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Synthesis and spectroscopy of nine isomeric methylacephenanthrylenes

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Abstract. The synthesis of nine isomeric methyl-substituted acephenanthrylenes is described. Three different approaches were used. 1-, 2-, And 6-methylacephenanthrylene (**1a**, **1c** and **1f**) were prepared by formylation of acephenanthrene (**2**) and 4,5,7,8,9,10-hexahydroacephenanthrylene (**17**), followed by Wolff–Kishner reduction and dehydrogenation. 4-, 5-, 7- And 10-methylacephenanthrylene (**1d**, **1e**, **1g** and **1j**) were synthesized by treating the corresponding acephenanthrenones with methyllithium, followed by dehydration and, in the case of **1g** and **1j**, dehydrogenation. 8- And 9-methylacephenanthrylene (**1h** and **1i**) were prepared by a Haworth synthesis starting with the reaction of methylsuccinic anhydride with acenaphthene. The spectroscopic properties of acephenanthrylene and its methyl derivatives were investigated with mass spectrometry, ^{1}H NMR and UV–VIS spectroscopy. According to the ^{1}H NMR spectra, steric hindrance between the methyl group and nearby protons decreases in the following order: 1, 10 > 6 > 7 > 3 > 4, 5, 8, 9.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are present in the environment due to natural and anthropogenic activity[1]. Many of these compounds display carcinogenic activity and in this way can affect the health of humans and other animals. The main problem in investigating their biological and medical effects is that many of these PAHs usually occur as traces in very complex mixtures. Therefore there is a continuous need for (substituted) PAHs synthesized in the laboratory.

Ten years ago we started a research program to prepare and study various PAHs, especially derivatives containing nitro[2,3] or methyl groups[4], one or more five-membered rings[5–8], or more than one functional group[9,10]. Rational syntheses have been developed to prepare these compounds in very pure form. These materials can be used for establishing structure–activity relationships. They are also available as reference materials for the study of complex matrices. In collaboration with others, we established that cyclopental[*cd*]pyrene (CPP) is a potent carcinogen in the adenoma bioassay of the newborn-mouse lung[11]. A report on the activity of aceanthrylene and acephenanthrylene, cyclopenta-fused derivatives of anthracene and phenanthrene, respectively, will be published soon.

The methyl derivatives of these PAHs are of interest as well, because they are present in many complex mixtures and it is known that methyl-substituted PAHs can be very potent carcinogens[12–14]. We have recently published[9] the synthesis of some methylated CPP derivatives. In this study we will focus on the preparation of the methyl derivatives of acephenanthrylene (AP) (**1**). We have developed strategies to synthesize nine out of the ten possible novel methyl isomers: 1-methyl-AP (**1a**), 3-methyl-AP (**1c**), 4-methyl-AP (**1d**), 5-methyl-AP (**1e**), 6-methyl-AP (**1f**), 7-methyl-AP (**1g**), 8-methyl-AP (**1h**), 9-methyl-AP (**1i**) and 10-methyl-AP (**1j**). Spectroscopic data on the methylacephenanthrylenes, obtained by means of mass spectrometry, ^{1}H NMR and UV–VIS spectroscopy will be presented and discussed.

Synthesis

Acephenanthrylene (**1**) and acephenanthrene (**2**) are not commercially available. Synthetic routes to these compounds which require six or seven steps have been published[15–17]. We found it profitable to investigate another route, starting from phenanthrene. We have modified and improved the synthesis of **1** and **2** in the following manner (Scheme 1). Phenanthrene was chloromethylated with formaldehyde and concentrated HCl according to the reaction conditions reported by *Fernández* et al.[18]. Unlike their report that only 9-(chloromethyl)phenanthrene (**3**) was formed, we isolated a mixture of **3** and 1-(chloromethyl)phenanthrene (**4**) in a ratio of 6 : 1, in high yield (95%). Both the 9 and the 1 position in phenanthrene are known to be susceptible to mild electrophilic attack[19].

The isomers **3** and **4** could not be separated by means of column chromatography. A mixture of **3** and **4** was converted into the corresponding homologous acids, by a two-step procedure. First they were treated with NaCN and triethylbenzylammonium chloride as a phase-transfer catalyst in CH_2Cl_2/H_2O under reflux for 16 hours. A

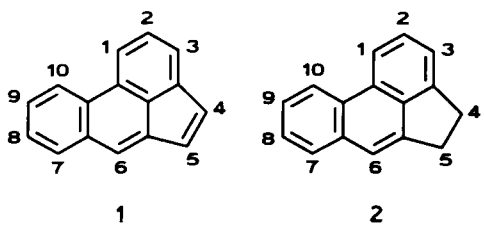
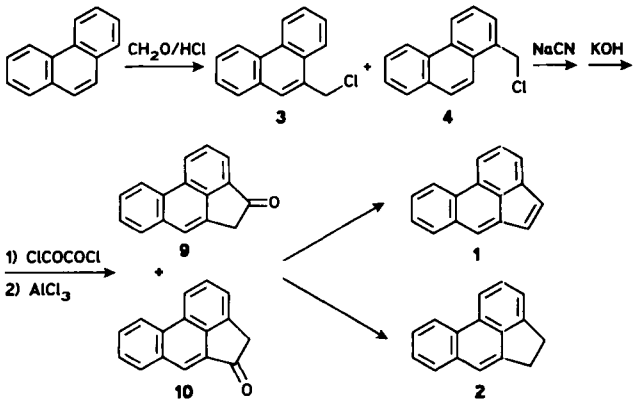


Figure 1. Acephenanthrylene (AP) (1) and acephenanthrene (2)



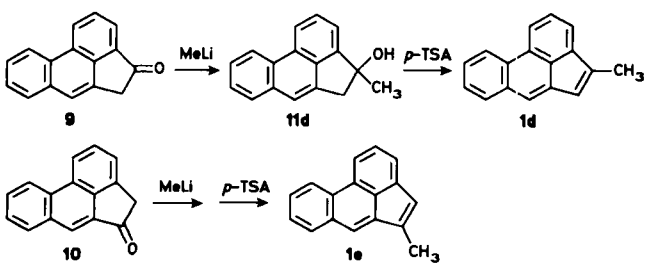
Scheme 1. Synthesis of acephenanthrylene (1) and acephenanthrene (2).

mixture of 9-phenanthreneacetonitrile (**5**) and 1-phenanthreneacetonitrile (**6**) (ratio 6:1) was isolated in 91% yield. Compounds **5** and **6** were hydrolyzed with KOH in refluxing aqueous ethanol to give, upon acidification, a mixture of 9-phenanthreneacetic (**7**) and 1-phenanthreneacetic acid (**8**) in 76% yield.

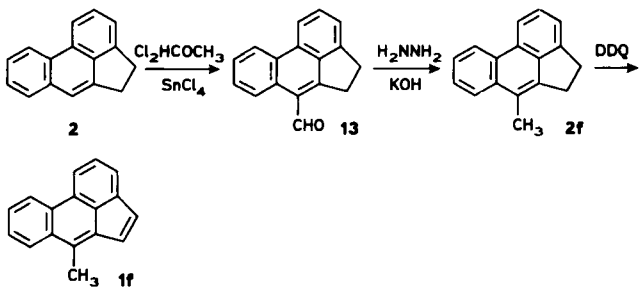
Acids **7** and **8** were cyclized to the corresponding five-membered ring ketones. The mixture of acids (6:1) was treated with oxalyl chloride[16] to yield the acid chlorides. Cyclization was performed with $AlCl_3$ under Friedel–Crafts conditions. After purification a mixture of 4(5*H*)-acephenanthrenone (**9**) and 5(4*H*)-acephenanthrenone (**10**) (4:1) was obtained in 44% yield. Ketones **9** and **10** could be separated by means of column chromatography. 4(5*H*)-Acephenanthrenone was prepared in 23% yield from phenanthrene and 5(4*H*) acephenanthrenone in 6% yield.

