

# First Examples of Fluorinated and Chlorinated Polycyclic Aromatic Hydrocarbon (PAH) Dications from Benzo[a]pyrene, Pyrene, and Their Alkyl-Substituted Derivatives

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Two-electron oxidations (SbF<sub>5</sub>/SO<sub>2</sub>ClF) of 6-fluoro-benzo[a]pyrene **3**, 6-chloro-benzo[a]pyrene **4**, and their corresponding 7-methyl derivatives **5** and **6** as well as 1-fluoropyrene, **7**, 1-chloropyrene, **8**, and 1-fluoro-2,7-di-*tert*-butylpyrene, **9**, allowed the charge delocalization mode, substituent effects, one-bond and long-range C/F coupling constants, and the tropicity of the resulting persistent PAH dications to be examined by NMR for the first time. For comparison, detailed NMR studies of the dications of 7-methylbenzo[a]pyrene, **2**, and the parent benzo[a]pyrene, **1**, are also reported. Total deshieldings  $\Sigma\Delta\delta$  <sup>13</sup>C in the resulting dications are ca. 195–211 ppm/e for the benzo[a]pyrenium and ca. 200–209 ppm/e for the pyrenium dications, respectively. Their AM1-calculated  $\Delta\Delta H_f^\circ$  values are between 421 and 427 kcal/mol and 444 and 449 kcal/mol, respectively, well within the previously predicted dication formation limit of  $463 \pm 4$  kcal/mol.

## Introduction

Numerous examples of  $\pi$ -conjugated dianions of alternant and nonalternant polycyclic, heterocyclic, and bridged annulenes are known. Contributions by several groups, notably those of Rabinovitz,<sup>1–7</sup> Müllen,<sup>8–10</sup> and Olah,<sup>11</sup> laid a strong foundation for understanding their NMR features in relation to topology, charge delocalization, tropicity, and ion pairing.

In comparison, the field of stable dication chemistry of alternant and nonalternant PAHs and bridged annulenes is relatively less extensive. Following initial feasibility studies using early, low-field <sup>1</sup>H NMR by Brouwer,<sup>12</sup> many of the subsequent investigations were reported by Olah and associates.<sup>13–17</sup> More recent examples were provided by Michl,<sup>18</sup> Laali,<sup>19–22</sup> Müllen,<sup>8,9</sup> and their associates; the topic has been reviewed.<sup>23</sup>

Because of the well-established relationship between <sup>13</sup>C NMR chemical shift and charge in structurally analogous ions, it became the primary tool for probing dications.<sup>1,2,24</sup> However, in many instances, only partial assignments were made. Moreover, except for anthracenium dications, whose alkyl (aryl) and chloro derivatives were reported,<sup>14</sup> and some polyalkylated naphthalenes<sup>16</sup> and biphenylenes,<sup>22,11</sup> the majority of the reported examples are those of the parent hydrocarbons. Therefore, substituent effects on charge delocalization and on tropicity in dications remained to be explored. Proton NMR data, which may allow an evaluation of ring current effects, were considerably less emphasized for dications.

Dications are theoretically interesting for comparison with solution NMR, since counterion effects are expected to be greatly reduced in SbF<sub>5</sub>/SO<sub>2</sub>ClF medium as compared to metal/THF for dianions and polyanions that are contact ion pairs.<sup>4–6,11</sup>

Benzo[a]pyrene (BaP) (**1**), 7-MeBaP (**2**), and 6-FBaP (**3**) are carcinogenic, with **2** and **3** being less active, but 6-ClBaP (**4**) (and 6-BrBaP) are very weakly active.<sup>25–28</sup> Because of the significance of the radical cation (RC) pathway in metabolic activation, the reactions of chemically generated RCs derived from the 6-halo and 6-methyl derivatives of **1** have been studied with model nucleo-

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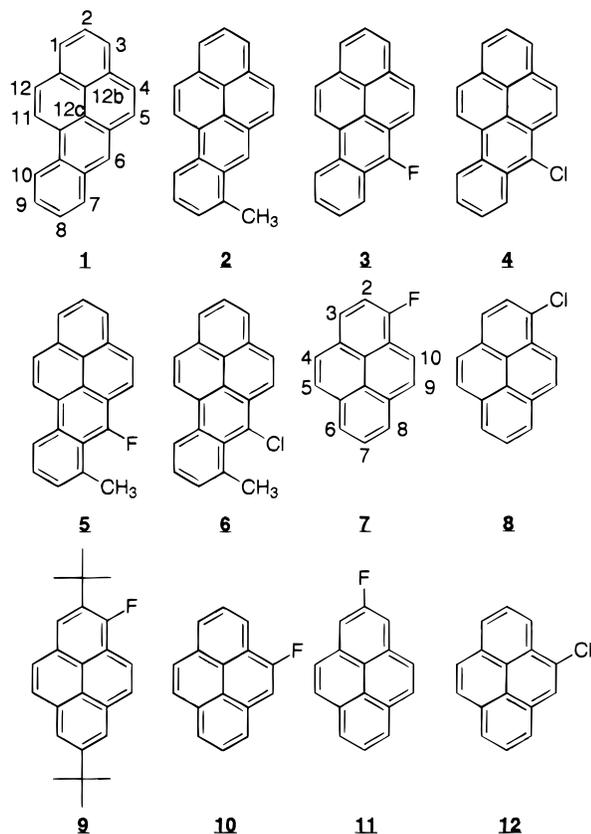
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**Figure 1.** Substrates.

