Medium-Sized Cyclophanes, 20[1]

Synthesis and Conformational Studies of *syn*- and *anti*-Dihydroxy[*n*.2]metacyclophanes

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syn- and *anti*-Dimethoxy[*n*.2]metacyclophanes **9** are obtained by pyrolysis of the corresponding *anti*-sulfones **8**, which are prepared by the reaction of 1,*n*-bis[3-(chloromethyl)-2-methoxyphenyl]alkanes **6** with Na_2S in ethanol under the high dilution conditions, followed by the oxidation of the obtained thiametacyclophanes **7** with *m*-chloroperbenzoic acid. Demethylation of *anti*-dimethoxy[*n*.2]metacyclophanes *anti*-**9** with BBr_3 in dichloromethane affords the corresponding *anti*-dihydroxy[*n*.2]metacyclophanes *anti*-**10**. On the other hand, demethylation of *syn*-dimethoxy[3.2]-*syn*- **9b** and -[4.2]metacyclophane syn-**9c** gives *syn*-dihydroxy[*n*.2]metacyclophanes *syn*-**10b**, **c**, but *syn*-dimethoxy[5.2]-*syn*-**9d** and -[6.2]metacyclophane *syn*-**9e** are converted into the corresponding *anti*-dihydroxy[*n*.2]metacyclophanes *anti*-**10d**, **e**. $AlCl_3 \cdot CH_3NO_2$-catalyzed de-*tert*-butylation of *tert*-butyl-*syn*- and -*anti*-dihydroxy[3.2]- and -[4.2]metacyclophanes *syn*/*anti*-**10b**, **c** has been carried out in benzene to give the desired metacyclophanes *anti*-**11a**–**c** and *syn*-**11c** except *syn*-dihydroxy-[3.2]metacyclophane *syn*-**11b** which is converted into 8,17-epoxy[3.2]metacyclophane **13**. The assignment of *syn* and *anti* conformations has been confirmed by ^{1}H-NMR analyses and X-ray diffraction studies. The dynamics of the ring inversion and UV spectra are also discussed.

The synthesis and stereochemical aspects of conformationally mobile [*m.n*]metacyclophanes (MCP = metacyclophane) have been of interest for the past decade[2], particular attention[3] being paid to [2.2]MCPs, which possess an *anti*-stepped conformation. The pioneering work of the conformational investigation of 2,11-dithia[3.3]MCPs has been performed by Vögtle et al.[4] Sato and his co-workers have also reported on the conformational behavior of the 2-thia[3.2]MCPs and their analogs[5]. While in [3.3]MCP the aromatic rings preferentially appear to adopt the *syn* arrangement, its lower and higher homologs, i.e. [3.2]-, [4.2]-, and [4.3]-MCPs, prefer the mobile *anti* conformation[6].

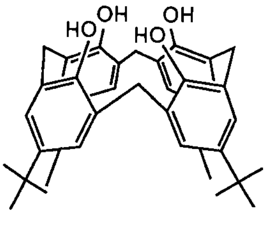
The ring inversion barriers for the higher [*m.n*]MCPs are estimated and found to decrease with increasing length of the bridges[6]. Most of the reported [*m.n*]metacyclophanes, however, are internally unsubstituted. The introduction of intra-annular substituents such as methyl increase the barrier to conformational flipping[7], for example both *syn*- and *anti*-9,18-dimethyl-2,11-dithia[3.3]MCP exist as discrete conformers, whereas 2,11-dithia[3.3]MCP is conformationally mobile[8,9]. Surprisingly, few of the higher MCPs containing internal methyl substituents have been studied[10] despite the fact that the chemical shift of the methyl group provides a convenient probe for ^{1}H-NMR studies of any possible conformational changes. Hence, the introduction of substituents into internal positions of higher [*m.n*]MCPs may influence not only the ring inversion but may also give rise to a change of the equilibrium position of *syn*- and *anti* conformers.

Recently, we have found[1] that *anti*-11,19-dimethyl-[5.2]MCP and *anti*-12,20-dimethyl[6.2]MCP are both conformationally rigid below 150°C, but *anti*-14,22-dimethyl-[8.2]MCP exhibits conformational flipping at the coalescence temperature of 140°C, and the estimated energy barrier to flipping is 20.5 kcal mol^{-1} in hexachloro-1,3-butadiene.

On the other hand, Gutsche and his coworkers[11–13] have reported that the stong intramolecular hydrogen bond of tetrahydroxy[1.1.1.1]MCP (calix[4]arene) may fix the "cone" shape conformation **A**.

Thus, there is substantial interest in investigating the effects of the intramolecular hydrogen bond of hydroxyl substituents on the conformations of dihydroxy[*n*.2]MCPs.

A



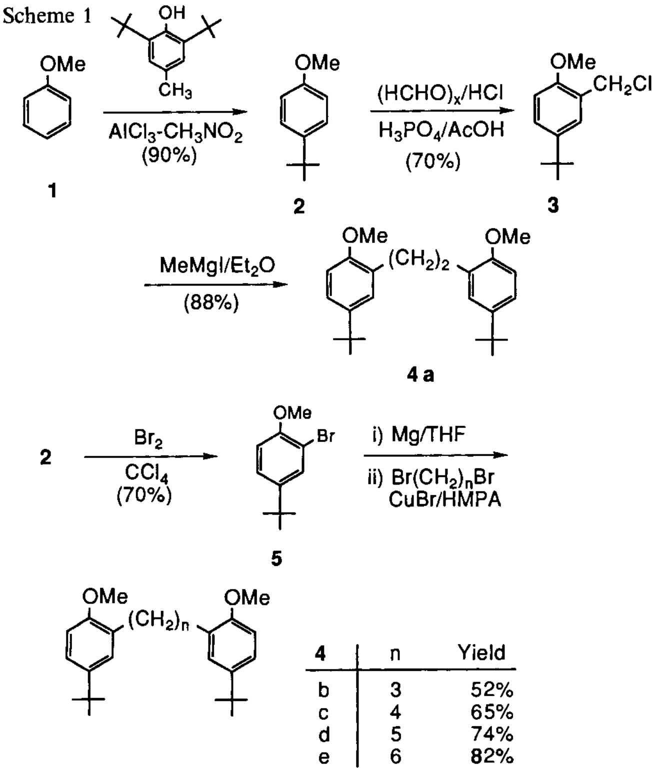
In this paper we report on the first example of the synthesis of two *syn* and *anti* conformers of intra-annularly hydroxyl-substituted [*n*.2]MCPs from anisole by using the *tert*-butyl function as a positional protective group and on the investigation of the ring inversion of these system.

Results and Discussion

A. Synthesis of 1,*n*-Bis(5-tert-butyl-2-methoxyphenyl)alkanes (4)

1,2-Bis(5-*tert*-butyl-2-methoxyphenyl)ethane (**4a**) has been prepared according our previous paper[14]. Although it has been reported previously that 1,3-bis(5-*tert*-butyl-2-methoxyphenyl)propane (**4b**) can be prepared in six steps form 4-*tert*-butylanisole[15], this route seems to be too long for practical purposes. Recently, we have found[16] a much more convenient method for the preparation of 1,3-bis(5-*tert*-butyl-2-substituted phenyl)propanes by using the cross coupling reaction of 5-*tert*-butyl-2-substituted phenylmagnesium bromide with 1,3-dibromopropane in the presence of cuprous bromide as a catalyst in a mixture of hexamethylphosphoric triamide (HMPA) and tetrahydrofuran at reflux temperature in good yields. The cross coupling reactions of 5-*tert*-butyl-2-methoxyphenylmagnesium bromide with other 1,*n*-dibromoalkanes have been carried out under the same conditions to give the desired 1,*n*-bis(5-*tert*-butyl-2-methoxyphenyl)alkanes (**4b**–**e**) in satisfactory yields (Scheme 1).

Scheme 1

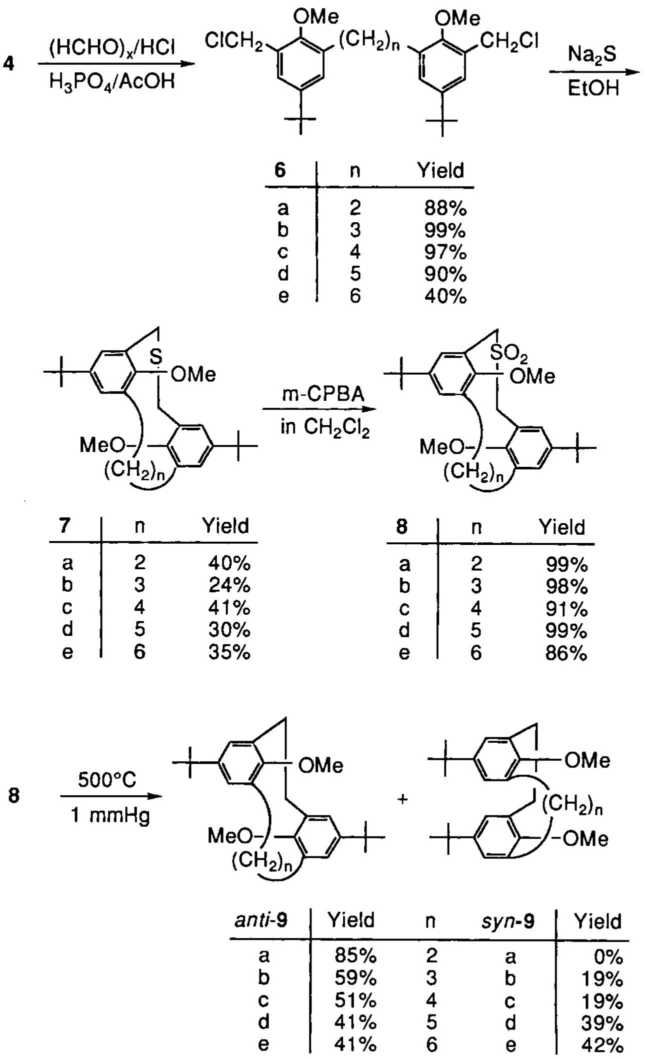


4	n	Yield
b	3	52%
c	4	65%
d	5	74%
e	6	82%

B. Synthesis of *anti*- (*anti*-9) and *syn*-Dimethoxy[*n*.2]MCP (*syn*-9)

The title compounds **9** have been prepared according to Scheme 2.

Scheme 2



6	n	Yield
a	2	88%
b	3	99%
c	4	97%
d	5	90%
e	6	40%

7	n	Yield
a	2	40%
b	3	24%
c	4	41%
d	5	30%
e	6	35%

8	n	Yield
a	2	99%
b	3	98%
c	4	91%
d	5	99%
e	6	86%

anti-9	Yield	n	*syn*-9	Yield
a	85%	2	a	0%
b	59%	3	b	19%
c	51%	4	c	19%
d	41%	5	d	39%
e	41%	6	e	42%

The chloromethylation of diarylalkanes **4a**–**e** with paraformaldehyde in the presence of HCl/H_3PO_4 affords the corresponding bischloromethyl derivatives **6a**–**e** in 40–99% yield. The cyclization of **6a**–**e** has been carried out under the conditions of high dilution and in ethanolic Na_2S to afford the corresponding dimethoxy-2-thia[3.*n*]-MCPs **7a**–**e** in 24–41% yield. Oxidation of the latter with *m*-

Table 1. Chemical shifts (δ) of the internal methoxy protons of dimethoxy-2-thia[3.*n*]MCPs **7** and dimethoxy-2-thia[3.*n*]MCP 2,2-dioxides **8**[a]

Number of methylene bridges, n	7	8
2	3.05	3.06
3	3.14	3.15
4	3.26	3.26
5	3.28	3.24
6	3.21	3.21

[a] Determined in $CDCl_3$ by using $SiMe_4$ as a reference.

chloroperbenzoic acid (*m*-CPBA) furnishes the corresponding sulfones **8a**−**e** in almost quantitative yields.

