Medium-sized cyclophanes. Part 52:† synthesis and structures of [2.*n*]metacyclophane-1,2-diones

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A series of *syn*- and *anti*-[2.*n*]metacyclophan-1-enes, **3**, and [2.*n*]metacyclophane-1,2-diols, **4**, were prepared in good yields by a McMurry cyclization of 1,*n*-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)alkanes, **2**. Upon increasing the length of the methylene bridge higher yields of **3** were obtained. The assignment of the *syn* and *anti* conformations has been confirmed by ^{1}H-NMR analyses. The 1,2-diol derivatives **4** were converted to the 1,2-diones **9** by Swern oxidation. However, [2.2]metacyclophane-1,2-dione, **9a**, was found to be quite labile under treatment by silica gel column chromatography and on refluxing in toluene to give the dicarboxylic acid **10** in quantitative yield. Thus, a trapping reaction of diketone **9a** was attempted, in which the crude diketone **9a** was treated with *o*-phenylenediamine in ethanol at room temperature for 24 h to afford in almost quantitative yield the desired [2.2]metacyclophane **11** having a quinoxaline skeleton. Similarly, in the case of [2.3]- and [2.4]metacyclophanes, Swern oxidation of the *trans*-diols *trans*-**4b,c** also afforded the desired diketones **9b,c** in quantitative yields as stable yellow prisms.

For many years various research groups have been attracted by the chemistry and spectral properties of [2.2]MCP ([2.2]MCP = [2.2]metacyclophane) skeleton.[2,3] Its conformation, which was elucidated by X-ray measurements,[4] is frozen into a chair-like non-planar form. Many attempts have been made to directly introduce functional groups into the methylene groups of [2.2]MCPs, but these have failed because of the deviation of the benzyl carbon atom from the plane of the benzene ring.[5]

Singler and Cram have reported that bromination of [2.2]paracyclophan-1-ene with bromine affords the corresponding *cis* adduct.[6] We have reported that di-*tert*-butyldimethyl[2.*n*]MCP-1-enes were treated with an equimolar amount of benzyltrimethylammonium tribromide (BTMA Br_3) in methylene dichloride to afford the *cis* adducts to the bridged double bond.[7–9] This result indicates the first success in the introduction of two bromo groups into the methylene groups of dimethyl[2.*n*]MCPs. We have extended the novel reaction mentioned above and reported on the acetolysis of bromine adducts with silver acetate in acetic acid and the conversion to dimethyl[2.*n*]MCP-1,2-diones *via* hydrolysis followed by Swern oxidation of the dihydroxy derivatives.[10]

However, we have not yet succeeded in preparing [2.2]MCP-1,2-dione due to the novel transannular reaction arising from the electronic interaction between two benzene rings, the proximity of the 8,16-positions and the release of the considerable strain energy to form the more stable annulene π-electron system, 10b,10c-dihydropyrene. Thus, the reaction of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP-1-ene[7] with bromine affords 4,5,9,10-tetrabromo-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene in good yield, but not the adduct to the bridged double bond, which can be converted to the corresponding [2.2]MCP-1,2-dione.[8]

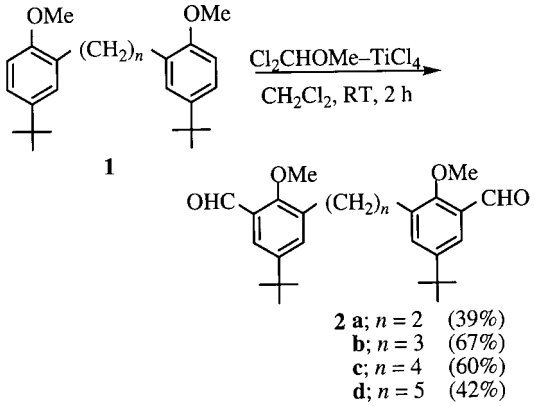
† Part 51: ref. 1.

On the other hand, in cyclophane chemistry, the reductive coupling of carbonyl compounds by low-valent titanium, the McMurry reaction,[11] has been used before by Mitchell and Weerawarna[12] to synthesize cyclophanes with glycol units as bridges. The McMurry reaction has also been used by Tanner and Wennerström,[13] and more recently by Hopf and Mlynek[14] and by Grützmacher and Neumann[15] to cyclize suitable dialdehydes to yield unsaturated cyclophanes. Thus, there is substantial interest in developing a more convenient preparation of [2.*n*]MCP-1-enes or -1,2-diols than the conventional sulfur method.[7–9] We report here on the use of the McMurry coupling reaction to prepare a series of [2.*n*]MCP-1,2-diols with internal methoxy substituents and their conversion to 1,2-diones by Swern oxidation.[16]

Results and discussion

The starting compounds, 1,*n*-bis(5-*tert*-butyl-2-methoxyphenyl)alkanes, **1**, are easily prepared in three steps from anisole by using the *tert*-butyl group as a positional protective group on the aromatic ring.[17] Formylation of **1** with dichloromethyl methyl ether in the presence of titanium tetrachloride in methylene dichloride at room temperature for 2 h yields 1,*n*-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)alkanes, **2**, in moderate yields (Scheme 1).

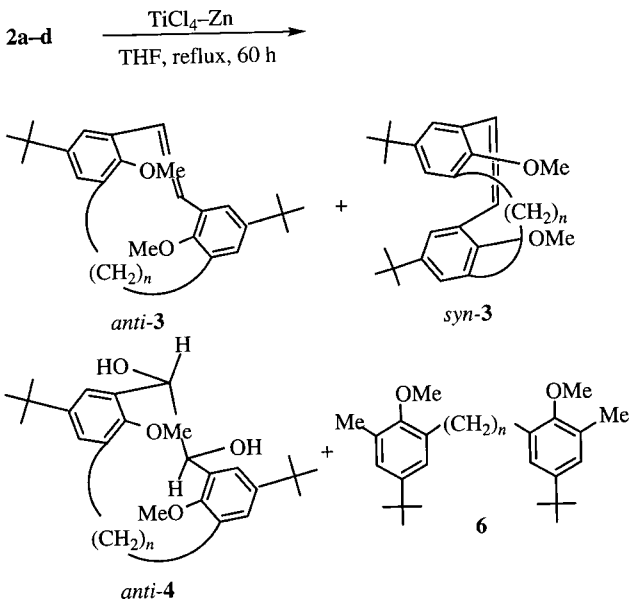
1,2-Bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)ethane, **2a**, was subjected to reductive coupling by the McMurry reaction following Grützmacher's procedure[15] (Scheme 2, Table 1). Although none of the desired [2.2]MCP-1-ene **3a** was observed, *anti*-[2.2]MCP-diol *anti*-**4a** was obtained in 18% yield along with a small amount of the dimer **5** and 1,2-bis(5-*tert*-butyl-2-methoxy-3-methylphenyl)ethane, **6a**. The same reaction in the presence of pyridine increased the yield of diol *anti*-**4a** to 68% from 18%, but the formation of [2.2]MCP-1-ene **3a** was not observed. This finding seems to be due to the much more strained structure of **3a** than diol **4a** during the



Scheme 1

formation of the unsaturated C=C linkage. Thus, during the McMurry reaction the deoxygenation of the diol to form the double bond might be quite difficult.

