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Spectroscopic and photochemical properties of mononitropyrenes

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Abstract. The influence of the nitro group on the aromatic π-system of pyrene has been studied by comparing the spectroscopic and photochemical properties of the three mononitropyrenes. Whereas the UV and mass spectra of 1- and 4-nitropyrene show an interaction normal for nitro-aromatic compounds, this is not observed for 2-nitropyrene. The lack of interaction is reflected in a UV spectrum very similar to that of pyrene and a mass spectrum with a very low abundance of M–NO. The photochemical behaviour of the three compounds is governed by the degree of interaction. 1-Nitropyrene shows the nitro-nitrite rearrangement leading to 1-hydroxypyrene (88%) and 1-hydroxy-2-nitropyrene (7%). The photoproducts of 4-nitropyrene are pyrene (9%) and unstable products which react with the solvent. 2-Nitropyrene is very stable under photochemical conditions due to lack of interaction. Similarly, the sterically hindered 1-methyl-2-nitropyrene is also very stable towards light. The photochemical nitro-nitrite rearrangement observed for nitro-aromatic compounds was found to be governed by electronic effects.

Introduction

Polycyclic aromatic hydrocarbons (PAH) and their nitro derivatives are widespread environmental contaminants[1a-c]. The availability of these compounds in the pure state will allow their identification in complex environmental samples and the study of their analytical, spectroscopic, chemical and biological properties.
Pyrene and its derivatives form the main subject of our studies in the polycyclic aromatic field[2a-c,3]. The three isomeric nitropyrenes occur in the environment. The nitro group in an aromatic compound may be converted into many other functional groups. The position of the substituent in the molecule can determine the biological properties of isomeric compounds[4]. These considerations motivated us to prepare 1-, 2- and 4-nitropyrene and to study their chemical, spectroscopic and photochemical properties. The results of this study are reported in the present paper and the biological properties will be the subject of a later paper.

Synthesis and purification

The nitro group is introduced into most aromatic systems by nitration. Position 1 and the equivalent positions 3, 6 and 8 in pyrene are reactive towards electrophilic substitution. Treatment of pyrene with nitric acid in acetic anhydride gives mainly 1-nitropyrene, pyrene and 1,3-, 1,6- and 1,8-dinitropyrene, since 1-nitropyrene is subject to further nitration. Unreacted pyrene and the dinitropyrenes can be removed by chromatography on silica. A cleaner conversion of pyrene into 1-nitropyrene (**1**) (Fig. 1) can be achieved via an oxidative nucleophilic aromatic substitution ($S_{ON}2$) reaction involving sodium peroxydisulfate as the oxidizing agent and nitrite as the nucleophile. Sodium peroxydisulfate, or rather the sulfate anion radical, is a powerful oxidant capable of oxidizing electron-rich arenes[5]. In acetonitrile, pyrene is oxidized to a radical cation[6] which then reacts with NO_2^-. After oxidative removal of a hydrogen atom, the electron-deficient aromatic compound **1** is formed, which cannot be oxidized any further by the sulfate anion radical and thus no dinitropyrenes are formed. Since there are no direct ways of introducing a nitro group at the 2 (or 4) position of pyrene, we required a pyrene derivative which can be substituted at position 2 (or 4) and can subsequently be converted into the corresponding nitropyrene.
4,5,9,10-Tetrahydropyrene (**4**), having a biphenyl system, is the material of choice in the preparation of 2-substituted 4,5,9,10-tetrahydropyrenes which can then be converted into 2-substituted pyrenes. Catalytic hydrogenation or dissolving metal reductions of pyrene give complicated mixtures containing several hydrogenated pyrenes[7]. A convenient way of obtaining **4** in very pure form (in small quantities) is the photochemical reduction of pyrene using triethylamine as electron donor[8]. In addition to **4**, however, more than 50% of the product mixture consists of hydrogenated pyrene amino adducts. We reasoned that these adducts result from the coupling of hydrogenated pyrenyl and amine radicals. The radicals may be trapped using triphenyltin hydride as hydrogen donor[9]. Indeed, upon irradiation in the presence of triphenyltin hydride, the formation of amino adducts was prevented. Pyrene, triethylamine and triphenyltin hydride were irradiated in acetonitrile using a medium-pressure mercury arc, until no further reaction took place. The mixture contained 4,5,9,10-tetrahydropyrene, but no pyrene, 4,5-dihydropyrene or

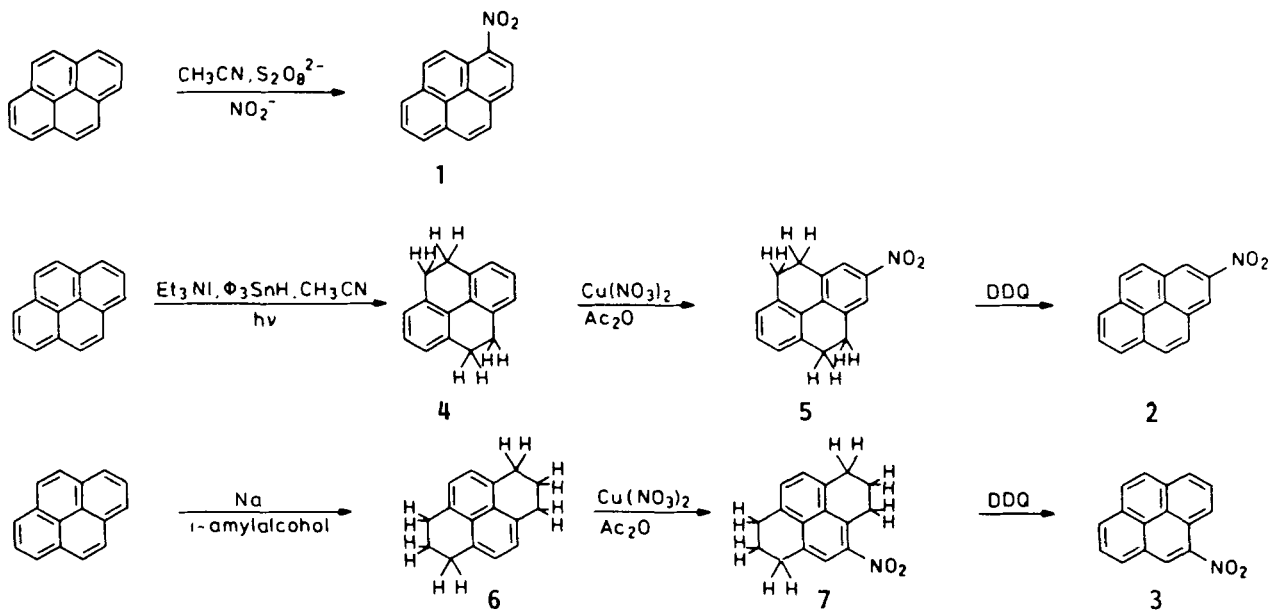


Fig. 1. The preparation of 1-, 2- and 4-nitropyrene.

1,2,3,6,7,8-hexahydropyrene. 4,5,9,10-Tetrahydropyrene (**4**) of high purity is obtained in excellent yield after chromatography on silica.

4 is a sensitive compound, which, under the usual nitration conditions, is partially oxidized to pyrene. Because of the high reactivity towards nitration, the product mixture always contains 1-nitropyrene, which cannot be removed by HPLC procedures on a preparative scale. Therefore, the nitration has to be carried out under non-oxidative conditions. Nitration of **4** with copper(II) nitrate in acetic anhydride yields 2-nitro-4,5,9,10-tetrahydropyrene (**5**) which was easily separated from unreacted **4** and acylated by-products. The presence of an electron-withdrawing group, however, renders the DDQ oxidation to the fully aromatic system somewhat difficult. A rapid conversion of **5** into 2-nitropyrene (**2**) by oxidation with DDQ was achieved in refluxing nitrobenzene. Nitrobenzene was removed by evaporation and **2** was further purified by chromatography on silica.

For the preparation of 4-nitropyrene (**3**), 1,2,3,6,7,8-hexahydropyrene (**6**) is the required starting material. It contains a naphthalenic system with 4 equivalent aromatic carbon atoms. Upon reduction with sodium and isoamyl alcohol as described by *Coulson*[10], pyrene is converted into a mixture of hydrogenation products containing mainly **6**. The latter can be obtained in very pure form by crystallization from ethanol. **6** was converted into 4-nitropyrene (**3**) using the same procedure as described for **2**.

