References and Notes

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(13) The term "van der Waals radius" has two different meanings in the literature. The crystallographer uses the expression to mean what can more properly be called the "contact radius", or the "distance of closest approach" in crystals. The "van der Waals radius" will be used here with the meaning accorded to the term by theoreticians, namely, one-half the distance between the interacting but otherwise isolated atoms (or groups) when the system is at an energy minimum. Contact radii are always a good deal shorter than van der Waals radii.

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Novel Aromatic Systems. 8.[1] Cyclooctatetraene Dications

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Abstract: Suitably substituted cyclooctatetraenes are oxidized by antimony pentafluoride in sulfuryl chloride fluoride solution to the corresponding C_8 6 π-electron Hückeloid cyclooctatetraene dications. The structures of the 1,4-dimethyl-, 1,3,5,7-tetramethyl-, 1,3,5,7-tetraphenyl-, and *sym*-dibenzocyclooctatetraene dications are discussed in terms of their ^{1}H and ^{13}C NMR spectra.

For over 150 years chemists have been intrigued by that group of unsaturated organic molecules which they termed "aromatic".[3] The concept and theory of aromaticity was first placed on a sound physical foundation during 1931–1937 with Hückel's[3-6] development of the basic pattern of molecular orbital theory of unsaturated and aromatic compounds. Hückel's rule and subsequent more highly refined theoretical treatments of aromaticity[7] have stimulated continued efforts to prepare molecules designed to provide the experimental tests for their predictions. This experimental work has led to the discovery of a substantial number of intriguing new "aromatic" molecules, highlighted by the cyclopropenium ion (**1**),[8] the cyclopentadienyl anion (**2**),[9] the tropylium ion (**3**),[10] the cyclononatetraenyl anion (**4**),[11] the cyclooctatetraene dianion (**5**),[12] the annulenes,[13] the bridged annulenes,[13] and the *trans*-15,16-dihydropyrenes.[14] Not withstanding their predicted aromatic stabilization,[3,5,7,15] several fundamental systems have remained elusive of preparation and experimental study. Perhaps the most notable Hückeloid absentee is the C_8 6 π-electron cyclooctatetraene dication (**6**). Despite repeated attempts,[16,17] neither **6** nor any of its substituted derivatives have yet yielded to synthesis.


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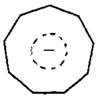
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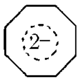
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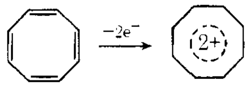
Cyclooctatetraene (**7**) is a nonplanar 8 π-electron system[18] which occupies an extremely interesting pivotal position for the preparation of the cyclooctatetraene dication (**6**) since a two-electron oxidation offers the possibility of its conversion into the 6 π-electron dication **6**.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In a communication[1b] we reported the first successful preparation of a cyclooctatetraene dication, namely, the 1,3,5,7-tetramethyl derivative, by the 2 π-electron oxidation of the respective cyclooctatetraene[19] with SbF_5 in SO_2ClF solution at low temperature. We now wish to report our complete studies in this area which includes the preparation and study of a series of cyclooctatetraene dications.

Results and Discussion

A. The 1,4-Dimethylcyclooctatetraene Dication. Antimony pentafluoride in sulfuryl chloride fluoride (SbF_5–SO_2ClF) solution has recently been shown to be an effective two-electron oxidizing agent, particularly for the oxidation of aromatic hydrocarbons to their respective dications.[20] Treatment of 1,4-dimethylcyclooctatetraene (**8**)[21] with SbF_5–SO_2ClF at −78 °C results in the formation of the corresponding 1,4-dimethylcyclooctatetraene dication (**9**). The ^{1}H NMR spec-

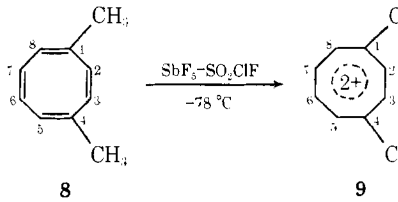

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Table I. Proton and Carbon-13 NMR Parameters of Cyclooctatetraenes and Their Dications[a]

Compd		Skeletal positions 1,4	2,3	5,8	6,7	Other
7[c]	δ^1H	5.75 (m)				
	$\delta^{13}C$	132.2 (d, 156.3)				
8[d]	δ^1H			← 5.35–5.75 (m) →		CH_3: 1.72 (s)
	$\delta^{13}C$	138.3 (s)	126.9 (d)[b]	127.6 (d)[b]	128.2 (d)[b]	CH_3: 24.1 (q)
9[e]	δ^1H		9.90[b]	9.96[b]	9.96[b]	CH_3: 3.98 (s)
	$\delta^{13}C$	208.8 (s)	160.2[b] (d, 167.2)	160.8[b] (d, 168.0)	164.8[b] (d, 166.8)	CH_3: 39.6 (q, 134.5)

