FULL PAPER

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Synthesis, structures and conformational studies of 1,2-dimethyl[2.10]metacyclophane-1-enes

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A series of 1,2-dimethyl[2.10]metacyclophane-1-enes (MCP-1-enes) containing different substituted groups has been synthesized. 4,22-Dimethoxy-1,2-dimethyl[2.10]MCP-1-ene **3** was synthesized by a Grignard coupling reaction, Friedel-Crafts acylation reactions and a McMurry coupling reaction from 1,10-dibromodecane. The formation of 4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **4** was carried out by demethylation of compound **3** with boron tribromide at room temperature. The *syn* type conformation of **4** was characterized by X-ray diffraction, and was found to form both intramolecular and intermolecular hydrogen bonds between two hydroxyl groups. From this reaction an interesting compound [10]tetrahydrobenzofuranophane **5** was afforded on prolonging the reaction time. 5,21-Diformyl-4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **6** has been prepared from 4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **4** by using the Duff method in the presence of hexamethylenetetramine. Structural analysis by ^{1}H NMR spectroscopy and X-ray diffraction confirmed that both the solution and the crystalline state of compound **6** adopts an *anti*-conformation which forms an intramolecular hydrogen bond between the formyl group and the hydroxyl group.

Introduction

In the world of organic chemistry, benzene and its derivatives are a pivotal class of compound. A small sub-division is the so-called cyclophanes, which are molecules that comprise of one aromatic part and a hydrocarbon chain that connects two carbon atoms of a ring. Additionally, they can be formed from two or more aromatic rings connected by either saturated or unsaturated chains.[1–3] The compound [2.*n*]metacyclophane has a fascinating molecular structure, and consists of two benzene rings cross-linked together by two ethylene chains at the *meta* positions.[3–5] Various [2.*n*]MCP (MCP = metacyclophane) derivatives have been prepared and characterized by a number of research groups, and have been found to exhibit unique properties.[6–8] In 1953, Brown and co-worker reported the X-ray crystallographic analysis of an MCP and the conformational evaluation thereof.[9] Hata et al.[10] measured the ring inversion of different MCPs, where the length of the cross-linking chain was systematically varied. The conformation of a monomer unit proved key in determining the behavior of such systems. Boekelheide[11] and Staab[12] accomplished the synthesis of *syn*-[2.2]MCPs, which are intra-annularly substituted.

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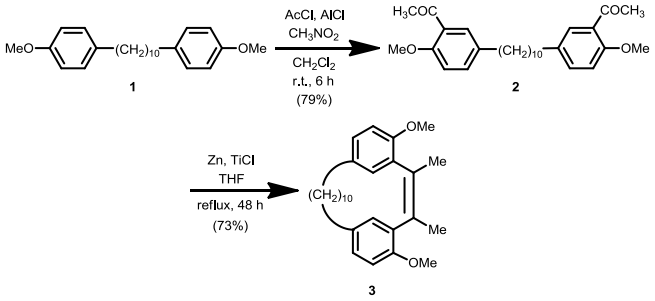
However, early papers on the synthesis and reactions of *syn*-[2.*n*]MCPs did not appear. Bodwell *et al.* described the synthesis of [2.2.*n*](1,3,5)cyclophane-1,9-dienes leading to 1,*n*-dioxa[*n*](2,7)pyrenophanes.[13] The rigid *syn*-conformation of cyclophanes was isolated by the overlaying of the aromatic rings. Mitchell and Weerawana group[14] synthesized cyclophanes bearing glycol units as bridges by the McMurry coupling reaction.[15] Latterly, Hopf and Mlynek,[16] Grützmacher et al.[17] reported the cyclization of dialdehydes to yield unsaturated cyclophanes. In more recent times, we have reported the preparation of 1,2-dimethyl[2.3]MCP- 1-enes[18–20] by using the reductive coupling reactions of carbonyl compounds in the presence of low-valent titanium. Here, the McMurry reaction was applied as a key step.[21–24] For the [2.3]MCP-1-enes, the aromatic rings are predicted to adopt 'mobile' *anti*- or *syn*-conformations. Additionally, the synthesis of and conformational studies on the [2.4]-MCP-1-ene system, together with it's conversion to *syn*-10-thia[2.3.4](1,3,5)-cyclophan-1-ene, has been reported.[25] In our laboratory, we are now focusing on the synthesis of small and medium sized metacyclophanes containing dihydrobenzofuran or benzofuran rings via intramolecular cyclization. This interest stems from interest in their conformations and also exploring their possible applications.[26] We report here the preparation of a series of [2.10]MCP-1-enes with different substituents as a monomer unit and their conformational studies in solution.