In this way, the three isomeric mononitropyrenes were obtained in reasonable quantities (~1–2 g) in very pure form.

Spectroscopic properties

Mass spectra

The electron impact mass spectra of **1**, **2** and **3** show the parent peak at the expected position and the high-resolution mass measurements are in agreement with the expected composition. $C_{16}H_9NO_2$ calcd. *m/z* 247.0633; found **1**: *m/z* 247.0644; **2**: *m/z* 247.0647; **3**: *m/z* 247.0652. In Table I, the relative abundances of the major peaks in the mass spectra of the three mononitropyrenes are given.

The electron-impact mass spectra were recorded at two different ion source temperatures. At 150°C, the base peak in the mass spectrum is, in all cases, observed at *m/z* 201 due to loss of $NO_2^{\bullet}$; a well known fragmentation for nitro aromatic compounds[11,12]. The spectra differ considerably in the intensity of the *m/z* 217 peak. For many aromatic nitro compounds, this $(M-30)^+$ is due to $NO^{\bullet}$ loss. Part of the $(M-30)^+$ peak is due to the molecular ion of the amino-PAH derivative[13]. We investigated the degree of reduction by measuring the exact mass of *m/z* 217 in the mass spectrum of **2**. At 150°C, at least 10% of the 217 peak consists of *m/z* 217.0894 corresponding to $C_{16}H_{11}N$ (calcd. *m/z* 217.0891), the amino derivative. The presence of *m/z* 216 is also in

Table I Relative abundance (%) of the major peaks in the electron impact mass spectra of 1-, 2- and 4-nitropyrene.

Compound	Probe T (°C)	247 (M^+)	217 ($M-NO^+$)	216	201 ($M-NO_2$)	200 ($M-HNO_2$)	189 ($M-NO-CO$)
1-nitropyrene	100	100	30	–	93	51	38
	150	89	62	–	100	76	65
2-nitropyrene	100	81	5	–	100	44	15
	150	96	8	1	100	61	38
4-nitropyrene	100	100	11	–	87	54	45
	150	69	35	1	100	83	90

agreement with reduction (loss of a proton from the amino parent ion). The other 90% (*m/z* 217.0660), corresponding to $C_{16}H_9O$ (calcd. *m/z* 217.0653), is attributable to the loss of NO from the M^+. The degree of reduction varies with compound structure, laboratory humidity and with the temperature and condition of the source. In order to obtain reproducible mass spectra, a freshly cleaned source was used at 100°C, *i.e.* 50°C below the usual source temperature. Special precautions were taken to exclude water and other H-donating solvents in order to keep the reduction at the lowest possible level. Under such conditions, the spectra were reproducible and reduction was not observed (*m/z* 216 is absent). At 100°C, the fragmentations and rearrangements have diminished. Exact measurement of the *m/z* 217 peaks at 100°C of **1**, **2** and **3** shows that they consist entirely of $(M-NO)^+$. In **2**, the $(M-NO_2)^+$ fragment is the base peak at both temperatures. The *m/z* 217 is very low, thus rearrangement of the nitro group does not occur easily. Comparison of the *m/z* 217 abundances in the EI mass spectra of the three isomers makes it possible to distinguish between **1**, **2** and **3**.

NMR spectra

The structures of **1**, **2** and **3** were elucidated using NMR spectroscopy. The ^{1}H NMR spectra of nitropyrenes are sensitive to concentration variations. In more concentrated solutions, the spectra are shifted upfield and the signals tend to overlap making interpretation difficult. This effect is caused by association of the molecules and persists until the concentration is as low as 1 mg per ml $CDCl_3$.
From the ^{1}H NMR spectra, the position of the nitro group is immediately clear. The most pronounced effects of the nitro group are the large downfield shifts of the protons *ortho* and *peri* to the substituent. In substituted pyrenes, the protons 1, 2, 3, 6, 7 and 8 show a normal aromatic *ortho* coupling of 7–8.5 Hz. The protons 4 and 5 (9 and 10) have a coupling constant of about 9.5 Hz. The latter value is indicative of the greater double bond character of the C(4)–C(5) [C(9)–C(10)] bond[3,14]. The spectrum of **1** consists of one ABX and three AB subspectra. Two doublets are downfield from the signals of the parent hydrocarbon. The first doublet is part of an AB subspectrum and it is characterised by the large coupling constant of 9.4 Hz. This must belong to the *peri* proton H(10), which is shifted +0.68 ppm downfield from the parent compound. By means of homonuclear decoupling, the B part H(9) of the AB system can be identified. The second doublet at low field, also part of an AB system, has a normal aromatic *ortho* coupling of 7.6 Hz, characteristic of H(2). The resonance is shifted +0.63 ppm downfield. H(3) is found by means of the double resonance technique. The AB spectrum of H(4) and H(5) has a coupling constant of 8.9 Hz. The signal of H(4) is assigned by a NOE experiment on H(3). The remaining peaks belong to the ABX spectrum. H(7), a triplet, is coupled to H(6) and H(8), which have the same chemical shift.
The spectrum of **2** shows a +0.86 ppm downfield shifted singlet due to H(1) and H(3). The remaining peaks constitute one A_2B and an AB system with double intensity. The A_2B spectrum consists of a triplet (H(7)) and a doublet of H(6) and H(8). The AB system of H(4) and H(5) is assigned by a NOE experiment on H(3).
The spectrum of **3** is composed of one singlet, one AB and two ABX spectra. A doublet of doublets (+0.67 ppm) with *J* 8.3 Hz and a singlet (+0.72 ppm) can be assigned to the *peri* H(3) and to the *ortho* proton H(5), respectively. In addition to the *ortho* coupling, H(3) shows a *meta* coupling with H(1) of 1.5 Hz. By homonuclear decoupling of H(3), the triplet of H(2) can be assigned. The other triplet in the spectrum belongs to H(7), which is coupled with H(6) and H(8). The signal of H(6) is found from a NOE experiment on H(5). H(1), H(6) and H(8) have almost the same chemical shift and cannot be irradiated separately. Therefore, it was not possible to discriminate between H(9) and H(10). The assignments and coupling constants given in Table II were checked using the Bruker NMR simulation programme PANIC.84.
^{13}C NMR assignments of pyrene, **1**, **2** and **3** are presented in Table III. The ^{13}C chemical shifts are not very sensitive to concentration variations in $CDCl_3$. The ^{13}C spectra of **1** and **3** both show sixteen peaks as expected. The spectrum of **2** only shows eight of the expected ten peaks. Quaternary carbon atoms of large symmetric molecules of this type have very long relaxation times[15]. Consequently, carbon atoms 10^b and 10^c of **2** were not observed in the normal ^{13}C measurement. Using the relaxation accelerator manganese triacetylacetonate[16], the relaxation times could be shortened sufficiently to make detection of these signals possible. No significant changes in the chemical shifts were observed upon addition of the reagent. Using APT and 2D ^{13}C–H correlated NMR spectroscopy, the signals of carbon atoms bearing protons were easily assigned in **1** and **2**. For **3**, a simple ^{13}C–H correlated spectrum was insufficient. H(1), H(6) and H(8) have almost the same chemical shift and, since these shifts are sensitive to concentration variations, an unambiguous assignment was not possible and consequently a ^{13}C–H relayed transfer experiment was used[17]. In addition to ^{13}C–H correlations, cross peaks from more distant protons appear via proton–proton couplings. It was thus possible to assign C(1) due to a coupling with H(2). With proper irradiation of H(5), in the same sample as used for the ^{13}C–H 2D NMR experiment, a definitive assign-

Table II *^{1}H resonance assignments[a] (300 MHz, $CDCl_3$) δ (ppm) of pyrene, 1-nitropyrene* (**1**), *2-nitropyrene* (**2**) *and 4-nitropyrene* (**3**).

