Medium-sized cyclophanes. Part 56.† 8-Substituted 5-*tert*-Butyl [2.2]metaparacyclophane-1,9-dienes. Preparation, X-ray diffraction study and their treatment with Lewis and protic acids

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The preparation of various 8-substituted 5-*tert*-butyl[2.2]metaparacyclophane-1,9-dienes **1**, using the thiacyclophane method, and an X-ray diffraction study of 5-*tert*-butyl-8-cyano[2.2]metaparacyclophane-1,9-diene **1e** are described. Lewis and protic acid-catalyzed reactions of 8-substituted [2.2]metaparacyclophane-1,9-dienes **1b**–**g** in dichloromethane proceeded by isomerization and transannular cyclization to afford the strainless pyrenes **10** in good yields. In contrast, similar treatment of 5-*tert*-butyl-8-methoxy[2.2]metaparacyclophane **11** with Lewis acids in dichloromethane under the same conditions only led to recovery of the starting compound. Treatment of 8-methoxy[2.2]metaparacyclophane-1,9-diene **1d** with $TiCl_4$ in dichloromethane also led to isomerization and transannular reactions to afford 2-*tert*-butylpyrene **10b** within 1 min in almost quantitative yield. However, the $TiCl_4$ catalyzed reaction of an electron-poor [2.2]metaparacyclophane-1,9-diene such as **1e** did not afford any product and the starting material was recovered in almost quantitative yield. These results suggest that the present novel isomerization reaction might be attributed to the bridged double bonds, which increase the strain in the molecule in comparison with the corresponding saturated [2.2]metaparacyclophane **11**. The characterization and the reaction pathway of these products are also discussed.

[2.2]MPCP-1,9-diene (MPCP = metaparacyclophane) **1a** was first prepared by Hylton and Boekelheide[2] *via* direct C–C coupling through nucleophilic alkylation. Later on, **1a** became available *via* other synthetic methods developed by various research groups.[3–6] A versatile procedure, appropriate for the synthesis of substituted derivatives, makes use of 2,11-dithia[3.3]MPCP as a precursor.[5] The *meta*-bridged benzene ring of **1a** has been shown to undergo conformational flipping[3–6] (Fig. 1) with a significantly lower energy barrier (*ca.* 35 kJ mol^{-1}) than that for [2.2]MPCP (*ca.* 80 kJ mol^{-1}), in which elevated temperatures (about 400 K) were required for the interconversion to be revealed on the NMR timescale. A large fraction 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.

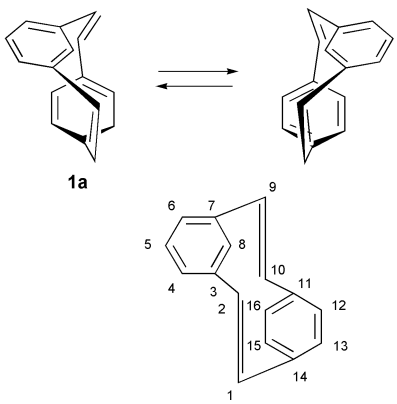


Fig. 1 Conformational flipping and numbering of [2.2]metaparacyclophane-1,9-diene.

Preliminary X-ray crystallographic studies of **1a** were carried out by Hanson.[7] The deformations of benzene rings in **1a** are similar to those of the corresponding rings in [2.2]para- and [2.2]metacyclophane, with *para*- and *meta*-bridged rings both bent into a boat-like form. The angle between the two aromatic planes defined by the carbon atoms 3, 4, 6, 7, on the one hand, and 12, 13, 15, 16, on the other, is about 18.4°. It should be noted that the angle between the (11, 12, 16)-plane and (10, 11)-bond vector [or between the (13, 14, 15)-plane and (1, 14)-bond vector] is even larger than the analogous angle in [2.2]paracyclophane.

Although Boekelheide and coworkers[3,5] have reported the preparation of various [2.2]MPCP-1,9-dienes in low total yields from readily available starting compounds in order to study their conformational ring flipping, these preparative routes seem to be too long for practical purposes. In spite of [2.2]MPCP-1,9-dienes being such highly strained compounds that are reactive toward many reagents, the known chemistry of [2.2]MPCP-1,9-dienes is very limited since their preparation from readily available compounds is very difficult. Furthermore, the preparation of other internally substituted [2.2]MPCP-1,9-dienes has not yet been reported. We report here the convenient preparation of the title compounds and their treatment with Lewis and protic acid catalysts in dichloromethane solution.

† For part 55, see: ref. 1.

