

Oxidation of Sterically Crowded Alkyl(cycloalkyl)pyrenes. Persistent Dications in $\text{SbF}_5/\text{SO}_2\text{ClF}$ and Radical Cations in $\text{FSO}_3\text{H}/\text{SO}_2$

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Sterically crowded alkylpyrenes 2-7 undergo two-electron oxidation with $\text{SbF}_5/\text{SO}_2\text{ClF}$ (or $\text{SbF}_5\cdot\text{FSO}_3\text{H}$ (9:1)/ SO_2ClF) to give persistent alkylpyrene dications. In agreement with the charge distribution pattern observed in the parent pyrene dication and with semiempirical calculations (AM1) on isomeric monoisopropylpyrenes dications, the deshielding order $C_\alpha > C_{\alpha\beta} > C_\beta$ was found in their carbon-13 NMR spectra regardless of the number and position of the alkyl substituents. In most cases, the observed $\Delta\delta_{13\text{C}}$ for the aromatic *ipso*-carbon signals of the alkylpyrenium dications relative to those of 1^{+2} were slightly larger than expected for a normal substituent effect in the alkylpyrene precursors. Only minor changes ($\Delta\delta_{13\text{C}}$) in the unsubstituted positions were observed, except for the ring carbons in highly crowded locations for which a noticeable upfield shift was detected. The ^1H NMR spectra of alkylpyrenium dications showed a much greater substituent dependency. Low temperature reactions of the less-reactive pyrene and 2,7-di-*tert*-butylpyrene with $\text{SbF}_5/\text{SO}_2\text{ClF}$ led primarily to sulfonylation σ -complexes rather than oxidation dications. Persistent alkylpyrene radical cations were found to coexist with the alkylpyrenium ions of protonation in $\text{FSO}_3\text{H}/\text{SO}_2$ (ESR detection) without any noticeable line broadening in the NMR spectra of the Wheland intermediates.

Introduction

In their pioneering work on persistent aromatic carbocations, Olah and co-workers¹ demonstrated that polycyclic aromatic hydrocarbons PAHs with sufficiently low ionization potentials (E_{HOMO}) undergo two-electron oxidation with $\text{SbF}_5/\text{SO}_2\text{ClF}$ to give stable dipositive ions. ^{13}C NMR provided a powerful tool for the study of structures and charge distribution patterns in arene dications.

A recent semiempirical study² showed that the ionization potentials (IPs) and the ability to generate dications are closely related, with IPs of ≤ 8.3 eV as the lower limit, provided that the geometry of the PAH remains unchanged. AM1 calculations predicted dication formation when $\Delta\Delta H_f \leq 463 \pm 4$ kcal/mol.

The presence of electron-releasing substituents on PAHs lowers their HOMO energy and generally increases the ease of oxidation. This is reflected in facile generation of persistent dications from octamethylnaphthalene,³ octamethylbiphenylene,^{4,5} and 1,4,5,8-tetramethylnaphthalene.⁶ Furthermore, the position of alkyl substituents could influence the degree of dication stabilization. For example, in the naphthalene dication the α -methyl substituents are more stabilizing than β -methyls.⁶

In their recent studies, Rabinovitz et al.^{7a} demonstrated that in a variety of arene dianions and dications the charges are nonuniformly distributed on every other carbon leading to donor-acceptor stabilization by charge alternation. Presence of methyls or phenyls at the 9,10 position of anthracene dication was shown to influence charge alternation; a reduction in the positive charge at the *meso* positions led to attenuation of charge alternation in the rest of the molecule.^{7a} Nonuniform charge distribution of diamagnetic ions was also suggested by Müllen based on ^{13}C NMR studies.^{7b}

Parent pyrene 1 with a calculated E_{HOMO} (Hückel) = 0.4450β ,³ the first and second IP's (AM1) of 8.1 and 12.3 eV, and $\Delta\Delta H_f = 416.5^2$ kcal/mol (MINDO/3) gives a persistent dication by ionization with $\text{SbF}_5/\text{SO}_2\text{ClF}$ ($-40^\circ\text{C} \rightarrow -10^\circ\text{C}$) and a radical cation in $\text{SbCl}_5/\text{CH}_2\text{Cl}_2$ (at room temperature).^{8a} Stable dications and radical cations of substituted (or functionalized) pyrenes have not been reported in the literature.

In relation to our previous studies of crowded alkylpyrenium ions,^{9,10} we report herein on generation and NMR studies of alkylpyrene dications of oxidation (Figure 1). Major objectives of the study were (a) to provide new examples of pyrene dications and (b) to explore whether the location and the number of inductively electron-releasing substituents (alkyl and cycloalkyl groups) (Figure 2) might perturb the mode or the extent of charge distribution in the dications. We demonstrate further that superacid solutions of the alkylpyrenium cation resulting

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(1) For reviews and summaries see: Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem. Int. Ed. Engl.* 1983, 22, 393-398; Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985; Chapt. 3.

(2) Mills, N. S. *J. Org. Chem.* 1992, 57, 1899.

(3) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* 1976, 98, 4086.

(4) Bausch, J. W.; Gregory, P. S.; Olah, G. A.; Prakash, G. K. S.; Schleyer, P. V. R.; Segal, G. A. *J. Am. Chem. Soc.* 1989, 111, 3633.

(5) Laali, K. *J. Chem. Res. (S)* 1988, 378.

(6) Lammertsma, K.; Olah, G. A.; Berke, C. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1979, 101, 6658.

(7) (a) Cohen, Y.; Klein, J.; Rabinovitz, M. *J. Am. Chem. Soc.* 1988, 110, 4634. (b) Müllen, K. *Helv. Chim. Acta* 1976, 59, 1357. Müllen, K. *Helv. Chim. Acta* 1978, 61, 1296.

(8) (a) Lewis, I. C.; Singer, L. S. *J. Chem. Phys.* 1965, 43, 2712. (b) Buchanan, A. C., III; Livingston, R.; Dworkin, A. S.; Smith, G. P. *J. Phys. Chem.* 1980, 84, 423. (c) Wang, H.; Kispert, L. D.; Sang, H. *J. Chem. Soc. Perkin Trans. 2* 1988, 1463.

(9) Laali, K. K.; Hansen, P. E. *J. Org. Chem.* 1991, 56, 6795.

(10) Laali, K. K.; Liang, T.-M.; Hansen, P. E. *J. Org. Chem.* 1992, 57, 1658.

