Medium-sized Cyclophanes. Part 18.[1] 5-*tert*-Butyl-8-substituted [2.2]Metaparacyclophanes: Preparation, X-Ray Diffraction Studies, and their Treatment with Lewis Acids in Benzene

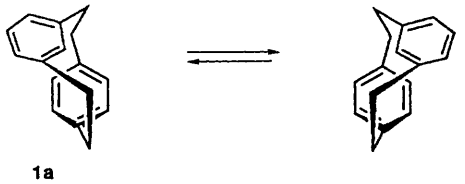
Takehiko Yamato,*[a] Jun-ichi Matsumoto,[a] Kiwamu Tokuhisa,[a] Katsuya Tsuji,[a] Kazuaki Suehiro[a] and Masashi Tashiro[b]

[a] *Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga 840, Japan*

[b] *Research Institute of Advanced Material Study, Kyushu University, 6-1, Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan*

The preparation of various 8-substituted 5-*tert*-butyl[2.2]metaparacyclophanes **8** using the sulfur method, and X-ray diffraction studies of dithia[3.3]metaparacyclophanes **6** and 8-methyl[2.2]-metaparacyclophane **1b**, are described. $AlCl_3$–$MeNO_2$-catalysed trans-*tert*-butylation of 8-alkyl- and 8-hydroxy-5-*tert*-butyl[2.2]metaparacyclophanes **8** in benzene gave the desired 8-alkyl- and 8-hydroxy-[2.2]metaparacyclophanes **1** in good yield. However, 5-*tert*-butyl-8-methoxy[2.2]metaparacyclophane **8c** was isomerized to the strainless 5-*tert*-butyl-8-methoxy[2.2]metacyclophane **13** and this was converted into the tetrahydropyrenes **11** and **12**. The mechanism of this reaction is also discussed.

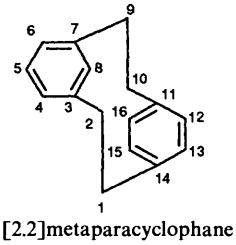
[2.2]Metaparacyclophane **1a** was first prepared by Cram *et al.*[2] *via* acid-catalysed rearrangement of [2.2]paracyclophane. Later on, compound **1a** became available through synthetic methods developed by other research groups.[3–11] A versatile procedure, appropriate for the synthesis of substituted derivatives, makes use of 2,11-dithia[3.3]metaparacyclophane as a precursor.[6,8,9] The *meta*-bridged benzene ring of compound **1a** has been shown to undergo conformational flipping[4,5,8,10,12–14] with a substantial energy barrier (~80 kJ mol^{-1}) [equation (1)], so that elevated temperatures (~400 K) were required for the interconversion to be revealed on the NMR timescale. A great part of this energy barrier is believed to arise from steric destabilization of the transition state in which the 8-hydrogen atom of the *meta*-bridged ring impinges into the π-electron cloud of the *para*-bridged one.



1a (1)

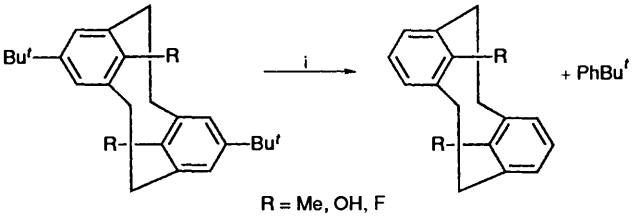
Preliminary X-ray crystallographic studies of compound **1a** were carried out by Trueblood and Crisp; their results have recently been refined by Renault *et al.*[15] The deformations of the benzene rings in compound **1a** are similar to those of the corresponding rings in [2.2]para- and [2.2]meta-cyclophane, with *para*- and *meta*-bridged rings bent in a boat- and a chair-like form, respectively. The angle between the two aromatic planes defined by the carbon atoms 3, 4, 6 and 7, on the one hand, and 12, 13, 15 and 16, on the other, is ~13°. It should be noted that the angle between the 11,12,16-plane and the 10,11-bond vector (or between the 13,14,15-plane and the 1,14-bond vector) is even larger than the analogous angle in [2.2]paracyclophane. The *para*-bridged moiety of **1a** is thus more strongly tilted than the moieties of the isomeric compound.

Although Boekelheide and his co-workers[6,8] have reported the preparation of various [2.2]metaparacyclophanes and 8-halogeno- and 8-cyano-[2.2]metaparacyclophanes in low total yields from simply available starting compounds in their studies of the conformational ring flipping, their preparative routes seem to be too long for practical purposes. In spite of the [2.2]metaparacyclophanes being such highly strained compounds that they may be reactive toward many reagents, the chemistry of [2.2]metaparacyclophanes is very limited since their preparation from easily available compounds was very difficult. Furthermore, as yet there has been no reported preparation of other internally substituted [2.2]metaparacyclophanes.



Numbering scheme for [2.2]metaparacyclophane **1a**

Previously we found that 8,16-dimethyl-,[16,17] 8,16-dihydroxy-,[18] and 8,16-difluoro-[2.2]metacyclophane[19] can be conveniently prepared by $AlCl_3$–$MeNO_2$-catalysed trans-*tert*-butylation of the corresponding *tert*-butyl derivatives (Scheme 1).



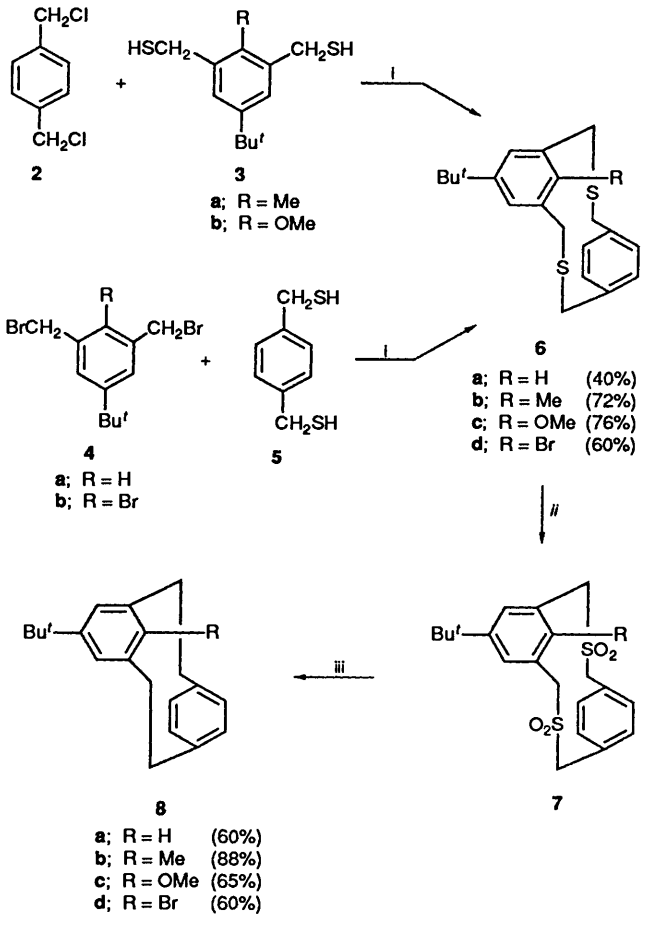
R = Me, OH, F

Scheme 1 *Reagents and conditions:* i, $AlCl_3$–$MeNO_2$, C_6H_6

These results suggest that 8-substituted metaparacyclophanes might be prepared from the corresponding *tert*-butyl derivatives, using the *tert*-butyl group as a positional protective group on the aromatic rings.[20,21] We report here the convenient preparation of the title compounds and their treatment with Lewis acid catalysts in benzene solution.

Results and Discussion

Preparation.—The route used to prepare the title compounds is summarized in Scheme 2.



