9.86; S, 16.51. Found: B, 59.8; C, 12.01; H (total), 9.9; S, 15.5.

Structural studies on the two new solvated B_{11} derivatives have not been completed. We believe, however, that $NaB_{11}H_{14}$ can be best pictured as possessing an electron pair in a bridge position; an available proton would be expected to attack this basic site to yield the parent borane species, $B_{11}H_{15}$. This view is supported by many observations of acid character of bridge hydrogens and the fact that the $B_{11}H_{15}$ product exhibits a significant increase in bridge hydrogen absorption in its infrared spectra at 1918 cm^{-1} in comparison to the sodium derivative. The loss of 1 mole of hydrogen from $B_{11}H_{15}$ to form $B_{11}H_{13}$ is accompanied by a substantial decrease in the bridging absorption in the infrared region of 1918 cm^{-1}, suggesting that $B_{11}H_{13}$ is derived through loss of at least one bridge hydrogen. Both of these boranes exhibit a new band of medium intensity at 820 cm^{-1}, not found in the sodium derivative.

Acknowledgment. We appreciate the financial assistance by the Department of the Navy, Ships Systems Command, for supporting this research under Contract NObs 92478.

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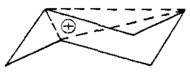
Received June 9, 1966

Monohomocyclooctatetraene Anion Radical. A Homoaromatic Nine-Electron System[1,2]

Sir:

A number of homoaromatic species with delocalized two- or six-electron systems have been reported and discussed. Examples are trishomocyclopropenyl[1] cations such as I[3a] and II,[3b] monohomotropylium ions[1] such as III,[4] and the 1,3-bishomocyclopentadienide ion[1,5] IV. We now report an example of a homoaromatic nine-electron system.



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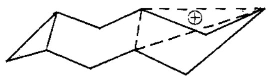

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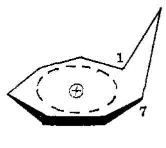

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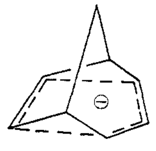

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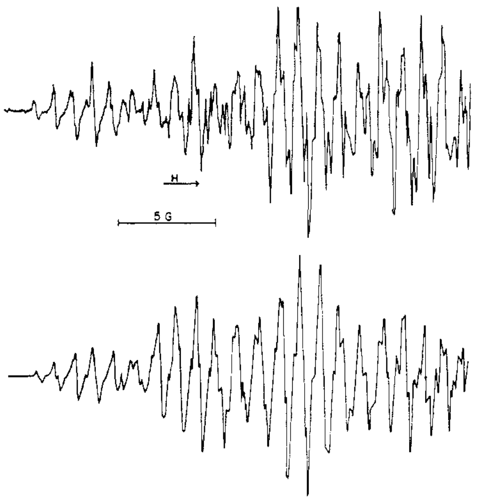

Figure 1. Esr spectra of VII: upper, observed; lower, calculated using 0.150-gauss line width and Lorentzian line shape; only half-spectra shown.

Instead of entering an antibonding olefinic molecular orbital, an additional electron supplied to tub cyclooctatetraene prefers to go into a nonbonding molecular orbital of a planar cyclooctatetraene.[6] The HMO delocalization energy of cyclooctatetraene anion radical V is so large (2.66β) that aromatization is induced by donation of an electron to cyclooctatetraene. Analogously, we have now observed that donation of an electron to the cyclooctatetraene monomethylene adduct[7] VI (monohomocyclooctatetraene) gives rise to monohomocyclooctatetraene anion radical VII.

Treatment of VI with a small amount of potassium in glyme at $-80°$ gives an anion radical whose esr spectrum has been observed at $-84°$. Compared to cyclooctatetraene anion radical V with a nine-line esr spectrum due to spin coupling of the odd electron with eight equivalent protons (a_H = 3.209 gauss), the monohomocyclooctatetraene anion radical displays a relatively complex esr spectrum showing eight major groups each split into seven lines (Figure 1). The observed spectrum is appropriate for a species with the symmetry of VII. The spectrum indicates a large hyperfine splitting constant (a_H) of 16.8 gauss assigned to one of the C_9 protons and an a_H value averaging 5.6 gauss for four protons. Further, the septet splitting averages *ca.* 1 gauss. The interpretation of the spectrum is further substantiated with the aid of the dideuterio analog of VII, namely VIID, prepared from VID containing two deuterium atoms on C_9. The latter was prepared by the use of CD_2Cl_2 in the reaction of cyclooctatetraene dianion with methylene chloride.[7b]

From the relative widths and other features of the spectra of the ordinary and dideuterio anion radicals VII and VIID, shown in Figures 1 and 2, it is clear that the sum of the hyperfine coupling constants of the two C_9 methylene protons is *ca.* 19 gauss, making a_H *ca.* 2 gauss for the second of the two C_9 protons. Setting

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(1) Reported at The Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6–8, 1966.

(2) (a) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of this fund. (b) Research was supported in part by the National Science Foundation.

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(7) (a) E. Vogel, *et al.*, *Ann.*, **653**, 55 (1962); *Tetrahedron Letters*, **No. 11**, 673 (1963); (b) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964).

