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Syntheses and Chemical Characterization of Tris-Bridged [2.2.2]Cyclophanes with a Triphenylmethyl Component[1]

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High-dilution coupling of 1,3,5-tris(mercaptomethyl)benzene (16) and 1,1,1-tris[(3-bromomethyl)phenyl]ethane (12) afforded the trithia derivative 17 which was converted, via the trisulfone 18, into 17-methyl[2.2.2](1,3,5)-benzeno(3,3′,3″)triphenylmethanophane (21). Starting from the methoxy derivative 15, the same sequence of conversions provided the 17-methoxy compound 22 which could be converted into the chloride 24. Chemical characteristics of the chloride 24 including failure to give the corresponding radical together with its reluctance toward various displacement reactions indicate lack of resonance stability in the intermediary chemical species. The temperature-dependent NMR spectral analysis of the hexadeuterio compound 35 gave $E_a = 15.5 \pm 1.0$ kcal/mol for the interconversion between two enantiomeric conformers with C_3 symmetry.

Ever since Gomberg's first discovery[2] of the triphenylmethyl radical in 1900, an enormous amount of effort has been exerted in modifying the aryl rings to see the effects of the modification on the stabilization of the radicals, which not only has contributed to our understanding of radical chemistry but eventually has led Nauta and coworkers[3] to their methylenecyclohexadiene structure of the dimer. Efforts have also been made to study the reactivity of triarylmethyl derivatives toward various displacement reactions at the central carbon atom, and these have provided a vast accumulation of information on intermediary radicals,[4] cations, and anions.[5]

Contrary to this overwhelming amount of research, however, it seems rather surprising to realize that few studies can be found in the preparation of the cage-shaped molecules 1 (Chart I), constraining the three aryl rings in a cage with the triphenylmethyl reaction center at the bridgehead position.

The only exception has been the 1-substituted triptycenes 2 whose feasible preparation together with the unique rigid stereochemistry prompted Bartlett and co-workers[6] to explore their bridgehead reactivity; failure of the triptycenes 2 to undergo various substitution reactions[6] and the related instabilities[7] of the radical and cation were attributed to lack of resonance stability in these intermediary species.

As an extension of their tris-bridged cyclophane study, Vögtle and Hohner[8] have reported the preparation of the cage-shaped compound 3, comprising two triphenylmethane components, and described detailed NMR spectral analysis of 3 which suggested a rigid D_3 propeller conformation for 3.

Chart I

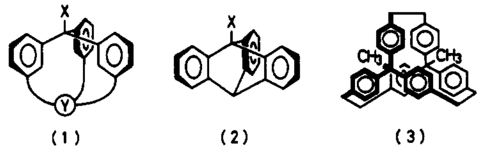


Chart II

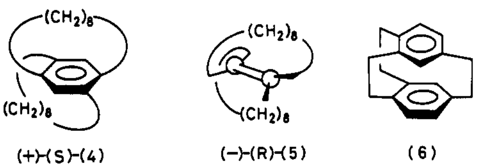
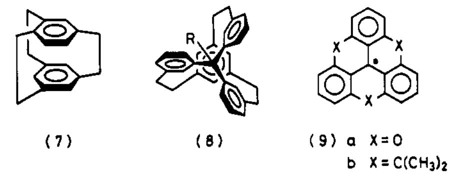
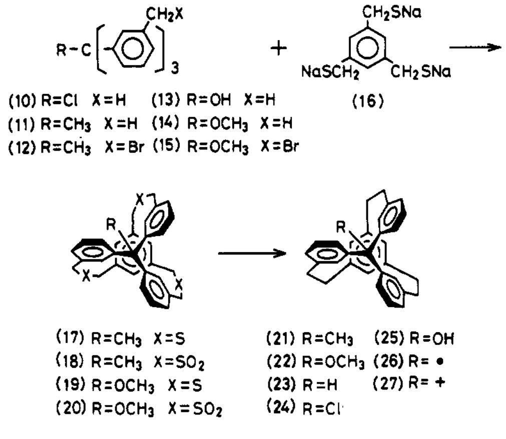


Chart III



Scheme I



In previous papers, we reported the preparation and chiroptical properties of (+)-(*S*)-[8][8]paracyclophane (4)[9] and (−)-(*R*)-trans doubly bridged ethylene 5[10] (Chart II) with twisted π-electron systems, and our continuing in-

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[1] A part of this paper has been reported in a short communication: Nakazaki, M.; Yamamoto, K.; Toya, T. *J. Org. Chem.* **1980**, *45*, 2553.

[2] Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757. For a historical account, see: McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

[3] Lankamp, H.; Nauta, W. T.; Maclean, C. *Tetrahedron Lett.* **1968**, 249.

[4] Bachmann, W. E. In "Organic Chemistry-An Advanced Treaties", 2nd ed., Gilman, H., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 6.

[5] Concise summaries on the bridgehead reactivity can be found in: Applequist, D. E.; Roberts, J. D. *Chem. Rev.* **1954**, *54*, 1065; Fort, R. C., Jr.; Schleyer, P. v. R. In *Adv. Alicyclic Chem.* **1966**, *1*, 283; Fort, R. C., Jr. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1973; Vol. 4, p 1783.

[6] Bartlett, P. D.; Lewis, E. S. *J. Am. Chem. Soc.* **1950**, *72*, 1005.

