

¹³C, ¹H and Two-dimensional NMR Studies of Charge Distribution in Sterically Congested Persistent Cycloalkyl- and Alkyl-pyrenium Ions Generated by Protonation in Superacid Media

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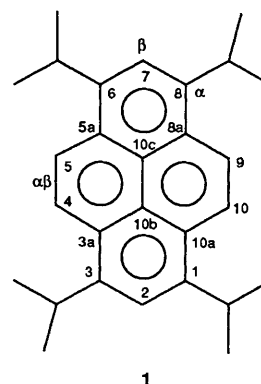
In FSO₃H-SO₂ClF at low temperature, the symmetrical all α -substituted tetraisopropylpyrene **1**, tetracyclohexylpyrene **2**, and tetracyclopentylpyrene **3** monoprotonate at the *ipso* position to give **1H**⁺, **2H**⁺ and **3H**⁺, respectively. Whereas **1H**⁺ is directly observable by low-temperature NMR spectroscopy before it rearranges to **1aH**⁺, the sterically more congested pyrenium ions **2H**⁺ and **3H**⁺ are not persistent, rearranging rapidly to the NMR-observable **2aH**⁺ and **3aH**⁺. These rearranged pyrenium cations are the first examples of pyrenium ions of $\alpha\beta$ attack. Ambient disproportionation of **2** in triflic acid 'TfOH' gives 1,3,6,8,7-pentacyclohexylpyrene.

The 1,3,6-triisopropylpyrene **4** is protonated at the available α position to give **4H**⁺. The 2,7-di-*tert*-pentylpyrene **5** and 2,7-di-*tert*-butylpyrene **6** are α monoprotonated, and 2-*tert*-pentylpyrene **7** is exclusively monoprotonated at the α position *ortho* to the *tert*-pentyl group (\rightarrow **7H**⁺). The 4-isopropylpyrene **8** is monoprotonated at the 'remote' α positions to give **8H**⁺ and **8aH**⁺ in near equal amounts. The charge distribution in the resulting monopyrenium ions was probed with ¹³C, ¹H and two-dimensional NMR (HECTOR, COLOC and COSY) experiments. The positive charge is extensively delocalized away from the site of attack and exists at the alternating carbons of the periphery. Thus the phenalenium ion character of the pyrenium ion of α attack and phenanthrenium ion character of the pyrenium ion of $\alpha\beta$ attack are shown. Low-temperature reaction of **2** with FSO₃H-SbF₅(4:1)-SO₂ClF gives a varying amount of sulfonylation σ -complex **2SO₂H**⁺, the oxidation dication **2**²⁺ and a 1,3-diprotonation species, **2D**²⁺ (D = dynamic). Likewise, protonation of **6** and **7** with FSO₃H-SbF₅(1:1) 'magic acid'-SO₂ClF leads to diprotonation forming, **6D**²⁺ and **7D**²⁺ in addition to dealkylation to give R⁺. The 1,3-diprotonation species consist of singly charged phenalenium ions and tertiary carbocations in which the alkyl group at the 2-position is dynamic and alkyl cation-like.

Synthesis, spectroscopic studies, electrophilic substitution and oxidation chemistry of pyrene derivatives, namely the benzo-, dibenzo-, ethylindeno-pyrenes and their cyclopenta-annulated and methylene-bridged derivatives continue to be the focal points of research directed toward their detection/characterization as proven environmental hazards, and understanding the pathways leading to carcinogenesis.¹⁻¹⁰

In a previous study,¹¹ we reported a ¹H NMR study of protonation of sterically crowded alkyl-(cycloalkyl)-pyrenes. Monoprotonation was observed in FSO₃H-SO₂ (or in CF₃SO₃H-SO₂) and sulfonylation occurred in 'magic/acid'^R-SO₂. Diprotonation was not achieved with 'magic acid'-SO₂ClF owing to competing oxidation. Our ¹H NMR studies pointed to delocalization of charge away from the site of attack and maximum proton deshielding at the 'remote' α and two of the $\alpha\beta$ positions with the proton at the *meta* position to the site of attack being shielded relative to the precursor.

The focus of the present study was four fold: (a) to provide a more complete picture pertaining to the charge distribution mode in congested cycloalkyl-(alkyl)-pyrenium ions of protonation by complete ¹³C NMR analysis of their persistent ions, (b) to explore the influence of the nature and the position of various substituents on the outcome of protonation, (c) to search for new examples of *ipso* attack in order to compare the ease of dealkylation/realkylation of alkyl (cycloalkyl) groups which may be exploited synthetically for one-pot preparation of inaccessible or difficult to prepare alkylpyrene isomers, and (d) to explore new alkylpyrene substrates which are likely to facilitate diprotonation.



NMR Analysis.—The ¹³C NMR assignments of the pyrenium ions are based on the chemical shifts, C/H heteronuclear correlation HETCOR (and long-range heteronuclear correlation COLOC)¹² experiments and/or multiplicities in proton-coupled spectra, alkyl and cycloalkyl substituent effects, relative intensities, and the chemical shifts of their attached proton. The data lead to a consistent set of protonation shifts on carbon chemical shifts (Fig. 1). The ¹H NMR analyses were based on symmetry properties of the molecules, chemical shifts, vicinal coupling constants, H/H COSY and a consistent set of protonation effects on ¹H chemical shifts (Fig. 2).

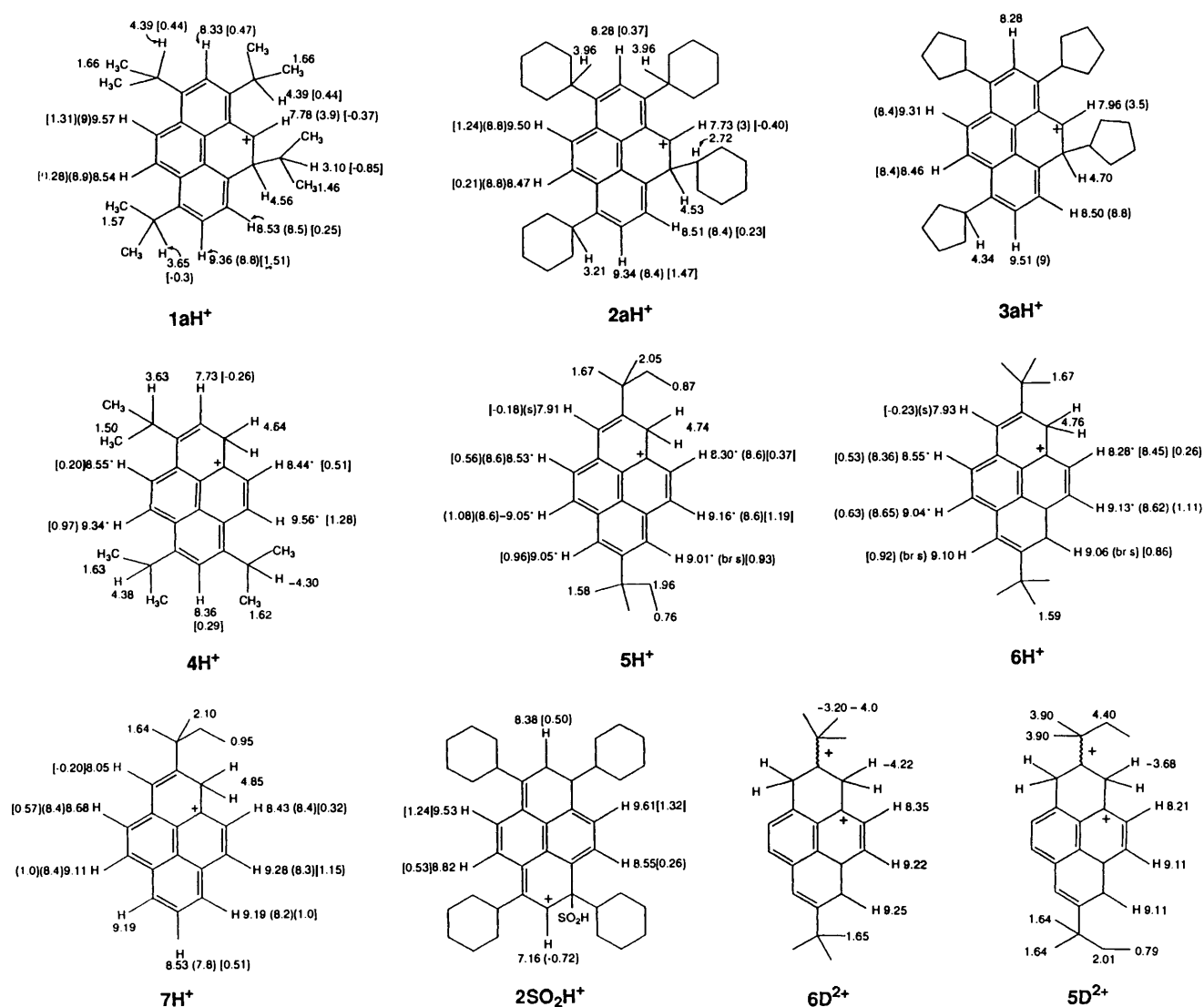


Fig. 1 Proton NMR data for alkyl-(cycloalkyl)-pyrenium ions. Numbers in parentheses are hydrogen-hydrogen coupling constants. Numbers in square brackets are protonation shifts. An asterisk indicates tentative assignment.