Scheme 2 *Reagents and conditions:* i, KOH–EtOH, high dilution; ii, 30% H_2O_2, AcOH (*ca.* 100%); iii, 500 °C, 1 mmHg

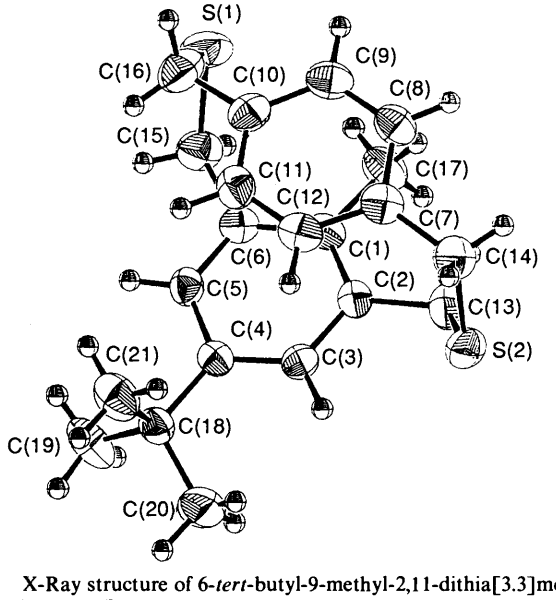


Fig. 1 X-Ray structure of 6-*tert*-butyl-9-methyl-2,11-dithia[3.3]metaparacyclophane **6b**

The preparation of 1,2,3,5-tetrasubstituted benzenes **3a**, **b** and **4a**, **b** have already been described in earlier papers.[17,22] 1,4-Bis(mercaptomethyl)benzene **5** was prepared from 1,4-bis(chloromethyl)benzene **2** according to the reported procedure.[8]

The cyclization of bis(halogenomethyl)benzenes **2** and **4**, and bis(mercaptomethyl)benzenes **3** and **5** was carried out under highly dilute conditions in 10% ethanolic KOH in the presence of a small amount of $NaBH_4$, giving the desired 9-substituted 6-*tert*-butyl-2,11-dithia[3.3]metaparacyclophane **6a–d** in 40–76% yield, respectively.

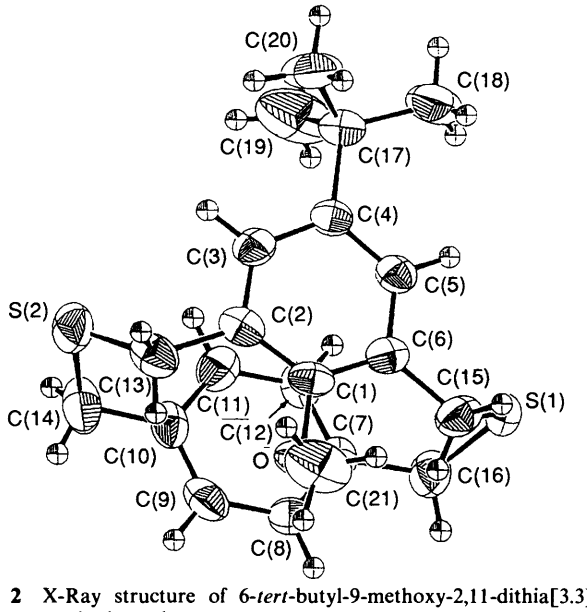


Fig. 2 X-Ray structure of 6-*tert*-butyl-9-methoxy-2,11-dithia[3.3]-metaparacyclophane **6c**

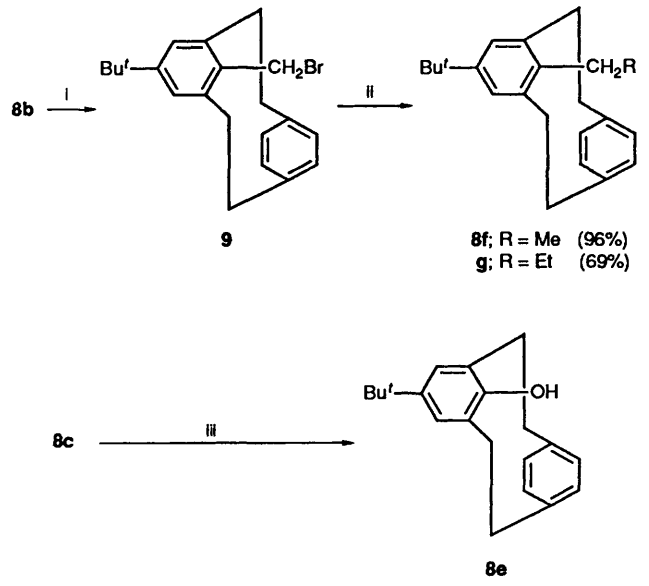
The assignment of structure **6** was readily apparent from the ^1H NMR spectrum of the corresponding compound. Thus the internal proton, methyl protons, and methoxy protons should show an upfield shift due to the ring current of the opposite aromatic ring. The ^1H NMR spectra of the dithia[3.3]metaparacyclophanes **6a**, **6b** and **6c** prepared in the present paper showed the internal proton, methyl protons and methoxy protons at δ 5.30, 1.80 and 3.31. The conformation of compounds **6b** and **6c** was also confirmed by X-ray analysis (Figs. 1 and 2).

X-Ray crystallographic studies of compounds **6b** and **6c** show that the compounds are probably conformationally more rigid than is **6a** (R = H) because their methyl or methoxy substituents are likely to impinge upon the electron cloud of the *para*-bridged ring. It is quite interesting that the conformation of the bridge chains of compounds **6b** (R = Me) and **6c** (R = OMe) are different since in compound **6b** the sulfur atoms occupy inequivalent positions with respect to the methyl group while in the more symmetric conformation of compound **6c** the sulfur atoms are both away from the corresponding methoxy substituent. This might be attributed to the interaction of the oxygen atom and the sulfur atoms of bridge chains.

Oxidation of compounds **6a** and **6d** with *m*-chloroperbenzoic acid (MCPBA) in chloroform, and of **6b** and **6c** with 30% hydrogen peroxide in acetic acid, afforded the corresponding bissulfones **7** in quantitative yield. Pyrolysis of compounds **7** under reduced pressure (1 mmHg) was carried out according to the reported method[16–18] to afford the corresponding 8-substituted 5-*tert*-butyl[2.2]metaparacyclophanes **8** in 60–88% yield.

Recently, we have reported[23] that reaction of 8-bromomethyl-16-methyl[2.2]metacyclophane with Grignard reagents afforded the corresponding 8-alkyl-16-methyl derivatives in good yield. Thus, we have carried out the rection of 5-*tert*-butyl-8-methyl[2.2]metaparacyclophane **8b** with *N*-bromosucinimide (NBS) in the presence of benzoyl peroxide in refluxing tetrachloromethane; the desired 8-bromomethyl-5-*tert*-butyl[2.2]-metaparacyclophane **9** was obtained in 59% yield. Reaction with bromide **9** with Grignard reagents afforded the corresponding 8-ethyl- **8f** and 8-propyl-5-*tert*-butyl[2.2]metaparacyclophane **8g** in 96 and 69% yield, respectively (Scheme 3).

The preparation of 5-*tert*-butyl-8-hydroxy[2.2]metaparacyclophane **8e** was carried out by treatment of the corres-



Scheme 3 *Reagents and conditions:* i, NBS (1.1 mol equiv.), CCl_4, benzoyl peroxide; ii, RMgBr, Et_2O; iii, BBr_3, CH_2Cl_2, room temperature for 4 h

Table 1 The Lewis acid-catalysed trans-*tert*-butylation of 8-substituted 5-*tert*-butyl[2.2]metaparacyclophanes **8** in benzene[a]

Run	Substrate	Catalyst[b]	Catalyst/**8** (mol/mol)	Time (*t*/h)	Product (%)[c]
1	**8a**	A	0.3	1.5	**1a** (80), **10** (85)
2	**8b**	A	0.3	1.5	**1b** (92), **10** (98)
3	**8b**	B	1.5	10	**1b** (81), **10** (85)
4	**8b**	C	1.5	15	**1b** (0), **10** (0)[d]
5	**8d**	A	0.3	1.5	**1d** (0), **10** (0)[d]
6	**8e**	A	1.2	12	**1e** (80), **10** (90)
7	**8f**	A	0.3	1.5	**1f** (76), **10** (90)
8	**8g**	A	0.3	1.5	**1g** (74), **10** (93)

[a] The reaction temperature was 50 °C. [b] A, $AlCl_3$–$MeNO_2$; B, $TiCl_4$; C, $SnCl_4$. [c] The isolated yields are shown. [d] Starting compound was recovered in quantitative yield.

ponding 8-methoxy derivative **8c** with boron tribromide[18,21] in dichloromethane.

