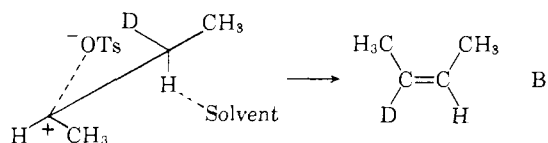the antiperiplanar position, essentially as in the concerted E2 elimination. Thus, the difference between E2 and E1 in basic solvents may only be a matter of degree

of polarization of the bond between the leaving group and the α-carbon.

Although it is not possible completely to rule out gegenion free carbonium ions in each of the solvents, it is clear that they do not play a major role in these solvolytic eliminations. Streitwieser and Walsh[7] have demonstrated that the solvolytic displacement of tosylate by acetate group in the 2-octyl system occurs with 100% inversion in glacial acetic acid. *All of these results are best accommodated by rejection of the idea that in these solvolytic processes the fate of the carbonium ion is independent of its origin.*

Acknowledgment.—This work was supported by the U. S. Army Research Office (Durham).

(7) A. Streitwieser, Jr., and T. D. Walsh, *Tetrahedron Letters*, 27 (1963).

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA
P. S. SKELL
W. L. HALL

The Cyclononatetraenyl Anion

Sir:

The cyclononatetraenyl anion I should have a closed shell configuration of 10 π electrons and should be highly resonance stabilized.[1] That it should be aromatic is, however, questionable for two reasons: (1) The energy required to distort the angles of its bonds might be excessively large[2] and (2) the nine-membered ring might valence tautomerize[3] spontaneously to form a single bond at the expense of a double. Nevertheless, the cyclononatetraenyl anion does appear to be aromatic. Its synthesis is the subject of this report.
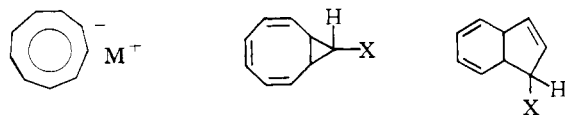
Ia, M⁺ = Li⁺
b, M⁺ = K⁺

IIa, X = Cl
b, X = OCH₃
c, X = H

IIIa, X = Cl
b, X = OCH₃
c, X = H

Cold chloroform reacts with dipotassium cyclooctatetraenide[4] in tetrahydrofuran (THF) to yield, after aqueous work-up, 9-chlorobicyclo[6.1.0]nonatriene (IIa), b.p. 28–32° (0.2 mm.), in 52% yield; λ_{max}^{EtOH} 248 mμ (log ϵ 3.57). *Anal.* Calcd. for C₉H₉Cl: C, 70.82; H, 5.94; Cl, 23.23. Found: C, 71.06; H, 6.06; Cl, 23.42. Similarly, dichloromethyl methyl ether reacts to yield 9-methoxybicyclo[6.1.0]nonatriene (IIb) in 26% yield; b.p. 54–56 (1.1 mm.); λ_{max}^{EtOH} 255 mμ (log ϵ 3.69). *Anal.* Calcd. for C₁₀H₁₂O: C, 81.09; H, 8.11. Found: C, 80.89; H, 8.18. Methylene chloride yields bicyclo[6.1.0]nonatriene[5] (IIc) in 45% yield.

IIa was identified by its ultraviolet spectrum and by its n.m.r. spectrum. The latter exhibited a multiplet

(1) Its Hückel molecular orbital delocalization energy is 3.5 β.

(2) The compressional barrier is, however, overcome by its next lower homolog, the cyclooctatetraenyl dianion [T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962), and references therein].

(3) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

(4) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).