Results

Alkyl-(Cycloalkyl)-pyrenium Ions of $\alpha\beta$ Attack via Skeletal Rearrangement of the ipso Protonated all α -Substituted Pyrenium Ions (Schemes 1 and 2, Figs. 1–4).—In a previous ^1H NMR study, we showed that **1** is ipso protonated ($\longrightarrow \text{1H}^+$) and subsequently undergoes a facile Pr^i migration ($\text{1H}^+ \longrightarrow \text{1aH}^+$). In the present study we explore the scope of this type of rearrangement and probe the charge distribution pattern in the resulting pyrenium ions of $\alpha\beta$ attack by ^{13}C NMR.

Protonation of 1. ^1H NMR monitoring of the $\text{1H}^+ \longrightarrow \text{1aH}^+$ rearrangement process in more concentrated ion solutions prepared for ^{13}C NMR studies showed that the rearrangement had already occurred. Thus slight increase in local overheating upon protonation is sufficient to induce skeletal rearrangement, indicative of a low barrier. Only careful preparation at low temperature with lower concentration of the substrate ensures initial detection of the almost pure 1H^+ .

The noteworthy features of the ^1H NMR spectrum of 1aH^+ [Fig. 3(a)] are: (a) the extreme anisotropic shielding of one of the two Pr^i methyls at the ipso position ($\alpha\beta$) appearing at 0.23 ppm (previously observed at 0.12 ppm in $\text{FSO}_3\text{H}-\text{SO}_2$)¹¹ as compared with 0.82 for the ipso $\text{Pr}^i(\text{Me})$ in 1H^+ ; its matching ipso $\text{Pr}^i(\text{Me})$ is only slightly shielded relative to other $\text{Pr}^i(\text{Me})$ doublets and appears as a doublet at 1.46 ppm; (b) vicinal coupling between H-10 (at 7.78 ppm) and the ipso proton (at

4.56 ppm); (c) presence of two well resolved deshielded aromatic AB systems and a singlet; (d) the spectrum was unchanged when examined again after storage for one week at ca. -50°C .

The ^{13}C NMR spectrum of 1aH^+ [Fig. 3(b)] exhibits fifteen aromatic carbons between 169.7–123.9 ppm. The two most deshielded carbon signals at 169.7 and 168.4 ppm are assigned to C-1 and C-3 based on (a) absence of attached proton (HETCOR; [Fig. 3(c)]), and (b) an observed $^3J_{\text{C-H}}$ with $\text{Pr}^i(\text{CH}_3)$ as deduced from a COLOC experiment. C-5a and C-8a give rise to deshielded signals at 166.4 and 152.6 ppm. The assignment of the hydrogen-bearing ring carbons is in line with charge alternation at the periphery observed in pyrenium ions of α attack. Thus C-4, C-7 and C-10 are most deshielded. In the aliphatic region, the diagnostic $\text{sp}^3(\text{CH})$ appears at 52.8 ppm (confirmed by HETCOR experiment, showing its connectivity to the ipso CH at 4.56 ppm). Four $\text{Pr}^i(\text{CH})$ absorptions between 29.5 and 41.4 and eight $\text{Pr}^i(\text{CH}_3)$ between 15.9 and 24.8 ppm are observed. The anisotropically shielded $\text{Pr}^i(\text{CH})$ multiplet at 3.10 is connected to the most deshielded $\text{Pr}^i(\text{CH})$ at 41.3 ppm. It seems reasonable that the geometrical change of the Pr^i group upon rehybridization at C-9 leads to tilting of the $\text{Pr}^i(\text{CH})$ and one of the $\text{Pr}^i(\text{Me})$ groups. The observed deshielding of $\text{Pr}^i(\text{CH})$ suggests that it lies in the proximity of C-8a. The HETCOR experiment shows that the most shielded $\text{Pr}^i(\text{CH}_3)$ at

