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Generation and NMR Studies of Persistent Fluoro(alkyl)pyrenium Ions and Their Tetrahydro and Hexahydro Derivatives in Superacid Media[†]

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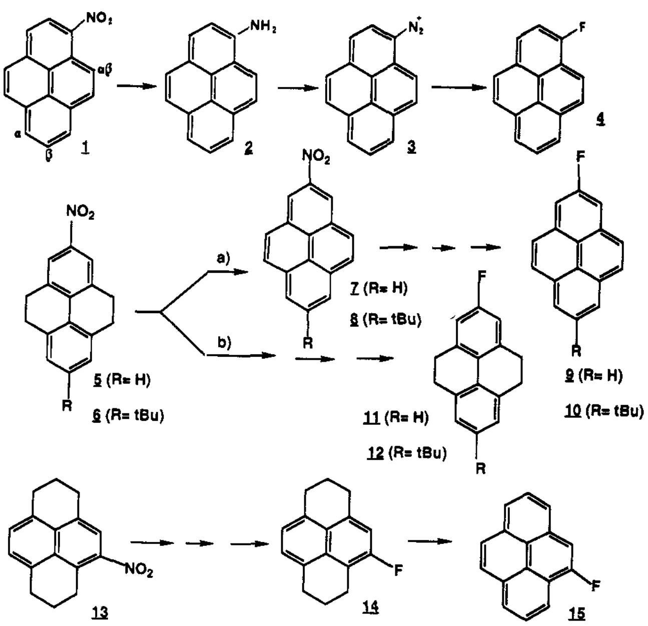
Low-temperature protonations of 2-fluoropyrene (**9**), 2-fluoro-7-*tert*-butylpyrene (**10**), their corresponding tetrahydro analogs **11** and **12**, 1-fluoropyrene (**4**), 4-fluoropyrene (**15**), and its hexahydro derivative **14** are studied in various superacid media. The isomeric fluoro(alkyl)pyrenes are fully monoprotonated in FSO_3H/SO_2ClF and their tetrahydro and hexahydro analogs **11**, **12**, and **14** are monoprotonated with $FSO_3H{\cdot}SbF_5$ (4:1)/SO_2ClF. The resulting persistent fluoro(alkyl)pyrenium ions are probed by multinuclear NMR (^1H, ^{13}C, ^{19}F). Whereas a vicinal fluorine in the β position increases the stability of the pyrenium ion of α protonation leading to a single α pyrenium ion, fluorine in the $\alpha\beta$ or α position is not sufficiently stabilizing to alter the normal site of protonation; α attack is still observed. ^{13}C, ^1H, and ^{19}F NMR data illustrate that the positive charge is extensively delocalized away from the site of attack and exists predominantly at the alternating carbons of the periphery, indicative of significant phenalenium ion character in the fluoro(alkyl)pyrenium ions of α attack. The fluoronium ion character of the resulting delocalized arenium ions is deduced based on the increase in ^1J(C–F), deshielding of the fluorine, and reduced deshielding of the fluorine-bearing carbons as compared to position of these carbons in the analogous non-fluorinated pyrenium ions. With **10** the presence of fluorine and the tBu group in 2, 7 positions (β) allows their relative stabilization effects on an adjacent carbenium ion formed by vicinal protonation (α) to be compared. Whereas kinetic protonation produces both **10**-H^+ and **10a**-H^+ in near equal amounts, subsequent thermodynamic equilibration gives almost pure **10**-H^+. A rearrangement of the tetrahydropyrene derivative (**12**-H^+ → **12a**-H^+) was also observed.

Introduction

Stabilization of a carbenium ion center by an α fluorine via a favorable 2p–2p back-bonding mechanism and the fluoronium ion character which overrides the unfavorable inductive electron withdrawal of F are well-investigated phenomena in fluorinated carbocation chemistry.[1a,b]

Pioneering studies of Olah and co-workers[1,2] on persistent fluorocarbenium ions since the sixties have greatly enhanced the present state of knowledge pertaining to the mechanism of electrophilic substitution of fluoroaromatics and addition to fluoroalkenes by shedding light on the structure/dynamics and charge-distribution patterns of their fluorocarbocation intermediates under long-lived ion conditions.

Scheme I. The "Berg Synthesis" of Monofluoropyrenes (ref 7a, 8)



In the fluoroarenium ion area, the benzene series was extensively probed by Olah et al.[1a] In the naphthalene series, the Russian workers provided examples of poly- and perfluoronaphthalenium ions by ionization of their corresponding 1,4-cyclohexadienes with SbF_5.[3a] A series of polyfluorinated indenyl cations have also been studied.[3b]

The lack of examples of stable fluoroarenium ions of large fused polycyclic aromatic hydrocarbons is probably due to inherent difficulty in selective fluorination of PAHs.

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(1) (a) Review: Olah, G. A.; Mo, Y. K. *Advances in Fluorine Chemistry*; Tatlow, J. C., Peacock, R. D., Hyman, H. H., and Stacey, M., Ed., 1973; Vol. 7, p 69. (b) Monograph: Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973.

(2) Selected examples: (a) Prakash, G. K. S.; Heiliger, L.; Olah, G. A. *J. Fluorine Chem.* **1990**, *40*, 33. (b) Olah, G. A.; Stephenson, M.; Shih, J. G.; Krishnamurthy, V. V.; Prakash, G. K. S. *J. Fluorine. Chem.* **1988**, *40*, 319. (c) Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1969**, *91*, 2955. (d) Olah, G. A.; Mo, Y. K. *J. Org. Chem.* **1973**, *38*, 2686. (e) Olah, G. A.; Chambers, R. D.; Comisarow, M. B. *J. Am. Chem. Soc.* **1967**, *89*, 1268. (f) Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1966**, *88*, 362. (g) Olah, G. A.; Kiovsky, T. E. *J. Am. Chem. Soc.* **1967**, *89*, 5692. (h) Olah, G. A.; Kiovsky, T. E. *J. Am. Chem. Soc.* **1968**, *90*, 2583.

