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$$O_2^{-}\cdot + e^- + 2H^+ \rightarrow H_2O_2 \quad E^\circ_{27a} = 0.87\ \mathrm{V}$$

$$H_2O_2 + e^- + H^+ \rightarrow H_2O + \cdot OH \quad E^\circ_{27b} = 0.38\ \mathrm{V}$$

as follows:

$$E^\circ_{27} = (E^\circ_{27a} + E^\circ_{27b})/2 = +0.63\ \mathrm{V}$$

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^1H and ^{13}C NMR Spectroscopic Study of 9-Fluorenyl Cations[1a]

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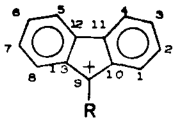
Abstract: A series of 9-substituted 9-fluorenyl cations were prepared and characterized by ^1H and ^{13}C NMR spectroscopy. Unsuccessful attempts were made to observe intramolecular interconversion of 9-methyl-9-fluorenyl cation via capped pyramidal ions with ring deuterated and methylated analogues. MINDO/3 calculations on isomeric structures of cyclopentadienyl, indenyl, and fluorenyl cations indicated strongly decreasing relative stabilities of the pyramidal forms due to benzoannulation. In deuterated fluorosulfonic acid solution, the 9-methyl-9-fluorenyl (**1**-CH_3) and 3,9-dimethyl-9-fluorenyl cations (**14**) underwent hydrogen-deuterium exchange consistent with a protonation-deprotonation mechanism.

Introduction

Diphenylmethyl and the related but "antiaromatic" fluorenyl cations have been compared previously.[2-6] Although the reported preparation of the parent 9-fluorenyl cation (**1**-H) in sulfuric acid now appears to be in doubt[3] (in fact, rapid polymerization to unidentifiable products occurs), the 9-phenyl-9-fluorenyl cation[2] (**1**-C_6H_5) was sufficiently stable in aqueous sulfuric acid to permit cryoscopic and ^1H NMR spectroscopic measurements. The low $pK_R{}^+$ value of **1**-C_6H_5 (-10.8) relative to that of more stable triphenylmethyl cation **2**-C_6H_5 ($pK_R{}^+ = -6.6$) provides direct evidence for antiaromatic destabilization of cyclopentadienyl-type cations.[7] Similarly, the solvolysis rates of a variety of 9-fluorenyl chlorides are significantly slower than those of their benzhydryl analogues.[6]



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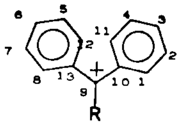

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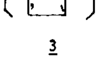
The square pyramidal $C_5H_5{}^+$ cation **3** was first predicted theoretically.[8,9] Molecular orbital calculations indicated that conversion into more stable forms such as **4** (singlet or triplet) should require high activation energies.[9,10]



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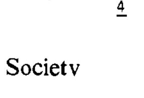

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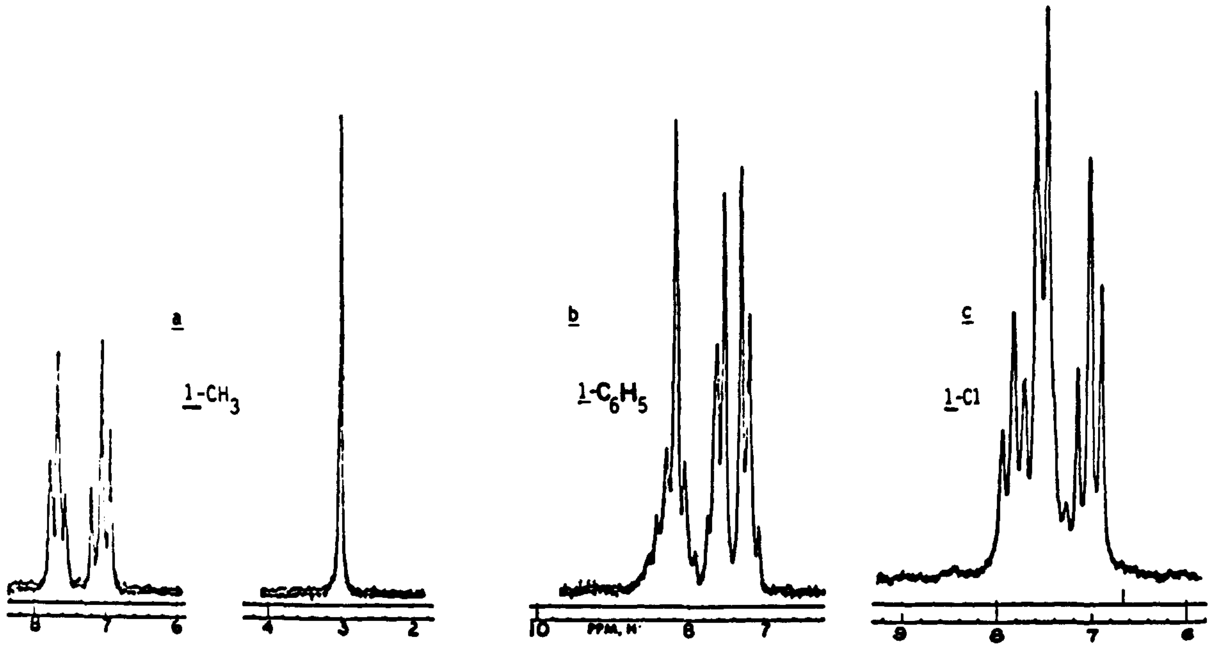
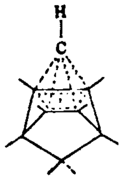


Figure 1. ^{1}H NMR (60 MHz) spectra: (a) of the 9-methyl-9-fluorenyl cation (**1**-CH$_3$) in SbF$_5$/SO$_2$ClF solution at −78 °C; (b) of the 9-phenyl-9-fluorenyl cation (**1**-C$_6$H$_5$); (c) of the 9-chloro-9-fluorenyl cation (**1**-Cl).