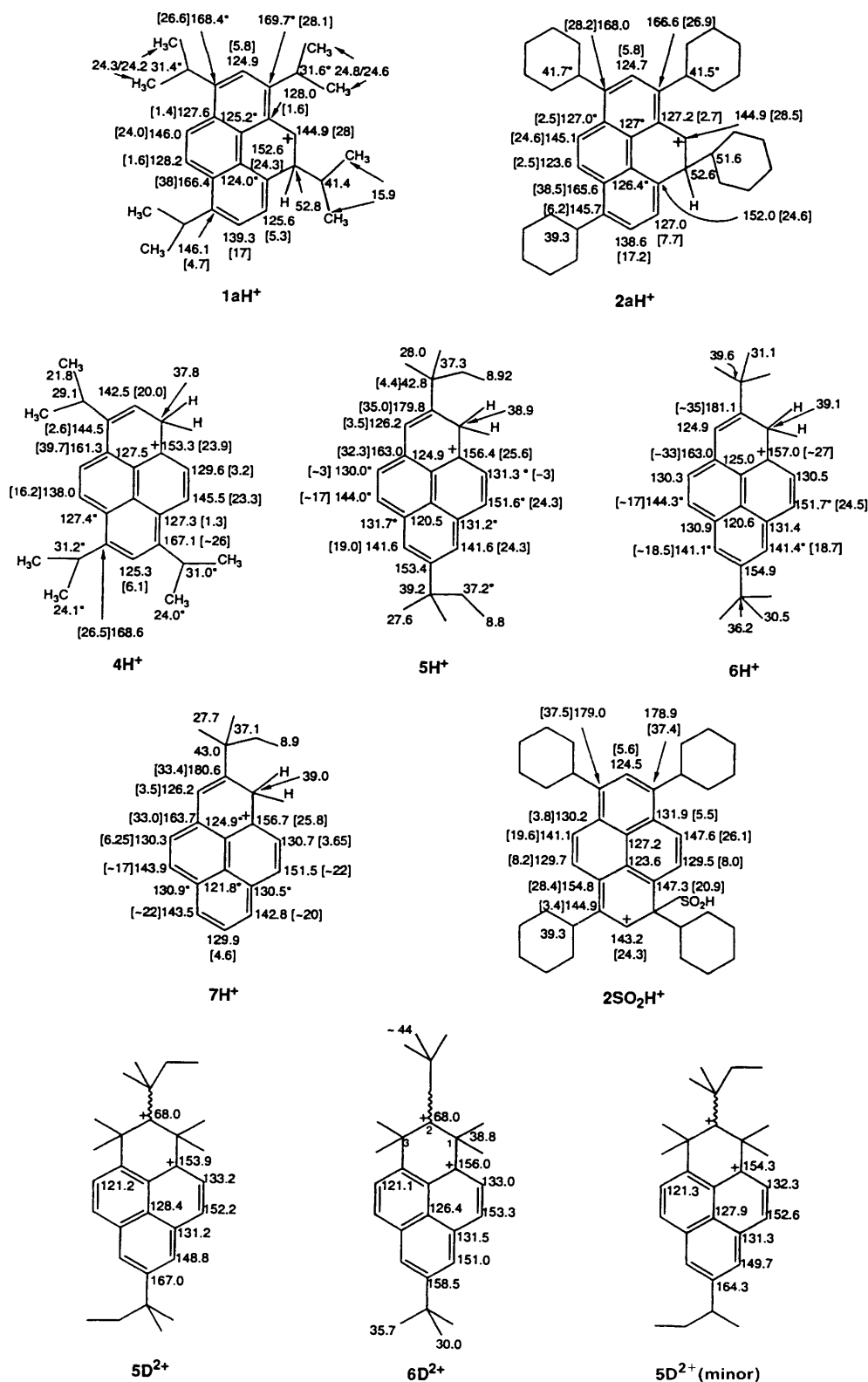


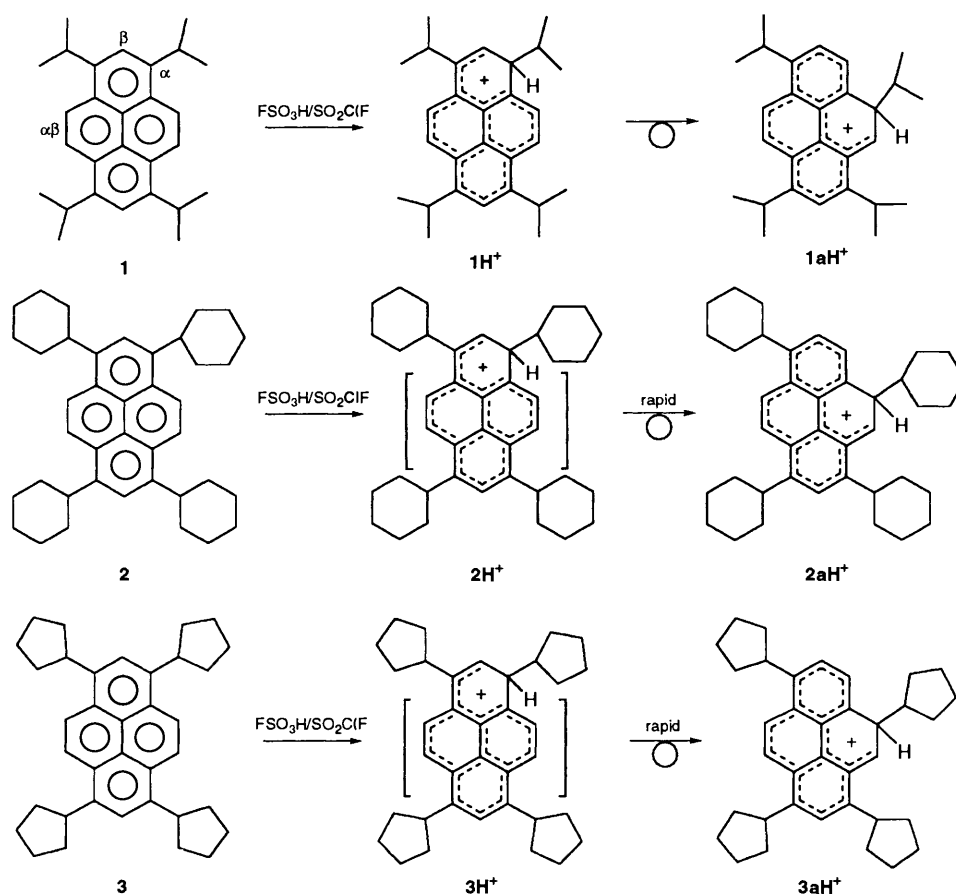
Fig. 2 ^{13}C NMR data for alkyl-(cycloalkyl)-pyrenium ions. Numbers in square brackets are ^{13}C $\Delta\delta$ values.

0.22 ppm is connected to the most upfield $\text{Pr}^i(\text{CH}_3)$ at 15.9 ppm, indicative of anisotropic shielding of a methyl group.

Quenching of the ion solution furnished the all α -substituted **1** (^1H NMR). The $1\text{aH}^+ \rightarrow \mathbf{1}$ transformation upon exothermic quenching (ice–bicarbonate), which was also observed in our previous studies,¹¹ suggests that realkylation (presumably by $\text{Bu}'\text{OSO}_2\text{F}$ or $\text{Bu}'\text{OH}-\text{FSO}_3\text{H}$) must occur in aqueous FSO_3H . To mimic such a process, a control experiment was

done by addition of FSO_3H to a suspension of 1,3,6-trisopropylpyrene **4** in Pr^iOH -ice. The heterogeneous mixture was allowed to mix efficiently for 1 h and subsequently quenched and extracted. The ^1H NMR spectrum of the organic extract in comparison with the ^1H NMR spectra of authentic **1** and **4** showed, apart from unchanged **4**, a ca. 30% yield of **1**.

Protonation of 2. The sterically congested tetracyclohexylpyrene **2** reacted rather sluggishly with $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ at dry

Scheme 1 Protonation of 1, 2 and 3 in FSO₃H–SO₂ClF

ice–acetone temperature. On vigorous mixing, a dark red colour slowly developed. The aromatic region of the ¹H NMR spectrum exhibits four 1/2 AB spin systems (1 H each; two overlapping), a singlet (1 H) and a 3.1 Hz doublet (1 H) as the most shielded aromatic resonance [Fig. 4(a)]. The sp³(CH) is a broad singlet resonance at 4.53 ppm (1 H). The cyclohexyl groups show four CH absorptions (as distorted triplets) the most upfield of which at 2.72 ppm is assigned to the *ipso* cyclohexyl group.

The positions and multiplicities of resonances in comparison with those of 1H⁺ and 1aH⁺ clearly indicate that cyclohexyl rearrangement had already occurred to give 2aH⁺, and that its precursor 2H⁺ escaped NMR detection. Similar results were obtained for the more dilute samples prepared with utmost care at dry ice–acetone temperature; only 2aH⁺ was observable.

The ¹³C NMR spectrum of 2aH⁺ exhibits all of the expected fifteen aromatic absorptions in the range 168.0–123.5 ppm and the sp³(C) at 52.6 ppm. The assignments of the individual carbons were facilitated by a HETCOR experiment; the four most deshielded aromatic carbons are those of C-1, C-3, C-5a and C-8a, followed by C-4/C-10. The C-5a/C-8a carbons are the most deshielded ring junction carbons. Other ring junction carbons do not sustain much positive charge including that of 10b (*para* to the formal site of attack).

The aliphatic region of the carbon spectrum exhibits four cyclohexyl CH carbons, the most deshielded one at 51.6 ppm is connected to the most upfield cyclohexyl CH attached to the *ipso* carbon (HETCOR). Thus as discussed for 1aH⁺, a geometrical change of the *ipso* cyclohexyl group leads to anisotropic shielding of CH with concomitant CH deshielding presumably due to its proximity to C-8a. The remaining three methine carbons are between 41.7 and 39.3 ppm, whereas eight methylene carbon resonances are observed between 35.4 and

27.4 ppm (1 C each). These are ascribed to C-2' carbons of the cyclohexyl rings and show clearly that the C-2' carbons of each ring are non-equivalent. In addition, four strong resonances between 26.8 and 26.6 ppm (2 C each) and three resonances at 26.4 (1 C), 26.1 (1 C) and 25.8 (2 C) are observed. The latter are C-4' of the cyclohexyl rings.

No change in the spectrum was observed on heating the sample to –40 °C. Quenching of the ion solution furnished the skeletally intact 2 (¹H NMR).

In another experiment, 2 reacted with excess TfOH at room temperature. After 12 h, the light-brown sample was quenched and examined by ¹H NMR spectroscopy. 1,3,4,6,8-Pentacyclohexylpyrene was obtained (>90% yield), showing four singlets at 8.24 (2 H), 8.01, 7.84 and 7.62 (1 H each) ppm. Therefore, superacid-catalysed cyclohexyl disproportionation at room temperature can be used for easy synthesis of this compound.

Protonation of 2 in FSO₃H·SbF₅(4:1)–SO₂ClF (Scheme 2). In an attempt to generate 2H⁺ more efficiently at lower temperatures for direct observation, protonation of 2 with FSO₃H·SbF₅(4:1)–SO₂ClF was tried. The major pyrenium ion detected under these conditions was 2SO₂H⁺, formed by initial *ipso* sulfonylation, with minor amounts of 2²⁺ and 2D²⁺ dications.

