Nitration of Isopropylpyrenes. Strained Models for Protonation and Transfer–Nitration in the Condensed Phase

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Protic mono- and dinitration of 1,3,5,7,9-pentaisopropylpyrene (**1**) occurred at the available α positions to give **2** and **3**. Despite steric crowding, **2** and **3** did not exhibit a torsional barrier to *i*-Pr rotation at ambient temperatures; however, buttressing of the peri *i*-Pr groups was evident (^{1}H NMR, UV, and force field energy minimizations). Persistent (dihydroxyiminium)pyrenium dications $\mathbf{2a}^{+2}$ and $\mathbf{3a}^{+2}$ were formed by low temperature protonation of **2** and **3** with CF_3SO_3H (TfOH)/SO_2 or with FSO_3H/SO_2. Intramolecular cyclization of the nitro group of $\mathbf{2a}^{+2}$ gave the rearranged pyrenium ion $\mathbf{2c}^+$. **1** reacted with $NO_2^+BF_4^-$ in acetonitrile solvent to give two pyrenium ions stable at rt, viz. the Wheland intermediate of α-nitration $\mathbf{2b}^{+2}$ and the (dihydroxyiminium)pyrenium dication $\mathbf{2a}^{+2}$; the latter was also the predominant pyrenium ion formed in the reaction of **1** with $NO^+BF_4^-$ in acetonitrile. Reaction of **1** with $NO_2^+BF_4^-$ in chloroform solvent gave α-nitration products and a persistent radical cation RC. The simultaneous presence of α-nitration products and a persistent pyrenium RC was also observed in the reaction of **1** with $NO^+BF_4^-$ in chloroform, where broader NMR line widths and a stronger ESR signal suggested more extensive oxidation. Protic and aprotic nitrations of 1,3,6,8-tetraisopropylpyrene (**10**) occurred at the $\alpha\beta$ positions; a minor addition product (**26**) was also found. A mixture of isomeric dinitropyrenes was obtained in NO_2^+ nitration of 1-isopropylpyrene (**13**). In line with low temperature protonation studies, aprotic nitrations of 2-isopropyl- and 4-isopropylpyrenes occurred predominantly at the α positions. The crowded pyrenium ion of **3** and **2** transfer nitrate to aromatics (toluene, mesitylene, benzene) under mild conditions in competition with a more facile transalkylation.

Introduction

Nitrated polycyclic aromatic hydrocarbons, PAHs, and especially nitropyrenes, are well-recognized environmental mutagens that are produced in the atmosphere through combustion processes.[1] Their mutagenic activity appears to be related to the number and position of the nitro group.[2] Gas-phase studies (EI/CAD-MS/MS) showed that 1-nitropyrene undergoes a ready loss of NO•, following intramolecular peri-H• transfer to the nitro group and OH• transfer to the peri position.[3] With 1-nitro-2-*tert*-butylpyrene, denitration (–NO_2•) was prominent and dealkylation was accompanied by H• transfer (from *t*-Bu) to the ring.[4] In agreement with theory,[5] and in line with sulfonation[6] and protonation studies in superacid media,[7] exclusive or predominant α attack was observed in electrophilic nitration of pyrenes in the condensed phase. Thus protic nitration of 2-*tert*-butylpyrene and 2,7-di-*tert*-butylpyrene gave exclusive α-nitration.[6,8]

Nitrations of PAHs with N_2O_4 led to a variety of results, depending upon the character of the aromatic compound and solvent.[9] PAHs with low reduction potentials, $E°$, usually form side products.

In relation to our low temperature protonation studies of crowded alkyl(cycloalkyl)pyrenes,[7] we now report on the protic and aprotic nitration of **1** and on the protonation/transfer–nitration chemistry of **2–3**. Aprotic nitrations of tetra- and isomeric monoisopropylpyrenes were also studied.

Results and Discussion

NMR Studies. Our protic and aprotic nitrations of isopropylpyrenes and subsequent protonation studies on nitroisopropylpyrenes focused on high field proton NMR as a probe because of its diagnostic nature with regard to substituent effects on chemical shifts and vicinal coupling constants in the pyrene skeleton and the implications of such effects on conformation in crowded nitropyrenes (nitropyrenium ions). Moreover, formation of isomeric mixtures in many instances coupled with limited availability of the purified nitroisopropylpyrenes made ^{1}H NMR more applicable than ^{13}C NMR. Assignments of the ^{1}H NMR spectra of nitrated products are based on the additivity of substituents on the chemical shifts and the magnitude of the coupling constants.

For a highly substituted pyrene skeleton, the assignments are often complicated due to the presence of up to four α, four α,β, and two β protons and several substituents. In general, $^3J(H_\alpha–H_\beta)$ is smaller than 9 Hz, whereas $^3J(H_{\alpha,\beta}–H_{\alpha,\beta})$ is larger than 9 Hz. α-Nitration increases the $^3J(H_\alpha–H_\beta)$ from 7.75 to 8.80 Hz and the $^3J(H_{\alpha,\beta}–H_{\alpha,\beta})$ from 8.98 to 9.50 Hz.

The substituent effects on chemical shifts of an unperturbed nitro substituent in the α position are H_2 (*ortho*) = 0.71, H_3 = 0.04, H_4 = 0.05, H_5 = 0.19, H_6 = 0.19, H_7 = 0.12, H_8 = 0.19, H_9 = 0.31, and H_{10}(peri) = 0.89 ppm. The presence of an isopropyl group ortho to the nitro group (as in **19** and **20**) results in a rather different, smaller, sub-

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‡ KSU senior undergraduate participant.

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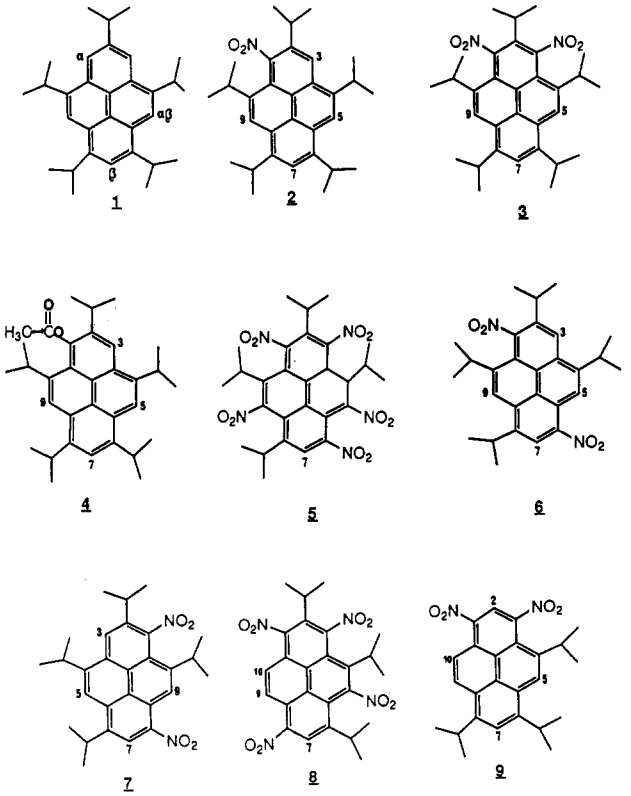
Scheme I. Protic and Aprotic Nitration of 1[a]



[a] Position numbers are indicated on the structures for clarity.

stituent effect: $H_3 = 0.06$, $H_4 = 0.03$, $H_5 = 0.16$, $H_6 = 0.00$, $H_7 = 0.10$, $H_8 = 0.19$, $H_9 = 0.02$, H_{10}(peri) = −0.33. The magnitude of the observed shielding of the peri proton in α-nitropyrenes is between those observed for the H_8 of 1-nitro-2-methyl- and 1-nitro-2-*tert*-butylnaphthalene.[10]

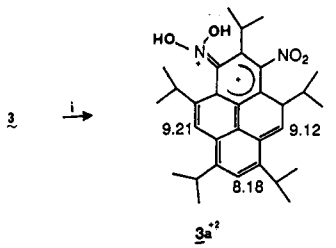
Substituent effects of out-of-plane nitro groups can also be obtained from comparisons of chemical shifts of **1**, **2**, and **3** or **10**, **11**, and **12**. However, in these cases, reorientation of isopropyl groups could influence chemical shifts.

Protic Nitration of 1,3,5,7,9-Pentaisopropylpyrene (1) (Scheme I and Table I). Protic nitration of **1** (HNO_3/HOAC) gave the 1-nitro product **2**. Further nitration led to the 1,3-dinitro product **3**. Whereas major products due to nitrodealkylation (e.g., **5**–**9**) were not found, ring acetoxylation (HOAC) occurred as a minor pathway to give the 1-acetoxy compound **4**.

