Stable Carbocations. 215.[1] ^{13}C Nuclear Magnetic Resonance Spectroscopic Study of the Benzenium, Naphthalenium, and Anthracenium Ions

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Abstract: The parent benzenium (1), naphthalenium (2), and anthracenium ions (3) have been prepared and studied by ^{1}H and ^{13}C NMR spectroscopy. The 270-MHz ^{1}H and 67.89-MHz ^{13}C NMR spectra of the parent benzenium ion display temperature dependence and at -135 °C ^{1}H and ^{13}C NMR spectra were obtained which corresponded to the observation of the "static" benzenium ion. The ^{13}C NMR chemical shifts of the "static" benzenium ion are interpreted in terms of the distribution of positive charge in this species. The pattern of the delocalization of positive charge in 1 suggests the approximate C_{2v} symmetry of this species and the absence of antihomoaromatic character in this potentially anti-Hückeloid system. The ^{13}C NMR shieldings of the "static" parent naphthalenium and anthracenium ions have also been measured and interpreted in terms of the change density distributions present in these respective species. Comparison of the ^{13}C NMR shielding of 2 and 3 with those obtained for a series of substituted naphthalenium and anthracenium ions, respectively, allowed the influence of these substituents upon the electronic structure of these arenium ions to be evaluated. The effect of benzannelation upon the electronic structure of a benzenium ion was also investigated through comparison of the ^{13}C NMR parameters of 1, 2, and 3.

Introduction

Arenium ions have been well established as intermediates in electrophilic substitution reactions, as well as in numerous acid-catalyzed transformations (i.e., isomerizations, transalkylations, etc.) of aromatics.[3] Thus it is understandable that a considerable effort has been expended over the past years to elucidate the electronic structures of arenium ions through their characterization by varied theoretical (quantum mechanical calculations) as well as experimental (basicity studies, X-ray crystallography, UV and IR spectroscopy, and ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy) methods.[3] To the present, however, the simplest arenium ion, namely, the benzenium ion (1),

1   2   3
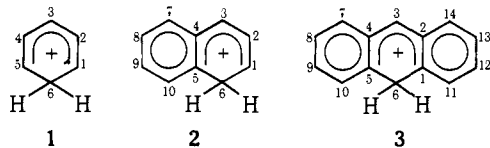
has eluded its observation by NMR spectroscopy as a "static" species.[4] Moreover, neither the naphthalenium (2)[5] nor the anthracenium (3)[6] ion has yet been fully characterized, particularly by ^{13}C NMR spectroscopy.

Since ^{13}C NMR spectroscopy is at the present time the most suitable technique available for the structural study and determination of charge distribution patterns in carbocations,[7] the application of this method to elucidate the electronic

structural features of these fundamentally important ions seemed particularly appropriate. We also wish to report our successful observation of the "static" parent benzenium ion allowing the detailed characterization of the "big three" of arenium ions by ^{13}C NMR spectroscopy under superacidic conditions. In each case we have also obtained the ^{13}C NMR parameters of a series of substituted derivatives which, upon comparison with those of the related parent ions, provide insight into the perturbing influence of these substituents on the arenium ions' electronic structure.

Results and Discussion

1. The Observation and Characterization of the Parent Benzenium Ion as a "Static" (Nonequilibrating) Species by ^{1}H and ^{13}C NMR Spectroscopy. In contrast to the extensive body of information which has become available over the past 2 decades on the preparations, properties, and structural features of a wide variety of substituted benzenium ions,[3] the parent benzenium ion (1) has remained elusive.[4] Indeed, the mere preparation of 1 has remained a longstanding challenge.[3,4] In our initial studies[4] in which we described the first preparation of 1 under superacidic, nonnucleophilic conditions the temperature-dependent 100-MHz ^{1}H and 25.1-MHz ^{13}C NMR spectra obtained for the parent benzenium ion did not correspond to those of the "static" benzenium ion 1, but rather to a set of benzenium ions 1a–f whose spectra were time averaged

Table I. ^{1}H and ^{13}C NMR Parameters of the Benzenium Ion[a]

	proton and carbon-13 chemical shifts and multiplicities							
	proton				carbon-13			
	$H_{1,5}$	$H_{2,4}$	H_3	$H_{6,6'}$	$C_{1,5}$	$C_{2,4}$	C_3	C_6
1	9.7 (br)[b,c]	8.6 (br)	9.3 (br)	5.6 (br)	186.6 (d, br)[b,d]	136.9 (d, br)	178.1 (d, br)	52.2 (t, br)
4	7.33 (s)[f]	7.33 (s)	7.33 (s)	7.33 (s)	129.7 (d)[g]	129.7 (d)	129.7 (d)	129.7 (d)

[a] Chemical shifts are in parts per million from external (capillary) Me$_4$Si. Multiplicities are given in parentheses: s = singlet, d = doublet, t = triplet, br = broad. [b] Spectrum recorded on Bruker HX-270 NMR spectrometer. [c] In SbF$_5$-FSO$_3$H-SO$_2$ClF-SO$_2$F$_2$ solution at -140 °C. [d] In SbF$_5$-FSO$_3$H-SO$_2$ClF-SO$_2$F$_2$ solution at -135 °C. [e] In CDCl$_3$ solution at ambient temperature. [f] Spectrum recorded on Varian Associates A-60A NMR spectrometer. [g] From ref 7a, converted to parts per million relative to external Me$_4$Si utilizing δ_{13C} (external Me$_4$Si) = δ_{13C} (internal) + 1.0.
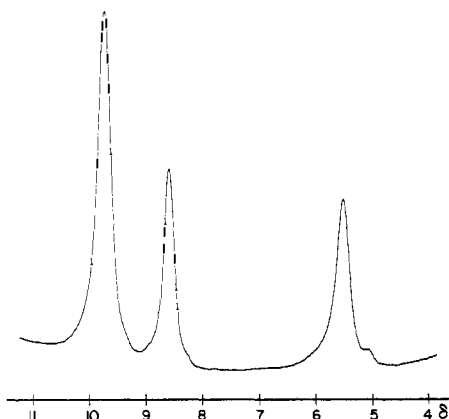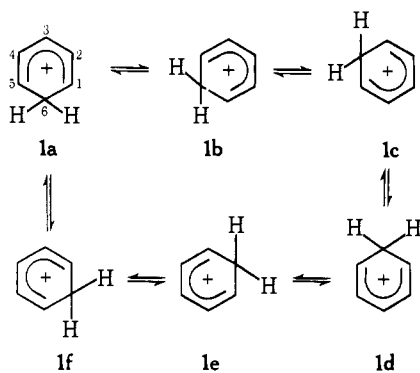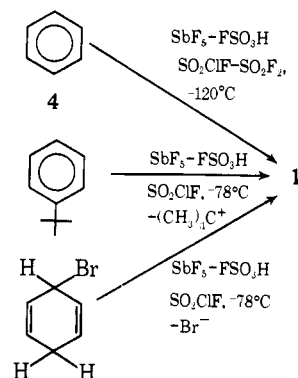

Figure 1. The 270-MHz FT ^{1}H NMR spectrum of the "static" benzenium ion in SbF$_5$-FSO$_3$H-SO$_2$ClF-SO$_2$F$_2$ solution at -140 °C.

