A STUDY
OF THE SYNTHESIS AND MESOMORPHISM OF CERTAIN AROMATIC CARBOXYLIC ACIDS

Thesis submitted to the Faculty of Science
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by

G.W.Gray

University College
HULL

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DISCUSSION OF SYNTHESES

EXPERIMENTAL SECTION B

Introduction.

A. Mesomorphism and nomenclature

Mesomorphism is a state of matter which is neither liquid nor crystalline,but intermediate between the two,and,as such, it automatically commands the interest and investigation of both physical and organic chemists,the former to examine the unique physical properties of the state,and the latter to synthesise compounds of the required molecular dimensions to exhibit the phenomenon.Therefore,only by collaboration of crystallographer,physical chemist and organic chemist can any substantial advancement be made in this field of study.

This is apparent from a study of the literature on mesomorphism.The discovery of mesomorphism,by Reinitzer in 1888, in melts of cholesteryl benzoate was followed,in a very short time,by the preparation of over two hundred and fifty organic compounds which show this phenomenon.This was achieved largely by D.Vorländer(1).It was immediately evident that all these compounds had one common feature — a very long molecule — and this has always been accepted as a necessary property of a mesomorphic substance.

Initially,various opinions on mesomorphism persisted. Tammann and Nernst maintained that the compounds were impure and that the mesophase is an actual emulsion of two liquids. Lehmann,Quincke and Wulff concluded that the mesophase is a colloidal suspension of crystals in the amorphous liquid,and Vorländer believed that the mesophase has a fixed space lattice.The microscopic examination of mesophases [Grandjean, Mauguin and G.Friedel(2 and 3)] soon dispelled these ideas and mesomorphism was established as a true physical state, intermediate between the crystalline solid and the amorphous liquid.

With a large number of compounds available for study, G.Friedel was able to make a further detailed microscopic examination of the mesophases and to name the phase types as smectic,nematic and cholesteric.A study of the optical properties of the first two made it possible to assign structures to these states,but,even now,little is known about the structure of the cholesteric phase.It is no longer considered that these structures extend uniformly throughout the melt but that they persist in groups or swarms of molecules. The whole melt is composed of a random orientation of these groups as proposed by the Swarm Theory of E.Bose(4) in 1909. Measurements of changes in refractive index and viscosity with temperature have given considerable support to this theory. The physical characteristics of these mesomorphs have therefore been closely examined and X-ray analysis of crystalline substances,which can form mesophases,may be of prime importance in furthering knowledge of mesomorphic structure.

Little progress has however been made on the question of the forces existing between the molecules in the mesophase swarm,and Vorländer alone has attempted to investigate the effect of functional groups, present in the molecule, on the phase-types and the phase-lengths. These factors are no doubt closely related to the inter-molecular forces which exist in the melt, and a closer study of the molecular dimensions necessary for mesomorphic systems is of importance. This thesis is largely concerned with such considerations.

The discovery and investigation of mesomorphism by G.M. Bennett and Brynmor Jones(5 and 6) in _p_-_n_-alkyloxy benzoic and _trans_-_p_-_n_-alkyloxy cinnamic acids has been of first importance in this connection, as it has given a much more simple molecular pattern to investigate than the complex azo- and azoxy-compounds studied by Vorländer. In such aromatic acids, the length and breadth of the molecule may be altered by changing the ether group, the aromatic ring-system or the substituent in the ring. In this way, deviations from strict linearity and symmetry have been found to decrease, but not necessarily to eliminate the mesomorphism. The results of these investigations on substituted and unsubstituted _n_-alkyloxy benzoic and _n_-alkyloxy naphthoic acids are therefore discussed.

Since the interpretation of these results depends upon the structural conceptions of mesomorphism, some account will first be given of theories which are relevant to this study.

The crystalline and amorphous states are two common conditions in which matter may exist, but there is no sharp line of demarcation between the two. Glasses are well known to give gradual transitions from one to the other. Lehmann found another such intermediate condition in ammonium oleate, which is deposited from alcoholic solutions in a form which is apparently crystalline. Here the particles seem to have a definite geometrical form, but closer examination shows that they are bounded by rounded surfaces and are capable of flowing into one another. Naturally, Lehmann called this intermediate state a liquid-crystal, and ammonium oleate was indeed one of the first mesomorphic substances to be examined. The salt is now described as showing lyotropic mesomorphism, because the liquid crystals are formed from solution and are modified in their behaviour by the amount of water present in the alcohol. Thus,

crystalline —water ⟶ liquid crystal -excess water → solution
or
NH_4 Oleate ← dehydration — state ← evaporation — colloidal
solution.

The water gradually breaks down the crystal lattice to give a solution <u>via</u> the liquid crystalline state. Soaps, the alkali metal salts of naphthenic and resin acids, and 9-bromophenanthrene-3-sulphonic acid show liquid crystalline states by the controlled action of water.

Lyotropic mesomorphs are relatively uncommon and it is surprising that one of the first mesomorphs to be discovered should belong to this class. Much more common are the mesomorphic states found in the molten states of compounds. In this case,the thermal effect breaks down the crystal lattice,so that,

$$\begin{array}{c}\text{crystalline state(I)} \overset{t_1}{\rightleftarrows} \text{liquid crystalline state(II)} \overset{t_2}{\rightleftarrows} \text{amorphous liquid(III)} \\ \xrightarrow{\text{increasing temperature}}\end{array}$$

These transitions take place at precise temperatures and are reversible.In I there is a high degree of order in the regular arrangement of repeating unit-cells.Heat causes the perfect orientation to become disordered and,if molecular conditions are suitable to mesomorphism, I will pass over into III at the m.p. If conditions,which will be discussed later,are suitable,the order breaks down by stages giving states(II),which have certain degrees of order and are therefore anisotropic.Further heating to t_2 will destroy this orientation and give III. These anisotropic melts are cloudy compared with the translucent amorphous liquid into which they finally pass.This type of mesomorphism was first found by Reinitzer in molten cholesteryl benzoate.An ever increasing number of such substances is now known.

An unfortunate feature of this phenomenon and its study has been the failure to find agreement on nomenclature.Many of the early publications are concerned with fruitless discussions as to the relative advantages of the names "liquid crystals" and "crystalline liquids".In effect neither name is satisfactory,as the state is neither crystalline nor liquid in the true senses of these words.Crystals have a three dimensional order,whereas the phases may have only one or two dimensional order.The word liquid is also inappropriate as the phase is often crystalline in hardness,for example in lecithin.G.Friedel proposed the name mesomorphism,thus emphasising a state intermediate between the crystalline and amorphous states.This name is more satisfactory and is now generally employed.The terms mesophase,mesomorph and mesoform, of the same derivation,will also be used throughout this thesis.

F.Rinne(7) has raised objections to this nomenclature.He points out that the name has no structural meaning and over-stresses the intermediate character.He classifies matter as showing either ataxy(a disordered or amorphous structure) or eutaxy(an ordered structure).Mesomorphic and crystalline substances will belong to this class of eutactites,since they possess an ordered structure.The name paracrystals is therefore substituted for mesomorphs.This introduces the word crystal to emphasise the natural proximity of the state to the crystalline condition,and the prefix para- emphasises that many of the organic compounds showing this type of eutaxy are para-substituted benzene derivatives.Thus,the classification is (1) Atactites --Isotropic liquids,gases and amorphous matter

(2) Eutactites

(a) Crystals —3-dimensional order

(b) Paracrystals -1- or 2-dimensional order.

B. Smectic, nematic and cholesteric phases.

More than one type of mesophase may be found for one compound, so that the changes with increasing temperature may be represented,

$$\text{Crystal} \xrightarrow{t_1} \text{Mesophase I} \xrightarrow{t_2} \text{Mesophase II} \xrightarrow{t_3} \text{Amorphous liquid.}$$

The reversible transition temperatures, t_1, t_2 and t_3, are completely reproducible for a pure compound. The most important types of mesophase are the smectic and nematic. These names were given by G. Friedel and are derived from the Greek words smectos- soap-like, and nematos- thread-like. The term nematic has a special significance in that many nematic phases have a threaded appearance. Smectic has less meaning, and was first used for ammonium oleate, a soap-salt, which was the first smectic substance recognised as such. The names have now been generally accepted, although Vorländer(8) has criticised them for their lack of significance, without being able to suggest any more satisfactory names.

There are, of course, many compounds which show only one or other of these phases. Some of these are given in the following table,

Smectic substances	Transition temperature	m.p.
Ethyl-p-azoxy-benzoate	114°	121°
Ethyl-p-azoxy-cinnamate	140°	249°

n-Octyl *p*-azoxy-cinnamate	94°	175°
Nematic substances		
p-Azoxyanisole	116°	135°
p-Azoxyphenetole	137°	167°
Anisaldazine	165°	180°
p-Methoxy-cinnamic acid	170°	186°

Ammonium oleate shows only a smectic phase,but no transition temperature can be quoted for it since it is a lyotropic mesomorph.

Ethyl *p*-anisal-amino-cinnamate(I) and many other compounds give both a smectic and a nematic phase.In all such cases,the smectic phase is formed from the crystals:at a higher temperature this changes into the nematic phase.Finally,at t_3, the isotropic liquid is produced.

$$\begin{array}{c}\text{Crystalline state}\\\text{of I}\end{array} \xrightarrow{107^\circ} \begin{array}{c}\text{smectic}\\\text{phase}\end{array} \xrightarrow{114^\circ} \begin{array}{c}\text{nematic}\\\text{phase}\end{array} \xrightarrow{133^\circ} \begin{array}{c}\text{isotropic}\\\text{liquid}\end{array}$$

In lyotropic mesomorphs(9),the same conditions apply.For example,9-bromo-phenanthrene-3-sulphonic acid shows both smectic and nematic phases with increasing amounts of water.

$$\text{Solid} \xrightarrow{\text{water}} \begin{array}{c}\text{thick paste}\\\text{(smectic)}\end{array} \xrightarrow{\text{water}} \begin{array}{c}\text{thin paste}\\\text{(nematic)}\end{array} \xrightarrow[\text{water}]{\text{excess}} \begin{array}{c}\text{true}\\\text{solution}\end{array}$$

It is therefore reasonable to say that the space lattice, with three dimensional symmetry,is broken down in stages,by thermal agitation or by solvent effect,to give the isotropic liquid or the true solution respectively.In passing from solid to smectic to nematic,there will be an increasing breakdown of orientation until the completely disordered state is reached. Therefore,the smectic phase must have a more highly ordered structure than the nematic,and this is evidenced by the latter's greater viscosity.

The cholesteric phase is found in the melts of several compounds,the majority of which contain the cholesteryl ring-system.These substances have properties which are similar to both smectic and nematic phases,with additional characteristic properties due to the broad,flat molecules.It is difficult to assign these compounds to one of the two mesophase types,and several authors regard them as belonging to a third mesophase group.G.Friedel is emphatic that they are a modification of the nematic phase however.His argument is that although many compounds have been reported to give more than one smectic or nematic phase,it has been proved in all cases that the authors have mistaken a change in the appearance of one phase for a change of phase.Thus,if two mesophases are found,the sequence is always one smectic followed by one nematic.Yet,several substances show a smectic phase at lower temperatures and a cholesteric phase at higher temperatures.Since two smectic phases are never found together,the cholesteric phase must therefore be equivalent to the nematic.However,cholesteric compounds are always optically negative,whereas smectic and nematic mesophases are always positive.This fact makes the assignment to any of the two classes more dubious.

The first mesomorph,discovered by Rainitzer,was of this type.Cholesteryl benzoate is converted into a cholesteric phase at 146°,and into the isotropic liquid at 178.5°.

As the temperature is increased,and the crystalline solid passes through the smectic and/or nematic phase to the isotropic liquid,there is an increasing disorder of the molecular arrangement.G.Friedel first introduced the conception of a mesomorphic structure,which he derived from the optical behaviour of the phases.This theory was used and developed by Vorländer and by Bose.In brief,the smectic phase is the more highly ordered and is equivalent to a one-dimensional liquid,as shown in fig.1.

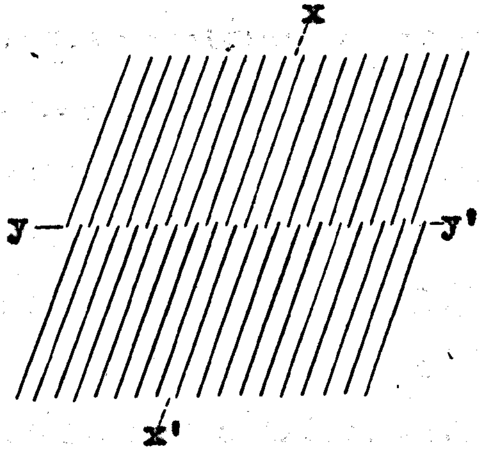


fig.1

This structure is also found in many long-chain,paraffinic substances,but in the smectic phase the layers are free to flow over one another.That is, there is a strong lateral adhesion along the direction xx' and a weak adhesion in the planes yy'. As the temperature rises,the adhesion along xx' diminishes,and the layer structure breaks down to give the nematic phase,which is a two-dimensional liquid.The molecules are still orientated in one direction,as shown in fig.2,but there is no

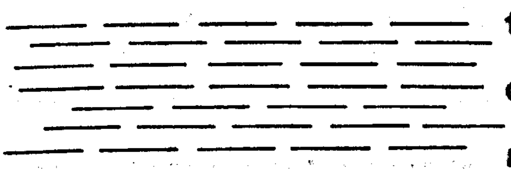


fig.2

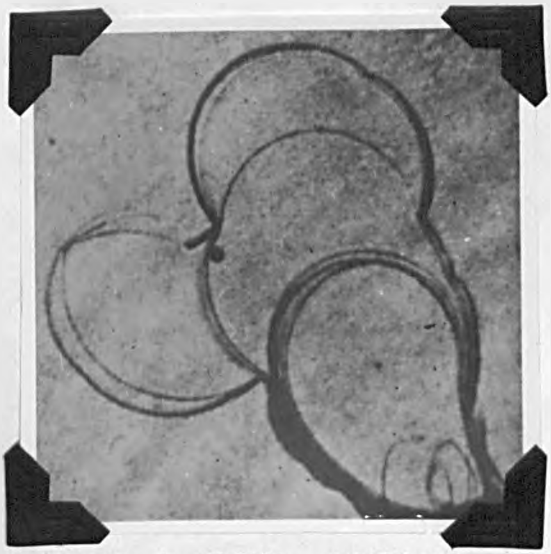
repeating spacing between the rods.Apart from a rather smaller intensity,the X-ray photograph is the same as that of an amorphous liquid.

The physical properties make it clear that there is no reason to suppose that these structures extend uniformly throughout a sample.The available data point rather to a whole made up of agglomerates of molecules,each swarm consisting of some one hundred thousand molecules.The molecules in a swarm will have a definite arrangement which will be one of the two mentioned above,so that the swarm will have a major axis lying parallel to the long axis of the individual molecules,due to the tendency of the molecules to link end to end.A magnification of the molecular anisotropies results, and this is evident in the optical,electric and magnetic properties.The forces existing between the swarms are very weak,and between any two there will be a region in which the molecules will gradually change their orientation from that of one swarm to that of the next.This transition will be similar to a diffusion.For many purposes,the swarm may be regarded as an elementary particle,capable of giving Brownian movement as a whole.This theory accounts for the known anisotropic and optical characteristics of mesophases and the first exact treatment of the theory was given by Ornstein and Zernike(10).Physical research on the viscosity,magnetic properties,electric properties and refractive index of mesophases gives increasing evidence for the existence of swarms. A summary of these measurements is given by Ornstein and Kast(11).

In general, the phases have been examined between a glass slide and a cover slip, for convenience of microscopic investigation. However, glass and many other surfaces have a profound orientating effect on the swarms, an effect which may extend 0.02mm. into the layer on each side (12),(13) and (14). This orientating effect causes the swarms to lie with their major axes parallel to one another and perpendicular to the surface. The whole film is therefore regularly ordered. For a thin, well mounted specimen, the whole sample may be orientated and appear transparent. Thus, the beautiful patterns, seen on microscopic examination of the phases, are due to external orientations of a fortuitous and variable nature. None the less, the effects depend on the phase type, and the textures, so thoroughly investigated by G. Friedel, are highly characteristic and invaluable for the identification of the phases. Some of the characteristic appearances of the smectic, nematic and cholesteric phases will therefore be described.

The smectic phase

The smectic phase shows pronounced layer flow, although this is seldom seen without complications from the surface itself. The flow arises from the layer structure discussed above and the gliding of the planes over one another, like the individual units in a pack of cards. The stepped drops (gouttes à gradins) are most easily obtained by mounting a drop of the smectic liquid over a hole in a glass slide or on a fresh cleavage surface of mica (Plate 1). In all other directions, other than parallel to the layers, the viscosity is high, and the behaviour is that of a solid. The distance between the layers approximates to the length of a molecule, deviations arising if the molecules are tilted. Such layers have a very homogeneous appearance. In ordinary light the planes resemble an isotropic liquid, but between crossed nicols, they are seen as homogeneous birefringent patches which have the optical properties of a positive uniaxial crystal. The optic-axial orientation varies from patch to patch, but is constant for any one. At the junction of two patches, the orientation changes from one to the other. The region of change is very small and is seen as a chain of very tiny focal-conic groups. In some cases, homogeneous patches may be obtained, wherein the optic axis is perpendicular to the slide surface. This homotropic condition may arise spontaneously or by movement of the cover slip. Such areas are extinct in parallel light and may be confused with the iso-



ETHYL p-AZOXY BENZOATE
Plate 1

tropic liquid.The homogeneous planes are also complicated at their edges by focal-conic groups.

More commonly,the smectic phase is obtained in the focal-conic structure which extends over all the specimen.In polarised light,this is seen particularly clearly as a series of fan-like structures with stepped edges.Friedel studied the optics of this structure and showed that the long axes of the molecules lie along the lines which may be drawn from an ellipse to a hyperbola with its plane at right angles to the ellipse.All such lines will form cones of revolution and the arrangement is that of Dupin's cyclides,the regular spacing of the cyclides resulting in a layer structure.Focal-conic structures are therefore further evidence for the layer theory of smectic substances. Excellent accounts of focal-conic structures and the geometry involved are given by G.Friedel(3) and by Sir William Bragg(16).A typical focal-conic structure is shown in Plate 2.


ETHYL p-AZOXY BENZOATE
Plate 2

Irrespective of the structure,the smectic mesophase is always positive and uniaxial and unaffected by magnetic fields. Electric fields have likewise no effect.A further characteristic of the smectic state lies in its appearance from the isotropic liquid in bâtonnets (fig.3).These resemble crystals, but have rounded edges and an ability to flow into one another. They extinct between crossed nicols, and are in effect none other than focal-conic groups.


fig.3

It may also be added that the homotropy mentioned above is rarely complete and oily streaks are often visible.These are birefringent and are the loops of very fine focal-conics,in which the hyperbolae are normal to the length of the band.

The nematic phase

This phase shows neither layer flow nor focal-conic structures and it is more similar to a true liquid.The phase may appear as large homogeneous areas(Plate 3) which are uniaxial and positive,showing extinction in four perpendicular positions.Unlike the immobile smectic phase,dust particles flow freely about from one patch to another.Yet,despite this Brownian movement,the whole is optically immobile,the swarms


p-AZOXY ANISOLE
Plate 3

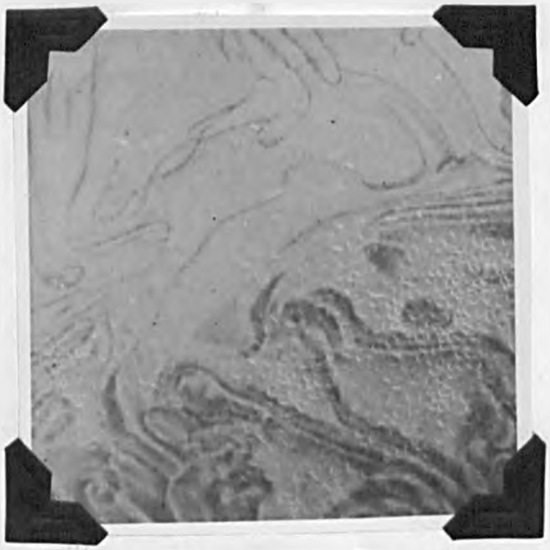
immediately assuming the orientation of the optic axis of any patch which they enter.The molecules have a marked tendency to adhere lengthwise to the glass,forming a pellicle or skin.This orientation may exist through a specimen from slide to cover slip.If it does,movement of the cover slip causes a doubling of the plane boundaries,the slide and cover slip pellicles becoming visible.Twisting of the cover slip gives a helicoidal transition from one pellicle orientation to the other.These pellicles have an extraordinary permanence, and if the nematic phase is heated to the isotropic liquid, the phase will often appear again on cooling in exactly the same distribution of homogeneous planes as before.Similarly, crystallisation from the nematic phase may give the crystals arranged in the pattern of the nematic patches.When the glass is rigorously clean,the pellicle has a low adhesion and homotropy may result.

In thick sections,the nematic phase more commonly appears in the characteristic threaded structure,after which the phase is named(Plate 4).The nature of the threads has been examined by Zocher and Birstein(15) who conclude that they are lines of optical discontinuity.They may be either the meeting place of optic axes at all points of their length or possibly lines round which the medium is circulating, corresponding to a vortex ring.In the latter case,the molecules and the optic axes are tangential to circles having the threads as axes. These threads may be free to move about in the bulk of the specimen, or they may have one end fixed to the glass and the other end free to move, or they may be attached along their length to the glass and remain at rest in the pellicle.

More rarely, the centred nematic structure is formed. Between crossed nicols, it appears as black brushes, which radiate from small centres in groups of two or four (Plate 5).

In contrast to the smectic, the nematic appears from the isotropic liquid as small spherical droplets. These show a black cross between nicols and are similar to spherulites of crystals which have developed as a result of growth from a centre. The droplets are here mobile, but they rapidly coalesce to give one of the nematic textures.

Also in contrast to smectic substances, the nematic phase is orientated by magnetic and



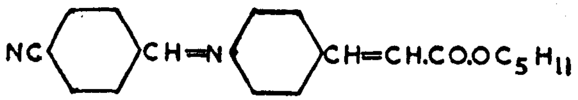
p-AZOXY PHENETOLE
Plate 4

p-AZOXY PHENETOLE
Plate 5

electric fields(15).

The cholesteric phase

This phase is shown by many cholesteryl esters and substituted cholesterols,and also by a few optically active substances which do not contain the cholesteryl ring system. For example,d-amyl-4-cyano-benzylidene-p-amino-cinnamate(I) shows this type of phase.



----(I)

The cholesteric phase resembles both types discussed above, but particularly the smectic.It has certain additional properties however,such as brilliantly iridescent interference colours in polarised light (varying from blue-violet to green or pink) and the optics of a negative uniaxial crystal.The distinctive properties are attributed to the shape of the molecule.In the lower esters the ring system predominates,and the system is cholesteric,whereas in the higher esters,which have marked paraffinic properties,smectic characteristics are shown.When non-cholesteryl molecules show this phase,e.g., I above,the molecular structure is found to be similar to a cholesteryl system.

The cholesteric phase appears from the isotropic liquid as bâtonnets and these coalesce to give a typical focal-conic structure.In this condition,no brilliant colour or high optical rotatory power is found.A slight cover slip displacement immediately produces the Grandjean plane structure, and brilliant colours and optical rotatory power at once appear. In these planes the optic axis is normal and there is a condition of homotropy. The planes are seen as strata which are equally spaced and separated by regions of discontinuity (Plate 6). These are analogous to the stepped drops in smectic substances, but the layer thickness is very much greater and varies in different cases from 2,000 to 80,000 Å. Cholesteric compounds are all optically active and are *dextro*- in the majority of cases. When in the plane structure the optical rotatory power is exceptionally high and scattered light is circularly polarised. If the incident light is circularly polarised it is reflected if the circulation is represented by a right-handed screw, and transmitted if the screw is left-handed. Sometimes this is reversed. The most remarkable feature is that the light which is scattered, like the light which is absorbed, is right-handed. In all other cases of reflection of circularly-polarised light the rotation sense is reversed--- these exceptions remain unexplained.

I IN ABOVE TEXT

Plate 6

The cholesteric phase is therefore considered as having a layer structure in which the plane of the ring system is at right angles to the optic axis. If the layers are 500 to 5,000 molecules thick, the interference colours and the very large optical rotation can be accounted for.

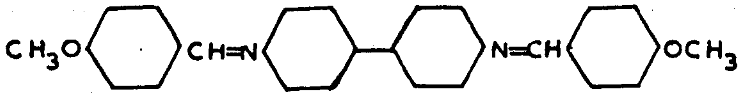
It has recently been reported that many esters of β-dihydro-cholesterols of the allo-series are mesomorphic(17), whereas the corresponding esters of the α-dihydro-cholesterols of the epi-series show no anisotropy in the melts.

C. Chemical properties of mesomorphic substances

The molecular formulae of a number of mesomorphic compounds make it clear that all possess the common feature of an elongated molecule. The molecules are rod-shaped and this leads to the closest possible packing in the crystalline or mesomorphic state. In this initial discussion of chemical characteristics no attempt will be made to discuss which structural types lead to smectic and which to nematic properties, as this will be detailed in the discussion of the results. Bernal and Crowfoot(18) have classified compounds as smectogenic or nematogenic on the basis of X-ray analysis of the crystalline solids. It may be pointed out here that what seems to be a suitable molecular pattern may not always produce a phase. Thus the long chain fatty acids have rod-shaped molecules, yet these apparently suitable systems show no mesomorphism. This is so, despite the fact that their melting points indicate a packing of linear molecules, with only slight differences in the arrangement of the terminal groups for odd and even carbon chains. The dimerisation of the molecules will also increase the favourable conditions, and the absence of mesomorphism must be due to the lack of cohesion between the carbon chains. Hence, once the lattice is destroyed the molecules will take up a random orientation and give no intermediate mesophase where molecules would be held together by cohesive forces. Thus, the molecule of a potential mesomorph must be long and capable of giving cohesive forces with which to attract neighbouring molecules. Normal van der Waal's forces will be insufficiently strong, and the cohesion must be increased by inter-molecular forces of a polar nature. Indeed many mesomorphic substances contain mildly active groups, such as $-\overset{|}{\underset{|}{C}}=N-$, $-N=\overset{|}{N}O$ or the azine group $-CH=N-N=CH-$, in the centre of the molecule, and these by their unsaturated nature increase the lateral adhesion. Aromatic rings have the same function, and the phase lengths and stabilities are increased with increasing number of benzene rings. The following examples bear this out.

$CH_3O.CO.C_6H_4.CO.OC_6H_4.CO.OC_6H_4.CO.OC_2H_5$ Phase length 140°

$CH_3O.CO.C_6H_4.CO.OC_6H_4.CO.OC_6H_4.CO.OC_6H_4.CO.OC_2H_5$ Here, the phase length is about 300°, from 187° to red heat, when decomposition occurs. Similarly, the compound ——



—prepared by Vorländer, contains two mildly active groups and four rings, and has been found to distil from the mesophase. That is, the isotropic liquid is unknown. These very stable phases must arise through the strong lateral adhesion of the molecules in the mesophase.

The salts of fatty acids, e.g., ammonium myristate and similar compounds, may show thermal as well as lyotropic mesomorphism. Ammonium myristate melts to a smectic phase which persists over some 30° to 35° before giving the isotropic liquid. These salts will be more polar than the free acids and so give greater cohesion. The thallous salts of the soaps show pronounced mesophases, e.g., thallous stearate shows a phase of 45° from 118° to 163°.

The nature of the terminal group is also important, and frequently it is an ether group (–OR) or an ester group (–CO.OR), where R– is a normal alkyl chain. These are called active groups. Because of their polar nature they increase the cohesion, and they do this not only laterally in the manner of the centre groups, but also in an end-to-end manner.

The terminal and central groups will give the molecule a dipole moment, with the result that the molecules will exert rotation moments on one another. This will tend to orientate them in parallel lines. Since the mutual attractive forces will be effective over only very small distances, the molecules will tend to link preferentially end to end, so that the swarm will be anisotropic and possess a long axis parallel to the long axis of the molecules.

These polar attractions must not be too great however or the melting point of the compound will become so high that the thermal agitation at this temperature will cause spontaneous disorder in the melt.

Hydrogen bonding may also bring about this result.Thus in hydroxy compounds,the extensive inter-molecular hydrogen bonding gives a very high melting point and an aggregate which is neither linear nor mesomorphic.Alkylation removes the ability to hydrogen bond,and the polar ether group,as well as lengthening the molecule,leads to cohesion of the molecules in the melt so that mesomorphism may result.In the carboxylic acids,hydrogen bonding will also occur,but in this case only a dimer is formed and moreover this will be linear.This was pointed out by G.M.Bennett and Brynmor Jones(6),who showed that ethyl *p*-*n*-propoxy-benzoate gives no phase,whereas the dimerisation of *p*-*n*-propoxy-benzoic acid results in nematic properties in the melt.In this respect the carboxyl group is very important in increasing molecule length.

An alkyl group (-R) replacing the alkyloxy group (-OR) usually results in destruction of the mesomorphic properties, since it is non-polar and the end-to-end cohesion is reduced.

The molecular requirements for mesomorphism may be summarised as follows:the molecule must have a rod-like shape containing active central groups to give lateral cohesion, and polar terminal groups which will give end to end cohesion, necessary for swarm formation. The individual effects of various groupings have been discussed by Vorländer(19).

D. Physical properties of mesoforms

The most picturesque features of mesophases examined on glass slides under the microscope are due to external orientating forces of the surface. The effect which these forces have is dependent on the inner mesophase structure, but as far as finding more precisely what this inner structure is, the examination of these textures (gouttes à gradins, focal-conics etc) can be of little help. Assuming that no drastic changes in structure occur on melting the crystalline state of a mesomorphic substance, Bernal and Crowfoot(18) have carried out an X-ray study of the crystalline states of several mesomorphic compounds. The results show that the unit-cells of nematic compounds contain the molecules arranged in parallel formation but the ends of the molecules are imbricated. This is the structure which has already been suggested as existing in the nematic phase. Similarly, the crystals of smectic and cholesteric substances have been shown to contain the molecules in parallel arrangement but with the ends of the molecules lying in line. This therefore represents a layer structure. It seems therefore to be possible to predict whether a compound will be smectic or nematic, and the names smectogenic and nematogenic are used to denote such substances.A combination of X-ray and optical methods is therefore likely to give a great deal of evidence for the structure of mesophases.

X-ray examination of the smectic phase itself provides evidence for the layer structure,and measurements give the layer thicknesses as equal to the length of a molecule,or less when the molecules are tilted.The angles of tilt in several thallous salts of the fatty acids have been measured by K. Herrmann(20).

Although nematic phases give no X-ray spacings they have been more extensively examined than the smectic phases in many of their physical properties.For example,Zocher(15) has carried out a mathematical treatment of the orientating effects of magnetic and electric fields on the swarms.Herzog and Kudar (21),Ostwald(22) and Vorländer(8) have studied the viscosity of nematic phases and find the viscosity to be greater than that of the isotropic liquid.In the region of the transition point a large increase in viscosity is found.In this anomalous region the Hagen-Poiseuille Law connecting shear and viscosity is disobeyed and,as far as viscosity is concerned,the sample behaves as a gelatine or a rubber sol.

Physical measurements have also given further evidence for the Swarm Theory in nematic mesoforms.Riwlin(13),using Ornstein and Zernike's relationship between refractive index and transparency in a system involving arbitrary gradients of refractive index,has found good agreement between transparencies for varying light and thickness of specimen of the mesophase. This shows that the mesophase is an aggregate of irregularly arranged doubly-refracting regions.That is,it contains molecular aggregates or swarms.Measurements of transparency in capillaries also give evidence for layers of high transparency in the regions orientated by the glass.These values agree with the results of the experiments of Moll and Ornstein (14) on transparency changes in magnetic fields.

Foëx(23) has shown that the magnetic rotation moment of a swarm may be calculated from the dielectric constant as a function of the magnetic field strengths applied.A value of 10^6 molecules per swarm is found.Jeżewski(24) arrives at a similar value for the swarm size on the basis of dielectric measurements(24).

X-ray work by Rinne(7) on lyotropic mesophases gives indication of a layer structure in the smectic phase from the sharp rings in the Debye-Scherrer photographs.

Excellent summaries of the general subject of mesomorphism are given by Sir W.Bragg(16) and (25) and by A.S.C.Lawrence (26).A general discussion of experimental work on mesomorphism to 1933 is to be found in the "Symposium on Liquid Crystals and Anisotropic Melts" in the Transactions of the Faraday Society of that year.

In conclusion the work of Weygand and Gabler(27) may be mentioned.These authors have examined a considerable range of azo- and azoxy-phenyl ethers and ether anils.They draw attention to the new case of monotropic mesomorphism.That is, the compound melts at t_1 to give the amorphous liquid which on cooling gives a nematic and/or smectic phase.These phases give transitions at t_2 or t_2 and t_3 which are higher than t_1. Moreover,they again claim the existence of two smectic phases, but in view of G.Friedel's investigations,the changes may be merely of structure in one phase.

E. <u>Mesomorphism of certain substituted and unsubstituted naphthoic and benzoic acids.</u>

The necessity for length in the molecule of a mesomorph has been well established,and yet broad systems such as the cholesteryl esters show distinct phases.The question arises— how far can breadth be increased without destroying the mesomorphic properties?

The study by Bennett and Jones of the mesomorphic properties of p-n-alkyloxy benzoic and cinnamic acids,both of which will form very long rod-shaped dimers,showed that comparatively simple molecules can exhibit mesomorphism.In these types of molecules containing an alkyloxy group to vary the length,an aromatic ring system to increase lateral adhesion,and a carboxyl group to further increase the length by dimerisation, it is comparatively easy to alter the ratio of length to breadth or flat-area.

The first ring system to be used was naphthalene — Vorländer having already shown that the anils of 2:6 and 1:4 diamino-naphthalene show mesomorphism. In the present study, the effective breadth of the molecules relative to the rotation axis was varied by altering the positions of the substituents. The 6-n-alkyloxy-2-naphthoic acids alone are mesomorphic; the 5:1, 4:1 and 7:2 n-alkyloxy naphthoic acids give isotropic liquids on melting. From this it seems that the breadth of the molecule cannot be increased greatly without destroying the mesophase(28). This view is supported by the observation that chlorination of p-n-amyloxy benzoic acid to give the 3:5 dichloro- derivative eliminates the mesomorphism although the m.p. of the latter is 22° lower than that of the parent acid. The disappearance of the phase results from the broadening effect of the two chlorine atoms. Even one halogen atom has a marked effect, and 3-bromo-4-n-alkyloxy benzoic acids show no mesomorphism. However, in the less broad 3-fluoro- and 3-chloro- derivatives short phases are found. Moreover the phases are shortest in the broader chloro- compounds(29).

Similar results have been found on halogenating and nitrating 6-n-alkyloxy-2-naphthoic acids in the 5-position. All these series exhibit mesomorphism, but the point at which it first appears depends upon the substituting atom or group.

present. The mesomorphism decreases from chloro- to bromo- to iodo- to nitro- with increasing molecular breadth(29).

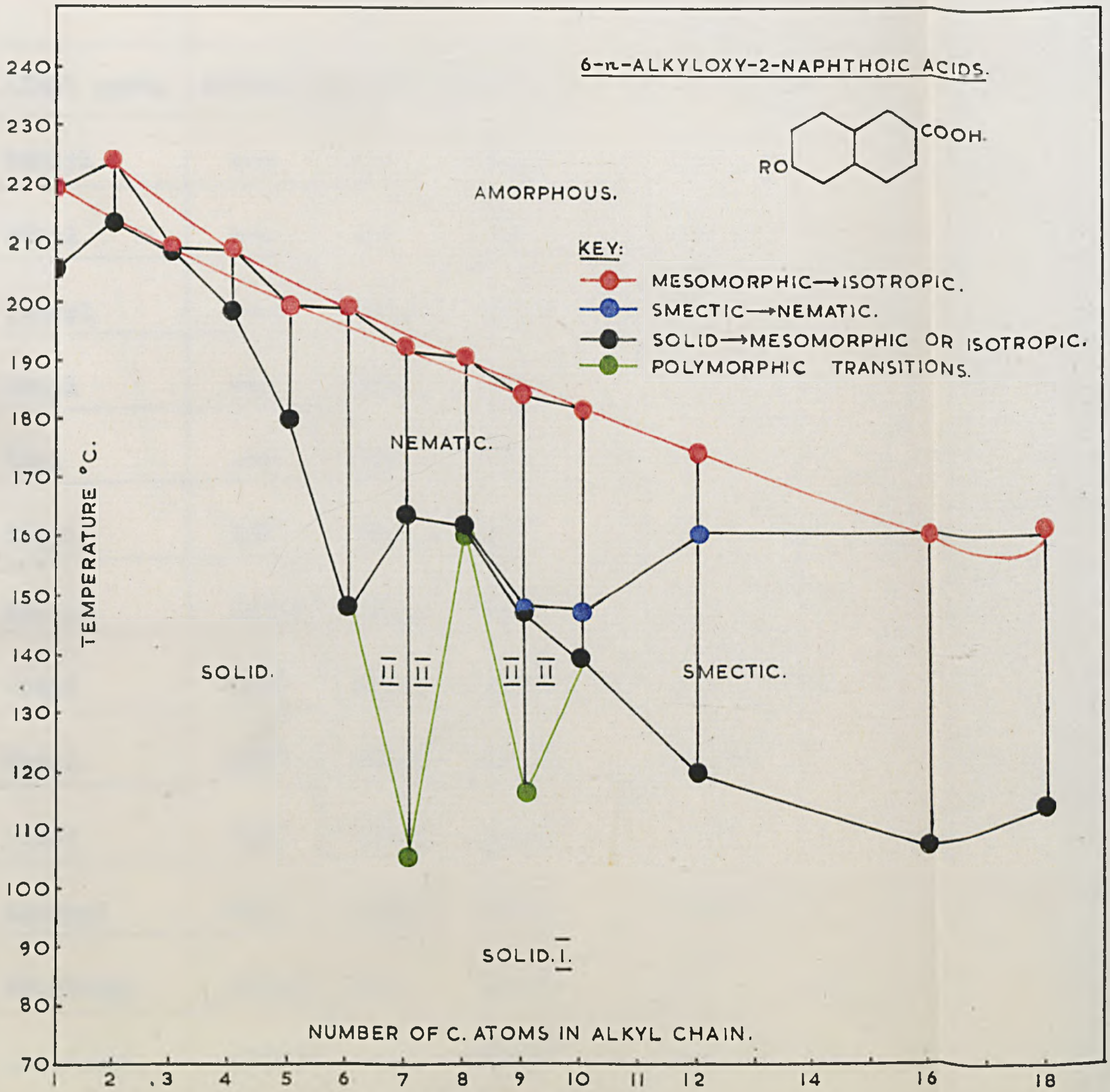
The interpretation of the results of varying the breadth of molecules, which are capable of showing mesomorphism, is dealt with under the discussion of results.

Tables and Graphs of Results.

6-n-alkyloxy-2-naphthoic acids.

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	206°	219°	—	13°
Ethyl	—	213°	224°	—	11°
Propyl	—	208°	208.5°	—	0.5°
Butyl	—	198°	208.5°	—	10.5°
Amyl	—	179.5°	199°	—	19.5°
Hexyl	—	147°	198.5°	—	51.5°
Heptyl	—	163°	192°	—	29°
Octyl	—	161.5°	190°	—	28.5°
Nonyl	146.5°	147.5°	183.5°	1°	36°
Decyl	139°	147°	181°	8°	34°
Dodecyl	119°	160°	174°	41°	14°
Hexadecyl	107°	—	159.5°	52.5°	—
Octadecyl	114°	—	161°	47°	—

TABLE I

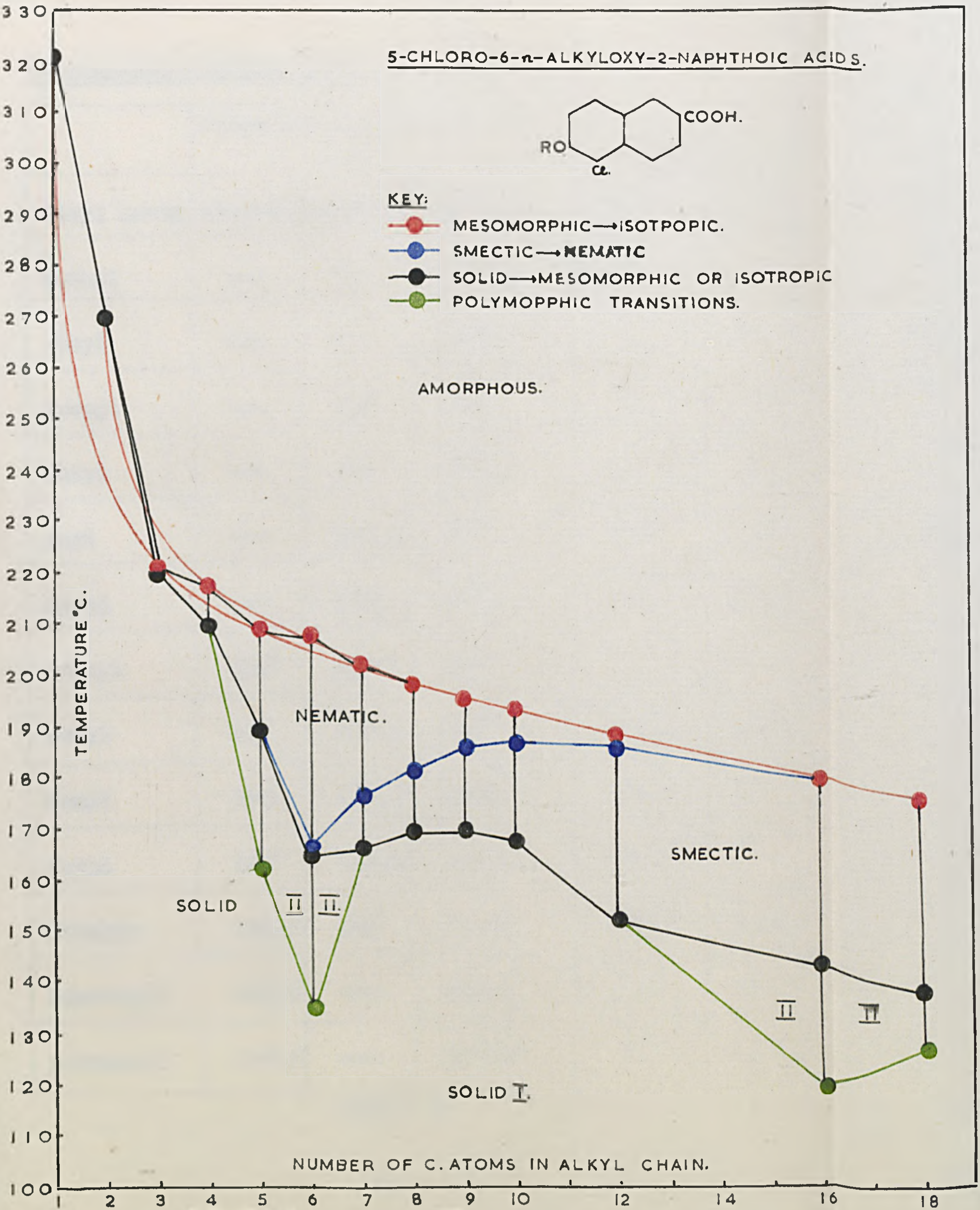

6-n-ALKYLOXY-2-NAPHTHOIC ACIDS.
RO
COOH.
AMORPHOUS.
KEY:
MESOMORPHIC → ISOTROPIC.
SMECTIC → NEMATIC.
SOLID → MESOMORPHIC OR ISOTROPIC.
POLYMORPHIC TRANSITIONS.
NEMATIC.
SOLID.
II
II
II
II
SMECTIC.
SOLID. I
TEMPERATURE °C.
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
NUMBER OF C. ATOMS IN ALKYL CHAIN.
1
2
3
4
5
6
7
8
9
10
11
12
14
16
18

GRAPH I

5-chloro-6-n-alkyloxy-2-naphthoic acids.

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	—	320.5°	—	—
Ethyl	—	—	269°	—	—
Propyl	—	219.5°	220.5°	—	1°
Butyl	—	209.5°	216.5°	—	7°
Amyl	—	189°	208°	—	19°
Hexyl	164°	166°	207°	2°	41°
Heptyl	165.5°	176.5°	201°	11°	24.5°
Octyl	169°	181.5°	197.5°	12.5°	16°
Nonyl	169°	185.5°	194.5°	16.5°	9°
Decyl	167°	186.5°	192.5°	19.5°	6°
Dodecyl	152°	185.5°	187.5°	33.5°	2°
Hexadecyl	142.5°	—	178.5°	36°	—
Octadecyl	138.5°	—	174.5°	36°	—

TABLE 2

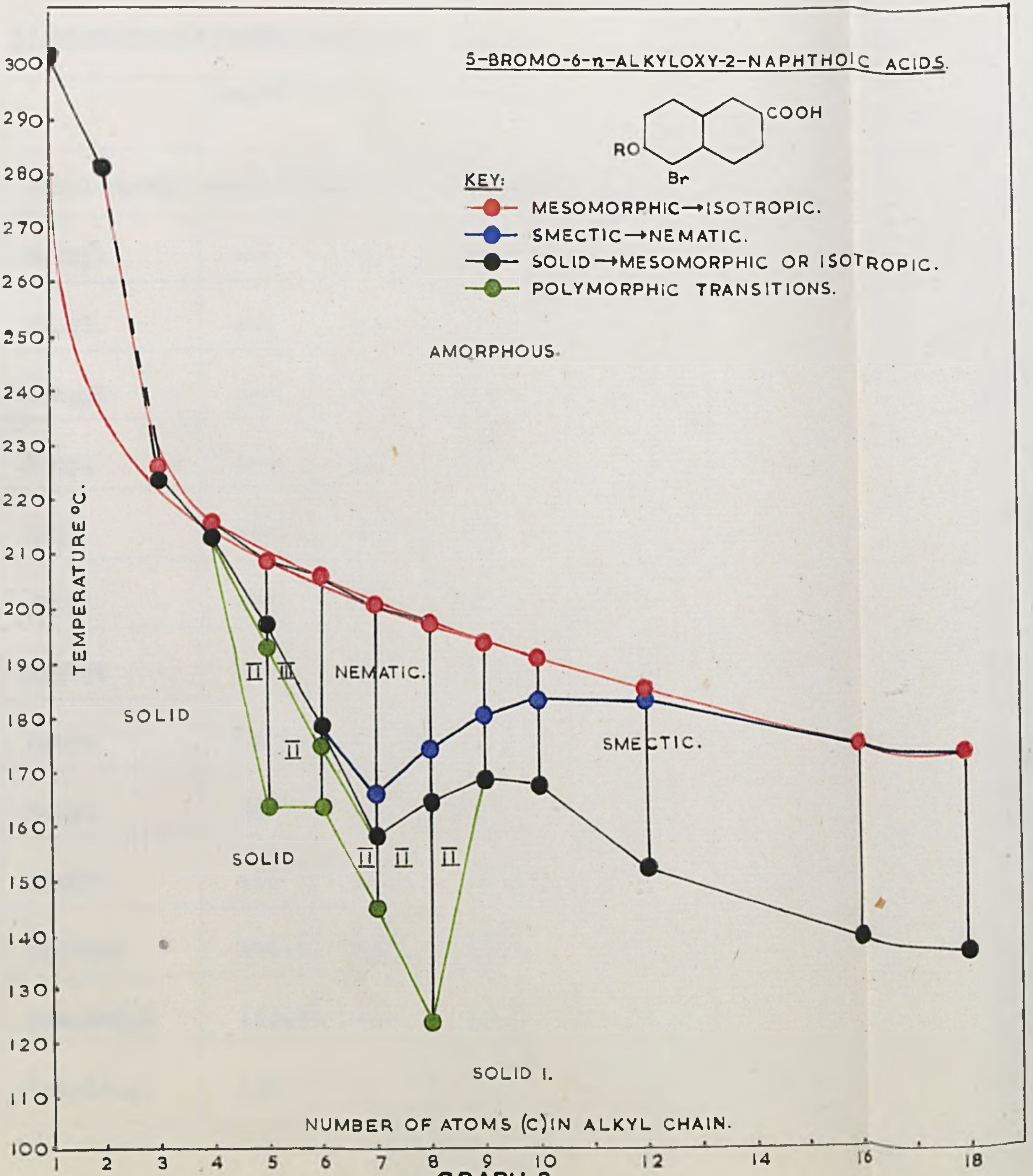

5-CHLORO-6-n-ALKYLOXY-2-NAPHTHOIC ACIDS.
RO
COOH.
Cl.
KEY:
MESOMORPHIC→ISOTPOPIC.
SMECTIC→NEMATIC
SOLID→MESOMORPHIC OR ISOTROPIC
POLYMOPPHIC TRANSITIONS.
AMORPHOUS.
NEMATIC.
SMECTIC.
SOLID
II
II.
II
II
SOLID I.
TEMPERATURE °C.
NUMBER OF C. ATOMS IN ALKYL CHAIN.
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
1
2
3
4
5
6
7
8
9
10
12
14
16
18

GRAPH 2

5-bromo-6-n-alkyloxy-2-naphthoic acids.

