Monohomocyclooctatetraene Dianion. A Homoaromatic Ten-Electron Species[1,2]

Sir:

Donation of one or two electrons to tub cyclooctatetraene (I) causes aromatization with formation of the planar cyclooctatetraene anion radical[3] (II) and cyclooctatetraene dianion[4] (III), respectively. As reported in the accompanying communication,[5] donation of an electron to cyclooctatetraene monomethylene adduct[6] (IV, monohomocyclooctatetraene) gives the homoaromatic anion radical V. We here report on the monohomocyclooctatetraene dianion species (VI) from donation of two electrons to IV.

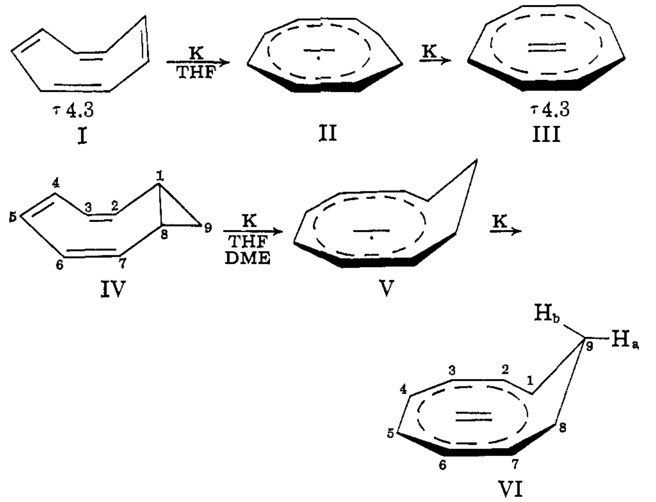
Allowing a dilute solution of IV in THF or 1,2-dimethoxyethane (DME) to stand at $-80°$ over a mirror of excess potassium gives rise to a solution of a potassium salt. Only dilute solutions of this material may be obtained since precipitation of the salt occurs if the concentration is too high (*ca.* 0.1 *M* in THF). If care is taken to obtain relatively complete reduction of the anion radical, satisfactory nmr spectra may be obtained for the salt species at $-60°$. Because of the relatively low concentration, it was necessary to record the spectrum with the aid of the Varian time-averaging computer (CAT). The nmr spectrum of the salt solution, compared with that of the original hydrocarbon IV, is appropriate for the dianion species VI.

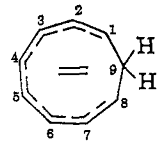
As shown in Table I for both THF and DME as solvents, the nmr spectrum[6] of the parent hydrocarbon IV contains a six vinyl proton multiplet centered at τ 4.1, a three-proton complex multiplet centered at τ 8.8 for the two tertiary cyclopropane $C_{1,8}$ protons plus one of the cyclopropane C_9 methylene protons, and a one-proton multiplet at τ 10.0 for the other C_9 proton. For the dianion species in THF-d_8, the nmr spectrum contains a multiplet for six protons in the τ 4.0–4.9 region, centerd at τ ~4.5, much more complex than the vinyl proton signal in IV, and multiplets for two protons at τ 6.0 and one proton at τ 10.0. The τ 6.0 signal overlaps one of the solvent signals (τ 6.40), so that the relative area of this signal is obtained by a difficult dissection and is therefore only approximate. In DME-d_{10} the six-proton multiplet is centered at τ ~4.8, and the two-proton signal at τ 6.1 is better separated from the nearby solvent peak at τ 6.58. Also visible is a one proton signal centered at τ 8.0 which was hidden in THF by the THF solvent peak at τ 8.25. Finally, the remaining one-proton signal occurs at τ 10.0.

