Probing the charge delocalization mode in methyl-, dimethyl- and methylene-bridged phenanthrenium ions. NMR studies of persistent mono- and di-cations and AM1 calculations

Kenneth K. Laali,*[a] Sandro Hollenstein[a] and Poul Erik Hansen[b]

[a] *Department of Chemistry, Kent State University, Kent, OH 44242, USA*
[b] *Roskilde University, Department for Chemistry and Life Sciences, Postbox 260, DK-4000 Roskilde, Denmark*

Superacid protonation studies are reported on 2-methyl- (1), 3-methyl- (2), 3,6-dimethyl-phenanthrene (3) and 4*H*-cyclopenta[*def*]phenanthrene (4).

In $FSO_3H–SO_2ClF$ persistent monocations $1H^+$–$4H^+$ are generated. 3 gives a symmetrical dication by protonation with $FSO_3H·SbF_5$ (4 : 1)–SO_2ClF or with 'magic acid'–SO_2ClF. 1 and 2 are partially diprotonated in 'magic acid'–SO_2ClF. The observed mono- and di-cations are in most cases those predicted by AM1 to be the most stable. Correlation between the magnitude of $\Delta\delta_{^{13}C}$ and AM1 calculated changes in carbon changes [$\Delta q = q_c$ (ion) − q_c (neutral)] is also examined.

The charge alternation paths in the mono- and di-cations are compared and discussed. A parallel is drawn between stable ion and AM1 studies of methylphenanthrenes and the solvolytic studies of K-region and non-K-region phenanthrene oxides.

Introduction

Involvement of dihydrotrihydroxycarbenium ions as reactive intermediates in the metabolic activation of polycyclic aromatic hydrocarbons PAHs *en route* to PAH–DNA adducts has been established through solvolytic studies of several classes of PAH–diol–epoxides (the ultimate carcinogens), probing the rate, stereochemistry and products.[1–3]

As proximate carcinogens, the synthesis and structural/mechanistic studies on PAH arene oxides have also received considerable attention.[4–9] Although phenanthrene itself is not a carcinogen, much of the early studies focused on its epoxides in order to compare K-region *versus* non-K-region epoxide reactivities.[5,10] It is generally agreed that an increase in carcinogenic activity observed by methyl group introduction in sterically crowded locations or by benzannelation is due to enhanced reactivity of the more hindered oxiranes.[4,6,8,11,12]

Stable ion studies on various classes of arenium ions derived from PAHs with varied degrees of carcinogenic activity provide the means to compare the mode of charge delocalization in the periphery of arenium ions as deduced from NMR studies, and carcinogenic/mutagenic activity determined through biological tests.[13]

In the early 1980s, Laali and Cerfontain[14] carried out a superacid protonation study of methylphenanthrenes using low temperature ^1H NMR spectroscopy. With $FSO_3H–SO_2ClF$ superacid, monocations were obtained, and in 'magic acid'–SO_2ClF representative dications were generated. The analyses of these cations were based solely on ^1H NMR studies (at 100 MHz) and ^{13}C NMR data on persistent phenanthrenium cations were hitherto unavailable to allow charge delocalization mapping in the mono- and di-carbocations.

In relation to our ongoing studies of PAH arenium ions,[15–18] and considering the importance of the phenanthrene core as a building block of biologically active PAHs,[12,19,20] we have generated several methyl- and dimethyl-phenanthrenium mono- and di-cations and examined their charge delocalization path by ^{13}C and 2D-NMR spectroscopies. As an entry into the methylene-bridged PAH–arenium ions and in connection with much current interest in the synthesis and biological activity of methylene-bridged PAHs,[21–27] protonation of cyclopenta[*def*]-phenanthrene was also carried out.

Table 1 Sum of the $\Delta\delta_{^{13}C}$ for mono- and di-cations of **1**, **3** and **4**

	$\Sigma\Delta\delta_{^{13}C}$ (Monocation)	$\Sigma\Delta\delta_{^{13}C}$ (Dication)
1	+162.5	+366.7
3	+158.4	+377.2
4	+163.8	—

AM1 energies and charges were calculated for all conceivable mono- and di-protonated phenanthrenes for comparison with experiment and as a means to obtain a more general picture of their relative stabilities and charge delocalization.

Results and discussion

NMR assignments

Detailed NMR assignments for the methyl- and dimethyl-phenanthrenes and cyclopenta[*def*]phenanthrene substrates (Fig. 1) were based on their ^1H and ^{13}C spectra, together with H–H COSY and C–H HETCOR relationships. In each case, a few proton and carbon assignments remain uncertain either because the proton chemical shifts were too close to allow definite assignments *via* H–H COSY, or some of the carbons had very similar chemical shifts in the ^{13}C NMR spectra.

NMR assignments for the phenanthrenium mono- and di-cations (Table 1 and later discussion) were based on ^1H and ^{13}C NMR chemical shifts, C/H coupled spectra and H–H COSY. In addition, C–H HETCOR spectra of $\mathbf{1H^+}$, $\mathbf{3H^+}$ and $\mathbf{4H^+}$ were recorded to clearly assign the H-bearing carbons.†

AM1-calculated carbon charges and in particular changes in carbon charges $\Delta q = q_c$(ion) − q_c(neutral) were used as an additional guideline to reduce the number of interchangeable carbon assignments, especially for quaternary carbons, experiencing low $\Delta\delta_{^{13}C}$ values with very similar chemical shifts (see also further discussion).

