Unsymmetrically Tris-Bridged [2.2.2]Cyclophane.[1] Syntheses of [2.2.2](1,2,4)(1,3,5)- and [2.2.2](1,2,4)(1,2,5)Cyclophanes[2]

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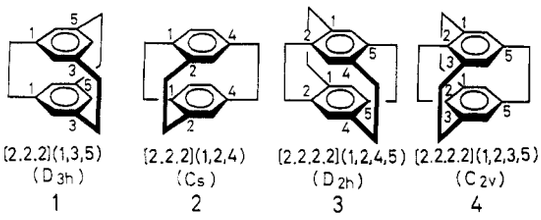
As the first members of [2.2.2]cyclophanes whose two benzene rings are unsymmetrically held together with three ethano bridges, [2.2.2](1,2,4)(1,3,5)cyclophane (C_1 symmetry) (**6**) and [2.2.2](1,2,4)(1,2,5)cyclophane (C_2 symmetry) (**7**) were synthesized and their unusually strained and skew structures were supported by their UV and NMR spectra.

As members of cyclophanes whose two benzene rings are held together with more than two ethano bridges, there have been prepared [2.2.2](1,3,5)- (D_{3h} symmetry) (**1**),[3] [2.2.2]-(1,2,4)- (C_s symmetry) (**2**),[4] [2.2.2.2](1,2,4,5)- (D_{2h} symmetry) (**3**),[5] and [2.2.2.2](1,2,3,5)cyclophanes (C_{2v} symmetry) (**4**).[6]

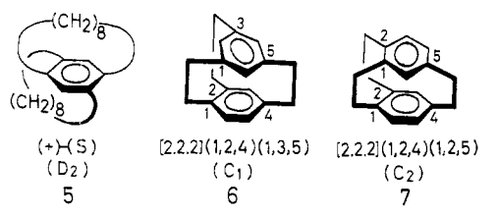
Chart I



Conspicuous features in these compounds are their deformed benzene rings and strong transannular π-electron interaction caused by intense interfacial crowding of the two aromatic rings.

We have been interested in the synthetic studies of high symmetry chiral(gyrochiral)[7] molecules,[8] and previous papers from our laboratory described the syntheses of various gyrochiral compounds with twisted π-electron systems: e.g., (+)-(*S*)-[8][8]paracyclophane[9] (D_2 symmetry) (**5**), (−)-(*R,R,R,R*)-[6]chochin[10] (D_2 symmetry) and (±)-*trans*-bicyclo[10.8.0]eicos-1(12)-ene[11] (C_2 symmetry). In [8][8]paracyclophane (**5**), the central benzene ring is dissymmetrically twisted by two octamethylene groups bridging two para positions, and the (+) Cotton effect at 240–360 nm reveals its skew structure.

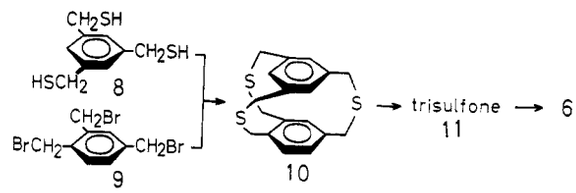
Chart II



An obvious extension of our interests in these dissymmetrically twisted cyclophanes led us to investigate the syntheses of [2.2.2]cyclophanes which have two benzene rings dissymmetrically held together with three ethano bridges, and this contribution is concerned with syntheses of [2.2.2](1,2,4)-(1,3,5)cyclophane (C_1 symmetry) (**6**) and [2.2.2](1,2,4)-(1,2,5)cyclophane (C_2 symmetry) (**7**).

Synthesis of [2.2.2](1,2,4)(1,3,5)Cyclophane (6). Guided by Cram's observation[12] that carbonyl groups attached to one deck of a [2.2]paracyclophane exert a strong influence directing electrophilic substitution to the pseudo-geminal position of the opposite deck, the syntheses of [2.2.2]cyclophane **2** and [2.2.2.2]cyclophanes **3** and **4** have been achieved all

Scheme I



starting from [2.2]paracyclophane precursors. This eventually led to the formation of achiral cyclophanes with a mirror plane which passes between two aromatic rings bisecting the molecules. Boekelheide's starting material in his elegant synthesis of [2.2.2](1,3,5)cyclophane (**1**)[3] was 1,3,5-tris(bromomethyl)-benzene whose D_{3h} symmetry again inevitably gives rise to the formation of the achiral cyclophane **1**.

