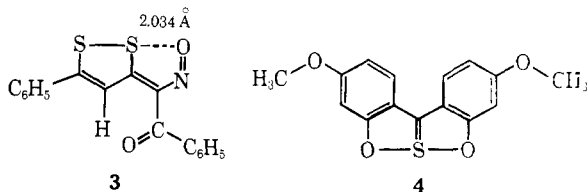


Figure 1. Stereoscopic drawing of **1**. The S–O lengths are 1.889 (4) and 1.916 (4) Å and the S–Cl lengths are 1.804 (6) and 1.810 (7) Å; the O–S–O angle is 175.1 (2), the C–S–C angle is 104.4 (3), and the O–S–C angles range from 86.4 (2) to 91.2 (2)°.

closely analogous to **1**. Its slightly distorted trigonal-bipyramidal geometry (Cl–S–Cl angle, 174.5 (1)°) is similar to that seen for **1** (O–S–O bond angle, 175.1 (2)°), although the distortion from 180° is away from the lone pair of electrons in **1** and toward the lone pair in **2**. The 0.2-Å elongation of the sulfurane S–Cl bonds, relative to the sum of covalent radii, was interpreted⁵ in terms of a bond order for the S–Cl bonds of approximately 0.5, in a three-center, three-orbital, four-electron bond.

The apical S–O bonds of **1** (1.889 (4), 1.916 (4) Å) are unusually long for single bonds when compared to the sum of the covalent radii for sulfur and oxygen (1.70 Å)⁷ and the lengths of 1.533–1.616 Å reported in organic sulfates^{8,9} and 1.594–1.627 Å found in sulfonates.¹⁰ S–O contacts ranging from 2.034 to 2.65 Å have been reported^{11,12} in a number of compounds, e.g., **3**; in many of these cases the oxygen atom lies along an extension of an S–S vector. The sum of the van der Waals radii for sulfur and oxygen is 3.25 Å.¹³ Another comparatively short S–O contact (2.81



(1) Å) has been found in 1-acetyl-1-thionia-5-thia-cyclooctane perchlorate,¹⁴ and in that case a distorted trigonal-bipyramidal arrangement, involving a trans-annular S–S interaction, was found around one of the sulfur atoms. A more pertinent comparison may be made with the structure of the fusion product (**4**)

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(11) J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Amer. Chem. Soc.*, **90**, 5800 (1968).

(12) P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc. B*, 946 (1971).

(13) Reference 7, pp 257–264.

(14) S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Chem. Soc. B*, 1603 (1970).

of captan and resorcinol.^{15,16} In the essentially coplanar molecule of **4**, the S–O lengths are 1.878 (2) and 1.879 (2) Å. While formally **4** appears as a tricoordinate sulfur(IV) compound, if one considers the equivalent orbital representation, in which the C=S double bond is represented as two equivalent bent bonds,^{17,18} the similarity to **1** is apparent. In both **4** and **1** the S–O bonds are elongated by ca. 0.2 Å from the usual value for S–O single bonds, as was seen⁵ for the S–Cl bonds of **2**. One picture of the bonding which is consistent with this would put two electrons into the three-center (O–S–O) bonding molecular orbital (giving a bond order of 0.5 for the two S–O bonds) and two into the nonbonding molecular orbital (putting negative charge on the electronegative apical substituents). Such an approximation, using no d orbitals on sulfur, has been discussed by Musher¹⁹ for a variety of compounds with what he calls hypervalent bonding.

Acknowledgment. Partial support for this research was provided by National Science Foundation Grant No. GP 13331 and by the Alfred P. Sloan Foundation.

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(17) Reference 7, pp 136–138.

(18) J. D. Dunitz and P. Strickler in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 595–602.

(19) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969). We also thank Professor Musher for a preprint of a paper which discusses the qualitative application of this theory to sulfurane structure problems.

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[20]Annulene¹

Sir:

All annulenes from [14]annulene to [24]annulene have been obtained as well-characterized crystalline compounds,² except for [20]annulene.³ We now report

(1) Unsaturated Macrocyclic Compounds. LXXXVI. For part LXXXV, see B. W. Metcalf and F. Sondheimer, *J. Amer. Chem. Soc.*, **93**, 5271 (1971).