For a given carbocation, the ^1H and ^{13}C chemical shifts varied in independent protonation experiments, depending on the

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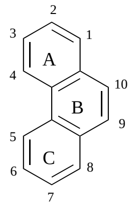
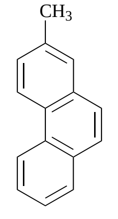
† Additional NMR spectroscopic data are available as supplementary material (SUPPL. No. 57285), (pp. 12) from the British Library. For details of the Supplementary Publications Scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1997.

nature and the amount of the superacid used to generate a given arenium ion.

The ^{1}H NMR shifts showed greater sensitivity (up to *ca.* 1 ppm) than the variations in the ^{13}C shifts (maximum variations of *ca.* 4 ppm) with the largest variations for protons and carbons which exhibit higher $\Delta\delta$ values (cation minus precursor). Similar variations in the ^{1}H (and ^{13}C) chemical shifts of the arenium cations of large PAHs (*e.g.* benzo[*a*]pyrene, benzo[*e*]pyrene and dibenzo[*ae*]pyrene) were observed in a previous study as a function of ion concentration.[15] Variation in the chemical shifts depending on the nature of the *in situ* generated radical cation has also been examined in our previous work.[16]

In order to fully monoprotonate the phenanthrenes **1**–**4**, a large excess (*ca.* 25–50-fold) of FSO_3H is usually needed. In selected cases (**1H$^+$** and **4H$^+$**), when the superacid : PAH ratio was lowered, a second set of resonances appeared whose ^{13}C resonances were at positions very close to those of the neutral PAH itself, but the ^{1}H chemical shifts were considerably shielded (up to 0.6 ppm) compared to the hydrocarbon. Upon addition of more FSO_3H to such a sample, the arenium ion resonances increased in intensity (^{1}H NMR) at the expense of the shielded peaks due to the hydrocarbon. Under comparable conditions in higher acidity superacids (FSO_3H–SbF_5, 4 : 1) the shielded resonances never appeared. Observation of the triad [PAHH]$^+$, and PAH and FSO_3H (excess) suggested the presence of the equilibrium (1) which must be too slow on the NMR timescale





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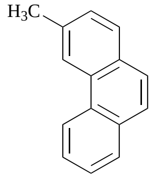

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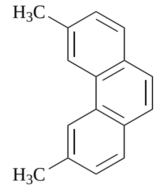

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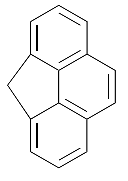


4

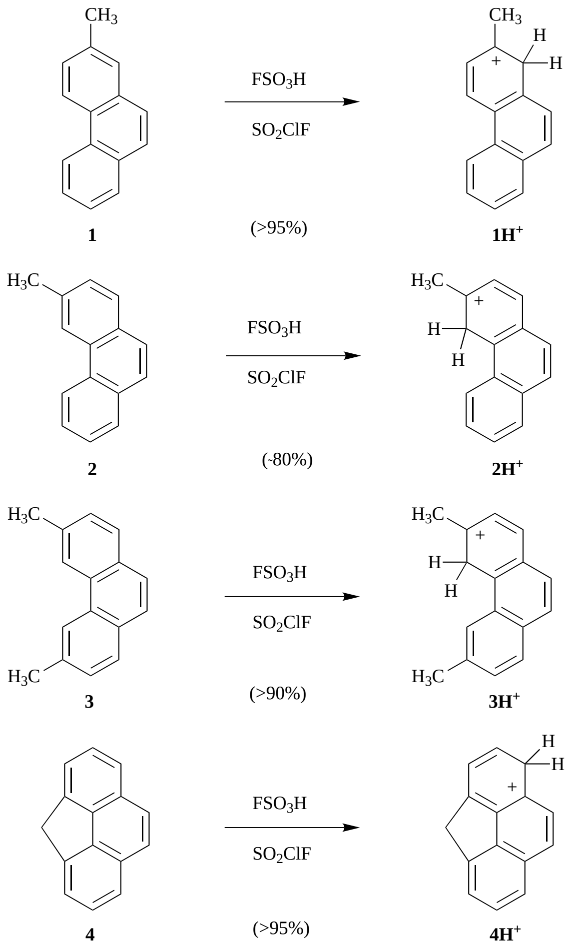
$$\mathrm{PAH} + \mathrm{FSO_3H} \rightleftharpoons [\mathrm{PAHH}]^+ + \mathrm{FSO_3}^- \qquad (1)$$

to cause broadening or averaging in the ^{1}H NMR spectra. Detailed NMR studies of this phenomenon, monitoring the variations in the chemical shifts of arenium ions of PAHs as a function of the PAH : superacid ratio and carbocation concentration, is the subject of a separate investigation.[28]

Stable ion studies (Schemes 1 and 2 and Fig. 1)

In the early ^{1}H NMR study, 1-, 3-, 4-, and 9-methylphenanthrenium cations were generated by monoprotonation with FSO_3H–SO_2ClF.[14] The present study began with a protonation study on the missing member 2-methylphenanthrene **1**.

Addition of cold FSO_3H to a slurry of **1** in SO_2ClF gave a deep-red homogeneous solution on mixing, whose ^{1}H NMR spectrum exhibited a major deshielded methyl group at 2.72 ppm, a CH_2 (carbocation) at 4.30 ppm and a highly deshielded aromatic doublet at 9.61 ppm, in addition to four doublets and two triplets between 8.50–7.70 ppm. The major phenanthrenium ion accounted for >95% of the product, identified as **1H$^+$** (Scheme 1). It exhibited 13 aromatic carbon resonances with the two most deshielded at 196.1 ppm (non-H bearing) and 163.7 (CH). The CH_2 (carbocation) and the methyl resonances were at 47.2 and 26.5 ppm respectively. Quenching of the ion solution returned the skeletally intact **1** (^{1}H NMR).