The structures **7** and **8** were readily apparent from their ^{1}H-NMR spectra (Table 1). Thus, the signals of the internal methoxy protons show an upfield shift due to the ring current of the opposite benzene ring[17,18]. The ^{1}H-NMR spectra of the 2-thia[3.*n*]MCPs **7** and 2-thia[3.*n*]MCP 2,2-dioxides **8** prepared in the present paper show that their structures correspond exclusively to the *anti* conformers. The conformation of **8d** has also been confiramed by an X-ray crystallographic analysis (Figure 1).

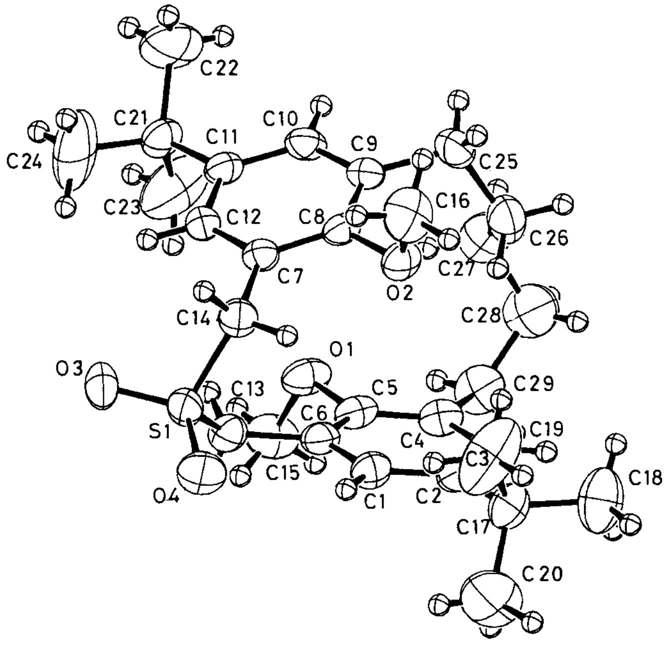


Figure 1. X-ray structure of 6,17-di-*tert*-butyl-9,20-dimethoxy-2-thia[3.5]MCP 2,2-dioxide (**8d**)

Pyrolysis of **8a**−**e** under reduced pressure (1 Torr) has been carried out according to the reported method[19−21] to yield **9**. The ^{1}H-NMR spectrum of **9** shows two kinds of methoxy protons, each as a singlet. By careful column chromatography (silica gel, Wako C-300), two conformers *anti*-**9** and *syn*-**9**, are separated. They are thermally stable and do not interconvert at 180°C in DMSO solution and at 400°C in the solid state.

The ^{1}H-NMR spectrum of conformer *anti*-**9b** and *syn*-**9b** shows the methoxy protons at $\delta = 3.02$ and 3.51, respectively. The aromatic protons of *syn*-**9b** are observed at much higher field ($\delta = 6.29$, 6.58) than those of *anti*-**9b** at $\delta =$ 6.92 and 6.96. The above data show that the structure of *anti*-**9b** is the *anti* conformer, whereas the structure of *syn*-**9b** is the *syn* conformer. The ^{1}H-NMR spectral data of the [*n*.2]MCPs obtained in the present work and of the *syn*-8,16-dimethoxy[2.2]MCP[22] are summarized in Table 2. The conformation of *anti*-**9e** has also been confirmed by an X-ray crystallographic analysis (Figure 2).

Although the parent [2.2]MCP was first reported as early as in 1899 by Pellegrin[23], the synthesis of *syn*-[2.2]MCP was not realized until 85 years later. Mitchel et al.[24] have successfully prepared *syn*-[2.2]MCP at low temperature by using (arene)chromiumcarbonyl complexation to control the stereochemistry. However, *syn*-[2.2]MCP isomerizes readily to the *anti* isomer above 0°C. More recently, Itô et al.[25] have isolated and characterized *syn*-[2.2]MCP without complexation. However, a pyrolysis of dithia[3.*n*]MCP dioxides to the corresponding *syn*-[*n*.2]MCPs has not yet been published.

Table 2. Chemical shifts (δ) of internal methoxy protons and aromatic protons of dimethoxy[*n*.2]MCPs **9**[a]

Compound	Methoxy protons	Aromatic protons
anti-**9a**	2.90	7.02
anti-**9b**	3.02	6.92, 6.96
anti-**9c**	3.16	6.77, 7.06
anti-**9d**	3.25	6.83, 7.10
anti-**9e**	3.18	6.94, 7.12
syn-**9a**	3.58	6.29
syn-**9b**	3.51	6.29, 6.58
syn-**9c**	3.54	6.48, 6.66
syn-**9d**	3.58	6.61, 6.68
syn-**9e**	3.59	6.72

[a] Determined in $CDCl_3$ by using $SiMe_4$ as a reference.

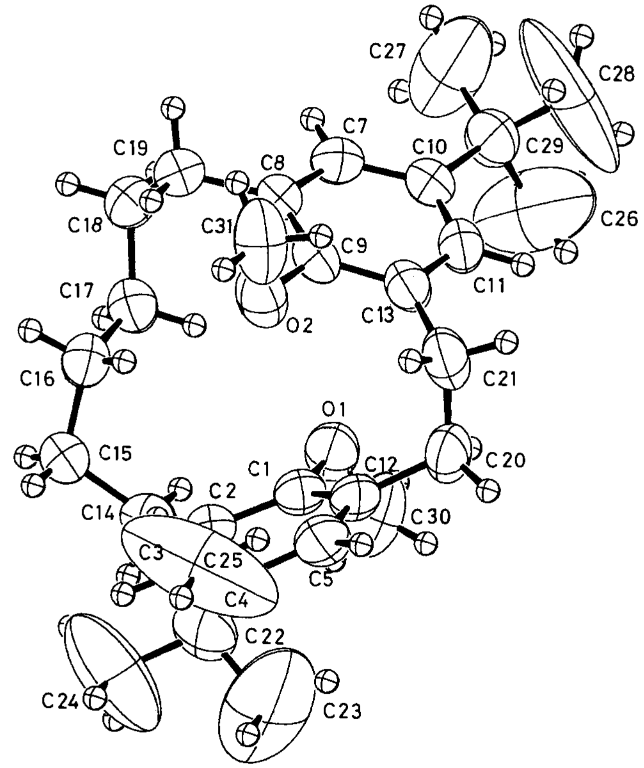


Figure 2. X-ray structure of *anti-9,17-di-tert*-butyl-12,20-dimethoxy[6.2]MCP (*anti*-**9e**)

Recently, we have found[1] that onyl *syn*-8,16-di-*tert*-butyl-11,19-dimethyl[5.2]MCP is obtained by pyrolysis of the corresponding 2-thia[3.5]MCP dicoxide, but that other analogs are exclusively converted into the *anti*-[*n*.2]MCPs.

In the present work, a mixture of *anti* and *syn* conformers **9a**–**e** is obtained by pyrolysis of the 2-thia[3.*n*]MCP dioxides **8b**–**e** with the exception of the [3.2]-analog **8a** which gives exclusively *anti*-[2.2]MCP (*anti*-**9a**). It has also been found that the ratio of the *anti* conformers decreases with increasing length of the methylene bridges and becomes equal to that of the *syn* conformers. These findings suggest that the aromatic π-π interaction of two opposite benzene rings may inhibit the formation of the *syn* conformer in the [2.2]MCP system. However, this interaction decreases with increasing number of the methylene bridges, and in turn the through-space interaction between the non-bonding electron pairs of the oxygen atom of the methoxy groups and the opposite aromatic π electrons of the *anti* conformer may disfavor the formation of the latter.

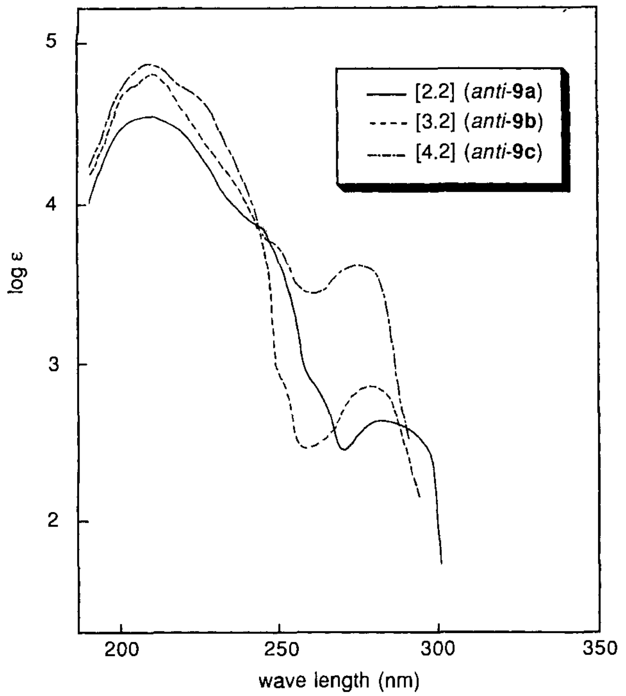


Figure 3. UV spectra of *anti*-dimethoxy[*n*.2]MCPs *anti*-**9** (cyclohexane)

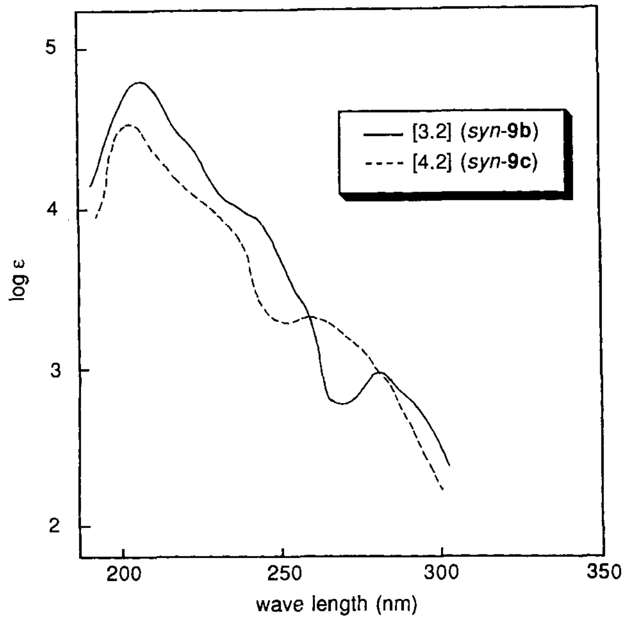
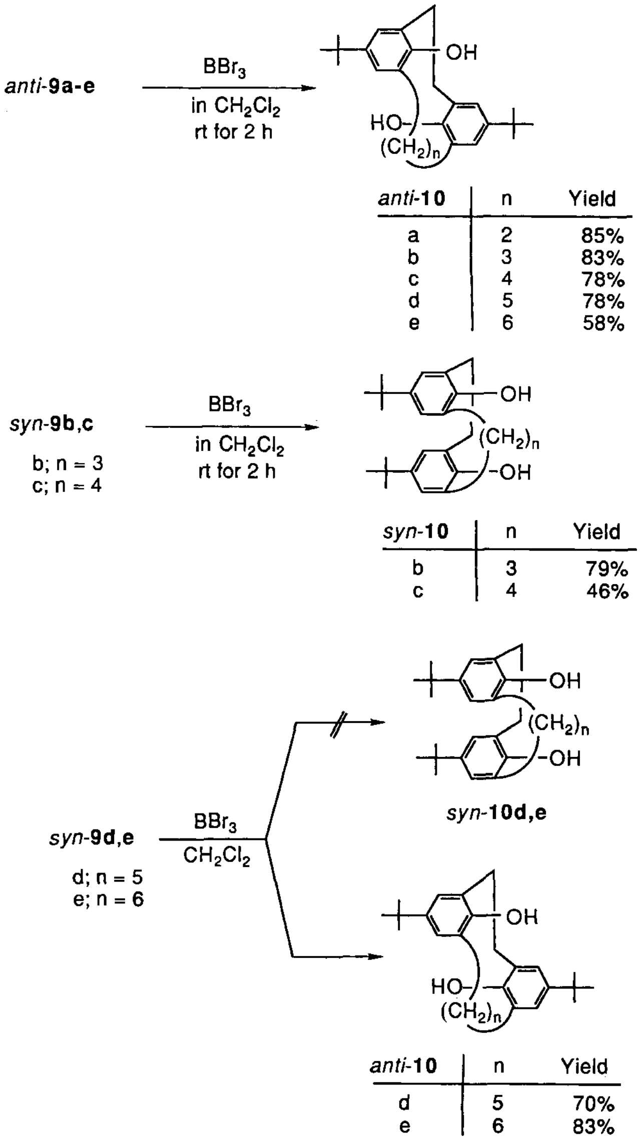


