

Persistent Oxidation Dications from Twisted Fluoranthenes, Benzo[*k*]fluoranthene and Dimethyldibenzo[*j,l*]fluoranthene: Charge Delocalization Mode, Tropicity, and Formation of Novel 8,8'-Bifluoranthenyls. An NMR and Theoretical Study

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Received June 7, 2001

First examples of persistent oxidation dications from fluoranthene-PAHs namely 1,3,4,6,7,10-hexamethyl- **2** and 3,4-dichloro-1,6,7,10-tetramethylfluoranthene **3**, benzo[*k*]fluoranthene **6**, and 3,6-dimethyldibenzo[*j,l*]fluoranthene **9** are reported. Charge delocalization mode and tropicity in the resulting *nonalternant* dications are examined. Quenching of the superacid solutions of the dications resulted in the formation of novel 8,8'-bifluoranthenyls **2a–4a**. AM1 was used as an initial guide for dication generation ($\Delta\Delta H_f^\circ$ and ionization potentials) and for probing the structures of the crowded fluoranthene substrates and their bifluoranthenyls. In selected cases, the dications and their neutral precursors were calculated at the B3LYP/6-31G(d,p) level. Charge delocalization mode (difference in NPA charges) and DFT/GIAO-derived NMR chemical shifts were obtained for comparison with experiment; aromaticity was assessed via nucleus independent chemical shift (NICS) calculations.

Introduction

The available literature on generation and NMR studies of persistent oxidation dications of fused polycyclic arenes is to a large extent based on *alternant* systems.^{1–6} In comparison, examples of *nonalternant* polyarene dications are relatively limited.^{7,9} Meaningful comparisons of structural features, substituent effects, charge delocalization modes, and tropicity between the two categories necessitate a continuing search for suitable non-

alternant polyarene precursors for dication generation and solution NMR studies.

Because of their environmental prevalence and mutagenic and carcinogenic activities, the electrophilic and oxidative chemistry of fluoranthene-PAHs is a topic of continuing recent interest.^{10–14} To our knowledge, no persistent oxidation dications are known from this class of *nonalternant* PAHs which are derivatives of parent fluoranthene **1** ring system (Figure 1).

Twisted fluoranthenes **2–4** were previously exploited in the synthesis of corannulene via reductive coupling of their bromomethyl derivatives.^{15,16} Severe steric crowding imposed by the substituents around the indeno moiety in **2–4** causes the fluoranthene core to become twisted. The X-ray crystal structure of 1,6,7,10-tetramethylfluoranthene shows a helical twist in the aromatic ribbon.^{15a}

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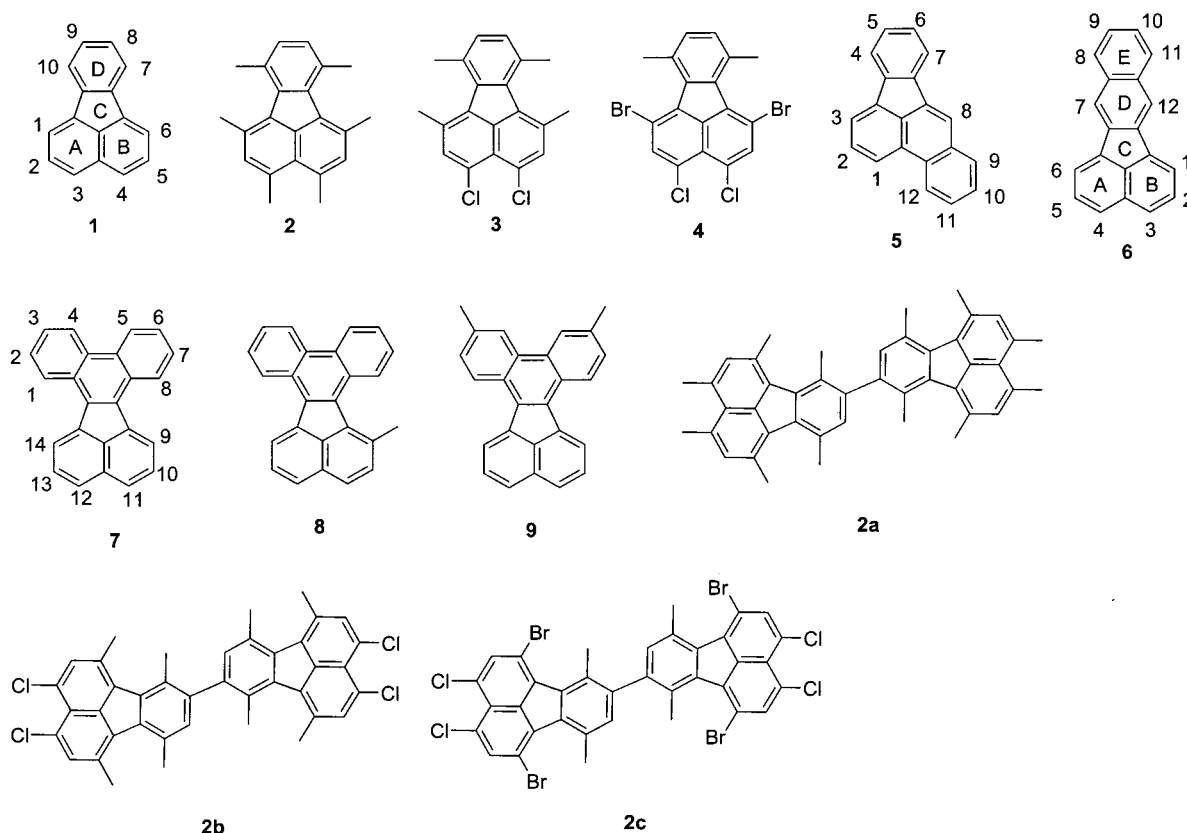


Figure 1. Fluoranthene, benzo[fluoranthene], and dibenzo[fluoranthene] substrates, and 8,8'-bifluoranthenyls.