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	—	303°(d)	—	—
Ethyl	—	—	281°(d)	—	—
Propyl	—	224°	224°	—	<0.2°
Butyl	—	213°	214.5°	—	1.5°
Amyl	—	196.5°	207°	—	10.5°
Hexyl	—	178°	204.5°	—	26.5°
Heptyl	158°	165°	199°	7°	34°
Octyl	164°	173.5°	196°	9.5°	22.5°
Nonyl	168°	179.5°	192.5	11.5°	13°
Decyl	167°	182.5°	189.5°	15.5°	7°
Dodecyl	151.5°	182°	183.5°	30.5°	1.5°
Hexadecyl	138.5°	—	173.5°	35°	—
Octadecyl	136.5°	—	172.5°	36°	—

TABLE 3


5-BROMO-6-n-ALKYLOXY-2-NAPHTHOIC ACIDS.
COOH
RO
Br
KEY:
MESOMORPHIC→ISOTROPIC.
SMECTIC→NEMATIC.
SOLID→MESOMORPHIC OR ISOTROPIC.
POLYMORPHIC TRANSITIONS.
AMORPHOUS.
NEMATIC.
SMECTIC.
SOLID
SOLID
SOLID I.
II
III
II
II
II
II
TEMPERATURE °C.
NUMBER OF ATOMS (C) IN ALKYL CHAIN.
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
1
2
3
4
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12
14
16
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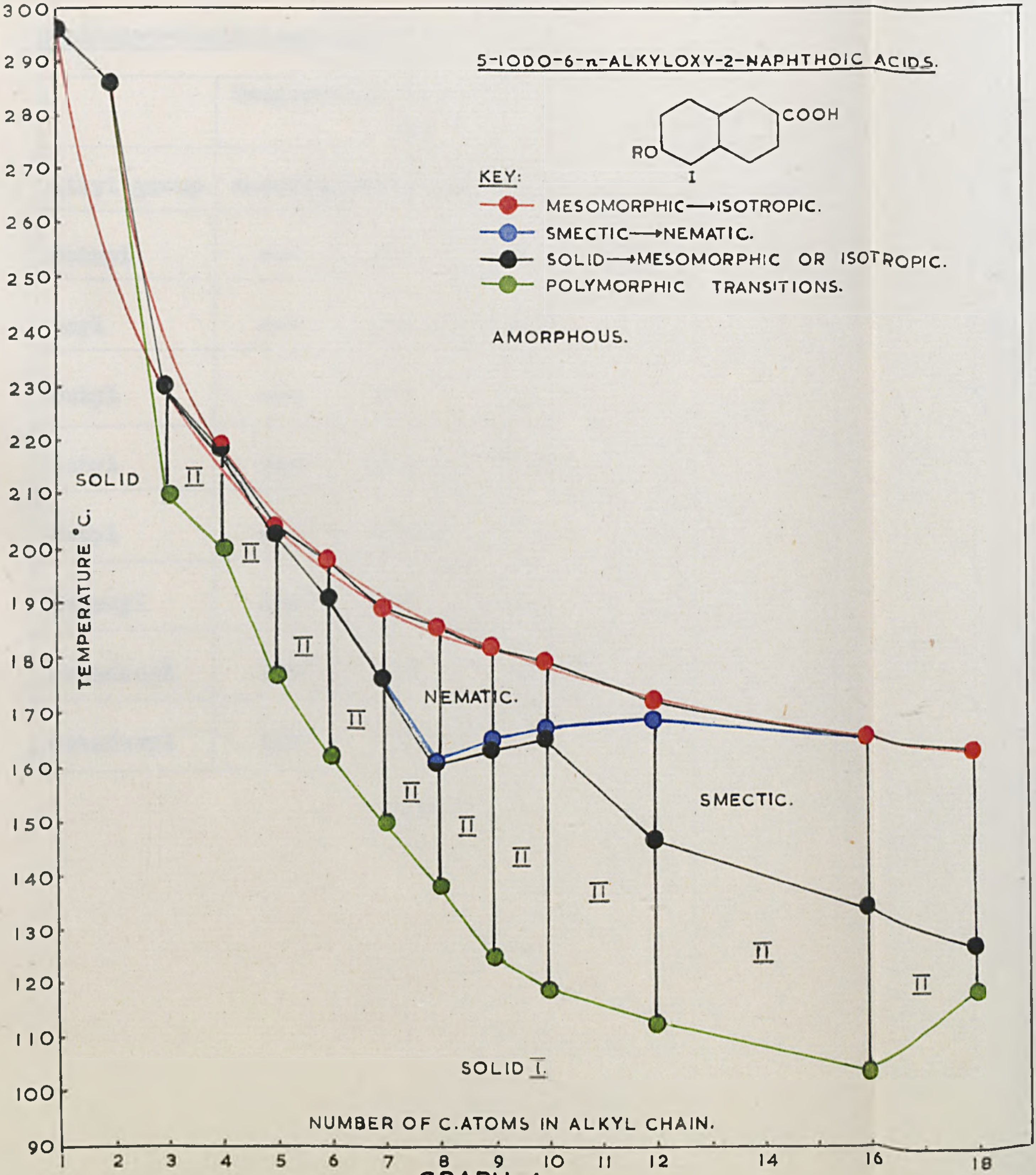
GRAPH 3

5-Iodo-6-n-alkyloxy-2-naphthoic acids.

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	—	296.5°(d)	—	—
Ethyl	—	—	286.5°	—	—
Propyl	—	—	230°	—	—
Butyl	—	219°	219°	—	<0.2°
Amyl	—	203°	204°	—	1°
Hexyl	—	191°	198°	—	7°
Heptyl	—	176°	189°	—	13°
Octyl	160.5°	161.5°	185.5°	1°	24°
Nonyl	163°	165°	182°	2°	17°
Decyl	165°	167°	179.5°	2°	12.5°
Dodecyl	146.5°	169°	172°	22.5°	3°
Hexadecyl	133.5°	—	165°	31.5°	—
Octadecyl	127°	—	163°	36°	—

TABLE 4


5-IODO-6-n-ALKYLOXY-2-NAPHTHOIC ACIDS.
COOH
RO
I
KEY:
MESOMORPHIC⟶ISOTROPIC.
SMECTIC⟶NEMATIC.
SOLID⟶MESOMORPHIC OR ISOTROPIC.
POLYMORPHIC TRANSITIONS.
AMORPHOUS.
SOLID
II
NEMATIC.
SMECTIC.
SOLID I.
TEMPERATURE °C.
NUMBER OF C.ATOMS IN ALKYL CHAIN.
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
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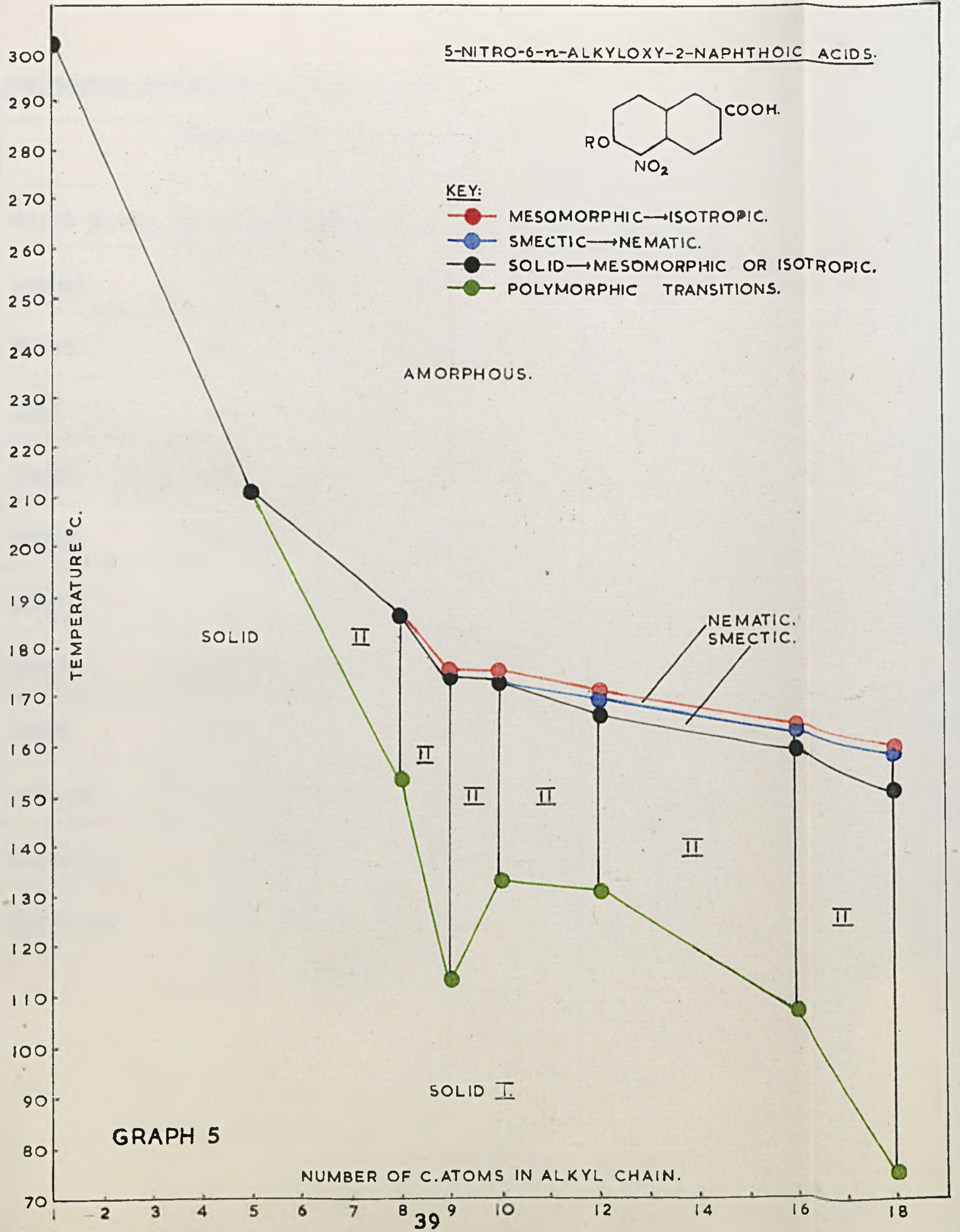
14
16
18

GRAPH 4

5-nitro-6-n-alkyloxy-2-naphthoic acids.

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	—	302°	—	—
Amyl	—	—	211°	—	—
Octyl	—	—	187°	—	—
Nonyl	—	174.5°	175°	—	0.5°
Decyl	—	173.5°	175°	—	1.5°
Dodecyl	167°	170°	171°	3°	1°
Hexadecyl	160°	164°	164.5°	4°	0.5°
Octadecyl	152°	159.5°	160°	7.5°	0.5°

TABLE 5


5-NITRO-6-n-ALKYLOXY-2-NAPHTHOIC ACIDS.
COOH.
RO
NO2
KEY:
MESOMORPHIC→ISOTROPIC.
SMECTIC→NEMATIC.
SOLID→MESOMORPHIC OR ISOTROPIC.
POLYMORPHIC TRANSITIONS.
AMORPHOUS.
NEMATIC.
SMECTIC.
SOLID
II
II
II
II
II
II
SOLID I.
TEMPERATURE °C.
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
NUMBER OF C.ATOMS IN ALKYL CHAIN.
1
2
3
4
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7
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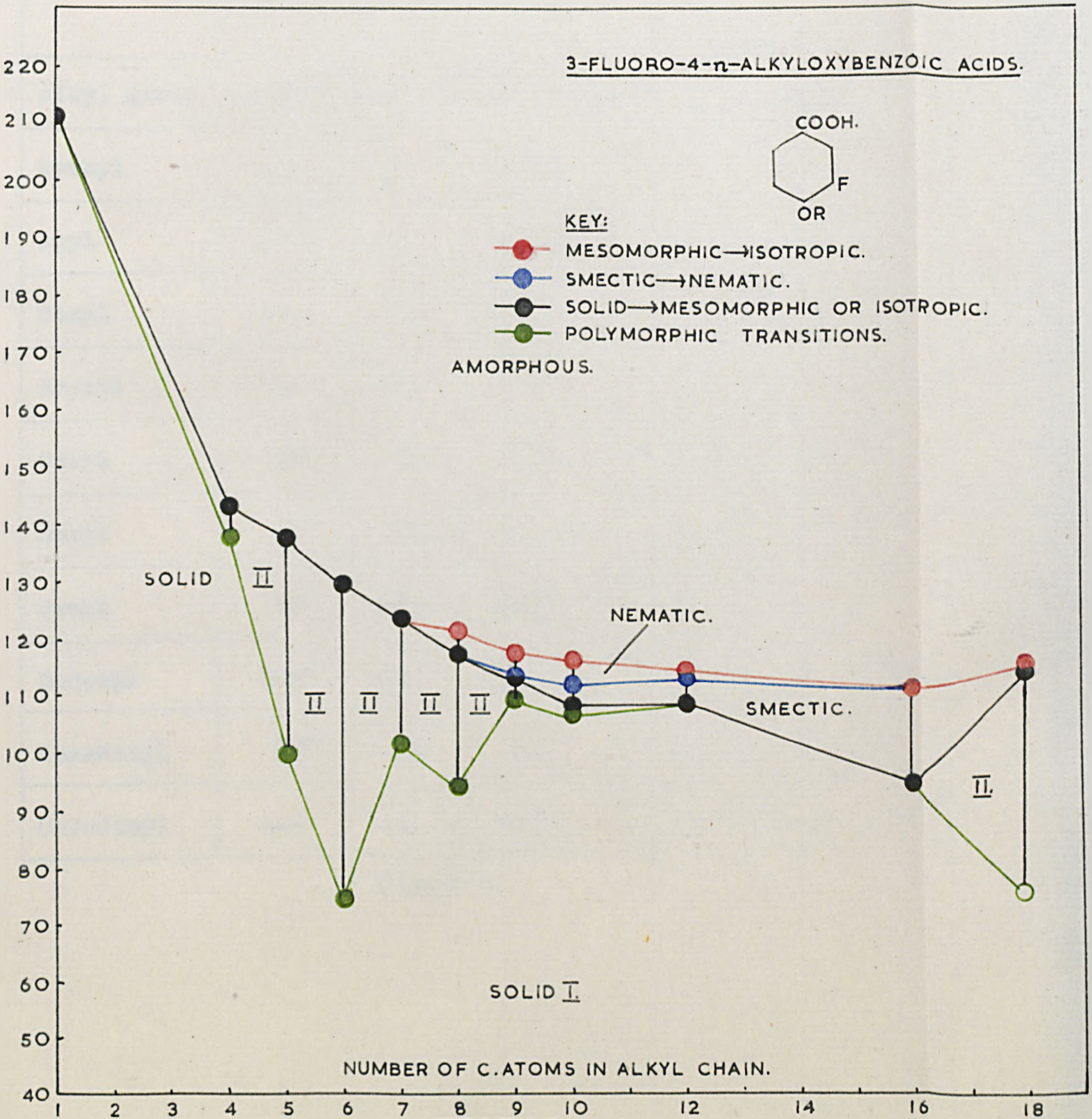
9
10
12
14
16
18

GRAPH 5

3-Fluoro-4-n-alkyloxy benzoic acids.

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	——	——	211.5°	——	——
Butyl	——	——	142.5°	——	——
Amyl	——	——	137°	——	——
Hexyl	——	——	129°	——	——
Heptyl	——	——	123°	——	——
Octyl	——	117°	121°	——	4°
Nonyl	112.5°	112.5°	116.5°	<0.2	4°
Decyl	108°	112°	116.5°	4°	4.5°
Dodecyl	108.5°	112.5°	114.5°	4°	2°
Hexadecyl	94°	——	111°	17°	——
Octadecyl	113°	——	115°	2°	——

TABLE 6


3-FLUORO-4-n-ALKYLOXYBENZOIC ACIDS.
COOH.
F
OR
KEY:
MESOMORPHIC→ISOTROPIC.
SMECTIC→NEMATIC.
SOLID→MESOMORPHIC OR ISOTROPIC.
POLYMORPHIC TRANSITIONS.
AMORPHOUS.
SOLID II
II
II
II
II
NEMATIC.
SMECTIC.
II.
SOLID I.
NUMBER OF C. ATOMS IN ALKYL CHAIN.
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
1
2
3
4
5
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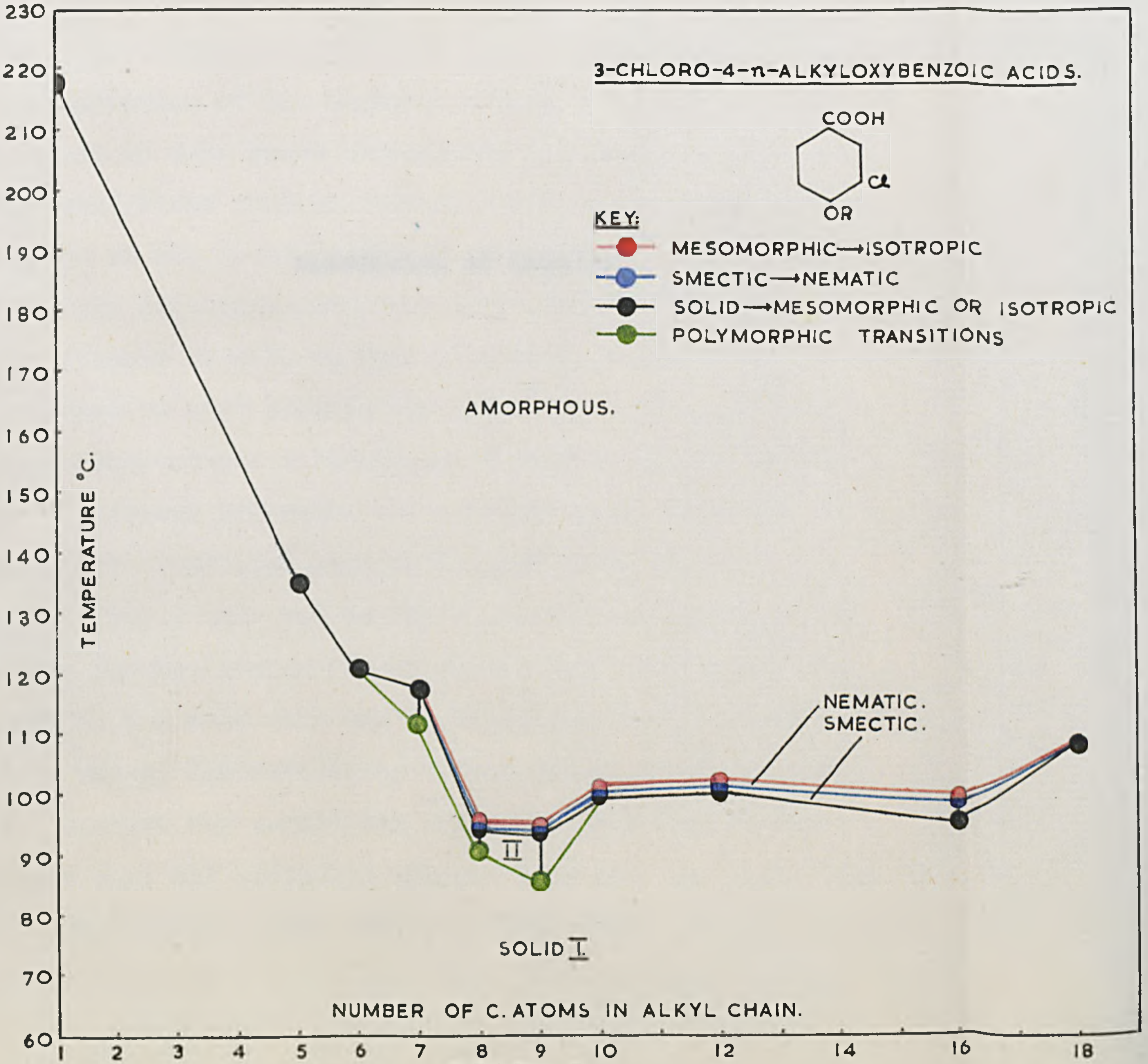
7
8
9
10
12
14
16
18

GRAPH 6

3-Chloro-4-n-alkyloxy benzoic acids.

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	—	217.5°	—	—
Amyl	—	—	134.5°	—	—
Hexyl	—	—	120°	—	—
Heptyl	—	—	117°	—	—
Octyl	94°	94°	95°	<0.2°	0.5°
Nonyl	93°	93.5°	94.5°	0.5°	1°
Decyl	99°	100°	101°	1°	1°
Dodecyl	100°	101°	102°	1°	1°
Hexadecyl	95°	98°	99°	3°	1°
Octadecyl	—	—	108°	—	—

TABLE 7


3-CHLORO-4-n-ALKYLOXYBENZOIC ACIDS.
COOH
Cl
OR
KEY:
MESOMORPHIC→ISOTROPIC
SMECTIC→NEMATIC
SOLID→MESOMORPHIC OR ISOTROPIC
POLYMORPHIC TRANSITIONS
AMORPHOUS.
NEMATIC.
SMECTIC.
II
SOLID I
TEMPERATURE °C.
NUMBER OF C. ATOMS IN ALKYL CHAIN.
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
1
2
3
4
5
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10
12
14
16
18

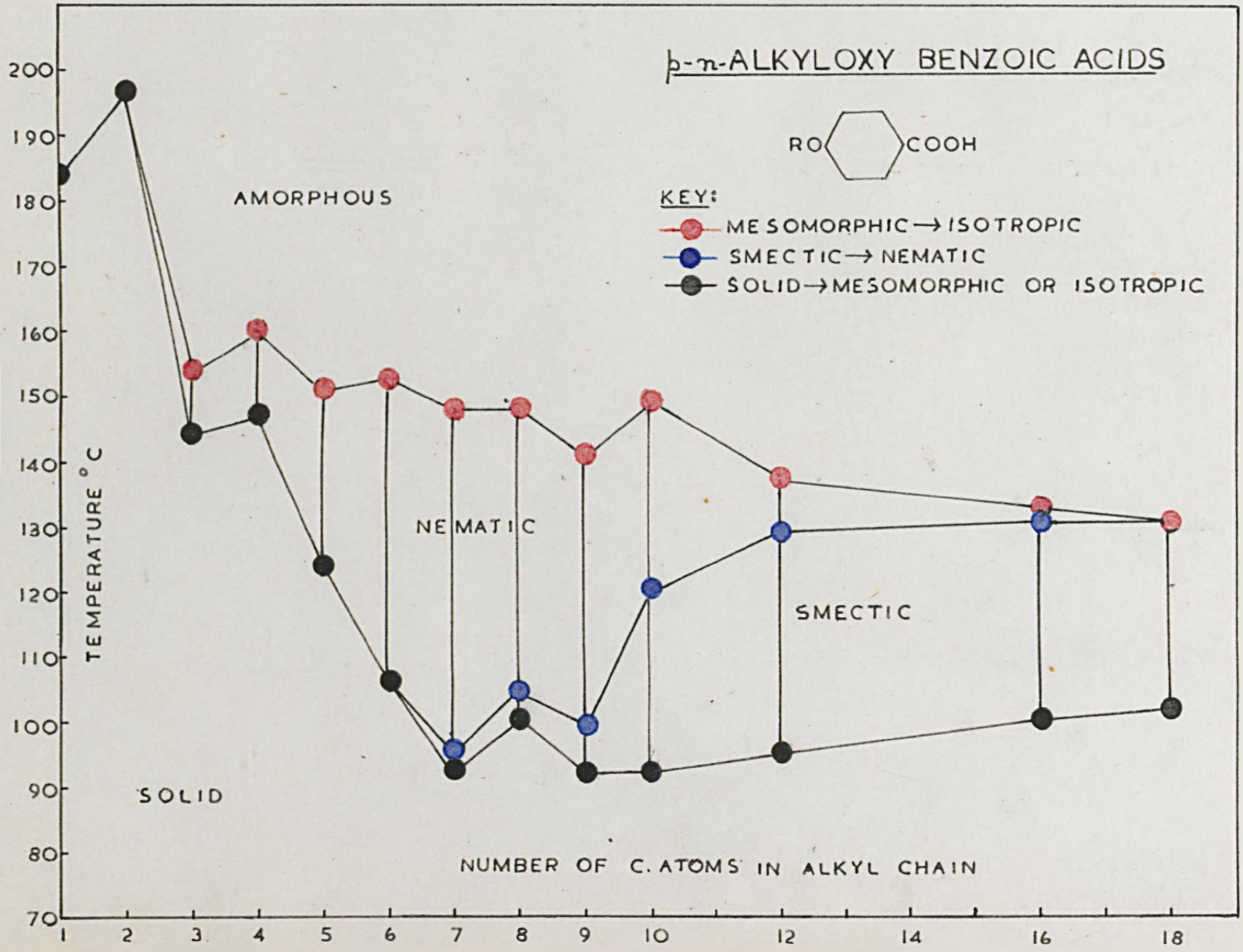
GRAPH 7

Discussion of Results

Compounds which possess mesomorphic properties are no longer a rare phenomenon and Vorländer,who was responsible for the preparation of a very large number,has remarked that the synthesis of a mesomorphic compound is a matter of no great difficulty,provided that certain conditions are observed. An examination of the physical constants and the formulae of a number of well known mesomorphic compounds shows clearly what conditions must be fulfilled.The most striking common feature is the great length of the molecules relative to the other two dimensions.Only the cholesteryl esters possess considerable breadth or flat-area,but,here also,length predominates over breadth and thickness.A long and narrow or a saucer-shaped molecule has therefore become recognised as a necessary criterion for a mesomorphic substance.However, two other conditions must obtain,and these are that the melting point must not be too high,and that sufficiently strong intermolecular forces must exist to preserve some order in the melt when the crystalline lattice breaks down. Since strong intermolecular forces result in high melting points,these two conditions are in opposition,with the result that all elongated molecules do not show mesomorphism. Thus,the melting point may be so high that when the lattice breaks down the thermal agitation gives spontaneous disorder in the melt,or,as in the case of the normal aliphatic carboxylic acids,the cohesive forces in the melt are not sufficiently strong to preserve order even at the low temperatures at which the liquid state exists. Although a large number of mesomorphic compounds has been prepared, these have been of widely different types and very little systematic research has been carried out. It is not possible to be more precise about the conditions for mesomorphism.

Of the few systematic investigations which have been made those of Bennett and Brynmor Jones(6) and Weygand *et al*(27 and 57) are the most important. Bennett and Brynmor Jones prepared homologous series of *p*-*n*-alkyloxy benzoic and *trans*-*p*-*n*-alkyloxy cinnamic acids in all of which the dimerisation through the carboxyl group yields a long narrow molecule, and the cohesive forces are sufficient to give orientation in the melt without raising the melting points too greatly. The *p*-*n*-alkyloxy benzoic acids first show mesomorphism when the alkyl group is *n*-propyl, and nematic properties alone are observed up to *n*-heptyl. This ether possesses an additional short smectic phase. Further increase in the length increases the smectic phase length at the expense of the nematic phase, which becomes progressively shorter, until the purely smectic *n*-octadecyl ether is reached. These results are summarised in graph 8, page 46. The importance of molecular length is shown by the fact that the *trans*-*p*-methoxy- and *p*-ethoxy cinnamic acids, which are longer than the corresponding benzoic acids, are mesomorphic. Again, as shown in graph 9, page47, the lower

GRAPH 8


p-n-ALKYLOXY BENZOIC ACIDS
RO COOH
KEY:
MESOMORPHIC → ISOTROPIC
SMECTIC → NEMATIC
SOLID → MESOMORPHIC OR ISOTROPIC
AMORPHOUS
NEMATIC
SMECTIC
SOLID
TEMPERATURE °C
NUMBER OF C. ATOMS IN ALKYL CHAIN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
1
2
3
4
5
6
7
8
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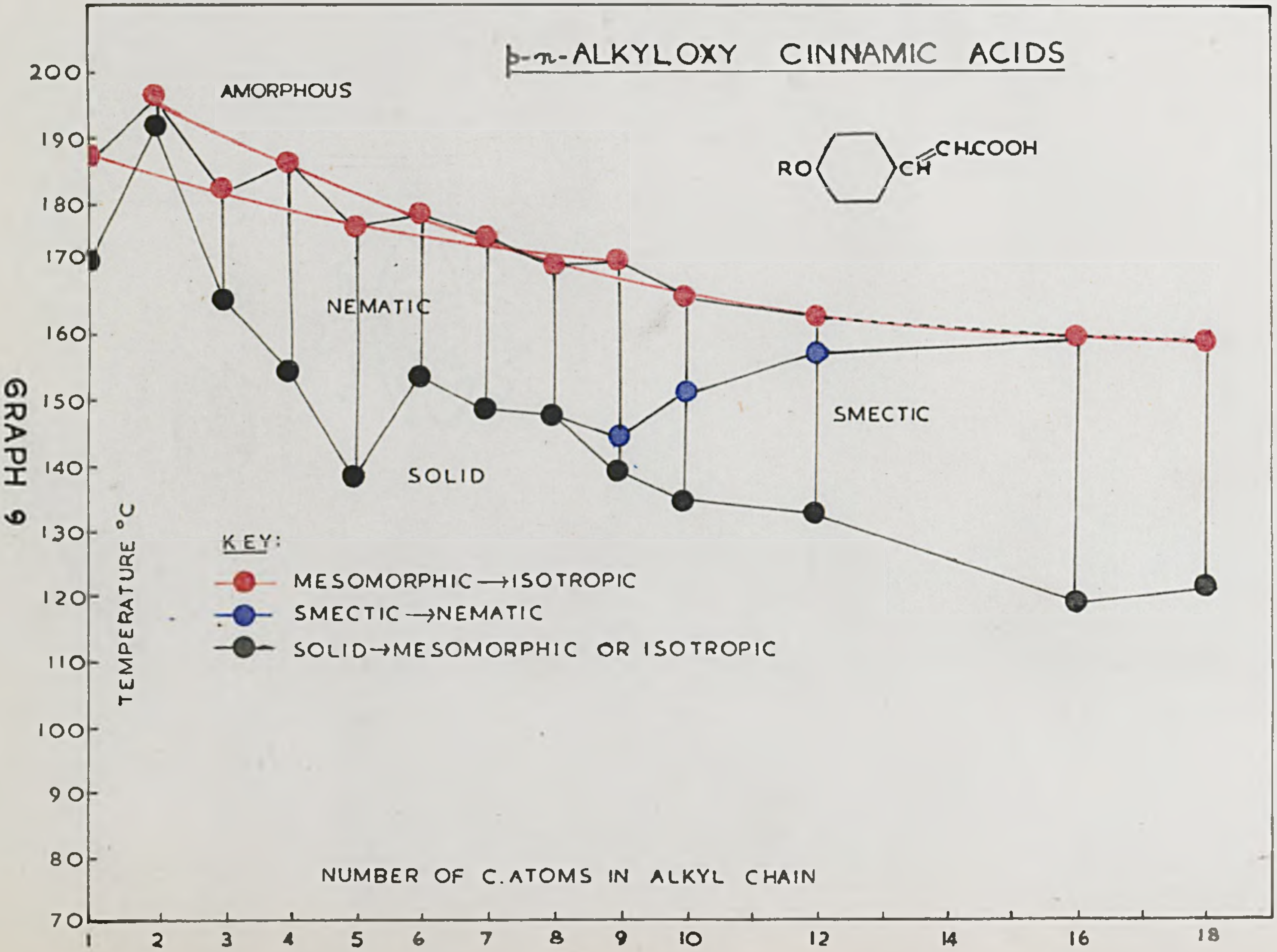
14
16
18



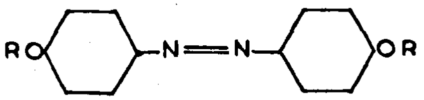
GRAPH 9

p-n-ALKYLOXY CINNAMIC ACIDS

members of the homologous series are purely nematic,and the n-nonyl ether is the first to show additional smectic properties.The smectic phase lengths then gradually increase with increasing length of the n-alkyl chain until, in the n-hexadecyl and n-octadecyl ethers,purely smectic properties are observed.These findings show very clearly the effect of systematic increases in the molecular length on the mesomorphism.

Weygand et al examined homologous series of n-alkyloxy anils,azo- and azoxy- compounds.Although monotropic mesomorphism is found in several of these compounds,the effect of increasing the length of the molecules by using longer n-alkyl chains agrees with the observations of Bennett and Brynmor Jones.Weygand's results are difficult to express graphically,due to the monotropic nature of the mesomorphism in some cases,so that the melting points are often higher than one or both of the transition points.However,the following figures in tables 8,9 and 10 show again that smectic properties appear with longer chain lengths,that nematic phase lengths then decrease,and that with sufficiently long n-alkyl groups the system becomes purely smectic.

Table 8

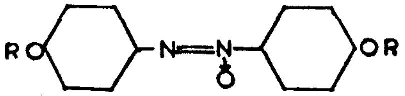


(R= n-alkyl group)

R	m.p.	s-n	n-i	s-i	Comments
Di-ethyl	159°	—	150°	—	Monotropic nematic
Di-butyl	135°	—	124°	—	" "
Di-amyl	112°	—	106°	—	" "
Di-hexyl	102°	—	114°	—	Enantiotropic nematic
Di-heptyl	102°	97°	109°	—	Monotropic smectic and enantiotropic nematic
Di-nonyl	103°	99°	107°	—	" " " " "
Di-dodecyl	106°	—	107°	—	Enantiotropic smectic

s-n smectic-nematic;n-i nematic-isotropic;s-i smectic-isotropic

Table 9

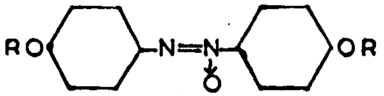


(R= n-alkyl group)

R	m.p.	s-n	n-i	s-i	Comments
Di-butyl	107°	—	134°	—	Enantiotropic nematic
Di-amyl	82°	—	119°	—	" "
Di-hexyl	81°	72°	127°	—	Monotropic smectic and enantiotropic nematic
Di-heptyl	74°	92°	122.5°	—	Enantiotropic s and n
Di-octyl	76°	106°	124.5°	—	" " " "
Di-nonyl	77°	113°	121°	—	" " " "
Di-decyl	78°	119.5°	123°	—	" " " "
Di-dodecyl	82°	—	—	122°	Enantiotropic smectic

s-n smectic-nematic;n-i nematic-isotropic;s-i smectic-isotropic

Table 10

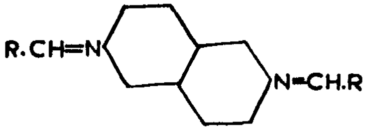


(R= n-alkyl group)

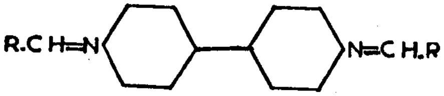
R	Smectic phase length	Nematic phase length
Di-butyl	—	27°
Di-amyl	—	37°
Di-heptyl	18°	30.5°
Di-octyl	30°	18.5°
Di-nonyl	36°	8°
Di-decyl	41.5°	3.5°
Di-dodecyl	40°	—

The same general effects of length increase on the mesomorphism have also been found in the present investigation.

By contrast, little was known about the effect of broadening the molecules and, apart from the trans-p-n-alkyloxy cinnamic acids, none of the compounds examined by the above authors has a breadth greater than that of a benzene ring. The only established fact would appear to be that the 27° nematic phase in p-n-amyloxy benzoic acid was eliminated completely by di-chlorination in the 3:5 positions. On the other hand, Vorländer prepared certain naphthalene derivatives, which are considerably broader than a benzene ring, and which possess mesomorphic properties. Among these are certain anils of 2:6-di-amino-naphthalene(I)



I

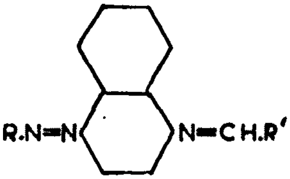


II

By comparing the properties of the naphthalene anils with those of type II,he proved that those based on naphthalene were less mesomorphic than the more linear anils derived from 4-4'-di-amino-diphenyl.

R	I	II
C_6H_5-	No mesomorphism	Mesomorphic
$C_6H_5.CH{=}CH$-	No mesomorphism	Mesomorphic
p-$CH_3.C_6H_5$- p-$CH_3O.C_6H_5$- p-$C_2H_5.OC_6H_5$-	Weakly mesomorphic	Strongly mesomorphic

These facts show that increase in molecular breadth will diminish the tendency to mesomorphism,but,the effect need not be marked.This last point was made clear when Vorländer (19) proved that certain 1:4-di-substituted naphthalene derivatives behave as varnishes or glazes with a strong tendency to supercool in the mesomorphic state.These compounds are of type III



III

When R=C_6H_5 and R'=$C_6H_5.OCH_3$ the amorphous melt supercools to a mesomorphic state,which can be obtained even at room temperature. When this is allowed to stand, or is warmed, crystallisation occurs, and on further heating the crystals pass over to the amorphous melt without forming a mesomorph. The mesomorphism is therefore monotropic.

When R and R' are $C_6H_5.OCH_3$, or when R is $C_6H_5.OC_2H_5$ and R' is $C_6H_5.OCH_3$, the tendency to supercool is lost, but in both, enantiotropic nematic phases are present. Clearly, these very broad molecules are well able to show the phenomenon of mesomorphism.

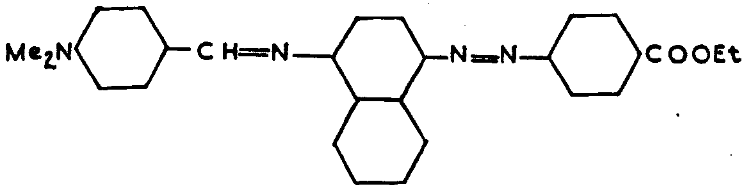
Existing evidence of the effect of broadening a molecule on its ability to show mesomorphism is scanty and ill-defined. The present investigation was undertaken in the expectation that it would be possible, by gradually increasing the breadth of one particular molecular type, to add to the knowledge of the effect of dimensions on mesomorphism.

The behaviour of Vorländer's anils and azo- compounds, and also those compounds prepared by Weygand, would however be difficult to relate to the findings of Bennett and Brynmor Jones on the alkyloxy benzoic and cinnamic acids, because of the fundamental differences in the molecule types. As has been pointed out in the introduction, an alkyloxy aromatic carboxylic acid has several advantages in that dimerisation ensures a very long molecule, and in that the length may be varied by changing the alkyl group. Moreover, the syntheses are less involved than are those for azo- and particularly azoxy- compounds. It was decided to use this molecular type, and to investigate fully the behaviour of series of naphthalene compounds by preparing _n_-alkyloxy naphthoic acids. In these, it is possible to vary the effective breadth of the molecules by altering the relative positions of the _n_-alkyloxy- and carboxyl groups. Thus, the narrowest molecules would be the 6-_n_-alkyloxy-2-naphthoic acids which would differ substantially from 4-_n_-alkyloxy-1-naphthoic acids. The study of such compounds would then allow comparisons to be made with the behaviour of the _p_-_n_-alkyloxy benzoic and _trans_-_p_-_n_-alkyloxy cinnamic acids.

1. Unsubstituted n-alkyloxy naphthoic acids

The first series to be investigated was that of the 4-_n_-alkyloxy-1-naphthoic acids in which the alkyl groups used were methyl to decyl, dodecyl, hexadecyl and octadecyl. Despite Vorländer's observation of mesomorphism in the 1:4-naphthalene azo-anils, these acids have no mesomorphic properties. The absence of anisotropy cannot be attributed to high thermal agitation in the molten state, which would cause spontaneous disorder, since the melting point values are not unusually high. Mesomorphism is not uncommon in the temperature range 200-250° and anisotropic melts existing at 250-300° are well established. In this series, the highest melting point, 248°, was found for 4-methoxy-1-naphthoic acid; thereafter, the melting point gradually decreased with increasing length of the alkyl group and the lowest melting point is for the 4-n-hexadecyloxy-1-naphthoic acid, at 136°. When the melting points for this series of acids are plotted against the number of carbon atoms in the alkyl group alternations in melting point are found, but these are irregular fluctuations, and the values for odd and even carbon chain ethers do not lie on two distinct curves. Such behaviour, although common in certain series of mesomorphic compounds, is not an essential characteristic of such a series. There is, however, no doubt that the melting point value is important in determining whether mesomorphism will occur, and what will be the length of the phase. Thus, the melting points of 184° and 197° for p-methoxy and p-ethoxy benzoic acids must be considered too high to cause mesomorphism, and that the absence of mesophases is not due to the fact that the molecules are too short. This has already been established since mixed melts of these two acids cannot contain a dimer longer than that of p-ethoxy benzoic acid and yet these melts are mesomorphic. This can only be attributed to the depression of the melting point below 184°, so diminishing the thermal agitations in the melt and permitting an ordered melt to exist for a detectible range of temperature. Mixed melts of 4-n-hexadecyloxy- and 4-n-octadecyloxy-1-naphthoic acids, with m.ps. of 136° and 137.5° respectively, were prepared which melted below 130°, but these exhibit no mesomorphism. Many other cases of anisotropy in mixed melts of two non-mesomorphic compounds have been previously reported(56,52 and 53).

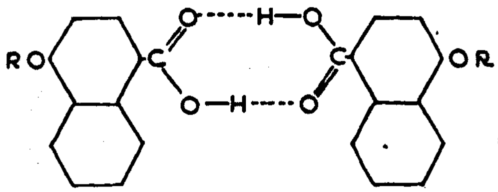
Since the melting points of these 1:4- naphthoic acids can hardly be considered to be too high, the absence of mesomorphism in their melts can only be attributed to the fact that the molecules are too broad. Yet, Vorländer reports that the 1:4-naphthalene azo-anils are mesomorphic. One of these, ethyl *p*-N.N.-di-methyl-amino-benzal-1-amino-naphthalene-4-azo-benzoate(IV) has m.p.188-189° and gives a mesophase which clears at 197°.



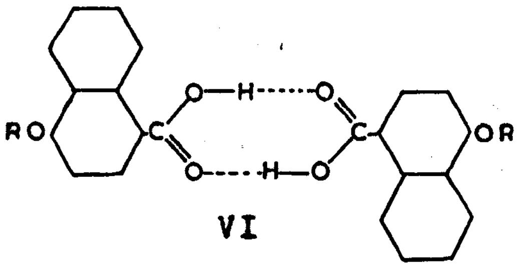
IV

In this case then there is mesomorphism, yet the molecule contains a naphthalene ring and, moreover, the melting point is higher than that of many of the 4-*n*-alkyloxy-1-naphthoic acids.

In the crystalline solids of the 4-*n*-alkyloxy-1-naphthoic acids the dimer may have either of the two extreme configurations(V and VI) shown below



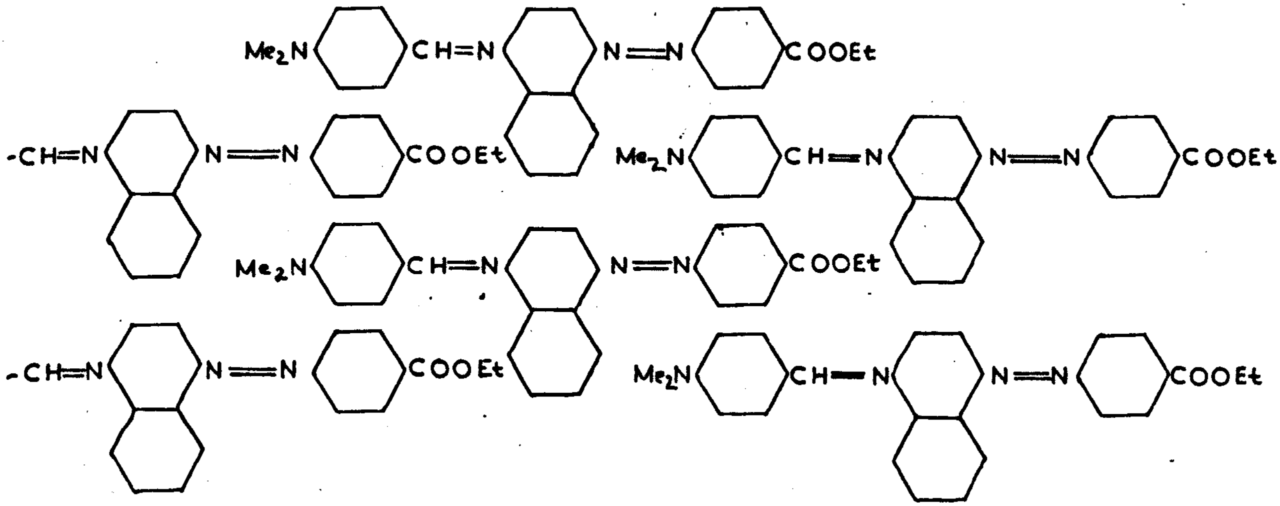
V



VI

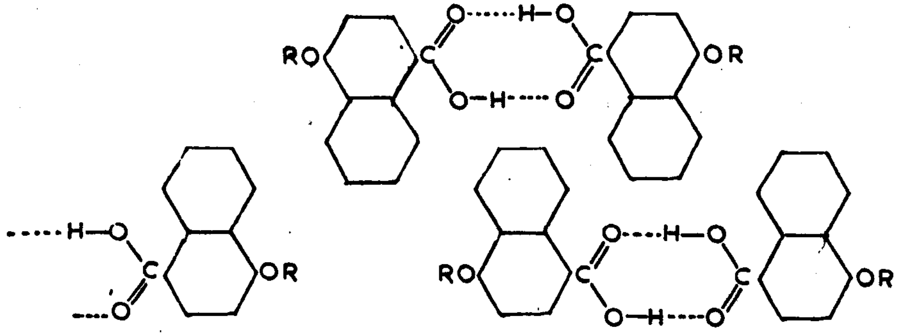
Configuration VI would give a very broad molecule, half as broad again as Vorländer's azo-anils, and, since it is possible that the molecular configuration of the solid is maintained when the lattice breaks down to give the mesophase or the amorphous liquid, this may account for the lack of mesomorphism. That is, the molecules are too broad to give a linear arrangement with sufficient cohesion to be maintained in the melt.