Acephenanthrylene (**1**) and acephenanthrene (**2**) could both be prepared from the ketones **9** and **10** in good yields. **1** was prepared in a two-step procedure, by reduction of the ketones with $NaBH_4$ and dehydration of the ensuing alcohols with *p*-toluenesulphonic acid monohydrate (*p*-TSA) in 86% yield. **2** was prepared by means of a Wolff–Kishner reduction of the ketones in 87% yield.

A straightforward manner for the introduction of a methyl group on the aromatic system has been explored earlier by our group in the preparation of methyl-substituted CPP derivatives[9]. In this method, the carbonyl-containing starting material is treated with methyllithium, giving monomethylation. The resulting tertiary alcohol can be dehydrated, leading to a double bond substituted with a methyl group. Ketone **9** was treated with excess methyllithium in dry THF to yield the corresponding methyl hydroxy compound **11d** (Scheme 2), which was then converted by reaction with a catalytic amount of *p*-TSA in refluxing toluene into 4-methylacephenanthrylene (**1d**) with an overall yield of 46%. Analogously, 5-methylacephenanthrylene (**1e**), was prepared in two steps from



Scheme 2. Synthesis of 4-methyl- and 5-methylacephenanthrylene (1d and 1e).



Scheme 3. Synthesis of 6-methylacephenanthrylene (1f).

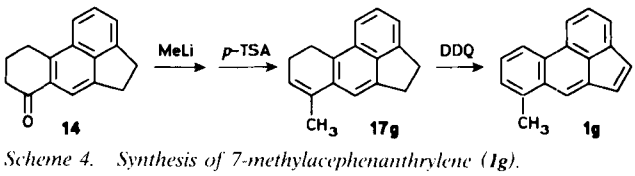
ketone **10** (67% yield) via the intermediate methyl hydroxy compound **12e**.

Another method that can be used for the introduction of a methyl group in a polycyclic aromatic system consists of formylation of the parent hydrocarbon, followed by Wolff–Kishner reduction of the aldehyde to the methyl derivative[20–22]. An especially mild formylating agent, dichloromethyl methyl ether with tin(IV) chloride as catalyst, has been described[23]. When acephenanthrene (**2**) was treated with these reagents, substitution occurred solely at the *meso* position 6[21,24] (Scheme 3). 6-Acephenanthrene carbaldehyde (**13**) was isolated as the single product in 69% yield after purification. Compound **13** was reduced under Wolff–Kishner conditions to 6-methylacephenanthrene (**2f**) in good yield (91%). **2f** Was dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (toluene, 70°C) to 6-methylacephenanthrylene (**1f**) in 60% yield.

Formylation of acephenanthrylene was attempted, but led under the reaction conditions only to decomposition, without even traces of methyl-substituted product. It is known that the double bond of the five-membered ring in cyclopenta-fused PAHs is very vulnerable to electrophilic attack[25,26]. The high reactivity of the electron-rich C4–C5 bond in **1** therefore leads to decomposition.

For the preparation of four of the remaining seven methyl isomers we have made use of the synthetic route to acephenanthrylene starting from acenaphthene. The preparation of 5,8,9,10-tetrahydro-7(4*H*)-acephenanthrylen one (**14**) in three steps from acenaphthene has been described[17]. We could improve the first step, the Friedel–Crafts reaction of acenaphthene with succinic anhydride. Normally this reaction is performed in nitrobenzene[27], which has as disadvantage that work-up is quite laborious. We found CH_2Cl_2 to be an excellent solvent for this reaction, making work-up much more facile. As an extra advantage, the formation of 3-substituted product could be diminished by lowering the reaction temperature to −10°C. 1,2-Dihydro-γ-oxo-4-acenaphthylenebutanoic acid (**15**) was isolated in 78% yield. Wolff–Kishner reduction of **15** and subsequent ring closure[17] afforded **14** in good overall yield.

Treatment of **14** with excess methyllithium in dry THF yielded the corresponding methyl hydroxy compound **16g**. Conversion of **16g** by reaction with a catalytic amount of *p*-TSA in refluxing toluene gave **17g** (Scheme 4). Compound **17g** was dehydrogenated with DDQ in toluene at 60–70°C to yield 7-methylacephenanthrylene (**1g**) in an overall yield of 43% from **14**.

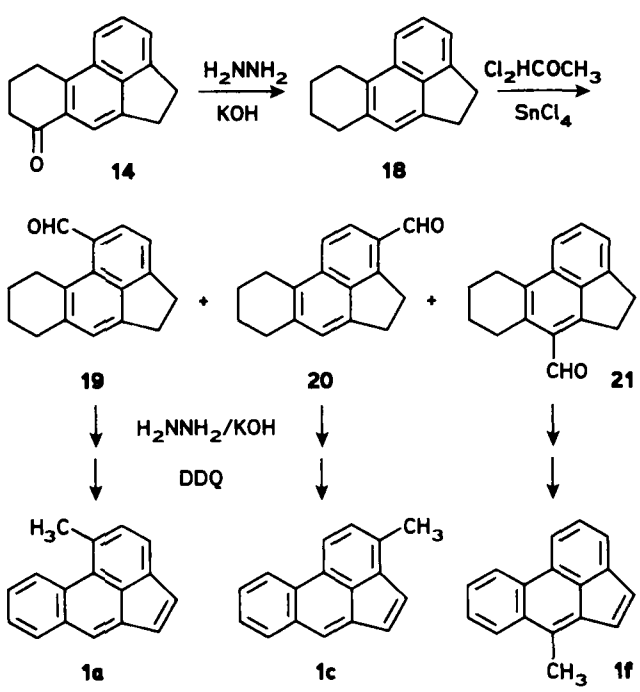


Scheme 4. Synthesis of 7-methylacephenanthrylene (1g).

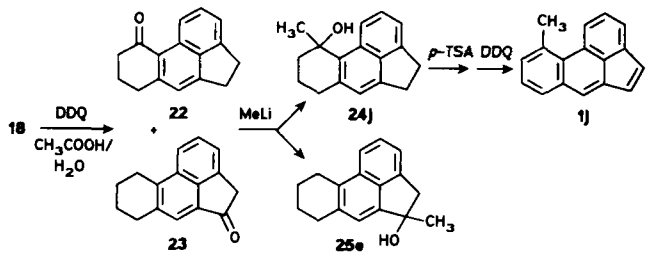
Compound **14** was converted via a Wolff–Kishner reduction into 4,5,7,8,9,10-hexahydroacephenanthrylene (**18**) in 55% yield (Scheme 5). Compound **18** can be regarded as an alkylated naphthalene nucleus. Three aromatic positions are activated: position 1, an α position of the naphthalene moiety, and positions 3 and 6, which are activated by the alkyl substituents. Indeed, when **18** was treated with dichloromethyl methyl ether and $SnCl_4$, a mixture of three isomers was formed with the formyl group at the 1-, 3-, and 6-position (**19–21**) in a ratio of 1.75 : 1 : 1.5 (total yield 98%). No trace of the 2-substituted isomer was present. We were able to separate the three isomers by careful column chromatography and recrystallization. The compounds were then deoxygenated under Wolff–Kishner conditions to **18a,c,f** (yields 84%, 79% and 77%). Dehydrogenation with 3 equivalents of DDQ (toluene, 60°C) yielded the corresponding 1-methyl-, 3-methyl-, and 6-methylacephenanthrylene (**1a,cf**) in yields of 42%, 35% and 36%, respectively. For the preparation of **1f** the synthetic route from **2** is to be preferred above that from **3**.