In relation to our previous studies of PAH oxidation dications,^{1–5} we report here the first examples of stable dications derived from **2** and **3**, and from the benzannulated derivatives of **1**, namely benzo[*k*]fluoranthene **6** and 3,6-dimethyldibenzo[*j,l*]fluoranthene **9** (Figure 1). Charge delocalization modes, structural features, and tropicity in the resulting dications are examined. We also report on facile formation of novel 8,8'-bifluoranthenyls **2a–4a** from **2–4** by quenching of their superacidic solutions.

For comparison, dications **1**²⁺, **2**²⁺, and **6**²⁺ and their neutral precursors were calculated at the B3LYP/6-31G(d,p) level. Their ¹³C and ¹H NMR chemical shifts were computed by the GIAO method, charge delocalization paths were deduced via differences in the NPA charges (dication minus neutral), and aromaticity in the dications was gauged via NICS calculations.

Results and Discussion

NMR Assignments (Figure 2). Detailed NMR assignments for the precursors (**2–4**; **6–9**), dications (**2**²⁺, **3**²⁺, **6**²⁺, **9**²⁺) and the dimeric products (**2a–4a**) were based on ¹H, ¹³C, H/H COSY, HMQC, HMBC, and NOED spectra.

NMR Features in the Neutrals. Specific assignments for hydrocarbons **1** and **5** were made recently in a protonation study.¹⁷ Only partial NMR data exist in the literature for fluoranthenes **2–4** and for the dibenzo[fluoranthenes **7–9**, and no specific assignments had been made.^{15,19} Complete NMR assignments for these compounds are given in this work (Figure 2).

The H-2/H-5 singlet is sequentially deshielded in going from **2** to **4** (δ 7.12; δ 7.41, δ 7.85) due to proximity to halogens and steric crowding in the ortho positions. These changes are also evident in the methyl groups at C-7/C-10 which are most deshielded in **4**. In **3**, NOE effects are observed between the methyl groups and their corresponding ortho ring protons. In benzo[*k*]fluoranthene **6**, NOE effects were observed between H-12/H-11 and H-1/H-12. The H-7/H-12 singlet is quite distinct and most deshielded (δ 8.31). In dibenzo[*j,l*]fluoranthenes the H-1/H-8 and H-4/H-5 protons are most deshielded. Introduction of a methyl at C-9 imposes a shielding effect on H-8 (from δ 8.90 to δ 8.60), suggesting increased compression and reorientation. NOE effects are observed between the “fjord-region” protons, e.g., H-8/H-9 (in **7** and **9**), and H-1/H-14 (in **8**). NOE effects were observed between the methyl and H-1 (in **8**) and between methyl groups and their ortho protons (in **9**).

AM1 Calculations as Guideline for Dication Generation. Previous AM1 calculations predicted an upper limit of $\Delta\Delta H_f^\circ = 463 \pm 4$ kcal/mol and the ionization potentials (IP's) = 8.3 eV as favorable indicators for dication formation from benzenoid hydrocarbons.¹⁸ A series of nonbenzenoid compounds were also computed including cyclooctatetraenes, bridged annulenes, and barrelenes.¹⁸ Comparable data for fluoranthene-PAHs are unavailable.

The $\Delta\Delta H_f^\circ$ for **1** calculated by AM1 method is 468.4 kcal/mol, and its first IP is about 8.6 eV (Table 1). AM1 calculations imply that dication generation from overcrowded, twisted, fluoranthenes **2–4** should be more