Figure 4. UV spectra of *syn*-dimethoxy[*n*.2]MCPs *syn*-**9** (cyclohexane)

C. UV Spectra of *anti*- (*anti*-9) and *syn*-Dimethoxy[*n*.2]MCP (*syn*-9)

The UV spectra of *anti*- and *syn*-dimethoxy[*n*.2]MCPs in cyclohexane are shown in Figure 3. A band of *anti*-[4.2]MCP (*anti*-**9c**) at 272 nm (lg ε_{max} = 3.65) indicates a bathochromic shift as the strain increases and the distance between the two aromatic rings decreases. The same phenomenon is also observed in *syn*-dimethoxy[*n*.2]MCPs, but the bathochromic shift (20 nm) between [3.2]- and [4.2]systems is larger than that of *anti* systems (6 nm) (Figure 4). These bathochromic shifts are ascribed to the

Scheme 3



anti-**10**	n	Yield
a	2	85%
b	3	83%
c	4	78%
d	5	78%
e	6	58%

syn-**10**	n	Yield
b	3	79%
c	4	46%

anti-**10**	n	Yield
d	5	70%
e	6	83%

rt = room temperature.

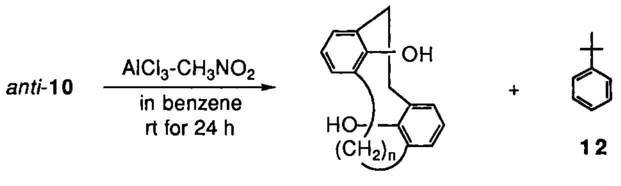
transannular interaction between the two benzene rings and the increase of the strain of these systems[26].

D. Synthesis of *anti*- (*anti*-11) and *syn*-Dihydroxy[*n*.2]MCP (*syn*-11)

Demethylation of *anti*-dimethoxy[*n*.2]MCPs (*anti*-**9a**–**e**) with BBr_3 in dichloromethane affords the corresponding *anti*-dihydroxy[*n*.2]MCPs (*anti*-**10a**–**e**). The same treatment of *syn*-dimethoxy[3.2]MCP (*syn*-**9b**) and [4.2]MCP (*syn*-**9c**) gives the corresponding *syn*-dihydroxy[*n*.2]-MCPs, i.e. *syn*-**10b** and *syn*-**10c** in 79 and 46% yield, respectively. However, the attempted demethylation of *syn*-dimethoxy-[5.2]MCP (*syn*-**9d**) and -[6.2]MCP (*syn*-**9e**) to give *syn*-dihydroxy[*n*.2]MCPs, i.e. *syn*-**10d** and *syn*-**10e**, has failed. Only *anti*-dihydroxy[*n*.2]MCPs (*anti*-**10d** and *anti*-**10e**) have been obtained in 70 and 83% yields, respectively. This finding suggests that the ring inversion to the thermodynamically stable *anti* conformation is possible in the dihydroxy[5.2]- and -[6.2]-MCPs, which seem to have sufficient space for the conformational flipping as demonstrated by the molecular models.

The $AlCl_3 \cdot CH_3NO_2$-catalyzed trans-*tert*-butylation of *anti*-**10a**, *anti*-**10b**, and *anti*-**10c** in benzene has been carried out at 50°C for 24 h to afford the correspnding *anti*-**11a**, *anti*-**11b**, and *anti*-**11c** in 70, 83, and 78% yield, respectively, along with *tert*-butylbenzene (**12**).

Scheme 4



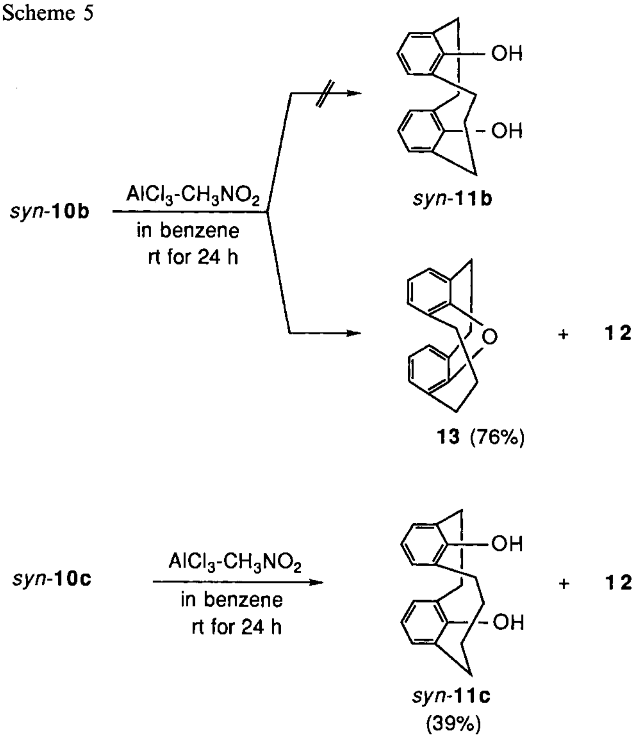
anti-11	n	Yield
a	2	70%
b	3	83%
c	4	78%

rt = room temperature.

However, the same treatment of *syn*-5,14-di-*tert*-butyl-8,17-dihydroxy[3.2]MCP (*syn*-**10b**) does not give the desired *syn*-8,17-dihydroxy[3.2]MCP (*syn*-**11b**), but gives 8,17-epoxy[3.2]MCP (**13**) in 76% yield. In contrast, the $AlCl_3 \cdot CH_3NO_2$-catalyzed trans-*tert*-butylation of *syn*-5,15-di-*tert*-butyl-8,18-dihydroxy[4.2]MCP (*syn*-**10c**) affords the corresponding *syn*-**11c** in 39% yield. No *syn*-*anti* isomerization catalyzed by Lewis acids has been observed under the reaction conditions used. These findings suggest that the above novel dehydration of hydroxyl groups in the *syn*-intra-annular positions is attributed to the release of strain in *syn*-8,17-dihydroxy[3.2]MCP (*syn*-**11b**) leading to the more strainless 9,17-epoxy[3.2]MCP (**13**) containing an ether linkage.

The structure **13** is supported by its elemental analysis and spectral data. The IR (KBr) spectrum shows the disappearance of ν_{OH}. The ^1H-NMR ($CDCl_3$) spectrum of **13** exhibits a pattern quite different from that of *syn*-8,18-dihydroxy[4.2]MCP (*syn*-**11c**).

Scheme 5



rt = room temperature.

E. Conformational Behavior of Hydroxy[*n*.2]MCPs

The conformations of dimethoxy[*n*.*m*]MCPs, such as **7**, **8**, *anti*-**9**, and *syn*-**9**, in solution are rigid, and the signals of the methylene bridge do not coalesce below 150°C. The energy barriers to flipping being above 25 kcal mol^{-1}. However, as already mentioned, dihydroxy[5.2]- and -[6.2]-MCPs seem to have sufficient space for conformational ring flipping as demonstrated by the molecular models. Therefore, we have studied the ring inversion of these systems by using variable temperature ^1H-NMR spectroscopy. The ^1H-NMR spectrum of *anti*-**10d** and *anti*-**10e** in $CDCl_3$ at room temperature exhibits the split pattern of the protons at the methylene bridge. In spite of an increase of the temperature

Table 3. Spectral data of dihydroxy[*n*.2]MCPs **10**

Number of methylene bridge, n		IR, ν_{OH} [cm^{-1}]	^1H-NMR (δ)[a] Hydroxy protons	Aromatic protons
2	*anti*	3575	2.14	7.08
3	*anti*	3530	2.15	7.08
	syn	3100 (broad)	-	6.35, 6.64
4	*anti*	3550	2.71	6.92, 7.10
	syn	3200 (broad)	5.42	6.52
5	*anti*	3527	3.06	6.92, 7.05
6	*anti*	3527	3.32	7.07, 7.09

[a] Determined in $CDCl_3$ at room temperature by using $SiMe_4$ as a reference.

to 130°C in $CDBr_3$ or hexachloro-1,3-butadiene, no change of the spectrum is observed for the [5.2] system. However, in the case of the [6.2] system, as the temperature of the solution of the respective compound in $CDBr_3$ is increased, the individual peaks of the benzyl protons merge and eventually a pair of single peaks is observed above 130°C. The energy barrier to the conformational ring flipping estimated from the coalescence temperature (T_c) is 20.6 kcal mol^{-1}.

In contrast, when the ^{1}H-NMR spectrum of [6.2]MCP (*anti*-**10e**) is measured in $[D_6]$DMSO, the spectrum shows a pattern quite different from that in $CDCl_3$ even at room temperature, e.g. two kinds of *tert*-butyl protons (δ = 1.05 and 1.24), hydroxyl protons (5.60 and 7.75), and aromatic protons (6.60 and 6.82, 7.00).

The ^{1}H-NMR spectrum of *anti*-dihydroxy[4.2]MCP (*anti*-**10c**) in $[D_6]$DMSO shows the *tert*-butyl protons at δ = 1.25, the hydroxyl protons at δ = 5.35, and the aromatic protons at δ = 6.69 and 6.97. However, the ^{1}H-NMR spectrum of *syn*-dihydroxy[4.2]MCP (*syn*-**10c**) in $[D_6]$DMSO exhibits the *tert*-butyl protons at δ = 1.06, the hydroxyl protons at δ = 7.88, and the aromatic protons at δ = 6.41 and 6.44. On the basis of these data it may be inferred that hydroxy[6.2]MCPs in $[D_6]$DMSO at room temperature exist as a mixture of *anti* and *syn* conformers in a ratio of 65:35. This phenomenon has also been observed in other polar solvents, such as CD_3CN or $[D_6]$acetone. The *anti*-*syn* ratios of hydroxy[6.2]MCPs in various solvents are compiled in Table 4.

The portion of the *syn* conformer increases with increasing dielectronic constant of the solvent. The polarity of the solvent may change the equilibrium position of *anti-syn* conformers by decreasing the energy difference of *anti-syn* conformers by stabilizing the much more polar *syn* conformer and the intramolecular hydrogen bond of the *syn* conformer.