Scheme 1 Protonations of **1**–**4** with fluorosulfonic acid–SO_2ClF

In agreement with NMR-based arguments, AM1 predicts that C-1 protonation is most favored among all possible sites of protonation (see also related discussion).

Protonation of **1** with higher acidity superacid $FSO_3H{\cdot}SbF_5$ (4 : 1)–SO_2ClF gave essentially the same monocation (**1H$^+$**), whereas the low temperature reaction of **1** with 'magic acid'–SO_2ClF produced the dication **1H$_2^{2+}$** and the monocation **1H$^+$**; in a mixture whose composition varied depending on temperature and the concentration of the samples (Scheme 2). The %**1H$^+$** was substantially lower in low concentration ion solutions studied between −90° and −70 °C.

In the ^{1}H NMR spectrum of **1H$_2^{2+}$**, H-4/H-8 (*para*) almost coincide (at 9.96 ppm) and H-6 (*ortho*) is at 9.87 ppm. In the ^{13}C NMR spectrum, the most deshielded resonances are at 224.5 (C) and 192.8 (CH) ppm for C-2/C-8 respectively.

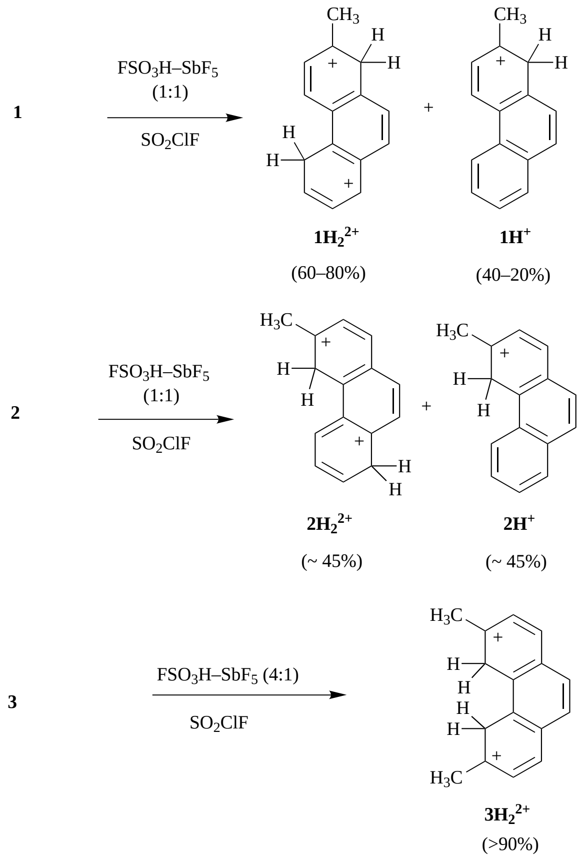
For comparison, we calculated (AM1) every conceivable diprotonated dication structure (23 combinations were considered). In agreement with the observed stable ion, the 1,5-diprotonated dication had the lowest energy (Table 2).

Mono- and di-protonation 2

Based on the early ^{1}H NMR study,[14] monoprotonation of 3-methylphenanthrene **2** was found to give a mixture of two monocations, identified as the C-4 and C-9 protonated phenanthrenium ions with the latter being more prominent. In the present study it was hoped that protonations at lower temperatures under more carefully controlled conditions may lead to a single monocation. In an attempt to provide complete ^{13}C and 2D-NMR data, protonation of **2** was reexamined and its diprotonation was also studied.

Table 2 AM1 calculated energies ($\Delta\Delta_fH°$, kcal mol^{-1}, in brackets) for the corresponding protonation sites of the phenanthrenes (observed sites are in italics)

	$\Delta\Delta_fH$/kcal mol^{-1}	
	Monocations	Dications
Phenanthrene	9 (170.5); 1 (170.5); 4 (171.9); 3 (172.6); 2 (173.6)	
1	*1* (167.5); 10 (169.1); 3 (169.6); 9 (169.7); 8 (169.9)	*1.5* (416.5); 1,8 (417.8); 1,7 (418.0); 1,6 (422.0); 4,8 (422.1)
2	9 (167.5); *4* (168.5); 8 (169.2); 1 (169.6); 10 (169.7)	*4.8* (416.9; 4,5 (420.5); 2,8 (420.5); 1,5 (422.2); 4,6 (422.7)
3	9 (166.9); *4* (167.8); 1 (168.3); 2 (170.3); 3 (174.2)	*4,5* (413.5); 1,5 (415.5); 1,7 (418.6); 2,5 (419.5); 1,8 (421.2)
4	*1* (167.0); 9 (168.1); 3 (169.8); 2 (171.0)	



Scheme 2 Diprotonation reactions of **1**–**3**

Careful low temperature protonation experiments using the vacuum line technique did not, however, lead to a single phenanthrenium ion; a mixture of two monocations were formed. Although high quality low temperature spectra could not be obtained (fast polymerization even at low temperature) the major ion (*ca.* 80%) was identified as the C-4 protonated **2H**$^+$, having two low field doublets at 8.73 (*para*) and 8.10 ppm, a deshielded methyl at 2.70 and the CH_2 at 4.42 ppm. In the ^{13}C NMR spectrum, the most deshielded resonances were at 203.5 (C) and 176.2 ppm (CH) for the *ortho* and *para* carbons; the annelated *ortho* carbon resonated at 159.5 ppm.

