Further insight *via* ^{15}N NMR spectroscopy into the reactive intermediates formed by superacid protonation of crowded nitro-PAHs: persistent dihydroxyiminiumpyrenium and hydroxyiminiumpyrenium dications

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Low temperature protonation of 1-nitropyrene and its ^{15}N-labelled isotopomer with $FSO_3H{\cdot}SbF_5$ (1 : 1) ('magic acid')–SO_2ClF (or SO_2) or with $FSO_3H{\cdot}SbF_5$ (4 : 1)–SO_2ClF generates either the dihydroxyiminiumpyrenium dication (NO_2 diprotonation) or the hydroxyiminiumpyrenium dication as the principle NMR observable persistent species (depending on the sample concentration, reaction time and the superacid). The latter is independently generated by diprotonation of authentic 1-nitrosopyrene. Variable formation of dihydroxyiminiumpyrenium and hydroxyiminiumpyrenium dications is also observed in the protonation of sterically crowded 1-nitro-2,7-di-*tert*-butylpyrene, which gives the corresponding dihydroxyiminiumpyrenium dication in $FSO_3H{\cdot}SbF_5$ (1 : 1)–SO_2ClF (or SO_2) and the hydroxyiminiumpyrenium dication by low temperature reaction with $FSO_3H{\cdot}SO_2ClF$ or $CF_3SO_3H{\cdot}SO_2$. Protonation of the buttressed 1-nitro-2,4,6,8,10-pentaisopropylpyrene and its ^{15}N-labelled isotopomer produces the dihydroxyiminiumpyrenium dication (no NMR evidence for the formation of the hydroxyiminiumpyrenium dication) which, as shown before (*J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 537), undergoes a facile cyclization to the oxazoline-fused pyrenium cation for which ^{15}N NMR data are now presented. Diprotonation and subsequent cyclization of the singly ^{15}N-labelled 1,3-dinitro-2,4,6,8,10-pentaisopropylpyrene are also studied. Whereas our work reaffirms the generality of NO_2 diprotonation in nitropyrenes, it focuses attention on an additional pathway leading to =NH(OH) dication formation.

PM3 calculations are used as a complementary tool to examine the geometries and energies of the resulting dications.

Introduction

Due to their wide-spread presence in the environment and variable genotoxic activities, the nitro derivatives of alternant and nonalternant polycyclic aromatic hydrocarbons (nitro-PAHs) continue to be intensely studied.[1–12] Nitro group reduction (→PAH–NHOH) and ring oxidation constitute the two principle pathways by which nitro-PAHs are activated.[1,3,4,7,10] Nitrenium ions are invoked as the reactive intermediates which bind to DNA. DNA-binding to a site remote from the amino group has also been observed and interpreted as an S_N1 process involving nitrenium ion formation and nucleophilic trapping of the mesomeric carbocations.[4,5]

Generally, the observed potencies of nitro-PAHs are very much structure dependent. Thus the mutagenicity order 4 > 2 > 1 has been established for the regioisomeric nitropyrenes. Some nitro-PAHs, such as dinitropyrenes, are 'super' mutagens.[2]

Several studies have emphasized the importance of nitro group orientation.[3,6,11] Planar nitro-PAHs showed increased bacterial mutagenicity and tumorigenicity whereas buttressed nitro-PAHs, where *peri*-strain forces the nitro group out of conjugation with the PAH, exhibited reduced activity.

A relationship has been found between the intensity of the $[M - 30]^+$ fragment ion (loss of NO) in the EI mass spectra and the degree of buttressing of the NO_2 group.[7] The NO_2→ONO rearrangement has been suggested with increasing torsion angle. Using MS/MS experiments with isomeric nitrofluoranthene (NF), it was found that a *peri*-H (1-NF) or a pseudo-bay-H (3-NF) can transfer to the nitro group and subsequently rearrange to a hydroxynitrosoarene which loses NO.[13]

Considering the biological importance and the available data, direct studies of the electrophiles formed from nitro-PAHs are quite relevant and may help provide a more comprehensive picture. As with the parent PAHs and their alkyl and fluoro derivatives,[14–18] we have been using low temperature protonation studies to model the biological electrophiles, in particular to address the protonation mode as a function of nitro group orientation.