Results and Discussion

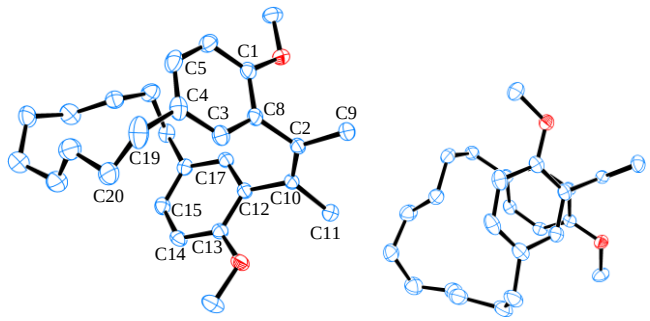
The starting compound 1,10-bis(4-methoxyphenyl)decane **1** was readily prepared from 1,10-dibromodecane according to our previous route.[27–33] In the presence of cuprous bromide (CuBr) as a catalyst, in a mixture of hexamethylphosphorictriamide (HMPA) and tetrahydrofuran (THF), the cross-coupling reaction of 4-methoxyphenylmagnesium bromide with 1,10-dibromodecane was carried out at reflux temperature to afford the required 1,10-bis(4-methoxyphenyl)decane **1** in 82% yield. This was followed by a regioselective Friedel-Crafts acylation reaction at the *meta* positions of the respective 1,10-diphenylalkanes. Compound **1** was then reacted in an $AlCl_3$–$MeNO_2$ catalyzed acetylation using acetyl chloride at 20 °C to afford 1,10-bis(3-acetyl-4-methoxy-phenyl)decane **2** in 79% yield (Scheme 1).[27–33] Under high dilution conditions, two carbonyl groups in the molecule of 1,10-bis(3-



acetyl-4-methoxy-phenyl)decane **2** were converted to a double bond, and a McMurry coupling reaction afforded the desired 4,22-dimethoxy-1,2-dimethyl[2.10]MCP-1-ene **3** in 73% yield.

Scheme 1. Synthesis of 4,22-dimethoxy-1,2-dimethyl[2.10]MCP-1-ene **3**.

The conformation of **3** was elucidated from it's ^{1}H NMR spectrum. [2.*n*]MCP-enes possessing overlaying aromatic rings adopt either a "staircase" *anti*-conformation or a *syn*-conformation.[34] The interconversion between the *syn*- and *anti*-conformers occurs by a ring flipping, the extent of which depends on the length of the bridge[35] and the presence or not of intra-annular substituents.[36–37] The ring current of the opposite benzene ring cause an upfield shift for the internal aromatic protons (δ = 6.59–6.81 ppm).[4–7] The ^{1}H NMR spectrum of **3** exhibited a doublet of doublets for the intra-annular proton H_i at δ = 6.81 (J = 8.3, 2.2 Hz) ppm. The other aromatic protons appear at δ = 6.59 and 6.67 ppm. The methyl protons of the bridging double bond were observed as a singlet at δ = 2.12 ppm, whilst the methoxy protons appear as a singlet at δ = 3.60 ppm. For a rigid *anti*-[2.10]MCP-1-ene structure, the protons of the decamethylene bridge introduce a complicated signal pattern. The benzylic CH_2 protons were observed as two multiplets centered at δ = 1.56 and 2.34 ppm, which are again split by coupling with the protons of the central CH_2 groups. These central CH_2 groups were also observed as a multiplet centered at δ = 1.21 ppm. These results suggested that the *anti*-conformation of [2.10]MCP-enes **3** might be controlled by the introduction of a double bond possessing substituents such as methyl or methoxy groups.

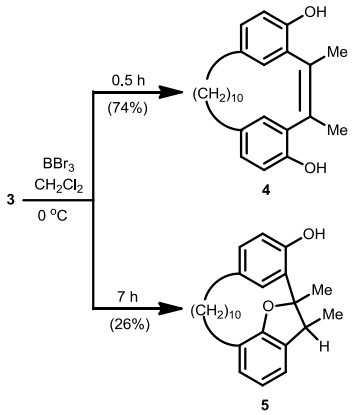


Top view Side view

Figure 1. ORTEP drawing of 4,22-dimethoxy-1,2-dimethyl[2.10]MCP-1-ene **3**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

The X-ray crystallography clearly shows that the conformation adopted by compound **3** is the *anti* conformation, in which two aromatic rings are part of a non-planar chain (Figure 1). Here the selected bond lengths of C19–C20 and C19–C3 in the decamethylene chains and C8–C2 and C9–C10 in the ethylenic chains have typical values at 1.54(3), 1.51(3), 1.49 (2) and 1.51(5) Å, respectively. The length of the double bond in C2–C10 is 1.34 Å, which is similar to that of ethylene. The bond angles defined by C8–C2–C10 and C2–C10–C12 are 120.3(2) and 121.0(2) Å, showing that **3** displays a slightly distorted conformation. The two benzene rings of **3** slightly deviate from planarity. The intramolecular distances of C8–C12, C1–C13, C5–C14, C4–C15, C16–C19, C3–C17 are 2.86, 4.82, 5.81, 5.21, 5.73 and 3.75 Å and the dihedral angle between the C3–C5–C6–C8 and C14–C15–C17–C12 planes is 61.36 Å. Both methoxy groups on the benzene rings of **3** point outwards, away from the decamethylene bridge chain. This contributes to the lack of steric crowding with hydrogens and carbons of the bridge chains.

To elucidate the substituents effect, we have tried to convert the methoxy groups into formyl groups. For the introduction of formyl groups at the 5,21-positions of 4,22-dimethoxy-1,2-dimethyl[2.10], MCP-1-ene **3** was treated with dichloromethyl ether and titanium tetrachloride (IV) in dichloromethane solution. However, the resulting product was a complex mixture. Therefore, we subsequently attempted to convert the methoxy groups into hydroxyl groups in order to introduce a formyl group using Duffs method. Firstly, demethylation was carried out using boron tribromide, and a dialcohol, namely compound 4,22-dihydroxy-1,2-dimethyl[2.10]MCP -1-ene **4**, was afforded within 0.5 h in 74% yield.



Scheme 2. Synthesis of 1-(2'-hydroxyphenyl)-7,8-dimethyl-[10](7,3') tetrahydrobenzofuranophane **5**.