Compd		1,3,5,7	2,4,6,8	Other
10[c]	δ^1H		5.50 (m)	CH_3: 1.73 (m)
	$\delta^{13}C$	138.9 (s)	128.8 (d, 148.4)	CH_3: 23.5 (q, 124.7)
11[f]	δ^1H		10.13 (s)	CH_3: 3.60 (s)
	$\delta^{13}C$	182.7 (s)	170.0 (d, 166.2)	CH_3: 33.5 (q, 134.3)
17[g]	δ^1H		7.08 (s)	C_6H_5: 7.6–8.0 (m)
	$\delta^{13}C$	144.7 (s)[b]	129.3 (d)[b]	C_i: 141.4 (s);[b] C_o: 129.7 (d);[b] C_m: 128.0 (d);[b] C_p: 129.1 (d)[b]
18[h]	δ^1H		9.62 (br s)	C_6H_5: 8.2–8.7 (m)
	$\delta^{13}C$	174.0 (s)	168.6 (d)	C_i: 125.8 (s); C_o: 135;[b] C_m: 132;[b] C_p: 137[b]

[a] ^1H and ^{13}C NMR shifts are given in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants are given in parentheses: d = doublet; s = singlet; q = quartet; m = multiplet. [b] Resonances are not specifically assigned. [c] In SO_2ClF solution at −70 °C. [d] In SO_2ClF solution at −80 °C. [e] In SbF_5-SO_2ClF solution at −80 °C. [f] In SbF_5-SO_2ClF solution at −70 °C. [g] In $CDCl_3$ solution at ambient temperature. [h] In SbF_5-SO_2ClF solution at −90 °C.

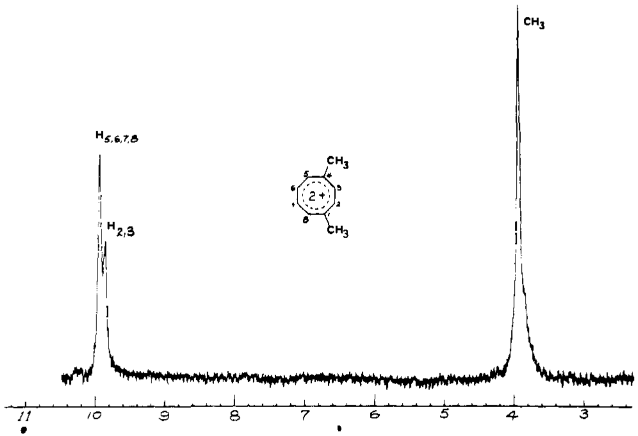


Figure 1. The 60-MHz ^1H NMR spectrum of the 1,4-dimethylcyclooctatetraene dication in SbF_5-SO_2ClF solution at −80 °C (impurity $H_3{}^+O$ deleted for clarity).

trum (60 MHz) of **9** obtained at −80 °C consists of three resonances at δ 9.96, 9.90, and 3.98 of relative areas 2:1:3, respectively (Table I, Figure 1).

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 with the slope of this relationship being approximately 10 ppm/π electron.[3a,b,22] On this basis an estimate of the vinylic proton deshielding attributable to those local diamagnetic shielding differences accompanying the transformation of the 8 π **8** to the 6 π **9** would be 2.5 ppm. The observed ^1H NMR chemical shift difference (ca. 4.0 ppm, Table I) is clearly enhanced and must arise because of the positioning of the ring protons in the deshielding region of the diamagnetic ring current generated by an aromatic species.[23] The observation of a ring current of this magnitude provides strong evidence that $C_{p\pi}{}^{ring}$–$C_{p\pi}{}^{ring}$ overlap in **9** is nearly optimal and hence the approximate coplanarity of the eight ring carbons is realized despite the adverse strain factors.[24]

The FT ^{13}C NMR of **9** in SbF_5-SO_2ClF solution at −80 °C consists of resonances at $\delta^{13}C$ 208.8 (s), 164.8 (d, 166.8), 160.8 (d, 168.0), 160.2 (d, 167.2), and 39.6 (q, 134.5). The resonances at $\delta^{13}C$ 208.8 and 39.6 are hence assigned unequivocally to $C_{1,4}$ and the methyl carbons, respectively. The remaining three resonances are nonspecifically assigned to the three expected sets of nonequivalent protiated cyclooctatrienediylium carbons (Table I, Figure 2).