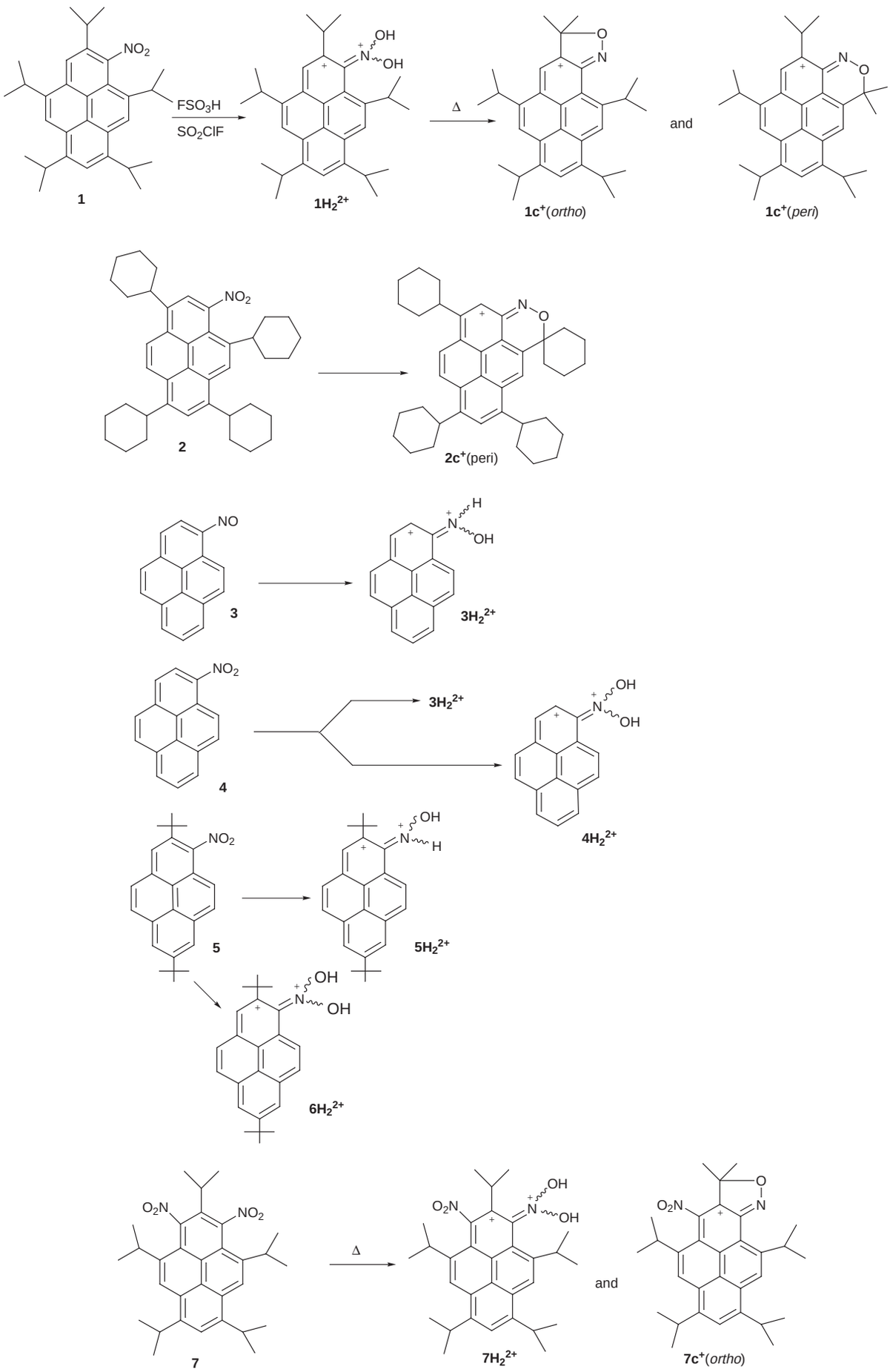
In previous studies,[19,20] nitro group diprotonation to form dihydroxyiminiumpyrenium dications was shown for a series of strained mono- and di-nitropyrenes, and the charge delocalization pathways in the resulting dications were examined based on the magnitude of $\Delta\delta_C$ values.[19]

Following the formation of dihydroxyiminium dications a facile cyclization involving the *ortho* and/or *peri* isopropyl group was observed, forming 5-membered ring oxazoline-fused and 6-membered ring oxazine-fused derivatives (Scheme 1), with 5-membered ring formation $\mathbf{1c}^+$ (*ortho*) being more facile than 6-membered ring $\mathbf{1c}^+$ (*peri*).[19]

The OH protons could not be observed as independent resonances, even in 'magic acid'. Although this may suggest oxoiminiumpyrenium dication formation, based on indirect NMR evidence, namely the equivalence and non-equivalence of the isopropyl groups in the case of $\mathbf{1H_2}^{+2}$, we argued that dihydroxyiminium formation was more probable.[19]

Nitro group cyclization was observed by Ridd and coworkers for nitroalkylbenzenes at high temperature in triflic acid, where for example anthranil is formed from 1-ethyl- and 1,3-diethyl-2-nitrobenzene.[21–23] Nitro reduction was also observed for 2-nitrobenzyl alcohol, 2-nitrobenzyl chloride and 2-nitrosobenzaldehyde by heating in triflic acid.[24]

In our case, although the iminiumpyrenium structure of the resulting dications was secured based on detailed ^{13}C and ^{1}H



Scheme 1 Superacid protonations of crowded nitroalkyl(cycloalkyl)pyrenes, nitropyrene and nitrosopyrene