philes (i.e., OAC<sup>-</sup>).<sup>27–29</sup> With **3** and **2**, there is a strong tendency for nucleophilic attack at C-6, whereas with **4** (and with 6-BrB<sub>a</sub>P), attack at C-1/C-3 also occurred (positions of second highest charge localization in the radical cation). With 6-methyl-BaP, benzylic cations were formed and nucleophilic attack occurred on the side chain. Ipso attack leading to defluorination was not observed under electrophilic substitution conditions (with TFAD and PyHBr<sub>3</sub>).<sup>28</sup>

In our previous studies, we reported on dications from a series of alkyl(cycloalkyl)pyrenes<sup>20</sup> and on alkylperylene.<sup>19</sup> In relation to our continuing interest in arenium ions and dications derived from different classes of PAHs and the significance of electrophiles derived from carcinogenic PAHs in adduct formation with DNA bases that could lead to cell damage, we report here the first examples of benzo[*a*]pyrenium dications, **2–6**, and pyrenium dications, **7–9**. Detailed assignments for parent **1** are also included for comparison.

On the basis of <sup>13</sup>C, <sup>19</sup>F, and <sup>1</sup>H NMR data, the charge delocalization mode, total deshieldings, one-bond and long-range C–F coupling constants, and tropicity of the systems have been evaluated. The AM1-calculated  $\Delta\Delta H_f^\circ$  values and carbon charges were also compared.

## Results and Discussion

**Dication Generation,  $\Delta\Delta H_f^\circ$  and Presence of Radical Cation.** Using SbF<sub>5</sub>/SO<sub>2</sub>ClF, two-electron oxidation of **1–6** (Figure 1) took place rapidly at dry-ice/acetone temperature (NMR) without the need to raise the

**Table 1.** AM1- $\Delta\Delta H_f^\circ$  and Total Deshielding  $\Sigma\Delta\delta^{13}\text{C}$  (ppm/e) for the Dications

dication	color	$\Delta\Delta H_f^\circ$	$\Sigma\Delta\delta^{13}\text{C}$ (ppm/e)
<b>1</b> <sup>2+</sup>	blue	412.4	210.7
<b>2</b> <sup>2+</sup>	blue	426.7	210.1
<b>3</b> <sup>2+</sup>	purple	427.2	195.1
<b>4</b> <sup>2+</sup>	green	427.6	207.4
<b>5</b> <sup>2+</sup>	blue	422.2	203.0
<b>6</b> <sup>2+</sup>	green	422.2	199.8
<b>7</b> <sup>2+</sup>	green	448.7	202.9
<b>8</b> <sup>2+</sup>	black	448.0	209.4
<b>9</b> <sup>2+</sup>	red-black	443.9	nd <sup>a</sup>

<sup>a</sup> nd, not determined.

sample temperature. With halopyrenes, dication formation was slower and required warming to  $-30\text{ }^\circ\text{C}$ ; increasing the oxidizing power of the medium by addition of SbCl<sub>5</sub> to bring about these oxidations at lower temperatures was ineffective. Dication generation from **8** and **9** was quite sluggish, requiring prolonged reaction times (several days) for completion. Attempted generation of persistent dications from halopyrenes **10–12** was unsuccessful (black solids were formed).

In agreement with these observations, the AM1-predicted  $\Delta\Delta H_f^\circ$  values (Table 1) for **8** and **9** are ca. 20 kcal/mol higher than those of benzo[*a*]pyrenium dications. The  $\Delta\Delta H_f^\circ$  for **10–12** are still higher (ca 451–458 kcal/mol range), close to the predicted set limit ( $463 \pm 4$  kcal/mol) for dication formation.<sup>30a</sup>

Monitoring the process of two-electron oxidation with <sup>1</sup>H NMR in the case of **11** showed broad aromatic resonances, which did not sharpen, even after 3 weeks. Solutions of **7** and **11** exhibited unresolved ESR signals, even after 2 months of storage at dry-ice/acetone temperature (**7**:  $g = 2.002$ ,  $\Delta H_{pp} = 7.4$  G at  $-57\text{ }^\circ\text{C}$ . **11**:  $g = 2.001$ ;  $\Delta H_{pp} = 13.6$  G at  $-60\text{ }^\circ\text{C}$ ), consistent with the concomitant presence of their radical cations (RC). Attempts to remove the RC by the introduction of oxygen or air into the sample were unsuccessful. A broad and shielded <sup>19</sup>F resonance was observed in the dication spectra for all of the fluorinated PAHs.