Table I. Summary of Chemical Shifts

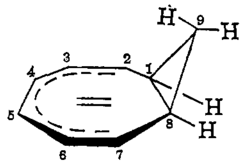
Solvent	Hydrocarbon IV			Dianion VI		
	H	Area	τ^a	H	Area	τ^a
THF-d_8	2-7	6.0	4.1	2-7	6.0	*Ca.* 4.5
	1,8,9	3.0	8.8	1,8	2.3	6.0
	9	1.00	10.0	9b	1.00	10.0
DME-d_{10}	2-7	6.0	4.1	2-7	6.1	*Ca.* 4.8
	1,8,9	3.0	8.8	1,8	2.2	6.1
				9a	1.00	8.0
	9	1.00	10.0	9b	1.0	10.0

[a] Based on the signals for the protonated solvents, τ 6.40 and 8.25 for THF, and τ 6.58 and 6.75 for DME, relative to TMS as internal standard.

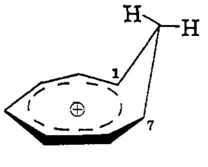




VII



VIII



IX

For the 9,9-dideuterio hydrocarbon[5] IV, the $C_{1,8}$ two-proton signal in THF appears as a broad singlet at τ 8.63, the width at half-height being 5 cps. The nmr spectrum of the dianion from the dideuterated IV contains the six-proton signal centered at τ ~4.5 (THF) and ~4.8 (DME), the two-proton signal centered at τ 6.0 (THF, 2.1 protons) or 6.1 (DME, 2.0 protons), and no other signal in the τ 6.8–10.5 range.

As regards assignments for the different signals in the dianion, the signal at τ 4.5 is assigned to the six C_{2-7} protons, somewhat upfield from the vinyl proton signal in the parent hydrocarbon. The signal at τ 6.0 is assigned to the two $C_{1,8}$ protons, considerably downfield from the position of the tertiary cyclopropane protons in IV. The signal at τ 8.0 is assigned to the "outside" C_9 proton, this being deshielded as compared to the same proton in IV, while the signal at τ 10.0 is assigned to the "inside" C_9 proton.

As in the case of the anion radical[5] V, the available evidence strongly supports a homoaromatic structure (VI) for the product from donation of two electrons to the monohomocyclooctatetraene IV. A classical planar structure VII with negligible 1,8 interaction is ruled out by the nonequivalence of the two C_9 protons as well as by the relatively low chemical shift of the C_{2-7} protons.

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[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.

[3] T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960); (b) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 2360 (1963).

[4] (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) C. A. Coulson, *Tetrahedron*, **12**, 193 (1961).

[5] R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4729 (1966).

[6] (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).

A classical structure VIII with a fully formed cyclopropane ring may also be rejected since the 1,8 protons and also the 2–7 protons are too deshielded. Further, it is not easy to account for the chemical shift between the "inside" and "outside" C_9 protons on the basis of VIII. On the other hand, all the features of the nmr spectrum are well accounted for by a homoaromatic structure VI with considerable 1,8 interaction and an appreciable ring current. On this basis, the intermediate value of the chemical shift of the $C_{1,8}$ protons is easily understandable. Further, the ring current in VI helps explain the chemical shift between the "inside" and "outside" C_9 protons, and also the low τ value for the C_{2-7} "vinyl" protons. From the known relationship[7] between the charge which a carbon atom bears and the chemical shift of a proton attached to it, one might expect the change from parent hydrocarbon IV to a dianion, with a double negative charge distributed over eight carbon atoms, to cause a shielding of the C_{2-7} protons by *ca.* 2.5 ppm from this cause alone. The observed net effect is only *ca.* 0.4–0.7 ppm (THF or DME); since charge density and ring current are very probably the two most important influences on the C_{2-7} proton chemical shifts, deshielding due to the aromatic ring current must be quite substantial.

Although ion pairing of the dianion with potassium ions must be very important[3,8] in the solvents employed, no information is yet available on the positioning of the potassium ions relative to the dianion or on the distribution between ion pairs involving one potassium ion and ion triplets involving two potassium ions. The slightly higher τ value for the C_{2-7} protons in DME relative to THF may be an indication of more intimate or more complete affiliation of the dianion with potassium ions in THF than in DME.

It is interesting to compare the C_{2-7} protons in VI with those in cyclooctatetraene dianion[4a] (III) as regards nmr. In THF, using the solvent τ values in Table I, the proton chemical shift[4a] in III has the value τ 4.3, not far from the τ 4.5 value for the homoaromatic analog VI. In the cyclooctatetraene dianion case, the blend of charge and ring-current effects is such as to leave the proton chemical shift in the dianion III identical with the value in the parent hydrocarbon[4a] I.