[7] Bartlett, P. D.; Greene, F. D. *J. Am. Chem. Soc.* **1954**, *76*, 1088.

[8] Hohner, G.; Vögtle, F. *Chem. Ber.* **1977**, *110*, 3052. For an analogous, rigid, cage-shaped compound with condensed triphenylmethane components, see: Wittig, G.; Shoch, W. *Justus Liebigs Ann. Chem.* **1971**, *74*, 38.

[9] (a) Synthesis of the racemic modification: Nakazaki, M.; Yamamoto, K.; Tanaka, S. *Tetrahedron Lett.* **1971**, 341; Nakazaki, M.; Yamamoto, K.; Tanaka, S. *J. Org. Chem.* **1976**, *41*, 4081. (b) Preparation of the optically active modification and chiroptical properties: Nakazaki, M.; Yamamoto, K.; Itho, M. *J. Chem. Soc., Chem. Commun.* **1972**, 433; Nakazaki, M.; Yamamoto, K. *Chem. Lett.* **1974**, 1051; Nakazaki, M.; Yamamoto, K.; Itho, M.; Tanaka, S. *J. Org. Chem.* **1977**, *42*, 3468.

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terests in these π-electron systems led us to synthesize the two unusually twisted, tris[2.2.2]-bridged cyclophanes **6** and **7**.[11] Displacing the (1,2,4)benzeno component of **7** (Chart III) with a triphenylmethane component, we have the tris[2.2.2]-bridged, cage-shaped cyclophane **8** whose molecular model could be constructed without much strain in a propeller conformation with C_3 symmetry. Being an intermediate between the two extremes **2** and **9**,[12] **2** with a noncoplanar triphenylmethane and **9** with a rigid coplanar triphenylmethane moiety, this [2.2.2]triphenylmethanophane **8**, together with **3**, should be an ideal compound for studing reactivity and radical stability in triphenylmethane derivatives. In this paper we describe the preparation, chemical characterization, and conformational mobility of this interesting class of compounds of type **8**.

Results and Discussion

Synthesis of 17-Methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (21)[13] (Scheme I). The Grignard reaction of tri-*m*-tolylmethyl chloride (**10**) with methylmagnesium iodide afforded the higher homologue **11**, whose photochemical *N*-bromosuccinimide bromination in CCl_4 gave a 41% yield of the tribromide **12**, mp 111–112 °C. High-dilution coupling of **12** with the sodium salt of 1,3,5-tris(mercaptomethyl)benzene (**16**) in a benzene–ethanol solution provided the trithia derivative **17** (mp 220–221 °C; 17% yield) which was further converted into the trisulfone **18** (mp >350 °C) in quantitative yield by the conventional hydroperoxide oxidation.

Pyrolysis of **18** was carried out in an evacuated Pyrex tube heated at 540 °C, and column chromatography followed by recrystallization from hexane purified the crude cyclophane **21** to melt at 213–214 °C (55% yield).

Synthesis of 17-Chloro[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (24, Scheme I). A deep red solution of the triphenylmethanol **13** in concentrated H_2SO_4 was poured into chilled methanol to give the methoxy derivative **14** which was converted, via the tribromide **15**, into the trithia derivative **19** by following a procedure similar to that descrbed for the methyl derivative **17**. Sodium tungstate mediated peroxide oxidation of the trithia compound **19** gave a 50% yield of the trisulfone **20**, which was pyrolyzed in an evaculated pyrolysis tube. On column chromatography of the pyrolysate, elution with hexane furnished fast-moving fractions containing the hydrocarbon **23**, and subsequent elution with hexane–benzene (2:1) gave fractions containing the methoxy derivative **22**; each was recrystallized to afford a 20% yield of **23** (mp >300 °C) and a 44% yield of **22** (mp 220–221 °C). This unexpected isolation of the hydrocarbon **23** could be explained by transient formation of the free radical **26** (vide infra) which should attack nearby molecules to substract a hydrogen atom, and this seems to be supported by our observation of an *m*/*e* 399 peak with an outstandingly high intensity in the mass spectrum of the methoxy derivative **22**.

Scheme II

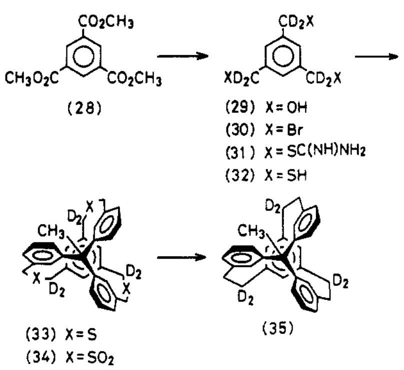
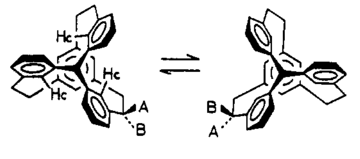


Chart IV



A solution of the methoxy derivative **22** in acetic acid was saturated with HCl gas to furnish a 68% yield of the chloride **24** (mp 219–220 °C) whose $LiAlH_4$ reduction afforded the hydrocarbon **23**, thus establishing its identity.

Synthesis of 17-Methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane-d_6 (35) (Scheme II). The deuterio derivative **35** was prepared for a temperature-dependent NMR analysis to secure information on the expected conformational mobility.