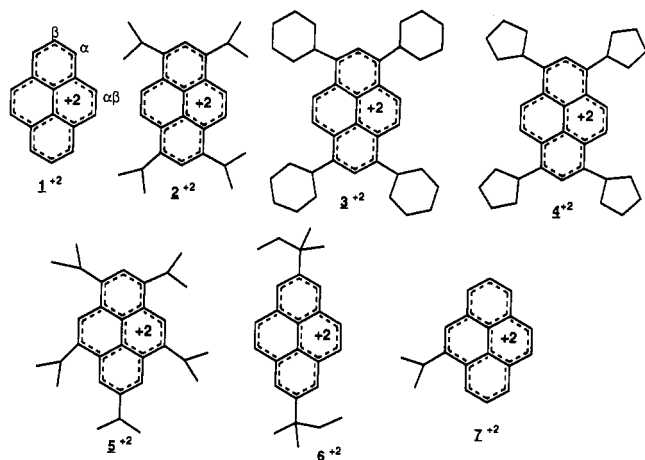


Figure 1. Persistent pyrene dication and alkylpyrene dications in $\text{SbF}_6/\text{SO}_2\text{ClF}$.

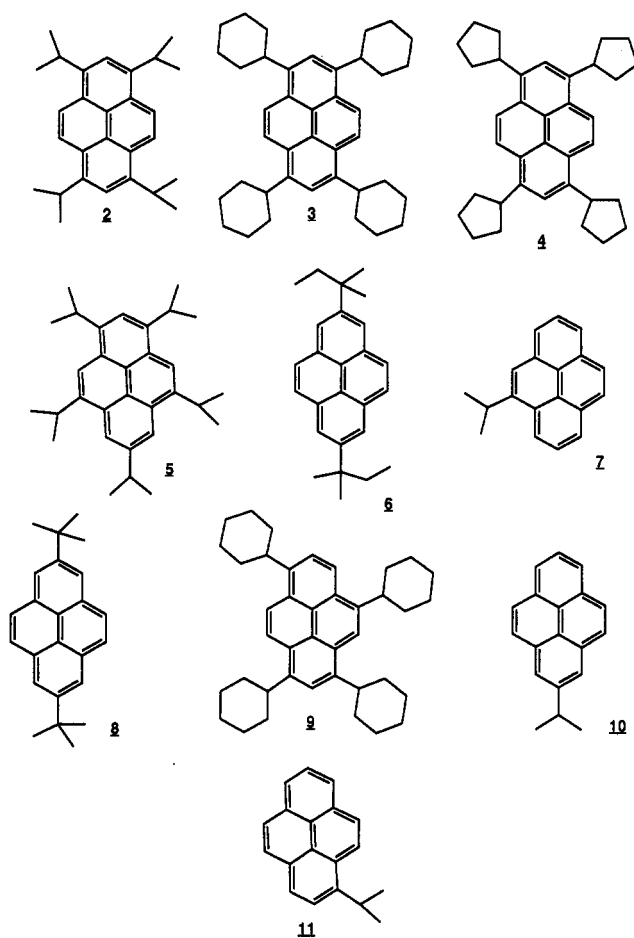


Figure 2. Parent pyrene and crowded alkylpyrene substrates.

from protonation contain ESR detectable amounts of their corresponding radical cations derived from oxidation and that the presence of this radical cation does not lead to noticeable line broadening in the NMR of the pyrenium ion.

Results and Discussion

As shown by Forsyth and Olah,³ the parent pyrene dication 1^{+2} shows three signals at 184.0, 156.2, and 143.3 ppm for the C_α , $C_{\alpha\beta}$, and C_β and two signals at 145.1 and 133.9 ppm for the ring junctions, consistent with the charge alternation model.^{7a}

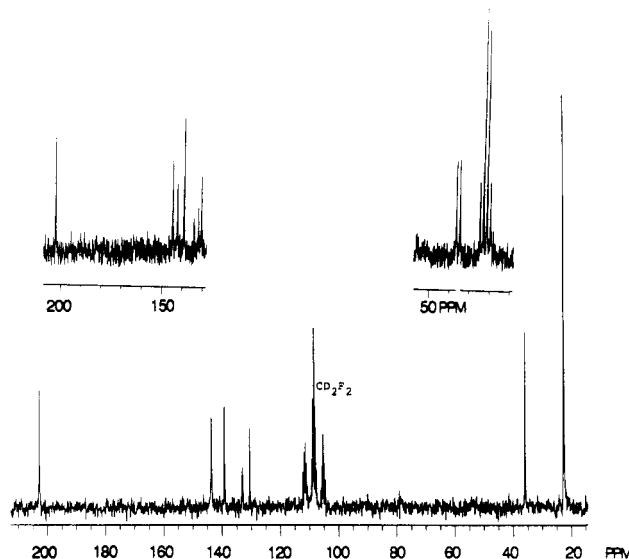


Figure 3. ^{13}C NMR spectrum of 2^{+2} [inset: proton-coupled spectrum].

Pertinent to this data are our recent ^{13}C NMR studies of persistent alkylpyrenium ions,¹¹ showing extensive positive charge delocalization away from the site of attack. Thus significant phenalenium ion character was found in the pyrenium ion from α attack, and phenanthrenium ion character in the Wheland intermediate from $\alpha\beta$ attack.

Oxidation of 1,3,6,8-Tetraisopropylpyrene (2), 1,3,6,8-Tetracyclohexylpyrene (3), and 1,3,6,8-Tetracyclopentylpyrene (4). Due to a high degree of symmetry and inherent simplicity of their NMR spectra, the all α -substituted 2 and 3 (and 4) are interesting models for comparison with 1.

Slow addition of cold $\text{SbF}_6/\text{SO}_2\text{ClF}$ to a slurry of 2 in SO_2ClF at dry ice/acetone temperature gave a dark red solution, the ^{13}C NMR spectrum of which (at -68°C ; Figure 3) demonstrates clean formation of a dipositive species without isopropyl disproportionation and loss of symmetry. Complete NMR assignments were made based on proton coupling, the chemical shifts (in analogy with 1), and relative signal intensities (Table I).

The observed total deshielding in 2^{+2} relative to its precursor is 209.6 ppm per electron charge (Table II) confirming dication formation. Presence of C_α resonance at 202.6 ppm corresponds to a deshielding of 61.1 ppm relative to the precursor. Comparison with the C_α resonance in 1^{+2} (Figure 4) gives a deshielding of 18.6 ppm, which is close to a normal *iPr* effect at C_α in 2, suggesting that the *iPr* groups have not greatly influenced the magnitude of the charge at the α -positions. It is noted, however, that the $C_{\alpha\beta}$ (with a *peri-iPr* group) and C_β (with two *ortho-iPr* groups) are both somewhat shielded relative to those carbons in 1^{+2} ($\Delta\delta_{13\text{C}}$ -12.7 and -10.4 ppm, respectively). The carbons at ring junctions are also somewhat shielded relative to those of 1^{+2} . Whereas the *iPr*(CH) in 2^{+2} is deshielded by 6.68 ppm compared to the precursor, the *iPr*(Me) is shielded by 1.56 ppm. These changes may indicate anisotropic shielding of the *iPr*-(Me) due to a change in the methyl geometry upon oxidation of the pyrene.¹²

(11) Laali, K. K.; Hansen, P. E., unpublished results.