The minor isomer (*ca.* 20%) shows two singlets at 9.35 and 8.20 ppm; except for a low field doublet at 8.40 ppm the remaining resonances are buried under the peaks belonging to **2H**$^+$. The assignment to the C-9 protonated cation is therefore tentative.

AM1 predicts C-9 protonation to be favored only slightly over C-4 protonation (by about 1 kcal mol^{-1}) and the C-4 and C-8 protonated cations to possess nearly identical energies. The lack of regioselectivity with **2** and variations observed in the relative ratio of the two phenanthrenium ions in independent studies are, therefore, not surprising.

The low temperature reaction of **2** with 'magic acid'–SO$_2$ClF gave the 4,8-diprotonated cation **2H**$_2^{2+}$, together with **2H**$^+$ (about 45% each) in addition to a minor monocation (10%). The dication exhibits a methyl group at 3.30 ppm, highly deshielded doublets at 10.28, 9.85 and 9.59 ppm, and two different CH_2 groups (5.68 and 5.59 ppm). In the ^{13}C NMR spectrum, the lowest field resonances are at 221.5 (C-3) and 195.5 ppm (C-5). Partial assignments of the dication were aided by C–H coupling and H–H COSY spectra. Quenching of the ion solutions in both cases returned the intact **2**.

Using AM1, various possible isomeric dication structures were calculated (24 combinations), among them, the experimentally observed 4,8-diprotonated dication had the lowest energy (Table 2).

Mono- and di-protonation of 3,6-dimethylphenanthrene 3

In accord with the formation of **2H**$^+$ from **2** (Scheme 1), the low temperature reaction of the symmetrical dimethyl derivative **3** with FSO$_3$H–SO$_2$ClF gave the C-4 protonated monocation **3H**$^+$ in better than 90% selectivity [the identity of the minor phenanthrenium ion(s) are undetermined]. The ^{1}H NMR spectrum of the resulting deep-red solution exhibited two methyl resonances at 2.74 and 2.65 ppm, the CH_2 at 4.85 and the lowest field doublet at 9.03 ppm for H-1 (*para*). In the ^{13}C NMR spectrum the expected 13 aromatic resonances were resolved, with C-3 (at 196.0 ppm) being the most deshielded.

AM1 predicts that for **3**, the C-9 protonated arenium ion has the lowest energy, closely followed by the observed C-4 protonated **3H**$^+$ (1 kcal mol^{-1} higher, Table 2).

The low temperature reaction of **3** with 'magic acid'–SO$_2$ClF (Scheme 2) cleanly produced the symmetrical dication **3H**$_2^{2+}$ in *ca.* 90% yield. The same dication was formed in the FSO$_3$H·SbF$_5$ (4 : 1)–SO$_2$ClF system. The dication exhibited a single low field methyl resonance at 3.48 and the CH_2 at 5.51 ppm, respectively. The aromatic region consisted of two doublets and one singlet with the most deshielded being the doublet for H-1/H-8 at 9.69 ppm. The aromatic region in the ^{13}C NMR spectrum consisted of just seven resonances with the most deshielded at 227.2 ppm for the methyl-bearing C-3 (*ortho*). Again, quenching experiments showed that the structural integrity of the PAH was preserved; **3** was recovered unchanged from the superacid solutions (^{1}H NMR).

In accord with experiment, AM1 predicts that the 4,5-diprotonated dication has the lowest relative energy, with the 1,5-diprotonated cation being the next possibility (Table 2).

Protonation of 4*H*-cyclopenta[*def*]phenanthrene 4

Methylene-bridged PAHs are principal components of coal tar and crude oil as well as environmental pollutants.[20,22,25,26] Compound **4** has also served as the starting material for synthesis of corannulene.[29] The electrophilic reactivity of **4** has been studied on several occasions. Taylor's protiodetritiation experiments established the reactivity order C-1 > C-2 > C-3 > C-8.[30,31] Bromination, acylation and nitration were shown to occur preferentially at C-1.[24] It has been suggested that strain reduces the steric hindrance at the C-1/C-8 of **4** relative to phenanthrene.[30]

AM1 calculations predict the reactivity order; C-1 > C-9 > C-3 > C-2, with protonation at C-1 being favored over C-3 (*peri* to the bridge) by 2.8 kcal mol^{-1}.

In concert with the protiodetritation studies and AM1, we believe that the C-1 protonated methanophenanthrenium