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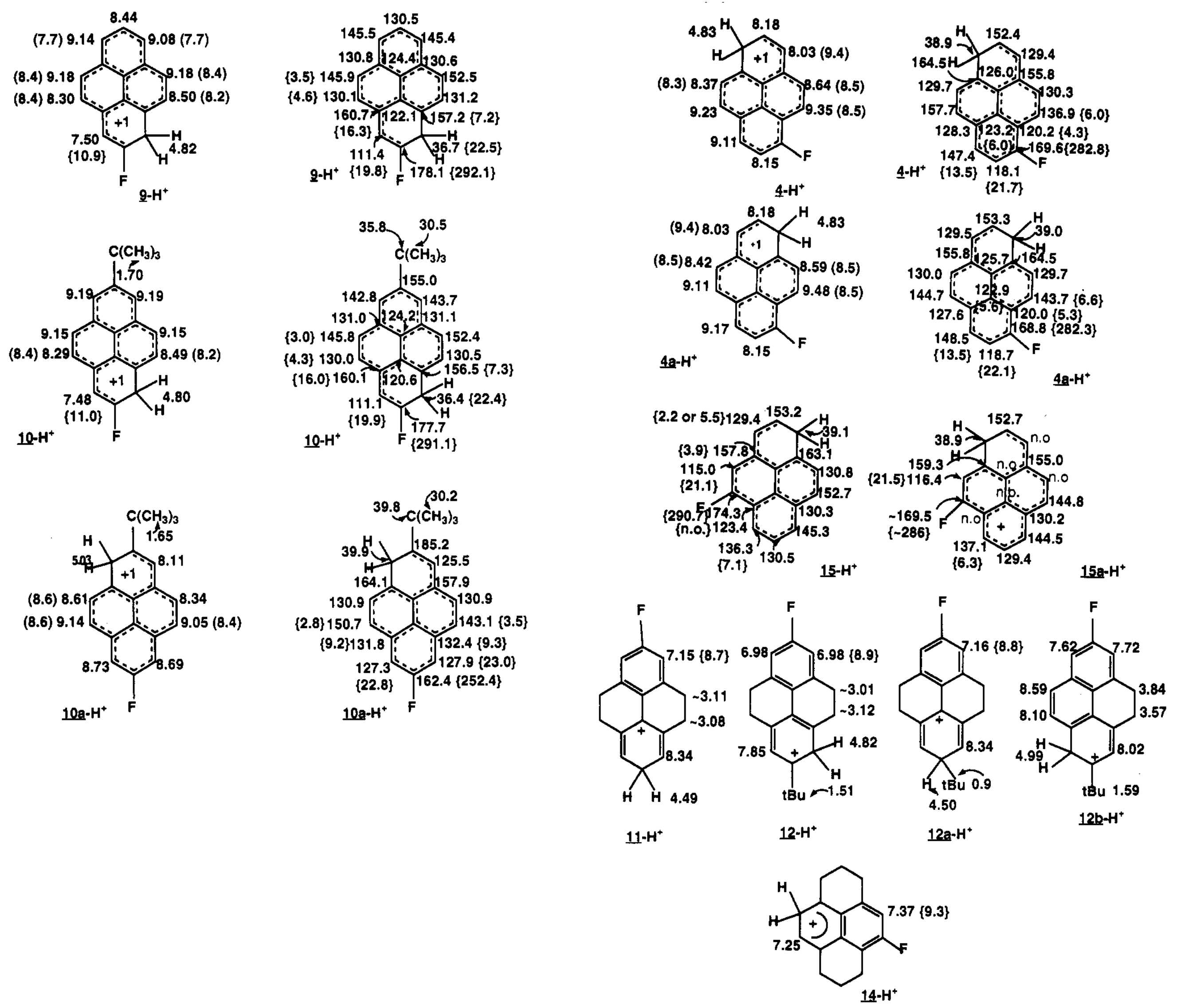
Chart I. Proton and Carbon-13 Chemical Shifts, and H–H, H–F, and C–F Coupling Constants in Fluoropyrenium Ions [H–H Coupling constants are given in parentheses; H–F and C–F coupling constants are shown in square brackets (n.o. = not observed.)]



Xenon difluoride fluorinations of anthracene, phenanthrene, and pyrene have been reported by Filler, Zupan, Agranat, and their collaborators.[4-6] With pyrenes a mixture of 1-, 2-, and 4-fluoropyrene isomers were obtained in low yields. Despite the need for a multistep process, selective preparations of isomeric fluoropyrenes via $ArNO_2 \rightarrow ArNH_2 \rightarrow ArN_2^+ \rightarrow ArF$ sequence developed by Berg[7a] provide the desired monofluoropyrenes. The 2-nitro and 4-nitro compounds are readily accessible by electrophilic nitration/aromatization of hexahydro- and tetrahydropyrene, respectively (Scheme I).[7a,b] Alternatively, the 2-aminopyrene is directly accessible via its aryne by cine substitution.[8]

The availability of isomeric monofluoro(alkyl)pyrenes **4**, **9**, **10**, **15**, and their tetrahydro and hexahydro precursors **11**, **12**, and **14** provided the impetus for the present investigation which probes their site(s) of protonation under stable ion conditions and the charge-distribution mode in the resulting fluoropyrenium ions by multinuclear NMR (^{13}C, ^1H, ^{19}F).

The present studies extend our previous and ongoing work on persistent arenium ions of protonation and nitration of crowded pyrenes and the dipositive alkylpyrenium ions of oxidation.[9-12]

Since the onset, an important question associated with this endeavor was whether fluorine can alter the sites of electrophilic attack in the PAHs and if so, might this eventually affect carcinogenic behavior, if indeed according to Miller's hypothesis,[13] carcinogenesis is initiated by electrophilic chemistry.

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Results and Discussion

Despite the presence of three sites of electrophilic attack in the pyrene skeleton, the higher stability of the Wheland intermediate of α-attack (as determined by DEWAR-PI and Hückel calculations and confirmed in a variety of electrophilic experiments)[14-16] practically governs its substitution chemistry, whereby the $\alpha\beta$ and especially the β products are not found even in cases where stabilizing alkyl(cycloalkyl) groups are strategically positioned.[9] Rearrangement of *ipso*-protonated 1,3,6,8-tetraisopropylpyrene provides a rare example for generation of a pyrenium ion of $\alpha\beta$ attack.[9]

The experiments described herein will demonstrate that fluoropyrenes **9**, **10**, **4**, and **15** are monoprotonated in FSO_3H/SO_2ClF and fluorotetrahydopyrenes **11**, and **12** and fluorohexahydropyrene **14** are monoprotonated in $FSO_3H{\cdot}SbF_5$ (4:1)/SO_2ClF.