Table I. ^{13}C NMR Data for Alkylpyrene Dications and Their Precursors

dication ^a	C_α	$C_{\alpha\beta}$	C_β	ring junction	alkyl (cycloalkyl) subst
2^{+2}	202.6 (s) ^c	143.5 (d)	132.9 (d)	139.0 (s), 130.3 (s)	35.8, 22.4
2^b	141.5	121.5	118.9	126.4, 126.1	29.1, 24.0
3^{+2}	199.8 (s)	142.7 (d)	133.1 (d)	138.6 (s), 130.2 (s)	47.4, 34.6, 25.7, 25.3
3^b	140.6	121.4	120.1	126.5, 126.1	40.0, 34.5, 27.34, 26.47
4^{+2}	199.3	142.2	129.1	138.7 ^d , 124.6 ^d	47.5, 37.2, 26.6
4	138.9	121.8	120.1	127.0, 126.2	41.6, 34.3, 25.0
5^{+2}	208.7 (s) (C_1, C_3), 180.5 (d) (C_6, C_8)	165.0 (s) (C_5, C_9), 142.0 (d) (C_4, C_{10})	160.6 (s) (C_7), 140.0 (d) (C_2)	141.0 (C_{5a}, C_{8a}), 140.0 (C_{3a}, C_{10a}), 131.5 (C_{10b}), ^d 130.0 (C_{10c}) ^d	37.0, 34.2, 33.7, 23.0, 22.5, 20.5
5^b	141.6, 117.5	141.0, 118.3	145.1, 118.8	125.4, 130.6	35.1, 29.1, 24.7, 24.0, 23.4
6^{+2}	183.1 (d)	155.3 (d)	166.6 (s)	146.6 ($C_{3a}, C_{5a}, C_{8a}, C_{10a}$), 134.3 (C_{10b}, C_{10c})	39.1, 33.4, 24.2, 8.5
6	127.4	122.6	145.8	130.8	39.0, 37.5, 29.0, 9.3
7^{+2} ^e	185.4 (C_1), 184.7 (C_8), 181.2 (C_6), 177.3 (C_3)	174.1 (C_4), 154.6 (C_{10}), 151.9 (C_9), 151.3 (C_3)	143.3 (C_7), 140.0 (C_2)	142.8 (C_{5a}), 141.8 (C_{8a}), 140.6 (C_{10a}), 132.5 (C_{10b}), 130.9 (C_{10c})	32.0, 21.0
7^b	124.1, 124.7, 124.6, 120.8	143.5, 122.3, 127.5, 127.0	128.7, 125.4	131.6, 131.4, 130.8, 130.1, 123.5	28.8, 23.3

^a The $^1J_{C-H}$ was typically 166–167 Hz; the $^1J_{C-H}$ 164–165 Hz and $^1J_{C-H}$ about 175 Hz. Chemical shifts are reported in ppm. ^b See ref 21. ^c Refers to multiplicity of coupled spectrum. ^d Tentative assignments. ^e Assignments within each category are tentative except for C_4 .

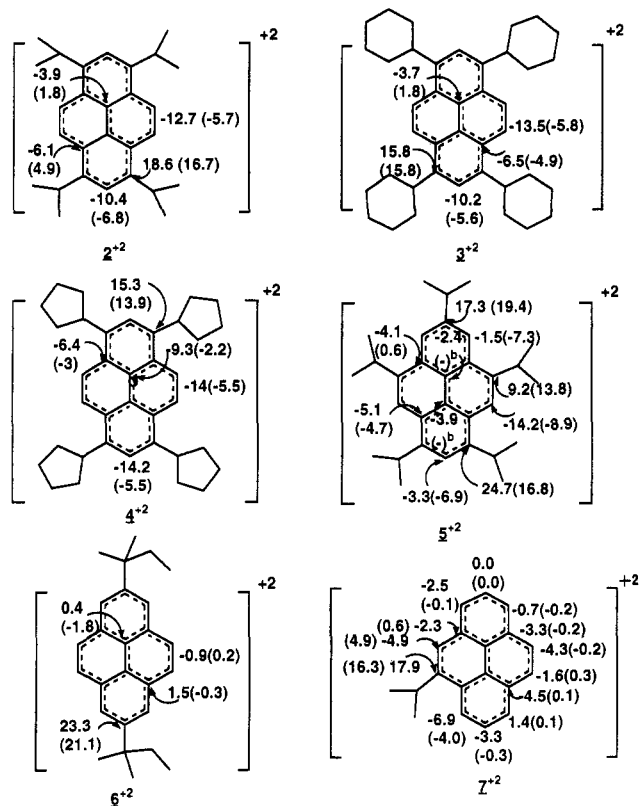


Figure 4. Substituent effects (^{13}C NMR) on alkylpyrenium dications. Values in parentheses are substituent effects in the noncharged species (see ref 21). The b designations indicate resonances not observed in the arene precursor. For 7^{+2} , assignments are tentative within a group of carbons, except for C_4 .

Quenching of the superacid solution of the dication furnished intact **2** (^1H NMR).

The closely related dication 3^{+2} was first observed as a byproduct when **3** reacted with $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ (1:1) "magic acid"/ SO_2ClF . At -65°C two isomeric *ipso*-protonated pyrenium dications were formed.¹¹ On raising the temperature to -50°C , the ^1H NMR spectrum showed two new singlets at 8.56 and 7.53 ppm. These peaks continued to grow with increasing temperature and accounted for

ca. 40% of the mixture at -40°C . The presence of 3^{+2} was confirmed by the ^{13}C NMR of the ion mixture (five distinct signals at 200.16, 144.60, 139.06, 134.24, and 130.71 ppm for the oxidation dication, in addition to the peaks for the isomeric pyrenium dications from *ipso* attack).

In subsequent studies 3^{+2} was independently generated by oxidation with $\text{SbF}_5\cdot\text{FSO}_3\text{H}$ (9:1)/ SO_2ClF (Table I). The latter dication (except of minor variations due to change in the superacid system) exhibited ^1H and ^{13}C NMR spectra identical with the cation produced in "magic acid" (see Table I and later discussion on ^1H NMR data). The total deshielding in 3^{+2} , the deshielding order, and the $\Delta\delta^{13}\text{C}$ values are given in Table II.

The structurally analogous 4^{+2} was similarly generated by oxidation with $\text{SbF}_5\cdot\text{FSO}_3\text{H}$ (9:1)/ SO_2ClF . The observed deshielding at C_α for 4^{+2} relative to C_α in 1^{+2} is 15.8 ppm, slightly larger than a cyclopentyl substituent effect, whereas C_β and $C_{\alpha\beta}$ are both shielded (Figure 4).

