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- (10) The yield of $\text{Me}_3\text{SiOSiMe}_3$ increased as the ratio of $\text{MeOK}/\text{Me}_3\text{SiSiMe}_3$ decreased.
- (11) Obtained from Alfa.
- (12) Obtained from Columbia Organics and used without further purification.
- (13) Cis- and trans-isomer ratios were determined on stationary phases that were independently shown to separate authentic mixtures. Product mixtures were coinjected with authentic olefin samples. Yields were determined after work-up by a weighed amount of internal standard and corrected for detector response (flame ionization detector-electronic integrator).
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- (17) National Science Foundation Predoctoral Fellow, 1973-1976.

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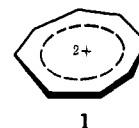
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Pasadena, California 91125
Received September 25, 1975

Novel Aromatic Systems. III.¹ The 1,3,5,7-Tetramethylcyclooctatetraene Dication, the First $8C-6\pi$ Hückeloid System

Sir:

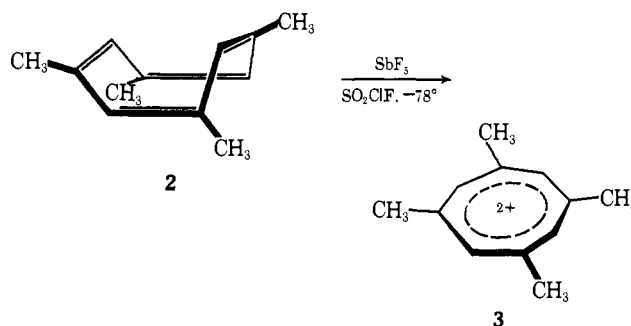
A most significant early triumph of simple MO theory was Hückel's prediction² that planar annulenes endowed with $(4n + 2)$ π -electrons should possess relative electronic stability as a consequence of their having closed-shell MO configurations with substantial electron delocalization (resonance) energies. The resultant relative electronic stability (aromaticity) which is achieved has been found to prevail as well, without known exception, in the related annular ions.³

Notwithstanding their predicted aromatic stabilization,²⁻⁴ several fundamental systems have remained elusive of preparation and experimental study. The most notable Hückeloid absentee is the $8C-6\pi$ cyclooctatetraene dication (**1**). Despite repeated attempts,⁵ neither **1** nor any of its substituted derivatives have yet yielded to synthesis.



We now wish to report the preparation and characterization by ¹H and ¹³C NMR spectroscopy of the first cyclooctatetraene dication, namely the 1,3,5,7-tetramethyl derivative **3**, showing it to be a fully delocalized, approximately planar, 6π -electron aromatic system.

The title substance (**3**) was obtained upon direct two-electron oxidation of 1,3,5,7-tetramethylcyclooctatetraene (**2**)⁶ by SbF_5 ⁷ in SO_2ClF solution at -78° .⁸ The FT ¹H NMR spectrum (100 MHz) of this solution at -50° consists of two sharp singlets at δ 4.27 and 10.80 of relative area 3:1, respectively (Figure 1, Table I). No spectral



change is noted over the temperature range -30 to -100° . Vinylic proton chemical shifts in a series of aromatic molecules have been shown to be a linear function of the π -electron densities of the carbon atoms to which they are bound,

Table I. Proton and Carbon-13 NMR Parameters of the 1,3,5,7-Tetramethylcyclooctatetraene Dication and Related Compounds^a

	Proton			Carbon-13			
	H ₁	H ₂	CH ₃	C ₁	C ₂	CH ₃	other
 3^b		10.80 (s)	4.27 (s)	182.7 (s)	170.0 (d, 166.2)	33.5 (q, 134.3)	
 2^c		6.17 (m)	2.40 (m)	138.9 (s)	128.8 (d, 148.4)	23.5 (q, 124.7)	
 c	6.42 (m)			132.2 (d, 156.3)			
 5^b	11.33 (s)		C ₇ H ₃ , 3.40 (s) C ₉ H ₃ , 3.02 (s)	230.6 (d)	164.5 (s)	20.8 (q) 14.6 (q)	C _{3a} , 88.3 (s)
 d	11.26 (d)	8.65 (t)		234.7 (d)	145.7 (s)		

^aChemical shifts are in parts per million from external capillary Me_4Si , coupling constants are in hertz: s = singlet, d = doublet, q = quartet, m = multiplet. ^bIn $\text{SbF}_5-\text{SO}_2\text{ClF}$ solution at -70° . ^cIn SO_2ClF solution at -70° . ^dIn $\text{SbF}_5-\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ solution at -60° ; data taken from ref 21 and converted to ppm from external capillary Me_4Si utilizing δ_{CS_2} 193.7.

