This work was supported in part by Grant AM 00608 of the National Institutes of Health and Grant GB-2762 of the National Science Foundation.

(14) National Institutes of Health Postdoctoral Fellow, 1965–1966.

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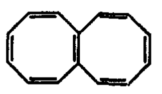
Received June 24, 1966

Octalene Derivatives

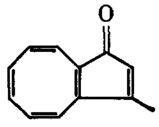
Sir:

One of the most interesting problems remaining in the field of novel aromatic systems is whether there is a class of aromatic compounds in which the magic number of $4n + 2$ electrons is attained by fusion of two antiaromatic rings, with $4n$ electrons each.[1] A possible example of such a system is octalene (I), a molecule with 14 π electrons. The system has substantial resonance energy by a Hückel calculation (4.1β), albeit much less with a more sophisticated treatment,[2] and it fits Craig's rule[3] for aromaticity as well. Of course, in this case one must be concerned not only with the usual cavils about simple MO predictions but also with the question of whether the putative aromaticity in a planar octalene would be sufficient to induce flattening of two cyclooctatetraene rings, with consequent strain.[4] The only evidence to date on such matters is our ambiguous finding[1] that a cyclooctatetraenocyclopentadienone (II) is quite unstable, but that it is also very basic. The instability suggests nonaromaticity, while the high basicity suggests that the bicyclic ten-π-electron cation may be aromatic. We have now prepared some derivatives and relatives of octalene (I) and wish to report their properties.

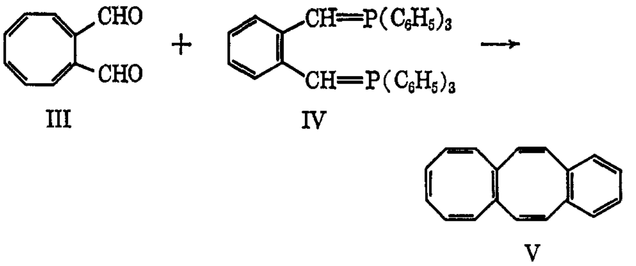
1,8-Diformylcyclooctatetraene (III), mp 124–125°, can be prepared in 10–40% yield from 1,8-bis(hydroxymethyl)cyclooctatetraene[5] by oxidation with MnO_2 or, better, NiO_2; it is separated from the concomitant furan and γ-lactone by alumina chromatography. Reaction of III with the bisphosphorane IV affords a 1–2% yield of benzo[*c*]octalene (V), which is isolated by chromatography and reversible extraction into 70% aqueous silver nitrate. The mass and nmr spectra are unchanged after vacuum distillation or preparative vpc; the mass spectrum shows a parent peak at m/e 230 ($C_{18}H_{14}$) and the nmr has a peak at δ 7.06, a sharp peak at δ 6.34, and a multiplet at δ 5.70 in a ratio of approximately 4:4:6. For comparison, *sym*-dibenzocyclooctatetraene, prepared as above but from *o*-phthalaldehyde, has the aromatic protons at δ 6.95 and the vinyl protons at δ 6.61; it has similar behavior on thin layer chromatography, and on vapor phase chromatography under the same conditions it shows a retention time of 100 sec compared with 130 sec for V. Hydrogenation of V in benzene for 2 hr (1 atm) with 10% Pd–C gives a substance with parent m/e 240 (residual benzene ring and tetrasubstituted double bond), while a further 2 hr with 10% Pd–C in ethanol gives m/e 242 (residual benzene ring).



I

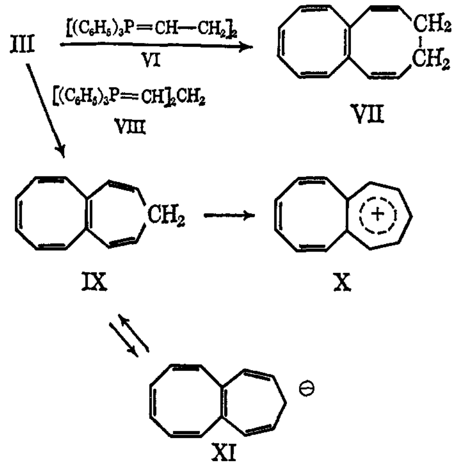


II



The ultraviolet spectrum of V shows only intense and absorption, with a shoulder at 245 mμ (ϵ ~17,000), and it resembles that[6] of benzocyclooctatetraene (which has a nonplanar eight-membered ring). By contrast, we calculate (Pariser–Parr–Pople) λ_{max} 328 mμ with a reasonable intensity for planar aromatic benzooctalene (the longest wavelength absorption is predicted to be 1.6 μ).[7] Furthermore, the protons in the terminal cyclooctatetraene ring are unshifted (δ 5.70) from normal cyclooctatetraene (δ 5.69). Benzooctalene is not particularly stable, being destroyed on chromatography on activity II alumina, exposure to air for a length of time, or (in part) vapor phase chromatography at 160–210°. From all this we conclude that the eight-membered rings have ordinary tub conformations, and the benzooctalene is not aromatic.