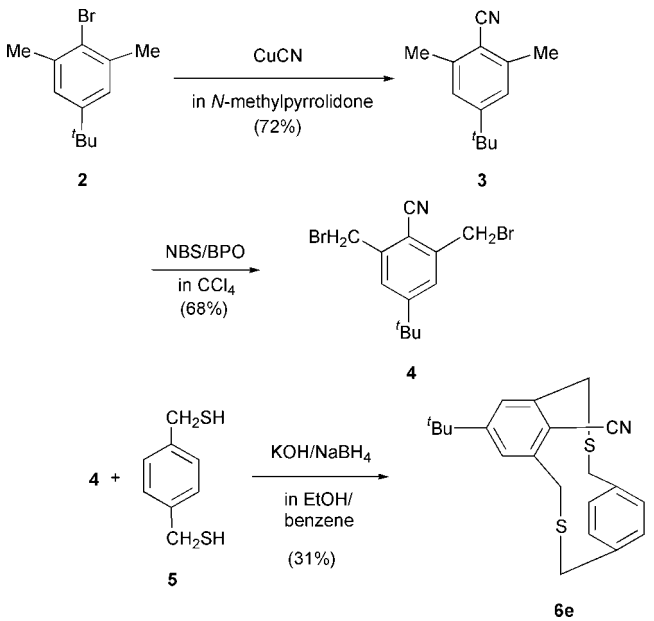
Results and discussion

Synthesis and structure

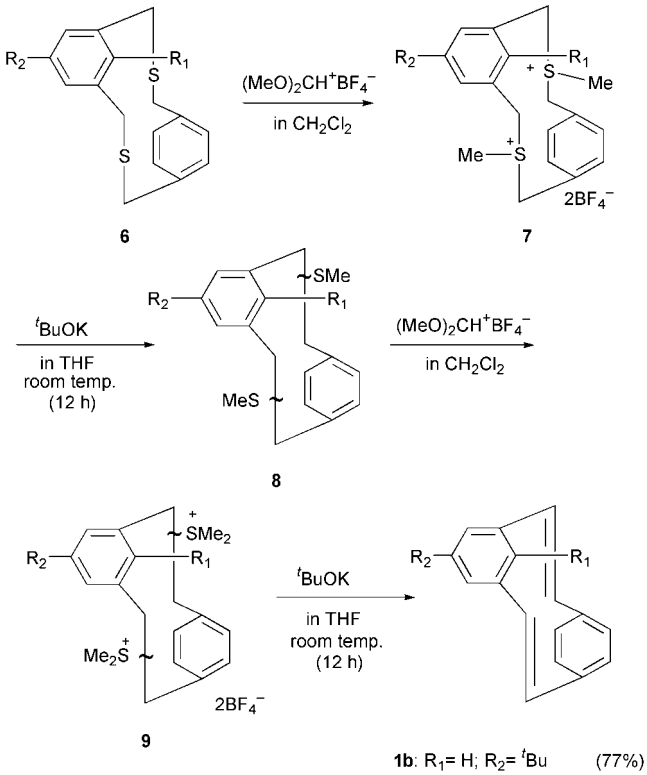
The route used to prepare 6-*tert*-butyl-9-cyano-2,11-dithia[3.3]MPCP **6e** is shown in Scheme 1. The cyclization of 2,6-bis(bromomethyl)-4-*tert*-butyl-1-cyanobenzene **4**, which was prepared from 4-*tert*-butyl-2,6-dimethylbromobenzene **2** in two steps and 1,4-bis(mercaptomethyl)benzene **5** was carried out under highly dilute conditions in 10% ethanolic KOH in the presence of a small amount of $NaBH_4$, giving the desired product **6e** in 31% yield.[8] The other intermediate dithiacyclophanes **6** were prepared in previous work.[9]

Attempted Wittig rearrangement of **6b** with *n*-butyllithium followed by treatment with methyl iodide under the same reaction conditions as for the preparation of bis(methylthio)[2.2]metacyclophane[10] failed. Only the starting compound was recovered. However, methylation of **6** with dimethoxymethylium tetrafluoroborate in dichloromethane followed by treatment with $KOBu^t$ in THF afforded the desired bis(methylthio)[2.2]MPCPs **8** in good yields (Scheme 2). Interestingly, depending on the internal substituents R_1, different yields (inversion of selectivity) of 2-*endo*,9-*endo*-**8** and 2-*endo*,10-*endo*-**8** were formed. Thus 9-methyl- and cyano-analogs are preferentially formed in the unsymmetrical 2,9-bis(thioether) isomer, but the 9-methoxyanalog is preferentially formed in the symmetrical 2,10-bis(thioether) isomer (Table 1). These findings suggest that in the case of 9-methoxyanalog, the through-space electronic interaction between the non-bonding electron pairs of the methoxy oxygen atom may inhibit the formation of the 2,9-bis(thioether) isomer in the Stevens rearrangement.

The structures of the products obtained in the present work were determined from their elemental analyses and spectral data. For example, the ^{1}H-NMR spectrum of 2,9-bis(thioether)-2-*endo*,9-*endo*-**8c** in $CDCl_3$ shows double doublets at δ 4.04 (J 7.0, 12.2 Hz) for the methine protons and a singlet at δ 7.35 for two aromatic protons of the *meta*-benzene ring ($H_{4,6}$), which are strongly deshielded by the sulfur atoms of the *endo*-SMe in the 2,9-*endo* positions on the ethylene bridges. These data strongly support the 2-*endo* and 9-*endo* arrangement of the two SMe groups. In contrast, a different spectral pattern was observed due to the unsymmetrical structure of 2,10-bis(thioether)-2-*endo*,10-*endo*-**8d** in $CDCl_3$. In particular, one aromatic proton resonance (H_{12}) of the outside *para* benzene



Scheme 1



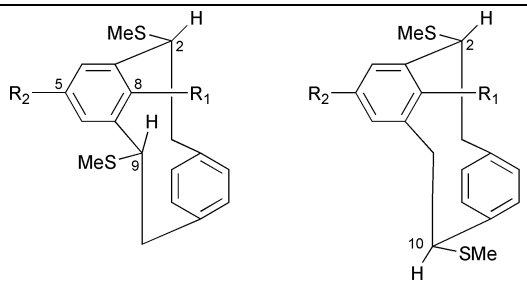
1b: R_1= H; R_2= ^{t}Bu (77%)
c: R_1= Me; R_2= ^{t}Bu (80%)
d: R_1= OMe; R_2= ^{t}Bu (77%)
e: R_1= CN; R_2= ^{t}Bu (70%)
f: R_1= OMe; R_2= H (40%)
g: R_1= OMe; R_2= Br (60%)

Scheme 2

ring was observed at δ 7.52 as a doublet (J 8.0 Hz), due to strong deshielding by the sulfur atom of the *endo*-SMe in the 10-*endo* position on the ethylene bridge.

Bis(methylthio)[2.2]MPCs **8** was methylated again to afford **9** from which the desired [2.2]MPCP-1,9-dienes **1b–g** were obtained (Scheme 2) in 60–80% yields, except for **1f** (40%). The assignment of the structure of **1** was readily apparent

Table 1 Product distribution of the Stevens rearrangement of sulfonium salt **7**



2-*endo*,9-*endo*-**8** 2-*endo*,10-*endo*-**8**

		Product distribution (%)[a]	
R_1	R_2	2-*endo*,9-*endo*-8	2-*endo*,10-*endo*-8
H	^{t}Bu	56	44
Me	^{t}Bu	77	23
CN	^{t}Bu	67	33
OMe	^{t}Bu	33	67
OMe	H	33	77
OMe	Br	6	94

[a] Determined from the ^{1}H NMR spectra.

from its ^{1}H-NMR spectrum. Thus, the internal, methyl and methoxy protons should show an upfield shift due to the ring current of the opposite *para* benzene ring. The ^{1}H-NMR spectra of the [2.2]MPCP-1,9-dienes **1b–d** prepared in the present work show peaks due to the internal, methyl and methoxy protons at δ 4.24, 1.32 and 3.26, respectively.

Single colorless crystals of suitable quality for X-ray diffraction were obtained by recrystallization of **1e** from chloroform–methanol. An ORTEP drawing of **1e** is shown in Fig. 2 with the atom numbering system. Compound **1e**, which crystallized in the orthorhombic space group $P2_12_12_1$ (no. 19), has two independent molecules ($Z = 8$) in equivalent positions. In Fig. 2, only one molecule is depicted. Two aromatic rings, which include the planes defined by the carbons 3, 4, 6, 7 and 12, 13, 15, 16, are tilted with a dihedral angle of about 15.7°. The strained rings are greatly different from each other. The *meta* benzene ring deviates from planarity and its conformation has a boat-like shape. The carbons 5 and 8 are out of the plane defined by the carbons 3, 4, 6, 7 on the opposite side of the *para* benzene ring; the dihedral angles between the plane defined by the carbons 3, 4, 6, 7 the planes defined by the carbons 3, 7, 8 and 4, 5, 6 are about 14.2 and 5.7°, respectively.