Although the parent ion **3** has not yet been reported experimentally, a number of derivatives and analogues (**5**–**6**) have now been described.[11]



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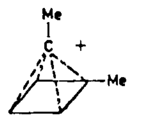

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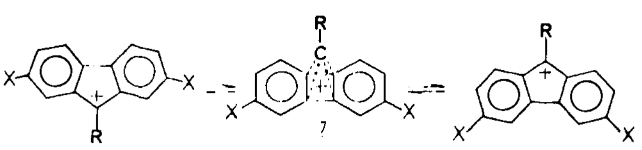
The parent antiaromatic cyclopentadienyl cation **4** has been obtained and its ESR spectrum studied.[12] The related pentaphenyl and pentachlorocyclopentadienyl cations were also reported previously.[12,13] In no case has the interconversion of ions of type **3** and **4** been observed.[14] A system readily available for such a test is the 9-fluorenyl cation. By choosing suitable substituents, X, possible rearrangements occuring via pyramidal structure **7** might be detected. This was a goal of our research.

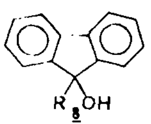


^{1}H NMR data for 9-aryl-9-fluorenyl cations (**1**-aryl) in sulfuric acid[3,15] and **1**-CH$_3$, **1**-C$_2$H$_5$, and **1**-*t*-C$_4$H$_9$ in SbF$_5$/SO$_2$ClF have been reported,[16] but no systematic analysis was carried out. We now report the preparation and ^{1}H and ^{13}C NMR spectroscopic study of a series of stable substituted 9-fluorenyl cations, which permit comparisons with corresponding diphenyl- and triphenylmethyl cations.[17]

Results and Discussion

Attempted Preparation of the Parent 9-Fluorenyl Cation. We were not able to generate the parent 9-fluorenyl cation **1**-H by slowly adding SO$_2$ or SO$_2$ClF solutions of possible precursors, 9-fluorenol, 9-chlorofluorene, and 9-bromofluorene, to FSO$_3$H, FSO$_3$H-SbF$_5$, or SbF$_5$ in SO$_2$ClF at −120 °C. The resulting solutions immediately became dark and unidentifiable polymeric materials were formed. No satisfactory ^{1}H NMR spectrum could be obtained, nor did electron paramagnetic resonance measurements reveal the presence of any appreciable concentration of radicals. Unlike 9-fluorenol, benzhydryl alcohol reacts readily with the above acids to give the stable diphenylmethyl cations, whose ^{1}H NMR spectral properties have already been reported.[17] We repeated Deno's experiments,[3] but obtained inconclusive results for the reaction of 9-fluorenol with sulfuric acid.[18] The ESR spectrum did not reveal the presence of any radical or diradical intermediate,[3,13] and the optical spectrum was quite different from those of 9-chloro- (**1**-Cl), 9-hydroxyl- (**1**-OH), and 9-methyl-9-fluorenyl cations (**1**-CH$_3$), which exist as bona fide cations in sulfuric acid. The observed behavior of 9-fluorenol may be due to radical-ion formation with subsequent Scholl-type oxidative condensation,[19] but this speculation is not based on direct experimental evidence.

9-Alkyl-9-Fluorenyl Cations. 9-Alkyl-substituted 9-fluorenyl cations[16] **1**-CH$_3$ and **1**-C$_2$H$_5$ were prepared from their respective alcohols **8** in FSO$_3$H, FSO$_3$H-SbF$_5$ or SbF$_5$/SO$_2$ClF solutions at −78 °C. The ^{1}H NMR spectrum of ion **1**-CH$_3$ is shown in Figure 1a, with assignments given in Table I. The C-3 and C-6 carbons can be considered para-like positions with respect to the 9 position. In most monosubstituted benzenes with a positively charged substituent, the para proton resonance is the most deshielded followed by ortho-proton resonances.[17] Therefore, H$_3$ and H$_6$ (as well as the ortho-like H$_1$ and H$_8$ resonance) are assigned to the multiplet at δ 7.5–7.9. The 100-MHz ^{1}H NMR spectra of **1**-CH$_3$ and **1**-C$_2$H$_5$ in SbF$_5$/SO$_2$ClF at −100 °C reported by Koptyug et al.[16] shows better resolution.



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We have also prepared ring deuterated 9-methyl-9-fluorenyl cations **9** and **10** from their corresponding alcohols. The ^{1}H NMR spectrum of **9** in the aromatic region is somewhat different from that of **1**-CH$_3$. With deuterium substitution at C$_2$, the lower field resonance (four protons) which is triplet-like in **1**-CH$_3$ became more complex in **9**. This is expected with deuterium at C$_2$; the signals for H$_1$ and H$_3$ should become