Oxidation of 1,3,5,7,9-Pentaisopropylpyrene (5). The low temperature reaction of **5** with $\text{SbF}_5/\text{SO}_2\text{ClF}$ gave a dark red solution, the ^{13}C NMR of which exhibited ten aromatic signals and three different *iPr* groups (in 2:2:1 ratio), illustrating the formation of a single dication (Table I). The two equivalent *iPr*-bearing C_α resonances are the most downfield and appear as a singlet at 208.7 ppm, deshielded by 24.7 ppm relative to the C_α resonance in 1^{+2} . The unsubstituted C_α peak is at 180.5 ppm and the peaks for the *iPr*-substituted and unsubstituted $C_{\alpha\beta}$ s are observed at 165.0 and 142.0 ppm and those for the C_β at 160.6 and 142.0 ppm, respectively. The unsubstituted $C_{\alpha\beta}$ having a *peri*- and an *ortho*-*iPr* is shielded by 14.2 ppm relative to this carbon in 1^{+2} (Figure 4).

The observed deshielding of substituted $C_{\alpha\beta}$ is less than expected based on a substituent effect alone on the precursor, suggesting a reduction in the positive charge at $C_{\alpha\beta}$ in 5^{+2} relative to 2^{+2} . The *iPr*-bearing C_β appears deshielded relative to that in 1^{+2} by 17.3 ppm, in range for just a substituent effect. The dicationic nature of the species is also evident based on the calculated total deshielding (Table II), and the deshielding order $C_\alpha > C_{\alpha\beta} > C_\beta$ is clearly observed.

Cold solutions of the dication stored at -25°C were stable for several weeks without decomposition. Quenching of the ion solutions regenerated the precursor.

Oxidations of 2,7-Di-*tert*-amylpyrene (6). Careful addition of $\text{SbF}_5/\text{SO}_2\text{ClF}$ to a slurry of **6** in SO_2ClF at -78°C gave a green-black solution, the ^{13}C NMR of which

(12) (a) For examples of anisotropic shielding of the *iPr*(Me) in alkylpyrenium σ -complexes see ref 9. (b) AM1 calculations on isomeric monoisopropylpyrenes do not indicate noticeable changes in *iPr*(Me) geometry upon oxidation (see later discussion).

Table II. Total Deshielding (ppm/e) and $\Delta\delta_{13C}$ of the Alkylpyrene Dications

dication	total ^a $\Delta\delta_{13C}$ ppm/e	$\Delta\delta_{13C}$ (relative to precursor)				
		C_α	$C_{\alpha\beta}$	C_β	$C_{3a,5a,8a,10a}$	$C_{10b,10c}$
1 ⁺²	231.5	59.2	29.0	17.6	14.1	9.3
2 ⁺²	209.6	61.1	22.0	14	12.6	4.2
3 ⁺²	207.0	59.2	21.3	13.0	12.1	4.1
5 ⁺²	223.5	67.1, 63.0	24.0, 21.2	15.5, 21.2	15.6, 9.4	0.6, 0.9
6 ⁺²	239.7	55.7	32.7	19.9	15.8	3.5
7 ⁺²	216.3	61.2, 56.5, 56.6, 60.1	30.6, 29.0, 24.9, 27.1	14.6, 14.6	9.5, 9.9, ^b 11.2, 11.0	7.4, 7.4

^a The alkyl groups are not included. ^b Approximated based on average position of the observed ring junction carbons.

showed five low-field aromatic absorptions and four aliphatic signals for the *tert*-amyl group (Figure 5; supplementary material).

The chemical shift of C_α in 6⁺² is close to that in 1⁺², showing little or no perturbation by the *tert*-amyl groups placed in the β positions (Table I). The δ_{13C} for C_β at 166.6 ppm represents a deshielding of 23.3 ppm relative to C_β in 1⁺². This difference is only slightly larger than a *tert*-amyl substituent effect on 5 and illustrates further that positive charge delocalization into the β positions is not noticeably enhanced by the presence of the *tert*-amyl groups. Intact 5 was isolated by quenching of the cold ion solution.

Oxidation of 4-Isopropylpyrene (7). The low temperature reaction of unsymmetrical 7 with SbF_5/SO_2ClF similarly gave a stable dication, the ¹³C NMR spectrum of which exhibited 16 aromatic signals (Figure 6; supplementary material) and one *iPr* group indicative of a single dication (Table I).

In line with the observed ¹³C NMR spectrum of 7 itself, loss of symmetry due to the *iPr* at the 4 position results in four C_α resonances, four $C_{\alpha\beta}$ resonances, and two C_β resonances in the dication. Only five types of ring junction carbons can be seen in the dication.

The four nonequivalent C_α 's are between 185.4 and 177.3 ppm. The C_α with a *peri*-*iPr* is shielded by 6.9 ppm as compared to the C_α in 1⁺² (Figure 4). The *iPr*-substituted $C_{\alpha\beta}$ is at 174.1 ppm, deshielded by 17.9 ppm relative to that in 1⁺².

The total deshielding observed is 216.3 ppm/e, and the deshielding order $C_\alpha > C_{\alpha\beta} > C_\beta$ has been maintained (Table II).

Oxidation of 2,7-Di-*tert*-butylpyrene (8). The low temperature reaction of SbF_5/SO_2ClF with a slurry of 7 gave a dark red solution whose ¹³C and ¹H NMR spectra clearly indicated the presence of the desired 8⁺² only as a minor species and the Wheland intermediate of sulfonylation⁹ as the prominent cation.

As expected, the ring carbon chemical shifts of 8⁺² (180.60, 167.2, 157.5, 149.1, and 135.2 ppm) are very close to those of 5⁺² with the *tBu* carbons of 8⁺² appearing at 33.6 and 25.9 ppm.

The prominent sulfonylation σ -complex shows a distinctly deshielded $sp^3(C)$ at 68.6 ppm, two nonequivalent, deshielded, *tBu* groups (38.3, 19.5, and 35.4, 27.9 ppm), and deshielded aromatic absorptions between 120–155 ppm.

In the ¹H NMR spectrum, the presence of the sulfonylation σ -complex is deduced based on a deshielded $sp^3(CH)$ at 6.33 ppm, a distinct upfield singlet at 7.85 (H_3 ; *meta*), a broad doublet at 8.30 ppm (H_{10}), a cluster of low-field aromatic absorptions between 9.10–9.21, and the SO_2H absorption as a sharp singlet at 9.50 ppm, leaving out two upfield aromatic singlets (1:1) at 7.05 and 7.83 ppm which must be ascribed to 8⁺² (see later discussion).

