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Synthesis and spectroscopy of nitroaceanthrylenes and nitroaceanthrenes

Patrick P.J. Mulder, Jos Olde Boerrigter, Ben B. Boere, Han Zuilhof, Cornelis Erkelens, Jan Cornelisse and Johan Lugtenburg

Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
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Abstract. The syntheses of nine mononitro derivatives of aceanthrylene (**1**) and nine mononitro derivatives of aceanthrene (**2**) are described. In addition to **1** and **2**, 1,2,6,10b-tetrahydroaceanthrylene (**3**), 6,10b-dihydro-2(1*H*)-aceanthrylenone (**5**), 1(2*H*)-aceanthrylenone (**4**) and 2(1*H*)-aceanthrylenone (**8**) were also used as starting materials. The resulting nitroaceanthrylenes and nitroaceanthrenes were characterized by their ^{1}H-NMR, ^{13}C-NMR, UV-VIS, IR and mass spectra. The conformation of the nitro group and the interaction between the nitro group and the aromatic system are discussed. In 2-nitroaceanthrylene (**1b**), the nitro group interacts exceptionally well with the aromatic nucleus. The 3-, 4-, 8- and 9-nitro derivatives of **1** and **2** display all the characteristics of normally conjugated planar nitroaromatic compounds. In the remaining nitro derivatives of **1** and **2**, conjugation is diminished owing to steric interactions with nearby protons. The order of decreasing conjugation and increasing twist angle is 5-nitro > 7-nitro > 6-nitro > 10-nitro. The twist angle of the nitro group was calculated using semi-empirical SCF methods PM3 and AM1. Although the values obtained by these methods deviate substantially, they both give the same order of increasing twist angles as the spectroscopically derived order.

Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) constitute an important group of widely distributed environmental contaminants[1-4]. Nitro-PAHs have been identified in emissions of combustion processes, for instance, in diesel exhaust[1,2,5], airplane emissions[6], and in airborne particulates[7,8]. They may be formed during incomplete combustion processes[1,9] and by thermal or photochemical nitration of the parent hydrocarbons in the atmosphere[8,10,11]. Photochemical (radical) nitration often yield other nitro isomers than ionic nitration.

Cyclopenta-fused PAHs (CP-PAHs) constitute another class of widely spread environmental pollutants that pose a significant threat to human health[12]. Cyclopenta[*cd*]pyrene (CPP) is a potent carcinogen in the newborn-mouse lung assay[13] and on mouse skin[14]. Aceanthrylene (AA) (**1**) and its dihydro derivative aceanthrene (DHAA) (**2**) are two other representatives of this class of compounds. Aceanthrylene has been shown to be mutagenic in the Ames test[15] and to form DNA adducts *in vitro*[16]. As with CPP, AA and DHAA are reactive compounds, which react quickly with traces of nitrogen oxides and nitric acid in the atmosphere or during combustion processes[9]. Therefore, nitro-substituted CPPs, AAs and DHAAs may well be present in the environment. Unequivocal identification of nitro-CP-PAHs in complex mixtures is often a problem because of the lack of reference materials and the large number of possible isomers[17]. Thus far, only a relatively small number of nitro-CP-PAHs have been identified[17-19]. The development of synthetic procedures for these nitro compounds may add significantly to the understanding of the occurrence and the structure–activity relationships of nitro-CP-PAHs in particular and nitro-PAHs in general. Several years ago, *Van den Braken-van Leersum* et al.[20,21] synthesized seven isomeric nitro-CPPs. We now wish to report the synthesis, purification and characterization of nine nitroaceanthrylenes: 2-nitro-AA (**1b**), 3-nitro-AA (**1c**), 4-nitro-AA (**1d**), 5-nitro-AA (**1e**) 6-nitro-AA (**1f**), 7-nitro-AA (**1g**), 8-nitro-AA (**1h**), 9-nitro-AA (**1i**), and 10-nitro-AA (**1j**), and nine nitroaceanthrenes: 1-nitro-DHAA (**2a**), 3-nitro-DHAA (**1c**), 4-nitro-DHAA (**2d**), 5-nitro-DHAA (**2e**), 6-nitro-DHAA (**2f**), 7-nitro-DHAA (**2g**), 8-nitro-DHAA (**2h**), 9-nitro-DHAA (**2i**), and 10-nitro-DHAA (**2j**), all being novel compounds. The biological properties of these compounds will be the subject of a forthcoming paper.

Synthesis

Preparation and nitration of aceanthrylene and its partially hydrogenated derivatives

Nitration of the parent aromatic hydrocarbon is the simplest way to introduce a nitro function. The parent systems, aceanthrylene (**1**) and aceanthrene (**2**), are not commercially available. Recently, we described a simple two-step procedure to prepare **2** in high yield (50%) from anthracene[22] (Scheme 1). 1,2-Aceanthraquinone can be prepared in one step from anthracene (56%)[23]. The double Wolff–Kishner reduction of the quinone proceeds with excellent efficiency (95% yield). Dehydrogenation of **2** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gives **1** in 76% yield. Both compounds are now available in gram quantities via this method, which can also be scaled up to higher quantities.

Aceanthrylene is reactive with respect to electrophilic substitution[9] and it is prone to undergo oxidation[24,25].

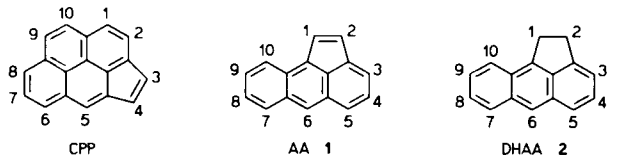
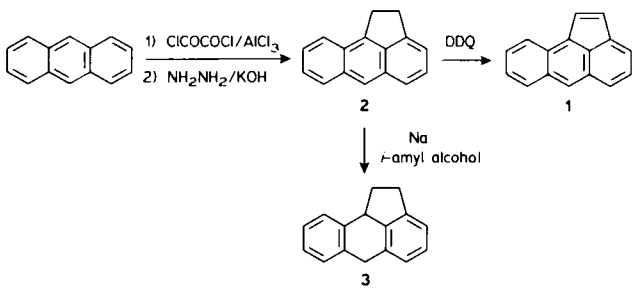


Figure 1. Cyclopenta[cd]pyrene (CPP), aceanthrylene (AA) (1) and aceanthrene (DHAA) (2).



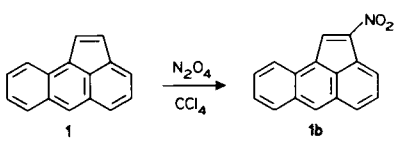
Scheme 1. Synthesis of aceanthrylene and partially hydrogenated derivatives.

Nitration with strong electrophilic or oxidative reagents, such as HNO_3, is expected to result in degradation or overnitration of the compound. It has been shown that similar CP-PAHs can be nitrated in good yields under non-oxidative water-free conditions[20,26]. AA was treated with N_2O_4 in dry CCl_4 (which also contained same K_2CO_3 to neutralize HNO_2 which was expected to be formed during the reaction[27]). Purple 2-nitroaceanthrylene (**1b**) was formed as the only nitro isomer in 55% yield.

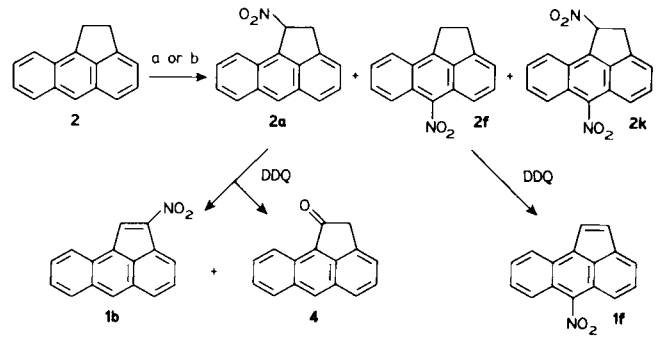
Aceanthrene (**2**) was treated with N_2O_4 in CH_2Cl_2[28] (Scheme 3). A mixture of 1-nitroaceanthrene (**2a**) and 6-nitroaceanthrene (**2f**) was isolated, in a ratio of 4:1. The isomers could easily be separated using column chromatography. Compound **2a** was obtained as yellow needles, and **2f** as orange needles. Small amounts of a dinitroaceanthrene were identified as the 1,6-dinitro isomer **2k**. When **2** was allowed to react with another mild nitrating agent, $NaNO_2/AgNO_3/I_2$ in acetonitrile[20], the ratio of **2a** and **2f** was reversed.

6-Nitroaceanthrene (**2f**) could be dehydrogenated to 6-nitroaceanthrylene (**1f**) with excess DDQ (3 eq.) in refluxing toluene (6 hours). TLC showed a small residue of starting material, which was easily removed by column chromatography. The yield of **1f**, collected as orange-red crystals, was 38%. In refluxing nitrobenzene[21], the reaction proceeded much faster but the yield (3–5%) of **1f** was discouragingly low.

1-Nitroaceanthrene (**2a**) is stable upon treatment with 3 equivalents of DDQ in refluxing toluene. Reaction occurred, however, when **2a** was treated with DDQ in refluxing nitrobenzene for 15 min. Chromatography yielded two fractions, the first containing a purple compound, which surprisingly turned out to be 2-nitro-AA (**1b**) (22%). As far as we know, this type of rearrangement reaction is unprecedented. The second fraction contained 1(2*H*)-aceanthrylenone (**4**) (28%).



Scheme 2. Nitration of aceanthrylene.



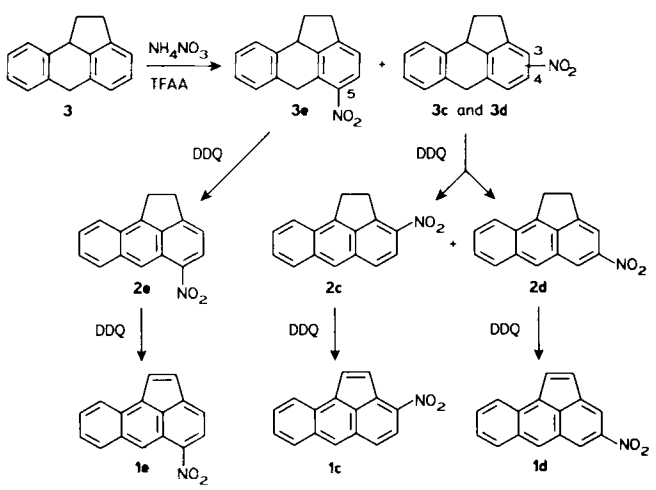
a. N_2O_4/CH_2Cl_2 b. $AgNO_3/NaNO_2/I_2$

Scheme 3. Nitration of aceanthrene, dehydrogenation of nitration products.

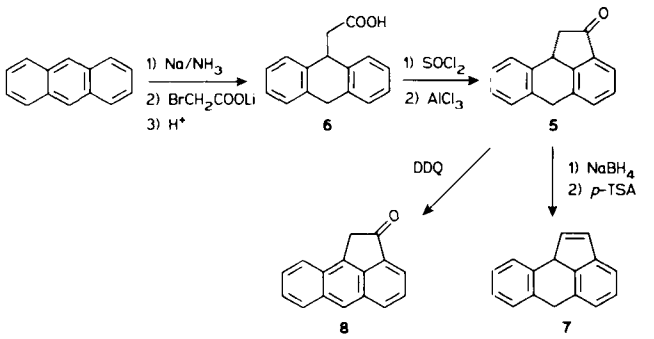
The other positions in **1** and **2** are not sufficiently reactive to undergo nitration. For the other nitro derivatives, synthetic strategies were employed similar to those used earlier in the preparation of the various nitro-CPPs. 1,2,6,10b-Tetrahydroaceanthrylene (THAA) (**3**) has the same skeleton as **1** and **2**, with two isolated benzene rings. Nitration is expected to take place in the most highly substituted benzene ring. The central ring of aceanthrene was reduced by reaction with sodium in refluxing isoamyl alcohol, yielding pure **3** in 91% yield (Scheme 1). Upon nitration with ammonium nitrate and trifluoroacetic anhydride (NH_4NO_3/TFAA) in acetonitrile[29] (Scheme 4), only the most substituted ring was attacked and a mixture of 3-, 4- and 5-nitro-THAA (**3c–e**) in a ratio of 1:1.3:3 was obtained. Chromatography yielded a first fraction containing the 5-nitro isomer **3e** and a second fraction consisting of the 3- and 4-nitro isomers **3c** and **3d**.

Compound **3e** was converted into 5-nitroaceanthrene (**2e**) by reaction with one equivalent of DDQ in refluxing toluene (45 min). Under these conditions, the reaction stopped at the dihydro stage. Compound **2e** was isolated in 27% yield as orange-red needles. 5-Nitroaceanthrylene (**1e**) was prepared from **2e** by reaction with 2 equivalents of DDQ in refluxing toluene for 2 hours. Some residual **2e** could be easily removed by column chromatography. Compound **1e** was isolated after purification as fine brown needles in 20% yield.

Similarly, the mixture of **3c** and **3d** was dehydrogenated with one equivalent of DDQ to 3- and 4-nitroaceanthrene (**2c** and **2d**), which were then separated by column chromatography. 3-Nitro-DHAA was isolated as dark-yellow



Scheme 4. Nitration of 3 and dehydrogenation of nitration products.



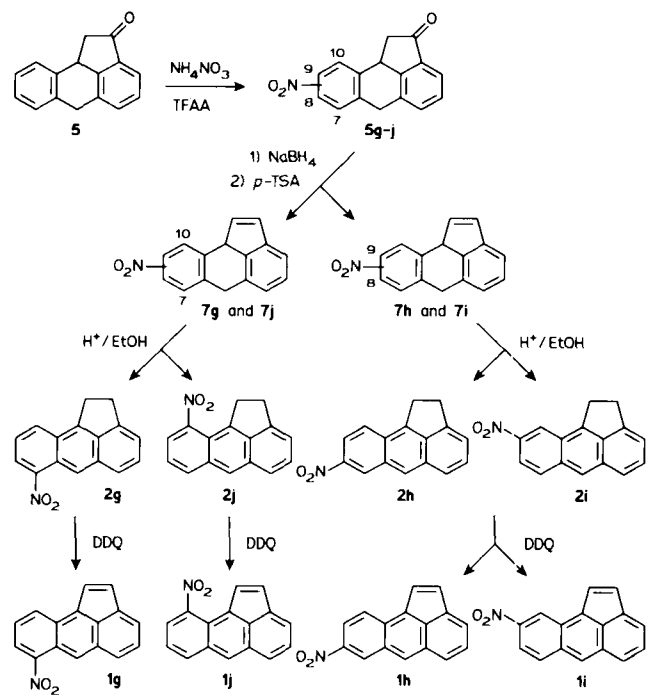
Scheme 5. Synthesis of aceanthrylenones and 6,10b-dihydroaceanthrylene.

needles (47% yield based on **3c**) and 4-nitro-DHAA as orange needles (43% yield based on **3d**).