The ¹H NMR spectrum of 2SO₂H⁺ exhibits four 1/2 AB systems and three singlets. The positions of the aromatic protons are very close to those of 1H⁺.¹¹ The –SO₂H resonance is at 9.71 ppm. Formation of 2SO₂H⁺ is corroborated by the ¹³C NMR spectrum showing the sp³(C–SO₂H) at 78.2 ppm in place of the 52.6 ppm signal observed for the sp³(CH) in 2aH⁺. The cyclohexyl CH resonances are between 40–47 ppm. The C-2' resonances of the rings show up as four pairs of resonances as also seen for 2aH⁺. In the aromatic region, the most de-

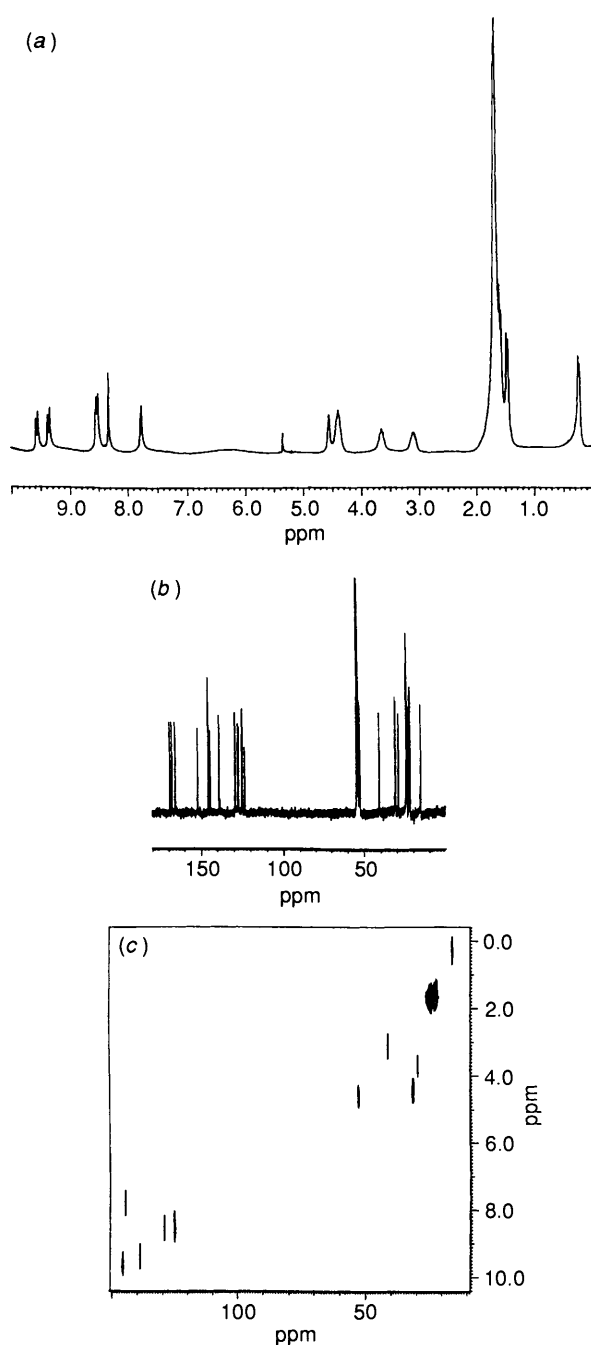


Fig. 3 (a) ^1H NMR, (b) ^{13}C and (c) HETCOR analysis for 1aH^+

shielded carbons are those of C-6/C-8 followed by C-3a/C-10a. The most deshielded aromatic CH absorptions are those of C-5/C-9. The assignments are tentative as more resonances are present due to the presence of other species.

In independent experiments, it was established that the extent of two-electron oxidation ($\longrightarrow 2^{2+}$) and *ipso* diprotonation ($\longrightarrow 2\text{D}^{2+}$) were both variable. In some cases 2^{2+} was absent, in one case 2D^{2+} was the major cation observed. The amount of 2^{2+} varied with time. The variations in amount and in time allowed an unambiguous separation of resonances. It is interesting that these products are different from those found in ref. 11.

Upon quenching $2\text{SO}_2\text{H}^+$ the original all- α substituted **2** was recovered (^1H NMR). We previously observed that sulfonated σ -complexes undergo desulfonylation on quenching.

The aromatic region of the ^1H spectrum of 2D^{2+} consists [Fig. 4(b)] of two doublets at 8.15 ppm and 8.30 ppm with a

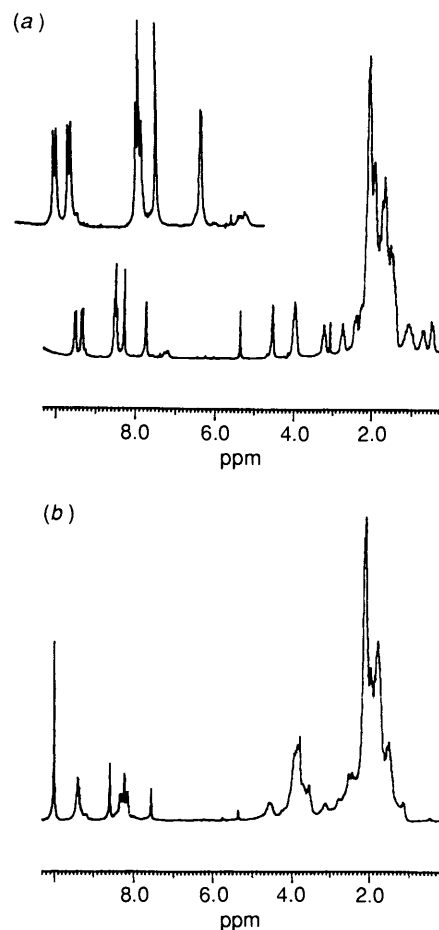
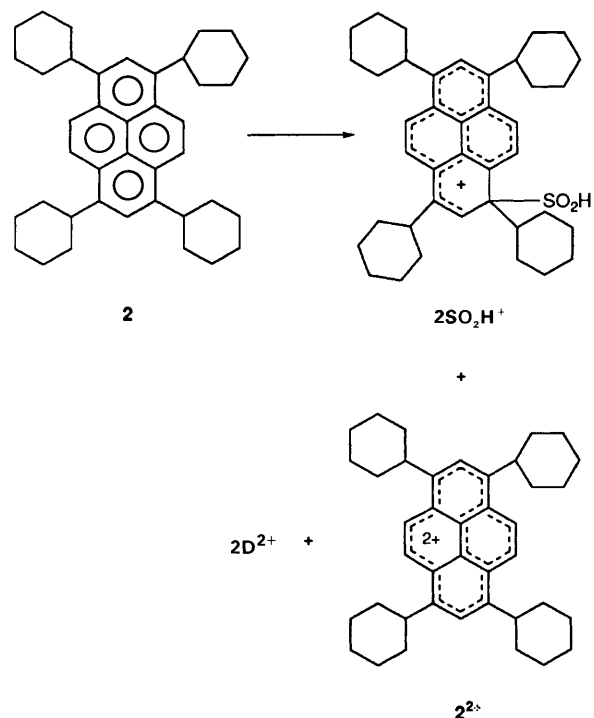
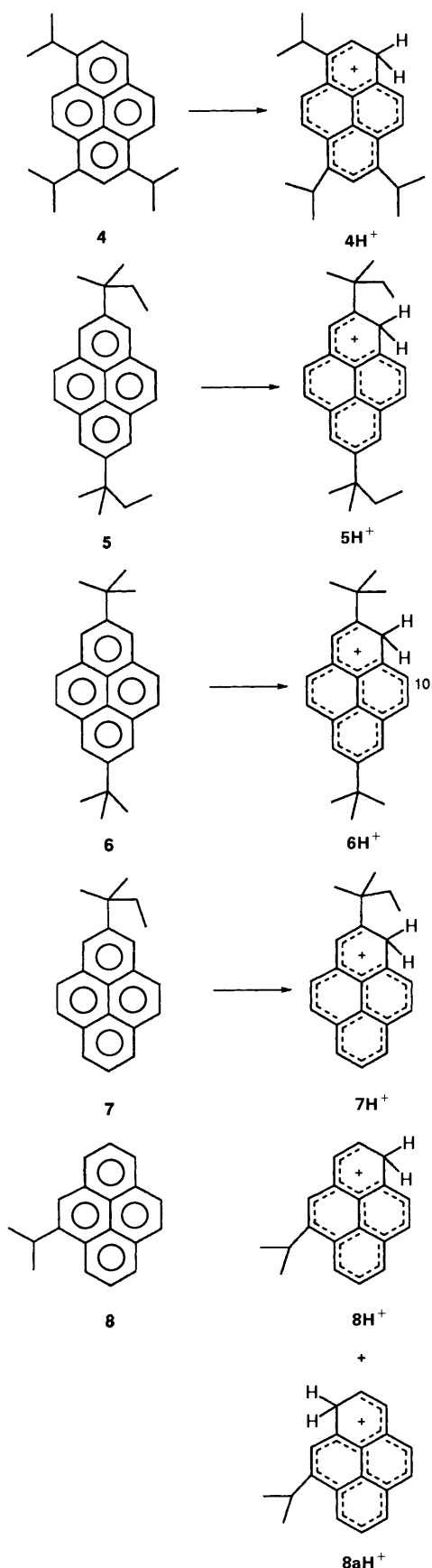