The cyanic carbon, 21, is about 2.9 Å above the plane defined by the carbons 12, 13, 15, 16. The compound **1e** is probably conformationally more rigid than **1a** (R = H) because its cyano substituent likely impinges upon the electron cloud of the *para*-bridged benzene ring. Indeed, the cyano moiety bends externally relative to the opposite *para* benzene ring; the bond angle between carbons 8 and 21 and the nitrogen 01, is about 171.8°, implying that the cyano moiety might be strongly influenced by the underlying *para* benzene ring. The angle between the (11, 12, 16)-plane and (10, 11)-bond vector [or between the (13, 14, 15)-plane and (1, 14)-bond vector] is about 108.0°.

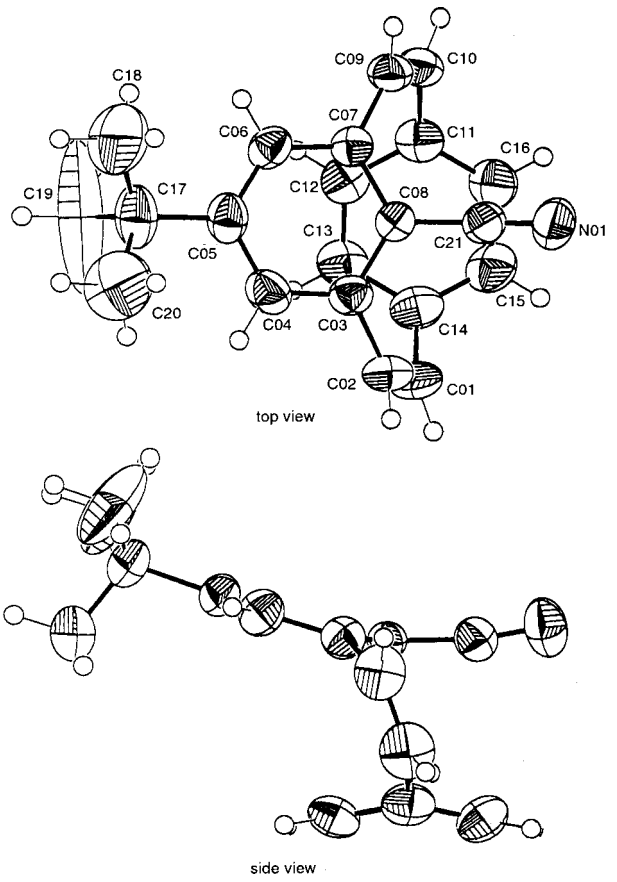


Fig. 2 X-Ray structure of 5-*tert*-butyl-8-cyano[2.2]metaparacyclophane-1,9-diene **1e**. Thermal ellipsoids are drawn at the 50% probability level.

The *para* benzene ring distorts into a boat-like shape outside of the molecule. It is quite interesting that the increased degree of deformation of the dihedral angle between the planes defined by the carbons 11, 12, 13, 14 and 11, 14, 15, 16 on the *para* benzene ring was estimated to be about 20.7°, which is larger than the 16.0° in 5-bromo-8-methoxy[2.2]MPCP.[9c] This might be attributed to the closer approach of two benzene rings caused by the introduction of double bonds into the bridging chains, resulting in increased electronic repulsion.

Acid-catalyzed reactions

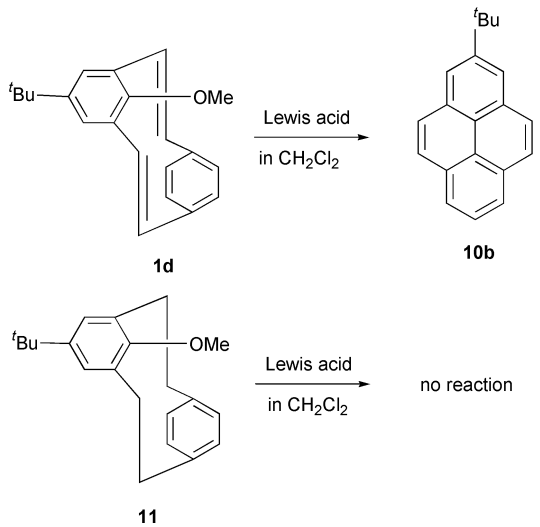
The Lewis and protic acid-catalyzed reactions of 5-*tert*-butyl-8-methoxy[2.2]MPCP-1,9-diene **1d** were carried out under various conditions and the results are summarized in Table 2. Treatment of **1d** with $AlCl_3$–$MeNO_2$ and $TiCl_4$ in dichloromethane led to isomerization and transannular reactions to afford 2-*tert*-butylpyrene **10b** (Scheme 3) within 1 min in almost quantitative yield. However, the less reactive $SnCl_4$ was needed in much larger amounts and with longer reaction times than was aluminium chloride or $TiCl_4$. A quantitative yield of **10b**, as with $AlCl_3$–$MeNO_2$ and $TiCl_4$, was obtained when the protic acid trifluoromethane sulfonic acid was used as a catalyst, but in the case of trifluoroacetic acid almost complete recovery of the starting compound was observed.

In contrast, similar treatment of 5-*tert*-butyl-8-methoxy[2.2]MPCP **11**[9a] with the Lewis acids described above in dichloromethane under the same conditions (Scheme

Table 2 The Lewis and protic acid-catalyzed reactions of 8-methoxy-5-*tert*-butyl[2.2]metaparacyclophane-1,9-diene **1d** in CH_2Cl_2[a]

Catalyst	**10b** (%)[b]
$SnCl_4$	50
$TiCl_4$	100
$AlCl_3$–$MeNO_2$	100
CF_3COOH[c]	3
CF_3SO_3H[d]	100

[a] Reaction temperature 0 °C, reaction time 1 min, [Lewis acid] : [**1d**] = 5 : 1, solvent CH_2Cl_2 unless otherwise indicated. [b] Yields determined by GLC analysis. The balance is accounted for by recovered **1d**. [c] Solvent CF_3COOH. [d] Solvent HOAc.



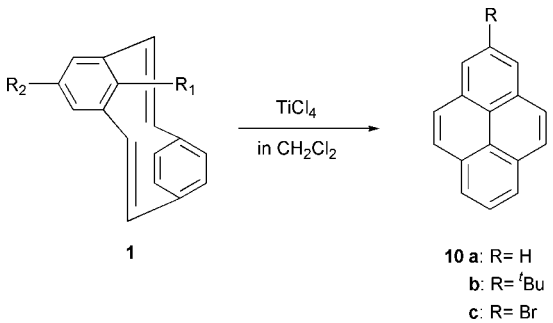
Scheme 3

3) only led to recovery of starting compound; prolonged reaction with $AlCl_3$–$MeNO_2$ gave the same result. This suggests that the present novel isomerization reaction might be attributed to the bridging double bonds, which increase the strain in the molecule in comparison with the corresponding saturated [2.2]MPCP **11**.