3-Nitroaceanthrylene (**1c**) was isolated as fine brown needles in 30% yield from **2c** by using the same reaction conditions as described for **1e**. 4-Nitroaceanthrylene (**1d**) was prepared from **2d** by treatment with 1.5 equivalent of DDQ in refluxing toluene for 2 hours. Compound **1d** was isolated as orange crystals in 30% yield after purification.

Preparation and nitration of aceanthrenones

6,10b-Dihydro-2(1*H*)aceanthrylenone (**5**) was used for the preparation of derivatives with the nitro group at positions 7, 8, 9 or 10. The carbonyl group in **5** will deactivate the adjacent aromatic ring and cause direct nitration to the least substituted ring. The preparation of 9,10-dihydro-9-anthraceneacetic acid (**6**) via reductive alkylation of anthracene with lithium bromoacetate in liquid ammonia/diethyl-ether (62% yield) has been described earlier[30]. Conversion of **6** into its acid chloride with $SOCl_2$ and cyclization under Friedel–Crafts conditions gave **5** in 69% yield (Scheme 5). Upon reaction of **5** with NH_4NO_3/TFAA in CH_3CN, a mixture of four isomeric products was obtained (Scheme 6). ^1H NMR revealed



Scheme 6. Preparation of 7-, 8-, 9- and 10-nitroaceanthrenes and -aceanthrylenes.

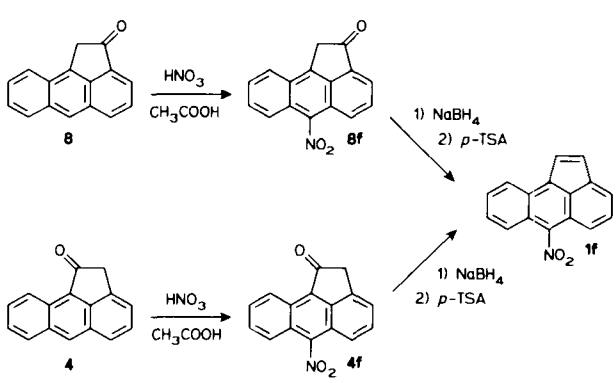
that substitution had taken place in the least substituted ring and that the 7-, 8-, 9- and 10-nitro derivatives **5g–j** were formed in a ratio of 4:4:4:1. The isomers could not be easily separated by column chromatography.

The nitro ketones were converted into the corresponding nitro alcohols by reduction with $NaBH_4$. Dehydration with p-TSA gave the corresponding nitro-6,10-b-dihydroaceanthrylenes (**7g–j**) (57%, two steps). The mixture of the four isomers could be separated into two fractions by chromatography. The first fraction contained the 7- and 10-nitro isomers **7g** and **7j** and the second fraction the 8- and 9-nitro isomers **7h** and **7i**.

Compounds **7g–j** are isomers of the nitroaceanthrenes **2g–j**, which will be more stable because they contain an anthracene nucleus. Isomerization could be effected by treating **7g–j** in refluxing ethanol with a few drops of concentrated HCl. A mixture of **7g** and **7j** was thus converted into a mixture of 7- and 10-nitroaceanthrene (**2g** and **2j**) in good yield. Separation of **2g** and **2j** was achieved by means of column chromatography. Compound **2g** was collected as orange-red crystals and **2j** as yellow-orange crystals. Isomerization of a mixture of **7h** and **7i** led to 8- and 9-nitroaceanthrene (**2h** and **2i**) which were separated using HPLC. Compound **2h** was collected as orange-red needles; **2i** as orange needles.

The nitroaceanthrylenes 7-, 8-, 9- and 10-nitro-AA (**1g–j**) were prepared from the corresponding nitro-DHAAs **2g–j** by treatment with 1.5 equivalent of DDQ in refluxing toluene for 45 min. 7-Nitroaceanthrylene (**1g**) was obtained in 60% yield from **2g** and 10-nitroaceanthrylene (**1j**) in 47% yield from **2j**. After purification, **1g** was obtained as red needles and **1j** as light-orange needles. For convenience, a mixture of **2h** and **2i** was used for the preparation of 8- and 9-nitroaceanthrylene (**1h** and **1i**), which were formed in 56% and 76% yields, respectively. After separation by HPLC, **1h** was obtained as orange needles and **1i** as orange-red needles. The preparation of 6-nitro-AA (**1f**) is described above. However, the overall yield in two steps from aceanthrene (8.5%) is not very high and, therefore, we investigated two other routes. 2(1*H*)-Aceanthrylenone (**8**) could be prepared from **5** by reaction with DDQ in refluxing toluene (74%) (Scheme 5). Nitration of **8** with HNO_3 (*d* 1.5) in glacial acetic acid gave the 6-nitro derivative **8f** (46% yield) (Scheme 7). This nitro ketone was converted into **1f** via reduction with $NaBH_4$ followed by dehydration with p-TSA (47% yield). Alternatively, 1(2*H*)-aceanthrylenone (**4**) can be prepared in one step from anthracene[31]. Nitration of **4** with HNO_3/CH_3COOH gave 6-nitro-1(2*H*)aceanthrylenone (**4f**) in 61% yield. Reduction and subsequent dehydration gave **1f** in 74% yield.

Nine of the ten nitro-AAs and nine of the ten nitro-DHAAs have been prepared. In an attempt to prepare 1-nitroaceanthrylene (**1a**), we synthesized 6,10b-dihydro-



*Scheme 7. Nitration of 2(1H)-aceanthrylenone (**4**) and 2(1H)-aceanthrylenone (**8**); preparation of 6-nitro-aceanthrylene (**1f**).*

aceanthrylene (**7**) (Scheme 5). Since nitration of styrene with $AgNO_2/I_2$ reportedly yields β-nitrostyrene[26], we hoped that nitration of **7** with $AgNO_3/NaNO_2$ and I_2 would occur at position 1. Compound **7** was prepared from ketone **5** by reduction with $NaBH_4$ and subsequent dehydration with p-TSA in good yield (82%). Unfortunately, nitration of **7** gave only traces of **2a**; other products, which could not be identified, were found in low yield.

A possibility to prepare 2-nitroaceanthrene (**2b**) would be reduction of the double bond of 2-nitroaceanthrylene (**1b**). Methods have been published in which a double bond is reduced in the presence of a nitro group[32,33] $NaBH_4$ in various solvents can be used. However, these methods failed to give **2b**, because the nitro group was reduced in preference to the double bond.

Purification of nitroaceanthrenes and the nitroaceanthrylenes

The nine nitro-AAs and the nine nitro-DHAAs were purified by column chromatography, in most cases followed by preparative HPLC. In this way, all compounds could be isolated in pure (> 99%) form. Best results were normally obtained by using reversed-phase HPLC (Zorbax ODS, CH_3CN/H_2O 6:1). For mixtures of 8- and 9-nitro-AA and of 8- and 9-nitro-DHAA, no satisfactory separation could be achieved in this way. Normal-phase HPLC (Zorbax Sil, CH_2Cl_2/petroleum ether 6:1) did, however, give good separation in these cases. All compounds were recrystallized from CH_2Cl_2/petroleum-ether and had sharp melting points with a melting range of 0.5–1.0°C.

Spectroscopic identification

Mass spectrometry

The electron-impact (EI) mass (low and high resolution) spectra of aceanthrylene, aceanthrene and their 18 nitro derivatives were recorded at 70 eV. The mass spectrum of AA shows little fragmentation, which is typical for unsubstituted PAH[34]. Only some loss of one and of two hydrogens (relative abundance: 14% and 20%) is observed. The loss of hydrogens in the spectrum of DHAA is more pronounced: M^+-1: 71%, M^+-2: 36%, M^+-3: 7% and M^+-4: 5%. No loss of the five-membered ring is observed.

The spectra of the nitro-AAs and the nitro-DHAAs were measured at the lowest possible source temperature (150°C and 100°C, respectively) in order to minimize reduction of the nitro group, which may occur in the inlet system at elevated temperatures[35]. For all compounds, the high-resolution mass data are in good agreement with the calculated values: $C_{16}H_9NO_2$ 247.0633 m/z; $C_{16}H_{11}NO_2$ 249.0789 m/z. The recorded values are given in the experimental section. The data of the low-resolution spectra of the nitro compounds are given in Tables I and II. Nitroaromatic compounds underwent two characteristic fragmentations under EI conditions: One route is the direct loss of NO_2/HNO_2 (M^+-46/M^+-47); the other is the loss of NO (M^+-30) after a nitro–nitrite rearrangement. The latter is often followed by loss of CO (M^+-58)[36]. For all nine nitro-AAs, the M^+ peak is the base peak. All isomers underwent considerable loss of NO_2/NO_2+H fragments (see Table I). 2-Nitro-AA gives the smallest loss of NO_2 of all nitro-AAs. A similar situation is observed in the series of nitro-CPPs[21], in which the derivative with the nitro group attached to the five-membered ring displays the smallest loss of NO_2.

The variation in loss of NO and NO + CO fragments is large. The 3-, 4-, 8- and 9-nitro derivatives gave low amounts of these fragments (the total of the relative abundance of M^+-30 and M^+-58 is between 9 and 17%), while for the 2-, 5-, 6-, 7- and 10-nitro isomers the loss of CO and of CO + NO was greatly enhanced (total relative abundance between 34 and 113%). It is known that the nitro–nitrite rearrangements is favoured when the nitro group is rotated out of the plane of the molecule[37], while simultaneously there will be good orbital overlap between the rotated nitro group and the aromatic π system[38]. A similar variation in NO loss is also found for the nitro-CPPs[21]: the unhindered 3-nitro-CPP has the lowest combined loss of M^+-30 and M^+-58 fragments (13%), while the other derivatives (which are more, or less hindered) display a clearly enhanced loss of these fragments (up to 108%). The observation that, for the 5-nitro derivative, the relative abundance of the M^+-30 and M^+-58 peaks is fairly low points to an only slightly hindered nitro group. The enhanced loss of NO observed in the mass spectrum of the planar 2-nitro-AA is also observed for 4-nitro-CPP[21].

A more diverse picture of fragmentation is seen in the spectra of the nitroaceanthrenes. In these spectra, the M^+ peak is not always the base peak. Especially for the 1-nitro derivative, the M^+ peak is rather small. The M^+-46 fragment is the base peak. This correlates with the fact that the nitro group is on a benzylic position and dissociation occurs easily. In the spectrum of 3- and 10-nitro-DHAA, the M^+-47 peak is the base peak. In both spectra, a strong M^+-17 fragment is observed as well. In these compounds, the nitro group is close to one of the benzylic protons of the five-membered ring. Loss of OH (M^+-17) will take place, which is followed by loss of NO (M^+-47)[36,39].

The other six isomers follow the fragmentation pathways discussed above for the nitroaceanthrylenes. The amounts of NO_2/NO_2+H loss are high for all compounds, while there is a large difference in NO loss. For the 4-, 8- and 9-nitro derivatives, no NO loss could be detected, while in the spectra of the 5-, 6-, 7- and 10-nitro derivatives this fragment has enhanced intensity. Surprisingly, the loss of

Table I Electron-impact (70 eV) mass spectra of nitro-AAs: double-focussed mass and relative abundance (%) of major peaks.

AA	M^+	M^+-30	M^+-46	M^+-47	M^+-58
2-nitro-AA	100	40	37	28	21
3-nitro-AA	100	1	73	41	16
4-nitro-AA	100	< 1	74	36	9
5-nitro-AA	100	10	47	39	24
6-nitro-AA	100	64	53	59	49
7-nitro-AA	100	33	51	59	79
8-nitro-AA	100	< 1	71	39	13
9-nitro-AA	100	1	71	30	9
10-nitro-AA	100	6	73	74	72

Table II Electron-impact (70 eV) mass spectra of nitro-DHAAs: double-focussed mass and relative abundance (%) of major peaks.

DHAA	M^+	M^+-17	M^+-30	M^+-46	M^+-47	M^+-58
1-nitro-DHAA	6	< 1	3	100	47	3
3-nitro-DHAA	62	33	3	24	100	< 1
4-nitro-DHAA	100	< 1	< 1	64	56	5
5-nitro-DHAA	100	< 1	86	57	97	9
6-nitro-DHAA	100	< 1	54	46	60	5
7-nitro-DHAA	100	< 1	7	31	69	5
8-nitro-DHAA	100	< 1	< 1	51	51	4
9-nitro-DHAA	100	< 1	< 1	50	57	5
10-nitro-DHAA	35	49	3	21	100	< 1

Table III ^{1}*H-NMR (300 MHz, $CDCl_3$) chemical shifts (ppm) of AA and nitro-AAs.*

AA	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
AA	7.61	7.14	7.81	7.59	8.00	8.47	8.10	7.46	7.59	8.27
2-nitro-AA	8.59		8.62	7.77	8.17	8.80	8.17	7.60	7.78	8.33
3-nitro-AA	7.66	7.57		8.21	8.06	8.41	8.02	7.48	7.60	8.15
4-nitro-AA	7.70	7.18	8.54		9.07	8.64	8.12	7.53	7.69	8.25
5-nitro-AA	7.67	7.01	7.75	8.56		9.26	8.10	7.50	7.63	8.14
6-nitro-AA	7.52	7.23	7.77	7.68	7.98		8.19	7.65	7.67	8.29
7-nitro-AA	7.55	7.18	7.83	7.64	8.03	9.12		8.20	7.61	8.53
8-nitro-AA	7.57	7.20	7.88	7.65	8.03	8.67	9.10		8.31	8.33
9-nitro-AA	7.58	7.21	7.83	7.65	7.99	8.50	8.19	8.16		9.19
10-nitro-AA	7.24	7.09	7.80	7.60	7.95	8.53	8.28	7.44	7.89	

Table IV ^{1}*H-NMR (300 MHz, $CDCl_3$) chemical shifts (ppm) of DHAA and nitro-DHAAs.*

DHAA	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
DHAA	3.78	3.58	7.23	7.45	7.73	8.19	8.06	7.47	7.47	7.99
1-nitro-DHAA	6.94	4.04 4.13	7.37	7.54	7.85	8.48	8.13	7.54	7.61	8.16
3-nitro-DHAA	3.88	4.10		8.16	7.80	8.26	8.12	7.60	7.63	8.08
4-nitro-DHAA	3.84	3.61	7.93		8.79	8.41	8.12	7.57	7.60	8.03
5-nitro-DHAA	3.82	3.58	7.27	8.65		9.24	8.20	7.62	7.59	8.04
6-nitro-DHAA	3.83	3.62	7.35	7.67	7.89		8.25	7.69	7.57	8.07
7-nitro-DHAA	3.83	3.62	7.34	7.57	7.82	8.91		8.25	7.50	8.29
8-nitro-DHAA	3.80	3.61	7.36	7.55	7.80	8.40	9.04		8.16	8.07
9-nitro-DHAA	3.85	3.62	7.34	7.58	7.77	8.24	8.12	8.14		9.00
10-nitro-DHAA	3.62	3.51	7.34	7.55	7.77	8.32	8.22	7.42	7.70	

NO is rather low for 7-nitro-DHAA, the cause of this is not clear.