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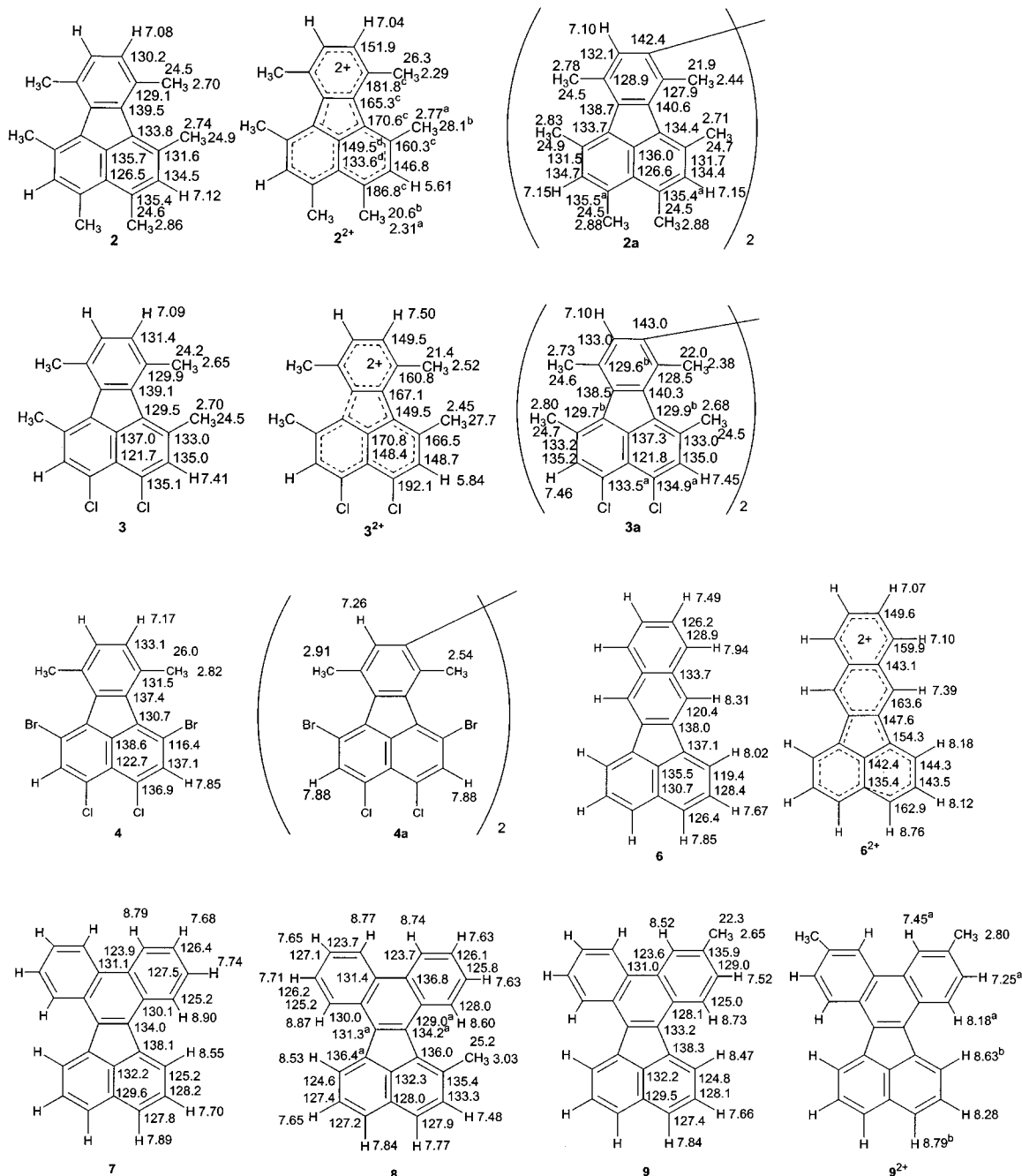


Figure 2. Summary of ^1H and ^{13}C NMR data for the fluoranthene-PAHs and the dications; a, b, c, d (superscripts) denote interchangeable assignments for a pair or a group of resonances (for 2^{2+} assignments for the quaternary carbons as given agree most closely with the calculated values).

favorable. Indeed, presence of methyl substituents and a twisted framework lead to a dramatic decrease in calculated $\Delta\Delta H_f^\circ$ for 2^{2+} generation (the IP is also lowered). Introduction of halogens (**3** and **4**) raises the $\Delta\Delta H_f^\circ$ as compared to **2** (and the IP's), but still imply reasonable prospects for dication formation.

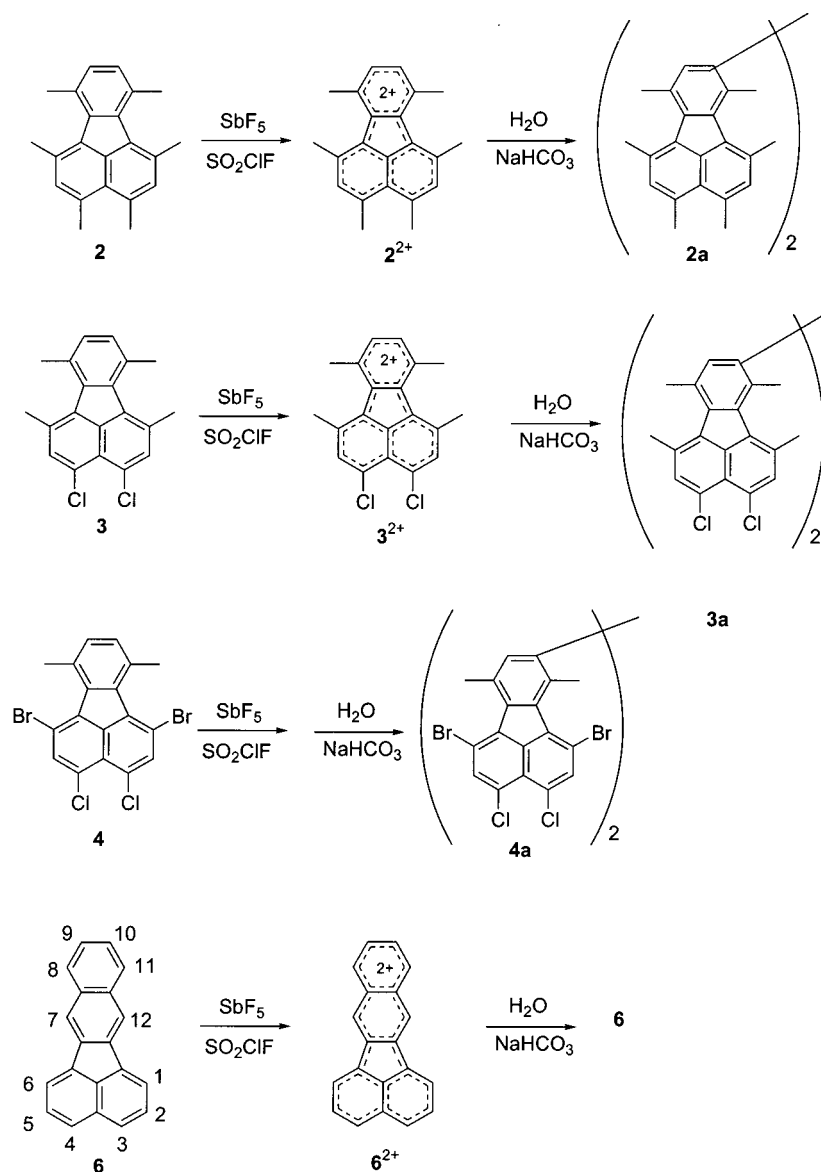
In neutral **2**, the twisted conformation is 1.2 kcal/mol lower in energy than the folded form (AM1). This difference increases in the dication (1.8 kcal/mol). Preference for a twisted dication becomes more pronounced with increasing steric crowding around the indeno moiety in going from **3** to **4** (Table 1).