Table I. ^{1}H NMR Parameters of[a] 9-Fluorenyl and Diphenylmethyl Cations

ion	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	others
1-CH_3	7.62	7.04	7.62	7.04	7.04	7.62	7.04	7.62	3.00 (CH_3)
1-$CH_2 \cdot CH_3$	7.80	7.22	7.70	7.22	7.22	7.70	7.22	7.80	3.04 (CH_2), 1.90 (CH_3)
1-C_6H_5	7.65	7.25	7.55	7.25	7.25	7.55	7.25	7.65	8.20 (C_6H_5)
1-OH	7.90	7.60	7.90	7.60	7.60	7.90	7.60	7.90	12.75 (OH)
1-Cl	7.50	7.10	7.82	6.95	6.95	7.82	7.10	7.50	
9	7.62		7.62	7.04	7.04	7.62	7.04	7.62	3.00 (CH_3)
10	7.62	7.04		7.04	7.04	7.62	7.04	7.62	3.00 (CH_3)
11	7.30		7.16	5.80	6.80	7.16		7.30	2.70 (CH_3), 2.10 (CH_3)
12	7.40	6.88		6.84	6.84		6.88	7.40	2.78 (CH_3), 2.45 (CH_3)
13	7.38		7.18	6.80	6.80		6.80	7.72	2.78 (CH_3), 2.42 (CH_3), 2.20 (CH_3)
14		6.80	7.70				multiplet		2.8 (CH_3), 2.4 (CH_3)
2-H	7.92	8.49	8.37						9.82 (H_9)
2-CH_3	7.96	7.53	8.12						3.70 (CH_3)
2-$CH_2 \cdot CH_3$	7.45	7.90	8.10						3.75 (CH_2), 1.40 (CH_3)
2-C_6H_5	7.56	7.74	8.12						
2-Cl	8.17	7.28	8.28						
2-OH	8.12	7.82	8.15						13.05 (OH)

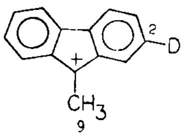
[a] ^{1}H NMR chemical shifts (δ) are in parts per million from external Me_4Si (capillary).

Table II. ^{13}C NMR Shifts[a] of Substituted Fluorenyl Cations in FSO_3H-SO_2ClF at −80 °C[b]

cation	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	others
1-CH_3	141.0	133.0	152.4	126.4	126.4	152.4	133.0	141.0	228.0	144.3	151.4	151.4	144.3	18.7 (CH_3)
13	139.1	144.1	147.8	125.6	127.0	171.5	133.1	141.0	220.8	142.1	145.1	153.1	144.3	23.80 (C_6 CH_3) 19.50 (C_9 CH_3) 17.30 (C_2 CH_3)
11	141.8	144.7	152.6	126.3	126.3	152.6	144.7	141.8	227.3	145.4	149.4	149.4	145.4	19.90 (C_2, C_7 CH_3) 18.60 (C_9 CH_3)
12	139.9	133.9	167.4	127.8	127.8	167.4	133.9	139.9	218.5	142.2	150.6	150.6	142.2	24.00 (C_3, C_6 CH_3) 17.70 (C_9 CH_3)
14	142.0	134.3	172.5	128.1	126.2	148.6	133.9	138.6	221.6	144.3	153.2	148.2	142.3	24.70 (C_3 CH_3) 18.1 (C_9 CH_3)
1-$CH_2 \cdot CH_3$	141.1	134.3	154.6	125.1	125.1	154.6	134.3	141.1	223.1	143.6	152.7	152.7	143.6	28.2 (CH_2) 18.8 (CH_3)
1-C_6H_5	141.4	134.6	153.4	126.8	126.8	153.4	134.6	141.4	224.2	143.8	151.4	151.4	143.8	137.7 (Ci), 135.8 (Co) 130.6 (Cm), 140.8 (Cp)
1-Cl	134.3	133.3	149.5	125.9	125.9	149.5	133.3	134.3	218.2	141.3	147.1	147.1	141.3	
1-OH	134.1*	132.5	146.8	125.3	125.3	146.8	132.5	133.1*	205.5	131.4†	149.1ⁿ	148.5ⁿ	130.1†	
2-H	143.8	134.1	151.2	134.1	134.1	151.2	134.1	143.8	191.1	138.6	143.8	143.8	138.6	
2-CH_3	141.6	132.8	148.2	132.8	132.8	148.2	132.8	141.6	217.5	142.8	141.6	141.6	142.8	$CH_3 = 31.9$
2-OH	144.3	131.3	144.1	131.3	131.3	144.1	131.3	144.3	211.9	140.9	144.3	144.3	140.9	
	140.2*	132.5	145.5	132.5	132.5	143.4	132.5	136.7*	209.2	131.4†	140.2*	136.7*	130.6†	

[a] Shifts are in parts per million from external capillary Me_4Si; assignments were confirmed by off-resonance experiments. [b] *, †, ⁿ = interchangeable values.

singlet and doublet, respectively, and will be superimposed on the pattern from the undeuterated ring. The ^{1}H NMR spectrum of cation **10** showed a similar complex pattern. Assignments for the ortho and para protons in **1**-CH_3 were further confirmed by comparison of ^{1}H NMR spectra of methyl-substituted cations **11**-**14**. When methyl groups were substituted onto the ring at C-2 and at C-7 in **11**, the low field aromatic signals became simplified. The H_1 and H_8 proton signals, doublets in **1**-CH_3, became a sharp singlet at δ 7.3 in **11**; H_3 and H_6 are doublets centered at δ 7.16, while H_4 and H_5 also are doublets centered at δ 6.8. The ^{1}H NMR chemical-shift assignments for all these ions are summarized in Table I.



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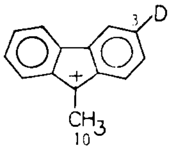

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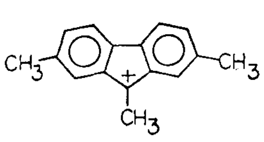

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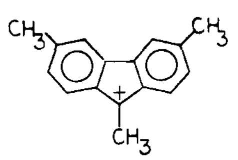

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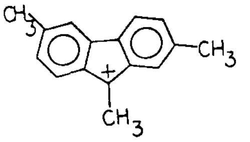

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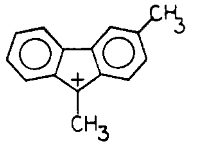

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We have also obtained ^{13}C NMR spectra of tertiary 9-fluorenyl cations **1**-CH_3, **1**-C_2H_5, and **11**-**14**. The ^{13}C NMR chemical shifts and their assignments, as well as those for model ions **2**, are shown in Table II. The ^{13}C NMR spectra (proton decoupled as well as proton noise coupled) of cation **1**-CH_3 is shown in Figure 2 as illustrative.