Interestingly, the intensity of the $M^+ - 58$ fragment is low for all nitro-DHAAs, and it is independent of the position of the nitro group. This is in contrast with the spectra of the nitro-AAs, where the intensity of the $M^+ - 58$ fragment is large in the spectra of the hindered isomers, but small in the spectra of the unhindered ones. The difference in fragmentation is not caused by the difference in source temperature (the intensity of the $M^+ - 58$ peak does not dramatically increase when the nitroaceanthrenes are measured at 150°C).

^{1}H-NMR spectroscopy

The ^{1}H-NMR (300 MHz) spectra of AA, DHAA and their nitro derivatives were recorded in $CDCl_3$. At concentrations of 3 mg/ml or higher, the spectra show the effects of association (generally upfield shifting of the proton signals). All spectra were, therefore, recorded at low concentration (1–2 mg/ml).

^{1}H NMR is the method of choice to establish the position of the nitro substituent on the aromatic nucleus. To facilitate the analysis of the spectra of the nitro derivatives, we first analysed the spectra of the parent systems. The proton signals were assigned by means of COSY and nuclear Overhauser effect (NOE) experiments (Tables III and IV). Computer simulations (PANIC) were performed to obtain the correct coupling constants. Coupling constants of 0.3 Hz and larger are summarized in Table V.

Table V Coupling constants (^nJ(H,H)[a] of aa and DHAA[b] (between parentheses) in Hz.

^3J(H,H)	^4J(H,H)	^5J(H,H)	^6J(H,H)
$J_{1,2}$ 5.2	$J_{3,5}$ 0.6 (0.6)	$J_{1,3}$ 0.4	$J_{1,5}$ 0.5
$J_{3,4}$ 6.6 (6.5)	$J_{6,7}$ 0.7 (0.7)	$J_{4,6}$ 0.3 (0.3)	$J_{2,6}$ 0.7
$J_{4,5}$ 8.4 (8.5)	$J_{7,9}$ 1.3 (1.2)	$J_{6,8}$ 0.5 (0.4)	
$J_{7,8}$ 8.6 (8.6)	$J_{8,10}$ 1.2 (1.2)	$J_{6,10}$ 1.0 (1.0)	
$J_{8,9}$ 6.6 (6.6)		$J_{7,10}$ 0.8 (0.8)	
$J_{9,10}$ 8.6 (8.6)			

[a] Coupling constants greater than 0.3 Hz. [b] For aceanthrene only coupling constants between aromatic protons were determined

The spectra are in full agreement with the simulated spectra.

When recorded under similar conditions as AA and DHAA, the protons of anthracene are observed at 8.01 (H1,4,6,8), 7.45 (H2,3,6,7) and 8.43 ppm (H9,10). Most protons of AA resonate at lower field with respect to anthracene. H3 of AA is the most strongly affected by the presence of the unsaturated five-membered ring (+0.36 ppm), but H10 (+0.26 ppm) and H4 and H9 (both +0.14 ppm) are also affected. Surprisingly, H5 and H6 display no notable shifts. In aceanthrene, H3, H5 and H6 are shifted upfield with respect to anthracene (0.22–0.28 ppm). The other protons display much smaller shifts. The electron-donating effect of the saturated five-membered ring is mainly felt by the protons situated ortho and para to the five-membered ring.

The ^3J coupling constants of the aromatic protons of AA and DHAA closely resemble that of anthracene[40]. The small ^3J of 5.2 Hz for the ethylene-bridge protons is typical for this kind of ring system[41]. The values of the meta ^4J between H7 and H9 and between H8 and H10 are close to those in anthracene[40]. The meta ^4J between H3 and H5 is significantly smaller, due to the presence of the five-membered ring. In AA, some interesting long-range couplings are visible, which are characteristic for this cyclopenta-fused hydrocarbon. H1 is coupled with H5 (0.5 Hz) and H2 with H6 (0.7 Hz), due to favourable *W* configurations of the intermediate σ bonds.

The ^{1}H-NMR spectra of the nitro-AAs and nitro-DHAAs were analysed in the same manner. The position of the nitro group and the assignment of all protons were determined unequivocally by HD and NOE experiments. Computer simulations were performed in cases in which higher order effects were observed in the spectra. The correct chemical shifts are given in Tables III (nitro-AAs) and IV (nitro-DHAAs). Coupling constants of the nitro derivatives, which have changed by more than 0.2 Hz with respect to the parent system, are given in Table VI. Only coupling constants of protons that are in the same aromatic ring as the nitro group are substantially altered. The nitro group induces an enlargement of the ortho ^3J by approximately 0.8 Hz and the meta ^4J by approximately 1.0 Hz.

Table VI $^1H-^1H$ *coupling constants of nitro-AAs and nitro-DHAAs (Hz)* [a].

	^3J(H,H)	^4J(H,H)
3-nitro-AA	$J_{4,5}$ 9.0	
4-nitro-AA		$J_{3,5}$ 1.7
5-nitro-AA	$J_{3,4}$ 7.3	
7-nitro-AA	$J_{8,9}$ 7.4	
8-nitro-AA	$J_{9,10}$ 9.4	$J_{7,9}$ 2.3
9-nitro-AA	$J_{7,8}$ 9.3	$J_{8,10}$ 2.3
10-nitro-AA	$J_{8,9}$ 7.3	

	^3J(H,H)	^4J(H,H)
3-nitro-DHAA	$J_{4,5}$ 9.3	
4-nitro-DHAA		$J_{3,5}$ 1.6
5-nitro-DHAA	$J_{3,4}$ 7.5	
7-nitro-DHAA	$J_{8,9}$ 7.4	
8-nitro-DHAA	$J_{9,10}$ 9.4	$J_{7,9}$ 2.3
9-nitro-DHAA	$J_{8,8}$ 9.4	$J_{8,10}$ 2.2
10-nitro-DHAA	$J_{8,9}$ 7.2	

[a] Coupling constants differing more than 0.2 Hz from those in AA and DHAA.

In ^{1}H-NMR spectra of nitro-PAH, protons ortho and peri to the nitro group are generally strongly shifted downfield. These shifts are caused by inductive and mesomeric interactions of the nitro group with the aromatic system via the σ and π bonds and by the electric-field effect of the nitro group[42,43]. We measured the change in chemical shift ($\Delta\delta$) of each aromatic proton ortho to a nitro group with respect to the corresponding proton in AA or DHAA (Table VII). It follows from this Table that the nitro-AAs display similar $\Delta\delta$ to the nitro-DHAAs. Most ortho protons have downfield shifts of 0.6–1.2 ppm. They appear to be clustered in two groups according to the magnitude of their ortho effects. One group of protons has $\Delta\delta$ between 0.6 and 0.8 ppm and a second group between 0.9 and 1.2 ppm. Only the values of the ortho protons of 10-nitro-AA and -DHAA are markedly smaller (0.30 and 0.23 ppm, respectively).

This difference in magnitude can be explained by taking into account the bond order of the C–C bond between the proton and the nitro group. The downfield shift will be high for protons which interact with the nitro group via a short C–C bond. In AA and DHAA, the C4–C5, C7–C8 and C9–C10 bonds are expected to be shorter (around 1.36 Å) than the C3–C4 and C8–C9 bonds (around 1.42 Å), as in anthracene[44]. The C1–C2 bond in AA will also be short. The data of Table VII correlate with the expected double bond order of the C–C bonds. Exceptions are H8 in the 7-nitro and H9 in the 10-nitro derivatives. These protons are connected with the nitro group via a short C–C bond, but their $\Delta\delta$ values are smaller than expected. This indicates that, in these molecules, the nitro group is forced out of the plane of the aromatic system by steric interactions. The rotation of the nitro group may be large in the 10-nitro isomers and moderate in the 7-nitro isomers. Interestingly, H4 in 5-nitro-AA and -DHAA has a large $\Delta\delta$, indicating that the twist angle of the nitro group is smaller than in the 7-nitro derivatives.

The $\Delta\delta$ of the peri protons of the nitro-AAs and nitro-DHAAs are summarized in Table VIII. A wide variation in $\Delta\delta$ is observed. The peri protons of the 2-, 3-, 5-, and 7-nitro derivatives have downfield shifts between 0.43 and 1.05 ppm. The peri protons of the 6-nitro- and 10-nitro derivatives, however, show small downfield or even upfield shifts. This corresponds with the findings for 9-nitroanthracene[45], which has an almost perpendicular nitro group.

The electron-withdrawing action of the nitro group causes protons are more remote positions to shift downfield[46]. The most pronounced shift is found for H6 in 2-nitro-AA (+0.33 ppm) (see Table III). In this compound, protons H4, H5, H6 and H9 are also "deshielded", by 0.17 ppm or more. Apparently, a very strong interaction exists between the nitro group and the aromatic system. H10 is strongly "deshielded" in 7-nitro-AA and -DHAA (0.26 and 0.30 ppm, respectively). These values agree well with the downfield shift of H4 in 1-nitronaphthalene (0.33 ppm)[47]. In the 10-nitro derivatives, protons H7 are less strongly "deshielded" (0.18 and 0.16 ppm). The severe twisting of the nitro group in these compounds will reduce resonance interactions. Finally, in 1-nitro-DHAA, a strong (π-inductive) interaction[48] of the nitro group with the proton at position 6 is observed (downfield shift of 0.29 ppm).

Table VII Effect of nitro group on its ortho protons. $\Delta\delta$ *(with respect to AA and DHAA) in ppm.*

AA	$\Delta\delta$ (ppm)	
2-nitro-AA	H1 0.98	
3-nitro-AA	H4 0.62	
4-nitro-AA	H3 0.73	H5 1.07
5-nitro-AA	H4 0.97	
7-nitro-AA	H8 0.74	
8-nitro-AA	H7 1.00	H9 0.71
9-nitro-AA	H8 0.69	H10 0.92
10-nitro-AA	H9 0.30	

DHAA	$\Delta\delta$ (ppm)	
3-nitro-DHAA	H4 0.71	
4-nitro-DHAA	H3 0.70	H5 1.09
5-nitro-DHAA	H4 1.20	
7-nitro-DHAA	H8 0.78	
8-nitro-DHAA	H7 0.98	H9 0.69
9-nitro-DHAA	H8 0.68	H10 1.01
10-nitro-DHAA	H9 0.23	

Table VIII Effect of nitro group on nearby peri protons. $\Delta\delta$ *(with respect to AA and DHAA) in ppm* [a].

AA	$\Delta\delta$ (ppm)	
2-nitro-AA	H3 0.81	
3-nitro-AA	H2 0.43	
5-nitro-AA	H6 0.79	
6-nitro-AA	H5 −0.02	H7 0.09
7-nitro-AA	H6 0.65	
10-nitro-AA	H1 −0.37	

DHAA	$\Delta\delta$ (ppm)	
3-nitro-DHAA	H2 0.54	
5-nitro-DHAA	H6 1.05	
6-nitro-DHAA	H5 0.16	H7 0.19
7-nitro-DHAA	H6 0.72	
10-nitro-DHAA	H1 −0.13	

[a] Negative sign denotes upfield shift.

Table IX ^{13}C NMR (100.6 MHz, $CDCl_3$); chemical shifts of AA [a] and nitro-AAs (ppm).

AA	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
AA	127.6	126.7	125.6	127.1	127.9	128.0	130.1	124.5	127.4	124.0
2-nitro-AA	129.8		130.5	128.0	130.3	135.8	131.1	126.0	130.5	123.5
3-nitro-AA	133.2	126.4		120.6	129.6	128.8	130.3	126.5	129.0	124.1
4-nitro-AA	130.4	126.8	118.5		125.8	131.2	130.6	125.9	129.6	124.2
5-nitro-AA	133.2	126.2	122.9	127.1		127.7	131.1	126.2	129.3	123.8
6-nitro-AA	127.4	131.1	126.4	130.5	123.6		123.5	128.4	127.8	124.4
7-nitro-AA	127.3	128.3	127.0	128.8	128.7	123.4		123.2	124.3	130.5
8-nitro-AA	127.4	128.4	127.7	128.6	128.2	131.6	127.7		120.0	125.7
9-nitro-AA	127.1	129.0	126.6	129.3	128.3	127.9	132.0	117.5		121.7
10-nitro-AA	129.0	128.0	127.1	128.6	128.1	129.4	135.2	122.2	123.3	

[a] Quaternary carbons: C2a 140.1; C5a 126.3; C6a 134.2; C10a 129.2; C10b 135.0; C10c 125.5 ppm.

Table X ^{13}C NMR (100.6 MHz, $CDCl_3$); chemical shifts of DHAA [a] and nitro-DHAAs (ppm).

DHAA	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
DHAA	29.4	30.3	117.1	127.6	122.1	121.2	129.3	125.0	124.3	124.6
1-nitro-DHAA	88.3	38.1	119.1	127.9	123.8	127.0	129.8	125.7	127.0	123.3
3-nitro-DHAA	30.2 [b]	33.6 [b]		121.1	124.8	122.3	129.5	127.6	126.0	125.1
4-nitro-DHAA	30.0 [b]	30.4 [b]	110.5		121.3	125.2	129.3	126.4	126.7	124.8
5-nitro-DHAA	29.8 [b]	30.7 [b]	115.3	129.3		120.5	130.1	127.0	126.1	124.5
6-nitro-DHAA	30.0 [b]	30.1 [b]	118.5	131.7	117.5		123.0	129.0	125.2	125.0
7-nitro-DHAA	30.1 [b]	30.3 [b]	118.9	129.5	123.0	117.4		124.0	121.7	131.5
8-nitro-DHAA	29.5 [b]	30.3 [b]	119.5	128.9	122.4	125.2	127.1		117.2	126.4
9-nitro-DHAA	29.9 [b]	30.5 [b]	118.9	130.1	122.5	121.9	131.1	117.9		122.8
10-nitro-DHAA	30.6 [b]	30.4 [b]	119.1	128.9	122.2	123.4	134.0	122.4	120.6	

[a] Quaternary carbons: C2a 147.0; C5a 129.7; C6a 133.6; C10a 127.0; C10b 142.4; C10c 137.3 ppm. [b] Chemical shifts may have to be interchanged.