As seen for benzo[*b*]fluoranthene **5** and benzo[*k*]fluoranthene **6**, the mode of benzannulation has a pro-

Table 1. Summary of AM1 Calculations

dication	$\Delta\Delta H_f^\circ$, kcal/mol	$\Delta\Delta H_f^\circ$, kcal/mol	first IP, ^a eV
1 ²⁺	468.4	---	8.6
2 ²⁺	435.2	1.22 (neutral) 1.8 (dication)	8.1
3 ²⁺	447.4	1.23 (neutral) 1.8 (dication)	8.4
4 ²⁺	459.0	1.56 (neutral) 2.6 (dication)	8.7
5 ²⁺	454.5	---	8.5
6 ²⁺	445.8	---	8.2
7 ²⁺	429.4	---	8.2
8 ²⁺	424.4	---	8.1
9 ²⁺	419.7	---	8.1

^a First ionization potential or the neutral.

Scheme 1. Formation of Oxidation Dications and 8,8'-Bifluoranthenyls

nounced influence on the computed $\Delta\Delta H_f^\circ$ values; whereas both substrates appear to meet the $\Delta\Delta H_f^\circ$ criterion, 6^{2+} formation is computed to be about 9 kcal/mol more favorable relative to 5^{2+} . Finally, AM1 calculations predicted that dibenzo[*j*,*l*]fluoranthenes 7–9 might also be suitable candidates for dication formation (see Table 1).

Stable Ion Studies on Fluoranthene-PAHs (Scheme 1, Figure 2, and Supporting Information).
Oxidation of 1 and 5. Initial studies focused on these substrates because they were available in larger quantities. Reaction of $\text{SbF}_5/\text{SO}_2\text{ClF}$ with **1** gave a dark-blue solution accompanied by a black precipitate. NMR of the liquid portion inferred that a persistent 1^{2+} was not produced. Instead, a complex mixture was obtained showing small, broad, paratropic shifted resonances (radical cation?) and a set of deshielded resonances likely due to dimer cation. Reaction of $\text{SbF}_5/\text{SO}_2\text{ClF}$ with benzo[*b*]fluoranthene **5** gave a dark-blue solution (with precipitate formation), whose proton NMR showed very broad featureless signals indicative of incomplete oxidation, and at best, a radical cation/dication equilibrium.

Oxidation of 2. The hexamethyl derivative **2** was reacted with $\text{SbF}_5/\text{SO}_2\text{ClF}$ (Scheme 1) to give a dark-blue solution, for which the NMR spectral data are consistent with the formation of dication 2^{2+} . The ^1H NMR spectrum (Supporting Information) consists of five singlets (three methyls and two ring protons). An important feature is paratropic shift of the proton resonances (only H-8/H-9 remain relatively unchanged). The center of gravity of the ring protons moves from δ 7.10 in the neutral to δ 5.36 (δ 6.32 after correcting for solvent bulk-effect; see Experimental Section) in the dication. Relative assignments of the ring proton singlets are based on NOE effects with the methyls and were determined based on the following information: irradiation of the δ 5.61 singlet caused NOE enhancement in two methyl resonances, whereas irradiation of δ 5.61 singlet gave NOE enhancement in only one methyl signal.

The paratropic shift for the ring protons in the naphthalene moiety (A/B rings) is significantly higher. In the ^{13}C NMR spectrum (Supporting Information) there are nine aromatic resonances and three methyls. The most deshielded resonances are the methyl-bearing ring car-

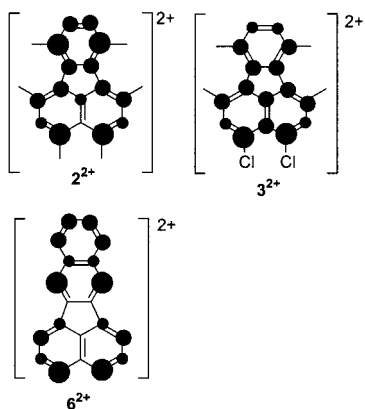


Figure 3. Charge delocalization mode in the dications.

bons (δ 186.8 and δ 181.8). A noteworthy feature is the charge delocalization mode in the dication (Figure 3). Positive charge is delocalized throughout the molecule including the ring junctions; only ring junction carbons in the naphthalene subunit bear less charge. Total deshielding ($\Sigma\Delta\delta^{13}\text{C}$) in 2^{2+} amounts to 481.7 ppm (240.8 ppm per electron charge), consistent with dication formation.^{1–6}

Quenching of the superacid solution gave the 8,8'-bifluorenyl dimer **2a** in ca. 90% yield (NMR). This dimer exhibits five types of methyl protons (in 2:1:1:1:1 ratio) with those at C-7/C-7' positions being most *upfield* (Figure 2). The latter methyl resonance exhibits NOE with the H-9 in the other unit. The observed proton shielding for methyls at C-7/C-7' in **2a** as compared to parent **2** (from δ 2.70 to δ 2.44) is probably a transannular effect, since in the AM1-minimized structure (Fig S1) these methyls appear suitably positioned to experience transannular shielding by the ring current effect. A noticeable feature in the ^{13}C NMR is deshielding of C-8/C-8' carbons in **2a** (δ 142.4 as compared to δ 130.2 in **2**). According to AM1 minimization, the dimer has nearly orthogonal twist angle between the fluorene units.²⁰ Electrospray mass spectrum of **2a** exhibited the m/z 571 cation (2aH^+) whose MS/MS gave m/z 285.