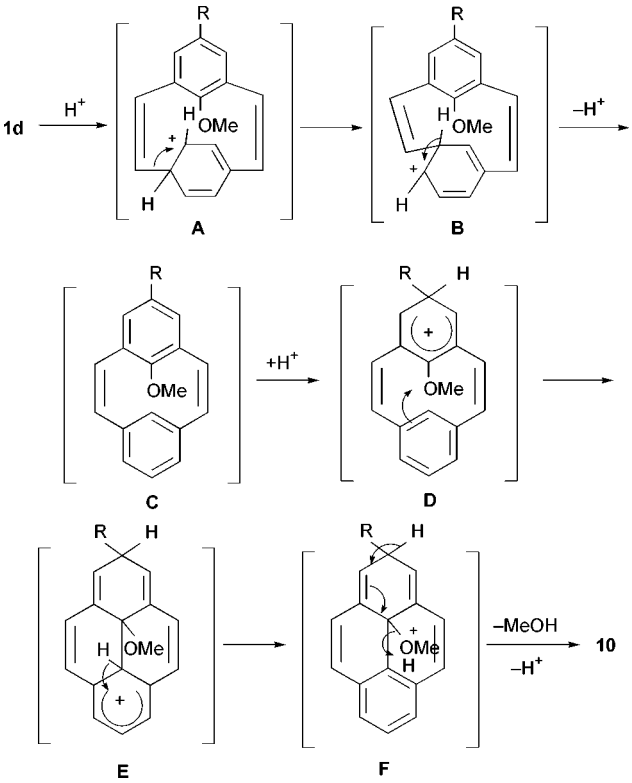
The $TiCl_4$-catalyzed reactions (Table 3) of 5-*tert*-butyl[2.2]MPCP-1,9-diene **1b** and 5-*tert*-butyl-8-methyl[2.2]MPCP-1,9-diene **1c** under the same reaction conditions for 1 min afforded the isomerization and transannular reaction product 2-*tert*-butylpyrene **10b** (Scheme 4) in 45 and 80% yields, respectively, along with recovery of the starting compound. However, in the case of 5-*tert*-butyl-8-cyano[2.2]MPCP-1,9-diene **1e**, the formation of the isomerization and transannular reaction product was not observed, and the starting material was recovered in almost quantitative yield. Thus, the nature of the substituent at the 8 position appears to have a major effect on these Lewis acid catalyzed isomerization reactions. In contrast, in the case of the 8-methoxy[2.2]MPCP-1,9-diene derivatives **1f** and **1g**, the corresponding pyrenes **10a** and **10c** were obtained in quantitative yields within 1 min, similarly to the 5-*tert*-butyl derivative **1d**. These findings strongly suggest that the 8-methoxy group might play an important role in the isomerization and transannular reactions.

We reported[9a] the $AlCl_3$ catalyzed isomerization of 8-methoxy[2.2]MPCP to the less strained [2.2]metacyclophane, followed by the transannular cyclization reaction, to afford 4,5,9,10-tetrahydropyrene. On the other hand, Boekelheide *et al.* reported[11] the oxidation of [2.2]metacyclophane-1,9-diene and 8-methyl[2.2]metacyclophane-1,9-diene to pyrene *via* 10*b*,10*c*-dihydropyrene. These results suggest that 8-substituted [2.2]metacyclophane-1,9-diene **C** (see Scheme 5) might be an intermediate for the formation of 2-substituted pyrene **10**.

Although the detailed mechanism of formation of **10** is not clear, a reaction pathway for the formation of **10** from **1** is tentatively proposed in Scheme 5. The protonation of the *ipso*-position of the ethylene bridge on the *para* benzene ring could afford the cation intermediate **A**, which could then isomerize to the less strained 8-substituted [2.2]metacyclophane-1,9-diene **C**. It assumes that when R (in **C**) is electron-donating, interannular bond formation at the 8- and 16-positions is concerted with protonation at the 5-position to form intermediate **E**. When the internal 8-substituent is an electron-withdrawing group such as CN (*e.g.* in **1e**), intermediate **C** does not form because of deactivation of the second *para* benzene ring by the CN group. The aromatization reaction transforming **E** to **10** can be facilitated by protonation of the methoxy group, followed by removal of methanol from **F**. This novel isomerization reaction might be attributed to the methoxy group at the 8 position, which increases the strain in the molecule in comparison with the unsubstituted [2.2]MPCP-1,9-diene **1a**. This interpretation is also supported by the increased deformation of the *para* benzene ring, which was estimated to be 20.7° from the X-ray crystallographic study of **1e**, compared with 18.4° in **1a**.[7] Furthermore, the good leaving ability of the methoxy group, particularly when complexed by Lewis acids, may be important, *e.g.* in preventing the reversal between intermediates **D** and **F**.



Scheme 4



Scheme 5

Table 3 $TiCl_4$-catalyzed reaction of 8-substituted [2.2]metaparacyclophane-1,9-dienes **1** in CH_2Cl_2[a]

Substrate	R_1	R_2	Product (%)[b]
1b	H	*t*Bu	10b(45)[c]
1c	Me	*t*Bu	10b(80)[c]
1d	OMe	*t*Bu	10b(100)
1e	CN	*t*Bu	10b(0)[d]
1f	OMe	H	10a(100)
1g	OMe	Br	10c(100)

[a] Reaction temperature 0 °C, reaction time 1 min, [$TiCl_4$] : [**1**] = 5 : 1. [b] Yields determined by GLC analysis. [c] Starting compounds **1b** and **1c** were recovered in 55 and 20% yields, respectively. [d] Starting compound **1e** was quantitatively recovered.

In conclusion, the preparation of 8-substituted [2.2]MPCP-1,9-dienes **1** using the thiacyclophane method appears to be a useful route to such compounds. Lewis and protic acid catalyzed reactions of **1** in dichloromethane led to the isomerization and transannular cyclization reactions affording the considerably less strained pyrenes **10** in good yields. These reactions are strongly affected by the bulk and properties of the 8-substituents, which increase strain in the molecule. Further studies on the chemical properties of [2.2]MPCP-1,9-dienes **1** are now in progress.

Experimental

All melting points (Yanagimoto MP-S1) are uncorrected. NMR spectra were taken at 270 MHz 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 on a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra were collected using 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 a GLC. Elemental analyses were obtained on a Yanaco MT-5. GLC analyses were performed using a Shimadzu GC-14A gas chromatograph (silicone OV-1, 2 m; programmed temperature rise 12 °C min^{-1}; carrier gas nitrogen, 25 mL min^{-1}).