Fig. 4 ^1H NMR spectrum (a) for 2aH^+ and (b) for 2D^{2+}



Scheme 2 Protonation of **2** in $\text{FSO}_3\text{H}\cdot\text{SbF}_5(4:1)\text{-SO}_2\text{ClF}$

singlet in between at 8.27 ppm and in addition overlapping resonances at 9.39 ppm (2 H). The aliphatic region is less clear cut. A resonance is seen at 4.55 ppm (2 H) and a broad multiplet is centred around 3.85 ppm, integrating approximately to 9 H, a finding that indicates that protons other than just the methine



Scheme 3 Protonation of 4–8 in $\text{FSO}_3\text{H-SO}_2\text{ClF}$

ones are present in this area. The finding of only five resonances in the aromatic region suggests that diprotonation has occurred. The resonance at 4.55 ppm could be two CH protons at the site

of protonation, thus suggesting diprotonation. The extra protons at 3.85 ppm suggest a cyclohexyl-like group having methylene protons at approximately the position of a free cyclohexyl ion (see also treatment of 5 and 6 with 'magic acid'). The corresponding ^{13}C spectrum shows 13 resonances in the aromatic region from 175.5 to 125.7 ppm, three of which are proton-carrying (128.0, 130.1 and 144.6 ppm). The quaternary resonance at high field, 125.7 ppm, is assigned to C-10b or C-10c. Other quaternary carbon resonances are seen at 127.1 (very weak), 128.9, 130.6, 132.1, 144.8, 162.2, 166.5, 174.6 and 175.2 ppm.

It is interesting to note that the ^{13}C chemical shifts are similar in magnitude to those found in the monoprotated species.

Protonation of 3. The symmetrical tetracyclopentylpyrene 3 was similarly reacted with $\text{FSO}_3\text{H-SO}_2\text{ClF}$ (at -75°C) to give a dark-red solution on vigorous mixing. Once again, the initially formed *ipso* protonated 3H^+ escaped NMR detection; the rearranged pyrenium ion 3aH^+ was observed instead. Its ^1H NMR spectrum exhibited the $\text{sp}^3(\text{CH})$ at 4.70 (1 H), the shielded H-8 as a doublet at 7.69 with a 3.5 Hz vicinal coupling to the *ipso* proton, in addition to two resolved AB systems with $^3J = 8.3$ and 9.0 Hz and a singlet at 8.28 ppm for H-7.

Exothermic quenching of the rearranged pyrenium ions 1aH^+ , 2aH^+ and 3aH^+ generates the original all- α substituted aromatics.

The α Protonated Pyrenium Ions (Scheme 3 and Figs. 1 and 2).—(a) **Protonation of 4.** Monoprotection of 4 with $\text{FSO}_3\text{H-SO}_2\text{ClF}$ occurs at the available α position to give 4H^+ . The ^1H NMR spectrum of the resulting red solution formed at dry ice-acetone temperature exhibits two AB systems for the $\alpha\beta$ protons and two singlets for the β hydrogens with H-2 (*ortho*) being the most upfield. The $\text{sp}^3(\text{CH})$ appears as a broad singlet at 4.64. The $\text{Pr}^i(\text{Me})$ at C-3 (*meta*) moves upfield relative to the other $\text{Pr}^i(\text{Me})$ doublets.

The ^{13}C NMR spectrum of 4H^+ exhibits fifteen deshielded aromatic signals between 168.6–125.0 ppm, the $\text{sp}^3(\text{CH}_2)$ at 37.8 ppm, three $\text{Pr}^i(\text{CH})$ and three $\text{Pr}^i(\text{Me})$ absorptions. Consistent with shielding of the $\text{Pr}^i(\text{Me})$ in the ^1H NMR, ^{13}C NMR indicates shielding of the Pr^i group at the *meta* position as compared with Pr^i groups at the 'remote' α which are attached to the more deshielded C-6/C-8. Analysis of the ^{13}C NMR data illustrates that the positive charge in 4H^+ is delocalized away from the site of attack at alternating carbons, residing predominantly at C-6/C-8, C-3a/C-10a and C-5/C-9. Whereas the positions of C-10a (*ortho*) and C-3a (*para*) carbons are clearly different, other ring junction carbons are very similar (all in the range 125–130 ppm). Thus 4 is monoprotated exclusively at the unsubstituted α position and no *ipso* attack is identified. Ion 4H^+ is quite stable; no deterioration of the solution was observed when the sample was stored in the cold ($-75^\circ\text{C} \rightarrow -40^\circ\text{C}$) for several days and re-examined by NMR spectroscopy. Quenching of 4H^+ furnished the skeletally intact 4 (^1H NMR).

(b) **Protonation of 5.** Low-temperature treatment of 5, with two *tert*-pentyl group strategically positioned at the β positions, with $\text{FSO}_3\text{H-SO}_2\text{ClF}$ led to a smooth reaction with exclusive formation of 5H^+ (α attack). The ^1H NMR spectrum (at -68°C) consists of two AB systems for the $\alpha\beta$ hydrogens all with H–H coupling of *ca.* 8.5 Hz, a shielded singlet for H-3 (*meta*) and broad singlets for the H-6/H-8. The $\text{sp}^3(\text{CH}_2)$ is at 4.74 ppm and the two *tert*-amyl groups do not exhibit a rotational barrier.

A well-resolved ^{13}C NMR spectrum was obtained for 5H^+ which in combination with a HETCOR experiment and the observation of C–H couplings allowed a complete analysis.

The aromatic region exhibits fourteen signals between 179.8–120.5 ppm with C-6/C-8 carbons coinciding (at 140.6 ppm). The

most deshielded hydrogen-bearing carbon is at 151.6 (C-9). The four most deshielded carbon signals are due to C-2, C-3a/C-10a and C-7. Analysis of the data leads to the conclusion that the inductive stabilization by the *tert*-pentyl group at C-2 has a profound stabilization effect on the cation, causing 35 ppm deshielding at C-2. This effect reduces the extent of positive charge delocalization into the 'remote' α and $\alpha\beta$ positions. Thus the *ortho* (C-2 and C-10a) and *para* (C-3a) positions sustain maximum positive charge. The $\text{sp}^3(\text{CH}_2)$ is at *ca.* 38.9 ppm, overlapping with a *tert*-pentyl($\text{CH}_2\text{-CH}_3$) at C-7.

(c) *Protonation of 6.* In our previous study,¹¹ we reported on monoprotection of **6** to give 6H^+ , based on a ^1H NMR analysis. In order to provide a more complete picture with regard to charge delocalization and an insight into the influence of the Bu' group for inductive charge stabilization at C-2, we repeated the protonation of **6** and carried out a complete ^{13}C NMR analysis. The low-temperature reaction of **6** with the higher acidity superacid $\text{FSO}_3\text{H}\cdot\text{SbF}_5(4:1)\text{-SO}_2\text{ClF}$ led to clean generation of 6H^+ the ^1H NMR spectrum of which was essentially identical with our previously reported data in $\text{FSO}_3\text{H}\text{-SO}_2\text{ClF}$. No diprotonation was evident.

The ^{13}C NMR spectrum exhibits fifteen resolved aromatic signals in the range 181.1–120.6 ppm, two Bu' groups and the $\text{sp}^3(\text{CH}_2)$ at 39.1 ppm. In line with the arguments proposed for 5H^+ , the most deshielded carbon signal for 6H^+ observed at 181.1 ppm is for C-2 (*ortho*). The extent of deshielding observed at C-2 is clearly larger than that at C-10a. Not unexpectedly, charge delocalization patterns for 5H^+ and 6H^+ are very similar, with the *ortho* and *para* positions being most deshielded and with a reduction in the positive charge present at the α and $\alpha\beta$ carbons being observed relative to *ipso* protonated cations as described earlier.