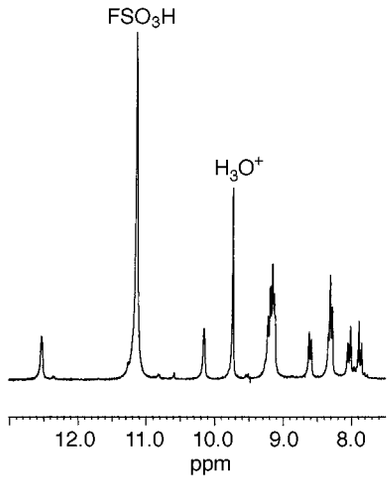


Fig. 1 ^{1}H NMR spectrum of $\mathbf{3H_2}^{2+}$

NMR studies, the exact identities of the cations formed were not unambiguous.

We now report complimentary studies emphasizing ^{15}N NMR analysis and a comparative protonation study on authentic nitrosopyrene in order to elucidate these structures more fully.

Results and discussion

Protonation of 1-nitrosopyrene 3

Low temperature reaction of 'magic acid'–SO_2ClF with nitrosopyrene in SO_2ClF (Scheme 1) gave a dark red–brown solution at dry ice–acetone temperature. Its ^{1}H NMR spectrum (Fig. 1) exhibits eight doublets and a triplet and ring protonation is clearly ruled out. Two distinct low-field resonances are observed at δ_H 12.64 (NH) and 10.27 (OH) (1H each). A $^{3}J_{H/H}$ of *ca.* 3 Hz is seen between the OH and NH protons. Absence of a NOE between the δ_H 10.27 resonance and the aromatic protons, taken together with NH/OH coupling, is indicative of the *syn*-stereochemistry for the =NH(OH) group (see also further). The observed ^{1}H NMR chemical shifts for NH and OH are comparable with those of diprotonated benzoquinone monooximes studied by Olah and Donovan.[25]

The natural abundance ^{15}N NMR spectrum gave rise to just one resonance at δ_H −156.5 which appeared as a 106.4 Hz doublet in the proton-coupled spectrum. The iminium carbon was observed at δ_C 150.1 in the ^{13}C NMR spectrum. The charge delocalization in $\mathbf{3H_2}^{2+}$ (Fig. 2) is similar to that of $\mathbf{4H_2}^{2+}$ except at C-1 (ref. 19), leading to a lower total deshielding ($\Sigma\Delta\delta_C$) of 189.3 for the former.

The relative energies of the four different geometrical isomers of hydroxyiminiumpyrenium dication $\mathbf{3H_2}^{2+}$ were calculated by the PM3 method (Fig. 3). It was predicted that the *syn*-1 and *anti*-2 conformations have nearly identical energies (within 0.1 kcal mol^{-1}), followed closely by the *syn*-2 conformation (*ca.* 0.3 kcal mol^{-1} higher), whereas *anti*-1 was clearly less favourable (3.6 kcal mol^{-1} higher than *syn*-1).

Protonation of 1-nitropyrene 4 revisited

As previously pointed out,[19,20] due to its reduced basicity (as compared to alkyl(cycloalkyl)nitropyrenes, frozen arenium ions can not be generated with FSO_3H or CF_3SO_3H

Addition of a cold solution of 'magic acid' in SO_2 (or in SO_2ClF) of $FSO_3H{\cdot}SbF_5$ (4:1)–SO_2ClF to a slurry of **4** in the same co-solvent led to the formation of either the hydroxyiminiumpyrenium or the dihydroxyiminiumpyrenium dication (usually as a dark red solution), depending on the superacid and ion concentration.

In the present study, the ^{15}N-labelled isotopomer was reacted with 'magic acid'–SO_2ClF. In the ^{15}N NMR spectrum two