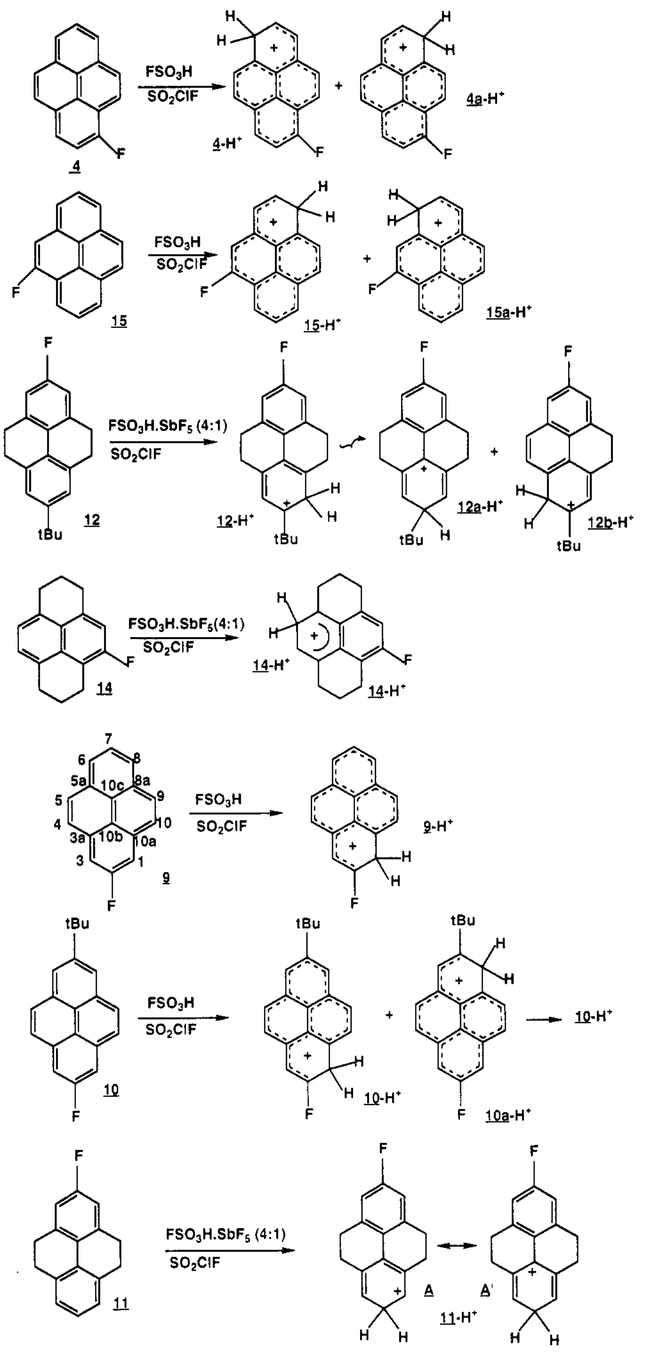
NMR Assignments. The ^1H NMR assignments are based on the chemical shifts, the relative intensities, the magnitude of vicinal H–H coupling constants for well-resolved absorptions, the vicinal and long-range H–F couplings, and a consistent set of protonation effects on chemical shifts in comparison with our previous studies of alkylpyrenium ions.[9]

The ^{13}C NMR assignments are based on the chemical shifts, the magnitude of one-bond and long-range C–F couplings in comparison with those in the fluoropyrene precursors, HETCOR experiments, and/or multiplicities in proton-coupled spectra.

The ^1H and ^{13}C NMR data for the fluoropyrenium ions are gathered in Chart I. The ^{13}C NMR data for the isomeric monofluoropyrenes **4**, **9**, and **15** and the 4-fluorohexahydro derivative **14** had been reported and their long-range C–F couplings had been assigned.[17a] The ^{13}C chemical shifts of the parent fluoropyrenes recorded in $CDCl_3$ are slightly different from the reported values,[17a] in which CS_2/acetone-d_6 was used as NMR solvent. However, the variations are less than +0.3 ppm, usually with the smallest variations for carbons next to the substituent. Hence, those assignments are adopted in the present study and used as interpretive guidelines. The ^1H NMR data for all the fluoropyrenes substrates and the ^{13}C data for those which are unreported are gathered in Chart IV (supplementary material).

Role of Fluorine in the β Position. Protonation of 2-fluoropyrene (**9**), 2-fluoro-7-*tert*-butylpyrene (**10**), 2-fluorotetrahydropyrene (**11**), and 2-fluoro-7-*tert*-butyltetrahydropyrene (**12**) (Scheme II, Figure 1, and Charts I-III).

Scheme II. Persistent Fluoropyrenium Ions Formed in Superacid Media



(a) Protonation of 9. Careful addition of a clear homogeneous solution of FSO_3H/SO_2ClF kept at dry ice/acetone temperature to a cold slurry of **9** in SO_2ClF gave a dark-green solution whose ^1H NMR consists of five 1H doublets, a 1H triplet, and a 2H doublet all between 7.50–9.18 ppm and a distinct 2H singlet at 4.82 for the sp^3-(CH_2). The most shielded aromatic signal is a 11-Hz doublet due to vicinal coupling to fluorine, confirming **9**-H$^+$ formation (Figure 1a).[17b] Absence of attack at a remote α position is also evident from overlapping low-field doublets at 9.18 and 9.14 (1H each) and the H-7 triplet at 8.44 ppm.

In the ^{13}C NMR spectrum (Figure 1b) all the expected 16 ring carbons were resolved: the sp^3(CH_2) is a doublet at 36.7 ppm with $^2J(CF)$ = 22.5 Hz corroborating **9-H**$^+$ formation. The assignments for C-1, C-2, C-3, C-3a, C-10a, and C-10b were assisted by observation of carbon–fluorine couplings similar to those in the parent compounds. In addition, carbon–fluorine long-range couplings were observed for two other ring carbons. Whereas in the pyrene precursor these are for C-4/C-10, for the pyrenium ion these carbons are assigned to C-4/C-5 which allow the most plausible C–F conjugation path. The C-6, C-7, and C-8

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[16] Cerfontain, H.; Laali, K.; Lambrechts, H. J. A. *Rec. Trav. Chim. Pays-Bas* **1983**, *102*, 210 and refs cited therein.

[17] (a) Hansen, P. E.; Berg, A.; Jakobsen, H. J.; Manzara, A. P.; Michl, J. *Org. Magn. Reson.* **1977**, *10*, 179. (b) Our previous studies of alkylpyrenium ions showed that for the pyrenium ion of attack at C_1, the proton at C_3 is most upfield (see ref 9).

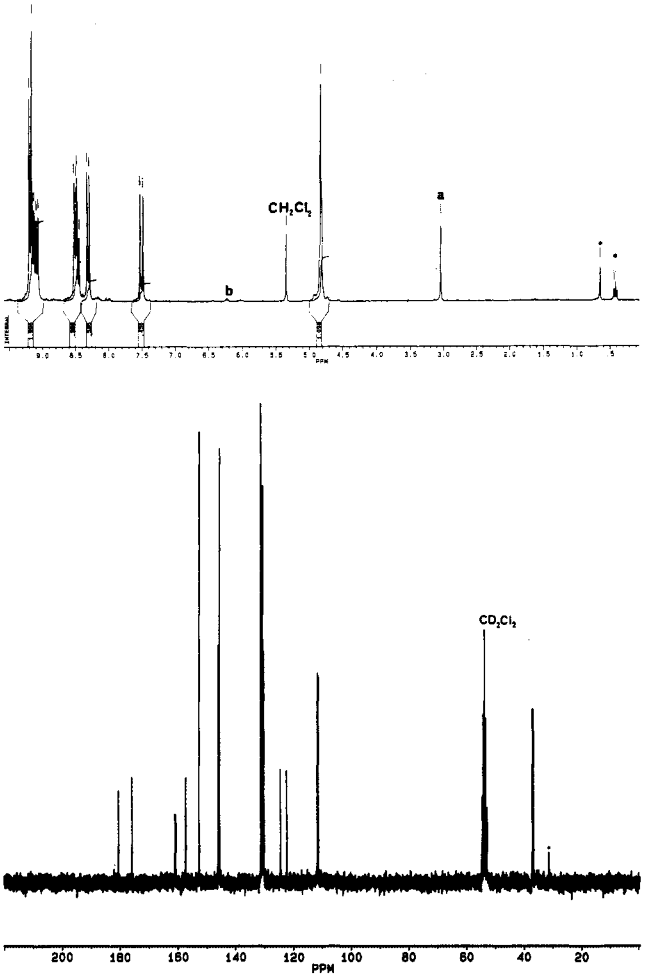

Figure 1. Proton and carbon-13 NMR spectra of protonation of **9**-H$^+$. The following designations apply: a, protonated acetone; b, CHDF$_2$; * denotes unknown impurities and their derived ions.

are identified based on a HETCOR experiment, as are C-9 and C-10 by default. The most deshielded non-hydrogen-bearing carbons are the C-2 (^1J(C-F) = 292 Hz), C-3a, and C-10a. Other deshielded carbons are located at alternating $\alpha\beta$ and α positions.

