Dependence of ^1H and ^{13}C NMR chemical shifts on the PAH : FSO_3H ratios for 4*H*-cyclopenta[*def*]phenanthrenium and pyrenium cations in SO_2ClF. Possible existence of cation–anion interactions and coexistence of $PAHH^+$–PAH †

Sandro Hollenstein and Kenneth K. Laali *

Department of Chemistry, Kent State University, Kent, OH 44242, USA

Received (in Cambridge) 24th December 1998, Accepted 24th February 1999

For two representative delocalized PAH-carbocations, namely the C-1 protonated 4*H*-cyclopenta[*def*]phenanthrenium cation $\mathbf{1H}^+$ and the C-1 protonated pyrenium cation $\mathbf{2H}^+$, generated in FSO_3H–SO_2ClF, the FSO_3H : PAH molar ratio and the absolute concentration of the arenium ions were systematically varied over a wide range (FSO_3H : PAH molar ratios were varied from 71 to 1 for $\mathbf{1H}^+$ and from 69 to 5 for $\mathbf{2H}^+$ in 0.3 mL of SO_2ClF and 0.05 mL of CD_2Cl_2 at −75 °C). In selected cases, the H/H COSY and C/H HETCOR spectra were used to fully assign the resonances. Shielding of the PAH-arenium ion protons and carbons was observed with decreasing FSO_3H : PAH ratios without noticeable line-broadening. This is attributed to cation–anion interactions in the low FSO_3H : PAH domain and possible formation of contact ion pairs. Lowering the ratio (below 35 in the case of **1** and below 10 for **2**) gave separate sets of resonances for the unprotonated PAH, indicative of the presence of the equilibrium: $PAH + FSO_3H \rightleftharpoons PAHH^+ + FSO_3^-$. The observed *shielding* of the unprotonated PAH in the equilibrium as compared to the starting material in $CDCl_3$, is attributed to solvation by FSO_3H, although possible formation of $PAHH^+\ FSO_3^-$–PAH ion pair–molecule clusters is not ruled out.

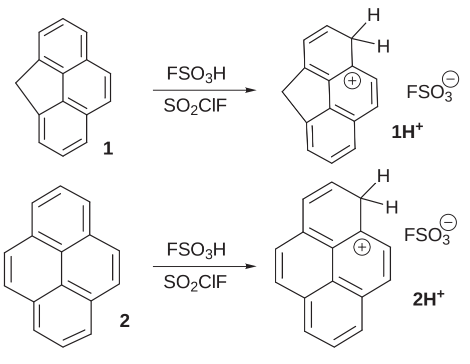
Introduction

The commonly practiced method for generation of persistent carbocations and acidic onium ions is to dissolve the substrates in excess of the superacid system in an appropriate low nucleophilicity cosolvent (*i.e.* SO_2, SO_2ClF, SO_2F_2) depending on the nature and reactivity of the cation(s) to be formed, so that the possibilities of self-condensation, oxidation and other side-reactions are minimized.[1] A large variation in the superacid : substrate ratios (from 4 fold excess to as much as 100 fold excess superacid) can be found in the literature both in protonation (using FSO_3H–SO_2ClF and $FSO_3H{\cdot}SbF_5$–SO_2ClF systems) and in two electron oxidation studies (with SbF_5–SO_2ClF).[2,3] Although working with dilute carbocation (or onium ion) solutions is advantageous because of reduced viscosity and substrate economy, it becomes less practical for low temperature 2D-NMR studies in protic superacids.

In the course of our studies on PAH arenium ions,[4–9] we have observed dramatic variations in the ^1H NMR chemical shifts as a function of FSO_3H : PAH ratios, whereas subsequent dilution with SO_2ClF had minimal effect. In some cases, the appearances of the ^1H NMR spectra were greatly influenced, with resonances moving around to various degrees (up to 2 ppm!), so that it was sometimes hard to believe that the more concentrated samples prepared for 2D-NMR studies were still due to the same arenium ions. The ^{13}C resonances also changed, but less severely.

