Synthesis and Structures of [2.*n*]Metacyclophan-1-enes and their Conversion to Highly Strained [2.*n*]Metacyclophane-1-ynes

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Abstract: The syntheses of s*yn*-[2.*n*]metacyclophan-1-enes (*n* = 5, 6, 8) in good yields using the McMurry cyclization of 1,*n*-bis(3-formyl-4-methoxyphenyl)alkanes are reported. Conversion of s*yn*-[2.6]- and [2.8]metacyclophan-1-enes to the corresponding highly strained *syn*-type [2.6]- and [2.8]metacyclophane-1-ynes was achieved by successive bromination and dehydrobromination reactions. An attempted trapping reaction of the putative corresponding [2.5]metacyclophane-1-yne by Diels-Alder reaction with 1,3-diphenylisobenzofuran failed due to its smaller ring size and strained structure. X-ray crystallographic analyses show that the triple bonds in *syn*-[2.6]- and [2.8]metacyclophane-1-ynes are distorted from linearity with bond angles of 156.7° and 161.4°, respectively. A DFT (Density Functional Theory) computational study was conducted to determine the stabilities of different conformations of the target compounds.

Introduction

Cyclophanes are an important class of compounds that have been shown to possess unique properties. This has attracted the interest of many research groups. These properties include having highly strained and unusual conformers with distorted aromatic ring components and this has resulted in much on-going research into the fundamental aspects of aromaticity.[1] Among the cyclophanes, the highly strained cyclophynes containing at least one ethyne bridging group have proven to be elusive. The formation of a paracyclophyne (Fig.1) was inferred by Psiorz and Hopf as the transient intermediate that led, via its cyclotrimerization reaction, to the formation of the novel C_3-symmetrical hydrocarbon trifoliaphane.[2] Meijere[3a,b] and Wong[3c,d] and their respective coworkers used reactive trapping reagents such as furan, to confirm the formation of other strained cyclophynes as transient intermediates leading to the observed formed cycloaddition products.

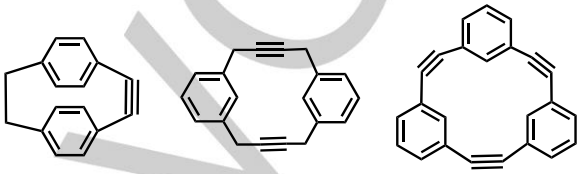

Figure 1. *Left:* Paracyclophyne; *middle:* [4.4]metacyclophyne and *right:* [2.2.2]metacyclophyne

The syntheses of several medium-sized [*n*.*n*]metacyclophane-diynes such as [4.*n*]metacyclophyne, were reported by Ramming and Gleiter.[4a] Under different reaction conditions the triple bonds of some of these diynes could be isomerized into the corresponding *cis* double bonds and in others into allenic moieties. Kawase and co-workers reported the syntheses of [2$_n$]metacyclophane-*n*-ynes such as [2.2.2]metacyclophyne (Fig. 1) which are considerably strained and have bent triple bonds, via sequential bromination-dehydrobromination reactions of the corresponding metacyclophan-*n*-enes.[4b–d]

Previously, we reported our own attempts to produce the shorter chain-length [2.3]- and [2.4]metacyclophane-1-ynes by the dehydrobromination of the corresponding 1,2-dibromo-[2.*n*]metacyclophanes, but only 1-bromo[2.*n*]metacyclophan-1-enes together with [2.*n*]metacyclophan-1-ones were obtained.[5a,b] Later, we reported the successful preparation of *syn*- and *anti*-[2.8]metacyclophan-1-enes using the low-valent titanium-induced McMurry coupling reaction and their conversion to *syn*- and *anti*-[2.8]metacyclophane-1-ynes, in a ratio of 35:65.[6] The bromine adduct of [2.10]metacyclophan-1-ene on the other hand, gave the [2.10]metacyclophane-1-yne as the major product, along with a monodehydrobrominated product 1-bromo[2.10]metacyclo-phan-1-ene as a by-product.[6] We also recently reported the synthesis, structures and DFT (Density Functional Theory) computational studies of several [2.*n*]metacyclophanes[7a–g] and [3.3]metacyclophanes[8] as well as ring-expanded metacyclophanes containing three aromatic rings.[9]

In this paper, in continuation of our previous work related to the synthesis of [2.*n*]metacyclophane-1-ynes,[6] we now report the first synthesis of highly strained [2.*n*]metacyclophane-1-ynes (*n* = 5, 6 and 8) using the bromination-dehydrobromination reactions of their corresponding [2.*n*]metacyclophan-1-ene precursors.

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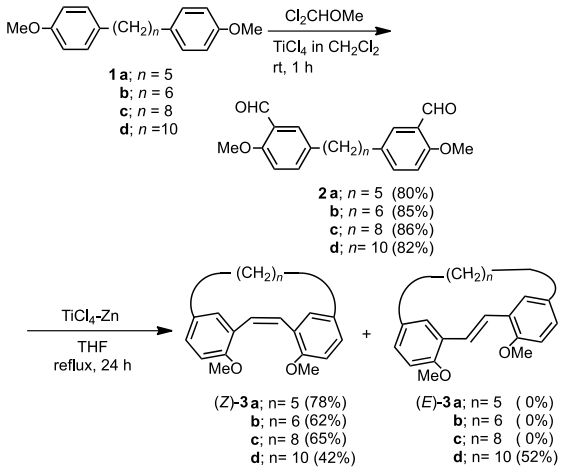
Results and Discussions

The starting compounds for the target [2.*n*]metacyclophane-1-ynes, *i.e.* 1,5-bis(4-methoxyphenyl)pentane **1a**, 1,6-bis(4-methoxyphenyl)hexane **1b** and 1,8-bis(4-methoxyphenyl)-octane **1c** were readily prepared in good yields via one-step cross-coupling reactions of 4-methoxyphenylmagnesium bromide with 1,*n*-dibromoalkanes (*n* = 5, 6 and 8) respectively, in the presence of CuBr, in a mixture of HMPA and THF, heated at reflux.[10–12] Dichloromethyl methyl ether-$TiCl_4$, regioselective Friedel-Crafts formylation reactions of 1,*n*-bis(4-methoxyphenyl)alkanes **1** (*n* = 5, 6 and 8) afforded the required 1,*n*-bis(3-formyl-4-methoxyphenyl)alkanes **2a** (*n* = 5), **2b** (*n* = 6) and **2c** (*n* = 8) in 80–86 % yields, respectively (Scheme 1).



Scheme 1. Synthesis of *syn*-dimethoxyl[2.*n*]metacyclophan-1-enes **3a–d**.