For further confirmation, in a control experiment, the sulfonylation σ -complex was independently generated by reacting a slurry of 7 in SO_2 with $FSO_3H \cdot SbF_5$ (1:1)/ SO_2 . The ¹³C NMR spectrum of the resulting deep red solution exhibited two *tBu* groups (38.5, 29.8 and 35.6, 28.4), the $sp^3(C)$ at 68.5 ppm, and deshielded aromatic absorptions, the positions of which were identical with those observed in the spectrum of the oxidized 8.¹³

In the ¹H NMR spectrum a distinct $sp^3(CH)$ absorption at 6.34 ppm (slightly broadened singlet), upfield aromatic protons at 7.85 (H_3 ; *meta*) and 8.26 ppm (8Hz doublet; H_{10}), a cluster of deshielded doublets between 9.03–9.27 ppm, and the SO_2H singlet at 10.11 ppm were present. Moreover, the two upfield aromatic singlets of 8⁺² are totally absent.

Oxidation of 1 at Lower Temperatures. We find that if 1 is treated with SbF_5/SO_2ClF at ca. -75 °C and the temperature is kept below -60 °C, two-electron oxidation is very slow and 1⁺² is not observable by NMR. Instead, the ¹H and ¹³C NMR spectra of the resulting green-black ion solution are consistent with the formation of a pyrenium ion.

Presence of a distinctly deshielded $sp^3(CH)$ which appeared as a broad singlet at 6.04 ppm and deshielded aromatic absorptions between 7.40–8.80 ppm argued in favor of a pyrenium ion of sulfonylation.⁹ In the ¹³C spectrum in place of the expected five aromatic signals of the dication,³ 16 aromatic signals were present (between 122–157 ppm), typical of a pyrenium ion with an $sp^3(C)$ resonance at 67.1 ppm.¹⁴

¹³C NMR Spectra of Alkylpyrene Dications. The substituent effects at the *ipso*-carbons are in most cases somewhat larger for the dications than for the noncharged arenes (Table II); exceptions are C-5, C-10, and C-7 of 5⁺² (Figure 4).

It is furthermore seen from 6⁺² that the effects of substitution beyond the *ipso*-carbon are very small. The assignments of the ¹³C spectrum of 7 are clearly tentative, but they show again only small substituent effects with the exception of the *ipso*-carbon and the carbon *peri* to the substituent, C-3.

The total deshielding values given in Table II must be considered approximate as the effects of charge delocalization into the alkyl substituents have not been included. Nevertheless, the values are for all ions close to those of a doubly charged ion. The effects of charge at each position are given in Figure 4. The effects at *ipso*-carbons at

(13) Presence of a second (more upfield) $sp^3(C)$ at 65.8 and additional deshielded aromatic absorptions in the sulfonylation spectrum corroborated the formation of another, less abundant, pyrenium ion whose *tBu* carbon positions coincided with those of the sulfonylation σ -complex. Presence of a second pyrenium ion was further evident from the ¹H NMR spectrum exhibiting additional peaks at 7.83 ppm (singlet), doublets between 8.51–8.61 ppm, and a SO_2H singlet at 10.20 ppm.

(14) A second less prominent absorption was also seen at 67.6 ppm together with other minor aromatic signals.

Table III. AM1 Calculations of $\Delta\Delta H^\circ_f$ and Charge Densities for Pyrene Dication and Isomeric Monoisopropylpyrene Dications

pyrene dication (iPr position)	ΔH°_f (neutral)	ΔH°_f (dication)	$\Delta\Delta H^\circ_f$	calculated charges at ring carbons in the dication ^a									
				C ₁ (α)	C ₂ (β)	C ₃ (α)	C ₄ ($\alpha\beta$)	C ₅ ($\alpha\beta$)	C ₆ (α)	C ₇ (β)	C ₈ (α)	C ₉ ($\alpha\beta$)	C ₁₀ ($\alpha\beta$)
1 ⁺²	67.3	515.7	448.4	+0.162	-0.209	+0.162	+0.011	+0.010	+0.162	-0.208	+0.162	+0.009	+0.010
11 ⁺² (α) ^b	54.5	493.5	439.1	+0.265	-0.222	+0.123	-0.025	+0.030	+0.162	-0.205	+0.143	+0.005	-0.011
11 ⁺² (α) ^c	52.7	491.7	439.0	+0.268	-0.219	+0.118	-0.028	+0.032	+0.161	-0.205	+0.143	+0.006	-0.009
10 ⁺² (β)	50.2	494.2	444.0	+0.156	-0.125	+0.143	-0.001	+0.015	+0.160	-0.208	+0.159	+0.011	+0.003
7 ⁺² ($\alpha\beta$) ^d	53.2	494.1	440.9	+0.156	-0.204	+0.134	-0.014	-0.000	+0.171	-0.209	+0.150	+0.005	+0.126
7 ⁺² ($\alpha\beta$) ^e	54.6	495.8	441.2	+0.157	-0.208	+0.134	-0.013	+0.004	+0.171	-0.210	+0.151	+0.000	+0.119

^a Excluding ring junctions and the iPr substituent. ^b Methine C-H bond syn to C1-C2 bond. ^c Methine C-H bond anti to C1-C2 bond. ^d Methine C-H bond anti to C9-10 bond. ^e Methine C-H bond syn to C9-C10 bond.

α -positions are all larger than for the unsubstituted cases, whereas for the β - and $\alpha\beta$ -positions a more varied picture is found probably related to the effects of substitution as described above. For the nonsubstituted positions a β -substituent has little effect, whereas large effects are seen at C- β and C $\alpha\beta$ as a consequence of α -substitution. This latter effect indicates that the steric effects are larger and more important in the dications.

Semiempirical Calculations on Model Pyrenium Dication Compounds. To complement our NMR studies, we calculated by the AM1 method the charge distributions and the $\Delta\Delta H^\circ_f$ ($= \Delta H^\circ_{f \text{ ion}} - \Delta H^\circ_{f \text{ neutral}}$) for pyrene dication 1⁺² and three isomeric monoisopropylpyrene dications, 11⁺², 10⁺², and 7⁺² (Table III), which served as models for the polyisopropylpyrene systems. It can be seen that a single isopropyl group lowers the energy for oxidative dication formation by 4–8 kcal/mol. Although the $\Delta\Delta H^\circ_f$ values for the isopropylpyrenes are within 5 kcal/mol of each other, the presence of an isopropyl group at the β position is least stabilizing. In all cases, the optimized structure has the isopropyl methine CH bond coplanar (within 0.4°) with the aromatic rings. There are two coplanar rotamers each for the α and $\alpha\beta$ isomers, and for both isomers the two rotamers are minima on the AM1 energy hypersurface, differing by less than 2 kcal/mol. The isopropyl methyls are symmetrically placed above and below the ring plane within a maximum dihedral angle difference of 0.9°.

