Recl. Trav. Chim. Pays-Bas **111**, 335–344 (1992) 0165–0513/92/7/8335–10$3.00

Full Papers

Synthesis and characterisation of nitro-, nitroso- and aminofluoranthenes

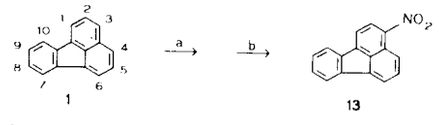
C. J. van Haeringen, N. F. Aten, J. Cornelisse and J. Lugtenburg

Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
(Received November 27th, 1991)

Abstract. The synthesis is reported of the five mononitrofluoranthenes. 1-Nitrofluoranthene was synthesized in 20% from fluoranthene, 2-nitrofluoranthene in 24% from 1,2,3,10b-tetrahydrofluoranthene, 3-nitrofluoranthene in 13% from fluoranthene and 7- and 8-nitrofluoranthene in 34% from 1,2,3,10b-tetrahydrofluoranthene. The pure nitrofluoranthenes were converted into their nitroso and amino analogues. The nitrosopyrenes were also synthesized. Characterisation of each compound is described.

Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAH) constitute a class of widespread environmental contaminants[1,2]. These nitro-PAH can be formed directly during incomplete combustion processes or indirectly via atmospheric reactions of their parent PAH[3,4]. Nitro-PAH are potent mutagens and carcinogens, which pose significant hazards to human health[1,2,5]. The position of the nitro group has a large effect on the biological activity[6,7,8]. During their metabolism, nitro-PAH may be converted into nitroso and amino derivatives[9,10,11]. These substituents also have a profound effect on the mutagenicity and carcinogenicity[9,12,13]. In order to detect and identify nitro-PAH and to obtain a better understanding of their chemical properties and biological activities, it is necessary to have available pure reference materials[14]. In previous papers, our group has described the synthesis of the mononitropyrenes and the mononitrocyclopenta[*cd*]pyrenes[15,16,17]. 2-Nitrofluoranthene is one of the most abundant nitro-PAH found in airborne particles[3]. 3-, 7- And 8-nitrofluoranthene are also found in polluted air[18]. 1-, 3-, 7- And 8-nitrofluoranthene are known to be present in diesel exhaust[19]. This motivated us to prepare each of the five possible nitrofluoranthenes in pure form at the 100-mg scale. Access to the pure nitrofluoranthene isomers allowed us also to prepare the corresponding nitroso and amino derivatives at the 100-mg scale in high purity. In this paper, we describe the preparation of 1-, 2-, 3-, 7- and 8-nitrofluoranthenes, 1-, 2-, 3-, 7-, and 8-nitrosofluoranthenes and 1-, 2-, 3-, 7- and 8-fluoranthenamines. The spectroscopic characterisation of each compound is also described. The biological activity of these compounds will be the subject of a future paper.



1 13

(a) NH_4NO_3, $(CF_3CO)_2O$; (b) column chromatography

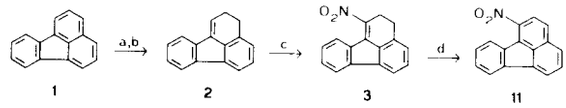
Scheme 1. Synthesis of 3-nitrofluoranthene (**13**).

Results and discussion

Synthesis

A common method for the introduction of a nitro group in a PAH is direct nitration of the parent PAH. Treatment of fluoranthene with ammonium nitrate and trifluoroacetic acid anhydride in acetonitrile[20] gave a mixture of four mononitrofluoranthenes with 3-nitrofluoranthene (**13**) as the main isomer. 3-Nitrofluoranthene could be isolated from this mixture in pure form by chromatography on silica (Scheme 1). In this way, 480 mg of 3-nitrofluoranthene was obtained from fluoranthene in 13% yield.

For the preparation of the other mononitrofluoranthenes, derivatives of fluoranthene with a partially hydrogenated skeleton were required. The synthesis of 1-nitrofluoranthene (**11**) is depicted in Scheme 2. Birch reduction of fluoranthene gave, via 1,10b-dihydrofluoranthene, 2,3-dihydrofluoranthene (**2**)[21] in quantitative yield. Position 1 is the reactive site of 2,3-dihydrofluoranthene towards nitration[22]. Treatment of **2** with ammonium nitrate and trifluoroacetic acid anhydride in acetonitrile gave as sole mononitro product 1-nitro-2,3-dihydrofluoranthene (**3**). Dehydrogenation of **3** by reaction with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in refluxing xylene gave 1-nitrofluoranthene. After purification by column chromatography on silica, 240 mg of 1-nitrofluoranthene was obtained in 20% yield based on fluoranthene.



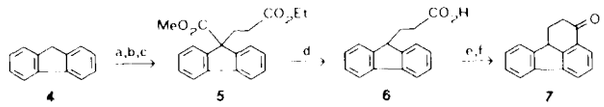
1 2 3 11

(a) Na, NH_3, THF; (b) NH_4Cl; (c) NH_4NO_3, $(CF_3CO)_2O$; (d) DDQ, xylene

Scheme 2. Synthesis of 1-nitrofluoranthene (**11**).

For the preparation of the other three mononitrofluoranthenes, 1,10b-dihydro-3(2*H*)-fluoranthenone (**7**) was the key intermediate. Compound **7** could be prepared in a few steps in 24% yield starting from fluorene (Scheme 3)[23].

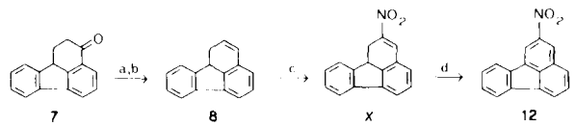
Fluorene was dissolved in tetrahydrofuran and treated with two equivalents of butyllithium. Addition of one equivalent of methyl chloroformate followed by one equivalent of ethyl 3-bromopropanoate gave the diester **5** in 83% yield. Treatment of **5** with potassium hydroxide in refluxing ethanol led to hydrolysis and monodecarboxylation giving 3-(9*H*-fluoren-9-yl)propanoic acid (**6**) in quantitative yield. Ring closure of the acid **6** to the required 1,10b-dihydro-3(2*H*)-fluoranthenone was effected by converting the acid **6** to the acid chloride and subsequent reaction with aluminum chloride in dichloromethane.



(a) 2 eq. BuLi; (b) ClCOOMe; (c) $BrCH_2CH_2COOEt$; (d) KOH; (e) $SOCl_2$; (f) $AlCl_3$

Scheme 3. Synthesis of 1,10b-dihydro-3(2H)-fluoranthenone (**7**).

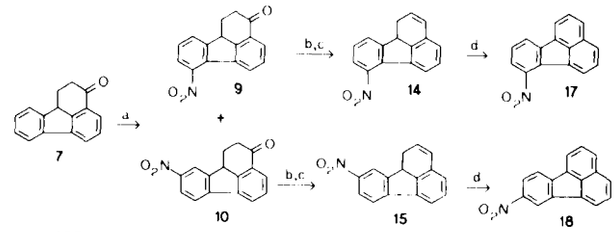
Scheme 4 illustrates how 1,10b-dihydro-3(2*H*)-fluoranthenone can be used as starting material for the preparation of 2-nitrofluoranthene (**12**). **7** was reduced to the corresponding alcohol by reaction with sodium borohydride. The alcohol was dehydrated with *p*-toluenesulfonic acid in refluxing toluene to give 1,10b-dihydrofluoranthene (**8**). **8** was nitrated with silver nitrite and iodine in acetonitrile. This resulted in selective nitration at the β-position of the conjugated double bond[24]. The single nitro derivative obtained was 2-nitrofluoranthene, most probably formed by nitration of compound **8** at position 2, yielding intermediate **X** which aromatized under the reaction conditions ($AgNO_2$, I_2, CH_3CN). In this way, 330 mg of 2-nitrofluoranthene was obtained in 24% yield from 1,10b-dihydro-3(2*H*)-fluoranthenone. Nitration of **8** with regular nitrating agents resulted in nitration in the aromatic moiety of the molecule.



(a) $NaBH_4$; (b) *p*-TsOH; (c,d) $AgNO_2$, I_2, CH_3CN.

Scheme 4. Synthesis of 2-nitrofluoranthene (**12**).

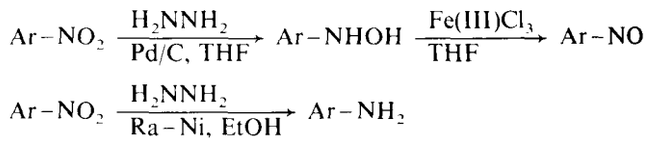
Scheme 5 shows the conversion of 1,10b-dihydro-3(2*H*)-fluoranthenone (**7**) into 7-nitrofluoranthene and 8-nitrofluoranthene similar to the approach of *Campbell* et al.[25]. Treatment of **7** with ammonium nitrate and trifluoroacetic acid anhydride in acetonitrile was expected to result in nitration at positions 7 and 9 due to the strong deactivating properties of the carbonyl group and the directing properties of the fluorene unit. The two products obtained were 7-nitro-1,10b-dihydro-3(2*H*)-fluoranthenone (**9**) and 9-nitro-1,10b-dihydro-3(2*H*)-fluoranthenone (**10**) in a ratio of 2 : 3. **9** and **10** could be separated completely by column chromatography on silica. The ketone **9** was reduced with sodium borohydride to the corresponding alcohol and this was dehydrated with *p*-toluenesulfonic acid in refluxing toluene to 7-nitro-1,10b-dihydrofluoranthene (**14**). **14** was dehydrogenated with DDQ in toluene to 7-nitrofluoranthene (**17**). The ketone **10** was reduced with sodium borohydride to the corresponding alcohol and this was dehydrated with *p*-toluenesulfonic acid to 9-nitro-1,10b-dihydrofluoranthene (**15**). **15** was dehydrogenated with DDQ in toluene to 8-nitrofluoranthene (**18**). In this way, 120 mg of 7-nitrofluoranthene and 190 mg of 8-nitrofluoranthene were obtained from **7** in 14% and 20% yields, respectively.



(a) NH_4NO_3, $(CF_3CO)_2O$, CH_3CN; (b) $NaBH_4$; (c) *p*-TsOH; (d) DDQ, toluene.

Scheme 5. Synthesis of 7-nitro- and 8-nitrofluoranthene (**17**, **18**).