Mononitration of **1** at position 6 (position 1 in **2**) forces the peri *i*-Pr group out of coplanarity and leads to an *upfield* shift in the ^{1}H NMR [$\Delta\delta$ = −0.75 (CH) and −0.13 (Me) ppm]. Further nitration of **2** at position 3 (**3**) reduces the buttressing of the peri *i*-Pr (CH) group [$\Delta\delta$ = −0.49 ppm], but increases methyl shielding [$\Delta\delta$ = −0.17 ppm]. In turn, the ortho *i*-Pr is forced out of the aromatic plane [$\Delta\delta$ = −0.17 (CH) and −0.03 (Me) ppm].

The *i*-Pr groups in **2** and **3** remain sharp in the NMR spectra, and no restricted rotation is observed at ambient temperatures. On the other hand, **4** exhibits a torsional barrier (CS_2 solvent), showing an envelope of *i*-Pr (Me) doublets from 0.55–2.05 ppm. The presence of an upfield methyl doublet at 0.55 ppm and a CH multiplet at 2.15 ppm are strongly indicative of a twisted *i*-Pr, anisotropically shielded by introduction of a bulky acetoxy group peri and ortho to two *i*-Pr groups. UV spectra of **2** and **3** showed vibrational fine structure typical of pyrene itself and a dramatic weakening of the ~390-nm absorption (diagnostic of planar nitroaromatics). The ~390-nm band from **2** is less intense than that from **24**.[11] The same band from **3** is slightly stronger than that from **2**, indicating a more twisted nitro group in **2**.

Scheme II. Protonation of 3[a]



[a] (i) $TfOH{\cdot}SO_2$ or $FSO_3H{\cdot}SO_2$.

In agreement with NMR and UV-based conclusions, MMX force field energy minimization of **2** and **3** indicated loss of coplanarity of the Ar–CH bond upon α-nitration (peri *i*-Pr, ca. 18° tilt; ortho *i*-Pr, ca. 10° tilt) and a twisted Ar–N bond [**2**, 18° (ONO angle 111°); **3**, 23° (position 1, ONO angle 102°) and 13° (position 3, ONO angle 111°)].

Calculated (MMX) van der Waals VDW radii surfaces for **1**–**3** are gathered in Figure 1 for comparison.

Protonation of 1,3-Dinitro-2,4,6,8,10-pentaisopropylpyrene (3) (Scheme II). Slow addition of a slurry of **3** in SO_2 to cold FSO_3H/SO_2 gave a dark red homogeneous solution, the ^{1}H NMR spectrum of which (at −65 °C) consisted of three deshielded aromatic singlets at 9.21, 9.12, and 8.18 ppm. The aliphatic region showed seven different *i*-Pr (Me) groups as broad doublets [1.71 (1 Me), 1.65 (1 Me), 1.58 (2 Me), 1.53 (2 Me), 1.48 (1 Me), 1.37 (2 Me), and 1.32 ppm (1 Me)], indicative of restricted rotation, and two *i*-Pr (CH) multiplets [4.40 and 3.10 ppm]. Relative integrals confirmed the absence of any protiodealkylation. Substantial deshielding of the aromatic protons clearly established pyrenium ion formation. Ipso protonation at C_2 was ruled out on the basis of (a) the absence of the CH (sp^3) proton, (b) the magnitude of $\Delta\delta$s (see ref 7), and (c) the higher energy content of the mesomeric structures of σ-complex of α attack in which positive charges (N^+ and C^+) are adjacent.

Parent nitrobenzene and its alkyl(halogeno) derivatives are O-protonated in Magic acid/SO_2 and the NO_2H^+ proton in the frozen ion is observed at 14.50–16 ppm.[12] With nitrosobenzene, an iminiumbenzenium dication is formed.[13] Isomeric mononitronaphthalenes are similarly diprotonated in TfOH at room temperature to give (dihydroxyiminium)naphthalenium dications (Scheme VI).[14] Due to rapid exchange in TfOH, the OH protons are not detectable. Trapping experiments on protonated (TfOH) *N*-arylhydroxylamines with arenes also suggested an iminiumbenzenium ion intermediate.[15a] In line with these studies and based on the similarity of the spectrum with

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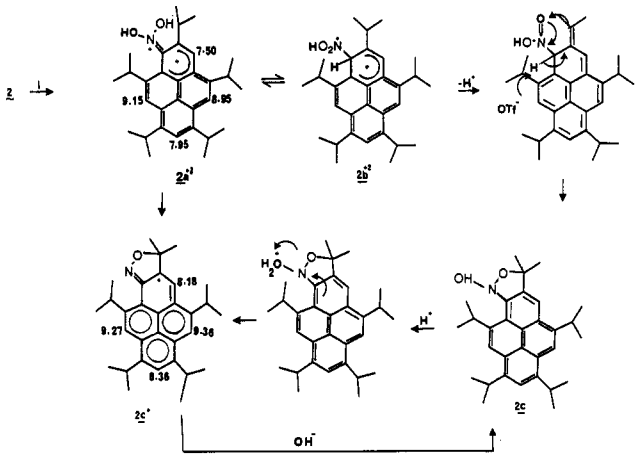
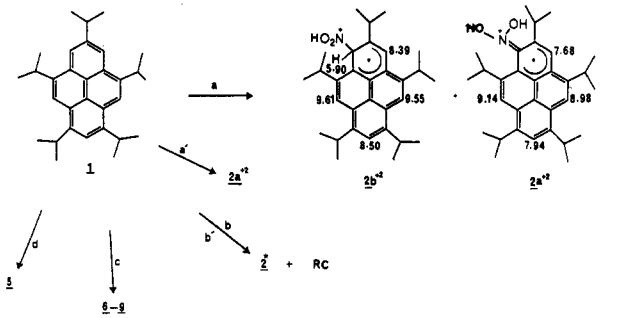
(15) (a) Schudo, K.; Ohta, T.; Okamoto, T. *J. Am. Chem. Soc.* **1981**, *103*, 645 and references therein. (b) Since the OH protons were not observable, formation of an oxo-iminiumpyrenium dication formed by O-diprotonation/dehydration may not be completely ruled out; formation of an oxo-iminiumnaphthalenium dication was, however, excluded by Shudo et al. (ref 14a) based on cryoscopy and quenching with H_2O.[18]

Scheme III. Protonation of 2 and Rearrangement of $2a^{+2}$ to $2c^{+}$ [c]



[a] (i) $TfOH{\cdot}SO_2$.

Scheme IV. Reaction of 1 with $NO_2^+BF_4^-$ and with $NO^+BF_4^-$ in CD_3CN and in $CDCl_3$ [a]

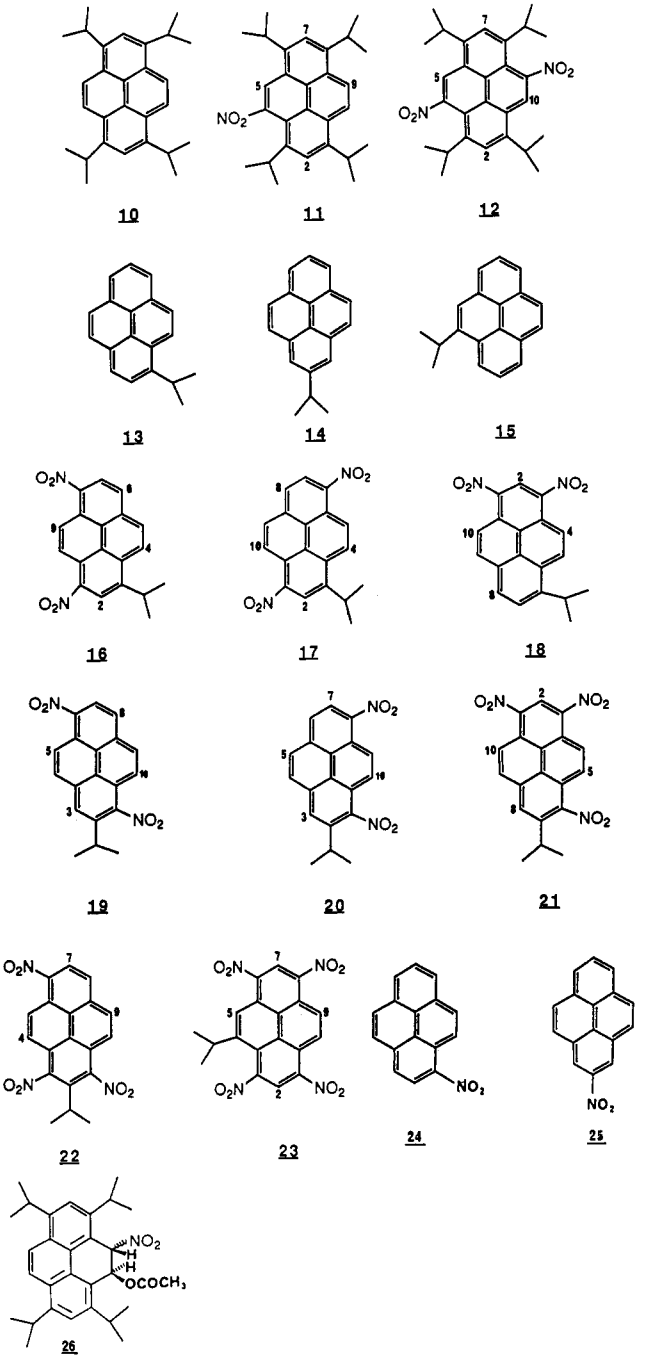


[a] (a) $NO_2^+BF_4^-/CD_3CN$/rt; (b) $NO_2^+BF_4^-/CDCl_3$/rt; (c) excess $NO_2^+BF_4^-$/MeCN/overnight; (d) excess $NO_2^+BF_4^-/CDCl_3$/overnight; (a') $NO^+BF_4^-/CD_3CN$/rt; (b') $NO^+BF_4^-/CDCl_3$/rt; (*) contains minor amounts of 3.

