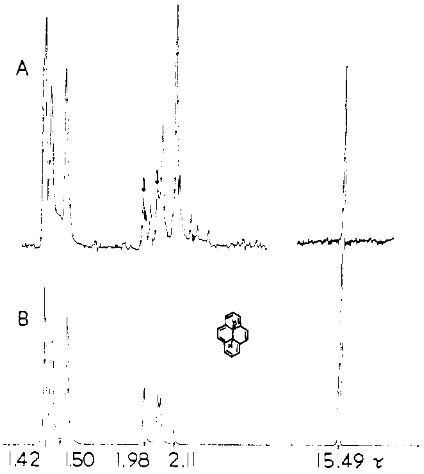

Figure 1. (A) The experimental nmr spectrum of *trans*-15,16-dihydropyrene (7) in cyclohexane. The signal in the region of 2.0 is due to the presence of pyrene with the underlying signals from 7 marked by arrows. B is a computer simulated nmr spectrum for 7 in which the signals due to pyrene have been subtracted from the experimental spectrum in A. Spectra recorded with a Varian HA-100 MHz spectrometer.

as a multiplet at 1.98–2.11, and H_x as a singlet at 15.49. In view of the fact that H_x is allylic, this is a remarkable upfield chemical shift, a proof of the strong diamagnetic ring current, and the aromatic nature of 7. Further, the visible spectrum of 7 is very similar to that of the other *trans*-15,16-dihydropyrenes.

Although such sealed, degassed cyclohexane solutions of 7 appear to be reasonably stable in the dark at room temperature, prolonged exposure to light at 2537 nm leads to a clean conversion to pyrene. Similarly, exposure of such solutions to oxygen leads to a rapid, but not instantaneous, conversion to pyrene. Finally, when such solutions are heated the intensity of the green color is lessened and this occurs very rapidly at temperatures above 60°. Although the structures of these thermal rearrangement products have not yet been established, they are presumably the result of a 1,5-sigmatropic rearrangement of the hydrogens from the interior to the periphery.[7] In retrospect, it is remarkable that 7 is so stable at room temperature and does not spontaneously undergo such a 1,5-sigmatropic rearrangement.

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Syntheses of Novel Tris-Bridged Cyclophanes. [2.2.2](1,3,5)Cyclophane-1,9,17-triene

Sir:

Recently, we reported on a method for the transformation of a sulfide linkage to a carbon–carbon double bond.[1] This has provided a convenient synthesis for *trans*-15,16-dimethyldihydropyrene,[1] both *trans*-[2.2]metacyclophane-1,9-diene and *trans*-15,16-dihydropyrene,[2] and [2.2]metaparacyclophane-1,9-diene.[3] Recent nmr studies provide evidence that the *cis* and *trans* conformers of 2,11-dithia[3.3]metacyclophane interconvert rapidly at room temperature.[4] In view of this it seemed possible that a suitably substituted derivative of 2,11-dithia[3.3]metacyclophane might undergo ring closure and be locked in a *cis* conformation. We now report the successful experimental test of this hypothesis and the consequent synthesis of 2,11,20-trithia[3.3.3](1,3,5)cyclophane, **2**. Furthermore, application of our method of transforming sulfide linkages to olefinic bonds has led to the conversion of **2** to the unusual tris-bridged cyclophane **6**.[5]

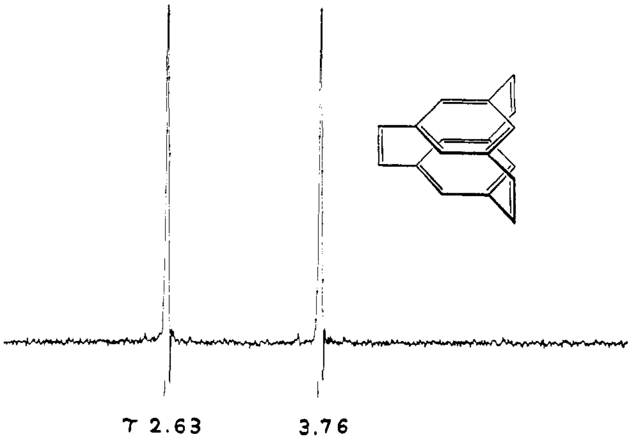

Figure 1. The nmr spectrum of [2.2.2](1,3,5)cyclophane-1,9,17-triene (6) in deuteriochloroform measured with a Varian 60-MHz spectrometer.