In our synthesis of unsymmetrical [2.2.2](1,2,4)(1,3,5)cyclophane (**6**), 1,3,5-tris(mercaptomethyl)benzene (**8**) was condensed with 1,2,4-tris(bromomethyl)benzene (**9**) following Vögtle's procedure[13] (Scheme I).[14] Whereas **8** possess two homotopic faces around the benzene ring, **9** has two enantiotropic faces which determine the chirality of the condensation product, trithia[3.3.3](1,2,4)(1,3,5)cyclophane (**10**). Refluxing an ethanolic solution of **8** and **9** with sodium hydroxide for 13 h completed the condensation reaction, affording a 74% yield[15] of **10**, mp 200–201 °C. After fruitless attempts for expulsion of sulfur by irradiation of a solution of **10** in triethyl phosphite,[16] the trisulfone **11** was prepared from the corresponding trisulfide **10** in quantitative yield following Vögtle's procedure.[13] Pyrolysis of the trisulfone **11** under conditions (0.1 mmHg, 520 °C) similar to those described by Staab[17] for sulfone pyrolysis led to the formation of [2.2.2](1,2,4)-(1,3,5)cyclophane (**6**) in 6% yield.[18]

Resinifying rather rapidly on standing at room temperature, the unsymmetrically tris-bridged cyclophane **6** was found to be very labile, and attempts to isomerize it into symmetrical [2.2.2](1,3,5)cyclophane (**1**) with aluminum chloride or trifluoroacetic acid failed, giving invariably a polymer as the product. This chemical instability undoubtedly reflects the extraordinarily strained structure **6** which is also responsible to the long-wavelength absorption band exhibited at 300 nm (Table I). The unsymmetrical structure of **6** reveals itself in its ^{13}C NMR spectrum[19] which shows six peaks at δ 35.3–39.2 for the methylene groups and 12 peaks at δ 128.2–148.1 for the aromatic carbon atoms. The ^1H NMR spectrum (Figure 1) contained other interesting features. The aromatic protons exhibited peaks at δ 5–7, and a meta-decoupling procedure assigned three peaks at δ 5.04 (t), 6.32 (t), and 6.80 (m) to the protons on the (1,3,5) deck. A molecular model of **6** indicated that, among these three aromatic protons on the (1,3,5) deck, H_f suffers the highest shielding from the opposite (1,2,4) deck followed by H_e and H_d, and this automatically assigned the peaks δ 5.04, 6.32, and 6.80 to H_f, H_e, and H_d, respectively. Among the remaining peaks corresponding to the aromatic

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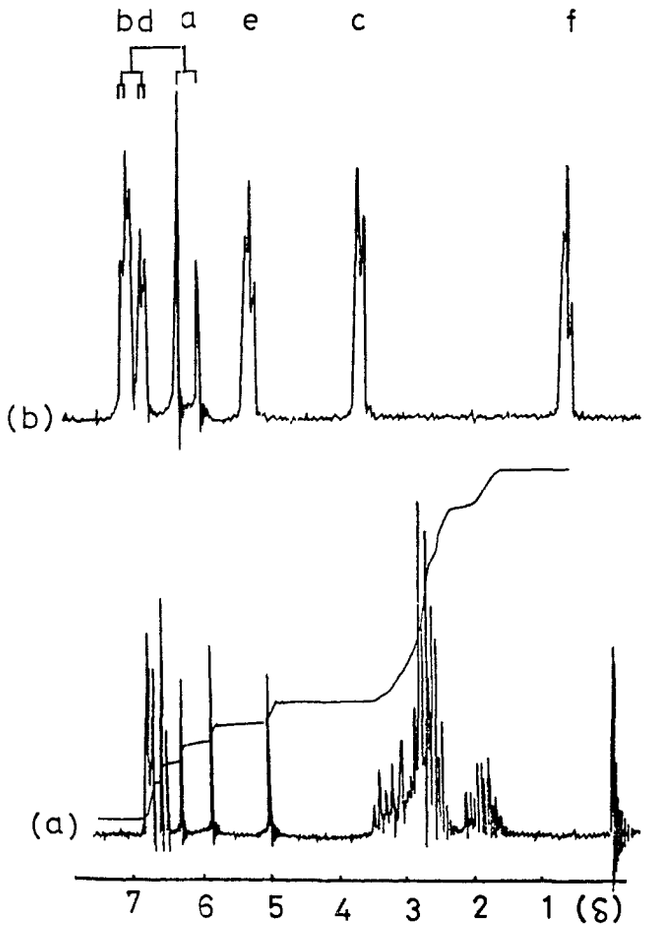