This experiment was repeated with FSO_3D (*ca.* 60% enrichment). Deuterium incorporation leads to a high-field shift of the CH carbon of 0.1 ppm. Judging from the integral of the CH_2 resonance, the compound was 30–40% deuteriated leading to an isotope effect of approximately 0.25–0.3 ppm.

From a fully coupled ^{13}C spectrum, $^1J(\text{C},\text{H})$ couplings of 6H^+ can be measured: C-3, 165.6; C-4, 166.8; C-5, 166.1; C-6, 162.5; C-8, 161.0; C-9, 163.7 and C-10; 165.2 Hz. They are found to be larger than those of **6** ($\text{C-}\alpha = 156$ Hz and $\text{C-}\alpha\beta = 159$ Hz).¹³ The difference in coupling constants between the charged and non-charged species is roughly inversely proportional to the difference in ^{13}C chemical shifts (Fig. 2).

(d) *Protonation of 7.* In order to assess whether a *tert*-amyl group at C-7 has an influence on the extent of positive charge delocalization, protonation of **7** was studied. The resulting red ion solution, formed by reacting **7** with $\text{FSO}_3\text{H}\text{-SO}_2\text{ClF}$ at dry ice–acetone temperature, exhibited well resolved NMR spectra consistent with exclusive α protonation at C-1 ($\longrightarrow 7\text{H}^+$).

The ^1H NMR spectrum shows two AB systems for the $\alpha\beta$ hydrogens with *ca.* 8.4 Hz vicinal coupling, a shielded singlet at 8.05 for H-3 (*meta*), a 2 H singlet for H-6/H-8, a triplet for H-7. This points towards protonation at position 1. The $\text{sp}^3(\text{CH}_2)$ of the protonation site is at 4.85 ppm. Fifteen well resolved deshielded aromatic signals are seen in the ^{13}C NMR spectrum, with the $\text{sp}^3(\text{CH}_2)$ at 39.0 ppm and four peaks for the *tert*-amyl group, indicative of a single pyrenium ion. The analysis of the carbon spectrum was facilitated by proton coupling, HETCOR analysis and by consideration of the charge delocalization pattern in other alkylpyrenium ions. Thus the most deshielded ring carbon is that of C-2 (*ortho*) followed by the C-3a/C-10a carbons. Hydrogen-bearing ring carbons carry less positive charge, with the most deshielded of such carbons being at 151.5 ppm. Again, the *tert*-pentyl group has a strong influence on charge stabilization at C-2, consequently the C-6/C-8 carbons are less deshielded relative to these positions in alkylpyrenium ions which are not substituted at C-2. The $\text{sp}^3(\text{CH}_2)$ at 39.1

is slightly more shielded relative to the *tert*-amyl(C) which appears at 42.9 ppm.

(e) *Protonation of 8.* We showed previously that **8** was monoprotated in $\text{CF}_3\text{SO}_3\text{H}\text{-SO}_2$ or in $\text{FSO}_3\text{H}\text{-SO}_2$ to give a mixture of two pyrenium ions of attack 8H^+ and 8aH^+ .¹¹ The analysis of the ^1H NMR spectrum was not trivial, since there is substantial overlap in the positions of the 1/2 AB systems for both ions at 300 MHz. In the present study our previous ^1H interpretations were re-evaluated by a H/H COSY experiment on the ion mixture generated by protonation of **8** in $\text{FSO}_3\text{H}\text{-SO}_2\text{ClF}$ at dry ice–acetone temperature. Furthermore, charge distribution in the isomeric ions was examined by ^{13}C NMR for comparison with other persistent alkylpyrenium cations. The COSY spectrum confirmed our previous assignments; namely coupling of H-1/H-3 (α) with H-2 (β), coupling of the $\alpha\beta$ protons (H-9/H-10) within each isomer, and coupling of the most upfield aromatic hydrogens of the two isomers (*ortho*) with the $\text{sp}^3(\text{CH}_2)$ at 4.73 ppm. The ^{13}C NMR spectrum of the ion mixture exhibited 27 aromatic signals between 175.6–139.2 ppm, showing that three ring carbons coincide. One of these coinciding carbons is of C-4 which is the most deshielded signal in the spectrum. The $\text{sp}^3(\text{CH}_2)$ absorptions for both ions are identical appearing at 38.4 ppm, their $\text{Pr}^i(\text{C})$ absorptions are different but the $\text{Pr}^i(\text{Me})$ signals are coincident.

Study of 5 and 6 in 'Magic Acid'^R-SO₂ClF and 'Magic Acid'^R-SO₂: Diprotonation and Sulfonylation (Schemes 4 and 5).—Taking advantage of the inductive stabilization of a Bu' or a *tert*-pentyl group at the β -position and the charge alternation in the ring system we examined the low-temperature reactions of 2,7-di-*tert*-butylpyrene **6** and 2,7-di-*tert*-amylpyrene **5** in 'magic acid'^R-SO₂ClF in an attempt to diprotonate these.

Reaction of **6** with 'magic acid'-SO₂ClF at dry ice–acetone temperature gave a deep-red ion solution the ^1H NMR spectrum of which initially recorded at -70°C shows [Fig. 5(a)] one sharp Bu' singlet at 1.65 ppm, a very broad more deshielded Bu' absorption barely visible in the baseline around 3.50 ppm, a very sharp resonance at 3.82 ppm, which is assigned to the free Bu'^+ methyl resonance, and the most deshielded resonance, which is a slightly broad singlet at 4.22 ppm (4 H) assigned to the CH_2 hydrogens. This is at higher field than in the monoprotated species. That the sharp resonance is indeed due to free Bu'^+ was supported by the ^{13}C NMR spectrum discussed below (peaks at 328.4 and 48.0 ppm; lit.,¹⁴ 335.2 and 47.5 ppm). The $\text{sp}^3(\text{CH})$ for 6H^+ (see the earlier discussion) was at 4.76 ppm. In the magic acid spectrum only a small peak was present at 4.80 ppm. The aromatic region of the ^1H NMR spectrum consists of only two absorptions at 8.35 ($J = 7$ Hz) accounting for 2 H, a doublet at 9.22 ppm (2 H), and a singlet at 9.28 ppm (2 H). The ^1H NMR spectrum at -60°C shows the broad Bu' group more clearly at 3.32 ppm. The broad resonance shows that this group is dynamic and Bu'^+ -like. The spectra show as indicated a clear temperature dependence, but also a dependence on acidity (H_0).

Quenching of the ion solution furnished the skeletally intact **6** with no alkyl disproportionation products being found (^1H NMR).

The ^{13}C NMR spectrum (recorded at -70°C) shows the Bu' group at C-7 at 30.0/35.7 ppm [these values are nearly identical with those for 6H^+ (see above)], the free Bu'^+ group at 328.4/48.0 ppm, the dynamic and Bu' -like methyl carbons as a broad hump at 43.6 and in addition a sharp signal at 68.0 ppm, which is possibly C-2. This leaves a broad hump at 79.5 ppm unaccounted for. The aromatic region shows eight major resonances between 158.7–121.1 ppm, three of which, at 153.3, 151.0 and 133.0, are proton-bearing. The appearance of the spectrum is consistent with symmetry in the diprotonated ion as shown in structure 6D^{2+} (see later discussion). In addition to