The structures of products *anti*-**4a** and **5** were determined on the basis of their elemental analyses and spectral data. Thus, we previously assigned[18] the ^{1}H-NMR signals of 1-*exo*-5,13-trichloro-8,16-dimethyl[2.2]MCP. We have assigned the ^{1}H-NMR signals of **4a** in a similar fashion. For example, the ^{1}H-NMR spectrum of **4a** shows two internal methoxy resonances as a singlet at δ 2.93, a bridge methine signal as a singlet at δ 4.51, and two aromatic protons as a pair of doublets at δ 7.09 and 7.40 (J = 2.5 Hz); the latter protons are in a strongly deshielding region of the oxygen atom of *endo*-OH on the ethylene bridge. The structure of the *anti*-conformer is also readily assigned from the chemical shift of the methoxy



Scheme 2

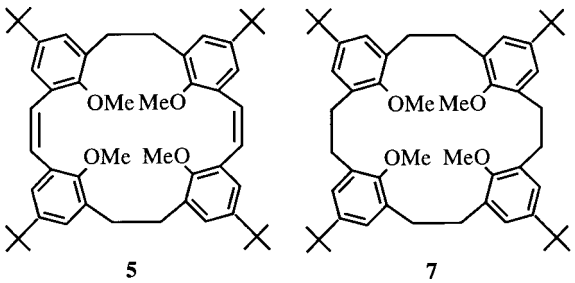
Table 1 McMurry reaction of 1,*n*-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)alkanes, **2a**–**2d**

		Product yield/%[a]			
Substrate	*n*	*anti*-**3**	*syn*-**3**	*anti*-**4**	**6**
2a	2[c]	0	0	18.3	3.2
2a[b]	2[c]	0	0	68.0	4.0
2b	3	0	1.0	29.1	2.0
2c	4	2.1	2.0	56.5	0
2d	5	0	27.4	15.3	0

[a] Isolated yields. [b] The reaction was carried out in the presence of pyridine. [c] The dimer (*Z*,*Z*)-**5** was obtained in 0.4 and 0.6% yields, respectively.

protons at δ 2.93. Thus, the methoxy protons should show an upfield shift due to the ring current of the opposite aromatic ring.[19] These data strongly support the assignment of both OH groups to *endo*-arrangement and therefore, *anti*-**4a** is found to be a *trans*-diol.

The mass spectral data for dimer **5** (M^+ m/z = 756) strongly support a cyclic dimeric structure. In the ^{1}H-NMR spectrum of tetramethoxyMCP **5**, protons of the *tert*-butyl and methoxy groups, ArCH_2CH_2Ar methylene protons, and the ArCH=CHAr olefinic protons each appear as a singlet at 27 °C. This behavior indicates that the rate of conformational ring flipping of macrocycle **5** is faster than the NMR time scale above this temperature. However, in dimer **5**, even at −60 °C in $CDCl_3$, the singlet signal of the ArCH_2CH_2Ar-ethylene protons and the ArCH=CHAr olefinic protons both remain unsplit. These observations indicate the flexible structure of **5**. In comparison with the corresponding tetramethoxy[2.2.2.2]MCP **7**,[20] the ring size of **5** is smaller and the methoxy group might come in close proximity to the aromatic ring and thus the signal of the methoxy group might shift to higher field. However, in fact the methoxy signal of [2.2.2.2]diene **5** appears around δ 3.51 and that of [2.2.2.2]MCP **7** resonates at δ 2.9. These findings might indicate that the conformation of **5** is quite different from that of **7** due to the two additional double bonds of the ethylene bridge.



The X-ray crystallographic analysis of **5** clearly shows that the four methoxy groups are located on the same side of the ring and that the two double bond adopt *cis*-configurations, resulting in a cone-conformation like *tert*-butylcalix[4]arene.[21] These results seem to indicate that the double bonds in **5** play an important role in the fixation of the conformation in the solid state (Fig. 1).

Similar McMurry cyclization of bis(formyl)diphenylpropane, **2b**, carried out under the same reaction conditions afforded diol *anti*-**4b** in 29% yield, along with trace amounts of *syn*-[2.3]MCP-1-ene, *syn*-**3b**, and 1,3-bis(5-*tert*-butyl-2-methoxy-3-methylphenyl)propane, **6b**. The same results were obtained in the case of bis(formyl)diphenylbutane, **2c**, except that two types of [2.4]MCP-1-enes, *anti*- and *syn*-**3c**, were formed. Interestingly, the increased and preferential formation

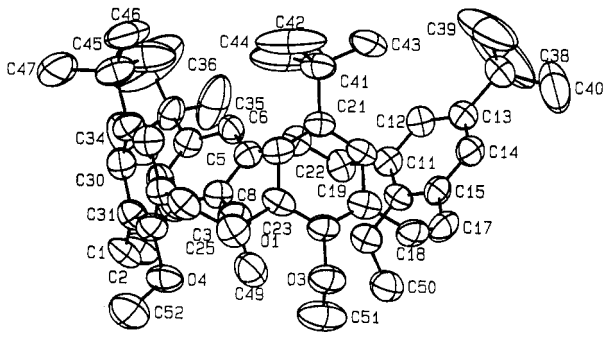


Fig. 1 Ortep drawing of 5,13,21,29-tetra-*tert*-butyl-8,16,24,32-tetramethoxy[2.2.2.2]MCP-1,18-diene, **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

of *syn*-[2.5]MCP-1-ene, *syn*-**3d**, in 27% yield was observed in the similar McMurry cyclization of bis(formyl)-diphenylpentane, **2d**. With increasing length of the methylene bridge higher yields of [2.*n*]MCP-1-enes were obtained. This finding seems to support the notion that the strain of the [2.2]MCP-1-ene compared to the higher [2.*n*]MCP-1-enes decreases as the length of the methylene bridge increases.