With increasing temperature of the solution of dihydroxy[6.2]MCP **10e** in $[D_6]$DMSO, the individual

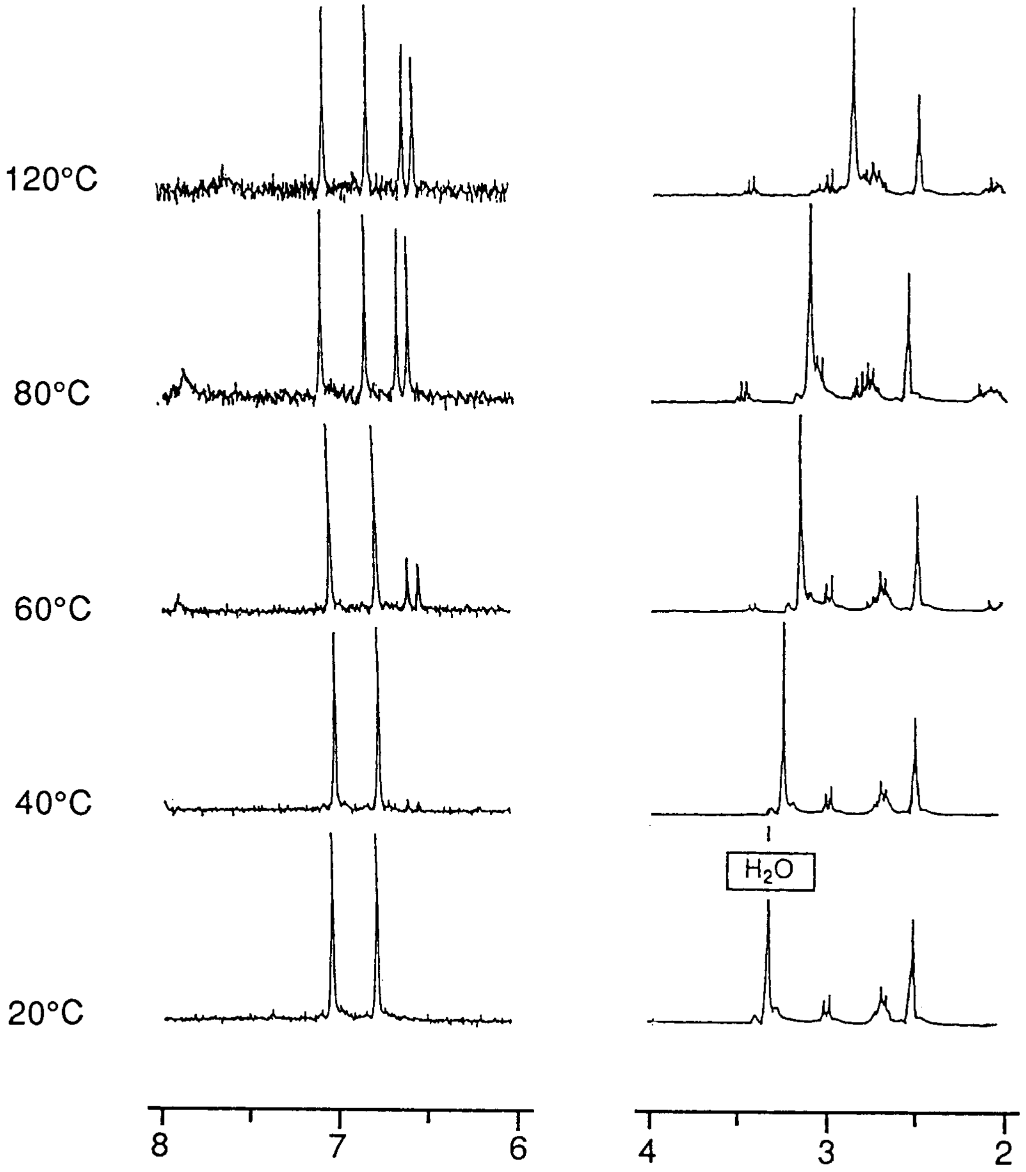
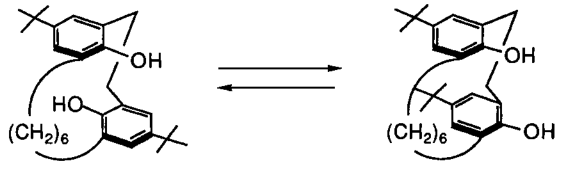


Figure 5. Dynamic ^{1}H-NMR spectrum of *anti*-**10d** at 270 MHz ($[D_6]$DMSO). δ scale

peaks of *anti* and *syn* conformers merge and eventually a single peak is observed above 80 °C for the *tert*-butyl, benzyl, aromatic, and hydroxyl protons. This behavior strongly suggests that conformational ring flipping occurs at the coalescence temperature of 80 °C giving an estimated energy barrier of 17.5 kcal mol^{-1}.

Table 4. Solvent effects for *anti-syn* ratios of dihydroxy[6.2]MCP **10e**[a]



anti-**10e** *syn*-**10e**

Solvent	Dielectric constant	*anti*-**10e**	*syn*-**10e**
[D$_6$]DMSO	45	65	35
CD_3CN	37.5	81	19
[D$_6$]acetone	21.5	90	10
$CDCl_3$	4.9	100	0

[a] *anti-syn* Ratios were determined by ^{1}H-NMR spectrometry at 20 °C.

In contrast, at room temperature the ^{1}H-NMR spectrum of dihydroxy[5.2]MCP **10d** in [D$_6$]DMSO is almost identical with that in $CDCl_3$ and no *syn* conformer is observed. However, the *syn* conformer is detected at 60 °C, and as the temperature is raised the ratio of the *syn* conformer to the *anti* conformer increases (Figure 5). The individual peaks of the *anti* and *syn* conformers do not coalesce below 140 °C, and the energy barrier to flipping is above 25 kcal mol^{-1}. It has also been found that the ^{1}H-NMR spectrum in $CDCl_3$ of the recovered hydroxy[5.2]MCP **10d** from the dynamic ^{1}H-NMR experiment in [D$_6$]DMSO still corresponds to a mixture of *anti* and *syn* conformers. However, in the case of hydroxy[6.2]MCP **10e** this phenomenon has not been observed. This difference may be attributed mainly to a higher barrier for **10d** to conformational ring flipping than that for **10e** by decreasing the length of the methylene bridge by one unit.

Conclusions

We have prepared intra-annularly-substituted *anti*- and *syn*-[*n*.2]MCPs and have investigated their solid and solution conformations for the first time. The conformation of dihydroxy[*n*.2]MCPs in solution is affected by the chain length of the bridges. The ring inversion barriers for the dihydroxy[*n*.2]MCPs are estimated and have beend found to decrease with increasing length of the bridges as expected. The conformations of dihydroxy[2.2]-, -[3.2]-, -[4.2]MCPs are rigid, but -[5.2]- and -[6.2]MCPs are flexible and exhibit conformational ring flipping. The ratio of *anti* to *syn* conformers has been found to be strongly affected by the solvents.

Further studies on the synthesis and conformational behavior of the higher dihydroxy[*n*.2]MCPs are in progress.

Experimental

Melting and boiling points are uncorrected. – IR (KBr or NaCl): Nippon Denshi JIR-AQ2OM. – ^{1}H NMR: Nippon Denshi Jeol FT-270 in $CDCl_3$, TMS as reference. – UV: Hitachi 220A spectrophotometer. – MS: Nippon Denshi JMS-01SA-2. – Elemental analyses: Yanaco MT-5.

1,3-Bis(5-tert-butyl-2-methoxyphenyl)propane (**4b**): To a solution of 3.4 g (143 mmol) of magnesium and a small amount of iodine in 5 ml of tetrahydrofuran was added a solution of 17.01 g (70 mmol) of 2-bromo-4-*tert*-butylanisole (**5**) in 25 ml of tetrahydrofuran, and the mixture was refluxed for 12 h. To a solution of 6.1 g (30 mmol) of 1,3-dibromopropane and 750 mg (5.25 mmol) of CuBr in 5 ml of HMPA was added dropwise a solution of 5-*tert*-butyl-2-methoxyphenylmagnesium bromide with gentle refluxing. After the reaction mixture was refluxed for additional 17 h, it was quenched with a 10% aqueous ammonium chloride solution and extracted with CH_2Cl_2 (3 × 50 ml). After the combined CH_2Cl_2 extracts were dried with Na_2SO_4, the solvent was evaporated in vacuo and the residue recrystallized from ethanol to give 5.78 g (15.7 mmol, 52%) of **4b**. Colorless plates (ethanol), m.p. 62–65 °C. – IR (KBr): $\tilde{\nu}$ = 2959, 1600, 1500, 1460, 1360, 1310, 1270, 1255, 1240, 1170, 1140, 1020, 1010, 880, 810, 770, 730, 655. – ^{1}H NMR ($CDCl_3$): δ = 1.28 (18 H, s), 1.70–2.04 (2 H, m), 2.68 (4 H, t, *J* = 8 Hz), 3.76 (6 H, s), 6.72 (2 H, d, *J* = 9 Hz), 7.07–7.16 (4 H, m). – MS (75 eV), *m/z*: 368 [M$^+$].

$C_{25}H_{36}O_2$ (368.6) Calcd. C 81.47 H 9.85
Found C 81.44 H 9.77

1,4-Bis(5-tert-butyl-2-methoxyphenyl)butane (**4c**): Synthesis in a similar manner as described above, yield 65%; colorless prisms (hexane), m.p. 102–105 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2850, 1610, 1500, 1460, 1440, 1360, 1320, 1270, 1245, 1180, 1150, 1090, 1030, 820. – ^{1}H NMR ($CDCl_3$): δ = 1.29 (18 H, s), 1.62–1.78 (4 H, m), 2.60–2.70 (4 H, m), 3.79 (6 H, s), 6.76 (2 H, d, *J* = 9 Hz), 7.15 (2 H, dd, *J* = 3/9 Hz), 7.16 (2 H, d, *J* = 3 Hz). – MS (75 eV), *m/z*: 382 [M$^+$].

$C_{26}H_{38}O_2$ (382.6) Calcd. C 81.62 H 10.01
Found C 81.69 H 10.17

1,5-Bis(5-tert-butyl-2-methoxyphenyl)pentane (**4d**): Synthesis in a similar manner as described above, yield 74%; colorless oil. – IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2953, 2853, 1504, 1463, 1362, 1288, 1247, 1144, 1036, 808. – ^{1}H NMR ($CDCl_3$): δ = 1.30 (18 H, s), 1.40–1.70 (6 H, m), 2.58–2.64 (4 H, m), 3.79 (6 H, s), 6.76 (2 H, d, *J* = 9 Hz), 7.15 (2 H, dd, *J* = 3/9 Hz), 7.16 (2 H, d, *J* = 3 Hz). – MS (75 eV), *m/z*: 396 [M$^+$].

$C_{27}H_{40}O_2$ (396.6) Calcd. C 81.76 H 10.17
Found C 81.88 H 10.30

1,6-Bis(5-tert-butyl-2-methoxyphenyl)hexane (**4e**): Synthesis in a similar manner as described above, yield 82%; colorless oil. – IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2954, 2858, 1503, 1483, 1382, 1267, 1247, 1151, 1038, 809. – ^{1}H NMR ($CDCl_3$): δ = 1.29 (18 H, s), 1.23–1.42 (4 H, m), 1.50–1.68 (4 H, m), 2.60 (4 H, t, *J* = 8 Hz), 3.77 (6 H, s), 6.75 (2 H, dd, *J* = 3/9 Hz), 7.15 (2 H, dd, *J* = 3/9 Hz), 7.16 (2 H, d, *J* = 3 Hz). – MS (75 eV), *m/z*: 410 [M$^+$].