^{13}C-NMR Spectroscopy

The proton, noise-decoupled, ^{13}C-NMR spectra of AA and DHAA and their nitro derivatives were recorded in $CDCl_3$ at 100.6 MHz. ^{13}C chemical shifts are not very sensitive to variations in concentration and we could, therefore use concentrations of 20 mg/ml. The chemical shift values of AA are in agreement with those already published[25]. So far, no assignment of the ^{13}C-NMR spectra of AA and DHAA has been published. Since we have made a complete assignment of their ^1H-NMR spectra, the tertiary carbons of AA and DHAA could easily be assigned by ^1H–^{13}C-correlated 2D-NMR (CH COSY) techniques (Tables IX and X). The quaternary carbons could be assigned by using the smaller $^3J(C,H)$ (typically 6–8 Hz) to observe the correlations. The ^1J and ^3J COSY spectra of aceanthrylene are shown in Figure 2.

The ten tertiary and six quaternary carbons of AA are found between 124 and 140 ppm, which is typical for non-alternant aromatic hydrocarbons[49]. The assignment of all but two tertiary carbons is straightforward. Carbons C4 and C9 cannot be assigned by ^1J CH COSY, because H4 and H9 overlap in the proton spectrum. By means of a $^3J(C,H)$ COSY experiment, these carbons could be easily distinguished. C4 has no three-bond couplings with protons, while C9 has one with H7. The quaternary carbons of AA are assigned by $^3J(C,H)$ COSY without difficulty. It appears that some ^3J correlations in the $^3J(C,H)$ COSY spectrum are absent, while some ^2J correlations are observed instead.

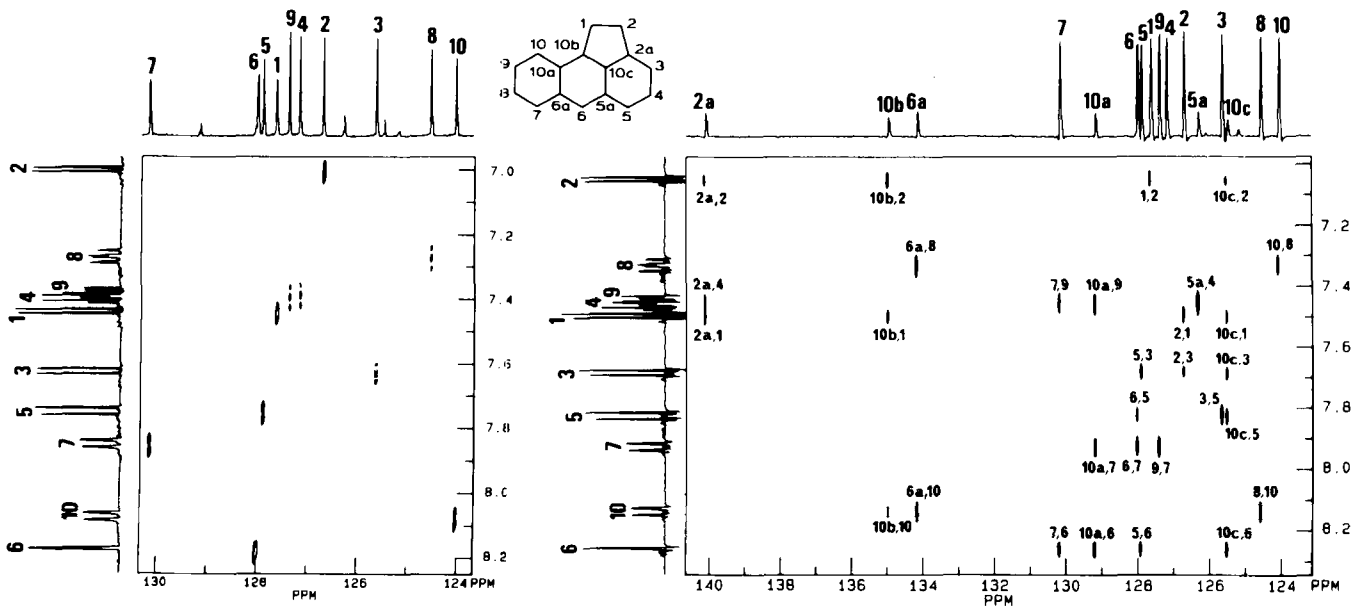


Figure 2. CH COSY spectrum of aceanthrylene, optimized for $^1J(C,H)$ couplings (left) and $^3J(C,H)$ couplings (right).

The assignment of the two secondary, eight tertiary and six quaternary carbons of aceanthrene is made in the same manner. The secondary and tertiary carbons are assigned by means of ^1J(C,H) COSY. C8 and C9 cannot be assigned in this way because H8 and H9 overlap in the ^{1}H-NMR spectrum. The ^3J(C,H) COSY experiment yields the correct assignment. Based on strong ^3J(C8,H10) and ^3J(C9,H7) correlations, C8 and C9 are attributed to the signals at 125.0 and 124.3 ppm, respectively. In the (aromatic part of the) ^3J(C,H) COSY spectrum, all ^3J and no ^2J cross peaks are observed.

The absence of some ^3J and the appearance of ^3J cross peaks in the spectrum of AA can be related to the unsaturated five-membered ring. Similar results have been found for CPP[41] and a number of benzofluoranthenes[50]. In alternant PAH the ^2J(C,H) are generally around 1 Hz and do not give rise to correlations in the spectrum. For five-membered ring systems such as azulene[51] and cyclopentadiene[52], the ^2J(C,H) can be large (4 Hz or more), while the ^3J(C,H) may be small (4 Hz or less). This has been attributed to the enlarged H–C–C and C–C–C angles in these systems[51–53].

The proton-gated ^{13}C-NMR spectrum of AA shows C_1 to have a ^2J with H2 of 4.4 Hz and C2 to have a ^2J with H1 of 3.7 Hz. The ^3J of C3 with H2, on the other hand, is only 2.4 Hz. The ^2J correlations observed between C10b and H1 and between C2a and H2 are related to enlarged H–C–C angles (the J values cannot be determined, because the quaternary carbons appear as complex multiplets). The absence of a ^3J cross peak between C10a and H1 is due to a large C1–C10b–C10a angle. We have calculated the geometry of aceanthrylene (PM3). The values obtained for the H1–C1–C2 (127.2°), H2–C2–C1 (127.5°), H1–C1–C10b (123.5°) and H2–C2–C2a (123.5°) angles are in agreement with the spectroscopic results. The C2–C2a–C3 angle (136.2°) and the C1–C10b–C10a angle (135.5°) are also substantially larger than in regular alternant PAH (120°).

The ^{13}C-NMR and ^1J(C,H) COSY spectra of the nitro-AAs and nitro-DHAAs were recorded at 100.6 MHz. The quaternary-carbon signals including that of the carbon bearing the nitro group could not always be observed, due to their longer relaxation times and the lower solubility of the compounds. Therefore, only the tertiary carbon atoms were assigned, their data are reproduced in Tables IX and X.

From the ^1J(C,H) COSY spectra, the tertiary carbons of the nitro compounds can easily be assigned. However, in the ^{1}H-NMR spectrum of 6-nitro-AA, the signals of H4, H8 and H9 coincide. The corresponding carbon atoms resonate at 127.8, 128.4 and 130.5 ppm. Fortunately, such overlap of protons is absent in the spectrum of 6-nitro-DHAA, in which the chemical shifts and the $\Delta\delta$ with respect to DHAA of C4, C8 and C9 are 131.7 (+4.1), 129.0 (+4.0) and 125.2 (+0.9) ppm, respectively. When we assume that similar differences in chemical shift exist between AA and 6-nitro-AA, we can make the following assignments: C4 130.5 (+3.4), C8 128.4 (+3.9) and C9 127.8 (+0.4) ppm.

In 1-nitro-DHAA, H4 and H8 overlap completely. The corresponding carbon resonances are found at 127.9 and 125.7 ppm. In DHAA, C4 and C8 resonate at 127.6 and 125.0 ppm, respectively, which are very close to the values found for 1-nitro-DHAA. If the signal at 127.9 ppm would belong to C8, C4 would have shifted to higher field (from 127.6 to 125.7 ppm) by interaction with the nitro group at C1. This is highly unlikely, because the π-inductive effect of the nitro group is known to lead to downfield shifts[48].

A nitro group induces pronounced changes in the chemical shifts of the carbon atoms. In ^{13}C NMR, the ortho carbons will experience both a downfield effect due to mesomeric and inductive interactions and an upfield effect due to the steric and electrostatic interactions of the attached protons with the nitro group[42,43,54]. In Table XI, the $\Delta\delta$ values of the ortho carbons with respect to the parent hydrocarbons are given.

Although there is a wide variation in $\Delta\delta$, two groups can be discerned. One group of carbons displays large but almost identical upfield shifts ranging between −7.5 and −6.5 ppm. A second group of carbons has a much wider variation in induced shifts and the shifts are found in a different range (between −4.1 and 2.2 ppm). The first group contains the carbons that interact with the nitro group via a long C–C bond, and the second those interacting via a short C–C bond. It is, therefore, likely that the electron-withdrawing effect of the nitro group on the ortho carbons is responsible for the observed differences[43,55]. Carbon atoms linked to the nitro group via short C–C bonds will experience a larger decrease in electron density than those connected via longer C–C bonds. In 2-nitro-AA, C1 is shifted downfield by 2.2 ppm, as a result of the strong conjugation of the nitro group with the aromatic system via the C1–C2 bond. C9 in 10-nitro-AA and -DHAA are the most strongly shielded members of the second group. Due to rotation of the nitro group the electron-withdrawing effect is diminished in these compounds[56], in accordance with our findings in ^{1}H NMR.

The changes in chemical shifts induced by the nitro group on peri carbon atoms display an even larger variation than is observed for the ortho carbons (see Tables IX and X). Substantial upfield shifts are observed for the peri carbons in the 6-nitro and 7-nitro derivatives (between −3.8 and −6.6 ppm). In contrast, upfield shifts are absent in the 3-, 5- and 10-nitro derivatives. C3 in 2-nitro-AA is "deshielded" by 4.9 ppm. It is difficult to draw pertinent conclusions from these data.

The data of Tables IX and X were searched for long-range effects, caused by mesomeric interactions of the nitro group with distinct carbons[43,55,57]. Some carbon atoms, four or more bonds away from the nitro group, display pronounced downfield shifts (3 ppm or more). These carbon atoms are found in pairs. For instance, both C6 in 4-nitro-AA (3.2 ppm) and C4 in 6-nitro-AA (3.4 ppm) are

Table XI Effect of nitro group on ortho-carbon atoms. $\Delta\delta$ (with respect to AA and DHAA) in ppm [a].

	$\Delta\delta$ (ppm)	
2-nitro-AA	C1 2.2	
3-nitro-AA	C4 −6.5	
4-nitro-AA	C3 −7.1	C5 −2.1
5-nitro-AA	C4 0.0	
7-nitro-AA	C8 −1.3	
8-nitro-AA	C7 −2.4	C9 −7.4
9-nitro-AA	C8 −7.0	C10 −2.3
10-nitro-AA	C9 −4.1	

	$\Delta\delta$ (ppm)	
3-nitro-DHAA	C4 −6.5	
4-nitro-DHAA	C3 −6.6	C5 −0.8
5-nitro-DHAA	C4 1.6	
7-nitro-DHAA	C8 −1.0	
8-nitro-DHAA	C7 −2.2	C9 −7.1
9-nitro-DHAA	C8 −7.1	C10 −1.8
10-nitro-DHAA	C9 −4.1	

[a] Negative sign means upfield shift.

shifted downfield. In 4- and 6-nitro-DHAA, the shifts of both of these carbons are 4.0 ppm. Such four-bond relationships are also observed between C6 and C8 and between C7 and C10 in both the AA and DHAA series. Interestingly, the downfield shifts of C7 in 10-nitro-AA and -DHAA (5.1 and 4.7 ppm) are diminished compared to the shifts of C10 in the 7-nitro derivatives (6.5 and 6.9 ppm). This is in agreement with a more strongly hindered nitro group in the 10-isomers. Carbon atoms C1 and C2 of the nitro-AAs display some strong long-range interactions. Six-bond interactions are observed between positions 2 (4.4 ppm in 6-nitro-AA) and 6 (7.8 ppm in 2-nitro-AA) and between positions 1 and 5 (5.6 ppm in 5-nitro-AA). There is a four-bond interaction between positions 1 and 3 (5.6 ppm in 3-nitro-AA). Finally, it is noteworthy that C6 is considerably shifted downfield in 1-nitro-DHAA, owing to a strong π-inductive interaction with the nitro group[48].

UV-VIS absorption spectroscopy

The electronic absorption spectra of AA, DHAA, the nitro-AAs and nitro-DHAAs were recorded in methanol (Figure 3). The spectra of AA and DHAA are in accordance with those already published[58,59]. Aceanthrene, colourless when in solution, has an anthracene nucleus substituted with a 1,10-ethano bridge, which only slightly perturbs the symmetry of the π-electron system of the molecule. The spectrum of DHAA, therefore, strongly resembles that of anthracene[60]. A bathochromic shift of the long-wavelength L_a band (ϵ 6550) of about 18 nm is observed, caused by the electron-rich methylene bridge. The intense absorption at 257 nm (ϵ 105 000), does not show much shift compared to anthracene. Aceanthrylene has an anthracene nucleus with a 1,10-etheno bridge, which leads to a strong perturbation of the UV spectrum of anthracene. The electronic spectrum has been assigned by *Plummer*[58]. The first clear long-wavelength transition is observed at 424 nm, but tailing occurs to wavelengths exceeding 500 nm. This tailing is probably responsible for the orange-red colour of solutions of AA. The absorption band at 253 nm is considerably less intense (ϵ 49 600) than that of DHAA.