The observed variations in the position and appearance of the ring protons were detected in a number of systems, namely pyrenium cations,[4] benzo[*a*]pyrenium,[5] benzo[*e*]pyrenium,[5] dibenzo[*a*,*e*]pyrenium,[5] dihydropyrenium,[6] phenanthrenium,[7] methylene-bridged phenanthrenium[7], chrysenium,[8] and indeno-PAH cations,[9] showing that it is a rather general phenomenon. This implied that the reported NMR data on various carbocations are not necessarily the same under a different set of experimental conditions, especially at *lower* superacid to substrate ratios.

Using two representative PAH arenium ions $\mathbf{1H}^+$ and $\mathbf{2H}^+$ (Scheme 1) we report here the first systematic carbocation concentration dependency study on NMR chemical shifts showing a dramatic counter ion effect at lower FSO_3H to arene ratios, and the appearance of the equilibrium: $FSO_3H + PAH \rightleftharpoons PAHH^+ + FSO_3^-$ which is slow enough on the NMR timescale not to give an exchange-averaged structure, but for the arenium ion and its precursor to coexist. Such an equilibrium was not observed in higher acidity superacid $FSO_3H{\cdot}SbF_5$ (4 : 1).



Scheme 1 Protonation of **1** and **2** with FSO_3H–SO_2ClF.

Based on the Δδ values determined for two extreme cases (low ratio/high ratio) for each carbocation, it is possible to identify the positions of high counter ion contacts (see Discussion). The approach is similar to the detection of contact ion pairs in the X-ray structures of carbocations,[10] where nucleophile–electrophile interactions and H-bonding have been observed in situations in which atoms of the counter ion and cation are closer than the sum of their van der Waals radii. A detailed analysis of carbocation–counter ion interactions in the solid state has been provided in a recent review by Laube.[11] In

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† Supplementary data (SUPPL. NO 57509, 11 pp.) are available from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC web page (http://www.rsc.org/authors).

Table 1 The FSO_3H:PAH ratios for spectra 1 through 12 given in Fig. 1–2

Spectrum number	PAH/mg	FSO_3H/ml	FSO_3H/mmol: PAH/mmol
1	19.5	0.05[a]	—
2	9.4	0.2	71
3	9.4	0.1	35
4	20.2	0.2	33
5	31.7	0.2	21
6	20.2	0.1	16
7	10.9	0.05	15
8	31.7	0.1	11
9	19	0.05	8
10	32.6	0.05	5
11	32.2	0.025	3
12	33.3	0.01	1

[a] Superacid: $FSO_3H{\cdot}SbF_5$ (4:1).

Table 2 The FSO_3H:PAH ratios for spectra 1 through 10 given in Fig. 3

Spectrum number	PAH/mg	FSO_3H/ml	FSO_3H/mmol: PAH/mmol
1	10.2	0.2	69
2	19.7	0.2	36
3	10.2	0.1	35
4	29.2	0.2	24
5	9.5	0.05	19
6	19.7	0.1	18
7	29.2	0.1	12
8[a]	19.7	0.05	9
9[a]	34.7	0.075	8
10[a]	34.5	0.05	5

[a] Not fully dissolved (some starting material on top of the solution).

solution, however, despite a great deal of progress in stable ion chemistry in superacid media, carbocation interactions with the counter ion and solvent are much less understood.[12] Such interactions are usually difficult to detect when they are not site-selective. Detection of counter ion interactions with onium ions were more successful and became the impetus for much of the elegant work directed towards developing "weakly-coordinating anions".[13,14] In a recent study, Mayr *et al.*[15] reported that the NMR of chloromethylene-ammonium ions exhibits interesting counter ion dependency in regular solvents indicative of contact ion pair formation, but no such effects could be observed in the less nucleophilic SO_2.