The McMurry $TiCl_4$/Zn reductive coupling reaction of carbonyl compounds catalyzed by low-valent titanium[13] has been extensively used to synthesize cyclophanes.[14,15] In the present work, using the reductive coupling reaction, intramolecular cyclization of 1,5-bis(3-formyl-4-methoxy-phenyl)pentane **2a** successfully afforded 4,17-dimethoxy[2.5] metacyclophan-1-ene **3a** in 78% yield. Similarly, 4,18-dimethoxy[2.6]-metacyclophan-1-ene **3b** and 4,20-di-methoxy[2.8]metacyclophan-1-ene **3c** were obtained in 62% and 65% yields, respectively. No formation of any of the corresponding (*E*)-isomers were observed with **2a–c** but with 1,10-bis(3-formyl-4-methoxyphenyl)decane **2d** as previously reported, a mixture of the corresponding (*E*)- and (*Z*)-4,22-dimethoxy[2.10]metacyclo-phan-1-enes (*E*)-**3d** and (*Z*)-**3d** was obtained (Scheme 1).[16]

[2.*n*]Metacyclophan-1-enes can adopt either a "staircase" *anti*-conformation or a *syn*-conformation by overlapping of their aromatic rings (Fig. 2).[17] *Syn-anti* interconversion can occur by ring flipping, and is dependent upon both the length of the bridges[18] and also on the nature of the intra-annular substituents.[19]

The ^{1}H-NMR spectrum of **3a** clearly showed the doublet of the intra-annular protons at δ 7.05 ppm (d, *J* = 2.2 Hz) separated from the other protons of the aromatic rings at δ 6.80 (d, *J* =8.4 Hz) and 6.91 (dd, *J* = 2.2, 8.4 Hz) ppm. Previously, we had reported that the intra-annular aromatic potons in the *anti*-[2.*n*]metacyclophan-1-enes (*n* = 3–6) were shifted upfield at δ 6.05–6.77 ppm, due to the shielding effect of the ring current of the opposite benzene ring.[20] Thus, the observed chemical shift for the intra-annular protons of **3a** strongly suggests that the molecule adopts a *syn*-conformation. Previous work has shown the chemical shifts of olefinic protons for *(E)*- and *(Z)*-olefins to be at δ >7.4 ppm and δ <6.9 ppm repectively.[21] In the case of **3a** the olefinic bridge protons were observed as a singlet at δ 6.79 ppm indicating that the structure of **3a** is a (*Z*)-*syn*-isomer. Similarly, the spectra of [2.6]metacyclophan-1-ene (**3b**) and [2.8]metacyclophan-1-ene (**3c**), indicate that they exisist as (*Z*)-*syn*-isomers.

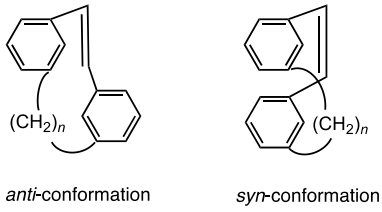
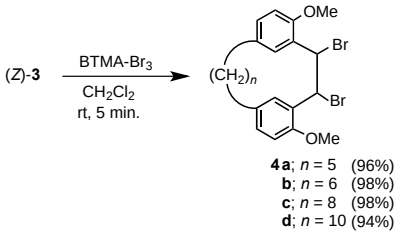


Figure 2. (*E*)-*Anti*- and (Z)-*syn*-conformations of [2.*n*]metacyclophan-1-enes.

Fast interconversion on the NMR timescale between the two conformations of **3a** can be observed since the three multiplets centered at δ 1.03, 1.28 and 2.32 ppm, which are due to the protons of the pentane bridge, do not change upon decreasing the temperature to –100°C in a 1:3 mixed $CDCl_3$-CS_2 solvent. Thus the larger cyclophane ring size and the smaller intra-annular protons in **3a** allow for a more flexible structure compared to, for example, *anti*-6,14-dimethoxy-1,2-dimethyl[2.4]metacyclophan-1-ene.[20a]



Scheme 2. Synthesis of dibromo-dimethoxyl[*n*.2]metacyclophanes **4a–d**.

Conversion of the double bonds to the corresponding triple bonds was accomplished by the bromination-dehydro-bromination sequence of reactions. First, using equimolar amounts of benzyltrimethylammonium tribromide (BTMA-Br_3)[22] in dichloromethane solution at room temperature, *syn*-**3a** and *syn*-**3b** afforded quantitatively the racemic *trans*-dibromo adducts *syn*-**4a** (*endo-exo*-Br) and *endo-exo syn*-**4b** (*endo-exo*-Br), respectively in which the bromine atoms are *endo* or *exo* to the macrocycle with *R,R* and/or *S,S* configurations (Scheme 2). However, with *syn*-**3c** a mixture of dibromo *meso-syn*-**4c** (*endo-endo*-Br) with the bromine atoms in *R,S* configurations and *syn*-**4c** (*endo-exo*-Br) was formed quantitatively in a 53:47 ratio. Interestingly, the bromination reactions of the *syn*-**3a–c** compounds afforded the corresponding *syn*-**4a–c** dibromo products, without any of the corresponding *anti*-conformers. In these bromination reactions no *syn*- to *anti*-ring inversion occurs.

The structures of these products were determined from their elemental analyses and spectral data. The ^{1}H-NMR signals of **4a–d** in $CDCl_3$, were assigned based upon the *trans*-addition of bromine to the double bonds with *endo*-*exo*- and *endo*-*endo*-arrangements of the two bromine atoms with respect to the macrocycle. The two intra-annular aromatic protons which are located *ortho* to the two bridging aromatic carbon atoms in **4a** now appeared as two distinct doublets at δ = 6.93 (J = 2.2 Hz) and 7.00 (J = 2.2 Hz) ppm, which is supportive for **4a** being in a *syn*-conformation. Furthermore, the methine protons at the dibromoethano bridge also appear as a pair of doublets (J = 10.4 Hz) at δ = 5.57 and 6.62 ppm. The lower field signal is attributed to one of the *exo*-methine protons which is in a strongly shielding region of the oxygen atom of the methoxy group on the aromatic ring. The data are strong evidence that the two methine protons at the ethano bridge are in an *exo*-*endo* arrangement with respect to the macrocycle (Figure S18). Thus, **4a** is assigned as being a racemic pair i.e. *rac*- or *dl*-*syn*-12-*endo*-bromo-13-*exo*-bromo-9,15-dimethoxy[5.2]metacyclophane, or *dl*-*syn*-**4a** as shown in Fig. 3 (where n = 5). None of the corresponding *anti*-isomer was observed under the conditions used here.

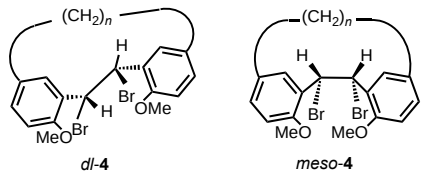


Figure 3. Possible structure of bromine adducts **4a–d.**

The protons of the –$(CH_2)_5$– bridge generated a complicated signal pattern, as to be expected for a rigid structure. The bridged methylene protons in *syn*-**4a** are clearly located in different spaces with one of them folded into the π-cavity formed by the two benzene rings and high-field signals at δ = –0.13– and δ = –0.03 ppm are observed. The individual signals of the methylene protons for the middle CH_2 group in the pentane bridge do not coalescence below 130°C in $CDBr_3$ and the energy barrier to conformational wobbling is above 25 kcal mol^{-1}.