The structure of **4** was elucidated from elemental analysis and spectral data. Notably, the cyclic structure was supported by the mass spectral data for **4** (M^+ = 378). The conformation of **4** was proposed from its ^{1}H NMR spectrum. If the conformation is of the *syn*-type, then the internally positioned aromatic protons (H_a) would receive a deshielding effect via the π electrons of the opposite side benzene ring. The other two aromatic proton (H_b, H_c) chemical shifts compared to (H_a) should be located at lower field positions. The ^{1}H NMR spectrum exhibited a doublet for the intra-annular proton H_i at δ = 6.75 (J = 1.9 Hz) ppm, indicating isomerization occuring between the *anti*- and *syn*-conformations (Figure 2). The aromatic protons of **4** are shifted to higher field at δ = 6.56, 6.72, 6.75 ppm than those of *anti*-compound **3** appearing at δ = 6.59, 6.67, 6.81 ppm.

The ^{1}H NMR spectrum of 4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **4** shows that its structure resembles entirely the *syn*-conformer. Furthermore, the protons of the decane bridge shows up as two multiplets centred at δ = 1.43 and 2.38 ppm, respectively, via ring flipping - fast *syn*–*syn* interconversion of the two *syn*-conformations of **4**; through this conversion **4** would exchange H_a and H_b of each CH_2 group. The peaks of the benzyl protons begin to merge and gradually a single peak is observed above 20 °C.

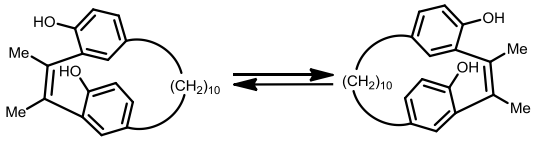


Figure 2. Conformational ring flipping of 4,22-dihydroxy-1,2-dimethyl[2.10] MCP-1-ene **4**.

Thus, a single benzyl peak at δ = 2.3 ppm is evident at 20 °C but when the temperature of the solution in $CDCl_3$ is decreased, it splits into two multiplets at δ = 2.3 and 2.5 ppm below –40 °C (Figure 3). This indicates that the rate of the conformational ring flipping of compound **4** is rapid on the NMR time-scale at this temperature. The energy barrier to the conformational ring flipping predicted from the coalescence temperature (T_c) is 64 kJ mol^{-1}. This suggests that the introduction of a double bond in the ethylene bridge as well as substituents such as methyl and methoxy groups can control the *syn*- and *anti*-conformations of [2.10]MCP-1-ene **4**.

In addition, intramolecular hydrogen bonding in compound **4** has been investigated in solution using NMR spectroscopy. In $CDCl_3$, the OH peak shifted to lower frequency at δ = 5.47 ppm. Notably, the stretching vibration of the OH groups are at a lower frequency, which together with the resonance of the protons of the OH groups at lower field is characteristic of intramolecular hydrogen bonding.[29–31] Selected regions of the ^{1}H NMR spectrum of **4** in three different solvents to provide solvation abilities were analyzed: acetone-d_6 and DMSO-d_6, which are exchanged by D_2O. In acetone-d_6, the peak shifted to lower frequency at δ = 7.47 ppm. In DMSO-d_6, a very sharp peak for the hydroxyl group was observed at δ = 8.42 ppm. These results indicating that the intramolecular hydrogen bonding is disrupted in polar solvents.

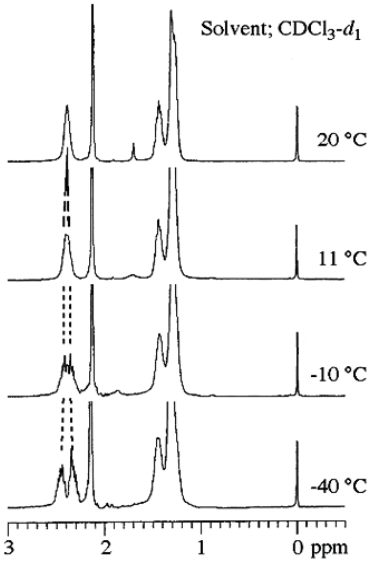


Figure 3. Dynamic ^{1}H NMR spectrum of **4** at 300 MHz ($CDCl_3$).

The crystal structure of **4** (Figure 4) was determined by X-ray crystallography. The X-ray structure is of the *syn* type, and the simultaneous formation of the partial hydrogen bonds between the two molecules was confirmed thereby forming an intramolecular hydrogen bond between the two hydroxyl groups of compound **4** as predicted from the ^{1}H NMR spectroscopic data. The distance between H1 (OH) and O2 (OH) is 2.46 Å, which is a reasonable distance for intramolecular hydrogen bonding and which is less than the distance between H2 (OH) and O1 (OH) 3.59 Å. From the above results, it can be assumed that the hydrogen bonds of **4** contribute to the immobilization of the conformation.

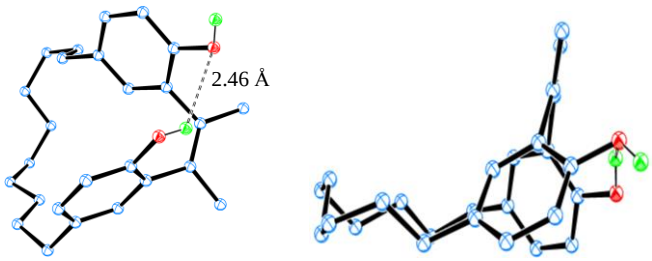
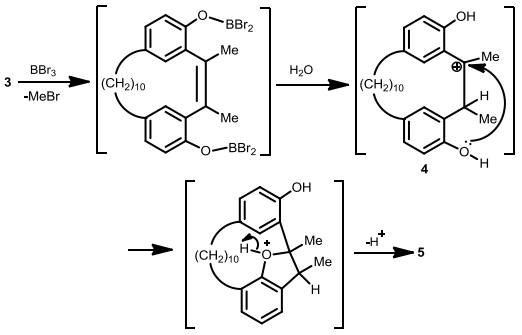


Figure 4. ORTEP drawing of 4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **4**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms except two are omitted for clarity.