For **7**, the initial <sup>1</sup>H NMR spectrum (recorded after 1 h) indicated the presence of two very similar species in a ca. 1:1 ratio; their chemical shifts can tentatively be assigned as follows: H-1, 6.2; H-3, 9.0; H-4, 7.8; H-5, 7.8; H-6, 9.3; H-7, 7.3; H-8, 8.9; H-9, 8.4; H-10, 8.2 ppm. There is a clear four-bond H/F coupling in both species. In relation to a previous study by Cornelisse et al.<sup>30b</sup> on the alkylation of pyrene using AlCl<sub>3</sub> in CS<sub>2</sub> solvent, where the formation of the phenalenium cation/allyl anion–AlCl<sub>3</sub> complex was suggested to explain the regioselectivity of alkylation, the initial spectrum via **7**/SbF<sub>5</sub>/SO<sub>2</sub>ClF may stem from two regioisomeric SbF<sub>5</sub> complexes (syn and anti to F); these disappear with time and are replaced by resonances for the dication.

Quenching of the dication solutions in all cases returned the skeletally intact PAH together with black unidentified oily byproducts, which were produced more extensively for the halobenz[*a*]pyrenes than for the pyrenes, especially in the case of **4**.

**NMR Assignments.** For the precursors, the <sup>13</sup>C NMR spectra of the proton-carrying carbons were assigned with HETCOR experiments and those of quaternary carbons

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were assigned by analyzing the C–F containing compounds and the others by analogy. The  $^{13}\text{C}$  NMR data for **7** and the  $^1\text{H}$  and  $^{13}\text{C}$  data for parent **1** had already been assigned;<sup>31a,b</sup> **3** was assigned by analogy. For the remaining compounds, the assignments were based on C/F coupling constants and comparisons of the chemical shifts with unsubstituted compounds.<sup>32</sup> For **5**, the assignments are tentative due to low solubility and the resulting low S/N ratio in the  $^{13}\text{C}$  spectra.

For the dications, the proton-carrying resonances were assigned by HETCOR experiments. For the quaternary carbons of  $7^{2+}$ ,  $9^{2+}$ ,  $3^{2+}$ , and  $5^{2+}$ , the assignments were based on C/F couplings and by analogy with the remaining dications.

The  $^1\text{H}$  NMR assignments for the dications and the precursors were based on the chemical shifts, H/H and H/F coupling constant, multiplicities, and H/H COSY and C/H HETCOR correlations.

For the methylated benzo[a]pyrene dications **2**, **5**, and **6**, NOED spectra assisted with the assignments of ortho and peri ring protons. Likewise, NOED spectra assisted in the assignment of H-3 for both the dication and the precursor.

**Charge Delocalization Mode.** Detailed  $^{13}\text{C}$  chemical shift assignments, the  $\Delta\delta$  values, and the one-bond and long-range C/F couplings (for fluorinated dications) are gathered in Figure 2 and Figure 3 for the benzo[a]pyrenium and pyrenium dications, respectively. In the benzo[a]pyrenium dications, the charge is extensively delocalized throughout the periphery including the annulated ring, with C-6, C-1/C-3, and C-9 carrying the highest positive charge density, whereas C-12b and C-12c remain relatively unchanged. There is a pronounced methyl substituent effect in comparing  $2^{2+}$  with  $1^{2+}$ .

The fluoronium ion character in the fluorinated benzo[a]pyrene dications is evident from significant  $\Delta\delta^{19}\text{F}$  values (given in Figure 3; for additional discussion see later sections) and enhanced one-bond C/F couplings. Back-bonding can also be inferred by a much larger  $\Delta\delta^{13}\text{C}$  for  $3^{2+}$  compared to  $4^{2+}$  (39.3 vs 68.9 ppm) and  $5^{2+}$  compared to  $6^{2+}$  (35.6 vs 57.0 ppm). The fluoronium ion character is also reflected in the decreased total carbon deshielding for  $3^{2+}$  and  $5^{2+}$  as compared to that for  $1^{2+}$ ,  $2^{2+}$ , and  $4^{2+}$  (see Table 1).

For the pyrenium dications, in line with previous examples,<sup>20</sup> the charge is extensively delocalized throughout the entire periphery, with those of C-1/C-3 and C-6/C-8 being most positive. Fluoronium ion character is similarly reflected in  $\Delta\delta^{19}\text{F}$  and a lower  $\Sigma\Delta\delta^{13}\text{C}$  for  $7^{2+}$  versus  $8^{2+}$ .

Using the data for **3**, **4**, and **6**, a plot of  $\Delta\delta^{13}\text{C}$  values versus the AM1-calculated Mulliken carbon charges  $\Delta q_c$  [ $q_c(\text{dication}) - q_c(\text{PAH})$ ] gave a good correlation for carbons with  $\Delta q_c > 0.1$ .<sup>33</sup>

**Analysis of the C/F Couplings.** Whereas the carbon–fluorine couplings for the PAHs **3**, **5**, and **9** are similar to those of other F–PAHs, very large  $^1J(\text{C},\text{F})$  and  $^3J(\text{C},\text{F})$  values can be seen in their dications. Large one-bond

and three-bond C/F couplings have previously been observed in fluorobenzenium,<sup>34</sup> fluoronaphthalenium cations,<sup>34</sup> and in fluoroallyl cations.<sup>35,36</sup> The absence of C/F couplings at the C-7 for **5** and  $5^{2+}$  is unexpected, as  $^3J(\text{C},\text{F})$  values greater than 3 Hz are seen at the C-8 of 1-fluoro-8-methylnaphthalene.<sup>37</sup>

For **5** and **9**, relatively large fluorine couplings are observed at Me and tBu(Me) both in the carbon and in the proton spectra. Similar couplings have been observed in 1-fluoro-8-methylnaphthalene<sup>37</sup> and 8-fluoro-*N*-methylquinoline.<sup>38</sup>

**$^2J(\text{C},\text{F})$ .** The two-bond couplings in noncharged molecules are thought to roughly depend on bond order<sup>20,39</sup> or bond length. This is confirmed in the present study.