The five pure nitrofluoranthenes could easily be reduced with Raney nickel and hydrazine monohydrate in ethanol to the five fluoranthenamines (Scheme 6). This way 1-, 2-, 3-, 7- and 8-fluoranthenamines (**21**, **22**, **23**, **27** and **28**) were each obtained in 95% yield from the corresponding nitrofluoranthenes. For the preparation of 1-, 2-, 3-, 7- and 8-nitrosofluoranthenes (**31**, **32**, **33**, **37** and **38**), the following procedure was followed: Catalytic reduction of the pure nitrofluoranthenes with Pd/C and hydrazine monohydrate in THF gave complete conversion to the five hydroxylamino derivatives[26]. After reduction was complete according to TLC, the solution was filtered to remove the catalyst. The hydroxylaminofluoranthenes were oxidized to the nitrosofluoranthenes by treatment with iron(III) chloride (Scheme 6). By using iron(III) chloride, no further oxidation to nitrofluoranthenes occurred. It is essential that all of the nitro compound is reduced to a hydroxylamino derivative because traces of the nitro compound are difficult to separate from the final nitroso product. At the same time, care must be taken to avoid further reduction to amino derivatives and loss of product. 2-Nitrosofluoranthene is a extremely unstable compound and must be handled ver carefully. The other nitrosofluoranthenes are stabl compounds. To obtain additional information about nitroso PAH, the nitrosopyrenes were also synthesized. Easy access to the nitropyrenes[15] enabled us to synthesize the nitrosopyrenes similarly as described for the nitrosofluoranthenes. 4-Nitrosopyrene is also a very unstable compound, whereas 1- and 2-nitrosopyrene are stable compounds.



Scheme 6. Reduction of 1-, 2-, 3-, 7- and 8-nitrofluoranthene to the corresponding nitroso- and aminofluoranthenes and of 1-, 2- and 4-nitropyrenes to the corresponding nitrosopyrenes

NMR spectroscopy

The ^1H NMR chemical shifts of the nitrofluoranthenes, nitrosofluoranthenes, nitrosopyrenes and fluoranthenamines are given in Tables I, II, III and IV, respectively. The values were assigned from COSY 2D NMR and NOE experiments. In the case of fluoranthenamines, the NOE experiments were performed on the amino group. The ^1H NMR chemical shifts of the nitrofluoranthenes are in good agreement with those published by *Squadrito* et al.[27].

All nitrofluoranthenes show downfield shifts of the protons *ortho* to the nitro group due to the electron-withdrawing properties of this group. The *peri* protons of 1-, 3- and 7-nitrofluoranthenes are also shifted downfield as a result of steric hindrance. For the fluoranthenamines, upfield shifts

were observed for the *ortho* positions due to the electron-releasing properties of the amino group. There is no *peri* effect. For the nitrosopyrenes and nitrosofluoranthenes, large downfield shifts were observed for *peri* protons (+1.85, +1.47, +0.89, +0.93 and 0.85 ppm for 1-NO-Py, 4-NO-Py, 3-NO-Fl, 7-NO-Fl and 1-NO-Fl, respectively). This was accompanied by large upfield shifts of the *ortho* positions of 1-NO-Py, 1-NO-Fl and 7-NO-Fl (−1.23, −1.00 and −0.86 ppm). No significant shift was observed for the *ortho* proton of 4-NO-Py, a downfield shift was observed for the *ortho* proton of 3-NO-Fl. In the other nitroso compounds, there are two protons ortho to the nitroso group. In the case of 2-NO-Py and 8-NO-Fl, both *ortho* protons were shifted downfield. 2-NO-Fl showed an exceptionally large downfield shift for H3 (+1.80 ppm) and an upfield shift for H1 (−0.55 ppm).

The ^{13}C NMR chemical shifts of the proton-bearing carbon atoms were assigned using ^{1}H–^{13}C 2D NMR. These values are given in Tables V, VI, VII and VIII for the nitrofluoranthenes, nitrosofluoranthenes, nitrosopyrenes and fluoranthenamines, respectively.

In the nitrofluoranthenes, carbon atoms *ortho* to the nitro

Table I ^{1}H *NMR chemical shifts of nitrofluoranthenes ($CDCl_3$, 300 MHz, 295K).*

Compound	H(*n*)									
	1	2	3	4	5	6	7	8	9	10
Fl	7.94	7.63	7.84	7.84	7.63	7.94	7.91	7.38	7.38	7.91
1-NO_2-Fl	–	8.21	7.91	7.83	7.72	7.95	7.89	7.48	7.43	8.49
2-NO_2-Fl	8.69	–	8.86	7.99	7.76	8.07	7.94	7.53	7.52	7.95
3-NO_2-Fl	7.93	8.60	–	8.66	7.79	7.94	7.87[a]	7.45[b]	7.40[b]	7.89[a]
7-NO_2-Fl	8.08	7.72	7.99	8.03	7.77	8.68	–	8.23	7.54	8.11
8-NO_2-Fl	8.11	7.75	8.01	7.99	7.75	8.10	8.76	–	8.31	8.03

[a,b] Interchangeable pair

Table II ^{1}H *NMR chemical shifts of nitrosofluoranthenes ($CDCl_3$, 300MHz, 295K).*

Compound	H(*n*)									
	1	2	3	4	5	6	7	8	9	10
Fl	7.94	7.63	7.84	7.84	7.63	7.94	7.91	7.38	7.38	7.91
1-NO-Fl	–	6.63	7.63	7.77	7.74	7.94	7.96	7.55	7.43	8.76
2-NO-Fl	7.39	–	9.64	8.24	7.81	8.11	7.91	7.43[a]	7.45[a]	7.91
3-NO-Fl	8.11[a]	8.26[a]	–	8.73	7.88	7.88	7.85[b]	7.46[c]	7.39[c]	7.92[b]
7-NO-Fl	8.11	7.77	8.03	8.10	7.84	8.87	–	6.52	7.37	8.24
8-NO-Fl	8.16[a]	7.75[b]	8.02[c]	7.97[c]	7.74[b]	8.10[a]	8.11	–	8.34	8.18

[a,b,c] Interchangeable pair.

Table III ^{1}H *NMR chemical shifts of nitrosopyrenes ($CDCl_3$, 300MHz, 295K).*

Compound	H(*n*)									
	1	2	3	4	5	6	7	8	9	10
Py	8.15	7.91	8.15	8.05	8.05	8.15	7.91	8.15	8.05	8.05
1-NO-Py	–	6.68	7.63	7.73	8.04	8.12	7.95	8.17	8.23	9.90
2-NO-Py	8.62	–	8.62	8.23	8.14	8.22	8.10	8.22	8.14	8.23
4-NO-Py	8.29	8.24	9.62	–	8.10	8.34[a]	8.05	8.48[a]	8.04[b]	8.10[b]

[a,b] Interchangeable pair

Table IV ^{1}H *NMR chemical shifts of fluoranthenamines ($CDCl_3$, 300MHz, 295K).*

Compound	H(*n*)									
	1	2	3	4	5	6	7	8	9	10
Fl	7.94	7.63	7.84	7.84	7.63	7.94	7.91	7.38	7.38	7.91
1-NH_2-Fl	–	7.02	7.72	7.76	7.48	8.01	8.03	7.36	7.42	7.75
2-NH_2-Fl	7.42[a]	–	6.99[a]	7.60	7.53	7.70	7.85	7.35	7.35	7.85
3-NH_2-Fl	7.73	6.78	–	7.83	7.60	7.97	7.89[a]	7.27[b]	7.34[b]	7.79[a]
7-NH_2-Fl	7.94	7.63	7.83	7.79	7.62	7.78	–	6.77	7.23	7.45
8-NH_2-Fl	7.75	7.56	7.71	7.80	7.59	7.85	7.25	–	6.69	7.67

[a,b] Interchangeable pair

Table V ^{13}C *NMR chemical shifts of nitrofluoranthenes ($CDCl_3$, 300MHz, 295K).*

Compound	C(*n*)									
	1	2	3	4	5	6	7	8	9	10
Fl	120.0	127.9	126.6	126.6	127.9	120.0	121.5	127.5	127.5	121.5
1-NO_2-Fl	–	122.9	127.9	126.7	130.8	121.2	121.3	130.0	128.8	127.5
2-NO_2-Fl	113.6	–	123.6	128.3	130.0	123.3	121.8	129.0	128.4	122.3
3-NO_2-Fl	118.1	127.3	–	124.7	131.6	121.4	121.9[a]	129.6[b]	128.3[b]	123.1[a]
7-NO_2-Fl	121.0	127.6	128.2	129.2	128.6	127.9	–	126.0	127.6	123.5
8-NO_2-Fl	122.3	128.3	128.7	128.0	128.4	121.6	116.7	–	123.0	121.3

[a,b] Interchangeable pair

Table VI ^{13}C *NMR chemical shifts of nitrosofluoranthenes ($CDCl_3$, 300MHz, 295K).*

Compound	C(*n*)									
	1	2	3	4	5	6	7	8	9	10
Fl	120.0	127.9	126.6	126.6	127.9	120.0	121.5	127.5	127.5	121.5
1-NO-Fl		106.7	126.7	132.2	126.7	121.3	121.7	130.0	128.5	129.5
2-NO-Fl	102.4	–	138.3	129.2	129.8	123.9	121.7[a]	128.3[b]	128.9[b]	122.4[a]
3-NO-Fl	119.1[a]	128.3[a]	–	125.2	133.6	121.1	122.0[b]	128.2[c]	129.8[c]	123.1[b]
7-NO-Fl	121.1	127.8	127.7	128.8	129.1	128.7	–	106.0	126.6	127.9
8-NO-Fl	122.6[a]	128.4[b]	128.7[c]	127.7[c]	128.4[b]	121.3[a]	110.9	–	125.5	121.7

[a,b,c] Interchangeable pair

Table VII ^{13}C *NMR chemical shifts of nitrosopyrenes ($CDCl_3$, 400MHz, 295K).*

Compound	C(*n*)									
	1	2	3	4	5	6	7	8	9	10
Py	125.2	126.3	125.2	127.5	127.5	125.2	126.3	125.2	127.5	127.5
1-NO-Py	–	103.8	124.1	126.8	133.1	127.6	126.7	127.7	131.4	121.9
2-NO-Py	117.1	–	117.1	128.9	129.3	126.1	128.0	126.1	129.3	128.9
4-NO-Py	126.7	128.4	122.0	–	123.6	129.5[a]	126.9	131.3[a]	126.9[b]	128.4[b]

[a,b] Interchangeable pair

Table VIII ^{13}C *NMR chemical shifts of fluoranthenamines ($CDCl_3$, 400MHz, 295K).*

Compound	C(*n*)									
	1	2	3	4	5	6	7	8	9	10
Fl	120.0	127.9	126.6	126.6	127.9	120.0	121.5	127.5	127.5	121.5
1-NH_2-Fl	–	121.0	128.9	126.0	124.0	120.4	121.5	125.1	126.8	121.7
2-NH_2-Fl	112.3[a]	–	107.3[a]	124.8	128.8	116.8	121.4[b]	127.6[c]	127.2[c]	121.3[b]
3-NH_2-Fl	122.0	110.3	–	120.3	126.2	120.1	121.4[a]	125.4[b]	127.5[b]	120.0[a]
7-NH_2-Fl	120.1	127.8	126.6	125.4	127.9	120.8	–	116.4	129.9	112.9
8-NH_2-Fl	118.3	128.0	124.9	126.7	127.6	119.7	108.8	–	114.0	122.4

[a,b] Interchangeable pair

group are shifted upfield due to the intramolecular electric field of the nitro group. Due to steric hindrance by the nitro group, the *peri* carbon atom of 3-nitrofluoranthene is shifted upfield. This is similar to what is found in 1-substituted naphthalenes and 9-substituted anthracenes. In these molecules, the *peri* positions are shielded. The *peri* carbon atoms of 1- and 7-nitrofluoranthene are shifted downfield.