It may also be argued that V, although the same breadth as the azo-anil molecules, is less likely to give an ordered melt, since the molecules contain two broad naphthalene rings and not, as in Vorländer's compounds, only one which, in any case, is almost symmetrically placed in an otherwise long and narrow molecule. This means that the molecules of the acid dimers are more bifurcated, and less likely to give a packing in their melts suitable for the formation of a mesophase. Vorländer's compounds may conceivably pack together as follows

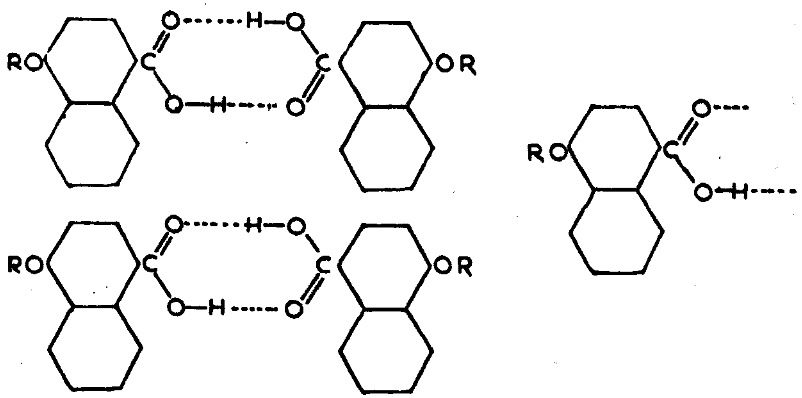


This,or some similar packing of the linear molecules,is possible and may well give considerable cohesion in the molten state because of the close proximity of all the parts of the molecules to one another.

On the other hand,molecules of type V are unlikely to give a closely interlocked packing which can repeat itself except, possibly,with the shorter chain ethers.Such a packing could be represented in the following way



With the longer carbon chains,the packing may be much more open and appear somewhat as follows



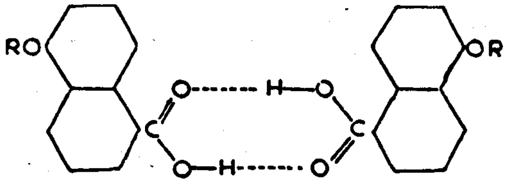
This may give sufficient lateral adhesion of the molecules in the crystal to give a reasonably high melting point,but in the molten state the open packing may make it possible for the molecules to swing round from their linear orientation and so to destroy the order.

In the 4-n-alkyloxy-1-naphthoic acids, there is an axis through the two -OR groups and the carboxyl group of the dimer, and another possible reason for the lack of mesomorphism in these acids may be in the rotation of the rings. In both of the extreme dimer types V and VI, such rotation will cause bifurcation of the molecules when the planes of the rings are not parallel. In both cases too, and particularly in type VI, the mechanical effect in disturbing any orientation will be very high, since the rotating naphthalene rings will act as paddles. This rotation of the naphthalene ring could also occur in Vorländer's azo-anils, but in these there is only one such ring and there is no other broad part of the molecule with which it can become out of phase. The mechanical effect of its rotation will also not be so great as that produced by two naphthalene rings in the dimerised naphthoic acids.

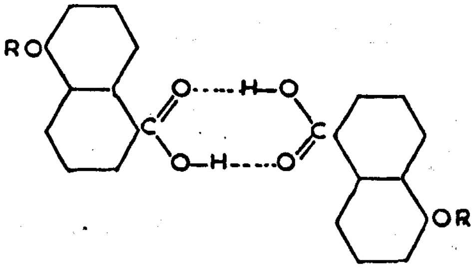
The explanation of the appearance of mesomorphism in Vorländer's compounds and the lack of anisotropy in melts of 4-n-alkyloxy-1-naphthoic acids requires a knowledge of the packing of the molecules in the crystals, and this can only be obtained by X-ray analysis.

The 5-n-alkyloxy-1-naphthoic acids are likewise not mesomorphic, and in this case the dimer may be represented by

VII or VIII



VII

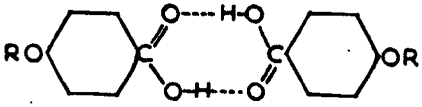


VIII

These alkyloxy acids, ranging from methyl to decyl, dodecyl, hexadecyl and octadecyl, again have reasonably low melting points which in themselves would be unlikely to mask the mesomorphism. The highest m.p. of 201° is found for the methyl ether, and the lowest of 117.5° for the hexadecyl ether. When the melting points are plotted against the number of carbon atoms in the alkyl chain their positions are irregular and two melting point curves are not present. The reasons for the absence of mesomorphism are therefore probably those which obtain in the isomeric 1:4 series. Again, such a dimer as VIII may be too broad to give a linear, ordered packing in the melt. The bifurcation in the dimer VII may mean that when the lattice breaks down the molecules are in such an open packing that the cohesive forces operate only at certain points and not along the entire length of the molecules. These are not strong enough to preserve a suitable orientation for anisotropy to result.

In this series it is seen that there is no axis through the two -OR groups and the dimerising carboxyl group.

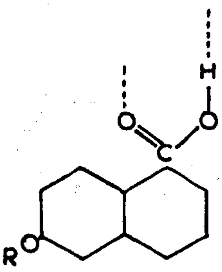
Therefore, irrespective of whether the dimer is of type VII or VIII, if rotation occurs about either of the ring-carboxyl bonds, the molecule will assume a highly bifurcated structure. This will not only destroy order in the melt but will also cause a mechanical disturbance to any order while the rotation occurs. In a strictly linear dimer, such as is present in the p-n-alkyloxy benzoic acids(IX),



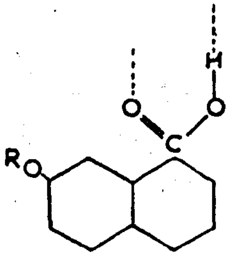
IX

it can be seen that rotation will not affect the packing of the rod-like molecules, since there will be little mechanical disturbance, and the dimer will not become bifurcated.

In the light of these results for the 4- and 5-n-alkyloxy-1-naphthoic acids, the remaining five possible alkyloxy-1-naphthoic acids were considered unlikely to give mesophases and these were not therefore synthesised. The 2-, 3- and 8-n-alkyloxy-1-naphthoic acids are analogous to ortho or meta substituted compounds which are known to have no mesomorphic properties, e.g., o- and m-n-alkyloxy benzoic acids show no mesomorphism. The 6- and 7-n-alkyloxy-1-naphthoic acids(X and XI) will give even greater branching and bifurcation in the dimers than the 5:1 compounds and would not therefore be expected to possess mesomorphic properties.

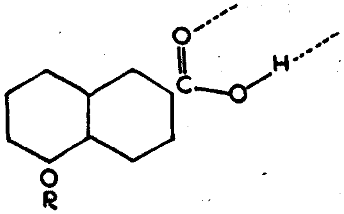


X



XI

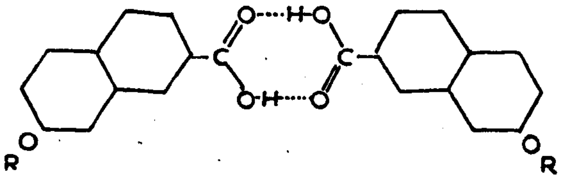
Similarly in the 2-naphthoic acids series,the 1-,3-,4- and 8-*n*-alkyloxy compounds are branched molecules similar to *ortho* or *meta* substituted systems and 5-*n*-alkyloxy-2-naphthoic acids(XII) will give a dimer which is far from linear.



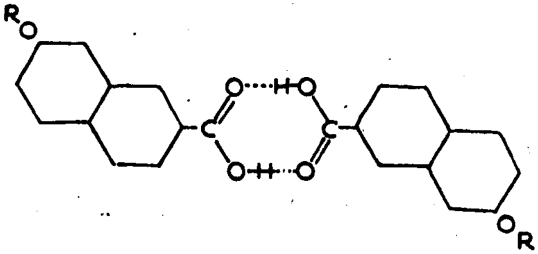
XII

The 7-*n*-alkyloxy- and 6-*n*-alkyloxy-2-naphthoic acids were the only two remaining naphthoic acids which seemed likely to be potential mesomorphic systems.

The 7-*n*-alkyloxy-2-naphthoic acids again have no axis through the -OR groups and the dimerising carboxyl group.Of the two extreme dimer configurations,XIII would be unfavourable to the orientation necessary in a mesomorphic melt,



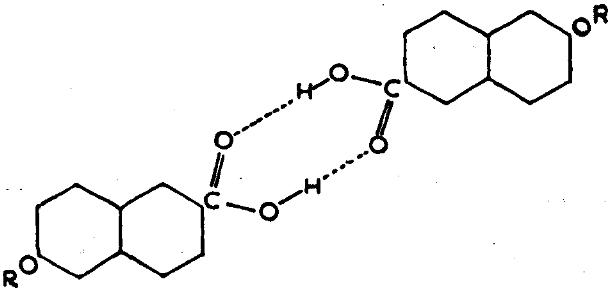
XIII



XIV

and XIV, although having the axes of the -OR groups approximately parallel, is also unlikely. Any free rotation in the melts of these acids will cause the system to lose any semblance of being rod-shaped, and it is not surprising therefore that the n-octyl and n-hexadecyl ethers, which were prepared and examined, are not mesomorphic. In this case too, the absence of mesomorphism cannot arise from high melting points for the n-octyl ether melts at 142.5° and the n-hexadecyl ether at 138°.

By contrast with the other n-alkyloxy naphthoic acids, the 6-n-alkyloxy-2-naphthoic acids seemed more likely to exhibit mesomorphism since they can give rise to a dimer with the rod-shaped configuration (XV) shown below.



XV

Although, unlike the dimers of the p-n-alkyloxy benzoic acids, this has no axis through the two -OR groups and the dimerising carboxyl group, there is a close approximation to one, but in such a molecule rotation may well cause considerable distortion. On the other hand, the dimer is long, narrow and essentially rod-shaped, and is obviously the most likely of the n-alkyloxy naphthoic acids to show mesomorphism. Indeed, the shortest molecule in this series, 6-methoxy-2-naphthoic acid, is mesomorphic, with a nematic phase length of 13° between 206° and 219°. The results for these 6-n-alkyloxy-2-naphthoic acids are summarised in graph 1 and table 1 (pages 30 and 31). The first eight members are all nematic, and, although there is no regular change in the phase lengths as the carbon chain increases in length, the melting points of these and of the whole series lie on two distinct curves (the red curves on the graph). That is, the upper clearing points alternate and lie on two curves which represent the odd and even carbon chain ethers. This suggests a packing of linear molecules with slight differences in the arrangement of the terminal groups for odd and even carbon chains(54). The fact that there is no regular increase in the nematic phase length with increase in the chain length was also found in the p-n-alkyloxy benzoic and trans-p-n-alkyloxy cinnamic acids. However, the very short phase length of 0.5° (208-208.5°) in 6-n-propoxy-2-naphthoic acid is outstanding.

At first sight, there seems to be no logical reason for this almost complete extinction of the mesomorphism, although narrowing of the phase length at n-propyl has been noticed to a lesser degree in certain series of n-alkyloxy anils which are at present being examined(55). It can only be concluded that the n-propyl chain favours some configuration which causes deviation from strict linearity in the dimer. Three possible configurations are shown in plates 7, 8 and 9.

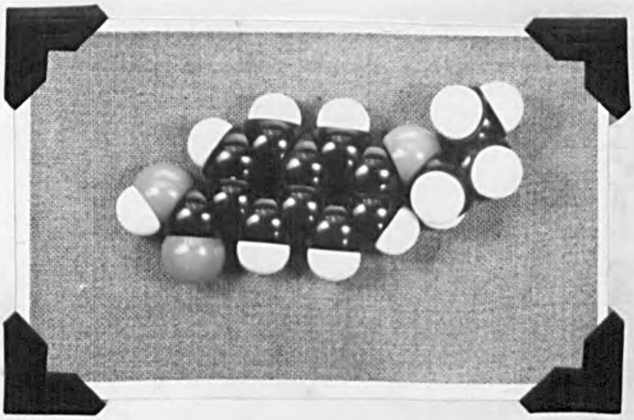


Plate 7

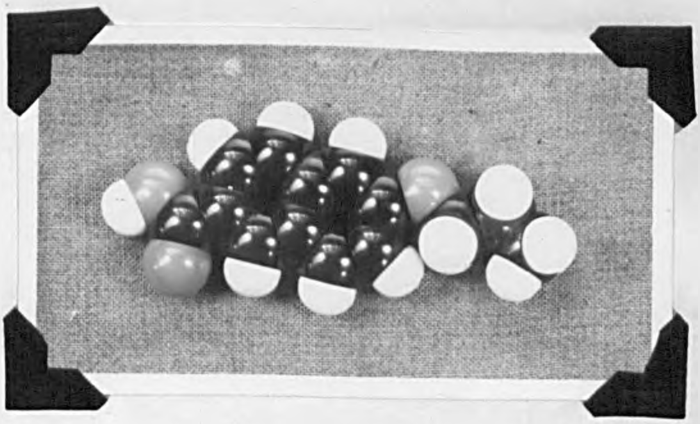


Plate 8

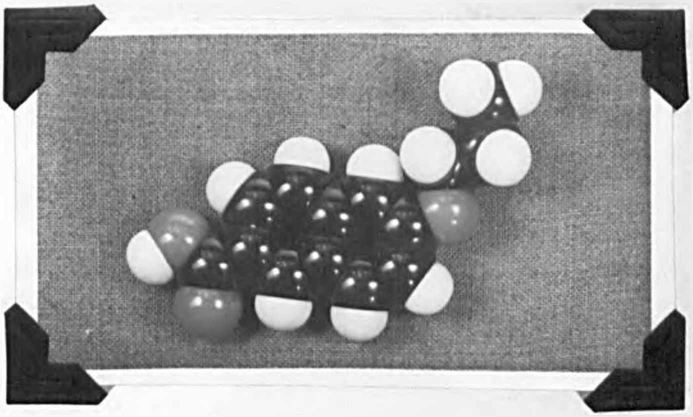


Plate 9

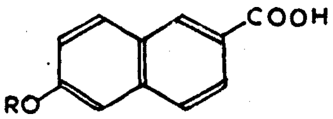
Configuration 7 would give a linear dimer which would be expected to be able to produce marked mesomorphism, whereas configurations 8 and 9 respectively would give increasing deviations from linearity. It need not be assumed that configuration 8 or 9 is suddenly assumed by n-propyl since the chain configurations in 7, 8 or 9 would give linear molecules in the methyl and ethyl ethers. It would, however, have to be assumed that the change to chain configuration 7 occurs in the n-butyl ether as a result of the addition of a further $-CH_2$ to n-propyl. This is not unreasonable since continuation of the chain types shown in plates 8 and 9 may be disfavoured in n-butyl and the higher ethers because the configurations involved may increase the potential energy of the system through preventing the closest packing. These and similar suggestions can only be tentative explanations. Definite evidence is required by X-ray methods of the crystal structure of 6-n-propoxy-2-naphthoic acid.

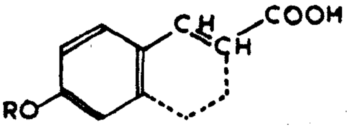
When the alkyl chain contains nine carbon atoms a short smectic phase appears in addition to the nematic phase.Further increments in the chain length increase the length of the smectic phase at the expense of the nematic phase,which decreases and is absent in the n-hexadecyl and n-octadecyl ethers.The increase in the smectic phase length is not entirely smooth and,indeed,that of the octadecyl ether is shorter(47°) than in the hexadecyl ether(52.5°).It is unlikely that this arises because the octadecyl ether has a smaller tendency to be mesomorphic.On the contrary,it is probably due to the increase in the transition point and the melting point of this particular ether.The values are 114° for the transition point and 161° for the melting point,compared with the corresponding values of 107° and 159.5° for the n-hexadecyl ether.The greater thermal agitation in the melt at the slightly higher temperatures may be sufficient to cause the order in the melt of the n-octadecyl ether to persist over a slightly shorter range.It is of course possible that with very long chains the system becomes more like a n-aliphatic acid,since the alkyl group is then the more preponderant part of the molecule.That is,the intermolecular forces which operate between the rings and the carboxyl groups of different molecules,will have to hold increasingly long molecules in position.This may cause a decrease in mesomorphism even in very long molecules.It is hoped in later investigations to determine whether this is so by preparing some *n*-alkyl ethers containing more than eighteen carbon atoms in a series which is known to be mesomorphic.

The sudden appearance of smectic properties at a certain alkyl chain length and finally the establishment of purely smectic properties in the higher ethers are characteristics of nearly all the series of mesomorphic compounds which have been examined.In such phases the molecules must lie parallel to one another with their ends in line as distinct from the parallel but imbricated orientation of molecules in a nematic melt.As the rather belated appearance of smectic properties is a common feature of all series,the origin of the smectic phase in a particular series will be examined later in this discussion.

2. trans-p-n-Alkyloxy cinnamic acids

That the molecules of 6-*n*-alkyloxy-2-naphthoic acids should exhibit mesomorphism is not surprising when the similarity of their structure to the mesomorphic *trans*-*p*-*n*-alkyloxy cinnamic acids is considered.This is particularly clear when the structures are drawn as follows.





The cinnamic acids differ only in the absence of the section of the naphthalene ring represented by the dotted lines. Indeed the similarity is so close that the behaviour of analogous members of the two series might well be expected to be identical. When the results published by Bennett and Brynmor Jones(6) were compared with those obtained for the 6-n-alkyloxy-2-naphthoic acids, very pronounced differences were observed. The three main points of difference are (1) in the cinnamic series there is no alternation of the upper transition points to give two curves for odd and even carbon chain ethers, (2) the n-hexadecyl ether has a short nematic phase in addition to the smectic phase and (3) the enantiotropic smectic phases do not appear until the n-decyl ether, although a monotropic smectic phase was reported for the n-nonyl ether. The above authors did not prepare the n-octadecyl ether and its preparation was undertaken to complete the series. The ether melts to a smectic state at 121° and clears at 158° without showing a nematic phase. This behaviour is in agreement with the purely smectic properties of 6-n-octadecyloxy-2-naphthoic acid, but the low m.p. of 121° seemed out of place when compared with the value reported for the lower n-hexadecyl ether in the cinnamic acid series. In order to establish this point, new samples of a number of trans-p-n-alkyloxy cinnamic acids were prepared. The results are shown in graph 9 (page 47) and in table 11 (page 69). For comparison, the transition points previously reported(6) are given in table12.

Table 11   trans-p-n-Alkyloxy cinnamic acids

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	171°	187°	—	16°
Ethyl	—	191.5°	196°	—	4.5°
Propyl	—	165°	182°	—	17°
Butyl	—	154°	186°	—	32°
Amyl	—	138°	176°	—	38°
Hexyl	—	153°	178°	—	25°
Heptyl	—	148°	174°	—	26°
Octyl	—	147°	170°	—	23°
Nonyl	138.5°	144°	170.5°	5.5°	26.5°
Decyl	134°	150.5°	165°	16.5°	14.5°
Dodecyl	132°	157°	162°	25°	5°
Hexadecyl	118.5°	—	159°	40.5°	—
Octadecyl	121°	—	158°	37°	—

Table 12 trans-*p*-*n*-Alkyloxy cinnamic acids Bennett,Jones(6)

	Temperature of transition to			Phase length	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	171°	187°	—	16°
Ethyl	—	191.5°	196°	—	4.5°
Propyl	—	165°	182°	—	17°
Butyl	—	154°	186°	—	32°
Amyl	—	138°	176°	—	38°
Hexyl	—	153°	182°	—	29°
Heptyl	—	150°	157°	—	7°
Octyl	—	147°	164°	—	17°
Nonyl	—	141°	163°	monotropic	22°
Decyl	133°	144°	163°	11°	19°
Dodecyl	132°	145°	153°	12°	8°
Hexadecyl	132°	154°	158°	22°	4°
Octadecyl	—	—	—	—	—

When the graph and these new transition points for the trans-p-n-alkyloxy cinnamic acids are compared with the graph and table of results (pages 30 and 31) for the 6-n-alkyloxy-2-naphthoic acids, the behaviour of the two series is found to be the same. In both, the first eight members are nematic, smectic properties first appear in the nonyl ether and occur with a nematic phase in the nonyl, decyl and dodecyl ethers, the hexadecyl and octadecyl ethers are purely smectic, and the upper clearing points now alternate regularly and lie on two curves for odd and even carbon chain ethers.

In these principal characteristics the parallelism between the two series is now very good. It was not expected that the agreement would be any closer than this and that, for example, the phase lengths would be identical for analogous ethers, or that the maximum phase lengths would occur at the same alkyl group in each series. The naphthoic acids, containing two naphthalene rings, will have different intermolecular cohesive forces from those in the cinnamic acids. On the whole, it might be expected that the cohesive forces would be stronger in the naphthoic acids and that their melting points would be higher. This is true in nine of the thirteen ethers examined, but probably other factors, such as the type of packing in the crystal lattice, will also have significant effects on the melting point. If the cohesive forces are stronger in the naphthoic acids, then the order in the mesophase should also require more energy to break it down. The transition points should therefore be higher. Indeed, in all cases the clearing points for the cinnamic acids are lower than for the corresponding naphthoic acids. This does not mean that the phase lengths of the naphthoic acids are always longer than the cinnamic acids, since the thermal effects at the higher temperatures will be greater in the former series and will cause the order to break down more quickly. The result is that in only ten of the naphthoic acids are the overall phase lengths longer than in the cinnamic acids. Further, a maximum phase length of 51.5° is found in 6-n-hexyloxy-2-naphthoic acid and of 38° in trans-p-n-amyloxy cinnamic acid.

In the series of cinnamic acids, there is no shortening of phase length at n-propyl and the short phase length of 4.5° in the ethyl ether is no doubt due to the sudden rise in the m.p. of this ether to 191.5°. In both cases, i.e., in the naphthoic and cinnamic series, the octadecyl ethers have shorter phase lengths than the hexadecyl ethers, and, as has been pointed out for the naphthoic acids, this is probably due to the slight rise in melting point.

The values obtained for the cinnamic acids in the present investigation agree exactly with those obtained by Bennett and Brynmor Jones for the first five members of the series. Thereafter, discrepancies of varying order are found. The reason for this was not clear until some of the original samples used by these authors were examined, when in many cases they were found to have lost almost all their mesomorphic characteristics. The nonyl ether, reported to have m.p. 141°, clearing point 163°, was found to melt to an amorphous liquid over the range 137-141°. On cooling, the melt slowly gave a turbid mesophase at 141-139° and crystallised at 137°. Moreover, mounted samples of the ethers prepared for this investigation were found to lose their mesomorphism when the sample was left to stand (the deterioration in sunlight was very rapid). It was also noticed that when samples were reheated they contained bubbles of gas. Such behaviour immediately suggests decarboxylation and this may be one reason for the disappearance of mesomorphic properties. It is possible that this occurs more readily in the longer chain ethers for which the discrepancies were found. Loss of carbon dioxide by substituted cinnamic acids is not uncommon and seems most liable to occur when more than one alkyloxy- group is present. 2:4-Di-methoxy cinnamic acid has been found to decarboxylate very readily. Professor Brynmor Jones has indeed verified that the samples used in his investigation may have been exposed to light during examination of their mesomorphic properties. Not only will the loss of carbon dioxide destroy the ability to dimerise and produce long molecules, but also, even although decarboxylation is slight, the styrenes produced will polymerise and cause depression of the melting point of the cinnamic acid. That light can have this effect on the transition points was confirmed in the case of trans-p-n-octadecyloxycinnamic acid. The constants for the freshly prepared material were 120.5° and 158°, but when the specimen (in a corked tube) had been exposed to ordinary light for three months these had fallen to 117° and 151-154°. The upper clearing point was so indefinite that, had the ether not been known to be purely smectic, the presence of a short nematic phase between 151° and 154° might have been expected. Such behaviour may well account for the reported observation of a short nematic phase in the hexadecyl ether which, when freshly prepared, has been found to be purely smectic.

Heating for quite short periods of time was also found to be detrimental to these ethers. The pure n-heptyl ether, with constants of 148° and 174°, was heated in an oil bath for one hour. On cooling, the nematic melt crystallised to a soft solid mass which suggested that polymerisation by decarboxylation had occurred to some extent. This material melted at 142-146°, and cleared indefinitely at 170-172°. The n-nonyl ether, with constants of 138.5°, 144° and 170.5° was much more affected by similar treatment and the crystals obtained on cooling were quite brown. When a thin film of this material was mounted on a slide and allowed to cool from the isotropic liquid, the smectic phase seemed to have decreased in length and all the changes were indistinct.The crystals softened at 126°,and flowed at 136° to a turbid melt which cleared at 157-164°.That is,no smectic phase was detectible on heating -which agrees with the report of a monotropic smectic phase in the n-nonyl ether(6).It is probable,therefore,that heating had a considerable effect on the ethers during the actual measurements made by Bennett and Brynmor Jones(6).As is described in the discussion of the methods of determining mesomorphic transition points,their procedure involved heating the samples,cooling them,and observing the number of transitions.This treatment was repeated several times, until at a certain temperature,the transition under consideration just failed to appear.It is clear now,that these successive heatings must have led to loss of carbon dioxide. In the present investigation,a fresh slide was mounted for each determination of a transition point,the instrument being pre-heated to some 5° below the approximate value as determined in an ordinary melting point apparatus,and the slide inserted and heated at a rate of 2° per minute until the transition occurred.In this way,a sample was exposed to the high temperatures for 2-3 minutes at the most and the risk of decarboxylation thereby reduced to a minimum.

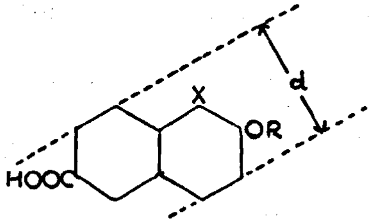
Some of the less significant differences in the constants may be due to the method of preparation of the trans-p-n-alkyloxy cinnamic acids.A specimen of n-octadecyl ether was prepared by alkylation of trans-p-hydroxy cinnamic acid, the method adopted for the whole series by Bennett and Brynmor Jones, but before the constant values of 121° and 158° were obtained, it was necessary to crystallise it twice from 98% acetic acid, thrice from benzene, and twice from absolute ethyl alcohol. The same compound, with the same constants, was obtained after only two crystallisations from glacial acetic acid when it was prepared by condensing p-n-octadecyloxy benzaldehyde and malonic acid in pyridine (with piperidine as catalyst). That a much less readily purified material is obtained by the alkylation method was verified in two other cases.

The close similarity in behaviour of these cinnamic acids and naphthoic acids verifies that mesomorphic behaviour is indeed a function of structure, and that similarity in structure can be taken as a criterion of similarity in mesomorphic behaviour.

3. The effect of broadening the molecules of 6-n-alkyloxy-2-naphthoic acids

(a) by substitution in the 5-position

6-Hydroxy- and 6-n-alkyloxy-2-naphthoic acid will substitute readily in the 5-position to yield molecules of structure XVI.



XVI

From this structure it can be seen that the breadth of the molecule is determined by the dotted lines and that there is a space between the uppermost of these lines and the 5-carbon atom.This space is such that certain substituting atoms may be accommodated without broadening the molecule.From scale drawings and models of these molecules,calculations were made to find what effect such substituents as the halogens and the nitro- group would have on molecular breadth.

Table 13

Substituent X	Covalent radius (A°)	van der Waal's radius (A°)	Breadth "d" in (A°)	Approach of X to upper line (A°)
H	0.30	1.2	7.9	-1.2
F	0.64	1.35	7.9	-0.73
Cl	0.99	1.80	7.9	0.0
Br	1.14	1.95	8.20	+0.30
I	1.33	2.15	8.59	+0.69
NO_2	———	———	8.38	+0.48

The figures in table 13 make it clear that 5-fluoro-6-n-alkyloxy-2-naphthoic acids will be no broader than the unsubstituted acids,and that even chlorine may be introduced without affecting the molecular breadth.In the case of the 5-chloro- compound,the outermost point on the circle representing the van der Waal's radius of the chlorine atom lies on the dotted line which represents one perimeter of the molecule.The 5-bromo- and 5-iodo-6-n-alkyloxy acids will however be increasingly broad,and will be 0.3 and 0.69 Å respectively broader than the unsubstituted, the 5-fluoro- or the 5-chloro-6-n-alkyloxy-2-naphthoic acids. The effect of a NO_2 group was obtained by drawing the planar nitro- group to scale in the 5-position of a scale drawing of a 6-n-alkyloxy-2-naphthoic acid.In this way,the maximum amount by which the group will project beyond the dotted line was measured as 0.48 Å ,so that the molecular breadth will be 8.38 Å .The nitro- group will therefore affect the breadth of the system to a degree intermediate between a bromine and an iodine atom.Plates 10,11 and 12 show scale models of 5-chloro-,5-bromo- and 5-iodo-6-n-butyloxy-2-naphthoic acids respectively.

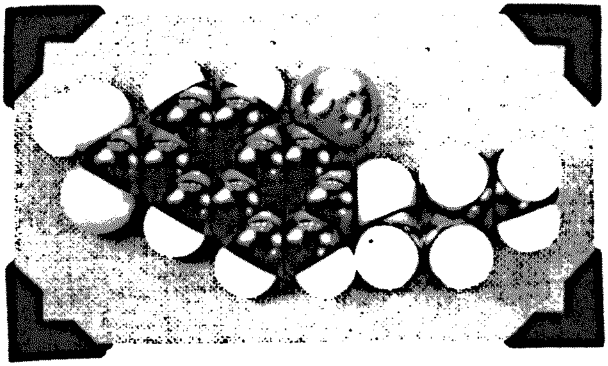


Plate 10

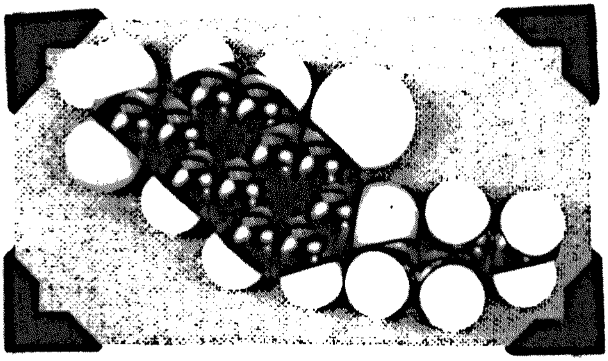


Plate 11

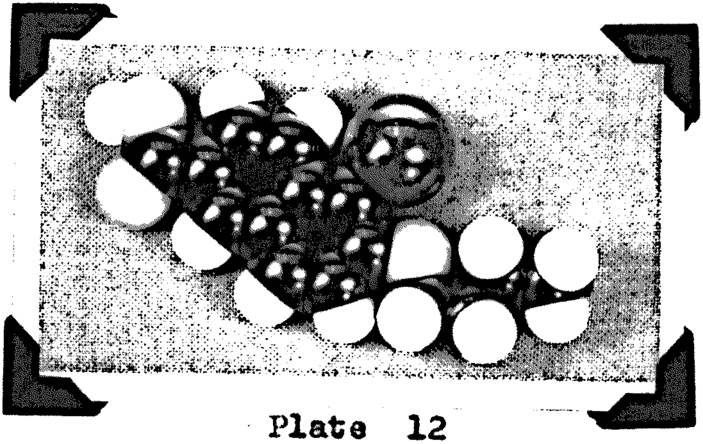


Plate 12

These substituted alkyloxy-naphthoic acids provide a means of investigating the effect of changes of breadth on mesomorphism. Thus, if breadth alone affects the mesomorphism, the 5-fluoro- and 5-chloro- compounds should behave in an identical manner to one another and to the unsubstituted 6-n-alkyloxy-2-naphthoic acids. Unfortunately, synthetic difficulties made it impossible to prepare the 5-fluoro- compounds, but the series of thirteen 5-chloro-6-n-alkyloxy-2-naphthoic acids was obtained. The melting point and transition point values for this series are summarised in table 2 and graph 2 (pages 32 and 33). The methyl and ethyl ethers are not mesomorphic: the first nematic phase occurs in the n-propyl ether. As usual, smectic properties are not found until later in the series, in this case in the n-hexyl ether, so that the n-propyl, n-butyl and n-amyl ethers are purely nematic. The n-hexyl ether has the maximum nematic phase length of 41° and a short smectic phase of 2°. As the length of the n-alkyl chain increases the smectic phase length gradually increases, while the nematic phase decreases in length and finally vanishes in the purely smectic hexadecyl and octadecyl ethers which have the same phase length of 36°.The upper transition points to the isotropic liquid for this series again lie on two distinct curves for odd and even carbon chain ethers.

There are,therefore,points of similarity and points of difference between the 5-chloro- acids and the unsubstituted acids,although for one particular alkyl group the two compounds will have the same length:breadth ratio.Obviously, some other factor,other than the molecular dimension,is operative,and this must be the cohesive forces which operate between molecules and which will undoubtedly be different for the two series.In the 5-chloro- compounds,the halogen atom will be able to approach a neighbouring molecule more closely than will the hydrogen atom in the 5-position of the unsubstituted compounds.It would therefore be reasonable to infer that the cohesive forces will be stronger in the chloro- compounds and that they will have higher melting points.Since the cohesive forces operate mainly between the aromatic parts of the molecules,these forces will become weaker per unit length of the molecule as the alkyl chain length is increased,and this is reflected in the general fall in melting point along a series.This is true in both series,and the melting points fall from the lower to the higher ethers with certain alternations for odd and even carbon chains.In all cases the m.p. values are higher for the 5-chloro- compounds and the differences are listed in table 14.

Table 14

n-Alkyl group	m.p. in 6-n-alkyloxy-2-naphthoic acids	m.p. in 5-chloro-6-n-alkyloxy-2-naphthoic acids	Difference
Methyl	206°	320.5°	114.5°
Ethyl	213°	269°	56°
Propyl	208°	219.5°	11.5°
Butyl	198°	209.5°	11.5°
Amyl	179.5°	189°	9.5°
Hexyl	147°	164°	17°
Heptyl	163°	165.5°	2.5°
Octyl	161.5°	169°	7.5°
Nonyl	146.5°	169°	22.5°
Decyl	139°	167°	28°
Dodecyl	119°	152°	33°
Hexadecyl	107°	142.5°	35.5°
Octadecyl	114°	138.5°	24.5°

It is doubtful whether any significance can be attached to the trend of the differences in the m.p. values without some knowledge of the crystal lattices of the individual members,since the manner of packing of the molecules will affect the cohesive forces and therefore the m.ps.The fact remains however that in all cases the chloro- compounds melt higher,and in the case of the first two,where no mesomorphism is found the melting points are very high.That is,although 5-chloro-6-methoxy and 5-chloro-6-ethoxy-2-naphthoic acids have molecular dimensions siutable for mesomorphism,the thermal agitation at the temperatures required to break down the crystal lattice nullify any tendency to orientation in the melt.The point at which mesomorphism commences in the two series can therefore be understood in terms of melting point differences.A further difference occurs in the point in the series at which smectic properties first appear,this being at n-nonyl in the unsubstituted compounds and at n-hexyl in the 5-chloro- compounds.Later in this discussion,the factors which may determine when smectic properties appear in a series will be discussed but for the moment all that need be said is that it is thought that melting point is not so important as the actual packing of the molecules in the solid lattice.Thus,although the unsubstituted and the 5-chloro-compounds will give the same rectangular projection,it is likely that,in the closely packed solids,differences will occur in the packing due to the presence of the larger chlorine in the 5-position.Since the type of packing in the solid probably determines the type of mesophase which is first formed,this difference in the point of origin of smectic properties may not be as anomalous as appears at first sight.

The two series are similar in that both give alternation of the upper transition points.These lie on two curves for the odd and even carbon chain ethers,and the last two members of the series (the C_{16} and C_{18}) are purely smectic.

The phase lengths of the respective members of the series are not in a simple ratio to one another nor to the melting points involved. This is evident from the list of melting points and total phase lengths given in table 15.

Table 15

n-Alkyl group	5-Substituent=H		5-Substituent=Cl	
	m.p.	Phase length	m.p.	Phase length
Methyl	206°	13°	320.5°	——
Ethyl	213°	11°	269°	——
Propyl	208°	0.5°	219.5°	1.0°
Butyl	198°	10.5°	209.5°	7.0°
Amyl	179.5°	19.5°	189°	19°
Hexyl	147°	51.5°	164°	43°
Heptyl	163°	29°	165.5°	35.5°
Octyl	161.5°	28.5°	169°	28.5°
Nonyl	146.5°	37°	169°	25.5°
Decyl	139°	42°	167°	25.5°
Dodecyl	119°	55°	152°	35.5°
Hexadecyl	107°	52.5°	142.5°	36°
Octadecyl	114°	47°	138.5°	36°

Reviewing these figures, it can be seen that in ten of the thirteen acids the overall phase length is less in the 5-chloro- compounds than in the unsubstituted acids which have considerably lower melting points. In the majority of cases, the shorter phases may be attributed to the greater thermal agitation which overcomes the stronger cohesive forces in the mesophases of the chloro- compounds. In the case of the heptyl and octyl ethers, the melting points of the chloro- compounds are only very slightly greater than those of the unsubstituted ethers and the phase lengths of the former are either greater or equal to the phase lengths of the latter. This would again indicate stronger cohesive forces in the chloro- compounds, such that, in approximately the same temperature range, the stronger cohesive forces between molecules containing chlorine are more able to withstand the same or even slightly greater thermal agitations than the unsubstituted compounds. That is, the effect of the cohesive forces predominates in these cases, and the chloro- compounds have the same or longer phase lengths at the higher temperatures.

Only the n-propyl ether remains to be discussed and this has a phase length which is twice as long in the 5-chloro- compound as it is in the unsubstituted molecule. It has already been explained that the latter is anomalous and three possible orientations of the alkyl chain (plates 10, 11 and 12, pages 64 and 65) have been suggested. Of these, the structure represented in plate 12 is the most likely to destroy or reduce the mesomorphism. In the 5-chloro- compounds, however, this orientation of the chain is unlikely due to the steric effect of the chlorine atom, and the chain may be forced into configurations of the kind shown in plates 10 and 11.These orientations of the propyl group will give a linear molecule, and the larger phase length in 5-chloro-6-n-propoxy-2-naphthoic acid,at a higher temperature,may be explained on these grounds.

At first sight then,these two series of acids should give identical results because of their identical molecular breadth,but differences in melting point and packing are other possible factors which are obviously of importance and can give rise to differences in behaviour.The effect of temperature on mesomorphism is thus shown to be very important and it explains why a mixture of p-methoxy- and p-ethoxy benzoic acids exhibit mesomorphism when the individual acids do not.This effect is explained entirely by the lower temperatures at which such a mixture melts.

There is therefore an inherent difficulty in comparing two series of mesomorphic compounds if the melting points vary from one to the other,and,of course it is not likely that two different series would have the same order of melting point throughout.However,it was found that the transition temperatures from the solid to the mesomorphic or isotropic states for the three series of 5-chloro-,5-bromo- and 5-iodo-6-n-alkyloxy-2-naphthoic acids are reasonably similar.This fact is made clear by the figures in table 16.This is particularly fortunate since there is a progressive increase in molecular breadth from chloro- to bromo- to iodo-, so that the differences may be attributed almost entirely to changes in molecular breadth, with only small fluctuations in phase length due to the differences in melting point.

Table 16

n-Alkyl group	Substituent in the 5-position		
	Cl	Br	I
	m.p.	m.p.	m.p.
Methyl	320.5°	303°(d)	296.5°(d)
Ethyl	269°	281°(d)	286.5°
Propyl	219.5°	224°	230°
Butyl	209.5°	213°	219°
Amyl	189°	196.5°	203°
Hexyl	164°	178°	191°
Heptyl	165.5°	158°	176°
Octyl	169°	164°	160.5°
Nonyl	169°	168°	163°
Decyl	167°	167°	165°
Dodecyl	152°	151.5°	146.5°
Hexadecyl	142.5°	138.5°	133.5°
Octadecyl	138.5°	136.5°	127°

Before comparing the three series, The individual characteristics of the bromo- and iodo- compounds will first be described.

5-Bromo-6-n-alkyloxy-2-naphthoic acids

The results for this series are summarised in table 3 and graph 3 (pages 34 and 35).The graph is very similar to that for the corresponding chloro- compounds.Mesomorphism is again first observed in the n-propyl ether,which has a transient nematic phase.The absence of mesomorphism in the methyl and ethyl ethers is again attributable to their high melting points and to their molecular breadth,which is of course greater in this series.Nematic properties alone are found until the alkyl chain contains 7 carbon atoms,when a short smectic phase appears in addition to the nematic phase.As the chain length is increased further,there is a gradual increase in the length of the smectic phase and a corresponding decrease in the nematic phase length,until the purely smectic n-hexadecyl and n-octadecyl ethers are reached.Again,the upper transition points lie on two distinct curves which represent the odd and even alkyl chains.

5-Iodo-6-n-alkyloxy-2-naphthoic acids

Table 4 and graph 4 (pages 36 and 37) summarise the results for this series.The greater molecular breadth,and the high melting points of the methyl,ethyl and n-propyl ethers, together account for the absence of mesomorphism in these three ethers.Thus,the n-butyl ether is the first to possess a phase which is nematic and very short.The nematic phase length then increases and reaches a maximum in the n-octyl ether. It is here too that a short smectic phase is found. With the growth in the length of the alkyl chain, the lengths of the smectic become greater, while the lengths of the nematic phase become gradually shorter. This again results in the *n*-hexadecyl and the *n*-octadecyl ethers becoming purely smectic in nature. The upper transition points fall as the length of the molecule increases and these points again lie on two curves representing the odd and even carbon chain lengths.

Table 17

n-Alkyl group	Length of mole. in Å (monomer)	Substituent					
		Cl		Br		I	
		Breadth in Å	Ratio	Breadth in Å	Ratio	Breadth in Å	Ratio
Methyl	13.02	7.9	1.66	8.2	1.59	8.59	1.52
Ethyl	14.3	7.9	1.81	8.2	1.74	8.59	1.66
Propyl	15.02	7.9	1.92	8.2	1.83	8.59	1.75
Butyl	16.3	7.9	2.06	8.2	1.99	8.59	1.90
Amyl	17.02	7.9	2.17	8.2	2.08	8.59	1.98
Hexyl	18.3	7.9	2.32	8.2	2.23	8.59	2.13
Heptyl	19.02	7.9	2.43	8.2	2.32	8.59	2.21
Octyl	20.3	7.9	2.57	8.2	2.48	8.59	2.36
Nonyl	21.02	7.9	2.68	8.2	2.56	8.59	2.45
Decyl	22.3	7.9	2.83	8.2	2.72	8.59	2.60
Dodecyl	24.3	7.9	3.08	8.2	2.96	8.59	2.83
Hexadecyl	28.3	7.9	3.58	8.2	3.45	8.59	3.3
Octadecyl	30.3	7.9	3.84	8.2	3.69	8.59	3.53

In these series, it is of interest to compare the relative length:breadth ratios for the various chloro-, bromo- and iodoalkyloxy naphthoic acids. These figures are summarised in table 17. The overall phase lengths in the three series are given in table 18.

Table 18

n-Alkyl group	Phase length of			n-Alkyl group	Phase length of		
	Chloro-	Bromo-	Iodo-		Chloro-	Bromo-	Iodo-
Methyl	—	—	—	Octyl	28.5°	31.5°	25°
Ethyl	—	—	—	Nonyl	25.5°	24.5°	19°
Propyl	1.0°	<0.2°	—	Decyl	25.5°	22.5°	14.5°
Butyl	7.0°	1.5°	<0.2°	Dodecyl	35.5°	32°	25.5°
Amyl	19°	10.5°	1.0°	Hexadecyl	36°	35°	31.5°
Hexyl	43°	26.5°	7.0°	Octadecyl	36°	36°	36°
Heptyl	35.5°	41°	13°				

In the three series, nematic properties begin at n-propyl in the chloro- and bromo- acids and at n-butyl in the iodo-acids. With the progressive broadening of the molecules, as a result of the increasing size of the substituting atoms, it might have been expected that the mesophases would make their first appearance later in the other series. This may well have been the case if molecular breadth were the only factor affecting mesomorphism. However, the temperature at which a compound melts is a further factor. The graphs show that in all three series the methyl and ethyl ethers melt at a much higher temperature than the other members of the series. There is a steep fall in the melting point curve at the beginning of the series. Although, therefore, 5-chloro-6-ethoxy-2-naphthoic acid may be capable of exhibiting mesomorphism as far as its molecular dimensions are concerned, its m.p. of 269° is high enough to involve rapid thermal agitation in the melt with the result that any molecular orientation is immediately destroyed. A further consideration is that the length:breadth ratios of the first three ethers which exhibit mesomorphism in the chloro-, bromo- and iodo- acids are 1.92, 1.83 and 1.90 respectively. The corresponding value for 5-chloro-6-ethoxy-2-naphthoic acid is only 1.81, which is probably too low for a compound which melts at 269°.

That broadening of the molecule does decrease the phase lengths and therefore the mesomorphism is shown in table 18. In eleven of the thirteen ethers, the phase lengths decrease in the chloro-, bromo- and iodo- ethers as the molecular breadth increases. The only exceptions are the heptyl and octyl ethers, which show an increase from chloro- to bromo- and, as expected, a decrease from bromo- to iodo-. It is difficult to account for this increase, because the decrease in melting point from chloro- to bromo- is only slight for these two ethers, and the thermal agitation in the melts of the chloro- and bromo- compounds will be very similar. Moreover, this anomaly occurs at the point in the series of bromo-compounds at which the maximum phase length appears and a big drop in the melting point from the hexyl to the heptyl ether is found. The heptyl ether is also the first bromo-compound to exhibit smectic properties, and it is possible that at this point in the series there is a difference in the nature of the packing of the molecules in the crystals. Later in this discussion it is suggested that the appearance of smectic properties in a series of compounds may coincide with the occurrence of a different packing in the crystal lattices,and,as this change may occur at different points in the three series of halogeno- compounds,it may well account for the partial deviations in the general trend of decreasing mesomorphism with increasing molecular breadth. Such discrepancies again emphasise how several different factors may well influence the mesomorphic behaviour of a series of compounds.

