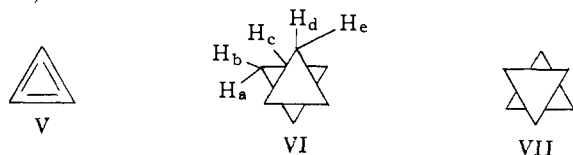


in VI. Thus, in its infrared spectrum, the hydrocarbon has five strong bands in the C-H stretching region, consistent with symmetric and asymmetric stretches of both kinds of methylene groups and a *tertiary* cyclopropane C-H stretch. The observed bands occur at 2840 (symmetric "ordinary" methylene stretch), 2900, 2942, 2990 and 3058  $\text{cm}^{-1}$  (asymmetric cyclopropane methylene stretch). Also, the hydrocarbon displays two methylene scissoring bands at 1465 and 1450  $\text{cm}^{-1}$ , respectively. Other pertinent strong bands occur at 1020, 1010 and 848  $\text{cm}^{-1}$ .



The proton magnetic resonance spectrum (Varian A-60) of the  $\text{C}_{12}\text{H}_{18}$  hydrocarbon in carbon tetrachloride solution with hexamethyldisiloxane as an internal standard shows three bands: (i) a doublet centered at 7.84  $\tau$  ( $J = 13$  c.p.s.) with very slight additional splitting of each member of the doublet; relative area 2.99; (ii) a broad complex multiplet centered at 9.32  $\tau$ ; relative area 12.1; (iii) an apparent pentuplet (with further additional fine structure) centered at 10.41  $\tau$ ; relative area 2.93. The signal from 3 protons at  $\tau = 10.41$  is indicative of three cyclopropane rings, since cyclopropane rings fused to other rings commonly<sup>6</sup> show one methylene proton ( $\text{H}_a$ ) at  $\tau$  above 10 and the other three at  $\tau$  ca. 9.3. On this basis, 9 of the 12 protons responsible for the broad band at  $\tau = 9.32$  are the 3 other cyclopropane methylene protons ( $\text{H}_b$ ) and the 6 *tertiary*-cyclopropane protons ( $\text{H}_c$ ). The remaining 3 of the 12 protons must be three of the "ordinary" methylene hydrogens ( $\text{H}_e$ ), while the three remaining methylene protons ( $\text{H}_d$ ) must be responsible for the signal at  $\tau = 7.84$ . Such discrimination between allycyclic methylene protons adjacent to a cyclopropane ring is usual,<sup>6</sup> one proton being shielded and the other deshielded.

The observed pattern of bands in the proton magnetic resonance spectrum of the  $\text{C}_{12}\text{H}_{18}$  hydrocarbon points to a *cis*-arrangement of the three cyclopropane rings in VI. With this arrangement, the three "ordinary" methylene groups each have one proton *cis* and one proton *trans* to two cyclopropane rings, consistent with the observed 3:3 split of these hydrogens. In the *trans*-isomer of VI, only one methylene group bears such a pair of protons, while the other two have four equivalent protons.<sup>7</sup>

The present evidence is that, even in the favorable isomer of VI, delocalization and compression energies do not blend in a way conducive to a homoaromatic structure (IV) under ordinary conditions. Isotopic labeling experiments are currently in progress to study the possible valency tautomerism  $\text{VI} \rightleftharpoons \text{VII}$ . Also, work is continuing on the syntheses of the more likely homoaromatic ionic species II and III.

(6) P. Radlick, R. Boikess and E. Friedrich, unpublished work.

(7) An illustrative example is provided by the *bis*-dideuteriomethylene adducts of 1,4-cyclohexadiene.<sup>6</sup> The *trans*-isomer shows methylene and *tertiary*-cyclopropane bands in a 4:4 ratio, while the *cis*-isomer shows methylene and combined methylene-*tertiary*-cyclopropane bands in a 2:6 ratio.

(8) National Science Foundation Post-Doctoral Fellow, 1962-1963.