(5) E. Vogel, *Angew. Chem.*, **73**, 548 (1961), and private communication.

at 4.1 (rel. int. 6) and a coupled (J = 4 c.p.s.) triplet at 7.54 (rel. int. 1) and doublet at 8.14 τ (rel. int. 2). IIb exhibited a similar n.m.r. spectrum: a multiplet at 4.2 (rel. int. 6), a singlet at 6.70 (rel. int. 3), and a coupled (J = 4 c.p.s.) triplet at 7.40 (rel. int. 1) and doublet at 8.40 τ (rel. int. 2). Only the *anti* isomers appear to be found, in striking contrast to the formation of mixtures of comparable amounts of *syn* and *anti* isomers, the former predominating, when chloro-[6] and methoxycarbene[7] are added to other olefins.[8]

Heating IIa to 70° yields 1-chloro-8,9-dihydroindene (IIIa; *Anal.* Found: C, 71.03; H, 6.01; Cl, 23.24), identified by its ultraviolet spectrum [$\lambda\lambda_{max}^{EtOH}$ 262 (3.52), 270 mμ (log ϵ 3.44)] and its n.m.r. spectrum (4.2, 5.27, 6.6 τ, rel. int. 6:1:2, all multiplets). Lithium aluminum hydride reduces IIIa to 8,9-dihydroindene[9] (IIIc) [$\lambda\lambda_{max}^{EtOH}$ 262 (3.57), 271 mμ (log ϵ 3.51), maleic anhydride adduct, m.p. 141.5°], which was identical with that obtained by heating IIc.[5]

IIa reacts with lithium in THF to give lithium cyclononatetraenide (Ia). On quenching with H₂O, IIIc is formed, and on quenching with D₂O, it is formed (24% yield) with the incorporation of 1 atom of deuterium.[10] Similarly, IIb reacts with potassium to give potassium cyclononatetraenide (IIb), which, on quenching with D₂O, yields monodeuterated IIIc.[11]

The n.m.r. spectra of potassium and of lithium cyclononatetraenide in completely deuterated THF consist of only one single very sharp peak at 2.96 and 3.15 τ, respectively.[12] These spectra show that the cyclononatetraenyl anion is aromatic.[13] If the cyclononatetraenyl anion and the cyclooctatetraenyl dianion are compared, their ring currents[14] should be similar,[15] but the protons in the former should be less shielded that in the latter because the negative charge density associated with each carbon atom is $1/9$ rather than $2/8$. That is, the cyclononatetraenyl anion's proton n.m.r. should[16,17] appear ($1/4$ − $1/9$) × 10 = 1.4 p.p.m. to lower fields than the resonance (4.3 τ) of the cyclooctatetraenyl dianion.[4] The agreement with the observed chemical shift is excellent.

The ultraviolet spectra of Ia [λ_{max}^{THF} 252 mμ (5.0), 318 mμ (3.9), 325 mμ (log ϵ 3.9)] and Ib are similar.[18]

It is remarkable that the cyclononatetraenyl anion has the all-*cis* stereochemistry.

(6) (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960); (b) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962).

(7) V. Schöllkopf, A. Lerch, and W. Pitteroff, *Tetrahedron Letters*, 241 (1962); *cf.* V. Schöllkopf and G. J. Lehman, *ibid.*, 165 (1962); V. Schöllkopf and H. Kuppers, *ibid.*, 105 (1963).

(8) The stereochemical assignment is based on the assumption that the small size of the spin–spin coupling constant implies the *anti* stereochemistry (after Closs, ref. 6b). The presence of a trace of the other isomer in samples of IIb is indicated by a small second methoxyl peak 0.05 p.p.m. above the main peak.

(9) K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

(10) Found: 9.40; 9.60; 9.38; atom % excess D. (Falling drop analyses by Josef Nemeth, Urbana, Ill.)

(11) 9.46 atom % excess D.

(12) Measured using the trace protonated solvent peaks as internal standards.

(13) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 180 ff.

(15) The point dipole approximation of Pople[14] leads to the prediction that the protons in cyclononatetraenide should be more shielded than those in cyclooctatetraenide by 0.02 p.p.m.

(16) (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (b) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(17) If the proportionality constant is 10.7[4b] the shift should be 1.5 p.p.m.

(18) The spectra are in agreement with that reported for tetraethylammonium cyclononatetraenide, synthesized independently by E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2853 (1963). We thank these authors for communicating this result to us prior to publication.

Acknowledgments.—We gratefully acknowledge the support of the National Science Foundation (NSF G-15561, GP-748), the Socony Mobil Oil Co., and the Alfred P. Sloan Foundation.