that of protonation of 2 (see below), the protonation spectrum is interpreted as the (dihydroxyiminium)pyrenium dication $3a^{+2}$.[15b]

Protonation of 1-Nitro-2,4,6,8,10-pentaisopropylpyrene (2) (Scheme III). Low temperature addition of a slurry of 2 in SO_2 to cold $TfOH/SO_2$ gave a dark red solution, the ^1H NMR of which at −65 °C consisted of four deshielded aromatic singlets at 9.15, 8.95, 7.95, and 7.50 ppm (1 H each), indicating the presence of a pyrenium ion. The aliphatic region consisted of four *i*-Pr (CH) multiplets [4.25 (2 H), 3.65, 3.52, and 3.20 ppm (1 H each)] and five *i*-Pr (Me) absorptions [1.65 (d, 1 Me), 1.55 (d, 4 Me), 1.45 (br s, 3 Me), 1.35 (d, 1 Me), and 1.25 (d, 1 Me)]. The presence of two shielded methyl doublets and a broad methyl singlet absorptions indicated that two methyl groups in the resulting pyrenium ion are buttressed and four exhibit hindered rotation due to peri strain. The spectrum is interpreted as the (dihydroxyiminium)pyrenium dication $2a^{+2}$. The assignment is consistent with the observed high field shift of the *i*-Pr (Me) doublets, and the number of such doublets is in accord with the asymmetry and restricted rotation in the ion. When the temperature was raised and the SO_2 evaporated under a stream of dry nitrogen, a persistent dark red solution resulted. Its ^1H NMR spectrum, at room temperature, showed the disappearance of $2a^{+2}$ at the expense of a new, more deshielded pyrenium ion having four (1 H) aromatic singlets at 9.36, 9.27, 8.36, and 8.18 ppm, three *i*-Pr (CH) multiplets [4.37 (2 H), 3.95 (1 H), and 3.85 (1 H)], three *i*-Pr (Me) doublets [1.67 (4 Me), 1.62 (2 Me), and 1.57 (2 Me)], and a methyl

Scheme V. Aprotic Nitration of Tetraisopropylpyrenes (10) and Isomeric Monoisopropylpyrenes 13–15 [a]



[a] Position numbers are indicated on the structures for clarity.

singlet at 2.15 ppm (2 Me).[16] As before, no ring CH (sp^3) signal was present.

The NMR data support the formation of the cyclized pyrenium ion $2c^+$. We propose that 2c is formed from $2b^{+2}$ (Wheland intermediate of protonation ipso to the nitro group) through a side-chain deprotonation/aromatization/cyclization sequence (Scheme III). $2b^{+2}$ was independently observed as a stable pyrenium ion in the reaction of 1 with $NO_2^+BF_4^-$ (Scheme IV). This crucial intermediate is also responsible for transfer-nitration to aromatics (see later). In situ O-protonation of 2c and pyrenium ion formation/dehydration leads to the observed

(16) The four (1 H) aromatic singlets and the 2.15 ppm methyl singlet absorptions of the rearranged pyrenium ion are observed as tiny peaks in the low temperature spectrum of $2a^{+2}$.

Table I. ^{1}H NMR Data (300 MHz) for Prominent Nitropyrenes in $CDCl_3$ Solvent

nitropyrene[c]	1	2	3	4	5	6	7	8	9	10	CH(Me[a])Me	CH(Me[b])Me
2			8.48 (Δδ = 0.20)		8.32 (Δδ = 0.07)		7.97 (Δδ = 0.06)		8.37 (Δδ = 0.12)		4.10 (2 H) [1,3] 3.22 (1 H) [5] (Δδ = −0.75) 3.55 (1 H) [7] (Δδ = 0.13) 3.90 (1 H) [9]	1.52 (4 Me) [1,3] 1.41 (2 Me) [5] (Δδ = −0.13) 1.47 (2 Me) [7] (Δδ = −0.05) 1.56 (2 Me) [9]
3					8.51 (Δδ = 0.11)		8.02 (Δδ = 0.26)		8.51 (Δδ = 0.26)		4.05 (2 H) [1,3] 3.48 (2 H) [5,9] (Δδ = −0.49) 3.25 (1 H) [7] (Δδ = −0.17)	1.54 (4 Me) [1,3] 1.37 (4 Me) [5.9] (Δδ = −0.17) 1.49 (2 Me) [7] (Δδ = −0.03)
5							8.60 (Δδ = 0.69)					1.2–1.4 (br)
6			8.59 (Δδ = 0.31)		8.53[c] (Δδ = 0.98)		8.75 (Δδ = 0.84)		8.56[c] (Δδ = 0.31)		2.90–3.60	1.57; 1.53; 149; 1.45
7			8.59 (Δδ = 0.31		8.37 (Δδ = 0.12)		8.63 (Δδ = 0.72)		8.95 (Δδ = 0.70)		2.90–3.50 1.52; 1.43	1.62; 1.55
8							8.62 (Δδ = 0.71)		8.92 (d; J = 9.85) (Δδ = 0.67)	8.57 (d; J = 9.85)	4.10	1.55
9		9.25 (Δδ = 1.34)			8.59 (Δδ = 0.34)		8.14 (Δδ = 0.23)		8.42 (d; J = 9.8) (Δδ = 0.17)	8.59 (d; J = 9.8) (Δδ = 0.34)	4.05–4.17	1.85 (d); 1.71 (d)
11		7.82			8.43 (Δδ = 0.13)		7.87		8.35	8.35	4.10; 3.90 (Δδ = −0.16)	1.53
12		7.88			8.48 (Δδ = 0.18)		7.88			8.48 (Δδ = 0.18)	4.10; 3.90 (Δδ = −0.16)	1.53; 1.25
16		8.67 (Δδ = 0.54)		~8.30	~8.30	~8.30	8.67 (Δδ = 0.57)		8.95 (Δδ = 0.80)	8.95 (Δδ = 0.80)	4.18[d]	1.55[d]
17		8.65 (Δδ = 0.52)									4.12[d] 4.12[d]	1.60[d] 1.60[d]
18		9.34 (Δδ = 1.37)		8.98	8.87		~8.29	8.23	8.46	~8.67	4.12[d]	1.60[d]
19			8.32 (Δδ = 0.26)	8.37 (0.34)	9.03 (Δδ = 1.0)		8.77 (Δδ = 0.80)	8.38	8.02	7.94	3.35–3.45	1.55–1.52
20			8.30 (Δδ = 0.24)	8.30	8.30	8.19	8.68 (Δδ = 0.71)		8.89 (Δδ = 0.86)	8.01		1.55–1.52
21		9.30 (Δδ = 1.33)		8.95 (Δδ = 0.92)	8.26 (Δδ = 0.23)			8.50 (Δδ = 0.44)	8.49 Δδ = 0.46)	9.01 (Δδ = 0.86)		1.55–1.52
22				8.05	8.92 (Δδ = 0.89)		8.67 (Δδ = 0.70)	8.17	8.24	8.28 (Δδ = 0.25)	4.01 (Δδ = 0.06)	1.58 (br, s) (Δδ = 0.01)
23		9.45 (Δδ = 1.44)			9.14 (Δδ = 1.07)		9.36 (Δδ = 1.35)		9.18 (Δδ = 1.11)	9.18 (Δδ = 1.11)	3.50 (Δδ = 0.45)	1.62 (Δδ = 0.04) 1.45 (Δδ = −0.13)

[a] All multiplets. [b] All 7–8 Hz doublets unless stated otherwise. [c] Assignment may be reversed. [d] May be interchanged. [e] ^{1}H NMR parameters (60 MHZ) for the byproduct 4 (CS_2 solvent): 7.75 (H_3), 7.0 (H_7), 7.0 (H_9), 2.15, 2.90, 3.20, 3.50, 3.70 [*i*-Pr (CH)], 1.55 (COMe), 0.55–2.05 ppm [*i*-Pr (Me)].