owing to their interconversion via a series of intramolecular 1,2-hydrogen shifts at rates exceeding that of the NMR time

scale even at the lowest obtainable solution temperature (-135 °C, below which viscosity broadening was encountered). Since the rate of interconversion at coalescence for exchanging sites is directly relatable to the differences in the resonating frequencies of the exchanging sites,[8] we decided to further study the temperature dependence of the ^{1}H and ^{13}C NMR spectrum of C$_6$H$_7^+$ at higher applied magnetic fields, specifically at 270 and 67.89 MHz, respectively.
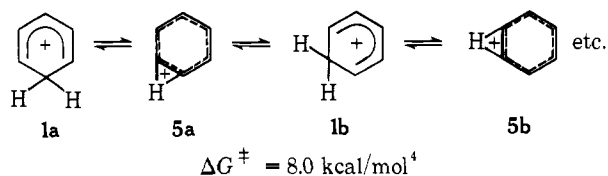
The parent benzenium ion was prepared by protonation of benzene (**4**) with SbF$_5$-FSO$_3$H in SO$_2$ClF or in SO$_2$ClF-SO$_2$F$_2$ at -120 °C. Alternatively solutions of **1** may also be prepared upon the dealkylation of *tert*-butylbenzene[9] or the ionization of 3-bromo-1,4-cyclohexadiene[10] in SbF$_5$-FSO$_3$H-SO$_2$ClF solution at -78 °C. The 270-MHz FT ^{1}H NMR spectrum of an SbF$_5$-FSO$_3$H-SO$_2$ClF-SO$_2$F$_2$ solution

of **1** was recorded at -140 °C (Figure 1, Table I). At this high field the coalescence temperature is raised sufficiently and consequently the spectrum obtained under these conditions corresponds to that of the "static" benzenium ion. The 270-MHz ^{1}H NMR spectrum of **1** in SbF$_5$-FSO$_3$H-SO$_2$ClF-SO$_2$ClF solution at -140 °C consists of three slightly broadened ($\nu_{1/2} \simeq 80$ Hz) resonances centered at δ 5.6, 8.6, and 9.7 of relative area 2:2:3, respectively. Irradiation of the absorption of δ 9.7 in a double resonance experiment revealed the presence of a previously enveloped broad resonance experiment revealed the presence of a previously enveloped broad resonance at about δ 9.3 (relative area 1). Thus, the band at δ 9.7 is due to near coincidence of the absorptions of the 1, 5, and 3 protons. The proton resonances are hence assigned to the methylene protons (H$_{6,6'}$), H$_{2,4}$, and the partially coincidental set of H$_{1,5}$ and H$_3$, respectively (Figure 1, Table I). The failure of these absorptions to display resolved fine structure is attributable to some limited equilibration of **1a-f**, which, even at -140 °C, is still sufficiently rapid relative to the NMR time scale to collapse the multiplets' structure.[8]

The close correlation of the ^{1}H NMR spectral parameters, exhibited by the "static" benzenium ion with those previously estimated[4] from a partially coalesced 100-MHz ^{1}H NMR spectrum of **1** at -129 °C, and the approximate C_{2v} symmetry of **1** (see subsequent discussion) certainly indicate that the Arrhenius activation energy of ca. 10 kcal mol^{-1} previously reported[4] on the basis of a complete line shape analysis of 100-MHz ^{1}H NMR spectra of **1** near coalescence provides a reasonable approximation of the E_a for the equilibration of **1a-f**. This E_a value, therefore, approximates the energy difference between the parent benzenium ion (**1**) and the parent benzonium ion (**5**), the presumed hydrogen-bridged intermediate (transition state) of this process.

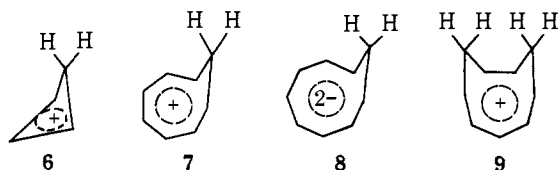The 67.889-MHz FT ^{13}C NMR spectra of **1** were obtained at -135 °C using a solution of C$_6$H$_7^+$ prepared by the protonation of benzene (65% ^{13}C) with SbF$_5$-FSO$_3$H in SO$_2$ClF

$$\Delta G^{\ddagger} = 8.0 \text{ kcal/mol}^4$$

Figure 2. The 67.89-MHz FT ^{13}C NMR spectra of the "static" benzenium ion in SbF_5–FSO_3H–SO_2ClF solution at −135 °C. The lower portion is the proton decoupled spectrum, and the upper is the proton coupled spectrum.

solution at −120 °C (see Experimental Section). The FT ^{13}C NMR spectra obtained under these conditions displayed resonances at δ_{13C} 52.2 (t), 136.9 (d), 178.1 (d), and 186.6 (d) which are assigned to the methylene carbon (C_6), $C_{2,4}$, C_3, and $C_{1,5}$, respectively (Figure 2, Table I). The assignment of the resonance at δ_{13C} 52.2 to the methylene carbon in **1** is unequivocal on the basis of its triplet multiplicity in the ^1H-coupled ^{13}C NMR spectrum and its typical aliphatic shift magnitude.[7a] The further assignments of the pentadienyl carbons in **1** were made as indicated in Table I based on the relative resonance intensities,[7a] by comparison of chemical shifts of the resonances with those observed in relation alkyl-substituted benzenium ions,[4] as well as by consideration of theoretical charge density distributions which have been calculated for **1** by quantum mechanical methods (see subsequent discussion).[11] Allowing the temperature of the solution of **1** to rise to −90 °C and recording its 67.889-MHz FT ^{13}C NMR spectrum (broad-band ^1H decoupled) at this temperature resulted in the obtainment of a single resonance at δ_{13C} 145.9 which indicates that rapid equilibration of **1a-f** is occurring under these conditions. The reversibility of this process was demonstrated upon recooling the sample to −135 °C and obtaining the originally observed ^{13}C NMR spectrum. The line widths of the resonances observed in these ^{13}C NMR spectra exhibited substantial broadening ($\nu_{1/2} > 175$ Hz) which is again attributed to a certain degree of exchange and viscosity broadening, as well as the presence of unresolved ^{13}C–^{13}C spin-spin couplings.

