normal vinyl one and the latter is typical of bis-allylic protons in related compounds, *e.g.*, 1,4-cycloöctadiene. At lower temperatures, *e.g.*, −10°, the methylene proton signal is split into two at 6.32 and 7.82 τ, respectively, with relative areas of 6.0:3.0:3.0 for the 4.68, 6.32 and 7.82 τ peaks.

Models suggest relatively rigid "crown" and quite flexible "saddle" conformations, IC and IS, respectively, for triene I. However, the "saddle" conformation suffers from an abnormally close approach of a methylenic hydrogen atom to an opposed olefinic group (*ca.* 1.2 Å. from Dreiding scale models), and it can be expected to be considerably less stable than the "crown." The proton magnetic resonance spectrum of triene I is in good accord with the crown conformation. At low temperatures, where crown → crown interconversion is slow, two separate resonances are seen for the H_a and H_b methylene protons. However, at higher temperatures crown → crown transformation is rapid, and a single resonance line is observed at the intermediate τ value. From the difference in chemical shift values for the two types of methylene protons[8] the estimated rate constant for the crown → crown interconversion is 200 sec.$^{-1}$ at the temperature at which the two lines appear to coalesce (*ca.* 30°). This leads to a value of *ca.* 11 kcal./mole for the free energy of activation for this process.

A simple LCAO–MO treatment of IC with $a = (\beta_{24}/\beta_{12})$ leads to molecular orbital energy levels $[(E - \alpha)/\beta]$ of $\pm(a + 1)$, $\pm\sqrt{a^2 - a + 1}$, and $\pm\sqrt{a^2 - a + 1}$, as compared to ±2, ±1 and ±1 for benzene. Contrary to the situation in bicycloheptadiene and barrelene,[9] where identically zero ground state delocalization energies (DE) are derived, a non-zero DE value is predicated for the ground state of triene I. In its ultraviolet spectrum the nonatriene shows evidence of considerable absorption shifted to relatively long wave lengths. Thus, in heptane solution it displays a band at 198 mμ (ϵ = 11,600) with an apparent shoulder at 200 mμ (ϵ = 11,200) and a prominent shoulder at 212 mμ (ϵ = 5,000). Attempts at analytic separation of the 198 mμ absorption from that at longer wave lengths indicate an absorption band at *ca.* 216 mμ with ϵ above 10^3.

---

(8) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1957).

(9) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

(10) U. S. Rubber Company Foundation Postgraduate Fellow in Physical and Engineering Science for 1961–1962.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA
PHILLIP RADLICK[10]
S. WINSTEIN

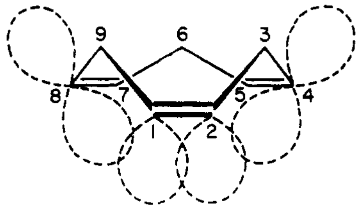
RECEIVED NOVEMBER 26, 1962

---

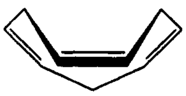
sym-cis,cis,cis-1,4,7-CYCLONONATRIENE,[1] AN UNUSUAL CYCLIC SIX PI ELECTRON SYSTEM

Sir:

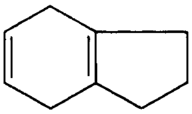
Our interest in *sym-cis,cis,cis*-1,4,7-cyclononatriene (I) was prompted by the possibility that the molecule would exhibit unusual properties and perhaps be aromatic. This cyclic system is unique in that electron delocalization may occur within six pi orbitals where only *half* of the lobes can overlap. The theoretical requirement[2] of like algebraic sign for all overlapping lobes is satisfied by I, unlike bicyclo[2,2,2]-2,5,7-octatriene, first cited by Hine[3] and synthesized by Zimmerman and Paufler.[4]



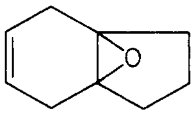
I



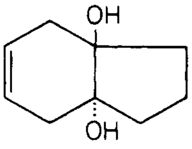
Ia



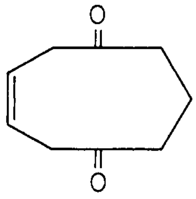
II



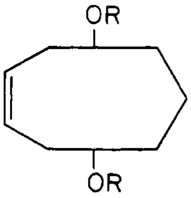
III



IV



V



VI, R = H

VII, R = COPh

We report herein the synthesis of this compound using indane as the starting material.