The $AlCl_3$–$MeNO_2$- and $TiCl_4$-catalysed trans-*tert*-butylation of compounds **8a–g** in benzene was carried out under various conditions and the results are summarized in Table 1. The $AlCl_3$–$MeNO_2$- and $TiCl_4$-catalysed trans-*tert*-butylation reactions of compound **8b** afforded the desired 8-methyl[2.2]metaparacyclophane **1b** and *tert*-butylbenzene **10** in good yield, but titanium tetrachloride was needed in much larger amounts and with longer reaction times than aluminium chloride. However, no trans-*tert*-butylation of compound **8b** was observed with $SnCl_4$ as catalyst.

The $AlCl_3$–$MeNO_2$-catalysed reactions of substrates **8a**, **8d**, **8f** and **8g** as well as **8b** afforded the expected products **1a**, **1d**, **1f** and **1g**, respectively (Scheme 4). However, in the case of 5-*tert*-butyl-8-hydroxy[2.2]metaparacyclophane **8e**, a large amount of the catalyst had to be used in order to obtain compound **1e** in good yield. The catalyst might react with the hydroxy group of compound **8e** to form a complex which could reduce both the catalytic activity and the basicity of substrate **8e**.

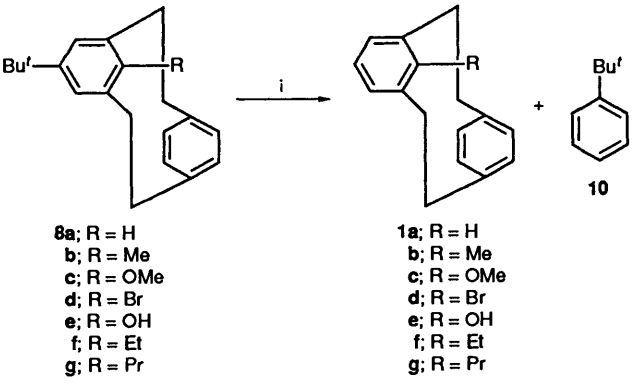
The $AlCl_3$–$MeNO_2$-catalysed trans-*tert*-butylation of electron-poor [2.2]metaparacyclophanes such as the 8-bromo derivative **8d** did not afford any product, but the starting material was recovered in almost quantitative yield.

The $AlCl_3$–$MeNO_2$-catalysed trans-*tert*-butylation of 5-*tert*-butyl-8-methoxy[2.2]metaparacyclophane **8c** in benzene under

Table 2 The Lewis acid-catalysed reaction of 5-*tert*-butyl-8-methoxy-[2.2]metaparacyclophane **8c** in benzene[a]

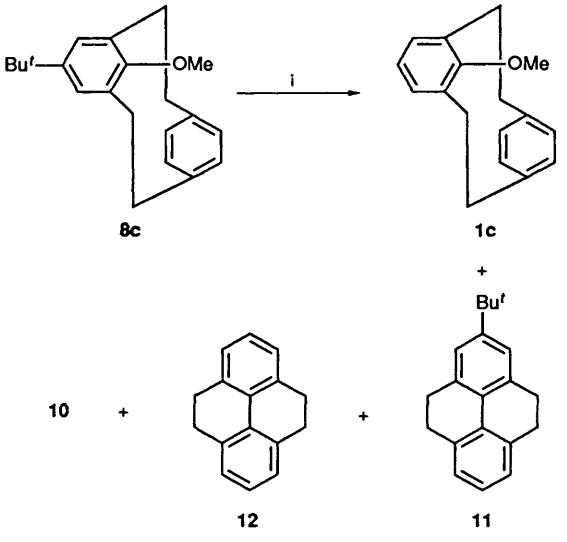
Run	Catalyst[b]	Catalyst/**8c** (mol/mol)	Time (*t*/h)	Product (%)[c]
1	A	1.2	24	**1c** (0)
2	B	1.2	6	**1c** (35), **11** (12), **12** (48), **10** (80)
3	B	1.2	19	**1c** (31), **11** (10), **12** (44), **10** (85)
4	B	3.0	6	**12** (86), **10** (90)
5	C	1.2	2	**1c** (17), **11** (5), **12** (65), **10** (85)

[a] The reaction temperature was 50 °C. [b] A, $TiCl_3$; B, $AlCl_3$–$MeNO_2$; C, $AlCl_3$. [c] Yields are determined by GLC analysis.



Scheme 4 (see Table 1) *Reagents and conditions:* i, Lewis acid, benzene

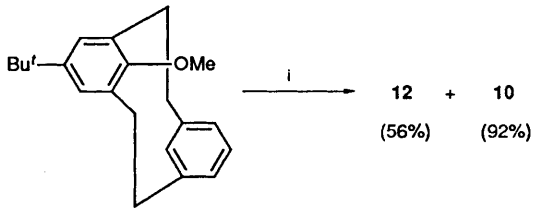
a variety of conditions (Table 2) afforded the expected compound 8-methoxy[2.2]metaparacyclophane **1c** in only low yield, along with formation of *tert*-butylbenzene **10** and the tetrahydropyrenes **11** and **12**; prolonged reaction with aluminium chloride gave only compound **12** (Scheme 5). This



Scheme 5 (see Table 2) *Reagents and conditions:* i, Lewis acid, benzene

result suggests that a compound **11** might be an intermediate in the formation of compound **12**. Indeed, compound **12** was also obtained in good yield when the *tert*-butyl derivative **11** was treated with $AlCl_3$–$MeNO_2$ in benzene under the same reaction conditions (50 °C for 30 min) (Scheme 6).

The $AlCl_3$–$MeNO_2$-catalysed reaction of 5-*tert*-butyl-8-methoxy[2.2]metacyclophane **13** in benzene was carried out at 50 °C for 30 min to afford 4,5,9,10-tetrahydropyrene **12** in 56% yield along with *tert*-butylbenzene **10**. It was also found that



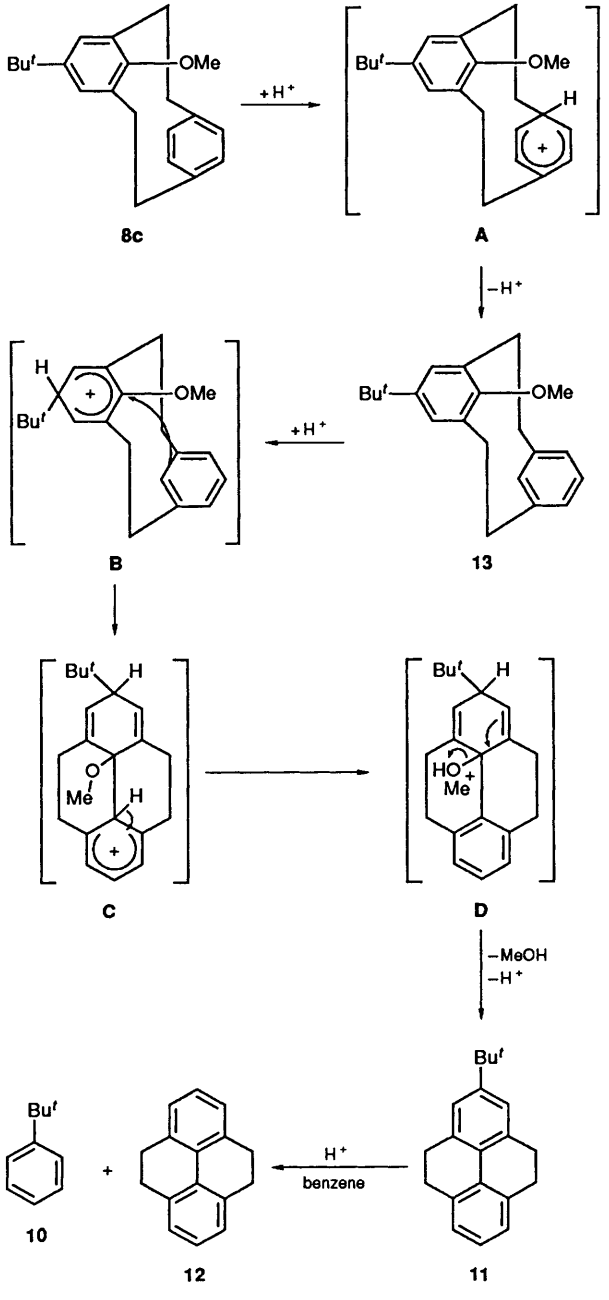
13

Scheme 6 *Reagents and conditions:* i, $AlCl_3$–$MeNO_2$ (1.2 mol equiv.), benzene, 50 °C for 30 min

the similar catalytic treatment of 5-*tert*-butyl-8-methoxy[2.2]-metacyclophane **13** with $TiCl_4$ in dichloromethane at 50 °C for 30 min afforded 2-*tert*-butyl-4,5,9,10-tetrahydropyrene **11** in 85% yield.

