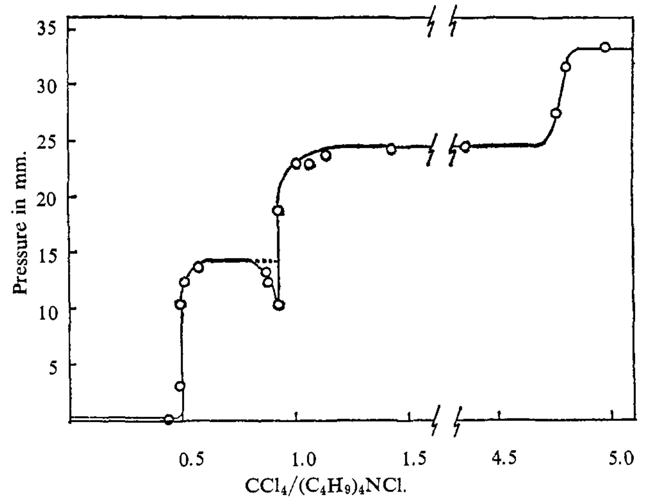

Figure 1. Pressure–composition isotherm at 0° for the system $(C_4H_9)_4NCl–CCl_4$.

action of CCl_4 with Cl^- does not occur when the tetrabutylammonium ion is replaced by the tetraethylammonium ion and it may thus be concluded that the reaction is lattice inhibited when the cation is as small as $(C_2H_5)_4N^+$.

Tetrabutylammonium chloride was prepared as described elsewhere.[1] Reagent grade carbon tetrachloride was purified by sublimation in the vacuum line prior to use. The materials were handled in a greaseless section of the vacuum line, and came into contact only with mercury and glass.

The bonding in CCl_5^- could be described either by a bicoordinate chlorine, $Cl_3C–Cl–Cl^-$, or by a pentacoordinate carbon, giving pentachlorocarbonate(IV) ion. The former would be analogous to I_3^- while the latter might resemble CH_5^+ with the occupancy of a nonbonding energy level by the additional electron pair.[2] The observed color could be explained using either model.

Reports in the literature indicate that carbon tetrahalides interact with many Lewis bases. The earliest work appears to be that of Dehn and Dewey[3] who studied the reaction of nitrogen bases with carbon tetrabromide. A survey of complexes of saturated molecules is available;[4] recent publications treat the interaction of carbon tetrachloride with iodide ions,[5] aromatic hydrocarbons,[6] aliphatic amines,[7,8] and alkyl sulfides.[9]

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work.

[1] D. H. McDaniel and R. E. Valleé, *Inorg. Chem.*, **2**, 996 (1963).

[2] For a qualitative MO treatment of CH_5^+, based on a trigonal bipyramidal geometry, see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 86.

[3] W. C. Dehn and A. H. Dewey, *J. Am. Chem. Soc.*, **33**, 1588 (1911).

[4] O. Hassel and Chr. Romming, *Quart. Rev.* (London), **16**, 1 (1962).

[5] M. C. R. Symons, *et al.*, *Trans. Faraday Soc.*, **62**, 301 (1966).

[6] R. F. Weimer and J. M. Prausnitz, *J. Chem. Phys.*, **42**, 3643 (1965).

[7] G. Heublein, *Z. Chem.*, **5**, 305 (1965).

[8] D. P. Stevenson and G. M. Coppinger, *J. Am. Chem. Soc.*, **84**, 149 (1962).

[9] H. L. Morris, *et al.*, *Inorg. Chem.*, **5**, 124 (1966).

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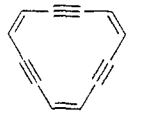
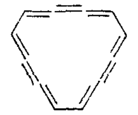
Received April 13, 1966

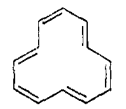
Cyclododecatrienetriyne

Sir:

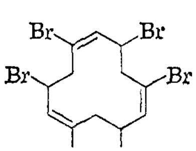
Cyclododecatrienetriyne[1] (I) should be a planar, strainless, conjugated monocyclic system containing $4n$ π electrons in parallel p orbitals. This molecule was suggested as a potential aromatic system by Sworski.[2] Although a canonical structure (II) can be written, I is predicted by the Hückel rule not to exhibit aromatic stability. Unlike the hypothetical cyclododecahexaene (III), I does not suffer from interior hydrogen atom repulsions.[3] Another unique aspect of I is that it contains six π electrons in p orbitals in the molecular plane which may contribute to a lowering of its ground-state energy by σ overlap.[4] An MO calculation ($\beta' = [S/(1 + S)]/[S_0/(1 + S_0)]$) predicts such a delocalization energy to be *ca.* 0.8 kcal/mole.