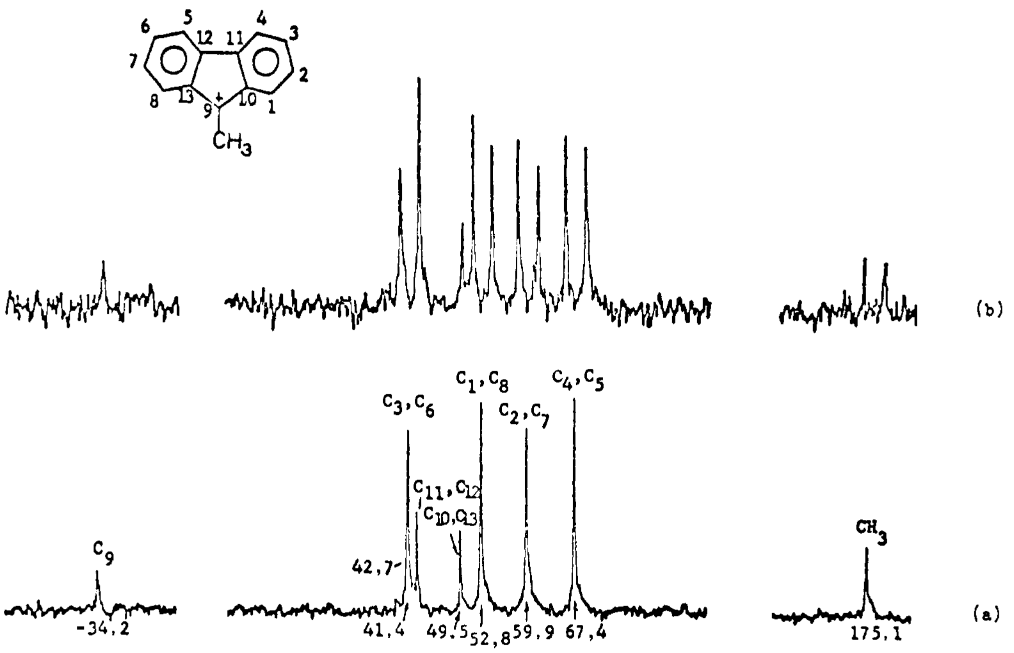


Figure 2. Fourier transform ^{13}C NMR spectra of the 9-methyl-9-fluorenyl cation (1-CH_3): (a) proton decoupled; (b) proton noise coupled.

The most deshielded signal in cation **1**-CH_3 at $\delta(^{13}C)$ 228.0 is assigned to the carbenium center C-9. "Off-resonance" measurements enabled assignment of C-10, C-13 and C-11, C-12 at $\delta(^{13}C)$ 144.3 and 151.4. The more shielded signal [$\delta(^{13}C)$ 144.3] is assigned to C-10 and C-13 carbons based on chemical shift data for a large number of monosubstituted benzenes in which a pronounced upfield shift is observed for ipso carbon adjacent to the neighboring carbocationic center.[20] The most deshielded of the remaining four ring carbon resonances is assigned to the para-like C-3 and C-6 [$\delta(^{13}C)$ 152.4], consistent with data for positively charged monosubstituted benzenes.[20] The ortho-like carbons 1 and 8 should experience more deshielding than both types of meta carbons at C-2, C-7 and at C-4, C-5 based on the same analogy. However, the meta carbon assignments are interchangeable. Similar assignments were made earlier in the dihydrobenzotropylium and the diphenylmethyl cations (**2**-CH_3) ions.[21] However, comparison of the data of **2**-CH_3 with those of **1**-CH_3 reveals significant differences. The carbenium shift (C-9) in **2**-CH_3 is 10 ppm more shielded than that of ion **1**-CH_3. In ion **1**-CH_3, the C-3 chemical shift is ~5 ppm more shielded, whereas the methyl and C-4 carbons are shielded by 13 and 6 ppm, respectively, than corresponding signals of ion **2**-CH_3. Perhaps, the shielding of resonances for C-4 and CH_3 may also result from the presence of an induced paramagnetic shielding ring current in the five-membered ring.[22,23] It would be necessary, of course, that both C-4 and CH_3 lie outside the toroidal path of the π-electron current. The deshielding of C-9 position by almost 10 ppm in ion **1**-CH_3 compared with that of **2**-CH_3 would result from this carbon being inside the toroidal path, and thus would not reflect the relative electron densities. It is also likely that ring strain in **1**-CH_3 is the reason for the deshielding of C-9 as similar effects are not observed in the case of dihydrobenzotropylium and dibenzotropylium cations.[21] The shielded resonance for CH_3 in **1**-CH_3 is also reflected in the shielded methylene resonance of **1**-C_2H_5 [$\delta(^{13}C)$ 28.2]. Although the ^{13}C NMR spectrum of **2**-C_2H_5 was not recorded, the methylene shift estimated[24] from data for **2**-CH_3 should be ~43 ppm. Despite these differences, the mode of charge delocalization into the aromatic ring skeleton in the fluorenyl cations **1**-CH_3 and **1**-C_2H_5 is similar to that of diphenylmethyl cations, indicating relative unimportance of antiaromatic destabilization[7] in the system. The charge density estimations on the parent fluorenyl system using simple HMO theory or MINDO/3 calculations also support such a conclusion.

The ^{13}C NMR spectra of ring methyl substituted ions **11** to **14** show significant ring methyl substituent effects. In ion **11**, the meta-like C-2 and C-7 methyl groups produce no significant difference in the chemical shifts of C-9 with respect to that of the parent ion **1**-CH_3. However, C-2 and C-7 show substantial deshielding ($\approx$11 ppm) compared with the parent ion **1**-CH_3, largely owing to a methyl substituent effect on the aromatic ring.[20,25] The *p*-methyl substituent effect (due to two methyl groups) in ion **12** shields the carbocationic center (by 10 ppm) compared with the parent ion **1**-CH_3. This effect is diminished both in ions **13** and **14**, which have only one *p*-methyl substituent.