Results

Low temperature protonation reactions of **1** and **2** with FSO_3H–SO_2ClF were selected for concentration dependency and NMR monitoring studies. A series of NMR samples with different concentrations and FSO_3H:PAH molar ratios were prepared (Tables 1 and 2) with good precision under carefully controlled conditions (see Experimental), and the ^1H and ^{13}C NMR spectra were recorded at −75 °C for comparison. The corresponding NMR spectra are shown as partial stackplots in Fig. 1–3.

Carbocation solutions whose FSO_3H:PAH ratios were in close proximity, were prepared several times to ensure reproducibility. Although minor changes (due to weighing errors) did exist, the overall picture for all spectra remained the same.‡

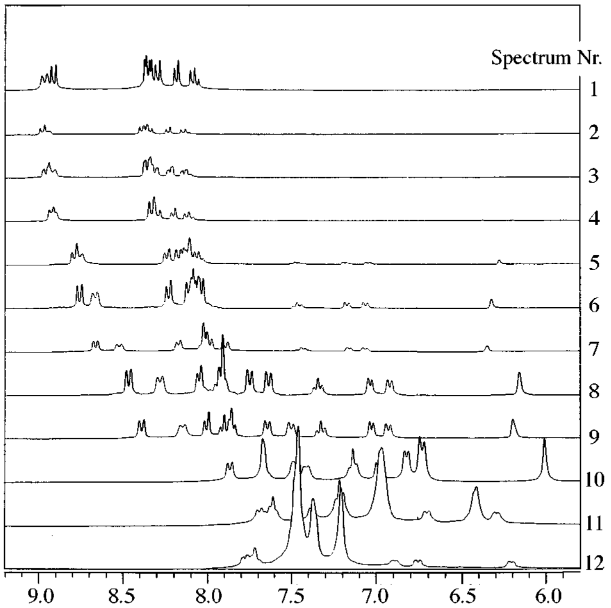

Fig. 1 ^1H NMR spectra (300 MHz; −75 °C) for $\mathbf{1H}^+$ as a function of FSO_3H:PAH ratios presented as partial stackplots (for FSO_3H:PAH ratios see Tables).

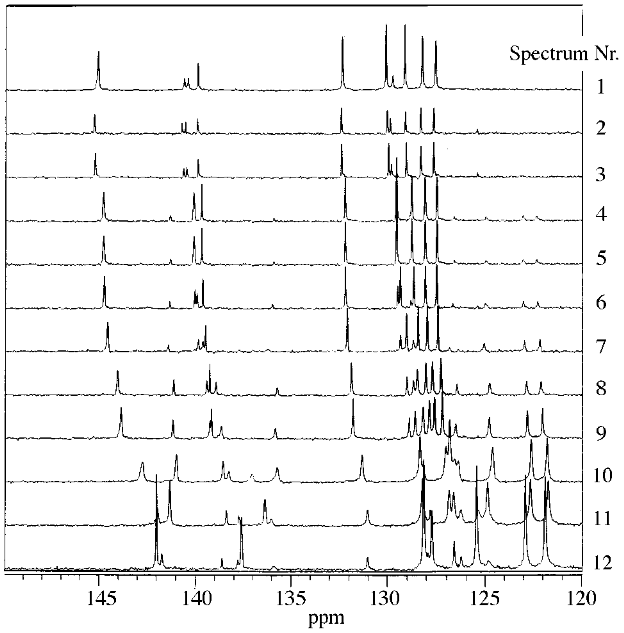

Fig. 2 ^{13}C NMR spectra (75 MHz; −75 °C) for $\mathbf{1H}^+$ as a function of FSO_3H:PAH ratios presented as partial stackplots (for FSO_3H:PAH ratios see Tables).