The *ortho* carbons of the fluoranthenamines are shielded as a result of the electron-releasing effect of the amino group. In 3-fluoranthenamine, there is an upfield shift of the *peri* carbon. In 1- and 7-fluoranthenamines, no *peri* effect is seen. 1-Nitrosopyrene, 4-nitrosopyrene and 3-nitrosofluoranthene showed upfield shifts of their peri carbons (– 5.6, – 3.2 and – 1.4 ppm). This may be caused by steric hindrance between the nitroso group and the *peri* position. The *peri* carbon atoms of 1- and 7-nitrosofluoranthene are shifted downfield (+ 8.0 and + 8.7 ppm). The *ortho* carbons of 1-nitrosopyrene, 1-nitrosofluoranthene and 7-nitrosofluoranthene showed large upfield shifts (– 22.5, – 21.2 and – 21.5 ppm) but the *ortho* carbons of 3-nitrosofluoranthene and 4-nitrosopyrene are only slightly influenced by the nitroso group (+ 0.4 and – 3.9 ppm). 2-Nitrosopyrene and 8-nitrosofluoranthene showed upfield shifts of both *ortho* carbons (– 8.1/ – 8.1 and – 10.6/ – 2.0 ppm, respectively).

2-Nitrosofluoranthene showed a large upfield shift of C1 (−17.6 ppm) and a large downfield shift of C3 (+11.7 ppm).

UV spectroscopy

The UV spectra of the nitrofluoranthenes and nitrosofluoranthenes are given in Figure 1. A characteristic UV spectrum of a nitro-PAH has a strong absorption band at high wavelength. 3-Nitrofluoranthene and 8-nitrofluoranthene possess this band with high intensity. For 2- and 7-nitrofluoranthene, this band is absent, whereas 1-nitrofluoranthene showed an absorption band at high wavelength with low intensity. For 1-, 3-, 7- and 8-nitrofluoranthenes, these phenomena can be explained by the orientation of the nitro group[28,29]. In 8-nitrofluoranthene, the nitro group is coplanar with the aromatic part of the molecule. In 3-nitrofluoranthene, the nitro group is only slightly hindered. This results in good interaction between the π system of the arene and the nitro group. The low intensity of the absorption band of 1-nitrofluoranthene and the absence of an absorption band at high wavelength in 7-nitrofluoranthene can be explained by steric interaction which forces the nitro group out of the plane of the aromatic part of the molecule. 2-Nitrofluoranthene is an exception, because the UV spectrum shows no absorption band at high wavelength although the nitro group is not sterically hindered. Therefore, the poor interaction between the nitro group and the π system of 2-nitrofluoranthene must be due to electronic factors. The nitrosofluoranthenes show UV spectra which roughly resemble those of the nitrofluoranthenes. 3- And 8-nitrosofluoranthene both have a strong absorption band at high wavelength. Compared with the nitrofluoranthenes, the intensity of this band is much stronger. 1- And 7-nitrosofluoranthenes show a weak absorption band at high wavelength, whereas in 2-nitrosofluoranthene no absorption band at high wavelength is observed.

Experimental

Warning:

Many polycyclic aromatic hydrocarbons and their nitro derivatives are potential mutagens and carcinogens.

Guidelines for safe handling and disposal of chemical carcinogens have been published by *Castegnaro* and *Sansone*[30].
All chemicals were commercially available and were used without further purification. All solvents were distilled prior to use. Petroleum ether with a boiling range from 60–80 °C was used. Column chromatography was performed on Merck (230–400 Mesh) silica gel. The ^{1}H NMR spectra were recorded on a Jeol FX-200 or a Bruker WM-300 spectrometer using tetramethylsilane (TMS, 0 ppm) as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. The ^{13}C–^{1}H-correlated 2D NMR spectra were recorded on a Bruker WM-300 spectrometer at 75.5 MHz or a Bruker WM-400 spectrometer at 100.6 MHz. The IR spectra were recorded on a Pye-Unicam SP3-200 spectrometer and the UV-VIS spectra on a Varian DMS-200 spectrophotometer. Double-focus Electron Impact mass spectra were recorded on a Kratos MS9/50 mass spectrometer (source 70 eV, temperature as reported).

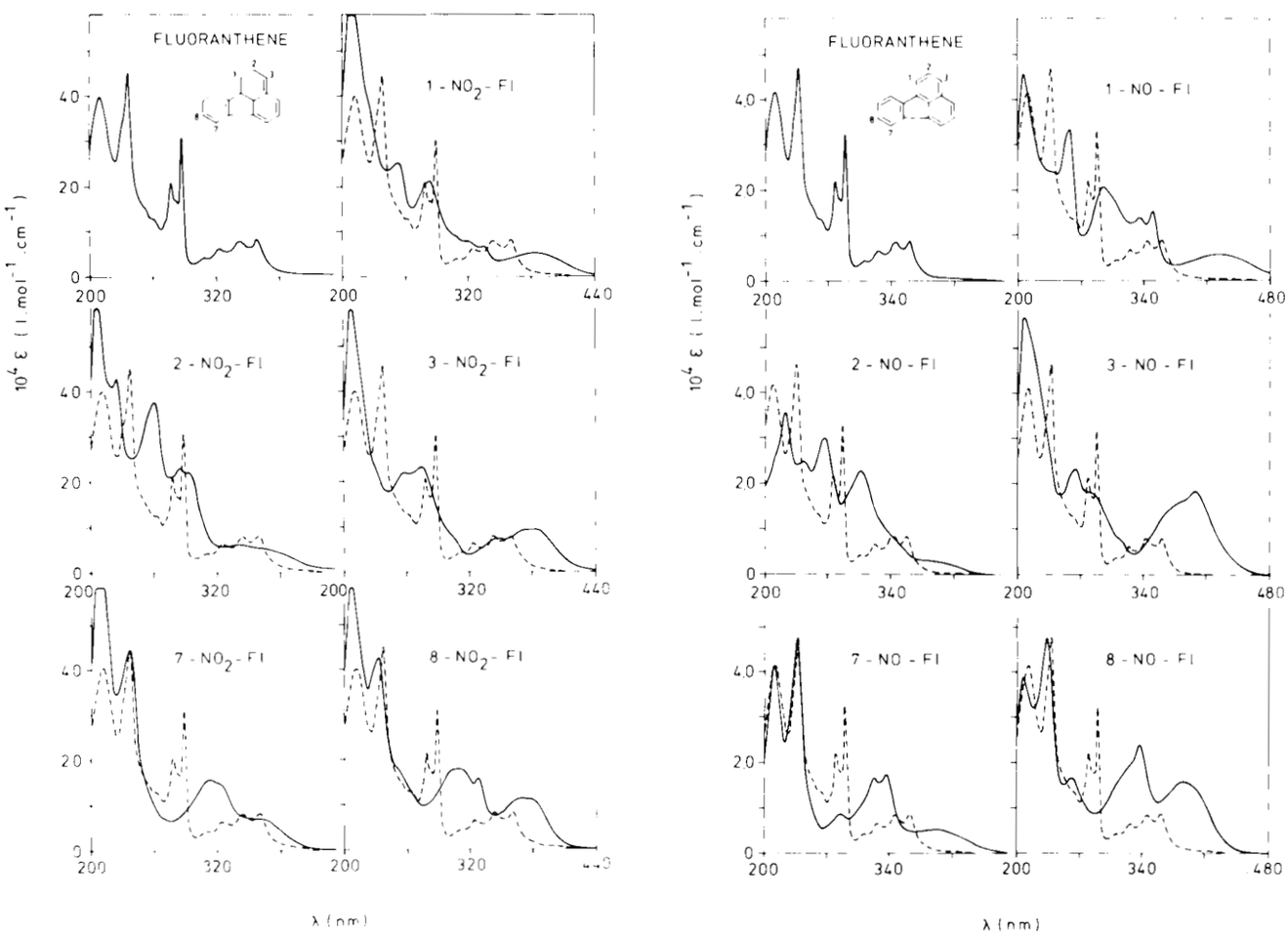


Figure 1. UV spectra of nitrofluoranthenes and nitrosofluoranthenes.

2,3-Dihydrofluoranthene (**2**)

Sodium (2.6 g, 104 mmol) was added at −50 °C under a nitrogen atmosphere to a well-stirred solution of fluoranthene (10 g, 50 mmol) in 500 ml ammonia and 500 ml freshly distilled THF. After stirring for 25 min at −50 °C, the reaction was quenched with 20 g of ammonium chloride. The ammonia was evaporated at room temperature. The remaining solution was dried over magnesium sulfate and the solvent was evaporated *in vacuo* giving 2,3-dihydrofluoranthene in quantitative yield. NMR showed no unreacted fluoranthene or 3,10b-dihydrofluoranthene. The product was used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.72–2.84 (m, 2H, 2-CH_2); 2.97 (t, 2H, *J* 8.0, 8.0, 3-CH_2); 6.58 (t, 1H, *J* 3.0, 3.0, H1); 7.06 (d, 1H, *J* 7.5, H4); 7.26–7.37 (m, 3H, H5,8,9); 7.51 (d, 1H, *J* 7.5, H6); 7.69–7.73 (m, 2H, H7,10).