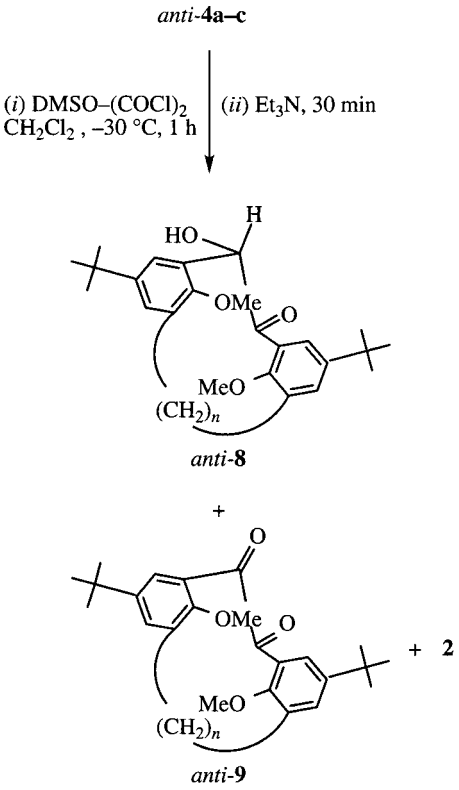
The structures of products **3b** and **3c** were determined on the basis of their elemental analyses and spectral data. For example, the ^{1}H-NMR spectrum of **3c** shows two kinds of methoxy protons, each as a singlet. By careful column chromatography (silica gel, Wako C-300), two conformers, *anti*-**3c** and *syn*-**3c**, were 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 spectra of conformers *anti*-**3c** and *syn*-**3c** respectively show the methoxy protons at δ 3.26 and 3.70. The aromatic protons of conformer *syn*-**3c** are observed at much higher field (δ 6.46, 6.56) than those of conformer *anti*-**3c** at δ 6.80 and 6.95, due to the ring current effect by the adjacent benzene ring,[22] a common consequence of face-to-face benzene rings. Also the *tert*-butyl protons of *syn*-**3c** were observed at higher field, δ 1.10, due to the strong shielding effect of the benzene ring. The above data show that the structure of *anti*-**3c** is the *anti*-conformer, whereas the structure of *syn*-**3c** is the *syn*-conformer. Chemical shifts similar to those of *syn*-**3c** were observed in *syn*-**3b** and *syn*-**3d**.

Although the parent [2.2]MCP was first reported as early as 1899 by Pellegrin,[23] the synthesis of *syn*-[2.2]MCP was not realized until 85 years later. Mitchell *et al.*[24] 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. Finally, Itô *et al.*[25] have isolated and characterized *syn*-[2.2]MCP without complexation. However, the preparation of internally substituted *syn*-[2.*n*]MCP-1-enes having internal substituents has not been published so far. We have thus accomplished for the first time the preparation of a series of *syn*-[2.3]-, *syn*-[2.4]- and *syn*-[2.5]MCP-1-enes, *syn*-**3b–d**. Also we have developed the convenient preparation of [2.*n*]MCPs **4** having a 1,2-diol unit on the ethylene bridge.

The ^{1}H-NMR spectrum of **4b** shows two internal methoxy protons as a singlet at δ 3.07, a bridged methine proton as a singlet at δ 4.53, and two aromatic protons as a set of doublets at δ 7.03 and 7.43 (J = 2.4 Hz). The higher field shift for the methoxy protons strongly supports the structure of **4b** as the *anti*-conformer. A deshielded aromatic proton was observed in the NMR spectrum of **4b** at δ 7.43, which is almost the same as that for the *endo*-OH arrangement of **4a** (δ 7.40). Similar findings were observed in the higher analogues **4c** and **4d**. On the basis of the spectral data, the two OH groups of **4b–d** are both in *endo*-arrangement as in **4a** and therefore, all of the diols *anti*-**4** are found to be *trans*-diol.

Although Mitchell and Weerawarna reported the first preparation of [2.2]MCP-1,2-dione from oxidation of the corresponding [2.2]MCP-1,2-diol,[12] the physical and chemical properties have not been established so far. Thus, there is substantial interest in the oxidation of [2.*n*]MCPs **4** having a 1,2-diol to afford [2.*n*]MCP-1,2-diones.

An attempted oxidation of the *trans*-diol *anti*-**4a** to the 1,2-dione *anti*-**9a** with pyridinium chlorochromate carried out in a methylene dichloride solution under the same reaction conditions as described above failed. Only the cleavage reaction product, the dialdehyde **2a** was obtained in 90% yield. This finding seems to support the strained nature of the diketone *anti*-**9a**. Fortunately, Swern oxidation[16] of *anti*-**4a** succeeded in affording the desired [2.2]MCP diketone *anti*-**9a** in 12% yield only, along with [2.2]MCP monoketone *anti*-**8a** and ring cleavage reaction product **2a** in 58 and 28% yields, respectively (Scheme 3, Table 2). Prolonging the reaction time to 24 h at room temperature under the same reaction conditions



Scheme 3

resulted only a mixture of *anti*-**8a** and *anti*-**9a** in almost the same ratio. This finding seems to support the strained nature of the diketone **9a** compared to the monoketone **8a**, in spite of these having the same ring size.

However, this diketone *anti*-**9a** was found to be quite labile under treatment by silica gel column chromatography and on refluxing in toluene to afford dicarboxylic acid **10** in quantitative yield. Thus, a trapping reaction of *anti*-**9a** with *o*-phenylenediamine was attempted, in which the crude diketone *anti*-**9a** was treated with *o*-phenylenediamine in ethanol at room temperature for 24 h to afford in almost quantitative yield the desired [2.2]MCP *anti*-**11** having a quinoxaline skeleton (Scheme 4).

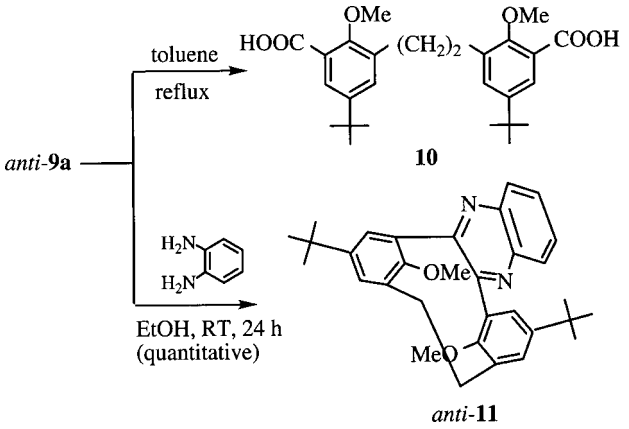
In contrast, in the case of [2.3]- and [2.4]MCPs, similar Swern oxidation of the *trans*-diols *anti*-**4b** and *anti*-**4c** also succeeded in affording the desired diketones *anti*-**9b** and *anti*-**9c** in 92 and 100% yields, respectively, as stable yellow prisms. This finding seems to support the notion that the strain of the [2.2]MCP diketone *anti*-**9a** compared to the [2.3]- and [2.4]MCP diketones *anti*-**9b** and *anti*-**9c** increases as the length of the methylene bridge decreases.

The structures of the diketones *anti*-**9a–c** were assigned on the basis of elemental analyses and spectral data. The internal methoxy protons and aromatic protons in the ^{1}H-NMR spectrum and the carbonyl frequency in the IR spectrum are tabulated in Table 3.

Table 2 Swern oxidation of [2.*n*]MCP-1,2-diols, *anti*-**4a–c**

Substrate	*n*	Product yield/%[a,b]		
		anti-**8**	*anti*-**9**	**2**
4a	2	58	12(8)	28
4b[c]	3	0	92(85)	0
4c	4	0	100(95)	0

[a] Relative yields were determined by ^{1}H-NMR spectroscopy. [b] Isolated yields are shown in parentheses. [c] The starting compound **4b** was recovered in 8% yield.