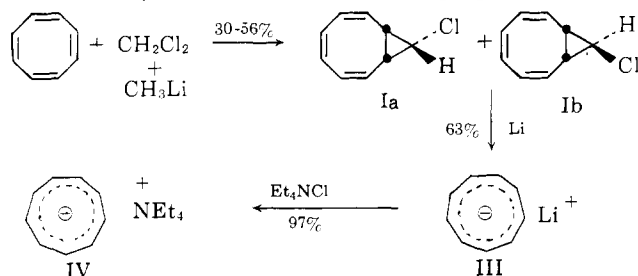## Cyclononatetraenide. An Aromatic 10-π-Electron System

Sir:

One area in which both theoretical and synthetic chemists share a common interest is that of non-benzenoid aromatic compounds. The guiding principle has been the well known Hückel rule[1] which states that carbomonocyclic compounds having a conjugated system of $(4n + 2)$ π electrons should exhibit aromatic character. For the case where $n = 2$, there was previously only a single example where this rule had been experimentally substantiated, *i.e.*, the cyclooctatetraene dianion.[2,3] We now wish to report the synthesis of cyclononatetraenide,[9,10] a 10-π carbocycle having D_{9h} symmetry, in two steps from cyclooctatetraene.

The reaction of cyclooctatetraene with methylene chloride and methyllithium under the general conditions described by Closs and Closs[11] for preparing chloro-

cyclopropanes led to a 3:1 mixture of *syn* and *anti* 9-chlorobicyclo[6.1.0]nona-2,4,6-triene (Ia and Ib). The structural assignment of Ia and Ib in the chlorocyclopropane fraction follows from: (a) H^1 n.m.r. [CDCl₃ solution, δ in p.p.m. *vs.* (CH₃)₄Si]: multiplet centered at 6.0 (olefinic H), triplet at 3.45 ($J = 7.6$ c.p.s., *syn*-CHCl), triplet at 2.52 ($J = 4.3$ c.p.s., *anti*-CHCl) and an unresolved multiplet centered at 1.83 (allylic cyclopropane H); (b) $\lambda_{max}^{isooctane}$ 248 mμ (ε 3080); (c) the presence of tertiary cyclopropyl hydrogens[12]: $\lambda_{max}^{CCl_4}$ 1.67 μ (ε 0.79); and (d) elemental

(1) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(2) (a) A. R. Ubbelohde, *Chem. Ind.* (London), 153 (1956); (b) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (c) H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 231 (1961).

(3) The reported⁴ synthesis of cyclodecapentaene has been shown to be in error.⁵ Attempts to prepare compounds having the 1,6-diazacyclodecapentaene ring system were unsuccessful,⁶ and recent studies⁷ of 2,3,6,7-dibenzo-1-methyl-1,4,5-triazacyclohepta-2,6-diene (and the 1-oxa and 1-thia analogs) have shown that these compounds exhibit no aromatic character attributable to the 10-π-electron system. Recently, the synthesis of 2,3-benzo-1,4-dioxacyclooocta-2,5,7-triene has been reported⁸ and it has been concluded that the molecule is not planar.

(4) W. Reppe, O. Schichting, and H. Meister, *Ann.*, **560**, 93 (1948).

(5) (a) L. E. Craig and C. E. Larrabee, *J. Am. Chem. Soc.*, **73**, 1191 (1951); (b) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1195 (1951), and references therein; (c) D. S. Withey, *J. Chem. Soc.*, 1930 (1952).

(6) A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 873 (1957).

(7) N. L. Allinger and G. A. Youngdale, *J. Am. Chem. Soc.*, **84**, 1020 (1962).

(8) W. Schroth, K. Kränke, and J. Reinhardt, *Angew. Chem.*, **75**, 303 (1963).

(9) Cyclononatetraenide has also been prepared independently by T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963).

(10) A theoretical study of the structure and electronic spectrum of cyclononatetraenide is being carried out in collaboration with Dr. H. E. Simmons and will be reported shortly.

(11) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

analysis. *Anal.* Calcd. for C₉H₉Cl: C, 70.82; H, 5.94; mol. wt., 152.6. Found: C, 70.76; H, 6.14; mol. wt., 152 (mass spec.)].