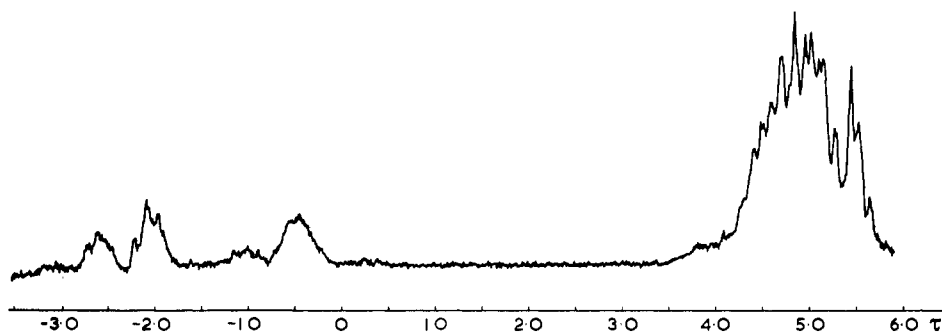


Figure 1. Nmr spectrum (100 MHz) of monodehydro[20]annulene (*e.g.*, 3), measured in tetrahydrofuran- d_8 at -90° , using a time-averaged computer (internal standard, TMS).

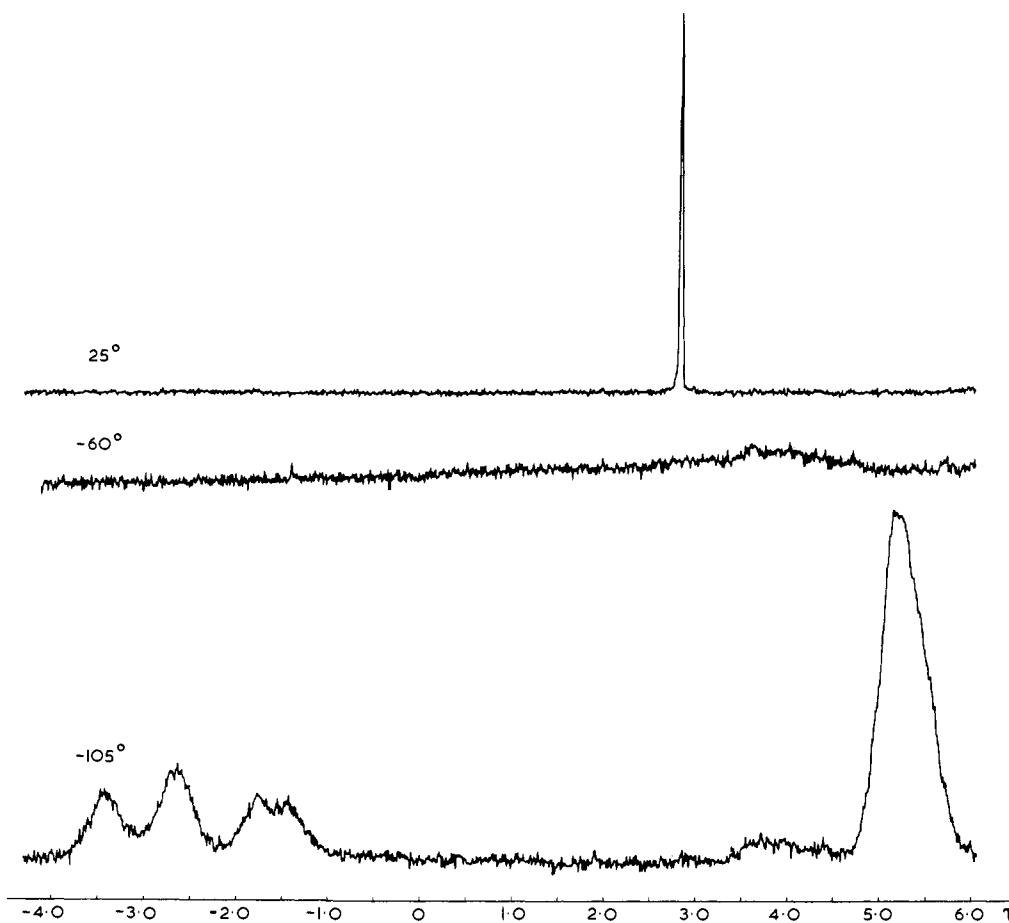


Figure 2. Nmr spectra (100 MHz) of [20]annulene (*e.g.*, 4), measured in tetrahydrofuran- d_8 at different temperatures (internal standard, TMS).

the synthesis and properties of [20]annulene (*e.g.*, 4), thus completing the series.

