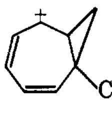
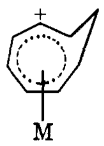
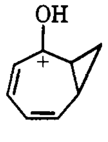


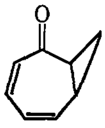
II



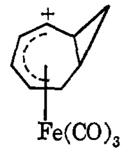
III, M = Mo(CO)$_3$
V, M = Fe$_2$(CO)$_6$



IV



VI



VII

pylium (IV),[8] the $C_8H_9^+Fe_2(CO)_6$ cation (V),[9] homotropone (VI),[8] and the $C_8H_9^+Fe(CO)_3$ cation (VII).[11]

The linearity of the plot of δ *vs.* Δ expected from eq 1 is very satisfactorily attained, and the deviations observed are no more than could be reasonably anticipated from the difficulty in getting a series of compounds of exactly the same geometry. The values of Δ range from almost zero in homotropone and the $C_8H_9Fe(CO)_3$ cation, indicating the absence of a ring current for these systems, to a value of 5.8 ppm for the homotropylium cation. The agreement with the theoretical expectations offers strong support for the argument that there exists a large ring current in the homotropylium cation. From the data given by Johnson and Bovey[5] it is seen that the value of 5.8 ppm for the difference in chemical shift for the protons H_a and H_b in I suggests that the size of the ring current in homotropylium is of the same order of magnitude as that present in benzene. This implies that the delocalization of electrons in the cation is extensive, and strongly supports the nonclassical formulation Ia or Ib over any classical formulation such as Ic.

Acknowledgment. We thank the administrators of the Petroleum Research Fund and the Robert A. Welch Foundation for financial assistance. We also thank Badische Anilin und Soda Fabrik for a gift of cyclooctatetraene.

(8) J. D. Holmes and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2531 (1963).

(9) Prepared by the addition of a proton to the cyclooctatetraene–$Fe_2(CO)_6$ complex[10] and by hydride abstraction from the cyclooctatriene–$Fe_2(CO)_6$ complex: C. E. Keller, G. F. Emerson, and R. Pettit, to be published.

(10) C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1389 (1965).

(11) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

(12) NASA Trainee, 1965–1966.

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A Dicarbanonaborane(13)

Sir:

We wish to report the preparation of a dicarbanonaborane(13), $B_7C_2H_{13}$, which is isoelectronic with an unknown $B_9H_{13}^{-2}$ ion and appears to contain two methylene groups. The latter feature has not been previously observed although isoelectronic BH_2^- groups are commonly observed in the boron hydrides.

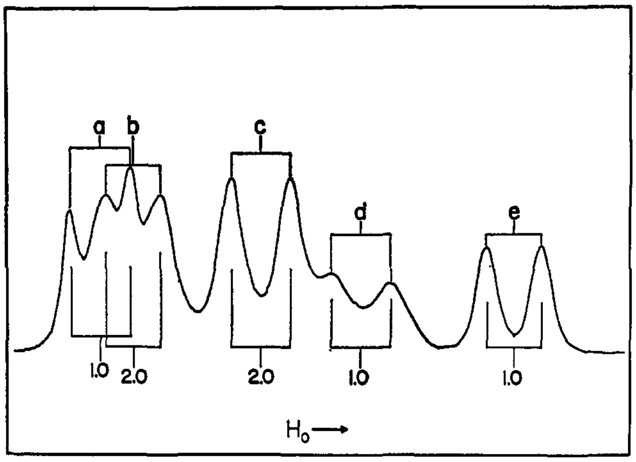

Figure 1. The ^{11}B nmr of $B_7C_2H_{11}(CH_3)_2$ at 19.3 Mc/sec. Chemical shifts, ppm (with reference to $BF_3O(C_2H_5)_2$), and coupling constants (cps) are (a) −7.44 (162), (b) −2.95 (147), (c) +14.9 (161), (d) +29.0 (156), and (e) +51.0 (148). Integrated areas are indicated beneath the peaks.