The structure of **4b** was similarly confirmed by elemental analysis, ^{1}H-NMR spectroscopic data and additionally, with a single crystal X-ray crystallographic analysis. The ^{1}H-NMR spectrum of **4b** exhibits two singlets at δ 3.71 and 3.82 ppm for the methoxy protons. The two intra-annular aromatic protons at δ = 6.96 and 6.99 ppm are at lower fields than those seen for the corresponding *anti*-[2.*n*]metacyclophan-1-enes.[20] The data is supportive for **4b** being in a *syn*-conformation. Furthermore, similar to *syn*-**4a** the two methine protons at the ethano bridge appear as a pair of doublets (J = 10.2 Hz) at δ = 5.66 and 6.67 ppm. The lower field absorption is attributed to the *exo*-methine proton in a strongly shielding region of the oxygen atom of the methoxy group on the aromatic ring (Figure S20). Thus, the two methine protons at the ethano bridge are similarly in an *exo*-*endo* arrangement and thus **4b** is assigned as being a racemic pair *i.e. rac*- or *dl*-*syn*-13-*endo*-bromo-14-*exo*-bromo-10,16-dimethoxy[6.2]metacyclophane *dl*-*syn*-**4b**. As in the case of **4a** the protons of the –$(CH_2)_6$– bridge generated a similarly complicated signal pattern.

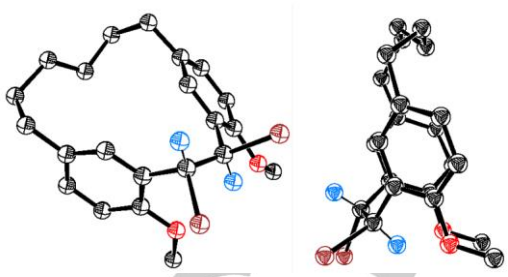
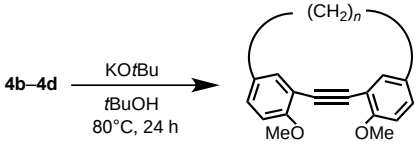


Figure 4. ORTEP figures of **4b** with top (*left*) and side (*right*) views. Thermal ellipsoids are drawn at the 50% probability level. Only hydrogen atoms at the ethano bridge are shown. Other hydrogen atoms are omitted for clarity.

The single crystal X-ray structure of *syn*-**4b** is illustrated in Fig. 4. The compound crystallized in the monoclinic space group P2*1/a* (CCDC 1547285 and SI Table S1) and clearly reveals that the conformation is *syn* in which two aromatic rings are face-to-face and mostly cause distortion in a boat-like shape and deviate from planarity to some extent as can be seen from the side view of the ORTEP drawing. Further, the X-ray analysis shows an unsymmetrical structure with a *staggered* orientation of the two methine protons on the ethano bridge and located distally from the bridging methylene groups. These results suggest that the introduction of the two bromine atoms at the ethano bridge might dominate the potential for interconversion of the two *syn* conformations of **4** by ring flipping.

Interestingly, the ^{1}H-NMR spectrum of **4c** showed it to be a mixture of *meso*-*syn*-**4c** (*endo*-*endo*-Br) and *dl*-*syn*-**4c** (*endo*-*exo*-Br) in the ratio of 53:47. The presence of the diastereomeric *meso*-*syn*-**4c** can be inferred by the presence of singlet signals for the its methoxy protons at δ = 3.54 ppm and for the ethylene bridge methine protons at δ = 6.12 ppm. The intra-annular protons appear as a broad singlet signal at δ = 7.30 ppm due to their being in the strongly deshielding region of the *endo*-Br atoms on the ethylene bridge. This data strongly supports the assignment of having the two Br atoms in an *endo*-arrangement. In contrast, *dl*-*syn*-**4c** showed a similar ^{1}H-NMR spectrum to those of **4a** and **4c**, which suggests an unsymmetrical *syn*-*endo*-*exo*-dibromo-structure.

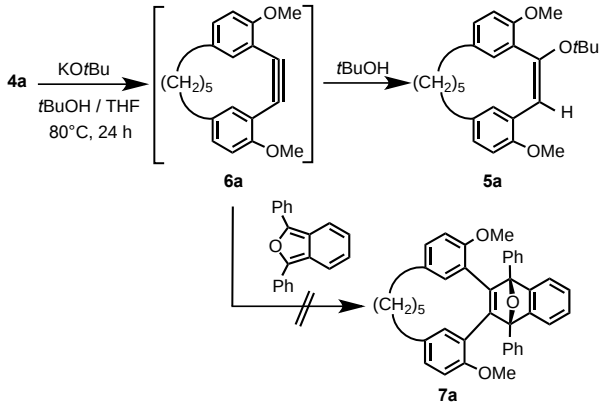


6 b; n = 6 (95%)
c; n = 8 (98%)
d; n = 10 (90%)

Scheme 3. Synthetic route of [2.*n*]metacyclophane-1-ynes **6b–d**.

Treatment of **4b** and **4c** with *t*-BuOK in *t*-BuOH at 80°C for 24 h gave the doubly dehydrobrominated products, [2.*n*]metacyclophane-1-yne **6b** and **6c** in 95% and 98% yields, respectively (Scheme 3). Similar treatment of **4a** however, afforded only the *t*-butoxide product **5a** in 83% yield and none of the desired [2.5]metacyclophane-1-yne **6a** (Scheme 4). In this case, it could be supposed that when the highly strained acetylenic moiety in **6a** formed in the dehydrobromination reaction, that it immediately reacts with the solvent *t*-BuOH to produce the addition product **5a**. Other attempts to

dehydrobrominate this shorter chain cross-linked compound **4a** using different *t*-BuOK/*t*-BuOH reaction conditions however failed. Attempts to trap putative **6a** as its Diels-Alder adduct **7a** with 3-diphenylisobenzofuran in *t*-BuOH were unsuccessful affording only **5a** again. However attempts to form the corresponding Diels-Alder adducts from the reaction of the isolated [2.*n*]metacyclophane-1-ynes **6b** and **6c** with 1,3-diphenylisobenzofuran under the same reaction conditions shown in Scheme 4 also failed and only the unreacted starting comounds were recovered. Presumably the sterically crowded bridged acetylene moiety having the methoxy groups on the benzene rings likely suppress the approach of the 1,3-diphenylisobenzofuran (Scheme 4).



Scheme 4. Trapping reaction of [2.5]metacyclophane-1-yne **6a** with 1,3-diphenylisobenzofuran.

The structure of **5a** was determined by elemental analyses and spectral data. The mass spectra showed the predicted molecular ion for **5a** at *m*/z = 380.19. The ^{1}H-NMR spectrum of shows the two methoxy protons as singlets at δ = 3.79 and 3.87 ppm. The *tert*-butoxy protons and the olefinic proton appear at δ = 1.31 ppm (9H) and 6.52 ppm (1H) as nine- and one-proton singlets, respectively.