Oxidation of 3. Low-temperature reaction of **3** with $\text{SbF}_5/\text{SO}_2\text{ClF}$ gave a dark-blue solution whose NMR spectral data (Figure 2 and Supporting Information) are consistent with the formation of 3^{2+} . The ^1H NMR spectrum consists of two methyls and two ring proton singlets. These were assigned based on NOE effects and in comparison with 2^{2+} . The center of gravity of the ring protons in the dication is at δ 5.71 (δ 6.67 after correction) as compared to δ 7.25 in the precursor. The dication is, therefore, strongly paratropic. This paratropic shift stems primarily from the naphthalene subunit (A/B rings). In the ^{13}C NMR, the most deshielded carbon resonance is due to the chlorine-bearing ring carbons (δ 192.1). Total deshielding in the dication amounts to 231.8 ppm per electron charge. Charge delocalization mode in 3^{2+} is similar to 2^{2+} except that the extent of positive charge localization at ring junction carbons in the naphthalene subunit has greatly increased in 3^{2+} (Figure 3).

Quenching of superacids solution of 3^{2+} produced the corresponding 8,8'-bifluorenyl dimer **3a** in ca. 90%

yield (NMR) with the same regiochemistry (connecting the C-8/C-8' bond). Dimer **3a** exhibits four methyls (1:1:1:1) with the C-7/C-7' methyls being most *upfield* (δ 2.38) (Figure 2). As in the case of **2a**, AM1 minimization for **3a** (Fig S2) supports the notion that this *upfield* shift may stem from a transannular shielding effect, and suggests that the two fluorene units in **3a** are orthogonal.²⁰ The C-8/C-8' carbons are at δ 143.0 (δ 131.4 in the precursor).

Oxidation of 4. The tetrahalogeno derivative **4** could not be oxidized cleanly to a dication. A dark-blue solution resulted the ^1H NMR spectrum which exhibited broad resonances indicative of incomplete oxidation and at best a dication/radical cation equilibrium. Quenching of the superacid solution produced the dimer **4a** (ca. 85% by NMR) together with minor amounts of **4**. The C-7/C-7' methyls in the dimer are at δ 2.54 (the AM1-minimized structure of **4a** is shown in Figure S3).

Oxidation of 6. Benzo[*k*]fluorene **6** gave a dark-blue solution upon reaction with $\text{SbF}_5/\text{SO}_2\text{ClF}$. The NMR spectral data (Supporting Information and Figure 2) are consistent with the formation of dication 6^{2+} . The ring protons appear as six broad singlets in the ^1H NMR (line-broadening masks the H/H couplings). Their relative assignments were secured based on NOE and H/H COSY. The center of gravity in the proton NMR is at δ 6.81 (δ 7.71 after correction), as compared to δ 7.88 for the precursor. On the basis of the magnitude of $\Delta\delta^1\text{H}$ values, paratropic shifts stem from the A/E rings. The carbon resonances appear between 162.9 and 135.5 ppm. Total deshielding in this dication is 216.1 ppm per electron charge. The proton-bearing carbons bear significantly more positive charge as compared to the ring junction positions. Among the former group, C-7/C-12 and C-3/C-4 carbons exhibit the largest $\Delta\delta^{13}\text{C}$ values (43.2 and 36.5 ppm) (Figure 3). Quenching of the dication solution returned the skeletally intact **6** (NMR).

Oxidation of Dibenzo[*h*,*j*]fluoranthenes 7–9. Parent **7** and the 9-methyl derivative **8** could not be transformed into their dications. In both cases, upon reaction with $\text{SbF}_5/\text{SO}_2\text{ClF}$, red-brown solutions were formed accompanied by formation of black precipitates. The NMR spectra of the liquid phase exhibited very broad features indicative of incomplete oxidation and predominant presence of the radical cations. With the 3,6-dimethyl derivative **9** a dication was slowly formed on prolonged contact, but it was not possible to convert the radical cation to dication in sufficient yields to obtain nicely resolved NMR spectra (the proton resonances were broadened, and the carbons signals were nearly wiped-out). The center of gravity in the ^1H NMR is at δ 7.13 (δ 8.09 corrected) as compared to δ 8.12 for the neutral. Taking the $\Delta\delta^1\text{H}$ values as a measure of tropicity, paratropic shifts stem primarily from the phenanthrene subunit.

Theoretical Study Using the DFT, GIAO-DFT and NICS Methods. To obtain more insight into the structures, charge delocalization mode, and aromaticity, neutral compounds **1**, **2**, and **6** and their dications were calculated at the B3LYP/6-31G(d,p) level. Parent fluorene **1** and its dication 1^{2+} were included for comparative purposes, even though 1^{2+} could not be directly observed by NMR.

Parent **1** has C_{2v} point group. Upon oxidation this symmetry becomes a first-order saddle-point. The imaginary vibration of the C_{2v} -optimized 1^{2+} represents a b2

(20) All attempts to grow crystals suitable for X-ray analysis were unsuccessful, as the dimer formed oils that would not subsequently crystallize (see also Experimental Section).

