Synthesis and structure of 1,2-dimethylene[2.10] metacyclophane and its conversion to chiral [10]benzenometacyclophanes

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Abstract: Bromination of 5,21-di-*tert*-butyl-8,24-dimethoxy-1,2-dimethyl[2.10]metacyclophan-1-ene (MCP-1-ene) **1** with benzyltrimethylammonium tribromide exclusively afforded 1,2-bis(bromomethyl)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-1-ene **2**. Debromination of **2** with Zn and AcOH in CH_2Cl_2 solution at room temperature for 24 h produced the identical dimethylene[2.10]MCP **7** in 92% yield, which is a stable solid compound. Subsequently, compound **7** was reacted with dimethyl acetylenedicarboxylate (DMAD) to provide 1,2-(3',6'-dihydrobenzo)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-4',5'-dimethylcarboxylate **8** in good yield. Diels-Alder adduct **8** was converted to a novel and inherently chiral areno-bridged dimethoxy[2.10]MCP-4',5'-dimethylcarboxylate **9** by aromatization with dichlorodicyano-*p*-benzoquinone (DDQ), possessing C_1 symmetry. Also a new type of *N*-phenyl-maleimide substituted 1,2-(3',6'-dihydrobenzo)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-4',5'-*N*-phenylmaleimide **10** was synthesised from **7** via treatment with *N*-phenylmaleimide in toluene at 110°C followed by aromatization with DDQ. Single crystal X-ray analysis of **9** revealed the adoption of a *syn*-isomer.

Introduction

Cyclophanes are a class of compound classes that has undergone extensive studies in recent decades.[1] Metacyclophanes (= MCPs) have been known for nearly 45 years,[2] with the short chain (*n* = 4–6) members having attracted the appreciation of chemists as exemplary compounds to test the limits of bending aromatic rings.[3] Some of the reports focus on synthesis and conformational studies of the macrocyclic compounds, but few researchers have investigated the flexible conformations of the synthesized macrocyclic compounds and their conversion into rigid structures to provide as suitable platforms for diverse complexation experiments.[4] Our interest in this field stems from investigations of cyclic diynes in which two double bonds were part of the ring system.[5]

The syntheses of [*n*]MCP-diynes and conversion of the propargylic moieties into allenic moieties in the presence of strong bases was reported by Ramming and Gleiter.[6] Kawase and co-workers described the synthetic procedure for [2.*n*]MCP-ynes by bromination–dehydrobromination of the corresponding MCP-enes, which are considerably strained with bent triple bonds.[7] On the other hand, although the parent [2.2]MCP was first explored as early as in 1899 by Pellegrin,[8] the synthesis of *syn*-[2.2]MCP was achieved 85 years later. A successful preparative method for *syn*-[2.2]MCP has been introduced which uses (arene) chromium–carbonyl complexation at low temperature.[9] Further, Boekelheide[10] and Staab[11] have succeeded in synthesizing intra–annularly substituted [2.2]MCP, respectively. For alkene-containing MCPs, the McMurry reaction holds is a promising one-step pathway, but this reaction route has a preference for coupling two identical functional groups to facilitate the synthesis of the direct cyclophanes precursors.[12–16]

However, reports on the synthesis of [2.*n*]MCP-dienes containing long carbon chain as well as their chirality have not yet been published. Inherent chirality is a property of molecules whose lack of symmetry does not originate from a classic stereogenic element, but is rather the effect of the presence of curvature within a structure that would be lacking of symmetry axes in any two-dimensional representation.[17] A large number of inherently racemic chiral macomolecules have been reported, and some of them have been resolved into enantiomerically pure form.[17] Applications of inherently chiral molecules in molecular recognition[18] and asymmetric catalysis[19] have been reported.