For $\mathbf{1H}^+$, samples corresponding to spectra 2 and 10 (in Fig. 1–2) and for $\mathbf{2H}^+$ those corresponding to spectra 1 and 10 (in Fig. 3) were studied by 2D-NMR (H/H COSY and C/H HETCOR) to provide complete assignments (the relative assignments of some of the quaternary carbons still remain interchangeable). Fig. 4 illustrates the NMR assignments for $\mathbf{1H}^+$ (based on spectrum #2) and for $\mathbf{2H}^+$ (based on spectrum #1). It also shows the $\Delta\delta$ values derived from two extreme cases for each arenium ion ($\mathbf{1H}^+$: spectra 2 and 10; $\mathbf{2H}^+$: spectra 1 and 10) (see also supplementary material for representative full spectra at selected FSO_3H:PAH ratios).

In order to gauge the temperature effect, a series of spectra were recorded between −50 and −85 °C (at 5° intervals) for comparison. The effects on ^1H NMR chemical shifts were small, with spectra recorded at −50 °C being on average 0.2 ppm more deshielded as compared to −85 °C, but no crossover

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‡ Except for the last three entries in Table 1, in all cases the solutions were homogeneous and no separation of the solution into two layers was observed. Entries for saturated solutions were included in order to provide a wider range of FSO_3H:PAH ratios, however the general conclusions derived remain unchanged if these entries are excluded.

resonances were detected and no noticeable changes in the integral ratios for PAHH$^+$: PAH were discernable.

It can be seen from stackplots shown in Fig. 1–3 and from the representative spectra (supplementary material) that the ^{1}H and ^{13}C NMR spectra vary dramatically as a function of FSO$_3$H : PAH molar ratios (Tables 1–2). For the PAHH$^+$, a general deshielding trend is observed with increasing amounts of the superacid.

With **1H**$^+$, when the FSO$_3$H : PAH is below 35, a separate set of resonances appear which belong to the PAH itself. The latter exhibits a triplet, two doublets and one singlet (1 : 1 : 1) on the shielded side of the aromatic region belonging to **1H**$^+$ with a corresponding shielded methylene. For **2H**$^+$, shielded resonances due to pyrene itself do not appear until the FSO$_3$H : PAH mmolar ratio is below 10; they appear broad in the ^{1}H NMR.

These observations can be explained by the presence of equilibrium (1).

$$\mathrm{PAH} + \mathrm{FSO_3H} \rightleftharpoons \mathrm{PAHH^+} + \mathrm{FSO_3^-} \qquad (1)$$

Because **2** is more basic than **1**, for a given FSO$_3$H : PAH ratio, its equilibrium lies more strongly to the right. In both cases, no unprotonated PAH remains when the acidity of the superacid is increased [protonation with FSO$_3$H·SbF$_5$ (4 : 1); spectra #1 in Fig. 1 and 3], whereby the ^{1}H and ^{13}C spectra become identical to those obtained with the highest FSO$_3$H : PAH ratios, except for **1H**$^+$ for which the two CH$_2$ resonances are coinciding in FSO$_3$H·SbF$_5$ (4 : 1)–SO$_2$ClF (see supplementary material).

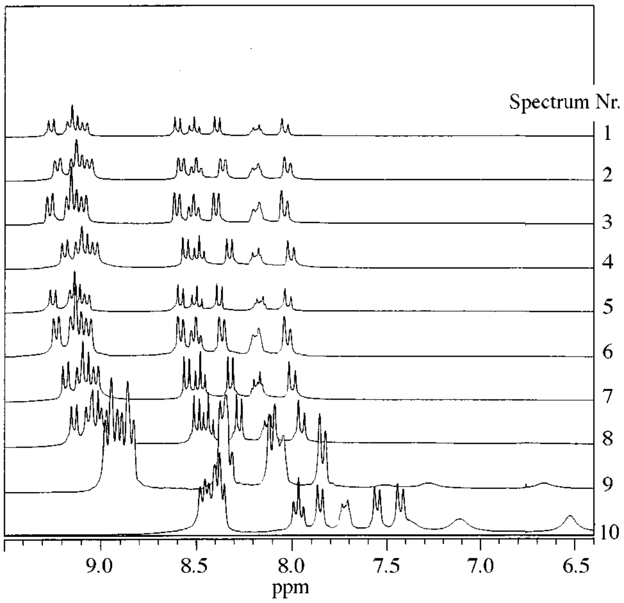


Fig. 3 The ^{1}H NMR spectra (300 MHz; −75 °C) for **2H**$^+$ as a function of FSO$_3$H : PAH ratios (for FSO$_3$H : PAH ratios see Tables).