^{13}C NMR shieldings (δ_{13C}) of aromatic systems have been demonstrated to depend primarily upon the local π-electron density (ρ) at each carbon nucleus.[7a,c,d] A least-squares analysis of the data obtained for the 2π-, 6π-, and 10π-electron monocyclic aromatics indicates the relationship (commonly termed the Spiesecke–Schneider relationship) for these systems to be $\delta_{13C} = -159.5\rho + 288.5$.[7a] O'Brien, Hart, and Russell[12] have recently extended the scope of ^{13}C NMR chemical shifts correlatable on the basis of the local π-electron densities at corresponding nuclei to include those of fully conjugated π systems in which all carbons are not necessarily equivalent ($\delta_{13C} = -156.8\rho + 289.9$). They were furthermore successful in relating the *average* π-electron densities (ρ_{av}) of such systems to *average* ^{13}C NMR chemical shifts ($\delta_{13C_{av}} = -156.8\rho_{av} + 289.9$). The consistency of the magnitude of the observed ^{13}C NMR shieldings with the assignment of the observed species as the parent benzenium ion (**1**) is thus readily demonstrated on this basis upon comparison of the *average* ^{13}C NMR shieldings of the olefinic carbons in **1** (δ_{13C} 165.0, Table I) with that predicted for a 4π-5C system (δ_{13C} 164.5).[12]

The question of the degree of overlap between the termini of a polyenyl fragment interrupted in one or more positions by an intervening saturated linkage[13] in systems such as the monohomocyclopropenium cation (**6**),[13,14] the monohomotro-

of significant overlap in the above cases may be attributed to the realization of additional delocalization energy upon partially completing the potentially Hückeloid aromatic array (homoaromaticity).[13] We therefore considered it to be of substantial interest to examine whether there is any indication of 1,5 overlap in **1**, since is this case a partial closure of the π array across the intervening methylene carbon would result in the formation of a homocyclopentadienyl cation (**10**), a

potentially Hückeloid *antihomoaromatic* 4π species. **1** may be envisioned as a resonance hybrid of the cyclohexadienyl cations **1'-1'''** and the 1,5 π-overlap contributors **1''''-1'''''**.
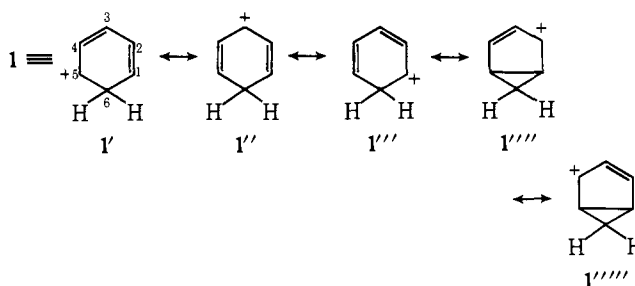
It is thus apparent that whereas the allylic contributors **1'-1'''** localize positive charge at $C_{1,5}$ and C_3, the homoallylic contributors **1''''-1'''''** localize charge at $C_{2,4}$. Hence, it is expected that the π-electron density distribution in **1** should accurately reflect the importance of 1,5 overlap in this species. Although a quantitative assessment of the π-electron densities of the carbon atoms incorporated into the pentadienyl fragment of **1** from their ^{13}C NMR chemical shifts would require that corrections be introduced into the ^{13}C NMR shieldings for the intervening methylene group,[7a,17] comparison of the ^{13}C NMR shieldings of the sp²-hybridized carbons in benzene,[7a,18] 1,3-cyclohexadiene (**11**),[7a,18] and cyclohexene (**12**)[7a,18] certainly suggests that the magnitude of these corrections is indeed small and hence their neglect is a reasonable approximation. Comparison of $C_{1,5}$, $C_{2,4}$, and C_3's ^{13}C NMR chemical shifts

pylium ion (**7**),[13,15] the monohomocyclooctatetraene dianion (**8**),[13] and the bishomotropylium ion (**9**)[15c,16] has been the subject of substantial controversy over the years. The existence
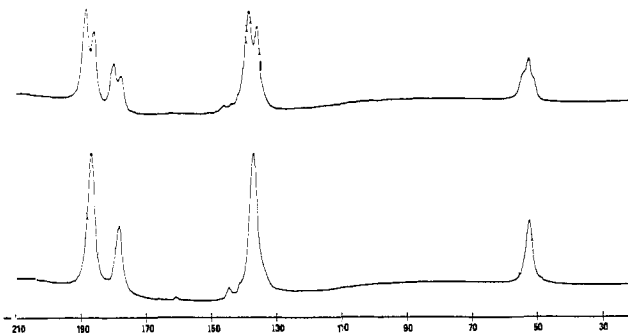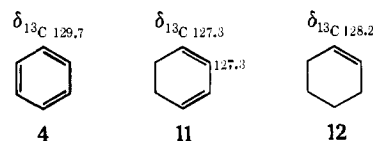
tainly suggests that the magnitude of these corrections is indeed small and hence their neglect is a reasonable approximation. Comparison of $C_{1,5}$, $C_{2,4}$, and C_3's ^{13}C NMR chemical shifts

in **1** with the chemical shift of benzene thus demonstrates that whereas the unit positive charge is distributed rather uniformly over C_1, C_5, and C_3 in **1** minimal charge development is indicated at C_2 and C_4.[7,12] We thus conclude that the π-electron density distribution in **1** is basically allylic in nature, with only minimal, if any, contributions from homoallylic delocalization. These experimental results are in accord with Hückel molecular orbital calculations which predict a decrease in the π-electron delocalization energy enjoyed by a pentadienyl cation upon increasing the π overlap between C_1 and C_5.[19]

Comparison of the ^{13}C NMR chemical shifts of **1** with those of the corresponding positions in the parent bicyclo[3.1.0]-hexenyl cation **13**[20] furthermore indicates that the equilibrium

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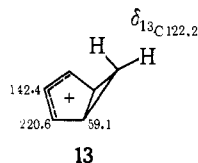
ground-state geometry of the parent benzenium ion contains either a planar or very nearly planar cyclohexadienyl ring since appreciable deformation from a planar C_{2v} structure, in a manner as depicted in **14**, would result in the development of


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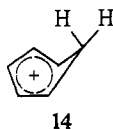
substantial σ overlap between C_1 and C_5 and hence, as evidenced in the ^{13}C NMR shieldings of **13**, a charge density distribution drastically modified from that expected of a cyclohexadienyl cation. The apparent magnetic equivalence of the methylene protons in the 270-MHz ^{1}H NMR spectrum of **1** even at -140 °C further reinforces this conclusion as does the reported X-ray crystal structure determination of **15**[21]


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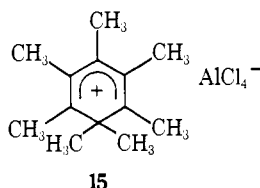
demonstrating the planarity of the cationic cyclohexadienyl ring in this case. Our experimental results hence accord well with the benzenium C_{2v} geometry predicted for the parent $C_6H_7^+$ ion by quantum mechanical calculations.[11]

In contrast to the ^{13}C NMR shieldings of the allylic positions in 3-alkylbenzenium ions, which evidence a rather strong polarization of positive charge toward C_3,[4] the similarity in magnitude of the ^{13}C NMR shieldings of C_1, C_5, and C_3 in **1** indicates a rather uniform distribution of positive charge over these three allylic positions with the 8.5-ppm deshielding of C_1 and C_5 relative to C_3 suggesting a slight polarization of the positive charge toward the terminal, methylene-substituted positions. The direction of this polarization may be rationalized on the basis that the terminal carbocation centers of the pentadienyl fragment interact hyperconjugatively with the methylene C–H bonds. Such hyperconjugative interaction has previously been suggested to be operative in arenium ions on the basis of evidence provided by an analysis of the infrared spectrum of the anthracenium ion[22] and quantum mechanical calculations[11,23] of benzenium ions. Comparison of the ^{13}C NMR shieldings of C_3 in **1** ($\delta_{^{13}C_3}$ 178.1) with that of the significantly more shielded corresponding position in the ethylenebenzenium ion **16** ($\delta_{^{13}C_3}$ 155.4),[24] however, indicates that the hyperconjugative donation of electron density into the electron-deficient pentadienyl fragment from the methylene's

exocyclic bonds is not as important in the former as it is in the latter case.