In 1-nitro-DHAA, the nitro group is not conjugated directly with the aromatic π system. As a result, its UV spectrum closely resembles that of DHAA; the long-wavelength absorption is hypsochromically shifted by 6 nm. Solutions of 1-nitro-DHAA are almost colourless. The other eight nitro derivatives of aceanthrene form light-orange to dark-orange solutions in methanol. Their spectra show broad absorption without vibrational fine-structure around 400–450 nm (see Table XII). The spectra of 5-, 6-, 7- and 10-nitro-DHAA show smaller changes, compared to the spectrum of DHAA, than the spectra of 3-, 4-, 8- and 9-nitro-DHAA. These observations agree with the consideration that the isomers of the first group contain a nitro group on a more or less hindered *peri* or *meso* position, while those of the second group all contain a planar nitro group. The 10- and the 6-nitro isomer show the smallest bathochromic shifts of the long-wavelength band (25 and 39 nm, respectively), in agreement with the expectation that these compounds are the most severely

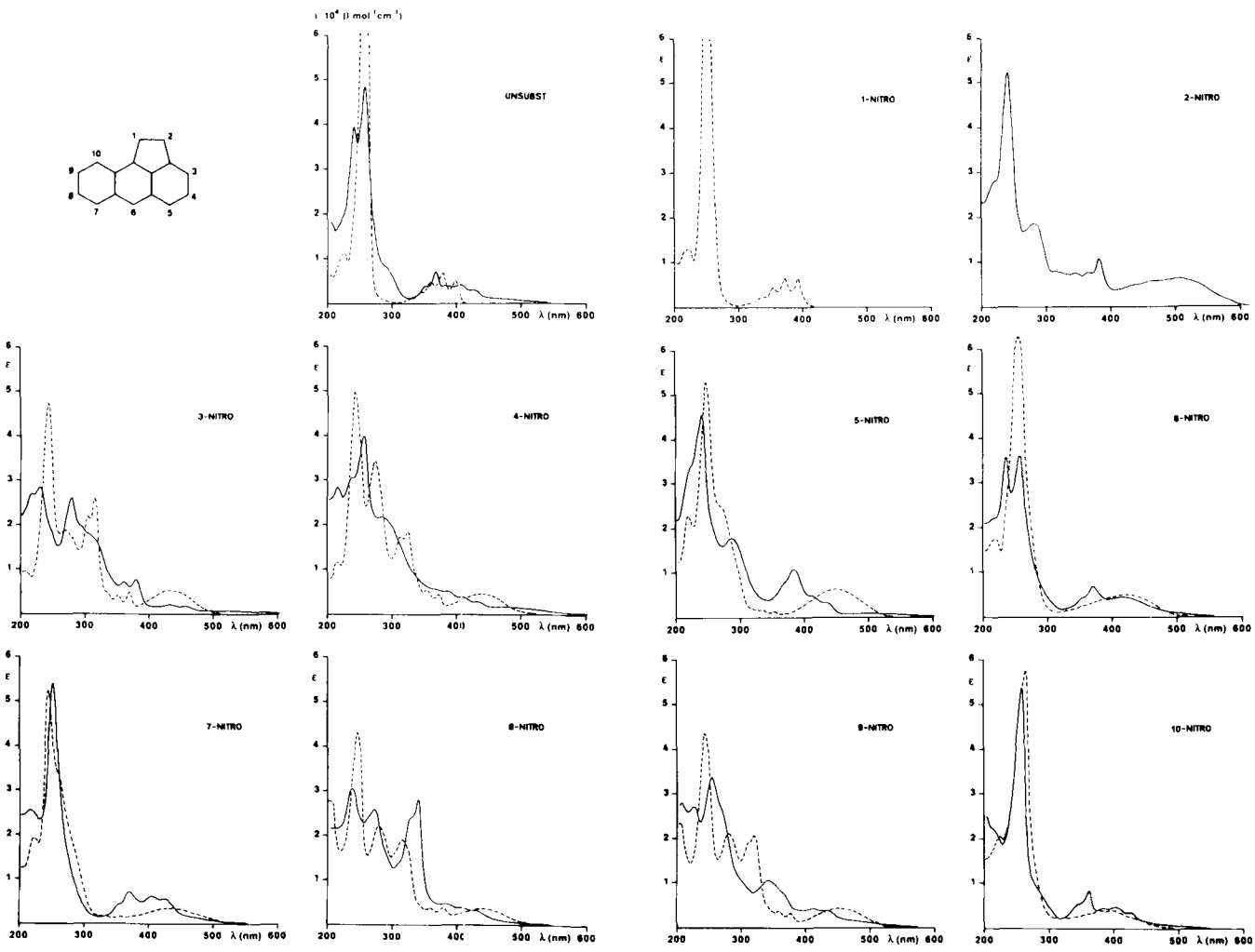


Figure 3. UV-VIS spectra (methanol) of AA (———), DHAA (- - - - -) and nitro derivatives.

hindered. The 5- and 7-nitro derivatives display large bathochromic shifts (72 and 57 nm), in the same range as those found in the unhindered nitro isomers. In these isomers, the interaction of the nitro groups with the aromatic system may not be seriously affected by steric hindrance.

The 257-nm absorption band of DHAA is also observed in its 5-, 6-, 7- and 10-nitro derivatives, although the ϵ value drops by a factor of 2. In the 3-, 4-, 8-, and 9-nitro derivatives, more absorption bands in the shorter wavelength part of the spectrum are visible, indicating a strong perturbation of the electronic π system.

The nitro-AAs with the nitro group on a six-membered ring give orange-red or brown solutions. They show absorption between 400 and 500 nm, but these are not as pronounced as in the nitro-DHAAs. The bathochromic shift of the longest-wavelength absorption in many instances is rather small (Table XII). As with AA, the nitro derivatives display tailing to wavelengths longer than 500 nm. The spectrum of 2-nitro-AA is a prominent exception, because it displays a very broad long-wavelength absorption, with a maximum at 500 nm, while the band begins at about 600 nm. The solution of 2-nitro-AA is purple-red. Similar intense long-wavelength absorptions have been reported in the case of 4-nitro-CPP[21] and of *trans*-9-(2-nitroethenyl)anthracene[61]. Very likely, exceptionally effective conjugation between the nitro group and the aromatic system via the etheno bridge lies at the basis of this behaviour in these compounds.

The electronic spectra of 5-, 6-, 7-, and 10-nitro-AA closely resemble that of AA. In these compounds, the nitro group is on a *meso* or *peri* position. The 6-, 7- and 10-nitro derivatives show no bathochromic shift of their longest-wavelength absorption band with respect to AA. The bathochromic shift of 11 nm in the case of 5-nitro-AA may indicate a less hindered nitro group in this compound. The 255 nm band of AA is also prominent in these isomers, the ϵ value varies between 35 000 and 54 000. The spectra of the 3-, 4-, 8- and 9-nitro isomers are very different compared to that of AA. This agrees with a conjugated, planar nitro group. As for the corresponding nitroaceanthrenes, the number of bands has increased in the region below 400 nm, indicating strong distortion of the aromatic π system.

IR spectroscopy

Infrared absorption spectra of nitroaromatic compounds exhibit two very characteristic vibrational bands associated with the nitro group[62]. These are the symmetric (ν_s) and the asymmetric (ν_{as}) stretching mode of the NO_2 group. In Table XIII, the ν_s and ν_{as} of the nitro-AAs and nitro-DHAAs are tabulated.

Table XIII Infrared frequencies (cm^{-1}) of symmetric and asymmetric N–O stretching vibration of nitro-AAs and nitro-DHAAs.

AA	ν_{as}(N–O)	ν_s(N–O)	DHAA	ν_{as}(N–O)	ν_s(N–O)
2-nitro-AA	1503 (m)	1328 (vs)	1-nitro-DHAA	1543 (vs)	1362 (m)
3-nitro-AA	1525 (m)	1335 (vs)	3-nitro-DHAA	1503 (m)	1317 (vs)
4-nitro-AA	1518 (m)	1334 (vs)	4-nitro-DHAA	1511 (s)	1335 (vs)
5-nitro-AA	1513 (s)	1321 (vs)	5-nitro-DHAA	1490 (s)	1309 (vs)
6-nitro-AA	1503 (s)	1332 (s)	6-nitro-DHAA	1497 (s)	1330 (s)
7-nitro-AA	1510 (s)	1320 (s)	7-nitro-DHAA	1509 (s)	1321 (vs)
8-nitro-AA	1512 (m)	1331 (vs)	8-nitro-DHAA	1505 (m)	1330 (vs)
9-nitro-AA	1511 (s)	1332 (vs)	9-nitro-DHAA	1505 (ms)	1323 (vs)
10-nitro-AA	1513 (vs)	1353 (s)	10-nitro-DHAA	1511 (vs)	1350 (s)

The ν_{as} of the nitro-AAs (including 2-nitro-AA) is observed between 1503 and 1525 cm^{-1}. In the nitro-DHAAs, it is found between 1490 and 1511 cm^{-1}. The ν_{as} of 1-nitro-DHAA is found at 1543 cm^{-1}, which corresponds with a benzylic nitro group[62]. A relationship between the magnitude of ν_{as}(N–O) and the degree of conjugation of the nitro group with the aromatic system[63] was not found. In general, there seems to be a rather random distribution of the values of ν_{as} among the compounds.

The ν_s of eight of the nine nitro-AAs is found between 1320 and 1335 cm^{-1}. Only the ν_s of 10-nitro-AA is observed at higher wavenumbers (1353 cm^{-1}). For seven nitroaceanthrenes, ν_s is observed between 1309 and 1335 cm^{-1}. 1-Nitro-DHAA (1362 cm^{-1}) with its benzylic nitro group and 10-nitro-DHAA (1350 cm^{-1}) are exceptions. It has been demonstrated[64,65] that there often exists a relationship between the frequency of the ν_s(N–O) and the occurrence of steric hindrance. When the nitro group is tilted out of the plane of the aromatic system, ν_s shifts to higher values (up to 40 cm^{-1} in the case of severely hindered nitro-*tert*-butylpyrenes[65]). In our compounds, only the 10-nitro derivatives give rise to a higher frequency of the ν_s. It should be noted that the ν_s is found in the fingerprint region, which means that it can be coupled with other vibrations in this part of the spectrum. This may be the reason why, for instance, the ν_s of the 6-nitro derivatives is not increased compared to that of some of the unhindered isomers.

Interesting differences are observed when the intensities of the ν_{as} and the ν_s are compared. In the planar 3-, 4-, 8-, and 9-nitro derivatives, the intensity of the ν_s is much higher than that of the ν_{as}. This is also the case for 2-nitro-AA. This correlates with a very good interaction of the nitro group with the aromatic π-system[66]. However, in the 10-nitro derivatives, the intensity of ν_{as} is higher than that of ν_s. In the 6-nitro derivatives, ν_s and ν_{as} are of about equal intensity, while the 5- and 7-nitro derivatives hold an intermediate position; their ν_s is somewhat more intense than the ν_{as}.

Table XII Absorption maxima (methanol) of longest-wavelength band of AA, DHAA and their nitro derivatives; shift induced by nitro substitution.

AA	λ_{max} (nm)	Shift (nm)	DHAA	λ_{max} (nm)	Shift (nm)
AA	424		DHAA	374 [a]	
2-nitro-AA	*ca.* 500	*ca.* 76	1-nitro-DHAA	368 [a]	−6
3-nitro-AA	456	32	3-nitro-DHAA	431	57
4-nitro-AA	435	11	4-nitro-DHAA	435	61
5-nitro-AA	435	11	5-nitro-DHAA	448	74
6-nitro-AA	425	1	6-nitro-DHAA	413	39
7-nitro-AA	425	1	7-nitro-DHAA	431	57
8-nitro-AA	428	4	8-nitro-DHAA	437	63
9-nitro-AA	430	6	9-nitro-DHAA	447	73
10-nitro-AA	425	1	10-nitro-DHAA	399	25

[a] Wavelength of (second) vibronic transition with largest ϵ.

Table XIV PM3- and AM1-calculated twist angles (τ) of nitro group and distance between oxygen and closest hydrogen in nitro-AAs.

AA	τ (deg)		n (O ··· H (Å)	
	PM3	AM1	PM3	AM1
1-nitro-AA	52.9	40.2	2.409	2.128
2-nitro-AA	0.0	0.1	2.625	2.557
3-nitro-AA	31.4	1.5	2.589	2.425
4-nitro-AA	0.8	0.1	2.487	2.423
5-nitro-AA	47.0	17.2	2.547	2.167
6-nitro-AA	89.7	44.6	2.941	2.215
7-nitro-AA	62.9	33.6	2.564	2.155
8-nitro-AA	0.9	0.0	2.498	2.449
9-nitro-AA	25.1	0.2	2.572	2.447
10-nitro-AA	85.6	70.1	2.739	2.379

Calculations using PM3 and AM1 methods

In an attempt to find correlations between the spectroscopic characteristics of the compounds studied and the conformation of the nitro group, we have carried out some calculations. Two semi-empirical SCF methods, AM1[67] and PM3[68], were used to calculate the twist angle (t) of the nitro group in the nitro-AAs (Table XIV). By some additional calculations, we verified that these values are also valid for the corresponding nitro-DHAAs. As is evident from Table XIV, the twist angles calculated using PM3 are in most cases considerably larger than those calculated using AM1. The difference may be as large as 45° (6-nitro). The difference in calculated twist angle between PM3 and AM1 is, for a number of isomers, 30° or even more.

Next to the twist angle, the distance between the oxygens of the nitro group and the nearby *ortho* and/or *peri* protons is an important parameter. From X-ray studies on a number of crystalline nitro-PAHs[69,70], we learned that, in hindered compounds, this distance is often approx. 2.3–2.5 Å. This is approximately the sum of the Van-der-Waals radii of an H and an O atom (2.4 Å). From Table XIV, it becomes clear that AM1 tends to give unrealistically small O to H distances for the sterically hindered isomers. Using AM1, we calculated for the 1-, 5-, 6- and 7-nitro derivatives O to H distances in the order of 2.1–2.2 Å, which is far below the combined Van-der-Waals radii. Consequently, the calculated twist angles must be too small. On the other hand, the distances we calculated using PM3 for the 6- and 10-nitro isomers are rather large. The PM3-calculated twist angle and O-to-H distance for 6-nitro-AA agree well with the values (85° and 2.97 Å, respectively) found for 9-nitroanthracene in the crystalline state[71]. In solution, the twist angle has been found to vary between 65 and 115°[72].

From the data of Table XIV, it seems reasonable to conclude that 10-nitro-AA contains the most seriously hindered nitro group. Furthermore, the difference in spectral behaviour between the 7-nitro and 5-nitro derivatives is reflected in the calculated twist angles. Using both PM3 and AM1, we calculated a difference in twist angle of 16° between the two isomers. This difference may be related to a difference in C–C–C angles. We used PM3 to calculate for AA the angle C5–C5a–C6 to be 128.7° and the C6–C6a–C7 angle to be 119.5°. The values obtained by AM1 are in full agreement with this. The angle C5–C5a–C6 is widened due to the five-membered ring. As a result, the nitro group in 5-nitro-AA is less hindered.