The structures of **6b** and **6c** were also determined by elemental analyses and spectral data. The intra-annular aromatic protons of **6b** appear as a doublet at δ 7.52 ($H_{8,20}$, *J* = 2.4 Hz) ppm and the other aromatic protons appear at δ 6.82 ($H_{5,17}$, d, *J* = 8.5 Hz) and 7.06 ($H_{6,16}$, dd, *J* = 2.4, 8.5 Hz) ppm. As with the previous examples, the *syn*-conformer structure is assigned to **6b**. The lower-field signal of the intra-annular protons in comparison with the other aromatic protons indicate that are situated within the deshielding region owing to the π-electrons of the triple bond.

The X-ray structure of a single-crystal **6b** obtained from slow evaporation of a saturated dichloromethane solution clearly indicates that it is also the *syn*-conformer in the solid state (Fig. 5). This compound crystallized in the same monoclinic space group P2*1/a* (CCDC 1547283; SI Table S2). The side view shown in Fig. 5 shows that the two methoxy groups are situated away from the direction of macrocyclic ring to constrain steric repulsion with the bridge chain. The C13–C14 bond distance is 1.203 Å, which is almost equal to the normal distance between the carbon atoms in acetylene. The C11–C13 and C14–C15 bond distances are both 1.440 Å, and are much shorter than those of C6–C7 (1.521 Å) and C1–C19 (1.521 Å). Interestingly, the acetylenic moiety in the bridge does not adopt a different linear structure than reference compound **11** shown below in Scheme 5. The C11–C13–C14 and C15–C14–C13 bond angles of 156.74° and 156.74° are unusual. This clearly shows that **6b** is a moderately bent molecule and is consistent with the lower field chemical shifts of the signals of the acetylenic carbons in its solution state ^{13}C NMR spectrum (see below).

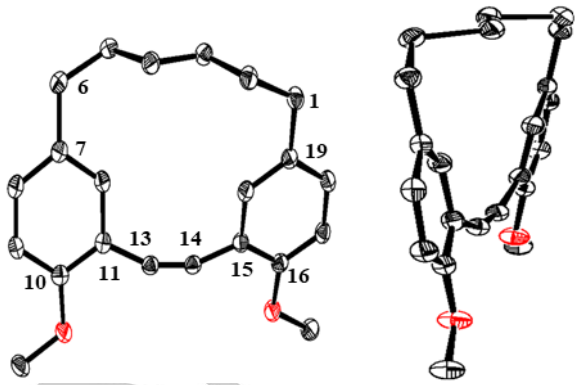


Figure 5. ORTEP figures of **6b** with top (*left*) and side (*right*) views. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity and the carbon numbering system is shown.

The structure of the *syn*-confomer for [2.8]metacyclophane-1-yne **6c** is also readily assigned from its NMR spectra and the chemical shift of the intra-annular aromatic protons at δ 7.50 ppm. The perspectives of the structure of the *syn*-**6c** are illustrated in Fig. 6. This compound crystallized in the same monoclinic space group P2*1/a* (SI Table S3). The X-ray crystallography (CCDC 1547284) clearly reveals that the conformation of **6c** is also *syn*. The bond distance of C14–C15 is 1.203 Å and the bond angles of C13–C14–C15 and C16–C15–C14 are unusual values, 161.91° and 161.43°. The two aromatic rings diverge similarly from planarity to some extent, to avoid π-electron repulsion.

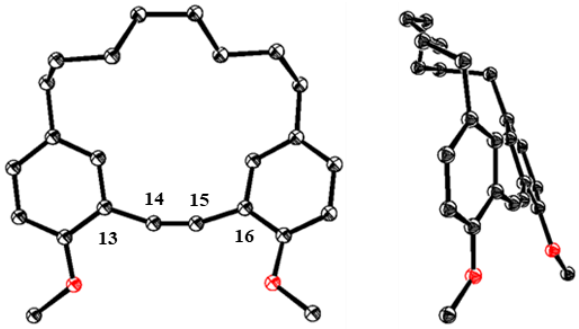
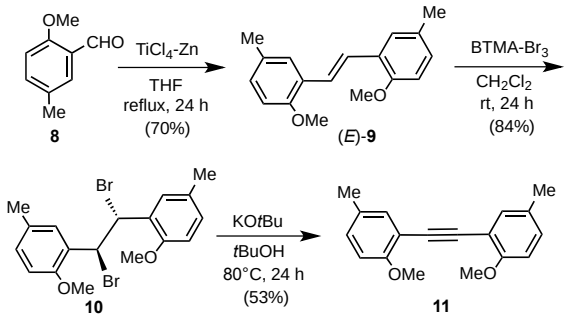


Figure 6. ORTEP figures of **6c** with top (*left*) and side (*right*) views. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

The chemical shifts of the ^{1}H- and ^{13}C-NMR signals arising from the benzene rings of **6b**, **6c** and **6d** (*n* = 10)[16] are comparable to those of the acyclic compound **11**, which was prepared from 2-formyl-6-methylanisole in 3 steps using the same procedure as for the [2.*n*]metacyclophane-1-ynes **6b–d** by following our previous report (Scheme 5).[16] The signals of the acetylenic carbons (Table 1) in **6b–d** are located at lower fields than those of **11** (δ 89.7 ppm). This reflects the appreciable strain in the triple bonds due to bending. In particular, the chemical

shift of the *sp* carbons in **6b** is at considerably lower field than that of **11** and has almost the same value as that of [2$_3$]metacyclophane-1,9,17-triyne (δ 99.86 ppm),[23] but is at lower field than that of [2$_4$]metacyclophane-1,9,17,25-tetrayne (δ 92.20 ppm) or 1,5-cyclooctadiyne (δ 95.8 ppm).[24]



Scheme 5. Synthetic route of the reference compound **11**.

Table 1. ^{13}C NMR data and dihedral angle of [2.*n*]metacyclophane-1-ynes **6b–d** and reference compound **11**.

Compounds	^{13}C NMR, δ ppm; ($CDCl_3$)		
	-$(CH_2)_n$-	C≡C	angle
6b	6	101.6	156.7
6c	8	95.6	161.4
6d	10	91.5	169.6
11	–	89.7	180.0

Computational Details

Computational studies were conducted to explore the conformational properties of the conformers of **3a–c** and **6b–6c**. All computations were carried out with the *Gaussian 09.e01* package.[25] The molecular geometries of the conformers shown were fully optimized in the gas phase, at the DFT level of theory using the B3LYP (Becke, three-parameter, Lee-Yang-Parr),[26] exchange–correlation with the 6-31G(d) basis set.