The preparation of $B_7C_2H_{13}$ and its C-substituted derivatives was carried out by oxidation of the corresponding $B_9C_2H_{11}$ carborane[1a,b] with dichromate ion in aqueous acetic acid solution at 0°. In a typical preparation 53.5 g (0.333 mole) of $B_9C_2H_9(CH_3)_2$ was dissolved in 450 ml of glacial acetic acid, and 900 ml of water was added with stirring under a nitrogen atmosphere. Toluene (400 ml) was added to the resulting solution to serve as an extractant for the reaction product. At 0°, a solution of 98.7 g (0.335 formula wt) of $K_2Cr_2O_7$ dissolved in 500 ml of water and 180 ml of glacial acetic acid was added to the carborane solution with vigorous stirring over a period of 60 min. The reaction mixture was added to 1.5 l. of water and the toluene layer separated. The aqueous layer was extracted four times with 100-ml portions of toluene. The combined toluene extracts were washed three times with 100-ml portions of 10% H_2SO_4 and dried over $MgSO_4$. The bulk of the toluene was removed by use of a rotary evaporator and the product isolated by sublimation under high vacuum. Table I reports relevant yield and characterization data.[2]

The 19.3-Mc/sec ^{11}B nmr spectrum of $B_7C_2H_{11}(CH_3)_2$ shown in Figure 1 contained five doublets with the relative intensities 1:2:2:1:1. Similar spectra were obtained for each of the compounds presented in Table I. The ^1H nmr chemical shifts and relative intensities obtained with the compounds reported in Table I are presented in Table II. The CH_3 resonance appeared as a doublet (J = 4.8 cps) in the spectra of $B_7C_2H_{12}(CH_3)$ and $B_7C_2H_{11}(CH_3)_2$. In addition, the spectra of $B_7C_2H_{12}(CH_3)$ and $B_7C_2H_{13}$ contained two broad singlets which represent two distinct types of CH (τ 9.9 and 10.7). In $B_7C_2H_{11}(CH_3)_2$, only the τ 10.7 resonance was observed. These results may be interpreted in terms of two CH_2 groups separated by a plane of symmetry in the parent compound. The two re-

(1) (a) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964); (b) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Letters*, 715 (1965).

(2) At 16 ev the mass spectrum of $B_7C_2H_{13}$ contains the parent peak, m/e 114, which corresponds to $^{11}B_7{}^{12}C_2{}^1H_{13}$.

Table I. Yield and Characterization Data for the $B_7C_2H_{11}RR'$ Species

				Analysis, %					
				Calculated			Found		
R	R'	Mp, °C	Yield, %	C	H	B	C	H	B
H	H	60.5-61.0	76	21.30	11.62	67.09	21.36	11.61	67.09
CH_3	H	23.5-24	62	28.41	11.92	59.67	28.40	11.71	59.58
CH_3	CH_3	50.5-51.8	65	34.11	12.17	53.73	34.34	12.43	53.65
C_6H_5	H	78.5	59	50.87	9.07	40.06	51.15	9.22	39.73

maining "extra" hydrogen atoms may be accounted for as a set of two B–H–B bridge groups which appear at 2020 cm^{-1} in the infrared spectrum of all the derivatives obtained thus far. The parent $B_7C_2H_{13}$ exhibited sharp C–H stretching bands at 3000 and 3060 cm^{-1}.

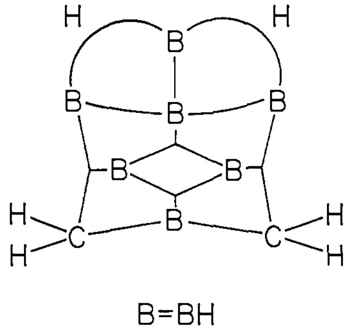

Figure 2. One topological representation of the proposed $B_7C_2H_{13}$ structure.