For the charged species, much less information is available, but  $^2J(\text{C},\text{F})$  is seen to decrease as compared to the uncharged compound, especially in cases where  $^3J(\text{C},\text{F})$  increases in the charged species (see below).

**$^3J(\text{C},\text{F})$ .** Three different types of three-bond carbon–fluorine couplings can be observed as exemplified in the following cases: for **7**,  $^3J(\text{C}-3,\text{F})$  and  $^3J(\text{C}-10\text{b},\text{F})$  both with bonds in an anti relationship but with widely different bond orders and  $^3J(\text{C}-10,\text{F})$  with a syn relationship and a short distance between C-10 and the fluorine and for **9**, the presence of  $^3J(\text{tBu}/\text{C})-\text{F}$ .

The marked increase in  $^3J(\text{C},\text{F})_{\text{anti}}$  in the dications can be related to the positive charge on fluorine as discussed in fluoroallylic ions.<sup>35,36</sup> An increase in  $^3J(\text{C}-3,\text{F})$  for protonated 1-fluoronaphthalene and fluorobenzenes was found by Olah et al.<sup>34</sup> An increase in  $^3J(\text{C}-3\text{a},\text{F})$  of the 2-fluoropyrenium cation has also been reported.<sup>40</sup> Olah et al.<sup>34</sup> correlated  $^3J(\text{C},\text{F})$  of para substituted fluorobenzenes with  $\delta\text{F}$ , but as  $^1J(\text{C},\text{F})$  also correlates with  $\delta\text{F}$ , a correlation between  $^1J(\text{C},\text{F})$  and  $^3J(\text{C},\text{F})$  can also be expected. In Figure 4, we have plotted the observed three-bond C/F (anti) couplings versus  $^1J(\text{C},\text{F})$  for a series of fluoroarenium cations and oxidation dications. The graph defines the maximal values.  $^3J(\text{C},\text{F})_{\text{anti}}$  depends on  $^1J(\text{C},\text{F})$  but possibly also on the bond order as seen by comparing different coupling paths within the same molecule. For  $7^{2+}$ , three-bond couplings of 32.7 and 15.1 Hz are observed. The larger coupling clearly relates to the higher bond order of the C-3–F bond.

Semiempirical calculations<sup>41</sup> on  $^1J(\text{C},\text{F})$  showed that this type of coupling is largely dominated by the Fermi contact term for neutral PAHs and the variations are relatively small, whereas for the charged species with large one-bond couplings, these in addition have a large orbital term. A similar trend is seen for  $^3J(\text{C},\text{F})$ . The  $^3J(\text{C},\text{F})_{\text{syn}}$  couplings have been observed in a series of fluorinated polycyclic aromatics with the result that  $^3J(\text{C}-4,\text{F})$  of 1-fluoronaphthalene and couplings in pyrenes, phenanthrenes,<sup>31a</sup> and benz[a]pyrenes<sup>39</sup> were of the order