In addition,the maximum phase lengths which appear in the three series below dodecyl decrease in the order chloro- to bromo- to iodo- and are 45°,41° and 25° respectively.These maxima occur one unit of the alkyl chain later in the three series of ethers at hexyl,heptyl and octyl respectively.With regard to the possibility that a change in the nature of the crystal packing occurs when smectic properties appear in a series,it is interesting to note that these maximum phase lengths,which are equivalent to a large drop in melting point,are found in these ethers which are the first in the series to exhibit smectic properties.A lattice change coinciding with the appearance of smectic properties may therefore be a possibility.The beginning of smectic properties in the series is therefore stepped back one unit of the alkyl chain with increasing molecular breadth,and this contrasts with the origin of nematic phases,where the stepping back is not regular due to fluctuations in the melting points for the three series.The following figures show that the melting points can have little or no effect on the appearance of smectic properties,but that this must be determined by the breadth of the molecules affecting the packing in the crystals.

Substituent	First ether to be smectic	m.p.	Length:breadth ratio
Cl	hexyl	164°	2.32
Br	heptyl	158°	2.32
I	octyl	160.5°	2.36

It is observed that,although nematic and smectic properties appear at different points in the three series,and the general tendency is for the phase lengths to decrease from chloro- to bromo- to iodo-,the last ether in each series to show nematic properties is dodecyl.Further,the octadecyl ethers have the same smectic phase length of exactly 36°.It would appear therefore that in the case of the longer molecules the effect on the mesomorphism of increasing the breadth is less marked than for the shorter molecules.This would be expected from a purely dimensional viewpoint.The octadecyl ethers in particular are so long that small changes in the breadth have little or no effect and a constant phase length is achieved despite variations in the substituent.

5-Nitro-6-n-alkyloxy-2-naphthoic acids

In this series no mesomorphism is detected until the alkyl group is increased to nonyl, and this ether has only a very short nematic phase persisting over 0.5°. The decyl ether is likewise nematic with a phase length of 1.5°. Thereafter in the dodecyl, hexadecyl and octadecyl ethers smectic and nematic phases are exhibited. The smectic phases increase in length with increasing number of carbon atoms in the alkyl chain. The complete series of ethers was not prepared but a sufficient number were examined to establish that the upper transition points of the even carbon chain ethers lie on a curve. Only three of the odd carbon chain ethers were however prepared.

In this series there is a considerable reduction in the mesomorphism compared with the 5-halogeno- compounds. This is seen by the absence of mesomorphism in the first eight members and by the shortness of the phases. A maximum overall phase length of only 8° is found in the octadecyl ether — despite the fact that the breadth of the nitro- compounds is intermediate to the breadth values for the bromo- and iodo- compounds. The extremes of the length:breadth ratios are given below.

n-Alkyl group	5-bromo-	5-nitro-	5-iodo-
Methyl	1.59	1.55	1.52
Octadecyl	3.69	3.62	3.53

Some other factor must therefore cause the unexpected diminution in mesomorphism and the effect of temperature must first be considered. Table 19 makes it possible to compare the lower transition points for the three series.

Table 19

n-Alkyl group	5-bromo-	5-nitro-	5-iodo-
Amyl	196.5°	211°	203°
Octyl	164°	187°	160.5°
Nonyl	168°	174.5°	163°
Decyl	167°	173.5°	165°
Dodecyl	151.5°	167°	146.5°
Hexadecyl	138.5°	160°	133.5°
Octadecyl	136.5°	152°	127°

Solely from the standpoint of molecular dimensions, the nitro- compounds would be expected to behave in a manner intermediate between the bromo- and iodo- compounds. For example, the n-propyl or n-butyl ether might have been expected to be the first to exhibit mesomorphism. It is evident from table 19 however that the 5-nitro- derivatives melt considerably higher than the 5-bromo- and 5-iodo- compounds, so that thermal agitations in the melts of the nitro- compounds will be greater. This will tend to diminish the mesomorphism, but, since the melting points are not markedly higher, this cannot be the sole reason for the deferment of mesomorphism until the n-nonyl ether and the shortening of the phases to such a marked degree. Some other property, other than an increase in molecular breadth and melting point, must be conferred on the molecule of the alkyloxy naphthoic acid by introduction of the nitro- group. This is probably stereochemical in character.

Models of the 5-nitro- compounds show that the nitro- group cannot lie in the plane of the naphthalene ring system without involving substantial strain in the molecule. The strain involved is so large that it seems more than likely that the hydrogen on the α-carbon atom in the ring maintains the plane of the nitro- group at an angle to the plane of the rings. Plate 13 shows the orientation of the nitro- group relative to this hydrogen atom.

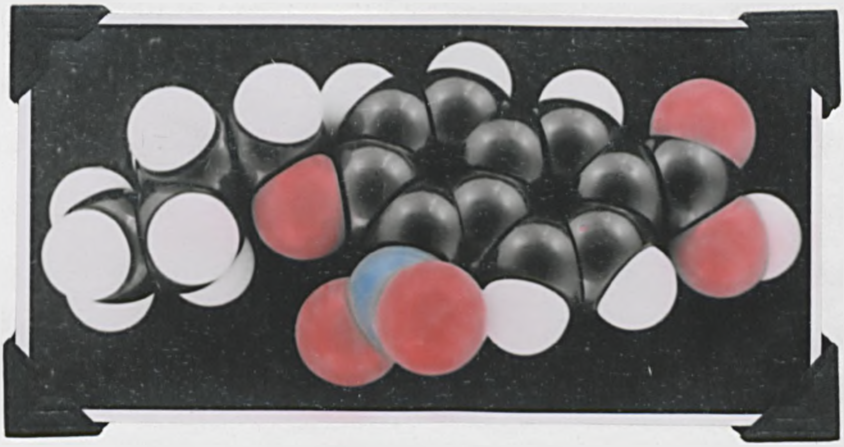


Plate 13

This means that the thickness of the molecules is increased to an extent that would prevent them from lying in parallel planes unless they are some distance apart. Because of the dipole of the nitro- group the cohesive forces between neighbouring molecules in one plane may be high, but between molecules in different planes they may be low. This would account very well for the relatively small difference in melting point between the nitro- and the bromo- and iodo-compounds.Furthermore,the greater intermolecular spacing between the planes would result in a decrease in adhesion in the mesophase so that random orientation in the melt would be more easily brought about.The rotation moment in the dimer would also cause the layers to slide over one another so that the orientation in one would not be that in the next layer.Such factors would cause a lesser degree of mesomorphism than would be expected at first sight.

The persistence of nematic properties even in the hexadecyl and octadecyl ethers may be due to a similar cause.If we assume that in the smectic mesophase we have numbers of micelles in which the molecules are arranged as in fig. 4(a), then two conditions may occur on further heating.Firstly,if, as will be the case in the nitro- compounds,the cohesion between the planes of the molecules is weak,then as the temperature rises,and the cohesion further decreases,the molecules may slide over one another to give an imbricated structure such as is proposed for nematic substances — fig 4(b).In other series,cohesion between the planes and the sides of the molecules may both be high,so that the first breakdown may occur at the ends of the dimer,and cause a sliding of the layers,as distinct from a sliding in a layer. Fig. 4(c) would represent such behaviour and the result would be equivalent to a smectic phase,which would disintegrate completely on further heating without necessarily passing through a nematic condition.Except in the case of the nitro-compounds,in which the interplanar cohesion will be low,this last state of affairs will be most likely to arise in the longer chain ethers,where interlocking of the chains may give a resistance to sliding of the molecules along their length.

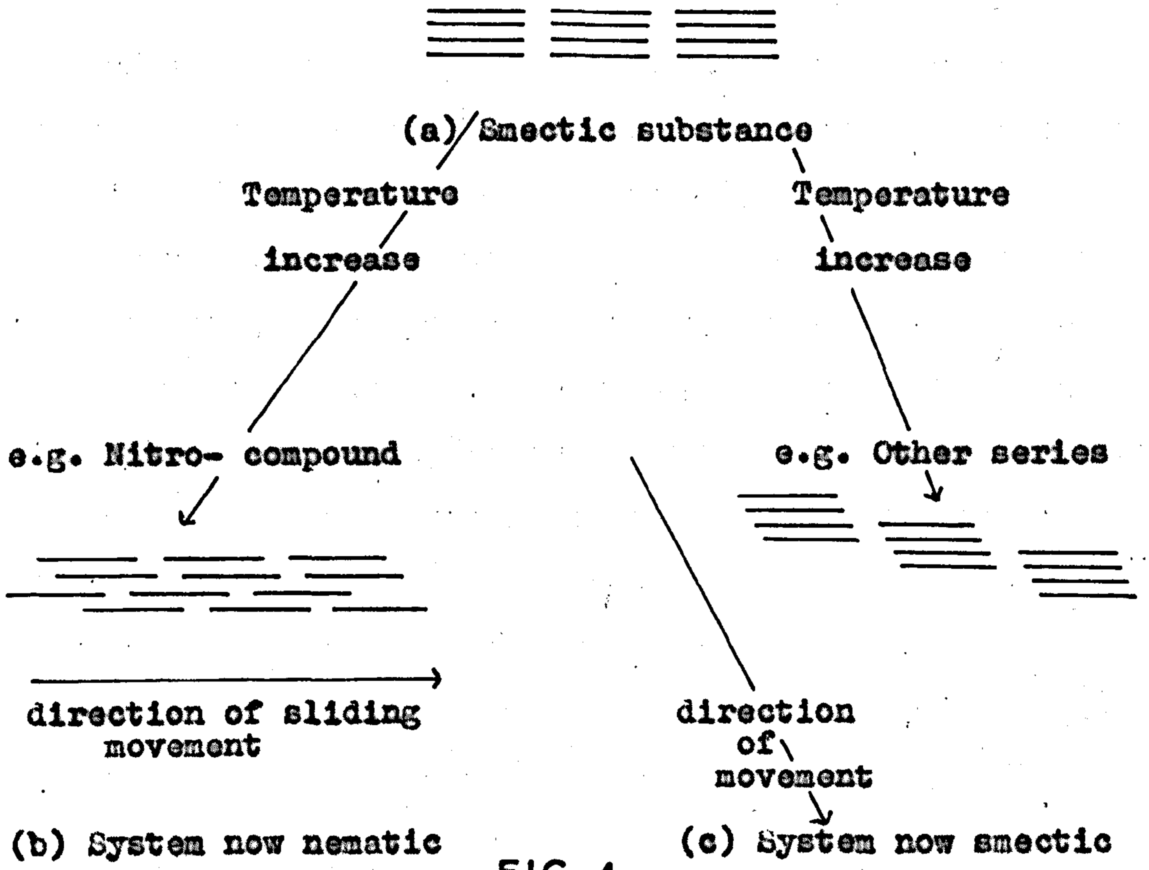
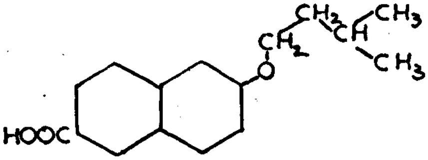


FIG. 4

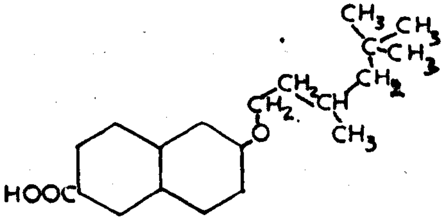
The behaviour of other series of nitro- compounds would be interesting in order to establish whether these results are reproduced.However,the production of a molecule in which the nitro- group is forced out of the plane of the rings and yet is capable of giving mesomorphism,will not often arise.

(b) *By replacing the n-alkyl group by branched groups*

The pronounced mesomorphic properties of the 6-*n*-alkyloxy-2-naphthoic acids are well emphasised by the study of the effect of substitution in the 5-position.However,when the *n*-alkyl group is replaced by a secondary alkyl group, as in *iso*-propyl ethers,the mesomorphic characteristics are greatly reduced or destroyed.It can be understood that the effect of branching in the alkyl group will have a greater effect than substitution in the 5-position,since the branching will force the molecules apart by preventing the close packing of the alkyl groups which is possible in the normal ethers.Thus,the *iso*-amyl ether,6-(3-methyl-butyloxy)-2-naphthoic acid (XVII) shows only a very short nematic phase between 194° and 194.5°,and the *iso*-nonyl ether,6-(3:5:5-trimethyl-hexyloxy)-2-naphthoic acid(XVIII) melts to an isotropic liquid at 170°.



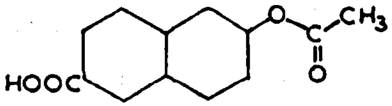
XVII



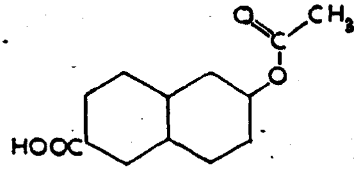
XVIII

The 6-*iso*-propoxy- and 6-(2-methyl-propoxy)-2-naphthoic acids are also non-mesomorphic,and melt to the isotropic liquid at 215° and 200° respectively.Only the broadening of the molecules and the prevention of close packing can account for the marked diminution in mesomorphic behaviour.

The acetate of 6-hydroxy-2-naphthoic acid has m.p.228°, and exhibits no mesomorphism, although the molecule will have the same length as 6-ethoxy-2-naphthoic acid — which has a nematic phase of 11° ,from 213° to 224°. The disappearance of the mesomorphic properties may be attributed to the broadening of the molecule, which, in its planar form, may have structures XIX or XX



XIX



XX

However, the acetate tends to decompose in the region of its melting point and this will contribute strongly to the destruction of the mesomorphism. That this is highly likely is shown by the fact that the benzoate, which is equally broad, shows a nematic phase of 2° between the m.p. of 257° and the clearing point of 259°. As would be expected, this melting point is much higher than that of the acetate, due to the greater molecular adhesion through the aromatic rings in the benzoyl group. This might have been expected to make mesomorphism less likely. However, the adhesion between molecules of the benzoate would also be greater when the crystal lattice breaks down, and the nett result would seem to favour mesomorphism. An exact comparison between the acetate and the benzoate cannot be made since the former decomposes on melting. Were this not so, it is possible that it, too, would exhibit mesomorphism.

The benzene sulphonate, m.p. 228.5°, is not mesomorphic, which is not surprising since the molecule will be very much broader, and also thicker, due to the bulky, non-planar benzene sulphonyl group.

The acetate, benzoate and benzene sulphonate of p-hydroxybenzoic acid and trans-p-hydroxy cinnamic acid have been prepared and found to show no mesomorphism, and these facts do emphasise the strong mesomorphic tendencies in compounds derived from 6-hydroxy-2-naphthoic acid.

It should be noted that the mesomorphic properties of such systems are completely destroyed when the molecules can no longer dimerise. The ethyl ester of 6-n-hexadecyloxy-2-naphthoic acid is itself a very long molecule, but, unlike the free acid, it cannot dimerise, and the compound melts to an isotropic liquid at 53°.

These results prove that an increase in molecular breadth can and does diminish and even destroy mesomorphism, but in a strongly mesomorphic system, such as the 6-n-alkyloxy-2-naphthoic acids, considerable increases in breadth can be tolerated without substantial loss of mesomorphism.

4. The effect of broadening the molecules of p-n-alkyloxy benzoic acids

Unlike the 6-*n*-alkyloxy-2-naphthoic acids which substitute in the 5-position and do not suffer a significant broadening of the molecule in every case, substitution of a *p*-*n*-alkyloxy benzoic acid in the 3-position must give a substantially broader molecule, since any substituting atom or group which may be introduced will be larger than a hydrogen atom. In table 20 are given the length:breadth ratios of the series of *p*-*n*-alkyloxy benzoic acids and the 3-fluoro-, 3-chloro- and 3-bromo- derivatives.

Table 20

3-Substituent		H	F	Cl	Br
Breadth in Å		6.8	7.29	8.09	8.39
n-Alkyl group	Length(Å)	Ratio	Ratio	Ratio	Ratio
Methyl	10.82	1.59	1.49	1.34	1.29
Ethyl	12.1	1.78	1.66	1.5	1.44
Propyl	12.82	1.89	1.76	1.59	1.53
Butyl	14.1	2.07	1.93	1.74	1.68
Amyl	14.82	2.18	2.03	1.83	1.77
Hexyl	16.1	2.37	2.21	1.99	1.92
Heptyl	16.82	2.47	2.31	2.08	2.0
Octyl	18.1	2.66	2.48	2.24	2.16
Nonyl	18.82	2.76	2.58	2.33	2.24
Decyl	20.1	2.96	2.76	2.49	2.4
Dodecyl	22.1	3.26	3.03	2.73	2.63
Hexadecyl	26.1	3.85	3.58	3.22	3.11
Octadecyl	28.1	4.14	3.86	3.47	3.35

From considerations of molecular dimensions alone, substitution of a p-n-alkyloxy benzoic acid would be expected to reduce the mesomorphism. Moreover, if it were assumed that the melting points of the substituted and the unsubstituted compounds would be of the same order, then, since a length: breadth ratio of 1.89 is consonant with the presence of mesophases in the p-n-alkyloxy benzoic acids, it might be expected that a substituted acid with the same ratio would be mesomorphic. This would mean that mesomorphism should begin at n-butyl(1.93), n-amyl(1.83) and n-hexyl(1.92) in the fluoro-, chloro- and bromo- compounds respectively. When these series of compounds were prepared this was found to be very far from true and the results, which are detailed in tables 6 and 7 and graphs 6 and 7 (pages 40 to 43), may be summarised as follows.

p-n-Alkyloxy benzoic acids(6)

A nematic phase first appears in the n-propyl ether and this gradually increases in length up to and including the n-heptyl ether which also possesses a short smectic phase. Further increase in the chain length causes the smectic properties to become more pronounced, until in the n-octadecyl ether the gradually decreasing nematic properties are extinct, and the ether, which melts at 101° to a smectic mesophase, becomes isotropic at 130°.

3-Fluoro-4-n-alkyloxy benzoic acids

Here nematic properties do not begin until the n-octyl ether which has a phase length of 4° .At the n-nonyl ether smectic properties appear,although the first smectic phase has a length of <0.2°.The maximum nematic phase length is 4.5° in the n-decyl ether,but further increases in the chain lengths reduce the nematic phase length until the purely smectic n-hexadecyl ether is reached.As the nematic phase lengths decrease,the smectic phase lengths increase,and reach a maximum of 17° in the hexadecyl ether.The n-octadecyl ether is likewise purely smectic,but the phase length is only 2°.As is frequently the case among these ethers there is a sharp increase in the melting point from the C_{16} to the C_{18} ether in this series.Here the temperature increase is 19° .Since the C_{18} ether must have dimensions which are suitable for mesomorphism,the decrease in phase length from 17° in the hexadecyl ether to 2° in the octadecyl ether must be due entirely to the greater thermal agitations at these higher temperatures.

3-Chloro-4-n-alkyloxy benzoic acids

As in the fluoro- substituted series,mesomorphic properties first appear with the n-octyl ether,but,unlike the fluoro- compound,this ether is both smectic and nematic with phase lengths of only <0.2° and 0.5° respectively.From the n-nonyl ether to the n-hexadecyl ether,the smectic phases increase from 0.5° to 3.0°, while the nematic phase lengths are constant at 1.0°. That is, unlike the fluoro- ethers, the n-hexadecyl ether is nematic as well as smectic. It is just possible that this may be due to a thickening of the molecule as a result of the presence of the chlorine atom. Such an explanation would allow the application of the same arguments which were used to account for the persistence of nematic properties in 5-nitro-6-n-alkyloxy-2-naphthoic acids. Admittedly, no such effect is found in the 5-chloro-, 5-bromo- or even 5-iodo-6-n-alkyloxy-2-naphthoic acids, but in these molecules the surface area is much greater, and there will be a greater surface for cohesion between the molecule planes. In the benzoic acids, the forcing apart of the smaller surfaces by the chlorine atoms may minimise the adhesion in the smectic state sufficiently to cause sliding, imbrication and the introduction of nematic properties, prior to the condition of isotropy. Plate 14 shows a model of 3-chloro-4-n-butyloxy benzoic acid, and when this is compared with plates 10, 11 and 12 for 5-chloro-, 5-bromo- and 5-iodo-6-n-butyloxy-2-naphthoic acids, the greater relative size of the halogen atom in the benzoic acids can be readily appreciated. The n-hexadecyl ether, m.p. 95°, has a smectic phase length of 3°, but the n-octadecyl ether, m.p. 108°, shows no mesomorphic properties. Here again, the rise in melting point may account for the disappearance of mesomorphism, in the same way as it resulted in the reduction in phase length in the fluoro- series

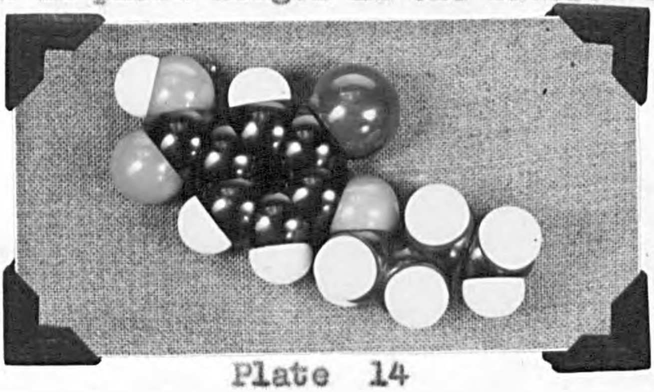


Plate 14

3-Bromo-4-n-alkyloxy benzoic acids

No mesomorphism was found in this series

The large deviation from the behaviour which might have been expected from a consideration of length:breadth ratios alone are therefore apparent,and other factors must be responsible for the absence of mesomorphism in so many of these compounds.The other factor which is known to affect mesomorphism is the temperature of melting,and a larger decrease in mesomorphism on substitution could be explained by an increase in melting point together with an increase in molecular breadth.In table 21 the melting points of the substituted and unsubstituted benzoic acids are listed for comparison,with the overall phase lengths of the ethers in parenthesis.

Table 21

Substituent	H	F	Cl	Br
n-Alkyl group				
Methyl	184°(-)	211.5°(-)	217.5°(-)	
Ethyl	195°(-)			
Propyl	145°(9°)			
Butyl	147°(13°)	142.5°(-)		
Amyl	124°(27°)	137°(-)	134.5°(-)	
Hexyl	106°(47°)	129°(-)	120°(-)	
Heptyl	92°(56°)	123°(-)	117°(-)	
Octyl	100°(48°)	117°(4°)	94°(0.5°)	111°(-)
Nonyl	92°(49°)	112.5°(4°)	93°(1.5°)	
Decyl	92°(57°)	108°(8.5°)	99°(2.0°)	
Dodecyl	95°(42°)	108.5°(6°)	100°(2.0°)	
Hexadecyl	100°(33°)	94°(17°)	95°(4.0°)	99°(-)
Octadecyl	101°(29°)	113°(2°)	108°(-)	

In all cases there is a progressive decrease in phase length on passing from the unsubstituted acid to the fluoro-, chloro- and bromo- acids.With regard to the melting points the position is less simple.Apart from one or two exceptions, there is a sharp rise on passing from the unsubstituted to the fluoro- acids,a decrease from the fluoro- to the chloro-acids and an increase from the chloro- to the bromo- acids.

Comparison of the fluoro- and chloro- series

The very large difference in behaviour between the unsubstituted acids and the fluoro- compounds might have been expected to have been accompanied by an equally large effect on passing from fluoro- to chloro-.Indeed,from considerations of the breadth of the molecules alone,the effect might have been expected to be greater in the case of the chloro-compounds since there is a larger increase in breadth (0.65Å) from fluoro- to chloro-,compared with an increment of 0.45Å from the unsubstituted acid to the fluoro- compound.This increase in breadth does lead to a diminution in phase length in all cases from the fluoro- to the corresponding chloro-compound,but the mesomorphism begins at the same point in each series.This can only be attributed to the decrease in melting point resulting in smaller thermal agitations in the melts—a feature which counteracts the increased breadth in the chloro- compounds.Thus,if the temperature of melting had been the same for the fluoro- and chloro- compounds,the origin of mesophases in the chloro- series might have been stepped back one unit of the alkyl chain to nonyl (as was the case in the naphthoic series),and the phase lengths would have been even shorter than those observed.It may be argued that the melting point differences are small and that to have these effects the influence of temperature must be critical.It does seem that this is indeed the case,and the effect in the n-octadecyl ethers has been mentioned above.In these cases temperature increases of 19° and 13° in the fluoro- and chloro- series diminish and eliminate mesomorphism respectively.Moreover,slight depressions of melting point have been shown both to increase phase lengths and, in some cases, to bring about the appearance of mesophases in mixtures of two non-mesomorphic components. The following results emphasise the significance of the effect of temperature.

Mixed melts of 3-fluoro-4-n-alkyloxy benzoic acids

(a) n-octyl ether - purely nematic. Phase length 4°, 117-121°
n-nonyl ether - smectic and nematic
overall phase length 4.0°, 112.5-116.5°
smectic phase length <0.2°
nematic phase length 4.0°

Mixture of equal parts of the octyl and nonyl ethers

A sample of this mixture was melted on a slide and a cover slip pressed down on the melt. On cooling, the sample behaved like the nonyl ether and showed a nematic and a short smectic phase. Although this latter phase is very short, and appears only a little in front of the crystals on sudden chilling or when crystallisation is nearly complete, it is obviously longer than the smectic phase in the pure n-nonyl ether.

M.p. of the mixture, 107° to 113°; runs to a cloudy nematic melt,
119°; clears and reverses sharply

Thus, taking only the upper limit of running at 113°, the phase length is now increased to 6°, compared with the phase lengths of 4° for each of the constituents. This corresponds to a depression of only 4° for the lower transition point of the *n*-octyl ether, and gives an increase in phase length of 2°. The preliminary softening in the mixed melt made it impossible to determine the length of the short smectic phase.

(b) *n*-octyl - nematic phase length 4°, 117-121°

n-heptyl ether - m.p. 123° —no mesomorphism

Mixture of the heptyl and octyl ethers in equal amounts

This mixture shows a nematic phase, which was determined as having a length of 2°, between the m.p. of 114-113°, and the clearing point of 120°. On the other hand, a mixture of the octyl ether and another substance incapable structurally of showing mesomorphism, in the ratio 1:1, would have destroyed its mesomorphism. It may be inferred then that the heptyl ether is structurally capable of mesomorphism, but that its melting point is too high, so that the phase length of 2° for the mixture may be said to be an infinite increase in the mesomorphism of the heptyl ether for a m.p. depression of only 3°.

(c) *n*-hexyl ether — m.p. 128.5°, no mesomorphism

n-heptyl ether - m.p. 123°, no mesomorphism

Mixture of the hexyl and heptyl ethers in equal amounts

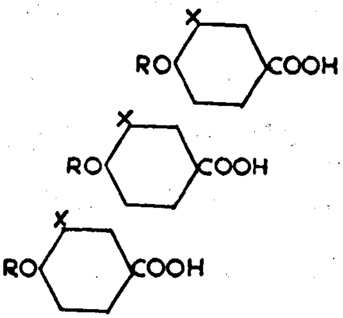
The mixture shows a nematic phase on cooling from the isotropic liquid. Although short, this phase is definite and it behaves as though its length were less than 0.1°, since it appears only on sudden chilling or when crystallisation of the sample is nearly complete. The melting point determination shows that the crystals pass over to the isotropic liquid between 120° and 122°, but, in this range, the sample is a mixture of a cloudy liquid and the isotropic liquid. It therefore represents a mesomorphic system, formed from non-mesomorphic components. Such behaviour suggests that the components are potential mesomorphs but that their melting points are too high for this to be seen in the usual way.

These and similar experiments illustrate just how critical melting point can be as far as mesomorphism is concerned. Although this will account for the behaviour of the fluoro-series relative to the chloro- series, it can hardly explain the influence of a fluorine atom in a p-n-alkyloxy benzoic acid. As has been seen, fluorination postpones the appearance of mesomorphism four units in the alkyl chain, and causes a marked diminution in the phase lengths, from a maximum of 57° in the unsubstituted to a maximum of 17° in the fluoro- series.

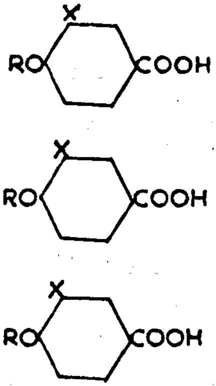
A gradual change from the unsubstituted to the substituted acids was not found either in the 6-n-alkyloxy-2-naphthoic acids, and the reason suggested for this was the high melting points of the 5-chloro- derivatives together with the stronger cohesive forces in such molecules. In both the naphthoic and the benzoic acid series, the change in breadth of the molecules will be the same from chloro- to bromo- and from bromo- to iodo-. However, since the lateral adhesion of the molecules along their edges will depend on the closeness of approach of the ring systems, it can be seen that, since part of the bulk of a substituent in the 5-position of the naphthoic acids does not contribute to the broadening of the molecule due to the recess in the naphthalene ring, the aromatic rings in the benzoic acids containing the same substituent will approach one another less closely. The following figures give the distance in Å to which the rings are forced apart by substituents.

	Naphthoic acids				Benzoic acids			
Substituent	H	Cl	Br	I	H	F	Cl	Br
Distance in Å	0	0	0.3	0.69	0	0.49	1.29	1.59

The lateral adhesion, which will be less in the benzoic acids than in the naphthoic acids, due to the smaller ring system in the former, will be further decreased by substitution, and the same substituent will have a greater effect in the benzoic acids. It may be argued that this should lead to a big reduction in the melting point of the ethers with increasing size of the substituent, whereas in fact the melting point increases on fluorination. However, the forcing apart of the molecules may only apply in the mesophases. That is, a packing such as is shown in XXI may be possible in the lattice, resulting in a high melting point. In the subsequent mesophase there must be a considerable molecular mobility for the lattice to break down into micelles, and the interlocked structure XXI may swell to give an arrangement of type XXII.



XXI



XXII

This will have a low lateral adhesion and will confer instability on the mesophases.If this occurs in the naphthoic acids the degree of separation will be less.It is possible, therefore,that,coupled with a high melting point,there is a low molecular adhesion in the mesophases,and a tendency for the molecules to turn and take up random orientations because of the wide spacing.As the molecules are made longer,this turning into a random orientation will become less easy and the molecules may persist over a range of temperature in a linear orientation in the melt.If this is so,then the lateness of appearance of mesomorphism can be explained and so can the shortness of the phases which do in practice exist.

Compared with the fluoro- compounds,the packing in the crystal lattice in the chloro- series would seem to be such that a decrease in melting point arises.The effects of this fall in temperature have been discussed, and the greater spacing in the mesophase would account for the shorter phases at a lower temperature.

The complete absence of mesomorphism in the 3-bromo-4-*n*-alkyloxy benzoic acids is the only remaining point which has not been discussed. It will be recalled that the very short mesophases of the chloro- compounds are here not merely diminished but completely extinguished. The ethers of the bromo- series must have a packing in the crystal lattice which causes higher melting than with the chloro- compounds and, moreover, there may be less cohesion in the melt itself when the lattice breaks down. These two effects will work together to make mesomorphism less likely and, indeed, they may be sufficient to destroy it. The maximum phase length in the chloro- series is 4°, and the minimum reduction in phase length from fluoro- to chloro- is from 4° to 1.5°. Obviously then, if this reduction of ⅜ which occurs on replacing fluorine by chlorine is repeated when chlorine is replaced by bromine, the maximum phase length in the bromo- series would be ⅜ of 4° = 1.5°. But, the melting points of the bromo-acids are higher than those of the chloro- acids and the critical nature of temperature in these series is such that these higher melting points may well be sufficient to annihilate so short a phase.

3:5-di-Halogeno-4-n-alkyloxy benzoic acids

3:5-di-Chloro-4-n-amyloxy benzoic acid has been previously examined and shown to be non-mesomorphic. It was decided to prepare a longer chain ether of this type and also to synthesise a long chain 3:5-di-fluoro-4-n-alkyloxy benzoic acid in order to establish the behaviour of such systems.

The following halogeno- substituted p-n-alkyloxy benzoic acids were therefore examined:

	m.p.
3:5-di-fluoro-4-methoxy benzoic acid	215° (211.5°)
3:5-di-fluoro-4-n-hexadecyloxy benzoic acid	72° (94°)
3:5-di-chloro-4-n-amyloxy benzoic acid	103° (134.5°)
3:5-di-chloro-4-n-hexadecyloxy benzoic acid	60.5°(95°)

The melting points of the corresponding 3-halogeno-4-n-alkyloxy benzoic acids are included above in parenthesis. With the exception of 3:5-di-fluoro-4-methoxy benzoic acid, the di-halogeno- compounds melt considerably lower than the mono-halogeno- derivatives. The above four di-halogeno-compounds exhibit no mesomorphism and so the systems are obviously too broad to show the phenomenon. This is hardly surprising in view of the short phases shown by the 3-chloro- and 3-fluoro-4-n-alkyloxy benzoic acids.

5. The origin of the smectic phase in the series

In all the homologous series examined in this investigation, and in the p-n-alkyloxy benzoic acids and the trans-p-n-alkyloxy cinnamic acids examined by Bennett and Brynmor Jones as well as in the series of compounds examined by Weygand et al, the following characteristics always arise—

(a) the shorter chain ethers show either no mesomorphism or purely nematic phases,

(b) as the chain length is increased smectic properties are introduced,

(c) further increases in the chain length give rise to more pronounced smectic properties, and in many cases nematic properties disappear.

These facts make it seem that smectic characteristics may depend on

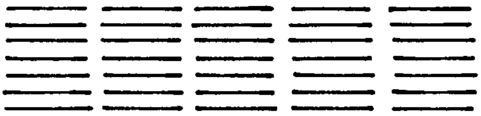
(1) predominantly aliphatic properties in the molecule

(2) the greater length of the long chain ethers

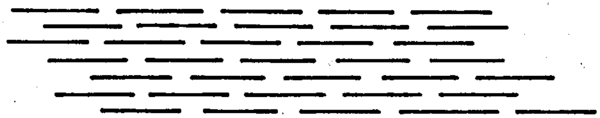
(3) the lower temperatures at which the higher members of the series melt.

The following discussion makes it clear that condition (3) is not a determining factor in smectic phases in any greater degree than it is to mesomorphism, and that the importance of conditions (1) and (2) may lie in their altering the nature of the packing of the molecules in the crystals at some stage in the series.

The molecular distribution in the micelles of smectic and nematic states is considered to be that of linear molecules which in the former lie with their ends parallel and in the latter with no regular arrangement of the ends of the molecules.



Smectic



Nematic

It can be understood that the longer alkyl chains may tend to interlock to some extent thus forcing the molecules to lie parallel to one another and with their alkyl groups alongside each other.This would eliminate the imbrication necessary to nematic states and so give rise to smectic properties.This idea is in agreement with the established fact that the longer chains favour smectic behaviour but it would not account for the variation in chain length in the different series at which smectic properties first develop.The chain lengths and the melting points at which smectic properties first appear in the series are listed below in table 22.This also includes the melting point of the preceding purely nematic ethers.

In this table,(A) represents *p*-*n*-alkyloxy benzoic acids,and
(E) represents 6-*n*-alkyloxy-2-naphthoic acids.

Table 22

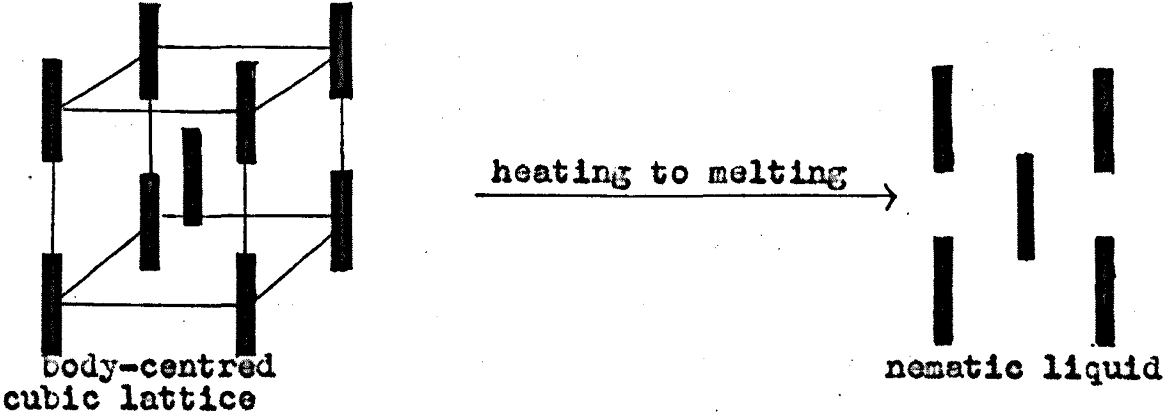
Series	Chain length	m.p.	m.p. of the preceding nematic ether
(A)	Heptyl (7)	92°	106°
3-Fluoro-(A)	Nonyl (9)	112.5°	123°
3-Chloro-(A)	Octyl (8)	94°	117°
(B)	Nonyl (9)	146.5°	161.5°
5-Chloro-(B)	Hexyl (6)	164°	189°
5-Bromo-(B)	Heptyl (7)	158°	178°
5-Iodo-(B)	Octyl (8)	160.5°	176°
5-Nitro-(B)	Dodecyl(12)	167°	173.5°
<u>trans-p-n</u>-alkyloxy-cinnamic acids	Nonyl (9)	138.5°	147°

In all cases there is a steep fall in melting point from the last purely nematic member to the first ether which shows smectic properties.The inference here may be that in all solids,which are capable of exhibiting mesomorphic properties,the molecules are arranged with their long axes parallel,and with their ends in line so as to form layers,or, in other words,with a smectic packing in the solid.If the melting point is high,isotropy may result from the breakdown of this lattice,because of the high thermal agitations.At a somewhat lower melting point,a lattice of this type may break down with a sliding motion of the molecules to form a mobile fluid in which the parallel distribution of the molecules is maintained but not the parallel distribution of the ends of the molecules.The imbrication will result in a nematic melt.At still lower melting points,as a result of smaller thermal agitations,such a lattice may give rise to a fluid with the same arrangement of the molecules as in the crystal lattice.This will give a smectic melt which,as the temperature is raised,may then give a nematic phase through a sliding action of the molecules along their lengths,or it may result in a complete thermal breakdown leading to an isotropic liquid.

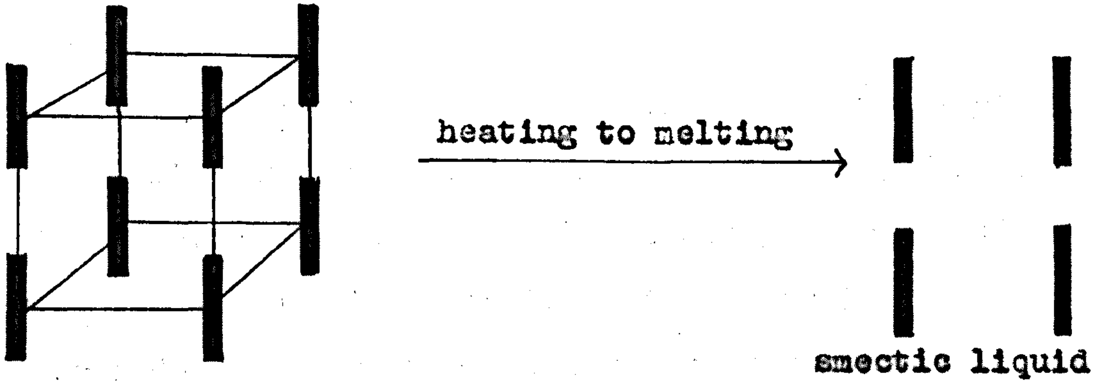
If this is the case,temperature alone will determine whether a system will be nematic or smectic.It would therefore seem reasonable to assume that it would be possible to induce a smectic phase in mixed melts of two purely nematic compounds through melting point depression,just as it has been shown to be possible to induce a nematic phase in mixed melts of two non-mesomorphic substances.The induction of a smectic phase in this way would be most likely if the mixed melt consisted of the last purely nematic ethers in any series.In no case has this been found to be possible,however.These negative results have been recorded on mixed melts of the last two purely nematic members of the nine series listed in table 22.

This leads to the idea that there are two separate packings of the molecules in the solid lattices of nematic and smectic substances.Taking the cubic unit cell as an example,the two possibilities may be represented diagrammatically as follows:

(a) Nematic



(b) Smectic



The crystals of the substituted and unsubstituted p-n-alkyloxy benzoic acids and 6-n-alkyloxy-2-naphthoic acids are not of course cubic,and,as would be expected from their great length compared to the other two dimensions,they are orthorhombic.However,the effect will be the same as above,so that a nematic substance would have a body-centred orthorhombic lattice and a smectic substance a non-body-centred orthorhombic lattice.

It was hoped to prove that different lattices obtained in smectic and nematic compounds in the same series by measuring the refractive indices along the crystal axes. However, these substances have very high refractive indices and no liquid of sufficiently high index could be found for a standard comparison. The refractive indices could of course be measured and calculated from a knowledge of the optics of individual crystals of the compounds, and it is hoped that this will be done at a later date. However, the examination will not be easy from the point of view of mounting individual crystals of these waxy, fragile compounds on a universal microscope stage.

X-ray powder photographs have been taken on 6-n-amyloxy-2-naphthoic acid (nematic) and on 6-n-decyloxy-2-naphthoic acid (smectic). Although these have not yet been fully interpreted there is an obvious difference in the two lattices, quite independent of the differences in spacing which will arise from the longer chains in the n-decyl ether.

It seems possible therefore that there is a change in lattice type which causes the fall in melting point from the last nematic to the first smectic ether in a series and that smectic and nematic characteristics are determined by the type of packing in the crystal lattice. The type of packing preferred by any compound will be that which is closest, and gives the maximum cohesion, and on this basis it would seem reasonable that the very long chain ethers, such as the hexadecyl and octadecyl ethers,should be,as indeed they are, smectic.Even by using atomic models it is however impossible to begin to predict which packing is most likely in different cases.Therefore,no predictions are possible about the point at which smectic properties start.The following regularities which have been found are,however,worth mentioning:

(a) the closely similar 6-n-alkyloxy-2-naphthoic acids and trans-p-n-alkyloxy cinnamic acids both start to show smectic properties at nonyl.Doubtless the closely similar molecules will give changes in the packing at the same alkyl chain length.

(b) the gradual increase in molecular breadth from 5-chloro- to 5-bromo- to 5-iodo-6-n-alkyloxy-2-naphthoic acids is marked by a regular displacement of one unit of the alkyl chain of the points at which smectic properties are first evident.These alkyl groups are hexyl,heptyl and octyl in the chloro-,bromo- and iodo- series respectively.It is possible that here,too,the gradual increase in size causes a gradual displacement of the alkyl chain length at which the crystal lattice type changes,and that the result of this is a displacement of the point at which smectic properties begin.

Yet the results in table 22 show that it cannot be said that increased molecular breadth will cause smectic properties to begin later in the series.For example,the 6-n-alkyloxy-2-naphthoic acids first show smectic phases at nonyl,and this is later in the series than any of the three halogeno-substituted series. Moreover, the increase in breadth from 3-fluoro- to 3-chloro-4-n-alkyloxy benzoic acids is accompanied by the smectic properties at a chain length which is one unit shorter. No explanation of these effects can be offered and it can only be said that it is possible that the many factors which govern molecular packing are probably responsible for the irregularity in the chain lengths in the series at which smectic properties are first evident. Until more is known of the crystallography of these many compounds these ideas on the origin of the smectic phase can however only be considered as tentative suggestions.

Summary of conclusions

Despite the number of compounds which have been examined, very few definite conclusions can yet be reached concerning the precise relationship between molecular shape and mesomorphism. The idea that broadening a long molecule will reduce its mesomorphism is amply justified and this reduction is made evident both by shorter phase lengths and by the appearance of mesophases only when longer alkyl groups are present. The effect of the breadth of a molecule on its mesomorphic behaviour is however difficult to dissociate from other variables such as temperature and the strength of the intermolecular forces. Thus it is only possible to equate breadth change to mesomorphic behaviour when the temperature conditions are closely similar. This is the case in the 5-halogeno-6-<u>n</u>-alkyloxy-2-naphthoic acids, but the melting points again vary sufficiently to make it impossible to say that the breadth changes are solely responsible for all the effects. When the melting points do vary for the same ether in two series, irregularities in mesomorphic behaviour will be found, and in all cases higher melting points lead to shorter phase lengths. In the 3-fluoro-4-<u>n</u>-alkyloxy benzoic acids, the effect of temperature has been shown to be very marked. The present study does show that certain conclusions can be reached between systems of different breadths, and it gives some indication of how much the breadth of molecules may be increased in different cases without destroying the mesomorphism. The wide difference which breadth increase has on the naphthoic and benzoic acids, due to the several variable factors which operate, make it clear that it would be very hazardous to predict the possible mesomorphic behaviour of an unknown compound merely from its molecular dimensions. Since the effect of breadth increments can vary both at different temperatures and for different molecule types, it is evident that many more homologous series of mesomorphic compounds must be studied before more firm conclusions can be reached on the molecular dimensions necessary for mesomorphism.

The comparison of the 6-<u>n</u>-alkyloxy-2-naphthoic acids and the trans-p-n-alkyloxy cinnamic acids does at least establish that similarly-shaped molecules can be expected to exhibit very similar mesomorphic properties.Clearly,molecular shape is of first importance in determining,not only whether mesomorphism will or will not occur,but also in deciding where the phase types will begin and end.

Considerations of the smectic phase,and in particular of the stage at which smectic properties first appear in a series would suggest that,here again,molecular shape is critical because of its effect in determining the packing of the molecules in the crystal lattices.Without doubt, examinations of the crystal structure of nematogenic and smectogenic substances will give valuable information in this respect.Both X-ray and pure crystallographic methods would be of value,and an interesting field of investigation lies ahead.

It is well established that the longer the molecule the more mesomorphic is the system likely to be,provided the lateral adhesion is increased in proportion with the length. That is,a simple increase in the length by indefinite increases in the alkyl chain would simply lower the cohesion and give an approximation to the aliphatic open chain carboxylic acids which are not mesomorphic.The preparation of compounds,whose molecules are even longer than the naphthoic types and which contain benzene rings to maintain the lateral adhesion, should give valuable information concerning the effect of temperature, in relation to the length and breadth of the molecules, on the mesomorphism. Investigations along these lines are being undertaken, with the object of obtaining results which can be compared with those for the series already described. Such studies should shed more light on the whole phenomenon of mesomorphism.

Discussion of the Phase Length

Determinations

Determination of the Phase Lengths

Using an ordinary melting point apparatus containing liquid paraffin, it is possible to determine the mesomorphic transition points, because the mesophase is a turbid fluid which is easily distinguished from the solid or the amorphous liquid. The high viscosity of the smectic phase prevents its flow as a normal liquid, causing adhesion to the capillary walls. In the nematic state, the turbid fluid runs like a normal liquid of low viscosity and has a well defined meniscus. The observations made are therefore:

A purely smectic substance

$$\text{Solid} \text{ --- } t_1 \longrightarrow \text{smectic} \text{ --- } t_2 \longrightarrow \text{isotropic}$$

At t_1 the solid is replaced by the turbid, viscous melt which adheres to the walls in the capillary tube. Only at t_2 does this show any mobility when it flows and clears at the same time. The transition is reversible exactly at t_2 and this effect is readily seen by the reappearance of the turbidity.