H (n)	Pyrene	*J* (n,m) Hz	**1**	*J* (n,m) Hz	**2**	*J* (n,m) Hz	**3**	*J* (n,m) Hz
1	8.15	d 7.6 (1,2)	–		9.01	s	8.23	dd 8.3 (1,2); 1.5 (1,3)
2	7.91	t 7.6 (2,1/3)	8.54	d 8.5 (2,3)	–		8.07	t 8.3 (2,1/2)
3	8.15	d 7.6 (3,1)	7.99	d 8.5 (3,2)	9.01	s	8.82	dd 8.3 (3,2); 1.5 (3,1)
4	8.05	s	7.95	d 8.9 (4,5)	8.16	d 9.1 (4,5)	–	
5	8.05	s	8.14	d 8.9 (5,4)	8.20	d 9.1 (5,4)	8.77	s
6	8.15	d 7.6 (6,7)	8.21	d 7.6 (6,7)	8.30	d 7.8 (6,7)	8.23	dd 8.3 (6,7); 1.5 (6,8)
7	7.91	t 7.6 (7,6/8)	8.03	t 7.6 (7,6/8)	8.16	t 7.8 (7,6/8)	8.02	t 8.3 (7,6/8)
8	8.15	d 7.6 (8,7)	8.19	d 7.6 (8,7)	8.30	d 7.8 (8,7)	8.27	dd 8.3 (8,7); 1.5 (8,6)
9	8.05	s	8.14	d 9.4 (9,10)	8.20	d 9.1 (9,10)	7.99[b]	d 9.3 (9,10)
10	8.05	s	8.73	d 9.4 (10,9)	8.16	d 9.1 (10,9)	8.04[b]	d 9.3 (10,9)

[a] s: singlet; d: doublet; dd: double doublet; t: triplet. [b] Peaks indicated by the same character may be interchanged.

Table III ^{13}C *Chemical shifts (75 MHz, $CDCl_3$) δ (ppm) of pyrene,* **1**, **2** *and* **3**.

	1	2	3	4	5	6	7	8	9	10	3a	5a	8a	10a	10b	10c
pyrene	125.2	126.3	125.2	127.5	127.5	125.2	126.3	125.2	127.5	127.5	131.1	131.1	131.1	131.1	124.3	124.3
1	142.4	122.5	123.3	126.6	130.5	127.5	127.0	126.9	131.2	121.4	134.8	130.5	129.8	124.5	123.3	124.5
2	118.6	145.0	118.6	127.4	129.4	126.2	127.8	126.2	129.4	127.4	131.7[a]	131.3[a]	131.3[b]	131.7[b]	123.7[c]	127.1[c]
3	126.7	127.0	121.6	146.0	126.5	127.6	128.0	128.5	126.7[d]	127.0[d]	125.2	127.6	131.0	131.0	122.1	125.2

[a-d] Peaks indicated by the same character may be interchanged.

ment of C(6) and C(8) was made. It was not possible to discriminate between H(9) and H(10) nor, consequently, between C(9) and C(10).

The most obvious shift in **1** is the downfield shift of the carbon atom attached to the nitro group (+ 17.2 ppm). The carbons *ortho* and *peri* to the nitro group show upfield shifts of − 3.8 and − 6.6 ppm due to the anisotropy of the nitro group. The more distant carbons show an alteration of charge density along the periphery of the molecule, attributed to the mesomeric interaction of the nitro group with the aromatic moiety. The same alteration of charge density, albeit very small, was observed for the peripheric carbon atoms of **2** and this information was used to assign the quaternary carbon atoms in **2**. The effect of the nitro group is more perceptible at 3^a (10^a) than at 5^a (8^a) which makes an upfield shift of − 0.6 ppm for the former and − 0.2 ppm for the latter plausible. The assignment of the quaternary carbon atoms 10^b and 10^c, detected with the relaxation accelerator, is based upon the downfield shift of position 3^a in **1**. The latter assignments are not definitive and may be interchanged. In **2**, the presence of the nitro group is mostly felt on C(2) (+ 18.7 ppm) and on the *ortho* carbons C(1) and C(3) (− 6.6 ppm); the other resonances are hardly affected. The same considerations as for **2** were used to assign the chemical shifts in **3**. For 3^a, an upfield shift is expected due to the influence of the nitro group, whereas a downfield shift is expected for 5^a. Since large shifts for 10^b and 10^c are not very plausible, and also because great differences for 8^a and 10^a are not to be expected, the chemical shifts were assigned as presented. For pyrene and **1**, the chemical shifts are in agreement with literature data[18]. A definitive assignment of all the quaternary carbon atoms in **1**, **2** and **3** should be possible using 2D ^{13}C INADEQUATE NMR techniques; unfortunately such techniques could not be used due to the poor solubility of the compounds.

UV spectra

In Fig. 2 the electronic spectra of **1**, **2**, **3** and pyrene in methanol are given. 1-Nitropyrene (**1**) shows the spectrum expected for a nitro-aromatic system, *viz.* a broad long-wavelength band at ~400 nm (ε: 11000) and no vibrational fine structure. In the case of 4-nitropyrene (**3**), the intensity of the long-wavelength absorption, typical for nitro-aromatic compounds, is much weaker and the second absorption region (280–300 nm) shows well defined vibrational fine structure. The UV spectrum of 2-nitropyrene (**2**), however, does not exhibit the characteristics of a nitro-aromatic compound. Surprisingly, from 300 nm up to 500 nm, the spectrum is almost identical with that of pyrene. The long-wavelength band is absent and there is a small absorption at 400 and at 420 nm corresponding to the forbidden transition to the first excited singlet state (as in pyrene). The second absorption region at 300–350 nm displays the same shape and intensity as does pyrene, indicating that there is very little interaction between the 2-nitro substituent and

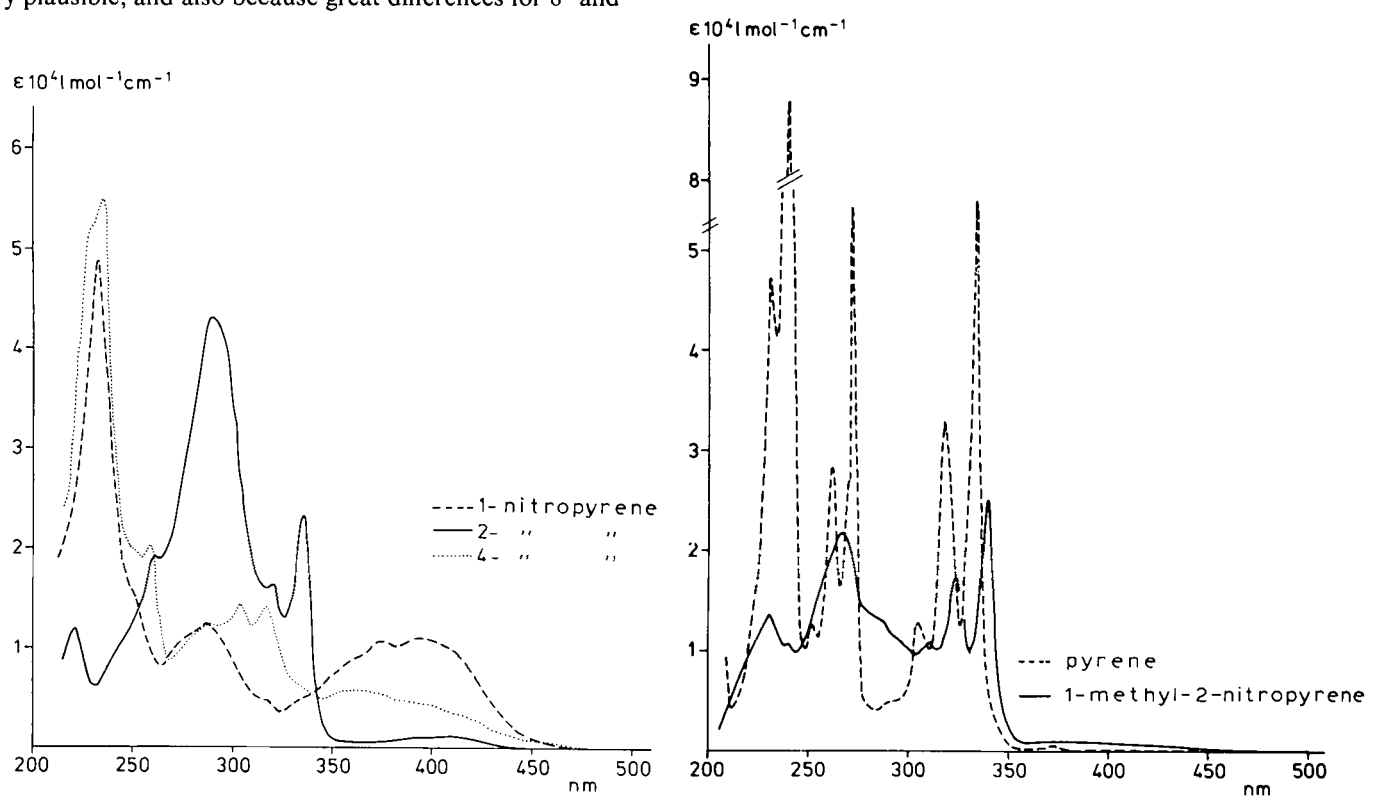


Fig. 2. The electronic absorption spectra of 1-, 2-, 4-nitropyrene, 1-methyl-2-nitropyrene and pyrene.