Indane was hydrogenated to 4,7-dihydroindane (II) with lithium metal in liquid ammonia.[5] Treatment of II with perbenzoic acid gave the epoxide (III), which was hydrolyzed to the crystalline 8,9-dihydroxy-4,7,8,9-tetrahydroindane (IV), m.p. 87–89° in 65–75% yield (*Anal.*[6] Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.90; H, 9.29). Cleavage of IV with lead tetraacetate in the presence of trichloroacetic acid[7] afforded the highly reactive cyclononene-4,8-dione (V), which was immediately reduced with sodium borohydride to cyclononene-4,8-diol (VI) in 70–80% yield (presumably a mixture of *cis* and *trans* diols). Part (approx. 60%) of the oily mixture was crystallized to give the solid isomer (assumed *cis*-diol), m.p. 82–83° (*Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.34; H, 10.27). Benzoylation of VI yielded (90%) 4,8-dibenzoyloxycyclononene (VII), an oil (*Anal.* Calcd. for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.95; H, 6.90). Pyrolysis (free flame) of VII gave benzoic acid (65–80%) and a mixture of neutral compounds which was fractionally distilled (25 mm.). The fraction collected at 75–90° was treated with excess 50% (w./w.) aqueous silver nitrate, which selectively gave a silver nitrate complex salt, m.p. (dec.) 243° (*Anal.* Calcd. for

---

(1) Applying the nomenclature introduced by S. Winstein, *J. Am. Chem. Soc.*, **83**, 3244 (1961), the molecule is trishomobenzene.

(2) C. A. Coulson, "Valence", Oxford University Press, London, 1952, Sections 4.7, 8.7 and 9.1.

(3) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, *J. Am. Chem. Soc.*, **77**, 594 (1955).

(4) H. E. Zimmerman and R. M. Paufler, *ibid.*, **82**, 1514 (1960).

(5) A. P. Krapcho, Ph.D. Thesis, Harvard University, 1957.

(6) The microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill., and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(7) C. A. Grob and P. W. Shiess, *Helv. Chim. Acta*, **43**, 1546 (1960).

$C_9H_{12}(AgNO_3)_3$: C, 17.16; H, 1.92; Ag, 51.38. Found: C, 17.46; H, 2.06; Ag, 51.40). I was regenerated by treating the silver nitrate adduct with excess ammonia. Sublimation at room temperature (25 mm.) gave white needles (having a high vapor pressure), m.p. 50–51° cor. (*Anal.* Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.92; H, 10.12). The found molecular weight[8] was 120 (mass spectrometric determination). The conversion of VII to I by a given pyrolysis was 9–14% of the neutral pyrolysate as determined by gas–liquid chromatography (5% Carbowax 1500 on Fluoropak 80, 4 m. × 6 mm., 100° column).[9]

Infrared (vapor phase): strong absorptions at 3.30, 3.36, 3.40, 11.40, 13.85 μ; medium absorptions at 3.47, 5.94, 6.07, 6.72, 6.75, 6.80, 11.36 μ; ultraviolet: λ_{max} = 198 mμ (9,300), $\lambda_{shoulder}$ = 210 mμ (4,600) in cyclohexane at 7.4 × 10^{-5} mole/l.

Exhaustive hydrogenation of I gave cyclononane whose g.l.c. retention time and infrared spectrum were identical with those of an authentic sample.

Together these data show that the isolated hydrocarbon is a cyclononatriene. The possible isomers (other than I and *cis,cis,trans*-1,3,5-cyclononatriene[10]) that were considered are *cis,cis,cis*-1,3,5-, *cis,cis,cis*-1,3,6- and *cis,cis,trans*-1,4,7-cyclononatrienes. Any isomer containing a *trans* olefin is less plausible because the infrared absorptions (7.6–7.7, 10.4–10.5 μ) attendant with dialkyl *trans* olefins[11] are absent in the spectrum of the new hydrocarbon.

The n.m.r. spectrum[12] (Fig. 1) of the isolated compound provides evidence to assign its structure. The symmetrical nonet (4.57 τ) is consistent with structure I wherein all the olefinic hydrogens are equivalent. The ratio of the two peak areas (4.57, 7.1 τ) are 1:1 (within 2%). The other cyclononatrienes are expected to show more complicated olefinic absorption patterns for the chemically, and presumably magnetically, non-equivalent olefinic hydrogens on adjacent double bonds. They should also exhibit more than one kind of methylene hydrogen due to chemical shift differences for doubly allylic, allylic and aliphatic hydrogens (note no absorption beyond a value of 8.2 τ).