In the remaining derivatives, the nitro groups are at relatively unhindered positions. The angle C2–C2a–C3 is of interest in the 2- and 3-nitro derivatives. In AA, this angle is 136.2° (PM3), which is sufficiently wide to allow a nitro group at positions 2 or 3 to be coplanar with the aromatic system. The calculated angle is, in fact, 0° for 2-nitro-AA. However, for 3-nitro-AA, PM3 gives an angle of 31°, whereas AM1 gives 1.5°. Using PM3, we calculated a considerable twist (26°) for the 9-nitro derivative, although it is beyond doubt that the nitro group is not sterically hindered in this case. According to PM3, the nitro group is completely planar in 4- and 8-nitro-AA, in agreement with the spectroscopic evidence. Additional calculations revealed that, when the nitro group was kept in the plane of the molecule, the heat of formation was only very slightly increased (PM3). This means that the nitro group in these compounds is not really hindered.

Spectroscopically, it was established that, in 2-nitro-AA, the nitro group is conjugated exceptionally well with the aromatic system. Using both methods, we calculated a completely planar nitro group. A much shorter C–N bond was calculated for this compound (1.469 Å, PM3) than for any of the other derivatives (1.495–1.503 Å, PM3). As a result of the conjugation, the C1–C2 bond is considerably lengthened (0.017 Å, PM3) with respect to AA, while the C10b–C1 bond has become shorter (0.014 Å, PM3). The other nitro-AAs show changes in bond lengths not exceeding 0.010 Å (PM3).

Conclusions

Efficient and short syntheses of aceanthrylene, 1,2,6,10b-tetrahydroaceanthrylene and 6,10b-dihydro-2(1*H*)-aceanthrylenone have been devised. These compounds have now become available in gram quantities, which gives access to the class of aceanthrylenes for further research. The double Wolff–Kishner reduction of 1,2-aceanthraquinone reduces the synthetic route from anthracene to DHAA to two steps and that to AA to three steps.

Nine mononitroaceanthrylenes and nine mononitroaceanthrenes were prepared, all being novel compounds. Three partially hydrogenated aceanthrylenes and three aceanthrenones were used as starting materials in the nitration step. The nitro derivatives were converted into the nitro-DHAAs and nitro-AAs. In the preparation of the latter, the most critical step was aromatization. The reaction conditions could be optimized in such a way that good-to-reasonable yields were obtained in all cases. Great care was taken in the separation and purification of the final products. Most compounds were purified with HPLC to ensure a purity of at least 99%. Although most compounds were prepared and purified only in relatively small quantities (usually several mg of each compound), this was sufficient to allow spectroscopic identification.

The position of the nitro group in each of the isomers was unambiguously established. A qualitative relationship was found between the degree of conjugation of the nitro group with the aromatic system and the spectroscopic characteristics of the compound. The following order of decreasing conjugation was established: 2-nitro-AA > 3-, 4-, 8-, and 9-nitro-(DH)AA > 5-nitro-(DH)AA > 7-nitro-(DH)AA > 6-nitro-(DH)AA > 10-nitro-(DH)AA. For the 5-, 7-, 6- and 10-nitro derivatives, the conjugation was found to be diminished owing to steric interactions with nearby *peri* protons. The twist angles were calculated using two semi-empirical SCF methods, PM3 and AM1. Although the methods yielded two rather different sets of twist angles, the order of decreasing conjugation in both cases was identical to the spectroscopically obtained order.

The nitroaceanthrylenes and nitroaceanthrenes are now available as reference compounds for their identification in the environment. It will now also be possible to determine the biological properties of these compounds and to establish structure–activity relationships.

Experimental

General

All reagents were commercially available and were used without further purification. Lithium bromoacetate was prepared by reaction of bromoacetic acid with 1-equivalent of lithium methoxide, it was thoroughly dried before use. All solvents were distilled before use and dried if necessary. Petroleum ether with a boiling range of 60–80°C was used. Silica gel (230–400 Mesh) was supplied by Merck. For HLPC purification, an LKB HPLC system (normal phase Zorbax Sil or reversed-phase Zorbax ODS 21.2 mm×25 cm) was used. Solvents were distilled and filtered before use. Melting points were determined on a Pleuger–Büchi melting point apparatus and are uncorrected. Melting points of the nitroaceanthrenes and nitroaceanthrylenes were measured of samples that were flushed with argon and sealed, in order to minimize decomposition.
The 300-MHz ^{1}H-NMR spectra were recorded on a Bruker WM-300 spectrometer. TMS (δ 0) was used as internal standard and $CDCl_3$ (99.8% D) as solvent unless stated otherwise. Concentrations were 1–2 mg/ml. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Spectra were simulated with the PANIC 84 program of Bruker. The 100.6-MHz proton-decoupled ^{13}C and ^{1}H–^{13}C-correlated 2D-NMR (CH COSY) spectra were recorded on a Bruker MSL-400 spectrometer, with $CDCl_3$ as solvent. In the ^1J(C,H) COSY experiments, the experimental setting was optimized for Js of 160 Hz. In the ^3J(C,H) COSY experiments, this was 7 Hz. An additional low-J pass filter[72] was used in the latter measurements.
IR spectra were recorded on a Pye-Unicam SP3-200 spectrophotometer and UV-VIS spectra on a Varian DMS 200 spectrophotometer. Mass spectra were determined on a KRATOS MS9/50 mass spectrometer (source 70 eV, source temperature as reported) and double-focused mass spectra on a Varian MAT 711 spectrometer.
AM1 calculations[67] were performed with the AMPAC 3.01 (QCPE 527) and were run on an Amdahl computer. PM3 calculations[68] were run on a CONVEX C-120. In this case, pre-optimization was carried out using the program MODEL, which includes an MM2-derived optimization mode. Further reduction of the value for the heat of formation was then achieved with a restricted Hartree–Fock calculation using the standard PM3 parameters as implemented in the VAMP program (based on AMPAC 1.0 and MOPAC 4.0). Either the Broyden–Fletcher–Goldfarb–Shanno algorithm (BFGS) or Bartels' Non-Linear Least-Squares method (NLLSQ) was used, always in combination with the keyword PRECISE.

*Aceanthrene (DHAA) (**2**)*

Hydrazine monohydrate (22.0 g, 0.44 mol) was added to a suspension of 1,2-aceanthrenequinone[23] (5.0 g, 21.4 mmol) in diethylene glycol (300 ml) under an argon atmosphere. Upon slight heating, the reactants dissolved. After 1 h, excess water and hydrazine were distilled off until the temperature of the reaction mixture reached 150°C. The solution was allowed to cool to 80°C and KOH (22 g) was added in portions. The solution was refluxed for 3 h and finally cooled to room temperature. Water (500 ml) was added and the reaction mixture was extracted with diethyl ether (2×). The combined organic layers were washed with water (2×), and dried over $MgSO_4$. Evaporation of the solvent gave the crude aceanthrene (**2**) as yellow plates. Column chromatography (silica/petroleum ether) gave **2** (4.1 g, 95%) as pale-yellow plates. Recrystallization (ethanol) gave **2** as silvery-white plates, m.p. 112–113°C (lit.[25]: 113–114°C; lit.[59]: 114–115°C). UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 257 (105000), 340 (2400), 356 (4750), 374 (6550), 394 (4800). IR (KBr): 3040, 2915, 1618, 1576, 1344, 880, 869, 836, 754, 742, 733 cm^{-1}. MS (25°C), m/z (%): 204 (100), 203 (71), 202 (36), 201 (7), 200 (5), 101 (24).

*Aceanthrylene (AA) (**1**)*

Under an argon atmosphere, **2** (204 mg, 1.0 mmol) was dissolved in dry toluene (90 ml). DDQ (250 mg, 1.1 mmol) was added under stirring and the solution was brought to reflux. After 90 min, no starting material could be detected on TLC. The reaction mixture was cooled to room temperature, filtered over hyflo and washed with saturated Na_2SO_3 solution (2×) and water. Drying over $MgSO_4$ and evaporation of solvent yield **1** as a dark-red viscous oil. Column chromatography (silica; petroleum ether) yielded **1** (153 mg, 76%) as red plates, m.p. 94–95°C (lit.[25]: 95–96°C; lit.[59]: 94–95°C). UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 237 (38900), 253 (47800), 346 (3700), 362 (7000), 382 (3550), 440 (4000), 424 (2800). IR (KBr): 1437, 1306, 1085, 881, 850, 816, 770, 750, 738, 717 cm^{-1}. MS (25°C): m/z (%): 202 (100), 201 (14), 200 (20), 101 (22).

Nitration of aceanthrylene with dinitrogen tetroxide

Aceanthrylene (**1**) (120 mg, 0.60 mmol) was dissolved under an argon atmosphere in dry, freshly distilled CCl_4 (100 ml). Some K_2CO_3 was added to neutralize HNO_2 which was expected to be formed during nitration. Into a dry three-necked round-bottomed flask equipped with rubber septum inlets, N_2O_4 gas from a lecture bottle was condensed with the aid of an ice–salt bath. One drop of liquid N_2O_4 was added to the stirred solution of **1** and the reaction was followed by TLC. After 15 min, another drop of N_2O_4 was added and stirring was continued until all starting material had reacted. The purple-red solution was stirred for 1 h at 35°C and then it was washed with water and with aqueous $NaHCO_3$. After, drying over $MgSO_4$, the solvent was evaporated. The dark-purple residue was purified using column chromatography (silica; CH_2Cl_2/petroleum-ether 2:3), yielding 2-nitroaceanthrylene (**1b**) (81 mg, 55%) as purple-red needles, m.p. 170–171°C (dec). UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 239 (52100), 280 (18400), 343 (7600), 362 (7700), 379 (10800), 500br (6300). IR (KBr): 1503, 1465, 1456, 1434, 1367, 1328, 1244, 1069, 954, 899, 818, 755, 735 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_2$: 247.0633 m/z; found: 247.0637 m/z.

Nitration of aceanthrene with dinitrogen tetroxide

A saturated solution of N_2O_4 in CH_2Cl_2 was added to a solution of **2** (1.0 g, 4.4 mmol) in CH_2Cl_2 (100 ml) in portions of 10 ml. The colour of the solution changed from yellow to dark red. After 90 ml had been added, TLC showed that all of the starting material had reacted. After additional stirring for 15 min, the reaction mixture was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The dark residue was purified by column chromatography (silica; CH_2Cl_2/petroleum ether 2:3). 6-Nitroaceanthrene (**2f**) eluted first (94 mg, 9%), followed by 1-nitroaceanthrene (**2a**) (390 mg, 36%). Both isomers were further purified by recrystallization (CH_2Cl_2/petroleum ether) and reversed-phase HPLC (acetonitrile/water 6:1) giving **2f** as orange needles, m.p. 166–167°C and **2a** as yellow needles, m.p. 159–160°C. Elution with CH_2Cl_2 gave 1,6-dinitroaceanthrene (**2k**) as a dark-red solid (55 mg, 4%).
1-Nitro-DHAA (**2a**). UV (methanol), λ_{max} nm (ϵ l.mol.cm^{-1}): 256 (100900), 320 (1200), 335 (2350), 350 (4400), 368 (6500), 388 (6400). IR (KBr): 1543, 1362, 1340, 1283, 900, 885, 871, 862, 802, 749, 737 cm^{-1}. Exact mass calculated for $C_{16}H_{11}NO_2$: 249.0790 m/z; found: 249.0789 m/z.
6-Nitro-DHAA (**2f**). UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 252 (64100), 413br (4700), IR (KBr): 1620, 1497, 1421, 1330, 1180, 817, 780, 749, 730 cm^{-1}. Exact mass calculated for $C_{16}H_{11}NO_2$: 249.0790 m/z; found: 249.0796 m/z.
1,6-Dinitro-DHAA (**2k**). ^{1}H NMR: δ 4.06–4.19 (m, H2,2′); 6.94 (dd, J 6.5, 3.1, H1); 7.48 (d, J 6.5, H3); 7.67–7.77 (m, H4,8,9); 7.87 (d, J 8.8, H5); 8.16 (m, H10); 8.22 (m, H(7). IR (KBr): 1620, 1550, 1508, 1425, 1367, 1333, 1280, 868, 847, 783, 755 cm^{-1}.

Nitration of aceanthrene with $NaNO_2$ and $AgNO_3$

A suspension of **2** (150 mg, 0.73 mmol), sodium nitrite (700 mg, 10 mmol) and silver nitrate (255 mg, 1.5 mmol) in dry acetonitrile (75 ml) was cooled to 0°C under a nitrogen atmosphere. Iodine (380 mg, 1.5 mmol) was added under stirring. A white-grey precipitate of silver iodide slowly separated. After 4 h, TLC showed that the starting material had completely reacted. Water was added and excess iodine was destroyed by washing with saturated Na_2SO_3 solution. Extraction with CH_2Cl_2 (2×), drying over $MgSO_4$ and evaporation of the solvent yielded a crude mixture of **2a** and **2f**. Purification (see above) yielded **2f** (39 mg, 22%) and **2a** (12 mg, 7%).

General procedure for dehydrogenation of nitroaceanthrenes with DDQ

All nitroaceanthrenes, except 1-nitroaceanthrene, were dehydrogenated with DDQ in refluxing dry toluene under an argon atmosphere. DDQ (1.1–3 equivs.) as used, depending on the reactivity of the nitroaceanthrene; the reaction time varied between 30 min and 6 h. When dehydrogenation was complete according to TLC, the reaction mixture was allowed to cool to room temperature. It was filtered under reduced pressure over a short column of silica and hyflo in order to remove insoluble products and unreacted DDQ. The solvent was evaporated and the product was further purified by means of column chromatography.

*6-Nitroaceanthrylene (**1f**)*

Compound **2f** (36 mg, 0.14 mmol) was dehydrogenated with DDQ (117 mg, 0.45 mmol) according to the general method. The reaction mixture was refluxed for 6 h, when most of the starting material had reacted according to TLC. Column chromatography gave **1f** as dark-orange crystals (14 mg, 39%). Recrystallization from CH_2Cl_2/cyclohexane yielded orange-red crystals, m.p. 156–157°C. UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 234 (35000), 255 (35600), 353sh (34100), 368 (6600), 413 br (4100). IR (KBr): 1503, 1441, 1405, 1353, 1332, 920, 836, 817, 778, 749, 712 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_2$: 247.0633 m/z; found: 247.0637 m/z.