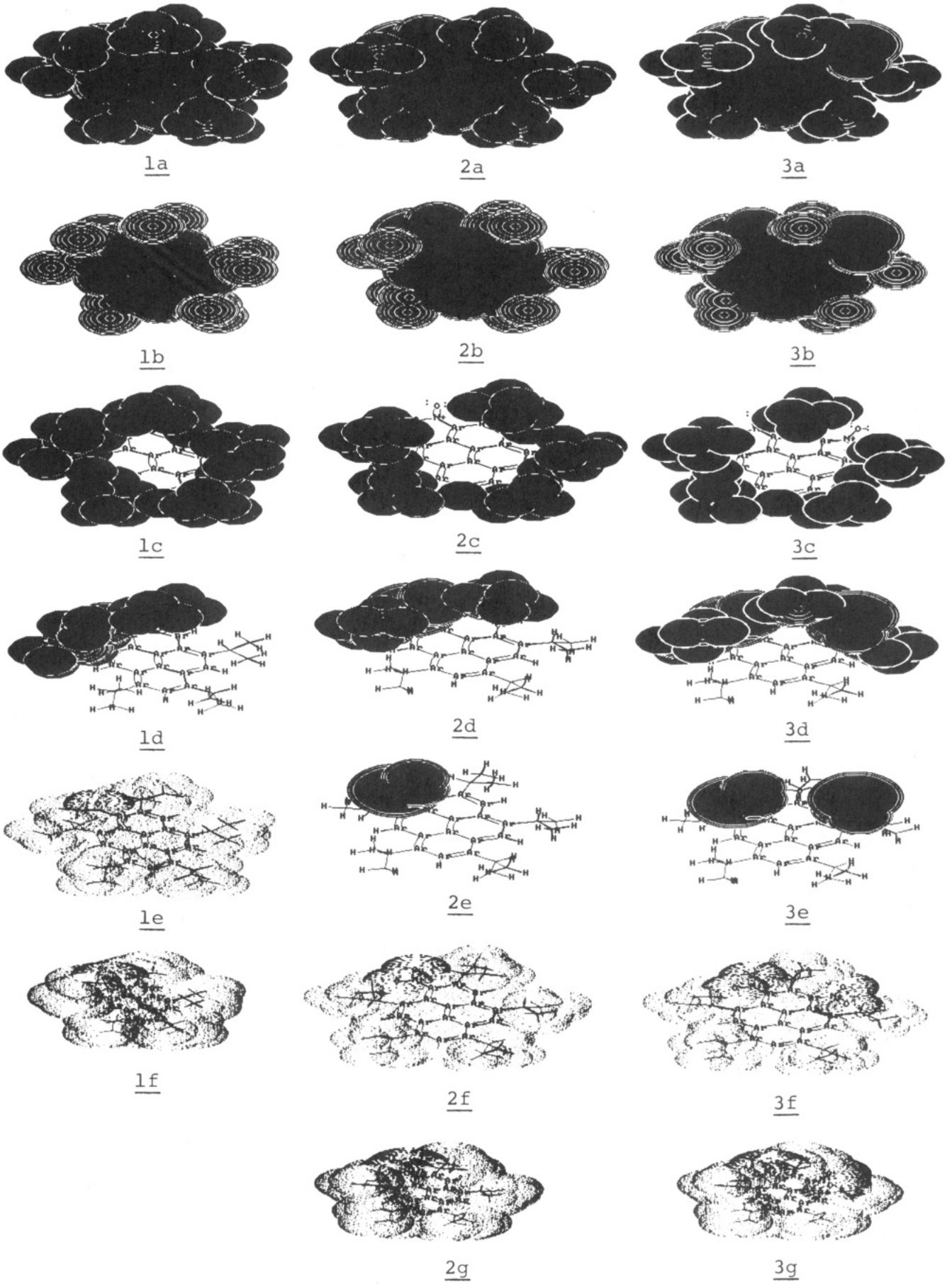
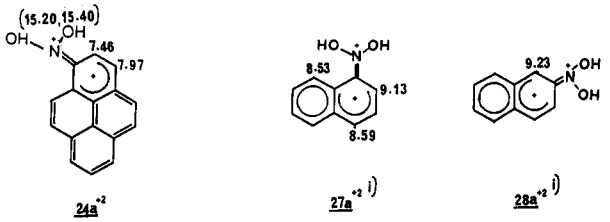


Figure 1. Calculated surface drawings for **1–3**. **1**: VDW radii for all atoms (a), C only (b), H only (c), *i*-Pr groups at the 5 and 7 positions (d), VDW surface [453 sq ang] (e), and water dot surface (f). **2**: VDW radii for all atoms (a), C only (b), H only (c), NO_2 plus ortho/peri *i*-Pr (d), NO_2 only (e), VDW surface [466 sq ang] (f), and water dot surface (g). **3**: VDW radii for all atoms (a), C only (b), H only (c), NO_2s plus ortho/peri *i*-Pr (d), NO_2s only (e), VDW surface [477 sq ang] (f), and water dot surface (g).

Scheme VI. Charge Distribution Patterns in Iminium-Arenium Dications of Pyrene and Naphthalene (Values for Isomeric Nitronaphthalene Are Taken from Ref 14a)[a]



24a^{+2} 27a^{+2} i) 28a^{+2} i)

[a] (i) From ref 14a.

persistent **2c**$^+$. A similar cyclization, ultimately leading to anthranil, was recently reported by Ridd et al.,[17] when 1-nitro-2-ethylbenzene was heated in TfOH. A related intramolecular cyclization of the nitro group (oxygen atom rearrangement) was observed by Schudo et al.[18] by protonation of 2-cyclopropyl-1-nitrobenzene with TfOH. **2c**$^+$ is indefinitely stable at room temperature. Upon quenching, a dark green solid was obtained (**2c**),[19] from which **2c**$^+$ was regenerated by addition of TfOH (identical NMR).

Protonation of 1- and 2-Nitropyrenes 24 and 25. In order to determine the generality of iminiumpyrenium dication formation vis-a-vis ipso attack and ring protonation in the less substituted nitropyrenes, we generated stable ions of protonation of **24** and **25** in control experiments and examined them by NMR at low temperature. Due to their reduced basicity, frozen σ-complexes of protonation could not be generated with $TfOH/SO_2$; the ^1H NMR spectra, even at −70 °C, showed coalescence of aromatic protons with the acid peak, indicative of dynamic systems. However, frozen ions could be obtained in the much higher acidity superacid [FSO_3H·SbF_5 (1:1); Magic acid in SO_2 solvent].

Addition of a cold homogeneous solution of Magic acid/SO_2 to a solution of **24** in SO_2 (dry ice/acetone temperature) gave a dark blue solution. The ^1H NMR spectrum at −65 °C exhibited a low field doublet at 9.51 ppm [1 H; ^3J = 8.29 Hz], four overlapping doublets between 9.10 and 9.25 ppm (4 H), an overlapping doublet and triplet centered at 8.30 ppm (2 H), and two doublets at 7.97 and 7.46 ppm [1 H each; ^3J = 10.01 and 10.09 Hz, respectively]. The absence of an sp^3 (CH) absorption (see 2-nitropyrene) and deshielding of the aromatic protons are strongly indicative of an iminiumpyrenium dication **24a**$^{+2}$ (Scheme VI); its corresponding N–OH absorptions were seen as two relatively broad singlets at 15.20 and 15.40 ppm. In agreement with our previous studies,[7] the upfield aromatic doublets at 7.46 and 7.97 ppm with enhanced vicinal coupling are due to H_2 (ortho) and H_3 (meta).

Similar addition of cold Magic acid/SO_2 to **25** in SO_2 gave a green brown solution; its ^1H NMR at −65 °C showed two distinct CH (sp^3) absorptions, a major peak at 5.20 ppm (slightly broad singlet), and a minor one at 6.70 ppm (4.5 Hz doublet). The aromatic region showed major doublets at 8.30, 8.60, 8.80, 9.25, and 9.35 ppm, a distinct low field triplet at 9.66 ppm in addition to two deshielded singlets at 9.85 and 10.4 (broad) ppm, and five minor aromatic doublets. O-Protonation (NO_2) was clearly evident (a broad singlet at 16.80 ppm).