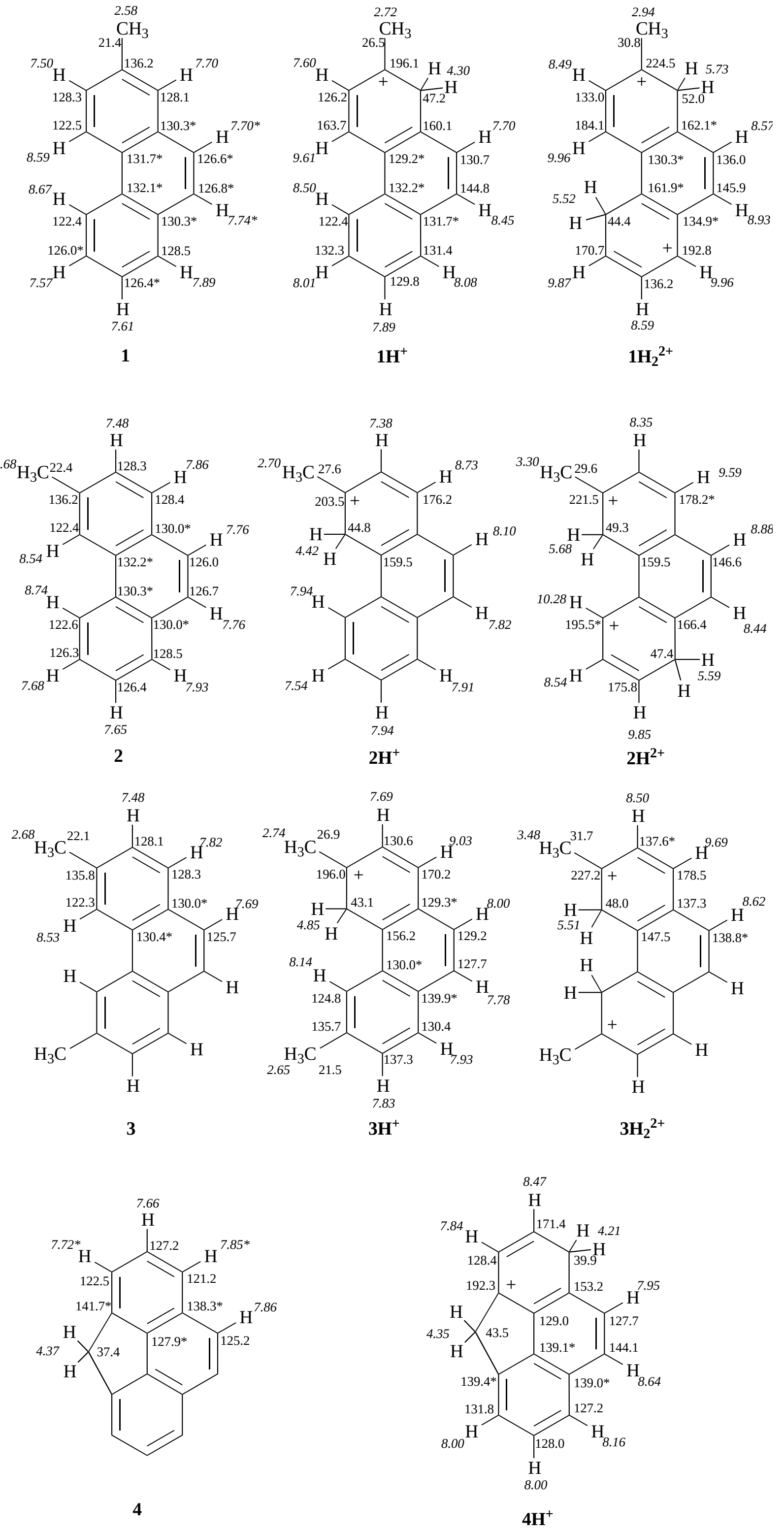


Fig. 1 ^1H (italic) and ^{13}C NMR chemical shifts of **1**–**4**, **$1H^+$**–**$4H^+$** and **$1H_2^{2+}$**–**$4H_2^{2+}$** (* indicates interchangeable assignments)

ion **$4H^+$** is formed exclusively (>95%) under stable ion conditions: the low temperature reaction of **4** with $FSO_3H–SO_2ClF$ gave a clear red solution whose ^1H NMR spectrum consisted of two CH_2 resonances at 4.35 and 4.21 ppm, six doublets and one triplet, the most deshielded of which was at 8.64 ppm. In the ^{13}C NMR spectrum, apart from the two CH_2 moieties, there are 13 aromatic resonances with the most deshielded one at 192.3 ppm. Detailed assignments were made (Fig. 1) based on H-H COSY, H-coupled, -decoupled ^{13}C and HETCOR spectra, and fine-tuned by taking into account the AM1-calculated charges. Protonation at C-1 rather than C-3 was deduced from AM1 calculations: the energy of C-1 protonated **$4H^+$** is *ca.* 3 kcal mol^{-3} lower than the C-3 protonated isomer; we were not able to clearly assign the protonation site of **4** based on the NMR data alone. Attempted diprotonation of **4** with $FSO_3H{\cdot}SbF_5$ (4 : 1)–SO_2ClF again produced the monocation **$4H^+$**.

The low temperature reaction of **4** with 'magic acid'–SO_2ClF did not produce a dication selectively, instead a complex mixture of mono- and di-cations were formed. Quenching of **$4H^+$** (generated in $FSO_3H–SO_2ClF$) gave in addition to intact **4** (*ca.* 45%), several (*ca.* 5–6) other as yet unidentified products, mostly having deshielded ^{13}C and ^1H methylene-bridge resonances.