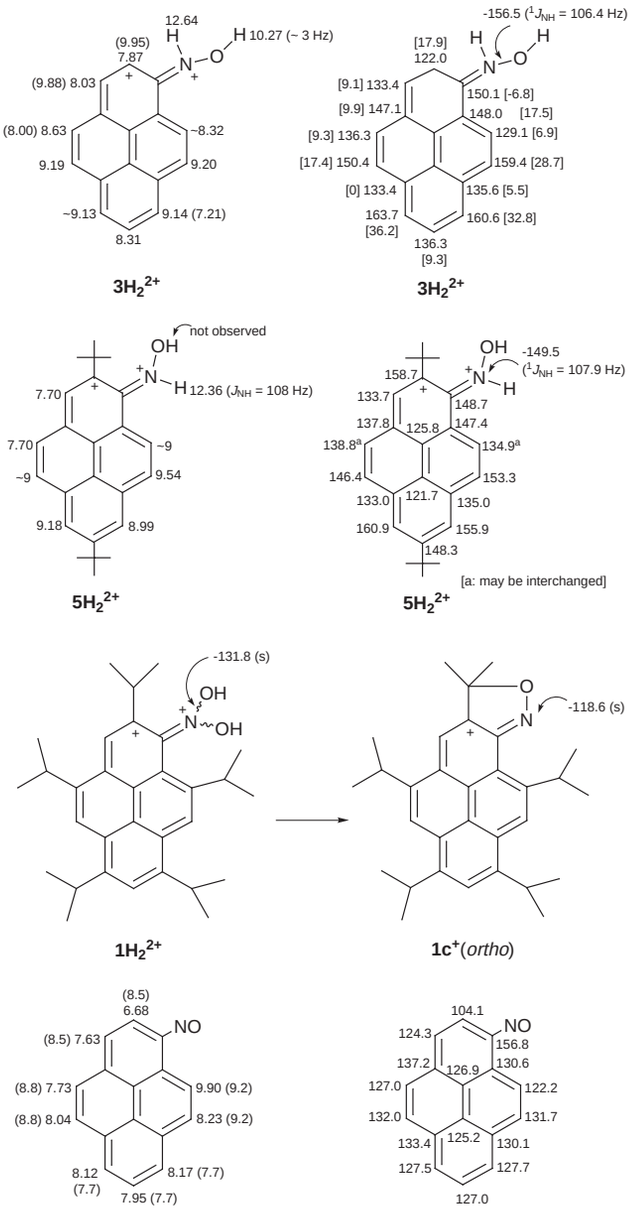


Fig. 2 ^{1}H, ^{13}C and ^{15}N NMR data for protonated nitroso- and nitropyrenes. NMR data for nitrosopyrene itself are included; ( ) coupling constants; [ ] $\Delta\delta_C$ values.

resonances were observed at δ_N −156.4 ($^{1}J_{NH}$ = 106.4 Hz) and −145.7 ($^{1}J_{NH}$ = 108 Hz). The former value is identical to that of dication $\mathbf{3H_2}^{2+}$ formed *via* nitrosopyrene **3**. The close chemical shifts of the NH doublets infers two closely related =NH(OH) dications, possibly as geometrical isomers. The absence of a NOE (see protonation of nitrosopyrene) once again argues in favour of the *syn*-stereochemistry; these may be the *syn*-1 and *syn*-2 forms having close energies (PM3).†

In the ^{1}H NMR spectrum the OH proton is observed at δ_H 10.39 and the NH is seen as a triplet at δ_H 12.71 ($^{1}J_{NH}$ = 107.3 Hz) for the major species. The second species exhibits a triplet at δ_H 12.56. The combined data in comparison with those of $\mathbf{3H_2}^{2+}$ formed *via* nitrosopyrene clearly point to hydroxyiminiumpyrenium dication formation from 1-nitropyrene in the superacid. In addition, there is a small amount of the dihydroxyiminium species [δ 11.26 (s) and 10.39 (s); δ_N −128.4 (s)].

Protonation of **4** and its ^{15}N-labelled isotopomer were studied in 'magic acid'–SO_2 in several independent reactions at lower

† Since PM3 calculations refer to gas phase stabilities, their reliability for dications in superacid solvents may be questionable.