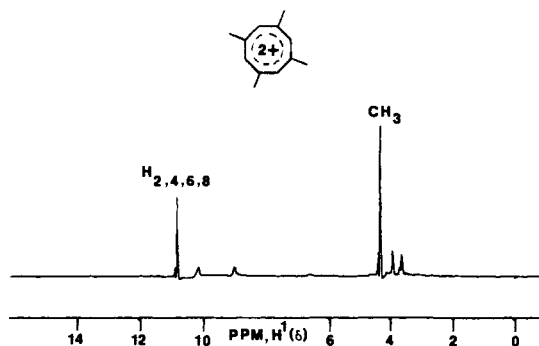
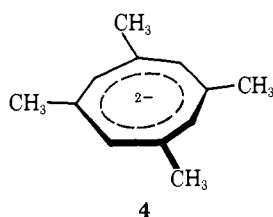


Figure 1. The 100-MHz FT ^1H NMR spectrum of the 1,3,5,7-tetramethylcyclooctatetraene dication (**3**) in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -50° . Resonances attributable to the 1,3,5,7-tetramethylhomotropylum ion i (see ref 8) are also present. The H_3O^+ resonance at δ 10.37 has been deleted for clarity.

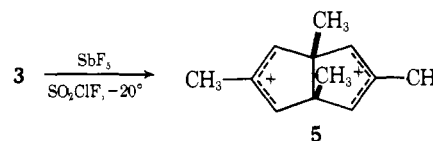
with the slope of this relationship being approximately 10 ppm/ π -electron.^{3c,10} On this basis, an estimate of the vinylic proton deshielding attributable to those local diamagnetic shielding differences accompanying the transformation of the 8π **2** to the 6π **3** would be 2.5 ppm. The observed ^1H chemical shift difference (4.6 ppm, Table I) is clearly enhanced and must arise because of positioning of the ring protons in the deshielding region of the diamagnetic ring-current generated from an aromatic species.¹¹ Assuming that such tetraalkyl substitution of the cyclooctatrienediylum ring represents only a minor perturbation, the expected deshielding of the vinylic protons in **3** due to diamagnetic anisotropy is 1.9 ppm as calculated by Pople's equivalent point magnetic dipole approximation.¹² The 2.1 ppm additional deshielding of the vinylic protons in **3** not attributable to the "charge" effect coincides therefore with the magnitude of deshielding anticipated from ring-current contributions. The observation of a ring-current of this magnitude provides strong evidence that $C_{p\pi}^{\text{ring}}-C_{p\pi}^{\text{ring}}$ overlap in **3** is nearly optimal and hence that approximate coplanarity of the eight ring carbons is realized despite adverse strain factors.¹³ This finding is to be compared with recent NMR¹⁴ and x-ray crystallographic studies¹⁵ of the analogous 10π Hückeloid dianion **4**.



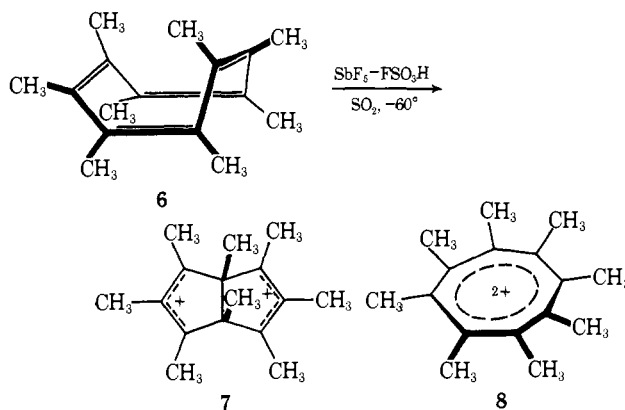
The FT ^{13}C NMR of **3** in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -70° consists of three resonances at δ 182.7 (s), 170.0 (d, 166.2), and 33.5 (q, 134.3) which are unequivocally assigned to $\text{C}_{1,3,5,7}$, $\text{C}_{2,4,6,8}$, and $\text{C}_{9,10,11,12}$, respectively (Table I). ^{13}C NMR shieldings of aromatic systems have been demonstrated to be primarily dependent upon the local π -electron density (ρ) at each carbon nucleus.^{3c,d,16} A least-squares analysis of the data obtained for 2π -, 6π -, and 10π -electron monocyclic aromatics indicates the relationship for these systems to be $\delta_{13\text{C}} = 159.5\rho + 288.5$.¹⁷ However, an accurate assessment of the π -electron densities at $\text{C}_{1,3,5,7}$ and $\text{C}_{2,4,6,8}$ in **3** requires that corrections be introduced into the ^{13}C NMR shieldings for the methyl substituents present.¹⁸ The difficulty of precisely estimating substituent effects on ^{13}C NMR shifts is well recognized,^{18,19} but values for these corrections can be determined to be approximately -6.7 and $+3.4$ ppm, respectively, by compar-