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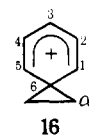
2. ^{13}C NMR Spectroscopic Study of the Parent, 1-Methyl-, and 3-Methylnaphthalenium Ions.

The parent (**2**), 3-methyl- (**17**), and 1-methylnaphthalenium ions (**18**) were prepared by

19, R = R' = H	**2**, R = R' = H
20, R = CH_3; R' = H	**17**, R = CH_3; R' = H
21, R = H; R' = CH_3	**18**, R = H; R' = CH_3
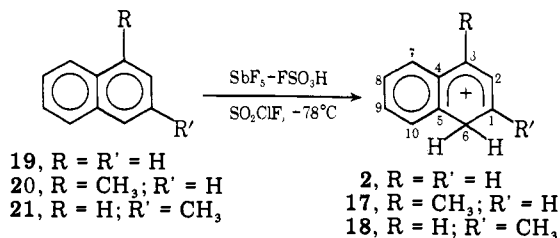
the protonation of the appropriate naphthalenes with SbF_5–FSO_3H (1:1) in SO_2ClF solution at -78 °C. In each case the obtained solutions displayed in their 60-MHz ^{1}H NMR spectra only resonances attributable to the indicated isomeric naphthalenium ion. These spectra obtained were identical with those previously reported by these laboratories for these ions.[5]

The FT ^{13}C NMR parameters of the "frozen-out" naphthalenium ions **2** (Figure 3), **17**, and **18** as well as those of their neutral precursors, **19–21**, respectively, are summarized in Table II. The assignment of the methylene carbon resonance in each of the naphthalenium ions is unequivocal on the basis of its triplet multiplicity in the corresponding off-resonance ^{1}H-decoupled ^{13}C NMR spectrum.[7a] Additional assignments of the ^{13}C NMR resonances of the studied naphthalenium ions were made on the basis of their multiplicities in the corresponding off-resonance ^{1}H-decoupled ^{13}C NMR experiments[7a] and comparison with the ^{13}C NMR chemical shifts of related positions in benzenium and anthracenium ions (see subsequent discussion), as well as those of the electronically related allyl cation **22**.[25] C_1 and C_3 in the parent naphthalenium ion were

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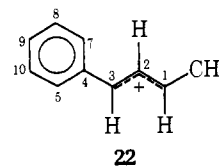
unequivocally assigned to the resonances centered at $\delta_{^{13}C}$ 185.6 and 180.9, respectively, in the ^{13}C NMR spectrum of **2** on the basis of experiments in which H_1 and H_3 were selectively off-resonance ^{1}H decoupled according to the procedure of Feeney.[28] The resonances which could not be specifically assigned based upon these criteria were assigned on a tentative basis and these assignments are designated as interchangeable.

Although, as previously suggested, an intervening sp^3-hybridized methylene carbon in an arenium ion precludes a quantitative interpretation of the π-electron population dispersed over the olefinic carbon framework on the basis of their ^{13}C NMR chemical shieldings which are not corrected for substituent effects,[7a,17] comparison of the ^{13}C NMR shieldings of the approximately corresponding olefinic carbons in naphthalene (**19**),[7a,18] 1,4-dihydronaphthalene (**23**),[29] and 1,2,3,4-tetrahydronaphthalene (**24**)[7a,18] suggests that these corrections are again small in magnitude relative to the charge-induced shifts which may be expected upon the conversion of **19** to **2**. Hence these corrections can be neglected in a first approximation. Comparison of the *average* ^{13}C NMR chemical shift on the olefinic carbons in **2** ($\delta_{^{13}C}$ 148.6) with that
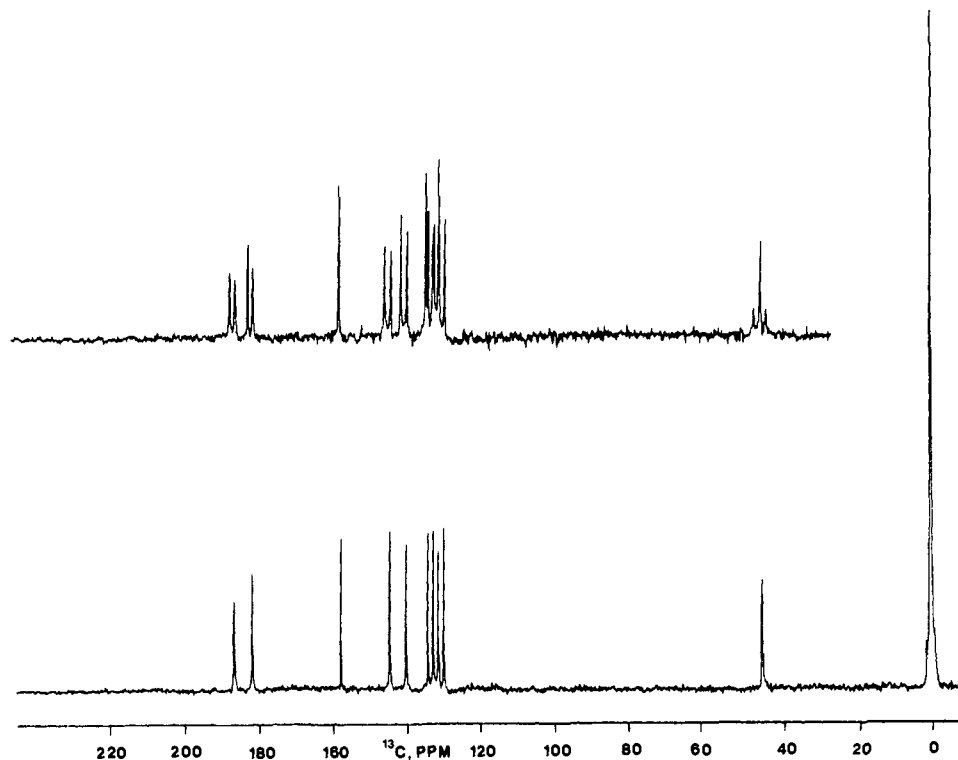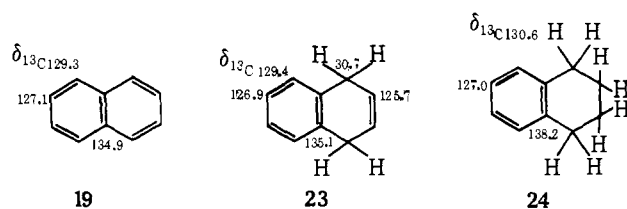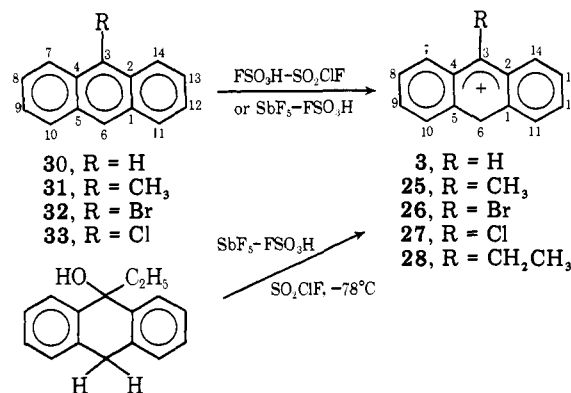
Figure 3. The 25.16-MHz FT ^{13}C NMR spectra of the parent naphthalenium ion in SbF_5-FSO_3H-SO_2ClF solution at -80 °C. The lower portion is the proton decoupled spectrum, and the upper is the off-resonance ^1H-decoupled spectrum.