The CF carbon is deshielded by 17.4 ppm relative to **9** and the ^1J(CF) has increased by 48 Hz. These findings indicate significant double bond character of the CF bond and charge stabilization by F back-bonding.

The ^{19}F NMR spectrum of the ion solution shows a doublet at −61.8 for **9**-H$^+$ deshielded by 53.3 ppm from its precursor, in addition to the peaks for the superacid system.[18]

Thus the presence of a fluorine at C-2 (β) directs the site of attack exclusively (within NMR detection limit) to C-1.

(b) Protonation of 10. Low-temperature protonation of **10** provides an opportunity to compare the relative efficiency of a vicinal tBu group versus a fluorine in directing the attack to their respective α positions. In our previous work, we showed that 2-isopropylpyrene and 2,7-di-*tert*-butylpyrene were monoprotonated exclusively at C-1.[9]

Slow addition of a cold solution of FSO$_3$H/SO$_2$ClF to a cold slurry of **10** in the SO$_2$ClF at dry ice/acetone temperature gave a deep red solution, the ^{1}H NMR spectrum of which (Figure 2a; supplementary material) showed two sp^3(CH_2) singlets at 4.80 and 5.03 ppm and two tBu(Me) singlets at 1.70 and 1.65 ppm, demonstrating the formation of **10-H$^+$** and **10a-H$^+$** in a 40:60 ratio (Scheme II). The most shielded aromatic doublet at 7.48 with an HF vicinal coupling of 11 Hz is specific for **10**-H$^+$ (H-3), whereas the upfield singlet at 8.11 ppm is the H-8 of **10a**-H$^+$.[9] As established with alkylpyrenium ions,[9] the most deshielded aromatic protons in both ions are those of remote α and two of the $\alpha\beta$ protons. The H-6/H-8 in **10**-H$^+$ appear at 9.19 ppm with 0.96 ppm deshielding relative to **10**. For the more abundant **10a**-H$^+$, the H-1/H-3 appear as overlapping doublets at 8.73 and 8.69 ppm. The vicinal coupling constants for the $\alpha\beta$ protons for both pyrenium ions are between 8.2-8.6 Hz.

Despite its complexity, the ^{13}C NMR spectrum of the ion mixture (Figure 2b; supplementary material) exhibited nearly all of the expected signals for the two pyrenium ions. Unequal abundances of the two pyrenium ions greatly assisted the preliminary assignments. The sp^3(C) carbon for **10**-H$^+$ is a doublet at 36.4 ppm with ^2J(CF) = 22.4 Hz. The fluorine-bearing C-2 in **10**-H$^+$ is the most deshielded absorption for this cation appearing as a 291-Hz doublet at 177.7 ppm, corresponding to a 18.2-ppm deshielding at C-2 and a 47.9-Hz increase in the CF coupling relative to **10**, indicating charge stabilization by fluorine by the back-bonding mechanism. The C-2 in **10a**-H$^+$ is more shielded (relative to that in **10**-H$^+$) appearing at 162.4 ppm with ^1J(CF) = 252.4 Hz. This signal is deshielded only by 2.9 ppm relative to **10**, consistent with charge delocalization at alternating ring carbons. Inductive stabilization by the tBu group at C-7 in **10a**-H$^+$ is manifested in >37 ppm deshielding at this carbon as well as in deshielding of the tBu carbons.

When the sample was stored for several days (ca. −65 °C) and examined again by NMR, ^{1}H NMR spectrum showed that the peaks due to **10**-H$^+$ grew at the expense of **10a**-H$^+$ (95 and 5% of the ion mixture, respectively; Figure 2c; supplementary material). Thus kinetic protonation gives a mixture of two pyrenium ions of α attack, and slow isomerization produces the more stable **10**-H$^+$. This isomerization greatly assisted the fine-tuning of our NMR assignments for individual positions of each pyrenium ion. Further support for the ^{13}C assignments were provided by comparison of the ^{13}C of the almost pure **10**-H$^+$ (Figure 2d; supplementary material) with the spectrum of the mixture and by a HETCOR experiment on **10**-H$^+$, in particular corroborating the assignments of the deshielded ring junctions.

Finally, the ^{19}F NMR spectrum of **10**-H$^+$ is a single peak at −62.6 ppm deshielded by 53.1 ppm from the precursor. The fluorine resonance for **10a**-H$^+$ was in the [SbF$_5$-(OSO$_2$F)$^-$] region of the fluorine spectrum.[18] It is tentatively placed at −104.6, corresponding to 11.0 ppm deshielding as compared to **10**.

(c) Protonation of 11. Low temperature reaction of **11** with FSO$_3$H·SbF$_5$ (4:1)/SO$_2$ClF at dry ice/acetone temperature gave a deep-red solution. Protonation at C-7 to give **11**-H$^+$ was clearly evident based on an ^{1}H NMR study. The resulting simple spectrum exhibits the sp^2-(CH_2) at 4.49 ppm as a broad unresolved absorption. Protonation at C-7 is deduced by observation of a 2H singlet at 8.34 ppm. The H-1/H-3 are intact and appear

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Chart II. Comparison of the observed $\Delta\delta^1H$ (cation − precursor) in fluoropyrenium ions and in alkylpyrenium ions (Py-H$^+$).