When 1,3,5-tris(bromomethyl)benzene (**1**) was treated with sodium sulfide in ethanol under the standard conditions for such reactions,[2] it was converted in 12% yield to 2,11,20-trithia[3.3.3](1,3,5)cyclophane (**2**), isolated as white crystals, mp 254–255°.[6] Treatment of **2** with dimethoxycarbonium fluoroborate[7] gave the tris-sulfonium salt (**3**) as fine white needles, but as a mixture of isomers, in 100% yield. This mixture was treated directly with sodium hydride in tetrahydrofuran to effect a triple Stevens rearrangement and to give the tris-sulfide **4** as a mixture of isomers in 38% yield. This, in turn, was again treated with dimethoxycarbonium fluoroborate to give the tris-sulfonium salt **5** in 100% yield. When **5** was suspended in ether at −78° and treated with *n*-butyllithium, it was converted to the desired triene **6** in 5% yield, isolated as white platelets, mp 203–204°, after recrystallization from petroleum ether (30–60°).

The nmr spectrum of **6** (see Figure 1) shows only two singlets of equal intensity at τ 2.63 and 3.76. In view of the fact that **6** represents a rigid molecule in

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(1) R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1197 (1970).

(2) R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3510 (1970).

(3) V. Boekelheide and P. H. Anderson, *Tetrahedron Lett.*, 1207 (1970).

(4) T. Sato, M. Wakabayashi, M. Kainosho, and K. Hata, *ibid.*, 4185 (1968).

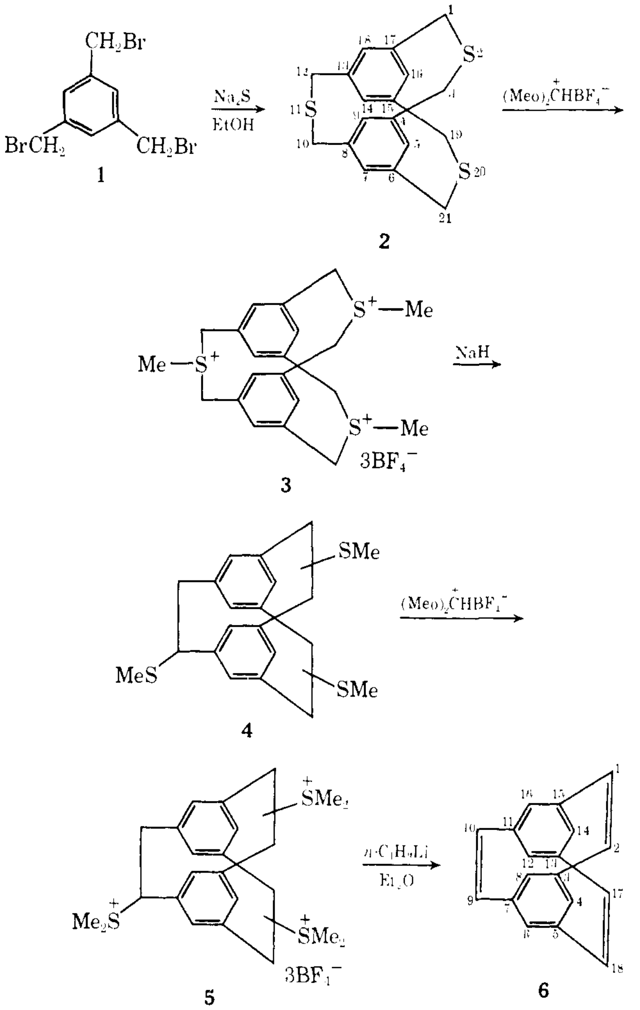
(5) Although tris-bridged cyclophanes have been reported previously (see D. J. Cram and R. A. Reeves, *J. Amer. Chem. Soc.*, **80**, 3094 (1958), and A. J. Hubert, *J. Chem. Soc. C*, 6, 10, 13 (1967)), these are the first examples where the bridges involve only two linking atoms.

(6) The empirical formulae of all new compounds have been substantiated by elemental analyses and/or high resolution mass spectra.