Syntheses

Preparation of 9-substituted-2,11-dithia[3.3]MCP **6** and 5-*tert*-butyl-8-methoxy[2.2]MPCP **11**[9a] was as previously described. 4-*tert*-Butyl-2,6-dimethylbromobenzene **2** was prepared as previously described.[12]

4-*tert*-Butyl-2,6-dimethyl-1-cyanobenzene (3). A mixture of 4-*tert*-butyl-2,6-dimethylbromobenzene (**2**, 3.38 g, 14.0 mmol) and cuprous cyanide (2.20 g, 24.6 mmol) in *N*-methylpyrrolidone (25 mL) was heated at 180–185 °C for 10 h, it was then poured into a mixture of water and concentrated aqueous ammonia (400 mL, 1 : 1 v/v). After the resulting mixture had been stirred in an ice bath at 0 °C for 3 h, the solid precipitate was collected by filtration, washed with water, and dried. The resulting solid was placed at the top of a silica gel column (Wako, C-300, 500 g), using CH_2Cl_2 as an eluent. Removal of the solvent from the eluted solution gave a white solid, which was recrystallized from hexane to afford **3** (1.89 g, 72%) as colorless prisms, mp 66–67 °C; υ_{max} (KBr)/cm^{-1}: 2221 (CN); δ_H ($CDCl_3$): 1.30 (9 H, s), 2.52 (6 H, s), 7.13 (2 H, s); *m*/z: 187 (M^+). Anal. calc. for $C_{13}H_{17}N$ (187.3): C, 83.37; H, 9.15; N, 7.48; found: C, 83.56; H, 9.11; N, 7.54%.

2,6-Bis(bromomethyl)-4-*tert*-butylcyanobenzene (4). A mixture of **3** (5.0 g, 26.7 mmol), *N*-bromosuccinimide (10.0 g, 56.1 mmol), and benzoylperoxide (100 mg, 0.376 mmol) in carbon tetrachloride (300 mL) was refluxed for 12 h. The reaction mixture was cooled to room temperature and washed with aqueous sodium hydroxide and water, dried over Na_2SO_4, and the solvent evaporated *in vacuo* to leave a residue. The residue was recrystallized from hexane to afford **4** (6.3 g, 68%) as colorless prisms, mp 91–93 °C; υ_{max} (KBr)/cm^{-1}: 2221 (CN); δ_H ($CDCl_3$): 1.35 (9 H, s), 4.64 (4 H, s), 7.49 (2 H, s); *m*/z: 343, 345, 357 (M^+). Anal. calc. for $C_{13}H_{15}NBr_2$ (345.1): C, 45.63; H, 4.64; N, 3.96; found: C, 45.25; H, 4.38; N, 4.06%.

6-*tert*-Butyl-9-cyano-2,11-dithia[3.3]metaparacyclophane (6e). A solution of **4** (5.67 g, 18 mmol) and 1,4-bis(mercaptomethyl)benzene (**5**, 3.07 g, 18 mmol) in 200 ml of benzene was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 3.29 g (58.6 mmol) of potassium hydroxide and 0.8 g (21.1 mmol) of sodium borohydride in 4.0 L of ethanol. When addition was complete (12 h), the reaction mixture was concentrated and the residue was extracted with CH_2Cl_2 (500 mL). The combined extracts were washed with water (100 mL × 2), dried over Na_2SO_4 and the solvent was evaporated *in vacuo* to leave a residue. The residue was chromatographed over silica gel (Wako, C-300; 300 g) with 1 : 1 benzene–hexane as eluent to give 2.5 g of **6e** as a white solid. Recrystallization from hexane gave 1.96 g (31%) of **6e** as colorless prisms, mp 177–179 °C; υ_{max} (KBr)/cm^{-1}: 2965, 2908, 2867, 2218 (CN), 1603, 1504, 1478; δ_H ($CDCl_3$): 1.34 (9 H, s), 3.65 (2 H, d, *J* 15.3), 3.74 (2 H, d, *J* 15.3), 3.76 (2 H, d, *J* 12.8), 3.96 (2 H, d, *J* 12.8), 6.36 (2 H, s), 7.14 (2 H, s), 7.31 (2 H, s); *m*/z: 352 (M^+). Anal. calc. for $C_{21}H_{23}NS_2$ (353.5): C, 71.34; H, 6.56; N, 3.96; found: C, 71.21; H, 6.78; N, 3.83%.

Typical procedure for the preparation of sulfonium salts (7). A solution of **6b** (4.78 g, 14.7 mmol) in CH_2Cl_2 (2 mL) was added with stirring to a suspension of dimethoxymethylium tetrafluoroborate (18.1 g, 94 mmol) in CH_2Cl_2 (25 mL) maintained at −30 °C under nitrogen. The mixture was allowed to warm to room temperature and was stirred for an additional 4 h. Then, 150 mL of ethyl acetate was added, the mixture stirred overnight, and the solvent decanted. The resulting crystalline precipitate was collected and dried, giving 7.3 g (93%) of **7b**. Compounds **7c**–**7g** were synthesized in the same manner as described for **7b** and compounds **7b**–**7g** were used directly without further purification.

7b. Yield 93%, colorless crystals, mp 207–209 °C; υ_{max} (KBr)/cm^{-1}: 2954, 1601, 1479, 1423, 1370, 1055, 885; δ_H ([D_6]DMSO): 1.27 (9 H, s), 3.20 (6 H, s), 4.35 (2 H, d, *J* 14.0), 4.62 (2 H, d, *J* 14.0), 4.63 (2 H, d, *J* 12.2), 5.11 (2 H, d, *J* 12.2), 5.30 (1 H, s), 6.77 (2 H, s), 7.47 (2 H, s), 7.68 (2 H, s).

7c. Yield 89%, colorless crystals, mp 240–242 °C; υ_{max} (KBr)/cm^{-1}: 3040, 2960, 1430, 1030, 989, 745; δ_H ([D_6]DMSO): 1.36 (9 H, s), 1.87 (3 H, s), 3.23 (6 H, s), 4.33–5.14 (8 H, m), 6.18 (1 H, d, *J* 7.93), 6.56 (1 H, d, *J* 7.93), 7.40 (1 H, d, *J* 2.2), 7.42 (1 H, d, *J* 2.2), 7.45 (1 H, d, *J* 7.9), 7.52 (1 H, d, *J* 7.9).

7d. Yield 89%, colorless crystals, mp 235–238 °C; υ_{max} (KBr)/cm^{-1}: 2960, 1645, 1420, 1060, 1040; δ_H ([D_6]DMSO): 1.30 (9 H, s), 3.23 (6 H, s), 3.44 (3 H, s), 4.46 (2 H, d, *J* 14.0), 4.52 (2 H, d, *J* 12.2), 4.62 (2 H, d, *J* 14.0), 5.02 (2 H, d, *J* 12.2), 6.56 (2 H, s), 7.42 (2 H, s), 7.51 (2 H, s).

7e. Yield 64%, colorless crystals, mp 204–209 °C; υ_{max} (KBr)/cm^{-1}: 2962, 2231 (CN), 1490, 1466, 1356, 1368; δ_H ([D_6]DMSO): 1.40 (9 H, s), 3.36 (6 H, s), 4.76 (2 H, d, *J* 14.0), 4.81 (2 H, d, *J* 12.2), 4.93 (2 H, d, *J* 14.0), 5.16 (2 H, d, *J* 12.2), 6.75 (2 H, s), 7.74 (2 H, s), 7.81 (2 H, s).

