Stable ion and electrophilic chemistry of fluoranthene-PAHs†

Kenneth K. Laali,*[a] Takao Okazaki[a] and Sergio E. Galembeck[b]

[a] *Department of Chemistry, Kent State University, Kent, OH 44242, USA*
[b] *Departamento de Química, FFCLRP, Universidade de São Paulo, 14040-901, Ribeirão Preto - SP, Brazil*

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The first examples of persistent carbocations derived from parent fluoranthene (four fused rings), benz[*e*]acephenanthrylene (benzo[*b*]fluoranthene) (five fused rings) and its C-10 substituted derivatives (X = OMe, F), as well as indeno[1,2,3-*cd*]pyrene (six fused rings) by protonation with FSO_3H–SO_2ClF are reported. NMR characteristics (500 MHz) of the resulting carbocations, their charge delocalization mode and tropicity are examined.

Relative arenium ion energies for all possible protonation sites were calculated by AM1 for comparison with the NMR-based assignments. The NMR chemical shifts for the observed arenium cations were computed by GIAO-DFT calculations at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level (their energies and those of their neutral precursors were also calculated at this level of theory). Relative aromaticity in various rings in the resulting PAH-arenium ions was gauged *via* nucleus independent chemical shift (NICS) calculations.

It has been shown that the site of protonation and nitration in 10-methoxybenz[*e*]acephenanthrylene are the same (C-9). Quenching of the superacid solutions of fluoranthene and 10-methoxybenz[*e*]acephenanthrylene produced the dimers 3,3′-bifluoranthenyl and 10,10′-dimethoxy-9,9′-biacephenanthrenyl as minor products (*ca.* 10% and *ca.* 33% respectively) in addition to the intact PAHs. It has also been demonstrated that fluoranthene-PAHs and their derivatives are easily protonated with $[NH_4][NO_3]$ and observed in the gas phase *via* electrospray mass spectrometry (ES-MS).

Introduction

In comparison with the *alternant* hydrocarbons for which a wealth of synthetic, chemical and biological reactivity data are available, *nonalternant* polycyclic aromatic hydrocarbons (PAHs) are relatively little studied.[1,2]

Polycyclic aromatic fluoranthenes constitute an important class of *nonalternant* PAHs for which parent fluoranthene **1** serves as the building block (Figs. 1, 2).[3] Fluoranthene triol-carbocations ($\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{4}^+$) have attracted attention as reactive intermediates which may be derived from the diol-epoxide metabolites (Fig. 1).[4] For **1**, three pairs of diastereoisomeric diol-epoxides are possible (**2a**,**2b**; **3a**,**3b**; **4a**,**4b**), among them **3a** and **3b** are equivalent to bay-region diol-epoxides. Diol-epoxide **3a**,**3b** and **4a**,**4b** were synthesized and tested for mutagenic activity. It was found that **3a**,**3b** are potent mutagens in the absence of metabolizing systems, whereas **4a** is weakly mutagenic and **4b** is inactive.[4]

The benz[*b*]annelated derivative **5** (Fig. 2) which has a bay-region is a common environmental pollutant with carcinogenic

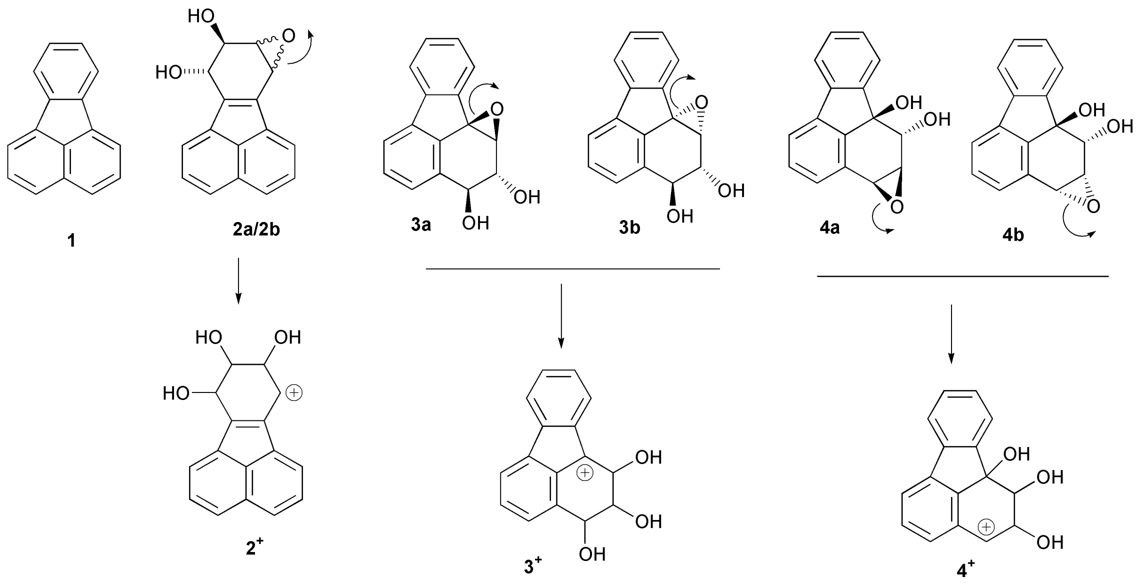

Fig. 1 Fluoranthene, its diol-epoxides and derived trihydroxy-carbocations.