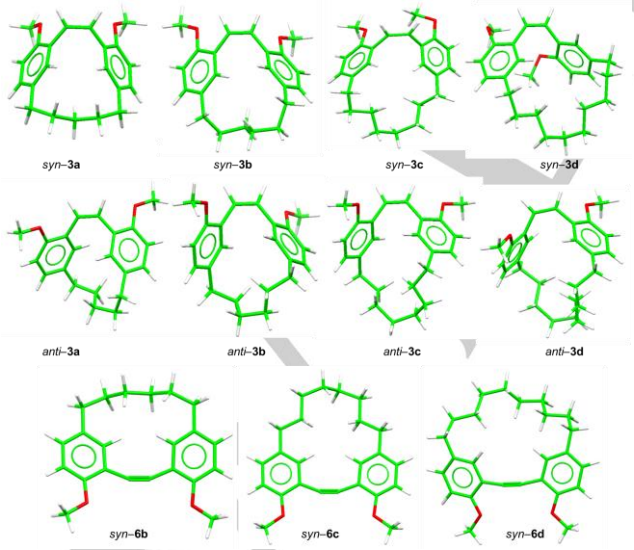


Figure 7. The B3LYP molecular geometry optimized structures of the various conformers of **3** and **6** MCPs in gas phase. Colour code: carbon = green; hydrogen = white; oxygen atom = red.

The individual geometry-optimized structures and their energies are summarized in Fig. 7 and Table 2. The energies of the less energetically-favoured conformers for each compound are presented as ΔE values relative to the most energetically-favoured conformer for that compound. As can be seen, the *syn* conformers are the lower energy ones in each case.

Table2. B3LYP/6-31G(d) gas phase calculated optimized relative energies (ΔE kJ mol^{-1}), HOMO/LUMO energies (E; eV); and HOMO–LUMO energy gaps (ΔE; eV), of the conformers of **3a–c** and **6b–c**.

Conformer	Optimized energy (E)	Relative Energy (ΔE)	HOMO energy	LUMO energy	HOMO-LUMO gap (ΔEg)
	(kcal mol^{-1})	(kcal mol^{-1})	(eV)	(eV)	(eV)
syn-**3a**	-605609.54	0.00	-5.15	-0.84	4.31
anti-**3a**	-605580.77	28.78	-5.08	-0.75	4.33
syn-**3b**	-630276.41	0.00	-5.22	-0.77	4.45
anti-**3b**	-630260.41	16.00	-5.06	-0.76	4.30
syn-**3c**	-679616.44	0.00	-5.07	-0.93	4.14
anti-**3c**	-679610.77	5.67	-4.97	-0.91	4.06
syn-**3d**	-728954.95	0.00	-5.32	-0.56	4.76
anti-**3d**	-728950.72	4.22	-5.11	-1.07	4.05
syn-**6b**	-629484.59	-	-5.10	-0.92	4.19
syn-**6c**	-678829.10	-	-5.04	-0.93	4.11
syn-**6d**	-728174.55	-	-5.08	-0.95	4.12

Conclusions

We have synthesized, for the first time, the highly strained *syn*-[2.6]metacyclophane-1-yne **6b** and [2.8] metacyclophane-1-yne *syn*-**6c**, of the metacyclophane-1-yne systems. Single-crystal X-ray structures of the dibromo precursors **4b** and **4c** adducts were determined and their NMR spectra analysed. The subsequent double-dehydrobromination of the bromine adducts of [2.*n*]metacyclophan-1-enes with base will also open up new mechanistic aspects for cyclophane chemistry. The conformations were also determined by DFT studies and were cosistent with the experimental results. Further studies on the chemical properties of [2.*n*]metacyclophane-1-ynes are now in progress.

Experimental Section

General procedures

All melting points (Yanagimoto MP-S1) are uncorrected. NMR spectra were determined at 300 MHz with a Nippon Denshi JEOL FT-300 spectrometer with Me_4Si as an internal reference: *J* values are given in Hz. IR spectra were measured for samples as KBr pellets or as liquid films on NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra were measured by a Shimadzu 240 spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70 eV using a direct inlet system through GLC. Elemental analyses were performed by Yanaco MT-5. G.L.C. analyses were performed with a

Shimadzu gas chromatograph, GC-14A; silicone O V-1, 2 m; programmed temperature rise, 12°C min^{-1}; carrier gas nitrogen, 25 mL min^{-1}.

Materials

4,22-Dimethoxy[2.10]metacyclophane-1-yne (**6d**) was prepared following previous reports.[16,27]

Preparation of 1,5-bis(4-methoxyphenyl)pentane (1a)

To a solution of magnesium (2.19 g, 90 mmol) and a small amount of iodine in THF (5 mL) was added a solution of 4-bromoanisole (14.3 g, 75 mmol) in THF (20 mL) and the mixture was refluxed for 12 h. To a solution of 1,5-dibromopentane (5.75 g, 25 mmol) and CuBr (750 mg, 5.2 mmol) in HMPA (3.5 mL) was added dropwise a solution of 4-methoxyphenylmagnesium bromide with gentle refluxing. After the reaction mixture was refluxed for an additional 24 h, it was quenched with a 10% aqueous ammonium chloride solution and extracted with CH_2Cl_2 (50 mL × 3). After the combined CH_2Cl_2 extracts were dried over Na_2SO_4 and concentrated. The residue was chromatographed over silica gel (Wako C–300, 200 g) with hexane–ethylacetate (5:1) as eluent to give **1a** (6.4 g, 90%) as a colourless solid. Recrystallization from hexane gave **1a** (5.7 g, 80%) as colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.37–1.43 (2H, m, *CH₂*), 1.60–1.68 (4H, m, *CH₂*), 2.57 (4H, t, *J* = 7.8 Hz, *CH₂*), 3.81 (6H, s, *OMe*), 6.84 (4H, d, *J* = 8.6 Hz, Ar-*H*) and 7.12 (4H, d, *J* = 8.6 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 28.96, 31.75, 35.08, 55.36, 113.79, 129.36, 135.01 and 157.75 ppm. MS: *m*/*z* 284 [M^+]. $C_{19}H_{24}O_2$ (284.39): calcd C 80.24, H 8.51; found: C 80.21, H 8.31.

1,6-Bis(4-methoxyphenyl)hexane (1b)

This compound was obtained as colourless prisms (from hexane). Yield 77%. M.p. 56–57 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.38–1.38 (4H, m, *CH₂*), 1.58–1.62 (4H, m, *CH₂*), 2.53 (4H, t, *J* = 7.8 Hz, *CH₂*), 3.80 (6H, s, *OMe*), 6.84 (4H, d, *J* = 8.6 Hz, Ar-*H*) and 7.10 (4H, d, *J* = 8.6 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz $CDCl_3$): δ = 29.21, 31.78, 35.12, 55.35, 113.77, 129.35, 135.05 and 157.73 ppm. MS: *m*/*z* 298 [M^+]. $C_{20}H_{26}O_2$ (298.42): calcd C 80.50, H 8.78; found: C 80.54, H 8.62.