The calculated positive charges at the ring carbons of the pyrene dications, regardless of substitution, are located primarily at the α positions, while negative charge accumulates at any unsubstituted β positions. The AM1 HOMO-LUMO symmetries for 11 are illustrated in Figure 8 (supplementary material). In the dications, the charges at the unsubstituted α positions are about 0.27 more positive than in the neutral species; those at the unsubstituted β positions about 0.08 more negative; those at the $\alpha\beta$ positions about 0.1 less negative, and those at the ring junction carbons about 0.05 more negative. The positive charge at the *ipso* position of the β and the $\alpha\beta$ isopropylpyrene dications is 0.18 higher than in the neutral species and 0.31 higher in the *ipso* position of the α isomer. The calculated absolute charges on the ring carbons are consistent with their observed ¹³C chemical shifts.

As is commonly seen in calculations on carbocations, the majority of the positive charge is carried by the hydrogens. In these dications the charges on the ring hydrogens are +0.20, for α and $\alpha\beta$ positions and +0.22 for the β positions, regardless of the position of substitution. For the alkyl hydrogens the charges are +0.11 to +0.15 each.

On the ¹H NMR Spectra of the Alkylpyrene Dications. In an early ¹H NMR study of arene dications,

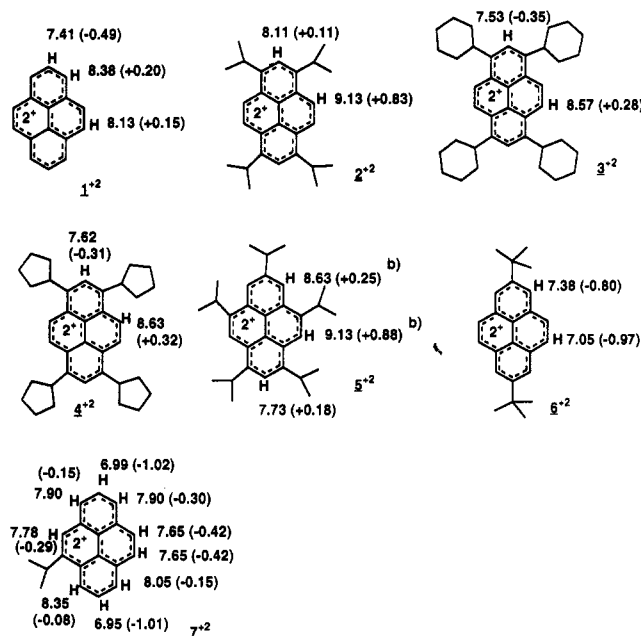


Figure 7. ¹H NMR positions ($\Delta\delta_{1H}$ between brackets) of the ring hydrogens of alkylpyrene dications. Values for 1⁺² taken from ref 17. Values indicated by b designations may be interchanged.

Brouwer¹⁵ showed that the total charge-induced shifts ranged from as little as 2.3 ppm per electron charge for anthracene to as much as 14 ppm for perylene.

In 1,4,5,8-tetramethylbiphenylene dications studied by Olah and Liang¹⁶ a total deshielding of 1.80 ppm was found for the four equivalent aromatic protons of the dication.

With 1⁺² the center of gravity of the ¹H NMR spectrum remains almost unchanged relative to that of the arene precursor.¹⁴ Whereas H_α and $H_{\alpha\beta}$ are both somewhat deshielded ($\delta H_\alpha > \delta H_{\alpha\beta}$), the δH_β resonance is actually more *upfield*. Thus the expected downfield shifts due to the positive charge are compensated by a *paramagnetic* ring current in the 12- π perimeter.¹⁷

The ¹H chemical shifts given in Figure 7 show a large degree of variation. Whereas large upfield shifts are seen in 6⁺² and 7⁺², relatively large downfield shifts are found for 2⁺² and 5⁺² as compared to their corresponding neutral species. For the charged species a paramagnetic ring current is operative.¹⁷ Furthermore, as shown by AM1 calculations (Table III) charge alternation occurs at the carbons of the periphery. This charge alternation is not to any large extent disturbed by substitution except at

(15) Brouwer, D. M.; van Doorn, J. A. *Rec. Trav. Chim. Pays. Bas.* 1972, 91, 1110.

(16) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* 1977, 99, 6045.

(17) Müllen, K. *Helv. Chim. Acta* 1978, 61, 2307.

the *ipso*-substituted carbons. β -Hydrogens must thus be expected to fall at higher field based on the charge arguments. The relatively small low-field shift of the H_α protons, despite the positive charge at C_α , may be explained by the paramagnetic ring current as stated above. The large variations are probably unrelated to charge variations as calculated by the AM1 method (Table III). They can neither be related to substituent effects in a traditional sense. In the neutral molecule these effects are very small and very localized except for a small *peri* effect. For pyrenes, substitution at the α -position leads to a substantial variation in position of the *para*-band in the UV spectrum.²¹ This transition is primarily of HOMO to LUMO type. As the HOMO orbitals are involved in the paramagnetic ring current, it seems plausible that substitution at these positions leads to a decrease in the paramagnetic ring current and thus to a low-field shift of all ^1H resonances, as observed for 2^{+2} and 5^{+2} . The much smaller positive effect observed for 3^{+2} appears to support this notion as the cyclohexyl substituent is shown from the UV spectra to interact less with the *para*-band of pyrene than the corresponding isopropyl substituents.²¹ Slightly larger positive effect observed with 4^{+2} is also in line with this suggestion.

Substitution at the β -position appears on the other hand to support the paramagnetic ring current, as judged from 6^{+2} . The perturbations imposed by an *iPr* group in the $\alpha\beta$ position in 7^{+2} are remarkable. This phenomenon clearly requires more studies, both of substituted pyrenes and other substituted polycyclic aromatics.

On Sulfonylation σ -Complex Formation in the $\text{SbF}_5/\text{SO}_2\text{ClF}$ System. Formation of the Wheland intermediate of sulfonylation as a competing reaction in oxidation of **8** and in low temperature oxidation of **1** is rather surprising. It is unlikely that its origin is SO_2 impurity in SO_2ClF since the same batch of SO_2ClF did not give sulfonylation with other alkylpyrenes under similar conditions. We propose that oxidation of **8** under our mild conditions at low temperatures proceeds mainly to give a radical cation and that the Wheland intermediate arises from this cation by reaction with SO_2 . The course of events which may lead to SO_2 formation from SO_2ClF (presumably by redox chemistry in SbF_5) are unclear. With **1**, possible formation of a dimeric dication formed by radical cation coupling must be ruled out since quenching of the ion solution furnished intact pyrene rather than 1,1'-dipyrenyl (^1H NMR). We found previously that authentic sulfonylation σ -complexes, formed by treating alkylpyrenes with "magic acid"/ SO_2 , desulfonylate on quenching to give alkylpyrenes.⁹

Alkylpyrene Radical Cations Formed in $\text{FSO}_3\text{H}/\text{SO}_2$. The green radical cation of pyrene, first reported by Lewis and Singer,^{8a} was formed by room temperature oxidation with SbCl_5 in methylene chloride solvent. The hyperfine coupling constants [5.83 G ($4H_\alpha$), 2.12 G ($4H_{\alpha\beta}$), and 1.18 G ($2H_\beta$)] show that the largest couplings are to H_α s. Pyrene radical cation was also generated by oxidation with $\text{SbCl}_5\text{-AlCl}_3$ melt,^{8b} and more recently by a Scholl