Reduction of 1,3,5-tris(carbomethoxy)benzene (**28**) with $LiAlD_4$ gave the deuterio triol **29** which was transformed into the trithiol **32** by the conventional sequence of conversions including PBr_3 bromination into the tribromide **30** followed by its mercaptization with thiourea. High-dilution coupling of the tribromide **12** with the sodium salt of the deuterio trithiol **32** gave a 14% yield of **33** whose peroxide oxidation afforded the trisulfone **34** in a quantitative yield. Pyrolysis followed by alumina chromatography of the pyrolysate gave the deuteriocyclophane **35**, mp 221–222 °C.

NMR Spectra and Conformational Mobility. Inspection of a molecular model (Chart IV) reveals that the [2.2.2]benzenotriphenylmethanophanes **36** have a strain-free rigid conformation with C_3 symmetry which can be converted into the enantiomer **37**[14] via various labile conformations with C_1 symmetry, and this is supported by its temperature-dependent NMR spectra.

Common to the derivatives **21**–**24** are two aromatic proton signals which are outstanding in the room-temperature NMR spectra: a doublet (3 H) in the δ 5.0–5.5 region and a singlet (3 H) in the δ 6.4–6.7 region. The observed meta coupling (J = 2 Hz) and fairly shielded nature assigned the doublet (3 H) to H_c (Chart IV) of the triphenylmethane component pointing to the inside of the cage structure, and the singlet (3 H) was assigned to the protons of the mesitylene component suffering a mild

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[10] (a) Synthesis of the racemic modification: Nakazaki, M.; Yamamoto, K.; Yanagi, J. *J. Chem. Soc., Chem. Commun.* **1977**, 346; Nakazaki, M.; Yamamoto, K.; Yanagi, J. *J. Am. Chem. Soc.* **1979**, *101*, 147. (b) An asymmetric synthesis and chiroptical properties: Nakazaki, M.; Yamamoto, K.; Maeda, M. *J. Chem. Soc., Chem. Commun.* **1980**, 294; *J. Org. Chem.* **1980**, *45*, 3229.

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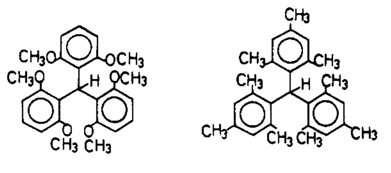
[12] Sabacky, M. J.; Johnson, C. S., Jr.; Smith, R. G.; Gutowsky, H. S.; Martin, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2054; Müller, E.; Moosmayer, A.; Rieker, A.; Scheffler, K. *Tetrahedron Lett.* **1967**, 3877; Neugebauer, F. A.; Hellwinkel, D.; Aulmich, G. *Ibid.* **1978**, 4871. For the 9,9″-bitriptycyl derivatives, see: Koukotas, C.; Mehlman, S. P.; Schwartz, L. H. *J. Org. Chem.* **1966**, *31*, 1970; Schwartz, L. H.; Koukotas, C.; Yu, C. S. *J. Am. Chem. Soc.* **1977**, *99*, 7710.

[13] Following the nomenclature proposed by Vögtle: Vögtle, F.; Newman, P. *Tetrahedron* **1970**, *26*, 5847.

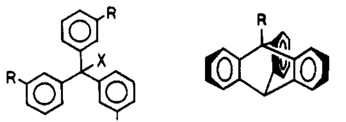
[14] The chirality of these enantiomers may be conveniently specified by *M* and *P* helicity, reflecting their unique propeller-shaped morphology: Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

Chart V



(38) (39)

Chart VI



(40)
(41) R=CH3 X=•
(42) R=CH3 X=+

(2) a R=•
b R=H
c R=CO2triptoyl
d R=I
e R=+

shielding from the three outer benzene rings.

Reflecting the expected conformational mobility, the methylene proton signals were found to be temperature-dependent: (a) the 17-methyl derivative **21** exhibited a complex multiplet (δ 2.3–3.3) at room temperature which coalesced to a broad singlet (δ 2.72) at 40 °C and then to a sharp singlet at 60 °C; (b) the broad singlet (δ 2.83) of the 17-chloro derivative **24** at room temperature was found to coalesce to a sharp singlet at 65 °C; (c) the sharp singlets centered at δ 2.75 and 2.83 exhibited by the methoxy derivative **22** and the hydrocarbon **23**, respectively, transformed into broad singlets on cooling of the sample to −60 °C. Detailed information on the rate of this racemization process was obtained by analysis of the temperature-dependent spectra of the deuterio derivative **35** whose typical AB quartet (J = 12.4 Hz) centered at δ 2.73 at −10 °C was found to coalesce to a broad singlet at 40 °C (T_c) and then to a sharp singlet at 60 °C. The computer-assisted simulation of the spectra by the line-shape method[15] gave E_a = 15.5 ± 1.0 kcal/mol for the racemization process, and the calculation[16] of $\Delta G_c^{\ddagger}$ afforded 14.7 kcal/mol at T_c = 40 °C, which can be compared with $\Delta G_c^{\ddagger}$ = 11.1 kcal/mol (T_c = −57 °C) and 8.8 kcal/mol (T_c = −90 °C) reported for the related rotational process in the *o,o'*-disubstituted triphenylmethanes **38**[17] and **39**[18] (Chart V).