7f. Yield 97%, colorless crystals, mp 198–202 °C; υ_{max} (KBr)/cm^{-1}: 2985, 1458, 1433, 1300, 1060; δ_H ([D_6]DMSO): 3.31 (6 H, s), 3.52 (3 H, s), 4.58 (2 H, d, *J* 14.0), 4.59 (2 H, d, *J* 12.0), 4.70 (2 H, d, *J* 14.0), 5.12 (2 H, d, *J* 12.0), 6.60 (2 H, s), 7.16 (1 H, t, *J* 7.2), 7.40 (2 H, d, *J* 7.2), 7.52 (2 H, s).

7g. Yield 85%, colorless crystals, mp 200–206 °C; υ_{max} (KBr)/cm^{-1}: 2950, 1478, 1431, 1331, 1262, 1056; δ_H ([D_6]DMSO): 3.22 (6 H, s), 3.46 (3 H, s), 4.49 (2 H, d, *J* 14.0), 4.54 (2 H, d, *J* 13.0), 4.59 (2 H, d, *J* 14.0), 4.70 (2 H, d, *J* 13.0), 6.78 (2 H, s), 7.52 (2 H, s), 7.67 (2 H, s).

Typical procedure for the Stevens rearrangement of 7 to give 8. To a solution of **7b** (1.7 g, 3.2 mmol) in tetrahydrofuran (THF, 30 mL) was added with stirring $KOBu^t$ (1.04 g, 9.2 mmol) at room temperature. The mixture was stirred for an additional 12 h. Then, 1 M hydrochloric acid (50 mL) was added and the solution extracted with CH_2Cl_2 (200 mL). The combined extracts were washed with water (2 × 50 mL), dried over Na_2SO_4 and the solvent was evaporated *in vacuo* to leave a residue. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with 1 : 1 benzene–hexane as eluent to give 720 mg of **8b** as a white solid. Recrystallization from hexane gave 650 mg (57%) of **8b**. Compounds **8c**–**8g** were synthesized in the same manner as for **8b**.

8b. Yield, 57%, colorless prisms, mp 123–126 °C; ν_{max} (KBr)/cm^{-1}: 2960, 2915, 2884, 2860, 1476, 1362; δ_H ($CDCl_3$): 1.24 (9 H, s), 1.89 (3 H, s), 2.06 (3 H, s), 1.80–2.20 (2 H, m), 3.32–3.34 (2 H, m), 3.69–3.74 (1 H, m), 5.05 (1 H, s), 5.72 (2 H, s), 6.72 (1 H, d, *J* 2.0), 7.11 (1 H, d, *J* 7.0), 7.22 (1 H, d, *J* 2.0), 7.55 (2 H, d, *J* 7.0); *m*/*z*: 356 (M^+). Anal. calc. for $C_{22}H_{28}S_2$ (356.6): C, 74.10; H, 7.91; found: C, 74.21; H, 8.04%.

8c. Yield 44%, colorless prisms (hexane), mp 131–134 °C; ν_{max} (KBr)/cm^{-1}: 2959, 1480, 1363; δ_H ($CDCl_3$): 1.38 (9 H, s), 1.79 (3 H, s), 2.06 (6 H, s), 2.39 (2 H, dd, *J* 12.2, 12.2), 3.53 (2 H, dd, *J* 7.0, 12.2), 4.04 (2 H, dd, *J* 7.0, 12.2), 5.83 (2 H, d, *J* 2.0), 7.00 (2 H, d, *J* 2.0), 7.35 (2 H, s); *m*/*z*: 370 (M^+). Anal. calc. for $C_{23}H_{30}S_2$ (370.6): C, 74.54; H, 8.16; found: C, 74.19; H, 7.96%.

8d. Yield 79%, colorless prisms (hexane), mp 126–129 °C; ν_{max} (KBr)/cm^{-1}: 2960, 1460, 1428, 1243, 1073; δ_H ($CDCl_3$): 1.32 (9 H, s), 2.05 (6 H, s), 2.26 (2 H, dd, *J* 12.2, 12.2), 3.14 (3 H, s), 3.49 (2 H, dd, *J* 7.0, 12.2), 4.09 (2 H, dd, *J* 7.0, 12.2), 5.82 (2

H, s), 6.77 (1 H, d, *J* 2.0), 7.12 (1 H, d, *J* 8.0), 7.27 (1 H, d, *J* 2.0), 7.52 (1 H, d, *J* 8.0); *m*/*z*: 386 (M^+). Anal. calc. for $C_{23}H_{30}OS_2$ (386.6): C, 71.46; H, 7.82; found: C, 71.63; H, 8.15%.

8e. Yield 54%, colorless prisms (hexane), mp 121–123 °C; ν_{max} (KBr)/cm^{-1}: 2958, 2212 (CN), 1469, 1439, 1361; δ_H ($CDCl_3$): 1.38 (9 H, s), 2.03 (6 H, s), 2.43 (2 H, dd, *J* 12.2, 12.2), 3.49 (2 H, dd, *J* 7.0, 12.2), 4.16 (2 H, dd, *J* 7.0, 12.2), 5.76 (2 H, s), 7.30 (2 H, s), 7.57 (2 H, s); *m*/*z*: 381 (M^+). Anal. calc. for $C_{23}H_{27}NS_2$ (381.6): C, 72.39; H, 7.13; N, 3.67; found: C, 72.19; H, 7.10; N, 3.72%.

8f. Yield 36%, colorless prisms (hexane), mp 123–126 °C; ν_{max} (KBr)/cm^{-1}: 2943, 2908, 1463, 1426, 1245, 1048; δ_H ($CDCl_3$): 2.03 (3 H, s), 2.20 (3 H, s), 2.29 (1 H, dd, *J* 12.2, 12.2), 2.57 (1 H, dd, *J* 12.2, 12.2), 2.77 (1 H, dd, *J* 7.0, 12.2), 3.14 (3 H, s), 3.51 (1 H, dd, *J* 7.0, 12.2), 3.69 (1 H, dd, *J* 7.0, 12.2), 4.14 (1 H, dd, *J* 7.0, 12.2), 5.87 (2 H, s), 6.79 (1 H, dd, *J* 2.0, 7.0), 6.88 (1 H, t, *J* 8.0), 6.03 (1 H, d, *J* 8.0), 7.14 (1 H, d, *J* 8.0), 7.29 (1 H, dd, *J* 2.0, 7.0); *m*/*z*: 328 (M^+). Anal. calc. for $C_{19}H_{22}OS_2$ (330.51): C, 69.05; H, 6.71; found: C, 69.26; H, 6.78%.