the aromatic pyrene system. Many other 2-substituted pyrene derivatives with electron-donating or electron-withdrawing groups show a similar lack of interaction. 2-Methoxypyrene, 2-aminopyrene, 2-hydroxypyrene, 2-pyrenecarboxylic acid and 2-pyrenecarboxaldehyde[19] all have UV spectra similar to that of unsubstituted pyrene. The nitro group in 2-nitropyrene (**2**) is not hindered by a *peri* proton as in **1** and **3**. In **2**, the substituent is expected to be in the plane of the aromatic π-system. In order to study the influence of non-planarity, we synthesized 1-methyl-2-nitropyrene (**8**) (*cf.* Exp.). A methyl group at position 1 is expected to force the nitro group at position 2 out of the plane. A methyl group at position 1 does not influence the shape and intensity of the UV spectrum of pyrene[19]. The changes in the UV spectrum will reflect the non-planarity of the nitro group. As can be seen in Fig. 2, the UV spectrum of **8** is very similar to that of **2**, showing even more fine structure, *i.e.* the interaction has further diminished due to the out-of-plane position of the nitro group. The non-planar conformation is obvious from the mass and ^{1}H NMR spectra. The mass spectrum shows a strong M−OH peak (55%) and, in the ^{1}H NMR spectrum, the downfield shift of proton H(3) is 0.59 ppm less than that of 2-nitropyrene. Both phenomena are characteristic of a sterically hindered nitro group[3,20]. When the nitro group is hindered to such an extent that it is almost perpendicular to the aromatic plane, as in 1-nitro-2-*tert*-butylpyrene, the UV spectrum is identical with that of pyrene and the compound shows a bright fluorescence[3]. The lack of interaction between the substituents at position 2 of pyrene can be explained by the fact that both the HOMO and the LUMO in pyrene have nodal planes on carbon 2 (7, 10[b] and 10[c])[21]. Substituents at position 2 therefore have little electronic interaction with the pyrene orbitals.

IR spectra

The infrared absorption region 900–600 cm^{-1} shows strong absorption bands due to H out-of-plane (HOOP) wagging vibrations of the aromatic C−H groups. These vibrations are very characteristic of the substitution pattern in pyrene and its derivatives[22]. The peaks due to the nitro substituent are also easily observed. Normal values for aromatic nitro vibrations are 1520 cm^{-1} (ν_{as}N−O), 1350 cm^{-1} (ν_sN−O) and 850 cm^{-1} (νC−NO$_2$). ν_{as} is influenced by the degree of conjugation of the nitro group and the aromatic moiety: strong conjugation decreases the N−O bond order and ν_{as}N−O is shifted to shorter wavenumbers[23]. Likewise, the C−N stretching vibration provides information about the C−N bond order. The coplanarity of the nitro group and the aromatic system is expressed by the ν_sN−O. When the nitro group is forced out of the aromatic plane by steric hindrance, the ν_s is shifted to longer wavenumbers[3]. In Table IV, the characteristic frequencies of the nitro group in **1**, **2** and **3** are shown.

Table IV Infrared absorptions of the nitro group in mononitropyrenes (in cm^{-1}).

Compound	νC−N	ν_sN−O	ν_{as}N−O
1-nitropyrene (**1**)	841	1330	1510
2-nitropyrene (**2**)	795	1340	1535
4-nitropyrene (**3**)	827	1348	1510
1-methyl-2-nitropyrene (**8**)	824	1342	1521
1-nitro-2-*tert*-butylpyrene	800	1368	1520

The frequencies are in the region expected for aromatic nitro compounds. Remarkably, it is compound **2** that differs significantly in the values of νC−N and ν_{as}N−O. Simple correlations between structure and IR characteristics cannot be given. Coupling with other vibrations and steric factors also play a role. Study of a larger collection of nitro aromatic compounds having weak interaction between the nitro group and the π-system may reveal correlations between νC−N, ν_sN−O and ν_{as}N−O and steric and electronic factors.

Photochemistry

Many aromatic nitro compounds show a rich photochemistry. Light is an important environmental factor which may

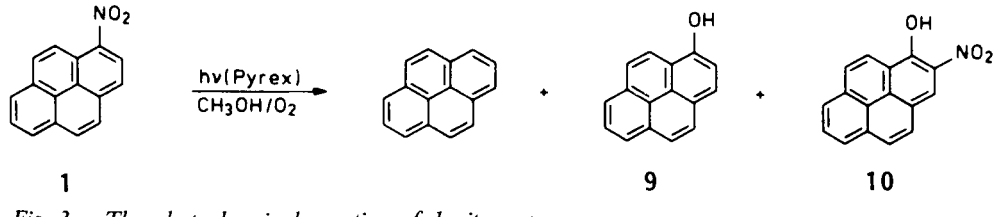


Fig. 3. The photochemical reaction of 1-nitropyrene.

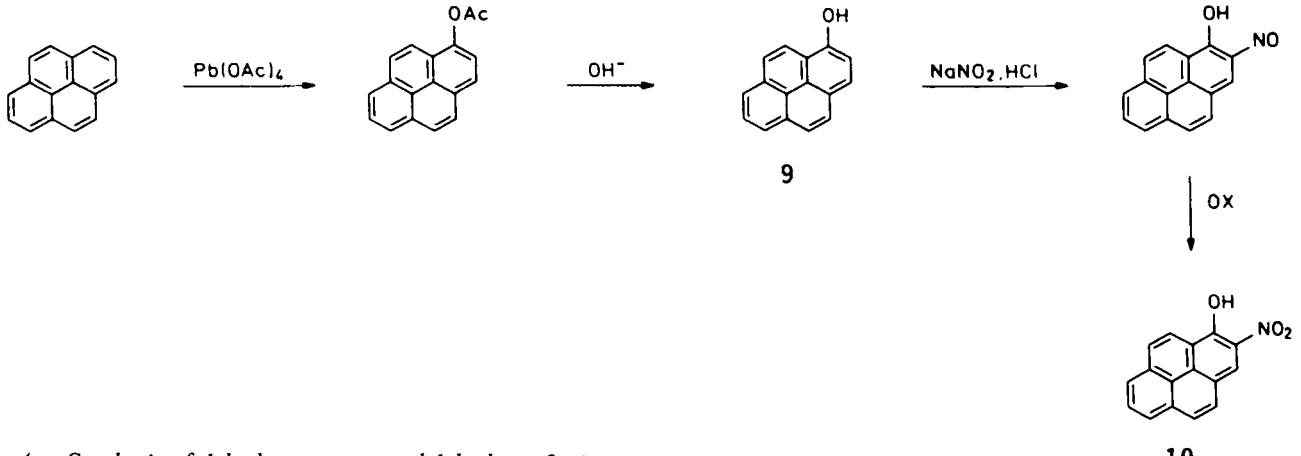


Fig. 4. Synthesis of 1-hydroxypyrene and 1-hydroxy-2-nitropyrene.

convert nitropyrenes into other (possibly harmful) products. These considerations led us to investigate the photochemistry of pure **1**, **2** and **3** in detail.