Scheme 4

The ^{1}H-NMR spectrum of *anti*-**8a** shows internal methoxy protons as singlets at δ 2.93 and 3.04, a bridged methine proton as a singlet at δ 4.33, and two aromatic protons as two sets of doublets at δ 7.09, 7.34 and 7.28, 7.32 (J = 2.4 Hz). We observed one of the methoxy protons to be deshielded by the carbonyl group on the ethylene bridge resulting in a downfield shift (δ 3.04 ppm). A deshielded aromatic proton was observed at δ 7.34 due to the *endo*-OH oxygen atom on the ethylene bridge, which is almost the same as that for the *endo*-OH arrangement of **4a** (δ 7.40).

The higher frequency of the C=O stretching vibration in the IR spectrum for **9a** (1678 cm^{-1}) in comparison with that for the reference compound benzil, **12** (1662 cm^{-1}), presumably reflects the deviation of the carbonyl group from the plane of the benzene ring rather than conjugation between the carbonyl group and the benzene ring. This finding is similar to those for the strained [2.2]paracyclophan-1-ones,[6,26] and [2.2]metacyclophan-1-ones,[27] for which absorptions are toward wavelengths characteristic of unconjugated ketones due to the expanded O–C–C bond angles. A similar high frequency was observed in the next member of the series, [2.3]MCP-1,2-dione **9b** (1675 cm^{-1}), but increasing by one the methylene bridge, the C=O stretching vibration appears at the normal position in [2.4]MCP-1,2-dione, **9c** (1667 cm^{-1}).

The UV spectra of the diketones **9a–c** along with that of the reference compound benzil, **12**, in cyclohexane are shown in Fig. 2. The UV spectra of the diketones **9** show different absorption curves than that of the model acyclic compound. The lack of a benzil-type chromophore in the UV spectra of the MCP ketones confirms the non-planarity of the aromatic ring and carbonyl group.

Bathochromic shifts were observed for the cyclophane diketones **9a–c**, which are ascribed to a transannular interaction between the two benzene rings and an increase in the strain of these systems.[28] With decreasing length of the methylene bridge red shifts of the absorption derived from n–π* transition were obtained. This supports the notion that the strain in the MCP-1,2-diones decreases as the length of the methylene bridge increases.

Single-crystal X-ray diffraction structures of the diketones *anti*-**9a** and *anti*-**9b** are shown in Fig. 3 and 4. For clarity all

Table 3 Spectral data of [2.*n*]MCP-1,2-diones (*anti*-**9a–c**)

		NMR/δ^a			
Compound	n	Methoxy protons	Aromatic Ha	Protons Hb	IR $\upsilon_{C=O}$/cm^{-1}
anti-**9a**	2	3.11	7.32	7.34	1678
anti-**9b**	3	3.19	7.33	7.49	1675
anti-**9c**	4	3.28	7.16	7.83	1667

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

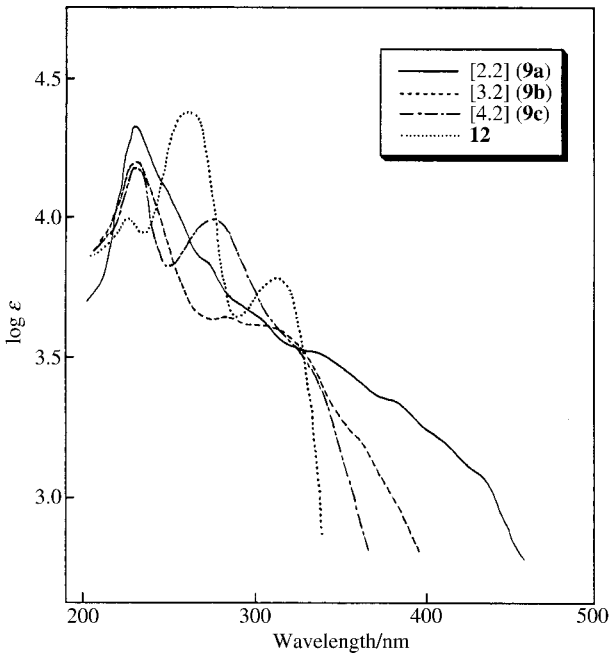


Fig. 2 UV absorption spectra of [2.*n*]MCP ketones **9** and benzil, **12**, in cyclohexane.

hydrogen atoms are not shown. The structures were solved by direct methods and refined using standard least-squares and Fourier techniques.

Compound *anti*-**9a** crystallized in the centrosymmetric space group $P2_1/a$. In contrast, compound *anti*-**9b** crystallized in the centroasymmetric space group Pa and there are two independent molecules (Z = 4) at general positions in the asymmetric unit of the crystal structure. Thus, one molecule is selected and depicted in Fig. 4. It is clear that both *anti*-**9a** and *anti*-**9b** adopt the *anti* conformation in which two benzene rings are in a non-planar chain form. In *anti*-**9a** the benzene

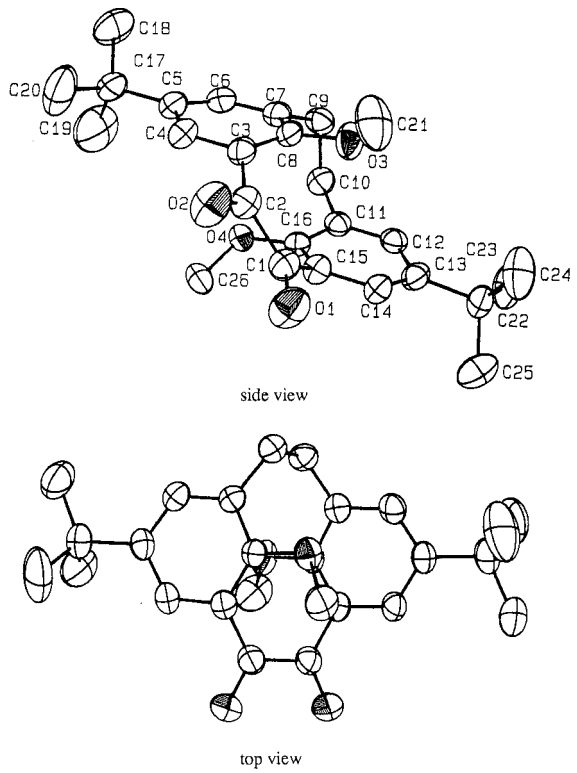


Fig. 3 Ortep drawing of *anti*-5,13-di-*tert*-butyl-8,16-dimethoxy[2.2]MCP-1,2-dione, *anti*-**9a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