(2) See (a) F. Sondheimer, *Proc. Roy. Soc., Ser. A*, **297**, 173 (1967); (b) F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Mayo, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc., Spec. Publ.*, No. 21, 75 (1967); (c) R. M. McQuilkin, B. W. Metcalf, and F. Sondheimer, *Chem. Commun.*, 338 (1971); (d) F. Sondheimer, *Accounts Chem. Res.*, in press.

(3) Indications have been obtained previously that [20]annulene is formed by the partial catalytic hydrogenation of 1,11-bisdehydro[20]annulene,⁴ as well as by the prototropic rearrangement of *trans,trans*-1,11-cycloicosadiene-5,7,15,17-tetrayne.⁵ However, this work was carried out over 10 years ago without the benefits of thin layer chromatography, nmr spectrometry, or mass spectrometry, and the structural evidence was not conclusive.

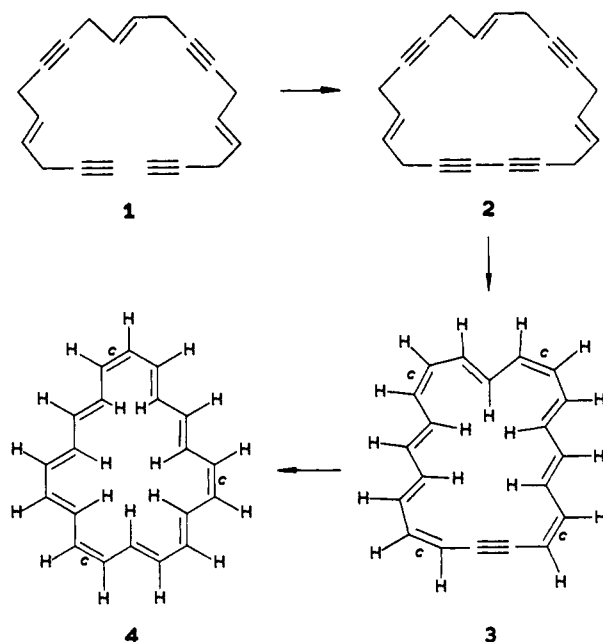
(4) F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **84**, 3520 (1962).

(5) F. Sondheimer, R. Wolovsky, and D. A. Ben-Efraim, *ibid.*, **83**, 1686 (1961).

The starting material was *all-trans*-1,7,13-cycloicosatriene-4,10,16,18-tetrayne (2),⁶ obtainable in $\sim 20\%$ yield by the oxidative coupling of *all-trans*-4,10,16-eicosatriene-1,7,13,19-tetrayne (1)⁷ with cupric acetate in pyridine and ether. Substance 2 in tetrahydrofuran was added during 3 min to freshly sublimed potassium *tert*-butoxide in tetrahydrofuran at -70° . After being stirred for 15 min at -70° , the product was isolated and chromatographed on silica. This procedure led

(6) Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *ibid.*, **90**, 4940 (1968).

(7) Substance 1 has been obtained previously⁸ as a by-product (2% yield) from the reaction of *trans*-1,4-dibromo-2-butene with ethynylmagnesium bromide. It has now been synthesized in 18% yield by the cuprous chloride catalyzed condensation between *trans*-1,4-dichloro-2-butene and 2 mol equiv of the mono-Grignard derivative of *trans*-4-octene-1,7-diyne.⁶



to 12% monodehydro[20]annulene (e.g., **3**)⁸ as purple-brown prisms which decomposed on attempted melting point determination: homogeneous when chromatographed on 0.5% silver nitrate-silica gel; mass spectrum m/e 258.140 (calcd for $^{12}\text{C}_{20}^{1}\text{H}_{18}$ 258.141); $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ 308 (sh) (ϵ 94,400) and 322 nm (124,000); $\nu_{\text{max}}^{\text{CHCl}_3}$ 2180 (w), 1000 (s), 980 (s), and 960 (s) cm^{-1} .⁹ Catalytic hydrogenation in tetrahydrofuran over platinum gave cycloicosane (mass spectrum m/e 280).