Compounds **1**, **2** and **3** were irradiated in methanol with light of wavelengths above 300 nm. Preliminary irradiations were performed on a small scale in the presence and in the absence of oxygen. **1** showed a rapid conversion, whereas **3** is more stable than **1** under identical circumstances. Under the same irradiation conditions, with or without oxygen, **2** is very stable and does not undergo a clear reaction. In order to isolate and identify the photoproducts, the irradiations were performed on a preparative scale. After irradiation of **1** (48.0 mg in 300 ml methanol) for $2\frac{1}{2}$ hours in the presence of oxygen, over 95% of the starting material was converted. Two products were identified, namely 1-hydroxypyrene (**9**), formed in high yield (88%), and 7% of a new compound, 1-hydroxy-2-nitropyrene (**10**) (Fig. 3). The spectroscopic properties of **9** and **10** were identical with those of the authentic samples, obtained by independent synthesis (Fig. 4). The structure of **9** and **10** was elucidated by means of NMR spectroscopy. The ^{1}H NMR spectrum of **10** shows a singlet due to H(3) at 8.72 ppm. This proton has a downfield shift of − 0.67 ppm consistent with a proton *ortho* to a nitro group. The proton *ortho* to the hydroxyl group has an upfield shift of + 0.65 ppm as can be seen in the ^{1}H NMR of **9** (*cf.* Exp.).

1-Hydroxy-2-nitropyrene must have been formed via 1-hydroxy-2-nitrosopyrene which is easily oxidized by oxygen. The reaction also proceeds in deaerated, anhydrous acetonitrile. In this case, 1-nitropyrene serves as the oxidant since 1-hydroxy-2-nitropyrene and 1-nitrosopyrene are formed in equimolar quantities. 1-Nitrosopyrene was identified by comparison with an authentic sample. Sweeping the solution with nitrogen gas during the irradiation leads to traces of pyrene.

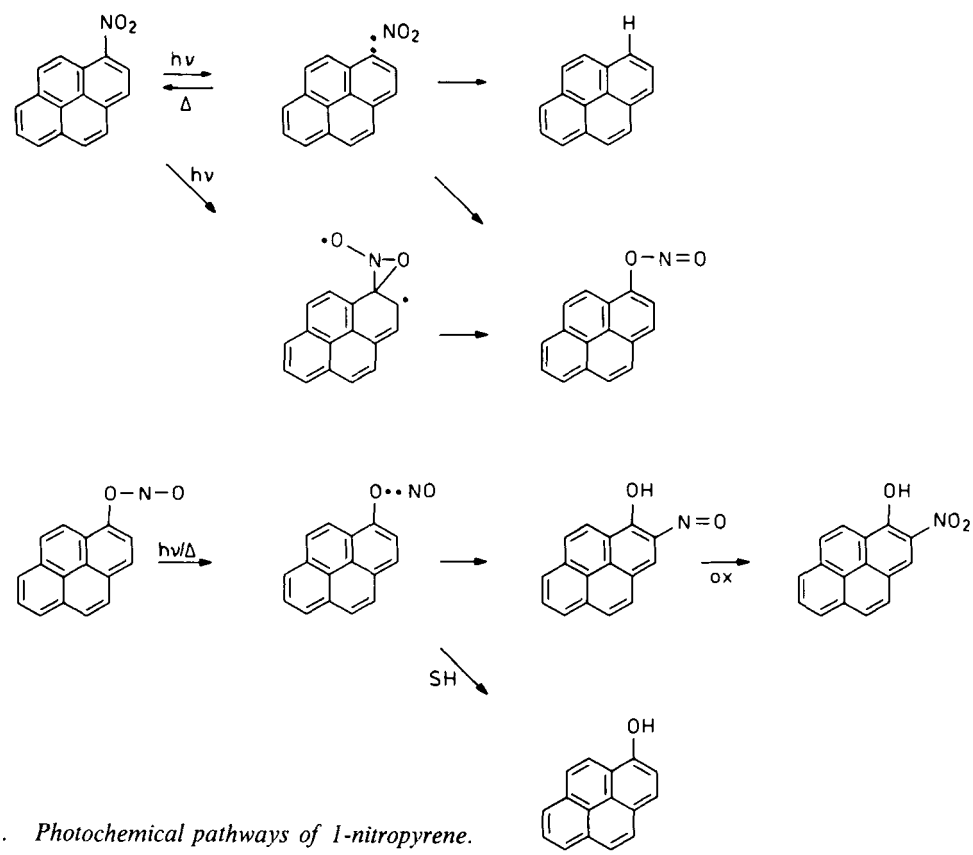
After irradiation of a solution of **2** three times longer than needed for 95% conversion of **1**, 81% of the starting material was recovered.

In contrast to the photoproducts of **1**, those of **3** appeared to be unstable. Pyrene is the most important product (9%) in addition to traces of nitrohydroxy-, nitrodihydroxy- and nitromethoxypyrenes, which were tentatively identified by means of mass spectrometry and proton NMR.

Discussion

The photochemistry of the three nitropyrenes correlates very well with both the electronic and the mass-spectroscopic properties. 2-Nitropyrene (**2**) is very stable towards light; even after prolonged irradiation, virtually all of **2** remains unconverted. This agrees well with the lack of interaction between the nitro group and the aromatic π-system. Compounds **1** and **3** show a high photochemical reactivity. For 1-nitropyrene (**1**), all photoproducts could be isolated and identified, and the percentage of isolated photoproducts (**9**) and (**10**) added up to the total amount of 1-nitropyrene converted.

In the literature[24], data can be found which indicate that the photoreaction described above proceeds via the electronically excited singlet state. In Scheme 1, the reaction pathways of **1**, on photoexcitation, are depicted. Both C–N bond scission and rearrangement may occur. The latter pathway leads directly to 1-pyrenyl nitrite. The major pathway for **1** is presumably via direct rearrangement. The radical pair formed by C–N scission may recombine to form either starting material or 1-pyrenyl nitrite. The pathway via scission is evident from the fact that sweeping the irradiation solution with nitrogen gas leads to an increase in the amount of pyrene. In the case of 4-nitropyrene, C–N bond scission is presumably more important, as, even without N_2 sweeping, the amount of pyrene formed is rather large. The formation of methoxy hydroxy compounds also points to the intermediacy of 4-pyrenyl radicals in methanol. In the mass spectrometer, the rearrangement takes place via the intramolecular mechanism. The amount of $(M-NO)^+$ for



Scheme 1. Photochemical pathways of 1-nitropyrene.

1, **2** and **3** is indicative of the observed photochemical rearrangement. Bond scission in this case only leads to loss of the nitro substituent, which is also a main fragment in the mass spectrum.

The intermediate nitrite esters are unstable; they decompose either thermally or photochemically to the pyrenyloxy radical and NO. The pyrenyloxy radical may react with the solvent to form the corresponding hydroxy compound. With 1-nitropyrene, 1-hydroxypyrene (**9**) is the major product (88%) under both oxidizing and reducing conditions. The NO radical may recombine with the pyrenyloxy radical at various positions, but only the product of attack at position 2 is found. The intermediate 1-hydroxy-2-nitrosopyrene is not isolated as such, but is converted, in the presence of air, into 1-hydroxy-2-nitropyrene (**10**). In the absence of air, 1-nitropyrene acts as oxidant and equimolar amounts of **10** and 1-nitrosopyrene are formed. 1-Hydroxypyrene has been synthesized directly from pyrene via a lead tetraacetate acetoxylation and subsequent saponification. Nitration of **9** does not lead to **10**: the NO_2^+ does not attack at position 2 in **9** but rather at positions 3, 6 and 8, as in pyrene. Reaction with NO^+, however, leads to formation of 1-hydroxy-2-nitrosopyrene, mixed with products of attack at the positions 3, 6 and 8. This mixture was oxidized with H_2O_2, converting the nitroso into nitro groups. Compound **10**, having a high R_f value on account of the hydrogen bond between the 1-OH and the adjacent nitro group, could easily be isolated from this mixture by chromatography. The thermal reaction is a very reliable method of obtaining **10** in high purity and reasonable (4%) yield. While in the literature[25a-b], 2-hydroxy-1-nitropyrene is reported to be the photoproduct of **1**, we found 1-hydroxypyrene (**9**) and 1-hydroxy-2-nitropyrene (**10**) as the photoproducts. This conclusion is based on the spectroscopic data and the independent synthesis.

Other aromatic nitro derivatives such as 9-nitroanthracene[26] and 4-nitroanisole[27,28] show the same photochemical rearrangement. In the case of 9-nitroanthracene, it has been argued that this photoreaction is related to an almost perpendicular arrangement of the nitro group. However, 9-nitroanthracene shows a normal nitro-aromatic electronic absorption spectrum, typical of the considerable interaction of the nitro orbitals with the anthracene system. We were able to establish that a perpendicular arrangement merely results in a lack of photochemistry. In 1-nitro-2-*tert*-butylpyrene, with the nitro group perpendicular to the pyrene system[3], no photochemical reaction is observed.