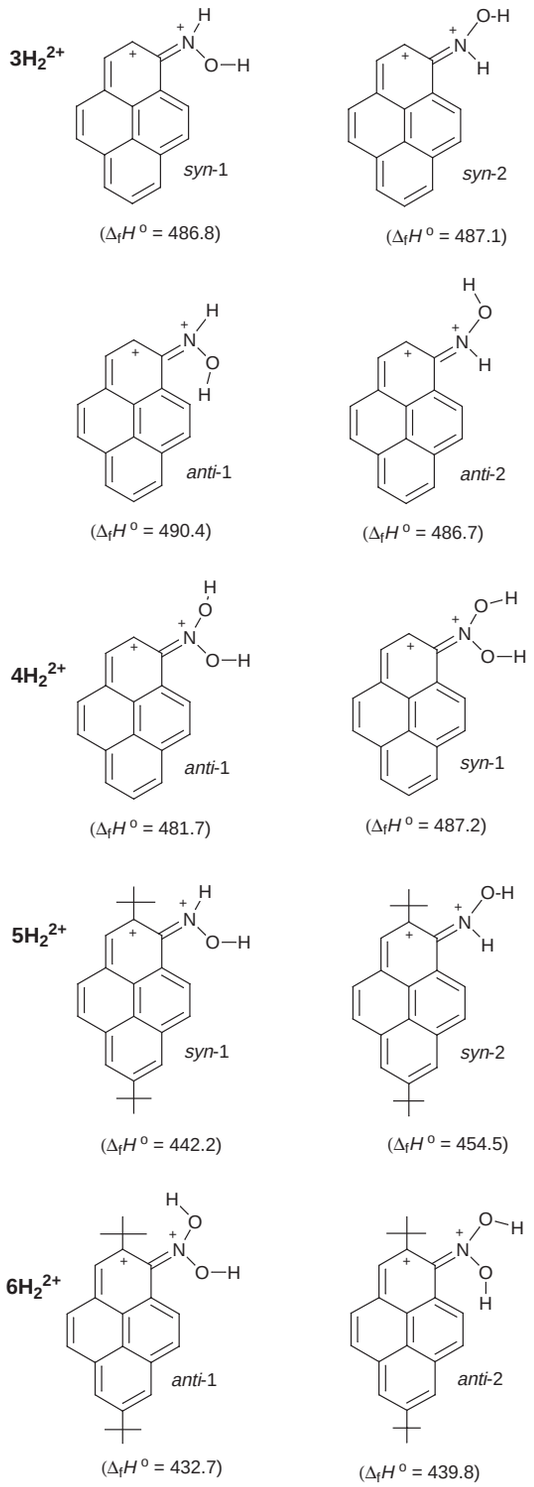


Fig. 3 PM3 energies for various isomeric hydroxyiminium- and dihydroxyiminium-pyrenium dications

concentrations suitable for ^{1}H NMR studies. In these cases, two low field resonances at δ_H 10.57 and 11.24 (1H each) were observed in between the superacid peak and H_3O^+ resonance. These are assigned to the two OH groups of dihydroxyiminiumpyrenium dication $\mathbf{4H_2}^{2+}$.‡

For the ^{15}N-labelled nitropyrene, protonation in 'magic acid'–SO_2 similarly led to dihydroxyiminiumpyrenium dication formation (the NH triplet was clearly absent). In this case, a by-product was also formed and increased with time and/or temperature. Whereas ring protonation could be excluded, the identity of the by-product remains undetermined.

PM3 energy minimizations suggest that for $\mathbf{4H_2}^{2+}$ the *anti*-1 form is favoured over *syn*-1 by 6.5 kcal mol^{-1} (Fig. 3). The dihydroxyiminium species with a W-conformation, with the OH groups both pointing towards the *ortho*- and *peri*-hydrogens, converged to the *anti*-1 form. The PM3-calculated C=N bond length (1.334 Å for *anti*-1) is slightly shorter than that for hydroxyiminium dication (1.338 Å for *anti*-1).

Quenching of the magic acid solution of 1-nitropyrene gave a mixture of 1-nitropyrene and 1-nitrosopyrene (assayed by ^{1}H NMR spectroscopy).

Protonation of 2,7-di-*tert*-butyl-1-nitropyrene 5

As part of a broader study of nitro diprotonation in sterically crowded nitroalkylpyrenes and their cyclization, we had also examined the protonation of **5** in various superacid media, namely FSO_3H–SO_2, CF_3SO_3H–SO_2 and 'magic acid'–SO_2 (or SO_2ClF).[19] Based on the ^{13}C and ^{1}H NMR spectral data (Fig. 2), the resulting dication was assigned to the dihydroxyiminium and the derived oxoiminium species in all cases, despite slightly more deshielded ^{13}C NMR values in 'magic acid'.

In the present study, the ^{15}N-labelled isotopomer was investigated in FSO_3H–SO_2ClF solvent. The ^{15}N NMR spectrum exhibited just one resonance at δ_N −149.5 which gave rise to a doublet on proton-coupling ($^1J_{NH}$ = 107.4 Hz). Increasing temperature had no effect on the ^{15}N NMR spectrum, in agreement with the lack of subsequent cyclization in this case as reported before.[19] The ^{1}H NMR spectrum of this sample clearly shows an NH triplet at δ_H 12.36 (J_{NH} = 108 Hz); these results are consistent with an hydroxyiminiumpyrenium dication $\mathbf{5H_2}^{2+}$. The OH is not observed as a separate resonance and either must be exchanging at these acidities or is hidden underneath the acid peak.

Independent protonation of **5** in 'magic acid'–SO_2 gave rise to the dihydroxyiminiumpyrenium dication $\mathbf{6H_2}^{2+}$ as previously assigned. In the ^{1}H NMR spectrum two low-field singlets at δ_H 10.46 and 11.13 (1H each) are tentatively ascribed to the two OH groups.

PM3 energy minimizations (Fig. 3) indicated that for $\mathbf{5H_2}^{2+}$, the *anti*-1 and *anti*-2 geometrical isomers were unfavorable. These converged to the *syn*-1 and *syn*-2, with the *syn*-1 form being strongly favoured (by 12.3 kcal mol^{-1}). For $\mathbf{6H_2}^{2+}$, the *anti*-1 conformer is preferred over *anti*-2 and the *syn*-1 conformer converged to *anti*-1.