In a control experiment, addition of sodium fluorosulfate to the NMR samples increased the relative integrals of the PAH resonances and correspondingly decreased the integral for the arenium ion, corroborating the equilibrium.

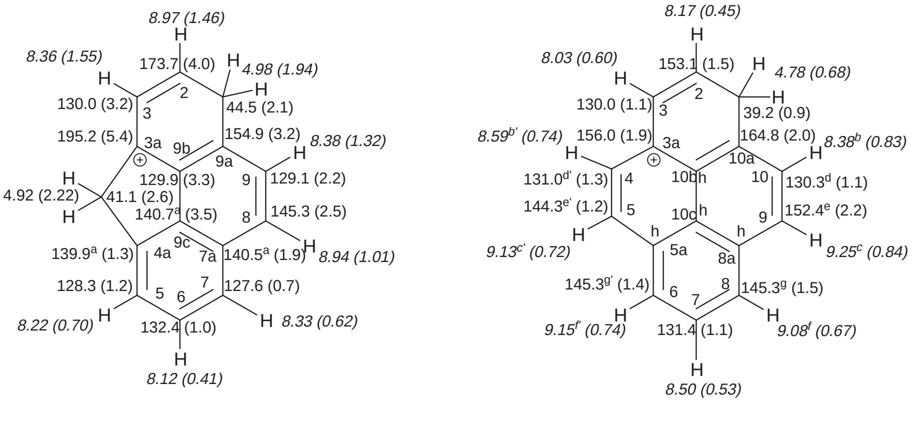
Increased deshielding of the arenium ion resonances as the amount of FSO$_3$H is gradually increased could be explained by a gradual reduction in cation–anion and H-bonding interactions, since the counter ion progressively becomes more solvated by FSO$_3$H and hence less nucleophilic. The $\Delta\delta$ values for low and high ratios shown in Fig. 4 represent these interactions, where large differences are observed for hydrogens and carbons that are more strongly associated with the counter ion. For **1H**$^+$ the largest changes for both carbons and hydrogens are in the AB rings which, as already determined,[7] are the most positive (we note that the strongest interactions are with C-2/C-3a and with the two CH_2 groups). For **2H**$^+$ the variations are more uniform corresponding to an extensively delocalized cation as deduced in previous NMR studies,[6,16] with positions 3a, 6, 8, 9, and 10a exhibiting stronger interactions. The observed changes may be attributed to the sum of the charge effect and cation–anion interactions.

The absolute concentrations of the arenium ions in the NMR samples appear to have only a minor influence on the chemical shifts. Thus for **2H**$^+$, a slight shielding of the resonances is observed when comparing high concentration samples with low concentration samples having similar FSO$_3$H:PAH ratios (compare for instance spectra 2 and 3 with 5 and 6 in Fig. 3). It may be concluded that FSO$_3^-$ anions are less effectively solvated by SO$_2$ClF and that the predominant effects are the cation–anion interactions which are controlled by FSO$_3$H : PAH ratios. The weakly nucleophilic nature of SO$_2$ClF was established by Olah and Donovan in their studies of alkyl cations.[17]

Concerning the observed shielding of both ^{1}H and ^{13}C NMR chemical shifts of the unprotonated PAH in equilibrium (if compared to the PAH resonances in CDCl$_3$), the following observations are noteworthy:

a) all resonances belonging to the PAH are shielded as compared to the neutral precursor;[6,7] b) at very low FSO$_3$H : PAH ratios (1→3) the shielding effect is less; it reaches a maximum at a FSO$_3$H : PAH ratio of 5 and beyond that a deshielding trend sets in, which depends on the absolute concentration of **1H**$^+$: **1**.