It is clear that exposure to light can change the properties of **1** and **3** (and presumably also other nitro-aromatic compounds). Structure-activity studies of nitro-aromatic compounds in particular (*e.g.* the mutagenic and carcinogenic properties) can be affected by photochemical or thermal[20] decomposition. In order to obtain reliable information about nitro-aromatic systems, constant attention must be paid to the purity of the samples. Pure samples may easily be contaminated by their own photoproducts and the (biological) properties of these compounds can differ considerably from those of the starting material[29]. It is also clear that photochemical processes in the environment may lead to highly mutagenic (and possibly carcinogenic) photoproducts.

Conclusion

The study of 1-, 2- and 4-nitropyrene and a few sterically hindered nitropyrenes has shed new light on the spectroscopic and photochemical properties of nitro-aromatic systems. A photochemical rearrangement of the nitro group ensues from electronic interaction of the nitro group with the aromatic π-system. In addition, an efficient and reliable synthesis of 1-hydroxy-2-nitropyrene, a very hazardous environmental contaminant, is presented.

Experimental

General

Pyrene was purchased from Janssen Chimica (99 + %) and used without further purification. All solvents were distilled prior to use. Acetonitrile was purified by method A as described by *Walter* et al.[30]. Silica (230–400 Mesh) ASTM was supplied by Merck. All other chemicals were commercial products and were used without further purification. All products are potential carcinogens and consequently all necessary safety precautions were taken. Irradiations were carried out in well-stirred solutions in a vessel fitted with an inner tube (quartz or pyrex) in which the light source Hanau TQ-150 medium pressure arc was mounted. The inner tube and the outside of the vessel were cooled with water. The ^1H and ^{13}C NMR spectra were obtained using a Jeol JNM-FX200 and a Bruker WM-300 spectrometer. The routine ^1H NMR spectra were measured on a Jeol PS 100. TMS ($\delta = 0$ ppm) was used as an internal standard. The coupling constants (J) are given in Hz. The IR spectra were obtained on a Pye-Unicam SP 3–200 spectrophotometer and the UV spectra on a Varian C-219 spectrophotometer. The mass spectra were determined on a KRATOS MS9/50 or an AEI MS 20 mass spectrometer (source 70 eV, temperature as reported). The mass spectrum of 1-methyl-7-nitropyrene was recorded on a Varian MAT-711 double focussing mass spectrometer. For HPLC purification, a DuPont HPLC system (normal phase Zorbax Sil or reversed phase Zorbax ODS 21.2 mm × 25 cm) was used. Melting points are uncorrected.

1-Nitropyrene **1**

Sodium nitrite (2.0 g, 96.6 mmol) and ammonium peroxydisulfate 2.0 g, 29.2 mmol) were added to a stirred solution of pyrene (0.5 g, 2.5 mmol) in 300 ml acetonitrile. The solution was stirred at room temperature for 21 h during which time the colour of the solution turned from colourless to dark yellow. The solution was filtrated, evaporated to dryness and chromatographed on silica (50 g) using hexane/dichloromethane 4/1 as eluent, yielding 0.6 g (2.4 mmol, 98%) 1-nitropyrene. Recrystallization from acetonitrile afforded yellow needles, m.p. 151–152°C (m.p. 151–152°C, hexane/2-propanol[1b]; 153–154°C, acetic acid[31]).

2-Nitropyrene **2**

Pyrene (0.5 g, 2.5 mol) and triphenyltin hydride (1.5 g, 4.3 mmol) were dissolved in a solution of acetonitrile (300 ml) and triethylamine (15 ml). The solution was irradiated for 1 h. The resulting yellowish white suspension was evaporated and dissolved in dichloromethane. The solution was extracted with sulfuric acid (M). The aqueous layer was washed with dichloromethane. The combined organic layers were washed with a 5% sodium hydroxide solution, a 5% sodium bicarbonate solution and water. After drying over magnesium sulfate, filtration and evaporation, the product was chromatographed on silica using hexane as eluent, yielding 0.35 g 4,5,9,10-tetrahydropyrene (1.7 mmol, 68%) as a white solid. ^1H NMR (100 MHz, $CDCl_3$) δ: 2.80 [s, 8H, H(4,4',5,5',9,9',10,10')]; 6.98–7.04 [m, 6H, H(1,2,3,6,7,8)].

4,5,9,10-Tetrahydropyrene (**4**) (0.8 g, 3.8 mmol) was dissolved in 100 ml of acetic anhydride. Copper(II) nitrate trihydrate (0.5 g, 2.1 mmol) was dissolved in 50 ml of acetic anhydride and added to the stirred solution of **4** in 1 h. After 24 h stirring at room temperature, the reaction mixture was poured onto ice (600 g) containing 2 ml sulfuric acid (M) in order to hydrolyse the acetic anhydride. After 15 h stirring, the mixture was extracted with dichloromethane, washed with water, a saturated sodium bicarbonate solution, a 5% sodium hydroxide solution, again with water, dried over magnesium sulfate, filtered and evaporated to dryness. The product was chromatographed on silica using hexane/dichloromethane 4/1 as the eluent, yielding 0.05 g **4** and 0.90 g **5** (3.6 mmol, 98%). ^1H NMR (100 MHz, $CDCl_3$) δ: 2.84 [s, 8H, H(4,4',5,5', 9,9'10,10')]; 7.02–7.20 [m, 3H, H(6,7,8)]; 7.82 [s, 2H, H(1,3)].

5 (0.85 g, 3.4 mmol) was dissolved in 50 ml nitrobenzene and added to a refluxing solution of 2.75 eq. DDQ (2.25 g, 9.9 mmol) in 100 ml nitrobenzene. After refluxing for 40 min, the reaction mixture was cooled and an aqueous sodium sulfite solution was added to remove excess DDQ. The mixture was filtered over hyflo and extracted with water. The aqueous layer was washed with ether and the combined organic extracts were dried over magnesium sulfate, filtrated, evaporated to dryness and chromatographed on silica (hexane/dichloromethane 4/1), yielding 0.79 g (3.2 mmol, 95%) **2** as a light yellow solid. Recrystallization from acetonitrile afforded yellow needles, m.p. 198.5–199.5°C (m.p. 197–199°C, benzene/ethanol[1b]; 201–202.5°C, benzene[32]).

4-Nitropyrene **3**

1,2,3,6,7,8-Hexahydropyrene (**6**), synthesized according to *Coulson*[10], (0.48 g, 2.3 mmol) was dissolved in 100 ml acetic anhydride, and copper(II) nitrate trihydrate (0.5 g, 2.1 mmol), dissolved in 50 ml of acetic anhydride, was then added. After stirring for 6 h at room temperature, the mixture was poured onto ice containing 2 ml sulfuric acid (M) and worked up as described under **2**. Chromatography on silica (hexane/dichloromethane 4/1) afforded 0.55 g **7** (2.2 mmol, 94%). ^{1}H NMR (100 MHz, $CDCl_3$) δ: 1.82–2.18 [m, 4H, H(2,2',7,7')]; 2.92–3.36 [m, 8H, H(1,1',3,3',6,6',8,8')]; 7.18 [s, 2H, H(9,10)]; 7.56 [s, 1H, H(5)].
7 (113 mg, 0.45 mmol) was dissolved in 20 ml of nitrobenzene and added dropwise to a refluxing solution of 3.3 eq. DDQ (339 mg, 1.49 mmol) in 80 ml nitrobenzene. The reaction was performed under nitrogen. After refluxing for ½ h, the reaction mixture was cooled and worked up as described under **2**. Chromatography on silica (hexane/dichloromethane 4/1) yielded 102 mg (0.41 mmol, 92%) **3**. Recrystallization from acetonitrile/water afforded orange needles, m.p. 185–186°C (m.p. 190–192°C, benzene/ethanol[1b]; 196–197.5°C, methanol/acetone[33]).