1-Nitro-2,3-dihydrofluoranthene (**3**)

Trifluoroacetic anhydride (2.0 ml) and 0.39 g (4.9 mmol) ammonium nitrate were added to a solution of 1.0 g (4.9 mmol) 2,3-dihydrofluoranthene in 40 ml acetonitrile at 0 °C. The solution was stirred for 1 h at 0 °C. Water was then added and the mixture was extracted with dichloromethane. The organic layers were washed with water and with a saturated solution of sodium chloride. The solution was dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed over silica, using dichloromethane/petroleum-ether (1 : 4) as eluent, yielding 0.46 g (1.9 mmol, 38%) of 1-nitro-2,3-dihydrofluoranthene. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.00–3.12 (m, 2H, 3-CH_2); 3.22–3.30 (m, 2H, 2-CH_2); 7.03 (d, 1H, *J* 8.0, H6); 7.25–7.46 (m, 4H, H5,7,8,9); 7.59 (d, 1H, *J* 8.0, H4); 8.42 (d, 1H, *J* 8.0, H10). IR (KBr): 1603, 1589, 1497, 1436, 1323, 782, 760, 749, 738 cm^{-1}. UV (methanol), λ_{max} nm (relative ε): 218.5 (1.00), 263.1 (0.89), 270.3 (0.94), 374.8 (0.29). MS *m/z* (%): 249 (14), 232 (19), 203 (44), 202 (100), 201 (18), 200 (23), 189 (10).

1-Nitrofluoranthene (**11**)

Dichlorodicyanobenzoquinone (DDQ 0.55 g, 2.4 mmol), was added to a solution of 0.46 (1.9 mmol) 1-nitro-2,3-dihydrofluoranthene in 40 ml dry xylene. The solution was refluxed for 48 h. During this period, an additional 0.2 g DDQ was added on 6 separate occasions. The reaction mixture was then cooled to room temperature, filtered over hyflo, washed with a saturated solution of sodium sulfite, water and then a saturated solution of sodium chloride. The solution was dried over magnesium sulfate, filtered and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using dichloromethane/petroleum-ether (1 : 4) as eluent, yielding 0.24 g (1.0 mmol, 53%) of 1-nitrofluoranthene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (dt, 1H, *J* 7.5, 7.5, 1.4, H9); 7.48 (dt, 1H, *J* 7.5, 7.5, 1.6, H8); 7.72 (dd, 1H, *J* 8.1, 6.7, H5); 7.83 (d, 1H, *J* 8.1, H4); 7.89 (dd, 1H, *J* 7.5, 1.4, H7); 7.91 (d, 1H, *J* 8.9, H3); 7.95 (d, 1H, *J* 6.7, H6); 8.21 (d, 1H, *J* 8.9, H2); 8.49 (dd, 1H, *J* 7.5, 1.4, H10). ^{13}C–^{1}H 2D NMR ($CDCl_3$): δ 121.2 C6, 121.3 C7, 122.9 C2, 126.7 C4, 127.5 C10, 127.9 C3, 128.8 C9, 130.0 C8, 130.8 C5. IR (KBr): 1590, 1519, 1470, 1339, 1185, 1140, 916, 833, 809, 778, 752 cm^{-1}. UV (methanol), λ_{max} nm (ε l·mol^{-1}·cm^{-1}): 205.0 (69750), 252.5 (26080), 281.9 (21830), 382.9 (5380). Exact mass, calcd. for $C_{16}H_9NO_2$: 247.0633 *m/z*; found: 247.0638. MS (75 °C) *m/z* (%): 247 (100), 201 (88), 200 (47), 189 (24).

Ethyl 3-[9-(methoxycarbonyl)-9H-fluoren-9-yl]propionate (**5**)

At −40 °C, 41 ml of 1.6 M (66 mmol) butyllithium in hexane was added to a solution of 5.0 g (30 mmol) fluorene in 75 ml of freshly distilled THF. The mixture was stirred for 30 min at −40 °C and 2.9 g (30 mmol) of methyl chloroformate was then added. The reaction mixture was stirred at 0 °C for 2 h. Then 5.5 g (36 mmol) ethyl 3-bromopropionate were added. After stirring the reaction mixture at room temperature for 3 h, water was added. The mixture was extracted with ether. The organic layer was washed with water and with a saturated solution of sodium chloride. The solution was dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using dichloromethane/petroleum-ether (20 : 80) as eluent, yielding 8.1 g (25 mmol, 83%) of **5**. ^{1}H NMR (200 MHz, $CDCl_3$), δ 1.11 (t, 3H, *J* 7.1, ethoxy-CH_3); 1.61–1.68 (m, 2H, fluorenyl-CH_2); 2.68–2.78 (m, 2H, CH_2-C=O); 3.60 (s, 3H, methoxy-CH_3); 3.95 (q, 2H, *J* 7.1, ethoxy-CH_2); 7.33 (dt, 2H, *J* 7.4, 1.4 H2,7/H3,6); 7.40 (dt, 2H, *J* 7.4, 1.4, H3,6/H2,7); 7.54 (dd, 2H, *J* 7.4, 1.4, H1,8/H4,5); 7.73 (dd, 2H, *J* 7.4, 1.4, H4,5/H1,8). IR (KBr): 2952, 1727, 1450, 1239, 1021, 745 cm^{-1}. UV (methanol), λ_{max} nm (relative ε): 224.5 (0.83), 260.8 (0.94), 267.0 (1.00), 290.5 (0.27), 302.0 (0.77). MS *m/z* (%): 324 (60), 265 (59), 251 (43), 237 (23), 236 (43), 219 (87), 205 (28), 195 (54), 192 (56), 191 (100), 189 (59), 180 (37), 179 (25), 178 (70), 165 (64), 164 (35), 163 (31).

3-(9H-Fluoren-9-yl)propanoic acid (**6**)

5 (6.0 g, 18.5 mmol) was dissolved in 100 ml of ethanol and 20 ml of 25% aqueous potassium hydroxide were added. The reaction mixture was refluxed for 48 h and then cooled to room temperature. Water and ether were added and the mixture was extracted with 5% aqueous sodium hydroxide. The aqueous layers were combined, acidified with concentrated hydrochloric acid and extracted with ether. This organic layer was washed with water and with a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The yield was 4.2 g (17.5 mmol, 95%) of 3-(9*H*-fluoren-9-yl)propanoic acid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.90–1.99 (m, 2H, fluorenyl-CH_2); 2.34–2.46 (m, 2H, CH_2-C=O); 4.05 (t, 1H, *J* 4.0, 4.0, H9); 7.29 (dt, 2H, *J* 7.5, 7.5, 1.0, H2,7/H3,6); 7.36 (dt, 2H, *J* 7.5, 7.5, 1.0, H3,6/H2,7); 7.50 (dd, 2H, *J* 7.5, 1.0, H1,8/H4,5); 7.74 (dd, 2H, *J* 7.5, 1.0, H4,5/H1,8).

1,10b-dihydro-3(2H)-fluoranthenone (**7**)

6 (2.6 g, 10.9 mmol) was dissolved in 50 ml of thionyl chloride and the solution was refluxed for 1 h. The thionyl chloride was distilled off under reduced pressure. The acid chloride was dissolved in 5 ml of dry dichloromethane and then added dropwise to a cold (−10 °C) solution of 3.2 g (24 mmol) of aluminum chloride in 200 ml of dry dichloromethane. After the mixture had been stirred for 20 min at 0 °C, it was poured into a solution of 10 g potassium tartrate in 500 ml ice/water and the resulting solution was extracted with dichloromethane. The organic layer was washed with water and with a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using dichloromethane/petroleum ether (4 : 1) as eluent yielding 0.7 g (3.2 mmol, 29%) of **7**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.66–1.88 (m, 1H, H1); 2.72–2.84 (m, 1H, H1'); 2.86–2.94 (m, 2H, H2,2'); 4.02 (dd, 1H, *J* 7.5, 2.5, H10b); 7.37 (dt, 1H, *J* 7.5, 7.5, 1.0, H8/H9); 7.42 (dt, 1H, *J* 7.5, 7.5, 1.0, H9/H8); 7.50 (t, 1H, *J* 7.5, 7.5, H5); 7.60 (bs, 1H, H7/H10); 7.78–7.84 (m, 2H, H6,7/H6,10); 7.90 (d, 1H, *J* 7.5, H4). IR (pure): 3050, 2940, 2870, 1677, 1592, 1481, 1450, 1432, 1311, 1275, 1200, 1113, 945, 900, 820, 799, 760, 750, 688 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 215.6 (1.00); 255.2 (0.86); 328.0 (0.56). MS *m/z* (%): 220 (52), 192 (14), 191 (20), 189 (12), 179 (13), 178 (100).

1,10b-Dihydrofluoranthene (**8**)

Sodium borohydride (0.50 g) was added to a solution of 0.70 g (3.2 mmol) of **7** in 150 ml dichloromethane/methanol (1 : 1). The mixture was stirred at room temperature for 2 h, and then water was added. The mixture was washed with a saturated solution of ammonium chloride, neutralized with a saturated solution of sodium bicarbonate, washed with water and with a saturated solution of sodium chloride. The organic layer was dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was dissolved in 100 ml of dry toluene. A catalytic amount of *p*-toluenesulfonic acid was added and the mixture was refluxed for 3 h. The reaction mixture was then cooled to room temperature, washed with a saturated solution of sodium bicarbonate, water and a saturated solution of sodium chloride. The organic layer was dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using petroleum-ether as eluent, yielding 0.59 g (2.9 mmol, 91%) of **8**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.90–2.08 (m, 1H, H1); 2.76–2.91 (m, 1H, H1'); 3.96 (dd, 1H, *J* 8.0, 4.0, H10b); 6.04–6.12 (m, 1H, H2); 6.70 (dd, 1H, *J* 8.0, 2.0, H3); 7.03 (d, 1H, *J* 7.5, H6); 7.30 (t, 1H, *J* 7.5, 7.5, H5); 7.33 (dt, 1H, *J* 7.5, 7.5, 1.0, H8/H9); 7.38 (dt, 1H, *J* 7.5, 7.5, 1.0, H9/H8); 7.53 (bs, 1H, H7/H10); 7.59 (d, 1H, *J* 7.5, H4); 7.79 (bs, 1H, H10/H7).