The data imply that not only cation–anion interactions but also solvation by FSO$_3$H and possibly PAHH$^+$–PAH inter-



a: assignment tentative

(bcde) might be interchanged with (b'c'd'e')
(fg) might be interchanged with (f'g')

h: 131.3 (1.4), 130.7 (1.6), 126.1 (1.9), 122.0 (1.5)

Fig. 4 ^{13}C and ^{1}H NMR shifts for **1H**$^+$ and **2H**$^+$ (based on spectrum #2 for **1H**$^+$ and #1 for **2H**$^+$) [$\Delta\delta$ values for two extreme (high–low) FSO$_3$H : PAH ratios (see text)].

actions play a role (the relative contribution of these effects to the overall trend is uncertain). Since the unprotonated PAH and FSO_3^- are the most basic species in the equilibrium, they are highly associated or build complexes with the excess FSO_3H molecules which may result in shielding. Alternatively, in the low FSO_3H : PAH domain, formation of $PAHH^+$ FSO_3^-–PAH ion pair–molecule clusters may occur. The case of tropylium cation salt complexes with naphthalenes, namely $C_7H_7^+$ SbF_6^-–naphthalene, $C_7H_7^+$ SbF_6^-–1,4-dimethylnaphthalene and $C_7H_7^+$ $SbCl_6^-$–naphthalene systems studied by Kochi *et al.*[18] (see also ref. 11), for which X-ray crystal structures are available, may be considered as a model for such clusters. PM3 modeling for both **1H$^+$ FSO$_3^-$** and **2H$^+$ FSO$_3^-$** resulted in deprotonation and convergence to π-complexes (inclusion of field solvation did not prevent π-complex formation in the gas phase; ionic point charge embedding calculations require knowledge of cation and anion locations). For comparison, the $PAHH^+$ FSO_3^-–PAH clusters were also examined by PM3: for **1H$^+$FSO$_3^-$–1** the minimized structure indicated arenium–arene periplanar stacking with the counter ion showing closest O–H distances with the H-2 and H-3 of **1H$^+$**(1.72 and 1.75 Å respectively). For **2H$^+$ FSO$_3^-$–2** the rings are also stacked but with the neutral deck rotated about 68° and closest O–H distances are with the CH**H** of the arenium ion and an α proton of the neutral PAH (1.61 and 1.81 Å respectively) (see supplementary material).

In an effort to shed more light on the cation–anion interactions from the counter ion perspective in the present systems, the ^{19}F NMR spectra of several cation solutions were measured; they consisted of two singlets for SO_2ClF (at 100.2 ppm) and FSO_3H (at 42.7 ppm). No separate resonance for the FSO_3^- counter ion could be found; its exchange with FSO_3H solvent must be too fast. Christe[19] has reported the ^{19}F value for the anion in NF_4^+ FSO_3^- in HF solvent at 33.5 ppm (verified by comparison with $CsFSO_3$ in HF). In a control experiment, using a 500 MHz instrument, we measured $KFSO_3$ in D_2O at 38.9 ppm.§

Summary

We have shown that the ^1H NMR chemical shifts of arenium ions of PAHs can vary considerably as a function of FSO_3H : PAH ratios; the ^{13}C shifts also change but less dramatically. Variations in the absolute concentration of the carbocation solutions and temperature have minor effects on chemical shifts. The observed changes are attributed to cation–anion interactions and can be mapped out based on $\Delta\delta^{13}C$ and $\Delta\delta^{1}H$ values between extreme cases (low–high PAH : FSO_3H ratios). By lowering the FSO_3H : PAH ratios, the $PAHH^+$ and the PAH can be made to coexist without noticeable line-broadening in the NMR (except for resonances due to pyrene and the CH_2 protons which appear broad at low FSO_3H to pyrene ratios). The counter ion effect and the equilibrium may be minimized by going to higher superacidity systems with lower nucleophilicity counter ions. Resonances due to the PAH itself are considerably shielded. Possible reasons for the observed shielding are solvation by FSO_3H and formation of ion pair–molecule stacks in the low FSO_3H : PAH domain.