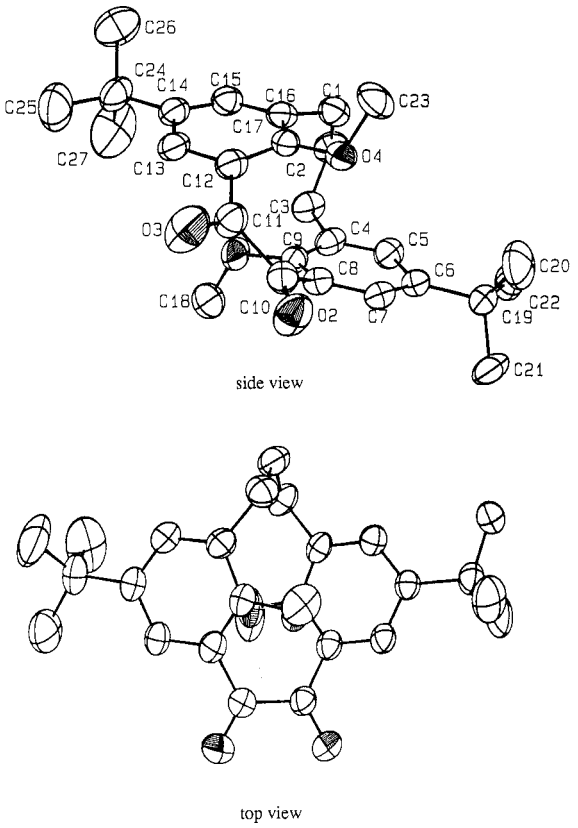


Fig. 4 Ortep drawing of *anti*-5,14-di-*tert*-butyl-8,17-dimethoxy[2.3]MCP-1,2-dione, *anti*-**9b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

rings deviate from planarity to some extent and the C5, C8, C13 and C16 carbons are out of the C3–C4–C6–C7 and C11–C12–C14–C15 planes. The dihedral angles of the C3–C4–C6–C7 plane between the C4–C5–C6 and C8–C3–C7 planes, and those of the C11–C12–C14–C15 plane between the C12–C13–C14 and C16–C11–C15 planes are 6.1°, 12.0°, 6.7° and 15.7°, respectively, showing that this molecule has an asymmetrical strain between the above and below rings, and that the amount of strain is much greater at the internal carbons, C8 and C16, than at the external carbons, C5 and C13. The C1–C2–C3–O2 and C15–C1–C2–O1 planes are twisted out of coplanarity and have a dihedral angle of 5.2°, and thus the two carbonyl groups, C1–O1 and C2–O2 do not lie in the same plane where the adjacent two carbon atoms are included. The angles of C1–C2–C3 and C15–C1–C2 are 119.8° and 122.4°, respectively, which are not so different from the values in the acyclic diaryl ketones in spite of the difference of 2.6°.

The two benzene ring framework in *anti*-**9b** also features a slight twisting of the dihedral angles from planarity and the C6, C9, C14 and C17 carbons are out of the C5–C7–C8–C4 and C12–C13–C15–C16 planes. The dihedral angles of the C5–C7–C8–C4 plane between the C4–C8–C9 and C5–C6–C7 planes, and those of the C12–C13–C15–C16 plane between the C16–C12–C17 and C13–C14–C15 planes are 11.4°, 5.3°, 9.6° and 6.3°, respectively. In the other independent molecule, the corresponding values for the dihedral angles are 11.0°, 5.6°, 9.5° and 6.6°. These imply that this molecule has less strain than *anti*-**9a**. However, it is noted that the C8–C10–C11–O2 and C10–C11–C12–O3 planes have a dihedral angle of 20.0°, which is significantly much larger than that in *anti*-**9a**. Similarly, in the other independent molecule, the corresponding values for the dihedral angles are 20.4°. The angles between C8–C10–C11 and C10–C11–C12 are almost the same, 121.3° and 120.5°, respectively. In the case of the other independent molecule, the corresponding values for the angles are 120.9° and 121.0°, respectively. Two methyl groups in internal and methoxy groups of *anti*-**9b** are located underneath and over two methyl ring planes. It is quite interesting that two internal methoxy groups of *anti*-**9a** point towards the carbonyl groups of the bridge chains. This might contribute to avoiding steric crowding among the oxygen and hydrogen atoms of the bridge chains.

In conclusion, we have developed the convenient preparation of a series of *syn*- and *anti*-[2.*n*]MCP-1-enes **3** and [2.*n*]MCP-1,2-diols **4** by a McMurry cyclization of 1,*n*-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)alkanes **2**. Also, [2.*n*]MCP-1,2-diols **4** were converted to the 1,2-diones **9** by Swern oxidation. Further studies on the chemical properties of the diketones **9** are now in progress.

Experimental

All melting points (Yanagimoto MP-S1) are uncorrected. NMR spectra were determined at 270 M Hz with a Nippon Denshi JEOL FT-270 NMR spectrometer with $SiMe_4$ 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-01SA-2 spectrometer at an ionization energy of 70 eV using a direct inlet system through GLC. Elemental analyses were performed by Yanaco MT-5. GLC analyses were performed with a Shimadzu gas chromatograph, GC-14A; silicone OV-1, 2m; programmed temperature rise, 12 °C min^{-1}, carrier gas nitrogen, 25 mL min^{-1}.

Synthesis of 1,*n*-bis(5-*tert*-butyl-2-methoxyphenyl)alkanes, **1**, was previously described.[17,29]

General procedure for the synthesis of 1,*n*-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)alkanes, 2

To a solution of 1,2-bis(5-*tert*-butyl-2-methoxyphenyl)ethane, **1a**,[29] (3.19 g, 9 mmol) and Cl_2CHOMe (2.28 mL, 25.2 mmol) in CH_2Cl_2 (20 mL) was added a solution of $TiCl_4$ (6.0 mL, 54.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 2 h, it was poured into a large amount of ice–water (200 mL) and extracted with CH_2Cl_2 (100 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, 200 g) with $CHCl_3$ as eluent to give crude **2a** (3.0 g, 81%). Recrystallization from hexane gave 1.44 g (39%) of 1,2-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)ethane, **2a**, as colourless prisms, mp 119–120 °C; υ_{max} (KBr)/cm^{-1}: 1683 (C=O); δ_H ($CDCl_3$): 1.26 (18H, s), 3.00 (4H, s), 3.87 (6H, s), 7.36 (2H, d, *J* 2.5), 7.70 (2H, d, *J* 2.5), 10.35 (2H, s); *m*/*z*: 410 (M^+). Anal. calcd. for $C_{26}H_{34}O_4$ (410.56): C, 76.06; H, 8.35. Found: C, 76.27; H, 8.49.

1,3-Bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)propane, 2b. **2b** was prepared as described above, yield 67%; yellow viscous oil; υ_{max} (NaCl)/cm^{-1}: 1688 (C=O); δ_H ($CDCl_3$): 1.32 (18H, s), 1.92–2.05 (2H, m), 2.76 (4H, t, *J* 7.6), 3.84 (6H, s), 7.50 (2H, d, *J* 2.4), 7.73 (2H, d, *J* 2.4), 10.36 (2H, s); *m*/*z*: 424 (M^+). Anal. calcd. for $C_{27}H_{36}O_4$ (424.59): C, 75.38; H, 8.55. Found: C, 75.64; H, 8.63.