Treatment of partially hydrogenated PAHs with DDQ in refluxing acetic acid/water leads to ketones via oxidation at benzylic positions[28]. Submitting compound **18** to these reaction conditions yielded two products: 5,7,8,9-tetrahydro-10(4*H*)-acephenanthrylen-one (**22**) and 7,8,9,10-tetrahydro-5(4*H*)-acephenanthrylenone (**23**) (Scheme 6). These are also the products that are expected, when the relative stability of the intermediate carbenium ions is considered[28]. The total yield of ketones was 31%, and the ratio of **22** to **23** was 4 : 5. They could not be separated by column chromatography.

The mixture of **22** and **23** was treated with MeLi to give 4,5,7,8,9,10-hexahydro-10-methyl-10- and -5-methyl-5-acephenanthrylenol (**24j** and **25e**). Compounds **24j** and **25e** could easily be separated by column chromatography. Dehydration of **24j** with *p*-TSA yielded 4,5,7,8-tetrahydro-10-methyl-acephenanthrylene (**26j**), dehydrogenation with DDQ furnished 10-methylacephenanthrylene (**1j**) in an overall yield of 28% from **22**. Similarly **25e** could be converted into **1e**. The preparation of **1e** by this route was not optimized because **1e** is more easily available starting from **10**.



*Scheme 5. Synthesis of 1-methyl-, 3-methyl-, and 6-methylacephenanthrylene (**1a,c,f**).*



*Scheme 6. Synthesis of 10-methylacephenanthrylene (**1j**).*

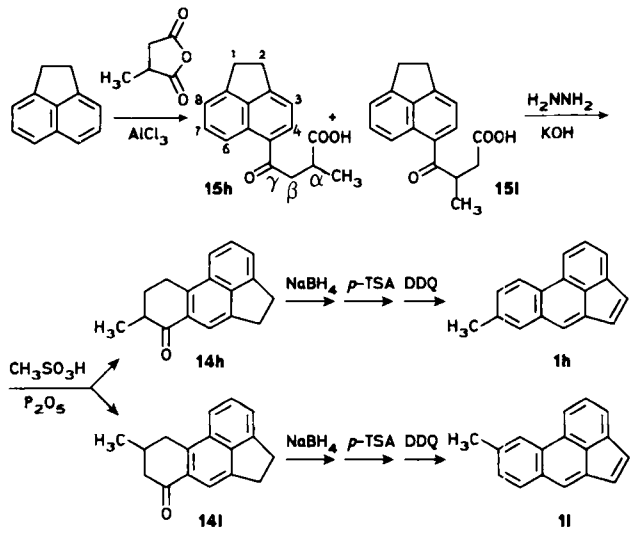
For the synthesis of 8-methyl- and 9-methylacephenanthrylene the Haworth approach of annulation was used. The Friedel–Crafts reaction of acenaphthene with methylsuccinic anhydride in CH_2Cl_2 at low temperature (−10°C) gave a 1 : 2 mixture of the two methyl keto acids **15h** and **15i** (92%) (Scheme 7). The isomer **15i** with the methyl group at the β-position with respect to the carboxyl group is, according to ^1H NMR, formed in two-fold excess over the isomer **15h** in which the methyl group is at the α position. The formation of the α isomer **15i** in considerable amounts is a somewhat unexpected outcome. It has been reported that in the reaction of pyrene with methylsuccinnic anhydride the β isomer was formed almost exclusively[29]. However, in this investigation nitrobenzene was used as solvent, which is known to stabilize the reactive species to a great extent[30]. As a result the reaction in nitrobenzene proceeds slowly, with high selectivity (high α-to-β ratios)[30]. In less stabilizing solvents, such as CH_2Cl_2, the reaction is much faster and the selectivity will be smaller (lower α-to-β ratios).

The isomers could not be separated nor could they be purified by means of recrystallization as with the unsubstituted ketoacid[27]. According to ^1H NMR, 3-substituted products constituted less than 5% of the reaction mixture. Wolff–Kishner reduction of keto acids **15h** and **15i** gave the corresponding acids **27h** and **27i** in reasonable yield (48%). Cyclization with methanesulphonic-acid/P_2O_5 gave a mixture of 5,8,9,10-tetrahydro-8- and -9-methyl-7(4*H*)-acephenanthrylenone (**14h** and **14i**). The cyclization of **27h** to **14h** proceeded in a higher yield (88%) than the cyclization of **27i** to **14i** (45%). The cause of the disappointing yield in the latter case remains unclear. It was possible to separate and purify the two methyl ketones **14h** and **14i** by column chromatography and recrystallization. The methyl ketones were obtained in very pure form. The ketones underwent conversion to 8-methyl- and 9-methylacephenanthrylene (**1h** and **1i**) by successive reduction ($NaBH_4$), dehydration (*p*-TSA) and dehydrogenation (DDQ) in an overall yield of 33% and 50%, respectively.

2-Methylacephenanthrylene cannot be easily prepared by the methods discussed above. We have not yet succeeded in devising a suitable synthesis of this compound. The methylacephenanthrenes, with their five-membered ring reduced, are biologically interesting compounds as well. 6-Methylacephenanthrene has been prepared. The other methylacephenanthrenes may be prepared from the corresponding methylacephenanthrylenes by hydrogenation over a Pd/C catalyst or by reduction with Raney-nickel/hydrazine[5] in high yield.

Purification of the methylacephenanthrylenes

The nine monomethylacephenanthrylenes were purified by column chromatography (silica; petroleum ether) followed by recrystallization (methanol). In this way 4- and 5-methylacephenanthrylene were isolated in pure form. The other methylacephenanthrylenes contained minute quantities of an orange-coloured contamination. We were



*Scheme 7. Synthesis of 8-methyl- and 9-methylacephenanthrylene (**1h** and **1l**).*

able to remove this impurity by column chromatography with caffeine-impregnated silica[4] and elution with petroleum ether. In all cases the yellow-coloured methylacephenanthrylenes eluted first. The isomeric purity was at least 98% as determined with high-resolution ^{1}H NMR. All compounds gave sharp melting points with a melting range of 0.5–1.0°C.

Spectroscopic analysis

Mass spectrometry

The electron-impact (70 eV) mass spectra of the methylacephenanthrylenes **1a–j** have been recorded at low and at high resolution. The double-focused mass spectral data of the parent peak are, within experimental error, in accordance with the calculated value for $C_{17}H_{12}$: 216.0939 *m/z*.

For the derivatives with a methyl group attached to a six-membered ring the parent peak is also the base peak. In contrast to this, for the compounds with the methyl group attached to the five-membered ring (**1d** and **1e**), the $(M - 1)^+$ peak is the base peak in the spectrum (the parent peak for both compounds has a relative intensity of 92%). Under electron impact conditions methyl-PAHs will lose a hydrogen to give a carbenium ion, which readily rearranges by ring expansion[31]. In the case of 4- and 5-methyl-AP the five-membered ring is expanded to a six-membered one, generating a favourable benzophenalene cation (I). This phenomenon has been observed for 1-methylacenaphthylene[32] as well. Due to the formation of a phenalene cation, 1-methylacenaphthylene gives a stronger $(M - H)^+$ fragment than the other isomers. 3-, 4- and 5-methylacenaphthylene all give rise to an identical tropylium ion[32].