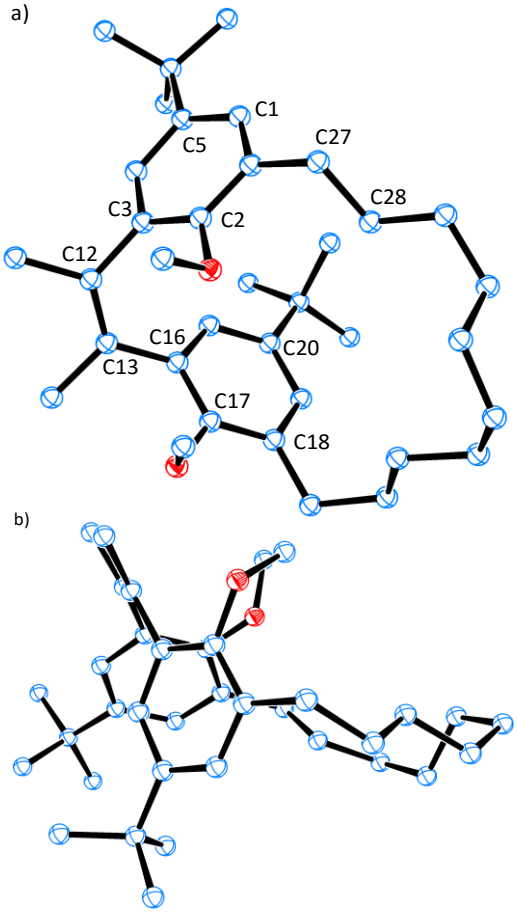
Our group has published a series of papers describing McMurry coupling reactions of tethered dialdehydes and ketones, in which the restrain length ranged from 2 to 10 and every accessible position on the aromatic rings was at some point substituted.[20] In this paper, we describe the first preparation of inherently chiral areno-bridged [2.10]MCP by using a bromination reaction and Diels–Alder reactions followed by aromatization with DDQ.

Results and Discussions

Very recently, we reported a synthesis and conformational study of [2.*n*]MCP-1-enes and the reaction with BBr_3 to afford tetrahydrobenzofuranophane.[21] We also reported inherent chirality in the MCP structure.[22] As part of our continued interest in the synthesis of inherently chiral MCPs, we undertook a systematic investigation of the starting compound 5,21-di-*tert*-butyl-8,24-dimethoxy-1,2-dimethyl[2.10]MCP-1-ene **1** containing both decane and ethylene bridges, which were synthesized from 1,10-bis(5-*tert*-butyl-2-methoxylphenyl)decane in four steps by using the *tert*-butyl group as a positional protective group on the aromatic ring.[23] Formylation of 1,10-bis(5-*tert*-butyl-2-methoxylphenyl)decane with dichloromethyl methyl ether (Cl_2CHOCH_3) in the presence of titanium tetrachloride in CH_2Cl_2 for 2 h afforded 1,10-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl) decane. The bisformylated compound was converted to the bis-alcohol derivative in 87% yield by reaction with the Grignard MeMgI in ether and then oxidation with pyridinium chlorochromate (PCC) to afford the bisacetyl derivative in 71% yield, which was subjected to reductive coupling by the McMurry reaction following the improved Grützmacher's procedure[16] to afford the desired compound **1** in 90% yield.[24]

None of the corresponding *anti*-isomer was observed under the conditions used. The structure of **1** was confirmed by comparing the melting point and ^{1}H NMR spectroscopic data with the reported data. Previously we failed to get single crystal of compound **1**, although we tried several times using different conditions. However, we have now succeeded in growing single crystals by slow evaporation of a saturated dichloromethane solution. The conformation was assigned by using both single crystal X-ray crystallography and ^{1}H NMR ($CDCl_3$, 300 MHz) spectroscopic analysis. The ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **1** exhibits a single peak at δ 3.65 ppm for the methoxy protons indicating that the two methoxy groups are outside of the two benzene rings (*syn*-