The NMR data support the formation of two pyrenium ions (ca. 4:1 ratio). For the major ion, the low field aromatic triplet at 9.66 ppm argues against α protonation at a "remote" position. Ipso protonation (β) and $\alpha\beta$ protonation were ruled out on the basis of the integrals, number, and multiplicities of the major aromatic absorptions. The data are best compatible with α protonation ortho to the nitro group (see Discussion). A clear presence of the low field CH (sp^3) doublet at 6.70 ppm and 9.85 singlet (SO_2H) showed that the minor pyrenium ion is a sulfinylation σ-complex.[7] Thus in the pyrene skeleton, iminiumpyrenium dication generation (nitro group diprotonation) was observed only for a nitro group in the α position.

Reaction of 1 with $NO_2^+BF_4^-$ and $NO^+BF_4^-$ in Acetonitrile: Stable Pyrenium Ions at Room Temperature (Schemes I and IV and Table I). A persistent dark red color developed upon slow addition of a homogeneous solution of $NO_2^+BF_4^-$ (2.2 equiv) in CD_3CN to **1** in the same solvent, at dry ice–acetone temperature. The sample was allowed to reach room temperature and examined by ^1H NMR without workup. The aromatic region showed a pair of four singlets between 7.68 and 9.61 ppm, indicative of two species in a 60:40 ratio. The highly deshielded nature of the aromatic peaks indicated the generation of two pyrenium ions stable at room temperature. The major pyrenium ion with aromatic singlets at 9.61, 9.55, 8.50, and 8.39 ppm exhibited a matching CH (sp^3) absorption (a distinct singlet at 5.90 ppm) and is assigned to **2b**$^{+2}$, viz., the pyrenium ion of ipso protonation of in situ formed mononitro product **2** or the Wheland intermediate of nitration of **1** (see Scheme IV and Discussion). The minor pyrenium ion with four aromatic singlets at 9.14, 8.98, 7.94, and 7.68 ppm and no CH (sp^3) absorption is assigned to the (dihydroxyiminium)pyrenium dication **2a**$^{+2}$. Comparison of the NMR spectrum of this ion with that generated independently by low temperature protonation of **2** with $TfOH/SO_2$ clearly supports the assignment. The pyrenium ion mixture exhibited an envelope of *i*-Pr (CH) multiplets between 2.70 and 4.60 ppm and *i*-Pr (Me) doublets between 0.6 and 1.70 ppm. The highly shielded methyls at 0.62 and 0.85 ppm are clear indications of their twisted conformation and anisotropic shielding. However, restricted *i*-Pr rotation is not evident at room temperature and the methyls are all seen as relatively sharp doublets. Finally, two exchange-broadened singlets at 11.40 and ca. 13.80 ppm are (tentatively) assigned to the N–OH absorption of the pyrenium ions, exchanging with HBF_4 proton (at ca. 12 ppm).

The relative proportion of **2b**$^{+2}$ and **2a**$^{+2}$ varied in different nitration reactions. In an experiment carried out following the general aprotic nitration procedure (see Experimental Section), the (dihydroxyiminium)pyrenium dication **2a**$^{+2}$ was dominant [aromatic absorptions at 9.15, 8.98, 7.95, and 7.70 ppm]. In addition, minor but distinct resonances appeared at 9.67, 9.61, 9.58, 9.54, 9.33, 9.25, 8.70, 8.49, 8.38, and 8.19 ppm. Absorptions at 9.67, 9.58, 9.54, 9.33, and 9.25 ppm were each two, nearly overlapping peaks (almost equally abundant). The low field singlets at 9.33, 9.25, and 8.19 ppm were close to those of **3a**$^{+2}$, independently generated by protonation of **3** with FSO_3H/SO_2 (vide supra), whereas those at 9.33, 9.25, 8.38, and 8.19 ppm were matching with **2c**$^+$ formed by rearrangement of **2a**$^{+2}$.[20]

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(19) The IR spectrum of **2c** (thin film) prior to addition of TfOH indicated that the nitro group absorptions at 1590, 1519, 1457, 1378, and 1360 cm^{-1} in **2** were replaced by strong peaks at 1472, 1388, and 1267. Similarly, in the 900–700 cm^{-1} region (previously shown to be diagnostic of substitution pattern in pyrene skeleton)[23b] the absorptions at 888, 822, 800, and 736 cm^1 in **2** were replaced by strong bands at 908 and 729 cm^{-1}.

(20) Facile formation of **2c**$^+$ in TfOH at rt and its minor presence in the ambient nitration of **1** in CD_3CN points to crucial role of TfO^- gegenion as "base" in the side-chain deprotonation and cyclization steps.

Upon workup, the low field absorptions were lost (spectrum contained no absorptions below 8.40 ppm). The crude reaction mixture showed, among other peaks, absorptions for 1, indicating a partial loss of the nitro group.

In another experiment, 1 was allowed to react with 2.2 equiv of $NO_2^+BF_4^-$ in dry CH_3CN solvent at room temperature overnight. The ^1H NMR spectrum of the crude reaction mixture following workup showed a complex aromatic region between 7.9 and 9.30 ppm and a cluster of broadened *i*-Pr groups. The reaction mixture was subjected to a series of preparative TLC analyses from which several fractions were separated. Comparison of R_f values and NMR spectra with those of authentic 2 and 3 confirmed that these were present only as minor products (ca. 10% each). Instead, nitration/nitrodealkylation/dealkylation products 6–9 were found (ca. 15–20% each). Both 6 and 7 showed four different *i*-Pr (Me) groups and four deshielded aromatic singlets. The chemical shifts of the two compounds were rather similar and not easily distinguished. The ^1H NMR spectrum of 8 consisted of two doublets (9.85 Hz, 1 H each) and a singlet (ca. 1 H) in the aromatic region and deshielded (coinciding) *i*-Pr (CH) groups. All chemical shifts except that of H_{10} were in accord with predictions. The 9.85-Hz coupling between H_9 and H_{10} is clearly indicative of a $^3J(H_{\alpha\beta}-H_{\alpha\beta})$ with substitutions at both peri positions. The spectrum of 9 showed two nonequivalent *i*-Pr groups, an AB system, and three singlets in the aromatic region. One singlet (H_2) at 9.25 ppm is deshielded by 1.34 ppm (relative to H_2 in 1) due to two ortho nitro groups. A structure like 9 explains the AB system (J = 9.8 Hz), and the chemical shifts were close to expected values.

A similar reaction of 1 with $NO^+BF_4^-$ in CD_3CN solvent at room temperature gave a dark brown solution, which was directly examined by ^1H NMR without workup. The spectrum consisted of four sharp aromatic singlets at 9.15, 8.98, 7.95, and 7.70 ppm (1 H each), indicative of a persistent pyrenium ion, structurally similar to that formed in NO_2^+ nitration of 1 in acetonitrile and low temperature protonation of authentic 2 with $TfOH/SO_2$. The *i*-Pr methyls appeared as slightly broadened doublets between 1.65 and 1.35 ppm and the *i*-Pr (CH) groups absorbed at 4.50 (2 H), 4.25 (2 H), 3.75 (1 H), and 3.25 (1 H) ppm. The 1.35 (Me) and 3.25 (CH) absorptions suggest that at least one *i*-Pr group is anisotropically shielded. The near identical positions of the aromatic protons, and especially the *i*-Pr (Me) pattern, with those of $\mathbf{2a}^{+2}$ corroborate the formation of the latter.

Reaction of 1 with $NO_2^+BF_4^-$ and $NO^+BF_4^-$ in Chloroform: α-Nitration and Oxidation (Schemes I and IV and Table I). 1 reacted exothermically with $NO_2^+BF_4^-$ (2.2 equiv) in dry $CDCl_3$ at room temperature to give a reddish brown solution, the ^1H NMR of which showed a broad envelope of isopropyl methyls [1.2–1.6 ppm] and CH groups [2.50–3.70] and a broad aromatic envelope in the base line [ca. 7.65 ppm], implying intervention by a radical cation RC, presumably involving the NO^+ impurity[9b,21] present in the commercial $NO_2^+BF_4^-$ samples (up to 15%). The HOMO–LUMO gap (E_{HOMO}) for the parent pyrene is 0.4450β,[22] which should decrease further due to the inductive effect of five *i*-Pr substituents in 1, in agreement with conclusions based on UV studies of isopropylpyrenes.[23a] Pyrenes and alkylpyrenes are, therefore, expected to be easily oxidized. NO^+ is a versatile ET oxidant ($E°$ = 1.51 V) for reactive polycyclic aromatics forming long-lived radical cation salts.[24-26]

In another experiment, 1 was reacted with excess $NO_2^+BF_4^-$ (8 equiv) in $CDCl_3$ solvent overnight. Following aqueous workup and TLC, NMR analysis of the product showed a single compound identified as 1,3,5,6,9-pentanitro-2,4,8,10-tetraisopropylpyrene (5), which exhibited restricted *i*-Pr rotation at room temperature as evidenced by broad-*i*-Pr groups between 1.2 and 1.4 ppm with no visible CH multiplets and a single aromatic absorption at 8.60 ppm [H_7; $\Delta\delta$ = 0.69]. Thus, whereas 3 is conformationally mobile, introduction of two additional nitro groups in the αβ positions induces a barrier. The degree of loss of coplanarity of the isopropyl groups (MMX) were in the order *i*-Pr (αβ positions, 33° and 27°) > *i*-Pr (β position, 24°) > *i*-Pr (α position, 15°). For the nitro groups, the degrees of buttressing ($ArNO_2$) were (αβ position, 27° and 23°; α position, 20–21°.