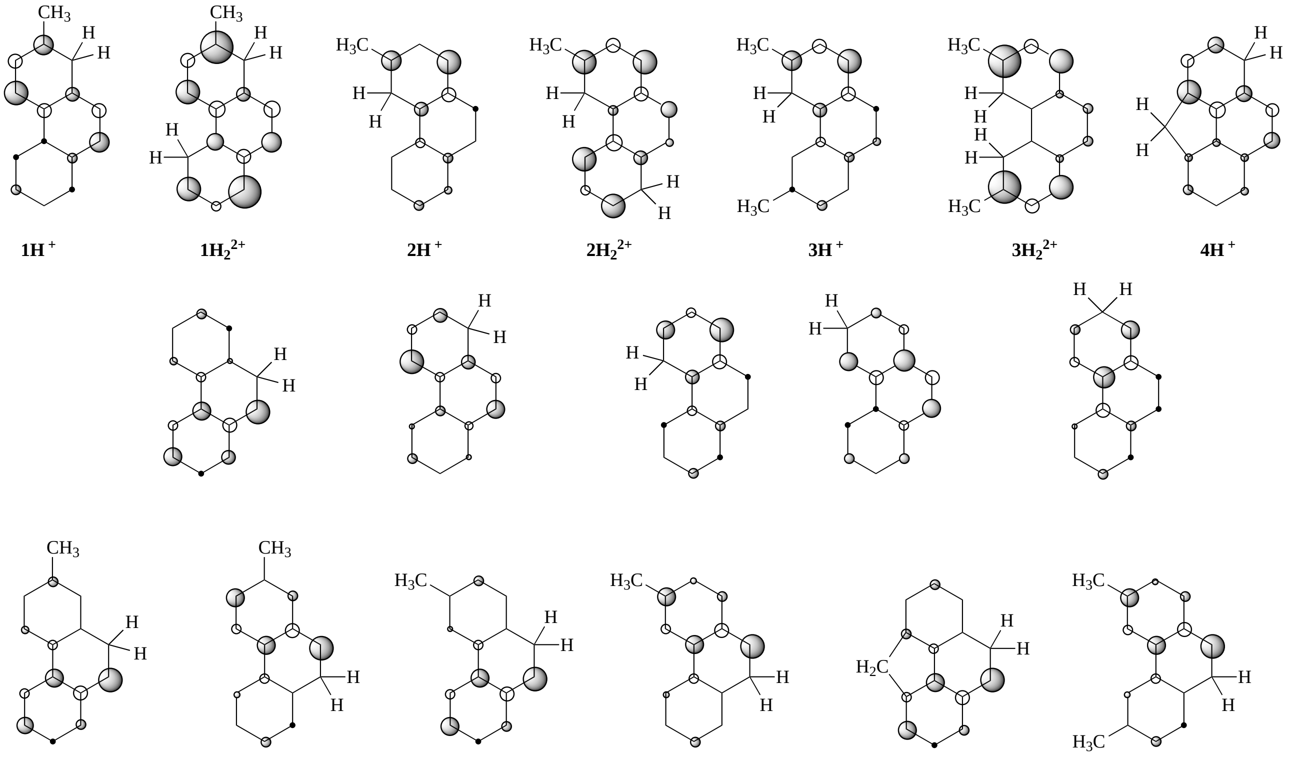


Fig. 2 Calculated charge delocalization pattern for **$1H^+$**–**$4H^+$** and **$1H_2^{2+}$**–**$4H_2^{2+}$** and other selected phenanthrenium cations

Parent phenanthrene

It was reported in an early study that attempted protonation of parent phenanthrene led to oxidation.[14] In the present study several attempts were made to generate the elusive phenanthrenium cation using a vacuum-line technique under more carefully controlled conditions. In all cases, blue solutions were formed showing very broad NMR features indicative of radical cation formation. In the protonation/oxidation manifold, the carbocation stabilizing effect of the methyl groups is, therefore, more important than their IP lowering effect; in accord with the early study, parent phenanthrenium ion remains elusive under superacid conditions.

Overall comparison of the charge delocalization mode (NMR and theory) in the mono- and di-cations

The total deshielding values ($\Sigma\Delta\delta_{^{13}C}$) in phenanthrenium monocations are between 158.4 and 163.8 ppm (Table 1). For the dications, the total deshielding amounts to 366.7 ppm for **3** (183.3 ppm e^{-1}) and 377.2 ppm for **1** (188.6 ppm e^{-1}), consistent with the dicationic nature of these arenium ions.[13]

Table 2 provides an overall comparison between the observed and predicted protonation sites and the corresponding differences in the heats of formation between the cations and the hydrocarbons. A plot of Δq (AM1 changes in carbon charges) and $\Delta\delta_{^{13}C}$ for representative phenanthrenium mono- and di-cations (**$1H^+$**, **$1H_2^{2+}$**, **$3H^+$**, **$3H_2^{2+}$**, **$4H^+$**) shows a reasonable correlation for carbons that do not carry much positive charge, but large deviations are observed for those with large $\Delta\delta_{^{13}C}$ values. Similar observations have been made with other delocalized carbocations.[15,32] Problems associated with a quantitative correlation have been addressed by Tolbert and Ogle[33] in the context of their work on delocalized carbanions. It is believed that the charge on carbon is exaggerated in AM1, since any quantitative meaning of Mulliken populations at this level of theory is uncertain. The use of these plots as a qualitative guideline is acceptable; there is good overall agreement between our stable ion work and the AM1 predictions.

Fig 2 provides a summary of charge delocalization patterns of the observed mono- and di-cations based on the magnitude of Δq values. Patterns for the elusive parent phenanthrene are also included (middle row). In view of the importance of K-region phenanthrene-9,10-epoxide,[5,10] the charge delocalization pattern for the *meso*-protonated substrates are also given in Fig. 2 (bottom row).

It becomes apparent that in the C-1 and C-4 protonated monocations, the positive charge is predominantly located in the AB rings with the *para* carbons always becoming more positive than the *orthos*, even when a methyl substituent is placed at an *ortho* carbon (as in **$1H^+$** and **$3H^+$**). The charge delocalization pattern in **$1H^+$** and the bridged **$4H^+$** is quite similar, except for the inductive stabilization of the C-2 methyl which enhances the positive charge at C-2 relative to C-10a.