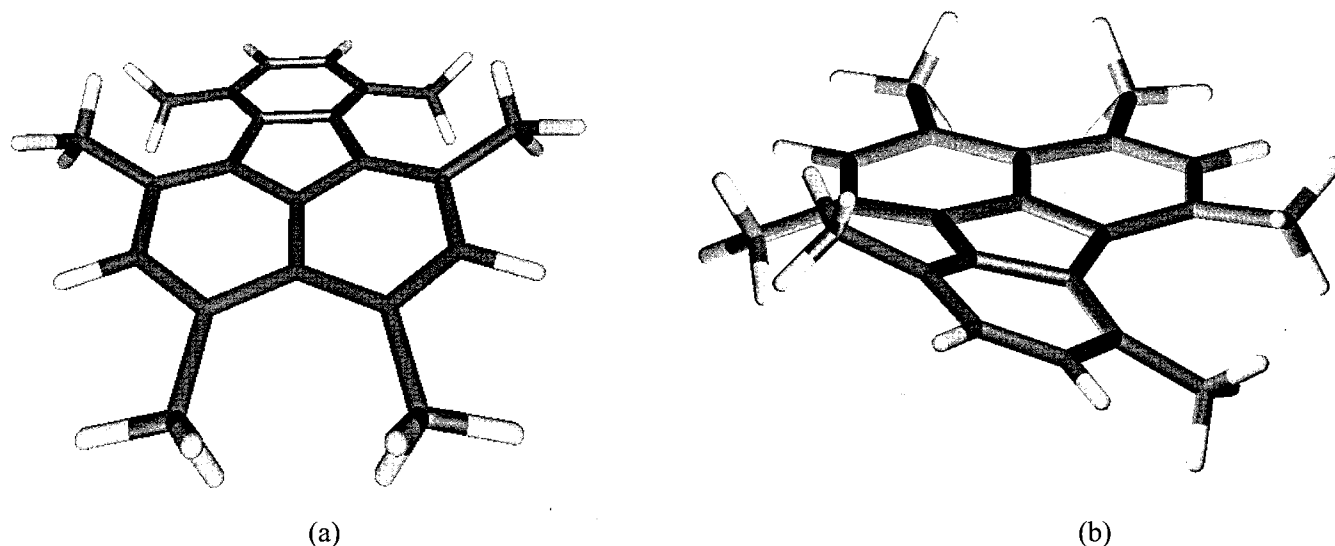


Figure 4. Optimized structures for (a) **2** and (b) **2**²⁺ by B3LYP/6-31G(d,p).

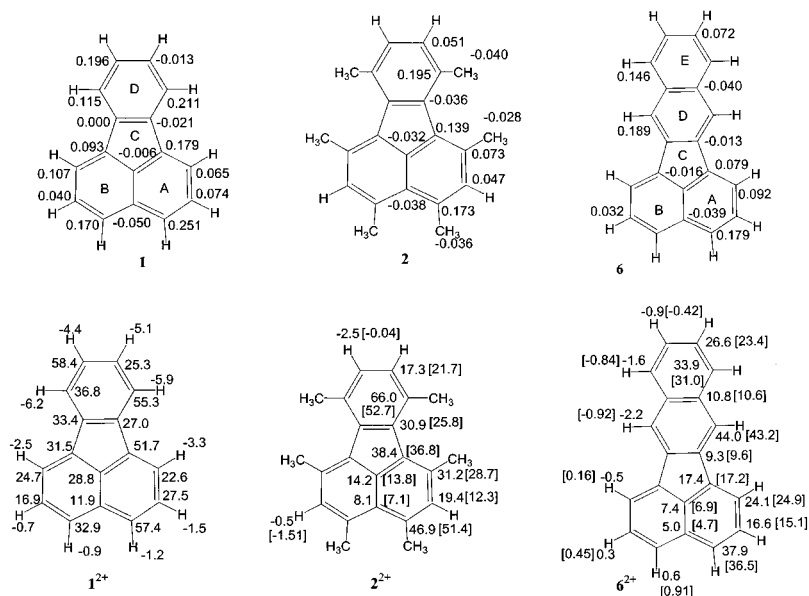


Figure 5. Difference in NPA charges (dication minus neutral) and computed $\Delta\delta^{13\text{C}}$ and $\Delta\delta^1\text{H}$ values; experimental $\Delta\delta$ values are given in brackets. Top row: differences in NPA charges; bottom row: differences in chemical shifts;

ring-breathing. Optimization in a lower symmetry (C_s) produced a stable structure, for which variations in bond lengths from neutral to dication did not present a clear pattern. The C_s structure is only 0.48 kcal/mol more stable than the C_{2v} one (including zero-point energies). Distortions in **1**²⁺ cause nonequivalence of the calculated charges and chemical shifts in otherwise equivalent atoms. In contrast to DFT results, the minimum for **1**²⁺ in the AM1 method has C_{2v} point group. Otherwise, two-electron oxidation of **6** causes small, symmetric distortions relative to the parent molecule, and optimized **6**²⁺ has a C_{2v} point group similar to the neutral compound. This indicates that benzannulation increases rigidity and precludes the distortion observed in **1** upon two-electron oxidation.

Figure 4 illustrates the B3LYP/6-31G(d,p) optimized structures for the neutral hexamethyl derivative **2** and its dication **2**²⁺, showing remarkable structural changes upon oxidation. In **2** (fold conformation), the naphthalene unit is convex and the indeno moiety is inclined in the

opposite direction. In **2**²⁺, the benzo ring becomes severely distorted. It is interesting to note that the optimized geometry for **2**²⁺ is qualitatively similar to that of neutral 1,6,7,10-tetramethylfluoranthene,^{15a} but not to neutral **2**, indicating the 3,4-methyl groups are important in determining the lowest-energy conformation for **2**. Distortions observed in the dication cannot be compared with experiment because there are no X-ray structures available for fluoranthene dications.