To focus on RC formation in chloroform, in an independent experiment, we added a cold solution of 1 in dry $CDCl_3$ to a suspension of $NO_2^+BF_4^-$ (2 equiv) in $CDCl_3$ at dry ice/acetone temperature, and the temperature was allowed to rise slowly to ambient with efficient mixing. The ^1H NMR spectrum of the resulting red brown solution at room temperature showed four rather sharp *i*-Pr (Me) doublets [1.57, 1.53, 1.49, and 1.42 ppm], four *i*-Pr (CH) multiplets [3.20, 3.40, 3.80, and 4.0 ppm; the latter was much broader], and three broadened aromatic singlet absorptions [8.49, 8.34, and 7.98 ppm]. The NMR data are consistent with the formation of a mixture of 2 and 3 (2 predominating) in which 2-H_7/3-H_7, 2-H_3/3-H_9, and 2-H_9/2-H_5 are overlapping due to line broadening. Similarly, the *i*-Pr (CH) resonances for 2 and 3 are coinciding, except for the 3.80 ppm multiplet, which is specific for 2. Reduced overall line broadening as compared to the room temperature reaction suggested that RC formation was less extensive. After 24 h at −70 °C, the sample was examined by ESR at 240 K, and a broad signal was detected with a g value of 2.0023 (ΔH_{pp} = ca. 7.1 gauss).

Excess $NO^+BF_4^-$ (4 equiv) was reacted with 1 as above to further clarify the role of NO^+ as oxidant in RC formation. The ^1H NMR spectrum of the reaction mixture showed much broader lines but essentially the same absorptions as those observed in the product from the $NO_2^+BF_4^-$ reaction.[27a] The ESR spectrum of the sample kept for 24 h at −70 °C was examined at 240 K; the same persistent pyrenium RC was observed [g = 2.0023; ΔH_{pp} = ca. 7.1] but the ESR signal was much stronger. Lack of hyperfine coupling precluded detailed structural analysis on the pyrenium radical cation. In control experiments 2 and 3 were reacted with $NO^+BF_4^-$ in $CDCl_3$ at room temperature to determine if 2 or 3 could be oxidized with NO^+. No color change of the orange yellow solutions was observed; their ^1H NMR spectra showed very sharp lines and remained identical with those of the authentic 2 and 3.

Nitration of 1,3,6,8-Tetraisopropylpyrene (10) (Scheme V and Table I). Protic nitration (HNO_3/HOAC) of the symmetrical pyrene 10 resulted in mono-

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(27) (a) Also present was a broad featurless hump centered around ~2.2 ppm. This signal is barely visible in reaction of 1 in $NO_2^+BF_4^-$/$CDCl_3$; it is tentatively ascribed to the *i*-Pr (Me) of the RC. (b) Experiments to determine the scope of this reaction for introduction of various functionalities into αβ positions are underway.

substitution in the $\alpha\beta$ position, viz. 11. A UV spectrum of 11 showed a weak 405-nm absorption and pyrene-like vibrational fine structure, indicative of NO_2 buttressing. In addition, product 26 was formed in some cases which could result from a nucleophilic attack of OAc^- on the pyrenium ion of $\alpha\beta$ nitration.[27b] Nitration of 10 with $NO_2^+BF_4^-$ (2.2 equiv) in $CDCl_3$ led to the 4,9-dinitro product 12. Peri strain, caused by the introduction of two nitro groups in the $\alpha\beta$ positions of 10, leads to peri-*i*-Pr groups buttressing and a sizable upfield shift of *i*-Pr (CH) in the NMR [$\Delta\delta$ = −0.16].

Aprotic Nitration of Isomeric Monoisopropylpyrenes 13–15 (Scheme V and Table I). In relation to our protonation studies,[7] and for comparison of isomer distributions with protonation, we also studied $NO_2^+BF_4^-$ nitration of 1-isopropylpyrene (13), 2-isopropylpyrene (14), and 4-isopropylpyrene (15) in dry acetonitrile solvent at room temperature.

1-Isopropylpyrene (13). Reaction of 13 with 2 equiv of $NO_2^+BF_4^-$ gave a complex mixture of nitrated products, which were separated by preparative TLC and fractional crystallization and examined by ^1H NMR. Three isomeric dinitro products, viz. 1,8-$(NO_2)_2$, 1,6-$(NO_2)_2$, and 1,3-$(NO_2)_2$ (16–18) were isolated in a single TLC layer in a 70:25:5 ratio. ^1H chemical shifts are gathered in Table I.

2-Isopropylpyrene (14). Nitration of 14 with 2.2 equiv of $NO_2^+BF_4^-$ in acetonitrile gave a mixture of two dinitro and two trinitro isomers, viz. 1,6-$(NO_2)_2$ (19, 50%), 1,8-$(NO_2)_2$ (20, 20%), the 1,6,8-$(NO_2)_3$ (21, 10%) and 1,3,6-$(NO_2)_3$ (22, 20%) showing three *i*-Pr doublets [1.55, 1.53, and 1.52 ppm] with their corresponding *i*-Pr (CH) absorptions as overlapping multiplets [3.35–3.45 ppm] and a complex aromatic region from 7.90 to 9.30 ppm. The 9.30 ppm singlet is specific for the H_2 of 21 [$\Delta\delta$ = 1.33 ppm].

Analysis of these spectra clearly established that a nitro group ortho to the 2-isopropyl group has a negative substituent effect at H-10, which explains the high field shift of this proton.

4-Isopropylpyrene. Following the reaction with 2.2 equiv of NO_2^+, TLC of the crude nitration mixture indicated only a minor presence of the dinitro isomers (ca. 10%) and no mononitro products. A major, more polar fraction was separated; its ^1H NMR showed that it contained ca. 70% of 1,3,6,8-tetranitro-4-isopropylpyrene (23). Compound 23 exhibited nonequivalent *i*-Pr (Me) groups at 1.62 and 1.45 ppm [$\Delta\delta$ = 0.04 and −0.13] and an upfield shifted CH multiplet at 3.50 ppm [$\Delta\delta$ = −0.45], illustrating anisotropic shielding. The aromatic absorptions for 23 were observed at 9.45 (1 H, s), 9.36 (1 H, s), 9.18 (2 H, s), and 9.14 (1 H, s) ppm; these positions are considerably more deshielded compared to dinitropyrenes.

Extensive formation of tri- and tetrasubstitution with 2.2 equiv of NO_2^+ in the present study provides a new example of mixing disguised selectivity in reactions between the highly electrophilic isopropylpyrene and the remarkably reactive NO_2^+. Similar observations were previously made in aprotic sulfonation of pyrene, perylene, and tetramethylphenanthrene with 0.9 equiv of SO_3 which led to predominant disulfonation.[6]

Transfer–Nitration Chemistry. Olah et al.[9a,28] have already demonstrated that an ipso-protonated 9-nitroanthracene or pentamethylnitrobenzene transfer-nitrates to aromatics (benzene, toluene, and mesitylene) in superacid media. With toluene, predominant para substitution was observed, indicative of the bulky nature of the nitrating agent and the crowded nature of the transition state of transfer–nitration. Regioselectivity dependence in toluene nitration was also recently demonstrated with acidic zeolites and silica gel as catalyst.[29,30] With metallic nitrates/acidic clay system a high para selectivity was observed (79%); a benzoyl nitrate/zeolite system gave 67% of the para isomer; and benzoyl nitrate/silica gave predominantly *o*-nitrotoluene.

Exploiting the observed ease of formation and unusual stability of the Wheland intermediate of ipso protonation of crowded isopropylnitropyrenes (Scheme IV), we studied the transfer–nitration chemistry of 3 and 2 with particular interest in regioselectivity control through steric factors.