9-Phenyl-9-Fluorenyl Cation. Although the 9-phenyl-9-fluorenyl cation **1**-C_6H_5 has been previously prepared in solution and even isolated as a salt,[13] no NMR study has been reported.

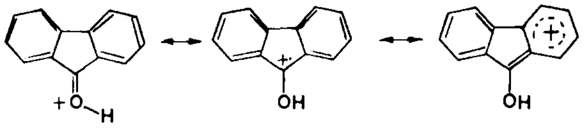
The ^1H NMR spectrum (Figure 1b) of ion **1**-C_6H_5, in superacid solution from its alcohol precursor **8**-C_6H_5, shows the phenyl ring protons as a complex multiplet centered at δ 8.2, indicating some charge delocalization from the carbenium center C-9. An examination of models reveals that the phenyl ring should be twisted out of the molecular plane of fluorene to relieve unfavorable steric interactions involving the *o*-phenyl protons. However, the degree of twisting should be less than in 9-*o*-methyl-substituted phenyl-9-fluorenyl cation, where the methyl proton shifts showed[15c] little charge delocalization into the 9-aryl ring.

The ^{13}C NMR spectrum of **1**-C_6H_5 (assignments shown in Table II) is similar to that of ion **1**-CH_3. The C-3 (C-6), C-10 (C-13), and C-11 (C-12) chemical shifts are almost identical with the corresponding shifts in **1**-CH_3. The 9-phenyl ring in **1**-C_6H_5 carries little excess positive charge. The C-9 resonance [$\delta(^{13}C)$ 224.2] is about the same as C-9 in **1**-CH_3 [$\delta(^{13}C)$ 228.0] indicating insignificant phenyl π-conjugation. Also the para and ortho carbons [$\delta(^{13}C)$ 140.8 and 135.8, respectively] of the phenyl ring in **1**-C_6H_5 are not very deshielded compared with those of phenylmethyl cations where p-π conjugation is significant.[20,21] Comparison of the para shift in **2**-C_6H_5 [$\delta(^{13}C)$ 144.1] with that of C-3 and C-6 in **1**-C_6H_5 [$\delta(^{13}C)$ 153.4] shows that more charge is delocalized to the fluorenyl ring positions in the latter ion.

9-Chloro-9-fluorenyl Cation. The 9-chloro-9-fluorenyl cation **1**-Cl was obtained from 9,9-dichlorofluorene in SbF_5/SO_2ClF at −78 °C. Ion **1**-Cl has previously been prepared in concentrated sulfuric acid/acetic acid solution, and its optical spectrum examined.[3] The ^{1}H NMR spectrum of **1**-Cl (Figure 1c) shows aromatic proton absorptions similar to those of other tertiary 9-fluorenyl cations.

The ^{13}C NMR spectrum provides evidence that the extent of electron "back-donation" [26] from the chlorine atom to the carbenium center C-9 in ion **1**-Cl is minimal. The carbenium center is deshielded only by ~8.8 ppm compared with those in **1**-CH_3 and other model ions.[26]

Protonated 9-Fluorenone (9-Hydroxy-9-fluorenyl Cation). Protonated 9-fluorenone 1-**OH** was obtained from 9-fluorenone in FSO_3H-SbF_5/SO_2ClF solution at −78 °C. The hydroxy proton shows a singlet ^{1}H NMR absorption at δ 12.75 shielded by ~2 ppm from the corresponding signal in protonated dialkyl ketones and by ~1 ppm from those in protonated aryl alkyl ketones.[27] A ^{1}H NMR study of several protonated para-substituted acetophenones indicate excellent correlation between the OH proton chemical shift and the σ^+ value for the substituent.[27] These and other data for di- and trihydroxycarbenium ions[27] indicate that the OH proton chemical shift is a good indicator of the electron delocalizing ability of the groups attached to the protonated carbonyl group. Therefore, the shielded OH signal for ion **1**-OH suggests that there is substantial charge delocalization into the fluorene rings.



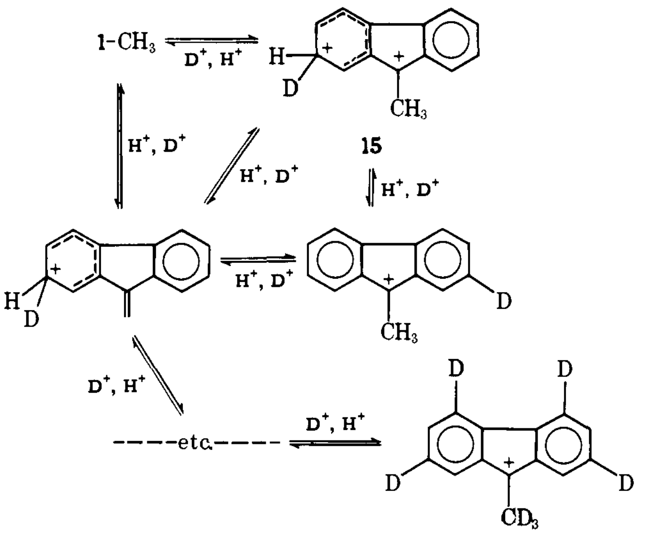
1-OH

In the ^{13}C NMR spectrum, the ion **1**-OH showed a total of eight resonances (Table II); hence the rotation about C_9–O bond is rather slow on the NMR time scale. However, the C-9 chemical shifts in **1**-OH and **2**-OH are similar.

Recently, Agranat and co-workers[28] have demonstrated the reversibility of aromatic Friedel–Crafts acylations in ortho and para fluorenones using polyphosphoric acid catalyst at elevated temperatures. However, no such rearrangements were observed in the case of 3-methyl-9-fluorenone under superacidic conditions up to 25 °C.