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† Electronic supplementary information (ESI) available: Table S1, NMR spectra and results of calculations. See http://www.rsc.org/suppdata/p2/b1/b108025n/

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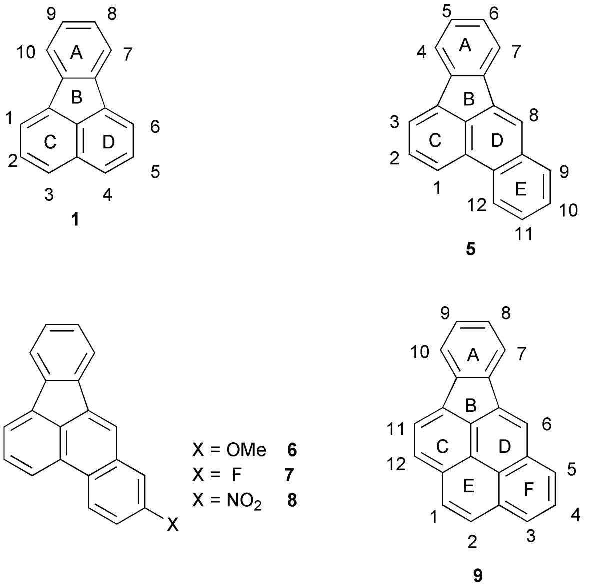


Fig. 2 Compounds under discussion.

and tumorigenic properties.[5] Indeno[1,2,3-*cd*]pyrene **9** is a ubiquitous environmental pollutant which acts as a complete carcinogen and an active tumor initiator.[1] Because of their biological activity and presence in the environment a number of oxidation products of **5** and **9** have been synthesized including phenols and dihydrodiols.[1,2,6]

Recent interest in fluoranthene-PAHs and their derivatives stimulated synthetic efforts to provide these compounds in reasonable quantities for chemical and biological activity studies.[3,7]

For **1**, electrophilic attack is predominantly directed to C-3 (nitration and bromination) whereas in Friedel–Crafts acetylation and benzoylation equal amounts of substitution at C-3 and C-8 were obtained.[2] Nitration of **5** resulted in substitution at C-8 and C-1 with the former predominating. Nitration, bromination and acetylation of **9** occurred predominantly at C-12.[2,8] These reactivity trends are in good agreement with those predicted by the Dewar-PI method based on relative arenium ion energies for substitution at various ring positions.[9]

In relation to our continuing interest in generation and NMR studies of carbocations derived from various classes of PAHs as models for biological electrophiles,[10] we report here on the first examples of persistent arenium ions for representative fluoranthene-PAHs.

Results

NMR assignments

Detailed NMR assignments for the precursors, carbocations and the substitution products (nitro derivatives and dimers) were based on ^{1}H, ^{13}C, H–H COSY, HMQC, HMBC and NOED spectra and are summarized in (Fig. 3a).

NMR features in neutral fluoranthenes. NMR assignments for **1**, **5** and **9** were previously reported by Jones *et al.*,[11] Ernst,[12] Cho and Harvey,[13] Sardella and Boger[14] at various levels of sophistication. These are in very close agreement with our assignments using 500 MHz NMR.

The reported NMR data[15] for the substituted benzo[*b*]fluoranthenes **6**–**8** were extended and fine-tuned. In **6** irradiation of methoxy protons gave concurrent NOE enhancement in H-9/H-11(*ortho*) but NOE enhancement for H-9 was larger suggesting closer proximity of O*Me* to H-9. Whereas OMe substitution (**6**) induces a shielding effect in H-9/H-11, NO$_2$-substitution (**8**) deshields these protons. Deshielding caused by NO$_2$-substitution at C-10 is consistent with its coplanarity with the arene π-system.[16] In **7**, fluorine substitution induces a shielding effect in protons in the D/E rings. The C/F couplings are detectable up to four-bonds within the D/E ring. For **5** and its substituted derivatives (**6**–**8**) NOE effects are observed between the diagnostic H-8 singlet and H-7/H-9. In **9** the diagnostic H-6 singlet is most deshielded (δ 8.53).

Stable ion and electrophilic chemistry (Scheme 1 and Figs. 3–5)

Protonation of 1. Low temperature reaction of **1** with FSO$_3$H–SO$_2$ClF gave a purple solution whose NMR spectral data are consistent with the formation of fluoranthenium cation **1H**$^+$ by protonation at C-3. An important feature in the proton spectrum is the upfield shift of the protons. The center of gravity in the ^{1}H NMR for the cation is at δ 6.89 as compared to the neutral at δ 7.73. The methylene protons (observed at δ 2.61) exhibit NOE with H-4. In addition to resonances for **1H**$^+$ the proton spectra showed broad resonances between δ 7.3–7.8. In concert with experiment, AM1 predicts that among five possible protonation sites, C-3 protonation has the lowest energy, with C-8 predicted to be the next best possibility (2 kcal mol^{-1} higher) (see Supplementary information †).