The other methylacephenanthrylenes all contain a methyl group attached to a six-membered ring. Under electron-impact conditions this will lead to a seven-membered ring, or tropylium ion. Three structurally different tropylium ions, II, III and IV, will be formed, depending on the position of the methyl group. 1- And 3-methyl-AP will generate tropylium ion II, 6-methyl-AP will lead to III and the 7-, 8-, 9- and 10-methyl isomers will give rise to tropylium ion IV. Depending on their stability these tropylium ions may give different relative intensities of the $(M - 1)^+$ peak. Tropylium ion III is expected to be the most stable of the three, because it is the most heavily substituted, followed by tropylium ion II, and IV, which is the least substituted. This difference is reflected in the relative intensity of the $(M - H)^+$ peak: for the 1-, 3- and 6-methyl derivatives this is around 67%, relative to the parent peak, while for the 7-, 8-, 9- and 10-methyl derivatives the intensity of the $(M - 1)^+$ peak is around 44%. Less intense peaks due to the loss of two or three hydrogens are observed in all spectra. When more than one hydrogen is lost, the differences between the isomers disappear, however. The loss of two hydrogens is for all isomers around 7%, and the loss of three hydrogens varies between 13 and 22%. The methylacephenanthrylenes are not prone to undergo further extensive fragmentation. No fragmentation due to the loss of a methyl group $(M - CH_3)^+$, 201 *m/z*, is observed. This is in agreement with the spectra of other methyl-substituted PAHs[28]. The small peak at 189 *m/z* which is present in all spectra (2–8% relative intensity) stems from loss of a C_2H_3 fragment.

^{1}H-NMR spectroscopy

The ^{1}H-NMR (300 MHz) spectra of acephenanthrylene (AP, **1**) and its methyl derivatives (**1a–j**) were recorded in $CDCl_3$. Above a concentration of 5 mg/ml the spectra were found to be concentration-dependent due to association. The spectra were therefore measured in a concentration range of 1–2 mg/ml. The spectra are in agreement with the expected structures. From the analysis of the aromatic proton signals, the locations of the methyl substituent could be established. The spectra indicate that the isomeric purity of all compounds is high (> 98%).

We first analysed the ^{1}H-NMR spectrum of acephenanthrylene in detail. Unequivocal assignments of the ten non-equivalent protons could be made by means of homonuclear decoupling (HD) and nuclear Overhauser effect (NOE) experiments. PANIC simulations were performed to check the assignments made and to obtain the correct chemical shifts and coupling constants. The chemical-shift values of AP are given in Table I, the coupling constants larger than 0.3 Hz are given in Table II.

The spectra of the methylacephenanthrylenes (**1a–j**) were analysed and assigned in the same manner. Besides nine aromatic protons, a methyl signal is observed in the region between 2.45 and 3.17 ppm. By means of HD and NOE experiments the position of the methyl group was determined in each of these compounds and all aromatic protons were assigned. When higher-order effects were observed in the spectra, simulations were performed with the PANIC programme to determine the correct chemical shifts and coupling constants. The chemical shifts are summarized in Table I. The coupling constants were found to be almost unchanged with respect to the values of acephenanthrene and are therefore not reproduced here.

From Table I the substituent effect of the methyl group in relation to its position in the acephenanthrylene system can be studied. The electron-donating effect of the methyl group causes nearby protons to shift upfield with respect to AP. This effect is mostly strongly felt by *ortho* protons, but *meta* and *para* protons are also affected. The *ortho*

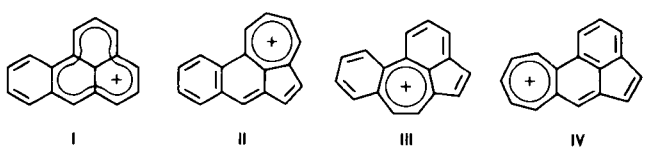


Figure 2. Possible structure of $(M - H)^+$ fragments from the methylacephenanthrylenes, generated under electron impact conditions.

Table I ^1H *NMR (300 MHz, $CDCl_3$) of acephenanthrylene and its methyl derivatives* [a].

AP	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	CH_3
AP	8.39	7.68	7.69	7.20	7.10	7.99	8.00	7.60	7.69	8.64	
1-methyl-AP		7.45	7.56	7.16	7.03	8.00	8.04	7.61	7.69	8.88	3.17
3-methyl-AP	8.30	7.46		7.30	7.08	7.99	8.00	7.57	7.67	8.61	2.69
4-methyl-AP	8.36	7.65	7.61		6.75	7.80	7.94	7.57	7.64	8.59	2.45
5-methyl-AP	8.27	7.59	7.51	6.83		7.92	8.01	7.59	7.67	8.62	2.48
6-methyl-AP	8.36	7.61	7.67	7.18	7.27		8.19	7.65	7.69	8.67	2.91
7-methyl-AP	8.40	7.65	7.68	7.20	7.12	8.24		7.46	7.58	8.54	2.82
8-methyl-AP	8.35	7.63	7.65	7.19	7.09	7.92	7.79		7.51	8.52	2.58
9-methyl-AP	8.37	7.64	7.68	7.18	7.09	7.95	7.89	7.43		8.43	2.63
10-methyl-AP	8.71	7.67	7.71	7.23	7.09	8.03	7.92	7.52	7.52		3.17

[a] Chemical shifts (δ) in ppm.

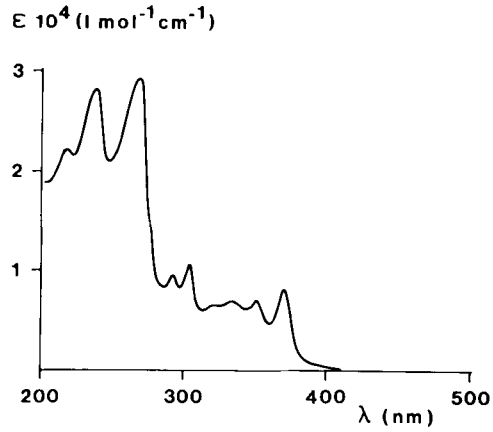


Figure 3. Electronic absorption spectrum of acephenanthrylene in cyclohexane.

protons of the derivatives with the methyl group attached to a six-membered ring can roughly be divided into two groups. The first group, consisting of H2 of 1- and of 3-methyl-AP, H7 of 8-methyl-AP, and H10 of 9-methyl-AP, displays upfield shifts of 0.21–0.23 ppm. The second group, consisting of H8- of 7- and of 9-methyl-AP, and H9 of 8- and of 10-methyl-AP displays smaller upfield shifts varying between 0.14 and 0.18 ppm. When the methyl group is attached to the five-membered ring, the upfield shift of the ortho proton is much larger: H5 of 4-methyl-AP and H4 of 5-methyl-AP are shielded by 0.35 ppm.

In the spectra of methylpyrenes the upfield shift of ortho protons was found to be typically 0.13–0.15 ppm[4]. In our series of methylacephenanthrylenes, the upfield shifts of the protons H8 and H9 are in this range, but those of H2, H7 and H10 are somewhat larger, in the order of 0.21–0.23 ppm. This difference has also been observed for 1- and 2-methylnaphthalene[33]: H1 in 2-methylnaphthalene is shielded by 0.20 ppm, while H3 is shielded by only 0.14 ppm. H2 in 1-methylnaphthalene is shielded by 0.21 ppm. 4- And 5-methyl-AP, with their methyl group attached at the C4–C5 bond of the five-membered ring, show a very strong shielding effect of the ortho proton (0.35 ppm). This is in good agreement with the upfield shift of 0.33 ppm found for cyclopenta[*cd*]pyrene (CPP) methylated at the five-membered ring[9] and with the shielding of 0.39 ppm for the analogous methylaceanthrylenes[34].