Figure 1. (a) 100-MHz NMR spectrum of [2.2.2](1,2,4)(1,3,5)cyclophane (**6**) in CCl_4. (b) An expanded spectrum (×2) of the aromatic protons.

Table I. Ultraviolet Absorption Data in Isooctane

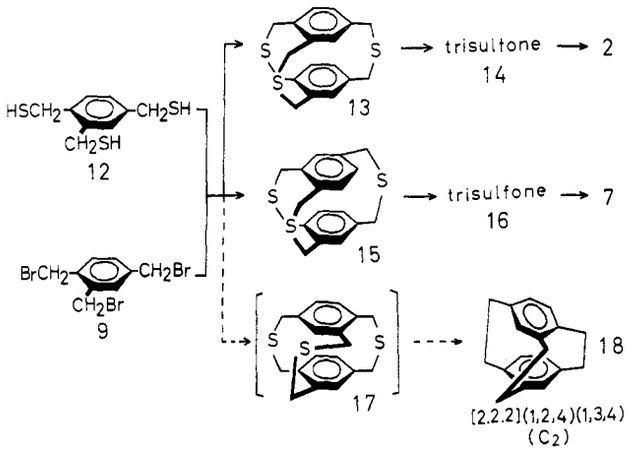
Compd	λ_{max}, nm (ϵ)
6	235 sh (10 030), 300 (380)
7	234.5 sh (10 010), 285.5 (640), 293.5 (530)
2	225 (12 300), 291 (450), 304 sh (250)

protons on the (1,2,4) deck, the peak at δ 5.88 (d) was assigned to H_c again on the basis of meta coupling with H_b, and this was supported by an inspection of the molecular model which indicates H_c suffers the highest shielding from the opposite (1,3,5) deck. Although overlapping with the H_d peak made the downfield AB quartet (J_{ab} = 8 Hz) difficult to discern, meta coupling with H_c assigned the downfield signal δ 6.82 to H_b.

Synthesis of [2.2.2](1,2,4)(1,2,5)Cyclophane (7) (Scheme II).[14] Although symmetrical trithia[3.3.3](1,2,4)cyclophane (C_s symmetry) (**13**) is an obvious candidate for the possible condensation products between 1,2,4-tris(mercaptomethyl)-benzene (C_s symmetry) (**12**) and 1,2,4-tris(bromomethyl)-benzene (C_s symmetry) (**9**), molecular models indicate that one can also expect the formation of trithia[3.3.3](1,2,4)-(1,2,5)cyclophane (**15**) and trithia[3.3.3](1,2,4)(1,3,4)cyclophane (**17**) both having C_2 symmetry.

The condensation reaction was carried out following the procedure described for the preparation of **10**, and column chromatography of the reaction product afforded two trisulfides in 39 and 14% yields, respectively. The major product **13** was converted into the trisulfone **14** whose pyrolysis gave a 12% yield of [2.2.2](1,2,4)cyclophane (**2**),[4] mp 167–168 °C,