The dark red ion solution formed by protonation of 3 with FSO_3H/SO_2 was quenched in cold toluene in dry methylene chloride. A persistent dark green solution was formed. Following 35 min of mixing at room temperature, GC analysis of the organic extract showed predominant transalkylation, forming isomeric cymenes in addition to a nitrotoluene isomer at an approximately 18:1 ratio (GC), indicative of transfer-nitration as a minor competing pathway. The isomer distribution of the cymene isomers, 80% meta, 4-5% ortho, and 15% para, corroborated isomerizing conditions (predominant meta). Capillary GC coinjections with authentic samples of nitrotoluene isomers showed it to be meta! In control experiments authentic para or ortho nitrotoluenes did not isomerize in FSO_3H under the reaction conditions. Toluene itself reacts with FSO_3H/SO_2 to give *p*-tolyl sulfoxide and *p*-tolyl sulfide (1:1) together with isomeric tolylsulfonyl fluorides.[31] Under our GC conditions, one of the isomeric tolylsulfonyl fluorides coincided with the nitrotoluene isomer produced via transfer–nitration. 3 was protonated in triflic acid/SO_2 to avoid sulfonyl fluoride formation, and the ion was quenched with toluene as before; the nitrotoluene isomer was again identified as meta. Control experiments similarly ruled out any isomerization of authentic nitrotoluenes in triflic acid. Reaction of 3 with Nafion-H in refluxing toluene was also studied. Although trans-isopropylation occurred (with meta predominating), only a trace of nitrotoluene could be detected.

Reaction of protonated 3 with cold mesitylene and benzene was examined. Although transalkylation was predominant, minor amounts of nitromesitylene and nitrobenzene were formed (GC).

Several other isopropylnitropyrenes were studied to probe the effect of structure on regioselectivity. Whereas 2 behaved analogously to 3, the less buttressed 12, with only two peri *i*-Pr groups, gave a nitrotoluene isomer distribution typical of NO_2^+ nitration, viz. 59% ortho, 30% para, and 11% meta, implying protiodenitration. The less crowded nitropyrenes such as 7 and 23 showed no transfer-nitration under the mild conditions employed (−70 °C → rt). The observed meta regioselectivity was also probed by molecular modeling (MMX). The calculated minimum energy structure for the ipso-protonated 3 indicated that steric crowding caused by the peri and ortho *i*-Pr groups would make a side-on approach by a toluene nucleophile highly unfavorable (a side-on approach would have made the toluene para position more available). The van der Waals (VDW) surface calculations on the nitropyrene precursors (Figure 1) also illustrated severe steric hindrance for nucleophile approach to C_1 (or C_3). Space-filling models suggested that an approach in which a toluene

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methyl group points away from the nitro groups and toward the "remote" phenyl rings seems least congested. In such a model the meta positions of the receptor (toluene) appear to be most accessible for transfer–nitration.

An Overall Comparison of the Protonation and Nitration Chemistry of Crowded Isopropylpyrenes. Protonation of 2 and 3: Iminiumpyrenium Dications. Nitro group diprotonation was observed (a) in the low temperature protonation of 2 and 3 (TfOH or FSO_3H; SO_2 solvent) and (b) in the reaction of 1 with $NO_2^+BF_4^-$ or $NO^+BF_4^-$ at rt presumably via deprotonation/reprotonation of the nitration σ-complex of 1. A dication was also formed in protonation of 1-nitropyrene in Magic acid/SO_2 and was previously reported for 1-nitro- and 2-nitronaphthalene in TfOH.[14a]

Comparison of the ^1H NMR shifts of the ring protons in iminiumpyrenium dications with isomeric iminiumnaphthalenium dications (Schemes II, III, and VI) reveals a dramatic difference in the charge distribution patterns. With nitronaphthalenes the ortho and para positions are most deshielded but in nitropyrenes extensive delocalization occurs in the $\alpha\beta$ (and remote α) positions with shielding in the ortho and meta positions. $\mathbf{2b}^{+2}$ exhibits an analogous delocalization pattern; thus the delocalization mechanisms for the pyrenium ions of protonation and nitration are similar.

For a planar nitroarenium ion, p–π overlap is possible, and despite the dicationic character of the resulting Wheland intermediates an overall contribution to stability may result. Thus 2-nitropyrene is ring protonated. Regarding the position of protonation (ortho to nitro), our previous protonation studies established a strong preference for α attack, irrespective of the position of alkyl substituents, and extensive delocalization away from that site. Thus, the resonance structure bearing adjacent positive charges (C^+ and N^+) may have little influence on the overall stability of the Wheland intermediate.

Loss of coplanarity of the nitro group in 2 and 3 as revealed by NMR, UV, and energy minimization should dramatically reduce any p–π overlap. The distinct pyrenium ion character of nitro group-diprotonated nitropyrene (NMR) shows that p–π overlap in the dication must be possible, i.e., that sufficient degree of overlap is achieved by change of bond order at nitrogen (NO_2 diprotonation).[32,33a]

Reaction of 1 with $NO_2^+BF_4^-$: Role of Solvent. Two persistent pyrenium ions $\mathbf{2a}^{+2}$ and $\mathbf{2b}^{+2}$ were observed in the reaction of 1 with $NO_2^+BF_4^-$ in acetonitrile. $\mathbf{2a}^{+2}$ was independently generated by protonation of 2. $\mathbf{2b}^{+2}$ may be formed either directly as a σ-complex of nitration of 1 or via in situ protonation of 2 (HBF_4). Observation of $\mathbf{2a}^{+2}$ as the only observable intermediate in the protonation of authentic 2 in superacids and the absence of an ipso-protonated pyrenium ion in $CDCl_3$ solvent argues in favor of the nitration σ-complex itself.

Deprotonation of the Wheland intermediate of aprotic nitration must presumably occur either by BF_4^- or by the solvent.[34a] We recently showed[34b] that $NO_2^+BF_4^-$/MeCN and $NO_2^+BF_4^-/CHCl_3$ show different regioselectivities in halopyridine nitration. In MeCN the electrophile has a larger steric demand and nitrates a less hindered position, indicative of initial complexation to MeCN and subsequent transfer–nitration. Complexation should also influence the steric demand of the associated gegenion (BF_4^-), hence ease of deprotonation in a highly crowded σ-complex; moreover, in a solvent of much higher dielectric constant (MeCN compared to $CHCl_3$), the gegenion is more solvated and deprotonation may be more uphill.

In chloroform solvent, apart from the nitration products, a persistent RC was formed; a stable pyrenium ion was not detectable. Oxidation of 1 by NO^+ impurity in NO_2^+ is consistent with the observation of more line broadening in the NMR spectrum and a stronger ESR signal in the reaction of authentic $NO^+BF_4^-$ with 1 in chloroform. Longer reaction times and higher NO_2^+/arene ratio in both solvents led to polynitration/nitrodealkylation, indicating denitration and renitration ipso to the *i*-Pr groups.

As the pyrenium ion of nitration and the RC of oxidation were not observed together (both of which would have been persistent), a branching reaction via $PyH^{+\bullet}\cdot NO_2$ seems unlikely. Our observations are also incompatible with homolytic dissociation of the Wheland intermediate to form RC.[21]

Observation of $\mathbf{2a}^{+2}$ in the reaction of 1 with $NO^+BF_4^-$ in MeCN may be explained in two ways: (i) initial ET to give a radical pair, followed by rapid autoxidation of $NO^\bullet$ and recombination to give the Wheland intermediate of nitration (deprotonation/reprotonation then gives $\mathbf{2a}^{+2}$), or (ii) autoxidation of the Wheland intermediate of nitrosation. The absence of a persistent RC in MeCN seems to argue in favor of the latter. The same reaction in chloroform solvent gave mono- and dinitration products together with the RC. Presence of the Wheland intermediate in MeCN and its absence in $CDCl_3$ is once again attributed to steric inhibition to deprotonation of the Wheland intermediate in MeCN.

The absence of a persistent RC in the reaction of $NO_2^+BF_4^-$ (containing NO^+ oxidant) in MeCN solvent and its pronounced presence in chloroform points to possible complexation of NO^+ with MeCN, which would modify its oxidative behavior.[35]

Experimental Section

Syntheses, purification, and spectral data (NMR, IR, UV, MS) of the isopropylpyrenes have already been reported.[23] Authentic 1-nitropyrene (Aldrich; 97%) was used as received. 2-Nitropyene was prepared as described.[11,23b] $NO_2^+BF_4^-$ (Aldrich; 85%) and $NO^+BF_4^-$ (Ozark-Mahoning) were stored under dry nitrogen in a freezer and used without further purification. The aromatics were high purity commercial samples which were distilled once under nitrogen and stored over molecular sieves. Rigorously dried methylene chloride and acetonitrile were used in aprotic nitrations.

NMR spectra were recorded on a wide-bore GN-300 instrument and GC analyses were performed on an HP 5890A instrument equipped with a 5-m HP methyl silicone gum capillary column. ESR spectra were obtained on an IBM 200 D-SRC instrument equipped with a ER4111 VT unit with 1 K precision.

General Procedure for the Protic Nitrations. In a typical experiment, 1 mmol of 1 was dissolved in warm glacial acetic acid (10 mL) and 1.3 mL of a mixture of concd HNO_3 and glacial acetic acid (1:10) was added to the warm solution. The reaction mixture was allowed to stand for 5 min before the addition of water. The precipitate was filtered off and the products were purified by preparative TLC on silica.