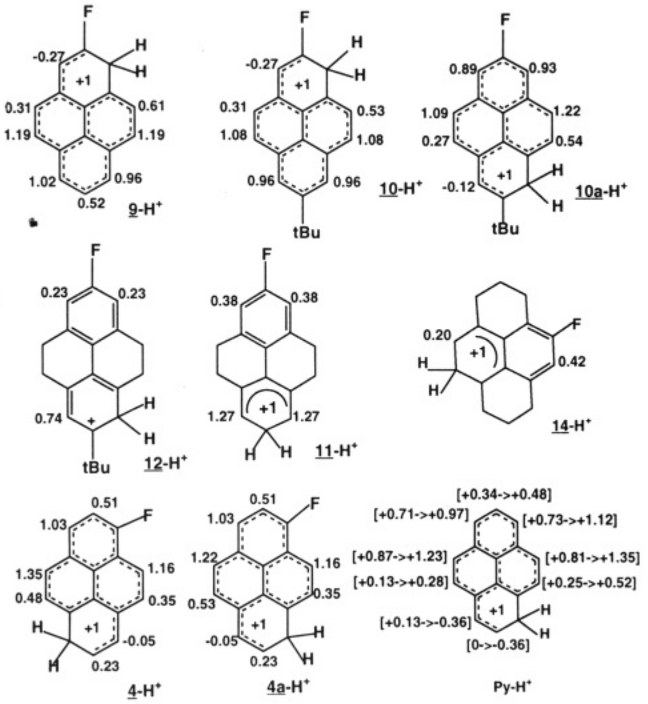
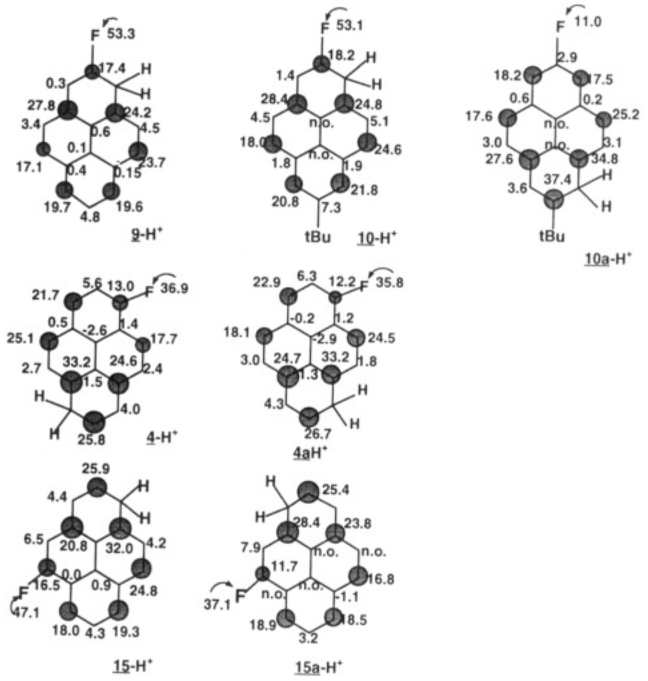


Chart III. A Comparison of $\Delta\delta^{13}C$ and $\Delta\delta^{19}F$ in Fluoropyrenium Ions (the positions of highest positive charge at the periphery are circled).



as a 8.7-Hz doublet at 7.15 deshielded by 0.38 ppm. The bridging CH$_2$'s appear as two broad singlets at 3.11 and 3.08 ppm.

The observed site of protonation under stable ion conditions is consistent with β attack observed in nitration and alkylation of tetrahydropyrene under normal Friedel–Crafts conditions.

Judging from the spectral appearance, the mesomeric form **A′** must be an important contributor (Scheme II). This form provides both a high degree of conjugation and symmetry.

The ^{19}F NMR position of **11**-H$^+$ was in the [SbF$_5$(OSO$_2$F)$^-$] region,[18] and was placed at −106.0 ppm ($\Delta\delta_{19_F}$ = *ca.* 10).

(d) Protonation of 12. Slow addition of the cold superacid FSO$_3$H·SbF$_4$ (4:1)/SO$_2$ClF to a suspension of **12** in cold SO$_2$ClF gave a dark-red solution whose ^1H NMR spectrum was consistent with the formation of **12**-H$^+$ as a major product (ca 80%); protonation at the fluorinated ring of tetrahydropyrene was not observed.

Ion **12**-H$^+$ exhibits a distinctive sp^3(CH_2) as a broad singlet at 4.82 ppm and a deshielded broad singlet at 7.85 ppm for H-6 (*meta*). The 2H doublet for H-1/H-3 are clearly intact and appear at 6.98 ppm (J = 8.9 Hz). This resonance is slightly deshielded as seen in Chart II. The bridging methylenes appear at 3.12 and 3.01 as unresolved broad absorptions. The ^{13}C NMR spectrum of **12**-H$^+$ is complicated due to the presence of minor impurities.

Monitoring the progress of reaction with time (^1H NMR) showed slow formation of **12a**-H$^+$ and **12b**-H$^+$. The ^1H NMR spectrum of **12a**-H$^+$ is characterized by its high degree of symmetry. The site of protonation is clearly away from fluorine. The tBu group is shielded appearing at 0.90 ppm compatible with *ipso* protonation at C-7 which is corroborated by the ^1H integral for the sp^3(CH) absorption observed at 4.50 ppm. An allylic coupling between the H-1 and the methylene protons of the bridge is also noted. These observations are consistent with the proposed structure **12a**-H$^+$ which is similar to the mesomeric **A′** form of **11**-H$^+$. The remaining protons are (2H, δ = 7.16 ppm, J = 8.8 Hz) and (1H, δ = 8.34 ppm, J = 2.3 Hz, t).

The second species exhibits two high-field doublets with large coupling, illustrating that it is not protonated at the fluorinated ring. Its methylene group at 4.99 integrates for 2H. Moreover, the bridge CH$_2$'s are deshielded (δ = 3.84 and 3.57 ppm). The position of the tBu singlet at 1.59 rules out *ipso* attack at the tBu. Five aromatic resonances are observed (δ 7.62 ppm, d, J = 9.1 Hz; δ 7.72 ppm, d, J = 8.6 Hz; δ 8.10 ppm, d, J = 8.6 Hz; δ 8.59 ppm, d, J = 8.6 Hz; δ 8.02, s). The data correspond to a protonated fluorodihydropyrene with the tentative structure **12b**-H$^+$. Oxidation of hexahydropyrene to pyrene in "magic acid" was observed in our previous studies.[9]

Fluorine in the α Position: Protonation of 1-Fluoropyrene 4 (Scheme II, Figure 3, and Charts I-III).

In our previous work[9] we showed that presence of an inductively stabilizing alkyl group in the α position does not reduce the energy of the Wheland intermediate of β attack sufficiently for it to become favored relative to the Wheland intermediate of attack at an unsubstituted "remote" α position. Thus monoprotonation of 1-isopropylpyrene gave a ca. 1:1 mixture two pyrenium ions of attack at C-6/C-8.[9]

Protonation of 1-fluoropyrene **4** provides a comparison with alkylpyrenes in terms of fluorine efficiency relative to alkyl groups to stabilize the positive charge in the α position by back-bonding

Low-temperature reaction of a slurry of **4** in SO$_2$ClF with cold FSO$_3$H/SO$_2$ClF gave a dark-green solution whose ^1H NMR spectrum shows a distinct sp^3(CH_2) absorption as a broad singlet at 4.83 ppm and a highly coupled aromatic region between 8.03–9.48 ppm (Figure 3, parts a and b). The most deshielded $^1/_2$ AB's at 9.48 and 9.35