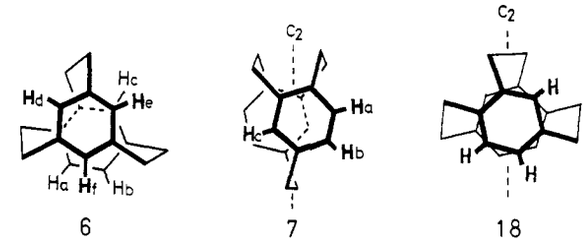
Scheme II



and this established the structure of the major trisulfide as **13**. The trisulfone **16** prepared from the minor product **15** was pyrolyzed to give a 5% yield of colorless platelets, mp 90–91 °C. In contrast to **6**, the dissymmetric cyclophane **7** was found to be more stable, apparently reflecting a less intense interfacial crowding, as the molecular model of **7** indicates. The ultraviolet spectrum of **7** shows absorption maxima at 285.5 (ϵ 640) and 293.5 nm (ϵ 530) (Table I), supporting again the less severely skewed structure of cyclophane **7**.

Structural evidences for the structure of **7** mainly came from its NMR spectum. In its ^{13}C NMR spectrum[19] the cyclophane **7** gives three peaks for the methylene carbon atoms in the δ 35.4–37.4 region, whereas the aromatic carbon atoms give rise to six peaks in δ 127.8–139.5 region. This simple spectrum is indicative of C_2 symmetry in **7** which was further supported by its ^1H NMR spectrum (Figure 2). As C_2 symmetry demands, **7** exhibited a rather simple pattern in its ^1H NMR spectrum; a doublet at δ 5.32 for two aromatic protons and a quartet (δ 6.79, 6.78, J_{ab} = 8 Hz) are downfield for four aromatic protons. Since the aromatic proton H_c is shielded by the opposite benzene ring, the upfield doublet at δ 5.32 can be safely assigned to this proton.[20] The remarkable upfield shift of the aromatic proton H_c clearly indicates a skewed geometry **7** than a less skewed one **18** (Chart III).

Chart III



Searches were made for the presence of another [2.2.2]-cyclophane **18** in the pyrolysate of trisulfone obtained from the crude condensation product between **12** and **9**, but its gas chromatography revealed only the presence of **2** and **7** in a ratio of 3:1 without a trace of the expected cyclophane **18** with C_2 symmetry.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectral data were measured from a Hitachi EPI-S2 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained from a JNM-MH-100 and a JNM-FX-100 spectrometer, respectively. UV spectra were recorded on a Hitachi EPS-3T spectrometer. Mass spectral data were measured on a Hitachi RMS-4 spectrometer. Elemental analyses were performed by a Yanagimoto CHN-Corder Type II.

1,2,4-Tris(bromomethyl)benzene (9). A solution of 1,2,4-tri-

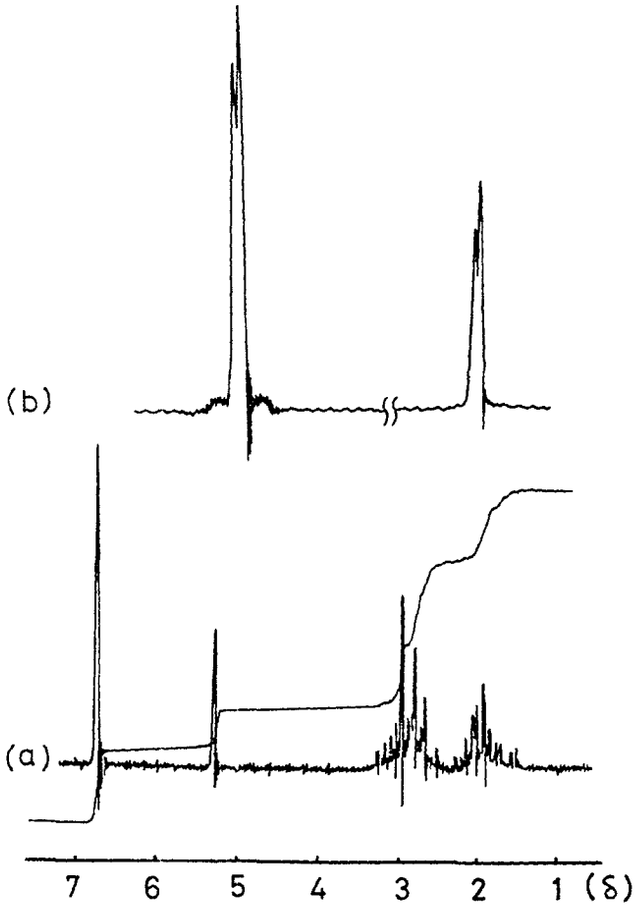


Figure 2. (a) 60-MHz NMR spectrum of [2.2.2](1,2,4)(1,2,5)cyclophane (**7**) in CCl_4. (b) An expanded spectrum (×5) of the aromatic protons.