$C_{28}H_{42}O_2$ (410.6) Calcd. C 81.90 H 10.31
Found C 81.69 H 10.18

1,3-Bis[5-tert-butyl-3-(chloromethyl)-2-methoxyphenyl]propane (**6b**): A mixture of 10 g (27.2 mmol) of **4b**, 20 g (0.67 mmol) of paraformaldehyde, 80 ml of acetic acid, 80 ml of H_3PO_4 (85%), and 80 ml of concentrated HCl (36%) was heated at 90–95°C with vigorous stirring for 36 h. Then the reaction mixture was extracted with benzene (3 × 100 ml). The combined extracts were neutralized with a 10% aqueous Na_2CO_3 solution, washed with water, dried with Na_2SO_4, and the solvent was evaporated in vacuo to leave a residue which was recrystallized from hexane to give 12.5 g (26.8 mmol, 99%) of **6b**. Colorless prisms (hexane), m.p. 79–80°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2960, 1600, 1480, 1460, 1435, 1390, 1360, 1300, 1270, 1205, 1110, 1000, 935, 880, 810, 785, 755, 685. – ^1H NMR ($CDCl_3$): δ = 1.29 (18H, s), 1.84–2.09 (2H, m), 2.70–2.80 (4H, m), 3.78 (6H, s), 4.64 (4H, s), 7.16 (2H, d, *J* = 2.5 Hz), 7.21 (2H, d, *J* = 2.5 Hz). – MS (75 eV), *m/z*: 464, 466, 468 [M^+].

$C_{27}H_{38}Cl_2O_2$ (465.5) Calcd. C 69.67 H 8.23
Found C 69.64 H 8.25

1,2-Bis[5-tert-butyl-3-(chloromethyl)-2-methoxyphenyl]ethane (**6a**): Synthesis in a similar manner as reported previously[19], yield 88%, m.p. 139–140°C (ref.[19] 139–140°C).

1,4-Bis[5-tert-butyl-3-(chloromethyl)-2-methoxyphenyl]butane (**6c**): Synthesis in a similar manner as described above, yield 97%; colorless prisms (hexane), m.p. 133–137°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2850, 1480, 1460, 1430, 1265, 1245, 1230, 1210, 1000, 885, 690, 605. – ^1H NMR ($CDCl_3$): δ = 1.38 (18H, s), 1.65–1.80 (4H, m), 2.62–2.78 (4H, m), 3.85 (6H, s), 4.68 (4H, s), 7.18 (2H, d, *J* = 2.5 Hz), 7.24 (2H, d, *J* = 2.5 Hz). – MS (75 eV), *m/z*: 478, 480, 482 [M^+].

$C_{28}H_{40}Cl_2O_2$ (479.5) Calcd. C 70.13 H 8.41
Found C 70.50 H 8.49

1,5-Bis[5-tert-butyl-3-(chloromethyl)-2-methoxyphenyl]pentane (**6d**): Synthesis in a similar manner as described above, yield 90%; colorless oil. – IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2950, 2850, 1480, 1460, 1360, 1265, 1240, 1208, 1170, 1110, 1005, 875. – ^1H NMR ($CDCl_3$): δ = 1.30 (18H, s), 1.40–1.57 (2H, m), 1.60–1.78 (4H, m), 2.60–2.70 (4H, m), 3.84 (6H, s), 4.67 (4H, s), 7.18 (2H, d, *J* = 2.5 Hz), 7.23 (2H, d, *J* = 2.5 Hz). – MS (75 eV), *m/z*: 492, 494, 496 [M^+].

$C_{29}H_{42}Cl_2O_2$ (493.6) Calcd. C 70.57 H 8.58
Found C 70.65 H 8.58

1,6-Bis[5-tert-butyl-3-(chloromethyl)-2-methoxyphenyl]hexane (**6e**): Synthesis in a similar manner as described above, yield 40%; m.p. 113–115°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3028, 2953, 2925, 2859, 2833, 1503, 1483, 1466, 1434, 1391, 1362, 1293, 1275, 1258, 1242, 1214, 1202, 1171, 1124, 1092, 1001, 885, 815, 782, 722. – ^1H NMR ($CDCl_3$): δ = 1.30 (18H, s), 1.33–1.45 (4H, m), 1.52–1.70 (4H, m), 2.63 (4H, t, *J* = 8 Hz), 3.83 (6H, s), 4.86 (4H, s), 7.17 (2H, d, *J* = 2.2 Hz), 7.24 (2H, d, *J* = 2.2 Hz). – MS (75 eV), *m/z*: 506, 508, 510 [M^+].

$C_{30}H_{44}Cl_2O_2$ (507.6) Calcd. C 70.99 H 8.74
Found C 70.62 H 9.02

6,15-Di-tert-butyl-9,18-dimethoxy-2-thia[3.3]metacyclophane (**7b**): A solution of 6.34 g (13.6 mmol) of **6b** in 400 ml of ethanol and 40 ml of benzene and a solution of 6.72 g (28 mmol) of $Na_2S \cdot 9\,H_2O$ in 400 ml of ethanol and 75 ml of water were added separately, but simultaneously, from two Hershberg funnels to boiling ethanol (4 l). When the addition was complete (21 h), the mixture was refluxed with stirring for 16 h. Then the reaction mixture was concentrated and the residue extracted with CH_2Cl_2 (3 × 200 ml). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was separated by silica gel column chromatography (eluent benzene/hexane, 5:1). Recrystallization from hexane afforded 1.37 g (3.22 mmol, yield 24%) of **7b**. Colorless prisms, m.p. 221–223°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3040, 2950, 1595, 1480, 1455, 1360, 1290, 1255, 1200, 1170, 1110, 1020, 920, 875, 810, 785, 650. – ^1H NMR ($CDCl_3$): δ = 1.34 (18H, s), 2.10–2.70 (6H, m), 3.14 (6H, s), 3.17 (2H, d, *J* = 14 Hz), 3.73 (2H, d, *J* = 14 Hz), 6.94 (2H, d, *J* = 2.5 Hz), 7.32 (2H, d, *J* = 2.5 Hz). – MS (75 eV), *m/z*: 426 [M^+].

$C_{27}H_{38}O_2S$ (426.6) Calcd. C 76.01 H 8.98
Found C 76.25 H 9.25

Compounds **7a**, **7c**, **7d**, and **7e** were prepared in the same manner as described above in 40, 41, 30, and 35% yield, respectively.

6,14-Di-tert-butyl-9,17-dimethoxy-2-thia[3.2]metacyclophane (**7a**): Colorless prisms (hexane/benzene, 1:1), m.p. 238–239°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2963, 2867, 1480, 1461, 1202. – ^1H NMR ($CDCl_3$): δ = 1.33 (18H, s), 2.66 (4H, s), 3.05 (6H, s), 3.38 (2H, d, *J* = 12.5 Hz), 3.88 (2H, d, *J* = 12.5 Hz), 7.06 (2H, d, *J* = 2.4 Hz), 7.26 (2H, d, *J* = 2.4 Hz). – MS (75 eV), *m/z*: 412 [M^+].

$C_{26}H_{36}O_2S$ (412.6) Calcd. C 75.68 H 8.79
Found C 75.52 H 8.70

6,16-Di-tert-butyl-9,19-dimethoxy-2-thia[3.4]metacyclophane (**7c**): Colorless prisms (hexane), m.p. 188–192°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3040, 2980, 1480, 1475, 1448, 1380, 1310, 1270, 1215, 1185, 1130, 1030, 910, 885, 670. – ^1H NMR ($CDCl_3$): δ = 1.34 (18H, s), 1.28–1.56 (4H, m), 1.90–2.00 (2H, m), 2.70–2.80 (2H, m), 3.24 (2H, d, *J* = 15 Hz), 3.26 (6H, s), 3.92 (2H, d, *J* = 15 Hz), 6.78 (2H, d, *J* = 2.4 Hz), 7.48 (2H, d, *J* = 2.4 Hz). – MS (75 eV), *m/z*: 440 [M^+].

$C_{28}H_{40}O_2S$ (440.7) Calcd. C 76.31 H 9.15
Found C 76.37 H 9.28

6,17-Di-tert-butyl-9,20-dimethoxy-2-thia[3.5]metacyclophane (**7d**): Colorless prisms (hexane), m.p. 143–144°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2850, 1600, 1475, 1455, 1360, 1300, 1255, 1230, 1195, 1170, 1110, 1014, 890, 809, 775, 705, 645. – ^1H NMR ($CDCl_3$): δ = 0.90–1.01 (2H, m), 1.35 (18H, s), 1.30–1.58 (4H, m), 2.16–2.28 (2H, m), 2.52–2.68 (2H, m), 3.24 (2H, d, *J* = 14.5 Hz), 3.28 (6H, s), 3.94 (2H, d, *J* = 14.5 Hz), 6.92 (2H, d, *J* = 2.4 Hz), 7.45 (2H, d, *J* = 2.4 Hz). – MS (75 eV), *m/z*: 454 [M^+].

$C_{29}H_{42}O_2S$ (454.7) Calcd. C 76.61 H 9.31
Found C 76.38 H 9.34

6,18-Di-tert-butyl-9,21-dimethoxy-2-thia[3.6]metacyclophane (**7e**): Colorless prisms (hexane), m.p. 200–202°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2992, 2962, 2952, 2903, 1481, 1448, 1391, 1362, 1315, 1300, 1281, 1246, 1194, 1172, 1160, 1118, 1105, 1008, 916, 888. – ^1H NMR ($CDCl_3$): δ = 0.85–1.00 (2H, m), 1.10–1.22 (2H, m), 1.34 (18H, s), 1.60–1.80 (4H, m), 2.30–2.44 (2H, m), 2.58–2.70 (2H, m), 3.21 (6H, s), 3.33 (2H, d, *J* = 15.3 Hz), 4.02 (2H, d, *J* = 15.3 Hz), 6.92 (2H, d, *J* = 2.4 Hz), 7.45 (2H, d, *J* = 2.4 Hz). – MS (75 eV), *m/z*: 468 [M^+].

$C_{30}H_{44}O_2S$ (468.7) Calcd. C 76.87 H 9.46
Found C 76.74 H 10.00

6,15-Di-tert-butyl-9,18-dimethoxy-2-thia[3.3]metacyclophane 2,2-Dioxide (**8b**): To a solution of 2.95 g (6.92 mmol) of **7b** in 300 ml of CH_2Cl_2 was added 3.58 g (17.65 mmol) of *m*-chloroperbenzoic acid. After the reaction mixture had been stirred at room temp. for 17 h, it was washed with a 10% aqueous $NaHCO_3$ solution and brine, dried with Na_2SO_4 and concentrated in vacuo to leave a residue which was recrystallized from hexane/benzene (1:1) to give 3.10 g (6.76 mmol, yield 98%) of **8b**. Colorless prisms (hexane/benzene, 1:1), m.p. 239–242°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3040, 2930, 1600, 1480, 1450, 1390, 1360, 1310, 1260, 1230, 1190, 1170, 1110, 1010, 920, 900, 880, 820, 805, 780, 700. – ^1H NMR ($CDCl_3$): δ = 1.34 (18H, s), 2.10–2.26 (2H, m), 2.46–2.70 (4H, m), 3.15 (6H, s), 3.81 (2H, d, J = 14 Hz), 4.35 (2H, d, J = 14 Hz), 7.13 (2H, d, J = 2.5 Hz), 7.54 (2H, d, J = 2.5 Hz). – MS (75 eV), m/z: 458 $[M^+]$.

$C_{27}H_{38}O_4S$ (458.7) Calcd. C 70.71 H 8.35
Found C 70.69 H 8.36

Compounds **8a**, **8c**, **8d**, and **8e** were prepared in the same manner as described above in 99, 91, 99, and 86% yield, respectively.

6,14-Di-tert-butyl-9,17-dimethoxy-2-thia[3.2]metacyclophane 2,2-Dioxide (**8a**): Colorless prisms (hexane), m.p. >300°C. – ^{1}H NMR ($CDCl_3$): δ = 1.33 (18H, s), 2.72 (4H, s), 3.07 (6H, s), 3.95 (2H, d, J = 13.7 Hz), 4.52 (2H, d, J = 13.7 Hz), 7.23 (2H, d, J = 2.4 Hz), 7.45 (2H, d, J = 2.4 Hz). – MS (75 eV), m/z: 444 $[M^+]$.