Experimental

Cyclopenta[*def*]phenanthrene and pyrene (both Aldrich) were highest purity commercial samples and were used without further purification. FSO_3H (Allied) was triply-distilled and stored in Nalgene bottles under argon. SbF_5 (Aldrich and Fluorochem) was distilled in an all-glass distillation unit under argon and stored in Nalgene bottles with teflon seals under argon. SO_2ClF was prepared from SO_2Cl_2 with NH_4^+ F^-–TFAH according to a modified procedure of Prakash *et al.*[20] Several distillations provided pure SO_2ClF as a colorless liquid (bp +7 °C).

Preparation of the carbocation solutions

An exact amount of PAH was weighed into a 5 mm NMR tube. The NMR tube was then connected to the HV-line (ace-thread port). After several cycles of evacuation and flushing with argon, the NMR tube was left under vacuum for *ca.* 5 min, after which it was cooled to liquid nitrogen temperature and into which exactly 0.30 mL of SO_2ClF was condensed from a Schlenk-tube reservoir. The liquid nitrogen bath was then exchanged for a dry ice–acetone bath, and 0.05 mL of CD_2Cl_2 was first added (under argon) followed by an exact amount of FSO_3H which was introduced *via* a glass microsyringe equipped with a flexible teflon needle (all under argon). The NMR tube was vigorously stirred at −78 °C (vortex). The concentration dependency spectra were recorded at −75 °C (±1°) on a GE GN 300 instrument [referenced to internal methylene chloride (^1H: 5.32 ppm; ^{13}C: 53.8 ppm)]. Although changes in the absolute value of the chemical shift of the internal standard were noted as a function of FSO_3H : PAH ratios, these variations were considerably smaller than the observed changes for $PAHH^+$ and PAH. Furthermore, since CH_2Cl_2 is exposed to the same environment as $PAHH^+$, the reported changes reflect *relative* NMR shift changes in counter ion interactions as compared to the internal standard. The ^{19}F NMR spectra were referenced to the SO_2ClF signal at 100.2 ppm.

PM3 calculations

These were performed using Hyperchem 5 (Hypercube Inc.; 1997) and the semiempirical package built into GAMESS.[21]

Acknowledgements

Support of our work in the PAH arenium ions area by the NCI of NIH (R15CA63595) is gratefully acknowledged. We thank Professor P. E. Hansen (Roskilde) for his involvement and interest, Dr Gangoda (KSU) for NMR assistance and helpful discussions, Dr Karl Christe (Hughes STX) for his input concerning the ^{19}F NMR of fluorosulfate salts and Dr Todd Raeker (Univ. of Michigan) for computational assistance. We are most grateful to one of the Referees for insightful comments.

Supplementary material

^1H NMR spectra of **1H$^+$** in $FSO_3H{\cdot}SbF_5$ (4 : 1) and using various FSO_3H : PAH mmolar ratios (between 35 and 1; corresponding to stackplots 3,7,9,12); ^1H NMR spectrum of **2H$^+$** in $FSO_3H{\cdot}SbF_5$ (4 : 1) and in FSO_3H at two different concentrations (corresponding to stackplots 6,10). PM3 minimized structures of **1H$^+$ FSO$_3^-$–1** and **2H$^+$ FSO$_3^-$–2**.

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§ In light of the present findings, a comparative study using a superacid with comparable acidity (H_o) but lower counter ion nucleophilicity, namely $HF{\cdot}BF_3$, would be instructive; however in our hands, this system does not meet the precision/reproducibility criteria that this study requires. Nevertheless, the results reported herein are significant since FSO_3H is the most widely used superacid in stable ion studies.

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