carbomethoxybenzene[21] (50 g, 0.2 mol) in dry tetrahydrofuran (200 mL) was added to a suspension of $LiAlH_4$ (16 g, 0.42 mol) in dry tetrahydrofuran (400 mL). The mixture was refluxed with stirring for 8 h, and the excess reducing agent was decomposed with water (40 mL). After the insoluble aluminum hydroxide was removed from the reaction mixture, the filtrate was concentrated under vacuum. The concentrate was distilled to give 1,2,4-tris(hydroxymethyl)benzene (25 g, 72%), bp 200–203 °C (1.5 mm), which was converted to the bromide **9**. To a stirred solution of the alcohol (92 g, 0.55 mol) in dry ether (1.5 L) was added dropwise a solution of phosphorus tribromide (180 g, 0.66 mol) in dry ether (400 mL) at room temperature. After the reaction mixture was stirred for 4 h at room temperature, water (400 mL) was slowly added. The organic phase was washed with dilute sodium bicarbonate solution and then with water and then dried. Removal of the ether afforded a solid which was recrystallized from methanol to yield **9** (122 g, 62%), mp 64–65 °C; MS *m/e* 356 (M^+).

Anal. Calcd for $C_9H_9Br_3$: C, 30.29; H, 2.55; Br, 67.17. Found: C, 30.56; H, 2.56; Br, 66.89.

2,11,20-Trithia[3.3.3](1,2,4)(1,3,5)cyclophane (10). To stirred and refluxed ethanol (2.2 L) were simultaneously added, in a period of 6 h, a solution of 1,2,4-tris(bromomethyl)benzene (**9**) (9.3 g, 0.026 mol) in ethanol (300 mL) and a solution of 1,3,5-tris(mercaptomethyl)benzene (**8**)[13] (5.6 g, 0.026 mol) in 80% ethanol (300 mL) containing sodium hydroxide (4.8 g, 0.12 mol). After being refluxed for 13 h, the mixture was concentrated in vacuum and the residue was extracted with boiling benzene. Removal of the solvent afforded a solid which was recrystallized from benzene to give **10** (19 g, 74%): mp 200–201 °C; IR (KBr) 2970, 2880, 2860, 1602, 1596, 1478, 1443, 1425, 1407, 1217, 1203, 1150, 1123, 1070, 918, 905, 891, 869, 810, 721, 702 cm^{-1}; NMR ($CDCl_3$) δ 3.09–4.08 (m, 12 H), 5.79 (s, 1 H), 6.40–7.21 (m, 5 H); UV (isooctane) λ_{max} 255 nm (ε 5020); MS *m/e* 330 (M^+).

Anal. Calcd for $C_{18}H_{18}S_3$: C, 65.41; H, 5.49; S, 29.10. Found: C, 65.38; H, 5.48; S, 28.91.

2,11,20-Trithia[3.3.3](1,2,4)(1,3,5)cyclophane Trisulfone (11). To a solution of **10** (1.4 g, 4.2 mmol) in benzene (400 mL) and acetic acid (250 mL) was added 35% hydrogen peroxide (6.3 g, 64.8 mmol). After the mixture was refluxed with stirring for 7 h, the resulting crystallines were collected by filtration, washed with ether, and dried: 1.75 g (98%); mp >300 °C; IR (KBr) 2960, 2880, 2860, 1600, 1496, 1475, 1456, 1413, 1400, 1320, 1291, 1277, 1122, 1110, 910, 853, 714, 692 cm^{-1}; MS *m/e* 426 (M^+).

Anal. Calcd for $C_{18}H_{18}S_3O_6$: C, 50.68; H, 4.25; S, 22.55. Found: C, 50.99; H, 4.28; S, 22.38.