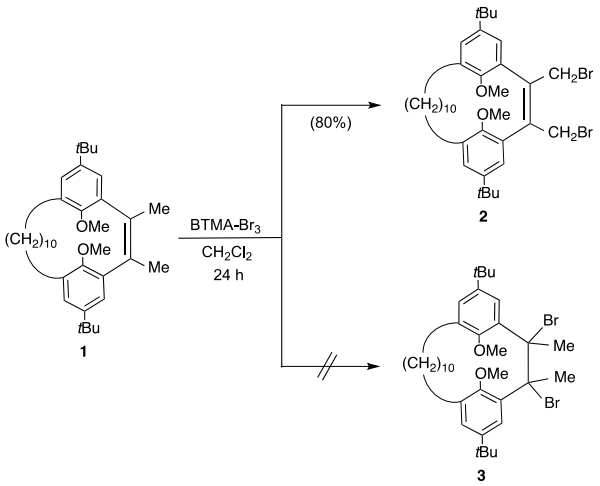
conformation) and methoxy protons appear at the normal position as for anisole. The aromatic protons appear in the high field region at δ 6.77 & 6.85 ppm due to shielding by the adjacent ring current; this is a common



consequence of face-to-face benzene rings due to the *syn*-conformation.[24] The crystal structure was found to belong to the monoclinic crystal system with space group *P* $2_1/n$ (SI Table S1) and is fully consistent with the ^{1}H NMR spectroscopic data for **1**.

The X-ray structure of **1** (Figure 1) clearly demonstrates that **1** exists as the *syn*-conformer in the solid state and that the two methoxy groups lie on the correlative side of the 18 membered inner ring, which contains the long bridging C1-10 chain pointing toward the outer direction thereby minimizing steric repulsion with the bridge chain. The selected bond lengths of C27–C28 and C1–C27 in the decamethylene chains and C3–C12 and C16–C13 in the ethylenic chains have typical values at 1.53, 1.50, 1.50 and 1.49 Å, respectively. The length of the double bond in C12–C13 is 1.34 Å, which is similar to that of ethylene. The bond angles defined by C3–C12–C13 and C12–C13–C16 are 123.6(2)° and 122.7(2)°, reveal that compound **1** displays a non-distorted conformation. The two benzene rings of **1** slightly deviate from planarity. The intramolecular distances of C3–C16, C2–C17, C5–C20, C4–C21, C1–C18, C6–C19 are 2.98, 4.18, 5.07, 3.59, 5.67 and 6.04 Å.

Bromination of **1** with 4.4 equiv. of benzyltrimethyl- ammonium tribromide (BTMA-Br_3)[25] in dry CH_2Cl_2 solution at room temperature for 24 h afforded the corresponding 1,2-bis(bromomethyl)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-1-ene **2** in 80% yield (Scheme 1). Here we use BTMA-Br_3 because it is easy to handle and a mild brominating reagent allowing us to control the reaction pathway. No bromination of compound **2** at the alkene bridge (double bond) was observed. This result is entirely different from the bromination of the corresponding [2.10]MCP-1-ene which afforded the *cis*–addition product (to the bridging double bond).[25] The presumed mechanism involves the initial formation of the bromonium ion followed by consecutive deprotonation and HBr elimination to afford diene **2**.[26,27]



Scheme 1. Synthesis of *syn*-1,2-bis(bromomethyl)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP **2**.