1,8-Bis(4-methoxyphenyl)octane (1c)

This compound was obtained as colourless prisms (from hexane). Yield 83%. M.p. 62–63 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.32 (8H, broad s, *CH₂*), 1.56–1.60 (4H, m, *CH₂*), 2.55 (4H, t, *J* = 7.9 Hz, *CH₂*), 3.80 (6H, s, *OMe*), 6.84 (4H, d, *J* = 8.6 Hz, Ar-*H*) and 7.10 (4H, d, *J* = 8.6 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz $CDCl_3$): δ = 29.38, 29.58, 31.87, 35.15, 55.37, 113.77, 129.36, 135.15 and 157.72 ppm. MS: *m*/*z* 326 [M^+]. $C_{22}H_{30}O_2$ (326.47): calcd C 80.94, H 9.26; found: C 80.67, H 9.32.

Preparation of 1,5-bis(3-formyl-4-methoxyphenyl)pentane (2a)

To a solution of **1a** (1.15 g, 4.5 mmol) and dichloromethyl methyl ether (1.14 mL, 12.6 mmol) in CH_2Cl_2 (10 mL) was added a solution of $TiCl_4$ (3.0 mL, 27.3 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was poured into a large amount of ice/water (50 mL) and extracted with CH_2Cl_2 (20 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was chromatographed over silica gel (Wako C–300, 200 g) with benzene as eluent to give **2a** (1.22 g, 80%) as a colourless solid. Recrystallization from hexane gave **2a** as colourless prisms. M.p. 64–65 °C. IR: ν_{max} (KBr): 2925, 2841, 1676 (C=O), 1596, 1500, 1439, 1280, 1260, 1207, 1121, 1019, 811 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.31–1.37 (2H, m, *CH₂*), 1.58–1.70 (4H, m, *CH₂*), 2.55 (4H, t, *J* = 7.9 Hz, *CH₂*), 3.90 (6H, s, *OMe*), 6.90 (2H, d, *J* = 8.5 Hz, Ar-*H*), 7.34 (2H, dd, *J* = 2.4, 8.5 Hz, Ar-*H*), 7.61 (2H, d, *J* = 2.4 Hz, Ar-*H*) and 10.40 (2H, s, CHO) ppm. MS: *m*/*z* 340 [M^+]. $C_{21}H_{24}O_4$ (340.42): calcd C 74.09, H 7.11; found: C 74.37, H 7.29.

Similarly, compounds **2b** and **2c** were prepared in the same manner as described above.

1,6-Bis(3-formyl-4-methoxyphenyl)hexane (2b)

This compound was obtained as pale-yellow prisms (from hexane). Yield 85%. M.p. 61–63 °C. IR: ν_{max} (KBr): 2924, 2841, 1682 (C=O), 1600, 1495, 1257, 1192, 1100, 1017, 812 and 641 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.30–1.33 (4H, m, *CH₂*), 1.54–1.61 (4H, m, *CH₂*), 2.56 (4H, t, *J* = 7.9 Hz, *CH₂*), 3.91 (6H, s, *OMe*), 6.91 (2H, d, *J* = 8.5 Hz, Ar-*H*), 7.35 (2H, dd, *J* = 2.4, 8.5 Hz, Ar-*H*), 7.62 (4H, d, *J* = 2.4 Hz, Ar-*H*) and 10.45 (2H, s, CHO) ppm. ^{13}C-NMR (100 MHz $CDCl_3$): δ = 29.00, 31.36, 34.79, 55.80, 111.70, 124.55, 127.99, 135.09, 136.17, 160.26 and 190.21 ppm. MS: *m*/*z* 354.25 [M^+]. $C_{22}H_{26}O_4$ (354.45): calcd C 74.55, H 7.39; found: C 74.54, H 7.42.

1,8-Bis(3-formyl-4-methoxyphenyl)octane (2c)

This compound was obtained as pale-yellow prisms (from hexane). Yield 86%. M.p. 62–64 °C. IR: ν_{max} (KBr): 2935, 2851, 1682 (C=O), 1598, 1495, 1258, 1131, 1022, 823 and 641 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.28 (8H, broad s, *CH₂*), 1.55–1.59 (4H, m, *CH₂*), 2.56 (4H, t, *J* = 7.9 Hz, *CH₂*), 3.91 (6H, s, *OMe*), 6.91 (2H, d, *J* = 8.5 Hz, Ar-*H*), 7.36 (2H, dd, *J* = 2.4, 8.5 Hz, Ar-*H*), 7.63 (2H, d, *J* = 2.4Hz, Ar-*H*) and 10.45 (2H, s, CHO) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 29.22, 29.47, 31.51, 34.86, 55.82, 111.69, 124.57, 128.05, 135.26, 136.19, 160.26 and 190.26 ppm. MS: *m*/*z* 382.47 [M^+]. $C_{24}H_{30}O_4$ (382.49): calcd C 75.36, H 7.91; found: C 75.52, H 8.00.

McMurry coupling reaction of 2 –Typical Procedure

The McMurry reagent was prepared from $TiCl_4$ [23.8 g (13.8 mL), 125 mmol] and Zn powder (18 g, 275 mmol) in dry THF (500 mL) under nitrogen. A solution of 1,5-bis(3-formyl-2-methoxyphenyl)pentane (**2a**) (2.81 g, 9.0 mmol) and pyridine (22.8 mL, 200 mmol) in dry THF (250 mL) was added within 60 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 additional 24 h, cooled to room temperature, and hydrolyzed with aqueous 10% K_2CO_3 (200 mL) at 0 °C. The reaction mixture was extracted with CH_2Cl_2 (200 mL

× 3). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was chromatographed over silica gel (Wako C-300, 300 g) with hexane–toluene (2:1) and $CHCl_3$–EtOAc (1:1) as eluents to give **3a** (2.17 g, 78%) as a colourless solid. Recrystallization of crude **3a** from methanol gave 4,17-dimethoxy[2.5]metacyclophan-1-ene (**3a**) as colourless prisms. M.p. 147–149 °C. IR: ν_{max} (KBr): 2919, 2858, 1608, 1498, 1249, 1121, 1035 and 828 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ =1.00–1.07 (2H, m, *CH₂*), 1.25–1.34 (4H, m, *CH₂*), 2.30–2.34 (4H, m, *CH₂*), 3.87 (6H, s, *OMe*), 6.79 (2H, s, *CH*), 6.80 (2H, d, *J* =8.3 Hz, Ar-*H*), 6.91 (2H, dd, *J* = 2.2, 8.3 Hz, Ar-*H*) and 7.05 (2H, d, *J* = 2.2 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 26.23, 30.32, 35.22, 55.72, 110.63, 125.24, 125.55, 128.91, 131.02, 133.60 and 155.52 ppm. MS: *m*/*z* 308.2 [M^+]. $C_{21}H_{24}O_2$ (308.42): calcd C 81.90, H 7.84; found: C 81.78, H 7.84.

Similarly, compound **3b** and **3c** were prepared in the same manner as described above.