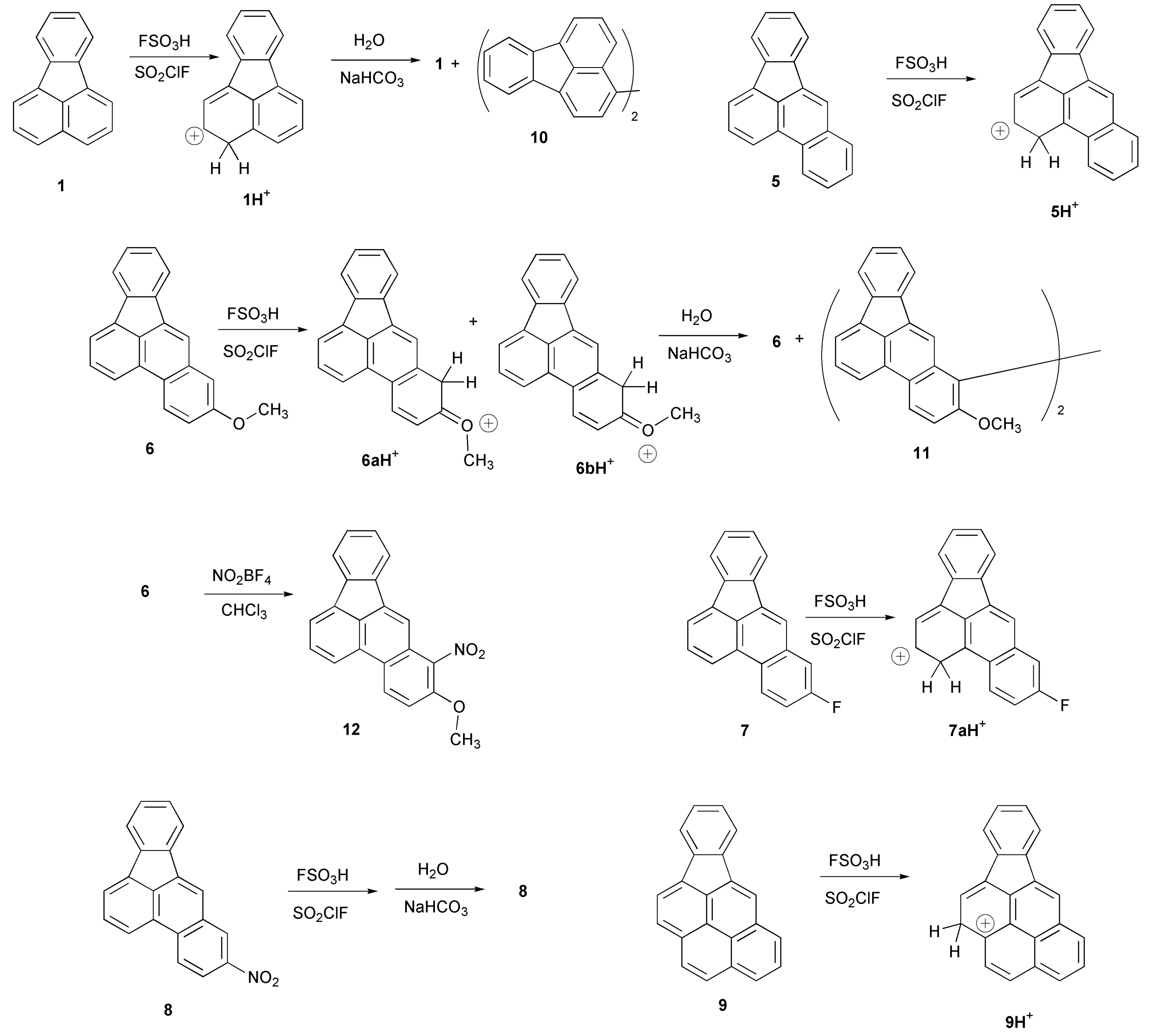
Based on the magnitude of $\Delta\delta^{13}$C values, positive charge is delocalized into the C and A rings plus one conjugated carbon in the D-ring (see Fig. 5). The most deshielded carbon resonances are C-2/C-3a/C-10b (*ortho*/*para*).

Quenching of the superacid solution gave intact **1**, together with minor amounts of another compound (*ca.* 10% yield by NMR) which was identified as 3,3′-bifluoranthenyl **10**.[17] Joining the two fluoranthene units *via* the C3–C-3′ bond causes deshielding of H-1′/H-2′ (from δ 7.93 to δ 8.06 and from δ 7.63 to δ 7.72), deshielding of H-3 (*peri*) (from δ 7.83 in **1** to δ 7.62 in **10**), and deshielding of C-3 (from δ 126.9 to δ 137.0), but the remaining resonances in **10** remain very close to those of parent **1**. The AM1-minimized structure of **10** shows that the two fluoranthene units are almost perpendicular to each other.

Protonation of 5. AM1 predicts that among all the possible protonation sites in **5**, C-1 protonation has the lowest energy, followed very closely by C-8, C-5, C-6, C-3 and C-9 (all within 0.5 kcal mol^{-1} of each other). As mentioned earlier, formation of both 1-nitro and 8-nitro derivatives had been reported in the nitration of **5** with the 8-nitro predominating.[2]

A purple solution was obtained when **5** was reacted with FSO$_3$H–SO$_2$ClF at low temperature. The NMR data (see Fig. 3a) are fully consistent with the formation of **5H**$^+$ by attack at C-1 (attack at C-8 or at other sites can be ruled out). As with **1H**$^+$, the proton signals for **2H**$^+$ are unusually shielded and additional broad resonances are present between δ 6.8–8.0. The most shielded aromatic proton is a singlet at δ 5.83 due to H-8. The latter exhibits NOE with H-7 and H-9. In addition, NOE was detected between H-3/H-4 and between C*H*$_2$ (at δ 1.99!) and H-12. The center of gravity of the aromatic region is at δ 6.80 as compared to the neutral substrate at δ 7.91. In the ^{13}C NMR, the most deshielded carbon resonances are C-2, C-3a and C-12b (*ortho*/*para*) and C-7a. Based on magnitude of the $\Delta\delta$ values it can be concluded that positive charge is primarily localized into the C/A rings (Fig. 5).

Protonation and nitration of 6. Low temperature reaction of **6** with FSO$_3$H–SO$_2$ClF gave a dark-red solution whose NMR spectral data are consistent with attack at C-9 to form two carboxonium ions as geometrical isomers, *viz.* **6aH**$^+$,**6bH**$^+$ in 2 : 1 ratio. Raising the temperature to −30 °C gave a conformationally averaged structure with broader proton resonances (the process was reversible indicative of conformational equilibrium). Relative assignment of the two conformers could not be decided based on NOE data, since irradiation of the OMe protons (δ 4.47/4.38) gave NOE enhancement in both H-9 and H-11. AM1 predicts that **6aH**$^+$,**6bH**$^+$ are the most stable pair of



Scheme 1 Stable ion and electrophilic chemistry of fluoranthene-PAHs.

carbocations to be formed and that **6aH**$^+$ is 2 kcal mol^{-1} lower in energy than **6bH**$^+$. On this basis the major conformer was assigned to **6aH**$^+$. Preference for **6aH**$^+$ relative to **6bH**$^+$ (by 2 kcal mol^{-1}) was further corroborated by DFT calculations (Table S1 †).

For both conformers, NOE was observed between the methylene protons (δ 4.01/3.82) and the H-8 singlets (δ 7.36/7.38). In addition, for the major conformer, NOE enhancement could be detected between the bay-region protons H-12/H-1. The most deshielded protons are those of H-12 (δ 9.08/8.94). The remaining protons are paratropically shifted as in earlier cases. Thus, the center of gravity of the aromatic protons in **6aH**$^+$,**6bH**$^+$ is δ 7.65 (for both conformers) and for neutral **6** is δ 7.83.