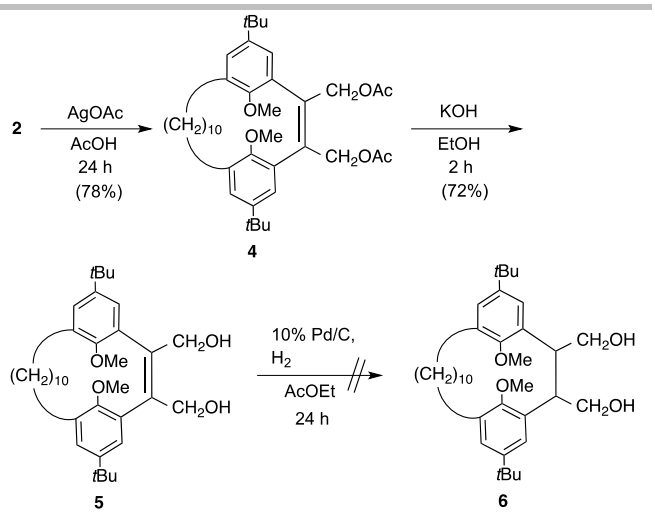
On changing the amount of BTMA-Br_3 used in this reaction there is the possibility of recovering the starting material. For example, when the compound **1** was treated with 1.2 equiv. of BTMA-Br_3 at room temperature for 24 h, **2** was formed in 30% yield with 60% recovery of compound **3** (Table 1). When the ratio was increased to around 2.4 equiv. under the same reaction conditions, the yield of compound **2** was increased to about 75% and became 100% when employing 4.4 equiv. of BTMA-Br_3.

Table 1. Bromination of 5,21-di-*tert*-butyl-8,24-dimethoxy-1,2-dimethyl[2.10]MCP-1-ene **1**.

Run	$BTMABr_3$ [equiv.]	Products yield [%][a,b]	
		2	Recovery of **1**
1	1.2	30(21)	60
2	2.4	75(65)	25
3	???	100(80)	0

[a] Yields determined by ^{1}H NMR spectroscopy. [b] Isolated yields are shown in parentheses.

The structure of product **2** was estimated on the basis of elemental analyses and spectral data. The mass spectral data for diene **2** (M^+ = 676, 678 and 680) strongly supported a dibominated structure. The ^{1}H NMR spectrum of **2** disclosed a singlet for the methoxy protons at δ 3.65 ppm as well as resonances at δ 6.67 and 6.91 ppm (*J* = 2.4 Hz) for the two protons of the aromatic rings. Previously reported[17b] 1,2-bis(bromomethyl)[2.3]MCP-1-ene exhibited a lower-field shift for the methoxy protons at δ 3.22 ppm along with δ 6.99 and 7.19 ppm (*J* = 2.4 Hz) for the two aromatic protons because of the short carbon chain length. The methylene protons of the bromomethyl group were observed as a doublet at δ 4.52 and 4.84 ppm (*J* = 10.0 Hz). Thus, the introduction of the bromo group at the methyl group might restrict the rotation throughout the single bond of C–CH_2Br, thereby causing the methylene protons to be in a diasterotopic environment.



Scheme 2. Synthetic strategy for debromination of 1,2-bis(bromomethyl)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-1-ene **2** *via* diol **6**.

To synthesize the diene body in the dehydration reaction for the Diels-Alder reaction, the reduction reaction of the double bonds does not proceed. Interestingly, treatment of **2** with Zn and dropwise addition of AcOH in dry CH_2Cl_2 solution at room temperature for 24 h afforded the identical 1,2-dimethylene[2.10] MCP **7** in 75% yield (Scheme 3). This type of reaction has been widely used to eliminate a bromine group to form a double bond.

Scheme 3. Synthesis of *syn*-1,2-dibenzo-5,21-di-*tert*-butyl-8,24-dimethoxy [2.10]MCP-4′,5′-dimethylcarboxylate **9**.