19   **23**   **24**

predicted by O'Brien's modified Spiesecke–Schneider treatment[12] for a 8π-9C system (δ_{13C} 150.5) consequently provides strong support for the assignment of **2** as the parent naphthalenium ion. The exact demonstration of the monocationic nature of **17** and **18** in a similar manner would require in each of these cases that additional corrections be introduced into the olefinic carbon shieldings for the methyl substituent.[7a,17] The expected similarity of the methyl substituent effects operative in naphthalenium ions and their related neutral precursors allows, however, the demonstration of the monocationic nature of these studied species by comparisons of the *total* increases in ^{13}C NMR shieldings of the olefinic carbons of the naphthalenium ions relative to their related carbons in the naphthalenes with the 156.8-ppm increase predicted by O'Brien's correlation[12] to accompany the π-electron oxidations. The observed *total* increases in the ^{13}C NMR shieldings of **17** and **18**, relative to **20** and **21**, respectively, are 173.7 and 179.7 ppm, respectively, which accord well with the assignment of **17** and **18** as naphthalenium ions. Comparisons of the ^{13}C NMR chemical shifts of the individual carbons in **2**, **17**, and **18** with the approximate positions in their neutral precursors, **19-21**, respectively, indicate that a significant degree of the unit positive charge in each of the naphthalenium ions is localized at C_1 and C_3 and detectable, but lesser, amounts of charge are developed at the formally conjugated positions C_5, C_7, and C_9. Moreover, the obviously enhanced deshieldings of the methylated carbons, relative to the protonated olefinic carbons, in **17** and **18**, as compared with those observed in their neutral precursors demonstrate that replacement of a hydrogen atom with a π donor at an allylic position in a naphthalenium
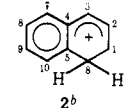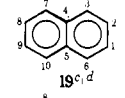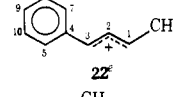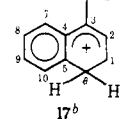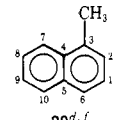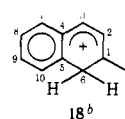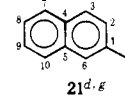
ion results in a further polarization of positive charge toward this center.

3. ^{13}C NMR Spectroscopic Study of the Parent and 3-Substituted Anthracenium Ions.

The parent (**3**), 3-methyl- (**25**), 3-bromo- (**26**), and 3-chloroanthracenium ions (**27**) were

30, R = H	**3,** R = H
31, R = CH_3	**25,** R = CH_3
32, R = Br	**26,** R = Br
33, R = Cl	**27,** R = Cl
	28, R = CH_2CH_3

prepared by the protonation of the appropriate anthracenes with FSO_3H or SbF_5-FSO_3H in SO_2ClF solution at temperatures between -60 and -78 °C. The 3-ethylanthracenium ion (**28**) was conveniently prepared by ionization of the alcohol **29**[30] in SbF_5-FSO_3H-SO_2ClF solution at -78 °C. In each case the only isomeric anthracenium ion detected by ^1H and ^{13}C NMR spectroscopy is that denoted which indicates that protonation of these anthracenes occurs exclusively at C_6. The second-order ^1H NMR spectra obtained for solutions of **3** (100 MHz),[31] **25** (60 MHz),[32] and **28** (60 MHz)[32] were identical with those previously reported in the literature and hence are not discussed here. We considered, however, it to be of importance to further define the ^1H NMR parameters of an ion as fundamental as **3**. To this effect, we obtained the 300-MHz ^1H NMR spectrum of **3**.[33] The 300-MHz ^1H spectrum of **3** (Figure 4) is interpretable on the basis of first-order theory[34] and provides the spectral parameters which are summarized in Table III. The assignments of the resonances of the same

Table II. ^{13}C NMR Parameters of Naphthalenium Ions and Related Compounds[a]

| | carbon-13 chemical shifts and multiplicities | | | | | | | | | | |
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
2[b]	185.6 (d)	132.9 (d)*	180.9 (d)	134.3 (s)	157.4 (s)	44.9 (t)	140.1 (d)**	130.1 (d)*	144.4 (d)**	131.6 (d)*	
19[c,d]	127.1 (d)	127.1 (d)	129.3 (d)	134.9 (s)	134.9 (s)	129.3 (d)	129.3 (d)	127.1; (d)	127.1 (d)	129.3 (d)	
22[e]	205.1 (d)	136.5 (d)	196.9 (d)	135.1 (s)	148.0 (d)		137.0 (d)	132.0 (d)*	149.9 (d)	132.2 (d)*	26.7
17[b]	180.1 (d)	133.4 (d)*	200.4 (s)	133.5 (s)	154.2 (s)	43.2 (t)	136.3 (d)**	130.1 (d)*	142.2 (d)**	131.0 (d)*	25.8
20[d,f]	126.6	127.8	135.3	134.3	135.3	127.8	125.2	126.7*	126.5*	129.8*	20.1
18[b]	210.9 (s)	133.0 (d)*	177.5 (d)	132.4 (s)	153.4 (s)	47.9 (t)	138.4 (d)**	129.4 (d)*	141.8 (d)**	130.8 (d)	28.0 (d)
21[d,g]	135.7	128.7	128.3	132.6	134.2	127.7	128.4	125.8	126.2	127.9	22.4

[a] Chemical shifts are in parts per million from external (capillary) Me$_4$Si. Multiplicities are in parentheses: s = singlet, d = doublet, t = triplet. Resonances within a spectrum which are labeled with an equivalent number of asterisks have interchangeable assignments. [b] In SbF$_5$–FSO$_3$H–SO$_2$ClF solution at −80 °C. [c] From ref 7a. [d] Converted to parts per million relative to external Me$_4$Si utilizing δ_{13C} (external Me$_4$Si) = δ_{13C} (internal Me$_4$Si) + 1.0. [e] From ref 25. [f] From ref 26. [g] From ref 27.
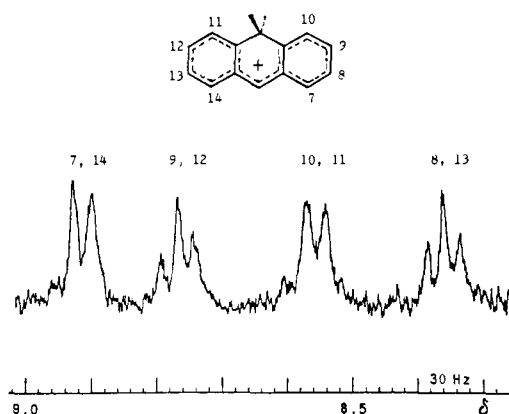

Figure 4. The 300-MHz ^{1}H NMR spectrum of the parent anthracenium ion in SbF$_5$–HF–SO$_2$ClF solution at −55 °C. The aliphatic region is not shown.