Compound **3** was subjected to a further attempted demethylation reaction with boron tribromide using methylene chloride as solvent at 0 °C and then prolonging the reaction time for 7 h. A new compound tetrahydrobenzofuranophane **5** was obtained in 26% yield (Scheme 2). 4,22-Dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **4** is considered as an intermidiate to **5**. Compound **3** was converted to the expected compound **5** by nucleophilic intramolecular cyclization reaction. Elemental analysis and spectral data were used to resolve the structure. The mass spectral data (M^+ = 378) strongly supported the cyclic structure. The generation of compound **5** was confirmed by the ^{1}H NMR spectrum; all the protons are non-equivalent. Seven aromatic protons are detected as a multiplet at δ = 6.66–7.03 ppm, which are correlated with the unsymmetrical structure of **5**. On the basis of the spectral data and the chemical conversion, compound **5** is assigned to the structure, 1-(2'-hydroxyphenyl)-7,8-dimethyl-[10](7,3') tetrahydrobenzofuranophane.

Although the mechanism of formation of compound **5** is not clear at this stage, one might consider that the reaction pathway is as shown in Scheme 3. We propose that cyclization of ketonic **3** with the phenolic hydroxyl group forms the furan moiety and then is immediately transformed to the tetrahydrofuran ring by hydrogen. Again, the BBr_3 induced conversion of **4** to **5** was probably followed by nucleophilic substitution at the C_2 carbon to afford the five membered tetrahydrofuran skeleton which led to the desired product 1-(2'-hydroxyphenyl)-7,8-dimethyl[10](7,3')tetrahydrobenzofurano- phane **5**.



Scheme 3. Possible reaction pathway of formation of **5**.

As an active site for launching potential reactions, hydrogen bonding can play a vital role in chemical reactions, the presence of which by analysis of crystal structure determinations. Furthermore, such bonding can be useful in controlling unwanted association of specific functional groups in complex molecules.[38] It is well known that intermolecular hydrogen bonds play a significant role in the development of organized organic networks.[39] Compound **5** consists of hydrogen bonding donor /acceptor sites in the molecule which form inter- or intramolecular hydrogen bond interactions. In the IR spectrum a peak at 3469 cm^{-1} was observed for OH. The ^1H NMR spectrum also provides the signal for one hydroxyl group at low field, δ = 7.22 ppm in $CDCl_3$, which is exchanged by D_2O. The ^1H NMR in three different solvents was recorded to evaluate solvation abilities: $CDCl_3$, acetone-d_6 and DMSO-d_6, which are exchanged by D_2O. In acetone-d_6, the peak shifted to lower frequency at δ = 8.37 ppm. In DMSO-d_6, a sharp peak for the hydroxyl group was observed at δ = 9.24 ppm. These results indicate that the intermolecular hydrogen bonding is disrupted in polar solvents. As shown in Figure 5, a single crystal X-ray diffraction analysis exposes the absence of intramolecular hydrogen bonding in the solid state.

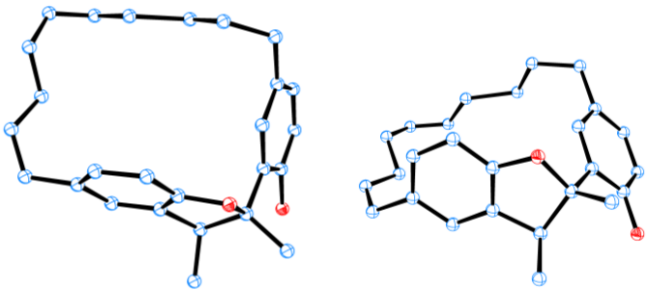
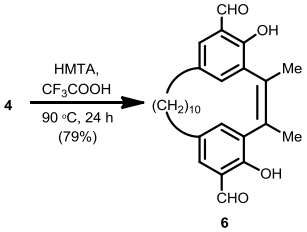


Figure 5. ORTEP drawing of 1-(2'-hydroxyphenyl)-7,8-dimethyl[10](7,3') tetrahydrobenzofuranophane **5**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Exploration of the crystal packing diagram of **5** reveals that the crystal lattice forms a hydrogen bonded network, where hydrogen bonding interactions between oxygen atoms and hydroxyl groups led to the construction of a chain extended along the crystal *c*-axis. The conformation of the molecule was influenced by these intermolecular OH···O hydrogen bonding. Parallel to the *ab* plane molecules are connected in *zig-zag* chain fashion. There is a lack of intramolecular hydrogen bonding involving the aromatic cores, which adopt the gauche conformation to abstain a strong repulsion between rings. This conformation is evident by inspection of the torsion angle between the two aromatic rings (C4–C3–C17–O1, 178.6(2)°). The observed C4–O2 bond in **5** is 1.38(3) Å, considerably shorter than C–O bond in phenol (1.38 Å).