The most deshielded carbon resonances are C-12 and C-10 with the $\mathit{C}{=}\mathrm{O}^+{-}\mathrm{CH}_3$ resonances at δ 202.0/205.4. Positive charge is localized in the E-ring plus one conjugated carbon (C-12b). Quenching of the superacid solution gave intact **6** together with a new compound which was identified by NMR and ES-MS (see later) as the 10,10′-dimethoxy-9,9′-biacephenanthrenyl **11** in a 2 : 1 ratio (NMR). Attempts to isolate the dimer by chromatography were unsuccessful. A notable feature in the ^{1}H NMR spectrum of **11** is the low field shift of the H-8 singlet as compared to **6** (δ 8.69 *versus* δ 8.15). This signal exhibits NOE with H-7 (δ 8.04). The AM1-minimized structure of the dimer **11** shows the almost perpendicular arrangement of the two acephenanthrylene units (Fig. 4). In addition, H-8 appears to be in close proximity to the –OMe oxygen, which could induce the observed deshielding in H-8. For comparison, dimer **11** was also optimized at the HF/3-21G level; the results were similar to those obtained by AM1.

Aprotic nitration of **6** (NO_2BF_4–$CHCl_3$) mainly yielded the 9-nitro isomer **12**. Whereas nitro substitution has a deshielding effect on OMe, it induces a rather significant upfield shift in the *peri* H-8 singlet ($\Delta\delta$ 0.34). This is indicative of nitro buttressing,[16] even though the NO_2 group is not in the bay-region.

Protonation of 7. Low temperature reaction of **7** with FSO_3H–SO_2ClF gave a dark red–purple solution whose NMR spectra were best interpreted as a mixture of two arenium ions (in almost equal amounts), one of which is **7aH**$^+$, which is formed by attack at C-1 (the other could not be positively assigned). The similarity of the chemical shifts between the two cations and extensive overlap of resonances precluded detailed assignments; only partial assignments for **7aH**$^+$ were feasible. For **7**, AM1 minimizations implied that the arenium ions of protonation at C-1 (**7aH**$^+$) and C-8 (**7bH**$^+$) have close to identical energies, with C-3/C-6/C-9 protonations computed to be equally favored as the next best possible site(s) (~2 kcal mol^{-1} higher). DFT calculations showed a clear preference for **7aH**$^+$ relative to **6bH**$^+$ (by 2.4 kcal mol^{-1}) (Table S1 † and Comparative discussion).

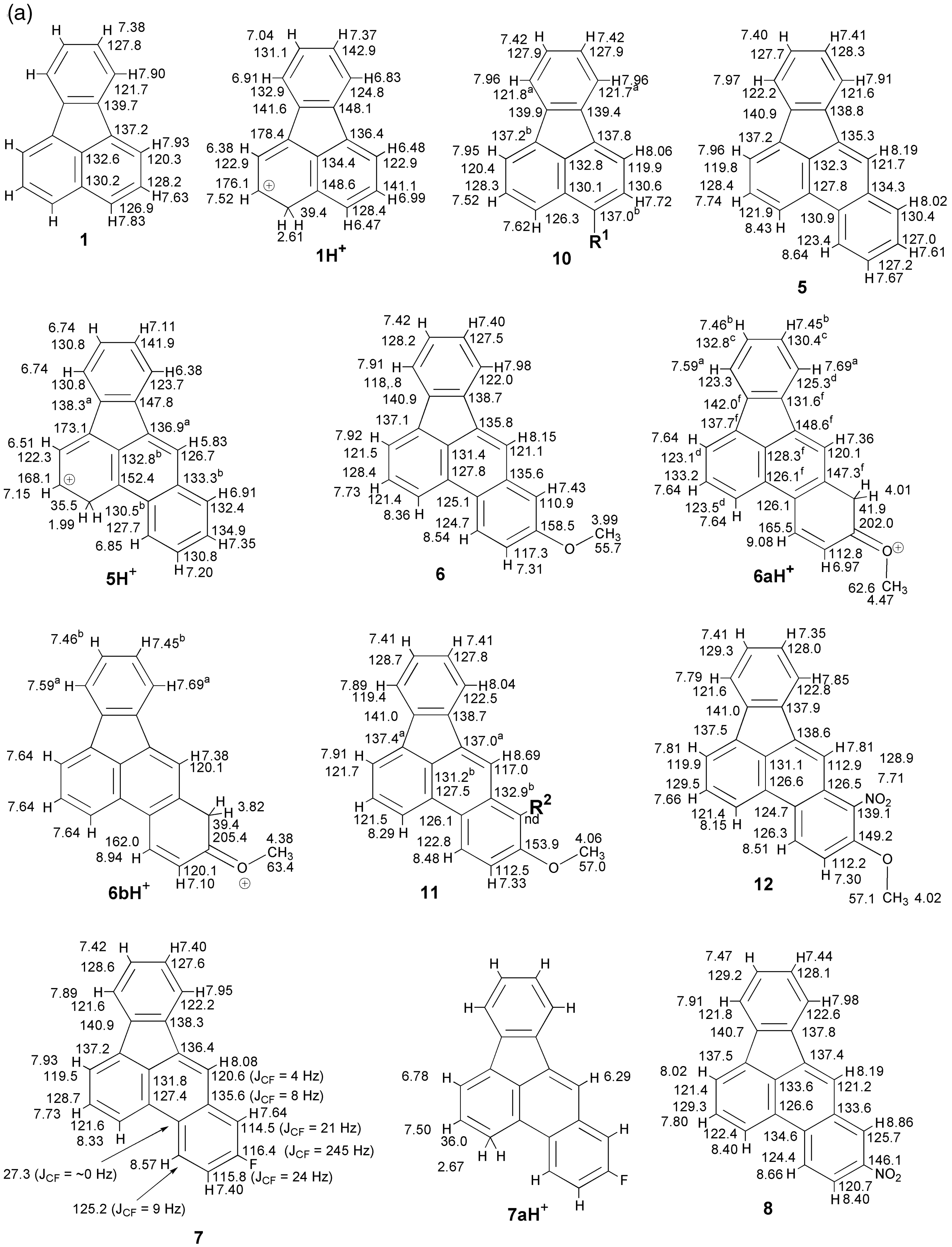


Fig. 3 (a) Summary of ^{1}H and ^{13}C NMR data for protonated carbocations and their precursors (R^1 = fluoranthen-3-yl; R^2 = 10-methoxybenz[*e*]acephenanthrylen-9-yl) (a, b, c, d, e, and f denote interchangeable assignments), nd = not detected. For **6aH**$^+$ assignment of the quaternary carbon resonances, designated by superscript f, took into account the computed GIAO NMR chemical shifts (b) GIAO-DFT computed NMR chemical shifts.