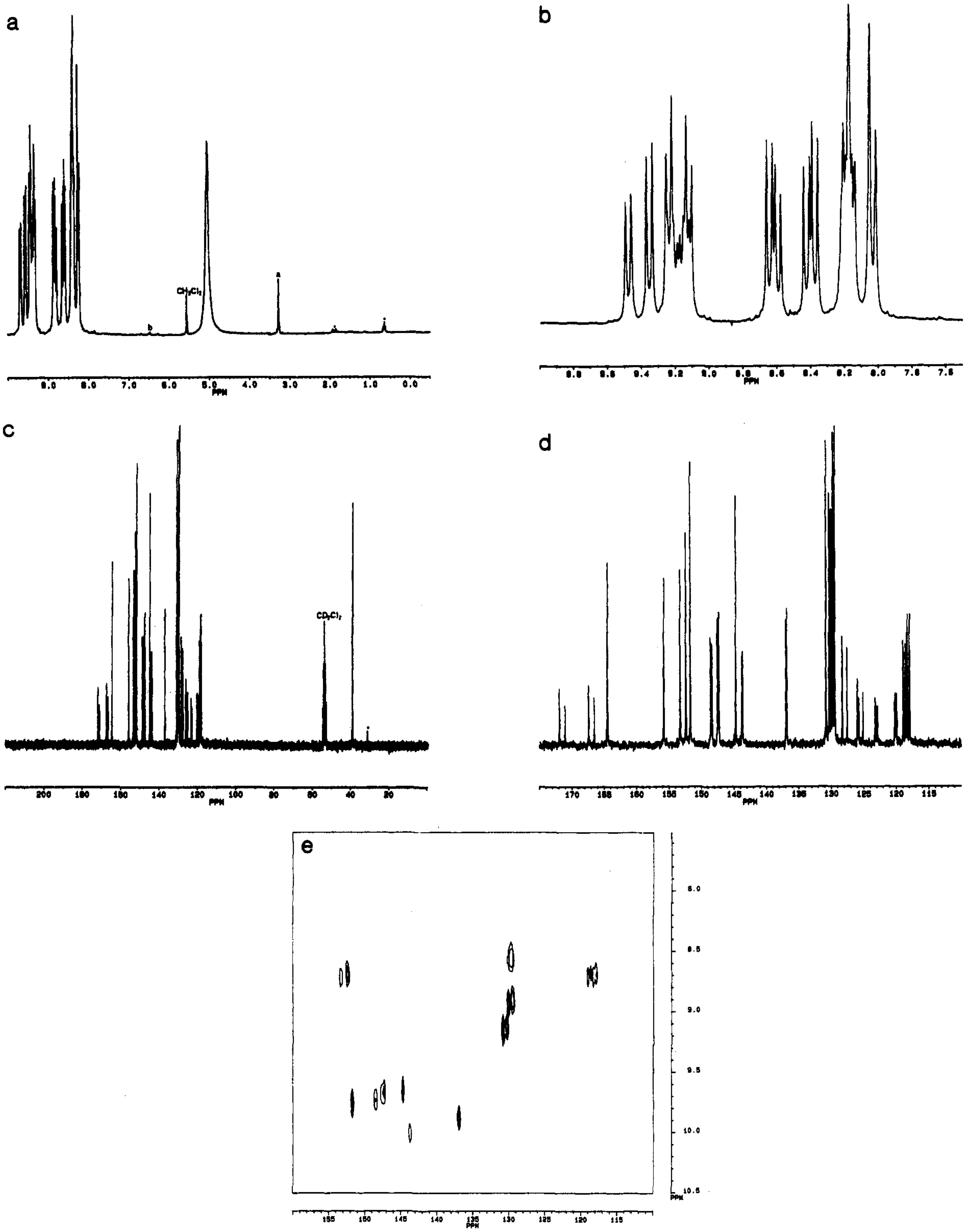


Figure 3. NMR spectra for 4-H$^+$ and 4a-H$^+$: (a) full ^{1}H NMR spectrum; (b) expansion of aromatic region; (c) full ^{13}C NMR spectrum; (d) expansion of aromatic region; (e) H/C HETCOR spectrum. The following designations apply: a, protonated acetone; b, CHDF$_2$; * denotes unknown impurities and their derived ions.

ppm exhibit matching $^1/_2$ AB's at 8.59 and 8.64 ppm, respectively, with vicinal coupling constants of 8.5 Hz. The most upfield aromatic $^1/_2$ AB systems are in between 8.03–8.18 ppm. The position, relative intensity, magnitude of the vicinal coupling constant, and comparison of the spectrum with that of protonation of 1-isopropylpyrene[9] led to the conclusion that there is no β attack and no α attack at the fluorinated ring. Instead, a 55:45 mixture of two pyrenium ions of attack at remote α positions viz 4-H$^+$ and 4a-H$^+$ with coinciding sp^3(CH$_2$'s) are formed. There was no change in the relative ratio of the pyrenium ions with time even after 1 week storage at *ca.* −40 °C.

The ^{13}C NMR spectrum of the mixture (Figure 3, parts c and d) exhibits two sp^3(*C*) absorptions at 38.9 and 39.0 ppm and 30 different types of aromatic absorptions between 118–171 ppm expected for the two pyrenium ions, the assignments of which were facilitated by a

HETCOR analysis (Figure 3e). The C–F in **4-H$^+$** and **4a-H$^+$** are at 169.6 and 168.8 ppm with ^1J(CF) = 284.7 and 284.4 Hz, respectively. These data correspond to 14 and 12 ppm deshielding at C-1 and a *ca.* 33 Hz increase in the C–F coupling compared to the precursor, indicative of fluorine back-bonding.

The resonances belonging to the two pyrenium ions could be separated due to their different intensities. However, the assignments for one set ascribed to **4-H$^+$** is tentative. The spectrum of the ion mixture is representative for its complexity and is, therefore, discussed in more detail: The assignments of C-1, C-2, C-3, C-10, and C-10b are assured *via* carbon–fluorine couplings; C-10c is then assigned by default. The C-3a, C-5a, and C-8a have widely different chemical shifts and C-3a can be assigned based on its position. The assignments of C-5a and C-8a are at present tentative. The C-5 and C-8 have been grouped based on a HETCOR experiment and C-4, C-7, and C-9 have been assigned based on a combination of HETCOR, ^{13}C chemical shifts, and the ^{1}H positions of their hydrogens.

Analysis of the ^{13}C data leads to the conclusion that the positive charge is delocalized at alternating carbons and resides primarily at C-1, C-3, C-4, C-10, C-5a, and C-8a. Consistent with the analysis based on ^{1}H and ^{13}C NMR, the ^{19}F NMR spectrum of the ion mixture exhibits two signals at −86.6 and −87.7 ppm (deshielded by 36.9 and 35.8 ppm, respectively, as compared to **4**). The more abundant cation is clearly one with the more deshielded fluorine, in accordance with a pyrenium ion in which the charge is most effectively delocalized *via* a mesomeric fluoronium ion.

Fluorine in the αβ Position: Protonation of 4-Fluoropyrene 15 and its Precursor 14 (Scheme II and Charts I-III). **(a) Protonation of 15.** In our previous studies we found that 4-isopropylpyrene was protonated at C-6 and C-8 to give a ca. 1:1 mixture of two pyrenium ions. In order to determine the directive effect of fluorine, **15** was protonated.

Slow addition of a cold solution of FSO_3H/SO_2ClF to a slurry of **15** in SO_2ClF at dry ice/acetone temperature gave a dark-green solution on mixing. The ^{1}H NMR spectrum shows just one sp^3(CH_2) absorption as a slightly broad singlet at 4.81 ppm and highly coupled aromatic absorptions within the ranges of 7.99–8.63 and 9.02–9.37 ppm. Absence of vicinal coupling for the 4.81 ppm peak for fluorine and a detailed analysis of the spectrum in comparison with that of protonation of 4-isopropylpyrene[9] led to the conclusion that the same two pyrenium ions formed by protonation at C-6/C-8 are formed with **15** viz **15-H$^+$** and **15a-H$^+$** (in ca. 60:40 ratio). Extensive overlap in the proton spectrum (and presence of Py-H$^+$ as impurity) precluded a complete analysis of the atomatic signals of **15-H$^+$**; only H-4 and H-7 (at 9.32 and 8.2 ppm, respectively) could be unambigously assigned.