I

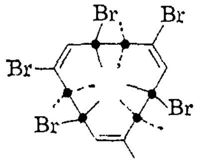

II


III

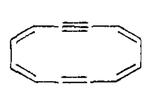
We wish here to report a synthesis and some properties of I. Bromination of 1,5,9-tribromo-*cis,cis,cis*-1,5,9-cyclododecatriene (IV)[4] with 3 equiv of N-bromosuccinimide (refluxing CCl_4, 25 min) gave an oily mixture of hexabromocyclododecatrienes. We assign structure V to compounds comprising at least the majority of this product. This assignment is based on the results of analogous reactions with 1-chlorocycloalkenes which gave the 3-bromo derivatives[5] and on the nearly quantitative yield (calculated for $C_{12}H_{12}Br_6$) obtained of a column chromatographically (SiO_2; $CHCl_3$) uniform product. Structure VI is assigned to one crystalline isomer of V, obtained after chromatography (SiO_2; hexane-CCl_4), mp 185°, *ca.* 15%, based on the complete analysis of its nmr spectrum as a four-spin system. The final proof of structure for this and other compounds present in this mixture will be reported later.



V



VI


VII

The hexabromocyclododecatriene mixture with excess sodium ethoxide in ethanol (35 min, 80°) gave I (65% yield, based on IV, after silicic acid column chromatography). Recrystallization (petroleum ether, bp 30–60°) provided pure I, dark brick-red needles,

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[1] 1,5,9-Cyclododecatriene-3,7,11-triyne or, using the nomenclature introduced by F. Sondheimer, tridehydro[12] annulene.

[2] T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

[3] For discussions of I, III, and related systems, see (a) W. Baker and J. F. W. McOmie in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter IX; (b) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952); (c) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **84**, 2844 (1962); (d) F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963); (e) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, 87, 5720 (1965), and references cited therein.

[4] K. G. Untch and D. J. Martin, *ibid.*, 87, 3518 (1965).

[5] B. Eistert and K. Schank, *Tetrahedron Letters*, No. 8, 429 (1964).

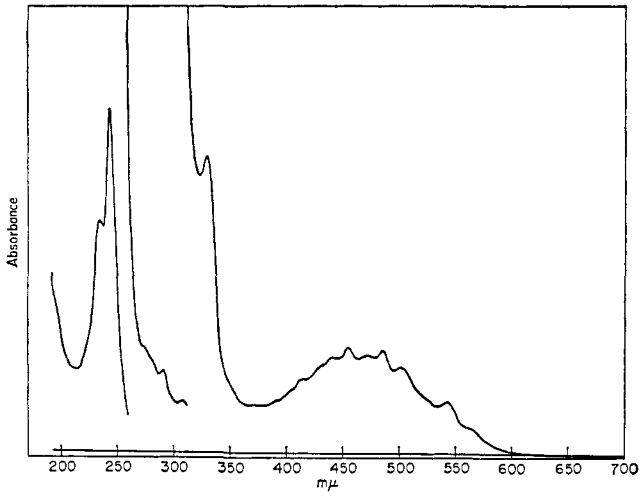

Figure 1. Ultraviolet absorption spectrum of cyclododecatrienetriyne in isooctane at 1.33 × 10^{-3}, 10^{-4}, and 10^{-5} mole/l. with a Jasco ORD/UV-5 spectrophotometer.