Bridgehead Reactivity. Reflection on the unexpectedly large molecular flexibility demonstrated by the dynamic NMR spectral study (vide supra) predicts that the bridgehead reactivity of the 17-substituted triphenylmethanophanes **8** as well as the stability of the corresponding radical **26** and the cation **27** would be between those of the unbridged triphenylmethanes **40** (Chart VI) and the rigid triptycenes **2**.

This was born out in our sterile attempts to generate the bridgehead radical **26** from the chloride **24** by reaction with silver amalgam in an ESR probe tube. Whereas the unbridged chloride **10** readily generated the radical **41**, which exhibited a trypical ESR spectrum characteristic of the triphenylmethyl radical, the same procedure failed to detect the signal expected for the bridgehead radical **26**. Our further attempts to generate the radical **26** or the corresponding dimer from the chloride **24** by means of various reducing reagents failed, and this reluctance seems to be parallel to the similar chemical characteristics reported in the triptycene derivatives.[7] Transient formation of a highly reactive free radical **2a** has been assumed by Bartlett and Greene[7] to account for the formation (40% yield) of triptycene (**2b**) on refluxing a benzene solution of triptoyl peroxide (**2c**), and our unexpected isolation of a 20% yield of the hydrocarbon **23** in the pyrolysis of the trisulfone **20** seems to suggest a similar unstable and avid nature of the transient cage-shaped radical **26**. Similar inertness was also observed in S_N displacement reactions of the cage-shaped chloride **24**; while 30 min refluxing of the control compound **10** with $AgNO_3$ in THF–H_2O solution was found to be enough for its quantitative conversion into the alcohol **13**, the bridgehead compound **24** was recovered unchanged when subjected to the same conditions, and 8 h of refluxing was necessary to afford an 87% yield of the alcohol **25**. This can be compared to the reported complete lack of reactivity of 1-iodotriptycene (**2d**),[7] which when refluxed with ethanolic $AgNO_3$ solution for 48 h did not precipitate any AgI, and these comparative studies seem to place the S_N reactivity of bridgehead **24** between those of the free triphenylmethyl chloride **10** and the rigid triptycene **2**. This conclusion was further supported by methanolysis experiments in pyridine at room temperature; after being allowed to stand for 10 min, the triphenylmethyl chloride **10** converted quantitatively into the methoxy derivative **14**, while the cage-shaped chloride **24** was recovered unchanged after being allowed to stand 48 h.

Contrary to Bartlett and co-worker's[6,7] fruitless attempt to detect triptyl cation **2e**, 11-methoxytriphenylmethanophane (**22**) dissolved in concentrated H_2SO_4 to give a deep red solution (λ_{max} 403 nm), indicating formation of the corresponding cation **27**. Dissolution of each of the chloro compound **24** and hydroxy derivatives **25** in concentrated H_2SO_4 gave the same deep colored solutions which upon being poured into ice–water and extracted afforded the alcohol **25**.

Finally, it seems pertinent to record here our failure in preparing the crystalline hexachloroantimonate of the cation **27** from the chloride **24**; the corresponding tri-*m*-tolylmethyl chloride **10** gave bright red crystals, mp 198–200 °C.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectral data were obtained from a Hitachi 260-10 infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained from a JNM-MH-100 spectrometer. Ultraviolet 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.

1,1,1-Tris(3-methylphenyl)ethane (11). A solution of **10**[19] (54.9 g, 0.171 mol) in dry benzene (300 mL) was added dropwise to a solution of methylmagnesium iodide, prepared from CH_3I (44 g, 0.323 mol) and Mg (7.3 g, 0.3 mol) in dry ether (100 mL). After being refluxed with stirring for 2 h, the reaction mixture was poured into cold 5% aqueous HCl solution and extracted with ether. The etheral extract was washed with 3% $NaHCO_3$ and water and then dried ($MgSO_4$). Evaporation of the solvent gave a solid, which was recrystallized from ethanol to give **11**: 44 g (85.6%); mp 73–74 °C; NMR (CCl_4) δ 2.07 (s, CH_3, 3 H), 2.26 (s, CH_3, 9 H), 6.61–7.24 (m, Ar H, 12 H).

Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.86; H, 7.94.

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[16] The calculation was based on the observed J_{AB} = 12.4 Hz, $\delta_{AB}{}^2$ = 19.8 Hz, at −10 °C: Kurland, R. J.; Rubin, M. B.; Wise, W. B. *J. Chem. Phys.* **1964**, *40*, 2426.

[17] Kossler, N.; Moosmayer, A.; Rieker, A. *Tetrahedron* **1969**, *25*, 287.

[18] Sabacky, M. J.; Johnson, S. M.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1969**, *91*, 7542.

[19] Brown, J. H.; Marrel, C. S. *J. Am. Chem. Soc.* **1937**, *59*, 1175.

1,1,1-Tris[3-(bromomethyl)phenyl]ethane (12). A mixture of 11 (8 g, 26.7 mmol), *N*-bromosuccinimide (15.7 g, 88.2 mmol), α,α'-azobis(isobutyronitrile) (20 mg), and CCl_4 (50 mL) was heated to reflux for 3 h. Removal of the deposited succinimide followed by concentration of the filtrate in vacuo gave a residue which was chromatographed over SiO_2 gel. Elution with hexane–benzene (1:1) gave **12** (13.8 g, 54%), which was recrystallized from hexane–benzene: mp 111–112 °C; NMR (CCl_4) δ 2.10 (s, CH_3, 3 H), 4.49 (s, CH_2, 6 H), 6.23–7.30 (m, Ar H, 12 H).