1,4-Bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)butane, 2c. **2c** was prepared as described above, yield 60%; colourless prisms (hexane–benzene, 5 : 1), mp 123–125 °C; υ_{max} (KBr)/cm^{-1}: 1688 (C=O); δ_H ($CDCl_3$): 1.31 (18H, s), 1.70–1.80 (4H, m), 2.70–2.80 (4H, m), 3.87 (6H, s), 7.48 (2H, d, *J* 2.4), 7.77 (2H, d, *J* 2.4), 10.36 (2H, s); *m*/*z*: 438 (M^+). Anal. calcd. for $C_{28}H_{38}O_4$ (438.61): C, 76.68; H, 8.73. Found: C, 77.00; H, 8.86.

1,5-Bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)pentane, 2d. **2d** was prepared as described above, yield 42%; colourless prisms (hexane), mp 89–90 °C; υ_{max} (KBr)/cm^{-1}: 1692 (C=O); δ_H ($CDCl_3$): 1.31 (18H, s), 1.48–1.53 (2H, m), 1.64–1.70 (4H, m), 2.65–2.71 (4H, m), 3.87 (6H, s), 7.47 (2H, d, *J* 2.4), 7.71 (2H, d, *J* 2.4), 10.36 (2H, s); *m*/*z*: 452 (M^+). Anal. calcd. for $C_{29}H_{40}O_4$ (452.64): C, 76.95; H, 8.91. Found: C, 77.01; H, 8.74.

General procedure for the McMurry coupling reaction of 2

The McMurry reagent was prepared from $TiCl_4$ (13.75 mL, 125 mmol) and Zn powder (18 g, 275 mmol) in 500 mL of dry THF, under nitrogen. A solution of 1,2-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)ethane, **2a**, (1.23 g, 3 mmol) in dry THF (100 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 an additional 8 h, cooled to room temperature and hydrolized 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.

For **2a** the residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane, benzene and $CHCl_3$ as eluents to give **6a**, (*Z*,*Z*)-**5** and *anti*-**4a**, respectively. The eluents were recrystallized from hexane, methanol and hexane–benzene (1 : 1) to afford **6a** (37 mg, 3.2%), (*Z*,*Z*)-**5** (4.3 mg, 0.38%) and *anti*-**4a** (230 mg, 18.3%), respectively.

The McMurry coupling reaction of **2a** was also carried out in the presence of pyridine (22.5 mL, 200 mmol added to the **2a**-THF solution) to afford **6a** (46 mg, 4.0%), (*Z*,*Z*)-**5** (6.8 mg, 0.6%) and *anti*-**4a** (855 mg, 68%).

For **2b**–**2d**, after concentration of the combined extracts, the residue was treated with hexane (10 mL) to give a precipitate. The precipitate was filtered and washed with hexane (5 mL) to give a colourless solid, which was recrystallized from hexane–benzene, 10 : 1, to afford *anti*-**4c** (746 mg, 56.5%) from **2c**. The filtrate was concentrated and the residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane–benzene (1 : 1) and benzene as eluents to give *anti*-**3c** (26 mg, 2%) and *syn*-**3c** (25 mg, 2%), respectively.

Compounds *syn*-**3b**, *syn*-**3d**, *anti*-**4b**, *anti*-**4d** and **6b** were similarly prepared. The yields are listed in Table 1.

1,2-Bis(5-*tert*-butyl-2-methoxy-3-methylphenyl)ethane, 6a. **6a** was obtained as colourless prisms (hexane), mp 100 °C; δ_H ($CDCl_3$): 1.28 (18H, s), 2.30 (6H, s), 2.91 (4H, s), 3.72 (6H, s), 7.02 (2H, d, *J* 2.4), 7.05 (2H, d, *J* 2.4); *m*/*z*: 382 (M^+). Anal. calcd. for $C_{26}H_{38}O_2$ (382.59): C, 81.62; H, 10.01. Found: C, 81.41; H, 10.05

(*Z*,*Z*)-5,13,21,29-Tetra-*tert*-butyl-8,16,24,32-tetramethoxy-[2.2.2.2]metacyclophane-1,18-diene, (*Z*,*Z*)-5. **5** was obtained as colourless prisms (MeOH), mp 227–228 °C; δ_H ($CDCl_3$): 1.11 (36H, s), 2.75 (8H, s), 3.51 (12H, s), 6.73 (4H, s), 6.79 (4H, d, *J* 2.5), 7.00 (4H, d, *J* 2.5); *m*/*z*: 756 (M^+). Anal. calcd. for $C_{52}H_{68}O_4$ (757.12): C, 82.49; H, 9.05. Found: C, 82.78; H, 8.98.

***anti*-1,2-*endo*-Dihydroxy-5,13-di-*tert*-butyl-8,16-dimethoxy-[2.2]metacyclophane, *anti*-4a.** *anti*-**4a** was obtained as colourless prisms (hexane–benzene, 1 : 1) mp 252 °C; υ_{max} (KBr)/cm^{-1}: 3426 (OH); δ_H ($CDCl_3$): 1.32 (18H, s), 2.52–2.71 (4H, m), 2.81 (2H, s, OH, H/D exchange with D_2O), 2.93 (6H, s), 4.51 (2H, s), 7.09 (2H, d, *J* 2.5 Hz), 7.40 (2H, d, *J* 2.5); *m*/*z*: 412 (M^+). Anal. calcd. for $C_{26}H_{36}O_4$ (412.57): C, 75.69; H, 8.8. Found: C, 75.69; H, 8.69.

***anti*-5,15-Di-*tert*-butyl-8,18-dimethoxy[2.4]metacyclophan-1-ene, *anti*-3c.** *anti*-**3c** was obtained as colourless prisms (MeOH), mp 168–169 °C; δ_H ($CDCl_3$): 1.20–1.40 (4H, m), 1.31 (18H, s), 1.96–2.08 (2H, m), 2.78–2.85 (2H, m), 3.26 (6H, s), 6.61 (2H, s), 6.80 (2H, d, *J* 2.8), 6.95 (2H, d, *J* 2.8); *m*/*z*: 406 (M^+). Anal. calcd. for $C_{28}H_{38}O_2$ (406.61): C, 82.71; H, 9.42. Found: C, 82.50; H, 9.60.

***syn*-5,15-Di-*tert*-butyl-8,18-dimethoxy[2.4]metacyclophan-1-ene, *syn*-3c.** *syn*-**3c** was obtained as colourless prisms (MeOH), mp 126–129 °C; δ_H ($CDCl_3$): 1.10 (18H, s), 1.30–1.42 (2H, m), 1.92–2.15 (4H, m), 2.72–2.82 (2H, m), 3.70 (6H, s), 6.46 (2H, d, *J* 2.4), 6.56 (2H, d, *J* 2.4), 6.97 (2H, s); *m*/*z*: 406 (M^+). Anal. calcd. for $C_{28}H_{38}O_2$ (406.61): C, 82.71; H, 9.42. Found: C, 82.41; H, 9.44

***anti*-1,2-*endo*-Dihydroxy-5,15-di-*tert*-butyl-8,18-dimethoxy-[2.4]metacyclophane, *anti*-4c.** *anti*-**4c** was obtained as colourless prisms (hexane–benzene, 10 : 1), mp 191–194 °C; υ_{max} (KBr)/cm^{-1}: 3521, 3378 (OH); δ_H ($CDCl_3$): 1.37 (18H, s), 1.22–1.38 (4H, m), 1.95–2.02 (2H, m), 2.71–2.82 (2H, m), 2.85 (2H, s, replaced by D_2O), 3.23 (6H, s), 4.70 (2H, s), 6.86 (2H, d, *J* 2.4), 7.49 (2H, d, *J* 2.4): *m*/*z*: 440 (M^+). Anal. calcd. for $C_{28}H_{40}O_4$ (440.63): C, 76.33; H, 9.15. Found: C, 76.17; H, 8.84.