[2.2.2](1,2,4)(1,3,5)Cyclophane (6). Following Staab's procedure,[17] the trisulfone (**11**) (1.2 g, 2.8 mmol) was pyrolyzed at 520 °C under vacuum (0.1 mm) using a nitrogen bleed, and the pyrolysate was subjected to alumina column chromatography. Elution with hexane gave **6** (40 mg, 6%), which when recrystallized from pentane gave: mp 87–88 °C; IR (KBr) 1970, 2950, 2880, 2820, 1572, 1475, 1437, 1426, 1395, 1188, 1177, 1150, 1078, 914, 886, 827, 797, 746, 725, 712, 654 cm^{-1}; UV (isooctane) λ_{max} 235 (sh), 300 nm (ε 10030, 380); ^1H NMR (CCl_4) δ 1.64–3.52 (m, 12 H), 5.04 (t, 1 H), 5.88 (d, 1 H), 6.32 (t, 1 H), 6.60, 6.82 (AB quartet, J_{ab} = 8 Hz, 2 H), 6.80 (m, 1 H); ^{13}C NMR ($CDCl_3$)[19] δ 35.3, 35.8, 36.7, 38.4, 38.6, 39.2, 128.2, 131.3, 132.5, 132.7, 135.9, 136.3, 136.7, 136.9, 139.5, 144.3, 147.5, 148.1; MS *m/e* 234 (M^+).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.26; H, 7.73.

1,2,4-Tris(mercaptomethyl)benzene (12). A mixture of **9** (66 g, 0.185 mol), thiourea (49 g, 0.644 mol), and 95% ethanol (900 mL) was refluxed with stirring for 13 h. The resulting trisisothiuronium salt was collected by filtration and dissolved in 6% sodium hydroxide solution (1.6 L). After refluxing under nitrogen for 8 h, the solution was allowed to cool and was then acidified with 6 N hydrochloric acid (200 mL). The resulting product was extracted with ether, and the ether extract was washed with water and then dried. After removal of the solvent, distillation of the residue gave **12** (29 g, 72%): bp 164–166 °C (0.1 mm), n^{26}_D 1.6627; IR (film) 2550 cm^{-1} (ν_{SH}); MS *m/e* 216 (M^+).

Anal. Calcd for $C_9H_{12}S_3$: C, 49.95; H, 5.59. Found: C, 50.13; H, 5.50.

2,11,20-Trithia[3.3.3](1,2,4)cyclophane (13) and 2,11,20-Trithia[3.3.3](1,2,4)(1,2,5)cyclophane (15). The method described for the preparation of **10** was followed for the condensation of 1,2,4-tris(bromomethyl)benzene (**9**) (11.5 g, 0.032 mol) and 1,2,4-tris(mercaptomethyl)benzene (**12**) (7 g, 0.032 mol). After an insoluble polymer was removed from the reaction mixture, the filtrate was concentrated to dryness under vacuum and the residue was chromatographed on neutral alumina. Elution with hexane–benzene yielded trithia[3.3.3](1,2,4)cyclophane (**13**) followed by trithia[3.3.3]-(1,2,4)(1,2,5)cyclophane (**15**). Compound **13** was recrystallized from chloroform: 4.2 g (39%); mp >300 °C; IR (KBr) 2960, 2870, 2850, 1595, 1482, 1415, 1219, 1148, 1138, 1078, 923, 895, 846, 830, 806, 788, 752, 703, 651 cm^{-1}; UV (isooctane) λ_{max} 271 (ε 3130); NMR ($CDCl_3$) δ 3.43–4.79 (m, 12 H), 6.85, 7.10 (AB quartet, J_{ab} = 8 Hz, 4 H), 7.13 (d, 2 H); MS *m/e* 330 (M^+).

Anal. Calcd for $C_{18}H_{18}S_3$: C, 65.41; H, 5.49; S, 29.10. Found: C, 65.50; H, 5.53; S, 29.02.