A mechanism for the formation of tetrahydropyrene **12** from compound **8c** is tentatively proposed in Scheme 7.

Cram *et al.* reported[2] the $AlCl_3$-catalysed isomerization of



Scheme 7

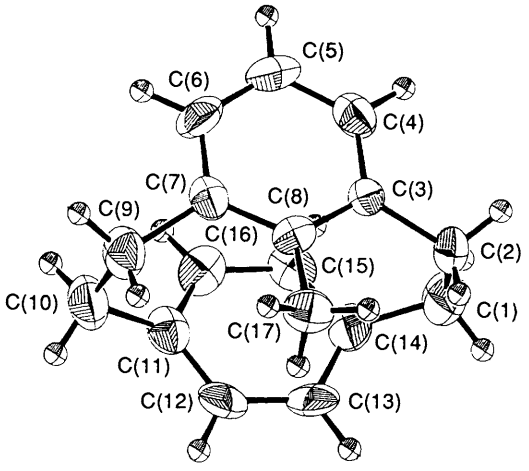


Fig. 3 X-Ray structure of 8-methyl[2.2]metaparacyclophane **1b**

[2.2]paracyclophane to the less strained [2.2]metaparacyclophane **1a** along with formation of the transannular isomerization products, 1,2,3,3a,4,5-hexahydropyrene and [2.2]metacyclophane. In the case of the 8-methoxy[2.2]metaparacyclophane **8c**, protonation of the *ipso*-position of the ethylene bridge on the *para*-benzene ring would afford the cation intermediate **A**, which could isomerize to the strainless 8-methoxy[2.2]-metacyclophane **13**. This novel isomerization reaction can be attributed to the methoxy group at the 8-position, which increases the strain in the molecule in comparison with the unsubstituted [2.2]metaparacyclophane **1a**. This fact is also supported by the increase in degree of deformation of the *para*-benzene ring, which was estimated to be 15° by X-ray crystallographic study of compound **1b** compared with that of the parent compound **1a** (13°; Fig. 3). Protonation at the *ipso*-position of the *tert*-butyl group of compound **13** to form intermediate **B**, from which product **11** might be produced *via* intermediates **C** and **D** as expected on the basis of previously reported observations that substrate **13** gives product **11** under electrophilic substitution conditions.[24–26] Furthermore, the good leaving-group ability of the methoxy group, particularly when complexed by Lewis acids, may be important, *e.g.* in preventing reversal of the steps between intermediates **B** and **D**. Finally, the trans-*tert*-butylation of compound **11** would give 4,5,9,10-tetrahydropyrene **12**.

Conclusions.—We propose that the above isomerization and transannular cyclization of 8-methoxy[2.2]metaparacyclophane to form tetrahydropyrene is strongly affected by the bulk of the methoxy group at the 8-position, which increases the strain in the molecule.

The preparation of 8-substituted [2.2]metaparacyclophane **1**, using a *tert*-butyl group as a positional protecting group on the aromatic ring, appears to be a useful route to such compounds, and studies of the scope and limitations of the route are in progress.

Experimental

All m.p.s and b.p.s are uncorrected. NMR spectra were determined at 270 MHz with a Nippon Denshi JEOL FT-270 NMR spectrometer with $SiMe_4$ as internal reference; *J*-values are given in Hz. IR spectra were measured for samples as KBr pellets or a liquid film on NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct-inlet system through GC.

Materials.—Preparation of bis(bromomethyl)benzenes **4** and bis(mercaptomethyl)benzenes **3** was previously reported.[17,22] 1,4-Bis(mercaptomethyl)benzene **5** was prepared from 1,4-bis(chloromethyl)benzene **2** according the reported procedure.[8] Preparation of 5-*tert*-butyl-8-methoxy[2.2]MCP **13** was as previously described.[24]

Preparation of 6-tert-*Butyl*-2,11-*dithia*[3.3]*metaparacyclophane* **6a**.—A solution of 1,4-bis(mercaptomethyl)benzene **5** (3.0 g, 18 mmol) and 1,3-bis(bromomethyl)-5-*tert*-butylbenzene **4a** (5.67 g, 18 mmol) in benzene (200 cm^3) was added dropwise from a Hershberg funnel under nitrogen to a stirred solution of potassium hydroxide (3.29 g, 58.6 mmol) and of sodium borohydride (0.8 g, 21.1 mmol) in ethanol (4 dm^3). When addition was complete (12 h), the reaction mixture was concentrated and the residue was extracted with dichloromethane (500 cm^3). The extract was concentrated and the residue was chromatographed over silica gel (Wako, C-300; 500 g) with a hexane as eluent to give a solid, which was recrystallized from hexane to afford the *title compound* **6a** (2.3 g, 40%) as prisms, m.p. 171–171 °C; ν_{max}(KBr)/cm^{-1} 3023, 2950, 1598, 1508, 1476, 1419, 1392, 1362 and 1232; δ_H($CDCl_3$) 1.20 (9 H, s), 3.31 (4 H, s), 3.67 (4 H, s), 5.30 (1 H, s), 6.67 (4 H, s) and 6.93 (2 H, s); *m/z* 328 (M^+) (Found: C, 73.2; H, 7.3. $C_{20}H_{24}S_2$ requires C, 73.12; H, 7.36%).

Similarly, compounds **6b–d** were synthesized in the same manner as described above. The yields are summarized in Scheme 2.

Preparation of 6-tert-*butyl*-9-*methyl*-2,11-*dithia*[3.3]*metaparacyclophane* **6b**. *Prisms* (from hexane); m.p. 106.5–107 °C; ν_{max}(KBr)/cm^{-1} 2967, 2953, 2943, 1511, 1478, 1463, 1420, 1358, 1220, 1202, 1191, 945, 903, 877, 818, 745 and 682; δ_H($CDCl_3$) 1.34 (9 H, s), 1.80 (3 H, s), 3.38–3.80 (8 H, m), 6.20 (2 H, d, *J* 1), 7.10 (2 H, d, *J* 1) and 7.19 (2 H, s); *m/z* 342 (M^+) (Found: C, 73.8; H, 7.6. $C_{21}H_{26}S_2$ requires C, 73.63; H, 7.65%).

Preparation of 6-tert-*butyl*-9-*methoxy*-2,11-*dithia*[3.3]*metaparacyclophane* **6c**. *Prisms* [from hexane–benzene (10:1)]; m.p. 135–137 °C; ν_{max}(KBr)/cm^{-1} 2925, 1590, 1460, 1425, 1240, 1210, 1180, 1160, 1070, 1020, 900, 815, 800, 770, 725 and 665; δ_H($CDCl_3$) 1.33 (9 H, s), 3.31 (3 H, s), 3.34 (2 H, d, *J* 15), 3.68 (2 H, d, *J* 13), 3.69 (2 H, d, *J* 15), 3.85 (2 H, d, *J* 13), 6.39 (2 H, d, *J* 1.2), 6.97 (2 H, d, *J* 1.2) and 7.19 (2 H, s); *m/z* 358 (M^+) (Found: C, 70.7; H, 7.4. $C_{21}H_{26}OS_2$ requires C, 70.34; H, 7.31%).