Figure 5. The 60-MHz ^{1}H NMR spectrum of **26** in FSO$_3$H–SO$_2$ClF solution at −60 °C.

multiplicity in the 300-MHz ^{1}H NMR spectrum of **3** were made on the basis of the anticipated deshielding of the protons bonded to carbons formally conjugated to the positive charge relative to those which are bonded to carbons which occupy formally nonconjugated positions. The ^{1}H NMR spectral parameters (60 MHz) of the heretofore unreported anthracenium ions **26** (Figure 5) and **27** (Figure 6) are also given in Table III. The low-field doublet in each of these two cases is assigned to H$_{7,14}$ on the basis of the expected deshielding of these protons by a peri (halogen) effect.[35]
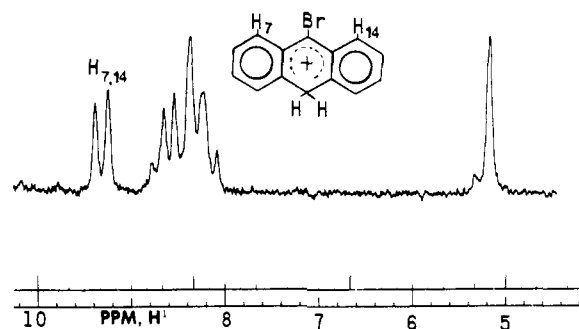
The FT ^{13}C NMR parameters of the anthracenium ions **3** (Figure 7) and **25–28** are summarized in Table IV. Assignments of the ^{13}C NMR resonances in **3**, **25** and **28** were made on the basis of their multiplicities in the off-resonance [1]H-decoupled spectra,[7a] relative resonance intensities,[7a] and comparison with the ^{13}C NMR chemical shifts of the approximately corresponding positions in the related benzhydryl (**34**)[36] or diphenylethyl cation (**35**).[36] In **3**, **25**, and **28**, the relative signal intensity of the resonances at about δ_{13C} 130.5 indicates that the chemical shifts of the C$_{10,11}$ and C$_{8,13}$ carbons were accidently coincidental in each of these cases. Assignments of the ^{13}C NMR spectra of **26** and **27** were made in a similar manner; only in these cases the ^{13}C shifts of the
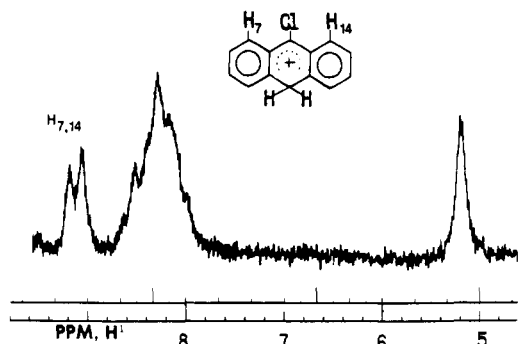
Figure 6. The 60-MHz ^{1}H NMR spectrum of 27 in FSO_3H-SO_2ClF solution at −60 °C.

Table III. ^{1}H NMR Parameters of the Parent, 3-Bromo-, and 3-Chloroanthracenium Ions[a]

	proton chemical shifts, apparent multiplicities, and coupling constants		
	H_3	$H_{6,6'}$	ring protons
3[b,c]	10.0^d	5.52 (s)	$H_{7,14}$: 8.92 (d, 8.5) $H_{8,13}$: 8.33 (t, 7.5) $H_{9,12}$: 8.76 (t, 7.5) $H_{10,11}$: 8.56 (d, 8.5)
26[e,f]		5.18 (s)	$H_{7,14}$: 9.35 (d, 8.5) H_{8-13}: 8.0–8.8 (m)
27[e,f]		5.20 (s, br)	$H_{7,14}$: 9.50 (d, 7.4) H_{8-13}: 7.9–8.6 (m)

[a] Chemical shifts are in parts per million from external (capillary) Me$_4$Si. Apparent multiplicities and coupling constants in hertz are in parentheses: s = singlet, d = doublet, t = triplet, br = broad. [b] Spectrum recorded on Varian Associates HR-300 NMR spectrometer. [c] In SbF$_5$-HF-SO$_2$ClF solution at −55 °C. [d] Obscured by internal lock signal. [e] Spectrum recorded on Varian Associates A56/60 NMR spectrometer. [f] In FSO$_3$H-SO$_2$ClF solution at −60 °C.

analogous bromodiphenylmethyl and chlorodiphenylmethyl cations, respectively, were not available for comparison. Hence several of the assignments in these spectra, as indicated, must be regarded as tentative.

As in the previously discussed cases comparison of the ^{13}C NMR shieldings of the corresponding olefinic carbons common to anthracene (30) and 9,10-dihydroanthracene (36)[7a,18] again
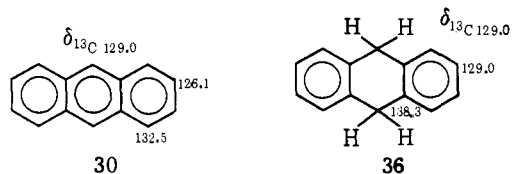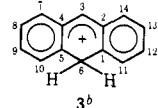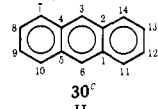

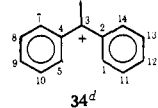30   36

suggests that the corrections[7a,17] which should be included into the ^{13}C NMR shieldings of the olefinic carbons of 3 before the average π-electron density about these positions can be accurately evaluated on this basis, indeed, may be disregarded as a first approximation. Hence comparison of the average ^{13}C shielding of the olefinic carbons in 3 (δ_{13C} 142.9) with that predicted by O'Brien's correlation[12] for a 12π-13C system

Figure 7. The 25.16-MHz FT ^{13}C NMR spectra of the parent anthracenium ion in FSO$_3$H-SO$_2$ClF solution at −80 °C. The lower portion is the proton noise-decoupled spectrum, and the upper is the proton coupled spectrum.

(δ_{13C} 145.2) demonstrates the consistency of these observed shieldings with those expected of an anthracenium ion 3. The carbocationic characters of 25-27 are readily demonstrated by the ob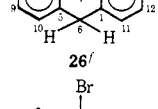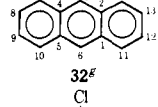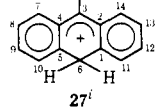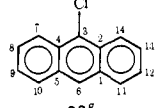servation that the totals of the ^{13}C NMR shieldings of the olefinic carbons in 25-27 exceed the totals of the shieldings of the approximately corresponding positions in 31-33, respectively, by 185.4, 182.2, and 173.8 ppm, respectively. Comparison of the ^{13}C NMR chemical shifts of 28 with those observed in 25 assures the carbocationic nature of the ethylated species.