The compound **15** was recrystallized from benzene: 1.5 g (14%); mp >300 °C; IR (KBr) 2970, 2880, 2860, 1596, 1483, 1440, 1409, 1213, 952, 912, 893, 834, 816, 777, 756, 718, 700, 672 cm^{-1}; UV (isooctane) λ_{max} 256 (ε 5920); NMR ($CDCl_3$) δ 3.25–4.87 (m, 12 H), 5.98 (s, 2 H), 7.15 (s, 4 H); MS *m/e* 330 (M^+).

Anal. Calcd for $C_{18}H_{18}S_3$: C, 65.41; H, 5.49; S, 29.10. Found: C, 65.49; H, 5.56; S, 28.97.

2,11,20-Trithia[3.3.3](1,2,4)cyclophane Trisulfone (14). The trisulfone **14** was prepared from **13** (4.0 g) in a quantitative yield (5.1 g) by the same method described for the preparation of **11**: mp >300 °C; IR (KBr) 2940, 2840, 1610, 1490, 1415, 1313, 1288, 1257, 1108, 906, 877, 857 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}S_3O_6$: C, 50.68; H, 4.25; S, 22.55. Found: C, 50.93; H, 4.31; S, 22.39.

[2.2.2](1,2,4)Cyclophane (2). The pyrolysis of **14** (1.5 g) was carried out by the same method described for the preparation of **6**. The pyrolysis product was recrystallized from benzene to give **2**:[4] 0.1 g (12%); mp 167–168 °C.

2,11,20-Trithia[3.3.3](1,2,4)(1,2,5)cyclophane Trisulfone (16). The trisulfone **16** was prepared from **15** (1.4 g) in a quantitative yield (1.8 g): mp >300 °C; IR (KBr) 2940, 2850, 1610, 1415, 1390, 1318, 1290, 1108, 909, 855 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}S_3O_6$: C, 50.68; H, 4.25; S, 22.55. Found: C, 50.41; H, 4.28; S, 22.69.

[2.2.2](1,2,4)(1,2,5)Cyclophane (7). The trisulfone **16** (2.0 g) was pyrolyzed by the same procedure described for the preparation of **6**. The pyrolysis product was chromatographed on neutral alumina. Elution with hexane produced **7** (55 mg, 5%), which when recrystallized from pentane gave: mp 90–91 °C; IR (KBr) 2960, 2930, 2820, 1575, 1480, 1434, 1426, 1402, 1192, 1166, 1150, 1120, 993, 910, 886, 802,

752, 740, 733, 706 cm^{-1}; UV (isooctane) λ_{max} 234.5 (sh), 285.5, 293.5 (ϵ 10 010, 640, 530); ^1H NMR (CCl_4) δ 1.60–2.30 (m, 4 H), 2.52–3.28 (m, 8 H), 5.32 (d, 2 H), 6.78, 6.79 (AB quartet, J_{ab} = 8 Hz, 4 H); ^{13}C NMR ($CDCl_3$)[19] δ 35.4, 35.7, 37.4, 127.8, 129.1, 134.5, 139.3, 139.4, 139.5; MS *m/e* 234 (M^+).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.80.

Registry No.—**2**, 58002-98-5; **6**, 63877-75-8; **7**, 64884,24,8; **8**, 38460-57-0; **9**, 61124-37-6; **10**, 63877-74-7; **11**, 64316-88-7; **12**, 64924-60-3; **13**, 64884-26-0; **14**, 64884-27-1; **15**, 64976-19-8; **16**, 64924-60-3; 1,2,4-tricarbomethoxybenzene, 2459-10-1; 1,2,4-tris(hydroxymethyl)benzene, 25147-76-7; phosphorus tribromide, 7789-60-8; thiourea, 62-56-6.