$C_{28}H_{40}O_4S$ (444.6) Calcd. C 70.24 H 8.16
Found C 70.30 H 8.15

6,16-Di-tert-butyl-9,19-dimethoxy-2-thia[3.4]metacyclophane 2,2-Dioxide (**8c**): Colorless prisms (hexane), m.p. 258°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 1485, 1460, 1318, 1292, 1278, 1290, 1280, 1250, 1196, 1170, 1120, 1010, 905, 770. – ^{1}H NMR ($CDCl_3$): δ = 1.34 (18H, s), 1.29–1.59 (4H, m), 2.00–2.15 (2H, m), 2.75–2.84 (2H, m), 3.26 (6H, s), 3.91 (2H, d, J = 15 Hz), 4.54 (2H, d, J = 15 Hz), 6.95 (2H, d, J = 2 Hz), 7.74 (2H, d, J = 2 Hz). – MS (75 eV), m/z: 472 $[M^+]$.

$C_{28}H_{40}O_4S$ (472.7) Calcd. C 71.15 H 8.53
Found C 71.30 H 8.51

6,17-Di-tert-butyl-9,20-dimethoxy-2-thia[3.5]metacyclophane 2,2-Dioxide (**8d**): Colorless prisms (hexane), m.p. >193°C (dec.). – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2850, 1476, 1465, 1360, 1314, 1285, 1250, 1190, 1170, 1100, 1008, 890, 760, 500. – ^{1}H NMR ($CDCl_3$): δ = 1.39 (18H, s), 1.05–1.08 (2H, m), 1.28–1.56 (4H, m); 2.17–2.30 (2H, m), 2.53–2.60 (2H, m), 3.24 (6H, s), 3.93 (2H, d, J = 15.3 Hz), 4.59 (2H, d, J = 15.3 Hz), 7.07 (2H, d, J = 2.4 Hz), 7.77 (2H, d, J = 2.4 Hz). – MS (75 eV), m/z: 486 $[M^+]$.

$C_{29}H_{42}O_4S$ (486.7) Calcd. C 71.57 H 8.70
Found C 71.63 H 8.78

6,18-Di-tert-butyl-9,21-dimethoxy-2-thia[3.6]metacyclophane 2,2-Dioxide (**8e**): Colorless prisms (hexane), m.p. 200–202°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2992, 2962, 2952, 2903, 2856, 1481, 1468, 1463, 1448, 1391, 1362, 1315, 1300, 1281, 1246, 1194, 1172, 1160, 1118, 1105, 1008, 916, 888, 766. – ^{1}H NMR ($CDCl_3$): δ = 0.85–1.00 (2H, m), 1.10–1.22 (2H, m), 1.34 (18H, s), 1.60–1.80 (4H, m), 2.30–2.44 (2H, m), 2.58–2.70 (2H, m), 3.21 (6H, s), 3.96 (2H, d, J = 15.7 Hz), 4.66 (2H, d, J = 15.7 Hz), 7.13 (2H, d, J = 2.0 Hz), 7.83 (2H, d, J = 2.0 Hz). – MS (75 eV), m/z: 500 $[M^+]$.

$C_{30}H_{44}O_4S$ (500.7) Calcd. C 71.96 H 8.86
Found C 71.84 H 9.22

Pyrolysis of Sulfone **8** *to* **9**. *Typical Procedure:* The sulfone **8b** (500 mg, 1.1 mmol) was pyrolyzed at 500°C/1 Torr according to ref.[19]. The sublimed product was collected and chromatographed on silica gel with hexane/benzene (1:1) and chloroform as the eluents to give 275 mg (59%) of *anti*-**9b** and 88.3 mg (19%) of *syn*-**9b**.

anti-6,14-Di-tert-butyl-9,17-dimethoxy[3.2]metacyclophane (*anti*-**9b**): Colorless prisms (methanol), m.p. 206–209°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2920, 2820, 1480, 1360, 1285, 1250, 1210, 1200, 1170, 1105, 1025, 870, 850, 810, 780, 705, 650. – ^{1}H NMR ($CDCl_3$): δ = 1.31 (18H, s), 1.85–2.10 (2H, m), 2.40–2.74 (8H, m), 3.02 (6H, s), 6.92 (2H, d, J = 2.5 Hz), 6.96 (2H, d, J = 2.5 Hz). – MS (75 eV), m/z: 394 $[M^+]$.

$C_{27}H_{38}O_2$ (394.6) Calcd. C 82.18 H 9.71
Found C 82.29 H 9.91

syn-6,14-Di-tert-butyl-9,17-dimethoxy[3.2]metacyclophane (*syn*-**9b**): Pale yellow oil. – IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2950, 2900, 2850, 1480, 1450, 1430, 1355, 1292, 1250, 1200, 1100, 1010. – ^{1}H NMR ($CDCl_3$): δ = 1.12 (18H, s), 1.27–1.43 (1H, m), 2.08–2.20 (1H, m), 2.46–2.64 (4H, m), 2.95–3.08 (2H, m), 3.43–3.50 (2H, m), 3.51 (6H, s), 6.28 (2H, d, J = 2.5 Hz), 6.58 (2H, d, J = 2.5 Hz). – MS (75 eV), m/z: 394 $[M^+]$.

$C_{27}H_{38}O_2$ (394.6) Calcd. C 82.18 H 9.71
Found C 81.66 H 9.69

Similarly, *anti*-**9a**, *anti*-**9c**, *anti*-**9d**, *anti*-**9e**, *syn*-**9c**, *syn*-**9d**, and *syn*-**9e** were prepared. The yields are compiled in Scheme 2.

anti-5,13-Di-tert-butyl-8,16-dimethoxy[2.2]metacyclophane (*anti*-**9a**): Colorless prisms (hexane), m.p. 242–243°C (ref.[19] 242–243°C).

anti-7,15-Di-tert-butyl-10,18-dimethoxy[4.2]metacyclophane (*anti*-**9c**): Colorless prisms (methanol), m.p. 174–176°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2880, 1450, 1430, 1365, 1295, 1280, 1190, 1160, 870. – ^{1}H NMR ($CDCl_3$): δ = 1.31 (18H, s), 1.56 (4H, s), 1.95–2.06 (2H, m), 2.68–2.79 (6H, m), 3.16 (6H, s), 6.77 (2H, d, J = 2.4 Hz), 7.06 (2H, d, J = 2.4 Hz). – MS (75 eV), m/z: 408 $[M^+]$.

$C_{28}H_{40}O_2$ (408.6) Calcd. C 82.30 H 9.87
Found C 82.38 H 9.93

syn-7,15-Di-tert-butyl-10,18-dimethoxy[4.2]metacyclophane (*syn*-**9c**): Pale yellow oil. – IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2940, 2900, 2850, 2800, 1480, 1464, 1360, 1240, 1204, 1100, 1020. – ^{1}H NMR ($CDCl_3$): δ = 1.12 (18H, s), 1.16–1.31 (2H, m), 1.92–2.08 (4H, m), 2.61–2.77 (4H, m), 3.50–3.60 (2H, m), 3.54 (6H, s), 6.48 (2H, d, J = 2.4 Hz), 7.66 (2H, d, J = 2.4 Hz). – MS (75 eV), m/z: 408 $[M^+]$.

$C_{28}H_{40}O_2$ (408.6) Calcd. C 82.30 H 9.87
Found C 82.22 H 9.66

anti-8,16-Di-tert-butyl-11,19-dimethoxy[5.2]metacyclophane (*anti*-**9d**): Colorless prisms (methanol), m.p. 142–144°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2920, 2850, 2800, 1482, 1460, 1450, 1360, 1290, 1200, 1170, 1110, 1020. – ^{1}H NMR ($CDCl_3$): δ = 0.85–1.00 (2H, m), 1.10–1.40 (4H, m), 1.31 (18H, s), 2.01–2.08 (2H, m), 2.51–2.58 (2H, m), 2.72–2.86 (4H, m), 3.25 (6H, s), 6.83 (2H, d, J = 2.4 Hz), 7.10 (2H, d, J = 2.4 Hz). – MS (75 eV), m/z: 422 $[M^+]$.

$C_{29}H_{42}O_2$ (422.7) Calcd. C 82.41 H 10.02
Found C 82.48 H 10.00

syn-8,16-Di-tert-butyl-11,19-dimethoxy[5.2]metacyclophane (*syn*-**9d**): Pale yellow oil. – IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2950, 2925, 2850, 1480, 1460, 1445, 1360, 1245, 1210, 1200, 1110, 1020, 910, 730. – ^{1}H NMR ($CDCl_3$): δ = 1.13 (18H, s), 1.10–1.40 (4H, m), 1.60–1.76 (2H, m), 2.08–2.20 (2H, m), 2.74–2.82 (4H, m), 3.58 (6H, s), 3.58–3.65 (2H, m), 6.61 (2H, d, J = 2.4 Hz), 6.68 (2H, d, J = 2.4 Hz). – MS (75 eV), m/z: 422 $[M^+]$.

$C_{29}H_{42}O_2$ (422.7) Calcd. C 82.41 H 10.02
Found C 82.49 H 10.05

anti-9,17-Di-tert-butyl-12,20-dimethoxy[6.2]metacyclophane (*anti*-**9e**): Colorless prisms (hexane), m.p. 110°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2957, 2928, 2850, 1482, 1460, 1445, 1424, 1391, 1362, 1292, 1240, 1202, 1170, 1105, 1018, 885, 867. – ^{1}H NMR ($CDCl_3$): δ = 0.76–1.10 (4H, m), 1.31 (18H, s), 1.51–1.56 (4H, m), 2.26–2.31 (2H, m), 2.47–2.57 (2H, m), 2.78–2.95 (4H, m), 3.18 (6H, s), 6.94 (2H, d, J = 2.9 Hz), 7.12 (2H, d, J = 2.9 Hz). – MS (75 eV), m/z: 436 $[M^+]$.

$C_{30}H_{44}O_2$ (436.7) Calcd. C 82.52 H 10.16
Found C 82.43 H 10.62

syn-9,17-Di-tert-butyl-12,20-dimethoxy[6.2]metacyclophane (*syn*-**9e**): Pale yellow prisms (methanol), m.p. 97–99°C. – IR (KBr): $\tilde{\nu}$

[cm^{-1}] = 2961, 2920, 2853, 1484, 1458, 1447, 1429, 1392, 1362, 1299, 1244, 1209, 1175, 1104, 1017, 885. – ^{1}H NMR ($CDCl_3$): δ = 0.50–0.60 (1H, m), 0.80–0.92 (1H, m), 1.14 (18H, s), 1.25–1.40 (4H, m), 1.67–1.82 (2H, m), 2.19–2.30 (2H, m), 2.64–2.92 (4H, m), 3.55–3.70 (2H, m), 3.60 (6H, s), 6.72 (4H, s). – MS (75 eV), *m/z*: 436 [M^+].

$C_{29}H_{42}O_2$ (436.7) Calcd. C 82.52 H 10.16
Found C 82.53 H 10.38

Demethylation of **9** *to* **10**. *Typical Procedure:* To a solution of 395 mg (1.0 mmol) of *anti*-**9b** in 10 m of dry CH_2Cl_2 at 0 °C was gradually added a solution of 0.4 ml (4 mmol) of BBr_3 in 2 ml of CH_2Cl_2 over a period of 14 min. After the reaction mixture has been stirred at room temp. for 4 h, it was poured into ice/water, washed with water, dried with Na_2SO_4, and concentrated in vacuo to leave a residue that after column chromatography (silica gel) afforded crude *anti*-**10b**. Recrystallization from methanol gave 303.8 mg (0.83 mmol, 83%).

anti-6,14-Di-tert-butyl-9,17-dihydroxy[3.2]metacyclophane (*anti*-**10b**): Colorless prisms (methanol), m.p. 190–193 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3530, 2950, 2850, 1480, 1445, 1360, 1290, 1188, 880. – ^{1}H NMR ($CDCl_3$): δ = 1.31 (18H, s), 2.15 (2H, s, replaced by D_2O), 2.00–2.17 (2H, m), 2.50–2.85 (8H, m), 7.08 (4H, s). – MS (75 eV), *m/z*: 366 [M^+].