The nmr spectrum of the monodehydro[20]annulene at -90° (Figure 1) consisted of very complex multiplets at τ -3.3 to -0.1 and 4.0 to 5.7 , the integrated areas being $\sim 5:13$.¹⁰ The integration shows these bands to be due to the inner and outer protons, respectively, and indicates a "tetra-cis" structure, such as **3**. The relative positions of the bands shows the existence of a paramagnetic ring current, as expected of a 20-out-of-plane- π -electron system.^{2b} A similar effect has already been observed in the low-temperature nmr spectrum of 1,11-bisdehydro[20]annulene, although in this case "averaging" of the trans double bond protons occurs at room temperature, due to the equivalence of the interconverting forms.^{2b}

The partial catalytic hydrogenation of monodehydro[20]annulene was carried out in benzene solution over a 5% palladium/calcium carbonate catalyst, the reaction being terminated when ~ 2 mol equiv of hydrogen had been absorbed. Chromatography on silica then gave 7% [20]annulene (**4**), followed by $\sim 35\%$ unchanged monodehydro[20]annulene. [20]Annulene formed brown-red needles (dark red in concentrated solution): mp 139 – 140° dec (sample placed on block at $\sim 120^\circ$); homogeneous when chromatographed on 0.5% silver nitrate-silica gel; mass spectrum m/e 260.156 (calcd for $^{12}\text{C}_{20}^{1}\text{H}_{20}$ 260.157); $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ 323 nm (ϵ 146,000); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1000 (s) and 980 (s) cm^{-1} . Catalytic

(8) For a preliminary study of the rearrangement of **2** to monodehydro[20]annulene, see F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **83**, 1259 (1961).

(9) Occasionally, small quantities of another monodehydro[20]annulene, with very similar properties, were isolated. However, this isomer was not investigated further.

(10) The nmr spectrum at room temperature was similar, but was less well resolved.

hydrogenation in tetrahydrofuran over platinum again gave cycloicosane (mass spectrum m/e 280).

The nmr spectrum of [20]annulene was found to be temperature dependent (Figure 2). At -105° , it consisted of a low-field multiplet at τ -3.9 to -0.9 due to the inner protons and a high-field multiplet at τ 3.4 – 5.9 due to the outer protons; the spectrum is again indicative of a paramagnetic ring current, as expected of a $[4n]$ annulene.^{2b} At higher temperatures, these bands broaden and then coalesce (coalescence temperature $\sim -60^\circ$). An "average" signal appears above the coalescence temperature, and at 25° this signal consisted of a sharp singlet at τ 2.82. This temperature effect is similar to that of most of the other annulenes investigated.^{2b}

The integrated areas of the low-field and high-field bands in the low-temperature nmr spectrum of [20]annulene were almost exactly 7:13, pointing to a "tricyclic" structure, such as **4**. However, the complexity of the spectrum indicates the presence of a stereoisomeric mixture in solution. The value of ΔG^\ddagger for the barrier to conformational interconversion, calculated as described previously,¹¹ was $9.2 \text{ kcal mol}^{-1}$.

The nmr spectra of all annulenes from the 6- to the 24-membered ring compounds have now been determined.^{2,12} With two exceptions, all the $[4n]$ annulenes show a paramagnetic ring current, and all the $[4n + 2]$ annulenes a diamagnetic ring current, in agreement with theory. The exceptions are [8]- and [10]annulene, which prove to have no ring current, presumably due to their nonplanarity.

Acknowledgments. We are indebted to the Royal Society for generous financial assistance.

(11) I. C. Calder and P. J. Garratt, *J. Chem. Soc. B*, 660 (1967).

(12) See R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 105 (1971).

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Tricarba-closo-octaborane(7), a Polyhedral Carborane Containing a "Bare" Carbon Atom

Sir:

The importance of isoelectronic sequences among boron compounds implies the existence of polyhedral carboranes containing more than two carbon atoms, which in theory would be generated from members of the known $\text{C}_2\text{B}_{n-2}\text{H}_n$ series by the formal replacement of one or more BH groups with carbon atoms. We wish to report the isolation and characterization of the first such molecule, $^1\text{C}_3\text{B}_5\text{H}_7$ (I), an isoelectronic analog of the known polyhedral species $\text{C}_2\text{B}_6\text{H}_8$ ^{2,3} and B_8H_8 ²⁻.⁴ Compound I was isolated quite unexpectedly during a

(1) Icosahedral carboranes containing unsubstituted Ge, Sn, or Pb atoms have been reported: R. L. Voorhees and R. W. Rudolph, *J. Amer. Chem. Soc.*, **91**, 2173 (1969); R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *ibid.*, **92**, 3351 (1970); L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, *ibid.*, **91**, 3376 (1969).

(2) (a) P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1907 (1969); (b) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968).

(3) R. E. Williams and F. J. Gerhart, *ibid.*, **87**, 3513 (1965).

(4) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).