Anal. Calcd for $C_{23}H_{21}Br_3$: C, 51.42; H, 3.95. Found: C, 51.38; H, 4.02.

Methoxytris(3-methylphenyl)methane (14). A deep red solution of the carbinol **13**[19] (5 g) in concentrated H_2SO_4 (20 mL) was added dropwise to stirred methanol (60 mL) chilled to −10 °C, and the resulting mixture was poured into an ice–water mixture (200 mL). An oily product which separated was extracted with ether, and the extract was washed with 3% $NaHCO_3$ and water and then dried ($MgSO_4$). Removal of the solvent followed by distillation in vacuo afforded the methyl ether **14**: 4.5 g (86%); bp 145–148 °C (0.1 mm); NMR (CCl_4) δ 2.30 (s, CH_3, 9 H), 2.97 (s, OCH_3, 3 H), 6.80–7.30 (m, Ar H, 12 H); mass spectrum, *m/e* 316 (M^+).

Anal. Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.64. Found: C, 87.50; H, 7.54.

Methoxytris[3-(bromomethyl)phenyl]methane (15). The preparation of **15** was carried out by the same method as described for the preparation of **12**, utilizing **14** (8.7 g, 27.5 mmol) and *N*-bromosuccinimide (16.3 g, 91.6 mmol). The product was chromatographed over SiO_2 gel to provide the tribromide **15**: 7.5 g (49.5% yield); colorless oil; NMR (CCl_4) δ 3.00 (s, CH_3, 3 H), 4.44 (s, CH_2, 6 H), 6.80–7.50 (m, Ar H, 12 H); mass spectrum, *m/e* 553 (M^+).

19-Methyl-2,11,27-trithia[3.3.3](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (17). A solution of the tribromide **12** (12.3 g, 23.8 mmol) in benzene and a solution of 1,3,5-tris(mercaptomethyl)benzene (**16**)[20] (5.16 g, 23.8 mmol) in 80% ethanol (400 mL) containing sodium hydroxide (4.4 g, 110 mmol) were synchronously added over a period of 24 h into a vigorously stirred and refluxed 1:1 mixture of ethanol and benzene (1.5 L). After being refluxed for another 13 h, the mixture was concentrated in vacuo to give a residue which was chromatographed on neutral alumina. Elution with benzene afforded the trisulfide **17** (2 g, 17% yield) which was recrystallized from ethyl acetate: mp 220–221 °C; IR (KBr) 3040, 2970, 2920, 1600, 1583, 1480, 1422, 1240, 1168, 1098, 940, 895, 796, 778, 776, 723, 705 cm^{-1}; NMR ($CDCl_3$) δ 1.97 (s, CH_3, 3 H), 3.47 (s, CH_2, 6 H), 3.68 (s, CH_2, 6 H), 6.16 (d, *J* = 2 Hz, Ar H, 3 H), 6.78 (s, Ar H, 3 H), 6.90–7.38 (m, Ar H, 9 H).

Anal. Calcd for $C_{22}H_{30}S_3$: C, 75.24; H, 5.92; S, 18.84. Found: C, 74.93; H, 6.00; S, 18.96.

19-Methyl-2,11,27-trithia[3.3.3](1,3,5)benzeno(3,3′,3″)triphenylmethanophane *S,S,S′,S′,S″,S″*-Hexaoxide (18). Aqueous hydrogen peroxide (30%; 4 g, 35.3 mmol) was added into a solution of the trisulfide **17** (1.0 g, 1.96 mmol) in benzene (400 mL) and acetic acid (200 mL), and the mixture was refluxed with stirring for 7 h. The deposited crystals were collected and washed with ether to yield the trisulfone **18**: 0.92 mg (77% yield); mp >300 °C; IR (KBr) 1305, 1105 cm.$^{-1}$

Anal. Calcd for $C_{32}H_{30}O_6S_3$: C, 61.71; H, 4.86; S, 15.85. Found: C, 61.27; H, 5.01; S, 16.01.

17-Methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (21). By use of Staab's procedure,[20] the vapor of the trisulfone **18** (400 mg, 0.66 mmol) carried with a slow stream of nitrogen was passed through an evacuated (0.1 mm) pyrolysis tube heated at 540 °C. The pyrolysate collected in a cold trap was chromatographed over neutral alumina. Elution with hexane gave **21** (150 mg, 55%) which was recrystallized from ethyl acetate: mp 213–214 °C; IR (KBr) 3040, 3025, 2990, 2970, 2960, 2920, 2880, 2840, 2820, 1595, 1576, 1473, 1432, 1412, 1193, 1177, 1090, 1054, 950, 903, 890, 850, 790, 778, 745, 694 cm^{-1}; NMR ($CDCl_3$) δ 2.22 (s, CH_3, 3 H), 2.32–3.26 (m, CH_2, 12 H), 5.05 (d, *J* = 2 Hz, Ar H, 3 H), 6.37 (s, Ar H, 3 H), 6.75–7.12 (m, Ar H, 9 H); UV (isooctane) λ_{max} 223 nm (sh, log ϵ 4.49), 256 (sh, 2.84), 263 (2.99), 271 (sh, 2.96); mass spectrum, *m/e* (relative intensity) 414 (100), 399 (79).