$C_{25}H_{34}O_2$ (366.5) Calcd. C 81.92 H 9.35
Found C 81.81 H 9.36

Similarly, *anti*-**10a**, *anti*-**10c**, *anti*-**10d**, *anti*-**10e**, *syn*-**10b**, and *syn*-**10c** were prepared. The yields are listed in Scheme 3.

anti-5,13-Di-tert-butyl-8,16-dihydroxy[2.2]metacyclophane (*anti*-**10a**): Colorless prisms (methanol), m.p. 267–268 °C (ref.[27] 267–268 °C).

anti-7,15-Di-tert-butyl-10,18-dihydroxy[4.2]metacyclophane (*anti*-**10c**): Colorless prisms (methanol), m.p. 132–135 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3550, 2950, 2880, 1490, 1460, 1365, 1280, 1260, 1195, 1110, 868, 855, 756, 730. – ^{1}H NMR ($CDCl_3$): δ = 1.31 (18H, s), 1.25–1.56 (4H, m), 2.09–2.17 (2H, m), 2.71 (2H, s, replaced by D_2O), 2.74–2.94 (6H, m), 6.92 (2H, d, J = 2.4 Hz), 7.10 (2H, d, J = 2.4 Hz). – ^{1}H NMR ([D_6]DMSO): δ = 1.20–1.30 (4H, m), 1.25 (18H, s), 1.90–1.99 (2H, m), 2.63–2.85 (6H, m), 5.35 (2H, s, replaced by D_2O), 6.69 (2H, d, J = 2.4 Hz), 6.97 (2H, d, J = 2.4 Hz). – MS (75 eV), *m/z*: 380 [M^+].

$C_{26}H_{36}O_2$ (380.6) Calcd. C 82.06 H 9.53
Found C 82.20 H 9.69

anti-8,16-Di-tert-butyl-11,19-dihydroxy[5.2]metacyclophane (*anti*-**10d**): Colorless prisms (methanol), m.p. 108–109 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3527, 3042, 2955, 2928, 2864, 1484, 1461, 1448, 1362, 1287, 1277, 1192, 1155, 816, 756. – ^{1}H NMR ($CDCl_3$): δ = 1.08–1.10 (2H, m), 1.31 (18H, s), 1.32–1.53 (4H, m), 2.09–2.17 (2H, m), 2.72–2.82 (2H, m), 2.92 (4H, s), 3.06 (2H, s, replaced by D_2O), 6.99 (2H, d, J = 2.4 Hz), 7.12 (2H, d, J = 2.4 Hz). – ^{1}H NMR ([D_6]DMSO): δ = 0.96–1.04 (2H, m), 1.25 (18H, s), 1.32–1.40 (4H, m), 1.95–2.08 (2H, m), 2.60–2.72 (4H, m), 2.96–3.00 (2H, s), 5.49 (2H, s, replaced by D_2O), 6.77 (2H, d, J = 2.4 Hz), 7.03 (2H, d, J = 2.4 Hz). – MS (75 eV), *m/z*: 394 [M^+].

$C_{27}H_{38}O_2$ (394.6) Calcd. C 82.18 H 9.71
Found C 82.45 H 10.03

anti-9,17-Di-tert-butyl-12,20-dihydroxy[6.2]metacyclophane (*anti*-**10e**): Colorless prisms (methanol), m.p. 87–89 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3527, 3222, 3046, 2933, 2905, 1458, 1392, 1362, 1299, 1271, 1253, 1242, 1194, 1100, 883, 815, 754. – ^{1}H NMR ($CDCl_3$): δ = 0.85–1.20 (4H, m), 1.32 (18H, s), 1.60–1.70 (4H, m), 2.19–2.30 (2H, m), 2.70–2.82 (2H, m), 2.88–3.10 (4H, m), 3.32 (2H, s, replaced by D_2O), 7.07 (2H, d, J = 2 Hz), 7.09 (2H, d, J = 2 Hz). – MS (75 eV), *m/z*: 408 [M^+].

$C_{28}H_{40}O_2$ (408.6) Calcd. C 82.30 H 9.87
Found C 81.95 H 10.16

syn-6,14-Di-tert-butyl-9,17-dihydroxy[3.2]metacyclophane (*syn*-**10b**): Colorless prisms (methanol), m.p. >188 °C (dec.). – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3100, 2950, 1480, 1358, 1292, 1240, 1190, 1100, 865. – ^{1}H NMR ($CDCl_3$): δ = 1.09 (18H, s), 1.28–1.41 (1H, m), 2.10–2.20 (1H, m), 2.62–2.96 (6H, m), 3.35–3.42 (2H, m), 6.35 (2H, d, J = 2.4 Hz), 6.64 (2H, d, J = 2.4 Hz). – MS (75 eV), *m/z*: 366 [M^+].

$C_{25}H_{34}O_2$ (366.5) Calcd. C 81.92 H 9.35
Found C 81.70 H 9.60

syn-7,15-Di-tert-butyl-10,18-dihydroxy[4.2]metacyclophane (*syn*-**10c**): Colorless prisms (methanol), m.p. 178–183 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3430, 3200, 2940, 2900, 2820, 1480, 1450, 1350, 1284, 1194, 860. – ^{1}H NMR ($CDCl_3$): δ = 1.12 (18H, s), 1.22–1.38 (2H, m), 2.16–2.22 (4H, m), 2.79–2.82 (4H, m), 3.45–3.48 (2H, m), 5.42 (2H, broad s, replaced by D_2O), 6.52 (4H, s). – ^{1}H NMR ([D_6]DMSO): δ = 1.06 (18H, s), 1.92–2.00 (2H, m), 2.11–2.14 (2H, m), 2.61–2.67 (2H, m), 2.81–2.86 (2H, m), 3.37–3.44 (4H, m), 6.41 (2H, d, J = 2.4 Hz), 6.44 (2H, d, J = 2.4 Hz), 7.88 (2H, broad s, replaced by D_2O). – MS (75 eV), *m/z*: 380 [M^+].

$C_{26}H_{36}O_2$ (380.6) Calcd. C 82.06 H 9.53
Found C 82.14 H 9.58

syn-8,16-Di-tert-butyl-11,19-dihydroxy[5.2]metacyclophane (*syn*-**10d**): ^{1}H NMR ([D_6]DMSO): δ = 1.07 (18H, s), 1.74–1.80 (2H, m), 1.94–2.02 (2H, m), 2.46–2.53 (4H, m), 2.65–2.79 (4H, m), 3.39–3.46 (2H, m), 6.54 (2H, d, J = 2.4 Hz), 6.60 (2H, d, J = 2.4 Hz), 7.07 (2H, broad s, replaced by D_2O).

trans-tert-Butylation of anti-**10** *to anti*-**11**. *Typical Procedure:* To a solution of 150 mg (0.409 mmol) of *anti*-**10b** in 6 ml of benzene was added a solution of 412 mg (3.09 mmol) of anhydrous aluminium chloride in 0.6 ml of nitromethane. After the reaction mixture has been stirred for 24 h at room temp., the reaction was quenched by the addition of 10% hydrochloric acid, and the solution was washed with water, dried with Na_2SO_4, and concentrated in vacuo to leave a residue that after recrystallization from hexane/benzene (1:1) furnished 86.3 mg (0.34 mmol, yield 83%) of *anti*-**11b**. The formation of *tert*-butylbenzene (**12**) was confirmed by GLC.

anti-9,17-Dihydroxy[3.2]metacyclophane (*anti*-**11b**): Colorless prisms (hexane/benzene, 1:1), m.p. 131–134 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3540, 2950, 2920, 2850, 1580, 1470, 1450, 1438, 1260, 1190, 1170, 1084, 785, 745. – ^{1}H NMR ($CDCl_3$): δ = 2.05–2.14 (2H, m), 2.60 (2H, s, exchanged by D_2O), 2.49–2.87 (8H, m), 6.90–7.10 (6H, m). – MS (75 eV), *m/z*: 254 [M^+].

$C_{17}H_{18}O_2$ (254.3) Calcd. C 80.28 H 7.13
Found C 80.03 H 8.04

Similarly, *anti*-**11a** and *anti*-**11c** were prepared in the same manner as described above. The yields are compiled in Scheme 4.

anti-8,16-Dihydroxy[2.2]metacyclophane (*anti*-**11a**): Pale yellow prisms (hexane), m.p. 223–228 °C (ref.[27] 223–228 °C).

anti-10,18-Dihydroxy[4.2]metacyclophane (*anti*-**11c**): Colorless prisms (methanol), m.p. 81–84 °C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3462, 2962, 2920, 2865, 1473, 1447, 1262, 1177, 1074, 746. – ^{1}H NMR ($CDCl_3$): δ = 1.30–1.60 (4H, m), 2.10–2.22 (2H, m), 2.70–3.00 (6H, m), 3.06 (2H, s, exchanged by D_2O), 6.84–7.15 (6H, m). – MS (75 eV), *m/z*: 268 [M^+].

$C_{18}H_{20}O_2$ (268.4) Calcd. C 80.56 H 7.51
Found C 80.20 H 7.69

Table 5. Crystallographic data and data-collection details for compounds **8d** and *anti*-**9e**

8d, formula: $C_{29}H_{42}O_4S$; mol. mass: 486.72; crystal size: 0.32 x 0.07 x 0.14 mm; space group: *P*-1; *Z* = 2; *a* = 1012.2, *b* = 1439.4, *c* = 996.2 pm; α = 90.63°, β = 92.28°, γ = 74.60°; *V* = 1398.16 x 10^{-30} m^3; D_c = 1.156 gm^{-3}; radiation: Cu-K_α ; total no. of unique reflections: 3518; R = 0.068, R_w = 0.091.

anti-**9e**, formula: $C_{30}H_{44}O_2$; mol. mass: 436.68; crystal size: 0.2 x 0.23 x 0.3 mm; space group: *P*2_1/*a*; *Z* = 4; *a* = 1243.9, *b* = 2243.3, *c* = 998.2 pm; α = 90.00°, β = 89.99°, γ = 90.00°; *V* = 2785.49 x 10^{-30} m^3; D_c = 1.041 gm^{-3}; radiation: Cu-K_α ; total no. of unique reflections: 1923; R = 0.098, R_w = 0.117.

*trans-tert-Butylation of syn-***10b** *to* **13**: To a solution of 150 mg (0.409 mmol) of *syn*-**10b** in 6 ml of benzene was added a solution of 412 mg (3.09 mmol) of anhydrous aluminium chloride in 0.6 ml of nitromethane. After the reaction mixture had been stirred at room temp. for 24 h, the reaction was quenched by the addition of 10% hydrochloric acid, and the solution was washed with water, dried with Na_2SO_4, and concentrated in vacuo to leave a residue that after column chromatography (silica gel, benzene) afforded crude **13**. Sublimation and recrystallization from methanol gave 76 mg (0.309 mmol, yield 76%) of **13**.