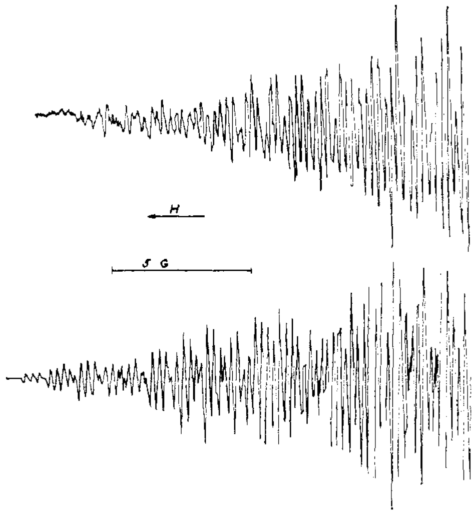
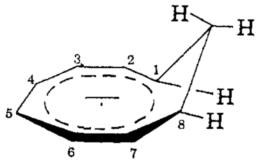


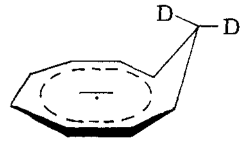
Figure 2. Esr spectra of VIID: upper, observed; lower, calculated using 0.050-gauss line width and Lorentzian line shape; only half-spectra shown.

a_D equal to $2a_H/13$, spectra of both the protonated and deuterated species can be fairly well simulated as regards line positions and intensities with the sets of a_H values listed in Table I. The comparison between actual and computer-simulated[8] spectra is shown in Figures 1 and 2.

Table I. Hyperfine Splitting Constants[a,b] for Computer-Simulated Esr Spectra



VII

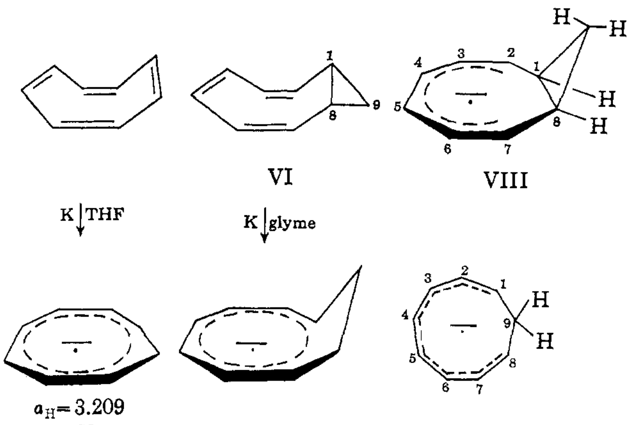


VIID

No.	H	a_H	a_H	a_D
1	9	16.80	....	2.58
1	9	2.00	....	0.25
2	1,8	6.70	6.70	
2	3,6	4.50	4.55	
2	4,5	1.10	1.10	
2	2,7	0.90	0.90	

[a] From the sensitivity of the computed spectra to changes in parameters, the error in the a_H values is estimated to be ±0.20 gauss for VII and ±0.03 gauss for VIID. [b] No splitting was observed due to the nuclear moment of the cation.

As regards the structure of the anion radical species from monohomocyclooctatetraene, it is clear that the classical structure VIII with a fully formed cyclopropane ring must be rejected. Such a structure would not accommodate the large a_H value (16.80 gauss) observed for one of the C_9 protons. The C_9 protons are γ to the nearest radical center in VIII, and any observed a_H values for γ protons are always very small.[9] The planar classical structure IX, with negligible 1,8 interaction, must also be rejected since the two C_9 protons are equivalent in this structure and would have equal a_H values. On the other hand, the nonclassical monohomocyclooctatetraene anion radical structure VII accommodates all the features of the esr spectra.



The specific assignment of a_H values shown in Table I for the protons on C_1 to C_8 is based on calculated[10] spin densities at C_1 to C_8 of the nonclassical anion radical VII. With either Hückel or the more sophisticated McLachlan[11] spin densities (ρ) one predicts the sequence of a_H values as $a_{1,8} > a_{3,6} > a_{4,5} > a_{2,7}$. Calculations[10] to simulate these observed a_H values with the aid of the McConnell relation,[12,13] $a_H = Q\rho$, support the nonclassical structure VII with appreciable 1,8 overlap and resonance integrals. The situation regarding the 1,8 interaction in VII is qualitatively analogous to that for the 1,7 interaction in monohomotropylium ion[4b] III.

After this communication was submitted we learned of the Katz and Talcott[14] work with VII generated electrolytically in liquid ammonia containing Me_4NI. There is substantial agreement regarding the structure and conformation of VII, the sequence of a_H values for the C_{1-8} protons ($a_{1,8} \simeq a_{3,6} > a_{4,5} > a_{2,7}$ *vs.* $a_{1,8} > a_{3,6} > a_{4,5} > a_{2,7}$), and Q (27.1 *vs.* 26.4). Some differences do exist in the actual assigned a_H values, the Katz and Talcott numbers not fitting our spectrum of VII. Further, these a_H values give too small an over-all spread in the spectrum of VIID. The extent to which solvent, ion pairing, and temperature effects contribute to these differences is still not clear.

Acknowledgment. We are grateful to Professor Daniel Kivelson and William Plachy, who made the esr facilities available to us and provided considerable assistance and helpful discussion.

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(8) Computing assistance was obtained from the Health Sciences Computing Facility, U.C.L.A., sponsored by National Institutes of Health Grant FR-3.

(9) See, for example, the situation in ethylcyclooctatetraene anion radical: A. Carrington and P. F. Todd, *Mol. Phys.*, 7, 533 (1963-64).

(10) R. Rieke, to be published separately.

(11) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

(12) H. M. McConnell, *J. Chem. Phys.*, 24, 632, 764 (1956).

(13) Taking Q equal to the sum of the a_H values on C_1 to C_8, the value is 26.4 gauss. This may be compared with the observed[6] value of 25.7 gauss for the cyclooctatetraene anion radical V. The g value observed for VII, 2.0026 ± 0.0006, is essentially identical with the value, 2.0025 ± 0.0001, reported[6] for the cyclooctatetraene anion radical V.

(14) T. J. Katz and C. Talcott, *J. Am. Chem. Soc.*, 88, 4732 (1966).

(15) National Institutes of Health Postdoctoral Fellow, 1965-1966.

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Received July 25, 1966