^{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.[3a,b,22c,25] A least-squares analysis of the data obtained for 2 π-, 6 π-, and 10 π-electron monocyclic aromatics indicates the relationship for these systems to be $\delta_{^{13}C}$ $-159.5\rho + 288.5$.[26] Although an accurate assessment of the π-electron densities at the cyclooctatrienediylium carbons requires that corrections be introduced in the ^{13}C NMR shieldings for the methyl substituents present,[27] the dicationic nature of **9** is readily apparent upon comparison of the observed average ring-carbon ^{13}C NMR shielding in **9** ($\delta^{13}C$ 173.3, Table I) with that predicted by the Spiesecke–Schneider relationship for a 6 π C_8 cyclooctatetraene dication ($\delta^{13}C$ 168.9).[26] Furthermore, a total increase of 347.2 ppm in the ring carbon shieldings of **9** relative to **8** accords well with the 319.0-ppm increase predicted by the Spiesecke–Schneider correlation for a 2 π-electron oxidation and hence with the formulation of **9** as a dicationic species.[3a,b,22c,25,26] The exaggerated deshielding of $C_{1,4}$ relative to $C_{2,3}$, $C_{5,8}$, and $C_{6,7}$ in **9**, as compared with that observed in the neutral precursor, further suggests that substantial polarization of the 6 π electrons exists in the dication[28] and substantially more positive charge is localized at a methylated cyclooctatrienediylium carbon than at any of the corresponding protiated sites.

Above −50 °C the dication **9** is unstable and rapidly decomposes to a number of yet unidentified products.

B. The 1,3,5,7-Tetramethylcyclooctatetraene Dication. The dication **11** was obtained by direct two-electron oxidation of 1,3,5,7-tetramethylcyclooctatetraene (**10**)[19] with SbF_5[20] in SO_2ClF solution at −78 °C.[29] The FT ^1H NMR spectrum (100 MHz) of this solution at −50 °C consists of two sharp

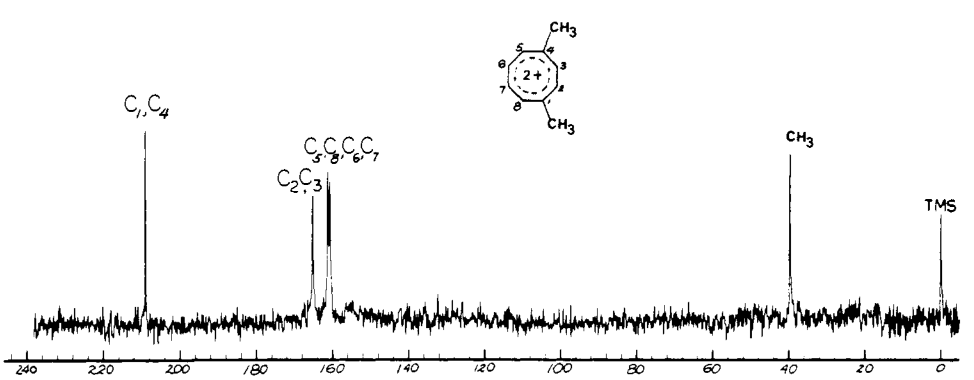
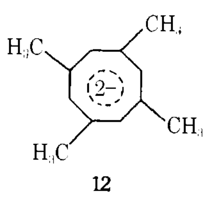


Figure 2. The proton noise decoupled 25.16-MHz FT ^{13}C NMR spectrum of the 1,4-dimethylcyclooctatetraene dication in SbF_5-SO_2ClF solution at −80 °C.

10 11

singlets at δ 3.60 and 10.13 of relative area 3:1, respectively (Table I, Figure 3). No spectral change was noted over the temperature range −30 to −100 °C.

Comparison of the vinylic proton shieldings of the 1,3,5,7-tetramethylcyclooctatetraene dication with those of its neutral precursor **10** again indicates that the observed difference of these shieldings (4.6 ppm, Table I) is clearly enhanced over the difference expected from the existence of nonequivalent local diamagnetic shielding contributions (approximately 2.5 ppm) in the two systems.[3a,b,22] Assuming that tetraalkyl substitution of the cyclooctatrienediylium ring represents only a minor perturbation, the expected deshielding of the aromatic protons in **11** due to diamagnetic anisotropy is 1.9 ppm as calculated by Pople's equivalent point magnetic dipole approximation.[31] The 2.1 ppm additional deshielding of the aromatic protons in **11** 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 presents strong evidence that $C_{p\pi}^{ring}$–$C_{p\pi}^{ring}$ overlap in **11** is nearly optimal and hence that, as in the case of **9**, approximate coplanarity of the eight ring carbons is realized despite adverse strain factors.[24] This finding is to be compared with recent NMR[32] and x-ray crystallographic studies[12b] of the analogous 10 π Hückeloid dianion **12**.