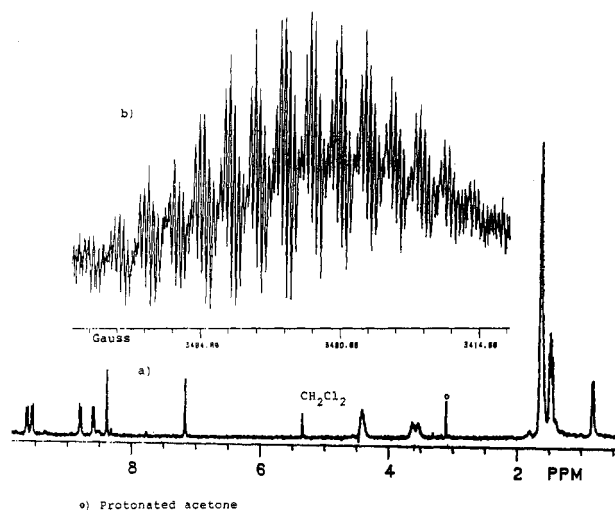


Figure 9. The ^1H NMR and ESR spectra of **2** in $\text{FSO}_3\text{H}/\text{SO}_2$. (a) ^1H NMR of pyrenium ion of *ipso* attack; (b) ESR of $2^{+•}$.

condensation of benzyl halides (via $\text{ClCH}_2\text{CH}_2\text{Cl}/\text{benzene}/\text{AlCl}_3$) followed by *in situ* oxidation.^{8c}

Davies and Shields¹⁸ found that in the $\text{FSO}_3\text{H}/\text{SO}_2$ solvent system, a superacid widely employed for generation of monocations by protonation, oxidation occurred as a minor competing pathway to give a radical cation. Since removal of dissolved oxygen had no effect on the ESR signal, it was suggested that electron transfer between the wheland intermediate and the precursor leads to radical cation formation.

The discovery of the simultaneous presence of the anthracenium cation (observed by ^1H NMR) and the anthracene radical cation (detected by ESR)¹⁸ is significant in that since the NMR line widths were not affected by radical cation formation, without an ESR measurement the presence of free radicals in arene/ $\text{FSO}_3\text{H}/\text{SO}_2$ systems could not have been suspected by solution NMR studies of arenium ions alone.

Among other examples, formation of the pyrene radical cation in a $\text{FSO}_3\text{H}/\text{SO}_2$ system was also shown by ESR by Davies and Shields.¹⁸

In relation to our previous studies of alkylpyrenium ions of protonation and sulfonylation⁹ and the present oxidation work, it was of interest to explore competing radical cation formation with $\text{FSO}_3\text{H}/\text{SO}_2$ and to determine its generality for crowded pyrenes.

We first repeated the reported oxidation of **1** with $\text{FSO}_3\text{H}/\text{SO}_2$, and as was already shown,¹⁸ detected the pyrene radical cation $1^{+•}$ by ESR.¹⁹

Focusing on competing oxidation of symmetrical **2**, the red ion solution formed by low temperature reaction of **2** with $\text{FSO}_3\text{H}/\text{SO}_2$ was examined both by ^1H NMR and ESR. Although the proton spectrum was identical to our previously reported spectrum showing an *ipso*-protonated pyrenium ion with no unusual line broadening (Figure 9a), the ESR spectrum (at -70°C) exhibited an intense and well-resolved signal for $2^{+•}$ (Figure 9b) [$g = 2.0019$; 2.1 G ($4H_{\alpha\beta}$) and 1.2 G ($2H_\beta$)] in which spin coupling to the four equivalent H_α observed in $1^{+•}$ has been eliminated. Instead, a much smaller hyperfine coupling occurs with the four equivalent α -*iPr*(*CH*) (0.31–0.35 G). The observed couplings to H_β and $H_{\alpha\beta}$ are very similar to those observed for $1^{+•}$.⁸

When the sample temperature was raised (-30°C), a broad, featureless, ESR signal was obtained. On recoiling,

(18) Davies, A. G.; Shields, C. J. *J. Chem. Soc. Perkin Trans. 2* 1989, 1001.

(19) Only ~42 lines out of the theoretically expected 75 were clearly discernible.

(20) Assuming that H_α 's and H_β 's remain equivalent, 120 lines would be expected.

(21) Berg, A.; Lam, J.; Hansen, P. E. *Acta Chem. Scand. Ser. B*: 1986, B40, 665.

some of the fine structure was recovered, but the signal lost intensity and remained broad.

We have already shown that the *ipso*-protonated cation 2-H⁺ rearranges on heating.⁹ The broadening of the ESR signal on heating probably also reflects such a rearrangement to form an unsymmetrical radical cation with more complex coupling.

In an independent experiment, 2 was treated with FSO₃H/SO₂ as before to give a bright red solution, exhibiting the same resolved ESR spectrum for the symmetrical radical cation. Subsequently, NO⁺BF₄⁻ was added; the solution turned green, and the ESR spectrum showed substantial broadening of the signal ($g = 2.0016$, $\Delta H_{pp} = 3.8$) and loss of hyperfine coupling, in agreement with further oxidation to a diamagnetic dication and the presence of a radical cation-dication equilibrium.

The advantage of FSO₃H/SO₂ as a medium for arene radical cation generation became apparent in our attempts to obtain the radical cation of 2 using SbCl₅/CH₂Cl₂. In this case, a broad, featureless signal was observed ($g = 2.0057$, $\Delta H_{pp} = 7.7$), and no hyperfine coupling could be seen.

The ESR spectrum of the dark red solution obtained by low temperature reaction of 5 with FSO₃H/SO₂ showed an intense signal which was broad and featureless (-70 to -40 °C). The signal was unaffected by removal of dissolved oxygen *via* repeated freeze-thaw cycles. The appearance of the ESR signal suggests a radical cation-dication equilibrium, as the arene becomes more easily oxidizable with more electron-donating substituents.

Presence of the radical cations of 6 and 8 was also confirmed when their low temperature protonation samples were examined by ESR at -70 °C (ca. 16 lines out of the theoretically expected 25 were observable).

The ESR spectrum of 7 in FSO₃H/SO₂ showed a rather weak signal which was not analyzed.²⁰

In our previous work,⁹ a single monopyrenium ion was generated from 1,3,5,8-tetracyclohexylpyrene 9 with TfOH/SO₂ or FSO₃H/SO₂ by protonation at the unsubstituted α position. In the present study, the ESR spectrum of the sample was examined. An intense, broad, and featureless signal was detected ($g = 2.0016$, $\Delta H_{pp} = 9.0$).