Oxidation of $B_9C_2H_{10}(CH_3)$ in D_2O solution produced the corresponding B_7 species, $B_7C_2H_8D_4(CH_3)$, with deuterium in the B–H–B bridge system and *two of the three* unsubstituted carbon positions. Thus, the B–H–B bridge band at 2020 cm^{-1} was missing, and a C–D stretching band appeared at 2230 cm^{-1}. The ^1H nmr spectrum of this material contained a singlet CH_3 resonance at τ 8.70 and the broad singlet CH resonance of relative intensity 1 at τ 9.82. The broad CH' resonance at τ 10.69 was absent. The ^{11}B nmr spectrum was sharpened in two regions which appeared to be associated with two types of boron atoms of relative intensities 1 and 2. This suggests the occurence of weak spin coupling of B–H–B bridge hydrogen atoms with neighboring B atoms in the isotopically normal compound.

Treatment of $B_7C_2H_{12}(CH_3)$ with deuterated phosphoric acid in D_2O-tetrahydrofuran afforded $B_7C_2H_{10}D_2(CH_3)$. No B–H–B bridge exchange was observed and the CH' ^1H nmr resonance at τ 10.69 was absent. The CH_3 proton resonance appeared as a sharp singlet and the τ-9.82 resonance remained.

Base-catalyzed deuterium exchange (D_2O-K_2CO_3) of $B_7C_2H_{12}(CH_3)$ resulted in $B_7C_2H_8D_4(CH_3)$ identical with that obtained from the oxidation reaction which was conducted in D_2O solution. Thus, base-catalyzed exchange occurs at the B–H–B bridge and CH' positions (τ 10.69 in the ^1H nmr spectrum).

The reaction of $B_7C_2H_{11}(CH_3)_2$ with aqueous hydroxide ion produced a monoanion which was isolated as its cesium or tetramethylammonium salt in high yield. *Anal.* Calcd for Cs $B_7C_4H_{16}$: C, 17.61; H, 5.91; B, 27.75. Found: C, 18.61; H, 6.32; B, 27.95.

Table II. ^1H Nmr Spectra of $B_7C_2H_{13}$ Derivatives

		Chemical shifts, τ^a		
	Solvent	CH_3	CH	CH'
$B_7C_2H_{13}$	$CDCl_3$		9.90 (1.0)	10.77 (1.0)
$B_7C_2H_{12}(CH_3)$	$C_6H_5CH_3$	8.66 (3.0)	9.82 (1.0)	10.69 (2.0)
$B_7C_2H_{11}(CH_3)_2$	CCl_4	8.70 (6.0)		10.73 (2.0)

[a] Relative areas in parentheses.

The instability of the $B_7C_2H_{10}(CH_3)_2^-$ ion precluded further reaction studies and nmr characterization. However, neutralization of the sodium salt of the anion with DCl produced $B_7C_2H_{10}D(CH_3)_2$ labeled at the more easily exchanged CH' positions (τ 10.73 in the ^1H nmr spectrum). These results again suggest that the easily exchanged CH' protons may be more acidic than those present in the proposed B–H–B bridge system.

The analytical and spectroscopic evidence cited above suggests, using the topological language of Lipscomb,[3] a 2532-A structure for $B_7C_2H_{13}$ which is probably based upon an icosahedral fragment. A tentatively suggested structure which satisfies these data is presented in Figure 2. The two hydrogen atoms attached to each carbon atom in $B_7C_2H_{13}$ form an axial–equatorial set similar to that found in chair-form cyclohexane. The tetrahedral hybridization at carbon would allow the transannular axial hydrogen–axial hydrogen distance to be greater than the 2-A minimum suggested by Lipscomb[4] for stable boron hydride species. Methyl substituents most likely lie in equatorial positions, and this serves to identify the readily exchanged CH' proton set at τ 10.7 as axial hydrogen atoms.

Pyrolysis of the C,C'-dimethyl and C-phenyl derivatives of $B_7C_2H_{13}$ at temperatures near 200° produced the correspondingly substituted $B_5C_2H_7$, $B_6C_2H_8$, $B_7C_2H_9$, and $B_8C_2H_{10}$ carboranes. The characterization of these products is described in the accompanying communication.

Acknowledgment. The authors gratefully acknowledge the support of this reserch by the National Cancer Institute, U. S. Public Health Service, under Grant CA-06773 MCHB.

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(4) W. N. Lipscomb, *Inorg. Chem.*, 3, 1683 (1964).

(5) Alfred P. Sloan Research Fellow.

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