***syn*-5,14-Di-*tert*-butyl-8,17-dimethoxy[2.3]metacyclophan-1-ene, *syn*-3b.** *syn*-**3b** was obtained as a colourless oil; δ_H ($CDCl_3$): 1.09 (18H, s), 1.82–2.60 (4H, m), 3.02–3.15 (2H, m), 3.71 (6H, s), 6.24 (2H, d, *J* 2.4), 6.58 (2H, d, *J* 2.4), 6.98 (2H, s); *m*/*z*: 392 (M^+). Anal. calcd. for $C_{27}H_{36}O_2$ (392.59): C, 82.61; H, 9.24. Found: C, 82.38; H, 9.07.

1,3-Bis(5-*tert*-butyl-2-methoxy-3-methylphenyl)propane, 6b. **6b** was obtained as a colourless oil; δ_H ($CDCl_3$): 1.28 (18H, s), 1.65–1.77 (2H, m), 2.28 (6H, s), 2.71 (4H, t, *J* 8.1), 3.69 (6H, s), 7.01 (2H, d, *J* 2.4), 7.05 (2H, d, *J* 2.4); *m*/*z*: 396 (M^+). Anal. calcd. for $C_{27}H_{40}O_2$ (396.62): C, 81.77; H, 10.17. Found: C, 81.51; H, 10.05.

***anti*-1,2-*endo*-Dihydroxy-5,14-di-*tert*-butyl-8,17-dimethoxy-[2.3]metacyclophane, *anti*-4b.** *anti*-**4b** was obtained as colourless prisms (hexane–benzene, 5 : 1), mp 235–237 °C; υ_{max} (KBr)/cm^{-1}: 3553, 3423 (OH): δ_H ($CDCl_3$): 1.33 (18H, s), 1.94–2.04 (2H, m), 2.37–2.49 (2H, m), 2.57–2.68 (2H, m), 2.76 (2H, s, replaced by D_2O), 3.07 (6H, s), 4.53 (2H, s), 7.03 (2H, d, *J* 2.4), 7.43 (2H, d, *J* 2.4); *m*/*z*: 426 (M^+). Anal. calcd. for $C_{27}H_{38}O_4$ (426.6): C, 76.02; H, 8.98. Found: C, 76.17; H, 8.84.

***syn*-5,16-Di-*tert*-butyl-8,19-dimethoxy[2.5]metacyclophan-1-ene, *syn*-3d.** *syn*-**3d** was obtained as colourless prisms (methanol), mp 125–127 °C; δ_H ($CDCl_3$): 1.12 (18H, s), 1.10–1.22 (4H, m), 1.53–1.69 (2H, m), 2.07–2.18 (2H, m), 2.91–3.02 (2H, m), 3.70 (6H, s), 6.58 (2H, d, *J* 2.7), 6.68 (2H, d, *J* 2.7), 6.96 (2H, s); *m*/*z*: 420 (M^+). Anal. calcd. for $C_{29}H_{40}O_2$ (420.64): C, 82.81; H, 9.58. Found: C, 82.55; H, 9.61.

***anti*-1,2-*endo*-Dihydroxy-5,16-di-*tert*-butyl-8,19-dimethoxy-[2.5]metacyclophane, *anti*-4d.** *anti*-**4d** was obtained as colourless prisms (hexane–benzene, 5 : 1), mp 224–226 °C; υ_{max} (KBr)/cm^{-1}: 3386 (OH); δ_H ($CDCl_3$): 1.32 (18H, s), 1.15–1.35 (6H, m), 1.98–2.11 (2H, m), 2.48–2.59 (2H, m), 2.81 (2H, s, replaced by D_2O), 3.32 (6H, s), 4.85 (2H, s), 6.93 (2H, d, *J* 2.4), 7.47 (2H, d, *J* 2.4); *m*/*z*: 454 (M^+). Anal. calcd. for $C_{29}H_{42}O_4$ (454.66): C, 76.61; H, 9.31. Found: C, 76.44; H, 9.33.

Oxidation of *anti*-4a with $C_5H_5NH^+CrO_3Cl^-$

To a solution of *anti*-**4a** (86.3 mg, 0.219 mmol) and CH_2Cl_2 (7.5 mL) was added $C_5H_5NH^+CrO_3Cl^-$ (480 mg, 1.86 mmol)

at 0 °C. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered and the filtrate was extracted with CH_2Cl_2 (10 mL × 3). The extract was dried over anhydrous sodium sulfate and concentrated. The residue was subjected to silica gel (Wako, C-300; 100 g) column chromatography using benzene as eluent to give 1,2-bis(5-*tert*-butyl-3-formyl-2-methoxyphenyl)ethane, **2a** (61 mg, 90%) as colourless prisms.

Swern oxidation of *anti*-4a

To a solution of oxalyl chloride (0.25 mL, 2.75 mmol) in CH_2Cl_2 (25.0 mL) was added DMSO (0.126 mL, 1.65 mmol) and then *anti*-**4a** (110 mg, 0.331 mmol) in CH_2Cl_2 (1.0 mL) at −30 °C under nitrogen. After the reaction mixture had been stirred at −30 °C for 1 h, triethylamine (380 mg, 3.75 mmol) was added. The temperature of the reaction mixture was maintained at −30 °C for 30 min under nitrogen, then allowed to warm up to room temperature and stirred for an additional 1 h. Then, water (10 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (10 mL × 3). The dichloromethane solution was washed with water, dried over Na_2SO_4 and evaporated *in vacuo* to a residue. The ^{1}H-NMR spectrum of this oil was in accord with its being a mixture of three components, *anti*-**8a**, *anti*-**9a** and **2a** in the ratio of 58 : 12 : 28, which was crystallized by adding a small amount of hexane to give a colourless solid. While attempts to isolate pure *anti*-**8a** failed, recrystallization from hexane–CH_2Cl_2, 10 : 1, afforded *anti*-5,13-di-*tert*-butyl-8,16-dimethoxy[2.2]metacyclophane-1,2-dione, *anti*-**9a** (10 mg, 8%) as orange prisms, mp 193 °C; υ_{max} (KBr)/cm^{-1}: 1678 (C=O); δ_H ($CDCl_3$): 1.33 (18H, s), 2.56 (2H, d, *J* 7.9), 2.86 (2H, d, *J* 7.9), 3.11 (6H, s), 7.32 (2H, d, *J* 2.4), 7.34 (2H, d, *J* 2.4); *m*/*z*: 408 (M^+). Anal. calcd. for $C_{26}H_{32}O_4$ (408.54): C, 75.44; H, 7.9. Found: C, 75.29; H, 8.09.