A purely nematic substance

$$\text{Solid} \text{ --- } t_1 \longrightarrow \text{nematic} \text{ --- } t_2 \longrightarrow \text{isotropic}$$

At t_1 the solid changes to a turbid melt of low viscosity, which flows sharply in the m.p. tube. At t_2 the turbidity disappears quite suddenly and this transition is again seen to be reversible at this temperature.

A substance showing a nematic and a smectic phase

$$\text{Solid} \text{ --- } t_1 \longrightarrow \text{smectic} \text{ --- } t_2 \longrightarrow \text{nematic} \text{ --- } t_3 \longrightarrow \text{isotropic}$$

The transition at t_1 is the same as for a purely smectic substance. At t_2 the viscous, turbid fluid runs to a cloudy nematic melt which then clears at t_3. The reverse change at t_3 is easily observed. Although the nematic-smectic transition is also reversible at t_2, it is not possible to see the change back to the smectic phase in the capillary, unless there happens to be a difference in the opacity of the two mesophases.

Of these transitions, the one most liable to be mistaken is the change of the solid to the smectic state. For example, there may be a slight softening and lattice disintegration in even a very pure solid, and, although the transition to the smectic phase is sharp, it may be difficult to distinguish the softening solid from the viscous smectic mesophase. This is particularly true in the long chain n-alkyl ethers such as dodecyl, hexadecyl and octadecyl, since solids containing these ether groups are largely paraffinic and quite wax-like. Moreover, the running of the smectic phase to the nematic phase is affected by external factors. Thus, if the capillary tube is wide and the amount of sample is small, the more mobile nematic phase may simply form a thin film on the wall and be unable to flow to any bulk of "liquid." Impurities and abrasions on the surface of the glass are also likely to prevent sharp flowing at the transition point. All the transition points in the tables and in section A of the experimental have therefore been rechecked by heating the sample on a slide and observing the actual changes in appearance of the phases under the microscope.The solid-solid transitions were determined in this way too.

The measurements made by G.M. Bennett and Brynmor Jones(6), on the p-n-alkyloxy benzoic and trans-p-n-alkyloxy cinnamic acids,were carried out in this way.The substance was melted on a small strip of microscope slide(1cm.×3cm.) and covered with a piece of cover slip.Solid-solid transitions were seen by the naked eye as a wave change in opacity which passed over the specimen.The mounted specimen was lowered by means of a thread into a test-tube serving as an inner air bath surrounded by the heated oil bath.The bulb of a thermometer was next to the specimen,and the upper end of the test-tube was closed with a cotton wool plug.The temperature of the oil bath was now slowly raised,and the specimen from time to time suddenly removed,placed on a cold slab and examined to see if any solid-solid transitions occurred.The actual transition temperature could thus be determined to about ±1° by finding two adjacent temperatures between which the observable transition just ceased to be detected.The mesomorphic and polymorphic transitions were thus determined.

In the present work,a more direct method has been used for the transition temperature determinations.A heating block was constructed which could be easily controlled by an external resistance at any required temperature between room temperature and 300°.The slide was housed in this block and the mounted specimen could be observed through a microscope. A plan and side elevation of this microscope heating block are shown in fig. 5 .To minimise temperature gradients in the block itself,high conductivity copper was used.The block is approximately 4¼ ins. in diameter and 1¼ ins. thick and consists of two parts which are bolted together.The block was made in two parts to facilitate the clean cutting of the slide slot and the thermometer pocket.The ½ in. hole is covered above and below by glass cover slips which are held in position by spring clips.These minimise air currents which may give localised cooling on the part of the slide being examined under the microscope.It may be mentioned that when operating at high temperatures,i.e. above 200°,considerable sublimation may occur and render the upper cover slip opaque.Since this could not be removed with ease for cleaning, when high temperatures obtained,the upper cover slip was discarded and replaced by an ordinary glass microscope slide which lies over the hole on top of the brass outer casing.As the slide became opaque it could be gradually pushed over to a clean part.This made continuous observation easy even when rapid sublimation occurred.The slide slot is cut to allow easy insertion and removal of a slide and the thermometer pocket is drilled in such a way that the surface of the bulb is exposed

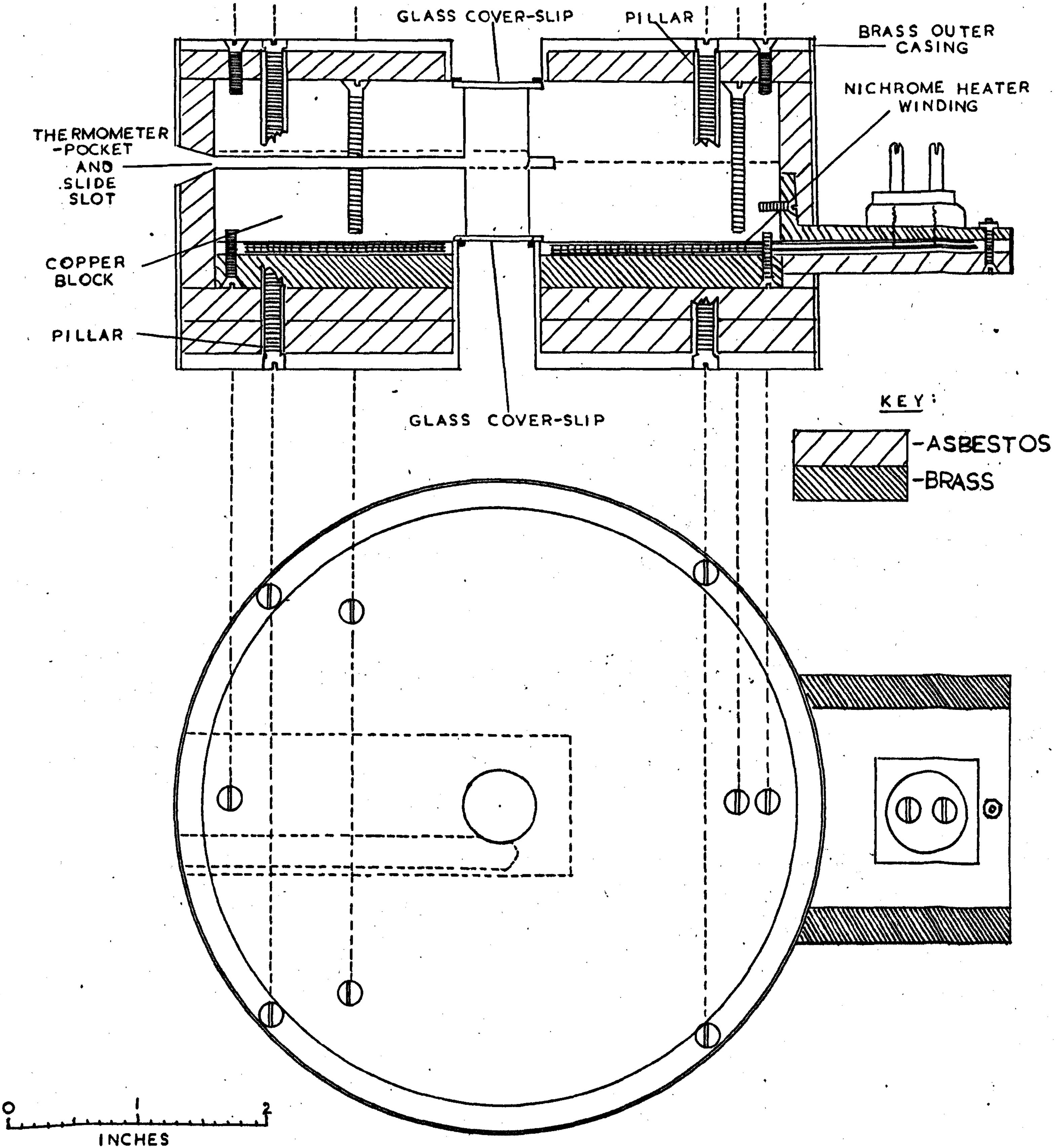


FIG. 5

MICROSCOPE HEATING-BLOCK

to the air in the hole between the cover slips.The temperature recorded is therefore that of the sample mounted on the end of the slide and not merely that of the copper block beside the hole.Samples were mounted,as described above,by melting between a glass slide and a cover slip to obtain a very thin film of the specimen.The heater consists of about 22 feet of 36 gauge,round Nichrome wire,diameter 0.0076 in.This has a total resistance of about 250 ohms.The wire is wound on a circle of mica sheet,3¾ in. in diameter,with a ¾ in. hole in the middle.Slightly larger mica sheets of the same pattern are placed on either side and the whole heater is secured against the underside of the block by a ¼ in. brass plate of the same pattern as the copper block to which it is bolted. The wire is led off from beneath the block to the plug at the side,which is attached to an L-shaped brass plate bolted to the side of the block.

A brass outer case for the block was constructed.Two ⅛ in. thick circular brass plates of approximately 5 in. diameter, with a ¾ in. hole in the centre,are supported some 2¾ in. apart by four pillars of brass tubing to which the plates are bolted.The thin brass outer casing is bent round the circular plates and bolted to the pillars.The heating block is housed in this outer case from the side of which the plug mounting protrudes.Two brass tubes are let into the top and bottom of the casing and meet the copper block beside the spring clips which secure the glass cover slips.These tubes are soldered and brazed in position and complete the outer jacket.Two ¼ in. layers of asbestos board below,one ¼ in. layer of asbestos board above and a ¼ in. of asbestos cement round the sides insulate the copper block.The upper plate of the outer casing is securely bolted through the upper insulation to the top of the copper block.

The whole instrument is mounted on the rotating stage of a Baker polarising microscope.The supporting bracket of this instrument had been cut through and a 4¼ in. brass column inserted,thus raising the barrel and focusing arrangement well above the stage.Using a 1½ in. objective,there is therefore a distance of 0.6 in. between the insulated top of the outer casing and the objective.The heavy insulation on the underside protects the lower optical system of the microscope from over-heating.

In this instrument,a sample mounted on the end of a slide may be heated gradually and observed under the microscope free from air currents.An 850 ohm variable resistance in the external circuit makes it possible to control the rate of heating so that it can range from very slow to fast over a considerable range of temperatures.The following figures, obtained while calibrating the instrument,illustrate this point.

Resistance in external circuit (Ω)	Temperature after (min.)							Rate of temp. rise (° per min.)	
	0	30	60	120	150	180	210	First 30min.	Last 30min.
0	9°	225°	320°	-	-	-	-	7.2°	3.2°
100	10°	130°	194°	248°	260°	268°	272°	4.0°	0.13°
200	10°	92°	135°	174°	184°	192°	195°	2.7°	0.1°
300	12°	60°	82°	123°	131°	136°	139°	1.6°	0.1°
400	17°	55°	74°	98°	103°	106°	109°	1.3°	0.1°
500	20°	44°	57°	76°	82°	85°	87°	0.8°	0.07°

The precision with which a m.p. value could be made was determined by taking the m.ps. of purified organic compounds covering a range of temperature from 40° to 300°. The m.p. values were then determined in the usual way. The corrected values obtained by the two methods agreed within ± 0.25°, provided that a slow rate of heating was employed in the region of the m.p. The optimum rate of heating was 2° per min.

The design of the instrument with a slide slot in one side has the advantage that the specimen under observation has a very slight temperature gradient across it. The melting begins at the far side from the opening of the slot and passes quickly, but as a well defined wave front, across the field of vision. This was particularly valuable in determining certain transitions which, had they occurred uniformly over the sample, would have been difficult to detect. This wave front effect made all transitions easily observed however.

Method of determining mesomorphic and polymorphic transitions

The compound was melted on a glass slide. A cover slip was pressed down on the melt and, when cold, a thin film of the solid was obtained. The specimen was observed visually and the number of polymorphic and mesomorphic transitions was counted. By heating over a small flame it was possible to determine how many of the polymorphic transitions were enantiotropic. Each of the solid states was then examined and characterised under a Cooke's polarising microscope. Unless the range of stability of a solid was very small, it was thus possible to determine the extinction, the relative birefringence using a quartz wedge in conjunction with polarised and ordinary light, and to ascertain at the same time whether the substance was uniaxial, biaxial, positive or negative, and to examine the general appearance of the crystals. If for example there were three solids, one monotropic and two enantiotropic, it was possible therefore, when the actual transition temperatures at which the solid-solid changes occurred in the heating block had been measured, to recognise which solid was monotropic by its non-appearance with rising temperature. Then, to measure these solid-solid transition temperatures, a fresh slide was mounted (to avoid prolonged heating of one sample) and inserted in the heating block. The temperature was allowed to rise fairly rapidly (say 5° per min.) and the approximate transition temperatures determined. The block was then allowed to cool until solid I reappeared and the measurements repeated using a rate of heating of 2° per min., from 10° below the transition point and until each transition had occurred. In this way the points for the solid-solid changes on the graphs were obtained. These changes were determined in either polarised or ordinary light depending upon which gave the better contrast in the specimen.

The mesomorphic transitions were of course known from ordinary m.p. determinations. The temperature was therefore raised quickly to within 10° of this value and then controlled, using a suitable resistance in the external circuit, to a rate of 2° per min. The transitions were seen as a wave front passing across the field of vision, and the phase type was easily recognised as being either smectic or nematic by comparing the appearance with those described for these phase types in the introduction to this thesis. A few of the characteristic appearances of the phases are illustrated by the photomicrographs shown in section A of the experimental work. These photographs were taken down the microscope with the sample in the copper block heated to the required temperature to render the phase stable. The magnification in all cases is approximately 25 diameters. The nematic phases were generally threaded or plated in appearance while the smectic phases always appeared in the focal-conic structure. These focal-conics were much smaller than the well defined example of ethyl *p*-azoxy-benzoate shown in the introduction (Plate 2).The general appearance of the smectic phases was that of a very fine mozaic.These mesomorphic transitions were always observed in polarised light in which the anisotropy gives well defined appearances to the phases.The transition to the amorphous liquid occurred when the field of view became completely black and extinct.The transitions,smectic-nematic,smectic-amorphous and nematic-amorphous are precisely reversible and the temperatures were recorded in both directions.Without exception,the two values were the same for each transition.

The accuracy of all measurements is ±0.25° and the temperatures measured were corrected for exposed stem.The very short phases found in a few of the compounds could not be measured accurately.In a m.p. capillary these transitions either passed unnoticed or were only just detectible,and are probably less than 0.2° in length.

Experimental Section A

Measurement of Phase Lengths

A. Measurements (all m.p. corrected).

1. 6-n-Alkyloxy-2-naphthoic acids.

The thirteen ethers examined (methyl to decyl, dodecyl, hexadecyl and octadecyl) are all mesomorphic. Nematic phases alone were identified in the first eight members, but increase of the alkyl chain to nine carbon atoms introduced, in addition, a very short smectic phase. The smectic phase length gradually increased with corresponding decrease in the nematic phase length, until, in the hexadecyl ether, a smectic phase alone was found. The transition point and melting point rise slightly for the octadecyl ether which is also purely smectic. Enantiotropic and monotropic transitions were observed in several of these ether acids.

6-Methoxy-2-naphthoic acid (amorphous-219°-nematic-206°-solid). The nematic phase appears as tiny droplets which coalesce to give a nematic plate structure with well defined nuclei and threads, and exhibiting high double refraction. The solid appears as arborescent crystals which show very high double refraction and straight extinction. Individual crystals are tabular and positive biaxial. Both changes are enantiotropic.

6-Ethoxy-2-naphthoic acid (amorphous-224°-nematic-213°-solid). The nematic phase first appears as tiny droplets, but these rapidly coalesce to form homogeneous planes which show high double refraction. The solid is acicular, positive biaxial and has high birefringence. The extinction is straight. Both changes are enantiotropic.

6-n-Propoxy-2-naphthoic acid(amorphous-208.5°-nematic-208°-solid).The nematic phase is very similar in its mobility to that in the ethoxy acid,but its double refraction is lower. The colours are 4th order in parallel light and between crossed nicols.The solid appears as blades or prisms.These have very high double refraction,straight extinction and parallel cleavage and give positive biaxial patterns.Again both changes are enantiotropic.

6-n-Butyloxy-2-naphthoic acid(amorphous-208.5°-nematic-198°-solid I.Solid II is monotropic).The nematic form,when coalesced, has a highly threaded structure with high flow properties and high double refraction.If the temperature is allowed to fall, the threads disappear and the mobility decreases until the structure becomes homogeneous.There is no change in double refraction.Solid II appears in large plates which show parallel cleavage,straight extinction and 4th order double refraction. This passes over to the more confused spherulitic structure of the stable solid I.This is similar to solid II in all its properties,except that the double refraction is higher.The crystals are positive and biaxial.The changes are enantiotropic,except those involving solid II.

6-n-Amyloxy-2-naphthoic acid(amorphous-199°-nematic - 179.5°-solid).When the threaded nematic phase first appears,the double refraction is only first order,but,as the temperature falls, the order rises to greater than 4th. The solid crystallises in blades which are arranged in spherulites. The blades show straight extinction, parallel cleavage and high double refraction and are positive biaxial. Both changes are enantiotropic.

6-n-Hexyloxy-2-naphthoic acid (amorphous-198.5°-nematic-147°-solid I. Solid II is monotropic). The nematic droplets coalesce to give a highly mobile threaded structure which rapidly develops centres and has 4th order double refraction. At about 180°, the double refraction becomes very high. Solid II appears as a fan-like structure of very fine needles showing straight extinction. The blades of stable solid I have straight extinction and parallel cleavage. Both solids have very high double refraction and are positive biaxial. All transitions are enantiotropic, except those involving solid II.

6-n-Heptyloxy-2-naphthoic Acid (amorphous-192°-nematic-163°-solid II-105°-solid I). The nematic form (Plate 15) is highly threaded and the double refraction increases from 4th to very high orders with falling temperature. Solid II crystallises in broad blades with parallel cleavage and straight extinction. Then solid I appears in very similar, but smaller blades. Both solids are positive biaxial and all changes are enantiotropic.

6-n-Octyloxy-2-naphthoic acid (amorphous-190°-nematic-161.5°-solid II-160.5°-solid I). The nematic form coalesces to a homogeneous threaded structure(Plate 15) which, on cooling, passes from 3rd to very high orders of double refraction. Moreover, the structure develops centres and becomes plated before the transition to solid II which, although of narrow range, supercools markedly. This solid is comprised of spherulites of broad clear blades. Solid I is much more opaque, and resembles solid I with the injection of tiny needles. Both solids have a high double refraction, straight extinction and parallel cleavage. Solid I was identified as positive biaxial and all changes are enantiotropic.

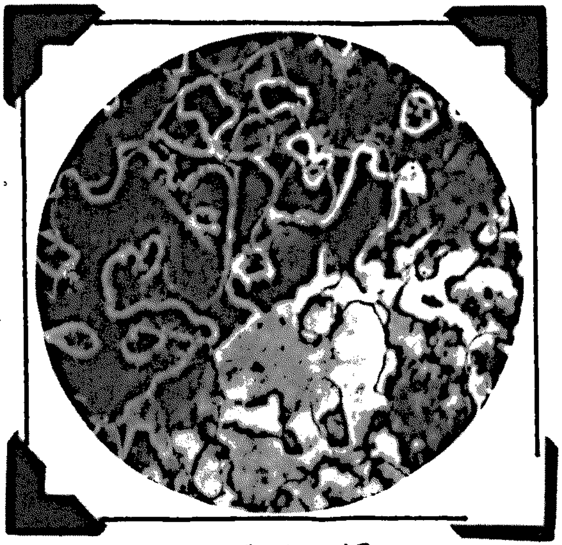


Plate 15

Plate 16

6-n-Nonyloxy-2-naphthoic acid(amorphous-183.5°-nematic-147.5°-smectic-146.5°-solid II -115°-solid I). The nematic phase is plate-like with well-defined centres(Plate 16) and the birefringence is high. The transition to the smectic is easily detectible, when the whole changes to a very minute focal-conic structure. Solid II is acicular, the crystals showing straight extinction,parallel cleavage and high double refraction.Solid I is similar,but has a denser structure with a higher birefringence and was identified as positive biaxial.All changes are enantiotropic.

6-n-Decyloxy-2-naphthoic acid(amorphous-181°-nematic-147°-smectic-139°-solid).The plated nematic phase is easily distinguished from the fine focal-conics and oily streaks of the smectic phase,although both have high double refraction. The solid crystallises in large sheets with straight extinction and parallel cleavage.The birefringence is high and the crystals are positive biaxial.All changes are enantiotropic.

6-n-Dodecyloxy-2-naphthoic acid(amorphous-174°-nematic-160°-smectic-119°-solid).The nematic and smectic phases are very similar to those described for decyl,but the smectic form has a lower (4th order) double refraction.The smectic phase is shown in Plate 17 .The solid is comprised of fairly large plates which are positive biaxial and of 4th order birefringence.All changes are enantiotropic.

6-n-Hexadecyloxy-2-naphthoic acid(amorphous-159.5°-smectic-107°-solid).The smectic phase first appears as a fine mozaic of focal-conics and the birefringence is high.If the temperature is allowed to fall,3rd order colours are seen in the larger areas which develop.The solid appears as a mass of tiny waxy plates which are positive biaxial.All changes are enantiotropic.

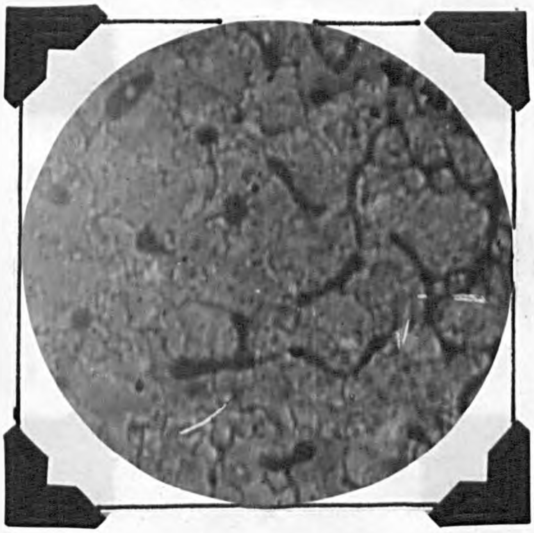


Plate 17

NEMATIC PHASE--- 5-CHLORO-6-n-BUTYLOXY-2-NAPHTHOIC ACID

Plate 18

6-n-Octadecyloxy-2-naphthoic acid(amorphous-161°-smectic-114°-solid).The smectic phase is very similar to that of the hexadecyl and the texture again becomes coarser as the temperature falls.The larger areas which develop have 1st order double refraction.The solid is a mass of waxy plates which are positive biaxial and have 1st order birefringence. All changes are enantiotropic.

2. 5-Chloro-6-n-alkyloxy-2-naphthoic acids.

Of the thirteen ethers examined (methyl to decyl,dodecyl, hexadecyl and octadecyl),methyl and ethyl alone are non-mesomorphic.From propyl to amyl the acids are purely nematic, but in hexyl,a short smectic phase appears.This gradually increases in length at the expense of the nematic,which makes its last appearance in the dodecyl ethor.The last two members of the series are purely smectic. The transition points to the amorphous liquid alternate for odd and even numbers of carbon atoms in the alkyl chain and lie on two distinct curves. This is shown in the graph for this series. Enantiotropic and monotropic polymorphism was exhibited by several of these acids.

5-Chloro-6-methoxy-2-naphthoic(amorphous-320.5°-solid), and 5-Chloro-6-ethoxy-2-naphthoic(amorphous-269°-solid) acids. In both cases, the solids appear as acicular crystals which show straight extinction and high double refraction. They are positive biaxial

5-Chloro-6-n-propoxy-2-naphthoic acid(amorphous-220.5°-nematic-219.5°-solid). Even when the amorphous liquid is cooled very slowly, the short nematic phase is over-taken by the crystalline solid which does not super-cool readily. This occurs before the nematic form has coalesced. The solid is acicular and the extinction is oblique. The double refraction is very high and the crystals are positive biaxial. Both transitions are enantiotropic.

5-Chloro-6-n-butyloxy-2-naphthoic acid(amorphous-216.5°-nematic-209.5°-solid I . Solid II is monotropic). When the nematic phase first forms, the birefringence is high and the structure is very mobile with many threads. As the temperature falls towards 210°, the double refraction decreases to 3rd or 4th order. Solid I crystallises in broad clear sheets, in contrast to the fine acicular structure of solid II.Both solids have high double refraction and oblique extinction,and are positive biaxial. The changes are enantiotropic,except those involving solid II.

5-Chloro-6-n-amyloxy-2-naphthoic acid(amorphous-208°-nematic-189°-solid III -162°-solid I.Solid II is monotropic).The highly birefringent nematic phase has characteristic plates and threads.The latter become less well-defined as the temperature falls.Solid III consists of clear blades and the appearance of solid II is marked by the injection of fine needles into this structure.The stable solid I crystallises as a mass of distorted blades and needles.The three solids have high double refraction and oblique extinction.Solid I was identified as positive biaxial.Except for transition to solid II , the changes are enantiotropic.

5-Chloro-6-n-hexyloxy-2-naphthoic acid(amorphous-207°-nematic-166°-smectic-164°-solid III -134°-solid I.Solid II is monotropic). The plated nematic phase has a high double refraction.The smectic form is of very narrow range,but has a characteristic focal-conic structure and high birefringence.The three solids are identical with those found in the hexyl ether.Again solid I was shown to be positive biaxial.

5-Chloro-6-n-heptyloxy-2-naphthoic acid(amorphous-201°-nematic-176.5°-smectic-165.5°-solid I.Solid II is monotropic). The coalesced droplets of the nematic phase form a very homogeneous structure,containing only a few threads.Nematic plates develop and the double refraction falls to about 4th order. Then the smectic form appears as a fine mozaic, with oily streaks. Solid II crystallises in large clear plates which soon pass over to the stable solid I. This is very similar, but the translucent areas are much larger. Both are positive biaxial, extinct obliquely and have high double refraction.

5-Chloro-6-n-octyloxy-2-naphthoic acid (amorphous-197.5°-nematic-181.5°-smectic-169°-solid I. Solid II is monotropic). The nematic phase has a highly centred structure of high birefringence, which falls with rising temperature and is only 4th order at 195°. The smectic form has a very homogeneous focal-conic structure. Solid II crystallises in large, clear sheets which have 4th order colours. Solid I appears in smaller sheets of much higher double refraction. Both solids extinct obliquely and are highly ordered, the whole section of the solids behaving as a positive biaxial crystal. All changes are enantiotropic, except those involving solid II.

5-Chloro-6-n-nonyloxy-2-naphthoic acid (amorphous-194.5°-nematic-185.5°-smectic-169°-solid I. Solid II is monotropic). The nematic form is almost homogeneous and the double refraction is only slightly greater than 4th order. The smectic phase consists of very minute focal-conics, but the double refraction is high. In Plate 19, the smectic form, on the right-hand side, is seen invading the more homogeneous nematic phase on the left. Solids I and II are identical with the corresponding solids of the octyl ether. However, in this case, both solids have a double refraction which is much higher than 4th order. Again, both solids are ordered and the sections behave as one positive biaxial crystal. Except for the changes to solid II, all are enantiotropic.

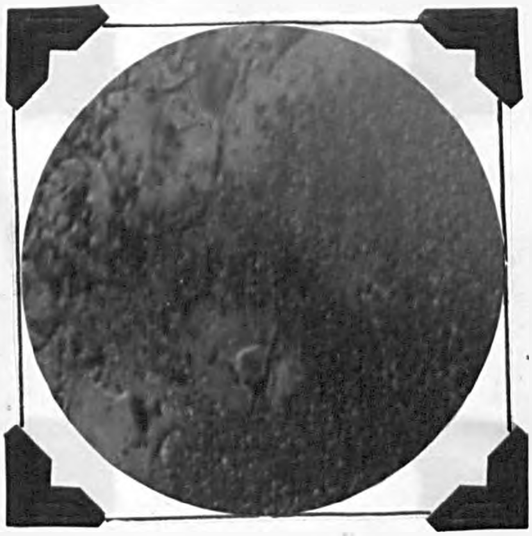


Plate 19

5-Chloro-6-n-decyloxy-2-naphthoic acid(amorphous-192.5°-nematic-186.5°-smectic-167°-solid). The nematic phase has a well-defined plate structure which has a very noticeable mobility. The smectic mozaic of focal-conics has slightly greater than 4th order birefringence. The solid crystallises in badly defined plates which are less translucent than the solids of the previous two ethers. The double refraction is still high but the degree of order of the crystals in a section is now lower, as indicated by the smaller number of positive biaxial patterns. All transitions are enantiotropic.

5-Chloro-6-n-dodecyloxy-2-naphthoic acid(amorphous-187.5°-nematic-185.5°-smectic-152°-solid). The short nematic phase is threaded and the birefringence is 3rd to 4th order, as is the case for the smectic form which appears in a fairly coarse focal-conic structure. The only solid crystallises in small waxy plates which have 4th order colours. Again, the solid is abundant in orientated positive biaxial crystals. All the transitions are enantiotropic.

5-Chloro-6-n-hexadecyloxy-2-naphthoic acid (amorphous-178.5°-smectic-142.5°-solid II -119°-solid I). On cooling, the amorphous liquid passes directly to the smectic form, which appears as small bâtonnets. These coalesce to a fine focal-conic structure of 1st to 2nd order double refraction. Solid II crystallises in distorted spherulites of fine needles; solid I consists of ill-defined waxy plates which show a fair number of positive biaxial patterns. Both solids have the same birefringence as the smectic phase and all the changes are enantiotropic.

5-Chloro-6-n-octadecyloxy-2-naphthoic acid (amorphous-174.5°-smectic-138.5°-solid II -126°-solid I). The smectic phase is identical in appearance and behaviour to that of the hexadecyl ether. In appearance and birefringence the two solids are also very similar to those of the latter ether. Solid I has fewer positive biaxial patterns. All transitions are enantiotropic.

In this series, the orientation of the stable solids on glass seems to increase up to octyl and then to decrease with further lengthening of the alkyl chain.

3. 5-Bromo-6-n-alkyloxy-2-naphthoic acids.

The methyl and ethyl ethers do not show mesomorphic properties. From propyl to hexyl, a nematic phase alone is observed, but in heptyl, a short smectic phase appears. This gradually increases in length at the expense of the nematic, which makes its last appearance in the dodecyl ether. The last two members of the series are purely smectic. As was found for the corresponding chloro- compounds, the transition points to the amorphous liquid lie on two distinct curves. Enantiotropic and monotropic polymorphism was observed in several of these acids.

5-Bromo-6-methoxy-2-naphthoic (amorphous-303°-solid), and 5-Bromo-6-ethoxy-2-naphthoic (amorphous-281°-solid) acids. Both crystallise in needles which extinct obliquely. The double refraction is very high and the crystals are positive biaxial.

5-Bromo-6-n-propoxy-2-naphthoic acid (amorphous-224°-nematic-224°-solid). The nematic phase is extremely short and is not longer than 0.2°. It is seen as a very narrow wave-front before the crystals. If the slide is suddenly cooled by a jet of air, the nematic form shoots ahead of the crystalline, but, on stopping the air supply, it is rapidly over-taken and frequently obliterated by the solid. By sudden chilling, the nematic form is seen to have a characteristic threaded structure of high double refraction. The solid crystallises in fine needles which have high double refraction, are positive biaxial and extinct obliquely. All changes are enantiotropic.

5-Bromo-6-n-butyloxy-2-naphthoic acid (amorphous-214.5°-nematic-

213°-solid I. Solid II is monotropic). The nematic phase is again short, contains many threads and is highly birefringent. The acicular crystals of monotropic solid II soon appear and, in turn, this changes to the stable solid I. The latter has a more dense acicular structure which becomes cracked and overgrown. Both solids show oblique extinction, high double refraction and positive biaxial patterns. With the exception of the transitions to solid II, the changes are enantiotropic.

5-Bromo-6-n-amyloxy-2-naphthoic acid (amorphous-207°-nematic-196.5°-solid III-193°-solid II-163°-solid I). When the minute droplets of the nematic form have coalesced, they give a homogeneous structure of 2nd order birefringence. Nematic plates soon develop and the double refraction increases to 4th order. Solids III and II are acicular and the transition between the two is not readily seen. The latter has a denser structure. Solid I has an extremely confused acicular structure. The high birefringence of solid I decreases slightly as the changes to the higher temperature crystal modifications are made. All are positive biaxial and extinct obliquely. Each transition is enantiotropic.

5-Bromo-6-n-hexyloxy-2-naphthoic acid (amorphous-204.5°-nematic-178°-solid III-174.5°-solid II-163°-solid I). The nematic form has a typical threaded structure (Plate 20) of high double refraction. Solid III crystallises in an open bladed structure which contrasts with the acicular solid II. The overgrown needles of solid I form a confused mass. The three solids are strongly birefringent and show oblique extinction. None of the solids was proved to be positive biaxial. All changes are enantiotropic.

Plate 20

5-Bromo-6-n-heptyloxy-2-naphthoic acid(amorphous-199°-nematic-165°-smectic-158°-solid II -144.5°-solid I). The mobile nematic form is threaded and the smectic form consists of small focal-conics. Both phases have a high double refraction, as is the case for solid II which crystallises in large translucent sheets, and for the mass of small plates which constitute solid I. Both solids extinct obliquely, but, again, no optic-sign patterns were found.

5-Bromo-6-n-octyloxy-2-naphthoic acid(amorphous-196°-nematic-173.5°-smectic-164°-solid II -122°-solid I). The threaded nematic form has 4th order double refraction which rapidly increases 2-3° before the appearance of the smectic phase. This is very homogeneous and is succeeded by solid II which crystallises in clear sheets. The stable solid I is made up of small plates. In both solids the double refraction is high and the extinction is oblique. Both solids are positive biaxial and all the transitions are enantiotropic.

5-Bromo-6-n-nonyloxy-2-naphthoic acid(amorphous-192.5°-nematic-179.5°-smectic-168°-solid). The nematic form appears as very large homogeneous patches which are separated by threads and show 4th order colours. The strongly birefringent smectic phase is a fine mozaic of focal-conics with oily streaks. The solid crystallises in large, clear, homogeneous plates. The extinction is oblique to the faint cleavage and the double refraction is high. The crystals are positive biaxial and all the changes are enantiotropic.

5-Bromo-6-n-decyloxy-2-naphthoic acid(amorphous-189.5°-nematic-182.5°-smectic-167°-solid). The 4th order colours of the plated nematic phase contrast with the bright whites of the strongly birefringent smectic form which appears as a fine mozaic of focal-conics. The extinction is oblique in the large sheets in which the solid crystallises. The double refraction is now beginning to decrease as the chain length increases and is only slightly greater than 4th order. The solid is positive biaxial and all changes are enantiotropic.

5-Bromo-6-n-dodecyloxy-2-naphthoic acid(amorphous-183.5°-nematic-182°-smectic-151.5°-solid). The very short nematic and the smectic phase are identical with those for the decyl ether. The solid is clear, but consists of a mass of plates. The double refraction has fallen to 2nd order and the extinction is oblique. The plates are positive biaxial and all the transitions are enantiotropic.

5-Bromo-6-n-hexadecyloxy-2-naphthoic acid(amorphous-173.5°-smectic-138.5°-solid).The smectic phase first appears from the amorphous liquid as bâtonnets which coalesce to a mozaic of small focal-conics.The solid crystallises as a mass of tiny plates.The solid and the mesophase have 1st to 2nd order birefringence.Individual determinations on separate crystals show that they are acicular and positive biaxial. Both transitions are enantiotropic.

5-Bromo-6-n-octadecyloxy-2-naphthoic acid(amorphous-172.5°-smectic-136.5°-solid).The smectic phase and the solid are very similar to those described above for the hexadecyl ether. The double refraction is slightly lower(2nd order),and in this case it was possible to show that separate crystals extinct obliquely.Both changes are again enantiotropic.

4. 5-Iodo-6-n-alkyloxy-2-naphthoic acids.

In this series,thirteen ethers were again examined.Methyl, ethyl and propyl are not mesomorphic,butyl to heptyl are nematic,octyl to dodecyl show both smectic and nematic properties,and hexadecyl and octadecyl are purely smectic. Enantiotropic and monotropic polymorphism is an outstanding feature of the series,but few of the solids were established as positive biaxial.

5-Iodo-6-methoxy-2-naphthoic acid(amorphous-296.5°-solid),and 5-Iodo-6-ethoxy-2-naphthoic acid(amorphous-286.5°-solid).Both of these ethers crystallise from the isotropic melt in blades which fan out and form spherulites.The cleavage lies parallel to the long axis of the blades.Individual crystals obtained from glacial acetic acid are almost perfect rectangular plates which are positive biaxial and show straight extinction. If the methyl ether is heated gently on a slide,the liberation of iodine is only slight and a clean isotropic melt can be obtained.

5-Iodo-6-n-propyloxy-2-naphthoic acid(amorphous-230°-solid III -213°-solid I.Solid II is monotropic).Solid III crystallises in very fine needles which pass over to the coarser acicular structure of solid II.The stable solid I crystallises in a very confused and overgrown acicular structure.The three solids have very high double refraction,show oblique extinction and are positive biaxial.

5-Iodo-6-n-butyloxy-2-naphthoic acid(amorphous-219°-nematic-219°-solid III -203°-solid I.Solid II is monotropic). The behaviour of the nematic is identical with that described for 5-bromo-6-n-propyloxy-2-naphthoic acid.The phase length is not greater than 0.2°.Only when the melt is rapidly cooled is the meso-phase seen as a threaded structure of high double refraction.Solid III quickly crystallises in large clear needles.Solids II and I are also acicular and all three are similar to the solids of the preceding ether.The changes are enantiotropic,except those involving solid II.

5-Iodo-6-n-amyloxy-2-naphthoic acid(amorphous-204°-nematic-203°-solid III -176.5°-solid I.Solid II is monotropic).The nematic phase is again threaded and has a high birefringence.The three solids are identical with those described for the propyl ether of this series.All transitions are enantiotropic with the exception of those involving solid II .

5-Iodo-6-n-hexyloxy-2-naphthoic acid(amorphous-198°-nematic-191°-solid III -162°-solid I.Solid II is monotropic).The nematic phase is homogeneous except for a few threads and the double refraction is again high.The three solids are again identical with those of the propyl ether,although solid I is less confused and overgrown.The transitions are enantiotropic except when they involve solid II .

5-Iodo-6-n-heptyloxy-2-naphthoic acid(amorphous-189°-nematic-176°-solid III -149.5°-solid I.Solid II is monotropic).On first appearing from the amorphous melt,the nematic phase is abundant in threads and the birefringence is high.This soon decreases however,and when the solid begins to crystallise the value is only 4th order.The three solids are again identical with the solid states of the propyl ether.The changes are enantiotropic,except those involving solid II .

5-Iodo-6-n-octyloxy-2-naphthoic acid(amorphous-185.5°-nematic-161.5°-smectic-160.5°-solid III -138°-solid I .Solid II is monotropic).The nematic phase has a plated structure and the double refraction is only 2nd order.The narrow smectic phase appears in characteristic, though small focal conics and has a high birefringence. Once more, the three solids are identical with those of the propyl ether and the changes are enantiotropic, except when they involve solid II.

5-Iodo-6-n-nonyloxy-2-naphthoic acid(amorphous-182°-nematic-165°-smectic-163°-solid II -125°-solid I. Solid III is monotropic). The highly birefringent nematic phase consists of large homogeneous areas containing a few well defined threads (Plate 21).

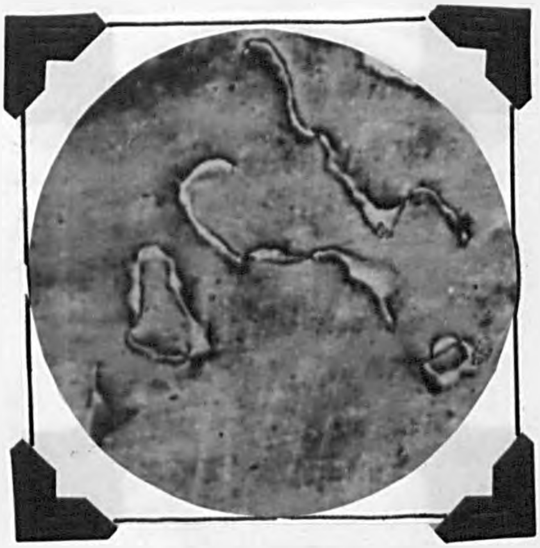


PLATE 21

The smectic phase is very similar to that of the octyl ether described above. Solid III crystallises in large clear sheets which have only a faint parallel cleavage. Solid II appears in radiating needles which then change into the confused bladed structure of the stable solid I. In all three solids the double refraction is high, the extinction is oblique and positive biaxial patterns are found. Except for changes to solid III, the transitions are enantiotropic.

5-Iodo-6-n-decyloxy-2-naphthoic acid(amorphous-179.5°-nematic-167°-smectic-165°-solid II -119°-solid I. Solid III is monotropic). The nematic phase, the smectic phase and the three solids are closely similar to those of the nonyl ether, and the only monotropic transitions are those to solid III.

5-Iodo-6-n-dodecyloxy-2-naphthoic acid(amorphous-172°-nematic-169°-smectic-146.5°-solid II -113°-solid I.Solid III is monotropic). The nematic phase is plated and the smectic phase consists of very fine focal-conics,but,in both,the double refraction has fallen to 1st-2nd order.The three solids are identical with those of the nonyl ether.The transitions are enantiotropic, except those involving solid III.

5-Iodo-6-n-hexadecyloxy-2-naphthoic acid(amorphous-165°-smectic-133.5°-solid II -103°-solid I).The smectic phase appears from the amorphous liquid in bâtonnets which coalesce to produce a fairly coarse focal-conic structure.Both solids crystallise in blades,but those of solid II are larger and clear.The double refraction is 1st-2nd order in the solids and in the meso-phases.The solids have only faint parallel cleavage and the extinction is oblique.The solids are positive biaxial and all transitions are enantiotropic.

5-Iodo-6-n-octadecyloxy-2-naphthoic acid(amorphous-163°-smectic-127°-solid II -118°-solid I).The smectic phase is identical with that of the hexadecyl ether.Solid II crystallises in waxy plates of 1st-2nd order birefringence.Solid I appears in even smaller plates of 1st order double refraction.When individual crystals of the solid were examined,these were found to be well defined prisms which show oblique extinction. All transitions are enantiotropic.

5. *5-Nitro-6-n-alkyloxy-2-naphthoic acids.*

The complete series of thirteen ethers was not prepared, since mesomorphic properties do not appear until the nonyl ether. Nematic properties persist beyond the dodecyl ether and are found in the hexadecyl and octadecyl ethers. Polymorphism is marked in the higher ethers which were examined.

5-Nitro-6-methoxy-2-naphthoic acid(amorphous-302°-solid). The solid crystallises in well defined prisms which extinct obliquely and are positive biaxial. The double refraction is very high.

5-Nitro-6-n-amyloxy-2-naphthoic acid(amorphous-211°-solid I. Solid II is monotropic). Solid II crystallises from the amorphous liquid in large clear plates which have a distinct parallel cleavage. Solid I appears in broad arborescent sheets. Both solids are positive biaxial and show oblique extinction. The double refraction is again very high.

5-Nitro-6-n-octyloxy-2-naphthoic acid(amorphous-187°-solid II - 153.5°-solid I). Solid II crystallises in well defined prisms which change over to solid I after standing for several minutes. Solid I has an opaque structure of small, distorted blades. Both solids have high birefringence and oblique extinction, and are positive biaxial. The transitions are enantiotropic.

5-Nitro-6-n-nonyloxy-2-naphthoic acid(amorphous-175°-nematic-174.5°-solid II -112°-solid I). The amorphous liquid frequently supercools and only crystallisation is seen. However, if the slide is chilled, the nematic phase is seen as a threaded structure of 1st order birefringence. Solid II crystallises in large clear sheets which show only very faint cleavage lines. Solid I has a more dense structure of smaller arborescent sheets. Both solids extinct obliquely, are highly birefringent and show many positive biaxial patterns. The transitions are enantiotropic.

5-Nitro-6-n-decyloxy-2-naphthoic acid (amorphous-175°-nematic-173.5°-solid II -133°-solid I). The nematic phase is very homogeneous and the double refraction is only 1st order. The solids are very similar to the corresponding solids of the nonyl ether, except that the birefringence is now lowered to 4th order. All transitions are enantiotropic.

5-Nitro-6-n-dodecyloxy-2-naphthoic acid (amorphous-171°-nematic-170°-smectic-167°-solid II -131°-solid I). The threaded nematic phase soon changes to focal-conic structures of the smectic phase. Both mesophases have 1st order birefringence. Again, the solids are closely similar to those of the nonyl ether but the double refraction is only 2nd-3rd order. All changes are enantiotropic.

5-Nitro-6-n-hexadecyloxy-2-naphthoic acid (amorphous-164.5°-nematic-164°-smectic-160°-solid II -107°-solid I). The nematic and smectic phases are identical with those described above for the dodecyl ether. Solid II crystallises in blades and solid I in small waxy plates and the double refraction of both is 1st-2nd order. They are positive biaxial. Crystals of the solid, obtained from ethyl alcohol, are acicular and show oblique extinction. All transitions are enantiotropic.

5-Nitro-6-n-octadecyloxy-2-naphthoic acid (amorphous-160°-nematic-159.5°-smectic-152°-solid II-75.5°-solid I). Both mesophases are again identical with those of the dodecyl ether. Solids II and I crystallise, in this order, in waxy plates, those of solid II being larger. Both solids are positive biaxial and their birefringence is 1st-2nd order. Crystals of the solid, obtained from ethyl alcohol, are acicular and show oblique extinction. All transitions are enantiotropic.

6. 3-Fluoro-4-n-alkyloxy benzoic acids.

The methyl and butyl to heptyl ethers have been prepared and show no mesomorphism. In the octyl ether, a short nematic phase appears and in the nonyl ether, an additional smectic phase which is too short to measure. In the decyl, dodecyl and hexadecyl ethers, the smectic phase increases in length with corresponding decrease in the length of the nematic phase which disappears in the last of the three. The octadecyl ether is likewise purely smectic but an increase in the m.p. accounts for the shorter phase-length than in the preceding ether. Polymorphism was observed in several of the ethers and all the solid states were established as positive biaxial.

3-Fluoro-4-methoxy benzoic acid (amorphous-211.5°-solid). The solid crystallises in well defined prisms which show oblique extinction and very high birefringence.

3-Fluoro-4-n-butyloxy benzoic acid(amorphous-142.5°-solid II -137.5°-solid I).Solid II crystallises in almost clear sheets and solid I in narrow,radiating blades.In both cases the double refraction is high and the extinction oblique.

3-Fluoro-4-n-amyloxy benzoic acid(amorphous-137°-solid II -99.5°-solid I).Solid II crystallises in broad blades.The long, fine needles of solid I give a very opaque structure,but, in both cases,the double refraction is high and the extinction oblique.

3-Fluoro-4-n-hexyloxy benzoic acid(amorphous-129°-solid II -74°-solid I).The solids are identical in appearance and properties to the corresponding solids of the amyl ether.

3-Fluoro-4-n-heptyloxy benzoic acid(amorphous-123°-solid II -101.5°-solid I).The solids are again identical in properties and appearance to the corresponding solids of the amyl ether.