Scheme 4. Synthesis of 5,21-diformyl-4,22-dihydroxy-1,2-dimethyl-[2.10]MCP-1-ene **6.**

Subsequently, use of Duffs method using 4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **4** in the presence of hexamethylene tetramine in trifluoroacetic acid at 90 °C for 24 h, allowed formyl groups to be introduced at the 5,21-positions, and [2.10]MCP-1-enes **6** was obtained in 79% yield (Scheme 4). The mass spectrometry data for **6** (M^+ = 378) supported the cyclic structure. The ^1H NMR spectrum exhibited a doublet for the intra-annular proton H_i at δ = 7.06 (J = 2.4 Hz), separated from the other aromatic protons of **6** at δ = 6.98 ppm. The data is consistent with the structure resembling the *anti*-conformer.

The attempted to immobilization of the molecules can be measured at the low temperature of 20 °C (Figure 6), since it is an upfield shift which allows for the estimation that 5,21-diformyl-4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **6** is of the *anti* type. Also, the hydroxyl group seems to be forming hydrogen bonds associated with at signal at δ = 11 ppm, which can be considered an *anti*-conformation conversion barriers along with [2.10]MCP-1-ene **4** (Figure 7).

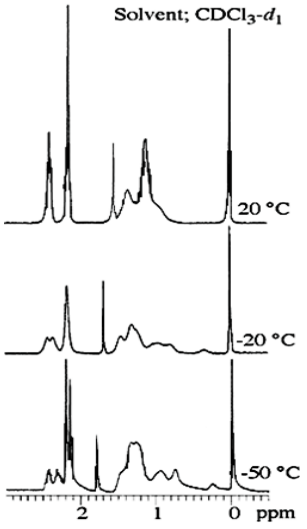


Figure 6. Dynamic ^1H NMR spectrum of 5,21-diformyl-4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **6** at 300 MHz ($CDCl_3$).

The energy barrier to the conformational ring flipping predicted from the coalescence temperature (Tc = –10 °C) is 57 kJ mol^{-1}. It is believed that an intramolecular hydrogen bond with a different unit has formed, which is presumed to be a formyl group with a hydroxyl group on the same benzene ring. There is a twist in the molecule and the two benzene rings are oriented in 180° with respect to each other. This is the result of the presence of the 10 cross-linking carbon atoms.

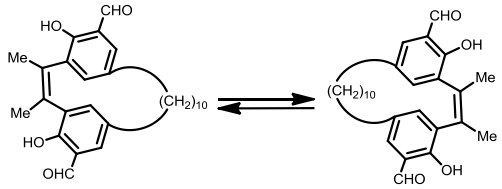


Figure 7. Conformational ring flipping of 5,21-diformyl-4,22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **6**.

Compound **6** was located at general positions in the asymmetric unit of the crystal structure. It forms an asymmetric conformation at –50 °C in solution as observed by the two sets of doublets for the methylene protons. Single crystals of **6** were grown from ethanol solution, and the structure was determined by X-ray crystallography to confirm the conformation. [2.10]MCP-1-ene **6** crystallized in the monoclinic space group $P2_1/n$ (Figure 8). The crystal structure using the Mercury program,[40] suggests that the two carbonyl groups and two hydroxyl groups are orientated outwards. It is also clear that the hydroxyl groups can form intramolecular hydrogen bonds with the oxygen atoms of carbonyl groups, as predicted from the ^1H NMR spectroscopic data. The distance between H1 (OH) and O2 (CHO)

is 1.78 Å, and that of H3 (OH) and O4 (CHO) is 1.71 Å, which are reasonable distances for intramolecular hydrogen bonding.

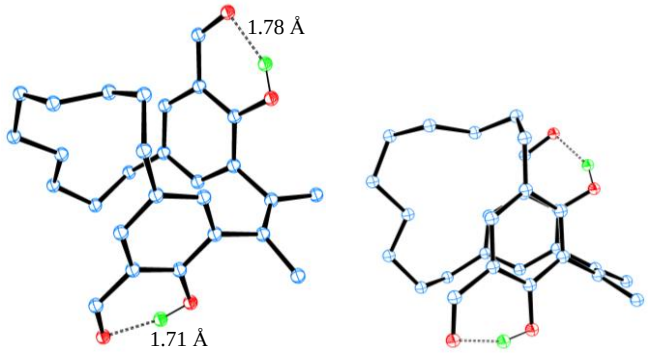
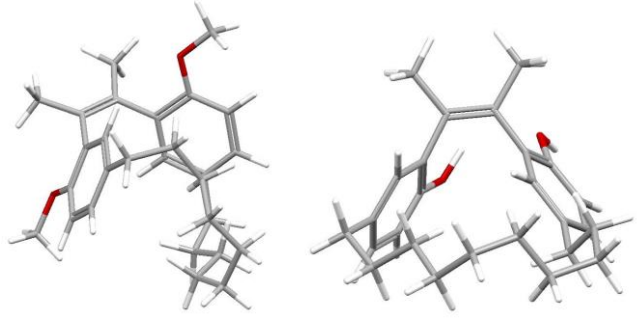


Figure 8. ORTEP drawing of 5,21-diformyl-4,22-dihydroxy-1,2-dimethyl-[2.10]MCP-1-ene **6**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms except two are omitted for clarity.