4,18-Dimethoxy[2.6]metacyclophan-1-ene (3b)

This compound was obtained as prisms (from methanol). Yield 62%. M.p. 193–194 °C. IR: ν_{max} (KBr): 2925, 1604, 1498, 1254, 1160, 1117, 1034, 912 and 822 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.01 (4H, broad s, *CH₂*), 1.60 (4H, broad s, *CH₂*), 2.33–2.37 (4H, m, *CH₂*), 3.81 (6H, s, *OMe*), 6.75 (2H, s, *CH*), 6.81 (2H, d, *J* = 8.4 Hz, Ar-*H*), 6.96 (2H, dd, *J* = 2.1, 8.4 Hz, Ar-*H*) and 7.24 (2H, d, *J* = 2.1 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 24.36, 30.72, 31.99, 55.81, 111.31, 123.98, 124.76, 128.20, 130.40, 133.15 and 155.40 ppm. MS: *m*/*z* 322.2 [M^+]. $C_{22}H_{26}O_2$ (322.45): calcd C 81.95, H 8.13; found: C 81.90, H 7.84.

4,20-Dimethoxy[2.8]metacyclophan-1-ene (3c)

This compound was obtained as colourless prisms (from methanol). Yield 65%. M.p. 131 °C. IR: ν_{max} (KBr): 2963, 2855, 1605, 1503, 1466, 1239, 1119, 1030 and 813 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.05–1.09 (4H, m, *CH₂*), 1.19 (4H, broad s, *CH₂*), 1.37–1.46 (4H, m, *CH₂*), 2.36–2.40 (4H, m, *CH₂*), 3.83 (6H, s, *OMe*), 6.73 (2H, s, *CH*), 6.80 (2H, d, *J* = 8.4 Hz, *CH*), 6.97 (2H, dd, *J* = 2.4, 8.4 Hz, Ar-*H*) and 6.99 (2H, s, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 25.38, 27.02, 29.84, 34.20, 110.13, 126.84, 129.85, 131.71, and 155.92 ppm. MS: *m*/*z* 350.23 [M^+]. $C_{24}H_{30}O_2$ (350.49): calcd C 82.24, H 8.63; found: C 82.33, H 8.62.

Bromination of 3 with BTMA-Br_3 –Typical Procedure

To a solution of **3a** (200 mg, 0.71 mmol) in CH_2Cl_2 (20 mL) was added BTMA-Br_3 (300mg, 0.78 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 5 min, it was poured into a large amount of ice/water (50 mL) and extracted with CH_2Cl_2 (50 mL × 2) The combined extracts were washed with water, dried with Na_2SO_4 and concentrated to afford **4a** (300 mg, 96%) as a colourless solid. Recrystallization from hexane gave 134 mg (43%) of 12,13-dibromo-9,15-dimethoxy[5.2]metacyclophane (**4a**) as colourless prisms. M.p. 116–117 °C. IR: ν_{max} (KBr): 2963, 2921, 2855, 1605, 1503, 1447, 1258, 1117, 1030, 810 and 775 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = –0.13– –0.03 (1H, m, *CH₂*), 0.78–0.89 (1H, m, *CH₂*), 1.40–1.54 (2H, m, *CH₂*), 1.57–1.68 (2H, m, *CH₂*), 2.28–2.43 (2H, m, *CH₂*), 2.49–2.69 (4H, m, *CH₂*), 3.75 (3H, s, *OMe*), 3.78 (3H, s, *OMe*), 5.58 (1H, d, *J* = 10.4 Hz, *CH*), 6.62 (1H, d, *J* = 10.4 Hz, *CH*), 6.52 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.55 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.73 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*), 6.80 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*), 6.93 (1H, d, *J* = 2.2 Hz, Ar-*H*) and 7.00 (1H, d, *J* = 2.2 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 22.69, 27.51, 28.29, 31.93, 33.15, 50.91, 55.36, 55.73, 59.05, 110.54, 111.43, 126.20, 127.17, 129.46, 129.71, 129.86, 132.22, 132.84, 133.42, 153.58 and 155.72 ppm. MS: *m*/*z*: 468.03 [M^+]. $C_{21}H_{24}O_2Br_2$ (468.23): calcd C 53.87, H 5.17. found: C 54.08, H 5.39.

Similarly, compound **4b** and **4c** were prepared in the same manner as described above.

13,14-Dibromo-10,16-dimethoxy[6.2]metacyclophane (4b)

This compound was obtained as colourless prisms (from hexane) in 98% yield. M.p. 116–117 °C. IR: ν_{max} (KBr): 2963, 2921, 2855, 1605, 1503, 1447, 1258, 1117, 1030, 810 and 775 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.41–0.52 (1H, m, *CH₂*), 0.68–0.79 (1H, m, *CH₂*),1.10–1.24 (2H, m, *CH₂*), 1.28–1.44 (2H, m, *CH₂*), 1.60–1.70 (1H, m, *CH₂*), 1.79–1.89 (1H, m, *CH₂*), 2.40 –2.61 (4H, m, *CH₂*), 3.71 (3H, s, *OMe*), 3.82 (3H, s, *OMe*), 5.66 (1H, d, *J* = 10.2 Hz, *CH*), 6.54 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.62 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.67 (1H, d, *J* = 10.2 Hz, C*H*), 6.82 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*), 6.87 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*), 6.96 (1H, d, *J* = 2.2 Hz, Ar-*H*) and 6.99 (1H, d, *J* = 2.2 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.76, 28.36, 28.89, 28.92, 33.68, 35.14, 51.92, 55.14, 55.71, 59.96, 110.77, 111.43, 126.47, 127.34, 128.40, 129.59, 130.14, 130.72, 133.48, 134.21, 153.46 and 155.49 ppm. MS: *m/z*: 480, 482, 484 [M^+]. $C_{22}H_{26}O_2Br_2$ (482.26): calcd C 54.79, H 5.43; found: C 54.87, H 5.49.