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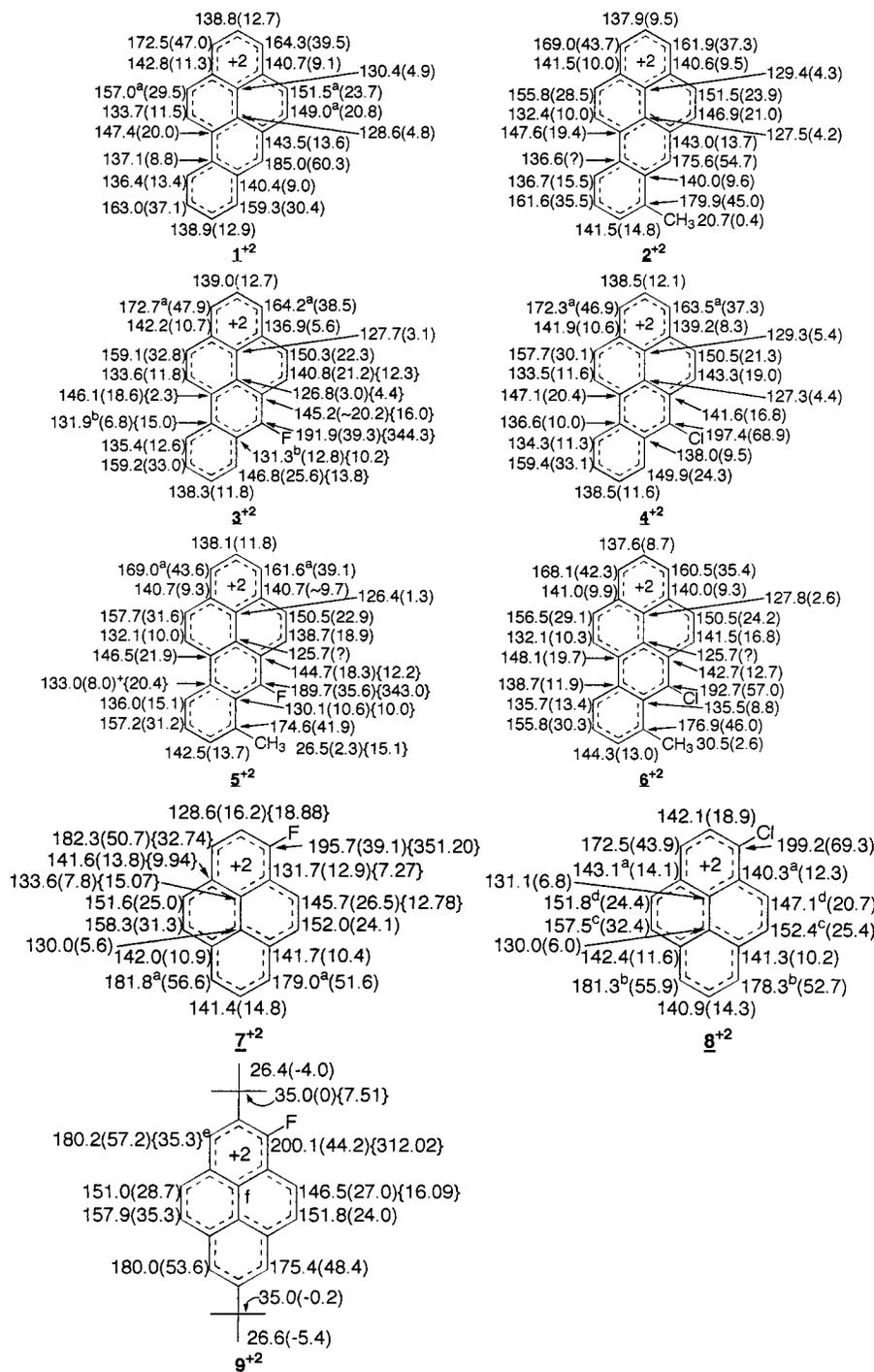
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C-F couplings for the parent compound s:

**3**:  $^1\text{J}(\text{C}, \text{F}) = \text{n.o.}$  (appearance of doublet is uncertain.);  $^3\text{J}(\text{C}-5, \text{F}) = 5.1\text{Hz}$ ;  $^4\text{J}(\text{C}-4, \text{F}) = 2.7\text{Hz}$ ;  $^3\text{J}(\text{C}-7, \text{F}) = 6.1\text{Hz}$ .

**5**:  $^1\text{J}(\text{C}, \text{F}) = 259.2\text{Hz}$ ;  $^3\text{J}(\text{C}-5, \text{F}) = 7.7\text{Hz}$ ;  $^4\text{J}(\text{C}-4, \text{F}) = 3.2\text{Hz}$ ;  $^2\text{J}(\text{C}-6\text{a}, \text{F}) = 15.2\text{Hz}$ ;  $^4\text{J}(\text{CH}_3, \text{F}) = 14.5\text{Hz}$ ;  $^4\text{J}(\text{C}-10, \text{F}) = 2.9\text{Hz}$ .

**7**: see Ref. 31a

**9**:  $^1\text{J}(\text{C}, \text{F}) = 254.1\text{Hz}$ ;  $^2\text{J}(\text{C}-10\text{a}, \text{F}) = 16.5\text{Hz}$ ;  $^3\text{J}(\text{C}-10, \text{F}) = 7.1\text{Hz}$ ;  $^4\text{J}(\text{C}-9, \text{F}) = 2.7\text{Hz}$ ;  $^6\text{J}(\text{C}-8, \text{F}) = 2.7\text{Hz}$ ;  $^6\text{J}(\text{C}-6, \text{F}) = 2.8\text{Hz}$ ;  $^9\text{J}(\text{C}-5, \text{F}) = 3.4\text{Hz}$ ;  $^5\text{J}(\text{C}-4, \text{F}) = 2.1\text{Hz}$ ;  $^4\text{J}(\text{C}-3\text{a}, \text{F}) = 3.1\text{Hz}$ ;  $^3\text{J}(\text{C}-3, \text{F}) = 6.3\text{Hz}$ ;  $^2\text{J}(\text{C}-2, \text{F}) = 12.7\text{Hz}$ ;  $^3\text{J}(\text{C}, \text{F}) = 2.2\text{Hz}$ ;  $^4\text{J}(\text{CH}_3, \text{F}) = 3.6\text{Hz}$ .