Related evidence comes from the reaction of III with VI, producing 5–10% yield of dihydrooctalene (VII). After vpc purification VII has m/e 182, with expected fragments at m/e 167 and 154; hydrogenation at 25° for 2 hr in benzene over 10% Pd–C gives a small peak at m/e 194 (perhydrooctalene) and the main peak at m/e 192 (residual hindered olefin). In the nmr VII has four protons in a broad (room temperature) peak at δ 2.4 and ten vinyl protons in a complex pattern near



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(1) R. Breslow, W. Vitale, and K. Wendel, *Tetrahedron Letters*, No. 6, 365 (1965).

(2) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 87, 685 (1965).

(3) D. P. Craig, *J. Chem. Soc.*, 3175 (1951). Octalene is specifically discussed at the end of this paper.

(4) N. L. Allinger (private communication) has calculated that the 50 kcal/mole lower E_π of planar octalene is insufficient to overcome a greater than 100 kcal/mole predicted strain advantage of the nonplanar structure. Although the validity of such calculations is not fully established, the prediction is in accord with our findings.

(5) J. Meili, Ph.D. Thesis, Massachusetts Institute of Technology, 1952.

(6) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, 619, 10 (1958).

(7) A similar spectrum has been calculated for octalene by N. Allinger (private communication).

δ 5.7; the ultraviolet spectrum has λ_{max} 240 mμ (ϵ 12,400). Attempts to dehydrogenate VII to octalene itself, either with N-bromosuccinimide and base or with dichlorodicyanoquinone, have so far led only to nonvolatile tarry materials, suggesting that octalene does not have striking stability.

Perhaps the most relevant evidence concerns cyclooctatetraenocycloheptatriene (IX), produced in 15% yield by reaction of III with VIII. After vpc purification, IX shows *m/e* 168 and a large fragment at *m/e* 167; hydrogenation in benzene over Pd-C gives material with *m/e* at 180 and 178. The nmr spectrum of IX is as expected, with the CH_2 at δ 2.27 and a complex ten-proton vinyl pattern. With trityl fluoroborate, IX is converted to the tropylium salt X, mp 99–100° (*Anal.* Found: C, 61.17; H, 4.69; nmr: five protons at δ 9.10, four protons at δ 6.16, two protons at δ 4.77). Since the anion XI derived from IX has a total of 14 π electrons, aromaticity of XI should be reflected in an increased kinetic acidity of IX compared with cycloheptatriene. However, with potassium *t*-butoxide in deuterated DMSO–*t*-butyl alcohol[8] IX exchanges 20–30-fold more slowly than does cycloheptatriene. Apparently fusion of tropylium anion to cyclooctatetraene does not appreciably stabilize it. We conclude that if there is any aromaticity associated with such fused ring systems it is not sufficient to induce planarity in our compounds, and it thus remains undetected.[9]

[8] This is the inverse of the system used by W. von E. Doering and P. P. Gaspar, *J. Am. Chem. Soc.*, **85**, 3043 (1963), to exchange protons into deuteriocycloheptatriene.

[9] This work was supported in part by grants from the National Science Foundation and the National Institutes of Health.

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Paramagnetic Relaxation of Trapped Electrons in Irradiated Alkaline Ices

Sir:

Electrons produced by γ radiation are trapped in alkaline ices at 77°K.[1,2] At hydroxide concentrations greater than 0.5 *M* the trapped electron is characterized by an epr singlet at $g = 2.001$[2,3] and a blue absorption band[1] with a maximum at 5850 A. Proof that the epr signal and the absorption band are associated with a trapped electron is demonstrated by experiments with electron scavengers.[3,4] Scavenging experiments show that a mobile electron, e_m^-, is formed in irradiated ice; the electron moves through the lattice until it finds a suitable site at which to be trapped or a species with which to react.[4] The nature of the trapping site has been discussed in terms of an F-center model in which the electron is trapped in a hydroxide anion vacancy.[4-6] We report here paramagnetic relaxation experiments which support this model. The anion vacancy should be formed in a radiation produced "spur"; the present results do indicate that the trapping site is located in a "spur." In addition, it is found that the trapped electron relaxes *via* cross relaxation with O^- which is also formed in irradiated alkaline ices.