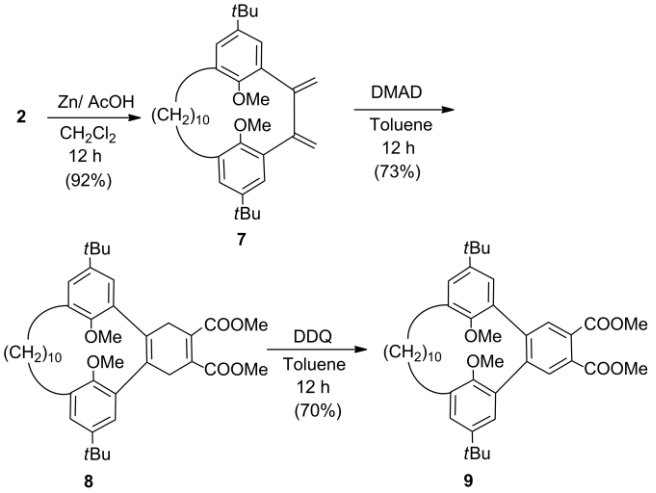
Figure 1. Single-crystal structure of **1** showing (a) the side view (b) the top view. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Treatment of 1,2-bis(bromomethyl)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-1-ene **2** with silver acetate in acetic acid at 100 °C for 24 h resulted in the analogous acetate compound **4** in 78% yield. Compound **4** was further converted to the 1,2-bis(hydroxymethyl) derivative **5** in quantitative yield by hydrolysis with KOH in presence of EtOH for 2 h in 72% yield (Scheme 2). After that, hydrogenation of compound **5** in presence of 10% Pd /C for 24 h failed to afford the expected compound **6**. This finding seems to support the strained nature of the diol **5**. Thus, the reduction reaction of the double bond does not proceed to the diene compound by palladium catalytic hydrogenation of diol **6**.

The cyclic dimeric structure was strongly supported by the mass spectral data for compound **4** (M^+ = 634). The 300 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$ showed a single peak at δ 3.68 ppm for the methoxy protons together with δ 6.79 and 6.95 ppm (*J* = 2.4 Hz) for the two aromatic protons. The methylene protons of the acetate group were observed as a doublet at δ 5.14 and 5.20 ppm (*J* = 12.6 Hz). On the basis of the spectral data and the chemical conversion, compound **4** is assigned to the structure, 1,2-bis(acetoxymethyl)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]- MCP -1-ene **4**.

Elemental analysis and spectral data were used to evaluate the structure of compound **5**. The structure of compound **5** was confirmed by the ^{1}H NMR spectrum. The methoxy protons were detected by a single peak at δ 3.76 ppm, and additional peaks at δ 6.79 and 6.95 ppm (*J* = 2.4 Hz) for the two aromatic protons. The methylene protons of the hydroxyl group were observed as a doublet at δ 4.50 and 4.80 ppm (*J* = 12.0 Hz). Using the spectral data, compound **5** is assigned to the structure *syn*-1,2-bis(hydroxymethyl)-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-1-ene **5**.

The structure of the diene obtained in the present work was determined from the elemental analyses and spectral data. The 300 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$ exhibited a doublet at δ 6.92 and 7.05 ppm for the two protons of the aromatic rings. The *exo*-methylene protons of the ethano-bridge were displayed as broad singlets at δ 5.53 and 5.69 ppm, and the protons of the methoxy group were observed at δ 3.64 ppm. The decamethylene bridge protons gave rise to a abstruse signal pattern as predicted for a rigid [2.10]MCP. The protons of the benzylic CH_2 group were observed as two multiplets at δ 2.11–2.38 and



2.73–2.90 ppm, which were additionally split by coupling with the protons of the central CH_2 groups. This central CH_2 groups was also observed as multiplets centered at δ 0.91–1.15 ppm. It was also observed that these methylene peaks did not merge up to 120 °C in $CDBr_3$. These findings suggested that the introduction of two double bonds of the ethano-bridge might inhibit the *syn–syn* conformational flipping of 1,2-dimethylene[2.10]MCP **7** above this temperature which

would exchange H_A and H_B of each CH_2 group. These perceptions suggested that the introduction of two double bonds of the ethano-bridge might restrict the *syn*- conformation of 1,2-dimethylene[2.10]MCP **7**.