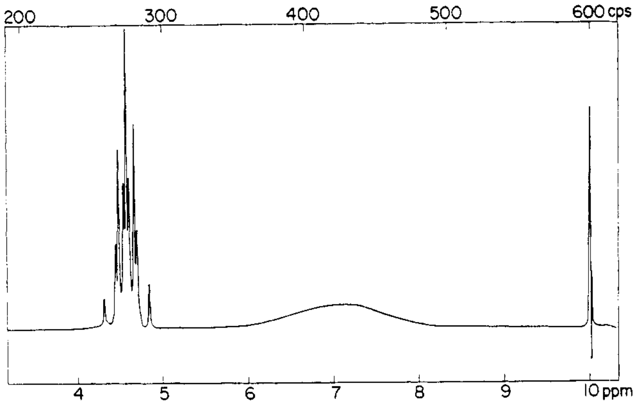


Fig. 1.—N.m.r. spectrum at 37° with tetramethylsilane as the internal reference standard (approx. 10% $CDCl_3$ solution).

cis,cis,cis-1,4,7-Cyclononatriene can assume different stereochemical forms, one being symmetric, I, and another less symmetric arrangement, Ia, which can exist in any of six equivalent conformations. The unusual absorption of the methylene hydrogens (Fig. 1, 7.17 τ) is the result of a dynamic equilibration. The appearance of this peak is extremely temperature dependent. Heating the sample causes the methylene absorption to narrow and sharpen up. Cooling causes the broad absorption to separate into two peaks of equal area which sharpen up with further cooling. Thus there is interconversion between two equivalent symmetrical conformers, I. N.m.r. spectra have been obtained at various temperatures ranging from −40 to 83.5°. These results are reported in a second paper.[13]

A completely rigid structure proof for I has been obtained by proton–proton spin decoupling experiments. These data along with a detailed analysis of the spectra will be reported.

Whether I shows aromatic character or not will be deferred until studies are completed on the "frozen" symmetrical conformer.[14] However, simple LCAO MO calculations have been carried out for I using angle parameters of 120° (sp^2 bonds) and 109°28″(sp^3 bonds). The result thus obtained is a lower limit for a predicted absolute value for any delocalized energy the molecule might possess since these parameters ignore steric repulsion of the three inner methylene hydrogens. This repulsion is undoubtedly present and would cause the homoallylic overlap to be greater than that calculated. The calculations give a value of 25.0% as much 2,4-overlap as that of 1,2-overlap and predicts negligible (0.02%) delocalization energy with the six pi electrons occupying three delocalized orbitals (degenerate pair at -0.985β and one at -1.03β).

The author gratefully acknowledges the able technical assistance of Mr. D. J. Martin throughout this research and helpful discussions with Drs. A. A. Bothner-By and H. Conroy.

---

[8] Performed by G. A. Muccini, Mellon Institute, Radiation Research Laboratories, Pittsburgh, Pa.

[9] Performed by C. J. Lindemann, Mellon Institute.

[10] This cyclononatriene has been prepared by K. Alder and H. A. Dortmann, *Ber.*, **87**, 1905 (1954), and its properties differ markedly from those of I.

[11] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p. 45.

[12] The n.m.r. spectrum was taken with a Varian Associates A-60 spectrometer.

[13] K. G. Untch and R. J. Kurland, *J. Am. Chem. Soc.*, **85**, 346 (1963).

[14] However, the infrared spectrum of V and a ferric chloride test showed no enol form present.

MELLON INSTITUTE K. G. UNTCH
PITTSBURGH 13, PENNSYLVANIA

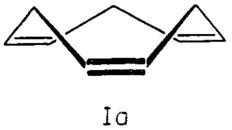
RECEIVED NOVEMBER 19, 1962

THE CONFORMATIONAL EQUILIBRATION OF *cis,cis,cis*-1,4,7-CYCLONONATRIENE; A DETERMINATION OF ACTIVATION ENERGY AND ENTROPY BY N.M.R. II.

Sir:

The synthesis and properties of *cis,cis,cis*-1,4,7-cyclononatriene (I) have been reported.[1] We wish to present the results of a detailed investigation of the temperature dependence of the n.m.r. spectra of I. This behavior is displayed (Fig. 1) by the n.m.r. spectra taken at three representative temperatures.

As pointed out previously[1] this temperature dependence reveals that the two equivalent forms of the conformation (Ia), hereafter called the "crown," are interconverting. After the interconversion of one crown to its mirror image, the inner and outer methylene hydrogens are exchanged. I may also attain a less symmetrical conformation (Ib), hereafter called the "saddle."



Ia

Ib

---

[1] K. G. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963).