a-d; interchangeable pairs

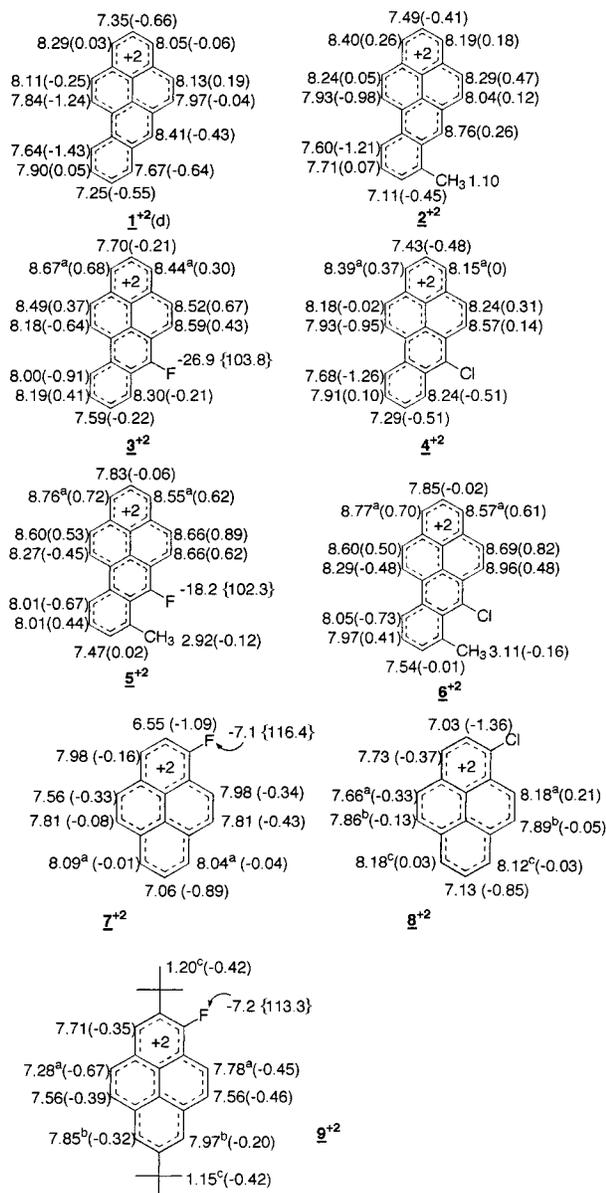
e; tentative because of overlap

f; quaternary carbons not assigned in dication

?; resonance not observed in precursor

+; assignment in parent tentative

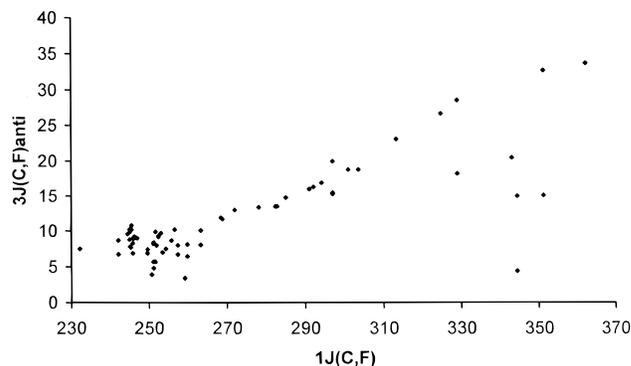
**Figure 2.**  $^{13}\text{C}$  NMR chemical shifts data ( $\Delta\delta^{13}\text{C}$ )  $\{\text{J}_{\text{C-F}}\}$  for the dications.



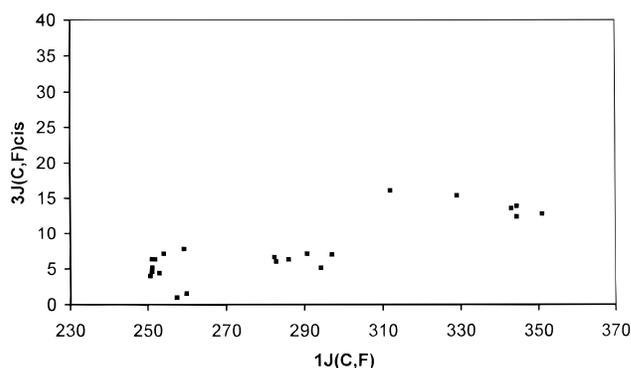
H-F couplings:  
**9**:  $^5J(\text{F}, \text{CH}_3)=0.9\text{ Hz}$ ;  $^4J(\text{F}, \text{H-3})=7.5\text{ Hz}$   
**9<sup>2+</sup>**:  $^5J(\text{F}, \text{CH}_3)=\text{n.o.}$ ;  $^4J(\text{F}, \text{H-3})=4.2\text{ Hz}$   
**5**:  $^5J(\text{F}, \text{CH}_3)=8.8\text{ Hz}$   
**5<sup>2+</sup>**:  $^5J(\text{F}, \text{CH}_3)=9.8\text{ Hz}$   
 a,b,c: interchangeable pairs  
 d: <sup>1</sup>H data taken from ref. 31b

**Figure 3.** <sup>1</sup>H NMR chemical shifts data ( $\Delta\delta^1\text{H}$ ) [ $\Delta\delta^{19\text{F}}$ ] for the dications.

of 4.6–6.3 Hz, with one exception, that of **5** in this study, showing a coupling of 7.7 Hz. In contrast to these couplings, very small values were seen for  $^3J(\text{C}-5,\text{F})$  in 4-fluoroacenaphthenes and acenaphthylenes and a  $^3J(\text{C}-4,\text{F})$  in 3-fluorofluoranthene. The small couplings in the latter three compounds were ascribed to a small through space (TS) contribution due to a large distance (large C–C–C angle).<sup>31a</sup> Larger  $^3J(\text{C},\text{F})$  values in **5** can possibly be related to steric strain imposed by the peri methyl group. A similar situation is seen in **9**, where the buttressing effect of ortho tBu group forces the C–F bond toward the C-10–H bond, leading to better orbital overlap.