Protonation of 8. When the nitro derivative **8** was carefully reacted with FSO_3H–SO_2ClF at low temperature, a black precipitate was formed leaving behind a pale brown solution. Inspection of the top liquid by ^{1}H NMR showed only weak resonances. Quenching of the entire superacid solution returned the intact **8** with no indication of a dimer. It is conceivable, then, that the black precipitate is the radical cation salt, but this was not further investigated.

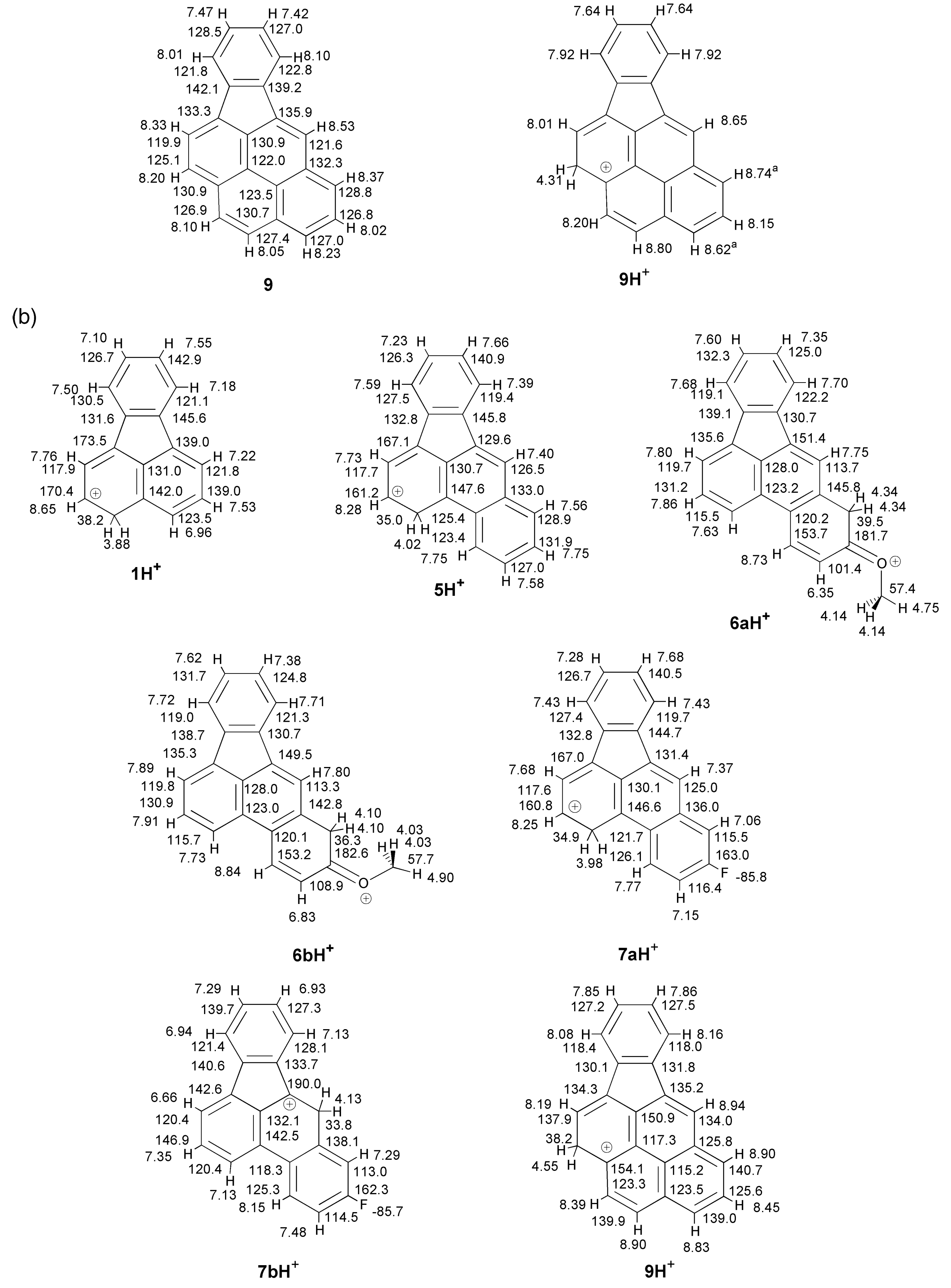


Fig. 3 continued.