3-Fluoro-4-n-octyloxy benzoic acid(amorphous-121°-nematic-117°-solid II -94°-solid I).The nematic phase first appears from the amorphous liquid as tiny droplets which coalesce to a threaded structure.The mesophase shows 3rd-4th order interference colours which fluctuate slightly.Solid II crystallises in large clear sheets and solid I in fine radiating needles. Both solids have high double refraction and show oblique extinction.All transitions are enantiotropic.

3-Fluoro-4-n-nonyloxy benzoic acid(amorphous-116.5°-nematic-112.5°-smectic-112.5°-solid II -109°-solid I).The nematic form closely resembles that of the preceding ether,but the double refraction is higher (slightly greater than 4th order).On sudden chilling,the smectic phase is seen as a fine mosaic of focal-conics.The double refraction is difficult to determine,since crystallisation occurs so quickly.The solids are also very similar to those of the octyl ether.All changes are enantiotropic and the smectic phase length is not greater than 0.2°.

3-Fluoro-4-n-decyloxy benzoic acid(amorphous-116.5°-nematic-112°-smectic-108°-solid II -106°-solid I).The threaded nematic phase is succeeded by the small focal-conics of the smectic phase and both have a double refraction which is considerably greater than 4th order.All transitions are enantiotropic.

3-Fluoro-4-n-dodecyloxy benzoic acid (amorphous-114.5°-nematic-112.5°-smectic-108.5°-solid I.Solids III and II are monotropic). The mesophases have the same appearance as those of the decyl ether,but the double refraction is only 4th order.Solid III crystallises in broad clear sheets,solid II in fairly large needles and solid I in very fine needles.The opacity increases in this order and the double refractions are 1st order, 2nd order and 4th order respectively.All the solids extinct obliquely.The transitions are enantiotropic,except when they involve solids II and III.

3-Fluoro-4-n-hexadecyloxy benzoic acid(amorphous-111°-smectic-94°-solid).The bâtonnets of the smectic phase appear from the amorphous liquid and coalesce to a typical focal-conic structure. This is shown in Plate 22 ,in which the amorphous liquid is black and completely extinct. The double refraction of the phase is only 1st order.The solid crystallises in small waxy plates which have 1st-2nd order colours.Both changes are enantiotropic.

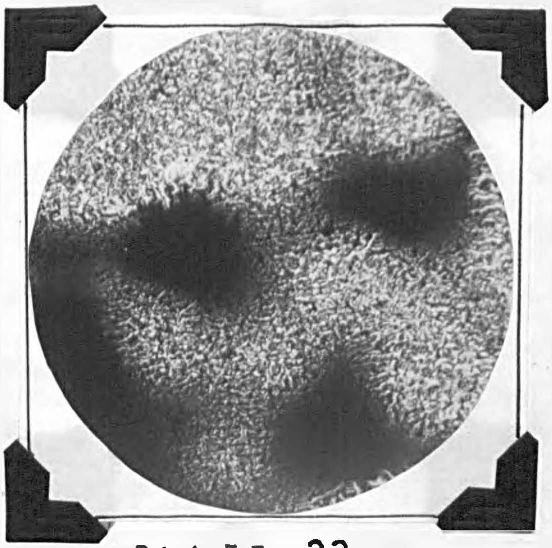


PLATE 22

3-Fluoro-4-n-octadecyloxy benzoic acid(amorphous-115°-smectic-113°-solid II -75.5°-solid I).The smectic phase is identical with that of the hexadecyl ether.Solid II crystallises in irregular blades and solid I in small waxy plates.Both have a first order birefringence and all changes are enantiotropic.

7. 3-Chloro-4-n-alkyloxy benzoic acids.

Like the corresponding fluoro- compounds,no mesomorphism is found until the alkyl group contains eight carbon atoms. In this series however,the phase lengths are very short.The longest is the 3° smectic phase in the hexadecyl ether.Those ethers which are mesomorphic have both a nematic and a smectic phase.The m.p. rises quite sharply in the octadecyl ether which is not mesomorphic.

3-Chloro-4-methoxy benzoic acid(amorphous-217.5°-solid).
3-Chloro-4-n-amyloxy benzoic acid(amorphous-134.5°-solid).
3-Chloro-4-n-hexyloxy benzoic acid(amorphous-120°-solid).
All three ethers crystallise in well defined needles which show oblique extinction and a high double refraction. No positive biaxial patterns were found in any of the solids.

3-Chloro-4-n-heptyloxy benzoic acid(amorphous-117°-solid II - 111°-solid I). Solid II crystallises in broad blades which extinct obliquely and have a high double refraction. These properties are also shown by the smaller, denser blades of solid I which was identified as positive biaxial. Both changes are enantiotropic.

3-Chloro-4-n-octyloxy benzoic acid(amorphous-95°-nematic-94°-smectic-94°-solid II -90°-solid I). The strongly birefringent nematic phase has a typical threaded appearance. The very short smectic phase is seen only if the slide is chilled suddenly, when it appears in a focal-conic structure. The phase length is less than 0.2° and no details can be seen before solid II appears. Solids II and I crystallise in blades, but the latter is much more dense and opaque. Both solids have very high double refraction, oblique extinction and positive biaxial properties. All transitions are enantiotropic.

3-Chloro-4-n-nonyloxy benzoic acid(amorphous-94.5°-nematic-93.5°-smectic-93°-solid II -85°-solid I). The threaded nematic phase and the focal-conic smectic phase are both strongly birefringent. The broad blades of solid II and the radiating needles of solid I are easily distinguished and have the same properties as the corresponding solids of the octyl ether. All the transitions are enantiotropic.

3-Chloro-4-n-decyloxy benzoic acid(amorphous-101°-nematic-100°-smectic-99°-solid I. Solid II is monotropic). The mesophases are similar to those of the nonyl ether, but the double refraction has fallen to 4th order. Solid II crystallises in well defined blades and solid I is a dense mass of needles. The crystals of both solids are positive biaxial and show oblique extinction and strong birefringence. The transitions are enantiotropic, except those involving solid II.

3-Chloro-4-n-dodecyloxy benzoic acid(amorphous-102°-nematic-101°-smectic-100°-solid I. Solid II is monotropic). The double refraction of the typical smectic and nematic phases is now only 2nd-3rd order. The solids, which are otherwise very similar to those of the decyl ether, are only of slightly greater than 4th order birefringence. The only monotropic transitions are those involving solid II.

3-Chloro-4-n-hexadecyloxy benzoic acid(amorphous-99°-nematic-98°-smectic-95°-solid). The double refraction of the mesophases is now 2nd order. The solid crystallises in very small needles. These extinct obliquely and show 3rd-4th order colours. No positive biaxial patterns were found. All changes are enantiotropic.

3-Chloro-4-n-octadecyloxy benzoic acid(amorphous-108°-solid). There is no mesomorphism in this ether and the solid appears from the amorphous liquid in well defined blades. The extinction is oblique, the double refraction is 3rd order and the crystals are positive biaxial.

Discussion of Syntheses

A. 4-n-Alkyloxy-1-naphthoic acids

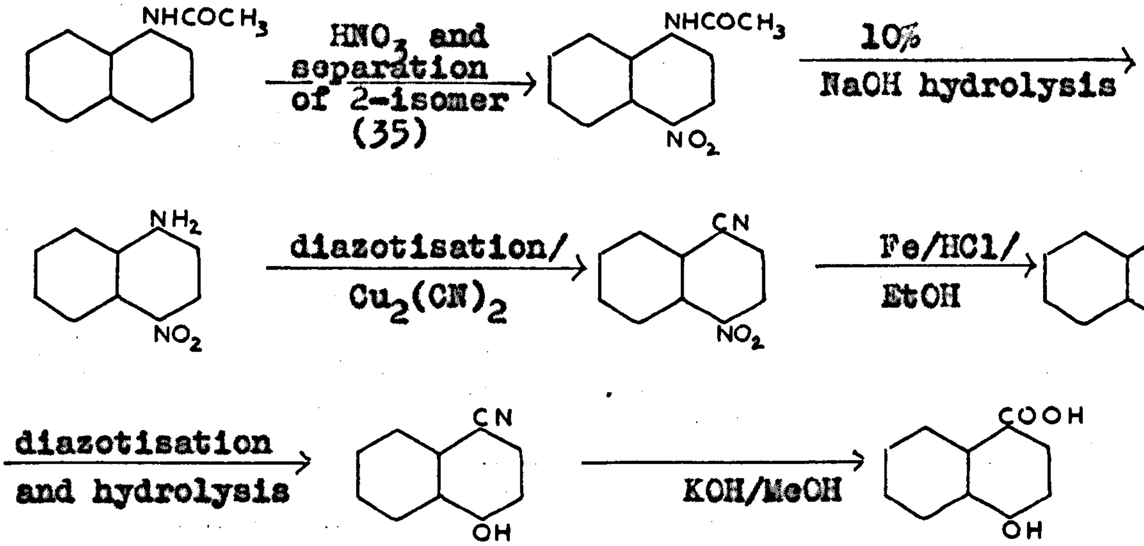
Each member of this series has been prepared separately from an available naphthalene derivative, and not simply by the homologous alkylation of 4-hydroxy-1-naphthoic acid. The reason is that the hydroxy acid is not readily obtainable in quantity by any convenient, direct method of preparation, and although 4-methoxy-1-naphthoic acid may be obtained in large amount, this ether cannot be demethylated to give the hydroxy compound without the occurrence of simultaneous decarboxylation.

4-Hydroxy-1-naphthoic acid was first prepared by Heller (30) in 1912 from the hydroxy aldehyde, which was obtained by the action of hydrogen cyanide and hydrogen chloride on an ether solution of 1-naphthol in the presence of zinc chloride, followed by hydrolysis of the imine hydrochloride(31). As the ring system and the hydroxy group are susceptible to attack by most oxidising agents, the conversion to the acid was effected by fusing the aldehyde with potassium hydroxide. The product is described as crystallising from water in fine yellow needles, m.p. 183-4°. Although the aldehyde is now more readily available by the Adam's modification of the Gattermann synthesis, the method of oxidation limits the amount of material which can be handled conveniently. M^{c}Cluggage and Lindstrom(32) have investigated methods of oxidising 4-ethoxy-1-naphthaldehyde and 4-ethoxy-1-naphthyl methyl ether —

prepared by the Friedel and Crafts reaction of acetyl chloride and 1-ethoxy-naphthalene.They claim that alkaline potassium permanganate oxidises the aldehyde to the acid and the ketone to 4-ethoxy-1-naphthoyl formic acid,which is converted by potassium permanganate in acetic acid solution, in quantitative yield,to 4-ethoxy-1-naphthoic acid.Repetition of these oxidations gave very poor yields due to the extensive degradation of the naphthalene ring system.Sodium hypochlorite oxidation of 4-ethoxy-1-naphthyl methyl ketone gives 40-50% yields of the acid,but the reaction is very slow and the large amounts of unreacted material render the product difficult to purify.M^{c}Cluggage and Lindstrom also emphasise the stability of the ketone to oxidation.

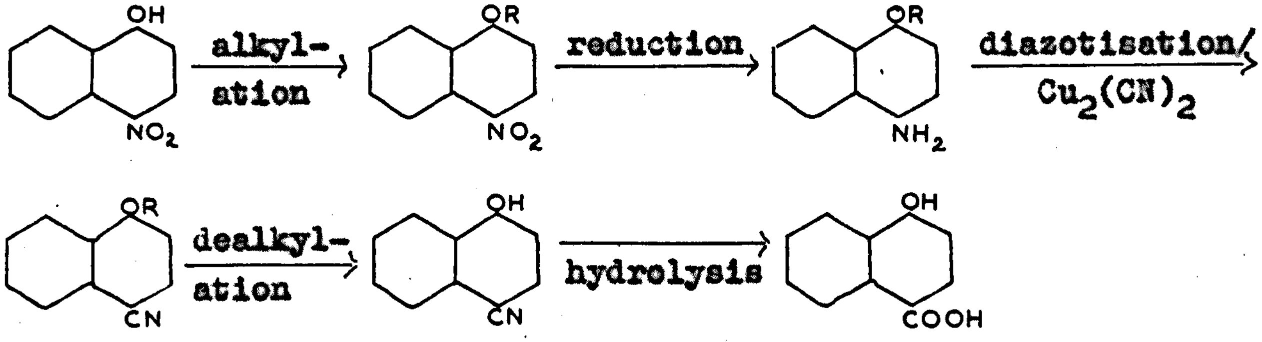
Methyl 4-hydroxy-1-naphthoate is described in an American patent(33).A solution of 1-naphthol in sodium hydroxide and methyl alcohol is stirred with carbon tetrachloride and copper powder for several hours at less than 50°.Neutralisation with an inorganic acid precipitates the methyl ester of 1-hydroxy-2:4-naphthalene di-carboxylic acid,m.p.144° after crystallisation from acetic acid.Removal of the methyl alcohol gives the methyl ester of 4-hydroxy-1-naphthoic acid,m.p.178° after crystallisation from methyl alcohol.Repitition of this procedure gave no products.

Friedlander and Weisberg(34) describe the preparation of 4-amino-1-naphthoic acid from 4-nitro-1-naphthonitrile by reduction, and hydrolysis of the 4-amino-1-naphthonitrile. A modification of their synthesis is a possible route to 4-hydroxy-1-naphthoic acid, as shown below—



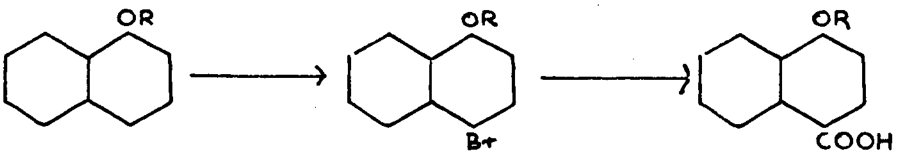
This route would be very tedious and, as is described later, the 4-hydroxy-1-naphthonitrile is very difficult to purify. Hydrolysis of the crude nitrile gives highly impure acid which cannot be purified.

The other possible route from 4-nitro-1-naphthol has also been eliminated as the 4-n-alkyloxy-1-naphthonitriles are very stable to dealkylation.



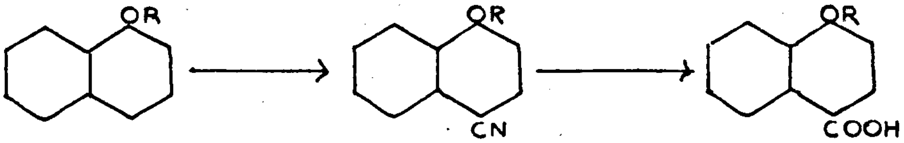
As no convenient method of preparing 4-hydroxy-1-naphthoic acid in quantity seemed possible,methods of synthesising the individual 4-n-alkyloxy-1-naphthoic acids were investigated. Two methods were found to give good results.

(1)



The 1-n-alkyloxy naphthalenes are brominated in 70-75% yield by the method of Militzer(36),using iodine monobromide in chloroform solution.The 4-bromo-1-n-alkyloxy naphthalene Grignard compound is prepared and carbonated(37) to give 80-85% yields of the carboxylic acids.4-Methoxy,ethoxy,propoxy and butyloxy-1-naphthoic acids were prepared by this method, but the higher members of the series were synthesised by method (2) below,which gives higher overall yields.Moreover the rate of formation of the Grignard derivatives of 4-bromo-1-n-amyloxy naphthalene and the higher bromo ethers is very slow

(2)



The nitriles are obtained in 80-90% yield directly from the 1-n-alkyloxy naphthalenes by the Friedel and Crafts reaction with aluminium trichloride and cyanogen bromide in dry carbon disulphide.The hydrolysis to the 4-n-alkyloxy-1-naphthoic acids is difficult, and it is necessary to use hot, saturated potassium hydroxide/methyl alcohol solution. The time of reflux until ammonia ceases to be evolved varies, depending on the alkyl group, between 15 and 25 hours. In this way, the acids are obtainable in 95-97% yield.

A large number of nitriles is preparable in this way(38) and despite the toxic properties of cyanogen bromide, it is conveniently handled and still further increases the scope of the Friedel and Crafts reaction.

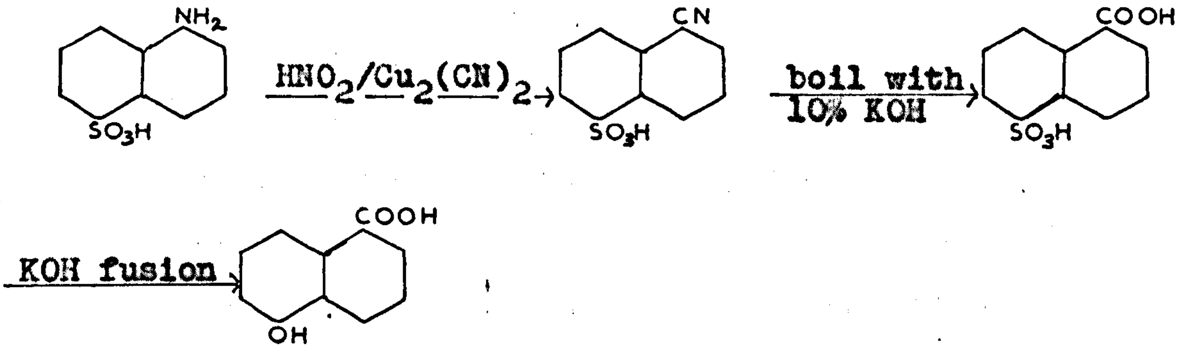
The yields obtained by the two methods compare as follows:-

Acid	Method	Overall yield(%) from 1-naphthyl ethyl ether
4-ethoxy-1-naphthoic	(1)	57
4-ethoxy-1-naphthoic	(2)	76

By these methods, 4-*n*-alkyloxy-1-naphthoic acids are preparable in good yield, but, as has been pointed out, neither offers a route to the hydroxy acid due to ready decarboxylation when dealkylation is attempted. In the Friedel and Crafts reaction, in method (2), only very small amounts (1-2%) of 4-hydroxy-1-naphthonitrile are formed, indicating the stability of the alkyloxy nitriles to dealkylation. Indeed, attempts to de-ethylate 4-ethoxy-1-naphthonitrile, by prolonged reflux with acetic acid and 48% hydrobromic acid, failed completely.

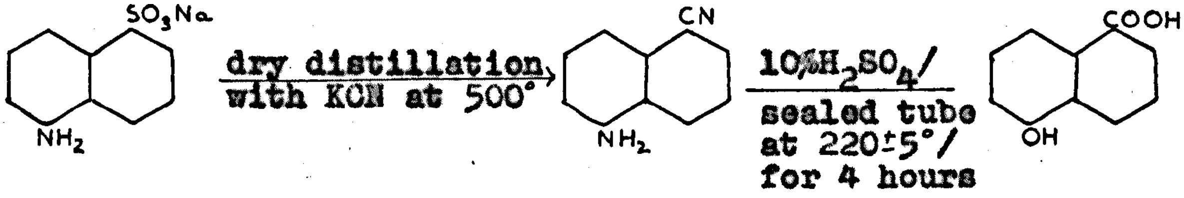
B. 5-Hydroxy-1-naphthoic acid and n-alkyl ethers

5-Hydroxy-1-naphthoic acid was first prepared from 5-aminonaphthalene-1-sulphonic acid by Royle and Schedler(39), who used the following synthesis.



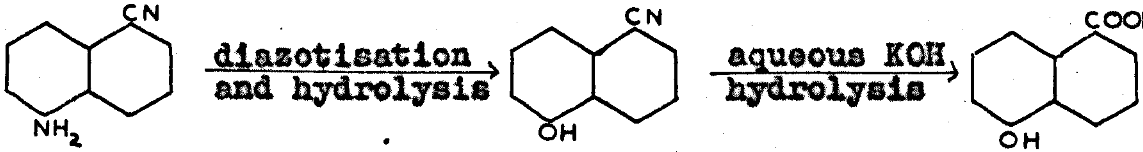
This procedure is apparently straightforward, but in practice is laborious due to the difficulty of isolating the product of diazotisation of an amino-sulphonic acid. The isolation involves the evaporation to dryness of the Sandmeyer reaction mixture and the extraction of the 5-cyano-naphthalene-1-sulphonic acid with alcohol. This is never obtained pure, and the 5-carboxy-naphthalene-1-sulphonic acid must be purified by crystallisation of its potassium salt. The synthesis was attempted twice, but the experimental difficulties in the evaporation of large volumes and the purification of intermediates make it a procedure with much to be desired. However, it is the only method recorded in the literature for the preparation of 5-hydroxy-1-naphthoic acid in quantity.

The only other method is due to Cason(40), who also started with the readily available 5-naphthylamine-1-sulphonic acid.



On repitition, the first stage to the nitrile went smoothly, the average yield of many experiments being 25%, but the hydrolysis of the nitrile could not be effected by Cason's procedure. Cason records that the temperature control is critical and that at 200±5° a product is obtained from which no pure hydroxy acid is isolable. In this work the hydrolysis was repeated at several temperatures. Temperatures higher than 225° gave mainly 1-naphthol by decarboxylation, at 200° to 225° the product was a mixture which could not be purified and between 180° and 200° only very slight hydrolysis to 5-amino-1-naphthoic acid occurred. The hydrolysis may be affected by the strength of the sulphuric acid and it is not stated whether Cason's 10% sulphuric acid is weight/weight or weight/volume. In these experimemts 10% weight/weight was used. In addition, the synthesis is not suitable for the preparation of any large quantity of the hydroxy acid, since the hydrolysis of even 0.2g. of nitrile requires 10c.c. of acid and hence the use of a fairly large sealed tube.

A different method was therefore required, using 5-amino-naphthalene-1-sulphonic acid as the starting material. The latter was converted to 5-amino-1-naphthonitrile, as described above, and this submitted to the following stages.



The finely divided amine sulphate is diazotised and the nitrite-free diazonium salt solution is hydrolysed by dropwise addition to boiling 40% weight/weight sulphuric acid.When cold,the solid and solution are extracted with ether.The crude hydroxy nitrile is extracted from the ether by shaking with aqueous sodium hydroxide.Precipitation with an inorganic acid, followed by crystallisation from 35% acetic acid gives a 65% yield of 5-hydroxy-1-naphthonitrile,m.p.203-5°.The nitrile is then hydrolysed with 30% aqueous potassium hydroxide to yield 90% of 5-hydroxy-1-naphthoic acid,m.p.238°(d).M.p. values quoted in the literature are 235-6°(d)(39) and 237-240°(d)(40). The acetyl derivative is found to have mp.205°.Recorded m.p. values are 202°(41) and 206°(40).Methylation gives 5-methoxy-1-naphthoic acid,m.p.227.5°.Fuson(41) quotes the m.p. of the methyl ether as 227.5°-228.5°.

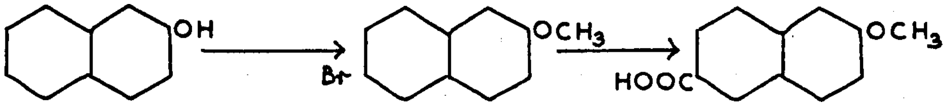
In this way,5-hydroxy-1-naphthoic acid is obtained by a shorter method than Royle and Schedler's,and although the synthesis involves one more stage than Cason's,the overall yield is slightly better.Moreover,the preparation may be carried out on any required scale.

The n-alkyl ethers are prepared in good yield by alkylation of the hydroxy acid in aqueous alcoholic potassium hydroxide solution.The ether acids are purified by crystallisation and sublimation until a constant m.p. is obtained.None of these 5-n-alkyloxy-1-naphthoic acids is mesomorphic.

C. 6-Hydroxy-2-naphthoic acid and n-alkyl ethers

6-Hydroxy-2-naphthoic acid is prepared by demethylation of the 6-methoxy compound which may be synthesised by either of the two methods described.The series of ethers is prepared by homologous alkylation of the hydroxy acid.

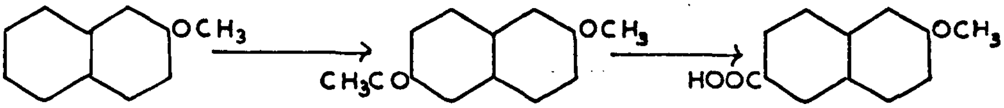
(1)



6-Bromo-2-naphthol is prepared in 90-95% yield by dibrominating 2-naphthol in acetic acid solution and,without isolation of the 1:6-dibromo-2-naphthol,reducing with mossy tin in hydrobromic acid/acetic acid solution(42).Methylation of this product gives 6-bromo-2-methoxy naphthalene in 60-70% yield after vacuum distillation.The unmethylated material is recovered from the alkaline reaction liquors.

The formation of the Grignard compound of 6-bromo-2-methoxy naphthalene is not quite straightforward.If 1g.atom of magnesium to 1g.mole. of the bromo compound is used,the yields of the acid on carbonation are consistently low (15-20%). Finally.the method of Fries and Schimmelschmidt(43) was adopted.The solvent is a mixture of dry benzene and ether, and a considerable excess of magnesium is used (1g.mole. of bromo compound to 1.67 g.atoms of magnesium).Throughout the reaction the magnesium is continually re-activated by the addition of small volumes of ethyl bromide.Carbonation of the reaction mixture and acidification gives the 6-methoxy-2-naphthoic acid which precipitates on evaporation of the ether. 50-55% of the purified acid is obtained. A further 10% may be extracted from the benzene, but this material can never be purified completely.

(2)



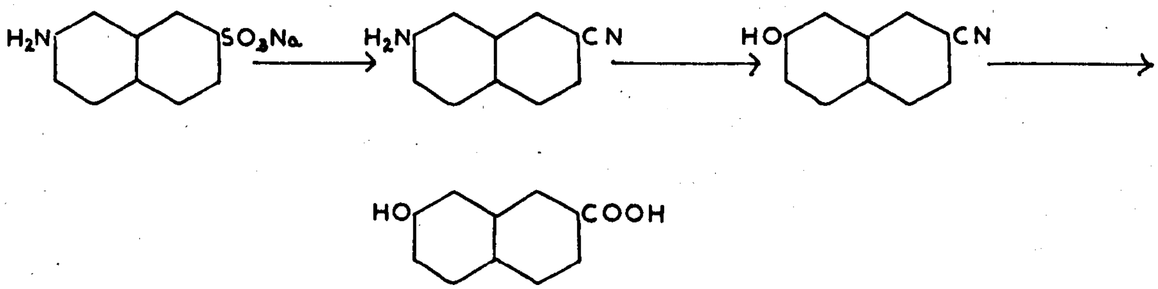
6-Acetyl-2-methoxy naphthalene is prepared by the method of Robinson and Rydon(44), who have shown that acetyl chloride and aluminium trichloride react with 2-methoxy naphthalene in nitrobenzene to give the 6-acetyl derivative and in carbon disulphide to give the 1-acetyl compound. The yield of purified 6-acetyl-2-methoxy naphthalene is consistently 50%. The acid is obtained in 70-75% yield when the ketone is oxidised by aqueous sodium hypochlorite, using dioxan as the organic solvent.

There is little to choose between the two methods, either in overall yield or in convenience of operation and both have been employed at various times.

6-Methoxy-2-naphthoic acid is demethylated by refluxing with a solution of 48% hydrobromic acid in acetic acid which has been saturated with hydrogen bromide. The product separates on cooling and may be crystallised from water to give 70-75% yields of 6-hydroxy-2-naphthoic acid.

The *n*-alkyl ethers are prepared by refluxing an aqueous alcoholic solution of the hydroxy acid and the theoretical amount of potassium hydroxide with the *n*-alkyl bromide or iodide.Acidification gives the ether acids which are purified by crystallisation from xylene and acetic acid to constant m.p.All the *n*-alkyl ethers prepared are mesomorphic.

D. 7-Hydroxy-2-naphthoic acid and n-alkyl ethers



This procedure is identical with that used for the preparation of 5-hydroxy-1-naphthoic acid.The yield of 7-amino-2-naphthonitrile,prepared by distillation of the sodium salt of the sulphonic acid with potassium cyanide at 500°,is much lower in this case(7%).However,only a small amount of 7-hydroxy-2-naphthoic acid was required and so this method was adopted.Diazotisation and hydrolysis yield 76% of the purified 7-hydroxy-2-naphthonitrile,which hydrolyses in 90% yield,with 2N potassium hydroxide,to the hydroxy acid.This procedure is a quick method of preparing small quantities of 7-hydroxy-2-naphthoic acid in a pure state.One crystallisation from 50% ethyl alcohol gives m.p.269°-270°.The acetate has m.p.

208-9°. The hydroxy acid has been prepared before from 7-amino-2-naphthonitrile by hydrolysing with 66% sulphuric acid to 7-amino-2-naphthoic acid, m.p. 240°, followed by diazotisation and hydrolysis to 7-hydroxy-2-naphthoic acid, m.p. 262° (45). Butler and Royle (46) prepared the same compound, m.p. 269°-270°, from 7-amino-naphthalene-2-sulphonic acid <u>via</u> 7-cyano-naphthalene -2-sulphonic acid. Holmes and Trevoy (47) prepared 7-methoxy-2-naphthoic acid, m.p. 195-6°, by dehydrogenation of 7-methoxy-3:4-dihydro-2-naphthoic acid, and demethylation yielded 7-hydroxy-2-naphthoic acid, m.p. 274-5°.

The 7-<u>n</u>-alkyloxy-2-naphthoic acids are prepared by the method described for the 6-<u>n</u>-alkyloxy-2-naphthoic acids. The ethers were crystallised to constant m.p. and show no mesomorphic properties.

Experimental Section B

Preparation of Materials

B. Preparation of materials(all m.p. corrected)

1. *n*-Alkyl halides

n-Nonyl,*n*-decyl,*n*-dodecyl and *n*-octadecyl bromides could not be purchased and were prepared by the following method(48).

48% Hydrobromic acid(71g.,0.42mole.) and concentrated sulphuric acid(12c.c.,0.23mole.) were mixed and the normal aliphatic alcohol(0.22mole.) added.After refluxing for 6 hours, the mixture was cooled.In one preparation the bromide was isolated by diluting the reaction mixture,separating the oily layer and washing with cold concentrated sulphuric acid,water and dilute sodium carbonate solution.During the concentrated acid wash,emulsions form easily and make the separation difficult.In subsequent preparations it was found easier to proceed as follows.On dilution of the mixture,the oily layer was extracted with ether and washed well with water.The unreacted alcohol was removed by shaking thoroughly with a saturated solution of calcium chloride and then,in the following order,with water,aqueous sodium carbonate and water. The ether extract was dried over calcium chloride,and the residue,after removal of the ether,was distilled under reduced pressure.

	Yield(%)	b.p.	m.p.
n-nonyl bromide	80	116° at 28m.m.	——
n-decyl bromide	77	136° at 32 m.m.	——
n-dodecyl bromide	70	175° at 32m.m.	——

n-octadecyl bromide	65	183° at 3m.m.	28°-28.5°

2. 4-n-Alkyloxy-1-naphthoic acids

(a) 1-n-Alkyloxy naphthalenes

1-Naphthol(144g.,1mole.) was dissolved in a cooled solution of sodium(23g.,1g.atom) in the minimum volume of absolute ethyl alcohol.n-Alkyl bromide or iodide was added in an amount equivalent to 1.2mole.,and the mixture refluxed for 8 hours.When cold,the sodium halide was dissolved out with water and the 1-naphthyl ether extracted with ether. 1-n-Octadecyloxy naphthalene was extracted with a mixture of equal parts of ether and benzene.The organic extract was washed with dilute sodium hydroxide and water,and dried over anhydrous sodium sulphate.After removing the solvent,the residue was distilled under reduced pressure.The pure ethers were obtained as colourless liquids or low melting solids in 65-75% yield.

Alkyl group	Yield	b.p.	m.p.
Methyl	74	134° at 13m.m.	
Ethyl	72	152° at 17m.m.	5°
Propyl	66	143° at 3m.m.	
Butyl	68	160° at 4m.m.	19.5°
Amyl	66	173° at 6m.m.	29.5°
Hexyl	66	166° at 4m.m.	-3°
Heptyl	67	171° at 5m.m.	
Octyl	67	189° at 5m.m.	

Nonyl	65	185° at 4m.m.	
Decyl	67	212° at 4m.m.	
Dodecyl	67	227° at 3m.m.	
Hexadecyl	65	258° at 1m.m.	31°
Octadecyl	65	236° at 10^{-2}m.m.	50.5°

(b) <u>4-Bromo-1-n-alkyloxy naphthalenes</u>(methyl to hexyl)

Powdered iodine(63.5g.,0.25mole.) was dissolved in chloroform(350c.c.) and bromine(40g.,0.25mole.) added.The solution was warmed to 50° to facilitate the formation of iodine monobromide,cooled to 25° and added during 1.5 hours to an efficiently stirred solution of the 1-<u>n</u>-alkyloxy naphthalene (0.25mole.) in chloroform(300c.c.),externally cooled in a water bath.After the addition,the mixture was stirred for a further hour at room temperature.Water(1,400c.c.) was next added and,while stirring vigorously,solid sodium hydrosulphite was sifted in until all the precipitated iodine was removed. The sulphurous acid and hydrobromic acid were then neutralised by adding an excess of solid sodium bicarbonate.The pale straw-coloured chloroform layer was separated,washed with aqueous sodium bicarbonate and water,and dried over anhydrous sodium sulphate.The chloroform was removed and the residue of 4-bromo-1-<u>n</u>-alkyloxy naphthalene distilled under reduced pressure.

<u>Alkyl group</u>	<u>Yield</u>(%)	<u>b.p.</u>	<u>m.p.</u>
Methyl	75	159° at 4m.m.	
Ethyl	70	158° at 3m.m.	48.5°

Propyl	72	188° at 8m.m.	31°
Butyl	67	199° at 5m.m.	25°
Amyl	70	181° at 3m.m.	47.5°
Hexyl	71	206° at 5m.m.	45°

	Analysis for $C_{10}H_6$.Br.OR	Analysis found
Ethyl	$C_{12}H_{11}OBr$ requires C,57.4 ;H,4.4	C,57.6;H,4.6%
Propyl	$C_{13}H_{13}OBr$ requires C,58.87;H,4.96	C,58.6;H,5.0%
Butyl	$C_{14}H_{15}OBr$ requires C,60.2 ;H,5.38	C,60.3;H,5.5%
Amyl	$C_{15}H_{17}OBr$ requires C,61.45;H,5.8	C,61.5;H,5.7%
Hexyl	$C_{16}H_{19}OBr$ requires C,62.6 ;H,6.2	C,63.1;H,6.3%

(c) <u>4-n-Alkyloxy-1-naphthonitriles</u>(ethyl,amyl to decyl, dodecyl,hexadecyl and octadecyl)

A mixture of bromine(36g.,0.2mole.)and a small amount of water(3.5c.c.) were placed in a round-bottomed flask(250c.c.), fitted with a mercury-sealed stirrer,condenser and dropping-funnel.The whole was cooled in ice and the mixture stirred vigorously during the addition of a solution of sodium cyanide (11.1g.,0.226mole.) in water(86c.c.).The addition time was 30 minutes.Stirring was continued for a further 2 hours, while maintaining the temperature below 30°.The cyanogen bromide was distilled off on a hot water bath,under an efficient hood.The product may be dried by shaking the molten cyanogen bromide with calcium chloride.This step was avoided by weighing the distillate directly,ignoring the very small amount of water which is carried over if the distillation is done slowly.The cyanogen bromide was then dissolved in carbon disulphide and the solution dried over anhydrous sodium sulphate.This solution,containing a known weight of cyanogen bromide per c.c.,was used for the Friedel and Crafts reaction.The cyanogen bromide distilled at 60°-62° as a colourless liquid which rapidly crystallised in colourless needles,m.p.52°.

A solution of cyanogen bromide(10.6g.,0.1mole.) in dry carbon disulphide(100c.c.) was added slowly to a stirred solution of the 1-n-alkyloxy naphthalene(0.1mole.) in dry carbon disulphide(75c.c.) containing powdered anhydrous aluminium trichloride(16g.,0.12mole.).The addition was made in 30 minutes and the reaction completed by warming at 45° in a water bath for 45 minutes.The reaction mixture was then poured onto crushed ice and left to stand overnight.The layer of carbon disulphide was diluted with ether and the total extract washed with sodium hydroxide to remove the small amounts of 4-hydroxy-1-naphthonitrile produced by dealkylation.After a final wash with water,the organic extract was dried over anhydrous sodium sulphate and the solvents distilled off.The solid residue was recrystallised from absolute ethyl alcohol to yield about 80% of the 4-n-alkyloxy-1-naphthonitriles in a sufficiently pure state for hydrolysis to the acids.Small amounts were recrystallised several times for analysis and m.p. determination.The nitriles are colourless crystalline solids which up to dodecyloxy are readily soluble in alcohol, but hexadecyloxy and octadecyloxy require moderately large volumes for crystallisation.

Alkyl Group	m.p.	Analysis for $C_{10}H_6.OR.CN$	Analysis found
C_2H_5	88°	$C_{13}H_{11}ON$ C,79.2 ;H,5.58;N,7.1	C,79.2;H,5.6;N,7.0%
C_5H_{11}	60°	$C_{16}H_{17}ON$ C,80.34;H,7.11;N,5.86	C,80.1;H,7.1;N,5.9%
C_6H_{13}	62°	$C_{17}H_{19}ON$ C,80.63;H,7.5 ;N,5.54	C,80.5;H,7.4;N,5.4%
C_7H_{15}	54°	$C_{18}H_{21}ON$ C,80.9 ;H,7.86;N,5.24	C,80.7;H,7.6;N,5.2%
C_8H_{17}	61°	$C_{19}H_{23}ON$ C,81.14;H,8.17;N,4.98	C,81.2;H,8.0;N,5.0%
C_9H_{19}	53°	$C_{20}H_{25}ON$ C,81.35;H,8.47;N,4.75	C,81.4;H,8.6;N,4.6%
$C_{10}H_{21}$	64°	$C_{21}H_{27}ON$ C,81.54;H,8.74;N,4.53	C,81.5;H,8.7;N,4.3%
$C_{12}H_{25}$	67°	$C_{23}H_{31}ON$ C,81.9 ;H,9.2 ;N,4.16	C,82.0;H,9.2;N,4.0%
$C_{16}H_{33}$	69°	$C_{27}H_{39}ON$ C,82.44;H,9.93;N,3.56	C,82.3;H,9.9;N,3.5%
$C_{18}H_{37}$	71°	$C_{29}H_{43}ON$ C,82.66;H,10.2;N,3.33	C,82.7;H,10.3;N,3.3%

Attempts to dealkylate any of these nitriles failed. Negative results were obtained by refluxing with 48% hydrobromic acid, with aluminium trichloride in carbon disulphide or nitrobenzene and with acetic acid saturated with hydrogen bromide.

Some 13g. of 4-hydroxy-1-naphthonitrile were accumulated by acidifying the alkali washes of the Friedel and Crafts reactions. The product proved to be very difficult to purify and the best sample, obtained by recrystallisation from 90% ethyl alcohol with heavy loss, had m.p.172-4°. This material gave poor analysis figures which were very low in nitrogen, and yielded impure acid on hydrolysing as described below.

4-Hydroxy-1-naphthonitrile(4g.),m.p.172-4°,was refluxed in hot saturated potassium hydroxide/methyl alcohol solution (125c.c.) for 32 hours,until ammonia was no longer evolved. The reaction mixture was poured into water(400c.c.) and acidified with concentrated hydrochloric acid.On cooling to 0°,the solution deposited 2.9g.,65%,of fine,light-brown needles, m.p.174-5° (d).This 4-hydroxy-1-naphthoic acid was very difficult to crystallise except from water,which did not improve the m.p.From the analysis figures the acid was very impure and the m.p. compares badly with the value of 183-4° quoted by Heller(30).

(d) <u>4-n-Alkyloxy-1-naphthoic acids</u>

<u>Method (1)</u>— from the 4-bromo-1-<u>n</u>-alkyloxy naphthalenes

Magnesium turnings(2.45g.,0.1g.atom) and a solution of the 4-bromo-1-<u>n</u>-alkyloxy naphthalene(2g.) in dry ether(20c.c.) were placed in a round-bottomed flask fitted with a three-necked adapter which carried a double-surface condenser and calcium chloride tube,a mercury-sealed stirrer and a dropping-funnel.The mixture was refluxed at 60° for a few minutes and if the reaction did not commence(i.e.,if a turbidity did not appear in the solution),a small crystal of iodine was added as a catalyst.The remainder of the bromo-compound(a total of 0.1 mole.) dissolved in dry ether(75c.c.) was added dropwise in 30 minutes to the boiling reaction mixture.Refluxing was then continued for 10 hours,after which time only a trace of magnesium remained unreacted in the dark brown mixture.The mixture was cooled and poured,with good stirring,into ether (75c.c.) saturated with solid carbon dioxide.The semi-solid addition compound separated out and was decomposed by stirring with 1:1 concentrated hydrochloric acid(50c.c.).The ether was allowed to evaporate and the brown free acid filtered.At this stage the product was always slightly tacky and tended to turn blue on standing,perhaps through oxidation of side reaction products.The acid was carefully washed free from magnesium ion with dilute hydrochloric acid and water,and finally dissolved in boiling 1N sodium hydroxide.Hot filtering removed any of the blue complex,and acidification of the pale orange filtrate precipitated the nearly white free acid, which after one crystallisation from glacial acetic acid was almost pure.All the acids crystallised in colourless needles.

Alkyl group	Yield(%)	Alkyl group	Yield(%)
Methyl	85	Propyl	80
Ethyl	82	Butyl	85

Method (2)— from the 4-n-alkyloxy-1-naphthonitriles

The 4-n-alkyloxy-1-naphthonitrile(0.1 mole.)was refluxed with a solution(250c.c.) prepared by saturating methyl alcohol with potassium hydroxide at 50°.Boiling was continued until ammonia was no longer detectible(15-25 hours).The hot solution was poured into water(1,000c.c.) and acidified.The acid was filtered,redissolved in boiling dilute sodium hydroxide and filtered hot. Acidification gave a quantitative yield of the white acid which crystallised from glacial acetic acid in colourless needles. The lowest yield of almost pure 4-*n*-alkyloxy-1-naphthoic acid after one crystallisation was 95%. This method was used to prepare all the acids listed below, except methyl, ethyl, propyl and butyl which were prepared by method (1). For the analyses and m.p. values, the acids were crystallised four times from glacial acetic acid.

Alkyl Group	m.p.	Analysis for $C_{10}H_6$.OR.COOH		Analysis found
Methyl	248°	$C_{12}H_{10}O_3$	C,71.29;H,4.94	C,71.2;H,5.2 %
Ethyl	220°	$C_{13}H_{12}O_3$	C,72.2 ;H,5.56	C,72.1;H,5.6 %
Propyl	203°	$C_{14}H_{14}O_3$	C,73.05;H,6.09	C,73.1;H,6.1 %
Butyl	213.5°	$C_{15}H_{16}O_3$	C,73.77;H,6.55	C,73.7;H,6.3 %
Amyl	207°	$C_{16}H_{18}O_3$	C,74.42;H,6.98	C,74.4;H,7.0 %
Hexyl	212°	$C_{17}H_{20}O_3$	C,75.0 ;H,7.35	C,74.9;H,7.5 %
Heptyl	189°	$C_{18}H_{22}O_3$	C,75.54;H,7.69	C,75.4;H,7.6 %
Octyl	183.5°	$C_{19}H_{24}O_3$	C,76.0 ;H,8.0	C,75.9;H,8.1 %
Nonyl	161°	$C_{20}H_{26}O_3$	C,76.44;H,8.28	C,76.3;H,8.2 %
Decyl	174.5°	$C_{21}H_{28}O_3$	C,76.8 ;H,8.54	C,77.0;H,8.6 %
Dodecyl	147.5°	$C_{23}H_{32}O_3$	C,77.54;H,8.99	C,77.5;H,9.0 %
Hexadecyl	136°	$C_{27}H_{40}O_3$	C,78.64;H,9.71	C,78.4;H,9.6 %
Octadecyl	137.5°	$C_{29}H_{44}O_3$	C,79.1 ;H,10.0	C,79.4;H,10.0%

3. 5-n-Alkyloxy-1-naphthoic acids

(a) Sodium 5-amino-naphthalene-1-sulphonate

Technical 5-amino-naphthalene-1-sulphonic acid was dissolved in the theoretical amount of cold 2N sodium hydroxide and the dark solution evaporated to dryness.The slightly purple sodium salt was powdered and completely dried by heating in an oven at 200° for two hours.

(b) 5-Amino-1-naphthonitrile

Sodium 5-amino-naphthalene-1-sulphonate(70g.) and potassium cyanide(140g.) were ground together and dry distilled in an all glass retort which had a short but wide side arm to act as a condenser.The heating was supplied by a high temperature salt bath at 500°-600°.Keeping the top of the retort warm with a flame,a dark,red-brown oil distilled and solidified immediately in the receiver.The distillate was dissolved in boiling 0.3N hydrochloric acid(1,300c.c.).The solution was cooled to 30° and a small amount of tar filtered off.The filtrate was neutralised with concentrated ammonium hydroxide and the orange-brown precipitate of 5-amino-1-naphthonitrile filtered with suction.The dried product(15.7g.) was distilled under reduced pressure and gave a pale yellow solid,11.3g., 23.5%,b.p.187°-193° at 2-3m.m.Although this material softened and melted over the range 120°-140°,it was found to give very satisfactory yields in the next stage of the synthesis.Two crystallisations from 80% ethyl alcohol gave yellow needles, m.p.140°.A large number of experiments gave yields which were consistently in the range 22-26%,after reduced pressure distillation(Found:C,78.4;H,4.8;N,16.7.$C_{11}H_8N_2$ requires

C,78.57;H,4.76;N,16.66%).

(c) 5-Hydroxy-1-naphthonitrile

5-Amino-1-naphthonitrile(5.04g.,0.03 mole.) was dissolved in glacial acetic acid at 80°.40% (w/w) Sulphuric acid(60c.c.), at 80°,was added to this hot solution and the mixture was cooled rapidly to 0°,with good agitation,to obtain the finely divided amine sulphate.An excess of sodium nitrite(4.2g.,0.06 mole.),dissolved in water(30c.c.),was added dropwise at 0°to the stirred solution and maintained under these conditions until a clear brown solution resulted.The excess sodium nitrite was destroyed by adding solid urea or sulphamic acid until a blank reaction to starch-iodide paper was obtained.The cold diazonium salt solution was added dropwise during 30 minutes to boiling 40% (w/w) sulphuric acid(180c.c.).As the addition was made a red oil separated,but this became granular after about 10 minutes.When all the diazonium solution had been added,refluxing was continued for one hour and the mixture then allowed to cool.Water(300c.c.) was added,and the crystals and the solution were extracted with ether.The ether layer was extracted twice with N sodium hydroxide and acidification gave a pink precipitate of 5-hydroxy-1-naphthonitrile,4.3g., 83%.One crystallisation from aqueous acetic acid(35c.c. of glacial acetic acid and 65c.c. of water) gave slightly orange needles,3.36g.,66-67%,m.p.204-6°.This material was used for the hydrolysis to the acid.Two further crystallisations from the above strength of aqueous acetic acid gave light yellow needles,m.p.209.5°(Found:C,77.8;H,4.14;N,8.2.$C_{11}H_7ON$ requires C,78.1;H,4.14;N,8.28%).