The calculated charge delocalization pattern in the parent phenanthrenium cations are shown in Fig. 2 (middle row); the C-9 protonated phenanthrene has the lowest energy according to AM1. The delocalization path in C-9, C-1, C-4 and C-3 protonated phenanthrene is mainly into ring A and B, and ring C does not carry any appreciable positive charge. In the case of the C-2 protonated phenanthrene the charge distribution is mainly into ring A and C.

The calculated delocalization path for the *meso*-protonated phenanthrenes are shown in Fig. 2 (bottom row). In the case of the C-9 protonated phenanthrenes most of the positive charge is delocalized into ring A and B, and C-8a never carries any significant charge. In the case of the C-10 protonated phenanthrenes, the positive charge is mainly delocalized into ring B and C, and C-10a does not carry much charge. In general, the *meso*-protonated phenanthrenes all show similar conjugation paths (β-protonated naphthalenes).

Based on energy calculations for the substituted phenanthrenes and the parent phenanthrene itself, it can be concluded that *ipso*-protonation is always disfavored. Protonation at a site which leads to a cation where both C-α atoms carry a proton (*e.g.* positions C-2 and C-3 of the parent phenanthrene) are always less favored. An *ortho* methyl substituent (α to the protonation site) usually stabilizes the cation, whereas a *meta* methyl substituent (β to the CH_2 group) raises the arenium ion energy. These results are in good agreement with the general pattern of stabilization of carbocations.

For the phenanthrenium dications, the conjugation path varies depending on the sites of protonation. With $\mathbf{1H_2}^{2+}$, the charge is delocalized over the entire system at alternating carbons of the periphery, whereas in $\mathbf{3H_2}^{2+}$ the B ring does not participate in charge delocalization and positive charge is heavily retained at the methyl-bearing *ortho* site and at C-1/C-8 (*para*) carbons. Absence of delocalization into the annelated *ortho* carbons C-4a/C–C-4b is logical since destabilizing charge–charge repulsion is being avoided.

For the diprotonated phenanthrenes one of the two protonation sites is always the protonation site which was already observed in the monocations. The calculations never predict diprotonation involving two new sites to have the lowest energy, only doubly protonated ions with one of the two protonation sites already observed in the monoprotonated phenanthrenes are predicted to be formed. Diprotonations with CH_2 groups at rings A and C are usually more favored than diprotonations at rings A and B or B and C, and they are much more stable than diprotonations at the same ring, according to AM1 calculations.

The parallel between stable ion studies and solvolytic studies on epoxide ring opening in water

For the non-K-region epoxides, solvolysis of phenanthrene-1,2- and -3,4-epoxide gave phenanthrols exclusively.[5b] With the K-region 9,10-epoxide, phenols were predominant (~72%), but in addition dihydrodiols were formed (Scheme 3). The rate of phenol formation was three times greater than solvent trapping.[5b]

The more facile formation of phenols from the non-K-region epoxides was attributed to the higher stability of the carbenium ions and a lower free-energy difference (as compared to the 9,10-epoxide) between the carbenium ions and the transition state for the hydride shift.[5b]

Even though epoxidation at the *meso* position is favored due to bond-fixation (the double bond is more alkene-like), the resulting carbocation is not as stable as those formed by epoxide ring opening of the non-K-region epoxides. Hence a K-region epoxide undergoes nucleophilic attack by amines (epoxide ring opening is slow because the carbocation is less stable), whereas for non-K-region epoxides nucleophilic trapping is not competitive with aromatization.[5b]

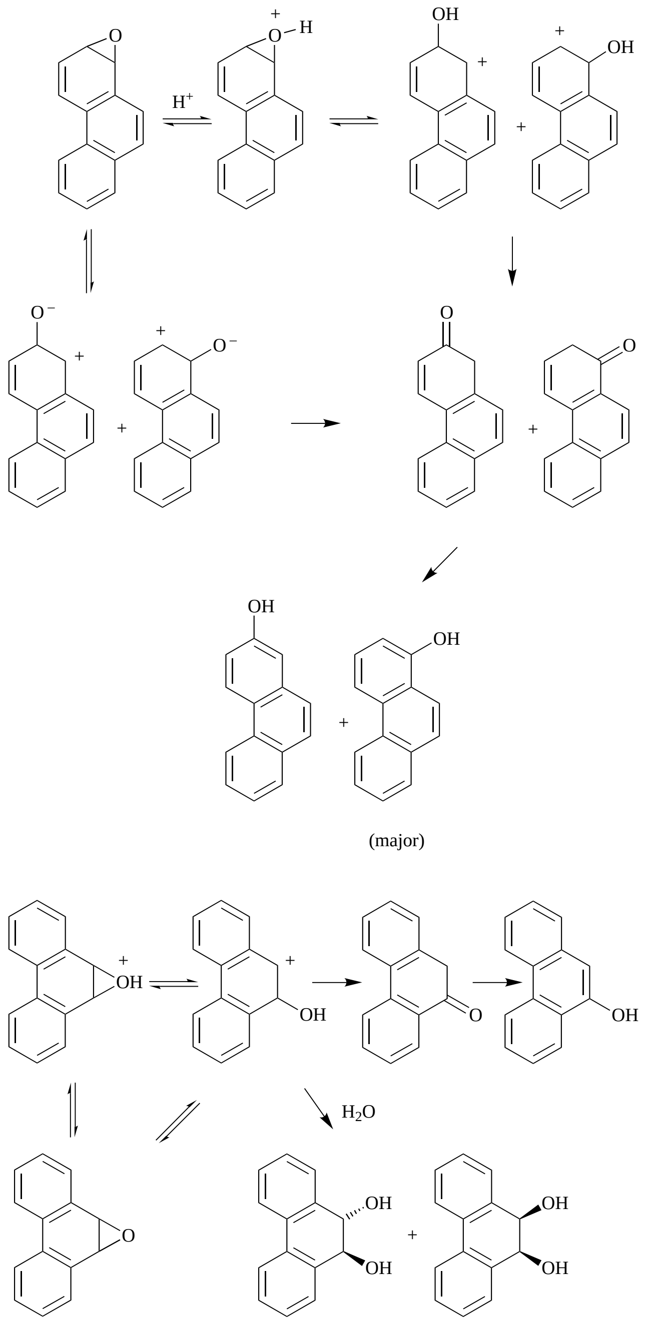
Our stable ion studies and AM1 calculations are in accord with the general conclusions made by Bruice and co-workers[5,10] based on solvolytic studies. The carbocation formed by opening of 1,2-epoxide closely resembles $\mathbf{1H}^+$ (and $\mathbf{4H}^+$) and the regiochemistry of phenol formation (1-phenanthrol) can be understood. Similarly, phenanthrenium cations $\mathbf{2H}^+$ and $\mathbf{3H}^+$ serve as models for carbocations formed by solvolysis of phenanthrene-3,4-epoxide (formation of 4-phenanthrol following hydride shift).