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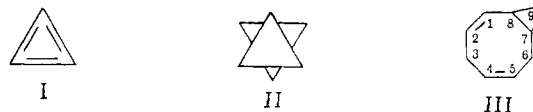
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*cis-cis-cis*-1,4,7-CYCLONONATRIENE, A  
HOMOCONJUGATED SIX  $\pi$ -ELECTRON SYSTEM<sup>1</sup>

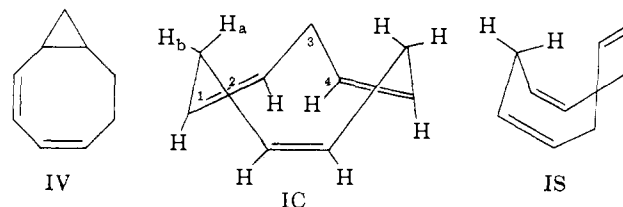
Sir:

Hydrocarbon I, *cis-cis-cis*-1,4,7-cyclononatriene, is of considerable interest in this Laboratory, mainly as a

stepping stone to "hexahomobenzene" (II),<sup>2</sup> but also as a conceivably homoconjugated six  $\pi$ -electron system.<sup>2</sup> We have come upon it during treatment of cyclooctatrienes with the Simmons-Smith<sup>3</sup> reagent in the course of other syntheses and are prompted<sup>4</sup> to report its preparation and its properties.



Hydrocarbon I, m.p., 49.5-50.0°, was first obtained in 30% yield, based on reacted starting material, when the product from treatment of 1,3,6-cyclooctatriene<sup>5</sup> with a 1.5 mole proportion of methylene iodide and excess zinc-copper couple<sup>3</sup> was subjected to vapor phase chromatography using a stainless steel preheater at 240°. It may also be prepared by passing either the crude reaction product or a mono-adduct fraction from the Simmons-Smith reaction through a stainless steel tube packed with stainless steel shavings at 240° in an atmosphere of helium, and then separating compound I by preparative vapor phase chromatography on a 4-methyl-4-nitropimelonitrile column at 100°. While it is not clear how hydrocarbon I arises, it is quite easy to visualize its formation from a mono-adduct (III) by C<sub>7</sub>-C<sub>8</sub> bond rupture and 9 → 8 hydrogen shift. However, compound I appears to be formed also from IV, since similar yields of I are obtained when 1,3,5-cyclooctatriene<sup>5</sup> is substituted for the 1,3,6-isomer in the above preparations.



Hydrocarbon I displays the correct C,H-analysis and mass spectral molecular weight<sup>6</sup> (120) for the formula  $\text{C}_9\text{H}_{12}$ . That the substance is indeed *cis-cis-cis*-1,4,7-cyclononatriene is clear from its infrared, proton magnetic resonance and ultraviolet spectra. In the infrared, I displays bands at 3018 (s), 2965 (m), 2932 (m), 2916 (m) and 2864 (mw)  $\text{cm}^{-1}$  in the C-H stretching region, peaks at 1675 (vw) and 1641 ( $\text{cm}^{-1}$ ) in the C=C stretching region, a *cis*-olefinic C-H out-of-plane deformation band at 717 (s)  $\text{cm}^{-1}$  and no bands corresponding to the C-H out-of-plane and in-plane deformation bands characteristic of *trans*-olefins. In carbon tetrachloride solution with the Varian A-60 instrument, the proton magnetic resonance spectrum of I at higher temperatures, e.g., 65°, shows two proton signals centered at 4.66 and 7.10  $\tau$ , respectively,<sup>7</sup> with relative peak areas of 6.0:6.0. The former value is a relatively

(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) (a) S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

(3) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(4) We have learned through Dr. Aksel Bothner-By that this same hydrocarbon has been prepared through a very different route by Dr. Kar Untch of the Mellon Institute [K. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963)]. We understand also that Dr. W. Roth of the University of Cologne in Germany has come upon this hydrocarbon during the study of "thermal reorganization" reactions [W. Roth, private communication], but we were not informed which hydrocarbons were involved in these re-organizations.

(5) A. C. Cope, *et al.*, *J. Am. Chem. Soc.*, **72**, 2515 (1950); **74**, 486 (1952).

(6) We are indebted to Dr. Richard Teeter of the California Research Corporation for the mass spectrum of this substance.