Attempted Observation of Equilibration Processes in 9-Methyl-9-fluorenyl Cations Involving Square Pyramidal Ion Intermediates. To study possible equilibration processes, ^{1}H and ^{13}C NMR spectra of ring substituted 9-methyl-9-fluorenyl cations **9**–**14** were recorded at various temperatures (+25 to −80 °C).

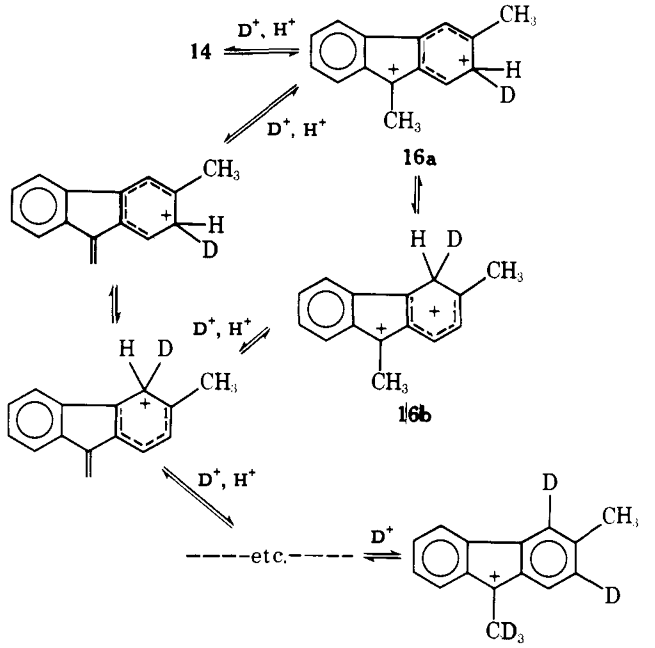
Ion **9** prepared in FSO_3H-SO_2ClF at −78 °C displayed a ^{1}H NMR spectrum slightly different from that of parent ion **1**-CH_3 as described in the earlier section. After the solution stood at −30 °C for 15 min, the deuterium label at C-2 position was lost and a spectrum identical with that of the parent ion **1**-CH_3 was obtained. The isomeric ion **10** also behaved similarly under these conditions. To ascertain the nature of this process, we prepared the parent ion **1**-CH_3 in FSO_3D-SO_2ClF at −78 °C. At −80 °C the ion **1**-CH_3 showed normal ^{1}H and ^{13}C NMR spectra. However, after solution was maintained at 0 °C for 1 day and the spectra were run, substantial changes in the aromatic and methyl resonances had occurred. The ^{13}C NMR spectrum clearly indicated deuterium substitution at C_2, C_4, C_5, C_7, and methyl carbons. This demonstrates a protonation–deprotonation mechanism at meta-like positions of the aromatic ring (relatively electron-rich positions). The methyl proton exchange should also occur through a similar mechanism.



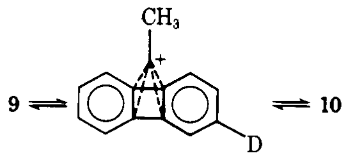
However, in deuterated magic acid ($FSO_3D + SbF_5$), the methyl proton exchange was totally suppressed. The aromatic proton exchange was also significantly reduced. In the case of phenyl substituted cation **1**-C_6H_5, such exchanges did occur, but at substantially reduced rates.

Similar proton exchange has been recently observed in the case of trityl cation in trifluoromethanesulfonic acid solution by Pagni and co-workers.[29] Weiss and Priesner[30] have also reported analogous phenomena in the case of aromatic cyclopropenyl cations. Hence, it is conceivable that proton exchange in fluorenyl cations may occur through a dicationic intermediate or transition state, such as **15**.

The cation **14** also behaved similarly in FSO_3D solution (at 0 °C for 24 h). The C-2, C-4 positions exchanged protons much faster than C-5, C-7 positions indicating enhanced stabilization of σ complexes **16a,b**. The methyl group at C_9 position also underwent rapid proton exchange.



Because of the rapid ring proton exchange in ions **9** and **10**, the possibility of pyramidal inversion through a pyramidal



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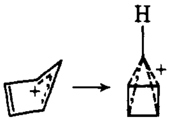
cation intermediate or transition state, such as **17** could not be ascertained. However, similar temperature dependent study on ions **11–14** even up to +25 °C did not show any evidence for such a conversion. The present study on 9-methyl-9-fluorenyl cations rule out any evidence for methyl substituted pyramidal ions of the $(CH)_5^+$ type indicating a very high energy barrier for such a process.[9,10]

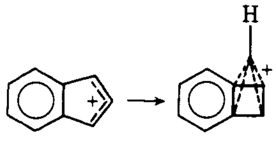
Theoretical Calculations

The possibility of degenerate rearrangement of fluorenyl cations via pyramidal intermediates (e.g., **7**) was examined by MINDO/3[31] semiempirical MO calculations. At this level of theory, the pyramidal $C_5H_5^+$ isomer **3** is calculated to be only 14.4 kcal/mol less stable than the lowest energy singlet cyclopentadienyl cation **4**.[10b] This result is in excellent agreement with the recent high level ab initio calculations including the effects of electron correlation.[10e] The use of MINDO/3 to explore the energies of a variety of pyramidal species, therefore, seems justified. We first examined the effect of annulation by a single benzene ring on the relative stability of the pyramidal cation, **18**. Relative to the indenyl cation **19**, **18** is much less stable. The calculated difference between the fluorenyl cation (**1**, R = H) and the dibenzannulated pyramid **7** (R = X = H) is even larger, 73.0 kcal/mol. The MINDO/3 relative energies for the pyramidal cations **20–22** provide further comparisons. The isomerizations leading to the formation of the pyramidal cations **7** (R = X = H) and **18** are, thus, indicated to be the least favorable.