Upon treating the isomeric mixture Ia and Ib in tetrahydrofuran with a lithium dispersion for 2 hr. at room temperature, the multiplet at 6.0 p.p.m. in the n.m.r. disappeared and a sharp line (width at half height no greater than 0.8 c.p.s.) was observed at 6.72 p.p.m. The lithium cyclononatetraenide (III) thus formed in 63% yield (n.m.r.) was stable in an inert atmosphere. The C¹³ n.m.r. of the lithium salt III in THF consisted of a doublet at 19.0 p.p.m. ($J = 137$ c.p.s.) to highfield from benzene.[13]

Metathesis of the lithium salt III with tetraethylammonium chloride produces tetraethylammonium cyclononatetraenide (IV, 97%) as a stable (inert atmosphere) white solid which was purified by recrystallization from anhydrous acetonitrile, dec. pt. 318° (*Anal.* Calcd. for C₁₇H₂₉N: C, 82.52; H, 11.81; N, 5.66. Found: C, 82.30; H, 11.55; N, 5.75); H¹ n.m.r. (d⁶ dimethyl sulfoxide): 6.82 (aromatic H, width at half height no greater than 0.6 c.p.s.), quartet at 3.03 (CH₂, $J = 7$ c.p.s.), triplet of triplets at 1.05 (CH₃, $J = 7$ c.p.s. and *ca.* 1.5 c.p.s.). The ultraviolet absorption spectrum is very simple, as expected for a molecule having a ninefold rotational axis: $\lambda_{max}^{CH_3CN}$ 250 mμ (ε >61,700) and doublet at 317 and 322 mμ (ε >6,170).[14]

Polarographic analysis of the tetraethylammonium salt IV in acetonitrile containing LiClO₄ (0.1 M) as the supporting electrolyte with a rotating platinum electrode shows what appears to be an irreversible one-electron oxidation at $E_{0.5} = -0.03$ v. (*vs.* s.c.e.). As expected from this result, the tetraethylammonium salt IV can be oxidized by either tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethan. Attempts to detect the resulting radical[15] in 1,2-dimethoxyethane solution *via* e.p.r. at ambient temperature or at $-80°$ have been unsuccessful although the spectrum of TCNE⁻ is observed.

Lithium cyclononatetraenide (III) does not undergo detectable electron exchange over a period of 45 days with cyclooctatetraene to give cyclooctatetraene dianion. However, the salt III reacts with cyclopentadiene to give lithium cyclopentadienide.

On the basis of the H¹ and C¹³ n.m.r. data and the strong absorption in the ultraviolet, it is concluded that cyclononatetraenide has aromatic character. Further studies are in progress.

(12) J. Meinwald, A. Lewis, and P. G. Gassman, *ibid.*, **84**, 977 (1962), and references therein.

(13) We are grateful to Dr. H. Foster for the C¹³ N.m.r. studies. The C¹³ chemical shift is in excellent agreement with the simple linear correlation between chemical shift and π-electron density as found recently for the aromatic series C₇H₇⁻, C₆H₆, C₅H₆⁻ and C₈H₈²⁻ [H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, **No. 14**, 468 (1961)]. Calculations using the least-squares method for their published data together with that found for C₈H₈⁻ gives the equation δC¹³ = 167.8ρ − 169.9. Although the value reported for C₆H₆⁻ appears to be anomalous, it has been confirmed by Dr. Foster.

As previously noted [T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963)] the prediction of the H¹ chemical shift from the π-electron density is less satisfying for larger ring aromatic compounds due to the difficulty of applying ring size corrections. The H¹ chemical shift for LiC₈H₉ from internal benzene was found to increase upon dilution (27.3 c.p.s. at *ca.* 3 mole % to 30.5 c.p.s. at *ca.* 0.4 mole %) as expected for decreasing ion association.

(14) Some difficulty was experienced in determining the exact value of the extinction coefficients since Beer's law was not followed upon carrying out the necessary dilutions, presumably because of reaction with trace impurities in the solvent.

(15) We are indebted to Dr. M. T. Jones for this experiment.

CONTRIBUTION NO. 909　　　　　E. A. LALANCETTE
CENTRAL RESEARCH DEPARTMENT　　　　　R. E. BENSON
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE
RECEIVED AUGUST 2, 1963