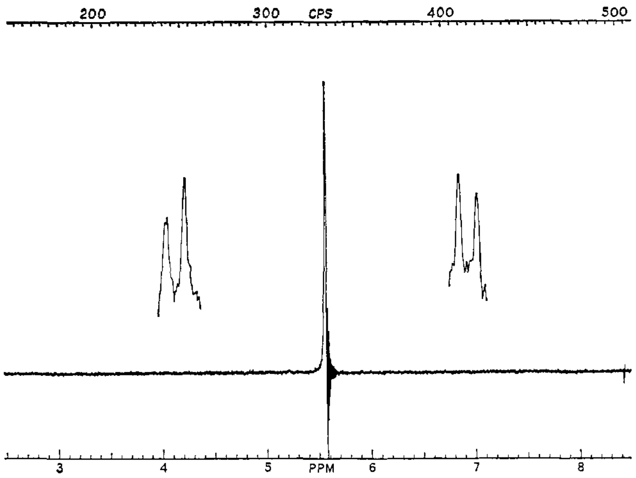

Figure 2. Nmr spectra of cyclododecatrienetriyne in carbon tetrachloride (*ca.* 15%) with tetramethylsilane as an internal reference. The continuous scan was recorded with a Varian A-60 spectrometer; the C^{13}–H satellites were recorded with a Varian HA-100 spectrometer and displayed after nine accumulated scans using a Varian C-1024 time-averaging computer.

mp 95–95.5°. Hydrogenation (Pt in EtOAc) gave cyclododecane (70%) and benzcyclooctene (15%), identified by glpc comparisons with authentic samples.[6] Mass measurement of the parent molecular ion provided the elemental composition[7] of I; calcd for $C_{12}H_6$: 150.04696; found 150.04695. The mass spectrum of I also shows clearly the doubly charged parent molecular ion *m*/2*e*, at 75 (the unrearranged $[C_{12}H_6]^{+2}$ ion containing ten out-of-plane π electrons?), and a doubly charged ion (*m* + 1)/2*e*, with the calculated intensity (13.2% for C^{13} natural abundance) at 75.5. The infrared spectra of I in CCl_4 and in KBr showed absorptions at or near 3.28 (w), 4.59 (w), 5.97 (m), 6.42 (m), 8.18 (s), 9.11 (s), 10.68 (w), and 13.42 μ (s), four of which are characteristic for triple and *cis* double bonds. The ultraviolet spectrum (Figure 1) exhibits intense absorptions at 239 mμ (ε 38,700) and 247.5 mμ (ε 57,200) and low-intensity maxima throughout the visible range, 457 mμ (ε 177). The nmr spectrum (Figure 2) shows a single, sharp absorption at τ 5.55. The C^{13}–H coupling constant is 169 ± 1 cps and the H–H coupling constant 10.5 ± 1 cps. These combined data establish the structure of this hydrocarbon as I.[8]

The properties of I that have been observed thus far indicate that it possesses little or no aromatic character. It is extremely reactive with oxygen, both in solutions and as a crystalline solid. In the absence of oxygen, however, it is stable. A dilute solution of I in hexane after 3 months showed no decrease in the amount of I present as determined by ultraviolet spectroscopy. It is readily hydrogenated. Its nmr spectrum demonstrates the absence of a diamagnetic ring current. We suspect that the cause for the relatively high-field chemical shift of the hydrogens of I may be a *paramagnetic* ring current.[9] On the other hand, part or all of this shift to high field may be due to the anisotropy of the triple bond. However, the corresponding hydrogens in vinylacetylene[10] and 1,10-deca-*cis*,*cis*-2,8-diene-4,6-diynediol[11] exhibit chemical shifts at τ 4.3.

Judging from identical, or nearly identical, colors, melting points, and infrared, ultraviolet, and nmr spectra, a compound isolated and assigned structure VII (bisdehydro[12]annulene) by Wolovsky and Sondheimer[3d,e] and the cyclododecatrienetriyne described here are one and the same substance. It is possible that a dehydrogenation (oxidation) occurred during their preparation or isolation procedure, similar to a process that occurred during Wolovsky's preparations of cyclooctadecahexaenetriynes and cyclooctadecapentaenetetrayne.[12]

The properties of I are in accord with the 4*n* + 2 Hückel rule for conjugated monocyclic systems. Previously prepared 4*n* π-electron monocyclic systems have been either nonplanar or highly strained due to angle deformation or nonbonded repulsions. In some cases (*n* = 1, 3) the presumed high strain energy has, thus

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(6) Identical retention times were obtained with silicone 710 on firebrick as the support, and each known compound added to a sample of the hydrogenation mixture caused an increase in the corresponding peak.

(7) An attempt to obtain the elemental composition by combustion analysis gave a very low carbon percentage. For similar observations with polyacetylenes, see F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959) (ref 6). In lieu of an elemental analysis by combustion, the much more accurate determination by high-resolution mass measurement was made with an AEI MS9 mass spectrometer.