Protonation of 9. The indenopyrene **9** reacted at low temperature with $FSO_3H–SO_2ClF$ to give a dark red solution together with some black precipitation. NMR studies of the superacid solution (at −50 °C) are consistent with the formation of $\mathbf{9H}^+$ by protonation at C-12. In addition to the resonances for $\mathbf{9H}^+$, which are somewhat broadened, there is a broad hump in the spectrum in the δ 5.40–7.10 range. Although the majority of aromatic protons for the carbocation appear deshielded relative

Table 1 NICS data for the carbocations (for structures see Figs. 3a and 3b)[a]

Rings	$1H^+$	$5H^+$	$6aH^+$	$6bH^+$	$7aH^+$	$7bH^+$	$9H^+$
A	−3.2 (−6.8)	−4.2 (−7.8)	−6.6 (−9.6)	−6.8 (−9.7)	−4.4 (−7.9)	−2.6 (−6.1)	−8.8 (−11.3)
B	13.2 (5.6)	9.9 (3.0)	7.2 (1.0)	6.8 (0.7)	9.8 (2.9)	15.5 (7.4)	1.9 (−3.6)
C	−0.7 (−5.1)	−0.2 (−4.5)	−6.9 (−9.8)	−7.0 (−10.0)	−0.1 (−4.4)	1.1 (−3.2)	0.8 (−3.1)
D	−3.4 (−7.0)	−1.7 (−5.2)	−7.2 (−10.3)	−7.4 (−10.4)	−1.8 (−5.2)	0.6 (−3.3)	−3.8 (−7.8)
E	—	−8.0 (−11.1)	0.8 (−3.0)	0.6 (−3.3)	−9.0 (−10.9)	−10.0 (−11.8)	−6.3 (−10.1)
F	—	—	—	—	—	—	−7.7 (−11.1)

[a] In each column: NICS(0) (NICS(1)). For benzene NICS(0) = −9.9; NICS(1) = −12.7. The A, B, C, D, E, F designations are adopted from Fig. 2.

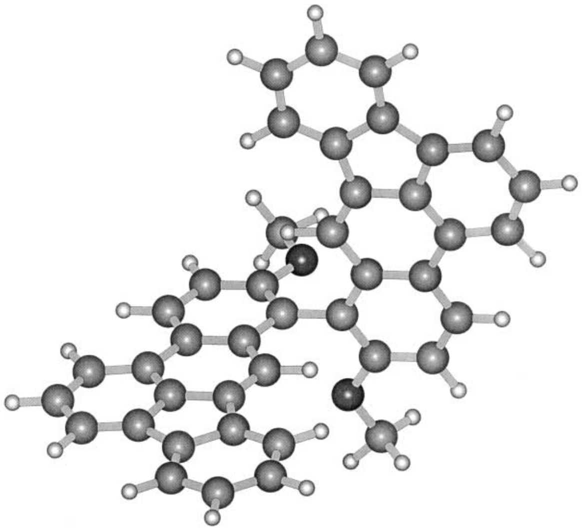
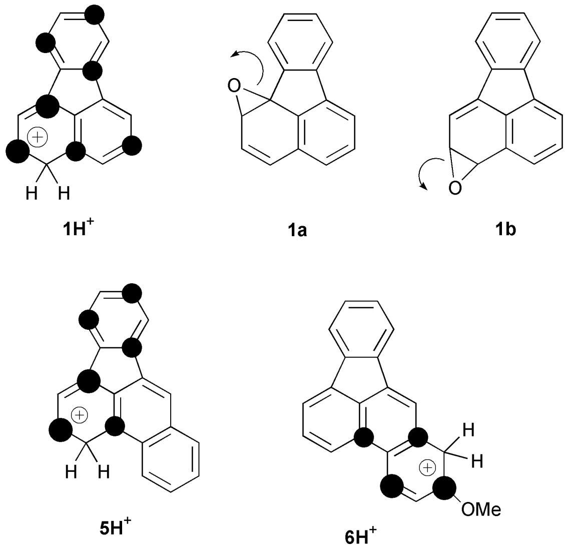


Fig. 4 AM1-minimized structure of the dimer **11**.



1H$^+$ **1a** **1b**

5H$^+$ **6H**$^+$

Fig. 5 Charge delocalization mode in the carbocations (and analogy with epoxide ring opening).

to the precursor, the magnitude of the deshielding is substantially less compared to that for the parent pyrenium cation as a model.[18]

Using AM1, relative arenium ion energies were computed for all possible protonated cations. In agreement with experiment, C-12 protonation is most favored, followed by protonation at C-5/C-3 which is equally favored. These sites are equivalent to the α-positions in pyrene, showing that annelation of the indeno moiety has not altered this preference.

Table 2 NICS data for the neutral substrates[a]

Rings	(**1**)	(**5**)	(**9**)
A	−8.4 (−10.9)	−8.4 (−11.0)	−8.2 (−10.8)
B	3.1 (−2.2)	2.9 (−2.3)	3.5 (−1.8)
C	−8.8 (−11.4)	−9.2 (−11.8)	−11.5 (−13.9)
D	−8.8 (−11.4)	−6.0 (−8.9)	−4.5 (−7.8)
E	—	−10.0 (−12.6)	−4.8 (−8.2)
F	—	—	−12.0 (−14.0)

[a] In each column: NICS(0) (NICS(1)). For benzene NICS(0) = −9.9; NICS(1) = −12.7. A, B, C, D, E, F designations are adopted from Fig. 2.

GIAO-DFT computed NMR chemical shifts and NICS calculations

High level *ab initio*-GIAO and DFT-GIAO calculations have proved invaluable in predicting the NMR parameters for various classes of carbocations.[19] Application of these computational methods to PAH arenium ions has been demonstrated in several recent studies.[20]

In an effort to provide further support for the interpretation of the NMR data, the NMR chemical shifts were computed for the **1H**$^+$, **5H**$^+$, **6aH**$^+$, **6bH**$^+$, **7aH**$^+$, **7bH**$^+$ and **9H**$^+$ carbocations using the GIAO-DFT method. Geometry optimizations and frequency calculations were performed at the B3LYP/6-31G(d) level and GIAO NMR chemical shifts were obtained at B3LYP/6-31G(d)//B3LYP/6-31G(d) level. The results are summarized in Fig. 3b (see also Comparative discussion). Energies [E in hartree (E_h)], zero-point corrections (ZPE) and energy differences between cation and neutral species (ΔE/kcal mol^{-1}) are collected in Table S1.†

Viewed as a single unit the PAH-arenium ion is devoid of cyclic conjugation (presence of an sp^3 center) and hence should not be subjected to the criteria of aromaticity. However, *relative* aromatic character in various rings in the resulting arenium cations may be assessed in comparison with neutral arene.‡ This feature was gauged in cations **1H**$^+$, **5H**$^+$, **6aH**$^+$, **6bH**$^+$, **7aH**$^+$, **7bH**$^+$ and **9H**$^+$ (Table 1) and compared with neutral PAHs **1**, **5**, and **9** (Table 2) by the NICS(0) (nucleus independent chemical shifts) and NICS(1) GIAO method,[21] employing the HF/3-21G level, at the ring centroid and at a point 1.0 Å above it, respectively.