The protons situated *meta* and *peri* towards the methyl group are shifted upfield as well. No discrimination can be made between the different positions; all protons are shielded between 0.08 and 0.13 ppm. Besides steric effects the influence of a methyl group, when attached to a six-membered ring, is relatively small on the protons of one of the other rings (0.07 ppm or less). For 4- and 5-methyl-AP this is otherwise: H6 in 4-methyl-AP is shielded by 0.19 ppm, and H3 in 5-methyl-AP by 0.18 ppm. In the latter compound H1 and H2 are also shifted upfield substantially. Similar effects are observed for the analogous methyl-substituted CPPs[9] and aceanthrylenes[34]. In several cases, substantial downfield shifts are observed in the spectra. The methyl group in 1- and 10-methyl-AP has a drastic effect on the opposite bay proton: H10 in 1-methyl-AP and H1 in 10-methyl-AP are deshielded by 0.22 and 0.24 ppm, respectively. Similar shifts are found for H7 in 6-methyl-AP (+0.19 ppm) and for H6 of 7-methyl-AP (+0.25 ppm). Introduction of a methyl group at position 3 or 6 has a similar effect on the protons of the five-membered ring (+0.10 ppm for H4 in 3-methyl- AP, +0.17 ppm for H5 in 6-methyl-AP), but the opposite is not observed: H3 of 4-methyl-AP and H6 of 5-methyl-AP are shielded by 0.08 and 0.07 ppm, respectively.

When the methyl group is situated in the bay region of the molecule, or next to a *peri* proton, downfield shifts, caused by a steric effect, of both proton and methyl group are observed[35]. This downfield shift is related to the degree of steric hindrance[4]. We conclude that, in our series, the two bay-region methyl-substituted AP's are the most strongly hindered. The bay protons of 1- and 10-methyl-AP are deshielded by about 0.23 ppm, while the methyl groups resonate at 3.17 ppm, 0.59 ppm downfield compared to the methyl group of 8-methyl-AP. The somewhat smaller, but significant downfield shifts observed for 6- and 7-methyl-AP indicate that the methyl groups in these compounds are experiencing some steric hindrance as well. In 6-methyl-AP the methyl group is found 0.33 ppm downfield with respect to 8-methyl-AP, while in 7-methyl-AP this figure is 0.24 ppm. In the spectra of 4- and 5-methyl-AP, protons 3 and 6, respectively, are not deshielded. Apparently the methyl groups in these compounds are not severely hindered.

Inspection of the three-bond coupling constants shows that the influence of the methyl group is rather small. The difference in ^nJ(H,H) is never more than 0.2 Hz compared with the unsubstituted compound. For AP and its methyl derivatives a characteristic ^3J of 5.3 Hz is observed for the five-membered ring protons[7,10,36]. The other ^3J of **1** and **1a–j** can be related to the corresponding couplings in phenanthrene[37]. The coupling constants between H1 and H2 (8.0–8.3 Hz); H7 and H8 (7.8–8.1 Hz); H9 and H10 (8.0–8.3 Hz) are larger than between H2 and H3 (6.9–7.1 Hz); and between H8 and H9 (7.0–7.2 Hz), similar to those of phenanthrene[35]. With respect to the ^4J *meta* coupling constants it is noteworthy that the coupling be-

Table II Coupling constants [^nJ(H,H)] of acephenanthrylene in Hz [a].

^3J(H,H)		^4J(H,H)		^5J(H,H)		^6J(H,H)	
$J_{1,2}$	8.2	$J_{1,3}$	0.7	$J_{1,10}$	0.4	$J_{1,5}$	0.5
$J_{2,3}$	7.0	$J_{6,7}$	0.6	$J_{3,5}$	0.3		
$J_{4,5}$	5.3	$J_{7,9}$	1.5	$J_{4,6}$	0.5		
$J_{7,8}$	7.9	$J_{8,10}$	1.4	$J_{6,10}$	0.7		
$J_{8,9}$	7.1			$J_{7,10}$	0.6		
$J_{9,10}$	8.1						

[a] Coupling constants larger than 0.3 Hz.

Table III

AP	λ_{max} (nm)	Shift (nm)
AP	365	
1-methyl-AP	366	1
3-methyl-AP	373	8
4-methyl-AP	366	1
5-methyl-AP	365	0
6-methyl-AP	367	2
7-methyl-AP	376	11
8-methyl-AP	368	3
9-methyl-AP	369	4
10-methyl-AP	368	3

tween H1 and H3 (0.7 Hz) is significantly smaller than the coupling between H7 and H9 (1.6 Hz) and between H8 and H10 (1.4 Hz). This must be due to the presence of the five-membered ring. Between H1 and H5 an interesting ^6J of 0.5 Hz can be seen. A favourable W configuration of the intermediate sigma bonds lies at the basis of this long-range coupling.

UV–VIS absorption spectroscopy

The electronic absorption spectrum of **1** is shown in Figure 3. Main absorptions are found at 233 (ϵ 27600), 264 (ϵ28800), 288 (ϵ 9200), 300 (ϵ 10400), 317 (ϵ 6200), 330 (ϵ 6750), 347 (ϵ 6800) and 365 (ϵ 7900) nm. These values are in agreement with the literature[16,17,38]. *Plummer*[38] has related the absorptions at 330 and 365 nm to the L_a and L_b transitions, while the absorptions at 317 and 347 nm can be attributed to higher vibrational levels of these absorptions.

We have investigated the bathochromic shift behaviour of the 365 nm absorption band upon methyl substitution (Table III). From this Table we can see that for most isomers the bathochromic shifts are modest or absent (4 nm or less). Exceptions are 3-methyl-AP (8 nm) and 7-methyl-AO (11 nm) for which larger bathochromic shifts are found. The cause of this behaviour remains unknown.

Conclusions

We have devised practical synthetic routes for the preparation of 9 of the 10 possible monomethylacephenanthrylenes. Starting from phenanthrene the synthetic scheme also allowed the efficient preparation of the parent system acephenanthrylene and its 4,5-dihydro derivative acephenanthrene. 1-, 3-, And 6-methylacephenanthrylene were prepared starting with formylation of two partially hydrogenated acephenanthrylene precursors. 4-, 5-, 7- And 10-methylacephenanthrylene were synthesized by reaction of methyllithium with the corresponding acephenanthrylenones. 8- And 9-methylacephenanthrylene were prepared by a Haworth synthesis starting with the reaction of methylsuccinic anhydride with acenaphthene. The methylacephenanthrylenes have been prepared with purities of at least 98% on a scale of 15–80 mg. We expect that scaling up these syntheses by a factor of ten will pose no serious problems.

We have investigated and characterized acephenanthrylene and its methyl derivatives by ^{1}H NMR and UV–VIS spectroscopy and mass spectrometry. Based on their ^{1}H-NMR behaviour we conclude that the methyl groups of the 1- and 10-methyl derivatives are the most strongly hindered ones on the series, due to interactions with the opposite angular bay proton. 6- And 7-methylacephenanthrylene are hindered due to interactions with *peri* protons. In the remaining derivatives the methyl groups appear to be unhindered.

The availability of these compounds makes it possible to obtain proof of their occurrence in environmental samples and to investigate their genotoxic properties. Moreover, the nearly complete set of methyl derivatives of acephenanthrylene can be used in a study aimed at finding relationships between the position of the substituent and the biological activity of the isomer.