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The FT ^{13}C NMR of **11** in SbF_5-SO_2ClF solution at −70 °C consists of three resonances at δ^{13}C 182.7 (s), 170.0 (d, 166.2), and 33.5 (q, 134.3) which are unequivocally assigned to $C_{1,3,5,7}$, $C_{2,4,6,8}$, and the methyl carbons, respectively (Table I). An accurate assessment of the π-electron densities at $C_{1,3,5,7}$ and $C_{2,4,6,8}$ in **11** from their ^{13}C NMR shieldings and the Spiesecke–Schneider correlation requires that corrections be introduced into the ^{13}C NMR shieldings for the methyl substituents present.[27] The difficulty of precisely estimating substituent effects on ^{13}C NMR shifts is well recognized,[27,33] but values for these corrections can be determined to be approximately −6.7 and +3.4 ppm, respectively, by comparison of the ^{13}C NMR shieldings for 1,3,5,7-tetramethylcyclooctatetraene and cyclooctatetraene (Table I). The adjusted ^{13}C NMR shieldings of $C_{1,3,5,7}$ and $C_{2,4,6,8}$ in **11** then become δ^{13}C 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 **7** (δ^{13}C 168.9).[26] The dicationic formulation of **11** is further substantiated by the observation that the total increase in the ring carbon shieldings of **11** relative to **10** is 340.0 ppm (Table I) which accords well with the 319.0-ppm increase predicted by the Spiesecke–Schneider correlation for a 2 π-electron oxidation.[3a,b,22c,25,26] The ^{13}C and ^{1}H NMR data thus indicate **11** to be a 6 π-electron aromatic system possessing substantial diamagnetic anisotropy.

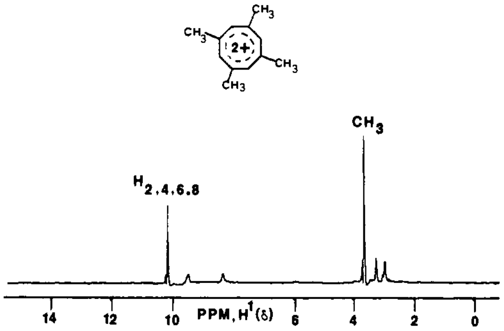
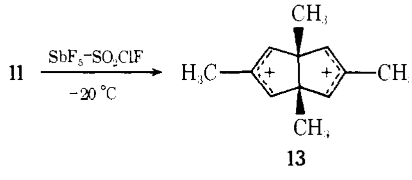


Figure 3. The 100-MHz FT ^{1}H NMR spectrum of the 1,3,5,7-tetramethylcyclooctatetraene dication in SbF_5-SO_2ClF solution at −50 °C. Resonances attributable to the 1,3,5,7-tetramethylhomotropylium ion (see ref 29) are also present (impurity H_3^+O peak deleted for clarity).

Warming the SbF_5-SO_2ClF solution of **11** to −20 °C results in its irreversible isomerization to the *cis*-2,3a,5,6a-tetramethyldihydropentalene dication **13**. Structure **13** is entirely consistent with the observed ^{1}H and FT ^{13}C NMR spectra,[1b,29] which closely resemble those of model cyclopentenyl cation systems,[34] and the previous observation that oxidation of octamethylcyclooctatetraene (**14**) in superacid media resulted in the formation of the octamethyldihydropentalene dication **15**.[35] The cis orientation of the 3a,6a methyl substituents in **13** is demonstrated by their ^{1}H NMR temperature dependence which results from their hindered rotation. This phenomenon has been previously observed in the case of **15**.[35]



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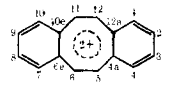
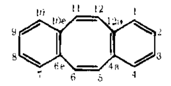
The conversion of **11** to **13** via a concerted mechanistic process is inconsistent with orbital symmetry arguments,[36] but

Table II. Proton and Carbon-13 NMR Parameters of the *sym*-Dibenzocyclooctatetraene Dication and *sym*-Dibenzocyclooctatetraene[a]

	Proton			Carbon-13			
	H_1	H_2	H_5	C_1	C_2	C_5	C_{4a}
 20[b]	9.80 (s)	9.80 (s)	10.87 (s)	145.5 (d)[d] 150.9 (d)[d]		160.1 (d)	148.6 (s)
 19[c]	7.06 (m)[d]		6.72 (s)	128.1 (d)[d] 130.4 (d)[d] 134.5 (d)[d]			138.4 (s)

[a] Chemical shifts are in parts per million from external (capillary) Me_4Si. Multiplicities are in parentheses: s = singlet, d = doublet, m = multiplet. [b] In SbF_5-SO_2ClF solution at −70 °C. [c] In $CDCl_3$ solution at ambient temperature. [d] Resonances are not specifically assigned.

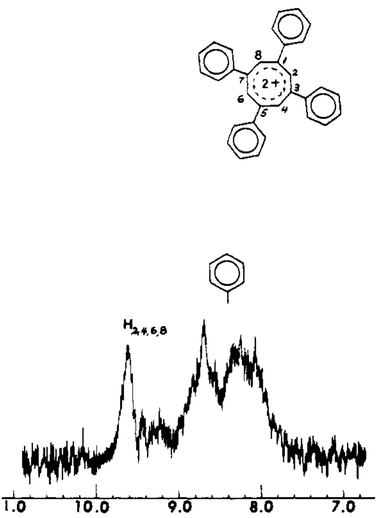
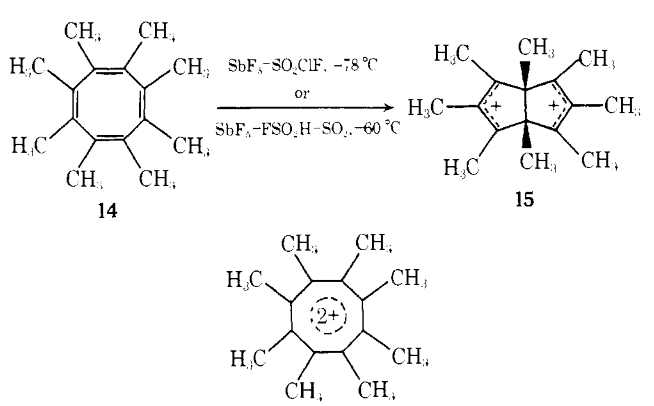