15,16-Dibromo-12,18-dimethoxy[8.2]metacyclophane (4c)

To a solution of **3c** (200 mg, 0.57 mmol) in CH_2Cl_2 (20 mL) was added BTMA-Br_3 (244 mg, 0.63 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 5 min, it was poured into a large amount of ice/water (50 mL) and extracted with CH_2Cl_2 (50 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated to afford **4c** (285 mg, 98%) as a colorless solid. Recrystallization from hexane gave 226 mg (78%) of a mixture of *meso-syn*-15-*endo*-bromo-16-*endo*-bromo-12,18-dimethoxy[8.2]metacyclophane (*meso*-**4c**) and *dl-syn*-15-*endo*-bromo-16-*exo*-bromo-12,18-dimethoxy[8.2]metacyclophane (*dl*-**4c**) in the ratio of 53:47 as colourless prisms. M.p. 122–123 °C. IR: ν_{max} (KBr): 2922, 1603, 1501, 1254, 1134, 1032 and 659 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): (*meso*-**4c**) δ = 0.86–1.83 (12H, m, *CH₂*), 2.36–2.61 (4H, m, *CH₂*), 3.54 (6H, s, *OMe*), 6.12 (2H, s, *CH*), 6.58 (2H, d, *J* = 8.4 Hz, $H_{11,19}$, Ar-*H*), 6.95 (2H, dd *J* = 2.4, 8.4 Hz, $H_{10,20}$, Ar-*H*) and 7.31 (2H, broad s, $H_{14,22}$, Ar-*H*) ppm. (*dl*-**4c**) δ = 0.86–1.83 (12H, m, *CH₂*), 2.36–2.61 (4H, m, *CH₂*), 3.77 (3H, s, *OMe*), 3.81 (3H, s, *OMe*), 5.65 (1H, d, *J* = 10.4 Hz, *CH*),

6.62 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.63 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.81 (1H, d, *J* = 10.4 Hz, CH), 6.87 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*), 6.90 (1H, d, *J* = 2.2 Hz, Ar-*H*), 6.92 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*) and 7.12 (1H, d, *J* = 2.2 Hz, Ar-*H*) ppm.MS: *m/z* 508, 510, 512 [M^+]. $C_{24}H_{30}O_2Br_2$ (510.31): calcd C 56.49, H 5.93; found: C 56.53, H 5.93.

Dehydrobromination of 4a with *t*-BuOK – Typical Procedure

To a solution of **4a** (100 mg, 0.214 mmol) in *t*-BuOH (20 mL) was added *t*-BuOK (995 mg, 8.51 mmol) at room temperature. After the reaction mixture was heated at 80 °C for 24 h, it was poured into a large amount of ice/water (50 mL) and extracted with CH_2Cl_2 (100 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was chromatographed over silica gel (Wako C-300, 300 g) with toluene as eluents to give 1-*tert*-butoxy-4,17-dimethoxy[2.5]metacyclophan-1-ene **5a** (68 mg, 83%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.83–0.92 (2H, broad s, *CH₂*), 1.12–1.21 (4H, m, *CH₂*), 1.31 (9H, s, *t*Bu), 2.35–2.45 (4H, m, *CH₂*), 3.79 (3H, s, OMe), 3.87 (3H, s, *OMe*), 6.52 (1H, s, *CH)*, 6.62 (1H, d, *J* = 2.2 Hz, Ar-*H*), 6.65 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.74 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*), 6.85 (1H, d, *J* = 8.4 Hz, Ar-*H*), 6.92 (1H, d, *J* = 2.2 Hz, Ar-*H*) and 7.02 (1H, dd, *J* = 2.2, 8.4 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 23.14, 25.37, 29.12, 29.72, 32.86, 34.13, 35.08, 55.40, 55.76, 110.05, 111.14, 112.01, 113.13, 127.27, 129.81, 131.42, 132.85, 133.76, 151.37, 154.99 and 154.74 ppm. MS: *m/z*: 380.19 [M^+]. $C_{25}H_{32}O_3$ (380.53): calcd C 78.91, H 8.48; found: C 78.83, H 8.55.

Dehydrobromination of 4b with KOBu^t

To a solution of **4b** (100 mg, 0.21 mmol) in *t*-BuOH (20 mL) was added *t*-BuOK (970 mg, 7.8 mmol) at room temperature. After the reaction mixture was heated at 80 °C for 24 h, it was poured into a large amount of ice/water (50 mL) and extracted with CH_2Cl_2 (100 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was recrystallized from methanol gave 64 mg (95%) of 4,18-dimethoxy[2.6]metacyclophane-1-yne (**6b**) as colourless prisms. M.p. 175–179°C. IR: ν_{max} (KBr): 2935, 2153, 1497, 1290, 1240, 1119, 1028 and 810 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.61–1.65 (4H, m, *CH₂*), 1.76–1.79 (4H, m, *CH₂*), 2.71 (4H, m, *CH₂*), 3.89 (6H, s, *OMe*), 6.82 (2H, d, *J* = 8.5 Hz, Ar-*H*), 7.06 (2H, dd, *J* = 2.4, 8.5 Hz, Ar-*H*) and 7.52 (2H, d, *J* = 2.4 Hz, Ar-*H*) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 26.53, 29.19, 30.76, 56.08, 101.60, 112.30, 113.15, 130.49, 133.22, 134.99 and 154.07 ppm. MS: *m/z*: 320.21 [M^+]. $C_{22}H_{24}O_2$ (320.42): calcd C 82.46, H,7.55; found: C 82.13, H 7.55.

Similarly, compound **4c** was treated with *t*-BuOK in *t*-BuOH at 80°C for 24 h to afford 4,20-dimethoxy[2.8]- metacyclophane-1-yne, **6c** in 98% yield as colourless prisms (methanol). M.p. 137 °C. IR: ν_{max} (KBr): 2925, 1504, 1228, 1240, 1100, 1030 and 811 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.47–1.51 (8H, broad s, *CH₂*), 1.65 (4H, broad s, *CH₂*), 2.63–2.66 (4H, m, *CH₂*), 3.88 (6H, s, O*Me*), 6.78 (2H, d, *J* = 8.4 Hz, Ar-*H*), 7.03 (2H, dd, *J* = 2.4, 8.4 Hz, Ar-*H*) and 7.50 (2H, d, *J* = 2.4 Hz, Ar-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.02, 29.19, 29.48, 32.17, 55.81, 95.68, 111.13, 112.63, 130.00, 134.05, 136.61 and 155.38 ppm. MS: *m/z*: 348.27 [M^+]. $C_{24}H_{28}O_2$ (348.49): calcd C 82.72, H 8.1; found: C 83.60, H 10.14.

Electronic Supplementary Information (ESI): ^{1}H, ^{13}C NMR and MS spectra of **2** to **6**. Details of single-crystal X-ray crystallographic data and DFT calculation.

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Keywords: [2.*n*]Metacyclophane-1-ynes• Structures• Strained molecule• Diels-Alder reaction • Conformational studies.

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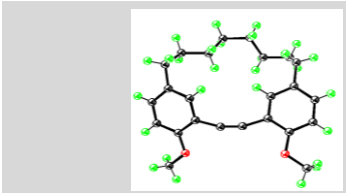
Synthesis and structures of [2.*n*]metacyclophan-1-enes and their conversion to highly strained [2.*n*]metacyclophane-1-ynes, in which the triple bonds are distorted from linearity with bond angles of 156.7°–161.4°, are discussed.



Metacyclophanes

T. Akther,[a] M. M. Islam,[a],[b] J. Kowser,[a],[c] T. Matsumoto,[d] J. Tanaka,[d] S. Rahman,[e],[f] A. Alodhayb,[f],[g] P. E. Georghiou,[e] C. Redshaw[h] and T. Yamato*[a]

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Keywords: [2.*n*]Metacyclophane-1-ynes• Structures• Strained molecule• Diels-Alder reaction • DFT Calculation.

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