Experimental

General

All reagents were commercially available and were used without further purification except for acenaphthene (Fluka, 97%), which was column-chromatographed before use. 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. Melting points were determined on a Pleuger–Büchi melting point apparatus and are uncorrected. 300-MHz ^{1}H-NMR spectra were recorded on a Bruker WM-300 spectrometer with $CDCl_3$ as solvent, unless stated otherwise. TMS (δ 0) was used as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. The spectra of the methylacephenanthrylenes were recorded at a concentration of 1–2 mg/ml. IR spectra were recorded on a Pye–Unicam SP3-200 and UV–VIS spectra on a Varian DMS 200 spectrophotometer. Mass spectra were determined on a Varian MAT 711 mass spectrometer (70 eV, source temperature 150°C, inlet temperature as reported) or on a Finnigan MAT TSQ-70 LC-MS spectrometer with a particle-beam interface. The solvent used was 50/50, methanol/water with a flow of 0.5 ml/min. The inlet and source temperature were 250°C at 70 eV. The double-focused mass spectra were recorded on a Varian MAT 711.**Warning!** Many polycyclic aromatic hydrocarbons (PAHs) are potential mutagenic and carcinogenic compounds.

9-(Chloromethyl)phenanthrene (3) and 1-(chloromethyl)phenanthrene (4)

Phenanthrene was chloromethylated according to the procedure of *Fernández* et al.[18] After work-up the crude product was purified by flash chromatography over a short column of silica. This procedure was sufficient to remove slow-running degradation components and to obtain the reaction products sufficiently pure for the next reaction step. ^{1}H NMR revealed, in addition to 9-(chloromethyl)-phenanthrene (**3**), some 1-(chloromethyl)phenanthrene (**4**) in the reaction mixture (ratio of **3** and **4**: 6:1). The total yield of **3** and **4** was 95%.

3. ^{1}H NMR: δ 5.11 [s, 2H, CH_2Cl]; 7.58–7.75 [m, 4H, H(2,3,6,7)]; 7.82 [s, H(10)]; 7.88 [m, H(8)]; 8.22 [m, H(1)]; 8.66–8.78 [m, 2H, H(4,5)]. The spectrum contained small signals which were due to the 1-(chloromethyl) derivative **4**.

9-Phenanthreneacetonitrile (5) and 1-phenanthreneacetonitrile (6)

A mixture of **3** and **4** (21.7 g, 95 mmol), NaCN (7.5 g, 145 mmol) and triethylbenzylammonium chloride (3.2 g, 14.5 mmol) was suspended in a mixture of CH_2Cl_2 (30 ml) and H_2O (6 ml) under stirring. The suspension was refluxed for 16 h and then allowed to cool to room temperature. A 5% NaOH solution was added and the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed twice with water and dried over $MgSO_4$. An equal amount of petroleum ether was added and the solution was filtered over a short column of silica and hyflo, to remove slow-running degradation products. Evaporation of the solvent yielded a mixture of **5** and **6** (ratio 6:1) (18.7 g, 91%) as a light-brown oil.

5. ^{1}H NMR: δ 4.20 [s, 2H, CH_2CN]; 7.61–7.77 [m, 5H, H(2,3,6,7,9)]; 7.89–7.93 [m, 2H, H(1,8)]; 8.67–8.79 [m, 2H, H(4,5)]. In the NMR spectrum the 1-isomer (**6**) is discernible by a singlet of the CH_2CN group at 4.27 ppm.

9-Phenanthrelacetic acid (7) and 1-phenanthreneacetic acid (8)

A mixture of **5** and **6** (18.0 g, 83 mmol) was dissolved in a mixture of ethanol (125 ml) and water (20 ml) under stirring. KOH (23.5 g) was added and the reaction mixture was refluxed for 24 h. The solution was allowed to cool to room temperature and water was added. The basic layer was extracted twice with diethyl ether in order to remove

unreacted products and a small amount of residual phenanthrene. The basic layer was acidified with concentrated HCl and extracted twice with diethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. Compounds **7** and **8** (ratio 6:1) were isolated as a white powder (14.7 g, 76%). They were not separated, but used directly in the next step.

7. ^{1}H NMR: δ 4.17 [d, J 1.5, 2H, H(α,α')]; 7.57–7.71 [m, 4H, H(2,3,6,7)]; 7.72 [s, H(10)]; 7.87 and 8.03 [2m, H(1 and 8)]; 8.67 and 8.75 [2m, H(4 and 5)]. MS (125°C) m/z (%): 236 (72), 222 (47), 205 (11), 191 (100), 189 (28), 177 (16), 176 (13), 165 (18). In the NMR spectrum the 1-isomer (**8**) is discernible by a singlet of the CH_2COOH group at 3.92 ppm.

4(5H)-Acephenanthrylenone (9) and 5(4H)-acephenanthrylenone (10)

A mixture of crude **7** and **8** (12.5 g, 53 mmol) was cyclized according to the procedure of *Amin* et al.[13]. After work-up and column chromatography (silica; CH_2Cl_2/petroleum ether 3:1) 5.0 g (44%) of a yellow-orange mass was obtained, consisting of **9** and **10** in a ratio of 4:1. A smaller amount (500 mg) was column-chromatographed (silica; CH_2Cl_2/petroleum ether, 1:1) in order to separate the two isomers, yielding a first fraction of pure **10** (65 mg), giving a blue fluorescence on TLC, a second fraction containing both compounds (125 mg) and a third fraction containing pure **9** (250 mg), giving a green fluorescence on TLC. Recrystallization (CH_2Cl_2/petroleum ether) yielded **9** as light-yellow needles, m.p. 155–157°C [Lit.[16] 158–160°C], and **10** as light-yellow needles, m.p. 150–151°C (lit.[39] 150–151°C).

9. ^{1}H NMR: δ 3.72 [s, 2H, H(5,5')]; 7.56 [s, H(6)]; 7.63 [m, 2H, H(8,9)]; 7.77 [dd, J 8.0, 7.3, H(2)]; 7.87 [m, H(7)]; 7.98 [d, J 7.3, H(3)]; 8.53 [m, H(10)]; 8.63 [d, J 8.0, H(1)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 236 (1.00), 267 (0.77), 277 (0.69), 305 (0.20), 318 (0.15), 336 (0.055), 353 (0.098), 371 (0.126).IR (KBr): 1705 (C=O), 1482, 1381, 1250, 1139, 1065, 1038, 1000, 940, 920, 879, 852, 822, 771, 752 cm^{-1}. MS (250°C) m/z (%): 218 (100), 190 (44), 189 (97), 188 (11), 187 (12), 163 (10).

10. ^{1}H NMR: δ 3.85 [s, 2H, H(4,4')]; 7.56 [d, J 7.1, H(3)]; 7.67 [m, H(9); 7.72 [dd, J 8.4, 7.1, H(2)]; 7.79 [m, H(8)]; 8.09 [d, J 8.0, H(7)]; 8.21 [s, H(6)]; 8.42 [d, J 8.4, H(1)]; 8.65 [d, J 8.3 H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 235 (1.00), 254 (0.90), 263 (0.98), 272 (0.73), 285 (0.49), 313sh (0.21), 322 (0.33), 338 (0.33), 355 (0.100), 370 (0.060). IR (KBr): 1712 (C=O), 1615, 1467, 1117, 1065, 888, 750 cm^{-1}. MS (250°C) m/z (%): 218 (100), 190 (45), 189 (76), 188 (10), 187 (9), 163 (9).