In the ^{13}C NMR spectrum the diagnostic sp^3(CH_2) for the two ions are coinciding and give rise to a peak at 38.95 ppm. The C–H connectivity of the latter with the 4.75 ppm signal (^{1}H NMR) is assured by a HETCOR analysis. The magnitude of the C,F coupling for resolved signals and the HETCOR analysis greatly assisted the assignments. The C-4 for the major ion is a doublet at 174.3 ppm with a ^1J(C–F) = 290.7 Hz, corresponding to 16.4 ppm deshielding and a 37.7 Hz increase in the C–F coupling constant. The less abundant cation shows a somewhat smaller doublet at 169.5 ppm with a C–F coupling of 286 Hz. The C-3, C-5, C-8a, C-6, and C-3a of **15-H$^+$** were assigned based on the magnitude of C,F couplings. Assuming a correct choice of the more abundant isomer, the data for C-4 and C-10 confirm that the protonation shift of C-10 is larger than that for C-5. The chemical shift of C-8a (assured based on C,F coupling arguments) is similarly larger than that of C-5a. These observations are of great importance in the interpretation of the protonation shifts.

Finally, the ions exhibit two ^{19}F absorptions with the major one at −77.4 ($\Delta\delta_{^{19}F}$ = 47.1 ppm) and the minor one at −87.4 ($\Delta\delta_{^{19}F}$ = 37.1).

(b) Protonation of 4-Fluorohexahydropyrene 14. It was previously shown[9,19] that hexahydropyrene itself is monoprotonated in FSO_3H/SO_2ClF (or SO_2) and diprotonated in $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2ClF. Slow oxidation to pyrene in magic acid was also observed.[9] To assess the possible role of fluorine in directing substitution hence the outcome of protonation, we studied mono- and diprotonation of **14**.

Careful addition of a cold solution of $FSO_3H{\cdot}SbF_5$ (4:1)/SO_2ClF to a slurry of **14** in the same solvent gave a red solution on mixing, whose ^{1}H NMR spectrum was consistent with monoprotonation in the nonfluorinated ring to give **14-H$^+$**.

The spectrum shows a distinct sp^3(CH_2) absorption as a broad singlet at 4.37 ppm. The vicinal proton (*ortho*) is a broad singlet at 7.25 deshielded by 0.20 ppm relative to **14**. The vicinal aromatic proton to fluorine is clearly intact and gives rise to a 9.3-Hz doublet (^3J, H–F) deshielded by 0.42 ppm. The bridge methylene protons give a number of broad singlets within the ranges of 3.48–2.98 and 2.28–2.04 ppm.

Similar protonation of **14** with "magic acid"/SO_2ClF gave a dark-red solution whose ^{1}H NMR spectrum shows five broad resonances in the aromatic region at 9.14, 8.96, 8.15, 7.81, and 7.42 ppm. The aliphatic region of the spectrum shows one unresolved sp^3(CH) absorption at 4.53 ppm and several bridge CH_2's as broad singlets (3.64, 3.43, 3.2, 3.03, 2.50, 2.26, and 2.0). The spectral appearance appears compatible with a mixture of mono- and dications. However, the number and relative integrals (and multiplicities) of the deshielded signals are incompatible with formation of a dication by a second protonation at the ring carbon vicinal to fluorine and/or by protonation *ipso* to fluorine.

A Comparative Discussion of the Sites of Attack and Charge Delocalization in Fluoro(alkyl)pyrenium Ions (Charts I-III).

Presence of a fluorine in the β position has clearly increased the stability of the pyrenium ion of α attack at the fluorinated ring relative to other available α positions leading to a single fluoropyrenium cation **9-H$^+$**.

A β fluorine and a β tBu group appear to provide equal kinetic stability to their respective pyrenium ions of α attack **10-H$^+$** and **10a-H$^+$** under stable ion conditions, but the *ortho* fluoropyrenium ion **10-H$^+$** is thermodynamically more stable.

The stabilization provided by a fluorine in the αβ position is obviously insufficient to overcome the predicted[14] 8.8 kcal/mol higher energy of the Wheland intermediate of αβ attack; protonation occurs at C-6/C-8 positions with the positive charge at C-4 being stabilized

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(19) Lammertsma, K. *J. Am. Chem. Soc.* **1981**, *103*, 2062.

by fluorine. Considering the much higher energy of the Wheland intermediate of β attack,[14] formation of **4**-H$^+$ and **4a**-H$^+$ by protonation of **4** are reasonable. Thus an α fluorine is very similar to an α alkyl group in controlling the electrophilic chemistry of pyrenes. Whereas the overall pattern of electrophilic substitution ($\alpha > \alpha\beta > \beta$) remains unaffected, α attack is highly responsive to the presence of a vicinal fluorine leading to a single Wheland intermediate after equilibration.

For direct comparison, the $\Delta\delta_{^1H}$ and $\Delta\delta_{^{13}C}$ observed for the fluoropyrenium ions are gathered in Charts II and III, respectively.

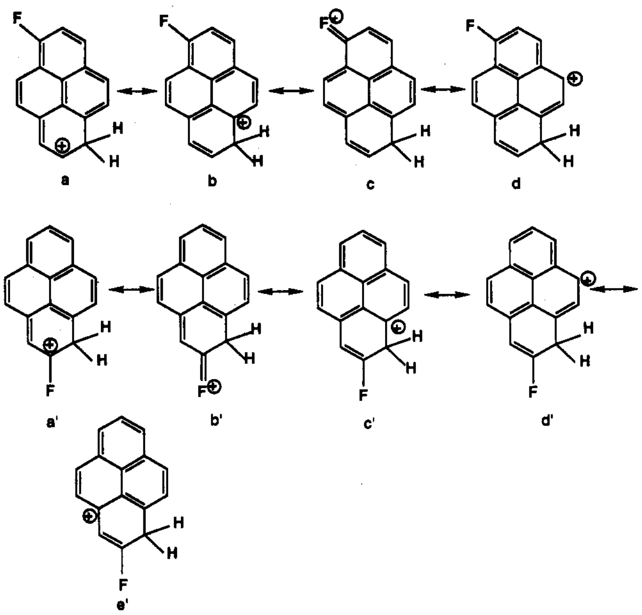
Comparison of the $\Delta\delta_{^1H}$ with the average $\Delta\delta_{^1H}$ established for alkylpyrenium ions[9] demonstrates that charge distributions are very similar, whereby the most deshielded protons are the remote α and two of the four $\alpha\beta$ protons in an alternating manner. The proton *meta* to the protonation site is *shielded* relative to the precursor. The ^{13}C chemical shifts provide an even more in-depth picture for charge distribution in the fluoropyrenium ions of protonation, demonstrating charge alternation at the periphery and away from the site of attack via their phenalenium ion character (Chart III).