Frozen solutions of 10.0 *M* NaOH and 7.3 *M* NaOD were irradiated at 77°K with cobalt-60. Slow passage progressive power saturation measurements at a modulation frequency of 40 cps were made over a 40-db power range on a Varian-4500 epr spectrometer. Measurements were made at 77°K unless otherwise noted. The electron line shape is nearly Gaussian and the saturation curves were interpreted as due to inhomogeneous broadening. The curves do not fit the ideal inhomogeneous case discussed by Portis,[7] but can be accounted for by the intermediate case discussed by Castner.[8] The inhomogeneous line is the envelope of individual spin packets where each spin packet is composed of those spins which "see" the same local magnetic field.[7,8] $(T_1T_2)^{1/2}$ was determined from the saturation curves; T_1 denotes the spin–lattice relaxation time and T_2 denotes the spin–spin relaxation time.

$(T_1T_2)^{1/2}$ was found to be about 2×10^{-5} sec. The most important results are: (a) $(T_1T_2)^{1/2}$ is independent of radiation dose from 0.3 to at least 2 Mrads (megarads) in both H_2O and D_2O matrices, (b) $(T_1T_2)^{1/2}$ is independent of temperature from 77 to 150°K, and (c) $(T_1T_2)^{1/2}$ is about 50% larger in D_2O as compared to H_2O matrices; this is on the borderline of being equal within our experimental error.

Observation a indicates no spin–spin interaction between trapped electrons at doses up to 2 Mrads. Thus the spin-packet width is due to spin–spin interactions within a radiation produced "spur" or it is limited by spin–lattice interactions. The lack of a temperature dependence eliminates the latter alternative. At higher doses at which the electron radiation yield has reached saturation (10^{19} electrons/g for both H_2O and D_2O), $(T_1T_2)^{1/2}$ does decrease as expected owing to *inter* "spur" interactions. We conclude that the electron trap is located within a "spur." This is to be expected if the trap is a hydroxide anion vacancy produced by the radiation.

Observations b and c yield information about the spin-lattice relaxation mechanism of the trapped electron. At temperatures of the order of and above the Debye temperature ($\theta_D = 192$°K for H_2O),[9] a two-phonon (Raman) spin-lattice relaxation mechanism is expected to dominate.[10] Since the trapped electron resonance line is broadened by hyperfine interaction with surrounding nuclear spins,[5] the logical candidate for the dominant spin-lattice relaxation mechanism is modulation of the hyperfine interaction by the lattice vibrations.[11] This and all other two-phonon processes in H_2O or D_2O matrices above 100°K predict $(T_1T_2)^{-1/2} \propto T^2$ where T is in °K. Instead a T^0 dependence is observed. Furthermore, hyperfine modulation by the phonons would require $(T_1T_2)^{1/2}$ to be several times

[1] D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch.*, **17a**, 445 (1962); **18a**, 199 (1963).

[2] B. G. Ershov, A. K. Pikaev, P. Ya. Glazunov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **149**, 363 (1963).

[3] P. N. Moorthy and J. J. Weiss, *Phil. Mag.*, **10**, 659 (1964).

[4] L. Kevan, *Progr. Solid-State Chem.*, **2**, 304 (1965).

[5] L. Kevan, *J. Am. Chem. Soc.*, **87**, 1481 (1965).

[6] M. J. Blandamer, L. Shields, and M. C. R. Symons, *Nature*, **199**, 902 (1963).

[7] A. M. Portis, *Phys. Rev.*, **91**, 1071 (1953).

[8] T. C. Castner, *ibid.*, **115**, 1506 (1959); a detailed analysis of the saturation curve shape will be published shortly.

[9] W. F. Giaugue and J. W. Stout, *J. Am. Chem. Soc.*, **58**, 1144 (1936).

[10] G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 121–133; eq 6–51 should have $1/T_1 \propto T^2$ instead of T^0.

[11] This mechanism is observed for F centers in KCl; see D. W. Feldman, R. W. Warren, and J. G. Castle, *Phys. Rev.*, **135**, A470 (1964).