To assess the role of a β-OH on carbenium ion stability and charge delocalization, the feasibility of directly studying PAH–epoxides and their ring opening under stable ion conditions should be tested. These studies have been initiated in our laboratory.

Experimental

Materials

Phenanthrene, 2-methylphenanthrene (**1**), 3,6-dimethylphenanthrene (**3**), 4,5-cyclopenta[*def*]phenanthrene (**4**, all Aldrich) and 3-methylphenanthrene (**2**, K&K Laboratories) were used without further purification. FSO_3H (Allied) and SbF_5 (Fluorochem) were purified by double distillation at atmospheric pressure under dry argon. The $FSO_3H{\cdot}SbF_5$ mixtures were freshly prepared by adding the required molar amounts of FSO_3H to preweighed samples of SbF_5 in Nalgene bottles under a fast flow of argon.



Scheme 3 Solvolysis of the non-K-region and K-region phenanthrene epoxides studied by Bruice and co-workers[5,10]

NMR spectra

^1H and ^{13}C NMR spectra were recorded on a GE GN-300 Instrument. All the starting materials were recorded at room temp. using $CDCl_3$ as solvent. The stable ion spectra were obtained at temperatures between −60 and −90 °C. Usually the low concentration samples (*ca.* 15 mg) showed the best resolution at −85 °C, whereas the samples with higher concentration (*ca.* 30 mg) had the best resolution at about −60 °C. Methylene chloride was used as internal standard [δ_H(300 MHz) 5.32, δ_C(75 MHz) 53.8] for protonation experiments with FSO_3H. With FSO_3H–SbF_5 4:1 or 1:1 as superacids the spectra were referenced to external TMS which was sealed in a capillary together with [$^2H_6$]acetone and added to the NMR tube. The corrected chemical shifts corresponding to internal methylene chloride were determined from Table 3. The correction values were established by adding both methylene chlorine and the capillary to a solution of the superacid in SO_2ClF.

Table 3 Correction applied for the use of external capillary reference

Superacid	δ_H correction	δ_C correction
$FSO_3H–SbF_5$ 4:1	+0.86	+0.95
$FSO_3H–SbF_5$ 1:1	+0.95	+0.95

General procedure for stable ion generation

In a typical experiment, about 15–30 mg of the phenanthrenes were placed in a 5 mm NMR tube. The NMR tube was then connected to the high vacuum line (ace-thread port). After several cycles of evacuation and flushing with argon, the NMR tube was left under vacuum for *ca.* 5 min. About 0.3 ml SO_2ClF were condensed into the NMR tube which was cooled to liquid nitrogen temperature. After completion of the SO_2ClF addition, the liquid nitrogen bath was changed to a dry ice–acetone bath, and about 0.1 ml of superacid (FSO_3H, $FSO_3H–SbF_5$ 4:1 or 1:1) was slowly added under argon. The color immediately turned deep-red in the case of the substituted phenanthrenes and blue in the case of parent phenanthrene. After vigorous stirring at −78 °C (vortex) either CD_2Cl_2 (FSO_3H as superacid) or a sealed capillary of [$^2H_6$]acetone and 5% TMS were slowly inserted into the NMR tube (vortex).

Quenching experiments

In quenching experiments, the NMR tube containing the cation/superacid solution was carefully poured into ice-bicarbonate. The aqueous slurry was then extracted three times with Et_2O, the combined organic extract was washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was dissolved in $CDCl_3$ for NMR studies. All the starting materials could be reisolated.

AM1 calculations

AM1 calculations and energy minimizations were performed with the Hyperchem package (HYPERCUBE, 1994).

Acknowledgements

Support of our work on reactive intermediates of carcinogenesis of PAHs by the NCI of NIH (R15CA63595) is gratefully acknowledged. We thank NATO for a collaborative research grant (CRG 930113).

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Paper 7/03742B
Received 29*th May* 1997
Accepted 9*th July* 1997