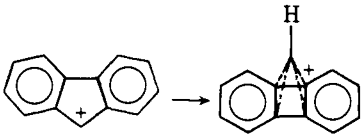
4 **3**

ΔH_f° 255.3 269.7 14.4 kcal/mol



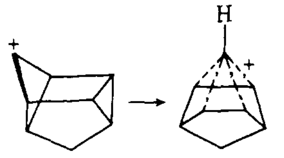
19 **18**

ΔH_f° 247.8 296.9 49.1 kcal/mol



1-H 7, R = X = H

ΔH_f° 253.9 326.9 73.0 kcal/mol



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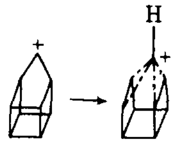
ΔH_f° 263.9 272.9 9.0 kcal/mol[32]



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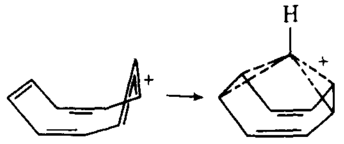
ΔH_f° 314.3 309.5[34] −4.8 kcal/mol[33]



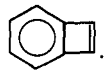
22

ΔH_f° 233.1 257.6 24.5 kcal/mol[35]

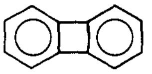
The large increase in the energy differences **4** → **3**, **19** → **18**, and **1** (R = H) → **7** (R = X = H) produced by benzannulation is due to decrease in destabilizing antiaromatic character along the series, **4** > **19** > **1** (R = H) and to decreasing stability of the pyramidal forms, **3** > **18** > **7** (R = X = H). The latter factor is independently confirmed by the following calculated (MINDO/3) "complexation" energies between a CH^+ cap and appropriate diene systems yielding the pyramidal cations.

 + CH^+ → **3**

ΔH_f° 94.4[36] 351.5 269.7 −176.2 kcal/mol

 + CH^+ → **18**

ΔH_f° 98.4 351.5 296.9 −153.0 kcal/mol

 + CH^+ → **7**

ΔH_f° 107.3 351.5 326.9 −131.9 kcal/mol

 + CH^+ → **20**

ΔH_f° 84.5[37] 351.5 272.9 −163.1 kcal/mol

 + CH^+ → **21**

ΔH_f° 123.1[37] 351.5 309.5 −165.1 kcal/mol

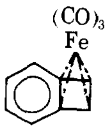
 + CH^+ → **22**

ΔH_f° 58.1[37] 351.5 257.6 −152.0 kcal/mol

These complexation energies are determined mainly by the degree of interaction between the doubly degenerate p LUMOs of the CH^+ cap and the π orbitals of appropriate symmetry of the diene systems. These π orbitals are lowered in energy on benzannulation. The coefficients on the four carbons coordinating to the cap are also reduced by delocalization. Therefore, the resulting CH^+ complexes become progressively less favorable, the more benzene rings are present.

In view of the isolobal nature of CH^+ and $Fe(CO)_3$ fragments,[38] it is interesting to compare the relative stabilities of ions **3**, **18**, and **7** (R = X = H) with those of the iron tricarbonyl complexes **23–25**. Complexes **23** and **24** are well known.[39] The X-ray structure of a derivative of **24** has recently been reported.[40] Apparently, **25** has never been prepared.[41]

23



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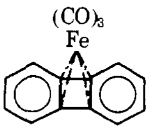
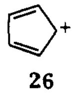


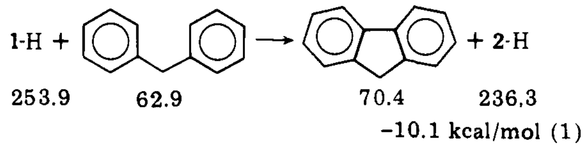
25

There is another factor responsible for the nonoccurrence of isomerization **1** → **7**. The electronic structure of **1** does not correspond to that of **4**, but rather to its lumomer **26**. While the isomerization **4** → **3** is symmetry allowed; **26** → **3** is not.[9a]

 $^+ \xrightarrow[\text{forbidden}]{} 3 \xleftarrow[\text{allowed}]{} 4$

26

Isomerization **1** → **7** along the C_s pathway is also *forbidden* by orbital symmetry. The allowed **4** → **3** conversion is calculated to have a barrier as high as 43 kcal/mol.[10b] Isomerization **1** → **7** should involve additional activation energy. We did not calculate the energy of the transition state since it was clear that the postulated reaction is much too unfavorable to be a viable experimental possibility. However, we cannot exclude the possibility that **7** (R = X = H) might be prepared in another way. In comparison with the other pyramidal cations, **7** (R = X = H) does not appear to be one of the more favorable goals. The antiaromatic destabilization of fluorenyl cation was estimated (MINDO/3) by isodesmic reaction 1. This result



(1)

is in qualitative agreement with the solvolysis results[6] and experimental $pK_R{}^+$ values.[7]

Key features of the calculated MINDO/3 structures and charge distributions of ions **1** (R = H), **3**, **4**, **7** (R = X = H), **18**, and **19** are presented in Chart I.

Conclusions

Although the parent 9-fluorenyl cation (**1**-H) could not be prepared in stable ion media, a number of 9-substituted derivatives are quite stable under such conditions. The ^1H and ^{13}C chemical shifts, on the whole, are quite similar to those of corresponding diphenylmethyl cation derivatives and do not reflect in any significant way the antiaromatic nature of 9-fluorenyl cations.

The possibility of degenerate rearrangements via pyramidal intermediates **7** was discounted both on the basis of negative experimental results and/or the basis of MINDO/3 calculations, which indicate **7**-H to be 73 kcal/mol less stable than **1**-H. However, our results do not exclude the possibility that ions like **7** would be generated in other ways.