Anal. Calcd for $C_{32}H_{30}$: C, 92.71; H, 7.29. Found: C, 92.70; H, 7.19.

19-Methoxy-2,11,27-trithia[3.3.3](1,3,5)benzeno(3,3′,3″)-triphenylmethanophane (19). Preparation of **19** was carried out by the same method described for the preparation of **17** with tribromide **15** (7.5 g, 13.6 mmol) and trithiol **16** (2.95 g, 13.6 mmol). The product was chromatographed over SiO_2 gel, and elution with benzene furnished the trisulfide **19** (1.8 g, 25%) which was recrystallized from ethyl acetate–hexane: mp >300 °C; IR (KBr) 3070, 3050, 2980, 2950, 2940, 2920, 2840, 1620, 1590, 1490, 1446, 1425, 1246, 1097, 1083, 906, 803, 796, 730, 715 cm^{-1}; NMR ($CDCl_3$) δ 2.89 (s, CH_3, 3 H), 3.44 (s, CH_2, 6 H), 3.74 (s, CH_2, 6 H), 6.45 (d, *J* = 2 Hz, Ar H, 3 H), 6.68 (s, Ar H, 3 H), 6.85–7.42 (m, Ar H, 9 H); mass spectrum, *m/e* 526 (M^+).

Anal. Calcd for $C_{32}H_{30}OS_3$: C, 72.96; H, 5.74; S, 18.26. Found: C, 72.64; H, 5.88; S, 18.15.

19-Methoxy-2,11,27-trithia[3.3.3](1,3,5)benzeno(3,3′,3″)-triphenylmethanophane *S,S,S′,S′,S″,S″*-Hexaoxide (20). An aqueous solution (80 mL) of sodium tungstate[21] ($Na_2WO_2 \cdot 2H_2O$, 264 mg) whose pH was adjusted to 6.2 with the addition of a few drops of acetic acid was added to a stirred and heated solution of the trisulfide **19** (100 mg, 0.19 mmol) in dioxane (3 mL). After being stirred 1 h, the turbid solution became clear. Addition of 30% hydrogen peroxide (76 mg) and stirring at room temperature for 15 h deposited crystals which were collected and washed with ether to give a 50% yield (62 mg) of the trisulfone **20**: mp >300 °C; IR (KBr) 1300, 110 cm^{-1}.

Anal. Calcd for $C_{32}H_{30}O_7S_3$: C, 61.71; H, 4.86; S, 15.45. Found: C, 61.01; H, 5.19; S, 15.76.

17-Methoxy[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (22) and [2.2.2](1,3,5)Benzeno(3,3′,3″)triphenylmethanophane (23). The trisulfone **20** (310 mg, 0.498 mmol) was pyrolyzed by the same procedure as described for the preparation of **21**. The pyrolysis product was chromatographed on neutral alumina. While elution with hexane yielded **23** (40 mg, 20%), further elution with hexane–benzene (2:1) gave **22** (95 mg, 44%).

The compound **23** was recrystallized from hexane: mp >300 °C; IR (KBr) 3040, 3010, 2940, 2920, 2910, 2850, 1600, 1580, 1475, 1440, 920, 895, 790, 743, 728, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.83 (s, CH_2, 12 H), 5.33 (s, CH, 1 H), 5.50 (d, *J* = 2 Hz, Ar H, 3 H), 6.72 (s, Ar H, 3 H), 6.90–7.32 (m, Ar H, 9 H); UV (isooctane) λ_{max} 224 nm (sh, log ϵ 4.56), 257 (sh, 3.32), 263 (3.31), 274 (sh, 3.09); mass spectrum, *m/e* 400 (M^+).

Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 92.94; H, 6.95.

The compound **22** was recrystallized from hexane–benzene: mp 220–221 °C; IR (KBr) 3040, 3010, 2940, 2930, 2920, 2860, 2840, 2820, 1598, 1580, 1480, 1438, 1421, 1080, 896, 850, 797, 782, 770, 702 cm^{-1}; NMR ($CDCl_3$) δ 2.75 (s, CH_2, 12 H), 3.74 (s, OCH_3, 3 H), 5.18 (d, *J* = 2 Hz, Ar H, 3 H), 6.47 (s, Ar H, 3 H), 6.82–7.33 (m, Ar H, 9 H); UV (isooctane) λ_{max} 223 nm (sh, log ϵ 4.46), 257 (sh, 2.89), 262 (2.94), 268 (sh, 2.86); mass spectrum, *m/e* (relative intensity) 430 (100), 415 (12), 399 (56).

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.58; H, 6.99.

1,3,5-Tris(hydroxymethyl)benzene-d_6 (29). A solution of 1,3,5-tris(carbomethoxy)benzene (**28**; 5.8 g, 23 mmol) in dry THF (35 mL) was added to a suspension of $LiAlD_4$ (99% D; 2 g, 48 mmol) in dry THF (35 mL). The mixture was refluxed with stirring for 10 h, and the excess reducing agent was decomposed with water (15 mL). After an insoluble solid was removed from the reaction mixture, the filtrate was concentrated in vacuo. The residual solid was recrystallized from benzene–hexane to give **29**: 2.8 g (67%); mp 74–75 °C; mass spectrum, *m/e* 174 (M^+).