Studies similar to those previously discussed have demonstrated the dependence of ^{13}C NMR chemical shifts of carbenium ion centers upon the electronic effects of attached aryl substituents.[39] Conversely there also has been found a complementary systematic dependence of the arene ^{13}C NMR shieldings upon the electronic demand of carbenium-type substituents.[7c,d] In each of these cases the systematic response of the ^{13}C NMR shielding of the correlatable sp^2-hybridized center to a distant substitutent is derived from the linear dependency of the ^{13}C NMR shielding of a sp^2-hybridized carbon on the local π-electron density at that position.[7a,c,d] These relationships thus suggest that a comparison of the delocalization patterns in the π-electron systems of an anthracenium ion (i.e., 3 and 25) and the related diphenylcarbenium ion (i.e., 34 and 35, respectively) should be possible by comparison of the ^{13}C NMR shieldings of the structurally related positions which are formally conjugated with the positive charge (maximization of detection of the difference in the π-density distributions) provided that they are remote from the site of perturbation (C$_6$) between the two systems (minimization of the contribution to the difference in ^{13}C NMR shieldings arising from non-charge-related factors, i.e., neighboring-group effects).[7a,c,d] On this basis, the decreased magnitude of the shieldings of C$_3$, C$_{7,14}$, and C$_{9,12}$ in 3 and 25, relative to those observed in 34 and 35, respectively, demonstrates the decreased conjugative electron demand upon these centers in the former, relative to the latter, systems. It further can be inferred that the decreased electron demand upon these formally conjugated centers in the anthracenium ions, relative to that in the corresponding diphenylcarbenium ions, is attributable to the additional hyperconjugative donation of π-electron density into

Table IV. ^{13}C NMR Parameters of Anthracenium Ions and Related Compounds[a]

	C$_{1,5}$	C$_{2,4}$	C$_3$	C$_6$	C$_{7,14}$	C$_{8,13}$	C$_{9,12}$	C$_{10,11}$	CH$_3$	other
3[b]	155.2 (s)	132.8 (s)	183.4 (d)	38.5 (t)	141.6 (d)	130.6 (d)	146.1 (d)	130.6 (d)		
30[c]	132.5 (s)	132.5 (s)	127.0 (d)	127.0 (d)	128.9 (d)	126.1 (d)	126.1 (d)	128.9 (d)		
34[d]	143.6 (d)	138.5 (s)	200.8 (d)		149.3 (d)	133.9 (d)	151.1 (d)	133.9 (d)		
25[e]	153.0 (s)	133.4 (s)	200.5 (s)	38.5 (t)	135.3 (d)	130.5 (d)	144.2 (d)	130.5 (d)	20.7 (g)	
31[c]	132.1 (s)	130.8 (s)	130.7 (s)	125.3 (d)	125.3 (d)	125.8 (d)*	125.3 (d)*	129.7 (d)	14.7 (q)	
35[d]	141.4 (d)	141.7 (d)	229.4 (s)		141.4 (d)	131.7 (d)	148.3 (d)	131.7 (d)	31.4 (q)	
26[f]	152.7 (s)	134.9 (s)	194.2 (s)	38.8 (t)	139.1 (d)*	131.6 (d)*	145.2 (d)	130.3 (d)*		
32[g]	131.7 (s)*	133.2 (s)*	123.4 (s)	128.3 (d)[h]	129.7 (d)**	128.7 (d)**	128.2 (d)**	126.6 (d)**		
27[i]	152.8 (s)	132.9 (s)	191.8 (s)	38.2 (t)	135.4 (d)	131.01 (d)*	145.1 (d)	130.2 (d)*		
33[g]	129.9 (s)*	132.9 (s)*	128.0 (s)*	127.0 (d)	129.5 (d)**	127.8 (d)**	126.6 (d)**	125.7 (d)**		
28[j]	153.6 (s)	132.2 (s)	205.1 (s)	38.6 (t)	134.8 (d)	130.7 (d)	144.2 (d)	130.7 (d)	18.9 (q)	CH$_2$ 27.6

[a] Chemical shifts are in parts per million from external (capillary) Me$_4$Si. Multiplicities are in parentheses: s = singlet, d = doublet, t = triplet, q = quartet. Resonances within a spectrum which are labeled with an equivalent number of asterisks have interchangeable assignments. [b] In FSO$_2$H–SO$_2$ClF solution at −80 °C. The $^1J_{CH}$'s are 162.9 (C$_3$), 129.9 (C$_6$), 168.6 (C$_{7,14}$), 168.0 (C$_{8,13,10,11}$), 168.8 (C$_{9,12}$) Hz. [c] From ref 37, converted to parts per million relative to external Me$_4$Si utilizing δ_{13C} (external) = δ_{13C} (internal) + 1.0. [d] From ref 36. [e] In SbF$_5$–FSO$_3$H–SO$_2$ClF solution at −80 °C. [f] In FSO$_3$H–SO$_2$ClF solution at −70 °C. [g] In CDCl$_3$ solution at ambient temperature. [h] Resonance of C$_6$ in 32 was not observed in this work presumably owing to its coincidence with other, more intense resonances quoted here was taken from ref 38 and converted to parts per million relative to external Me$_4$Si utilizing δ_{13C} (external Me$_4$Si) = δ_{13C} (SCS) (ref 38) + 128.0. [i] In FSO$_3$H–SO$_2$ClF solution at −80 °C. [j] In SbF$_5$–FSO$_3$H–SO$_2$ClF solution at −75 °C.

the former system by the methylene group. These results hence provide the most direct experimental evidence obtained to date for the hyperconjugative interaction of the methylene group

with the termini of the pentadienyl fragment in an arenium ion.

It is further informative to evaluate the relative ability of

the various C_3 substituents (H, CH_3, C_2H_5, Cl, Br) to donate π-electron density in the series of anthracenium ions summarized in Table IV. Since it is fully expected (see preceding discussion) that the $C_{9,12}$ ^{13}C NMR shieldings of these ions should directly reflect their relative π-electron densities,[7a,c,d] the evaluation may be accomplished on this basis. The implementation of this comparison indicates that the relative π-donor ability of the 3-substituents in anthracenium ions increases in the order $CH_3 \simeq C_2H_5 > Cl \simeq Br > H$; this ordering is consistent with that which would be expected on the basis of the σ_R values of these several substituents.[40] The enhanced deshieldings of C_3, relative to the remaining carbons, in **3** and **25-28**, as compared with those observed in the neutral precursors, demonstrate that significant positive charge is localized at the C_3's in the anthracenium ions. Moreover, the substantially enhanced deshielding of C_3 in **25** relative to **3**, as compared with the chemical shift shielding difference observed between the C_3 shifts in the neutral precursors, indicates that replacement of a hydrogen with a π donor at C_3 in an anthracenium ion results in a further polarization of the positive charge toward this center.

4. The Effect of Benzannelation upon the Electronic Structure of the Benzenium Ion. In the preceding discussion we have been primarily concerned with the characterization of the electron delocalization in each of the arenium ions **1-3** and have expanded these discussions to include the effect of substituents within each series. It is informative to proceed further to compare the electron delocalization patterns exhibited in each series of these arenium ions with each other.