Compounds *anti*-**9b**,**c** were similarly prepared. The yields are listed in Table 2.

Diketone *anti*-**9a** was found to be quite labile to treatment by silica gel column chromatography and on refluxing in toluene, affording dicarboxylic acid **10** in quantitative yield as colourless prisms (benzene), mp 213–215 °C; υ_{max} (KBr)/cm^{-1}: 3410–2965, 1696 (C=O), 1603, 1479, 1274, 1238, 891; δ_H ($CDCl_3$): 1.28 (18H, s), 3.02 (4H, s), 3.92 (6H, s), 7.33 (2H, d, *J* 2.4), 7.98 (2H, d, *J* 2.4), 11.15 (2H, s, OH); *m*/*z*: 442 (M^+). Anal. calcd. for $C_{26}H_{34}O_6$ (442.56): C, 70.56; H, 7.74. Found: C, 70.39; H, 7.89.

***anti*-5,13-Di-*tert*-butyl-2-*endo*-hydroxy-8,16-dimethoxy-[2.2]metacyclophan-1-one, *anti*-8a.** δ_H ($CDCl_3$): 1.30 (9H, s), 1.32 (9H, s), 2.93 (3H, s), 3.04 (3H, s), 2.56–2.86 (4H, m), 4.33 (1H, s), 5.26 (1H, s, OH, H/D exchange with D_2O), 7.09 (1H, d, *J* 2.4), 7.28 (1H, d, *J* 2.4), 7.32 (1H, d, *J* 2.4), 7.34 (1H, d, *J* 2.4).

***anti*-5,14-Di-*tert*-butyl-8,17-dimethoxy[2.3]metacyclophane-1,2-dione, *anti*-9b.** *anti*-**9b** was obtained as yellow prisms (hexane–benzene, 5 : 1), mp 274–276 °C; υ_{max} (KBr)/cm^{-1}: 1675 (C=O); δ_H ($CDCl_3$): 1.34 (18H, s), 1.90–2.05 (2H, m), 2.36–2.44 (4H, m), 3.19 (6H, s), 7.33 (2H, d, *J* 2.4 Hz), 7.49 (2H, d, *J* 2.4); *m*/*z*: 422 (M^+). Anal. calcd. for $C_{27}H_{34}O_4$ (422.57): C, 76.74; H, 8.11. Found: C, 76.93; H, 7.98.

***anti*-5,15-Di-*tert*-butyl-8,18-dimethoxy[2.4]metacyclophane-1,2-dione, *anti*-9c.** *anti*-**9c** was obtained as yellow prisms (hexane–benzene, 5 : 1), mp 245–246 °C; υ_{max} (KBr)/cm^{-1}: 1667 (C=O); δ_H ($CDCl_3$): 1.17–1.39 (4H, m), 1.34 (18H, s), 2.07–2.24 (2H, m), 2.78–2.91 (2H, m), 3.28 (6H, s), 7.16 (2H, d, *J* 2.4), 7.83 (2H, d, *J* 2.4); *m*/*z*: 436 (M^+). Anal. calcd. for $C_{28}H_{36}O_4$ (436.6): C, 77.03; H, 8.31. Found: C, 77.00; H, 8.41.

Trapping reaction of *anti*-9a with *o*-phenylenediamine

To a solution of crude *anti*-**9a** (10.6 mg, 0.026 mmol) in ethanol (10 mL) was added *o*-phenylenediamine (28.3 mg, 0.262 mmol) at room temperature. After the reaction mixture had been stirred at room temperature for 24 h, the solvent was evaporated *in vacuo* to leave a residue. The residue was washed successively with 10% aqueous hydrochloric acid, water, and ethanol to afford *anti*-**11** (12.5 mg, 100%) as a brown solid, mp >300 °C; δ_H ($CDCl_3$): 1.34 (18H, s), 2.55–2.80 (4H, m), 2.98 (6H, s), 7.19 (2H, d, *J* 2.4), 7.32 (2H, d, *J* 2.4), 7.78 (2H, dd, *J* 3.7, 6.3), 8.23 (2H, dd, *J* 3.7, 6.3); *m*/*z*: 480 (M^+). Anal. calcd. for $C_{32}H_{36}N_2O_2$ (480.66): C, 79.97; H, 7.55; N, 5.83. Found: C, 79.69; H, 7.76; N, 5.62.

Crystal data for 5, *anti*-9a and *anti*-9b

Crystallographic data for **5**, *anti*-**9a** and *anti*-**9b** are given in Table 4.

As a typical procedure, the unit cell constants for **5** were derived from least-squares analysis of the settings of a CAD4 FR 586 diffractometer for 25 reflections, in the range of $24.0 < \theta < 27.4°$. The intensities of all independent reflections with $6.16° < 2\theta < 129.90°$ were measured with ω scan width ($0.8 + 0.140 \tan \theta$); Ni-filtered Cu K_α radiation ($\lambda = 1.581\,84$ Å) was used. The X-ray analysis was performed with MolEN program package[30] and the structure was solved uneventfully by direct methods (SIR88).[31] The refinement was used by full-matrix least squares.

CCDC reference number 440/167.

Table 4 Crystallographic data and data collection details for 5,13,21,29-tetra-*tert*-butyl-8,16,24,32-tetramethoxy[2.2.2.2]MCP-1,18-diene (**5**), *anti*-5,13-di-*tert*-butyl-8,16-dimethoxy[2.2]MCP-1,2-dione (*anti*-**9a**) and *anti*-5,14-di-*tert*-butyl-8,17-dimethoxy[2.3]MCP-1,2-dione (*anti*-**9b**)

	5	*anti*-**9a**	*anti*-**9b**
Formula	$C_{52}H_{68}O_4$	$C_{26}H_{32}O_4$	$C_{27}H_{34}O_4$
FW	757.1	408.54	422.57
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No.14)	*Pa* (No.7)
a/Å	17.1301(1)	23.052(2)	12.834(1)
b/Å	26.617(3)	9.7452(1)	19.5775(16)
c/Å	10.267(1)	10.1413(8)	10.3418(5)
β/°	95.978(8)	93.239(6)	111.643(5)
U/Å^3	4656.0(8)	2274.5(3)	2415.3(3)
Z	4	4	4
T/K	295	297	298
μ/cm^{-1}	4.80	5.95	5.74
R^a	0.085	0.095	0.076
R_w [a]	0.114	0.155	0.108
No. of reflections	8587	6260	5128
Unique reflections	7423	4685	4707

[a] $w = 4(F_o)^2/[(\sigma I_o)^2 + 0.0016(F_o)^4]$.

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