2-Nitrofluoranthene (**12**)

Silver nitrite (1.3 g, 8.4 mmol), 5.7 g (84 mmol) of sodium nitrite, 2.1 g (8.4 mmol) of iodine and 2 g of potassium carbonate were added to a solution of 850 mg (4.2 mmol) **8** in 150 ml acetonitrile at 0 °C. The mixture was stirred at room temperature for 48 h. A saturated solution of sodium sulfite was then added and the mixture was extracted with ether. The organic layer was washed with a saturated solution of sodium sulfite, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using dichloromethane/petroleum-ether (1 : 9) as eluent yielding 329 mg (1.5 mmol, 32%) of 2-nitrofluoranthene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (dt, 1H, *J* 7.5, 7.5, 1.4, H9); 7.53 (dt, 1H, *J* 7.5, 7.5, 1.4, H8); 7.76 (dd, 1H, *J* 7.0, 8.2, H5); 7.94 (m, 1H, H7); 7.95 (m, 1H, H10); 7.99 (d, 1H, *J* 8.2, H4); 8.07 (d, 1H, *J* 7.0, H6); 8.69 (d, 1H, *J* 1.6, H1); 8.86 (d, 1H, *J* 1.6, H3). ^{13}C–^{1}H 2D NMR ($CDCl_3$): δ 113.6 (C1); 121.8 (C7); 122.3 (C10); 123.3 (C6); 123.6 (C3); 128.3 (C4); 128.4 (C9); 129.0 (C8); 130.0 (C5). IR (KBr): 1526, 1485, 1346, 892, 809, 776, 761, 743 cm^{-1}. UV (methanol) λ_{max} nm (ε l · mol^{-1} · cm^{-1}): 204.3 (64810), 223.2 (44020), 259.1 (38680), 283.9 (23420), 341.0 (6320). Exact mass calcd. for $C_{16}H_9NO_2$: 247.0633 *m/z*; found: 247.0630. MS (75 °C) *m/z* (%): 247 (100), 202 (53), 201 (84), 200 (44), 189 (18).

3-Nitrofluoranthene (**13**)

Ammonium nitrate (1.2 g, 15.0 mmol) and 6.3 ml (45 mmol) trifluoroacetic anhydride were added to a solution of 3.0 g (14.9 mmol) fluoranthene in 150 ml acetonitrile at room temperature. The mixture was stirred at room temperature for 3 h. Water was then added and the mixture was extracted with ether. The organic layer was washed with a saturated solution of sodium bicarbonate, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using dichloromethane/petroleum ether (1 : 9) as eluent, yielding 2.0 g of mononitrofluoranthenes. The mononitrofluoranthenes were chromatographed on silica using dichloromethane/petroleum-ether (3 : 97) as eluent, yielding 0.48 g of **13** and 1.5 g of a mixture of mononitrofluoranthenes. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (dt, 1H, *J* 7.5, 7.5, 1.4, H9); 7.45 (dt, 1H, *J* 7.5, 7.5, 1.4, H8); 7.79 (dd, 1H, *J* 8.6, 7.0, H5); 7.87 (dd, 1H, *J* 7.5, 1.4, H7); 7.89 (dd, 1H, *J* 7.5, 1.4, H10); 7.93 (d, 1H, *J* 7.7, H1); 7.94 (d, 1H, *J* 7.0, H6); 8.60 (d, 1H, *J* 7.7, H2); 8.66 (d, 1H, *J* 8.6, H4). ^{13}C–^{1}H 2D NMR ($CDCl_3$): 118.1 (C1); 121.4 (C6), 121.9 (C7); 123.1 (C10); 124.7 (C4); 127.3 (C2); 128.3 (C9); 129.6 (C8), 131.6 (C5). IR (KBr): 1723, 1610, 1516, 1487, 1455, 1440, 1328, 1185, 850, 778, 760, 747 cm^{-1}. UV (methanol), λ_{max} nm (ε l · mol^{-1} · cm^{-1}): 205.0 (60220), 256.5 (22580), 273.6 (23610), 347.3 (7660), 380.9 (9680). Exact mass calcd. for $C_{16}H_9NO_2$: 247.0633 *m/z*; found: 247.0640. MS (75 °C) *m/z* (%): 247 (100), 217 (16), 201 (59), 200 (43), 194 (89), 189 (27).

*7-Nitro-1,10b-dihydro-3(2*H*)-fluoranthenone and 9-nitro-1,10b-dihydro-3(2*H*)-fluoranthenone* (**9** and **10**)

Ammonium nitrate (0.60 g, 7.4 mmol) and 5.2 ml (37.0 mmol) trifluoroacetic anhydride were added to a solution of 1.64 g (7.4 mmol) **7** at room temperature. The mixture was stirred overnight at room temperature. Water was added and the mixture was extracted with dichloromethane. The organic layer was washed with a saturated solution of sodium bicarbonate, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using dichloromethane as eluent, yielding 0.32 g (1.2 mmol, 16%) of **9** and 0.50 g (1.8 mmol, 25%) of **10**. **9**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.68–1.92 (m, 1H, H1); 2.74–2.84 (m, 1H, H1′); 2.90–3.00 (m, 2H, H2,2′); 3.99 (dd, 1H, *J* 7.5, 2.0, H10b); 7.48–7.61 (m, 4H, H4,5,9,10); 7.86 (dd, 1H, *J* 7.5, 1.0, H8); 7.91 (d, 1H, *J* 7.5, H6). IR (KBr): 3050, 2940, 2875, 1683, 1599, 1531, 1472, 1450, 1409, 1372, 1310, 1274, 1197, 1112, 1098, 972, 867, 843, 799, 783, 750 cm^{-1}. UV (methanol), λ_{max} nm (relative ε): 218.1 (1.00), 254.4 (0.73), 335.5 (0.29), MS *m/z* (%): 265 (100), 220 (84), 193 (61), 191 (76), 189 (100), 179 (66), 178 (66). **10**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.74–1.96 (m, 1H, H1); 2.84–2.90 (m, 1H, H1′); 2.92–3.00 (m, 2H, H2,2′); 4.12 (dd, 1H, *J* 8.0, 4.0, H10b); 7.61 (t, 1H, *J* 7.5, 7.5, H5); 7.94–8.04 (m, 3H, H4,6,7); 8.39 (dd, 1H, *J* 7.5, 1.0, H8; 8.47 (d, 1H, *J* 1.0, H10). IR (KBr): 3080, 2930, 1732, 1680, 1609, 1591, 1513, 1448, 1344, 1318, 1280, 1260, 1198, 914, 852, 822, 801, 760, 750, 710 cm^{-1}. UV (methanol), λ_{max} nm (relative ε): 208.5 (1.00), 228.0 (0.73), 259.2 (0.40), 334.2 (0.59). MS *m/z* (%): 265 (19), 237 (15), 223 (100), 209 (40), 193 (24), 191 (23), 189 (21).

7-Nitro-1,10b-dihydrofluoranthene (**14**)

Sodium borohydride (0.16 g, 4.4 mmol) was added to a solution of 0.32 g (1.2 mmol) of **9** in 150 ml dichloromethane/methanol (1 : 1). The mixture was stirred at room temperature for 2 h. Water was then added and the mixture was extracted with dichloromethane. The organic layer was washed with a saturated solution of ammonium chloride, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was dissolved in 100 ml of toluene. A catalytic amount of *p*-toluenesulfonic acid was added and the mixture was refluxed for 3 h. The mixture was cooled to room temperature, washed with a saturated solution of sodium bicarbonate, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The product was chromatographed on silica using dichloromethane petroleum-ether (1 : 4) as eluent yielding 0.22 g (0.88 mmol, 74%) of **14**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.92–2.12 (m, 1H, H1); 2.86–3.02 (m, 1H, H1′); 3.96 (dd, 1H, *J* 8.0, 4.0, H10b); 6.12–6.20 (m, 1H, H2); 6.68 (dd, 1H, *J* 8.0, 2.0, H3); 7.14 (d, 1H, *J* 7.5, H4); 7.34–7.46 (m, 2H, H5,9); 7.76 (d, 1H, *J* 7.5, H10); 7.98–8.04 (m, 2H, H6,8). IR (KBr): 1612, 1575, 1519, 1480, 1431, 1345, 1328, 1311, 1288, 1260, 1162, 1061, 918, 832, 811, 750, 711, 701 cm^{-1}. UV (methanol), λ_{max} nm (relative ε): 209.8 (1.00), 257.0 (0.92), 341.2 (0.30). MS *m/z* (%): 249 (11), 232 (35), 203 (18), 202 (100), 201 (21), 200 (21), 189 (10).

7-Nitrofluoranthene (**17**)

Dichlorodicyanobenzoquinone (0.24 g, 1.10 mmol) was added to a solution of 0.22 g **9** in 50 ml dry toluene. The mixture was refluxed for 2 h. It was then cooled to room temperature, washed with a saturated solution of sodium sulfite, water and saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The product was chromatographed on silica using dichloromethane/petroleum-ether (1 : 4) as eluent yielding 0.12 g (0.50 mmol, 56%) of **17**. ^{1}H NMR (300 MHz, $CDCl_3$): 7.54 (dd, 1H, *J* 7.5, 8.2, H9); 7.72 (dd, 1H, *J* 6.9, 8.2, H2); 7.77 (dd, 1H, *J* 7.4, 8.1, H5); 7.99 (d, 1H, *J* 8.2, H3); 8.03 (d, 1H, *J* 8.1, H4); 8.08 (d, 1H, *J* 6.9, H1); 8.11 (dd, 1H, *J* 8.2, 1.1, H10); 8.23 (dd, 1H, *J* 7.5, 1.1, H8); 8.68 (d, 1H, *J* 7.4, H6). ^{13}C–^{1}H 2D NMR ($CDCl_3$): δ 121.0 (C1); 123.5 (C10); 126.0 (C8); 127.6 (C9); 127.6 (C2); 127.9 (C6); 128.2 (C3); 128.6 (C5); 129.2 (C4). IR (KBr): 1565, 1515, 1435, 1425, 1337, 1312, 1275, 1182, 851, 827, 811, 768, 738 cm^{-1}. UV (methanol), λ_{max} nm (ε l · mol^{-1} · cm^{-1}): 206.0 (69360), 235.7 (45550), 312.3 (15710). Exact mass calcd. for $C_{16}H_9NO_2$: 247.0633 *m/z*; found: 247.0638. MS (75 °C) *m/z* (%): 247 (100), 202 (13), 201 (78), 200 (40); 189 (18).