(8) The vibrational isomer, II, and I may both be expected to have a $J_{C^{13}\text{-}H}$ value near 167 cps based on the correlation between C^{13}–H *J's* and s character of the C^{13} hybrid atomic orbital [H. S. Gutowsky and C. S. Juan, *ibid.*, **84**, 307 (1962), and references therein]. The observed $J_{H\text{-}H}$ value of 10.5 cps suggests that cyclododecatrienetriyne is best represented as I. Fourteen model systems for II give observed $J_{H\text{-}H}$ values within the range of 5–7 cps; some representative examples are 1,3-cyclohexadiene, $J_{H_2H_3}$ = 5.14 cps (S. Manatt, private communication), 2-methyl-2-acetoxycyclohexadienone, $J_{H_4H_5}$ = 6.58 cps (E. Moser, private communication), and cycloheptatriene, $J_{H_2H_3}$ = 5.26 cps [J. B. Lambert, J. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965)]. The range of *J* values for the vicinal sp^2–sp^2 bonded hydrogens in cycloalkenes (six to eight membered) is 9–11 cps; see A. A. Bothner-By in "Advances in Magnetic Resonance," Vol. I, J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, p 195.

(9) This explanation was first suggested to us by Professor J. A. Pople. Though Pullman [*J. Chim. Phys.*, **49**, 641 (1952)] has calculated a paramagnetic induced ring current for 4*n* π-electron cyclic systems little attention has been paid to this effect on chemical shifts. Dauben [*J. Am. Chem. Soc.*, **83**, 4659 (1961)] has cited Pullman as predicting "a pronounced diminution of diamagnetic susceptibility in heptalene (and pentalene)." We (J. A. P. and K. G. U) are presently carrying out calculations and assembling experimental data which may corroborate a paramagnetic induced ring current for monocyclic 4*n* π-electron systems. These calculations and conclusions will be presented in a subsequent paper.

(10) R. C. Hirst and D. M. Grant, *ibid.*, **84**, 2009 (1962).

(11) L. D. Colebrook, private communication.

(12) R. Wolovsky, *J. Am. Chem. Soc.*, **87**, 3638 (1965).

far, prevented isolation; other systems (n = 2, 4, 5, 6) are predicted to be nonplanar, judging from molecular models.

Further work in progress (X-ray diffraction, C^{13} nmr) should provide more information about the properties and character of this molecule.

Acknowledgments. The authors are grateful to Mr. R. Rabinowitz for his able technical assistance, to Mr. R. E. Rhodes for obtaining the mass spectrometric measurements, to Mr. R. Pitcher of Varian Associates for the C^{13}–H coupling constants, and to Dr. A. A. Bothner-By for helpful discussions.

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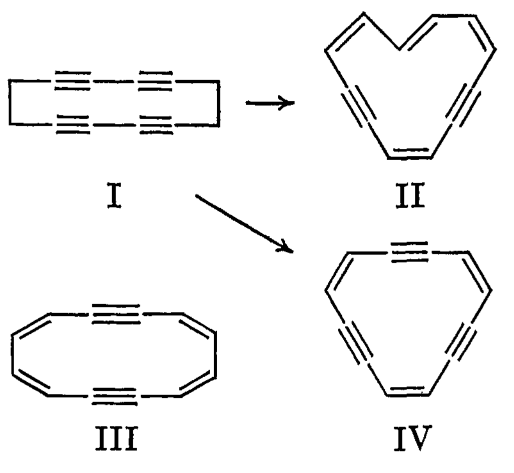
Received February 18, 1966

1,5,9-Tridehydro[12]annulene[1]

Sir:

It has been reported by our group[2] that treatment of 1,3,7,9-cyclododecatetrayne (I, $C_{12}H_8$) with potassium t-butoxide leads to two different dehydro[12]annulenes. The elemental analysis[2b] of each of these substances indicated the anticipated empirical formula $C_{12}H_8$, and they were therefore both considered to be bisdehydro[12]annulenes. The dehydroannulene obtained in larger amount ("isomer A," complex nmr spectrum) was assigned structure II, while the one obtained in lesser amount ("isomer B," nmr singlet at τ 5.58 in CCl_4)[3] was assigned structure III.