1-Hydroxypyrene **9**

Pyrene (2.0 g, 9.9 mmol) was dissolved in 50 ml chloroform and lead tetraacetate (5.0 g, 11.2 mmol) dissolved in 50 ml chloroform was then added. After the mixture had been stirred at room temperature for 60 h, it was filtrated and evaporated to dryness. The crude product was dissolved in 100 ml methanol containing KOH (4.0 g) and refluxed for 2 h. The solvent was removed by evaporation and the resulting mixture was dissolved in dichloromethane, filtrated over hyflo and extracted with an aqueous 5% sodium hydroxide solution. The dark blue fluorescent solution was acidified with hydrogen chloride and the resulting precipitate was filtered and purified by column chromatography on silica using toluene as eluent. 0.32 g **9** (1.5 mmol, 15%) was isolated as a white solid rapidly turning brown on contact with air. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.50 [d, 1H, H(2) *J* 8.2]; 7.85 [d, 1H, H(4 or 5) *J* 8.9]; 7.92 [t, 1H, H(7) *J* 7.5]; 7.93 [d, 1H, H(5 or 4) *J* 8.9]; 8.00 [dd, 2H, H(3) *J* 8.2 and H(9) *J* 9.2]; 8.06 [d, 2H, H(6,8) *J* 7.5]; 8.40 [d, 1H, H(10) *J* 9.2]. UV (methanol) λ_{max} nm (relative ε): 241 (1.00); 267 (0.39); 278 (0.60); 347.5 (0.40); 365 (0.22); 385 (0.16).

1-Hydroxy-2-nitropyrene **10**

9 (316 mg, 0.69 mmol) was nitrosated in a methanol/water solution with sodium nitrite at 0°C. The reaction mixture was acidified with a concentrated hydrogen chloride solution until pH 5. After stirring for 1 h, the mixture was extracted with dichloromethane, dried over magnesium sulfate, filtrated and evaporated to dryness. The resulting mixture was dissolved in 50 ml methanol with 50 ml of 5% aqueous sodium hydroxide and 10 ml of a 5% hydrogen peroxide solution was then added. After refluxing for 1 h, the mixture was extracted with dichloromethane. The aqueous layer was acidified with hydrogen chloride (pH 5), extracted with dichloromethane, washed with water and with a saturated sodium bicarbonate solution, dried over magnesium sulfate, filtrated and evaporated to dryness. After chromatography on silica using toluene as eluent, two fractions could be isolated: a red fraction 7.9 mg (0.03 mmol, 4%) of **10** and an orange fraction (19.0 mg) of other hydroxynitropyrene isomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.83 [d, 1H, H(5) *J* 9.1]; 7.87 [d, 1H, H(4) *J* 9.1]; 8.04 [t, 1H, H(7) *J* 7.8]; 8.09 [dd, 1H, H(6) *J* 7.8, *J* 1.7]; 8.12 [d, 1H, H(9) *J* 9.1]; 8.55 [d, 1H, H(10) *J* 9.1]; 8.15 [dd, 1H, H(8) *J* 7.8, *J* 1.7]; 8.72 [s, 1H, H(3)]; 11.59 [s, 1H, OH]. IR (KBr): 1624, 1595, 1530, 1470, 1422, 1405, 1325, 1284, 1268, 1200, 1150, 1136, 1110, 1064, 983, 950, 872, 838, 821, 800, 771, 756, 699, 678, 620 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 472 (0.08), 348 (0.50), 307.5 (1.00), 271 (0.50), 264 (0.80), 257 (0.51), 240 (0.38), 220 (0.57). MS (150°C) *m/z* (%): 263 (100); 246 (20); 233 (3); 217 (20); 216 (32); 189 (28); 188 (55); 187 (31).

1-Methyl-2-nitropyrene **8**

1-Methylpyrene (0.26 g, 1.2 mmol), synthesized from pyrene via a *Vilsmeyer–Haack* formylation followed by the *Huang–Minlon* modification of the *Wolff–Kishner* reduction, was dissolved in a solution of acetonitrile (300 ml), triethylamine (4 ml) and triphenyltin hydride (0.5 g, 1.4 mmol). The solution was irradiated for 1 h. The resulting yellowish white suspension was evaporated to dryness and dissolved in dichloromethane. The solution was extracted with sulfuric acid (M). The aqueous layer was washed with dichloromethane. The combined organic layers were washed with a 5% sodium hydroxide solution and subsequently with a 5% sodium bicarbonate solution followed by water. After drying over magnesium sulfate, filtration and evaporation, the product was chromatographed on silica using hexane as eluent, yielding 0.15 g 1-methyl-4,5,9,10-tetrahydropyrene (0.7 mmol, 54%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.31 [s, 3H, CH_3]; 2.84 [s, 8H, H(4,4',5,5',9,9',10,10')]; 6.98 [d, 1H, H(2) *J* 7.7]; 7.01 [d, 1H, H(3) *J* 7.7]; 7.05–7.13 [m, 3H, H(6,7,8)].
1-Methyl-4,5,9,10-tetrahydropyrene (53.1 mg, 0.24 mmol) was dissolved in acetic anhydride (20 ml). Copper(II) nitrate trihydrate (32.0 mg, 0.13 mmol) in acetic anhydride was added and the mixture was stirred at room temperature for 18 h. The mixture was poured onto ice containing 5 ml sulfuric acid (M) to hydrolyse the acetic anhydride and extracted with dichloromethane. The organic layer was washed with an aqueous sodium bicarbonate solution, a 5% sodium hydroxide solution and water. After drying over magnesium sulfate, the mixture was filtered and evaporated to dryness. Chromatography on silica (hexane/dichloromethane 4/1) afforded 10.5 mg (20%) of the starting material and 39.9 mg (0.15 mmol, 62%) of nitro-substituted 1-methyltetrahydropyrene, a mixture consisting of 25% 1-methyl-7-nitro-4,5,9,10-tetrahydropyrene and 75% 1-methyl-2-nitro-4,5,9,10-tetrahydropyrene. ^{1}H NMR (300 MHz, $CDCl_3$) 1-methyl-2-nitro-4,5,9,10-tetrahydropyrene δ: 2.43 [s, 3H, CH_3]; 2.89 [s, 8H, H(4,4',5,5',9,9',10,10')]; 7.10 [dd, 2H, H(6,8) *J* 7.4, *J* 1.5]; 7.21 [t, 1H, H(7) *J* 7.4]; 7.54 [s, 1H, H(3)]. ^{1}H NMR (300 MHz, $CDCl_3$) 1-methyl-7-nitro-4,5,9,10-tetrahydropyrene δ: 2.32 [s, 3H, CH_3]; 2.86 [s, 8H, H(4,4',5,5',9,9',10,10')]; 7.03 [d, 1H, H(2) *J* 7.7]; 7.10 [d, 1H, H(3) *J* 7.7]; 7.94 [t, 2H, H(6,8)]. The mixture was dissolved in nitrobenzene (10 ml) and added to a refluxing solution of DDQ in 10 ml nitrobenzene (71.9 mg, 31.5 mmol). After refluxing for ½ h, the reaction was cooled and worked up as described under the synthesis of **2**. Chromatography on silica (hexane/dichloromethane 4/1) yielded 39 mg (0.15 mmol, 99%) 1-methyl-2-nitro- and 1-methyl-7-nitropyrene. 1-Methyl-2-nitropyrene (**8**) was purified with HPLC (reversed phase) using acetonitrile/water (9/1), flow 20 ml/min., as eluent. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.98 [s, 3H, CH_3]; 7.84 [d, 1H, H(10) *J* 8.9]; 8.04 [d, 1H, H(9) *J* 8.9]; 8.06 [t, 1H, H(7) *J* 7.6]; 8.13 [d, 1H, H(5 or 4) *J* 9.3]; 8.19 [d, 1H, H(8 or 6) *J* 7.6]; 8.21 [d, 1H, H(6 or 8) *J* 7.6]; 8.24 [d, 1H, H(4 or 5) *J* 9.3]; 8.42 [s, 1H, H(3)]. IR (KBr): 1521, 1490, 1342, 880, 841, 824, 758, 731, 700 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 341 (1.00); 325 (0.72); 311 (0.48); 285 (0.60); 268 (0.93); 240 (0.59); 231 (0.77). Exact mass calcd. for $C_{17}H_{11}NO_2$: 261.0790 *m/z*; found: 261.0804 *m/z*. MS (150°C) *m/z* (%): 261 (88); 244 (55); 231 (8); 217 (19); 216 (82); 215 (98); 214 (49); 213 (78); 202 (26); 189 (100).
^{1}H NMR (300 MHz, $CDCl_3$) of 1-methyl-7-nitropyrene δ: 3.01 [s, 3H, CH_3]; 7.99 [d, 1H, H(2) *J* 7.8]; 8.07 [d, 1H, H(5 or 4) *J* 8.9]; 8.14 [d, 1H, H(4 or 5) *J* 8.9]; 8.18 [d, 1H, H(3) *J* 7.8]; 8.18 [d, 1H, H(9) *J* 9.3]; 8.36 [d, 1H, H(10) *J* 9.3]; 8.93 [d, 1H, H(6 or 8) *J* 2.3]; 8.94 [d, 1H, H(8 or 6) *J* 2.3]. IR (KBr): 1535, 1470, 1340, 1310, 888, 847, 829, 810, 779, 745, 705 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 345 (0.64); 329 (0.46); 295 (1.00); 266 (0.53); 222 (0.45); 217 (0.43). Exact mass calcd. for $C_{17}H_{11}NO_2$: 261.0790 *m/z*; found: 261.0779 *m/z*. MS (90°C) *m/z* (%): 261 (72); 231 (10); 216 (21); 215 (100); 214 (46); 213 (56); 203 (26); 202 (21); 189 (19); 187 (19).