(d) <u>5-Hydroxy-1-naphthoic acid</u>

5-Hydroxy-1-naphthonitrile(8.4g.,0.05 mole.) was dissolved in a solution of potassium hydroxide(50g.) in water(100c.c.). The light brown solution was refluxed until ammonia ceased to be evolved (4 to 5 hours).The solution was cooled,diluted with water(100c.c.) and filtered.Concentrated hydrochloric acid precipitated the light brown 5-hydroxy-1-naphthoic acid,8.46g., 90%,m.p.238°(d).This product was used for the alkylations,since two crystallisations from water did not raise the m.p.

Acetylation and two crystallisations of the product from benzene gave small,colourless plates,m.p.204-5°.

(e) <u>5-Methoxy-1-naphthoic acid</u>

5-Hydroxy-1-naphthoic acid(1.88g.,0.01 mole.),10% aqueous sodium hydroxide(5c.c.) and dimethyl sulphate(2.5g.,0.02 mole.) were stirred at 40°-60° for 30 minutes.During this time the mixture was kept alkaline by adding small portions of 10% sodium hydroxide.10% methyl alcoholic sodium hydroxide(20c.c.) was then added and the whole refluxed for one hour to remove any ester.The solution was filtered hot and acidified to give the pale yellow 5-methoxy-1-naphthoic acid,1.8g.,90%,m.p.220-227°.Two crystallisations from 95% ethyl alcohol and one sublimation at 190° at 2m.m. gave colourless needles,m.p.232.5°

(Found:C,71.3;H,5.18.$C_{12}H_{10}O_3$ requires C,71.3;H,4.94%).

(f) 5-n-Alkyloxy-1-naphthoic acids

5-Hydroxy-1-naphthoic acid(1.88g.,0.01 mole.),potassium hydroxide(0.7g.,0.02 mole.),water(5c.c.),ethyl alcohol(40c.c.) and the n-alkyl bromide or iodide(0.011 mole.) were refluxed for 8 hours when using an iodide and for 16 hours with a bromide.10% aqueous potassium hydroxide(10c.c.) was added and the reflux continued for a further 2 hours to hydrolyse any ester.The mixture was cooled,diluted and acidified,and the pale yellow or light brown 5-n-alkyloxy-1-naphthoic acid filtered.The acids were purified for analysis and m.p. determination by two crystallisations from glacial acetic acid and one from 95% ethyl alcohol.Except for the last three members of the following table,the crystallised acids were also sublimed at 175°-185° at 2m.m.However,after only one crystallisation from glacial acetic acid the acids were almost pure and the yields at this stage were between 80 and 90%.

Alkyl Group	m.p.	Analysis for $C_{10}H_6$.OR.COOH	Analysis found
Ethyl	201°	$C_{13}H_{12}O_3$ C,72.2 ;H,5.56	C,71.9;H,5.8 %
Propyl	189°	$C_{14}H_{14}O_3$ C,73.05;H,6.09	C,72.9;H,5.9 %
Butyl	172°	$C_{15}H_{16}O_3$ C,73.77;H,6.55	C,73.7;H,6.4 %
Amyl	143°	$C_{16}H_{18}O_3$ C,74.42;H,6.98	C,74.2;H,7.1 %
Hexyl	154°	$C_{17}H_{20}O_3$ C,75.0 ;H,7.35	C,74.7;H,7.4 %
Heptyl	135.5°	$C_{18}H_{22}O_3$ C,75.54;H,7.69	C,75.5;H,7.6 %
Octyl	142.5°	$C_{19}H_{24}O_3$ C,76.0 ;H,8.0	C,75.9;H,7.9 %

Nonyl	143°	$C_{20}H_{26}O_3$	C,76.44;H,8.23	C,76.4;H,8.3 %
Decyl	137°	$C_{21}H_{28}O_3$	C,76.8 ;H,8.54	C,76.7;H,8.4 %
Dodecyl	125°	$C_{23}H_{32}O_3$	C,77.54;H,8.98	C,77.4;H,9.0 %
Hexadecyl	117.5°	$C_{27}H_{40}O_3$	C,78.64;H,9.71	C,78.6;H,9.8 %
Octadecyl	122°	$C_{29}H_{44}O_3$	C,79.1 ;H,10.0	C,79.2;H,10.1%

4. 6-n-Alkyloxy-2-naphthoic acids

Method (1)

(a) Mossy tin

Stannous chloride(112g.,0.5 mole.) was dissolved in water (150c:c.) and zinc dust(30g.,0.46g.atom) added to the solution with shaking.Heat was evolved and the mossy tin precipitated immediately.When cold,the tin was filtered with suction,washed well with cold water and desiccated in vacuo.The yield was about 55g.

(b) 6-Bromo-2-naphthol

2-Naphthol(144g.,1 mole.) was suspended in glacial acetic acid(400c.c.) contained in a 3 litre round-bottomed flask fitted with a dropping-funnel and a reflux condenser.A solution of bromine(320g.,2 moles.) in glacial acetic acid(100c.c.) was added in 15 to 30 minutes,keeping the flask well shaken.The 2-naphthol dissolved during this time and heat was evolved, necessitating cooling towards the end of the addition to prevent excessive loss of hydrogen bromide.Water(100c.c.) was added and the mixture heated to boiling,cooled to 100°,mossy tin(25g.) added and boiling continued until the metal had dissolved.A second portion of mossy tin(25g.) was dissolved by boiling and finally a third portion of tin(100g.) was introduced.The mixture was boiled for 3 hours,cooled to 50° and filtered with suction.The crystalline tin salts so removed were washed in the funnel with cold glacial acetic acid (100c.c.).The filtrate and washings were stirred into cold water(3 litres) and the pink 6-bromo-2-naphthol,which precipitated,was filtered.The solid was removed from the funnel and washed by stirring with water(1 litre).After refiltering and drying at 50°,the yield was 214-223g.,96-100%.This product contained some tin salts,but was pure enough for the next stage.The m.p. was 123-7°.

(c) <u>6-Bromo-2-methoxy naphthalene</u>

6-Bromo-2-naphthol(223g.,1 mole.) was dissolved in a solution of sodium hydroxide(80g.,2 moles.) in water(3 litres). Methylation was effected by heating to 70° with two portions of dimethyl sulphate(126g.,1 mole. and 63g.,0.5 mole).The mixture was thoroughly cooled after each addition and finally the product was filtered off.The solid was dried and distilled under reduced pressure.Over a large number of methylations the yield was 145-170g.,60-70%,of white crystalline solid, m.p.103-5°,b.p.189°-199° at 20m.m.One crystallisation from ethyl alcohol gave colourless needles,m.p.106-7°.

The recovery of unmethylated 6-bromo-2-naphthol from the alkaline reaction liquors by acidification was quantitative.

(d) 6-Methoxy-2-naphthoic acid

6-Bromo-2-methoxy naphthalene(23.7g.,0.1 mole.),m.p.106-7°,was dissolved in hot Analar benzene(75c.c.).Magnesium turnings(4g.,0.17g.atom) were placed in a 500c.c. round-bottomed flask,fitted with a three-necked adapter which carried a mercury-sealed stirrer,a double-surface condenser and calcium chloride tube,and a dropping-funnel.The magnesium was covered with dry ether(75c.c.),and etched by heating with ethyl bromide(0.5c.c.) and a crystal of iodine.When the iodine colour had disappeared and the reaction mixture was turbid,the hot benzene solution of the bromo-compound was added in 15 minutes.During the addition the contents of the flask were thoroughly stirred and heated in a water bath at 50°-60°.The mixture became dark brown and stirring and refluxing were continued for two hours.Ethyl bromide(5c.c.) was then added at half-hour intervals in the following quantities— 6 portions of 0.5c.c.,2 portions of 0.75c.c. and 1 portion of 0.5c.c.—and boiled for a further 30 minutes.The overall time of reflux was 6.5 hours and only a very small amount of magnesium remained undissolved.The cooled reaction mixture was poured steadily,with stirring,into dry ether(75c.c.) saturated with solid carbon dioxide.The carbonated Grignard compound separated as a viscous semi-solid and,when all the excess carbon dioxide had evaporated,the free acid was liberated by thoroughly stirring in 1:1concentrated hydrochloric acid(75c.c.).The ether was evaporated and the white precipitate of the acid was filtered and pressed dry.The benzene layer in the filtrate was retained.The acid was dissolved in hot N sodium hydroxide,filtered,acidified and the precipitated acid filtered and dried.One crystallisation from xylene yielded 10.1 to 11.2g.,50-55%,m.p.206°,over a number of experiments.

The benzene layer was extracted twice with cold N sodium hydroxide and acidification of these extracts gave some light brown acid.This material was very impure and had m.p.170-3°. Three crystallisations from xylene gave about 2g.(10% of the theoretical yield),m.p.196-8°.

Method (2)

(a) 6-Acetyl-2-methoxy naphthalene

Aluminium trichloride(200g.,1.5 mole.) was powdered and dissolved in dry,redistilled nitrobenzene(1,200c.c.).To this solution was added 2-methoxy naphthalene(192g.,1.22 mole.) and the homogeneous mixture cooled well in ice water.Acetyl chloride(120g.,1.53 mole.) was added dropwise with shaking during 20 minutes.The dark,bottle-green reaction mixture was allowed to stand at room temperature with occasional shaking for 48 hours,after which it was poured into a vigorously stirred mixture of ice(1,000g.),water(400c.c.) and concentrated hydrochloric acid(400c.c.).As the complex decomposed,the green colour disappeared and the brown nitrobenzene layer separated. This was washed twice with water by decantation and the nitrobenzene steam-distilled off, leaving a solid cake of the acetyl compound which was filtered. The dried solid was distilled at 165°-170° at 3-4m.m. This gave 184g., 76-77%, of a pale yellow oil which rapidly solidified, but the m.p. was low. One crystallisation from absolute methyl alcohol(250c.c.) yielded colourless blades, 120g., 50%, m.p. 104-5°.

(b) 6-Methoxy-2-naphthoic acid

A solution of sodium hypobromite was prepared by dissolving sodium hydroxide(140g.) in water(600c.c.) and adding bromine (50c.c.) with stirring at 0°-5°. The thoroughly cooled hypobromite solution was added dropwise to a stirred solution of 6-acetyl-2-methoxy naphthalene(50g.) dissolved in dioxan(350c.c.). During the 30 minute addition the temperature rose gradually and was maintained at 35°-40° by cooling in a water bath. The temperature was then raised to 50°-55° to ensure complete oxidation. The excess bromine was destroyed by stirring in solid sodium hydrosulphite and the mixture diluted by pouring into water(2 litres). 500c.c. of liquid were distilled off to remove the dioxan and bromoform and the alkaline solution filtered hot. Acidification with concentrated hydrochloric acid yielded the pale yellow acid, 48.7g. One crystallisation from xylene gave nearly colourless needles of 6-methoxy-2-naphthoic acid, 35-37g., 70-75%, m.p. 205-6°.

6-Methoxy-2-naphthoic acid, prepared by either of the above methods (1) or (2), was then demethylated and the 6-hydroxy-

2-naphthoic acid homologously alkylated.

6-Hydroxy-2-naphthoic acid

6-Methoxy-2-naphthoic acid(8.4g.,0.042 mole.) was suspended in a mixture of glacial acetic acid(33c.c.),48% hydrobromic acid(33c.c.) and glacial acetic acid(20c.c.) saturated with hydrogen bromide.During the reflux time of 2.5 hours the methoxy acid dissolved.The dark solution was cooled thoroughly and the light brown crystals collected and washed well with water.One crystallisation from water(1,200c.c.) gave 5.4g., 69-70%,of pale tan needles,m.p.249°.One further crystallisation from water gave almost white needles,m.p.250°.In a number of experiments the yields were between 70 and 75%.

Derivatives

Acetate

6-Hydroxy-2-naphthoic acid(0.5g.) was dissolved in 0.5N sodium hydroxide(5c.c.) and the solution cooled thoroughly in ice water while acetic achydride(0.35c.c.) was added dropwise with stirring.A white precipitate formed immediately and after stirring for a few minutes at 0°,the solution was found to be acid.The acetate was filtered,washed well with water and after two crystallisations from ethyl acetate had the constant m.p. 228°(d).Knowles(49) has reported the m.p.221-3°.

Benzoate

6-Hydroxy-2-naphthoic acid(0.5g.)was dissolved in N sodium hydroxide(5c.c.) and the solution well shaken with benzoyl chloride(0.5c.c.).The mixture became warm and was allowed to stand for 15 minutes,with periodic shaking,until it had cooled to room temperature.The suspension of the sodium salt was stirred thoroughly with concentrated hydrochloric acid and the benzoate of the free acid filtered off.The benzoic acid was dissolved out by stirring with cold ethyl alcohol(30c.c.) and the insoluble benzoate refiltered.The white powder was crystallised twice from ethyl acetate and gave small needles m.p.257°.

Benzene sulphonate

The preparation was exactly as described above for the benzoate,using benzene sulphonyl chloride(0.6c.c.) for 0.5g. of the hydroxy acid.The buff coloured product obtained on acidification was crystallised twice from glacial acetic acid and once from ethyl acetate.The fine colourless needles had m.p.228.5°.

6-n-Alkyloxy-2-naphthoic acids.

The method of alkylation was exactly as described for the preparation of the 5-n-alkyloxy-1-naphthoic acids(page 190). After one crystallisation from glacial acetic acid the ethers were obtained as colourless needles in 85-90% yield.The m.p. values and analysis figures listed below were obtained on samples of the 6-n-alkyloxy-2-naphthoic acids which had been crystallised twice from glacial acetic acid and twice from xylene

Alkyl Group	m.p.	Analysis for $C_{10}H_6$.OR.COOH	Analysis found
Methyl	206°	$C_{12}H_{10}O_3$ C,71.29;H,4.94	C,71.2;H,5.0 %
Ethyl	213°	$C_{13}H_{12}O_3$ C,72.2 ;H,5.56	C,72.3;H,5.4 %
Propyl	208°	$C_{14}H_{14}O_3$ C,73.05;H,6.09	C,72.9;H,6.1 %
Butyl	198°	$C_{15}H_{16}O_3$ C,73.77;H,6.55	C,73.9;H,6.4 %
Amyl	179.5°	$C_{16}H_{18}O_3$ C,74.42;H,6.98	C,74.3;H,6.9 %
Hexyl	147°	$C_{17}H_{20}O_3$ C,75.0 ;H,7.35	C,74.9;H,7.4 %
Heptyl	163°	$C_{18}H_{22}O_3$ C,75.54;H,7.69	C,75.1;H,7.7 %
Octyl	161.5°	$C_{19}H_{24}O_3$ C,76.0 ;H,8.0	C,75.9;H,8.0 %
Nonyl	146.5°	$C_{20}H_{26}O_3$ C,76.44;H,8.28	C,76.6;H,8.4 %
Decyl	139°	$C_{21}H_{28}O_3$ C,76.8 ;H,8.54	C,76.8;H,8.6 %
Dodecyl	119°	$C_{23}H_{32}O_3$ C,77.54;H,8.99	C,77.4;H,9.1 %
Hexadecyl	107°	$C_{27}H_{40}O_3$ C,78.64;H,9.71	C,78.9;H,9.7 %
Octadecyl	114°	$C_{29}H_{44}O_3$ C,79.1 ;H,10.0	C,79.2;H,9.9 %

6-*iso*-amyloxy-2-naphthoic acid was prepared by the above method. This 3-methyl-butyl ether was crystallised three times from glacial acetic acid and had m.p. 194° (Found: C,74.3;H,7.0. $C_{16}H_{18}O_3$ requires C,74.42;H,6.98%).

6-*iso*-nonyloxy-2-naphthoic acid was also prepared. This was the 3:5:5-trimethyl-hexyloxy acid and after three crystallisations from glacial acetic acid the m.p. was 170° (Found: C,76.6; H,8.2. $C_{20}H_{26}O_3$ requires C,76.44;H,8.28%).

5. 5-Chloro-6-n-alkyloxy-2-naphthoic acids

5-Chloro-6-hydroxy-2-naphthoic acid may be prepared either by the demethylation of 6-methoxy-2-naphthoic acid and chlorination of the hydroxy compound or by chlorination of the methoxy acid and subsequent demethylation.The overall yield from 6-methoxy-2-naphthoic acid is better by the latter method. The relative yields were 50-51% and 63-64%.The 5-chloro-6-hydroxy-2-naphthoic acid was then homologously alkylated to give the n-alkyl ethers.

(a) 5-Chloro-6-hydroxy-2-naphthoic acid

6-Hydroxy-2-naphthoic acid(18.8g.,0.1 mole.) was dissolved in glacial acetic acid(170c.c.) and a hot solution of dichloramine-T(12g.,0.05 mole.) in glacial acetic acid(60c.c.) followed by concentrated hydrochloric acid(0.5c.c.) were added. The mixture was heated on the water bath for 4 hours,cooled and the light brown crystalline product filtered.All the p-toluene-sulphonamide was retained in the mother liquors. The solid was washed with a little glacial acetic acid and several times with water.One crystallisation from a small volume of absolute methyl alcohol gave light fawn needles of 5-chloro-6-hydroxy-2-naphthoic acid,16g.,72-73%,m.p.278°(d). Sublimation at 160°-180° at 1-2m.m. gave a white product,m.p. 279°(d) (Found:C,59.1;H,3.3;Cl,16.0.$C_{11}H_7O_3Cl$ requires C,59.4; H,3.15;Cl,15.9%).

(b) 5-Chloro-6-methoxy-2-naphthoic acid

6-Methoxy-2-naphthoic acid(5.05g.,0.025 mole.) was dissolved in glacial acetic acid(150c.c.) at 40°.Dichloramine-T (3g.,0.013 mole.) dissolved in glacial acetic acid(20c.c.) at

40° and 2-4 drops of concentrated hydrochloric acid were then added. The mixture was refluxed for 4 hours. On cooling 4.75g., 81.5%, of white crystalline product separated, leaving the p-toluene-sulphonamide in solution. The solid was washed with a little glacial acetic acid and with water, and dried. One crystallisation from glacial acetic acid gave an 80% yield of white needles of 5-chloro-6-methoxy-2-naphthoic acid, m.p. 320.5°.

(c) 5-Chloro-6-hydroxy-2-naphthoic acid

5-Chloro-6-methoxy-2-naphthoic acid(23.65g., 0.1 mole.), 48% hydrobromic acid(250c.c.) and glacial acetic acid(250c.c.) were refluxed until a solution was obtained(14-16 hours). The reaction mixture was poured into water(1 litre) and the pale pink precipitate(20g., m.p. 270°-275°) filtered, washed with water and dried. Soxhlet extraction with ether removed some high melting material which was insoluble, and evaporation of the ether gave 18.5g., 83%, m.p. 271°(d). One crystallisation from a small volume of absolute methyl alcohol yielded 17.6g., 79%, of light brown needles, m.p. 278-9°(d). Sublimation at 160°-180° at 1-2m.m. gave a white product, m.p. 279°(d).

(d) 5-Chloro-6-n-alkyloxy-2-naphthoic acids

The method of alkylation was exactly as described under the preparation of the 5-*n*-alkyloxy-1-naphthoic acids(page 190). After one crystallisation from glacial acetic acid the yields of 5-chloro-6-*n*-alkyloxy-2-naphthoic acids were 80-90%.

Complete purification was effected by carrying out an additional crystallisation from glacial acetic acid and one from 95% ethyl alcohol. For the analyses and m.p. determinations the hexyl, heptyl, nonyl, decyl, dodecyl and hexadecyl ethers were also sublimed at 1-2m.m.

Alkyl Group	m.p.	Analysis for $C_{10}H_5$.Cl.OR.COOH		Analysis found
Methyl	320.5°	$C_{12}H_9O_3Cl$	C,60.9;H,3.8 ;Cl,15.01	C,60.7;H,3.9; Cl,15.3%
Ethyl	269°	$C_{13}H_{11}O_3Cl$	C,62.3;H,4.39;Cl,14.17	C,62.3;H,4.4; Cl,14.3%
Propyl	219.5°	$C_{14}H_{13}O_3Cl$	C,63.5;H,4.92;Cl,13.42	C,63.5;H,5.0; Cl,13.5%
Butyl	209.5°	$C_{15}H_{15}O_3Cl$	C,64.6;H,5.39;Cl,12.75	C,64.8;H,5.5; Cl,12.8%
Amyl	189°	$C_{16}H_{17}O_3Cl$	C,65.6;H,5.8 ;Cl,12.13	C,65.8;H,5.8; Cl,12.05%
Hexyl	164°	$C_{17}H_{19}O_3Cl$	C,66.6;H,6.2 ;Cl,11.58	C,66.6;H,6.2; Cl,11.4%
Heptyl	165.5°	$C_{18}H_{21}O_3Cl$	C,67.4;H,6.55;Cl,11.08	C,67.4;H,6.6; Cl,11.1%
Octyl	169°	$C_{19}H_{23}O_3Cl$	C,68.2;H,6.88;Cl,10.61	C,68.6;H,6.9; Cl,10.6%
Nonyl	169°	$C_{20}H_{25}O_3Cl$	C,68.9;H,7.17;Cl,10.19	C,68.9;H,7.2; Cl,10.1%
Decyl	167°	$C_{21}H_{27}O_3Cl$	C,69.5;H,7.45;Cl, 9.79	C,69.5;H,7.5; Cl, 9.8%
Dodecyl	152°	$C_{23}H_{31}O_3Cl$	C,70.7;H,7.94;Cl, 9.09	C,70.7;H,8.0; Cl, 9.1%
Hexadecyl	142.5°	$C_{27}H_{39}O_3Cl$	C,72.6;H,8.74;Cl, 7.95	C,72.4;H,8.9; Cl, 7.7%
Octadecyl	138.5°	$C_{29}H_{43}O_3Cl$	C,73.3;H,9.06;Cl, 7.48	C,73.4;H,9.1; Cl,7.4%

6. 5-Bromo-6-n-alkyloxy-2-naphthoic acids

These ether acids were prepared by alkylation of 5-bromo-6-hydroxy-2-naphthoic acid.Compared with the corresponding chloro compounds,the greater steric factors involved,due to the larger bromine atom ortho-to the hydroxy group,always gave rise to a product which was contaminated with unreacted hydroxy acid.The latter has a high solubility in ethyl alcohol and a low solubility in benzene.Thus,crystallisation from alcohol followed by crystallisation from benzene with hot filtration from insoluble material yielded the pure 5-bromo-6-n-alkyloxy-2-naphthoic acids.The amount of unreacted hydroxy compound increased with the length of the alkyl chain to be introduced.The above method proved to be inefficient for chain lengths greater than nonyl.The higher ethers were therefore prepared by bromination of the 6-n-alkyloxy-2-naphthoic acids, when quantitative yields of the bromo ethers were obtained. Starting from 6-hydroxy-2-naphthoic acid,this latter process has the disadvantage of necessitating an alkylation and a bromination for each ether.

(a) 5-Bromo-6-hydroxy-2-naphthoic acid

6-Hydroxy-2-naphthoic acid(18.8g.,0.1 mole.) was dissolved in hot glacial acetic acid(200c.c.).Bromine(16g.,0.1 mole.) dissolved in glacial acetic acid(30c.c.) was added at 80° and, as the bromination proceeded smoothly,the product precipitated out.The reaction mixture was warmed for one hour on the water bath at 80° to complete the reaction and remove most of the hydrogen bromide. The mixture was cooled, diluted to 700-800c.c. and the pale pink solid filtered. The yield was 25g., 92-93%, m.p. 263-5°. One crystallisation from glacial acetic acid gave light tan needles of 5-bromo-6-hydroxy-2-naphthoic, 19g., 70%, m.p. 266° (Found: C, 49.5; H, 2.8; Br, 29.5. $C_{11}H_7O_3Br$ requires C, 49.44; H, 2.62; Br, 29.66%).

(b) 5-Bromo-6-n-alkyloxy-2-naphthoic acids

(1) Methyl to nonyl

By alkylating 5-bromo-6-hydroxy-2-naphthoic acid according to the procedure described for the 5-*n*-alkyloxy-1-naphthoic acids (page 190), the crude ethers were obtained. One crystallisation from ethyl alcohol (95%) and one from benzene (filtering from any unreacted hydroxy compound) gave the almost pure acids. The yields, which were between 60 and 80%, decreased with increasing length of the alkyl group. Two further crystallisations from glacial acetic acid gave the constant m.p. values and analysis figures listed below.

(2) Decyl, dodecyl, hexadecyl and octadecyl

The 6-*n*-alkyloxy-2-naphthoic acid (1 mole.) was dissolved in the minimum volume of glacial acetic acid at 80° and treated with bromine (1 mole.) dissolved in twice its volume of glacial acetic acid. The mixture was stirred at 80° for 20 minutes, crystallisation occurring almost immediately the addition had been made. The reaction mixture was cooled and an almost quantitative yield of the crystalline 5-bromo-6-*n*-alkyloxy-2-naphthoic acid filtered off. Two crystallisations from glacial acetic acid gave the constant m.p. values and analysis figures listed below.

Alkyl Group	m.p.	Analysis for $C_{10}H_5.Br.OR.COOH$		Analysis found
Methyl	303°(d)	$C_{12}H_9O_3Br$	C,51.25;H,3.2;Br,28.47	C,51.1;H,3.1; Br,28.5%
Ethyl	281°(d)	$C_{13}H_{11}O_3Br$	C,52.9;H,3.73;Br,27.12	C,52.8;H,3.8; Br,26.9%
Propyl	224°	$C_{14}H_{13}O_3Br$	C,54.36;H,4.2;Br,25.9	C,54.2;H,4.1; Br,25.9%
Butyl	213°	$C_{15}H_{15}O_3Br$	C,55.7;H,4.64;Br,24.77	C,55.5;H,4.6; Br,24.8%
Amyl	196.5°	$C_{16}H_{17}O_3Br$	C,57.0;H,5.04;Br,23.74	C,57.2;H,4.9; Br,23.6%
Hexyl	178°	$C_{17}H_{19}O_3Br$	C,58.1;H,5.41;Br,22.8	C,58.1;H,5.3; Br,22.7%
Heptyl	158°	$C_{18}H_{21}O_3Br$	C,59.2;H,5.75;Br,21.92	C,59.3;H,5.8; Br,21.7%
Octyl	164°	$C_{19}H_{23}O_3Br$	C,60.2;H,6.07;Br,21.1	C,60.3;H,6.0; Br,20.9%
Nonyl	168°	$C_{20}H_{25}O_3Br$	C,61.1;H,6.36;Br,20.36	C,61.0;H,6.3; Br,20.5%
Decyl	167°	$C_{21}H_{27}O_3Br$	C,61.9;H,6.63;Br,19.66	C,61.9;H,6.6; Br,19.4%
Dodecyl	151.5°	$C_{23}H_{31}O_3Br$	C,63.44;H,7.13;Br,18.4	C,63.4;H,7.0; Br,18.4%
Hexadecyl	138.5°	$C_{27}H_{39}O_3Br$	C,66.0;H,7.94;Br,16.3	C,66.1;H,7.9 Br,16.2%
Octadecyl	136.5°	$C_{29}H_{43}O_3Br$	C,67.04;H,8.29;Br,15.4	C,67.1;H,8.3; Br,15.4%

7. 5-Iodo-6-n-alkyloxy-2-naphthoic acids

5-Iodo-6-hydroxy-2-naphthoic acid was prepared by iodination of 6-hydroxy-2-naphthoic acid,but the product was very difficult to alkylate.In this case the iodine atom *ortho*-to the hydroxy group will exert an even larger steric effect than that which operates in the corresponding bromo-compound,which was itself very difficult to alkylate.The ethers were therefore prepared by iodination of the individual 6-*n*-alkyloxy-2-naphthoic acids.

(a) 5-Iodo-6-hydroxy-2-naphthoic acid

Sodium iodide(3g.,0.02 mole.) was dissolved in boiling glacial acetic acid(10c.c.) and added to a solution of di-chloramine-T (2.4g.,0.01 mole.) in warm glacial acetic acid (5c.c.).During the addition the mixture was cooled and well stirred.The resulting solution of iodine monochloride(0.02mole.) was clear and light brown in colour.This solution was added with stirring to 6-hydroxy-2-naphthoic acid(3.76g.,0.02 mole.) dissolved in glacial acetic acid(35c.c.) at 80°.The iodo-compound began to crystallise almost immediately,and after 20 minutes,when the reaction was complete,the mixture was cooled thoroughly.The product was filtered,washed with glacial acetic acid(25c.c.) and dried to yield 5-iodo-6-hydroxy-2-naphthoic acid,5g.,as buff coloured needles,m.p.235°(d).Iodine was slowly given off from 220° and the decomposition became vigorous at the m.p.The yield after one crystallisation from glacial acetic acid was 80% and the m.p. remained unchanged (Found:C,42.1; H,2.3;I,39.9.$C_{11}H_7O_3I$ requires C,42.05;H,2.23;I,40.44%). The recovery of 5-iodo-6-hydroxy-2-naphthoic acid was quantitative if the iodination liquors were diluted to 75% acetic acid. Further dilution will precipitate p-toluene-sulphonamide. This precipitated material had m.p.225°(d),and several crystallisations from glacial acetic acid failed to raise the m.p. above 230°(d).

(b) 5-Iodo-6-n-alkyloxy-2-naphthoic acids

The 6-n-alkyloxy-2-naphthoic acid(1 mole.) was dissolved in the minimum volume of glacial acetic acid at 80°,and a solution of iodine monochloride(1 mole.) in glacial acetic acid was added rapidly with stirring.The iodo-compound began to crystallise 2 minutes after the addition was complete,but the temperature was maintained at 80° for 20 minutes to ensure complete reaction.After cooling, the crystalline 5-iodo-6-n-alkyloxy-2-naphthoic acid was filtered washed with glacial acetic acid and dried.One crystallisation from glacial acetic acid gave 85 to 95% yields of highly pure material.The acids were crystallised to constant m.p. from glacial acetic acid and in all cases only two crystallisations were sufficient.

The m.p. values and analysis figures are listed in the following table.

Alkyl Group	m.p.	Analysis for $C_{10}H_5$.I.OR.COCH		Analysis found
Methyl	296.5°(d)	$C_{12}H_9O_3I$	C,43.9 ;H,2.74;I,38.72	C,44.0;H,2.7; I,38.5%
Ethyl	286.5°	$C_{13}H_{11}O_3I$	C,45.6 ;H,3.22;I,37.14	C,45.7;H,3.3; I,37.45%
Propyl	230°	$C_{14}H_{13}O_3I$	C,47.2 ;H,3.65;I,35.68	C,47.4;H,3.8; I,35.5%
Butyl	219°	$C_{15}H_{15}O_3I$	C,48.67;H,4.06;I,34.34	C,48.6;H,4.1; I,34.4%
Amyl	203°	$C_{16}H_{17}O_3I$	C,50.0 ;H,4.43;I,33.08	C,50.1;H,4.4; I,32.9%
Hexyl	191°	$C_{17}H_{19}O_3I$	C,51.25;H,4.77;I,31.91	C,51.4;H,4.7; I,31.8%
Heptyl	176°	$C_{18}H_{21}O_3I$	C,52.43;H,5.09;I,30.82	C,52.5;H,5.0; I,30.6%
Octyl	160.5°	$C_{19}H_{23}O_3I$	C,53.52;H,5.4 ;I,29.82	C,53.6;H,5.3; I,30.05%
Nonyl	163°	$C_{20}H_{25}O_3I$	C,54.56;H,5.68;I,28.86	C,54.4;H,5.8; I,28.75%
Decyl	165°	$C_{21}H_{27}O_3I$	C,55.5 ;H,5.95;I,27.97	C,55.5;H,5.9; I,27.7%
Dodecyl	146.5°	$C_{23}H_{31}O_3I$	C,57.27;H,6.43;I,26.35	C,57.4;H,6.5; I,26.6%
Hexadecyl	133.5°	$C_{27}H_{39}O_3I$	C,60.22;H,7.25;I,23.6	C,60.2;H,7.4; I,24.0%
Octadecyl	127°	$C_{29}H_{43}O_3I$	C,61.49;H,7.59;I,22.4	C,61.5;H,7.7; I,22.6%

8. 5-Nitro-6-n-alkyloxy-2-naphthoic acids

The 6-*n*-alkyloxy-2-naphthoic acid(0.5g.) was dissolved in the minimum volume of glacial acetic acid at 55-60°.Due to the lower solubility of the hexadecyl and octadecyl ethers,which however give nitro-derivatives of fairly high acetic acid solubility, a suspension of these ethers(0.5g.) in glacial acetic acid(25c.c.) was used. In both cases complete solution resulted during the nitration. A solution of fuming nitric acid (2c.c.) in glacial acetic acid(2c.c.) was added with stirring, the temperature was raised to 75° and these conditions maintained for 10 minutes. The mixtures were diluted until crystallisation began at about 70°. On cooling, the yellow needles of the crude 5-nitro-6-n-alkyloxy-2-naphthoic acids were filtered, washed well with water and dried. The yields at this stage were between 85 and 95%. Purification of these compounds involved a number of crystallisations, as the mesophases were of very short range and the transitions had to be obtained as sharp as possible to avoid error. The solvents used and the number of crystallisations in parenthesis are summarised below. The constant m.p. values and analysis figures are also listed.

Alkyl Group	Solvents and number of crystallisations
Methyl	Glacial acetic acid(3)
Amyl	Glacial acetic acid(3)
Octyl	Glacial acetic acid(2), toluene(1)
Nonyl	Absolute EtOH(4), toluene(1)
Decyl	Absolute EtOH(4), toluene(2)
Dodecyl	Absolute EtOH(1), glacial acetic acid(1), toluene(4)
Hexadecyl	Absolute EtOH(4), toluene(1)
Octadecyl	Absolute EtOH(5), toluene(1)

Alkyl Group	m.p.	Analysis for $C_{10}H_5.NO_2.OR.COOH$		Analysis found
Methyl	302°	$C_{12}H_9O_5N$	C,58.3 ;H,3.64;N,5.67	C,58.2;H,3.6; N,5.55%
Amyl	211°	$C_{16}H_{17}O_5N$	C,63.37;H,5.61;N,4.62	C,63.4;H,5.7; N,4.7%
Octyl	187°	$C_{19}H_{23}O_5N$	C,66.1 ;H,6.66;N,4.06	C,66.2;H,6.8; N,4.1%
Nonyl	174.5°	$C_{20}H_{25}O_5N$	C,66.85;H,6.96;N,3.9	C,67.0;H,6.9; N,3.9%
Decyl	173.5°	$C_{21}H_{27}O_5N$	C,67.56;H,7.24;N,3.75	C,67.5;H,7.2; N,3.8%
Dodecyl	167°	$C_{23}H_{31}O_5N$	C,68.83;H,7.73;N,3.49	C,68.5;H,7.7; N,3.5%
Hexadecyl	160°	$C_{27}H_{39}O_5N$	C,70.9 ;H,8.54;N,3.06	C,71.1;H,8.6; N,3.05%
Octadecyl	152°	$C_{29}H_{43}O_5N$	C,71.75;H,8.87;N,2.89	C,71.9;H,8.9; N,2.85%

9. 7-n-Alkyloxy-2-naphthoic acids

(a) Sodium 7-amino-naphthalene-2-sulphonate

7-Amino-naphthalene-2-sulphonic acid(223g.,1 mole.) was dissolved in a solution of sodium hydroxide(40g.,1 mole.) in water(1,800c.c.) at 80°.The solution was evaporated to dryness, the residue was powdered and the light brown sodium salt completely dried in an oven at 100°.

(b) 7-Amino-2-naphthonitrile

Sodium 7-amino-naphthalene-2-sulphonate(35g.) and potassium cyanide(70g.) were powdered and thoroughly mixed.The mixture was dry distilled in an all glass retort heated to 500°-600° in a high temperature salt bath.A pale brown oil distilled and rapidly solidified to give 3.8g. of pale yellow solid. This was dissolved at 80° in a solution of concentrated hydrochloric acid (10c.c.) in water(350c.c.), cooled and filtered from a little tar. Concentrated ammonium hydroxide was added until the solution was just alkaline, and the pale yellow precipitate of 7-amino-2-naphthonitrile, 3.3g., m.p. 140°-160°, was filtered. One crystallisation from benzene or absolute ethyl alcohol gave slightly yellow needles, 1.7g., 7.1%, m.p. 194-6°. This material was pure enough for the conversion to the hydroxy-nitrile. Two further crystallisations from benzene gave m.p. 197° (Found: C, 78.4; H, 4.8; N, 16.7. $C_{11}H_8N_2$ requires C, 78.57; H, 4.76; N, 16.66%).

(c) <u>7-Hydroxy-2-naphthonitrile</u>

7-Amino-2-naphthonitrile(5.04g., 0.03 mole.) was dissolved in boiling glacial acetic acid(60c.c.) and to this solution at 80° was added 40% (w/w) sulphuric acid(60c.c.), also at 80°. The mixture was rapidly cooled to 0° to obtain the finely divided amine sulphate. Sodium nitrite(4.2g., 0.06 mole.) in water(30c.c.) was added dropwise at 0° to the stirred suspension and maintained under these conditions until a clear brown solution was obtained. The excess sodium nitrite was destroyed by adding sulphamic acid until a blank reaction was given by starch-iodide paper. The cold diazonium salt solution was added dropwise during 30 minutes to a stirred and boiling 40% (w/w) sulphuric acid solution(180c.c.). Nitrogen was evolved, the solution became red and some dark oil separated. Boiling wascontinued for one hour. When cold, the crystals and solution were extracted with ether and the 7-hydroxy-2-naphthonitrile removed from the ether by shaking with two portions of 0.5N sodium hydroxide. Acidification gave a pale pink precipitate which was filtered. One crystallisation from 35% acetic acid gave orange-yellow plates, 3.85g., 76%, m.p. 183-5°. Two further crystallisations from the same solvent yielded pale yellow plates, m.p. 186.5° (Found: C, 77.9; H, 4.3; N, 8.2. $C_{11}H_7ON$ requires C, 78.1; H, 4.14; N, 8.28%).

(d) 7-Hydroxy-2-naphthoic acid

7-Hydroxy-2-naphthonitrile (2.5g.) was dissolved in 2N potassium hydroxide (50c.c.) and refluxed until no more ammonia was evolved (4 to 5 hours). The solution was cooled, diluted with an equal volume of water and acidified with concentrated hydrochloric acid. 7-Hydroxy-2-naphthoic acid precipitated as a pale pink solid which was filtered and dried, yielding 2.4g., 90%, m.p. 266-9°. This material was used for the alkylations. Two crystallisations from water gave pale yellow needles, m.p. 269°-270° (Found: C, 70.1; H, 4.4. $C_{11}H_8O_3$ requires C, 70.21; H, 4.14%).

(e) 7-n-Alkyloxy-2-naphthoic acids

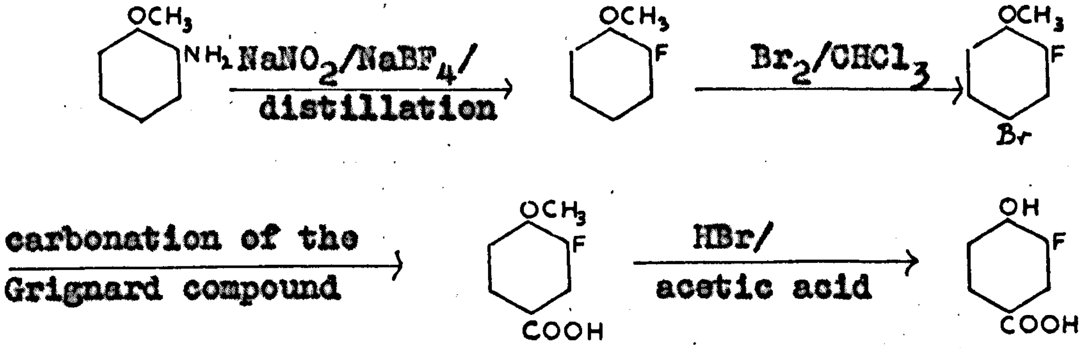
Only the n-octyl and n-hexadecyl ethers were prepared. The method used was the same as that for the preparation of the 5-n-alkyloxy-1-naphthoic acids (page 190). The ethers were purified as follows.

7-n-Octyloxy-2-naphthoic acid was obtained in 90% yield after one crystallisation from 90% ethyl alcohol as pale yellow needles,m.p.139.5°-141.5°.Further crystallisation from glacial acetic acid and xylene raised the m.p. to 141.5°,but failed to remove all the colour.White needles were obtained by subliming at 170° at 2-3m.m.,and this material had m.p.142.5°(Found: C,76.0;H,7.9.$C_{19}H_{24}O_3$ requires C,76.0;H,8.0%).

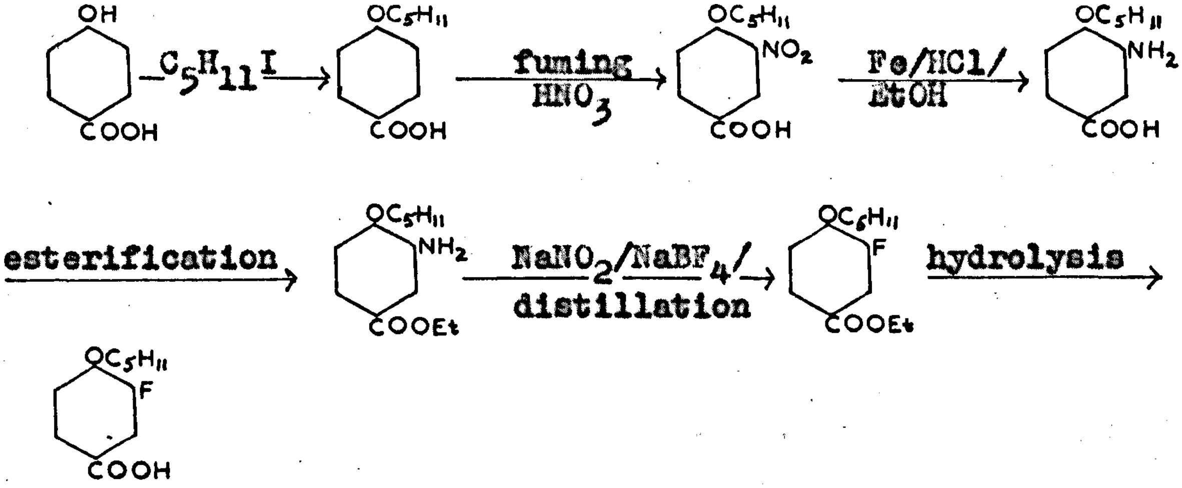
7-n-Hexadecyloxy-2-naphthoic acid was obtained in 90% yield, m.p.133-5°,after one crystallisation from 90% ethyl alcohol. Crystallisation from glacial acetic acid and xylene gave pale pink needles,m.p.135°.The colour was removed by subliming at 210°-220° at 4m.m.,whereby colourless needles were obtained, m.p.138°.Further crystallisation did not alter the m.p.(Found: C,78.6;H,9.7.$C_{27}H_{40}O_3$ requires C,78.64;H,9.71%).

10. 3-Fluoro-4-n-alkyloxy benzoic acids

These ethers were prepared by alkylating 3-fluoro-4-hydroxy benzoic acid,which was obtained by the following reactions.



Neither the hydroxy acid nor the ethers have been reported in the literature and the intermediate 2-fluoro-4-bromo-anisole is also unknown. Therefore there was a degree of assumption involved in accepting that o-fluoro-anisole brominates in the 4-position. It is made highly probable that it does since Ingold and Holmes(50) have proved that nitration of o-fluoro-anisole gives 2-fluoro-4-nitro-anisole. However, to verify the position of substitution, 3-fluoro-4-n-amyloxy benzoic acid was prepared by the following unambiguous route.



This method is much longer and the yields are much poorer, but some 3-fluoro-4-n-amyloxy benzoic acid was obtained. This material had the same m.p. as the amyl ether prepared by the first method, and a mixture of the two gave no m.p. depression. The orientation in 2-fluoro-4-bromo-anisole was therefore proved.

The preparation from p-hydroxy benzoic acid will be described first, followed by the more direct method used for the series of ethers.

(1) 3-Fluoro-4-n-amyloxy benzoic acid

(a) p-n-Amyloxy benzoic acid

This ether was prepared from p-hydroxy benzoic acid by the same method of alkylation as described for the preparation of the 5-n-alkyloxy-1-naphthoic acids. One crystallisation of the crude product from glacial acetic acid gave colourless needles, 180g., 86-87%, m.p. 122-3°.

(b) 3-Nitro-4-n-amyloxy benzoic acid

p-n-Amyloxy benzoic acid(104g., 0.5 mole.), glacial acetic acid(600c.c.) and fuming nitric acid(320c.c.) were heated for 5 hours at 70°, cooled and allowed to stand over-night. The suspension of yellow crystals in the nitration liquors was poured into water(3 litres) and the nitro-compound filtered. One crystallisation from glacial acetic acid gave pale yellow needles, 90g., 71-72%, m.p. 148.5°. Two further crystallisations from the same solvent gave m.p. 150° (Found: C, 56.7; H, 5.9; N, 5.5. $C_{12}H_{15}O_5N$ requires C, 56.9; H, 5.9; N, 5.5%).

(c) 3-Amino-4-n-amyloxy benzoic acid

3-Nitro-4-n-amyloxy benzoic acid(22.3g., 0.1 mole.), 95% ethyl alcohol(280c.c.), water(25c.c.), concentrated hydrochloric acid(56c.c.) and iron pin dust(21g., 0.375g. atom) were refluxed on the water bath for 24 hours with vigorous agitation. Concentrated ammonium hydroxide was added to the hot reaction mixture until alkaline, and the whole allowed to stand over-night to ensure that all the ferrous hydroxide was oxidised to the more readily filtered ferric oxide. The inorganic oxide was filtered off and well washed with dilute ammonium hydroxide, until the washings gave no precipitate on just acidifying with dilute acetic acid. The filtrate and washings were concentrated to about 300c.c., refiltered, cooled to 0° and made slightly acid with acetic acid. The light brown precipitate 16.2g., 80%, of 3-amino-4-n-amyloxy benzoic acid was filtered and dried. The m.p. was 100°-102°. The amino-compound was very difficult to purify by crystallisation and the above material was esterified. Some pure amino-acid was obtained by hydrolysis of the pure ester and this product had m.p. 104° (Found: C, 64.3; H, 7.4; N, 6.4. $C_{12}H_{17}O_3N$ requires C, 64.5; H, 7.6; N, 6.3%).

(d) Ethyl 3-amino-4-n-amyloxy benzoate

3-Amino-4-n-amyloxy benzoic acid (13g.), ethyl alcohol (100c.c.) and concentrated sulphuric acid (4c.c.) were refluxed for 5 hours. The reaction mixture was poured into water (100c.c.) neutralised with aqueous sodium bicarbonate and the colourless oil extracted with ether. The extract was dried, the solvent removed and the residue distilled under reduced pressure. The yield was 11.9g., 80%, of a colourless oil, b.p. 210° at 5m.m. On standing, the oil became a colourless solid, m.p. 34°-36°.