NMR spectroscopy is also a primary medium to explore intramolecular hydrogen bonding for compound **6** in solution. The ^{1}H NMR spectrum of **6** in three different solvents was recorded to afford solvation abilities: DMSO-d_6, acetone-d_6 and $CDCl_3$, which are exchanged by D_2O. In $CDCl_3$, the peak shifted to δ = 10.94 ppm. In acetone-d_6, the peak shifted to higher frequency at δ = 11.07 ppm. In DMSO-d_6, a sharp peak for hydroxyl group was observed at δ = 10.61 ppm, which indicates that the intramolecular hydrogen bonding is disrupted in polar solvents.

In comparison with [2.10]MCP-1-ene **4**, for compound **6** it can be seen that the distance between the two benzene rings is somewhat greater. Also the intramolecular hydrogen bond can be affected by the steric hindrance between the formyl group and hydroxyl group. This result suggests that the introduction of formyl group is best undertaken when the *anti*-type conformation is prevalent. The crystalline state of compound **6** is of the *anti*-type with the two benzene rings orientated at 180º to one another.

Density functional theory (DFT) computational studies were carried out to determine the geometry-optimized energies of compounds **3**–**6** (Figure 9). The starting structures were generated with the initial geometries based upon their X-ray crystal structures. The DFT level of theory using the popular B3LYP (Becke, three-parameter, Lee-Yang-Parr)[41] exchange-correlation functional with the 6-31G(d) basis set. The individual geometry-optimized structures of these molecules were first conducted in the gas phase and then in solvent (chloroform) with the B3LYP/6-31G(d) basis set using Gaussian-*09*.[42] The DFT optimized B3LYP/6-31G(d) energies for **3**–**6** conformers are −1240.30 kJ mol^{-1} for **3**, −1161.70 kJ mol^{-1} for **4**, −1161.72 kJ mol^{-1} for **5** and −1388.37 kJ mol^{-1} for **6** respectively in gas phase.



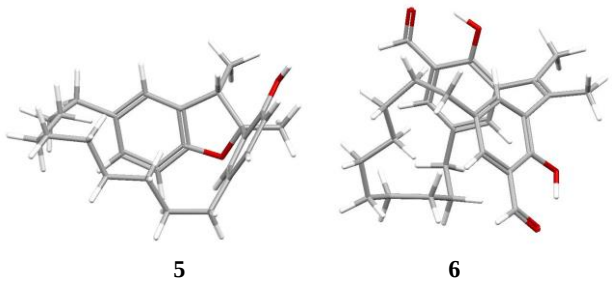


Figure 9. Geometry-optimized structures of **3**–**6** (in gas phase). Colour code: hydrogen = white, carbon = dark grey and oxygen atom = red.

Both the single crystal and DFT-optimized structures of **6** indicate that it adopts an *anti*-conformation and that the hydroxyl groups are pointed opposite to the benzene rings (Figure 7 and 8).

Conclusions

In conclusion, a new synthetic route has been developed for *syn*- and *anti*-[2.10]MCP-enes with various derivatives. We report an expedient preparation procedure of 5,21-diformyl-4, 22-dihydroxy-1,2-dimethyl[2.10]MCP-1-ene **6** from *p*-bromoanisole using a step by step reaction strategy. ^{1}H NMR spectroscopy and X-ray analysis of **3**–**6** confirmed the conformations present both in solution and in the solid state. The results from DFT computations were consistent with the observed experimental results. Further studies on the chemical behavior of compound **6** are now in progress.

Experimental Section

General Remarks: All melting points were uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Nippon Denshi JEOL FT-300 spectrometer and Varian-400MR-vnmrs400 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal Me_4Si. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyser. Elemental analyses were performed by Yanaco MT-5. Gas–liquid chromatograph (GLC) analyses were performed by Shimadzu gas chromatograph, GC-14A; silicone OV-1, 2 m; programmed temperature rise, 12 °C min^{-1}; carrier gas nitrogen, 25 mL min^{-1}.

Materials: 1,10-bis(4-methoxyphenyl)decane **1** was prepared following previous reports.[32]

Preparation of 1,10-bis(3-acetyl-4-methoxyphenyl)decane (2) (Typical Procedure): 1,10-Bis(4-methoxyphenyl)decane **1** (5.32 g, 15.0 mmol) was dissolved into acetyl chloride (3.2 mL, 45.0 mmol) and methylene chloride (60 mL) at 0 °C. Aluminum chloride (8.91 g , 68.0 mmol) and nitromethane (15 ml) solution was slowly added to the solution of compound **1** at 0 °C. After the reaction mixture was stirred at room temperature for 3 h, it was poured into ice-water (100 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined extracts were washed with water (2 × 50 mL), dried over $MgSO_4$ and concentrated *in vacuo* to leave a residue. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane-$CHCl_3$ (1:3) and $CHCl_3$ as eluent to give crude compound **2** as a colorless solid. Recrystallization from MeOH gave 1,10-bis(3-acetyl-4-methoxyphenyl)-decane **2** (5.19 g, 79%) as colorless prisms; m.p. 72–76 °C. IR (KBr): ν_{max} = 3002, 2922, 2842, 2362, 1671, 1605, 1561, 1496, 1460, 1416, 1256, 1168, 1038, 804, 762 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (broad s, 16 H), 1.55 (broad s, 4 H), 2.63 (s, 6 H), 3.73 (s, 6 H), 7.25 (dd, *J* = 8.4, 2.4 Hz, 2

H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 2.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.18, 29.41, 29.50, 31.47, 31.81, 34.78, 55.30, 55.52, 111.51, 114.13, 114.21, 126.96, 127.68, 127.87, 127.94, 129.95, 133.45, 133.50, 135.00, 157.11, 158.66, 200.06 ppm. MS (EI): *m*/*z* 438 [M$^+$]. $C_{28}H_{38}O_4$ (438.60): calcd. C 76.68, H 8.73; found C 76.54, H 8.71.