Figure 5 summarizes the difference in the NPA charges for the ring carbons (dication minus neutral) and the calculated $\Delta\delta^{13\text{C}}$ and $\Delta\delta^1\text{H}$ values for the ring positions in dications **1**²⁺, **2**²⁺, and **6**²⁺ using the GIAO-DFT method. For comparison, the experimental $\Delta\delta$ values for **2**²⁺ and **6**²⁺ are also gathered. It can be seen that whereas correspondence between experimentally observed and computed ¹³C shifts for **6**²⁺ is very good, the fit for **2**²⁺ is rather poor. This is likely due to a stronger role that solvation plays in this case, where (as predicted) more drastic geometrical changes have taken place upon

Table 2. NICS Values for 1^{2+} , 2^{2+} , and 6^{2+}

ring ^a	(1)	(1 ²⁺)	(2)	(2 ²⁺)	(6)	(6 ²⁺)
A	-8.8 (-11.4)	-12.7 (-5.4)	-7.7 (-10.6)	8.5 (2.3)	-8.8 (-11.4)	1.3 (-3.7)
B	-8.8 (-11.4)	0.2 (4.8)	-7.7 (-10.5)	8.5 (4.0)	-8.8 (-11.4)	1.3 (-3.7)
C	3.1 (-2.2)	35.1 (25.3)	2.0 (-2.3)	22.4 (25.3)	3.1 (-2.1)	11.3 (5.5)
D	-8.4 (-10.9)	25.5 (17.8)	-7.3 (-8.3)	16.6 (22.3)	-8.3 (-10.9)	19.9 (14.0)
E	---	---	---	---	-9.7 (-12.2)	9.6 (4.0)

^a Rings A–E are marked in Figure 5. ^b NICS(1) in parentheses. For benzene NICS(0) = -9.0; NICS(1) = -12.7.

oxidation (see Figure 4). The overall correspondence between difference in NPA charges for the ring carbons and the charge delocalization patterns which are deduced based on experimental $\Delta\delta^{13C}$ values (Figure 3) is reasonable. Calculated proton shifts for 1^{2+} indicate a strong paratropic shift in the dication. For 2^{2+} the gas-phase structure has six different methyls as compared to three in the superacid solution. For 6^{2+} the computed proton shifts produce a somewhat better fit with the experimental values if they are not corrected for bulk solvent effect! Computed proton shifts for the A/B rings in 6^{2+} deviate the most from experiment. It follows that proton chemical shifts are much more sensitive to solvation effects than carbon shifts.

Table 2 summarizes the NICS data, calculated by GIAO/HF/3-21G, for the dications and their neutral precursors, measured at the ring centroid and 1 Å above it. In the neutral fluoranthenes, the five-membered ring is nonaromatic and all other rings are strongly aromatic. For 1^{2+} and 6^{2+} , NICS calculations predict that only the naphthalene moiety (A/B rings) are slightly aromatic and rings C and D are anti-aromatic. Ring C is more anti-aromatic in 1^{2+} than in 6^{2+} , and this is probably due to the low symmetry of the former. For 6^{2+} , ring E is nonaromatic. In the case of 2^{2+} , rings A and B become nonaromatic, and the indeno moiety (C/D rings) is anti-aromatic due to geometrical distortions observed on oxidation.

Comparative Discussion of Tropicity and Charge Delocalization Mode. A paramagnetic ring current operates in the twisted fluoranthene dications 2^{2+} and 3^{2+} . On the basis of solution ¹H NMR, paratropic shifts are more pronounced for the naphthalene moiety (A/B rings). However, NICS calculations predict that the C/D rings should be more anti-aromatic. It may be argued that the origin of reduced paratropicity (antiaromaticity) in the benzannelated ring is its distortion upon two-electron oxidation. Reduced degree of paratropicity was previously observed for dianions derived from distorted (4,5-substituted) phenanthrenes;^{21a} it was suggested that this property may originate from the system's driving force to reduce its anti-aromaticity.

In contrast to **2**, two-electron oxidation in **6** causes only small symmetrical distortions. A paramagnetic ring current operates in 6^{2+} with the D/E rings showing the largest paratropic shifts. These rings are those predicted to be most anti-aromatic using NICS.

Charge delocalization pattern in dications 2^{2+} , 3^{2+} , and 6^{2+} is similar to those of previously studied *alternant* systems benz[*a*]anthracenium dications (16π)³ and dibenzoperylene dication (20π periphery),⁴ where localized and adjacent positive charges are distributed over the entire framework. This pattern is clearly different from that

observed in anthracenium dication and dianion and pyrenium dication and dianion where positive (cation) or negative (anion) charges are located on alternating carbons of the periphery (with positive charge in the dication located on the same carbons as the negative charge in the corresponding dianion).^{21b}

MNDO calculations suggested that the negative charge in fluoranthene dianion (1^{2-}) predominantly resides on the naphthalene unit.^{21c} In the present study, changes in the NPA charges calculated from the DFT wave functions show that for 1^{2+} the charge is in fact more delocalized, and delocalization to a large extent involves the benzo ring.

Formation of Bifluoranthenyls. In the present study, quenching of the dication solutions (SbF₅/SO₂ClF solvent) led to *efficient* formation of crowded bifluoranthenyls which are connected via the benzo ring (at C-8/C-8'). It is noteworthy that the regiochemistry of this dimerization is different from the dimer formed in low yield by quenching of the superacid solution of **1H**⁺ in FSO₃H/SO₂ClF, which produced 3,3'-bifluoranthenyl.¹⁷ We believe that the present quench experiments signify radical cation dimerization, whereas the bifluoranthenyl formed in protonation studies is due to a Scholl-type condensation (arenium ion–arene alkylation) and subsequent skeletal isomerization upon exothermic quenching.¹⁷

Formation of fluoranthenyl dimers **2a–4a** from twisted fluoranthenes represent a potentially interesting (and seemingly facile) route to large hydrocarbons with “curved” subunits, and we are beginning to pursue this angle.