*Dehydrogenation of 1-nitroaceanthrene (**2a**)*

Compound **2a** (90 mg, 0.36 mmol) was dissolved in nitrobenzene (40 ml) and DDQ (90 mg, 0.40 mmol) was added while stirring under an argon atmosphere. The solution was rapidly brought to reflux and, after 15 min, quickly cooled down to room temperature. After evaporation of the solvent under reduced pressure, the resulting black residue was thoroughly extracted with CH_2Cl_2. The organic layer was washed with saturated Na_2SO_3 solution and with water and dried over $MgSO_4$. The solvent was evaporated and the dark product was purified by column chromatography (silica: CH_2Cl_2/petroleum-ether 1:1). Two fractions were collected, the first consisting of starting material (13 mg) and the second of 2-nitroaceanthrylene (**1b**) (20 mg, 22%). When the column was eluted with CH_2Cl_2, 1(2*H*)-aceanthrylenone (**4**) (25 mg, 28%) was isolated.

*1,2,6,10b-Tetrahydroaceanthrylene (THAA) (**3**)*

In a 250-ml reaction vessel with a vibromixer, **2** (612 mg, 3.0 mmol) was dissolved in 3-methyl-1-butanol (150 ml) and the solution was brought to reflux. Sodium (3.0 g, 130 mmol) was added in small pieces over a period of 15 min and the reactants were vigorously mixed for an additional 45 min. When all of the sodium had dissolved, the solution was allowed to cool to room temperature. The solution was washed with water (2×) and dried over $MgSO_4$. Evaporation of the solvent yielded THAA (**3**) as a light-brown viscous oil. Column chromatography (silica/petroleum-ether) gave **3** (560 mg, 91%) as a colourless oil, which solidified on standing. Recrystallization (ethanol) gave **3** as white needles, m.p. 81–82°C (lit.[74]: 82°C).
^{1}H NMR: δ 2.06 (m, H1′); 2.91 (m, H1); 3.00 (dd, *J* 15.5, 8.3, H2′); 3.18 (m, H2); 3.88 (d, *J* 16.9, H6′); 4.05 (dd, *J* 16.9, 4.7, H6); 4.08 (m, H10b); 7.10–7.32 (m, 7H, arom.). Our spectrum of **3** is in agreement with a 500-MHz spectrum that has been published[74]. UV (cyclohexane), λ_{max} nm (relative ϵ): 260 (1.00), 342 (0.015), 356 (0.035), 375 (0.050), 396 (0.040). Exact mass calculated for $C_{16}H_{14}$: 206.1096 m/z; found: 206.1081 m/z. MS (25°) m/z (%): 206 (66), 205 (100), 204 (20), 203 (20), 202 (22), 178 (21).

*Nitration of 1,2,6,10b-tetrahydroaceanthrylene (**3**)*

Compound **3** (300 mg, 1.46 mmol) and trifluoroacetic anhydride (TFAA) (4.5 ml) were dissolved in dry acetonitrile (40 ml) and then ammonium nitrate (116 mg, 1.46 mmol) was added. After 10 min, the ammonium nitrate had dissolved and the colour of the solution had changed to orange-red. Water was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$ and the solvent was evaporated. Column chromatography (silica; CH_2Cl_2/petroleum-ether 1:1) yielded a mixture of 3-, 4-, and 5-nitro-THAA (**3c–e**) (220 mg, 63%) as a yellow-brown oil (ratio 1:1.3:1). It was possible to isolate the 5-nitro isomer from the mixture by two careful column-chromatography separations (silica; CH_2Cl_2/petroleum-ether 1:3). From a crude mixture (144 mg), the 5-nitro isomer (31 mg) was collected as a yellow-brown oil and a mixture of 3- and 4-nitro isomers (68 mg) as a yellow-brown oil.
Mixture of **3c** and **3d**. ^{1}H NMR: δ 2.13 (m, H1′); 2.94–3.69 (m, H1,2,2′); 3.92–4.11 (m, H6,6′); 7.20–7.34 (m, 4H, arom.); 7.99–8.03 (m, 2H, arom.). MS (150°C) m/z (%): 251 (100), 250 (58), 234 (44), 217 (13), 205 (39), 204 (65), 203 (57), 202 (42), 190 (10), 189 (12), 178 (11), 165 (11), 101 (12).
Compound **3e**. ^{1}H NMR: δ 2.16 (m, H1′); 2.93–3.27 (m, H1,2,2′); 4.16 (m, H6,10b); 4.60 (d, *J* 18.2, H6′); 7.21–7.36 (m, 5H, arom.); 7.97 (d, *J* 8.4, H4). MS (150°C) m/z (%): 251 (38), 234 (100), 217 (17), 205 (22), 204 (53), 203 (61), 202 (46), 190 (10), 189 (10), 101 (21).

*5-Nitroaceanthrene (**2e**)*

Compound **3e** (30 mg, 0.12 mmol) was dehydrogenated with DDQ (30 mg, 0.13 mmol) by the usual procedure (reaction time 45 min). Column chromatography (silica; CH_2Cl_2/petroleum ether 2:3) gave 5-nitroaceanthrene (**2e**) (9 mg, 30%) as red needles. Reversed-phase HPLC (acetonitrile/water 6:1) was used to remove a minor amount of **2c**. Compound **2e** was collected as light-red needles, m.p. 168–169°C. UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 246 (52500), 273 (24300), 333 (1600), 351 (1300), 448br (6200). IR (KBr): 1615, 1572, 1530, 1490, 1435, 1350, 1309, 1284, 895, 840, 741 cm^{-1}. Exact mass calculated for $C_{10}H_{11}NO_2$: 249.0790 m/z; found: 249.0783 m/z.

*3-Nitro- and 4-nitroaceanthrene (**2c** and **2d**)*

A mixture of **3c** and **3d** (65 mg, 0.26 mmol) was dehydrogenated with DDQ (65 mg, 0.29 mmol) according to the general procedure (reaction time 45 min). Column chromatography (silica; CH_2Cl_2/petroleum ether 2:3) yielded two fractions. The first fraction contained 4-nitroaceanthrene (**2d**) (15 mg, 43% from starting material) as brown-red needles and the second 3-nitroaceanthrene (**2c**) (14 mg, 47% from starting material). Both nitroaceanthrenes were further purified with reversed-phase HPLC (acetonitrile/water 6:1) yielding **2c** as yellow-orange needles, m.p. 205–207°C and **2d** as orange needles, m.p. 154–155°C.
3-Nitro-DHAA (**2c**). UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 244 (47000), 271 (18800), 305 (21700), 316 (25700), 336 (4600), 351 (4100), 370 (5050), 431br (5200). IR (KBr): 1610, 1503, 1435, 1343, 1317, 1135, 897, 841, 809, 748, 722 cm^{-1}. Exact mass calculated for $C_{16}H_{11}NO_2$: 249.0790 m/z; found: 249.0791 m/z.
4-Nitro-DHAA (**2d**): UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 241 (49500), 271 (34200), 313 (17400), 323 (18300), 352 (5250), 371 (4500), 435br (4400). IR (KBr): 1535, 1511, 1477, 1448, 1420, 1335, 912, 844, 803, 745 cm^{-1}. Exact mass calculated for $C_{16}H_{11}NO_2$: 249.0790 m/z; found: 249.0787 m/z.

*3-Nitroaceanthrylene (**1c**)*

Compound **2c** (25 mg, 0.10 mmol) was dehydrogenated with DDQ (50 mg, 0.22 mmol) in 2 h according to the general method. Column chromatography (silica; CH_2Cl_2/petroleum-ether 2:3) furnished 3-nitroaceanthrylene (**1c**) (9 mg, 36%) as brown crystals. Reversed-phase HPLC (acetonitrile/water 5:1) gave **1c** as brown fine needles, m.p. 170–171°C. UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 230 (28400), 278 (26000), 315sh (16900), 358 (7300), 377 (7800), 406 (1900), 429 (2200), 456 (1800). IR (KBr): 1618, 1525, 1467, 1438, 1335, 882, 828, 755, 715 cm^{-1}. Exact mass calculated for $C_{10}H_9NO_2$: 247.0633 m/z; Found: 247.0625 m/z.

*4-Nitroaceanthrylene (**1d**)*

Compound **2d** (20 mg, 0.08 mmol) was allowed to react with DDQ (30 mg, 0.13 mmol), according to the general method, for 2 h. Column chromatography (silica; CH_2Cl_2/petroleum-ether 2:3) gave 4-nitroaceanthrylene (**1d**) (6 mg, 30%) as an orange-brown crystalline mass. Reversed-phase HPLC (acetonitrile/water 6:1) gave **1d** as orange crystals, m.p. 130–131°C. UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 235 (26500), 254 (39700), 286 (21700), 298sh (20400), 368sh (4750), 384 (4050), 408 (3150), 435 (2150). IR 9KBr): 1624, 1533, 1518, 1334, 905, 822, 755, 740, 711 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_2$: 247.0633 m/z, found: 247.0630 m/z.

*5-Nitroaceanthrylene (**1e**)*

Compound **2e** (30 mg, 0.12 mmol) was treated with DDQ (70 mg, 0.31 mmol) according to the general method for 4 hours, after which most of the starting material had reacted (TLC). Column chromatography (silica gel, CH_2Cl_2/petroleum-ether, 2:3) gave 5-nitroaceanthrylene (**1e**) (6 mg, 20%) as brown crystals. Reversed-phase HPLC (acetonitrile/water 5:1) gave **1e** as fine brown needles, m.p. 141–142°C. UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 239 (45200), 286 (17800), 367sh (7500), 381 (10800), 413 (4500), 435 (3200). IR (KBr): 1513, 1437, 1321, 1175, 910, 882, 866, 850, 829, 760, 752, 717 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_2$: 247.0633 m/z; found: 247.0639 m/z.

*9,10-Dihydro-9-anthraceneacetic acid (**6**)*

The reaction was carried out in a 1-litre reaction vessel under an argon atmosphere while stirring with a vibromixer. Diethyl ether (300 ml) was freshly distilled from $LiAlH_4$ into the reaction vessel containing anthracene (7.0 g, 39.3 mmol). The resulting solution was cooled to −60°C and kept at this temperature with a solid-CO_2/ethanol bath. Liquid ammonia (300 ml) was added directly from a gas cylinder. After 15 min, sodium (2.1 g, 91.3 mmol) was added in

small lumps. The colour changed from dark-blue to brown-red under vigorous mixing, which was continued for 45 min. Lithium bromoacetate (6.8 g, 41.4 mmol) was added and the colour of the reaction mixture changed to yellow. Mixing was continued for 1 h, whereupon ammonium chloride (5 g) was added. After 30 min, the mixing was stopped and the cooling bath removed. Evaporation of the ammonia occurred when the mixture was left to stand overnight. The remaining ether layer was extracted with 5% NaOH solution (2×). The combined basic layers were acidified to pH 2 with concentrated H_2SO_4 and then extracted with CH_2Cl_2. The organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent gave **6** (5.8 g, 62%) as a light-yellow solid, m.p. 160–162°C, which was used without further purification. ^{1}H NMR: δ 2.66 (d, J 7.6, $-CH_2-COO$); 3.90 (d, J 18.4, H10'); 4.02 (d, J 18.4, H10); 4.52 (t, J 7.6, H9); 7.20–7.39 (m, 8H, arom.). UV (methanol), λ_{max} nm (relative ϵ): 214 (1.00), 258 (0.08), 264 (0.11), 271 (0.09). IR (KBr): 3300–2500 (COOH), 2260, 1708, 1694, 1482, 1455, 1438, 1411, 1302, 968, 770, 762, 733 cm^{-1}. Exact mass calculated for $C_{16}H_{14}O_2$: 238.0994 m/z; found: 238.0999 m/z. MS (150°C) m/z (%): 236 (13), 179 (68), 178 (100).

6,10b-Dihydro-2(1H)-aceanthrylenone (**5**)

Compound **6** (4.95 g, 16.6 mmol) was dissolved in thionyl chloride (80 ml) and the solution was refluxed for 1 h. Excess thionyl chloride was distilled off under reduced pressure and the residue was dissolved in nitrobenzene (50 ml). This solution was added in 30 min to a suspension of $AlCl_3$ (6.7 g, 50 mmol) in nitrobenzene (300 ml) at 10°C. The reaction mixture was stirred overnight at room temperature. It was poured out in a mixture of ice (200 g), water (100 ml) and potassium tartrate (20 g). Upon standing, the organic layer separated and it was washed with saturated Na_2CO_3 solution and dried over $MgSO_4$. The organic layer was filtered over hyflo and the solvent was removed under reduced pressure. The resulting dark-brown oil was purified by column chromatography (silica; CH_2Cl_2). Compound **5** (3.18 g, 69%) was collected as a brown oil, which solidified upon standing. Recrystallization from CH_2Cl_2/cyclohexane gave **5** as yellow cubes, m.p. 114–115°C. ^{1}H NMR: δ 2.92 (dd, J 17.8, 5.9, H1'); 3.40 (dd, J 17.8, 7.3, H1); 4.01 (d, J 17.7, H6'); 4.12 (dd, J 17.7, 4.0, H6); 4.24 (m, H10b); 7.24–7.42 (m, 5H, arom.); 7.56 (d, J 7.4, H5); 7.63 (d, J 7.6, H3). UV (cyclohexane), λ_{max} nm (relative ϵ): 242 (1.00), 252sh (0.88), 273 (0.13), 287 (0.24), 295 (0.24). IR (KBr): 1703 (C=O), 1598, 1472, 1450, 1408, 1270, 1065, 1040, 798, 783, 750, 682 cm^{-1}. Exact mass calculated for $C_{16}H_{12}O_1$: 220.0889 m/z; found: 220.0890 m/z. MS m/z (%): 220 (100), 219 (23), 192 (77), 191 (58), 189 (28), 179 (22), 178 (57), 165 (10).

Nitration of 6,10b-dihydro-2(1H)-aceanthrylenone (**5**)

Compound **5** (1.00 g, 4.6 mmol) was nitrated with ammonium nitrate (400 mg, 5.0 mmol) and TFAA (10 ml) in acetonitrile (80 ml) in a similar way to compound **3**. Column chromatography (silica; CH_2Cl_2) yielded a mixture of 7-, 8-, 9- and 10-nitro-6,10b-dihydro-2(1H)-aceanthrylenone (**5g–j**) (945 mg, 83%) as a yellow-brown foaming oil (ratio 4:4:4:1). ^{1}H NMR of the mixture of nitro isomers: δ 2.94 ("ddd", H1'); 3.47 ("dt", H1); 4.18 (m, H6,6'); 4.30 (m, H10b); 7.42–7.68 (m, 4H, arom.); 8.10–8.25 (m, 2H, arom.). MS (125°C) m/z (%): 265 (96), 248 (32), 237 (37), 220 (22), 219 (23), 218 (26), 192 (31), 191 (42), 190 (60), 189 (100).