Conclusions

We have provided the first examples of crowded alkylpyrene dications 2-7 by two-electron oxidation with SbF₅/SO₂ClF at low temperature. The position and number of the alkyl substituents greatly facilitate ¹³C NMR assignments of the resulting dications. We find that for the dications, substituent effects at the *ipso*-carbons are in most cases slightly larger and the effects due to steric interactions are strongly enhanced relative to their precursors. The ¹H NMR spectra of the alkylpyrene dications exhibit rather strong perturbations relative to unsubstituted 1⁺. Examination by ESR of the superacid solutions of alkylpyrenes protonated with FSO₃H/SO₂ shows competing formation of radical cations whose presence could not have been suspected based on ¹H NMR line widths of the pyrenium Wheland intermediates.

Experimental Section

Materials. Some of the alkylpyrenes used in this study were gifts donated by Professor Arne Berg of Aarhus University. The syntheses and NMR data of these alkylpyrenes have already been reported.²¹ SbF₅ (Aldrich) and FSO₃H (Allied) were twice

distilled in an all-glass distillation unit under a fast flow of dry nitrogen. SO₂ClF (Aldrich) and SO₂ (anhydrous; Linde) were used as received.

NMR Spectra were recorded on a GN-300 wide-bore or a Bruker AC 250 instrument. The probe was cooled while shimming with an acetone-*d*₆ sample. The cold ion solutions were introduced quickly into the cold probe and the sample spun for 2-3 min prior to data collection.

ESR Spectra. X-band ESR spectra were obtained using an IBM 200D-SRC spectrometer with an ER 4111 temperature controller which has a precision of 1 K. The spectrometer frequency was measured using a Hewlett-Packard 5351A microwave frequency counter, and the magnetic field was measured by the Hall probe of the spectrometer which had been previously calibrated near $g = 2$ using a NMR gaussmeter. The IBM ESR software used these results to calculate the reported g and line width data. The ESR spectrum of 2⁺ was simulated using the program SUPER provided by Prof. Philip Riger (Brown University).

MO Calculations. The MO calculations were carried out on an IBM 3090 using MOPAC 5 (QCPE 581). The input geometries were obtained from molecular mechanics calculations using PCMODEL (Serena Software; 4th edition) on an IBM PC-AT.

Stable Dication Generation. In a typical experiment, a clear homogeneous solution of SbF₅ (1.8 g, 8.3 mmol; ca. 20-fold molar excess) was prepared in a dry 10-mm NMR tube under nitrogen by addition of 1 ml of SO₂ClF. A cold slurry of 7 (0.1 g, 0.41 mmol) in SO₂ClF (1 mL) was prepared in a separate 10-mm NMR tube under nitrogen and was poured directly into the SbF₅ solution at dry ice/acetone temperature under a dry nitrogen atmosphere with efficient vortex mixing, whereupon a green-black solution was immediately formed. An aliquot was transferred into a precooled 5-mm NMR tube *via* a pipet precooled in liquid SO₂-ClF. Cold CD₂Cl₂ (6-7 drops) was carefully added to the sample with vortex mixing just prior to NMR analysis (see below).

Use of CD₂Cl₂ as Internal Lock and Halogen Exchange with SbF₅. CD₂Cl₂ does not react with cold FSO₃H or CF₃SO₃H superacids and is widely used as internal lock and reference in these media. With FSO₃H-SbF₅ mixtures, especially at high SbF₅ content (magic acid and higher), CD₂Cl₂ slowly undergoes Cl→F exchange to give CD₂F₂ showing a small triplet of triplets (CDHF₂) at 6.20 ppm ($J_{HF} = 52$ Hz) in ¹H NMR.²² Since methylene fluoride formation is quite slow under these conditions, CD₂Cl₂ still serves as a convenient internal lock (and reference) in low temperature NMR studies of stable cations, thus avoiding the use of external capillaries which in many instances lead to sample inhomogeneity due to inherent viscosity of the solutions and in to spinning side-band formation in superconducting magnets.

Olah and Bruce²³ found that methylene chloride reacts with neat SbF₅ (2-fold excess)/SO₂ClF at -130 °C to give bis-(chloromethyl)chloronium ion (δ_{1H} 7.0 and δ_{13C} 78.5 ppm) which decomposed to difluoromethane at -85 °C.

In the present study, addition of few drops of cold CD₂Cl₂ to solutions of oxidation dications generated in SbF₅/SO₂ClF at dry ice/acetone temperature, led to rapid Cl→F exchange. The resulting deuterated difluoromethane exhibited a distinct triplet of multiplets in the ¹³C spectrum centered at 108.5 ppm (lit.²⁴ 111.2 ppm) with a J_{C-F} of 232 Hz and a J_{C-D} of 28 Hz. Although the *in situ*-formed difluoride has a limited lifetime in the superacid, it can be used conveniently as an internal lock.

Alternatively, we have used acetone-*d*₆/acetone (ca. ~10:1 v/v) mixtures as internal lock with the SbF₅-FSO₃H (9:1) system, where the *in situ*-formed carboxonium ion serves as the NMR reference.

Generation of Radical Cations. (a) In FSO₃H/SO₂: In a typical experiment, a clear solution of FSO₃H in SO₂ was prepared by adding ca. 0.5 mL of SO₂ to ca. 1 mL of FSO₃H in a 10-mm NMR tube under dry nitrogen. In a second NMR tube, ca. 7 mg

(22) At infinite dilution in cyclohexane or in TMS, CH₂F₂ has been reported at 5.45 ppm ($J_{HF} = 50.2$ Hz); see S. G. Frankiss *J. Phys. Chem.* 1963, 67, 752.

(23) Olah, G. A.; Bruce, M. R. *J. Am. Chem. Soc.* 1979, 101, 4765.

(24) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH: Weinheim, 1987; p 199.

of **2** was slurried with ca. 0.5 mL of SO₂. The superacid was added slowly to the substrate at dry ice/acetone temperature with efficient vortex mixing. The resulting red solution was first examined with ¹H NMR which showed the formation of the pyrenium ion obtained by protonation. An aliquot was transferred into a cold ESR tube and the sample repeatedly flushed with dry nitrogen to remove dissolved oxygen. Control experiments showed that the ESR signals were not improved when the samples were sealed *in vacuo* after repeated freeze and thaw.

(b) **Oxidation of 2 with SbCl₅/CH₂Cl₂:** To **2** (10 mg) dissolved in 1 mL of dry methylene chloride was added a solution of SbCl₅ (1 mL) diluted in CH₂Cl₂ (1 mL) at dry ice/acetone temperature to give a dark brown and somewhat heterogeneous sample. Upon raising the temperature, the color turned purple and the solution became homogeneous. An aliquot was trans-

ferred under dry nitrogen into an ESR tube just prior to recording the spectrum.

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Supplementary Material Available: Figures 5, 6, and 8 (3 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.