1,3,5-Tris(bromomethyl)benzene-d_6 (30). To a stirred solution of the alcohol **29** (2.7 g, 15.5 mmol) in dry ether (90 mL) was added dropwise a solution of phosphorus tribromide (5.8 g, 21.5 mmol) in dry ether (30 mL) at room temperature, and the mixture was sitrred for 4 h at room temperature. Addition of water (100 mL) separated an organic layer which was washed with water

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and then dried ($MgSO_4$). Removal of the solvent afforded a solid which was recrystallized from hexane–benzene to yield the tribromide **30**: 4.8 g (86%); mp 93–94 °C; IR (KBr) 2380, 2180, 1602, 1450, 1193, 970, 862, 602 cm^{-1}; mass spectrum, *m/e* 362 (M^+).

1,3,5-Tris(mercaptomethyl)benzene-d_6 (32). A mixture of **30** (4.6 g, 12.7 mmol), thiourea (4.4 g, 57.8 mmol), and 95% ethanol (40 mL) was refluxed with stirring for 13 h. The resulting triisothiuronium salt **31** was collected by filtration and dissolved in 6% sodium hydroxide solution (150 mL). After being refluxed for 8 h in an atmosphere of nitrogen, the solution was allowed to cool and was acidified with 6 N HCl (25 mL). The resulting product was extracted with ether, and the extract was washed with water and then dried. Removal of the solvent followed by distillation of the residue gave **32**: 2.1 g (72.6%); bp 158–160 °C (0.1 mm); IR (film) 2506, 2230, 2150, 1600, 1442, 1173, 1003, 905, 870, 815, 700 cm^{-1}; mass spectrum, *m/e* 222 (M^+).

19-Methyl-2,11,27-trithia[3.3.3](1,3,5)benzeno(3,3′,3″)triphenylmethanophane-*3,3,10,10,26,26-d*$_6$ (33). The same procedure described for the preparation of **17** was followed in the condensation of tribromide **12** (4.74 g, 8.82 mmol) and 1,3,5-tris(mercaptomethyl)benzene-d_6 (**32**; 1.96 g, 8.82 mmol). The deuterated trisulfide **33** was purified by column chromatography on neutral alumina and recrystallized from ethyl acetate: 620 mg (13.6%); mp 219–220 °C; IR (KBr) 3070, 3040, 3020, 2960, 2930, 2860, 2180, 1600, 1580, 1480, 1440, 1430, 1240, 1175, 1100, 1057, 935, 832, 800, 772, 730, 703 cm^{-1}; NMR ($CDCl_3$) δ 1.97 (s, CH_3, 3 H), 3.67 (s, CH_2, 6 H), 6.12 (d, J = 2 Hz, Ar H, 3 H), 6.73 (s, Ar H, 3 H), 6.90–7.24 (m, Ar H, 9 H); mass spectrum, *m/e* 516 (M^+).

Anal. Calcd for $C_{32}H_{24}D_6S_3$: S, 18.62. Found: S, 18.68.

19-Methyl-2,11,27-trithia[3.3.3](1,3,5)benzeno(3,3′,3″)triphenylmethanophane-*3,3,10,10,26,26-d*$_6$ *S,S,S′,S′,S″,S″*-Hexaoxide (34). The deuterated trisulfone **34** (0.52 g, 84%) was prepared from **33** (0.52 g, 1.01 mmol) by the same method as described for the preparation of **18**: mp >300 °C; IR (KBr) 1310, 1141, 1110 cm^{-1}.

Anal. Calcd for $C_{32}H_{24}D_6O_6S_3$: S, 15.70. Found: S, 15.92.

17-Methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane-*2,2,8,8,16,16-d*$_6$ (35). The pyrolysis of the deuterated trisulfone **34** (400 mg, 0.653 mmol) was carried out in the same manner as described for the undeuterated compound, providing a 44% yield of **35**: 120 mg; mp 211–212 °C; IR (KBr) 3070, 3040, 3010, 2960, 2930, 2860, 2180, 2080, 1600, 1582, 1483, 1440, 1420, 1375, 1181, 1057, 930, 900, 807, 786, 760, 730, 706 cm^{-1}; NMR ($CDCl_3$) δ 2.22 (s, CH_3, 3 H), 2.73 (br d, CH_2, 6 H), 5.22 (d, J = 2 Hz, Ar H, 3 H), 6.53 (s, Ar H, 3 H), 6.90–7.30 (m, Ar H, 9 H); mass spectrum, *m/e* 420 (M^+).

[2.2.2](1,3,5)Benzeno(3,3′,3″)triphenylmethanophane (23). A mixture of the chloride **24** (15 mg, 0.0035 mmol), $LiAlH_4$ (10 mg), and THF (3 mL) was heated to reflux for 6 h with stirring. The usual procedure afforded the crude hydrocarbon **23** which was column chromatographed over SiO_2 gel (1 g). Fractions eluted with hexane were collected, and removal of the solvent gave **23** (9 mg) which was recrystallized from hexane; mp >300 °C. The infrared spectra (KBr disk) of this specimen and the hydrocarbon obtained from the pyrolysate of the trisulfone **20** were indistinguishable.