In the parents fluoranthene **1**, benz[*e*]acephenanthrylene **5** and in indeno[1,2,3-*cd*]pyrene **9** the 5-membered ring (B-ring) is non-aromatic. In **9**, rings D/E are noticeably less aromatic relative to the other 6-membered rings in the skeleton. Upon protonation, the B-ring becomes strongly anti-aromatic, except in the indeno-pyrene **9** where the change is rather small. In **1H**$^+$ and **5H**$^+$, ring C (site of protonation; formally a cyclohexadienyl cation) is non-aromatic. In the methoxy derivatives the site of protonation moves to the E-ring and

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‡ This approach was recently applied by Schleyer and associates to gauge aromaticity in individual rings in a homologous series of linear acenes.[28]

this ring is predicted to be non-aromatic. In the fluorinated carbocations **7aH**$^+$ and **7bH**$^+$, rings C and D respectively are the sites of attack and are hence non-aromatic, and in **9H**$^+$, C-ring is non-aromatic.

Detection of fluoranthene-PAH cations by ES-MS

Because of the earlier mentioned environmental significance of fluoranthene-PAHs and for comparison with solution studies, the utility of ES-MS was explored as a gentle technique to produce fluoranthene carbocations in the gas phase. When the neutral compounds were mixed with $[NH_4][NO_3]$–MeOH in MeCN solvent, protonated fluoranthene-PAH cations were formed in abundance. In addition, PAH–NH_4^+ cluster ions were detected in most cases. This method was also exploited to examine mixtures of PAH and dimers (formed *via* quenching of **1H**$^+$ and **6H**$^+$) and the nitro derivative **12**. In selected cases, addition of AgOTf to the PAH in MeOH gave the Ag$^+$–PAH clusters. The ES-MS data are summarized in the Experimental section.

Comparative discussion

In concert with ambient nitration and bromination, and as predicted by AM1 calculations, the parent fluoranthene **1** is protonated at C-3 under stable ion conditions. Benz[*e*]acephenanthrylene, **5**, is exclusively protonated at C-1 (same site as in parent **1**) which is also the site predicted by AM1 to be most favored. The resulting carbocations exhibit analogous charge delocalization patterns which involve mainly the C and A rings (Fig. 5). A similar charge delocalization pattern would be expected from epoxide ring opening in **1a** or **1b** (the former is equivalent to a bay-region epoxide related to the highly mutagenic **3a**,**3b** (see also Fig. 1). Introduction of an OMe group at C-10 directs the attack to C-9 (protonation and nitration). Positive charge in the resulting carboxonium ion is localized in the annelated ring. The NMR spectral data for the nitration product **12** are indicative of a nitro group buttressing and steric inhibition to conjugation.

There is very good overall agreement between the experimental and computed ^{13}C NMR chemical shifts (Figs. 3a and 3b). In the case of **7**, theory provides reasonable evidence that C-1 protonation is most important, since **7aH**$^+$ is 2.4 kcal mol^{-1} lower in energy relative to **7bH**$^+$ at the B3LYP/6-31G(d) level (after correction for zero-point energy) (Table S1). Furthermore, whereas the ^{13}C chemical shifts in **7aH**$^+$ are close in range to the experimental values for the parent **5H**$^+$ (as expected), in **7bH**$^+$ (C-8 protonated) several carbon resonances are predicted to be substantially more deshielded. Although, based on relative arenium ion energies, protonation(s) at C-3, C-6 or C-9 may well account for the remaining carbocation formed, extensive overlap and the large number of resonances in the NMR spectra preclude a definitive decision.

A noteworthy feature in the spectra of the fluoranthene-PAH carbocations are the observed paratropic shifts in the proton NMR spectra. The observed upfield shifts are larger in **5H**$^+$than in **1H**$^+$. This phenomenon is also detected in the substituted derivatives **6H**$^+$and **7H**$^+$, although with lower magnitude. In indeno[1,2,3-*cd*]pyrene **9** the net outcome is proton deshielding, but the magnitude of deshielding is significantly less as compared to the parent pyrenium cation,[18] suggesting that an opposing shielding effect is operative. Proton shielding in the carbocations relative to the neutral precursors is also predicted by GIAO-B3LYP/6-31G(d) (Fig. 3b).

Carbocations **1H**$^+$(14π) and **5H**$^+$(18π) are formally $4n + 2$ whereas **9H**$^+$ (20π) is a $4n$ system. NICS calculations (Tables 1 and 2) predict that the 5-membered rings in the carbocations develop strong anti-aromatic character. These rings exhibit the most positive NICS values, except in **9H**$^+$ ($4n$ system), where the change in aromatic character is least pronounced. In all cases, as expected, the ring undergoing protonation is non-aromatic.

In comparing the carbocations derived from benz[*b*]acephenanthrylenes and indeno[1,2,3-*cd*]pyrene with the previously studied phenanthrenium[22] and pyrenium cations,[23] striking differences are found in their tropicity and charge delocalization modes, showing that annelation with the indeno moiety has a significant effect.

The predicted anti-aromaticity in fluoranthene-PAH carbocations (NICS) may well be the origin of the observed paratropicity and proton shielding in these *nonalternant*-PAH carbocations. The observed broadening in the proton spectra in several cases, the appearance of upfield-shifted, broad humps, and the formation of insoluble precipitates (which upon quenching returned the intact PAH) are taken as evidence for the concomitant presence of the radical cation which could additionally contribute to proton shielding.