7-Nitro-, 8-nitro-, 9-nitro- and 10-nitro-6,10b-dihydroaceanthrylene (**7g–j**)

A mixture of nitro ketones **5g–j** (1.20 g, 4.54 mmol) was dissolved in a mixture of 75 ml CH_3OH and 75 ml CH_2Cl_2. $NaBH_4$ (0.80 g, 23.0 mmol) was added in portions over a period of 30 min. Stirring was continued for an additional 30 min. Water was added and the mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated to dryness. A mixture of nitro alcohols was collected as a yellow-brown foaming oil (1.10 g, 90%), which was not further purified.

The mixture of nitro alcohols (1.07 g, 4.02 mmol) was dissolved in toluene (80 ml), and a catalytic amount of p-TSA was added. The solution was refluxed for 30 min. When the solution had cooled to room temperature, it was washed with saturated $NaHCO_3$ solution and with water. The solution was dried over $MgSO_4$ and evaporated to dryness, yielding a mixture of nitro-6,10b-dihydroaceanthrylenes (**7g–j**) (620 mg, 63%) as a red oil. Separation of this mixture into two fractions of two isomers each was achieved by careful column chromatography (silica; CH_2Cl_2/petroleum-ether 1:2). A crude mixture of isomers (300 mg) yielded a first fraction containing the 7- and 10-nitro isomers (**7g** and **7j**) (90 mg, ratio 3:1) as an orange oil, and a second fraction containing the 8- and 9-nitro isomers (**7h** and **7i**) (174 mg, ratio 3:3) as an orange oil.

Mixture of **7g** and **7j**. ^{1}H NMR: δ 4.19 (dd, J 17.5, 4.2, H6); 4.32 (s, H10b); 4.35 (d, J 17.5, H6'); 7.15–8.03 (m, H1,2, 6 arom.).

Mixture of **7h** and **7i**: ^{1}H NMR: δ 4.03 (d, J 17.5, H6); 4.22 (dd, J 17.5, 4.1, H6); 4.32 (br.s, H10b); 7.08–8.10 (m, H1,2, 6 arom.).

Mixture of isomers **7g–j**: MS m/z (%): 249 (80), 203 (81), 202 (100), 191 (22), 101 (19).

7-Nitro- and 10-nitroaceanthrene (**2g** *and* **2j**)

A mixture of **7g** and **7j** (90 mg, 0.36 mmol) was dissolved in absolute ethanol (80 ml) and four droplets of concentrated HCl were added under stirring. The solution was refluxed under a nitrogen atmosphere for 2 h. The reaction mixture was allowed to cool to room temperature and water was added, followed by extraction with diethyl ether. The organic layer was washed with saturated $NaHCO_3$ solution and with water and then dried over $MgSO_4$. The solvent was evaporated and the resulting brown-red oil was purified by column chromatography (silica; CH_2Cl_2/petroleum-ether 1:2). 10-Nitroaceanthrene (**2j**) (20 mg, 90% from starting material) eluted first and was collected after recrystallization (CH_2Cl_2/cyclohexane) as yellow-orange needles, m.p. 177–178°C. The second fraction contained 7-nitroaceanthrene (**2g**) (62 mg, 92% from starting material) as red crystals, m.p. 154–155°C (after recrystallization).

7-Nitro-DHAA (**2g**): UV (methanol), λ_{max} nm (ϵ l.mol^{-1}. cm^{-1}): 246 (52600), 260sh (33800), 352 (1900), 431br (3500). IR (KBr): 1620, 1509, 1443, 1321, 869, 802, 740, 722 cm^{-1}. Exact mass calculated for $C_{16}H_{11}NO_2$: 249.0790 m/z; found: 249.0788 m/z.

10-Nitro-DHAA (**2j**): UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 259 (56600), 381 (3500), 399br (3600), IR (KBr): 1620, 1511, 1350, 1335, 1285, 866, 830, 759, 745, 709 cm^{-1}. Exact mass calculated for $C_{10}H_{11}NO_2$: 249.0790 m/z; found: 249.0791 m/z.

7-Nitroaceanthrylene (**1g**)

Compound **2g** (25 mg, 0.10 mmol) was treated with DDQ (35 mg, 0.15 mmol) according to the general procedure; the reaction was completed in 45 min. Column chromatography (silica; CH_2Cl_2/petroleum-ether 2:3) yielded 7-nitroaceanthrylene (**1g**) (15 mg, 60%) as red needles, m.p. 126–127°C. UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 253 (54200), 354sh (4400), 366 (7300), 401 (6200), 425 (5600). IR (KBr): 1508, 1320, 1085, 871, 800, 745, 712 cm^{-1}. Exact mass calculated for $C_{10}H_9NO_2$: 247.0633 m/z; found: 247.0633 m/z.

10-Nitroaceanthrylene (**1j**)

Compound **2j** (15 mg, 0.06 mmol) was dehydrogenated with DDQ (20 mg, 0.09 mmol) according to the general procedure, the reaction was completed within 45 min. Column chromatography (silica; CH_2Cl_2/petroleum-ether 2:3) yielded 10-nitroaceanthrylene (**1j**) as an orange solid (7 mg, 47%). Reversed-phase HPLC (acetonitrile/water 6:1) gave **1j** as light-orange crystals, m.p. 137–138°C. UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 253 (52800), 345 (4800), 361 (7800), 384 (3900), 402 (4400), 425 (3200). IR (KBr): 1513, 1435, 1353, 1333, 887, 831, 759, 741, 712 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_2$: 247.0633 m/z; found: 247.0634 m/z.

8-Nitro- and 9-nitroaceanthrene (**2h** *and* **2i**)

Isomerization of a mixture of **7h** and **7i** (174 mg, 0.65 mmol) with concentrated HCl in absolute ethanol was performed in the same way as that of **7g** and **7j**. Column chromatography (silica; CH_2Cl_2/petroleum-ether 2:3) yielded a mixture of 8- and 9-nitroaceanthrene (**2h** and **2i**) (170 mg, 98%) as an orange-red crystalline mass. The isomers were separated by normal-phase HPLC (CH_2Cl_2/petroleum ether 1:6), yielding **2h** as dark-orange needles, m.p. 185–186°C and **2i** as orange needles, m.p. 170–171°C.

8-Nitro-DHAA (**2h**): UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 241 (42200), 275 (21400), 310 (18300), 357 (3300), 377 (3400), 437br (3400). IR (KBr): 1615, 1503, 1330, 918, 862, 818, 808, 767, 752, 720 cm^{-1}. Exact mass calculated for $C_{16}H_{11}NO_2$: 249.0790 m/z, found: 249.0785 m/z.

9-Nitro-DHAA (**2i**): UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 242 (43500), 276 (21100), 309sh (19200), 317 (20700), 355 (3750), 374 (3250), 447br (4200). IR (KBr): 2920, 2845, 1615, 1549, 1504, 1465, 1323, 1090, 892, 860, 762, 732 cm^{-1}. Exact mass calculated for $C_{16}H_{11}NO_2$: 249.0790 m/z; found: 249.0791 m/z.

*8-Nitro- and 9-nitroaceanthrylene (**1h** and **1i**)*

A mixture of **2h** and **2i** (50 mg, 0.20 mmol) was dehydrogenated with DDQ (60 mg, 0.27 mmol) according to the general procedure (reaction time 45 min). Column chromatography (silica gel; CH_2Cl_2 / petroleum-ether, v/v 1:2) yielded two fractions: the first contained 9-nitroaceanthrylene (**1i**) (22 mg, 7.6% from starting material; 90% pure) as a red crystalline mass, and the second 8-nitroaceanthrylene (**1h**) (12 mg, 56% from starting material, 90% pure) as a brown-orange crystalline mass. Normal-phase HPLC (CH_2Cl_2 /petroleum ether 1:5) gave **1h** as orange needles, m.p. 156–157°C and **1i** as dark-orange crystals, m.p. 181–182°C.
8-Nitro-AA (**1h**): UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 234 (29200), 268 (24800), 328sh (22900), 335 (27500), 384 (4100), 408 (3400), 428 (2900). IR (KBr): 1614, 1544, 1512, 1331, 1086, 912, 867, 822, 804, 770, 751, 716 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_2$: 247.0633 m/z; found: 247.0636 m/z.
9-Nitro-AA (**1i**): UV (methanol), λ_{max} nm (ϵ l.mol^{-1}.cm^{-1}): 252 (33700), 267sh (26600), 339 (10500), 406 (4300), 430 (3750). IR (KBr): 1621, 1551, 1511, 1440, 1332, 1088, 900, 873, 838, 819, 773, 740, 720 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_2$: 247.0633 m/z; found: 247.0623 m/z.

*6,10b-Dihydroaceanthrylene (**7**)*

Compound **5** (1.33 g, 5.6 mmol) was reduced with $NaBH_4$ (900 mg, 25 mmol) in a mixture of CH_2Cl_2 (40 ml) and CH_3OH (40 ml). The resultant crude alcohol (1.18 g, 95%) was dehydrated with p-TSA in refluxing toluene (80 ml). Work-up and column chromatography (silica gel; CH_2Cl_2 /petroleum-ether, 1:9, v/v) gave 6,10-dihydroaceanthrylene (**7**) as a yellow oil (1.05 g, 97%). ^{1}H NMR: δ 3.90 (d, J 17.1, H6'); 4.16 (dd, J 17.1, 4.0, H6); 4.30 (br. s, H10b); 7.04 (dd, J 5.5, 2.3, H1); 7.12 (dd, J 5.5, 2.0, H2); 7.15–7.45 (m, 7H, arom.). UV (cyclohexane), λ_{max} nm (relative ϵ): 259 (1.00), 318 (0.002), 342 (0.015), 363 (0.025), 375 (0.030), 396 (0.025). Exact mass calculated for $C_{16}H_{12}$: 204.0940 m/z; found: 204.0926 m/z. MS (25°) m/z (%): 204 (100), 203 (76), 202 (56), 201 (9), 200 (16), 101 (30).

*2(1H)-Aceanthrylenone (**8**)*

Compound **5** (380 mg, 1.7 mmol) was dehydrogenated with DDQ (430 mg, 1.9 mmol) as described for the preparation of **1**. Column chromatography (silica/CH_2Cl_2) yielded 2(1*H*)-aceanthrylenone (**8**) (280 mg, 74%) as yellow crystals, m.p. 164–165°C (lit.[25]: 165–166°C; lit.[31]: 167°C). ^{1}H NMR: δ 4.14 (s, H1); 7.50–7.60 (m, H8,9); 7.72 (dd, J 8.5, 6.7, H4); 7.96 (m, H10); 7.97 (d, J 6.7, H3); 8.10 (m, H7); 8.23 (d, J 8.5, H5); 8.44 (s, H6). UV (methanol), λ_{max} nm (relative ϵ): 243 (1.00), 266 (0.69), 352 (0.025), 371 (0.040), 402 (0.060), 421 (0.060). IR (KBr): 1703 (C=O), 1430, 1395, 1257, 1225, 1015, 883, 842, 750, 740 cm^{-1}. MS (150°C) m/z (%): 218 (95), 190 (85), 189 (100), 188 (17), 187 (18), 163 (12).

*6-Nitro-2(1H)-aceanthrylenone (**8f**)*

Compound **8** (114 mg, 0.50 mmol) was dissolved in glacial acetic acid (50 ml). Fuming nitric acid (500 μl) was added under stirring, whereupon the colour of the solution changed from yellow to orange. After 30 min, water was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ solution (2×). Drying over $MgSO_4$ and evaporation of the solvent gave **8f** as a dark-orange oil. Column chromatography (silica; CH_2Cl_2) and recrystallization (CH_2Cl_2 /cyclohexane) gave **8f** (59 mg, 46%) as dark-yellow plates, m.p. 209–211°C. ^{1}H NMR; δ 4.24 (s, H1,1'); 7.70 (m, H9); 7.78 (m, H8); 7.95 (dd, J 8.6, 6.9, H4); 8.08 (d, J 6.9, H3); 8.08 (d, J 8.5, H10); 8.30 (d, J 8.9, H7); 8.38 (d, J 8.6, H5). UV (methanol), λ_{max} nm (relative ϵ): 241 (0.62), 264 (1.00), 376 (0.07), 418br (0.12). IR (KBr): 1713 (C=O), 1507, 1428, 1398, 1363, 1342, 1284, 1263, 1230, 919, 846, 811, 759 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_3$: 263.0582 m/z; found: 263.0584 m/z. MS (125°C) m/z (%): 263 (100), 233 (36), 217 (13), 189 (65), 177 (20), 176 (23), 145 (22).

*Synthesis of 6-nitroaceanthrylene (**1f**) from **8f***

The reduction ($NaBH_4$) and subsequent dehydration (p-TSA) of **8f** (110 mg, 0.42 mmol) was performed as described for the preparation of **7g–j**. Column chromatography (silica; CH_2Cl_2 /petroleum-ether 2:3) yielded 6-nitroaceanthrylene (**1f**) (51 mg, 53%) as a red solid, which was purified as described above.

*6-Nitro-1(2H)-aceanthrylenone (**4f**)*

1(2*H*)-Aceanthrylenone[31] (**4**) (220 mg, 1.0 mmol) was nitrated with fuming nitric acid (750 μl) in glacial acetic acid (50 ml) as described for **8**. After column chromatography (silica gel; CH_2Cl_2) and recrystallization (CH_2Cl_2 /cyclohexane), **4f** was collected (160 mg, 61%) as yellow-orange crystals, m.p. 245°C dec. ^{1}H NMR: δ 3.99 (s, 2H, H2,2'); 7.53 (d, J 6.6, H3); 7.73 (dd, J 9.0, 6.6, H4); 7.80 (m, H8,9); 7.86 (d, J 9.0, H5); 8.09 (m, H7); 9.27 (m, H10). UV (methanol), λ_{max} nm (relative ϵ): 260 (1.00), 342sh (0.03), 377 (0.09), 422br (0.12). IR (KBr): 1690 (C=O), 1510, 1452, 1419, 1350, 1165, 1103, 1053, 868, 792, 762 cm^{-1}. Exact mass calculated for $C_{16}H_9NO_3$: 263.0582 m/z; found: 263.0585 m/z. MS (125°C) m/z (%): 263 (100), 233 (20), 217 (19), 208 (22), 189 (55), 176 (22).

*6-Nitroaceanthrylene (**1f**) from **4f***

Compound **4f** (220 mg, 0.83 mmol) was reduced ($NaBH_4$) and subsequently dehydrated (p-TSA) as described for **7g–j**. Column chromatography (silica; CH_2Cl_2 /petroleum-ether 2:3) gave **1f** (151 mg, 73%) as red crystals. Further purification was performed as described above.

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