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).

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

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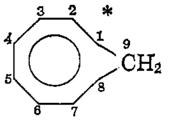
The Cyclononatetraene Anion Radical

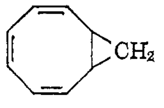
Sir:

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.

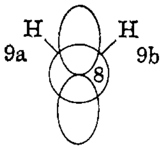
The synthesis of the anion radical was attempted for still another reason. The symmetry of the molecular frame of cyclic radicals or radical ions $(CH)_{n-1}CH_2{}^{m-}$ requires in the molecular orbital approximation that the wave function of the unpaired electron have a node through the plane of the 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-

[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).

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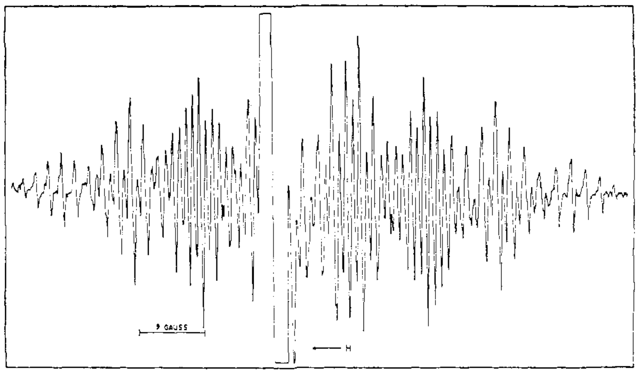

Figure 1. Esr spectrum of R_1, with that of E superimposed.

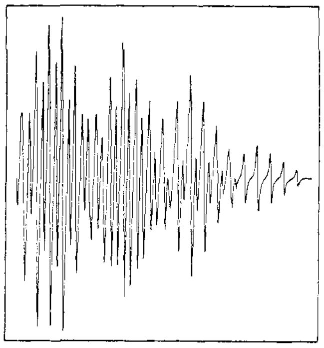

Figure 2. Calculated esr spectrum of Ia. Lines are assumed Lorentzian with a half-width of 0.15 gauss.

monia.[10,11] With further increase in current the spectrum of R_1 decreased in intensity, and that of a new radical, R_2 (superimposed by E), became visible, increased in intensity, and finally vanished, leaving only E. When the current was turned off E disappeared in 5 min and subsequently the signal of R_2 reappeared.

Table I. Esr Spectral Parameters of Ia

Position assignment[a]	No. of protons	Spin density, $\rho_i{}^b$	Splitting constants a_i gauss This work	Ref 9
1,8	2	+ 0.194	5.24 ± 0.1[c]	6.7
2,7	2	+ 0.038[a]	1.02 ± 0.05	0.9
3,6	2	+ 0.194	5.24 ± 0.1[c]	4.5
4,5	2	+ 0.075[a]	2.04 ± 0.05	1.1
9a	1		4.80 ± 0.1	2.0
9b	1		12.00 ± 0.1	16.8

[a] Based on HMO and McLachlan calculations. [b] $\rho_i = a_i/\sum_1^8 a_i$. [c] The constants used to derive Figure 2 are 5.19 and 5.29 gauss. The intensities suggest that the two sets differ by an unresolved 0.1 gauss.

The spectrum of R_1 (Figure 1) is believed to be that of the cyclononatetraene anion radical (Ia). A set of coupling constants that account for the spectrum is recorded in Table I, and the spectrum calculated shown in Figure 2.

The radical R_2 was identified as the methylcyclooctatetraene anion radical by the similarity of its esr spectrum and spectral parameters, $a_1 = 1.42 \pm 0.05$ gauss (4 H), $a_2 = 5.03 \pm 0.05$ (3 H), $a_3 = 5.51 \pm 0.05$ (3 H), with those reported: 1.6 gauss (4 H), 4.8 (3H), 5.1 (3H).[12] For R_1, $Q = \sum_1^8 a_i = 27.1$ gauss, similar to the 26.26 found for $C_7H_8\cdot^-$[6]. The spin densities, ρ_i ($i = 1, \ldots, 8$), evaluated[13] as a_i/Q, are given in the table. The dissimilarity in the splittings a_i ($i = 1, \ldots, 8$) does not provide a strong basis for believing that the electronic structure of Ia resembles that of the cyclooctatetraene anion radical.

The spectrum of R_1 implies that reduction is accompanied by valence tautomerism, for otherwise the olefin proton couplings would have been similar to those in cycloheptatriene (7.64, 0.59, 4.90 gauss),[6] and coupling to the distant C_9 protons a magnitude smaller.[7,14,15] But all the carbons do not lie in one plane because the two C_9 protons are not equivalent. If the hyperfine splittings of these two have as their origin a hyperconjugative interaction of the C–H bonds with adjacent 2p orbitals, then the dihedral angles subtended by the plane containing H_9, C_9, and C_8 and that containing C_9 and the axis of the 2p orbital on C_8 might be estimated as $\cos^{-1} [a_9/(40)(4)\rho_8]^{1/2}$,[5,7,16] or 52 and 67° for H_{9a} ahd H_{9b}. Since the dihedral angle between the planes H_{9a}–C_9–C_8 and H_{9b}–C_9–C_8 must be approximately 120° (for sp^3 hybridization), the two C–H bonds at C_9 presumably flank the adjacent 2p orbitals as in III.

The formation of methylcyclooctatetraene anion radical may have its origin in the reduction of Ia to Ib, isomerization to methylcyclooctatetraene dianion, and loss of an electron to the solvent to yield the corresponding anion radial.

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New Photochromic Compounds with *p*-Nitrobenzyl Structures

Sir:

Four new photochromic compounds are described in Table I. They each contain an aromatic nitro group only in the position *para* to an alkyl substituent. Previously, only nitrobenzyl derivatives containing *o*-