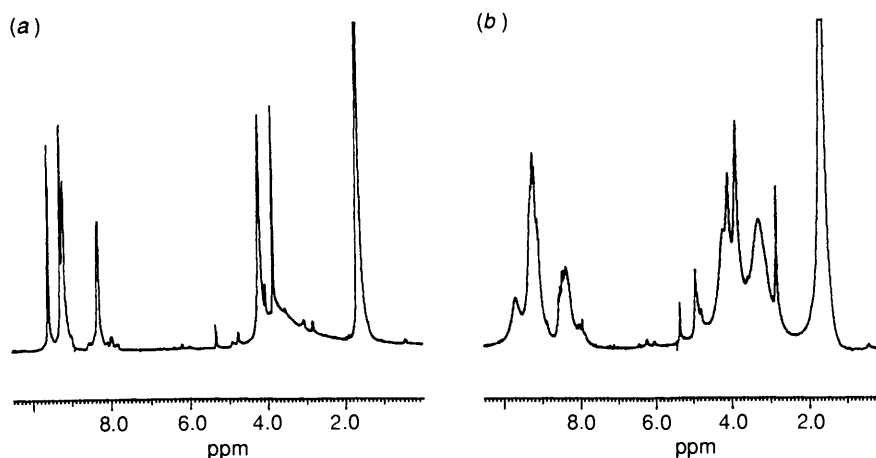
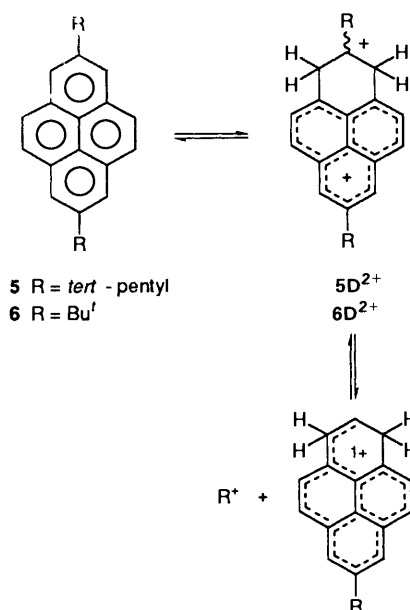


Fig. 5 ^1H NMR spectrum of 6D^{2+} at (a) 208 K and (b) 223 K

the major resonances weak minor resonances are also observed at positions very similar to those of the major species (6D^{2+}). It is tempting to assign these to the pyrene moiety that has lost a Bu^t -group (Scheme 4).

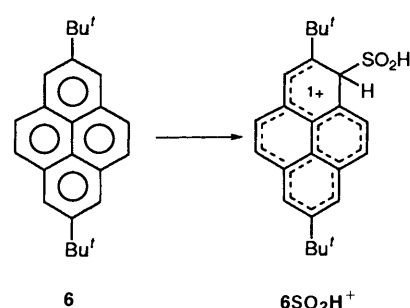


Scheme 4 Protonation of **5** and **6** with 'magic acid'- SO_2

Sulfonylation of 6 in 'magic acid'- SO_2 (Scheme 5). We showed previously in our ^1H NMR studies of persistent pyrenium ions¹¹ that sulfonylated σ -complexes were formed in SO_2 with the 'magic acid' system. In the present study and in relation to NMR studies of 6H^+ and the dynamic 6D^{2+} , it was of interest also to generate $6\text{SO}_2\text{H}^+$.

A dark-red solution resulted when **6**, slurred in SO_2 , was reacted with the superacid- SO_2 . Formation of $6\text{SO}_2\text{H}^+$ became quickly evident from the ^1H NMR spectrum showing non-equivalent Bu^t singlets (having non-equivalent abundances!), a distinctly deshielded $\text{sp}^3(\text{CH})$ at 6.32 ppm, and the $-\text{SO}_2\text{H}$ at 10.2 ppm close to H_3O^+ . In line with the ^1H NMR spectrum of alkyipyrenium ions of protonation and sulfonylation,¹¹ the H-3 (*meta*) is the most upfield aromatic signal in the spectrum (7.85 ppm, singlet), followed by a doublet at 8.24 ppm ($J = 8.1$ Hz) and a double doublet at 8.5 ppm ($J = 8.85$ and 2.2 Hz). This pattern points toward a single sulfonylation at the α -position (Scheme 5) although the small coupling of 2.2 Hz is thus unexpected. The remaining resonances are close to those of $6\text{SO}_2\text{H}^+$, but are not readily assigned due to overlap.

Consistent with the formation of two alkyipyrenium ions of



Scheme 5 Pyrenium ion of sulfonylation of **6** in 'magic acid'- SO_2

sulfonylation, the ^{13}C NMR spectrum shows two deshielded $\text{sp}^3(\text{C})$ signals at 65.8 and 68.6 ppm, two non-equivalent $\text{Bu}^t(\text{Me})$ signals at 29.9 and 28.4 ppm and two $\text{Bu}^t(\text{C})$ signals at 35.6 and 38.5 ppm. The aromatic region is more complex than expected showing over 30 signals in the region 120–158.7 ppm.

Reaction of 5 with 'magic acid'- SO_2ClF (Scheme 4). When reacted with 'magic acid' in SO_2ClF solvent at low temperature, the di-*tert*-pentylpyrene substrate, **5** shows similar behaviour to that of **6**. The intermolecular process (dealkylation/realkylation) also operates as evidenced from the presence of *tert*-pentyl cation in the solution (see below).

The ^1H NMR spectrum (Fig. 6) shows resonances belonging to a *tert*-pentyl group at 0.78 ppm (CH_3), 1.65 ppm (CH_2) and 2.01 ppm (CH_2). In addition resonances due to a *tert*-pentyl cation-like ion (as discussed for 5D^{2+}) or to a free *tert*-pentyl group is seen. The positions at 3.96 and 3.89 ppm can be assigned to $(\text{CH}_2)_2$, the CH_2 protons are most likely seen at 3.47 ppm and the CH_3 resonance is at 0.78 ppm, indistinguishable from the normal *tert*-pentyl group. The CH_2 group due to protonation is tentatively assigned to the signal at 4.40 ppm in analogy with 5D^{2+} . That one of the *tert*-pentyl groups is dynamic on the NMR timescale is seen from the slightly broadened, featureless, aliphatic absorptions. The aromatic region shows just two deshielded unresolved signals at 8.21 (2 H) and 9.11 (4 H) indicative of a rather symmetrical dication. The total integral shows that all the expected hydrogens for a structure like 5D^{2+} are accounted for.

The ^{13}C NMR spectrum of a freshly prepared sample provided additional information. Two sets of resonances are clearly observed in the ratio (4:1). The *tert*-pentyl cations of the major set were observed at 334.6, 59.8, 45.9 and 8.7 ppm and those of the minor at 328.2, 44.7 and 8.6 ppm. The resonance for the minor ion supposed to be at approximately 60 ppm could not be observed. These may be compared with literature values:¹⁴ 335.4, 57.5, 44.6 and 9.3 ppm. The *tert*-pentyl group at C-7 has absorptions very close to those of *tert*-pentyl in 5H^+ ,

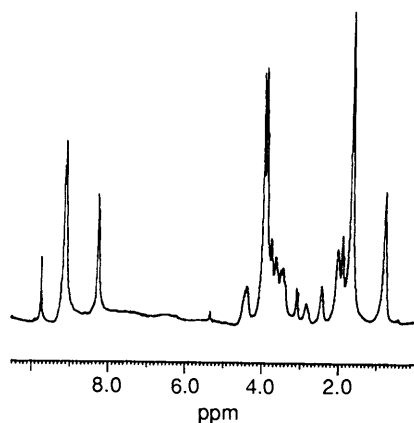


Fig. 6 ^1H NMR spectrum of 5D^{2+}

and the $\text{sp}^3(\text{CH}_2)$ is at *ca.* 39 ppm. The symmetry of the species and its similarity to 6D^{2+} is deduced from the number and position of the aromatic signals showing eight major peaks in the range 166.9–121.3 ppm, the positions of which closely match those of 5D^{2+} except for the most deshielded signal. The minor peaks fall in the same region and very close to those of the major species (Fig. 2). Quenching of the ion solution returned the structurally intact **5** (*ca.* 90%, ^1H NMR).

The spectra obtained by treatment of **5** and **6** with $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ (1:1) show unusual features as just described. This is likewise true for the spectra of **2**. In all three cases the ^{13}C chemical shifts of the aromatic carbons show that only one charge resides in the aromatic region as seen from the sums of $\Delta\delta$ values (Fig. 2). The finding of only eight aromatic resonances for **5** and **6** shows the presence of a symmetry axis through C-2, C-7 on the NMR timescale. The simplicity of the aromatic part of the ^1H NMR spectrum again indicates symmetry and thus excludes, *e.g.*, one protonation and one sulfonylation site. For **6** the finding of a methyl resonance near 4 ppm (in addition to the Bu^+ cation) shows that the *tert*-butyl group has to be very similar to the Bu^+ ion although not exactly the same. For **6** the *tert*-butyl group is broad and the position varies with temperature. This is not the case for **5**. Based on the above findings, structures like 5D^{2+} and 6D^{2+} are suggested (Scheme 4). The exact nature of the dynamic arrangement cannot be given. For **2** similar features are found. The general picture is thus that the pyrene derivatives upon protonation can only accommodate approximately one charge at the remaining aromatic circuit, although they can be transformed into dications on oxidation.¹⁵

Discussion

A Comparative Discussion of the Structural Features of Persistent Alkylpyrenium Ions.—Our studies with all α -substituted pyrenes demonstrate that facile cyclohexyl, cyclopentyl and isopropyl migration to a *peri* position following *ipso* attack at an α position can be used as a driving force to generate the energetically less favourable σ -complex of $\alpha\beta$ attack. Relief of steric strain apparently overrides the unfavourable energetics.