McMurry coupling reaction of 1,10-bis(3-acetyl-4-methoxy-phenyl) decane (2): The McMurry reagent was prepared from $TiCl_4$ (13.79 mL, 130 mmol) and Zn powder (18 g, 278 mmol) in dry THF (200 mL), under nitrogen. A solution of 1,10-bis(3-acetyl-4-methoxyphenyl)decane **2** (4.0 g, 0.091 mmol) in dry THF (150 mL) was added within 24 h to the black mixture of the McMurry reagent by using a high-dilution technique with continuous refluxing and stirring. The reaction mixture was refluxed for an additional 5 h, cooled to room temperature and hydrolyzed with aqueous 10% K_2CO_3 (500 mL) at 0 °C. The reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL), and the combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako C-300, 500 g) with hexane/$CHCl_3$ (1:2) as eluent to give crude compound **3** as a colorless solid. Recrystallization from EtOH gave 4,22-dimethoxy-1,2-dimethyl[2.10]metacyclophane-1-ene **3** (2.71 g, 73%) as colorless prisms; m.p. 123–124 °C. IR (KBr): ν_{max} = 2994, 2931, 2849, 2363, 2329, 1596, 1487, 1459, 1446, 1227, 1179, 1103, 1055, 1035, 891, 802, 753 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (broad s, 12 H), 1.56 (broad s, 4 H), 2.12 (s, 6 H), 2.34 (broad s, 4 H), 3.60 (s, 6 H), 6.59 (d, J = 8.3 Hz, 2 H), 6.67 (d, *J* = 2.2 Hz, 2 H), 6.81 (dd, *J* = 8.3, 2.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.30, 26.13, 26.36, 26.88, 29.87, 34.33, 55.12, 109.99, 126.71, 130.00, 133.61, 154.36 ppm. MS (EI): *m*/*z* 406 [M$^+$]. $C_{28}H_{38}O_2$ (406.60): calcd. C 82.71, H 9.42; found C 82.43, H 9.30.

Demethylation of 4,22- dimethoxy-1,2-dimethyl [2.10]metacyclophane-1-ene 3 with BBr_3: To a solution of 4,22-dimethoxy-1,2-dimethyl[2.10] metacyclophane-1-ene **3** (1.01 g, 0.248 mmol) in CH_2Cl_2 (30 mL) at 0 °C was gradually added a solution of BBr_3 (4.8 mL, 49.62 mmol) in CH_2Cl_2 (50 mL) over 1 h. After stirring the reaction mixture at room temperature for 30 min, it was poured into ice-water (50 mL), extracted with CH_2Cl_2 (2 × 30 mL). The combined extracts were washed with water (2 × 30 mL), dried over $MgSO_4$ and concentrated *in vacuo* to leave a residue. Recrystallization from EtOH gave 4,22-dihydroxy-1,2-dimethyl[2.10]metacyclophane-1-ene **4** (789 mg, 74%) as colorless prisms; m.p. 126–127 °C. IR (KBr): ν_{max} = 2942, 2850, 2359, 1601, 1496, 1453, 1428, 1256, 1180, 1143, 1112, 1068, 1024, 894, 808, 764 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (broad s, 12 H), 1.43 (broad s, 4 H), 2.12 (s, 6 H), 2.38 (broad s, 4 H), 5.47 (s, 2 H), 6.56 (d, *J* = 8.4 Hz, 2 H), 6.72 (dd, *J* = 8.4, 1.9 Hz, 2 H), 6.75 (d, *J* = 1.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.73, 26.24, 26.88, 27.41, 30.27, 34.87, 114.94, 127.62, 129.69, 130.28, 131.51, 134.42, 149.77 ppm. MS (EI): *m*/*z* 378 [M$^+$]. $C_{26}H_{34}O_2$ (378.55): calcd. C 82.49, H 9.05; found C 82.83, H 9.06.

Preparation of 1-(2'-hydroxyphenyl)-7,8-dimethyl[10](7,3')tetrahydro-benzofuranophane 5: To a solution of 4,22-dimethoxy-1,2-dimethyl[2.10] metacyclophane-1-ene **3** (600 mg, 1.48 mmol) in CH_2Cl_2 (20 mL) at 0 °C was gradually added a solution of BBr_3 (2.99 mL, 31.7 mmol) in CH_2Cl_2 (40 mL). After the reaction mixture has been stirred at room temperature for 7 h, it was poured into ice-water (50 mL), extracted with CH_2Cl_2 (2 × 30 mL). The combined extracts were washed with water (2 × 30 mL), dried over $MgSO_4$ and concentrated *in vacuo* to leave a residue. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane/ethyl acetate (5:1) as eluent to give crude compound **5** as a colorless solid. Recrystallization from hexane gave 1-(2'-hydroxyphenyl)-7,8-dimethyl[10](7,3')tetrahydrobenzofuranophane **5** (186 mg, 26%) as colorless prisms. ; m.p. 159–161 °C. IR (KBr): ν_{max} = 3454, 2929, 2849, 1612, 1511, 1489, 1460, 1424, 1380, 1336, 1263, 1220, 1199, 1125, 1088, 1052, 907, 884, 804, 703 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–1.17 (m, 16 H), 1.29 (d, *J* = 5.3 Hz, 3 H), 1.80 (s, 3 H), 2.46 (t, *J* = 6.3 Hz, 2 H), 2.55 (t, *J* = 9.3 Hz, 2 H), 3.73 (q, *J* = 10.6, 5.3 Hz, 1 H), 6.66–7.03 (m, 6 H), 7.22 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.94, 21.98, 25.37, 27.32, 27.53, 27.55, 27.67, 28.49, 29.34, 31.17, 34.01. 34.88, 43.95, 93.63, 109.12, 116.84, 124.59, 125.72, 128.03, 128.96, 130.40, 133.63, 133.70, 135.01, 152.13, 154.61 ppm. MS (EI): *m*/*z* 378 [M$^+$]. $C_{26}H_{34}O_3$ (378.26): calcd. C 79.15, H 8.69; found C 79.01, H 8.79.