Compound **7** is a stable solid and easy to purify. Compound **7** is conveniently employed in the reaction with dimethyl acetylenedicarboxylate (DMAD) to provide **8** in good yield. Diels-Alder adduct **8** was converted to areno-bridged [2.10]MCP **9** by aromatization with dichlorodicyano-*p*-benzoquinone (DDQ). The present Diels-Alder reaction of **7** with DMAD was completed within 24 h in toluene at reflux. Thus, the Diels-Alder reactivity of compound **7** exceeds that of 2,3-diphenyl-1,3-butadiene. This result suggests that the energy of the fixed s-*cis* conformation in

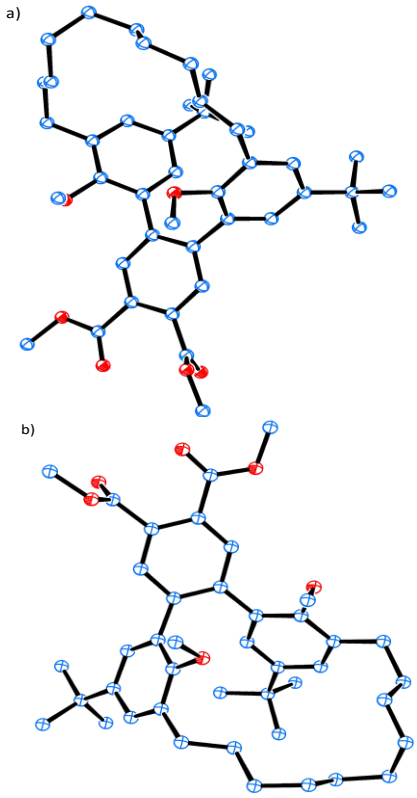


Figure 2. Single-crystal structure of **9** showing (a) the side view (b) the top view. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

7 in the ground and transition state might lower the Diels-Alder barriers due to the inflexibility of the MCP ring. The Diels-Alder reaction of **7** with suitable dienophiles followed by aromatization can be used to prepare a range of areno-bridged [2.*n*]MCPs.

Owing to the intrinsic structural features, we envisaged that MCP **9** would led to inherent chirality macrocycles due to intramolecular overcrowding like helicenes[28] or MCPs.[29] The synthesis and optical resolution of inherently chiral MCPs are challenging, but because of their potential uses in supramolecular chemistry, they remain attractive.[30] The design and synthesis of inherently chiral MCPs with novel structures therefore is a topic of great significance.

The structure of product **9** was determined by spectroscopic methods (^{1}H NMR and ^{13}C NMR), mass spectrometry and elemental analyses. The cyclic dimeric structure was confirmed by the mass spectral data for compound **9** (M^+ = 657). The 300 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$ exhibited a single peak at δ 3.68 ppm for the methoxy protons together with δ 6.79 and 6.95 ppm (J = 2.4 Hz) for the two aromatic protons. The methylene protons of the acetate group were observed as a doublet at δ 5.14 and 5.20 ppm (J = 12.6 Hz). On the basis of the spectral data and the chemical conversion, compound **9** is assigned to the structure, 1,2-dibenzo-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10]MCP-4',5'-dimethylcarboxylate (**9**).

In anticipation of future investigations into the ability of MCPs to be employed as chiral catalysts and ligands, efforts were made to access the solid-state structures and also the high-resolution NMR spectral data. Inherent chirality is a particular feature associated with some MCPs and **9** is predicted to have a plane of chirality. This is because it has two different types of substituents and bridged linkages which are fixed in a C_1 symmetrical structure and does not sustain a conformational change at or near ambient temperature.