Acephenanthrylene (1)

A mixture of **9** and **10** (270 mg, 1.2 mmol) was dissolved in a mixture of CH_2Cl_2 (25 ml) and CH_3OH (25 ml). To the stirred solution $NaBH_4$ (230 mg, 6 mmol) was added. Stirring was continued for 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. The crude mixture of alcohols was dissolved in dry toluene (50 ml) and a catalytic amount of p-toluenesulphonic acid monohydrate (*p*-TSA) (15 mg) was added. The solution was refluxed for 30 min and allowed to cool to room temperature. It was washed with a saturated $NaHCO_3$ solution and with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Column chromatography (silica; CH_2Cl_2/petroleum-ether, 1:9) and recrystallization (methanol) gave acephenanthrylene (**1**) (215 mg, 86%) as yellow plates, m.p. 140–141°C (lit.[16] 140–141°C; lit.[17] 141–142°C). ^{1}H NMR: δ 7.10 [d, J 5.3 H(5)]; 7.20 [d, J 5.3, H(4)]; 7.60 [m, H(8)]; 7.63–7.72 [m, 3H, H(2,3,9)]; 7.99 [s, H(6)]; 8.00 [d, J 7.9, H(7)]; 8.39 [dd, J 7.6, 1.8, H(1)]; 8.64 [d, J 8.1, H(10)]. UV (cyclohexane), λ_{max} nm (ϵ l. mol^{-1}. cm^{-1}): 233 (27600), 264 (28800), 288 (9200), 300 (10400), 317 (6200), 330 (6750), 347 (6800), 365 (7900), IR (KBr): 3070, 1448, 1390, 1222, 1173, 1093, 1035, 952, 921, 903, 829, 755, 720 cm^{-1}. Exact mass calculated for $C_{16}H_{10}$: 202.0782 m/z, found 202.0781 m/z. MS (25°C) m/z. MS (25°C) m/z (%): 202 (100), 201 (13), 200 (17), 101 (19).

Acephenanthrene (4,5-dihydroacephenanthrylene, 2)

A mixture of **9** and **10** (5.0 g, 22.9 mmol) was suspended in diethylene glycol (150 ml) under an argon atmosphere. Hydrazine monohydrate (15 ml, 190 mmol) was added and under slight heating the reactants dissolved. After 1 h, excess water and hydrazine were distilled off until the temperature of the reaction mixture reached 160°C. The solution was allowed to cool to 80°C and KOH (15 g) was added in portions. The solution was refluxed for 3 h and finally cooled to room temperature. Water (300 ml) was added and the reaction mixture was extracted twice with diethyl ether. The combined organic layers were washed twice with water, and dried over $MgSO_4$. Evaporation of the solvent gave the crude acephenanthrene (**2**), which was purified by column chromatography (silica; CH_2Cl_2/petroleum-ether, 1:9). Recrystallization (methanol) yielded **2** (4.05 g 87%) as white plates, m.p. 106–106.5°C (lit.[40] 106°C). ^{1}H NMR: δ 3.45 [s, 4H, H(4,4',5,5')]; 7.46 [d, J 7.0, H(3)]; 7.52 [s, H(6)]; 7.57 [m, 2H, H(8,9)]; 7.62 [dd, J 8.1, 7.0, H(2)]; 7.85 [m, H(7)]; 8.31 [d, J 8.1, H(1)]; 8.59 [m, H(10)]. UV (cyclohexane), λ_{max} nm (ϵ l. mol^{-1}. cm^{-1}): 252sh (60500), 258 (71400), 269sh (24400), 280 (12900), 292 (12200), 304 (16000), 321 (820), 331sh (630), 336 (1600), 347 (640), 353 (2000). Exact mass calculated for $C_{16}H_{12}$: 204.0939 m/z, found 204.0943 m/z. IR (KBr): 2920, 1628, 1599, 1446, 1385, 1032, 950, 899, 883, 858, 766, 749 cm^{-1}. MS (25°C) m/z (%): 204 (100), 203 (54), 202 (41), 201 (15), 200 (9), 101 (26).

4,5-Dihydro-4-hydroxy-4-methylacephenanthrylene (11d)

4(5*H*)-Acephenanthrylenone (**9**) (150 mg, 0.69 mmol) was dissolved in dry THF (50 ml) under an argon atmosphere. The solution was cooled with a dry-ice/alcohol bath to −60°C and MeLi (5.0 ml, 1.4 M as complex with LiBr in Et_2O) was added with a syringe. The solution turned orange and was stirred for 30 min at −60°C. The solution was allowed to warm up to room temperature and stirring was continued for 1 h. A saturated NH_4Cl solution was slowly added and the reaction mixture was extracted twice with diethyl ether. The combined organic layers were washed with water and dried over $MgSO_4$. Evaporation of the solvent yielded **11d** as a yellow oil. Column chromatography (silica; CH_2Cl_2) yielded a rapidly eluting fraction containing starting material (40 mg) and a slowly eluting fraction containing pure **11d** (116 mg, 72%) as a yellow viscous oil. ^{1}H NMR: δ 1.75 [s, 3H, CH_3]; 2.25 [br.s, OH]; 3.44 [d, J 17.6, H(5 or 5')]; 3.53 [d, J 17.6, H(5 or 5')]; 7.49 [s, H(6)]; 7.56–7.63 [m, 3H, H(3,8,9)]; 7.70 [dd, J 8.1, 7.2, H(2)]; 7.86 [m, H(7)]; 8.42 [d, J 8.1, H(1)]; 8.59 [m, H(10)]. MS (250°C) m/z (%): no M^+ peak was observed, 216 (52), 215 (100), 214 (7), 213 (20).

4-Methylacephenanthrylene (1d)

Compound **11d** (114 mg, 0.49 mmol) was dehydrated with a catalytic amount of *p*-TSA as described for the preparation of **1**. 4-Methylacephenanthrylene (**1d**) (67 mg, 64%) was purified by means of column chromatography (silica; petroleum ether). Recrystallization (methanol) yielded **1d** as yellow plates, m.p. 112–113°C. ^{1}H NMR: δ 2.45 [d, 3H, J 1.6, CH_3]; 6.75 [q, J 1.6, H(5)]; 7.57 [m, H(8)]; 7.60–7.69 [m, 3H, H(2,3,9)]; 7.80 [s, H(6)]; 7.94 [d, J 7.8, H(7)]; 8.36 [dd, J 7.3, 1.5, H(1)]; 8.59 [d, J 8.0, H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 235 (1.00), 262 (0.85), 291 (0.26), 301 (0.37), 317 (0.17), 331 (0.18), 348 (0.24), 366 (0.30). IR (KBr): 1468, 1443, 1380, 1217, 1157, 947, 902, 860, 837, 760, 750 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 m/z, found 216.0924 m/z. MS (25°C) m/z (%): 216 (93), 215 (100), 214 (5), 213 (21), 189 (3), 108 (12).

4,5-Dihydro-5-Hydroxy-5-methylacephenanthrylene (12e)

The reaction of **10** (109 mg, 0.50 mmol) with MeLi (3.5 ml, 1.4 M as LiBr complex in diethyl ether) was performed analogously to that of **9**. Column chromatography (silica; CH_2Cl_2) yielded some unreacted starting material (15 mg) together with **12e** (86 mg, 74%) as a yellow viscous oil. ^{1}H NMR: δ 1.75 [s, 3H, CH_3]; 2.30 [br.s, (OH)]; 3.46 [d, J 17.4, H(4 or 4')]; 3.54 [d, J 17.4, H(4 or 4')]; 7.43 [d, J 7.1 H(3)]; 7.57–7.69 [m, 4H, H(2,6,8,9)]; 7.93 [m, H(7)]; 8.34 [d, J 8.2, H(1)]; 8.61 [m, H(10). MS (250°C) m/z (%): no M^+ peak was observed, 216 (55), 215 (100), 214 (9), 213 (14).