The all α -substituted pyrenium ions **1**, **2** and **3** protonate at the *ipso* position and subsequently rearrange to give 1aH^+ , 2aH^+ and 3aH^+ . Only the *ipso* protonated pyrenium ion 1H^+ could be directly observed by NMR spectroscopy in dilute samples prior to the onset of rearrangement. In the case of sulfonylated species $2\text{SO}_2\text{H}^+$ could be observed in $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ (4:1). Facile migration of an *ipso* Pr^+ , cyclohexyl or cyclopentyl group to the *peri* position provides access to the otherwise less stable pyrenium ions of $\alpha\beta$ attack.

Exothermic quenching of the skeletally rearranged pyrenium

ions returns the original all α -substituted pyrenes, suggesting that dealkylation/realkylation must occur in aqueous acid upon quenching, a process which is borne out by our control experiment in which **4** could be transformed into **1** (albeit in low yields) in aqueous FSO_3H with Pr^+OH .

Protonation of **4** ($\longrightarrow 4\text{H}^+$) illustrates that attack at an unsubstituted α position is preferred over *ipso* attack at the α position.

Protonations of **5** and **6** demonstrate that the alkyl group in the neighbouring β position has a significant stabilizing effect on the pyrenium ion of α attack. This is borne out both by a study of charge delocalization at the periphery and by protonation of **7** where only the pyrenium of attack at C-1 is formed ($\longrightarrow 7\text{H}^+$). Alkyl substituents in remote α -positions likewise stabilize the charge as seen in $2\text{SO}_3\text{H}^+$.

Presence of an inductively stabilizing group in the $\alpha\beta$ position is insufficient to overcome the higher energetics of the σ -complex of $\alpha\beta$ attack; hence two isomeric pyrenium ions of attack at the 'remote' α positions with very similar energy content (1:1 ratio of the ions) and very similar NMR features are formed. H/H COSY helped to identify the spin systems of the two ions 8H^+ and 8aH^+ and ^{13}C NMR chemical shift patterns provide corroboratory evidence for formation of the two ions. In general, ^{13}C NMR analyses provide a more complete picture as to charge delocalization in pyrenium cations and complement our previous conclusions drawn on the basis of ^1H NMR data. Thus charge alternation at the periphery and away from the site of attack is shown for all of the crowded pyrenium ions probed in this study.

The presence of a β Bu^+ or a *tert*-pentyl group increases the extent of positive charge present at C-2. The ring junction carbons C-3a/C-10a, the remote α carbons C-6/C-8 and the $\alpha\beta$ carbons C-5/C-9 are the most deshielded. The positive charge at C-6/C-8 can be modulated by alkyl substitution at these positions.

Analysis of the carbon spectrum of alkylpyrenium ions of $\alpha\beta$ attack (1aH^+ , 2aH^+ , 3aH^+) demonstrates that the positive charge in these derivatives is located predominantly at C-1/C-3, C-4/C-10, C-5a/C-8a and at C-7. The chemical shifts of the *ortho* carbons C-8a and C-10 show that the ring-junction carbon sustains more positive charge. The positive charge at *para* carbon C-10b is quite small. This underlines the differing nature of arenium ions of pyrene as compared with those of smaller PAHs, where the positive charge is primarily located at the ring undergoing attack. Thus the ions exhibit significant phenanthrenium ion character and charge alternation in the phenanthrene moiety.

For pyrenium ions of α attack (at C-1) the *para* carbon (C-3a) is significantly deshielded, but the *para* carbon in the pyrenium ion of $\alpha\beta$ attack (C-10b) is little altered relative to the precursor unlike the *ortho* positions (C-8a/C-10) which are significantly deshielded.

The charge distribution in 5D^{2+} and 6D^{2+} is different from those of the α -monoprotonated in the sense that more charge is delocalized into the distal ring of the diprotonated species again underlining the stabilizing effect of the alkyl groups at C-2 of 5H^+ and 6H^+ .

Diprotonation of lower PAHs (naphthalene, phenanthrene and [10]annulenes) and stable dication generation have been demonstrated in a number of previous investigations.¹⁶ Because of ease of oxidation (lower HOMO–LUMO gap) in larger fused PAHs, protonation and oxidation compete. The usual requirement of higher H_0 s to effect arene diprotonation necessitates the use of SbF_5 or other oxidizing Lewis superacids, this in turn facilitates the oxidation as is observed with **2** in $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ (4:1)– SO_2ClF . Formation of $2\text{SO}_2\text{H}^+$ in this superacid system appears unusual. In connection with a similar previous observation,¹⁵ we suggested that the *in-situ* formed

arene radical cation may be reacting with SO_2 . The latter is presumably formed by redox chemistry with SbF_5 . Competing diprotonation remains a minor pathway. In agreement with ^1H NMR studies of charge distribution, ^{13}C NMR spectroscopy shows that the mode of charge distribution in the sulfonylation and protonation σ -complexes are very similar. The highly deshielded nature of both $\text{sp}^3(\text{C})$ and the $\text{sp}^3(\text{CH})$ which bear the $-\text{SO}_2\text{H}$ group is noteworthy.

Experimental

The synthesis, analytical and spectroscopic data on the cycloalkyl- and alkyl-pyrene substrates used in this study have already been published.¹⁷

FSO_3H (Linde), SbF_5 (Fluorochem), TfOH (Aldrich) were freshly distilled in an all-glass distillation unit under a fast flow of dry nitrogen at atmospheric pressure. SO_2ClF (Aldrich) and SO_2 (Linde, anhydrous) were used as received.

$\text{FSO}_3\text{H}\cdot\text{SbF}_5(4:1)$ and $\text{FSO}_3\text{H}\cdot\text{SbF}_5(1:1)$ were prepared by transfer of freshly distilled SbF_5 into a Nalgene bottle and by direct addition of the required amount of FSO_3H weighed inside a second Nalgene bottle (exothermic!).

The NMR spectra were recorded on a Bruker: AC 250 (at Roskilde) and a GE: GN-300 (at KSU). The probe was cooled while shimming with an $[\text{D}_6]\text{acetone}$ sample. CD_2Cl_2 served as both internal lock and NMR reference for the low-temperature measurements. For details see ref. 11. For the heterocorrelated spectrum the sweep width was 1375 in F_1 (^1H) and 11 362 Hz in F_2 (^{13}C). The 2D spectra were collected in 256×2048 data matrices and sine bell apodization was used in F_1 and Gauss multiplication in F_2 . The pulse sequence was optimized for a one-bond coupling of 150 Hz. 16 scans were measured for every increment. For the COSY spectra 2252 and 1126 Hz were used in the two dimensions with sizes of 1 K and 512 words in F_2 and F_1 , respectively. Both dimensions were apodized with a sine bell function.

Stable Ion Generation.—Typically, a clear homogeneous solution of the superacid (*ca.* 1 cm^3) diluted with SO_2ClF (*ca.* 1 cm^3) was prepared inside a 10 mm NMR tube under nitrogen in the cold (vortex). A slurry of the alkyl-(cycloalkyl)-pyrene substrate was prepared by addition of cold SO_2ClF (*ca.* 1 cm^3) to *ca.* 30–40 mg of the compound inside a second 10 mm NMR tube under nitrogen (vortex). The cold superacid solution was slowly poured into the pyrene- SO_2ClF tube with vigorous mixing whereby a light- or deep-red solution resulted. The homogeneous sample (vortex) was carefully poured directly into a precooled 5 mm NMR tube fully immersed in a dry ice-acetone bath. The sample was flushed with dry nitrogen, after which 5–8 drops of cold CD_2Cl_2 were added dropwise on top

of the acid solution. The cold two-phase sample was vortexed until homogeneous. The sample was flushed with dry nitrogen and sealed with a plastic cap and Teflon tape. The spectra were recorded within a few hours of sample preparation unless otherwise stated.

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