Protonation of 1-nitro-2,4,6,8,10-pentaisopropylpyrene 1

Protonation of **1** with FSO_3H–SO_2 (or SO_2ClF) and CF_3SO_3H–SO_2 was examined previously and the resulting dication was assigned a dihydroxyiminiumpyrenium dication $\mathbf{1H_2}^{2+}$, which subsequently undergoes rapid cyclization to form $\mathbf{1c}^+$ (*ortho*) (Scheme 1). In the present study, the ^{15}N-labelled isotopomer was synthesized and protonated at low temperature with FSO_3H–SO_2ClF. In the proton-decoupled ^{15}N NMR spectrum, a singlet was observed at δ_N −131.8, shielded from the precursor by 134.2 ppm. This resonance remained a singlet on proton coupling. Upon gentle warming and recooling the ^{1}H NMR spectrum clearly indicated the onset of cyclization, which was complete within minutes. The ^{15}N NMR spectrum of the oxazoline-fused cation $\mathbf{1c}^+$ (*ortho*) moved to δ_N −118.6 ppm ($\Delta\delta_N$ = 13.2). The ^{1}H NMR spectra of the ^{15}N labelled isotopomer before and after cyclization were very similar to those observed previously and reported for these dications.[19,20]

The PM3 geometries and energies for the cyclized oxazoline and oxazine monocations were also examined. Both were predicted to be nearly planar, with the *peri*-fused analogue being 5.5 kcal mol^{-1} more stable. Our superacid solution studies suggest that the formation of *peri*-cyclized cation is kinetically less favored (entropic reason?) in solution.

‡ In previous work, in line with observations of protonated aliphatic nitro compounds, we had assumed that two much smaller broad low field peaks at δ_H 15.20 and 15.40 were due to the OH protons.

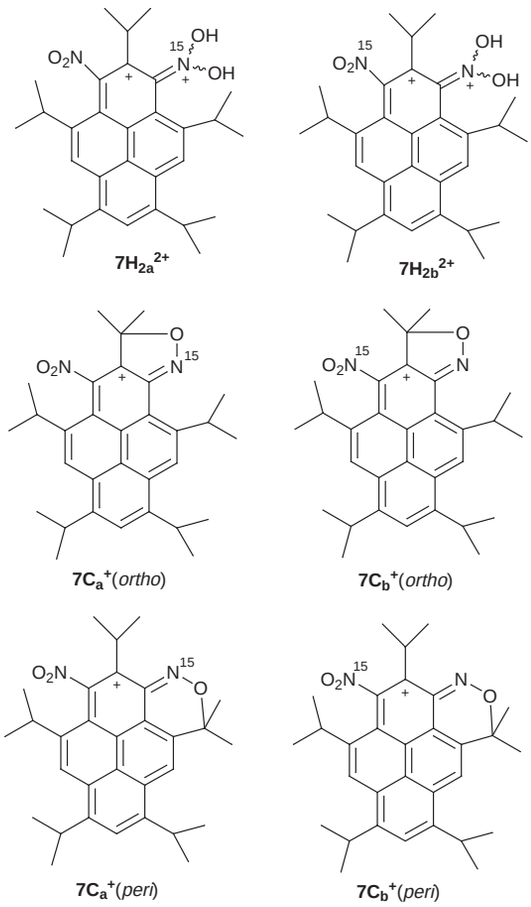


Fig. 4 Dications formed by NO_2-diprotonation of the singly ^{15}N-labelled **7**

Protonation of singly ^{15}N-labelled 1,3-dinitro-2,4,6,8,10-pentaisopropylpyrene 7

Since a pure sample of mono-labelled dintropentaisopropylpyrene could not be obtained, a mixture of **7** and **1**, whose ^{15}N NMR spectrum had shown a major resonance at δ_N 2.7 for the mononitro and a minor one at δ_N −2.25 (assigned to the singly-labelled dinitro compound), was reacted with FSO_3H–SO_2ClF and examined by ^{15}N NMR spectroscopy. Apart from the dihydroxyiminiumpyrenium dication $\mathbf{1H_2}^{2+}$ (Scheme 1) and its cyclized derivative $\mathbf{1c}^+$ (*ortho*), other ^{15}N NMR resonances were present at δ_N −135.76 and −112.5 which are tentatively assigned to $\mathbf{7H_{2a}}^{2+}$ and $\mathbf{7H_{2b}}^{2+}$ respectively (Fig. 4). In time or upon gentle heating the diprotonated species were converted into $\mathbf{7C_a}^+$(*ortho*) and $\mathbf{7C_b}^+$(*ortho*) (appearance of resonances at δ_N −112.5 and −9.8). The ^1H NMR spectra support the presence of the cyclized species, showing aromatic resonances at δ_H 9.54, 9.41 and 8.36. In addition to these, the resonances of $\mathbf{1c}^+$(*ortho*) are clearly present together with some broad less intense resonances. The ^{15}N NMR spectra show in addition unidentified peaks at δ_N −121.7 (disappears upon warming), 0.4, 0.08 and −0.1. The two former are unchanged by heating. Increasing sample temperature led to the appearance of resonances at δ_N −112.45 and −11.40. The latter may possibly be due to the *peri*-cyclized cations $\mathbf{7C_a}^+$(*peri*) and $\mathbf{7C_b}^+$(*peri*).

