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.

[7] NASA Trainee, 1965–1966.

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Received December 3, 1965

The Electronic Structure of the Homotropylium Cation

Sir:

There exists an interesting problem concerning the electronic structure of the homotropylium cation (I).[1] The nmr spectrum of the cation displays absorptions at τ 1.4, 3.4, 4.8, and 10.6 (areas 5:2:1:1) which can be assigned to the five protons on C_2–C_6, the two equivalent protons H_1 and H_7, and the protons H_b and H_a, respectively. Primarily on the basis of the extraordinarily large difference in chemical shift (5.8 ppm) between the two protons H_a and H_b which, as far as we are aware, is the biggest separation in chemical shift ever reported for two protons attached to the same carbon atom, we have suggested that there exists a ring current in the molecule. H_a which is over the ring is shielded, while H_b which is more nearly in the plane of the ring is deshielded. The system is thus presumed to have the nonclassical homotropylium structure I which can be represented either in molecular orbital terms as a or, what is equivalent, in valence bond terms as a resonance hybrid, *e.g.*, b.

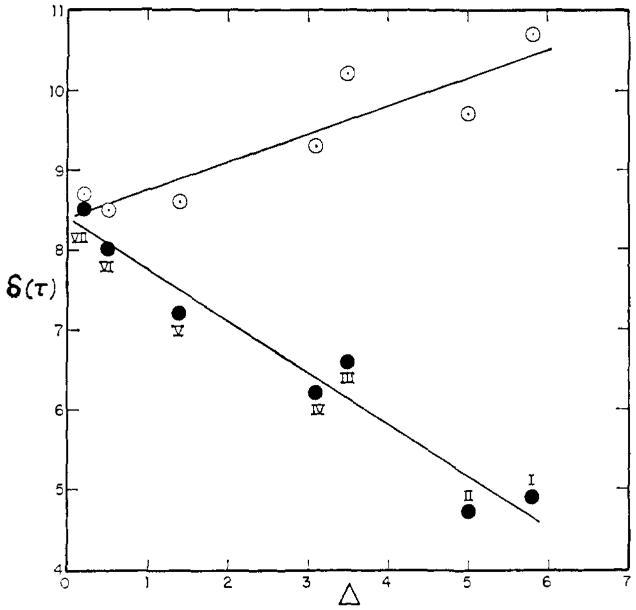
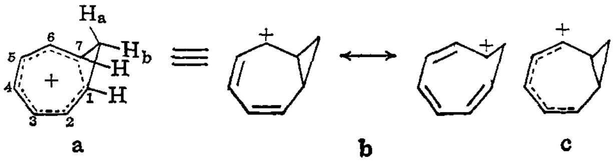


Figure 1. Plot of δ *vs.* Δ for the systems related to the homotropylium cation. The roman numerals refer to the compounds indicated in the text. The open circles refer to the proton H_a while the full circles refer to H_b. δ is given in τ units while Δ is in parts per million.



I

Deno on the other hand has stated that the properties of the cation are in accord with structure Ic and implies that nothing more than the normal stabilization of a cation by a cyclopropane ring is operative.[2] However, for the following three reasons there would seem to be no scientific basis for this statement. (a) The chemical shifts of the four protons in the "cyclopropyl" ring in homotropylium differ by 7.2 ppm whereas those in the several "normal" cyclopropylcarbonium ions studied by Deno and co-workers when they differ at all do so at most by 0.6 ppm.[3] (b) In homotropylium the coupling constant $J_{b,1}$ is 7.6 cps, whereas $J_{1,7}$ is close to 0.0 cps, at most 1.5 cps.[4] (c) We have been unable to isolate bicyclo[5.1.0]octane derivatives upon reaction of the homotropylium cation with such nucleophiles as $LiAlH_4$ or sodium acetate. There is therefore no evidence that the cation possesses a conventional cyclopropyl ring as is implied in Ic, and we consider that the nonclassical formulation remains the best description of the system.