(e) 3-Fluoro-4-n-amyloxy benzoic acid

Ethyl 3-amino-4-n-amyloxy benzoate (2.5g., 0.01 mole.) was stirred vigorously with water (8c.c.) and concentrated hydrochloric acid (8c.c.), to obtain the finely divided hydrochloride.The suspension was cooled to 0°-5° and a solution of sodium nitrite(1.03g.,0.015 mole.)in water(3c.c.) was added dropwise with stirring.After about 90 minutes a pale yellow solution resulted.This was filtered to remove a small amount of tar.The solution was added dropwise to a suspension of sodium borofluoride(1.6g.,0.015 mole.) in a small volume of water (3c.c.) at less than 10°.Stirring was continued for one hour and the precipitated diazonium borofluoride was filtered.The solid was dried in a vacuum desiccator and gave 2.73g.,78%, m.p.93-5°(d).The dry solid was heated in an all glass distillation apparatus until most of the nitrogen and boron trifluoride had been expelled.The temperature was raised to 180°,but only a few drops distilled even when the pressure was reduced to 20m.m.The distillate and the still residues were extracted with ether and the solvent removed.The residual dark brown oil was hydrolysed by refluxing for 2 hours with 5N methyl alcoholic potassium hydroxide.The hydrolysate was filtered free from some charred material and acidified with 1:1 concentrated hydrochloric acid.The dark brown precipitate of 3-fluoro-4-n-amyloxy benzoic acid was filtered,dried and crystallised from 70% ethyl alcohol.The light brown needles were recrystallised from 50% acetic acid and the yellow needles were sublimed at 140° at 1-2m.m.The white sublimate,0.4g.,16% had m.p.137°.

(2) 3-Fluoro-4-n-alkyloxy benzoic acids

(a) o-Fluoro-anisole

Redistilled o-anisidine(92.3g.,1 mole.),concentrated hydrochloric acid(190c.c.) and water(100c.c.) were vigorously stirred at 0° to obtain the finely divided hydrochloride.Sodium nitrite(54.8g.,1.05 mole.) in water(100c.c.) was added drop-wise,with stirring,to this suspension at 0°.Stirring at 0° was continued until a clear brown solution was obtained.This was filtered to remove a small amount of tar,and added gradually to a suspension of sodium borofluoride(130g.,1.5-1.6 mole.) in water(100c.c.) at less than 10°.The mixture was then stirred for one hour.The pale yellow diazonium borofluoride was filtered with suction and dried in a vacuum desiccator.The yield was 140g.,84%,m.p.95°-100°(d).The dry solid was decomposed by heating with a flame in an all glass distillation apparatus.The distillate was diluted with ether,washed twice with 0.5N sodium hydroxide,twice with water and dried over anhydrous sodium sulphate.The solvent was removed and the residue of o-fluoro-anisole distilled.The yield of colourless oil was 35-39g.,37-43%,b.p.160°-164°.

(b) 2-Fluoro-4-bromo-anisole

o-Fluoro-anisole(18.9g.,0.15 mole.) was dissolved in chloroform(50c.c.) and a solution of bromine(24g.,0.15 mole.) in chloroform(50c.c.) was added in small portions in 10minutes. The mixture became warm and eventually began to reflux with copious evolution of hydrogen bromide. When the first reaction had subsided, refluxing was continued until the bromine colour had disappeared(2.5 hours). The chloroform was distilled off and the pale yellow oily residue was distilled under reduced pressure. The yield of colourless oil was 26.7g., 95%, b.p. 148°-150° at 14m.m. The yield in a large number of brominations lay consistently between 92 and 96% (Found: C, 41.0; H, 3.0; Br, 38.9. C_7H_6OBrF requires C, 40.97; H, 2.92; Br, 39.02%).

(c) 3-Fluoro-4-methoxy benzoic acid

2-Fluoro-4-bromo-anisole(51.3g., 0.25 mole.) was dissolved in Analar benzene(190c.c.). Magnesium turnings(10g., 0.42g. atom) were placed in a 500c.c. round-bottomed flask, fitted with a three-necked adapter which carried a mercury-sealed stirrer, a double-surface condenser and calcium chloride tube and a dropping-funnel. The magnesium was covered with dry ether(190 c.c.) and etched by warming to 50°-60° after adding ethyl bromide(0.5c.c.) and a crystal of iodine. The iodine colour gradually disappeared and the solution became turbid. While refluxing on a hot water bath, the benzene solution of the bromo-compound was added dropwise in 20 minutes. The mixture soon became brown and occasionally the reaction had to be modified by removing the water bath. Refluxing was continued for two hours when the magnesium was reactivated by adding ethyl bromide(12.5c.c.) at half-hour intervals in the following quantities—6 portions of 2 c.c., and 1 portion of 0.5c.c.

After the overall reflux time of 5 hours,only a trace of magnesium remained unreacted.The cooled reaction mixture was poured steadily,with stirring,into ether(100c.c.) saturated with solid carbon dioxide.The carbonated Grignard compound separated as a viscous semi-solid.When all the excess carbon dioxide had evaporated,the free acid was liberated by stirring in 1:1 concentrated hydrochloric acid(75c.c.).The ether was evaporated off and the white acid which precipitated,was filtered and washed with water.The benzene layer in the filtrate contained only a small percentage of impure acid.The 3-fluoro-4-methoxy benzoic acid,28.5g.,67%,m.p.209°-211.5°,was quite pure, but without appreciable loss in yield the m.p. was raised to 211.5° by dissolving in hot dilute sodium hydroxide,filtering and reprecipitating with concentrated hydrochloric acid.This material was used for the demethylation.The m.p. was not changed from 211.5° by one crystallisation from glacial acetic acid and two from absolute ethyl alcohol (Found:C,56.4;H,4.1. $C_8H_7O_3F$ requires C,56.5;H,4.11%).

(d) <u>3-Fluoro-4-hydroxy benzoic acid</u>

3-Fluoro-4-methoxy benzoic acid(42.5g.,0.25 mole.) was refluxed for 6-7 hours with 48% hydrobromic acid(100c.c.) and glacial acetic acid(100c.c.).The brown solution gave a solid mass of crystals on cooling.These were filtered and dried,to give 24g.,61-62%.The product is quite soluble in acetic acid and in water and dilution of the mother liquors does not precipitate the remaining 3-fluoro-4-methoxy benzoic acid.The acetic acid was therefore distilled off under reduced pressure, and the solid residue completely dried,giving an overall yield of 38.5g.,99%,m.p.148°-157°.Although this light brown material was quite impure,it was satisfactory for the preparation of the ethers.

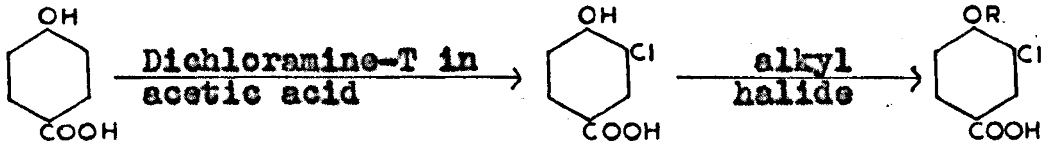
A small amount of the hydroxy acid was purified for analysis.For colourless needles,m.p.145-7°,one crystallisation from water was necessary,with hot filtration to remove a trace of high m.p. impurity.Further crystallisation from a mixture of water(2 parts) and acetic acid(1 part) gave small colourless needles,m.p.146-7°.No other means of purification attempted improved this m.p. or the analysis (Found:C,53.0; H,3.8.$C_7H_5O_3F$ requires C,53.9;H,3.22%).However,the ethers were very readily purified and the use of the impure hydroxy compound was not a disadvantage.

(e) 3-Fluoro-4-n-alkyloxy benzoic acids

These ethers were prepared using the same method of alkylation employed for preparing the 5-n-alkyloxy-1-naphthoic acids (page 190).After one crystallisation from absolute ethyl alcohol the yields of almost pure ethers were between 80 and 85%.The constant m.p. values and analysis figures listed below were obtained on samples which had been further crystallised twice from benzene and once from glacial acetic acid.

Alkyl Group	m.p.	Analysis for C_6H_3.F.OR.COOH		Analysis found
Methyl	211.5°	$C_8H_7O_3F$	C,56.5 ;H,4.11	C,56.5;H,4.2%
Butyl	142.5°	$C_{11}H_{13}O_3F$	C,62.3;H,6.13	C,62.4;H,6.3%
Amyl	137°	$C_{12}H_{15}O_3F$	C,63.7 ;H,6.64	C,63.7;H,6.7%
Hexyl	129°	$C_{13}H_{17}O_3F$	C,65.0 ;H,7.08	C,65.2;H,7.1%
Heptyl	123°	$C_{14}H_{19}O_3F$	C,66.15;H,7.48	C,66.2;H,7.35%
Octyl	117°	$C_{15}H_{21}O_3F$	C,67.16;H,7.83	C,67.3;H,7.8%
Nonyl	112.5°	$C_{16}H_{23}O_3F$	C,68.1 ;H,8.15	C,68.2;H,8.3%
Decyl	108°	$C_{17}H_{25}O_3F$	C,68.9 ;H,6.64	C,69.1;H,6.7%
Dodecyl	103.5°	$C_{19}H_{29}O_3F$	C,70.4 ;H,8.95	C,70.6;H,8.8%
Hexadecyl	94°	$C_{23}H_{37}O_3F$	C,72.63;H,9.73	C,72.5;H,9.8%
Octadecyl	113°	$C_{25}H_{41}O_3F$	C,73.5 ;H,10.05	C,73.4;H,9.9%

11. 3-Chloro-4-n-alkyloxy benzoic acids



(a) 3-Chloro-4-hydroxy benzoic acid

p-Hydroxy benzoic acid(13.8g.,0.1 mole.) was dissolved in glacial acetic acid(100c.c.).A solution of dichloramine-T (12g.,0.05 mole.) in glacial acetic acid(100c.c.),and concentrated hydrochloric acid(0.5c.c.) were added and the mixture refluxed for 5 hours.Acetic acid(100c.c.) was distilled off under reduced pressure and the mother liquors,on cooling, deposited colourless crystals,14g.,80-81%,m.p.169°-172°.One crystallisation from water gave pure 3-chloro-4-hydroxy benzoic acid,12.3g.,70-71%,m.p.172.°

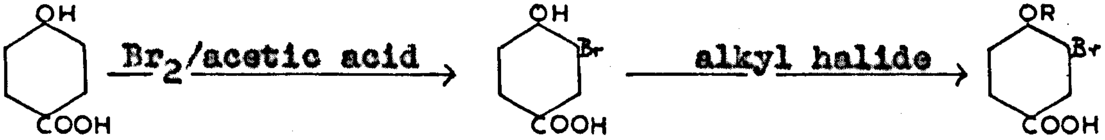
(b) 3-Chloro-4-n-alkyloxy benzoic acids

3-Chloro-4-hydroxy benzoic acid was alkylated by the same procedure as was used for the preparation of the 5-*n*-alkyloxy-1-naphthoic acids(page 190).The yields of crude ethers were 85-95%.Certain of these ethers gave very short mesophases and to avoid error in determining the transition points,they were crystallised several times from various solvents.The solvents, the number of crystallisations in parenthesis,the constant m.p. values and the analysis figures are summarised below.

Alkyl Group	Solvent and number of crystallisations	m.p.
Methyl	Absolute ethyl alcohol(3)	217.5°
Amyl	90% ethyl alcohol(2),glac.acetic acid(1)	134.5°
Hexyl	Absolute ethyl alcohol(1),benzene(3)	120°
Heptyl	Absolute ethyl alcohol(2),benzene(1)	117°
Octyl	90% ethyl alcohol(2),glac.acetic acid(1)	94°
Nonyl	Absolute ethyl alcohol(2),benzene(1)	93°
Decyl	80% ethyl alcohol(2),benzene(2)	99°
Dodecyl	Absolute ethyl alcohol(3),benzene(2)	100°
Hexadecyl	Glac.acetic acid(2),90% ethyl alcohol(3), benzene(2)	95°
Octadecyl	Absolute ethyl alcohol(1),benzene(4)	108°

Alkyl Group	Analysis for C_6H_3.Cl.OR.COOH		Analysis found
Methyl	$C_8H_7O_3Cl$	C,51.5;H,3.75;Cl,19.04	C,51.5;H,3.8;Cl,19.1%
Amyl	$C_{12}H_{15}O_3Cl$	C,59.4;H,6.19;Cl,14.66	C,59.6;H,6.3;Cl,14.6%
Hexyl	$C_{13}H_{17}O_3Cl$	C,60.8;H,6.63;Cl,13.84	C,60.7;H,6.6;Cl,13.9%
Heptyl	$C_{14}H_{19}O_3Cl$	C,62.1;H,7.03;Cl,13.12	C,62.2;H,7.2;Cl,13.1%
Octyl	$C_{15}H_{21}O_3Cl$	C,63.27;H,7.4;Cl,12.47	C,63.3;H,7.5;Cl,12.5%
Nonyl	$C_{16}H_{23}O_3Cl$	C,64.33;H,7.7;Cl,11.9	C,64.4;H,7.7;Cl,12.0%
Decyl	$C_{17}H_{25}O_3Cl$	C,65.27;H,8.0;Cl,11.36	C,65.3;H,7.8;Cl,11.5%
Dodecyl	$C_{19}H_{29}O_3Cl$	C,66.95;H,8.5;Cl,10.42	C,66.9;H,8.5;Cl,10.4%
Hexadecyl	$C_{23}H_{37}O_3Cl$	C,69.6;H,9.33;Cl, 8.95	C,69.6;H,9.5;Cl, 8.9%
Octadecyl	$C_{25}H_{41}O_3Cl$	C,70.66;H,9.7;Cl,8.36	C,70.7;H,9.7;Cl, 8.4%

12. 3-Bromo-4-n-alkyloxy benzoic acids



(a) 3-Bromo-4-hydroxy benzoic acid

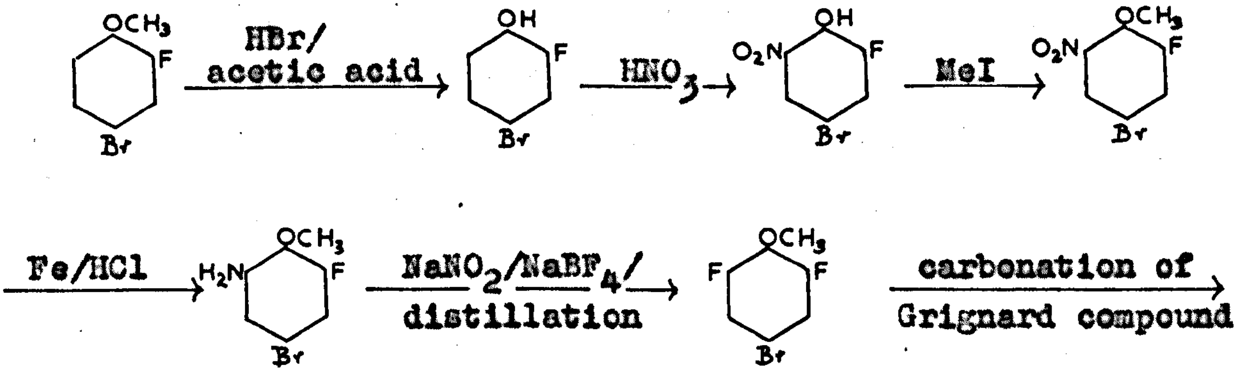
p-Hydroxy benzoic acid(27.6g.,0.2 mole.) was dissolved in glacial acetic acid(200c.c.) at 60°.Bromine(32g.,0.2 mole.) in glacial acetic acid(30c.c.) was added gradually to this solution. The reaction mixture became hot and hydrogen bromide was evolved. After the addition,the solution was refluxed for 2 hours by which time the bromine colour had disappeared.The solution was poured into water(500c.c.) and the thick white precipitate filtered off.This was dissolved in dilute sodium bicarbonate solution,filtered,acidified with concentrated hydrochloric acid and refiltered.The dry solid weighed 43.4g.,95-96%.One crystallisation from water(2 litres) gave colourless needles of 3-bromo-4-hydroxy benzoic acid,34.5g.,80%,m.p.177.5°.

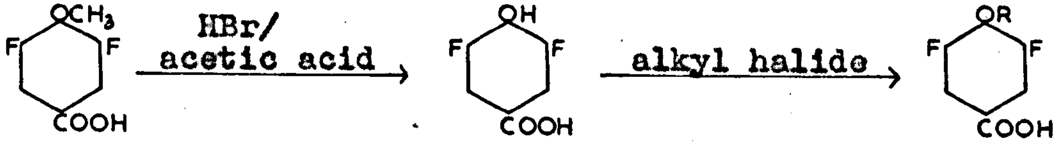
(b) 3-Bromo-4-n-alkyloxy benzoic acids

Only the _n_-octyl and _n_-hexadecyl ethers were prepared. The alkylation method was the same as that which was used for the preparation of the 5-_n_-alkyloxy-1-naphthoic acids.In each case,the yield of crude ether was 91-92%.Three crystallisations from glacial acetic acid gave colourless plates of 3-bromo-4-_n_-octyloxy benzoic acid,m.p.111° (Found:C,55.0;H,6.5;Br,24.4. $C_{15}H_{21}O_3Br$ requires C,54.8;H,6.39;Br,24.3%).Two crystallisations from benzene and one from glacial acetic acid gave small colourless plates of 3-bromo-4-_n_-hexadecyloxy benzoic acid,m.p.99° (Found:C,62.6;H,8.36;Br,18.2.$C_{23}H_{37}O_3Br$ requires C,62.58;H,8.38;Br,18.14%).

13. 3:5-di-Fluoro-4-n-alkyloxy benzoic acids

These were prepared according to the following set of reactions,using 2-fluoro-4-bromo-anisole as starting material.





It was not possible to introduce the nitro group directly into 2-fluoro-4-bromo-anisole,as nitration only occurred at 35° and at this temperature the reaction was uncontrollable.

(a) 2-Fluoro-4-bromo-phenol

2-Fluoro-4-bromo-anisole(206g.,1 mole.) was dissolved in glacial acetic acid(350c.c.) and 48% hydrobromic acid(200c.c.) added.The reaction mixture consisted of two layers,but,after refluxing for 2-3 hours,the whole became homogeneous.The total reflux time was 7 hours,when demethylation was complete.Acetic acid(400c.c.) was distilled off under reduced pressure and the residue,again consisting of two layers,was poured into water. The light brown layer of the phenol was extracted with ether, washed twice with water,twice with aqueous sodium bicarbonate, and once with water,and finally dried over anhydrous sodium sulphate.Removal of the ether and reduced pressure distillation of the residue yielded 2-fluoro-4-bromo-phenol as a colourless oil,135g.,71-72%,b.p.70°-72° at 0.5m.m.

(b) 2-Fluoro-4-bromo-6-nitro-phenol

2-Fluoro-4-bromo-phenol(192g.,1 mole.) was dissolved in glacial acetic acid(300c.c.) and the solution cooled to between 5° and 10°.A solution of fuming nitric acid(450c.c.) in glacial acetic acid(450c.c.) was added dropwise with good agitation, while maintaining the temperature below 10°.The addition time was 1.5 hours, after which the mixture was poured into a large excess (6 litres) of water. The yellow crystalline solid was filtered, washed with water and dried in a vacuum desiccator. This material had m.p. 59°-60° and one crystallisation from 50% methyl alcohol gave pale yellow needles, 143g., 62%, m.p. 61°.

(c) <u>2-Fluoro-4-bromo-6-nitro-anisole</u>

2-Fluoro-4-bromo-6-nitro-phenol (47.2g., 0.2 mole.) was dissolved in cyclohexanone (425c.c.). Powdered anhydrous potassium carbonate (235g., 1.7 mole.) was sifted into the solution with shaking to obtain the finely divided, deep orange potassium salt. Methyl iodide (85g., about 0.6 mole.) was added, and, with good stirring, the mixture was refluxed in an oil bath at 160° for 6 hours. The colour of the potassium salt rapidly disappeared and, on completion of the reflux, the yellow-brown solution and suspended potassium carbonate were stirred into sufficient water to dissolve all the solid. The organic layer was separated and the solvent distilled off under reduced pressure. Distillation of the oily residue gave a yellow oil, b.p. 117°-121° at 3-4m.m. The oil soon solidified and had m.p. 49°-50°. One crystallisation from a small volume of absolute ethyl alcohol (2c.c. for 3g.) gave pale yellow needles, 41g., 70-71%, m.p. 53.5°. Further crystallisation did not raise the m.p. of this material (Found: C, 33.5; H, 2.1; N, 5.4; Br, 32.0. $C_7H_5O_3NFBr$ requires C, 33.6; H, 2.0; N, 5.6; Br, 32.0%).

(d) 2-Amino-4-bromo-6-fluoro-anisole.

2-Fluoro-4-bromo-6-nitro-anisole(75g.,0.3 mole.) was dissolved in 90% ethyl alcohol(450c.c.).Concentrated hydrochloric acid(27c.c.) and iron pin dust(60g.,about 1g.atom) were added and the whole refluxed over-night on a water bath, with good agitation.The theoretical amount of sodium carbonate (14.5g.) was added and boiling continued for a further 2 hours. The mixture was filtered hot and the precipitated ferric oxide washed thoroughly with hot ethyl alcohol.The alcohol and water were removed under reduced pressure and the dark oily residue distilled.The 2-amino-4-bromo-6-fluoro-anisole was collected as a colourless oil,66g.,83-84%,b.p.109°-112° at 3-4 m.m. (Found:C,38.1;H,3.2;Br,36.4;N,6.35. C_7H_7ONFBr requires C,38.18;H,3.18;Br,36.35;N,6.36%).

(e) 2:6-di-Fluoro-4-bromo-anisole

2-Amino-4-bromo-6-fluoro-anisole(55g.,0.25 mole.) was stirred vigorously into 1:1 concentrated hydrochloric acid (130c.c.).The finely divided hydrochloride was diazotised at 0°-5° by the dropwise addition of a solution of sodium nitrite (17.3g.,0.25 mole.) in water (35c.c.).A clear brown solution of the diazonium chloride was obtained after filtering off a small amount of tar.This solution was added to a stirred suspension of sodium borofluoride(55g.,0.5 mole.) in water (150c.c.),at less than 10°.After stirring at less than 10° for 30 minutes,the yellow diazonium borofluoride was filtered, pressed dry and thoroughly desiccated in vacuo.Dry distillation of the borofluoride under reduced pressure gave a red-brown oil which was diluted with ether.The extract was washed with water,aqueous sodium hydroxide and again with water,and dried over anhydrous sodium sulphate.Removal of the solvent and distillation of the residue gave 2:6-di-fluoro-4-bromo-anisole as a colourless oil,10.6g.,17-18%,b.p.213°-218° (Found:C,37.55; H,2.3;Br,35.9. $C_7H_5OF_2Br$ requires C,37.66;H,2.24;Br,35.87%).

(f) 3:5-di-Fluoro-4-methoxy benzoic acid

In a round-bottomed flask fitted with a three-necked adapter which carried a mercury-sealed stirrer,a double-surface condenser and calcium chloride tube and a dropping-funnel,were placed magnesium turnings(1.2g.,0.05g.atom),dry ether(25c.c.), 2:6-di-fluoro-4-bromoanisole(0.5g),ethyl bromide(0.15c.c.) and a small crystal of iodine.The mixture was warmed slightly and after 5-10 minutes the magnesium was thoroughly etched,as indicated by the disappearance of the iodine colour and the turbidity in the solution.The stirrer was then started,the flask immersed in a water bath at 50°-60° and a solution of 2:6-di-fluoro-4-bromo-anisole(7g., a total of 0.03 mole.) in Analar benzene(25c.c.) added dropwise in 30 minutes.A vigorous reaction commenced and the water bath was lowered once or twice to control the reflux rate.The mixture became dark brown and,after the addition,boiling was continued for 2 hours. Ethyl bromide(1.75c.c.) was then added at half-hour intervals in the following quantities—6 portions of 0.15c.c.,2 portions of 0.35c.c. and one portion of 0.15c.c.The total reflux time was therefore 7 hours.The reaction mixture was cooled and decanted,from a small amount of unreacted magnesium,into dry ether(100c.c.) saturated with solid carbon dioxide.The carbonated Grignard compound separated as a grey sludge.When all the carbon dioxide had evaporated,the acid was liberated by stirring in 1:1 concentrated hydrochloric acid(100c.c.)The organic layer was separated,washed twice with water and extracted twice with 0.5N sodium hydroxide.The pale orange solution of the sodium salt was acidified with concentrated hydrochloric acid and the yellow precipitate of 3:5-di-fluoro-4-methoxy benzoic acid filtered.Crystallisation from glacial acetic acid gave colourless needles,2.8g.,45-46%,m.p.213-4°.Two crystallisations from 80% ethyl alcohol raised the m.p. to 215°.The thrice crystallised material was analysed (Found:C,51.0;H,3.2. $C_8H_6O_3F_2$ requires C,51.06;H,3.13%).

(g) <u>3:5-di-Fluoro-4-hydroxy benzoic acid</u>

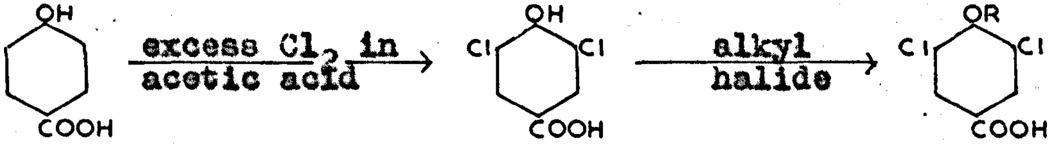
3:5-di-Fluoro-4-methoxy benzoic acid(0.7g.),glacial acetic acid(10c.c.) and 48% hydrobromic acid(10c.c.) were refluxed for 5 hours.The light orange solution was then evaporated to dryness under reduced pressure.The light brown powder,m.p.158°-165°,was recrystallised from water to give colourless needles, 0.5g.,78%.m.p.167-8°.One sublimation at 3m.m. gave a white powder,m.p.168° (Found:C,48.4;H,2.2.$C_7H_4O_3F_2$ requires C,48.28;

H,2.3%).

(h) 3:5-di-Fluoro-4-n-hexadecyloxy benzoic acid

The hydroxy acid was alkylated by the method used to prepare the 5-*n*-alkyloxy-1-naphthoic acids.Two crystallisations of the crude ether from 60°-80° petroleum ether gave colourless, waxy plates,m.p.72°,in 75% yield (Found:C,69.3;H,8.9.$C_{23}H_{36}O_3F_2$ C,69.34;H,9.0%).

14. 3:5-di-Chloro-4-n-alkyloxy benzoic acids



(a) 3:5-di-Chloro-4-hydroxy benzoic acid

p-Hydroxy benzoic acid(20g.) was dissolved in glacial acetic acid(170c.c.) at 40°.The temperature was raised to 60°-80° and maintained in this range for 4 hours while chlorine was bubbled through the mixture.After 2 hours the chloro-compound began to separate and in a further hour,when the mixture was saturated with chlorine,the whole was a thick paste.When cold,the solid was filtered,freed from chlorine by stirring with aqueous sodium hydrosulphite,refiltered,washed with water and dried.The yield of nearly pure product was 23.6g.,76%, m.p.265-7°.Crystallisation from a large volume of glacial acetic acid gave small,colourless needles,m.p.267°.Ugryumov(51) reports m.p.265°.

(b) 3:5-di-Chloro-4-n-alkyloxy benzoic acids

3:5-di-Chloro-4-hydroxy benzoic acid was alkylated by the method used to prepare the 5-*n*-alkyloxy-1-naphthoic acids. Only the *n*-amyl and *n*-hexadecyl ethers were prepared. In each case, due to the steric effect of the two chlorine atoms on the hydroxy group, a little unreacted hydroxy acid had to be separated from the product.

3:5-di-Chloro-4-n-amyloxy benzoic acid

The crude ether was shaken with cold benzene. 30c.c. of this solvent were used when starting with 2.07g., 0.01 mole., of the hydroxy acid. The insoluble hydroxy compound, 0.3g., m.p. 250-5°, was filtered off. Evaporation of the benzene and crystallisation of the residue from glacial acetic acid gave white needles of the *n*-amyl ether, 1.9g., 68%, m.p. 100°-102°. Two crystallisations from 60°-80° petroleum ether gave colourless blades, m.p. 103° (Found: C, 60.0; H, 5.1; Cl, 25.6. $C_{12}H_{14}O_3Cl_2$ requires C, 51.99; H, 5.05; Cl, 25.64%).

3:5-di-Chloro-4-n-hexadecyloxy benzoic acid

Starting with 2.07g., 0.01 mole., of the hydroxy acid, the crude ether was again freed from unreacted hydroxy compound by shaking with cold benzene (70c.c.) and filtering. The filtrate was concentrated and allowed to crystallise. This gave colourless prisms of the *n*-hexadecyl ether, 3.1g., 72%, m.p. 60.5°. One crystallisation from 40°-60° petroleum ether did not raise this m.p. (Found: C, 64.1; H, 8.3; Cl, 16.5. $C_{23}H_{36}O_3Cl_2$ requires C, 64.03;

H,8.34;Cl,16.47%).

15. trans-p-n-Alkyloxy cinnamic acids

These ethers were prepared both by alkylating *trans*-*p*-hydroxy cinnamic acid and by condensing the *p*-*n*-alkyloxy benzaldehydes with malonic acid.The latter is the better method,since the ethers are much more easily purified.Only those ethers,which showed any serious discrepancy in m.p. and transition point values from the figures previously published(6),were analysed.

(a) trans-p-hydroxy cinnamic acid

A solution of *p*-hydroxy benzaldehyde(12.2g.,0.1 mole.) and malonic acid(23g.,0.22mole.) in pyridine(75c.c.) containing piperidine(1c.c.) was allowed to stand,protected by a soda lime tube,for 3 weeks.The mixture was then poured into ice(100g.) and concentrated hydrochloric acid(60c.c.).The white precipitate was filtered,washed with 5% hydrochloric acid(10c.c.) and twice with water(10c.c.),and dried.The acid was crystallised from water and gave colourless needles,8.6g., 52-53%,m.p.215.5°-216.5°.

(b) trans-p-n-Alkyloxy cinnamic acids

The *n*-decyl and *n*-octadecyl ethers were prepared by alkylation of *trans*-*p*-hydroxy cinnamic acid.The method used was the same as that for the preparation of the 5-*n*-alkyloxy-naphthoic acids.The crude *n*-decyl ether was crystallised thrice from glacial acetic acid and had m.p.133°.The yield of almost pure product, after one crystallisation, was 79%. The n-octadecyl ether was obtained in 80% yield, m.p. 118°, after one glacial acetic acid crystallisation. The ether was further crystallised twice from glacial acetic acid, twice from benzene and twice from absolute ethyl alcohol, and had m.p. 120.5°.

Alkyl Group	Analysis for $C_8H_6 \cdot OR \cdot COOH$	Analysis found
Decyl	$C_{19}H_{28}O_3$ requires C, 75.0; H, 9.3	C, 74.8; H, 9.2%
Octadecyl	$C_{27}H_{44}O_3$ requires C, 77.9; H, 10.6	C, 78.1; H, 10.7%

(c) p-n-Alkyloxy benzaldehydes

p-Hydroxy benzaldehyde (12.2g., 0.1 mole.), anhydrous potassium carbonate (60g., 0.4 mole.), cyclohexanone (80c.c.) and the n-alkyl bromide or iodide (0.16 mole.) were refluxed and agitated as vigorously as possible. Alkylation was complete when the orange colour of the potassium salt of p-hydroxy benzaldehyde had disappeared and the solution was yellow or colourless. The time varied between 1 and 3 hours. The solution was decanted from the potassium carbonate which was thoroughly washed with ether. The ether washings were added to the cyclohexanone solution and both solvents distilled off on the water bath under reduced pressure. The residue of crude p-n-alkyloxybenzaldehyde was then distilled under reduced pressure.

Alkyl Group	Yield(%)	b.p.	Alkyl	Yield(%)	b.p.
Ethyl	75	106° at 3m.m.	Amyl	50	145° at 3 m.m.
Propyl	64	144° at 14m.m.	Hexyl	60	158° at 4m.m.
Butyl	61	165° at 17 m.m.	Heptyl	74	154° at 5m.m.

Alkyl group	Yield(%)	b.p.	m.p.
Octyl	66	160° at 1-2m.m.	
Nonyl	72	185° at 5m.m.	
Decyl	78	185° at 4m.m.	
Dodecyl	69	194° at 8m.m.	24°
Hexadecyl	50	230° at 3m.m.	34°
Octadecyl	59	240° at 2m.m.	48.5°

(d) trans-p-n-Alkyloxy cinnamic acids

The p-n-alkyloxy benzaldehyde(0.02 mole.),malonic acid (3.2g.,0.04 mole.),pyridine(8c.c.) and piperidine(3 drops) were heated on a boiling water bath for 3 hours.The evolution of carbon dioxide could no longer be seen after 2 hours.The reaction mixture was poured onto ice(25g.) and concentrated hydrochloric acid(25c.c.).The precipitate was filtered,washed well with dilute hydrochloric acid and water,and crystallised once from 98% acetic acid.In all cases,the yields of colourless needles were between 90 and 100%.Constant m.p. values were obtained after a total of three crystallisations from 98% acetic acid.The m.p. values and the necessary analyses are listed below.

Alkyl group	m.p.	Alkyl group	m.p.
Methyl	171°	Butyl	154°
Ethyl	191.5°	Amyl	138°
Propyl	165°	Hexyl	153°

Alkyl Group	m.p.	Analysis for C_8H_6.OR.COOH	Analysis found
Heptyl	148°	$C_{16}H_{22}O_3$ requires C,73.3;H,8.4	C,73.3;H, 8.5 %
Octyl	147°		
Nonyl	138.5°	$C_{18}H_{26}O_3$ requires C,74.5;H,9.0	C,74.3;H, 9.0 %
Decyl	134.5°	$C_{19}H_{28}O_3$ requires C,75.0;H,9.3	C,74.8;H, 9.2 %
Dodecyl	132°	$C_{21}H_{32}O_3$ requires C,76.1;H,9.65	C,76.1;H, 9.5 %
Hexadecyl	118.5°	$C_{25}H_{40}O_3$ requires C,77.3;H,10.3	C,77.3;H,10.4 %
Octadecyl	120.5°	$C_{27}H_{44}O_3$ requires C,77.9;H,10.6	C,78.1;H,10.65%

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The transition points and melting points quoted in the thesis vary slightly in certain cases from the values in these publications, which are only preliminary reports of some of the observations before these had been redetermined with complete accuracy in the heating instrument.

INFLUENCE OF SUBSTITUENTS ON THE MESOMORPHISM OF *p*-*n*-ALKOXYBENZOIC AND 6-*n*-ALKOXY-2-NAPHTHOIC ACIDS

By G. W. GRAY and Prof. BRYNMOR JONES

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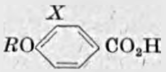
INFLUENCE OF SUBSTITUENTS ON THE MESOMORPHISM OF *p*-*n*-ALKOXYBENZOIC AND 6-*n*-ALKOXY-2-NAPHTHOIC ACIDS

By G. W. GRAY and PROF. BRYNMOR JONES
University College, Hull

SINCE Reinhitzer's discovery of mesomorphism in 1888, a large number of organic compounds which show this phenomenon have been prepared. Their physical appearance and the texture of their mesophases have been extensively studied by Friedel and others; but there is at present little or no information concerning the molecular dimensions which determine whether a system will show mesomorphism, or of the effect of substituents on the range and character of the mesophases. Vorländer[1] discussed the significance of certain structural features, and Bernal and Crowfoot[2] attempted to indicate the types of structure which would lead to the formation of nematic and smectic phases. Weygand *et al.*[3] made a systematic study of certain homologous series of alkoxyanils, azo- and azoxy-compounds. Nevertheless, all that can be said is that to show mesomorphism an organic molecule must either be predominantly one-dimensional or rod-shaped, as in *p*-azoxyanisole, or saucer-shaped, as in the cholesteryl esters, thus allowing the close packing in both the crystalline and mesomorphic states. In no series, hitherto, has the influence of substituents been systematically studied.

In an attempt to enlarge existing knowledge regarding the molecular dimensions which would appear to be necessary for mesomorphism to occur, an examination was recently made of the relative importance of length to breadth, or flat-area, in such molecules as the 4 : 1-, 5 : 1-, 6 : 2- and 7 : 2-*n*-alkoxynaphthoic acids[4]. Here, only the 6-*n*-alkoxy-2-naphthoic acids are mesomorphic. This investigation has now been followed by a study of the influence of substituents, particularly of the halogens, in the 3-position of *p*-*n*-alkoxybenzoic acids and in the 5-position of 6-*n*-alkoxy-2-naphthoic acids.



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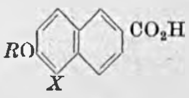

(II)

Table 1

	First appearance of : (a) nematic phase	(b) smectic phase	Smectic phase only	Maximum phase-length
X = H	$R = C_3H_7$	C_7H_{15}	$R = C_{18}H_{37}$	57° ($R = C_{10}H_{21}$)
F	C_8H_{17}	C_9H_{19}	$C_{16}H_{33}$	16° ($R = C_{16}H_{33}$)
Cl	C_8H_{17}	C_8H_{17}		4·5° ($R = C_{16}H_{33}$)

Table 2

	First appearance of : (a) nematic phase	(b) smectic phase	Smectic phase only	Maximum phase $R < C_{12}H_{25}$
X = Cl	$R = C_3H_7$	$R = C_6H_{13}$	$R = C_{16}H_{33}$ and $C_{18}H_{37}$	42° ($R = C_6H_{13}$)
Br	C_3H_7	C_7H_{15}	$C_{16}H_{33}$ and $C_{18}H_{37}$	40° ($R = C_7H_{15}$)
I	C_4H_9	C_8H_{17}	$C_{16}H_{33}$ and $C_{18}H_{37}$	25° ($R = C_8H_{17}$)
NO_2	C_9H_{19}	$C_{12}H_{25}$		1·5° ($R = C_{10}H_{21}$)

In the benzoic acids the effect of substituents is very marked. Introduction of the large bromine atom eliminates the mesomorphism completely. With chlorine and fluorine the mesophases persist, but their length is reduced, and their appearance in the series delayed. Thus, even with a fluorine atom, the nematic phase, which first appears in the unsubstituted acids in *p*-*n*-propoxybenzoic acid, is not found until the hydrocarbon chain is lengthened to octyl, in 3-fluoro-4-*n*-octyloxybenzoic acid. Moreover, in the unsubstituted acids a maximum phase-length of 57° is found in *p*-*n*-decyloxybenzoic acid[5,6]. In the fluoro-substituted acid the maximum phase-length is reduced to 16°, and in the chloro-acids it is only 4·5°. Both maxima are found in the *n*-octyloxybenzoic acids. Some of the data are summarized in Table 1; the alkyl groups used were CH_3 to $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{18}H_{37}$.

In view of these results, the absence of mesomorphism in 3 : 5-dichloro-4-*n*-alkoxy- and in 3-nitro-4-*n*-alkoxy- benzoic acids is not surprising.

A substituent in the alkoxynaphthoic acid (type II) affects its breadth (looked at along the line of axis of the O*R* and COOH groups) less than it does in the benzoic acid; even with a chlorine atom in the 5-position, the molecule is only a little broader than the parent acid. As a result, the decrease in the mesomorphism is far less marked than in the benzoic acids and, in all but the first members, mesomorphism persists throughout the chloro-, bromo- and iodo-alkoxynaphthoic acids. The influence of a nitro-group is much more striking, since its size and its polar character will probably affect orientation in the melt. The first eight acids in this series show no mesomorphism, but a short nematic phase appears in 5-nitro-6-*n*-nonyloxy-2-naphthoic acid. By contrast, a nematic phase is found in the unsubstituted 6-alkoxy-2-naphthoic acids in the 6-methoxy-acid, and the maximum phase-length in the first twelve members is 49° in 6-*n*-hexyloxy-2-naphthoic acid. The influence of increasing group size on the mesomorphism is shown in Table 2.

A particularly interesting feature of these results is the appearance of the smectic phase. In the chloro-acids, it emerges when *R* is hexyl, with bromine as substituent when *R* is heptyl, and with iodine when *R* is octyl. Thus, as the size of the halogen atom increases, this phase appears progressively later in the series.

It might have been expected that the appearance of the nematic phase would be affected similarly. That is, since a nematic phase is found with iodine and bromine as substituents in the butoxy- and

Table 3

	Phase-length			
	X = Cl	Br	I	NO_2
$R = C_{12}H_{25}$	35°	31°	24°	4°
$C_{16}H_{33}$	35°	34°	31°	4·5°
$C_{18}H_{37}$	35°	35°	35°	8°

propoxy- acids respectively, it might be found in the chloro-series in the ethoxy-acid. Actually, the lengths of the phases in 5-bromo-6-*n*-propoxy-2-naphthoic acid and in 5-iodo-6-*n*-butoxy-2-naphthoic acid are so short that they cannot be measured by normal methods (they persist for less than 0·1°). Moreover, the melting points of the ethoxynaphthoic acids are much higher than those of the propoxy-acids, and it is therefore not surprising that so short a phase is not found in 5-chloro-6-ethoxy-2-naphthoic acid with its high melting point of 264°.

When the alkyl group contains twelve or more carbon atoms, the effect of an increase in the size of the substituent, particularly of the halogen, is not so marked, and the halogeno-stearyloxynaphthoic acids become identical in their mesomorphic behaviour.

These compounds are the first extended series of substituted mesomorphic substances to be examined in detail. The gradual decrease in mesomorphism in the naphthoic acids as the size of the substituent is increased, together with its elimination in the benzoic acids, are noteworthy.

A fuller account of this work will be published later. [Feb. 21.

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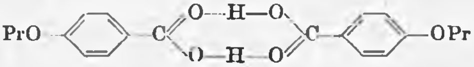
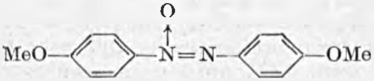
Mesomorphism of some Alkoxynaphthoic Acids

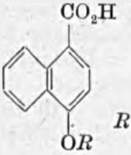
THE existence of mesophases in the melts of *p*-*n*-alkoxybenzoic and *p*-*n*-alkoxycinnamic acids has already been established[1,2]. In these acids the length of the rod-shaped molecules is enhanced by hydrogen-bond formation, and the mesomorphism arises from the association of the acids in double molecules. In this way, *p*-*n*-propoxybenzoic acid, which has the simplest molecular structure yet found to give a mesomorphic form, acquires a structure which is similar in length and shape to that of a typical nematic compound, such as azoxyanisole.





The structural features necessary for the occurrence of double refraction in a liquid have been discussed by Vorländer; but the relative importance of length and flat-area as factors in bringing about this phenomenon is not clear. It is well known that the cholesteryl esters of the saturated fatty acids exhibit marked mesomorphism.

In an attempt to determine more clearly the significance of these factors, the study of the alkoxy-aromatic carboxylic acids has been extended to 4-*n*-alkoxy-1-naphthoic and 6-*n*-alkoxy-2-naphthoic acids, and some twenty-six of these acids have been synthesized and examined.



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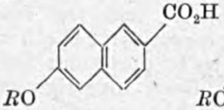
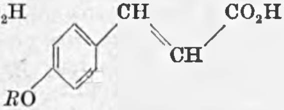


II



III

Of the thirteen 4-*n*-alkoxy-1-naphthoic acids (I) prepared, none shows mesomorphism ($R = CH_3$ to $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{18}H_{37}$). The first members of this series ($R = CH_3$ to C_8H_{17}), like *p*-methoxy- and *p*-ethoxybenzoic acids, melt at temperatures above 180° C., but the melting points of the higher members are much lower. The absence of mesophases in these acids may be due to the fact that the broad naphthalene nuclei, lying at right angles to the long axis of the dimerized molecules, prevent them from orientating themselves in such a way that mesomorphism becomes possible. It is significant in this connexion that the introduction of chlorine atoms into the ortho-positions of *p*-*n*-amyloxybenzoic acid destroys its mesomorphism.

Unlike the 4-*n*-alkoxy-1-naphthoic acids, the isomeric 6-*n*-alkoxy-2-naphthoic acids (II) show mesophases. In the case of twelve of the thirteen acids prepared ($R = CH_3$, C_2H_5, C_4H_9 to $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{18}H_{37}$) the mesomorphism is readily observed; but with the *n*-propoxy- acid the temperature-range of the nematic form is only a fraction of a degree. A nematic phase only is found in the first nine members of this series, the temperature-range of which reaches a maximum of 49° in the hexyloxy- acid. With the decyloxy- acid a smectic phase appears, the nematic henceforth becoming less pronounced as the length of the alkyl group is increased. These 6-*n*-alkoxy-2-naphthoic acids, which show structural similarities to the *trans* *p*-*n*-alkoxycinnamic acids (III), are long molecules without the breadth found in their isomers of structure (I), and therefore able to orientate themselves so that mesomorphism can occur.

Examples of mesomorphism in naphthalene compounds are not common; the best known are the anils of 2 : 6-diaminonaphthalene, but Vorländer[3] has shown that certain 1 : 4-disubstituted naphthalene systems exhibit mesomorphism. These, however, are resins or lacquers, such as anisal-1-amino-naphthalene-4-azobenzene. In such complex structures the broad naphthalene nucleus is near the centre of the molecule and, as a result, is probably of less importance than it is in the dimerized 4-*n*-alkoxy-1-naphthoic acids.

In view of the difference in behaviour between the 4-*n*-alkoxy-1-naphthoic and the 6-*n*-alkoxy-2-naphthoic acids, the properties of the 5-*n*-alkoxy-1-naphthoic acids may be of particular interest.

A fuller account of these investigations will be published elsewhere. In the meantime, other series of compounds are being examined.

G. W. GRAY
BRYNMOR JONES

University College,
Hull.
Sept. 12.

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[2] Bennett and Jones, Brynmor, *J. Chem. Soc.*, 420 (1939)

[3] Vorländer, *Trans. Farad. Soc.*, 899, 907 (1933).

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300 Word Summary

In order to determine more clearly the relative effects of length and breadth on mesomorphism,certain series of substituted and unsubstituted alkyloxy naphthoic and benzoic acids have been synthesised.The 4- and 5-*n*-alkyloxy-1-naphthoic acids and the 7-*n*-alkyloxy-2-naphthoic acids are not mesomorphic.On the other hand,the 6-*n*-alkyloxy-2-naphthoic acids show pronounced mesomorphism,as is also the case in the 5-chloro-,5-bromo- and 5-iodo- derivatives.The 5-nitro-6-*n*-alkyloxy-2-naphthoic acids exhibit mesomorphism only when the alkyl group contains nine or more carbon atoms.As the breadth of the molecules increases from the unsubstituted 6-*n*-alkyloxy-2-naphthoic acids to the chloro-,bromo-,iodo- and nitro- derivatives,the phase lengths decrease and the point at which mesomorphism commences becomes later in the series. A decrease in mesomorphic behaviour is also found with increasing breadth in the sequence *p*-*n*-alkyloxy benzoic acids to the 3-fluoro- and 3-chloro- derivatives.The appearances of the polymorphic states and the mesophases of the individual members have been examined in a heating instrument which was specially constructed for this purpose and for the measurement of the transition points.In the discussion of results,some attempt has been made to relate the differences in behaviour of these series to the molecular shapes

The mesomorphism in the *trans*-*p*-*n*-alkyloxy cinnamic acids has been re-examined and the previously published physical constants and transition points have been amended.

In the synthetic section, the best methods of preparing the unsubstituted naphthoic acids, and, wherever possible, the hydroxy naphthoic acids, have been described and compared with previously published routes to these compounds.