Formation of dimers in low yield upon quenching could either stem from a Scholl-type condensation between the arenium ion and neutral substrate through an equilibrium (*via* exothermic quenching and/or prolonged storage) or occur *via* a radical cation (RC) dimerization process. The following observations/evidence point to a Scholl condensation process: (a) dimer formation on quenching was not observed in all cases (only in the case of **1** and **6**); (b) the previously observed RC-induced shifts in arenium ions of *alternant* PAHs[18a] are significantly smaller than those observed here; (c) the bifluoranthenyl dimers which are formed in quenching experiments involving alkylfluoranthene oxidation dications have 8,8′-regiochemistry (*i.e.* connection is *via* the benzo ring).[24]

For a Scholl-type dimerization starting with **1H**$^+$ and **6H**$^+$, formation of the 2,3′-dimer in the case of **1** and 9,12′-dimer in the case of **6** may be most readily envisioned because electrophilic attack occurs at C-3 and C-9 in **1** and **6** respectively and since C-2 and C-12 are the most logical sites for subsequent nucleophile attachment in the carbocations (large $\Delta\delta^{13}$C values). However, the NMR data clearly rule out these dimers (absence of singlets in the proton spectra), suggesting that the "initial" Scholl condensation products must undergo subsequent skeletal rearrangements under exothermic quenching conditions to produce 3,3′- and 9,9′-dimers.

Finally, the facile generation of fluoranthene-PAH carbocations in the gas phase utilizing ES-MS and the use of ammonium nitrate to protonate the PAH are noteworthy from environmental and toxicological perspectives.

The present stable ion and computational study will provide the basis for further work on *nonalternant*-PAH carbocations in an effort to build up relative carbocation-based structure–reactivity trends.

Experimental

Compounds **1** and **2** were commercially available (Aldrich). Compound **9** was a gift from Professor Ronald Harvey (University of Chicago). Compounds **6**, **7** and **8** were kindly provided by Professor Antonio Echavarren (University of Madrid).[15]

FSO_3H (Allied and Aldrich) was freshly distilled in an all-glass distillation unit under a dry nitrogen atmosphere and stored under nitrogen in Nalgene bottles with Teflon seals.

SO_2ClF was prepared from SO_2Cl_2, NH_4F and TFAH according to a modified procedure of Prakash *et al.*[25] Several distillations provided pure SO_2ClF. Other chemicals and reagents were commercially available and were used as received.

NMR spectra were recorded on a Varian INOVA 500 MHz instrument; those of neutral PAHs were recorded in $CDCl_3$ at room temperature. Carbocations were studied between −70 and −30 °C. NMR analyses included ^{1}H, ^{13}C, H–H COSY, HMQC, HMBC and NOED experiments.

Electrospray mass spectra were recorded on a Bruker Esquire-LC instrument with MS/MS capability. MeOH or MeOH–MeCN 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). Frequency calculations confirmed that in all cases the carbocations were *bona fide* minima (no imaginary frequency) (see Supplementary information). DFT calculations were performed using Gaussian-98 software.[26] Optimized geometries were obtained at the B3LYP/6-31G(d) (Cartesian coordinates are provided as Supplementary information). NMR shifts were computed according to the GIAO method.[27] NICS calculations were carried out by GIAO/HF/3–21G at the ring centroid (NICS(0)) at 1.0 Å above this point.[21]

General procedure for stable ion generation

SO_2ClF (*ca.* 0.4 mL) was distilled into a 5 mm NMR tube containing the substrate (5–10 mg) cooled to dry ice–acetone temperature. To the resulting suspension cold FSO_3H (2–3 drops) was added with efficient mixing until homogeneous (vortex). Subsequently, 2 drops of CD_2Cl_2 were added on top of the cold solution and the mixture was thoroughly mixed.

Quenching experiments

The superacid solution was carefully poured into ice–bicarbonate and the mixture was extracted with CH_2Cl_2. The organic extract was washed (10% NaCl) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was analyzed by NMR. In the case of **1H**$^+$, apart from intact **1**, *ca.* 10% of **11** was formed (NMR in Fig. 3; ES-MS: see below). In the case of **6**, dimer **11** was present in *ca.* 33% yield. Separation of **11** from **6** by silica chromatography proved unsuccessful; the dimer was analyzed by NMR (Fig. 3a) and ES-MS (see below) directly in the mixture.

Nitration of 11

The methoxy derivative (10 mg) was reacted with NO_2BF_4 (2 equiv.) in $CHCl_3$ at rt. After 5 minutes' stirring, the reaction was quenched (ice–bicarbonate). The organic phase was separated, the solvent was removed and the residue was chromatographed on silica (hexane–CH_2Cl_2 1 : 1). NMR analysis indicated the formation of the 9-nitro isomer (~90%) **11** together with other minor isomers (or by-products) which could not be further separated [NMR data (Fig. 3a); ES-MS (see below)].

Summary of ES-MS data

Compound **1**: *m*/*z* 203 $(M + H)^+$; *m*/*z* 220 $(M + NH_4)^+$. Compound **5**: *m*/*z* 253 $(M + H)^+$; *m*/*z* 270 $(M + NH_4)^+$. Compound **6**: *m*/*z* 283 $(M + H)^+$ [MS/MS: *m*/*z* 263 (methyl loss)]; *m*/*z* 300 $(M + NH_4)^+$; *m*/*z* 391 $(M + Ag)^+$ [MS/MS: Ag^+]. Compound **7**: *m*/*z* 271 $(M + H)^+$; *m*/*z* 288 $(M + NH_4)^+$. Compound **8**: *m*/*z* 298 $(M + H)^+$ [MS/MS: *m*/*z* 252 (loss of nitro)]; *m*/*z* 315 $(M + NH_4)^+$. Compound **9**: *m*/*z* 277 $(M + H)^+$; *m*/*z* 294 $(M + NH_4)^+$. Compound **10**: *m*/*z* 282 $(M + 2H)^{+2}$; *m*/*z* 580 $(M + NH_4)^+$. Compound **11**: *m*/*z* 563 $(M + H)^+$; *m*/*z* 580 $(M + NH_4)^+$. Compound **12**: *m*/*z* 328 $(M + H)^+$ [MS/MS: *m*/*z* 311 and *m*/*z* 282]; *m*/*z* 345 $(M + NH_4)^+$.

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