17-Chloro[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (24). A solution of **22** (58 mg, 0.135 mmol) in acetic acid (35 mL) and benzene (1.5 mL) was saturated with dry HCl gas. After being allowed to stand for 1 h at room temperature, the reaction mixture was poured into cold water (20 mL) to precipitate solids. The mixture was extracted with ether, and the ethereal extract was washed with 3% $NaHCO_3$ solution and water and then dried ($MgSO_4$). Evaporation of the ether gave a solid, which was recrystallized from hexane to give **24**: 40 mg (68%); mp 219–220 °C; IR (KBr) 3070, 3030, 3010, 2930, 2910, 2860, 2840, 1600, 1590, 1484, 1445, 1424, 1180, 1087, 960, 896, 833, 800, 765, 752, 701 cm^{-1}; NMR ($CDCl_3$) δ 2.83 (br s, CH_2, 12 H), 5.18 (d, J = 2 Hz, Ar H, 3 H), 6.51 (s, Ar H, 3 H), 7.07–7.82 (m, Ar H, 9 H); UV (isooctane) λ_{max} 224 nm (sh, log ϵ 4.42), 257 (2.95, 264 (2.99), 270 (sh, 2.93); mass spectrum, *m/e* (relative intensity) 434 (100), 399 (69).

Anal. Calcd for $C_{31}H_{27}Cl$: C, 85.59; H, 6.26; Cl, 8.15. Found: C, 85.59; H, 6.25; Cl, 8.13.

17-Hydroxy[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (25). A mixture of **24** (25 mg, 0.057 mmol), $AgNO_3$ (30 mg, 0.176 mmol), and THF–H_2O (4:1, 20 mL) was refluxed with stirring for 6 h. The reaction mixture was diluted with water, and the product was extracted with ether. The ether extract was washed with water and then dried ($MgSO_4$). After evaporation of the solvent, the resulting solid was recrystallized from benzene–hexane to give **25**: 19 mg (79%); mp 173–174 °C; IR (KBr) 3550, 3470 cm^{-1}; NMR ($CDCl_3$) δ 2.86 (s, CH_2, 12 H), 3.17 (s, OH, 1 H), 5.33 (d, J = 2 Hz, Ar H, 3 H), 6.61 (s, Ar H, 3 H), 6.90–7.43 (m, Ar H, 9 H); UV (isooctane) λ_{max} 223 nm (sh, log ϵ 4.48), 257 (2.88), 262 (2.93), 268 (sh, 2.86); mass spectrum, *m/e* 416 (M^+).

Anal. Calcd for $C_{31}H_{28}O$: C, 89.38; H, 6.78. Found: C, 89.35; H, 6.77.

Methanolysis of Tri-*m*-tolylmethyl Chloride (10). A mixture of the chloride **10** (10 mg), methanol (0.2 mL), and pyridine (2 mL) was stirred at room temperature for 20 min. The routine workup yielded an oily product (10 mg) whose identity with the methoxy derivative **14** was established by TLC and mass spectroscopy: *m/e* 316 (M^+).

Hydrolysis of 14 with Concentrated H_2SO_4. A deep red solution of **14** (1 mg) in 2 drops of concentrated H_2SO_4 was diluted with water and extracted with ether. Removal of the solvent left a residue whose TLC analysis (SiO_2, 1:2 benzene/hexane development) showed the formation of the alcohol **13**.

Hydrolysis of the Methoxy Derivative 22 to the Alcohol 25. The methoxy derivative **22** (1 mg) was placed on a slide glass and dissolved in 2 drops of concentrated H_2SO_4 to give a bright red solution which discolored within 20 s. After dilution with water, the mixture was extracted with ether. TLC analysis (SiO_2, 1:1 benzene/hexane, development) of the extract detected the alcohol **25**.

Tri-*m*-tolylmethyl Hexachloroantimonate. A mixture of the chloride **10** (50 mg, 0.156 mmol) and $SbCl_5$[22] (46 mg, 0.156 mmol) in 5 mL of CCl_4 was stirred at room temperature for 1 h to precipitate a red solid which, after being washed with CCl_4 and recrystallized from nitromethane, gave 65 mg of the hexachloroantimonate, mp 198–200 °C.

Anal. Calcd for $C_{22}H_{21}SbCl_6$: C, 42.62; H, 3.42; Cl, 34.32. Found: C, 42.50; H, 3.49; Cl, 34.43.

The same procedure failed to prepare the crystalline hexachloroantimonate salt of the carbonium ion **27**.

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Registry No. **10**, 76499-47-3; **11**, 76499-48-4; **12**, 76499-49-5; **13**, 51226-48-3; **14**, 76499-50-8; **15**, 76499-51-9; **16**, 63877-73-6; **17**, 73663-55-5; **18**, 73651-36-2; **19**, 76499-52-0; **20**, 76499-53-1; **21**, 73651-37-3; **22**, 76499-54-2; **23**, 76499-59-7; **24**, 76499-55-3; **25**, 76499-56-4; **28**, 2672-58-4; **29**, 76499-57-5; **30**, 76499-58-6; **31**, 76499-60-0; **32**, 76499-61-1; **33**, 76499-62-2; **34**, 76499-63-3; **35**, 76499-64-4; tris(*m*-tolylmethyl)hexachloroantimonate, 980-93-8.

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