8g. Yield 42%, colorless prisms (hexane), mp 121–123 °C; ν_{max} (KBr)/cm^{-1}: 2949, 1496, 1240, 1101, 1086; δ_H ($CDCl_3$): 2.03 (3 H, s), 2.22 (3 H, s), 2.28 (1 H, dd, *J* 12.2, 12.2), 2.53 (1 H, dd, *J* 12.2, 12.2), 2.76 (1 H, dd, *J* 7.0, 12.2), 3.15 (3 H, s), 3.51 (1 H, dd, *J* 7.0, 12.2), 3.74 (1 H, dd, *J* 7.0, 12.2), 4.10 (1 H, dd, *J* 7.0, 12.2), 6.01 (2 H, d, *J* 2.0), 6.97 (1 H, d, *J* 2.0), 7.15 (1 H, d, *J* 8.0), 7.43 (1 H, d, *J* 2.0), 7.56 (1 H, d, *J* 8.0); *m*/*z*: 408, 410 (M^+). Anal. calc. for $C_{19}H_{21}OS_2Br$ (409.4): C, 55.74; H, 5.17; found: C, 56.02; H, 5.12%.

Typical procedure for the preparation of sulfonium salts (9). A solution of **8b** (1.1 g, 3.1 mmol) in CH_2Cl_2 (10 mL) was added with stirring to a suspension of dimethoxymethylium tetrafluoroborate (18.1 g, 94 mmol) in CH_2Cl_2 (25 mL) maintained at −30 °C under nitrogen. The mixture was allowed to warm to room temperature and was stirred for an additional 4 h. Then, ethyl acetate (150 mL) was added, the mixture was stirred overnight, and the solvent was decanted. The resulting crystalline precipitate was collected and dried, giving **9b** (1.3 g, 94%). Compounds **9c**–**9g** were synthesized in the same manner as for **9b** and compounds **9b**–**9g** were used directly without further purification.

9b. Yield 94%, colorless crystals, mp 262–270 °C; ν_{max} (KBr)/cm^{-1}: 2970, 1593, 1479, 1366, 1207, 1035; δ_H ([D_6]DMSO): 1.31 (9 H, s), 2.76 (3 H, s), 3.02 (3 H, s), 3.20 (3 H, s), 3.22 (3 H, s), 2.40–3.40 (3 H, m), 3.71 (1 H, dd, *J* 7.0, 11.0), 4.38 (1 H, d, *J* 7.0, 11.0), 4.77 (1 H, dd, *J* 7.0, 11.0), 5.29 (1 H, s), 5.99 (2 H, s), 7.11 (2 H, s), 7.44 (2 H, d, *J* 8.0).

9c. Yield 84%, colorless crystals, mp >300 °C; ν_{max} (KBr)/cm^{-1}: 2960, 2890, 1465, 1365, 1083, 1055; δ_H ([D_6]DMSO): 1.44 (9 H, s), 1.95 (3 H, s), 2.88 (6 H, s), 3.31 (6 H, s), 3.16 (2 H, t, *J* 11.0), 3.75 (2 H, dd, *J* 7.0, 11.0), 3.92 (2 H, dd, *J* 7.0, 11.0), 6.06 (2 H, s), 7.26 (2 H, s), 7.36 (2 H, s).

9d. Yield 74%, colorless crystals, mp >300 °C; ν_{max} (KBr)/cm^{-1}: 2955, 2914, 1460, 1363, 1204, 1065; δ_H ([D_6]DMSO): 1.41 (9 H, s), 2.94 (6 H, s), 3.07 (6 H, s), 3.22 (3 H, s), 3.02–3.20 (2 H, m), 3.64–3.80 (2 H, m), 4.84–4.95 (2 H, m), 6.08 (2 H, s), 7.22 (2 H, s), 7.43 (2 H, s).

9e. Yield 70%, colorless crystals, mp 275–278 °C; ν_{max} (KBr)/cm^{-1}: 2948, 2223 (CN), 1498, 1456, 1369; δ_H ([D_6]DMSO): 1.44 (9 H, s), 2.85 (6 H, s), 3.82 (6 H, s), 3.10–5.00 (6 H, m), 5.99 (2 H, s), 7.53 (2 H, s), 7.57 (2 H, s).

9f. Yield 85%, colorless crystals, mp >300 °C; ν_{max} (KBr)/cm^{-1}: 2944, 1463, 1426, 1245, 1048; δ_H ([D_6]DMSO): 2.83 (3 H, s), 3.01 (3 H, s), 3.22 (3 H, s), 3.24 (3 H, s), 3.25 (3 H, s), 2.60–3.60 (3 H, m), 4.69 (1 H, dd, *J* 7.0, 11.0), 4.65 (1 H, dd, *J* 7.0, 11.0), 4.84 (1 H, dd, *J* 7.0, 11.0), 6.05 (1 H, d, *J* 8.0), 6.12 (1 H, d, *J* 8.0), 7.12 (1 H, t, *J* 7.2), 7.36 (2 H, d, *J* 7.2), 7.31 (1 H, d, *J* 8.0), 7.39 (1 H, d, *J* 8.0).

9g. Yield 60%, colorless crystals, mp >300 °C; ν_{max} (KBr)/cm^{-1}: 2963, 1464, 1438, 1250, 1083; δ_H ([D_6]DMSO): 2.87 (3 H, s), 3.02 (3 H, s), 2.80–3.40 (3 H, m), 3.21 (3 H, s), 3.24 (3 H, s), 3.26 (3 H, s), 3.69 (1 H, dd, *J* 7.0, 11.0), 4.72 (1 H, dd, *J* 7.0, 11.0), 4.82 (1 H, dd, *J* 7.0, 11.0), 6.22 (1 H, d, *J* 8.0), 6.72 (1 H, d, *J* 8.0), 7.31 (1 H, d, *J* 8.0), 7.36 (1 H, d, *J* 2.0), 7.40 (1 H, d, *J* 8.0), 7.42 (1 H, d, *J* 2.0).

Typical procedure for the preparation of 1. To a solution of **9b** (1.2 g, 2.14 mmol) in THF (80 mL) was added with stirring $KOBu^t$ (0.72 g, 6.41 mmol) at room temperature. The mixture was stirred for an additional 12 h. Then, 1 M hydrochloric acid (50 mL) was added and extracted with CH_2Cl_2 (200 mL). The combined extracts were washed with water (50 mL × 2), dried over Na_2SO_4 and the solvent was evaporated *in vacuo* to leave a residue. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with 1 : 1 benzene–hexane, as eluent to give **1b** (430 mg, 77%). Compounds **1c**–**1g** were synthesized in the same manner as for **1b**.