Preparation of 9-*Bromo*-6-tert-*butyl*-2,11-*dithia*[3.3]*metaparacyclophane* **6d**. *Prisms* (from hexane), m.p. 102–104 °C; ν_{max}(KBr)/cm^{-1} 2980, 2910, 2884, 1508, 1478, 1436, 1432, 1415, 1402, 1393, 1362, 1225, 1157, 1099, 1019, 872, 748, 741 and 683; δ_H($CDCl_3$) 1.34 (9 H, s), 3.53–3.86 (8 H, m), 6.32 (2 H, d, *J* 2.2), 7.09 (2 H, d, *J* 2.2) and 7.35 (2 H, s); *m/z* 406, 408 (M^+) (Found: C, 58.7; H, 5.9. $C_{20}H_{23}BrS_2$ requires C, 58.96; H, 5.69%).

Preparation of 6-tert-*Butyl*-2,11-*dithia*[3.3]*metaparacyclophane* 2,2,11,11-*Tetraoxide* **7a**.—To a magnetically stirred solution of the bis-sulfide **6a** (2.97 g, 9.04 mmol) in dichloromethane (184 cm^3) was added MCPBA (85% purity; 8.12 g, 40 mmol), at 0 °C. After the solution had been stirred for 48 h at room temperature, the solvent was evaporated off under reduced pressure to leave a residue, which was washed successively with 10% aq. sodium hydrogen carbonate, water and ethanol to afford the *title compound* **7a** (3.10 g, 96%) as prisms, m.p. >300 °C; ν_{max}(KBr)/cm^{-1} 2869, 1360, 1149, 1024 and 818; δ_H($CDCl_3$) 1.31 (9 H, s), 4.07 (4 H, s), 4.45 (4 H, s), 5.43 (1 H, br s), 7.13 (4 H, s) and 7.42 (2 H, s); *m/z* 392 (M^+) (Found: C, 61.4; H, 6.1. $C_{20}H_{24}O_4S_2$ requires C, 61.2; H, 6.16%).

Compound **7d** was prepared according to the method described above in 92% yield.

Preparation of 9-*bromo*-6-tert-*butyl*-2,11-*dithia*[3.3]*metaparacyclophane* 2,2,11,11-*tetraoxide* **7d**. *Prisms*, m.p. >300 °C; ν_{max}(KBr)/cm^{-1} 2965, 1323, 1298, 1271, 1245, 1208, 1168, 1115, 894 and 862; δ_H($CDCl_3$) 1.36 (9 H, s), 4.07 (2 H, d, *J* 15.6), 4.35 (2 H, d, *J* 14.0), 4.53 (2 H, d, *J* 14.0), 4.77 (2 H, d, *J* 15.6), 6.72 (2 H, d, *J* 1.1), 7.30 (2 H, d, *J* 2.2) and 7.80 (2 H, s); *m/z* 470 and 472 (M^+) (Found: C, 50.8; H, 4.9. $C_{20}H_{23}BrO_4S_2$ requires C, 50.95; H, 4.92%).

Preparation of 6-tert-*Butyl*-9-*methyl*-2,11-*dithia*[3.3]*metaparacyclophane* 2,2,11,11-*Tetraoxide* **7b**.—A mixture of compound **6b** (5.0 g, 14.6 mmol), 30% hydrogen peroxide (14 cm^3), and glacial acetic acid (100 cm^3) was heated at 85–90 °C for 12 h. The reaction mixture was then poured into cold, aq. 20% sodium hydroxide (220 cm^3), and the resulting paste was allowed to cool to room temperature. The crude sulfone was filtered off, and washed with a small amount of ethanol to give *compound* **7b** (5.5 g, 93%) as prisms, m.p. >300 °C; ν_{max}(KBr)/cm^{-1} 2980, 2950, 2900, 1520, 1490, 1460, 1430, 1390, 1360, 1320, 1300, 1270, 1210, 1180, 1150, 1120, 1030, 950, 900, 875, 820 and 780; δ_H($CDCl_3$) 1.37 (9 H, s), 1.82 (3 H, s), 3.98–4.51 (8 H, m), 6.54 (2 H, d, *J* 1), 7.28 (2 H, d, *J* 1) and 7.55 (2 H, s); *m/z* 406 (M^+) (Found: C, 61.9; H, 6.5. $C_{21}H_{26}O_4S_2$ requires C, 62.04; H, 6.45%).

Compound **7c** was similarly prepared according to the method described above, in 95% yield.

6-tert-*Butyl*-9-*methoxy*-2,11-*dithia*[3.3]*metaparacyclophane* 2,2,11,11-*tetraoxide* **7c**. *Prisms*, m.p. >300 °C; ν_{max}(KBr)/cm^{-1} 2950, 1605, 1510, 1480, 1425, 1360, 1320, 1300, 1270, 1170, 1110, 1000, 900, 870, 830, 760 and 680; δ_H($CDCl_3$) 1.31 (9 H, s), 3.32 (3 H, s), 3.72–4.55 (8 H, m), 6.60 (2 H, d, *J* 1.2), 7.20 (2 H, d, *J* 1.2) and 7.65 (2 H, s); *m/z* 422 (M^+) (Found: C, 59.7; H, 6.1. $C_{21}H_{26}O_5S_2$ requires C, 59.69; H, 6.20%).

Pyrolysis of Disulfones **7** *to give* [2.2]*Metaparacyclophanes* **8**.—*Typical procedure.* Pyrolysis of disulfones of [2.2]metaparacyclophane (compounds **7**) was carried out in an apparatus consisting of a horizontal tube (15 mm in diameter) passing through two adjacent tube furnaces, each of which was 20 cm long. The first furnace provided a temperature that would induce sublimation of the sulfone; the second was used at a higher temperature (500 °C) that would assure pyrolysis. A vacuum pump was connected at the exit from the second furnace. Disulfone **7a** (1 g) was pyrolysed at 500 °C under reduced pressure (1 mmHg) in the above apparatus as follows. The sample of disulfone was placed in the first furnace and small glass beads were packed into the second furnace. The product which sublimed was collected and chromatographed on silica gel (100 g) with hexane to yield the desired 5-tert-*butyl*[2.2]*metaparacyclophane* **8a** (404.1 mg, 60%) as prisms (from hexane), m.p. 78–80 °C; ν_{max}(KBr)/cm^{-1} 2948, 2922, 2890, 1587, 1438, 1436, 1430, 1174, 928, 806, 780, 711 and 602; δ_H($CDCl_3$) 1.30 (9 H, s), 2.09–3.16 (8 H, m), 5.19 (1 H, s), 5.77 (2 H, s), 6.76 (2 H, s) and 7.14 (2 H, s); *m/z* 264 (M^+) (Found: C, 90.6; H, 9.2. $C_{20}H_{24}$ requires C, 90.85; H, 9.15%).

Compounds **8b–d** were prepared according to the method described above. The yields are summarized in Scheme 2.

5-tert-*Butyl*-8-*methyl*[2.2]*metaparacyclophane* **8b**. *Prisms* (from hexane), m.p. 44–45 °C; ν_{max}(KBr)/cm^{-1} 2950, 1480, 1355, 1280, 1200, 1175, 940, 880, 810 and 730; δ_H($CDCl_3$) 1.30 (9 H, s), 1.70 (3 H, s), 2.22–3.22 (8 H, m), 5.96 (2 H, d, *J* 1), 6.71 (2 H, s) and 7.00 (2 H, d, *J* 1); *m/z* 278 (M^+) (Found: C, 90.2; H, 9.8. $C_{21}H_{26}$ requires C, 90.59; H, 9.41%).

5-tert-*Butyl*-8-*methoxy*[2.2]*metaparacyclophane* **8c**. *Prisms* (from MeOH), m.p. 97–98 °C; ν_{max}(KBr)/cm^{-1} 2940, 2900, 1590, 1500, 1470, 1455, 1430, 1360, 1285, 1200, 1170, 1090, 1070, 930, 900, 880 and 860; δ_H($CDCl_3$) 1.31 (9 H, s), 2.34–3.17 (8 H, m), 3.13 (3 H, s), 5.78 (2 H, d, *J* 1.2), 6.74 (2 H, s), 7.06 (2 H, d, *J* 1.2); *m/z* 294 (M^+) (Found: C, 85.4; H, 8.9. $C_{21}H_{26}O$ requires C, 85.66; H, 8.90%).