The facility with which the ^{13}C NMR shieldings may be related to charge densities in each of these systems provides a convenient basis on which such a comparison can be accomplished.[7a,c,d] Thus the magnitude of the deshieldings observed for the central allylic carbons (C_3's) in the cyclohexadienyl fragments of the benzenium, naphthalenium, and anthracenium ions relative to the corresponding positions in the respective neutral hydrocarbons are 48.4, 51.6, and 55.3 ppm, respectively. The proximity of these values indicates the presence of comparable amounts of positive charge at each of these positions, with the degree of positive charge localization at this position actually increasing slightly in the series $1 < 2 < 3$. Analogous arguments readily demonstrate that monobenzannelation of a cyclohexadienyl cation (i.e., the transformation of **1** to **2**) does not decrease the electron density about the remaining protiated terminal allylic carbon of the cyclohexadienyl fragment (i.e., C_2 in **2**). One is therefore forced on the basis of these data to conclude that mono- or dibenzannelation of a cyclohexadienyl cation does not result in the expected positive charge delocalization away from remote, formally conjugated positions of the cationic polyenyl fragment (as, for example, occurs upon dibenzannelation of a cyclooctatetraene dication),[41] but rather actually appears to slightly polarize additional positive charge *toward* these positions. This rather remarkable effect observed in this series of arenium ions presumably reflects the resistance of the benzenoid moities incorporated into **2** and **3** to disrupt their aromatic sextets by delocalization of excess π-electron density to remote carbenium centers. This conclusion is in good accord with, and, moreover, provides insight into, the previously reported observation that the effect of enhancing the basicity for anthracene by methyl substitution at C_3 is an order of magnitude greater than that for the analogous substitution at C_{10}.[42]

Experimental Section

Materials. Benzene, alkylbenzenes, naphthalenes, and anthracenes, unless otherwise designated, were commercially available reagents of high purity. 3-Bromo-1,4-cyclohexadiene[10] and the alcohol **29**[30] were prepared according to literature procedures. Benzene (65% ^{13}C)

was obtained from Merck Sharp and Dohme of Canada, Ltd. Fluorosulfuric acid and antimony pentafluoride were each twice distilled before use. FSO_3H-SbF_5 refers to a 1:1 M solution of these two reagents.

Preparation of Ions. A. The Benzenium Ion (1). $SbF_5-FSO_3H-SO_2ClF$ solutions of **1** were prepared upon the dropwise addition of a SO_2ClF solution of either *tert*-butylbenzene or 3-bromo-1,4-cyclohexadiene at -78 °C to an approximately fourfold molar excess of SbF_5-FSO_3H in SO_2ClF at -78 °C which was vigorously stirred with a Vortex-Genie. Alternatively, $SbF_5-FSO_3H-SO_2ClF$ and $SbF_5-FSO_3H-SO_2ClF-SO_2F_2$ solutions of **1** were obtained upon the dropwise addition of a SO_2ClF solution of benzene at -120 °C to an approximately fourfold molar excess of SbF_5-FSO_3H in SO_2ClF or $SO_2ClF-SO_2F_2$ (2:1 v/v) at -120 °C, respectively, which was vigorously stirred with a Vortex-Genie. For the ^{13}C NMR spectroscopic study of **1** it was found to be necessary to utilize dilute (ca. 0.05 M) solutions of **1** to avoid unacceptable heat generation in the sample during ^1H decoupling. Consequently, benzene (65% ^{13}C) was employed for the preparation of **1** in these cases to allow obtainment of well-resolved ^{13}C NMR spectra over an acceptable time period of data accumulation.

B. Naphthalenium Ions. Solutions of these ions were prepared upon the dropwise addition of either a slurry or solution of the precursor in SO_2ClF at -78 °C to an approximately fivefold molar excess of SbF_5-FSO_3H in SO_2ClF at -78 °C which was vigorously stirred with a Vortex-Genie.

C. Anthracenium Ions. Solutions of these ions were prepared upon the dropwise addition of either a slurry or solution of the precursor in SO_2ClF at -78 °C to an approximately fivefold molar excess of SbF_5-HF, SbF_5-FSO_3H, or FSO_3H in SO_2ClF at -78 °C which was vigorously stirred with a Vortex-Genie.

Nuclear Magnetic Resonance Spectroscopy. A. ^1H NMR Spectra. ^1H NMR spectra (60 MHz) were obtained on a Varian Associates Model A56/60 NMR spectrometer. The 270-MHz FT ^1H NMR spectra of **1** were obtained on a Bruker Model HX-270 NMR spectrometer at the NIH Southern New England High Field NMR Facility at Yale University. The 300-MHz ^1H NMR spectrum of **3** was obtained on a Varian Associates Model HR-300 NMR spectrometer at Varian Associates, Palo Alto, Calif. All these instruments were equipped with variable temperature accessories, and proton chemical shifts are referenced to external (capillary) Me_4Si.

B. ^{13}C NMR Spectra. ^{13}C NMR spectra were obtained by the Fourier transform method on a Varian Associates Model XL-100 NMR spectrometer capable of either selective or broad-band ^1H decoupling. The complete details of this instrumentation and techniques employed have been described previously.[36] The 67.889-MHz FT ^{13}C NMR spectra were obtained on the Bruker Model HX-270 NMR spectrometer equipped with a broad-band ^1H decoupler and variable temperature accessory at the NIH Southern New England High Field NMR Facility located at Yale University. ^{13}C NMR chemicals shifts are referenced to external (capillary) Me_4Si. Proton-carbon coupling constants were measured directly from spectra recorded in the gyro-gate mode[7a] of operation. The resolution of the resonances in the gyro-gate ^1H-coupled ^{13}C NMR spectrum of **1** precluded the measurement of the $^1J_{CH}$'s in **1** (see discussion in text). In the cases of other ^{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[7a] ^1H-decoupled experiments.

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Dipole Moment, Optical Anisotropy, and Molar Kerr Constant of Triacetin

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Abstract: A rotational isomeric state treatment of unperturbed triacetin is presented. The objective is to determine conformational preferences of the glycerol moiety in unperturbed triglycerides. Calculations based on the model provide excellent agreement with the experimental dipole moment, optical anisotropy, and molar Kerr constant. The orientation of the ester group dipole moment and composition of the anisotropic part of the ester group polarizability tensor are among the critical parameters in the calculation. Experimental results are reproduced using values for these parameters which differ only slightly from those utilized successfully for methyl acetate. Statistical weights deduced from the analysis reveal that a variety of configurations are accessible to the glycerol moiety in an unperturbed triglyceride. Among the accessible configuration is the one adopted by β-tricaprin and β-trilaurin in the crystalline state. About 1% of the triacetin molecules exist with the glycerol moiety in this configuration. Certain other configurations are ten times more prevalent than the one found in the crystalline state.

Lipids derived from glycerol are important components of biological membranes.[3,4] They also occur in complexes with specific proteins in solution.[5] Depending upon temperature, their conformational freedom may either be severely restricted or they may exist in a fluid environment. Reversible transitions between these two states have been characterized by a variety of techniques. The temperature at which lipid components of membranes undergo the transition depends upon the chain length and extent of unsaturation of fatty acids esterified to the glycerol moiety.[3,4] Models have been proposed which view the hydrocarbon portion as a rigid planar zigzag below the

transition temperature. Disorder is introduced at higher temperatures, perhaps via the presence of a single bond in a gauche state[6] or a β-coupled gauche kink.[7] More extensively disordered states are also likely to be present. Three rotational states for each single bond about which rotation can occur would dictate 10^{25} configurations for unperturbed tristearin.

Configurational properties for unperturbed molecules which possess such a large number of configurations are most conveniently handled using rotational isomeric state theory.[8,9] This approach would be most appropriate for the bulk amorphous