**Figure 4.** Plot of  $^3J(\text{C},\text{F})$  anti versus  $^1J(\text{C},\text{F})$  (coupling constants are from the present study and from refs 31a, 38–40, and 52).



**Figure 5.** Plot of  $^3J(\text{C},\text{F})$  syn versus  $^1J(\text{C},\text{F})$  (coupling constants are from the present study and from refs 31a, 34, 39, 40, and 52).

The  $^3J(\text{C},\text{F})_{\text{syn}}$  couplings are unusually large for  $^3J(\text{C}-5,\text{F})$  for the dications **3<sup>2+</sup>** and **5<sup>2+</sup>** and for 1-fluoronaphthalenium ion.<sup>34</sup> For a number of neutral fluoro-PAHs, the  $^1J(\text{C},\text{F})$  value is close to 251 Hz. The variation in their  $^3J(\text{C},\text{F})_{\text{syn}}$  (Figure 5) can, as mentioned above, be in part due to a TS contribution. The very large values obtained for the dications cannot be ascribed to an increase in the TS contribution, as the F...H distance is at best the same as that in the neutral compounds. Furthermore, the positive charge at fluorine should lead to reduced C/F coupling as shown by Hsee and Sardella<sup>42</sup> who found that presence of an electron-withdrawing substituent para to fluorine (more positive charge at fluorine) had the effect of reducing the TS contribution. For the dications, the likely cause of the increase can best be ascribed to a larger bond order as also suggested for neutral molecules.<sup>39</sup> For charged species, a reasonable correlation between  $^1J(\text{C},\text{F})$  and  $^3J(\text{C},\text{F})_{\text{cis}}$  is seen (Figure 4).

The  $J(\text{CH}_3,\text{F})$  coupling in **9** is formally a coupling over four bonds, but this coupling most likely has a large TS contribution. In a similar manner, a coupling is observed in **5** and **5<sup>2+</sup>** whose magnitude is actually similar in the dication and the neutral PAH.

**Tropicity in the Dications.** The <sup>1</sup>H NMR chemical shifts and  $\Delta\delta^1\text{H}$  values for the benzo[a]pyrenium and pyrenium dications are gathered in Figure 3, which also contains the <sup>19</sup>F NMR data for the fluorinated dications **3**, **5**, **7**, **9**. The concomitant presence of the RC did not

(42) Hsee, L. C.; Sardella, D. J. *Magn. Reson. Chem.* **1990**, *28*, 688.

interfere with the assignments of the  $^1\text{H}$  NMR spectra of the dications, which usually contained additional broad features. Whereas the  $^1\text{H}$  spectra of the benzo[a]pyrenes are rather similar, those of the dications vary considerably. A common feature in the benzo[a]pyrenium dication is a significant shielding of the bay-region protons (H-10/H-11) by about 1 ppm. With the pyrenium dications **7–9**, a more or less general proton shielding trend is apparent.

The parent benzo[a]pyrenium dication is an  $18\pi$  system with a  $16\pi$  periphery and would sustain a paramagnetic ring current, which opposes the deshielding effect due to charge; it is hence paratropic. Among the studied benzo[a]pyrenium dications, several hydrogens (H-2, H-7, H-8, H-10, and H-11) are consistently shifted upfield; others are mainly deshielded. The latter are mostly attached to carbons with large  $\Delta\delta^{13}\text{C}$  values.

It has been shown that the HOMO–LUMO gap and tropicity correlate.<sup>1–3</sup> In dianions, smaller paratropic shifts are associated with larger HOMO–LUMO gaps. In the present study, the total  $\Delta\delta^1\text{H}$  values (difference in the center of gravities between the dication and the neutral PAH) in the parent **1**<sup>2+</sup> amounts to  $-4.73$  ppm. The substituted dications exhibit a pronounced substituent dependency, with paratropicity decreasing in the order **1**<sup>2+</sup> ( $-4.73$  ppm) > **4**<sup>2+</sup> ( $-2.79$  ppm) > **2**<sup>2+</sup> ( $-1.64$  ppm) > **3**<sup>2+</sup> ( $0.85$  ppm) > **6**<sup>2+</sup> ( $2.31$  ppm) > **5**<sup>2+</sup> ( $2.65$  ppm), while the AM1-predicted HOMO–LUMO gaps remain very close, for example, **1**<sup>2+</sup> ( $5.77$  eV), **2**<sup>2+</sup> ( $5.65$  eV), and **5**<sup>2+</sup> ( $5.67$  eV). Whereas a paratropic  $\rightarrow$  diatropic switch for **6**<sup>2+</sup> and **3**<sup>2+</sup> may well have a steric origin, the difference between **1**<sup>2+</sup> and **3**<sup>2+</sup> is not clear-cut. It is unlikely that variations in the total  $\Delta\delta^1\text{H}$ s are due to the presence of the RC, as the resonances for the dications remain sharp. Moreover, since chemical shift changes due to radicals result from contact, charge repulsion between the dication and the RC should minimize such interactions.