Table 3 Fractional atomic co-ordinates for the non-hydrogen atoms, with estimated standard deviations in parentheses, for 6-*tert*-butyl-9-methyl-2,11-dithia[3.3]metaparacyclophane **6b**

Atom	*x*	*y*	*z*
S(1)	0.725 6(1)	0.015 66(5)	0.943 40(6)
S(2)	0.413 8(1)	−0.262 70(5)	0.558 33(5)
C(1)	0.527 9(3)	−0.166 3(2)	0.833 6(2)
C(5)	0.797 9(3)	−0.219 3(2)	0.914 8(2)
C(3)	0.638 8(3)	−0.288 3(2)	0.773 5(2)
C(2)	0.515 6(3)	−0.228 6(2)	0.762 6(2)
C(4)	0.781 8(3)	−0.286 4(2)	0.849 4(2)
C(15)	0.709 7(4)	−0.091 3(2)	0.984 4(2)
C(6)	0.676 3(3)	−0.160 7(2)	0.908 3(2)
C(9)	0.621 1(4)	0.003 0(2)	0.706 6(2)
C(8)	0.531 9(4)	−0.038 3(2)	0.624 0(2)
C(12)	0.742 9(3)	−0.140 3(2)	0.643 5(2)
C(14)	0.477 1(4)	−0.163 9(2)	0.514 6(2)
C(16)	0.855 0(4)	0.007 3(2)	0.860 8(2)
C(7)	0.587 8(3)	−0.112 7(2)	0.593 4(2)
C(11)	0.831 6(3)	−0.099 3(2)	0.726 6(2)
C(10)	0.769 9(4)	−0.029 1(2)	0.762 0(2)
C(13)	0.368 9(4)	−0.233 7(2)	0.672 8(2)
C(18)	0.919 3(3)	−0.350 1(2)	0.858 1(2)
C(17)	0.387 9(4)	−0.107 9(2)	0.831 7(2)
C(19)	0.995 5(4)	−0.375 2(2)	0.964 5(2)
C(20)	0.857 3(4)	−0.430 4(2)	0.800 0(3)
C(21)	1.051 6(4)	−0.311 9(2)	0.816 3(3)

8-*Bromo*-5-tert-*butyl*[2.2]*metaparacyclophane* **8d**. *Prisms* [from hexane–benzene (1:1)], m.p. 64–66 °C; ν_{max}(KBr)/cm^{-1} 2950, 2930, 2859, 1476, 1428, 1360, 1023, 1008, 805 and 728; δ_H($CDCl_3$) 1.31 (9 H, s), 2.50–2.71 (4 H, m), 3.08–5.28 (4 H, m), 5.75 (2 H, d, *J* 2.2), 6.76 (2 H, s) and 7.18 (2 H, d, *J* 2.2); *m/z* 341, 343 (M^+) (Found: C, 70.2; H, 6.9. $C_{20}H_{23}Br$ requires C, 69.97; H, 6.75%).

Preparation of 8-*Bromomethyl*-5-tert-*butyl*[2.2]*metaparacyclophane* **9**.—After a mixture of compound **8b** (3.03 g, 10.88 mmol), NBS (2.32 g, 13.06 mmol), and benzoyl peroxide (100 mg) in tetrachloromethane (150 cm^3) had been refluxed for 7 h, the formed precipitates were filtered off. The filtrate was washed successively with 10% aq. sodium hydroxide and water. The organic layer was dried over sodium sulfate, and evaporated under reduced pressure to leave a solid, which was recrystallized from hexane to give *title compound* **9** (2.30 g, 59%) as prisms, m.p. 163–164 °C; ν_{max}(KBr)/cm^{-1} 2970, 2920, 2850, 1580, 1550, 1500, 1470, 1455, 1440, 1355, 1320, 1220, 1190, 1180, 1105, 995, 935, 875, 815 and 800; δ_H($CDCl_3$) 1.32 (9 H, s), 2.65–2.82 (6 H, m), 3.16–3.20 (2 H, m), 4.23 (2 H, s), 5.77 (2 H, d, *J* 1.2), 6.81 (2 H, s), 6.96 (2 H, d, *J* 1.2); *m/z* 355 and 357 (M^+) (Found: C, 70.7; H, 7.1. $C_{21}H_{25}Br$ requires C, 70.59; H, 7.05%).

Preparation of 5-tert-*Butyl*-8-*ethyl*[2.2]*metaparacyclophane* **8f**.—To a solution of MeMgI [prepared from iodomethane (3.3 g, 23.5 mmol) and magnesium (480 mg, 19.6 mmol)] in refluxing diethyl ether (10 cm^3) was added a solution of bromide **9** (700 mg, 1.96 mmol) in diethyl ether (6.5 cm^3). After the reaction mixture had been refluxed for 12 h, it was quenched with 10% aq. ammonium chloride and extracted with dichloromethane; the extract was dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue, which was recrystallized from hexane to give the *title compound* **8f** (550 mg, 96%) as prisms, m.p. 92 °C; ν_{max}(KBr)/cm^{-1} 3025, 1600, 1480, 1450, 1355, 1170, 890, 870 and 800; δ_H($CDCl_3$) 0.53 (3 H, t, *J* 7.0), 1.32 (9 H, s), 2.16 (2 H, q, *J* 7.0), 2.51–3.16 (8 H, m), 5.74 (2 H, s), 6.71 (2 H, s), 6.95 (2 H, s); *m/z* 292 (M^+) (Found: C, 90.3; H, 9.7. $C_{22}H_{28}$ requires C, 90.35; H, 9.65%).

Preparation of 5-tert-*Butyl*-8-*propyl*[2.2]*metaparacyclophane* **8g**.—To a solution of EtMgI [prepared from iodoethane (714.8 mg, 7.2 mmol) and magnesium (146 mg, 6 mmol)] in refluxing diethyl ether (5 cm^3) was added a solution of compound **9** (214.2 mg, 0.6 mmol) in diethyl ether (3.0 cm^3). After the reaction mixture had been refluxed for 12 h, it was worked up as described above to afford *compound* **8g** (126 mg, 69%) as prisms (from hexane), m.p. 66–69 °C; ν_{max}(KBr)/cm^{-1} 2960, 2889, 1480, 1460, 1362 and 1018; δ_H($CDCl_3$) 0.65 (3 H, t, *J* 7.0), 0.84 (2 H, m), 1.31 (9 H, s), 2.12 (2 H, t, *J* 7.0), 2.52–3.17 (8 H, m), 5.73 (2 H, s), 6.70 (2 H, s) and 6.96 (2 H, s); *m/z* 306 (M^+) (Found: C, 89.9; H, 9.9. $C_{23}H_{30}$ requires C, 90.13; H, 9.87%).

Demethylation of the Ether **8c** *to give the Alcohol* **8e**.—To a solution of compound **8c** (1.46 g, 5 mmol) in dry dichloromethane (25 cm^3) at 0 °C was gradually added a solution of BBr_3 (1 cm^3, 10 mmol) in dry dichloromethane (5 cm^3) during 10 min. After the reaction mixture had been stirred at room temperature for 4 h it was poured into ice–water, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue, which was chromatographed on silica gel (100 g) with hexane–benzene (1:1) to give a solid. Recrystallization from hexane afforded the *alcohol* **8e** (1.14 g, 82%) as prisms, m.p. 130–132 °C; ν_{max}(KBr)/cm^{-1} 3450, 2900, 1580, 1470, 1450, 1430, 1350, 1280, 1200, 1170, 990, 930, 900, 880, 870, 810 and 800; δ_H($CDCl_3$) 1.31 (9 H, s), 2.42–3.21 (8 H, m), 3.53 (1 H, br s, exchanged by D_2O), 5.91 (2 H, s), 6.68 (2 H, s) and 7.11 (2 H, s); *m/z* 280 (M^+) (Found: C, 85.7; H, 8.6. $C_{20}H_{24}O$ requires C, 85.67; H, 8.63%).