Experimental Section

All ring unsubstituted 9-fluorenyl derivatives were prepared according to literature procedures.[3-6,15]

9-Methyl-*2-d*- and 9-Methyl-*3-d*-9-Fluorenols. 2-Bromofluorene (Aldrich) and 3-bromofluorene [prepared from 3-bromofluorenone (Aldrich) by Huang-Minlon reduction] were each reacted with Mg and 1,2-dibromoethane in boiling ether to give the corresponding Grignard reagents, which were then hydrolyzed with D_2O. The crude products were then oxidized with $Na_2Cr_2O_7$ in acetic acid to give the monodeuterated fluorenones which, after chromatography on silica gel and crystallization from benzene, had mp 81.5–83.5 (*2-d*) and 82.4–83.5 °C (*3-d*). Each was treated with methylithium in ether to obtain the 9-methyl-9-fluorenols, mp 174.4–176.5 (*3-d*) and 173.8–175.7 °C (*2-d*). The alcohols, 2,7,9-trimethyl-, 3,6,9-trimethyl-, 2,6,9-trimethyl-, and 9,3-dimethylfluorenols were prepared by addition of methyllithium to the corresponding ketones[31] in ether soltuion. All the alcohols exhibited satisfactory spectral data.

Preparation of Ions. A cold solution of the 9-fluorenyl precursor in SO_2ClF was added slowly with vigorous stirring to a solution of $FSO_2H(D)$-SbF_5 (1:1) or SbF_5 in SO_2ClF at −78 °C. ^1H NMR spectra were obtained using Varian Associates Model A56/60A and HA 100 spectrometers equipped with variable-temperature probes. External tetramethylsilane (capillary) was used as reference. ^{13}C NMR spectra were obtained using a Varian Model XL-100 spectrometer, equipped with FT accessory and a variable-temperature probe, or a Varian Model FT-80 spectrometer, equipped with multinuclei variable-temperature broad-band probe and FT accessory. External capillary Me_4Si was used as the reference signal.

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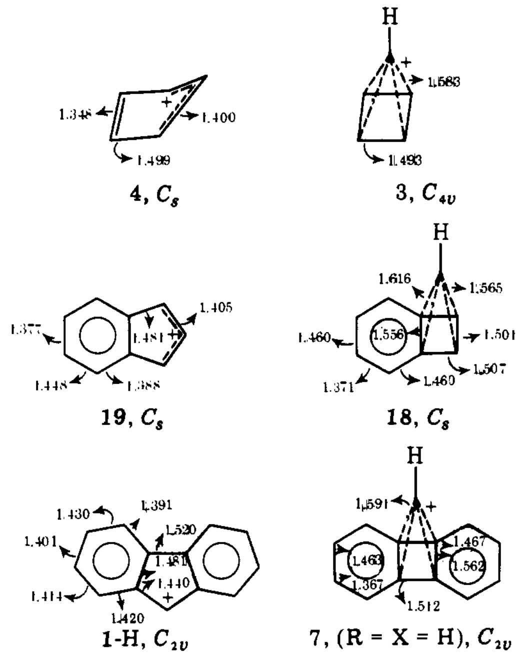
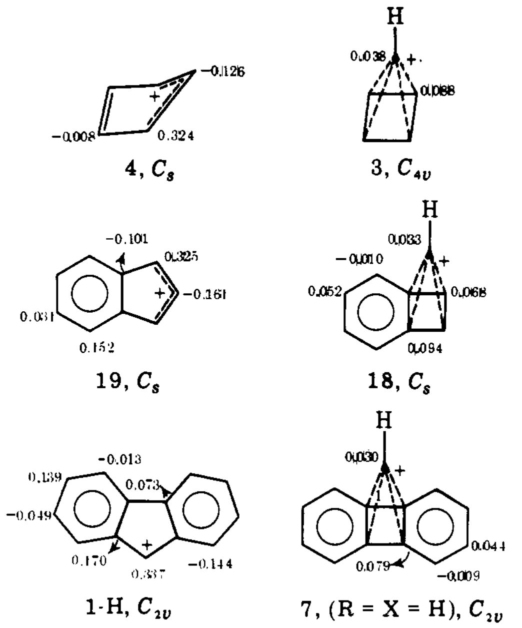
Chart I. MINDO/3 Geometries and Charge Distributions of $C_5H_5{}^+$, $C_9H_7{}^+$, and $C_{13}H_9{}^+$ Ions

A. Bond Lengths, Ångstroms



B. Charges



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Electronic Control of Ferroporphyrin Ligand-Binding Kinetics

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Abstract: Measurements of the rates of CO binding to ferrous porphyrins have been used to examine two different mechanisms which have been proposed to explain protein control of heme reactivity. The results indicate that electronic control through π-donor/acceptor interactions with the macrocyclic porphyrin ring is *not* important in controlling the heme reactivity of hemoglobin or of other hemoproteins. However, hydrogen bonding to the metal-bound imidazole can have a powerful influence on heme reactivity.

Introduction

The primary control of heme reactivity in proteins is achieved by the axial ligand(s) arrived at through molecular evolution. However, powerful secondary control mechanisms also exist. As the best-known example, cooperative ligation of hemoglobin reflects a conformational equilibrium between one protein form (T)[1] with low ligand affinity and a second form (R) with $\sim 10^2$-fold higher affinity, yet the single endogenous heme-ligand is the same in both forms.[2-4] This influence of conformation on reactivity is correspondingly expressed in the modulation of ligand-binding kinetics: for example, the CO on-rate for the T state is $\sim$20- to 60-fold less than for the R state.[5] This paper discusses two different control mechanisms involving purely electronic effects local to the heme, one associated with protein-induced perturbations of the proximal histidine which we shall call a "proximal" effect, the other with perturbations of the porphyrin ring which we call a "peripheral" effect.

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