As shown previously,<sup>10,20</sup> a pyrenium dication having a  $12\pi$  perimeter sustains a paramagnetic ring current, which compensates the deshielding due to charge to the extent that the center of gravity remains more or less unchanged, with only H- $\beta$  shifted upfield. For the substituted derivatives, considerable variation in the  $\Delta\delta^1\text{H}$  values was detected within the series pyrene, 4-isopropylpyrene, 2,7-di-*tert*-butylpyrene, and 1,3,6,8-tetrasubstituted- and 1,3,5,7,9-penta-isopropylpyrene.<sup>20</sup> The present  $^1\text{H}$  NMR data on dications **7–9** provide additional substituent effect information in 1-substituted and 1,2,7-trisubstituted dications. The 1-substituted derivatives exhibit small and similar effects at the H- $\alpha$  protons, very large and negative effects at H- $\beta$  and medium negative effects for H- $\alpha\beta$ . The pattern is similar to that seen in the 4-isopropylpyrenium dication.<sup>20</sup> The pattern for **9**<sup>2+</sup> is analogous to that of 4-isopropylpyrene and quite different from that for the 2,7-di-*tert*-butylpyrenium dication.

In summary, we have provided a detailed comparative NMR analysis for the first series of persistent fluorinated and chlorinated benzo[a]pyrene dications and pyrenium dications. For parent **1**, the similarity in the positions of highest spin density localization in the radical cation<sup>43,28</sup> and highest charge localization in the dication (C-6, C-1, C-3; followed by C-9, C-7, C-12, C-4, C-5) suggests that dications may be suitable models for NMR studies of large carcinogenic PAHs whose radical cations

can bind to DNA. Radical cations of isomeric monomethyl-BaP have been generated electrochemically, and their stabilities (estimated from rate constants for reaction with water) showed some parallel with animal carcinogenicity data.<sup>44</sup> Although chemically generated RCs of several halo-PAHs have been studied as models for metabolic activation,<sup>28</sup> their radical cations have not been directly examined. The present study provides the first insight into their doubly charged analogues.

## Experimental Section

**PAHs.** High purity samples of parent **1** and its 7-methyl derivative **2** were purchased from Aldrich and used without further purification. The isomeric fluoro-<sup>45</sup> and chloropyrenes<sup>46</sup> were synthesized according to the literature. Synthesis of **3** by  $\text{XeF}_2$  fluorination of **1** has been reported.<sup>47</sup> In the present study, compounds **3**, **5**, and **9** were prepared either by  $\text{XeF}_2$  fluorination, using the literature procedure, or by fluorination with *N*-fluoro-2,4-dinitroimidazole in refluxing dichloroethane, for which the procedures are been reported elsewhere.<sup>48</sup> Synthesis of **4** by chlorination of **1** with sulfuryl chloride has been reported by Cho and Harvey.<sup>49</sup> In the present study, **4** and **6** were prepared accordingly.

Typically, sulfuryl chloride (0.11 mmol) was added to a solution of **1** or **3** (0.1 mmol) with 20 mL of dry dichloroethane in a 50 mL three-necked flask. The reaction mixture was stirred for 1 h at room temperature, after which it was poured into water and extracted with chloroform. After removal of solvent under pressure, the residue was separated by column chromatography using hexane as an eluent. The yields were 88% and 83% respectively.

The PAHs were subjected to a complete NMR analysis ( $^{13}\text{C}$ ,  $^1\text{H}$ ,  $^{19}\text{F}$ , H/H COSY, C/H HETCOR, and NOED experiments). The data are incorporated into the data for the dications gathered in Figures 2 and 3.

**Other Materials.**  $\text{SbF}_5$  (Aldrich or Fluorochem) was distilled twice under a dry argon atmosphere in an all-glass distillation unit.  $\text{SO}_2\text{ClF}$  was prepared by fluorination of  $\text{SO}_2\text{Cl}_2$  with  $\text{NH}_4\text{F}$  and  $\text{CF}_3\text{COOH}$  according to a modified procedure of Prakash et al.<sup>50</sup>

**AM1 Calculations.** Energy minimizations and AM1 calculations were performed with the Hyperchem Package (Hypercube, Inc, 1994).

NMR spectra were recorded on a wide-bore GE-GN300 instrument using a 5 mm C/H switchable probe using very short (ca. 3 cm) external sealed capillary tubes (made from melting point tubes) added to 5 mm NMR tubes containing the dication solution. The reported  $^1\text{H}$

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NMR shifts are corrected for the use of an external capillary as previously described.<sup>51</sup>

**General Procedure for Stable Dication Generation.** SbF<sub>5</sub> (1 mL) was charged into a 10 mm NMR tube under argon. SO<sub>2</sub>ClF (2 mL) was condensed into a 5 mm NMR tube using a high vacuum line and was subsequently poured directly into SbF<sub>5</sub> in the 10 mm tube at dry-ice/acetone temperature. Upon vigorous mixing (vortex) and slight periodic warming, a clear homogeneous solution resulted. A slurry of the PAH substrate (30 mg) in SO<sub>2</sub>ClF (0.3 mL) was prepared in another 5 mm NMR tube at dry-ice/acetone temperature to which the solution of SbF<sub>5</sub>/SO<sub>2</sub>ClF was subsequently added under argon

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with vigorous mixing (the resulting colors are included in Table 1).

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**Supporting Information Available:** Selected 1D and 2D NMR spectra for the dications (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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