9-Nitro-1,10b-dihydrofluoranthene (**15**)

Sodium borohydride (0.34 g, 9.2 mmol) was added to a solution of 0.50 g (1.8 mmol) **10** in 150 ml dichloromethane/methanol (1 : 1). The mixture was stirred at room temperature for 2 h. Water was then added and the mixture was extracted with dichloromethane. The organic layer was washed with a saturated solution of ammonium chloride, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was dissolved in 100 ml of dry toluene. A catalytic amount of *p*-toluenesulfonic acid was added and the mixture was refluxed for 3 h. The mixture was cooled to room temperature, washed with a saturated solution of sodium bicarbonate, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The product was chromatographed on silica using dichloromethane/petroleum-ether (1 : 4) as eluent yielding 0.34 g (1.4 mmol, 73%) of **15**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.98–2.16 (m, 1H, H1); 2.91–3.06 (m, 1H, H1′); 4.00 (dd, 1H, *J* 8.0, 4.0, H10b); 6.14–6.26 (m, 1H, H2); 6.72 (dd, 1H, *J* 8.0, 2.0, H3); 7.14 (d, 1H, *J*, H4/H6/H7); 7.40 (t, 1H, *J* 7.5, 7.5, H5); 7.67 (d, 1H, *J* 7.5, H4/H6/H7); 7.84 (d, 1H, *J* 7.5, H4/H6/H7); 8.32 (dd, 1H, *J* 7.5,

1.5, H8); 8.39 (d, 1H, *J* 1.5, H10). IR (KBr): 1611, 1586, 1510, 1454, 1443, 1435, 1331, 1282, 1154, 1074, 890, 848, 834, 811, 753, 701 cm $^{-1}$. UV (methanol), λ_{max} nm (relative ε): 207.5 (1.00), 227.3 (0.82), 333.2 (0.79). MS *m/z* (%) 249 (25), 232 (26), 219 (20), 203 (29), 202 (100), 201 (39), 200 (31), 191 (29), 189 (20).

8-Nitrofluoranthene (**18**)

Dichlorodicyanobenzoquinone (0.38 g, 1.6 mmol) was added to a solution of 0.34 g (1.4 mmol) **15** in 50 ml of dry toluene. The mixture was refluxed for 2 h. It was then cooled to room temperature, washed with a saturated solution of sodium sulfite, water and a saturated solution of sodium chloride, dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The product was chromatographed on silica using dichloromethane/petroleum-ether (1 : 4) as eluent yielding 190 mg (0.76 mmol, 56%) of **18**. ^{1}H NMR (300 MHz, $CDCl_3$): 7.75 (dd, 1H, *J* 8.1, 7.0, H5); 7.75 (dd, 1H, *J* 8.1, 7.0, H2); 7.99 (d, 1H, *J* 8.1, H4); 8.01 (d, 1H, *J* 8.1, H3); 8.03 (d, 1H, *J* 8.3, H10); 8.10 (d, 1H, *J* 7.0, H6); 8.11 (d, 1H, *J* 7.0, H1); 8.31 (dd, 1H, *J* 8.3, 2.1, H9); 8.76 (d, 1H, *J* 2.1, H7). ^{1}H–^{13}C 2D NMR ($CDCl_3$): δ 116.7 (C7), 121.3 (C10), 121.6 (C6), 122.3 (C1), 123.0 (C9), 128.0 (C4), 128.3 (C2), 128.4 (C5), 128.7 (C3). IR (KBr): 1610, 1586, 1518, 1489, 1454, 1426, 1338, 1140, 1121, 893, 870, 823, 776, 737 cm $^{-1}$. UV (methanol) λ_{max} nm (ε l·mol $^{-1}$·cm $^{-1}$): 204.7 (60760), 231.4 (43420), 304.7 (18030), 326.8 (15860), 349.9 (8150), 369.4 (11360). Exact mass calcd. for $C_{16}H_9NO_2$: 247.0633; found: 247.0638. MS (75°C) *m/z* (%): 247 (100), 217 (5), 201 (69), 200 (45), 189 (16).

1-Nitrosofluoranthene (**21**)

Pd/C (10 mg, 10%) was added to a solution of 130 mg **11** in 50 ml of freshly distilled THF. At 0°C, 150 µl hydrazine monohydrate was added. The solution was stirred for 1 h at 0°C and filtered. $FeCl_3 \cdot 6H_2O$ (360 mg) was added to the cold solution and the solution was stirred for 15 min. Water was added to the solution and the mixture was extracted with ether. The organic layer was washed with water and with a saturated solution of sodium chloride. The solution was dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica giving 60 mg (0.26 mmol, 49%) of **21**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.63 (d, 1H, *J* 8.8, H2); 7.43 (dt, 1H, *J* 7.6, 7.6, 1.1, H9); 7.55 (dt, 1H, *J* 7.6, 7.6, 1.1, H8); 7.63 (d, 1H, *J* 8.8, H3); 7.74 (dd, 1H, *J* 8.2, 7.5, H5); 7.77 (d, 1H, *J* 8.2, H4); 7.94 (d, 1H, *J* 7.6, H6); 7.96 (d, 1H, *J* 7.5, 1.2, H7); 8.76 (dd, 1H, *J* 7.6, 1.2, H10). ^{13}C–^{1}H 2D NMR: δ 106.7 (C2); 121.3 (C6); 121.7 (C7); 126.7 (C5); 126.7 (C3); 128.5 (C9); 129.5 (C10); 130.0 (C8); 132.2 (C4). IR (KBr): 1610, 1493, 1454, 1406, 1353, 1298, 1216, 1164, 1130, 1090, 914, 832, 807, 780, 751 cm $^{-1}$. UV (methanol) λ_{max} (ε l·mol $^{-1}$·cm $^{-1}$): 206.5 (43380, 256.7 (32110), 294.6 (19730), 333.6 (13210), 348.4 (14280), 422.0 (5270). Exact mass calcd. for $C_{16}H_9NO$: 231.0684 *m/z*; found: 231.0680. MS (75°C) *m/z* (%): 231 (36), 217 (2), 202 (15), 201 (100), 200 (30).

2-Nitrosofluoranthene (**22**)

The experimental procedure was the same as for **21**. The yield was 43%, after chromatography on silica. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, 1H, *J* 1.2, H1); 7.43 (m, 1H, H8/H9); 7.45 (m, 1H, H8/H9); 7.81 (dd, 1H, *J* 8.2, 7.0, H5); 7.89–7.92 (m, 2H, H7,10); 8.11 (d, 1H, *J* 7.0, H6); 8.24 (d, 1H, J 8.2, H4), 9.64 (d, 1H, *J* 1.2, H3). ^{1}H–^{13}C 2D NMR ($CDCl_3$): δ 102.4 (C1); 121.7 (C7/C10); 122.4 (C10/C7); 123.9 (C6); 128.3 (C8/C9); 128.9 (C9/C8); 129.2 (C4); 129.8 (C5); 138.3 (C3). IR (KBr): 1616, 1490, 1451, 1383, 1359, 1264, 1222, 1172, 1121, 1092, 1070, 890, 808, 777, 742 cm $^{-1}$. UV (methanol) λ_{max} nm (ε l·mol $^{-1}$·cm $^{-1}$): 224.0 (34510), 243.8 (24260), 267.9 (29240), 308.8 (22130). Exact mass calcd. for $C_{16}H_9NO$: 231.0684 *m/z*, found: 231.0682. MS (75°C) *m/z* (%): 231 (43), 217 (2), 202 (16), 201 (100), 200 (33).

3-Nitrosofluoranthene (**23**)

The experimental procedure was the same as for **21**. The yield was 47% after chromatography on silica using dichloromethane/petroleum-ether (15 : 85) as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (dt, 1H, *J* 7.3, 7.3, 1.2, H8/H9); 7.46 (dt, 1H, *J* 7.3, 7.3, 1.2, H9/H8), 7.85 (m, 1H, H7/H10); 7.83–7.90 (m, 2H, H5,6); 7.92 (m, 1H, H10/H7); 8.11 (d, 1H, *J* 7.5, H1/H2); 8.26 (d, 1H, *J* 7.5, H2/H1); 8.73 (dd, 1H, *J* 7.8, 1.2, H4). ^{1}H–^{13}C 2D NMR ($CDCl_3$): δ 119.1 (C1); 121.1 (C6); 122.0 (C7/C10); 123.1 (C10/C7); 125.2 (C4); 128.2 (C8/C9); 128.3 (C2); 129.8 (C9/C8); 133.6 (C5). IR (KBr): 1613, 1472, 1454, 1439, 1410, 1372, 1344, 1178, 1139, 1052, 843, 781, 754 cm $^{-1}$. UV (methanol) λ_{max} cm^{-1} (ε l·mol $^{-1}$·cm $^{-1}$): 205.5 (54700), 262.6 (22820), 397.6 (18300). Exact mass calcd. for $C_{16}H_9NO$: 231.0684 *m/z*; found: 231.0682. MS (75°C) *m/z* (%): 231 (53), 217 (11), 202 (50), 201 (100), 200 (42).

7-Nitrosofluoranthene (**27**)

The experimental procedure was the same as for **21**. The yield was 70% after chromatography on silica using dichloromethane/petroleum-ether (15 : 85) as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.52 (dd, 1H, *J* 8.2, 0.9, H8); 7.37 (dd, 1H, *J* 8.2, 7.2, H9); 7.77 (dd, 1H, *J* 8.2, 6.9, H2); 7.84 (dd, 1H, *J* 8.1, 7.0, H5); 8.03 (d, 1H, *J* 8.2, H3); 8.10 (d, 1H, *J* 8.1, H4); 8.11 (d, 1H, *J* 6.9, H1); 8.24 (dd, 1H, *J* 7.2, 0.9, H10); 8.87 (d, 1H, *J* 6.9, H6). ^{1}H–^{13}C 2D NMR ($CDCl_3$): δ 106.0 (C8); 121.1 (C1); 126.6 (C9); 127.7 (C3); 127.8 (C2); 127.9 (C10); 128.7 (C6); 128.8 (C4); 129.1 (C5). IR (KBr): 1483, 1460, 1444, 1427, 1394, 1276, 1199, 1188, 1166, 1156, 1110, 1054, 991, 931, 838, 828, 804, 770, 740 cm $^{-1}$. UV (methanol) λ_{max} (ε l·mol $^{-1}$·cm $^{-1}$): 208.6 (41790), 234.7 (48120), 280.9 (9490), 319.0 (17390), 333.6 (18230), 387.0 (5780). Exact mass calcd. for $C_{16}H_9NO$: 231.0684 *m/z*; found: 231.0684. MS (75°C) *m/z* (%): 231 (40), 217 (2), 202 (16), 201 (100), 200 (31).