Comparative discussion of the protonation features: the parent nitro-PAHs

The NMR, UV and MMX force field minimization data for **1** and **6** have been previously discussed.[20] The ^{15}N NMR chemical shifts in nitromesitylene (δ_N −0.5)[26] and nitrobenzene (δ_N −9.8)[27] suggest a deshielding trend with increased steric crowding. The observed ^{15}N values for **4** (δ_N −7.1), **5** (δ_N 0.1), **1** (δ_N 2.7) and **7** (δ_N −2.2) are indicative of an upfield trend, but this is complicated by the fact that *ortho*/*peri* alkyl buttressing effects are also operating.

Nitrosopyrene is diprotonated in 'magic acid'–SO_2ClF to form the =NH(OH) dication $\mathbf{3H_2}^{2+}$. With nitropyrene either the hydroxyiminiumpyrenium dication or the dihydroxyiminiumpyrenium species can be observed depending on sample concentration, reaction time and the superacid. In view of the fact that PAH–NHOH compounds are ultimate carcinogens and the reported higher mutagenic activity of planar PAH–NO_2 facile formation of =NHOH dications in nitro(alkyl)pyrenes in superacid media is noteworthy.

The ^1H and ^{13}C NMR data for $\mathbf{3H_2}^{2+}$, $\mathbf{4H_2}^{2+}$ and $\mathbf{5H_2}^{2+}$, $\mathbf{6H_2}^{2+}$ are pairwise similar though not identical (Fig. 2 and ref. 19). Hence, the structures suggested in Scheme 1 are now in very good agreement with both the ^{15}N and ^1H/^{13}C NMR data. The previously suggested oxoiminium dications can now be better understood as hydroxyiminium ions.

It is interesting that the ^{15}N NMR chemical shifts for PAH=NHOH (δ_N *ca.* −130) and PAH=N(OH)$_2$ dications (δ_N *ca.* −150) are fairly close, showing that the effect of the extra oxygen is small. They fall in the general range for iminium ions (δ_N (−126 to −260).[28] The reported value of δ_N −30 for NO_2-diprotonated 1-nitronaphthalene falls clearly out of this range.[29]

The observed ^{15}N NMR chemical shifts for the oxazoline-fused iminium ion $\mathbf{7c}^+$(*ortho*) (δ_N −118.6) differs considerably with those of oximes[30] or benzofurazan 1-oxide,[31] which infers that in superacids the oxazoline is most likely N-protonated, despite the fact that the NH is not observable as a separate resonance and no one-bond NH coupling can be detected.

The NO_2 group protonation shifts obtained by comparing the data for $\mathbf{4H_2}^{2+}$ and **4**, $\mathbf{1H_2}^{2+}$ and **1** and $\mathbf{6H_2}^{2+}$ and **5** are similar, suggesting that steric crowding has no major influence. The NO protonation shifts are expected to be much larger (*ca.* 670 ppm). The ^{15}N NMR chemical shift of **3** has not been measured, but for PhNO it is δ_N 532,[32] and that of **3** close, judging from the similarity of the NO_2 group chemical shifts.

Comment on possible mode of *in situ* reduction in the superacid

Nitro group reduction was observed by Austin and Ridd,[23] where *via* heating in triflic acid, 4-amino-3-carboxyphenyl triflate was obtained in good yield from 2-nitrobenzyl alcohol. A mechanism involving *ortho*-cyclization, hydride shift and ring-opening was suggested. In our case, persistent hydroxyiminiumpyrenium dications are formed from nitropyrene and 2,4-di-*tert*-butyl-1-nitropyrene where benzylic-hydrogens are unavailable.

In a different context, we previously observed reduction in highly oxidizing superacids when simple arenes reacted with 'magic acid'–SO_2 to give diaryl sulfoxides and diaryl sulfones.[33] It is tentatively proposed that nitro reduction may originate from nucleophilic attack at the nitrogen of the oxoiminium dication (present in equilibrium) by FSO_3^- (or TfO^-) and O-protonation to form =NOH(OSO_2F) dication, which undergoes 'nucleophilic' displacement (by FSO_3^-) and N-protonation to form the =NHOH species.§

Experimental

Syntheses of **1**, **5** and **7** have previously been reported.[20] The ^{15}N-labelled nitropyrene was prepared by mild nitration of the pyrene precursor with 64% enriched sodium nitrate in warm glacial acetic acid. The singly-labelled dinitro compound was prepared by protic mononitration of the singly-labelled **1** with HNO_3–H_2SO_4.

FSO_3H (Aldrich or Linde), SbF_5 (Aldrich or Fluorochem)

§ Bis(fluorosulfonyl) peroxide $S_2O_6F_2$ would be the oxidation product!

and TfOH (Aldrich) were doubly distilled and stored in Nalgene bottles under argon.

The procedures for stable ion generation and low temperature NMR studies were similar to those previously described.[16–19]

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 and a GN-GE300 instruments. The ^{15}N NMR spectra were recorded at 25.35 MHz on a Bruker AC-250 using 10 mm NMR tubes and $MeNO_2$ as external reference.