Figure 4. The 60-MHz ^1H NMR spectrum of the 1,3,5,7-tetraphenylcyclooctatetraene dication in SbF_5-SO_2ClF solution at −80 °C.



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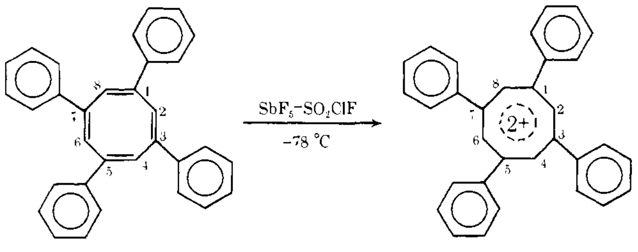
reflects the thermodynamic stability of *cis*-dihydropentalene derivatives relative to the trans isomers[37] and the importance of maintenance of optimal $C_{p\pi}-C_{p\pi}$ overlap in the allylic fragments of the dications. The thermodynamic stability of **13** relative to **11** is further indicated and is in accord with previous studies in which exclusive formation of **15**, in preference to **16**, was observed,[35] and our observation that oxidation of **14** with SbF_5 in SO_2ClF solution at −78 °C results only in the formation of **15**.

C. The 1,3,5,7-Tetraphenylcyclooctatetraene Dication. 1,3,5,7-Tetraphenylcyclooctatetraene (**17**) was prepared according to the procedure of White and Dunathan.[38] The careful addition of a suspension of **17** in SO_2ClF to excess SbF_5-SO_2ClF at −78 °C immediately resulted in the formation of a deep red solution. The ^1H NMR spectrum of this solution displays a broad singlet at δ 9.62 and two broad multiplets at δ 8.7 and 8.2, of relative area 1:2:3, respectively, which can be assigned to the corresponding dication **18** (Figure 4, Table I). The ^{13}C NMR spectrum of dication **18** was obtained at −90 °C and exhibited the two cyclooctatetraene dication carbon absorptions at $\delta^{13}C$ 174.0 (s) and 168.6 (d), the phenyl rings ipso carbon absorptions at $\delta^{13}C$ 125.8 (s), and the remainder of the phenyl ring carbons as broadened resonances at $\delta^{13}C$ 137, 132, and 135 which only became slightly sharpened at −30 °C (Table I). Owing to the availability of only small quantities of **17** it was not possible to further resolve the phenyl carbon shifts and, therefore, these data and assignments must be considered tentative.



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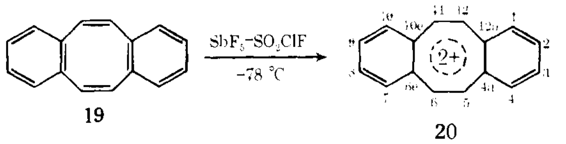
D. The *sym*-Dibenzocyclooctatetraene Dication. The *sym*-dibenzocyclooctatetraene dication (**20**) was prepared by the direct two-electron oxidation of *sym*-dibenzocyclooctatetraene (**19**)[39] by SbF_5[20] in SO_2ClF solution at −78 °C.



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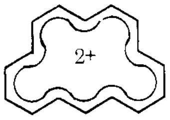
The ^1H NMR spectrum of **20** in SbF_5-SO_2ClF solution at −70 °C consists of two sharp singlets at δ 10.87 and 9.80 of relative area 1:2, respectively (Table II). Hence the signal at δ 10.87 is assigned to $H_{5,6,11,12}$ and that at δ 9.80 to the coincidental set $H_{1,4,7,10}$ and $H_{2,3,8,9}$.