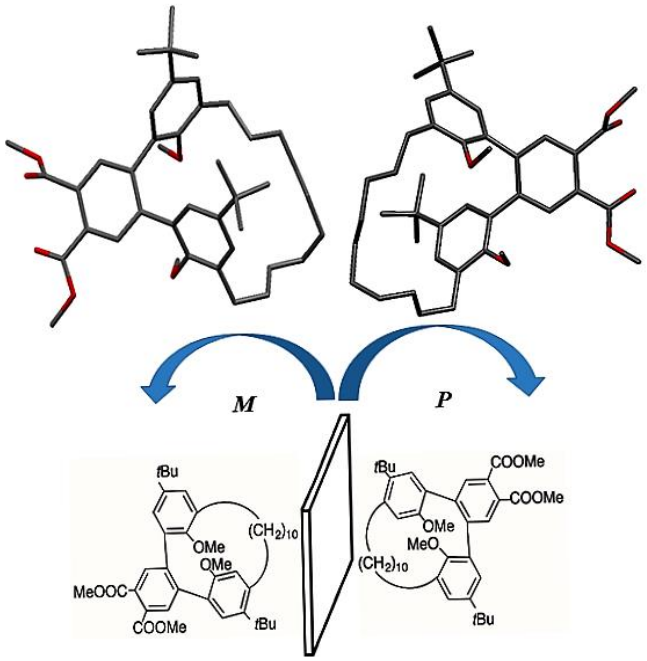
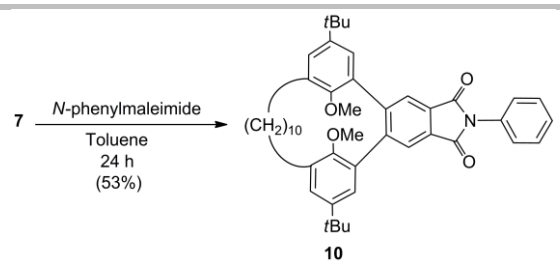


Figure 3. Schematic diagram of *M*-**9** (left side) and *P*-**9** (right side).

Compound **9** was crystallized by the slow, room temperature evaporation of a dichloromethane solution, into the space group *P-1*. Interestingly, the X-ray analysis disclosed that areno-bridged **9** adopts helical chirality, yet surprisingly, the dihedral angle of the arylenes connected by the phenyl unit is 33.98°. As a consequence, the compound is chiral and the (*M*)- and (*P*)-isomers are packed alternatively in the crystal as depicted schematically in Figure 3.

The removal of the external substituted COOMe group in compound **9** is more preferable than that of the internal substituted OMe group. However, this process required very high temperatures and also prolonged reaction times. In order to improve the reaction conditions to more suitable milder conditions, the reaction pathway was initiated from 1,2-dimethylene[2.10]MCP **7**. Compound **7** was treated with *N*-phenylmaleimide with toluene at 110 °C for 24 h to synthesized compound **10** (53% yield) as illustrated in Scheme 4.



Scheme 4. Synthesis of 1,2-dibenzo-5,21-di-*tert*-butyl-8,24-dimethoxy[2.10] MCP-4′,5′-*p*-dimethylbenzylamine **10**.

The structure of **10** was characterized by ^{1}H and ^{13}C NMR, mass spectra and elemental analysis. The cyclic dimeric structure was strongly supported by the mass spectral data for compound **10** (M^{+} = 689). The ^{1}H NMR spectrum of **10** (300 MHz, $CDCl_3$) exhibits a single peak at δ 3.64 ppm for the methoxy protons together with six aromatic protons appeared as doublets at δ 6.69, 6.89 and a singlet at δ 7.33 ppm, respectively, which are associated with the unsymmetrical structure of **10**.

Conclusions

We have described a simple and effective method for the synthesis of areno-bridged [2.10]MCP **9** by successive Diels-Alder reaction from 1,2-dimethylene[2.10]MCP **7**, and also its chiral conformation. To explore the rates of conformational behaviour of the described [2.10]MCPs, a series of electrophilic substitution reactions such as bromination, acylation and hydroxylation reactions of [2.10]MCPs were studied. Further mechanistic details of [2.10]MCP derivatives are being explored (by introducing different groups) and will be reported in due course.

Electronic Supplementary Information (ESI) available: Details of single-crystal X-ray crystallographic data. ^{1}H, ^{13}C NMR and MS spectra of **1** to **10**.

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Keywords: 1,2-Dimethylene[2.10]metacyclophane • Chirality • Diels-Alder reaction • Conformation studies

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