Very recently, Untch and Wysocki[5] have carried out an elegant synthesis of 1,5,9-tridehydro[12]annulene (IV, $C_{12}H_6$)[6] and have observed that this compound possesses properties essentially identical with those reported by us for isomer B. Dr. Untch kindly informed us of his work prior to publication, and we therefore reexamined the structure of isomer B. The mass spectrum was determined (AEI MS9 spectrometer), and the molecular ion (found 150.048) revealed that the empirical formula was in fact $C_{12}H_6$ (calcd 150.047) and not $C_{12}H_8$ (calcd 152.063).[7] Consequently, dehydrogenation must have taken place during the base treatment of I.[8] Isomer B was then shown to be identical with Untch's compound by direct comparison (thin layer chromatography, mass and ultraviolet spectra), and thus is 1,5,9-tridehydro[12]annulene (IV).[10]

The mass spectrum of "isomer A" (molecular ion, found 152.063) clearly showed the $C_{12}H_8$ formula to be correct, and the arguments[2] for assigning structure II to this compound remain unchanged.

Acknowledgment. We wish to thank Dr. K. G. Untch for kindly providing a sample of IV, and to C.S.I.R.O. for an Overseas Postgraduate Studentship (to I.C.C.).

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[1] Part XLI in the series Unsaturated Macrocyclic Compounds. For part XL, see R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **88**, 1525 (1966).

[2] (a) F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963); (b) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **87**, 5720 (1965).

[3] Whereas the nmr spectrum of isomer A provided confirmation for a $C_{12}H_8$ formulation, such confirmation could not be provided by the spectrum of isomer B. The fact that the latter spectrum showed only a sharp singlet was disturbing (since III possesses two different types of protons), although this type of observation is not without precedent.[4] Separation can occur by change of solvent,[4] but the spectrum of isomer B, determined in different solvents, in all cases exhibited only a singlet ($CDCl_3$, τ 5.52 at 20°, 5.44 at −60°; $(CD_3)_2CO$, 5.34 at 20°, 5.20 at −80°; C_6D_6, 6.00 at 20°).

[4] *Inter alia*, G. Farges and A. S. Dreiding, *Helv. Chim. Acta*, **49**, 552 (1966); F. Sondheimer and P. J. Garratt, unpublished observations.

[5] K. G. Untch and D. C. Wysocki, *J. Am. Chem. Soc.*, **88**, 2608 (1966).

[6] See T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

[7] The previously reported microanalysis (Found: C, 95.02; H, 5.01.[2b] Calcd for $C_{12}H_8$: C, 94.70; H, 5.30. Calcd for $C_{12}H_6$: C, 95.97; H, 4.03) must have been in error. This points to the inherent danger in assigning an empirical formula merely on the basis of microanalytical data.

[8] Analogous dehydrogenations have already been observed to occur in the C_{14}[2a,9a] and the C_{18} series.[9b]

[9] (a) F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *J. Am. Chem. Soc.*, **84**, 4595 (1962); (b) R. Wolovsky, *ibid.*, **87**, 3638 (1965).

[10] It is of interest that the tribenzo analog of IV has been prepared very recently by two groups (H. A. Staab and F. Graf, *Tetrahedron Letters*, 751 (1966); I. D. Campbell, G. Eglinton, W. Henderson, and R. A. Raphael, *Chem. Commun.*, 87 (1966)).

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Received March 23, 1966

Electron Spin Resonance Determination of the Heat of Reaction for Triphenylmethyl Radical and Oxygen[1]

Sir:

We wish to report an experimental determination of the heat of reaction for the formation of a peroxy radical from a hydrocarbon radical and oxygen. This value has been obtained for triphenylmethyl radicals trapped in a crystal lattice permeable to oxygen.

Triphenylmethyl radicals were produced in the solid state by radiolysis of triphenylmethyl chloride, triphenylmethyl bromide, or triphenylacetic acid.[2]

$$Ph_3CX \rightsquigarrow Ph_3C\cdot \qquad (1)$$

$$X = Cl, Br, COOH$$

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[1] Electron Spin Resonance Studies of Thermal Decomposition Mechanisms. Peroxides. I.

[2] γ-Radiation from cobalt-60 was used. The total dose was 4–10 × 10^{18} ev/g. The dose rate was 5 × 10^{15} ev/g sec^{-1}.