son of the ^{13}C NMR shieldings of 1,3,5,7-tetramethylcyclooctatetraene and cyclooctatetraene (Table I). The adjusted ^{13}C NMR shieldings of $^{13}\text{C}_{1,3,5,7}$ and $^{13}\text{C}_{2,4,6,8}$ in **3** then become 176.0 and 173.4 ppm, respectively, the magnitudes of which are in close agreement with the ^{13}C NMR shift predicted for parent dication **1** (168.9).¹⁷ Hence, hyperconjugative donation by the methyl substituents in **3** appears to be minimal. This conclusion is reinforced by the observation that the total increase in the ring carbon shieldings of **3** relative to **2** is 340.0 ppm (Table I) which accords well with the 319.0 ppm increase predicted by the Spiesecke-Schneider correlation for a 2π -electron oxidation.^{3c,d,10c,11} Moreover, although the uncertainties involved in these corrections of $\delta_{13\text{C}_{1,3,5,7}}$ and $\delta_{13\text{C}_{2,4,6,8}}$ preclude quantitative interpretation of the π -electron density distribution in **3**, the near identity of the two values suggests that the π -polarization induced by methyl substitution^{19,20} in this dication is not significantly accentuated relative to the electronically neutral **2**. The ^{13}C nmr data thus indicate **3** to be a 6π -electron aromatic system possessing a rather symmetrical π -density distribution over the ring carbon nuclei.

Warming the $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution of **3** to -20° results in its irreversible isomerization to the *cis*-2,3a,5,6a-tetramethyldihydropentalene dication **5**. Structure **5** is entirely



consistent with the observed ^1H and FT ^{13}C NMR spectra, which closely resemble those of model cyclopentenyl cation systems (Table I),²¹ and the previous observation that oxidation of octamethylcyclooctatetraene (**6**) in superacid media resulted in the formation of the octamethyldihydropentalene dication **7**.²² The *cis* orientation of the 3a,6a-methyl substituents in **5** is demonstrated by their ^1H NMR temperature dependence which results from their hindered rotation. This phenomenon has been similarly observed in the case of **7**.²²



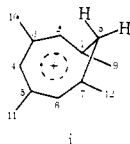
The conversion of **3** to **5** via a concerted mechanistic process is inconsistent with orbital symmetry arguments,²³ but reflects the thermodynamic stability of *cis*-3a,6a-dihydropentalene derivatives relative to the *trans* isomers²⁴ and the importance of maintenance of optimal $C_{p\pi}-C_{p\pi}$ overlap in the allylic fragments of the dications. The thermodynamic stability of **5** relative to **3** is further indicated and is in accord with previous studies in which exclusive formation of **7**, in preference to **8**, was observed.²²

We are extending our investigations of cyclooctatetraene dications to other derivatives. In addition, we are examining the possibility of generation of cyclooctatetraene dications by electrochemical methods.

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the protic impurities which are always present in the SbF_5 , despite careful purification.⁹ Cation **1** is not an intermediate in the formation of **3** and was prepared independently by protonation of **2** with FSO_3H in SO_2ClF solution at -78° .

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$$\Delta\sigma = -\frac{e^2 a^2}{2mc^2 R^3}$$

where $\Delta\sigma$ = the ring-current contribution to the mean screening constant of the proton, a = the radius of the aromatic ring, and R = the distance from the center of the aromatic ring to the proton. For the calculation, the MINDO/2 optimized geometry of **1** from ref 4a was utilized. The C–H bond lengths in **1** were assumed to be the same as in cyclooctatetraene (1.09 Å).

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Spin-Lattice Relaxation of Protons. A General, Quantitative Evaluation of Contributions from the Intramolecular Dipole-Dipole Mechanism

Sir:

The demonstration^{1–4} of several chemically useful stereospecific dependencies for the spin-lattice relaxation times (T_1 values) of the protons of organic molecules provides a compelling need for the development of methods for the accurate measurement of the relaxation contributions between individual protons via the intramolecular dipole-dipole (IDD) mechanism. Although such measurements can be made via nuclear Overhauser enhancement (NOE)^{5,6} experiments, a number of difficulties somewhat limit the overall scope of that approach. We now describe an alternative method, based on the selective measurement of T_1 values, which appears to have a wide generality.

For a coupled spin system,⁷ the relaxation is, in general, nonexponential but the initial rate of relaxation, R_1 , is a function of the initial perturbation. The conventional two-⁸ or three-pulse⁹ Fourier transform methods, in which a 180° pulse inverts the populations of all transitions, provide a routine source of the nonselective R_1 value, $R_1^A(\text{NS})$. A different value, $R_1^A(\tilde{A})$ is obtained by selective^{10–13} inversion of the spin states of a single nuclear species (A). The ratio $R_1^A(\text{NS})/R_1^A(\tilde{A})$ then gives the extent to which that particular species is relaxed via dipole-dipole interaction with other spins inverted by the nonselective pulse. For complete proton dipolar relaxation, this ratio is⁶ 1.5. For a