As regards 1,8-orbital overlap and ring-current effects, there is considerable qualitative analogy between the situations in the dianion VI and in monohomotropylium ion[1,9] (IX) (1,7 overlap). Crude HMO calculations on the monohomocyclooctatetraene system show the fourth molecular orbital (MO) to be 1,8 antibonding, while the fifth MO is 1,8 bonding. As $\beta_{1,8}$ is increased for the dianion, the over-all 1,8 bond order increases. For example, it is 0.42 for $\beta_{1,8} = 0.50\beta_0$ and 0.52 for $\beta_{1,8} = 0.75\beta_0$.

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[8] *E.g.*, G. L. Hoijtink, *et al.*, *Rec. Trav. Chim.*, 74, 277 (1955); **75**, 487 (1956).

[9] (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965); (b) S. Winstein, C. G Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966); (c) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, 84, 2842 (1962).

[10] National Institutes of Health Postdoctoral Fellow, 1965–1966.

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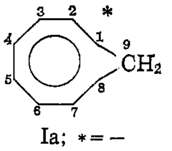
The Cyclononatetraene Anion Radical

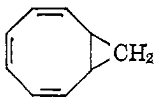
Sir:

Physical properties associated with electron conjugation in aromatic rings appear not to vanish if conjugation is interrupted by one methylene group.[1,2] To examine whether the cyclononatetraene (homocyclooctatetraene) anion radical (Ia) and dianion (Ib) are preparable and exhibit properties resembling those of the cyclooctatetraene anion radical[3] and dianion,[4] their synthesis was attempted.

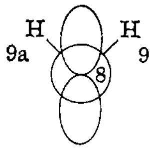
The synthesis of the anion radical was attempted for still another reason. The symmetry of the molecular frame of cyclic radicals or radical ions $(CH)_{n-1}CH_2{}^{m-}$ requires in the molecular orbital approximation that the wave function of the unpaired electron have a node through the plane of the CH_2 group if $n + m = 4k$ (k integral), but not if $n + m = 4k + 2$. If hyperconjugation is a major contributor to the methylene hyperfine interaction, then when $n + m = 4k$, the interaction should be small and when $n + m = 4k + 2$, large.[5,6] In cyclohexadienyl radical it is large (47.71 gauss)[7] and in cycloheptatriene anion radical, small (2.16 gauss),[6] but no homologous series of such radicals is known.



Ia; * = –
b; * = =



II



III

To prepare Ia, bicyclo[6.1.0]nonatriene[8] (II) was reduced. For although the bicyclic hydrocarbon does not spontaneously isomerize to cyclononatetraene, its reduction might, to allow more extensive delocalization of the additional electrons, be accompanied by a valence tautomerism.

While this research was in progress, Winstein[9] reported that reduction of II in cold glyme by potassium gives the anion radical Ia, with hyperfine splitting constants shown in Table I, and that further reaction gives the dianion Ib. Our results are reported below.

Bicyclo[6.1.0]nonatriene (II) was electrolyzed in liquid ammonia saturated with tetramethylammonium iodide in a cell mounted in the microwave cavity of an esr spectrometer.[6,10] As the amperage was increased, the spectrum of a radical, R_1, was observed which with time or amperage increased in intensity and was superimposed by the signal, E, of electrons in liquid am-

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[1] (a) C. E. Keller and R. Pettit, *J. Am. Chem. Soc.*, **88**, 604, 606 (1966); J. L. von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962); (b) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

[2] T. J. Katz and E. H. Gold, *ibid.*, **86**, 1600 (1964).

[3] (a) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960); (b) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 2360 (1963).

[4] T. J. Katz, *ibid.*, **82**, 3784 (1960).

[5] D. H. Whiffen, *Mol. Phys.*, **6**, 223 (1963).

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[8] (a) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964); (b) E. Vogel, *Angew. Chem.*, **74**, 829 (1962); (c) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963).

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