8-Nitrosofluoranthene (**28**)

The experimental procedure was the same as for **21**. The yield was 61% after chromatography on silica using dichloromethane/petroleum-ether (15 : 85) as eluent: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (dd, 1H, *J* 7.1, 8.3, H5/H2); 7.75 (dd, 1H, *J* 7.1, 8.3, H2/H5); 7.97 (d, 1H, *J* 8.3, H4/H3); 8.02 (d, 1H, *J* 8.3, H3/H4); 8.10 (d, 1H, *J* 7.1, H6/H1); 8.11 (d, 1H, *J* 1.5, H7); 8.16 (d, 1H, *J* 7.1, H1/H6); 8.18 (d, 1H, *J* 8.1, H10); 8.34 (dd, 1H, *J* 8.1, 1.5, H9). ^{1}H–^{13}C 2D NMR ($CDCl_3$): δ 110.9 (C7); 121.3 (C6/C1); 121.7 (C10); 122.6 (C1/C6); 125.5 (C9); 127.7 (C4/C3); 128.7 (C3/C4); 128.4 (C2); 128.4 (C5). IR (KBr): 1610, 1482, 1463, 1455, 1388, 1278, 1230, 1185, 1128, 1072, 909, 842, 816, 768, 740 cm $^{-1}$. UV (methanol) λ_{max} nm (ε l·mol $^{-1}$·cm $^{-1}$): 204.9 (37280), 230.9 (45650), 258.7 (15800), 334.9 (22680), 385.0 (15150). Exact mass calcd. for $C_{16}H_9NO$: 231.0684 *m/z*; found: 231.0681. MS (75°C) *m/z* (%) 231 (53), 217 (3), 202 (17), 201 (100), 200 (38).

1-Fluoranthenamine (**31**)

Raney Ni was added to a solution of 100 mg (0.40 mmol) 1-nitrofluoranthene in 50 ml of ethanol. Hydrazine monohydrate (0.1 ml) was added and the solution was refluxed for 2 h. The reaction mixture was then filtered, water was added and the solution was extracted with ether. The organic layer was washed with water and with a saturated solution of sodium chloride. The solution was dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was chromatographed on silica using dichloromethane/petroleum-ether (50 : 50) as eluent, giving 84 mg of **31** (0.39 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (d, 1H, *J* 8.6, H2); 7.36 (dt, 1H, *J* 7.4, 7.4, 1.4, H8); 7.42 (dt, 1H, *J* 7.4, 7.4, 1.4, H9); 7.48 (dd, 1H, *J* 8.1, 7.1, H5); 7.72 (d, 1H, *J* 8.6, H3); 7.75 (dd, 1H, *J* 7.4, 1.4, H10); 7.76 (d, 1H, *J* 8.1, H4); 8.01 (d, 1H, *J* 7.1, H6); 8.03 (dd, 1H, *J* 7.4, 1.4, H7). ^{1}H–^{13}C 2D NMR ($CDCl_3$): δ 120.4 (C6); 121.0 (C2); 121.5 (C7); 121.7 (C10); 124.0 (C5); 125.1 (C8); 126.0 (C4); 126.8 (C9); 128.9 (C3). IR (KBr): 3380, 3040, 1723, 1713, 1626, 1600, 1455, 1372, 1284, 1147, 824, 803, 777, 743 cm $^{-1}$. UV (methanol) λ_{max} nm (ε l·mol $^{-1}$·cm^{-1}): 204.0 (41950), 223.2 (43290), 259.1 (38320), 284.9 (16200), 326.8 (8120), 399.1 (8770). Exact mass calcd. for $C_{16}H_{11}N$: 217.0891 *m/z*; found: 217.0893. MS (50°C) *m/z* (%): 217 (100), 189 (13).

2-Fluoranthenamine (**32**)

The experimental procedure was the same as for **31**. The yield was 94% after chromatography on silica using dichloromethane/petroleum-ether (50 : 50) as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99 (d, 1H, *J* 1.7, H3/H1); 7.34–7.37 (m, 2H, H8,9); 7.42 (d, 1H, *J* 1.7, H1/H3); 7.53 (dd, 1H, *J* 8.2, 6.7, H5); 7.60 (dd,1H, *J* 8.2, 0.6, H4); 7.70 (dd, 1H, *J* 6.7, 0.6, H6); 7.81–7.87 (m, 2H, H7,10).

^1H–^{13}C 2D NMR ($CDCl_3$): δ 107.3 (C3/C1); 112.3 (C1/C3); 116.8 (C6); 121.3 (C10/C7); 121.4 (C7/C10); 124.8 (C4); 127.2 (C9/C8); 127.6 (C8/C9); 128.8 (C5). IR (KBr): 3430, 3350, 3210, 3045, 1622, 1489, 1467, 1441, 1418, 1314, 1298, 1282, 1241, 1180, 1164, 1151, 1113, 938, 870, 838, 815, 803, 780, 755, 746 cm^{-1}. UV (methanol) λ_{max} nm (ε $l \cdot mol^{-1} \cdot cm^{-1}$): 228.8 (28900), 243.9 (32180), 283.5 (20220), 332.4 (4230), 349.9 (4540). Exact mass calcd. for $C_{16}H_{11}N$: 217.0891 *m/z*; found: 217.0892. MS (50°C) *m/z* (%): 217 (100), 189 (17).

3-Fluoranthenamine (**33**)

The experimental procedure was the same as for **31**. The yield was 96% after chromatography on silica using dichloromethane/petroleum-ether (50 : 50) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ 6.78 (d, 1H, *J* 7.4, H2), 7.27 (dt, 1H, *J* 7.4, 7.4, 1.3, H8/H9); 7.34 (dt, 1H, *J* 7.4, 7.4, 1.3, H9/H8); 7.60 (dd, 1H, *J* 8.4, 6.9, H5); 7.73 (d, 1H, *J* 7.4, H1); 7.79 (dd, 1H, *J* 7.4, 1.3, H10/H7); 7.83 (d, 1H, *J* 8.4, H4); 7.89 (dd, 1H, *J* 7.4, 1.3, H7/H10); 7.97 (d, 1H, *J* 6.9, H6). ^1H–^{13}C 2D NMR ($CDCl_3$): δ 110.3 (C2); 120.0 (C10/C7); 120.1 (C6); 120.3 (C4); 121.4 (C7/C10); 122.0 (C1); 125.4 (C8/C9); 126.2 (C5); 127.5 (C9/C8). IR (KBr): 3480, 3390, 3210, 1621, 1499, 1433, 1402, 1362, 1300, 1285, 1256, 1157, 1110, 825, 817, 772, 756 cm^{-1}. UV-VIS (methanol) λ_{max} nm (ε $l \cdot mol^{-1} \cdot cm^{-1}$): 225.1 (38360), 246.3 (35380), 307.0 (19440), 327.1 (8860), 367.7 (5880), 414.2 (6780). Exact mass calcd. for $C_{16}H_{11}N$: 217.0891 *m/z*; found: 217.0894. MS (50°C) *m/z* (%): 217 (100), 189 (18).

7-Fluoranthenamine (**37**)

The experimental procedure was the same as for **31**. The yield was 95% after chromatography on silica using dichloromethane/petroleum-ether (50 : 50) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ 6.77 (d, 1H, *J* 8.0, H8); 7.23 (t, 1H, *J* 8.0, 8.0, H9); 7.45 (d, 1H, *J* 8.0, H10); 7.62 (dd, 1H, *J* 8.2, 6.9, H5); 7.63 (dd, 1H, *J* 8.1, 7.0, H2); 7.78 (d, 1H, *J* 6.9, H6); 7.79 (d, 1H, *J* 8.2, H4); 7.83 (d, 1H, *J* 8.1, H3); 7.94 (d, 1H, *J* 7.0, H1). ^1H–^{13}C 2D NMR ($CDCl_3$): δ 112.9 (C10); 116.4 (C8); 120.1 (C1); 120.8 (C6); 125.4 (C4); 126.6 (C3); 127.8 (C2); 127.9 (C5); 129.9 (C9). IR (KBr): 3390, 3130, 2910, 1722, 1610, 1582, 1471, 1446, 1424, 1401, 1320, 1290, 1161, 1139, 822, 794, 774, 728 cm^{-1}. UV (methanol) λ_{max} nm (ε $l \cdot mol^{-1} \cdot cm^{-1}$): 204.7 (41040), 216.9 (43800), 235.4 (35340), 275.0 (16630), 286.2 (16800), 321.5 (4490), 344.6 (5100), 360.5 (5960). Exact mass calcd. for $C_{16}H_{11}N$: 217.0891 *m/z*; found: 217.0894. MS (50°C) *m/z* (%): 217 (100), 189 (25).

8-Fluoranthenamine (**38**)

The experimental procedure was the same as for **31**. The yield was 96% after chromatography on silica using dichloromethane/petroleum-ether (50 : 50) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ 6.69 (dd, 1H, *J* 8.0, 2.2, H9); 7.25 (d, 1H, *J* 2.2 H7); 7.56 (dd, 1H, *J* 8.0, 6.9, H2); 7.59 (dd, 1H, *J* 8.1, 6.9, H5); 7.67 (d, 1H, *J* 8.0, H10); 7.71 (d, 1H, *J* 8.0, H3); 7.75 (d, 1H, *J* 6.9, H1); 7.80 (d, 1H, *J* 8.1, H4); 7.85 (d, 1H, *J* 6.9, H6); ^1H–^{13}C 2D NMR ($CDCl_3$): δ 108.8 (C7); 114.0 (C9); 118.3 (C1); 119.7 (C6); 122.4 (C10); 124.9 (C3); 126.7 (C4); 127.6 (C5); 128.0 (C2). IR (KBr): 3410, 3320, 3198, 1615, 1578, 1457, 1448, 1399, 1324, 1240, 1222, 1182, 877, 814, 773 cm^{-1}. UV (methanol) λ_{max} nm (ε $l \cdot mol^{-1} \cdot cm^{-1}$): 216.6 (42340), 235.4 (53830), 277.6 (22080), 288.5 (39000), 305.3 (9460), 321.2 (4450), 342.0 (9070), 357.2 (9100). Exact mass calcd. for $C_{16}H_{11}N$: 217.0891 *m/z*; found: 217.0897. MS (50°C) *m/z* (%): 217 (100), 189 (14).