(7) With the Varian HR-40 instrument the vinyl signal appears as nonet and the methylene as at least an octet.

normal vinyl one and the latter is typical of bis-allylic protons in related compounds, *e.g.*, 1,4-cyclooctadiene. At lower temperatures, *e.g.*,  $-10^{\circ}$ , the methylene proton signal is split into two at 6.32 and 7.82  $\tau$ , respectively, with relative areas of 6.0:3.0:3.0 for the 4.68, 6.32 and 7.82  $\tau$  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  $\rightarrow$  crown interconversion is slow, two separate resonances are seen for the H<sub>a</sub> and H<sub>b</sub> methylene protons. However, at higher temperatures crown  $\rightarrow$  crown transformation is rapid, and a single resonance line is observed at the intermediate  $\tau$  value. From the difference in chemical shift values for the two types of methylene protons<sup>8</sup> the estimated rate constant for the crown  $\rightarrow$  crown interconversion is 200 sec.<sup>-1</sup> at the temperature at which the two lines appear to coalesce (*ca.* 30 $^{\circ}$ ). 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  $\pm 2$ ,  $\pm 1$  and  $\pm 1$  for benzene. Contrary to the situation in bicycloheptadiene and barrelene,<sup>9</sup> 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 m $\mu$  ( $\epsilon = 11,600$ ) with an apparent shoulder at 200 m $\mu$  ( $\epsilon = 11,200$ ) and a prominent shoulder at 212 m $\mu$  ( $\epsilon = 5,000$ ). Attempts at analytic separation of the 198 m $\mu$  absorption from that at longer wave lengths indicate an absorption band at *ca.* 216 m $\mu$  with  $\epsilon$  above 10<sup>3</sup>.

(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.

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### *sym-cis,cis,cis*-1,4,7-CYCLONONATRIENE,<sup>1</sup> AN UNUSUAL CYCLIC SIX PI ELECTRON SYSTEM

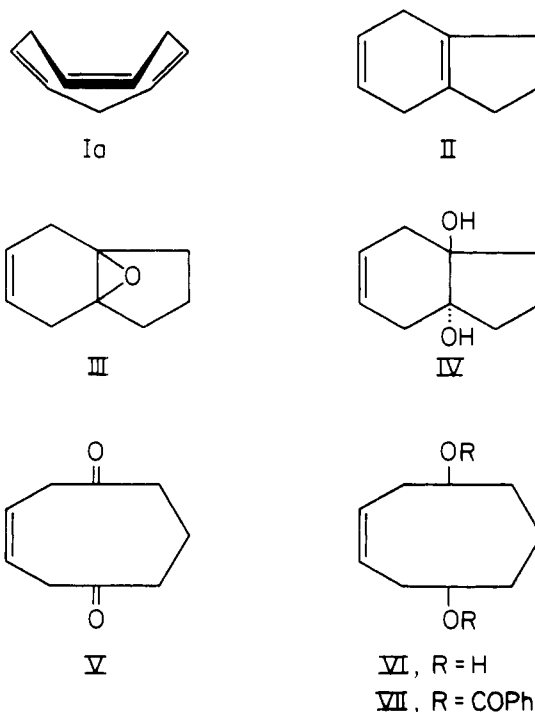
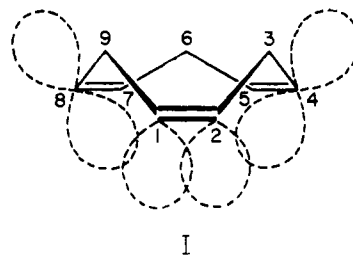
Sir:

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<sup>2</sup> 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<sup>3</sup> and synthesized by Zimmerman and Paufler.<sup>4</sup>

(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).



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.<sup>5</sup> 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 $^{\circ}$  in 65-75% yield (*Anal.*<sup>6</sup> Calcd. for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>: 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<sup>7</sup> 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 $^{\circ}$  (*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>: 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<sub>22</sub>H<sub>24</sub>O<sub>4</sub>: 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 $^{\circ}$  was treated with excess 50% (w./w.) aqueous silver nitrate, which selectively gave a silver nitrate complex salt, m.p. (dec.) 243 $^{\circ}$  (*Anal.* Calcd. for

(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).