A large part of the support for the homoaromatic formulation rests on the assumption that the origin of the large difference in chemical shift between protons H_a and H_b is the presence of a significant ring current in the system. We now wish to present evidence for the validity of this explanation.

Johnson and Bovey[5] have deduced that in a constant applied magnetic field the chemical shift (δ') of a proton due to the presence of a ring current in the molecule is related in the manner

$$\delta' \alpha I \times \mathrm{f}(xyz) \qquad (1)$$

where I is the magnitude of the ring current and $\mathrm{f}(xyz)$ is a function of the coordinates of the position of the proton relative to the ring.

If we now consider a series of related structures in which the geometry of the carbon skeleton remains fixed and in which two protons H_a and H_b experience different shielding due to the presence of a ring current in the system, then it follows from eq 1 that for differing values of the size of the ring current there should exist a linear relationship between δ, the chemical shift of one proton, and Δ, the difference in chemical shift between the two protons. In the present case of the $C_8H_9^+$ cation the further upfield is proton H_a, or downfield is proton H_b, then proportionately larger should be the separation between H_a and H_b. In Figure 1 we have plotted the position of H_a and H_b (δ) *vs.* the chemical shift separation of H_a and H_b (Δ) for homotropylium and six other systems which would be expected to have a closely related carbon skeleton. The systems plotted are homotropylium (I),[1] methylhomotropylium (II),[6] the $C_8H_9^+Mo(CO)_3$ cation (III),[7] 2-hydroxyhomotro-

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[1] J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

[2] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 157 (1964).

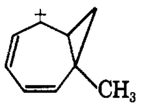
[3] N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Am. Chem. Soc.*, **87**, 4533 (1965).

[4] J. L. von Rosenberg, J. E. Mahler, J. C. Davis, and R. Pettit, unpublished observations. The coupling between the equivalent protons H_1 and H_7 was obtained from calculation of the theoretical spectrum.

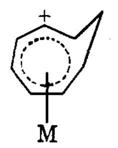
[5] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[6] C. E. Keller and R. Pettit, *J. Am. Chem. Soc.*, **88**, 604 (1966).

[7] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965).

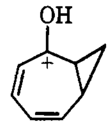


II

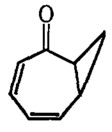


III, M = $Mo(CO)_3$

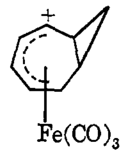
V, M = $Fe_2(CO)_6$



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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Received December 3, 1965

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.

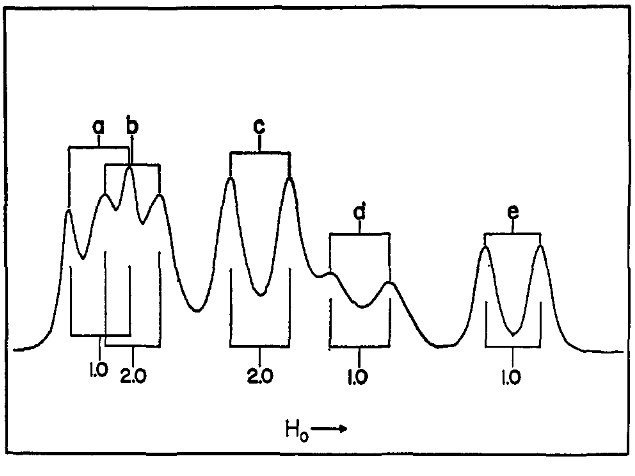

Figure 1. The ^{11}B nmr of $B_7C_2H_{11}(CH_3)_2$ at 19.3 Mc/sec. Chemical shifts, ppm (with reference to $BF_3O(C_2H_5)_2$), and coupling constants (cps) are (a) −7.44 (162), (b) −2.95 (147), (c) +14.9 (161), (d) +29.0 (156), and (e) +51.0 (148). Integrated areas are indicated beneath the peaks.

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 $^{11}B_7{}^{12}C_2{}^1H_{13}$.