Trans-tert-*butylation of Compounds* **8** *to give Products* **1** *with* $AlCl_3$–$MeNO_2$ *in Benzene.—Typical procedure.* To a solution of compound **8a** (180 mg, 0.68 mmol) in benzene (31 cm^3) was added a solution of $AlCl_3$ (27.2 mg, 0.204 mmol) in $MeNO_2$ (0.05 cm^3). After the reaction mixture had been stirred for 1.5 h at 50 °C, it was poured into ice–water and extracted with diethyl ether. The ethereal solution was dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue, which was recrystallized from methanol to give conpound **1a** (113 mg, 80%) as prisms, m.p. 80–81 °C (lit.,[27] 80–81 °C).

Compounds **1b** and **1e–g** were also obtained from substrates **8b** and **8e–g** under various conditions (see Table 1).

8-*Methyl*[2.2]*metaparacyclophane* **1b**. *Prisms* (from MeOH); m.p. 130–132 °C; ν_{max}(KBr)/cm^{-1} 2925, 2850, 1490, 1440, 1370, 1310, 1195, 1175, 1155, 1060, 935, 890 and 810; δ_H($CDCl_3$) 1.73 (3 H, s), 1.98–3.28 (8 H, m), 5.77 (2 H, d, *J* 1.0, 6.67–6.82 (3 H, m) and 6.95 (2 H, d, *J* 1.0); *m/z* 222 (M^+) (Found: C, 91.9; H, 8.25. $C_{17}H_{18}$ requires C, 91.84; H, 8.16%).

8-*Hydroxy*[2.2]*metaparacyclophane* **1e**. *Pale yellow prisms* (from hexane); m.p. 132–134 °C; ν_{max}(KBr)/cm^{-1} 3570, 2900, 1582, 1448, 1175, 900, 773 and 729; δ_H($CDCl_3$) 2.44–3.22 (8 H, m), 3.69 (1 H, s, exchanged by D_2O), 5.97 (2 H, d, *J* 1.2), 6.69 (3 H, s) and 7.13 (2 H, d, *J* 1.2); *m/z* 224 (M^+) (Found: C, 85.3; H, 7.2. $C_{16}H_{16}O$ requires C, 85.68; H, 7.19%).

8-*Ethyl*[2.2]*metaparacyclophane* **1f**. *Prisms* (from hexane–benzene (1:1); m.p. 148–152 °C; ν_{max}(KBr)/cm^{-1} 2982, 2963, 2923, 2874, 2854, 1455, 1442, 1429, 1178, 896 and 812; δ_H($CDCl_3$) 0.53 (3 H, t, *J* 7.5), 2.23 (2 H, q, *J* 7.5), 2.45–2.66 (4 H, m), 2.73–2.86 (2 H, m), 3.10–3.20 (2 H, m), 5.80 (2 H, d, *J* 1.6), 6.70–6.85 (3 H, m) and 6.98 (2 H, d, *J* 1.6); *m/z* 236 (M^+) (Found: C, 91.4; H, 8.5. $C_{18}H_{20}$ requires C, 91.47; H, 8.53%).

8-*Propyl*[2.2]*metaparacyclophane* **1g**. *Prisms* (from hexane); m.p. 230–235 °C; ν_{max}(KBr)/cm^{-1} 2922, 2872, 1588, 1500, 1456, 1377, 1260, 1178, 1101, 898, 804 and 770; δ_H($CDCl_3$) 0.64 (3 H, t, *J* 7.3), 0.79–0.94 (2 H, m), 2.18–2.24 (2 H, m), 2.50–2.64 (4 H, m), 2.72–2.86 (2 H, m), 3.10–3.20 (2 H, m), 5.80 (2 H, d, *J* 2), 6.70–6.85 (3 H, m), 6.99 (2 H, d, *J* 2); *m/z*

Table 4 Fractional atomic co-ordinates for the non-hydrogen atoms, with estimated standard deviations in parentheses, for 6-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metaparacyclophane **6c**

Atom	*x*	*y*	*z*
S(1)	0.706 79(9)	0.141 97(5)	0.842 5(1)
S(2)	1.353 9(1)	0.222 87(6)	0.697 0(1)
O(1)	0.991 6(3)	0.105 5(1)	0.567 6(2)
C(2)	1.085 2(3)	0.223 1(2)	0.616 9(3)
C(5)	0.855 0(3)	0.267 3(2)	0.705 3(2)
C(7)	0.969 4(3)	0.105 0(2)	0.918 6(3)
C(1)	0.979 8(3)	0.175 7(2)	0.614 3(3)
C(6)	0.866 8(3)	0.195 7(2)	0.665 2(3)
C(4)	0.952 7(3)	0.318 0(2)	0.700 0(3)
C(11)	1.152 0(3)	0.185 4(2)	0.924 1(3)
C(12)	1.028 6(3)	0.170 1(2)	0.953 8(3)
C(10)	1.220 5(3)	0.135 9(2)	0.858 4(3)
C(9)	1.162 6(4)	0.069 8(2)	0.827 1(4)
C(3)	1.068 6(3)	0.293 6(2)	0.657 4(3)
C(8)	1.038 5(3)	0.054 7(2)	0.856 6(4)
C(17)	0.939 9(4)	0.396 7(2)	0.742 8(3)
C(16)	0.830 3(4)	0.090 2(2)	0.941 0(4)
C(13)	1.215 9(4)	0.198 4(2)	0.580 7(4)
C(15)	0.760 4(4)	0.141 4(2)	0.683 0(4)
C(20)	0.975 9(5)	0.448 0(2)	0.637 9(5)
C(14)	1.352 8(4)	0.153 7(3)	0.819 9(4)
C(18)	0.800 9(5)	0.415 8(2)	0.763 8(6)
C(21)	0.952 8(5)	0.099 0(3)	0.432 1(4)
C(19)	1.025 5(7)	0.407 8(3)	0.870 0(6)

Table 5 Fractional atomic co-ordinates for the non-hydrogen atoms, with estimated standard deviations in parentheses, for 8-methyl[2.2]-metaparacyclophane **1b**

Atom	*x*	*y*	*z*
C(14)	0.5746(5)	0.1148(3)	0.094(1)
C(5)	0.8288(6)	0.2246(3)	0.074(1)
C(3)	0.6872(5)	0.1907(3)	−0.0958(9)
C(7)	0.8464(5)	0.1366(3)	−0.0776(9)
C(15)	0.6464(6)	0.1266(3)	0.216(1)
C(12)	0.6752(6)	0.0328(3)	0.021(1)
C(4)	0.7291(5)	0.2298(3)	0.013(1)
C(13)	0.5842(5)	0.0637(3)	0.010(1)
C(11)	0.7576(5)	0.0513(3)	0.114(1)
C(6)	0.8851(5)	0.1762(3)	0.033(1)
C(16)	0.7370(6)	0.0943(3)	0.2269(9)
C(8)	0.7502(5)	0.1460(3)	−0.1558(8)
C(2)	0.5704(5)	0.1915(3)	−0.126(1)
C(1)	0.5108(5)	0.1628(3)	0.025(1)
C(9)	0.8995(5)	0.0787(3)	−0.087(1)
C(10)	0.8690(6)	0.0392(3)	0.066(1)
C(17)	0.7177(5)	0.1107(3)	−0.302(1)

250 (M^+) (Found: C, 91.1; H, 8.75. $C_{19}H_{22}$ requires C, 91.14; H, 8.86%).

$AlCl_3$–$MeNO_2$-*Catalysed Trans*-tert-*butylation of Compound* **8c** *in Benzene.—Typical procedure.* To a solution of compound **8c** (200 mg, 0.68 mmol) in benzene (31 cm^3) was added a solution of $AlCl_3$ (108.8 mg, 0.816 mmol) in $MeNO_2$ (0.20 cm^3). After the reaction mixture had been stirred for 6 h at 50 °C, it was poured into ice–water and extracted with diethyl ether. The extract was dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue, which was analysed by GLC. The structures were determined by ^1H NMR spectroscopy and by comparison of the retention time on GLC with authentic samples. In the case of run 2 in Table 2, from the reaction mixture a trace amount of 8-methoxy[2.2]metaparacyclophane **1c** was obtained by recrystallization from hexane.