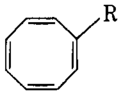
The FT ^{13}C NMR spectrum of **20** in SbF_5-SO_2ClF solution at −70 °C consists of four resonances at $\delta^{13}C$ 145.5 (d), 148.6 (s), 150.9 (d), and 160.1 (d) (Table II). The resonance at δ 148.6 can be unequivocally assigned to $C_{4a,12a,6e,10e}$ on the basis of its unique multiplicity in the off-resonance ^1H-decoupled ^{13}C NMR spectrum of **20**. The further assignment of $C_{5,6,11,12}$ to the most deshielded resonance at $\delta^{13}C$ 160.1 is reasonable as both the ^1H NMR spectrum and HMO calculations[40] of **20** indicate that $C_{5,6,11,12}$ are substantially electron deficient relative to $C_{1,4,7,10}$ and $C_{2,3,8,9}$. The resonance of $C_{1,4,7,10}$ and $C_{2,3,8,9}$ in **20** at considerably lower field than in **19** (Table II) does, however, indicate that the donation of π-electron density from these positions into the cyclooctatrienediylium ring in **20** is occurring.[3a,b,22c,25] Hence delocalization of *all* 14 π electrons in **20** about the 16 carbon atom periphery is indicated. This observation suggests an electronic and structural similarity between **20** and the [16]annulene dication (**21**),[42] and indicates that evidence for the dicationic nature of **20** might be obtained by comparison of the average ^{13}C NMR shift of **20** with that of **21**. In doing this the dicationic nature of **20** becomes apparent as the *average* ^{13}C NMR shift of **20** is calculated to be δ^{13}C 151.3 (Table II), which is indeed very similar in magnitude to both the *average* ^{13}C NMR shift predicted for **21** by the Spiesecke–Schneider relationship (δ^{13}C 148.9)[26] and to that recently determined experimentally for **21** (δ^{13}C 154.3).[42,43] The dicationic nature of **20** is further demonstrated by the observation that the total increase in the ^{13}C NMR shielding of **20** relative to **19** is 294.8 ppm (Table II), which accords well with the 319.0-ppm increase predicted by the Spiesecke–Schneider correlation to accompany a two π-electron oxidation.[3a,b,22c,25,26]



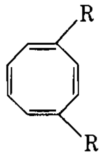
21

An SbF_5–SO_2ClF solution of **20** may be heated to at least 0 °C without undergoing isomerization or thermal decomposition.

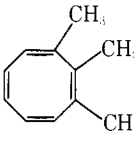
E. Attempted Preparation of the Parent (Unsubstituted), Methyl-, Bromo-, Chloro-, 1,4-Diethoxy-, 1,4-Diphenyl-, 1,2,3-Trimethyl-, and Octaphenylcyclooctatetraene Dications. Attempts were also made to directly oxidize the cyclooctatetraenes **7** and **22–28** to the corresponding dications. In all cases attempted two-electron oxidation of the above cyclooctatetraene precursors to the dication with SbF_5[20] in SO_2ClF at various temperatures resulted in the obtainment of a solution whose ^{1}H NMR spectrum consisted only of broadened, nondiscernible absorptions which provided no evidence for the formation of the desired aromatic dications.



7, R = H
22, R = CH_3
23, R = Br
24, R = Cl



25, R = OCH_2CH_3
26, R = C_6H_5



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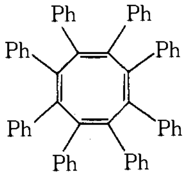
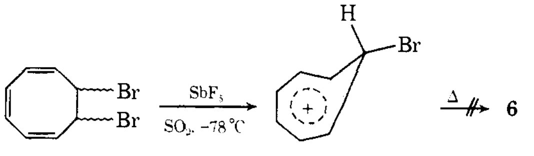


28

A second approach utilized in our efforts to prepare the unsubstituted cyclooctatetraene dication **6** was attempted ionization of the *exo*-8-bromohomotropylium ion **29**[17e] with SbF_5 in SO_2 solution. Heating an SbF_5–SO_2 solution of **29** at 55 °C for 50 min or at approximately −10 °C for 1 year resulted only in decomposition with no evidence for the formation of **6**.



29

Summary

The ^{1}H and ^{13}C NMR spectroscopic characterization of the reported new cyclooctatetraene dications indicates these ions possess those characteristics expected of a C_8 6 π aromatic system and hence further extends the evidence for the great predictive utility of the 4*n* + 2 Hückel rule.

Experimental Section

A. Materials. Cyclooctatetraene (Badische Anilin und Soda Fabrik AG) was redistilled at 30 °C (15 mm) before use. Methyl-,[45] bromo-,[45] chloro-,[45] 1,4-dimethyl-,[21] 1,3,5,7-tetramethyl-,[19] 1,3,5,7-tetraphenyl-,[38] 1,2,3-trimethyl-,[46] and *sym*-dibenzocyclooctatetraene[39] were prepared according to literature procedures. 1,4-Diethoxy- and 1,4-diphenylcyclooctatetraene were kindly provided by Dr. M. Oda (Tohoku University, Japan) and octaphenylcyclooctatetraene[47] similarly by Dr. H. H. Freedman (Dow Chemical Co.) to whom we are grateful for the samples. Fluorosulfuric acid was doubly distilled, and antimony pentafluoride triply distilled, before use.