Irradiations

1 (48.0 mg, 0.19 mmol) was dissolved in 300 ml methanol. The solution was irradiated for $2\frac{1}{2}$ h. The brown solution was evaporated to dryness, the residue dissolved in hexane/dichloromethane 1/1 and chromatographed on silica. During the elution, the polarity of the eluent was increased by changing from hexane/dichloromethane 1/1 to dichloromethane (100%) and then to dichloromethane/methanol 9/1. Three main fractions were collected: A. 2.5 mg **1** (5%); B. 3.4 mg **10** (7%); C. 37.3 mg **9** (88%). Alternatively, after evaporation, the reaction mixture was dissolved in dichloromethane and extracted with a 5% aqueous sodium hydroxide solution. The aqueous layer was purple and fluorescent. Upon acidification with hydrogen chloride, a pink precipitate appeared which could be extracted with dichloromethane. Combination of the organic layers, drying over magnesium sulfate, filtration and evaporation afforded an orange-red product which was chromatographed on silica using toluene as eluent. Compounds **10** (red needles) and **9** (grey solid) could now be easily separated.
2 (99.1 mg, 0.40 mmol) was dissolved in 300 ml methanol. The solution was irradiated for 9 h. After evaporation of the solvent, the orange product was chromatographed on silica using hexane/dichloromethane 1/1 as eluent. After elution of the light orange band of **2** (80.5 mg, 0.32 mmol 81%), the eluent was slowly changed to 100% dichloromethane. A yellow oily mixture (12.2 mg) of unidentifiable products was isolated.
3 (48.6 mg, 0.20 mmol) was dissolved in 300 ml methanol. The solution was irradiated for 5 h. TLC showed no remaining starting material. Evaporation of the reaction mixture followed by chromatography on silica using hexane/dichloromethane 1/1 afforded many fractions, amongst which was 3.5 mg (9%) pyrene.

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References

[1a] *H. S. Rosenkranz* and *R. Mermelstein*, Mutat. Res. **114**, 217 (1983);
[b] *M. C. Paputa-Peck, R. S. Marano, D. Schuetzle, T. L. Riley, C. V. Hampton, T. J. Prater, L. M. Skewes, T. E. Jensen, P. H. Ruehle, L. C. Bosch* and *W. P. Duncan*, Anal. Chem. **55**, 1946 (1983);
[c] *J. N. Pitts Jr., J. A. Sweetman, B. Zielinska, A. M. Winer* and *R. Atkinson*, Atmos. Envir. **19**, 1601 (1985).
[2a] *C. Tintel, J. Cornelisse* and *J. Lugtenburg*, Recl. Trav. Chim. Pays-Bas **102**, 14 (1983);
[b] *C. Tintel, J. Cornelisse* and *J. Lugtenburg*, Recl. Trav. Chim. Pays-Bas **102**, 228 (1983);
[c] *A. M. van den Braken-van Leersum, J. Cornelisse* and *J. Lugtenburg*, Tetrahedron Lett. **26**, 4823 (1985).
[3] *L. Rodenburg, R. Brandsma, C. Tintel, J. van Thuijl, J. Lugtenburg* and *J. Cornelisse*, Recl. Trav. Chim. Pays-Bas **105**, 156 (1986).
[4] *P. P. Fu, M. W. Chou, W. Chou, D. W. Miller, G. L. White, R. H. Heflich* and *F. A. Beland*, Mutat. Res. **143**, 173 (1985).
[5] *C. Giordano, A. Belli, A. Citterio* and *F. Minisci*, J. Chem. Soc. Perkin I 1574 (1981).
[6] *C. V. Ristagno* and *H. J. Shine*, J. Am. Chem. Soc. **93**, 1311 (1971).
[7] *R. G. Harvey*, Synthesis 161 (1970).
[8] *N. C. Yang* and *J. Libman*, J. Am. Chem. Soc. **95**, 5783 (1973).
[9] *H. G. Kuivila*, Synthesis 499 (1970).
[10] *E. A. Coulson*, J. Chem. Soc. 1298 (1937).
[11] *J. H. Beynon, G. R. Lester* and *A. E. Williams*, J. Chem. Soc. 1861 (1959).
[12] *T. Ramdahl, J. A. Sweetman, B. Zielinska, R. Atkinson, A. M. Winer* and *J. N. Pitts Jr.*, J. High Res. Chrom., Chrom. Comm. **8**, 849 (1985).
[13] *M. A. Quilliam, F. Messier, P. A. D'Agostino, B. E. McCarry* and *M. S. Lant*, Spectros. Int. J. **3**, 33 (1984).
[14] *E. Clar, B. A. McAndrew* and *M. Zander*, Tetrahedron **23**, 985 (1967).
[15] *G. C. Levy*, "Topics in carbon-13 NMR Spectroscopy", Vol. I, J. Wiley & Sons N.Y., 1974.
[16] *K. Hayamizu, M. Murata* and *O. Yamamoto*, Bull. Chem. Soc. Jpn. **48**, 1842 (1975).
[17] *P. H. Bolton*, J. Magn. Reson. **54**, 333 (1983).
[18] *S. Kaplan*, Org. Magn. Reson. **15**, 197 (1981).
[19] *R. N. Jones*, J. Am. Chem. Soc. **67**, 2127 (1945).
[20] *H. Svendsen, H. P. Rønningsen, K. Sydnes* and *T. Greibrokk*, Acta Chem. Scand. B **37**, 833 (1983).
[21] *A. Streitwieser Jr.* and *J. I. Brauman*, "Supplemental tables of molecular orbital calculations", Vol. I, Pergamon Press, 1965.
[22] *P. E. Hansen* and *A. Berg*, Acta Chem. Scand. B **35**, 131 (1981).
[23] *G. Varsányi* in "Vibrational spectra of benzene derivatives", Acad. Press, N.Y., 1969, p. 384.
[24] *R. Scheerer* and *A. Henglein*, Ber. Bunsen Gesellschaft **81**, 1234 (1977).
[25a] *A. Yasuhara* and *K. Fuwa*, Chem. Lett. 347 (1983);
[b] *A. Yasuhara* and *M. Morita*, Res. Rep. Natl. Inst. Environ. Stud. Jpn. **79**, 103 (1985).
[26] *O. L. Chapman, D. C. Heckert, J. W. Reasoner* and *S. P. Thackaberry*, J. Am. Chem. Soc. **88**, 5550 (1966).
[27] *L. B. Jones, J. C. Kudrna* and *J. P. Foster*, Tetrahedron Lett. **38**, 3263 (1969).
[28] *E. Lippert* and *J. Kelm*, Helv. Chim. Acta **61**, 279 (1978).
[29] *G. Löfroth, L. Nilsson, E. Agurell* and *A. Yasuhara*, Z. Naturforsch. **39c**, 193 (1984).
[30] *M. Walter* and *L. Ramaley*, Anal. Chem. **45**, 165 (1973), method A.
[31] *H. Vollmann, H. Becker, M. Corell* and *H. Streeck*, Justus Liebigs Ann. Chem. **531**, 1 (1937).
[32] *R. Bolton*, J. Chem. Soc. 4637 (1964).
[33] *P. M. G. Bavin*, Can. J. Chem. **37**, 1614 (1959).