Formylation reaction of 4,22-dihydroxy-1,2-dimethyl[2.10] metacyclophane-1-ene 4: 4,22-Dihydroxy-1,2-dimethyl[2.10] metacyclophane-1-ene **4** (386 mg, 1.02 mmol) was added into trifluoroacetic acid (3 mL) with hexamethylenetetramine (358 mg, 2.55 mmol) and the mixture stirred for 24 h at 90–100 °C. After cooling the reaction mixture to room temperature, it was again stirred for additional 1 h with 10% HCl (10 mL) and extracted with styrene (3 × 10 mL). The combined extracts were washed with 10% HCl and water (2 × 10 mL), dried over $MgSO_4$ and concentrated *in vacuo* to leave a residue. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane/$CHCl_3$ (1:3) as eluent to give the crude compound **6** as a colorless solid. Recrystallization from EtOH gave 5,21-diformyl-4,22-dihydroxy-1,2-dimethyl[2.10]metacyclophane-1-ene **6** (350 mg, 79%) as yellow prisms; m.p. 139–140 °C. IR (KBr): ν_{max} = 2922, 2849, 2356, 2318, 1641, 1445, 1372, 1256, 1227, 1088, 768, 718 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): δ = 1.12 (broad s, 12 H), 1.36 (broad s, 4 H), 2.14 (s, 6 H), 2.40 (broad s, 4 H), 6.98 (d, *J* = 2.4 Hz, 2 H), 7.06 (d, *J* = 2.4 Hz, 2 H), 9.76 (s, 2 H), 10.94 (broad s, 2 H) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C): δ = 1.31 (broad s, 12 H), 1.78 (broad s, 2 H), 2.16 (m, 6 H), 2.35 (broad s, 4 H), 6.95 (d, *J* = 2.4 Hz, 2 H), 7.06 (d, *J* = 2.4 Hz, 2 H), 9.75 (s, 2 H), 10.93 (broad s, 2 H), 11.23 (broad s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.40, 26.22, 26.26, 26.48, 29.05, 30.86, 33.58, 119.90, 131.41, 133.14, 133.46, 137.88, 156.84, 196.35, 206.8 ppm. MS (EI): *m*/*z* 434 [M$^+$]. $C_{28}H_{34}O_4$ (434.57): calcd. C, 77.39; H, 7.89; found: C, 77.32; H, 7.89.

The estimation of the activation energy of the ring flipping

By using Eqn (1) the rate constant (k_c) of the revealed conformational interconversion at the coalescence (T_c) can be calculated. The free energy of activation ($\Delta G_c^{\neq}$) at coalescence can be predicted by applying the Eyring equation [Eqn (2)].[43–44]

$$k_c = \pi\Delta\upsilon / 2^{1/2} \quad (1)$$

$$\Delta G_c^{\neq} = 2.303RT_c(10.32 + \log T_c - \log k_c) \quad (2)$$

Supporting Information (See footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra for all final products and X-ray structure of compounds **3, 4, 5** and **6**.

Acknowledgments

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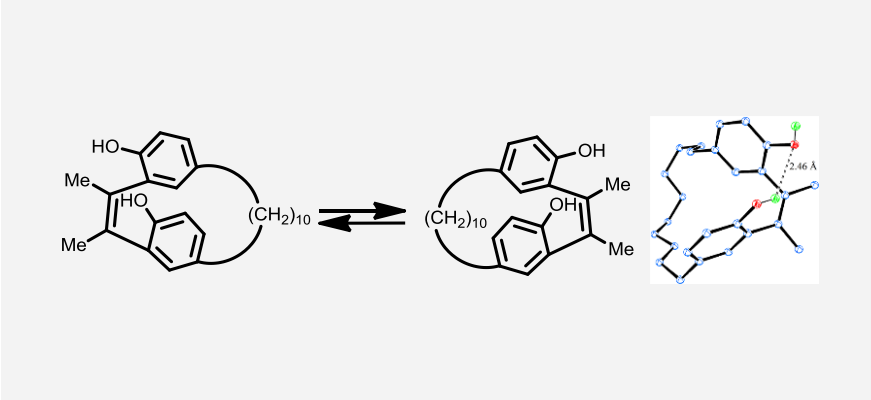

A series of 1,2-dimethyl[2.10] metacyclophane-1-enes containing different substituted groups has been synthesized and the structural properties were investigated by ^{1}H, ^{13}C, VT-^{1}H NMR spectroscopy and X-ray crystallography.

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Synthesis, structures and conformational studies of 1,2-dimethyl[2.10]metacyclophane-1-enes

Keywords: metacyclophane derivatives/ demethylation/ McMurry cyclization/ conformational studies/ intramolecular hydrogen bond