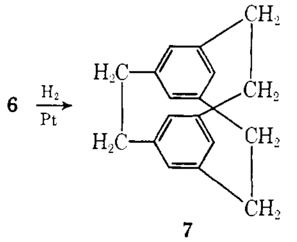
(7) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).

which the two benzene rings are held face to face in very close proximity by the three ethylene bridges, its nmr spectrum seemed at first glance to be singularly unexciting. However, since the assignment of which signal represented the vinyl protons and which represented the aromatic protons could not be made *a priori*, it seemed worthwhile to carry out a deuterium labeling experiment to settle this point.

Reduction of trimethyl 1,3,5-benzenetricarboxylate with lithium aluminum deuteride gave the corresponding deuterated 1,3,5-tris(hydroxymethyl)benzene. This, on treatment with phosphorus tribromide, gave 1,3,5-tris(bromomethyl)benzene, **1**, in which all of the benzylic hydrogens are replaced by deuterium. When the deuterated derivative of **1** was carried through the same reaction sequence as shown above, it gave a sample of **6** in which all of the vinyl hydrogens are replaced by deuterium. Examination of the nmr spectrum of this deuterated derivative of **6** showed a singlet at τ 3.76. Thus, it can be stated unambiguously that the aromatic protons of **6** appear at τ 3.76, whereas the vinyl protons appear as a singlet at τ 2.63. Actually, the upfield shift of the aromatic protons to τ 3.76 is not unexpected, since such upfield shifts of aromatic protons are a common consequence of bringing two benzene rings face to face in a *cis* relationship.[8-10] The more unusual observation is the downfield shift of the vinyl protons. Presumably, this is related to the unusual strain present in the rigid tris-bridged, *cis*-metacyclophane structure of **6**. In this regard the strain present in **6** should exceed that of [2.2]paracyclophane-1,9-diene, a molecule which previously had represented the outstanding example of severe ring-bridged strain.[11]



Since the aromatic protons of **6** probably are deshielded by the bridging vinyl groups, it was of interest to hydrogenate **6**. This occurred readily over a platinum catalyst to give **7** as white crystals, mp 204–206°. The nmr spectrum of **7** shows two singlets at τ 4.27, corresponding to the aromatic protons, and at 7.25, corresponding to the benzylic protons. To the extent that the upfield shift of aromatic protons is a measure of the proximity of two aromatic rings, the two aromatic rings of **7** (Ar-*H*, τ 4.27) are appreciably closer than in [2.2]paracyclophane (Ar-*H*, τ 3.63).[9]



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In view of the extensive theoretical interest in the long wavelength (302 nm) band of [2.2]paracyclophane,[12-14] it should be noted that both **6** and **7** show a similar band but at even longer wavelength. Thus, the ultraviolet spectrum of **6** in hexane shows absorption maxima at 252 (ϵ 1960) and 325 nm (ϵ 90), while a solution of **7** in hexane has absorption maxima at 258 (ϵ 1340) and 312 nm (ϵ 14).

Further studies of the physical and chemical properties of **6** and **7** are under investigation.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

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(8) R. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 530 (1968).

(9) D. J. Cram, C. K. Dalton, and G. R. Knox, *ibid.*, **85**, 1088 (1963).

(10) R. H. Martin, G. Morren, and J. J. Shurter, *Tetrahedron Lett.*, 3683 (1969).

(11) K. C. Dewhurst and D. J. Cram, *J. Amer. Chem. Soc.*, **80**, 3115 (1958).

(12) See R. Gleiter, *Tetrahedron Lett.*, 4453 (1969), and references cited therein.

(13) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter, and E. Heilbronner, *J. Amer. Chem. Soc.*, **81**, 5977 (1959).

(14) D. T. Longone and H. S. Chow, *ibid.*, **92**, 994 (1970).

(15) N.D.E.A. Fellow, University of Oregon, 1967–1970.

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Nuclear Magnetic Resonance Disclosure of the Anomalous Hydrogen in Pentaborane(11)

Sir:

The structure of pentaborane(11) has been generally settled, except for the nature of one particular hydrogen which is believed to be located somewhere in the vicinity of boron atoms 1, 2, and 5. The X-ray data[1] suggest

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(1) (a) L. R. Levine and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 2087 (1953); **22**, 614 (1954); (b) E. B. Moore, Jr., R. E. Dickerson, and W. N. Lipscomb, *ibid.*, **27**, 209 (1957).