2: mp 136.5–137.1 °C; ^1H NMR (Table I); MS *m/z* 457 (M^+), 414 ($M - i\text{-}Pr)^+$; IR (KBr) 2980 (s), 2940 (m), 2880 (m), 1620 (m), 1600 (m), 1530 (s), 1470 (m), 1390 (m), 1380 (m), 1370 (m), 1355 (m), 1340 (m), 1262 (m), 1100 br (m), 1050 (m), 1020 (w), 973 (w),

(32) We have begun probing this suggestion by semiempirical theory.

(33) (a) Iminiumnaphthalenium dication formation from 2-nitronaphthalene (no peri buttressing) does not fit this argument. (b) Slight changes observed in NMR shifts must be due to vast differences in the solvent and temperature.

(34) (a) If proton transfer from the pyrenium ion to solvent was important, $\mathbf{2b}^{+2}$ would not have been expected to be persistent at rt in MeCN. (b) Duffy, J. L.; Laali, K. K. *J. Org. Chem.* **1991**, *56*, 3006.

(35) An alternative explanation is that solvent reorganization energy $\lambda°$ for an outer-sphere ET by NO^+ has increased in the more polar solvent MeCN, compared to chloroform.

900 (m), 887 (w), 829 (w), 805 br (w), 739 (w), 650 (w); UV λ_{max} (EtOH) 209.3, 240.9, 249.9, 276.9, 286.1, 330.3, 361.3.

3: mp 164.7–165.2 °C; ^{1}H NMR (Table I); MS m/z 502 (M^+), 459 ($M - i\text{-}Pr)^+$; IR (KBr) 2980 (s), 2929 (m), 2872 (m), 1610 (w), 1568 (w), 1530 br (s), 1462 (m), 1387 (m), 1369 (s), 1335 (w), 1290 (w), 1275 (w), 1260 (w), 1050 (m), 979 (w), 898 (w), 817 (w), 779 (w), 762 (w), 660 (w); UV λ_{max} (EtOH) 205.3, 252.9, 289.7, 360.9.

11: mp 172.1–172.9 °C; ^{1}H NMR (Table I); MS m/z 415 (M^+), 398; UV λ_{max} (EtOH) 205.3, 246.1, 273.5, 284.9, 345.7, 405.9.

26 (*air-sensitive yellow substance*): ^{1}H NMR (250 MHz, $CDCl_3$) 8.07 (2 H, s), 7.60 (2 H, s), 7.56 (1 H, s), 7.35 (1 H, d, J = 3.14 Hz), 6.50 (1 H, d, J = 3.14 Hz), 1.92 (3 H, s), 4.05, 3.95, 3.25 [m, *i*-Pr (CH)] 1.55–1.27 [d, *i*-Pr (Me)].

Aprotic Nitration. (a) In $CHCl_3$. In a typical experiment, a slurry of the nitronium salt (usually 2.2 molar equiv) in dry $CHCl_3$ was added to a solution of the isopropylpyrene substrate (0.15–0.20 mmol) in ca. 8 mL of $CHCl_3$ with vigorous mixing inside a drybox. After 30–45 min at room temperature the reaction mixture was removed from of the drybox, quenched with ice–bicarbonate, extracted (CH_2Cl_2), dried ($MgSO_4$), and separated. Solvent was removed and the residue was taken up in $CDCl_3$ for NMR analysis. In experiments in which the reaction mixture was examined directly by NMR prior to workup, $CDCl_3$ was used as solvent and an aliquot was directly withdrawn and transferred into a 5-mm NMR tube.

(b) In CH_3CN. The procedure was similar except that a homogeneous solution of the nitronium salt was prepared in dry acetonitrile inside the drybox (vortex) and slowly injected via a syringe into a solution of the isopropylpyrene in acetonitrile with vigorous mixing. CD_3CN was used as solvent in reactions which were examined by NMR prior to workup.

Reaction of 1 with $NO_2^+BF_4^-$ in CD_3CN. (a) $NO_2^+BF_4^-$ (0.113 g, 0.85 mmol; 2.2 equiv) was charged into a dry 5-mm NMR tube inside the glovebox. CD_3CN (0.5 mL) was added via a pipet and the mixture was vigorously mixed (vortex) until homogeneous. The content of the NMR tube was slowly poured into a solution of 1 (0.165 g, 0.4 mmol) in CD_3CN (0.5 mL) prepared in a 10-mm NMR tube under dry nitrogen at dry ice/acetone temperature with vigorous mixing (vortex), whereupon a dark red homogeneous solution was immediately formed. It was allowed to reach room temperature while mixing. After 10 min, an aliquot was transferred via a pipet into a 5-mm NMR tube and examined directly by ^{1}H NMR, prior to workup.

(b) Alternatively, the general procedure outlined for aprotic nitration in acetonitrile was adopted, with the initial reaction temperature of ca. –60 °C, followed by room temperature mixing.

Reaction of 1 with $NO_2^+BF_4^-$ and $NO^+BF_4^-$ in $CDCl_3$. $NO_2^+BF_4^-$ (12 mg, 0.09 mmol; 2 equiv) was charged into a dry 5-mm NMR tube under a dry nitrogen atmosphere and diluted with 5 drops of $CDCl_3$. The tube was cooled in a dry ice/acetone bath and a solution of 1 (18 mg, 0.045 mmol) in 0.4 mL of $CDCl_3$ was slowly added. The temperature was allowed to rise slowly to rt to give a deep red brown solution which was directly examined by NMR. Following 24 h at –70 °C, the same sample was studied by ESR at 240 K.

Following the same procedure, to $NO^+BF_4^-$ (19 mg; 0.16 mmol; 4 equiv) slurried in $CDCl_3$ (ca. 10 drops) was added 1 (16 mg, 0.04 mmol) at low temperature. Following vortex mixing and a raise in temperature, a persistent red brown solution was obtained which was studied by ^{1}H NMR and ESR.

Protonation of Nitropyrenes. Typically, to 20 mg of the nitropyrene substrate suspended or dissolved in ca. 0.5 mL of SO_2 was added a clear solution of the superacid (1 mL) diluted in ca. 1 mL of SO_2 at dry ice/acetone temperature with efficient vortex mixing. The resulting dark red (**2** and **3**), dark blue (1-nitropyrene), or green brown (2-nitropyrene) solution was transferred into a pre-cooled NMR tube under nitrogen with CD_2Cl_2 as internal lock and reference. The cold NMR tube was quickly inserted into the pre-cooled NMR probe at –70 °C; the sample was spun for ca. 5 min prior to data collection.

Transfer–Nitration. The cold ion solution, generated as indicated above, was carefully added to a cold solution of 5 mL of the aromatic (toluene, mesitylene, or benzene) diluted in 20 mL of dry CH_2Cl_2 at dry ice–acetone temperature with vigorous magnetic stirring; a dark green solution was formed. The cold bath was removed and the reaction mixture was allowed to reach room temperature. Stirring was continued for an additional 30 min, prior to workup and GC analysis.

Calculations. MMX force field energy calculations and structure minimizations were performed with a PCMODEL program (Serena Software). Good convergence was achieved usually after 100–150 iterations. All carbons of the pyrene skeleton were assigned π-atoms (SCF-π calculations were not available). The π-system in the minimized structures was planar. For the pyrenium ion of transfer–nitration, C_2 (ortho) was specified as C^+.

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Supplementary Material Available: ^{1}H NMR spectra of **2** and its protonation in $TfOH/SO_2$ at –65 °C and in TfOH at room temperature, **3** and its protonation in FSO_3H/SO_2, protonation of **24** and **25** in Magic acid/SO_2, and reaction of **1** with $NO_2^+BF_4^-$ and with $NO^+BF_4^-$ in acetonitrile and in chloroform, ESR spectra of reaction of **1** with $NO_2^+BF_4^-/CDCl_3$ and $NO^+BF_4^-/CDCl_3$, aprotic nitration of **10**, and UV spectra of **1**, **2**, and **11** (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Chemical Modification of Halogenated Polystyrene Resins Utilizing Highly Reactive Calcium and the Formation of Calcium Cuprate Reagents in the Preparation of Functionalized Polymers

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Polymeric organocalcium reagents have been prepared from highly reactive calcium and cross-linked polystyrene resins containing halogens (Br, Cl, F, CH_2Cl) and subsequent addition of electrophiles to yield functionalized polymers. Transmetalation with CuCN·2LiBr yields calcium cuprate reagents which react with a variety of electrophiles to prepare highly derivatized polymers.

The chemical modification of cross-linked polymers has received considerable interest since the discovery of Merrifield's resin and its use in peptide syntheses.[1] For almost 30 years, cross-linked polystyrene resins have been

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