Comparison of the ^{13}C positions of C-5a and C-8a in **4**-H$^+$ and **4a**-H$^+$ (*ortho* and *para* to the protonation site) shows much larger deshielding at the *ortho* position. A similar situation exists for **10a**-H$^+$. In contrast, the C-3a and C-10a positions (*ortho* and *para* to the protonation site) in **9**-H$^+$ and **10**-H$^+$ show a similar degree of positive charge delocalization. This similarity is due to fluorine perturbation and charge stabilization at C-2, enhancing conjugation at both C-3a and C-10a. The more upfield position of the fluorine-bearing C-2 in **9**-H$^+$ and **10**-H$^+$ as opposed to the position of C-2 in **4**-H$^+$, **4a**-H$^+$, **15a**-H$^+$ is a clear indication that positive charge stabilization at C-2 is achieved by fluorine back-bonding. For all protonated compounds it is seen that C-9 is at lower field than C-5.

Focusing on the magnitude of three-bond couplings as an indicator of bond-order, it is generally seen that three-bond couplings between the $\alpha\beta$ protons have decreased in the fluoropyrenium ions, whereas they are generally unaffected at the nonprotonated end of the molecules; instead large vicinal couplings are encountered for H-6/H-7 (9.4 Hz) in **4**-H$^+$ and for H-8/H-7 (9.4 Hz) in **4a**-H$^+$ which can be compared with 8.3 Hz vicinal coupling observed in the alkylpyrenium ions, again indicative of the importance of the mesomeric forms with fluoronium ion character (Scheme III). The magnitude of one-bond ^{13}C–^{19}F NMR coupling constants as a measure of fluorine back-bonding in fluorocarbenium ions and its sensitivity to the electron demand at the cationic center have been well demonstrated by Olah et al. in a number of occasions.[2a,2b,20]

The ^3J(C-3,F) coupling for **4**-H$^+$ and **4a**-H$^+$ (Chart I) are much larger than for the uncharged precursors, whereas ^2J(C-10a,F) are much smaller. An increase in ^3J(C-3a,F) is observed for **9**-H$^+$ and **10**-H$^+$, but not for **10a**-H$^+$. Long-range C,F couplings are clearly smaller in the cations than in the neutral precursors. However, a large long-range coupling, ^5J(C-5,F) is detectable for **9**-H$^+$ and **10**-H$^+$ which is in accord with the large ^3J(C-3a,F) coupling.

Scheme III. Charge Delocalization in Fluoropyrenium Ions and the Fluoronium Ion Character



The ^{19}F chemical shifts of the protonated species exhibit a very regular deshielding pattern (Chart III). For a fluorine *ortho* to the site of attack (as in **9**-H$^+$ and **10**-H$^+$), a large downfield shift of 53 ppm is observed. For protonation at the "remote" α position with fluorine placed at the α or $\alpha\beta$ positions (as in **15**-H$^+$, **15a**-H$^+$, **4**-H$^+$, and **4a**-H$^+$), the deshielding effects are 35–47 ppm, and for a fluorine in the β position (as in **10a**-H$^+$) the $\Delta\delta_{^{19}F} = 11$ ppm. The observed $\Delta\delta_{^{19}F}$ for fluoropyrenium ions are all smaller than those observed in fluoro(alkyl)benzenes.[1a] The observed ^{19}F shifts underline the effective charge delocalization and alternation in pyrenium ions. This taken together with the large ^3J(C-3a,F) and the long-range ^5J(C-5,F) coupling underline the importance of mesomers like a′ and b′ (Scheme III). The charge pattern of the remaining compounds seems to be dominated by mesomers like b as judged from the difference in protonation shifts of C-3a and C-10a and the large ^3J(Hα,Hβ) coupling at the protonated end of the molecule. For all compounds, mesomers of d type are important. The fluorine substituents are thus seen to have a major impact on the charge distribution of the protonated ions of phenalenium character.

Donor-acceptor stabilization and charge alternation was observed by Rabinovitz[21] in a series of dianions and dications of PAHs. More recenty, we have observed the same type of charge distribution pattern in the oxidation dications of crowded alkylpyrenes.[11] Detailed NMR studies of charge distribution in crowded alkylpyrenium ions of protonation strongly point to the substituent influence of the Wheland intermediate of α attack as also found by Cornelisse et al.[22] based on the observed isomer distribution in nitration of cyclopenta[*cd*]pyrene.

Further studies directed toward fluorine control of electrophilic chemistry of carcinogenic PAHs and synthesis of model compounds, which may allow such perturbations to be tested under stable ion and normal Friedel–Crafts conditions, have been initiated in our laboratories.

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Experimental Section

Materials. Some of the fluoro(alkyl)pyrene substrates used in this study were gifts donated by Prof. Arne Berg (Aarhus University), synthesis (as outlined in Scheme I)[7a,8] and ^{13}C NMR spectra of which had already been reported.[17a] The important IR features of these compounds have also been discussed.[23] In the present study these compounds were subjected to a complete multinuclear NMR analysis (^{1}H, ^{13}C, ^{19}F) prior to the stable ion study [see discussion, Chart III (supplementary material) and ref 17a].

FSO_3H (Aldrich) and SbF_5 (Fluorochem and Aldrich) were distilled in an all-glass distillation apparatus under dry nitrogen at atmospheric pressure. SO_2ClF (Aldrich) was used as received.

The $FSO_2H{\cdot}SbF_5$ mixtures were freshly prepared by adding the required molar amounts of FSO_3H (by weight) to preweighed samples of SbF_5 in Nalgene bottles under a fast flow of dry nitrogen.

NMR spectra were recorded on a Bruker AC 250 (at Roskilde) and a GE GN-300 (at KSU) instruments.

The probe was cooled by shimming with an acetone-d_6 sample. Unless otherwise stated, the cold ion solutions were studied at 210-213 K. CD_2Cl_2 served as both the internal lock and NMR reference for the low-temperature spectra. ^{19}F NMR spectra were externally referenced relative to $CFCl_3$.

General Procedure for Stable Ion Generation. In a typical experiment, a clear homogeneous solution of the superacid (ca. 1 mL) diluted with SO_2ClF (1:1 v:v) prepared in a 10-nm NMR tube was carefully added to a cold slurry of the pyrene (ca. 30 mg) in SO_2ClF (ca. 0.5 mL) prepared inside a second 10-mm NMR tube with vigorous mixing (vortex) under nitrogen. The fluoropyrenium ions produced a dark-green color whereas the alkylated derivatives were red. A cold aliquot was then transferred (either by pouring directly or *via* a precooled pipet) into a 5-mm NMR tube fully immersed in a dry ice/acetone bath, and precooled CD_2Cl_2 (ca. 8 drops) was subsequently added (vortex) just prior to NMR analysis.

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Supplementary Material Available: Copies of NMR spectra of **10-H$^+$** (Figure 2a,b), the **10-H$^+$/10a-H$^+$** mixture (Figure 2c,d), and Chart IV (the NMR data on fluoro(alkyl)pyrenes and their tetrahydro and hexahydro derivatives not previously reported in the literature) (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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