B. Two-Electron Oxidation of Cyclooctatetraenes in SbF_5–SO_2ClF. In general, the cyclooctatetraene dications were prepared by the slow addition of the precursors in SO_2ClF (either dissolved or as a suspension) at −78 °C directly to a well-stirred SbF_5–SO_2ClF solution at −78 °C to give an approximately 10% solution of the dication which was immediately transferred to a precooled NMR tube for direct study. Details of the preparation of the dications were similar to those previously reported.[48]

C. Nuclear Magnetic Resonance Spectroscopy. 1. Proton Nuclear Magnetic Resonance Spectra. ^{1}H NMR spectra were obtained on either a Varian Associates Model A56/60 or HA-100 NMR spectrometer. The FT ^{1}H NMR spectra were obtained from the latter instrument equipped with a FT-100 Fourier transform accessory (V-4357 pulsing and control unit). Field/frequency regulation was maintained by the spectrometer's homonuclear lock system. The free induction signal derived after each pulse was digitized and accumulated in a Varian 620/1 computer (8K). Fourier transform of the accumulated free induction signal gave the frequency spectrum.[49] All these instruments were equipped with variable temperature accessories, and proton chemical shifts are referenced to external (capillary) Me_4Si.

2. Carbon Nuclear Magnetic Resonance Spectra. ^{13}C NMR spectra were obtained by the Fourier transform method on a Varian Associates Model XL-100 NMR spectrometer equipped with a broad-band proton decoupler and variable temperature probe. The complete details of the instrumentation and techniques employed have been described previously.[50] Proton-carbon coupling constants were measured directly from spectra recorded in the gyro-gate mode[25a,b] of operation. In the cases of ^{13}C NMR spectra where only the multiplicities of the carbon resonances are reported, the multiplicities of these resonances were obtained from the off-resonance ^{1}H-decoupled experiments.[25a,b]

Acknowledgment. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

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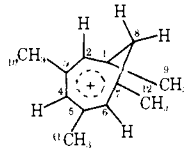
(29) In addition to obtaining 11 this reaction was accompanied by the formation of varying amounts of homotropylium ion i. ^{1}H NMR (SbF_5–SO_2ClF, −70 °C, δ_{Me_4Si}) $H_{2,6}$ 7.81 (s); H_4 7.96 (s); H_8 (endo) 1.16 (d, $J = 10.0$ Hz), H_8 (exo) 3.88 (d, $J = 10.0$ Hz), $H_{9,12}$ and $H_{10,11}$ 2.70 (s), 2.98 (s). ^{13}C NMR (SbF_5–SO_2ClF, −70 °C, δ_{Me_4Si}) $C_{1,7}$ and $C_{3,5}$ 164.7 (s), 174.1 (s); $C_{2,6}$ 140.9 (d, ~160); C_4 139.6 (d, ~160), C_8 45.6 (unresolved (d,d) or (t), ~142); $C_{9,12}$ and $C_{10,11}$ 29.0 (q, 129.9), 27.6 (q, 130.3). i presumably results from pro-



i

tonation of **10** by the protic impurities which are always present in the SbF_5, despite careful purification.[30] Cation i is not an intermediate in the formation of 11 and was prepared independently by protonation of **10** with FSO_3H in SO_2ClF solution at −78 °C. The ^{1}H NMR shifts of 7, **10**, **11**, **13**, and i reported here are uniformly 0.67 more shielded than those reported in ref 1b and are considered to be more accurate.

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(32) Reduction of **10** with potassium in ND_3, a medium where solvation factors gain considerable importance, gives rise to a highly symmetrical planar dianion species: δ_{Me_4Si} 5.47 (s, 4 H) and 2.82 (s, 12 H) utilizing Me_3N as internal standard. The NMR of this dianion, when generated by K/THF reduction, indicates reduced symmetry, probably due to the presence of tighter ion pairing with the potassium ions: L. A. Paquette, J. F. Hansen, and T. Kakihana, *J. Am. Chem. Soc.*, **93**, 168 (1971).

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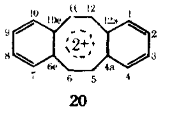

20

$q_{4a,12a,6e,10e} = 0.873$

$q_{5,6,11,12} = 0.766$

$q_{1,4,7,10} = 0.951$

$q_{2,3,8,9} = 0.911$

The following assumptions were made in the HMO calculation for **20**: (a) $\int \phi_r \phi_s d\tau = 0$ for $r \neq s$; $\int \psi_r \psi_s d\tau = 1$ for $r = s$; (b) all $\int \psi_r H \psi_s d\tau = \beta$ for $r \neq s$ and atom r σ-bonded to atom s, all $\int \psi_r H \psi_s d\tau = \alpha$ for $r = s$.

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(43) The dicationic nature of **20** is further reinforced by the observation that the *average* ^{13}C NMR shielding observed in **20** is δ ^{13}C 151.3 which is in good accord with the *average* ^{13}C NMR shielding of δ ^{13}C 152.7 predicted for **20** by a related Spiesecke–Schneider treatment which correlates *average* π-electron densities to *average* ^{13}C NMR chemical shifts in fully conjugated π systems ($\delta\,^{13}C_{av} - 156.8\,\rho_{av} + 289.9$)[44].