Experimental Section

Compounds **2–4** were synthesized by Siegel et al.¹⁵ Compound **5** and **6** was purchased from Aldrich. Since NMR analysis indicated that they had adequate purity, they were used as received. Compounds **7–9** were gifts from Dr. Doug Klumpp (Cal State–Pomona). Their synthesis and characterization had previously been reported.¹⁹

SbF₅ (Aldrich and Fluorochem) was freshly distilled in all-glass distillation unit under a dry-nitrogen atmosphere and stored under nitrogen in Nalgene bottles with Teflon seals.

SO₂ClF was prepared from SO₂Cl₂, NH₄F, and TFAH according to a modified procedure of Prakash et al.²² Several distillations provided pure SO₂ClF. Other chemicals and reagents were commercially available and were used as received.

NMR spectra were recorded on a 500 MHz instrument. Those of neutral PAHs were recorded in CDCl₃ at room temperature. Dications were studied between -70 °C and -30 °C in 5 mm NMR tubes, using short (ca. 6 cm) external sealed capillary tubes (made from melting point tubes) containing 0.1% TMS in acetone-*d*₆ (these were added to the 5 mm NMR tubes containing the dication solution). The reported ¹H NMR shifts were corrected for bulk solvent effect according to Edlund et al. (Eliasson, B.; Johnels, D.; Sethson, I.; Edlund,

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U. *J. Chem. Soc. Perkin. Trans. 2* **1990**, 897) by adding 0.96 ppm to the ^1H shift values. Proton spectra gathered in Supporting Information are actual, uncorrected spectra. NMR analyses included ^1H , ^{13}C , H/H COSY, C/H HETCOR (or HMQC), COLOC (or HMBC), and NOED experiments.

Mass spectra were obtained using electrospray MS (an ion-trap instrument with MS/MS capability). Acetonitrile–water (1:1) was used as solvent to which 0.01% NH_4NO_3 was added to protonate the PAH.

AM1 Calculations. These were carried out using standard methods implemented in the Hyperchem package version 5.11 (Hypercube Inc, 1999) or Insight II Release 97.0 (MSI, 1999).

In each case minima were verified via frequency calculations (confirming no imaginary frequency).

DFT calculations were performed using Gaussian-98 software.²³ Optimized geometries, charges, and chemical shifts were obtained in the 6-31G(d,p) basis²⁴ and B3LYP hybrid functional.²⁵ NMR chemical shifts were calculated according to the GIAO method²⁶ and charges with the NPA (natural population analysis) method.²⁷ Aromatic character was calculated via NICS(0) (nucleus independent chemical shifts) and NICS(1) GIAO method,²⁸ with the HF/3-21G level, at the ring centroid and at a point 1.0 Å above it, respectively. For five- and six-membered rings, the most negative NICS values were found at the ring centroid for the five membered rings and 1.0 Å above this point for the six-membered ring.²⁹ Acceptability of GIAO/HF/3-21G for NICS calculations has been well documented by Schleyer and associates.²⁹ Our previous work³⁰ also indicated that GIAO/HF/3-21G produces results that are

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coherent with experimental results for arenium ions derived from several classes of large *alternant* PAHs. In test calculations, we found that NICS using GIAO/B3LYP/6-31G(d,p) produced very large values for the D-ring in 2^{2+} .

General Procedure for Dication Generation. SO_2ClF (ca. 0.3 mL) was distilled via a vacuum line into a 5 mm NMR tube containing the substrate (10 mg) cooled to dry ice/acetone temperature. To the resulting suspension, ca. 0.3 mL (ca. 500 mg) of cold SbF_5 dissolved in SO_2ClF (1 mL) was added under a dry nitrogen atmosphere with efficient mixing until homogeneous (vortex). Subsequently, the external capillary was added to the cold NMR tube.

Quenching Experiments. The NMR tube containing the superacid solution was carefully poured into ice/bicarbonate. After allowing the mixture to stand in the fume-hood at rt overnight, the organic phase was extracted with CH_2Cl_2 . The combined organic extract was washed (10%NaCl) and dried (MgSO_4). Removal of the solvent under reduced pressure gave pale-yellow solids which were dissolved in CDCl_3 (in the case of **2** and **3**) or in $\text{CDCl}_3/\text{CS}_2$ (1:1) (in the case of **4**) and analyzed directly by NMR (see Figure 2). The NMR spectra showed the presence of dimers **2a** and **3a** as predominant products (ca. 90% based on NMR integrals) together with minor amounts of high molecular weight side-products (showing broad peaks); no intact substrates had remained. With **4**, apart from **4a** (about 85% based on NMR integration), some intact **4** could be detected. Following NMR analysis, the recovered solids were passed through short silica columns (using CH_2Cl_2 as solvent), but NMR analysis indicated that the purity had not improved. The resulting products were then subjected to fractional crystallization in attempts to grow suitable crystals for X-ray analysis.²⁰

Acknowledgment. Support of our work in the area of PAH reactive intermediates by the NCI of NIH (R15 CA 78235-01A1) is gratefully acknowledged. We thank Dr. M. Gangoda for assistance with NMR and ES-MS. S.E.G. thanks LCCA-USP for generous allocation of computer resources and Brazilian foundations FAPESP, CNPq, and CAPES for financial support.

Supporting Information Available: AM1-minimized structures of **2a–4a** and selected NMR spectra for the dications. Energies and Cartesian coordinates for all compounds studied by B3LYP/6-31G(d,p) and by AM1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO010571P

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