5-tert-buty1[*2.2*]*metaparacyclophane-1,9-diene* (***1b***). Yield 77%, colorless oil; ν_{max} (NaCl)/cm^{-1}: 2959, 1585, 1572, 1476, 1361; δ_H ($CDCl_3$): 1.25 (9 H, s), 4.24 (1 H, s), 6.66 (2 H, d, *J* 10.3), 6.79 (2 H, s), 6.86 (4 H, s), 7.18 (2 H, d, *J* 10.3); *m*/*z*: 260 (M^+). Anal. calc. for $C_{20}H_{20}$ (260.38): C, 92.26; H, 7.74; found: C, 92.21; H, 7.84%.

5-tert-Butyl-8-methyl[*2.2*]*metaparacyclophane-1,9-diene* (***1c***). Yield 80%, colorless oil; ν_{max} (NaCl)/cm^{-1}: 2962, 2866, 1463, 1392; δ_H ($CDCl_3$): 1.28 (9 H, s), 1.32 (3 H, s), 6.11 (2 H, s), 6.66 (2 H, s), 6.80 (2 H, d, *J* 9.8), 6.97 (2 H, d, *J* 9.8), 7.02 (2 H, s); *m*/*z*: 274 (M^+). Anal. calc. for $C_{21}H_{22}$ (274.41): C, 91.92; H, 8.08; found: C, 91.70; H, 8.26%.

5-tert-Butyl-8-methoxy[*2.2*]*metaparacyclophane-1,9-diene* (***1d***). Yield 77%, colorless oil; ν_{max} (NaCl)/cm^{-1}: 2958, 1483, 1360, 1244, 1021; δ_H ($CDCl_3$): 1.27 (9 H, s), 3.26 (3 H, s), 6.20 (2 H, s), 6.63 (2 H, s), 6.68 (2 H, d, *J* 9.8), 7.06 (2 H, d, *J* 9.8), 7.13 (2 H, s); *m*/*z*: 290 (M^+). Anal. calc. for $C_{21}H_{22}O$ (290.41): C, 86.81; H, 7.64; found: C, 86.60; H, 7.76%.

5-tert-Butyl-8-cyano[*2.2*]*metaparacyclophane-1,9-diene* (***1e***). Yield 70%, colorless prisms (hexane), mp 87–90 °C; ν_{max} (KBr)/cm^{-1}: 2958, 2281 (CN), 1437; δ_H ($CDCl_3$): 1.26 (9 H, s) 6.09 (2 H, s), 6.74 (2 H, d, *J* 10.0), 6.82 (2 H, s), 7.26 (2 H, d, *J* 10.0), 7.34 (2 H, s); *m*/*z*: 285 (M^+). Anal. calc. for $C_{21}H_{19}N$ (285.39): C, 88.38; H, 6.71; N, 4.91; found: C, 88.31; H, 6.80; N, 4.89%.

8-Methoxy[*2.2*]*metaparacyclophane-1,9-diene* (***1f***). Yield 40%, colorless oil; ν_{max} (NaCl)/cm^{-1}: 2954, 1438, 1363, 1226, 1164; δ_H ($CDCl_3$): 3.22 (3 H, s), 6.22 (2 H, s), 6.61 (3 H, s), 6.64 (2 H, d, *J* 9.8), 7.04 (2 H, d, *J* 9.8), 7.12 (2 H, s); *m*/*z*: 234 (M^+). Anal. calc. for $C_{17}H_{14}O$ (234.3): C, 87.15; H, 6.02; found: C, 87.40; H, 6.34%.

5-Bromo-8-methoxy[*2.2*]*metaparacyclophane-1,9-diene* (***1g***). Yield 60%, colorless oil; ν_{max} (NaCl)/cm^{-1}: 2949, 1496, 1240, 1101, 1086; δ_H ($CDCl_3$): 3.25 (3 H, s), 6.64 (2 H, s), 6.59 (2 H, d, *J* 9.8), 6.78 (2 H, s), 7.11 (2 H, d, *J* 9.8), 7.14 (2 H, s); *m*/*z*: 312, 314 (M^+). Anal. calc. for $C_{17}H_{13}OBr$ (313.20): C, 65.2; H, 4.18; found: C, 65.41; H, 4.35%.

Typical procedure for the Lewis and protic acid catalyzed transannular reaction of 1. To a solution of compound **1d** (100 mg, 0.35 mmol) in methylene dichloride (20 mL) was added a solution of $TiCl_4$ (0.17 mL, 1.5 mmol) or trifluoromethane sulfonic acid in CH_2Cl_2 (5 mL). After the reaction mixture had been stirred for 1 min at 0 °C, it was poured into ice water and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue. GLC analysis of the residue showed a single product, **10b**. The residue was recrystallized from methanol to give 75.7 mg (95%) of 2-*tert*-butylpyrene (**10b**), using $TiCl_4$. Com-

Table 4 Crystallographic data and data collection details for 5-*tert*-butyl-8-cyano[2.2]metaparacyclophane-1,9-diene **1e**

Formula	$C_{21}H_{19}N$
FW	285.39
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
a/Å	15.683(2)
b/Å	18.737(3)
c/Å	11.044(1)
U/Å^3	3245.3
Z	8
T/K	298
μ/cm^{-1}	5.0
No. of reflections	11 648
Unique reflections	5512
R	0.044
R_w [a]	0.117

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

pounds **10a** and **10c** were synthesized by the reaction of **1f** and **1g** in the presence of $TiCl_4$ as described for **10b**.

Pyrene (***10a***). Yield 95%, colorless prisms (hexane), mp 151–154 °C [lit.[13] mp 152.2–152.9 °C].

2-tert-Butylpyrene (***10b***). Yield 95%, colorless prisms, mp 109–112 °C [lit.[8h] mp 109–110 °C]; ν_{max} (KBr)/cm^{-1}: 2970, 1480, 1390, 1380; δ_H ($CDCl_3$): 1.59 (9 H, s), 7.96 (2 H, d, J 8.0), 8.05 (3 H, s), 8.15 (2 H, d, J 8.0), 8.21 (2 H, s).

2-Bromopyrene (***10c***). Yield 90%, colorless prisms (hexane), mp 131–133 °C [lit.[14] 132–133 °C].

X-Ray crystallography

Crystallographic data for **1e** are given in Table 4. The unit cell constants were derived from least-squares analysis of the settings, on an Enraf–Nonius CAD4 FR 590 diffractometer, for 25 reflections in the range $21° < \theta < 43°$. The intensities of all independent reflections with $4° < 2\theta < 130°$ were measured with $\omega - 2\theta$ scans (ω scan width $= 0.6 + 0.22 \tan \theta$); Ni-filtered Cu-Kα radiation ($\lambda = 1.541\,84$ Å) was used. The structure was solved uneventfully by direct methods (SIR97[15]) and difference Fourier syntheses, and refined by a full-matrix least-squares method. All calculations were performed on Micro VAX 3100 and IBM RISC System 6000 3100 computers using the SHELXL-97 program package.[16]

CCDC reference number 156030. See http://www.rsc.org/suppdata/nj/b0/b009932p/ for crystallographic data in CIF or other electronic format.

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