* For details, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

8-*Methoxy*[2.2]*metaparacyclophane* **1c**. *Prisms* (from MeOH); m.p. 112–113 °C; $\delta_H(CDCl_3)$ 2.38–3.18 (8 H, m), 3.14 (3 H, s), 5.83 (2 H, s), 6.76 (3 H, s) and 7.07 (2 H, s); *m/z* 238 (M^+) (Found: C, 85.7; H, 7.7. $C_{17}H_{18}$ requires C, 85.67; H, 7.61%).

In the case of run 4 in Table 2, from the reaction mixture was obtained a crop (57.4 mg, 41%) of 4,5,9,10-*tetrahydropyrene* **12**, which was obtained by recrystallization from hexane as prisms (from hexane), m.p. 136–138 °C (lit.,[24] 136–138 °C).

$TiCl_4$-*Catalysed Transannular Reaction of Compound* **13** *in Dichloromethane.*—To a solution of compound **13** (100 mg, 0.34 mmol) in dichloromethane (10 cm^3) was added a solution of $TiCl_4$ (77.4 mg, 0.408 mmol) in dichloromethane (5 cm^3). After the reaction mixture had been stirred for 30 min at 50 °C, it was poured into ice–water and extracted with diethyl ether. The extract was dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue, which was recrystallized from hexane to give 2-*tert*-butyl-4,5,9,10-tetrahydropyrene **11** (75.7 mg, 85%) as prisms (from hexane), m.p. 108–109.5 °C (lit.,[24] 108–109.5 °C).

$AlCl_3$–$MeNO_2$-*Catalysed Trans*-tert-*butylation of Compound* **13** *in Benzene.*—To a solution of compound **13** (100 mg, 0.34 mmol) in benzene (15 cm^3) was added a solution of $AlCl_3$ (54.4 m,g 0.408 mmol) in $MeNO_2$ (0.10 cm^3). After the reaction mixture had been stirred for 30 min at 50 °C, it was poured into ice–water and extracted with diethyl ether. The extract was dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue, which was recrystallized from hexane to give compound **12** (39.2 mg, 56%). The formation of *tert*-butylbenzene **10** was confirmed by GLC.

Crystal Data and Refinement Details.—The space groups were determined from single-crystal photographs. The unit-cell constants were derived from least-squares analysis of the settings, on a Rigaku AFC5 diffractometer, for 12 or more reflections, mostly in the range $100° < 2\theta < 130°$. The intensities of all independent reflections with $2\theta < 130°$ were measured with θ–2θ scans of width $(1.5 + 0.285 \tan\theta)$; Ni-filtered Cu-Kα radiation (λ = 1.54178 Å) was used.

All structure were solved uneventfully by direct methods (TEXAN Version 2.0, MJ201SP) which was also used for refinement calculations. The refined non-hydrogen atomic co-ordinates are listed in Tables 3–5 whilst the hydrogen co-ordinates, temperature factors (anisotropic for carbon atoms), scale factors, and secondary extinction coefficients are available, on request, from the Cambridge Crystallographic Data Centre.*

Crystal Data for 6-tert-*Butyl-9-methyl-2,11-dithia*[3.3]*metaparacyclophane* **6b**.—$C_{21}H_{26}S_2$, M = 342.56, monoclinic, a = 8.474(9), b = 15.976(9), c = 14.137(9) Å, β = 105.70(6)°, V = 1842(2) Å^3, Z = 4, D_c = 1.23 Mg m^{-3}. Space group $P2_1/c$, Cu-Kα radiation, R = 0.046, R_w = 0.066 for 2269 unique reflections.

Crystal Data for 6-tert-*Butyl-9-methoxy-2,11-dithia*[3.3]-*metaparacyclophane* **6c**.—$C_{21}H_{26}OS_2$, M = 358.56, monoclinic, a = 10.327(6), b = 18.431(6), c = 10.409(6) Å, β = 96.73(4)°, v = 1968(2) Å^3, Z = 4, D_c = 1.21 Mg m^{-3}. Space group $P2_1/c$, Cu-Kα radiation, R = 0.049, R_w = 0.064 for 2088 unique reflections.

Crystal Data for 8-*Methyl*[2.2]*metaparacyclophane* **1b**.—$C_{17}H_{18}$, M = 222.33, orthorhombic, a = 12.96(4), b = 23.58(2), c = 8.02(2) Å, V = 2451(10) Å^3, Z = 8, D_c = 1.20 Mg m^{-3}. Space group *Pbca*, Cu-Kα radiation, R = 0.080, R_w = 0.101 for 2088 unique reflections.

References

1 Part 17, T. Yamato, J. Matsumoto, K. Tokuhisa, K. Suehiro, S. Horie and M. Tashiro, *J. Org. Chem.*, in the press.
2 D. J. Cram, D. L. Helgeson, D. Lock and L. A. Singer, *J. Am. Chem. Soc.*, 1966, **88**, 1324.
3 T. Hylton and V. Boekelheide, *J. Am. Chem. Soc.*, 1968, **90**, 6887.
4 S. A. Sherrod and V. Boekelheide, *J. Am. Chem. Soc.*, 1972, **94**, 5513.
5 S. A. Sherrod and R. L. da Costa, *Tetrahedron Lett.*, 1973, 2083.
6 V. Boekelheide, I. D. Reingold and M. Tuttle, *J. Chem. Soc., Chem. Commun.*, 1973, 406.
7 R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1547.
8 S. A. Sherrod, R. L. da Costa, R. A. Barnes and V. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1565.
9 R. H. Mitchell, T. Otsubo and V. Boekelheide, *Tetrahedron Lett.*, 1975, 219.
10 F. Vögtle, *Chem. Ber.*, 1969, **102**, 3077.
11 P. Neumann and F. Vögtle, *Synthesis*, 1973, 85.
12 D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.*, 1970, **92**, 1073.
13 D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.*, 1971, **93**, 4767.
14 S. Akabori, S. Hayashi, M. Mawa and K. Shiomi, *Tetrahedron Lett.*, 1969, 3727.
15 A. Renault, C. Cohen-Addad, J. Lajzerowicz-Bonneteau, J. P. Dutasta and M. J. Cris, *Acta Crystallogr., Sect. B.*, 1987, **43**, 480.
16 M. Tashiro and T. Yamato, *Synthesis*, 1978, 435.
17 M. Tashiro and T. Yamato, *J. Org. Chem.*, 1981, **46**, 1543.
18 M. Tashiro, K. Koya and T. Yamato, *J. Am. Chem. Soc.*, 1982, **104**, 3707.
19 M. Tashiro and T. Yamato, *J. Org. Chem.*, 1985, **50**, 2939.
20 T. Yamato, T. Arimura and M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1.
21 M. Tashiro, A. Tsuge, T. Sawada, T. Makishima, S. Horie, T. Arimura, S. Mataka and T. Yamato, *J. Org. Chem.*, 1990, **55**, 2404.
22 M. Tashiro and T. Yamato, *Org. Prep. Proced. Int.*, 1981, **13**, 1.
23 M. Tashiro and T. Yamato, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2165.
24 M. Tashiro, T. Yamato, K. Kobayashi and T. Arimura, *J. Org. Chem.*, 1987, **52**, 3196.
25 M. Tashiro, S. Mataka, Y. Takezaki, T. Arimura, T. Tsuge and T. Yamato, *J. Org. Chem.*, 1989, **54**, 451.
26 T. Yamato, S. Ide, K. Tokuhisa and M. Tashiro, *J. Org. Chem.*, 1992, **57**, 271.
27 V. Boekelheide, P. H. Anderson and T. A. Hylton, *J. Am. Chem. Soc.*, 1974, **96**, 1558.

Paper 2/02781J
Received 28*th May* 1992
Accepted 11*th June* 1992