References and Notes

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(13) F. Vögtle, *Justus Liebigs Ann. Chem.*, **735**, 193 (1970).
(14) The structural formula of **6, 7, 10, 15, 17,** and **18,** respectively, represent one of their possible enantiomers.
(15) Vögtle has shown that the condensation of 1,3,5-tris(bromomethyl)benzene with 1,3,5-tris(mercaptomethyl)benzene (**8**) proceeded with only 5.3% yield.[13]
(16) J. Bruhin and W. Jenny, *Tetrahedron Lett.*, 1215 (1973); V. Boekelheide, I. D. Reingold, and M. Tuttle, *J. Chem. Soc., Chem. Commun.*, 406 (1973).
(17) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, 3585 (1970); *Chem. Ber.*, **106**, 2190 (1973).
(18) [2.2.2](1,3,5)Cyclophane (**1**) has been reported to be prepared by pyrolysis of the corresponding trisulfone in a 20% yield.[3]
(19) Chemical shifts are expressed in parts per million relative to Me_4Si.
(20) The heavily shielded proton in [2.2]metaparacyclophane is exhibited at δ 5.24; D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Am. Chem. Soc.*, **88**, 1324 (1966).
(21) 1,2,4-Tricarbomethoxybenzene, bp 171–173 °C (0.1mm), was prepared by the esterification of 1,2,4-benzenetricarboxylic acid with methanol containing sulfuric acid.

Rearrangement of 2-Cyano-3-(1-methylcyclopentyl)indenone to 4a-Methyl-9-oxo-10-cyano-1,2,3,4,4a,9-hexahydrophenanthrene[1a]

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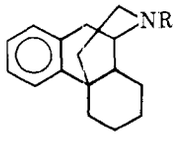
The possibility of preparing partially saturated phenanthrenes with 2-aminoethyl side chains at the 4a position, key precursors in the synthesis of the pharmacologically important morphinan ring system, by a complex carbonium ion rearrangement of the title compounds was explored. Thus, treatment of 1-methylcyclopentanecarbonitrile (**1**) with phenyllithium followed by malononitrile quench gave α-cyano-β-(1-methylcyclopentyl)cinnamonitrile (**2**), which on treatment with sulfuric acid gave a low yield of 3-(1-methylcyclopentyl)-2-cyanoindenone (**3**). Treatment of **3** with sulfuric acid gave 4a-methyl-9-oxo-10-cyano-1,2,3,4,4a,9-hexahydrophenanthrene (**4**) by a rearrangement involving migration of a cyclopentyl carbon followed by a phenyl migration. The structure expected by the reverse sequence of migrations, 2′-methyl-3′-cyanospiro[cyclopentane-1,1′(4′*H*)-naphthalene]-4′-one (**5**), was eliminated as a possible structure of the product by unambiguous synthesis of its Michael cyanide adduct **6** from a known compound (the parent enone of **5**) and comparison of **6** with the Michael cyanide adduct of **4**, with which it was not identical. Attempted cyclization of compounds analogous to **2** with side chains larger than methyl (methoxymethyl, phenyl, and benzyl) was not successful.

The morphinan ring system (**1**) is contained in a number of drugs being studied for use as narcotic antagonists or nonaddictive analgetics. The synthesis of this ring system from partially saturated phenanthrenes with an angular side chain such as **2** (R = $CH_2CH_2NH_2$) has now been studied in some detail.[2–6] The known rearrangement of 3-*tert*-butyl-2-cyanoindenone to give 2-cyano-3,4,4-trimethyl-1-oxo-1,4-dihydronaphthalene,[7] which has a quaternary carbon atom, suggested the possibility of preparing compounds of type **2**



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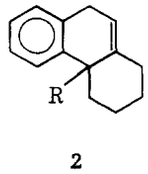

2

by carbonium ion rearrangement of suitably substituted indenones.[8a]

The use of ylidenemalononitriles as precursors to indenones has recently been reviewed.[8a] An example[7] is the cyclization of pivalophenylidenemalononitrile to 2-cyano-3-*tert*-butylindenone, which probably involves as an intermediate an iminium species, the stability of which prevents further acid rearrangement. The ylidenes may be prepared from ketones by condensation with malononitrile, or, alternatively, by malononitrile quench of the imine salts formed by the addition of organometallic reagents to nitriles, e.g., phenyl Grignard to pivalonitrile. The latter method is especially advantageous when the required ketone would be hindered.[8b]

If two of the methyl groups of the *tert*-butyl group were linked by a two-carbon bridge, as in **3** (Scheme I), the reaction would be a possible example of a double ring expansion approach to the phenanthrene ring system. The tertiary carbo-

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