1-Nitrosopyrene

1-Nitrosopyrene was prepared from 1-nitropyrene[15]. The experimental procedure was the same as for **21**. The yield was 56% after chromatography on silica using dichloromethane/petroleum-ether (15 : 85) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ 6.68 (d, 1H, *J* 8.5, H2); 7.63 (d, 1H, *J* 8.5, H3); 7.73 (d, 1H, *J* 8.8, H4); 7.95 (t, 1H, *J* 7.7, 7.7, H7); 8.04 (d, 1H, *J* 8.8, H5); 8.12, (dd, 1H, *J* 7.7, 1.1, H6); 8.17 (dd, 1H, *J* 7.7, 1.1, H8); 8.23 (d, 1H, *J* 9.2, H9); 9.90 (d, 1H, *J* 9.2, H10); ^1H–^{13}C 2D NMR ($CDCl_3$): δ 103.8 (C2); 121.9 (C10); 124.1 (C3); 126.7 (C7); 126.8 (C4); 127.6 (C6); 127.7 (C8); 131.4 (C9); 133.1 (C5). IR (KBr): 3420, 1725, 1585, 1440, 1395, 1318, 1171, 1138, 1085, 1050, 878, 841, 775, 750, 713 cm^{-1}. UV (methanol) λ_{max} nm (ε $l \cdot mol^{-1} \cdot cm^{-1}$): 234.0 (47960), 259.5 (18240), 313.1 (14580), 399.0 (9580), 439.8 (14170). Exact mass calcd. for $C_{16}H_9NO$: 231.0684; *m/z* found: 231.0674. MS (150°C) *m/z* (%): 231 (57), 202 (29), 201 (100), 200 (15).

2-Nitrosopyrene

2-Nitrosopyrene was prepared from 2-nitropyrene[15]. The experimental procedure was the same as for **21**. The yield was 61% after chromatography on silica using dichloromethane/petroleum-ether (15 : 85) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ 8.10 (t, 1H, *J* 7.6, 7.6, H7); 8.14 (d, 2H, *J* 9.0, H5,9); 8.22 (d, 2H, *J* 7.6, H6,8); 8.23 (d, 2H, *J* 9.0, H4,10); 8.62 (s, 2H, H1,3); ^1H–^{13}C 2D NMR ($CDCl_3$): δ 117.1 (C1,3); 126.1 (C6,8); 128.0 (C7); 128.9 (C4,10); 129.3 (C5,9). IR (KBr): 3400, 1450, 1415, 1390, 1315, 1276, 1252, 1082, 1070, 951, 877, 839, 815, 703 cm^{-1}. UV-VIS (methanol) λ_{max} nm (ε $l \cdot mol^{-1} \cdot cm^{-1}$): 224.8 (13890), 255.2 (13380), 312.8 (48700), 457.0 (1110). Exact mass calcd. for $C_{16}H_9NO$: 231.0684 *m/z*; found: 231.0692. MS (150°C) *m/z* (%): 231 (58), 202 (17), 201 (100), 200 (32).

4-Nitrosopyrene

4-Nitrosopyrene was prepared from 4-nitropyrene[15]. The experimental procedure was the same as for **21**. The yield was 16% after chromatography on silica using dichloromethane/petroleum-ether as eluent. ^1H NMR (300 MHz, $CDCl_3$): 8.04 (d, 1H, *J* 9.1, H9/H10); 8.05 (t, 1H, *J* 7.5, 7.5, H7); 8.10 (s, 1H, H5); 8.10 (d, 1H, *J* 9.1, H10/H9); 8.24 (t, 1H, *J* 7.7, 7.7, H2); 8.29 (dd, 1H, *J* 7.7, 1.2 H1); 8.34 (d, 1H, *J* 7.5, H6/H8); 8.48 (d, 1H, *J* 7.5, H8/H6); 9.62 (dd, 1H, *J* 7.7, 1.2, H3); ^1H–^{13}C 2D NMR ($CDCl_3$): 122.0 (C3); 123.6 (C5); 126.7 (C1); 126.9 (C7); 126.9 (C9/C10); 128.4 (C2); 128.4 (C10/C9); 129.5 (C6); 131.3 (C8). IR (KBr); 3410, 3140, 2920, 1629, 1509, 1396, 1260, 1175, 1115, 1094, 1029, 917, 828, 768, 718 cm^{-1}. UV-VIS λ_{max} nm (ε $l \cdot mol^{-1} \cdot cm^{-1}$): 229.8 (28140), 311.3 (11600), 435.9 (2960). Exact mass calcd. for $C_{16}H_9NO$: 231.0684 *m/z*; found: 231.0682. MS (50°C) *m/z* (%): 231 (47), 202 (23), 201 (100), 200 (30).

Acknowledgements

The authors wish to thank Mr. *A. W. M. Lefeber* and drs. *C. Erkelens* for recording the 2D NMR spectra. Mr. *R. H. Fokkens* (University of Amsterdam) and Mr. *J. J. van Houte* are acknowledged for recording the mass spectra.

References

[1] *H. S. Rosenkranz* and *R. Mermelstein*, Mutat. Res. **114**, 217 (1983).
[2] *H. Tokiwa* and *Y. Ohnishi*, CRC Critical Reviews in Toxicology **17**, 23 (1986).
[3] *T. Ramdahl, B. Zielinska, J. Arey, R. Atkinson, A. M. Winer* and *J. N. Pitts Jr*, Nature **321**, 425 (1986).
[4] *J. Arey, B. Zielinska, R. Atkinson* and *S. M. Aschmann*, Int. J. Chem. Kin. **21**, 755 (1989).
[5] *P. G. Wislocki, E. S. Bagan, A. Y. H. Lu, K. L. Dooley, P. P. Fu, H. Han-Hsu, F. A. Beland* and *F. F. Kadlubar*, Carcinogenesis **7**, 1317 (1986).
[6] *R. Mermelstein, E. C. McCoy* and *H. S. Rosenkranz*, in *D. E. Rickert* ed. Toxicity of nitroaromatic compounds, Chemical Industry Institute of Toxicology series, pp. 205–230.
[7] *B. Zielinska, J. Arey, W. P. Harger* and *R. W. K. Lee*, Mutat. Res. **206**, 131 (1988).
[8] *W. A. Vance, H. S. Okamoto* and *Y. Y. Wang* in *C. M. King, L. J. Romano* and *D. Schuetzle* ed. Carcinogenic and mutagenic responses to aromatic amines and nitroarenes, Elsevier Science Publishing Co. Amsterdam, New York (1988), pp. 291–302.
[9] *P. P. Fu, C. E. Cerniglia, K. E. Richardson* and *R. H. Heflich*, Mutat. Res. **209**, 123 (1988).
[10] *P. P. Fu*, Drug Metabolism Reviews **22**, 209 (1990).
[11] *K. El-Bayoumy* and *S. S. Hecht*, Cancer Research **43**, 3132 (1983).
[12] *W. A. Vance, Y. Y. Wang* and *H. S. Okamoto*, Environ. Mutagen. **9**, 123 (1987).

[13] *L. Fishbein*, Studies in Environmental Science 4: Potential industrial carcinogens and mutagens, Elsevier, Amsterdam, Oxford, New York (1979), p. 356.
[14] *W. Karcher*, in *A. Bjorseth* and *T. Ramdahl*, Handbook of Polycyclic Aromatic Hydrocarbons ed. *A. Bjorseth, T. Ramdahl*, M. Dekker, New York (1985) p. 385.
[15] *A. M. van den Braken-van Leersum, C. Tintel, M. van 't Zelfde, J. Cornelisse* and *J. Lugtenburg*, Recl. Trav. Chim. Pays-Bas **106**, 120 (1987).
[16] *A. M. van den Braken-van Leersum, N. M. Spijker, J. Cornelisse* and *J. Lugtenburg*, Recl. Trav. Chim. Pays-Bas **106**, 628 (1987).
[17] *A. M. van den Braken-van Leersum, J. Cornelisse* and *J. Lugtenburg*, Tetrahedron Lett. **26**, 4823 (1985).
[18] *J. Arey, B. Zielinska, W. P. Harger, R. Atkinson* and *A. M. Winer*, Mutat. Res. **207**, 45 (1988).
[19] *P. Ciccioli, A. Cecinato, E. Brancaleoni, R. Draisci* and *A. Liberti*, Aerosol Science and Technology **10**, 296 (1989).
[20] *J. V. Crivello*, J. Org. Chem. **46**, 3056 (1981).
[21] *R. G. Harvey, D. F. Lindow* and *P. W. Rabideau*, Tetrahedron **28**, 2909 (1972).
[22] *C. Finger*, Chem. Ber. **104**, 2567 (1971).
[23] *J. von Braun* and *E. Anton*, Chem. Ber. **62**, 145 (1929).
[24] *W.-W. Sy* and *A. W. By*, Tetrahedron Lett. **26**, 1193 (1985).
[25] *N. Campbell, J. T. Craig* and *K. Nichol*, Proc. Roy. Soc. Edin. Sect. A **65**, 223 (1960).
[26] *A. M. Dietrich, C. R. Guenat, K. B. Tomer* and *L. M. Ball*, Carcinogenesis **9**, 2113 (1988).
[27] *G. L. Squadrito, B. S. Shane, F. R. Fronczek, D. F. Chureh* and *A. Pryor*, Chem. Res. Toxicol. **3**, 231 (1990).
[28] *H. Svendsen, H.-P. Ronningsen, L. K. Sydnes* and *T. Greibrokk*, Acta Chem. Scan. B **37**, 833 (1983).
[29] *L. Rodenburg, R. Brandsma, C. Tintel, J. van Thuijl, J. Lugtenburg* and *J. Cornelisse*, Recl. Trav. Chim. Pays-Bas **105**, 156 (1986).
[30] *M. Castegnaro* and *E. B. Sansone*, "Chemical Carcinogens. Some Guidelines for Handling and Disposal in the Laboratory", Springer-Verlag, Berlin, 1986.