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Photochemistry of Bicyclo[3.2.1]octan-6-ones. Stereoselectivity of Hydrogen Transfer in Disproportionation of Biradical Intermediates[1,2]

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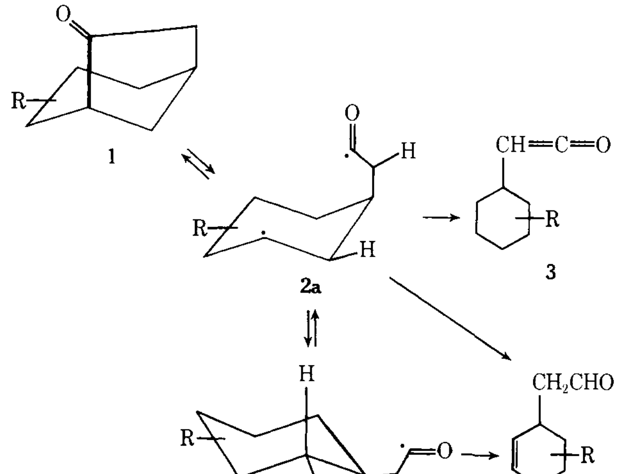
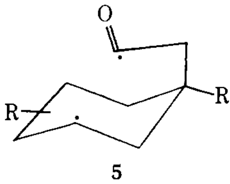
Abstract: The stereoselectivity of disproportionation of biradicals derived from three bicyclo[3.2.1]octan-6-ones, **6–8**, has been investigated through preparation and photolysis of the stereospecifically deuterated species **10**, **11**, and **24–27**. The results collected in Table I indicate that in disproportionation of **2e** (R = H) to aldehyde **4** (R = H) axial hydrogen is transferred $\sim$95% of the time, and it is suggested that this is primarily a stereoelectronic effect favoring scission of the carbon–hydrogen bond lying closest to the plane of the adjacent p orbital bearing free spin. The results in Tables II, III, and IV show an important element of steric control in disproportionation of **2a** to form ketene **3** and aldehyde **4**. In **46** with a geminal methyl substituent at C(1) this occurs $\sim$94% from **48** (transfer of exo hydrogen) and $\sim$6% from **49** (transfer of endo hydrogen). In biradical **47** with only hydrogen at C(1) the side chain has more freedom of rotation, and hydrogen is transferred from all three possible rotational conformers, $\sim$52% from **48**, $\sim$19% from **49**, and 29% from **50** (transfer of ring hydrogen).

In earlier investigations of substituted bicyclo[3.2.1]-octan-6-ones (**1**) we showed that **2a**, the biradical intermediate formed on photochemical α-cleavage of these ketones, undergoes conformational relaxation before disproportionation.[3] Thus in ketones for which the inverted conformer **2e** is more stable, all disproportionation occurs from **2e** and leads only to aldehyde **4**. For systems in which the initially formed conformer **2a** is the more stable, the situation is somewhat more complicated, since disproportionation to either ketene **3** or aldehyde **4** is geometrically possible. In practice, however, both **3** and **4** are formed only when the geminal substituent (R′ in **5**) is hydrogen. The ketones examined which disproportionate solely from **2a** and in which this substituent was an alkyl group (methyl or *tert*-butyl) yielded only ketene **3** on irradiation. This result was ascribed to a steric effect of the geminal substituent, acting to disfavor certain conformations of the acyl radical side chain. The behavior of ketones for which significant populations of both **2a** and **2e** could be expected on conformational grounds also was qualitatively consistent with these principles. In addition to these conformational and steric factors, we suggested that stereoelectronic effects might play a role in disproportionation of **2a** and **2e**.



With this fund of information at hand we undertook deuterium labeling experiments designed to explore the stereoselectivity for transfer of hydrogen in disproportionation of **2a** and **2e**. We were interested not only in a more complete description of the rearrangements of specific bicyclo[3.2.1]-octan-6-ones but also more broadly in the possibility of defining the roles of both steric and stereoelectronic effects in such hydrogen transfer processes. Previous studies[4-6] in other systems have shown that intramolecular disproportionation of acyl alkyl biradicals is sometimes quite stereoselective, but in general the reasons for this stereoselectivity are poorly understood and the question of thermodynamic or kinetic control is unanswered. In this report we describe the preparation and photolysis of appropriate deuterated isomers of **6–8**, three bicyclooctanones from our earlier work[3] which were chosen for the present study. The results demonstrate that highly stereoselective behavior can result from operation of both steric and stereoelectronic factors in these intermediates. Furthermore, they provide qualitative evidence that the rates of ring inversion and side chain rotation can be faster or slower than



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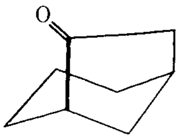

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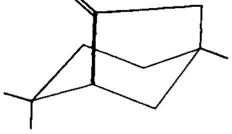

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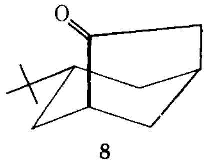

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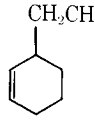

9