9,17-Epoxy[3.2]metacyclophane (**13**): Colorless prisms (methanol), m.p. 94–98°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2922, 2899, 2851, 1468, 1460, 1433, 1424, 1265, 1207, 1184, 885, 877. – ^1H NMR ($CDCl_3$): δ = 1.30–1.40 (1H, m), 2.33–2.42 (1H, m), 2.68–2.81 (4H, m), 3.24–3.33 (2H, m), 3.55–3.63 (2H, m), 6.90–6.99 (6H, m). – MS (75 eV), *m/z*: 236 [M^+].

$C_{17}H_{16}O$ (236.3)	Calcd.	C 86.41 H 6.82
	Found	C 86.61 H 6.85

Table 6. Atomic coordinates for the non-hydrogen atoms of **8d** with their estimated standard deviations in parentheses and the isotropic equivalent displacement parameters $B_{eq} = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ac(\cos\beta)B_{13}]$

atom	x	y	z	B_{eq}
S(1)	0.9311(1)	0.34972(7)	0.44359(8)	3.49(5)
S(8)	0.7617(3)	0.3753(2)	0.7903(3)	2.8(2)
C(2)	0.6339(3)	0.1643(2)	0.5293(3)	3.1(2)
C(11)	1.0294(3)	0.3509(2)	0.8942(3)	2.9(2)
C(6)	0.8656(3)	0.1851(2)	0.5480(3)	3.0(2)
C(1)	0.7357(3)	0.2051(2)	0.4851(3)	3.2(2)
C(10)	0.9271(3)	0.3338(2)	0.9721(3)	3.2(2)
C(12)	0.9934(3)	0.3819(2)	0.7627(3)	2.9(2)
C(4)	0.7983(4)	0.0762(2)	0.7008(4)	3.5(2)
C(5)	0.8950(3)	0.1210(2)	0.6559(3)	3.2(2)
C(7)	0.8605(3)	0.3929(2)	0.7090(3)	3.5(2)
C(3)	0.6689(4)	0.1004(3)	0.6357(4)	3.6(2)
C(9)	0.7930(3)	0.3451(2)	0.9235(3)	3.0(2)
C(13)	0.9768(4)	0.2282(3)	0.5021(4)	3.6(2)
O(2)	0.6282(2)	0.3854(2)	0.7379(2)	3.3(1)
O(3)	1.0588(3)	0.3765(2)	0.4413(3)	4.6(2)
O(1)	1.0230(2)	0.1034(2)	0.7228(2)	3.9(1)
O(4)	0.8496(3)	0.3568(2)	0.3198(2)	5.2(2)
C(14)	0.8233(3)	0.4217(3)	0.5646(3)	3.3(2)
C(21)	1.1783(4)	0.3316(3)	0.9503(4)	3.6(2)
C(17)	0.4904(4)	0.1930(3)	0.4604(4)	3.9(2)
C(15)	1.1263(4)	0.0260(3)	0.6665(4)	4.9(2)
C(16)	0.5414(4)	0.4811(3)	0.7486(5)	5.3(3)
C(18)	0.3886(4)	0.1490(4)	0.5275(6)	6.5(3)
C(19)	0.4362(5)	0.3017(4)	0.4622(7)	8.5(4)
C(22)	1.1824(5)	0.3698(5)	1.0935(5)	7.8(4)
C(23)	1.2420(5)	0.2247(4)	0.9473(7)	8.7(4)
C(20)	0.4993(5)	0.1542(5)	0.3158(5)	8.5(4)
C(24)	1.2620(5)	0.3811(5)	0.8689(6)	9.1(5)
C(26)	0.6605(4)	0.2230(3)	0.9678(4)	4.6(2)
C(25)	0.6865(4)	0.3210(3)	1.0091(4)	4.0(2)
C(27)	0.7808(5)	0.1368(3)	0.9974(4)	5.4(3)
C(29)	0.8302(4)	0.0061(3)	0.8171(4)	4.8(2)
C(28)	0.7576(5)	0.0425(4)	0.9462(5)	6.3(3)

*trans-tert-Butylation of syn-***10c** *to syn-***11c**: To a solution of 150 mg (0.409 mmol) of *syn*-**10c** in 6 ml of benzene was added a solution of 412 mg (3.09 mmol) of anhydrous aluminium chloride in 0.6 ml of nitromethane. After the reaction mixture had been stirred at room temp. for 24 h, the reaction was quenched by the addition of 10% hydrochloric acid, and the solution was washed with water, dried with Na_2SO_4, and concentrated in vacuo to leave a residue that after column chromatography (silica gel, benzene) afforded crude **12**. Sublimation and recrystallization from methanol gave 42.7 mg (0.159 mmol, yield 39%) of *syn*-**11c**.

syn-10,18-Dihydroxy[4.2]metacyclophane (*syn*-**11c**): Colorless prisms (hexane), m.p. 136–140°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3250, 2920, 2855, 1465, 1450, 1370, 1240, 1210, 1205, 1070, 755, 735. – ^1H NMR ($CDCl_3$): δ = 1.24–1.42 (2H, m), 2.13–2.20 (4H, m), 2.80–2.87 (4H, m), 3.39–3.46 (2H, m), 5.33 (2H, broad s, replaced by D_2O), 6.40–6.56 (6H, m). – MS (75 eV), *m/z*: 268 [M^+].

$C_{18}H_{20}O_2$ (268.4)	Calcd.	C 80.56 H 7.51
	Found	C 80.36 H 7.43

Estimation of the Activation Energy of the Ring Flipping: The rate constant (k_c) of the observed conformational interconversion at the coalescence (T_c) can be calculated by using eq. (1)[28]. The free energy of activation ($\Delta G_c^{\ddagger}$) at coalescence can be estimated by using the Eyring equation (eq. (2))[28].

$$k_c = (\pi/2)^{1/2}(\Delta\nu^2 + 6J^2)^{1/2} \qquad (1)$$

$$\Delta G_c^{\ddagger} = 2.303\,RT_c(10.32 + \lg T_c - \lg k_c) \qquad (2)$$

Crystal Structure Analysis of **8d** *and anti-***9e**: The space groups were determined from single-crystal photographs. The unit cell constants were derived from least-squares analysis of the settings of a Rigaku AFC5 diffractometer for twelve or more reflections, mostly

Table 7. Atomic coordinates for the non-hydrogen atoms of *anti*-**9e** with their estimated standard deviations in parentheses and the isotropic equivalent displacement parameters $B_{eq} = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ac(\cos\beta)B_{13}]$

atom	x	y	z	B_{eq}
C(1)	0.7315(5)	-0.0707(3)	0.3302(7)	4.5(4)
C(2)	0.8155(5)	-0.1089(3)	0.2892(7)	4.6(3)
C(4)	0.6988(6)	-0.1522(3)	0.1202(8)	5.4(4)
C(3)	0.7957(6)	-0.1484(3)	0.1858(8)	5.4(4)
C(5)	0.6199(5)	-0.1114(3)	0.1616(8)	5.5(4)
C(7)	0.7960(5)	0.1480(3)	0.3133(7)	5.5(4)
C(9)	0.7318(5)	0.0713(3)	0.1711(7)	5.1(4)
C(8)	0.8146(5)	0.1086(3)	0.2090(7)	4.9(3)
C(10)	0.6970(6)	0.1516(3)	0.3795(7)	5.6(4)
C(11)	0.6200(5)	0.1121(3)	0.3421(7)	5.4(4)
O(1)	0.7462(3)	-0.0317(2)	0.4339(5)	6.0(3)
O(2)	0.7468(3)	0.0315(2)	0.0667(6)	6.2(3)
C(12)	0.6340(5)	-0.0714(3)	0.2625(8)	4.8(4)
C(13)	0.6324(5)	0.0711(3)	0.2368(7)	5.2(4)
C(16)	0.9980(5)	-0.0248(3)	0.1998(7)	5.9(4)
C(17)	0.9981(5)	0.0248(3)	0.3030(7)	5.5(4)
C(19)	0.9255(5)	0.1056(3)	0.1451(7)	5.1(3)
C(20)	0.5448(5)	-0.0270(3)	0.2961(8)	6.0(4)
C(21)	0.5455(5)	0.0272(3)	0.2049(8)	5.9(4)
C(15)	1.0129(5)	-0.0868(3)	0.2571(8)	6.3(4)
C(14)	0.9244(5)	-0.1062(3)	0.3550(7)	5.7(4)
C(18)	1.0146(5)	0.0865(3)	0.2416(8)	5.8(4)
C(29)	0.6781(7)	0.1974(3)	0.4924(9)	7.4(5)
C(22)	0.6759(7)	-0.1969(4)	0.007(1)	7.2(5)
C(30)	0.7184(6)	-0.0570(5)	0.5637(8)	9.0(6)
C(31)	0.7183(7)	0.0572(5)	-0.059(1)	9.3(6)
C(24)	0.768(1)	-0.2392(6)	-0.018(1)	17(1)
C(27)	0.765(1)	0.2393(6)	0.514(1)	17(1)
C(28)	0.581(1)	0.2326(8)	0.454(2)	25(2)
C(26)	0.648(2)	0.1661(6)	0.617(1)	20(1)
C(23)	0.583(1)	-0.2339(8)	0.041(2)	23(1)
C(25)	0.657(2)	-0.1660(6)	-0.118(1)	23(2)

in the range $100^\circ < 2\Theta < 130^\circ$. The intensities of all independent reflections with $2\Theta < 130^\circ$ were measured with $\Theta - 2\Theta$ scans of width $(1.5 + 0.285 \tan \Theta)$; Ni-filtered Cu-$K_\alpha$ radiation ($\lambda = 1.54178$ Å) was used.

The structure was solved by direct methods (TEXAN Version 2.0, MJ201SP) which also used for refinement calculations.

The parameters refined were atomic coordinates, temperature factors (anisotropic for carbon atoms), scale factor, and secondary extinction coefficient. Results in Tables 5–7.

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CAS Registry Numbers

4b: 108656-63-9 / **4c**: 132098-45-4 / **4d**: 132098-46-5 / **4e**: 132098-47-6 / **5**: 41280-65-3 / **6a**: 76447-56-8 / **6b**: 125665-98-7 / **6c**: 143105-48-0 / **6d**: 143105-49-1 / **6e**: 143105-50-4 / **7a**: 143105-51-5 / **7b**: 143105-52-6 / **7c**: 143105-53-7 / **7d**: 143105-54-8 / **7e**: 143105-55-9 / **8a**: 143105-56-0 / **8b**: 143105-57-1 / **8c**: 143105-58-2 / **8d**: 143105-59-3 / **8e**: 143105-60-6 / *anti*-**9a**: 72523-20-1 / *anti*-**9b**: 143105-61-7 / *syn*-**9b**: 143168-60-9 / *anti*-**9c**: 143121-03-3 / *syn*-**9c**: 143105-62-8 / *anti*-**9d**: 143105-63-9 / *syn*-**9d**: 143105-64-0 / *anti*-**9e**: 143105-65-1 / *syn*-**9e**: 143105-66-2 / *anti*-**10a**: 71777-27-0 / *anti*-**10b**: 143168-61-0 / *syn*-**10b**: 143105-67-3 / *anti*-**10c**: 143168-62-1 / *syn*-**10c**: 143105-68-4 / *anti*-**10d**: 143168-63-2 / *syn*-**10d**: 143105-69-5 / *anti*-**10e**: 143168-64-3 / *anti*-**11a**: 81688-21-3 / *anti*-**11b**: 143105-70-8 / *anti*-**11c**: 143105-71-9 / *syn*-**11c**: 143168-65-4 / **13**: 143121-04-4 / $\mathrm{Br(CH_2)_3Br}$: 109-64-8 / $\mathrm{Br(CH_2)_4Br}$: 110-52-1 / $\mathrm{Br(CH_2)_5Br}$: 111-24-0 / $\mathrm{Br(CH_2)_6Br}$: 629-03-8