PM3 calculations were performed with the HYPERCHEM package (Hypercube 1994).

Acknowledgements

We thank Dr Simon Bolvig for assistance with the synthesis of ^{15}N-labelled substrates. Financial assistance by the Danish Natural Science Research Council, NATO (CRG930113) and the NCI of NIH (R15 CA63595-01A1) is gratefully acknowledged.

References

1 P. Upadhaya, L. S. von Tunglen, P. P. Fu and K. El-Bayoumy, *Chem. Res. Toxicol.*, 1994, **7**, 690.
2 B. P. Cho, *Org. Prep. Proced. Int.*, 1995, **27**, 243.
3 K. Fukuhara, M. Takei, H. Kageyama and N. Miyata, *Chem. Res. Toxicol*, 1995, **8**, 47.
4 D. Herrerno-Saez, F. E. Evans and P. P. Fu, *Chem. Res. Toxicol.*, 1994, **7**, 806.
5 W. A. Vance and R. Chan, *Environ. Mutagen.*, 1983, **5**, 859.
6 P. P. Fu, Y.-C. Ni, Y.-M. Zhang; R. H. Heflich, Y.-X. Wang and J.-S. Lai, *Mutat. Res.*, 1989, **225**, 121.
7 S.-T. Lin, Y.-F. Jih and P. P. Fu, *J. Org. Chem.*, 1996, **61**, 5271.
8 B. P. Cho, M. Kim and R. G. Harvey, *J. Org. Chem.*, 1993, **58**, 5788.
9 A. M. van den Braken van Leersum, J. Cornelisse and J. Lugtenburg, *Tetrahedron Lett.*, 1985, 4823.
10 Y.-S. Yu, J.-S. Lai and P. P. Fu, *J. Org. Chem.*, 1993, **58**, 7283.
11 K. Fukhari, M. Takei, H. Kageyama and N. Miyata, *Chem. Res. Toxicol.*, 1994, **7**, 357.
12 F. E. Evans, J. Deck and P. C. Howard, *Chem. Res. Toxicol.*, 1994, **7**, 357.
13 A. M. Dietrich, C. R. Guenat and L. M. Ball, *Abstracts of 35th ASMS conference on Mass Spectrometry and Allied Topics*, Denver, CO, May 1987.
14 Review: K. K. Laali, *Chem. Rev.*, 1996, **96**, 1873.
15 K. K. Laali, S. Hollenstein, R. G. Harvey and P. E. Hansen, *J. Org. Chem.*, 1997, **62**, 5804.
16 K. K. Laali and P. E. Hansen, *J. Org. Chem.*, 1997, **62**, 5804.
17 K. K. Laali, M. Tanaka, S. Hollenstein and M. Cheng, *J. Org. Chem.*, 1997, **62**, 7752.
18 K. K. Laali, S. Hollenstein and P. E. Hansen, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 2207.
19 K. K. Laali, S. Bolvig and P. E. Hansen, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 537.
20 K. K. Laali, T.-M. Liang and P. E. Hansen, *J. Org. Chem.*, 1992, **57**, 2658.
21 J. V. Bullen, J. H. Ridd and O. Sabek, *Gazz. Chim. Ital.*, 1990, **120**, 291.
22 J. V. Bullen and J. H. Ridd, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 1681.
23 R. P. Austin and J. H. Ridd, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 1411.
24 R. P. Austin and J. H. Ridd, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 1229.
25 G. A. Olah and D. J. Donovan, *J. Org. Chem.*, 1978, **43**, 1743.
26 S. Berger, S. Braun and H.-O. Kalinowski, *^{15}N NMR Spectroscopie*, Thieme Verlag, Stuttgart, 1992, vol. 2.
27 D. J. Craik, G. C. Levery and R. T. C. Brownlee, *J. Org. Chem.*, 1983, **48**, 1601.
28 G. J. Martin, M. L. Martin and J.-P. Gouesnard, *^{15}N NMR Spectroscopy*, in *NMR Basic Principles and Progress*, ed. P. Diehl, E. Fluck and R. Kosfeld, 1981.
29 T. Ohta, K. Shudo and T. Okomoto, *Tetrahedron Lett.*, 1984, **25**, 325.
30 *Nitrogen NMR*, ed. M. Witanowski and G. A. Webb, Plenum, London, 1973.
31 I. Yavari, R. E. Botto and J. D. Roberts, *J. Org. Chem.*, 1978, **43**, 2542.
32 G. C. Levy and R. L. Lichter, *Nitrogen*-15 *Nuclear Magnetic Resonance Spectroscopy*, Wiley Interscience, New York, 1979.
33 (*a*) K. K. Laali and D. S. Nagvekar, *J. Org. Chem.*, 1991, **56**, 1867; (*b*) K. K. Laali and J. J. Houser, *J. Phys. Org. Chem.*, 1992, **5**, 244.

Paper 8/00208H
Received 6*th January* 1998
Accepted 27*th February* 1998