5-Methylacephenanthrylene (1e)

The dehydration of **12e** (84 mg, 0.36 mmol) with *p*-TSA was performed as described for **1**. Column chromatography (silica; petroleum ether) and recrystallization (methanol) furnished 5-methylacephenanthrylene (**1e**) (67 mg, 89%) as yellow crystals, m.p. 117–118°C. ^{1}H NMR: δ 2.48 [d, 3H, J 1.6, CH_3]; 6.83 [q, J 1.6, H(4)]; 7.51 [d, J 6.9, H(3)]; 7.59 [dd, J 8.0, 6.9, H(2)]; 7.59 [m, H(8)]; 7.67 [m, H(9)]; 7.92 [s, H(6)]; 8.01 [d, J 7.8, H(7)]; 8.27 [d, J 8.0, H(1)]; 8.62 [d, J 8.0, H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 234 (1.00), 262 (0.80), 290 (0.22), 302 (0.31), 318 (0.19), 331 (0.21), 347 (0.21), 365 (0.25. IR (KBr): 1600, 1445, 1384, 1230, 1031, 895, 832, 765, 752 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 m/z, found 216.0935 m/z. MS (25°C) m/z (%): 216 (92), 215 (100), 214 (4), 213 (17), 189 (2), 108 (10).

4,5-Dihydro-6-acephenanthrylene carbaldehyde (13)

Acephenanthrene (**2**) (24 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (40 ml) under a nitrogen atmosphere. The solution was cooled to 0°C and tin(IV) chloride (600 μl) and dichloromethyl methyl ether (140 mg, 1.2 mmol) were added. The solution immediately turned red and stirring was continued for 2 h. Water was carefully added and the resulting yellow reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$ solution and dried over $MgSO_4$. Evaporation of the solvent, followed by column chromatography (silica; CH_2Cl_2/petroleum ether 1:1) furnished **13** (158 mg, 69%) as white crystals, m.p. 160.5–161.5°C (lit.[21] 161.5°C). ^{1}H NMR: δ 3.52 [t, 2H, *J* 6.0, H(4,4')]; 3.82 [t, 2H, *J* 6.0, H(5,5')]; 7.54 [d, *J* 7.1, H(3)]; 7.67 [m, 2H, H(8,9)]; 7.79 [dd, *J* 8.2, 7.1, H(2)]; 8.32 [d, *J* 8.2, H(1)]; 8.61 [m, H(10)]; 9.20 [m, H(7)]; 10.84 [s, CHO]. UV (cyclohexane), λ_{max} nm (relative ϵ): 236sh (0.57), 247sh (0.87), 254 (1.00), 268 (0.87), 292 (0.33), 319sh (0.25), 331 (0.29), 351 (0.16), 370 (0.17). IR (KBr): 2920 (CHO), 2740 (CHO), 1670 (C = O), 1600, 1442, 1379, 1238, 1153, 1002, 770 cm^{-1}. Exact mass calculated for $C_{17}H_{12}O$: 232.0888 *m/z*, found 232.0886 *m/z*. MS (50°C) *m/z* (%): 232 (100), 231 (21), 203 (82), 202 (39), 201 (9), 200 (11).

4,5-Dihydro-6-methylacephenanthrylene (2f)

Compound **13** (140 mg, 0.60 mmol) was reduced with hydrazine hydrate (0.3 ml, 6 mmol) in diethylene glycol (20 ml) as described for the preparation of **2**. 6-Methylacephenanthrene (**2f**) (121 mg, 91%) was purified by column chromatography (silica; CH_2Cl_2/petroleum ether 1:9) and by recrystallization (methanol). **2f** Was isolated as fine white needles, m.p. 127–128°C (lit.[21] 125°C). ^{1}H NMR: δ 2.62 [s, 3H, CH_3]; 3.35–3.46 [m, 4H, H(4,4',5,5')]; 7.42 [d, *J* 7.1, H(3)]; 7.55 [dd, *J* 8.1, 7.1, H(2)]; 7.60 [m, 2H, H(8,9)]; 8.05 [m, H(7)]; 8.28 [d, *J* 8.1 H(1)]; 8.62 [m, H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 254sh (0.86), 259 (1.00), 271 (0.38), 281 (0.21), 292 (0.19), 304 (0.25), 324 (0.015), 340 (0.030), 350 (0.018), 357 (0.041). IR (KBr): 2910, 1619, 1425, 1370, 1318, 1028, 760 cm^{-1}. Exact mass calculated for $C_{17}H_{14}$: 218.1095 *m/z*, found 218.1093 *m/z*. MS (25°C) *m/z* (%): 218 (100), 217 (12), 216 (5), 215 (14), 203 (59), 202 (32).

6-Methylacephenanthrylene (1f)

Compound **2f** (114 mg, 0.52 mmol) was dehydrogenated with DDQ (144 mg, 0.63 mmol) in dry toluene (40 ml) under an argon atmosphere. The reaction mixture was stirred at 70°C for 2 h. It was then washed twice with a saturated Na_2SO_3 solution. The solvent was dried over $MgSO_4$ and removed under reduced pressure. A two-step column-chromatographic purification was performed. First column: silica; CH_2Cl_2/petroleum-ether 1:9. Second column: caffeine-impregnated silica (5% by weight); petroleum ether. **1f** (68 mg, 60%) Was isolated after recrystallization (methanol) as light-yellow plates, m.p. 110.0–110.5°C. ^{1}H NMR: δ 2.91 [s, 3H, CH_3]; 7.18 [d, *J* 5.3, H(4)]; 7.27 [d, *J* 5.3, H(5)]; 7.61 [dd, *J* 7.9, 7.0, H(2)] 7.62–7.72 [m, 3H, H(3,8,9)]; 8.19 [m, H(7)]; 8.36 [d, *J* 7.9, H(1)]; 8.67 [m, H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 230 (1.00), 259sh (0.77), 265 (0.92), 277sh (0.41), 292 (0.22), 303 (0.28), 320 (0.20), 332 (0.23), 349 (0.26), 367 (0.31). IR (KBr): 1610, 1442, 1371, 1337, 1314, 1218, 1160, 1030, 900, 819, 746, 713 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 *m/z*, found 216.0936 *m/z*. MS (25°C) *m/z* (%): 216 (100), 215 (70), 214 (7), 213 (18), 189 (5), 108 (9).

1,2-Dihydro-7-oxo-4-acenaphtylenebutanoic acid (15)

A solution of acenaphthene (7.7 g, 50 mmol) in CH_2Cl_2 (300 ml) was cooled with an ice-salt bath to −10°C and $AlCl_3$ (16.5 g, 125 mmol) was added. Succinic anhydride (5.5 g, 55 mmol) was added in portions over a 30-min period. Stirring at −10°C was continued for 2 h, in which period the colour of the solution changed from dark-brown to orange and crystals precipitate. The reaction mixture was poured out on ice. When the ice had melted, the reaction mixture was acidified with 3N HCl. The white-grey precipitate was collected by filtering over a Büchner funnel. Further purification was performed according to the procedure of *Fieser*[27]. **15** (10.3 g, 78%) Was collected as a white powder, m.p. (lit.[27] 204–206°C).

4,5,7,8,9,10-Hexahydro-7-methyl-7-acephenanthrylenol (16g)

5,8,9,10-Tetrahydro-7(4*H*)-acephenanthrylenone (**14**) (prepared from **15** according to a literature[17]) (200 mg, 0.90 mmol) was treated with MeLi (7.0 ml, 1.4 M as complex with liBr in Et_2O) in the same way as described for **9**. Column chromatography (silica; CH_2Cl_2) furnished **16g** (192 mg, 90%) as a light-yellow viscous oil. ^{1}H NMR: δ 1.63 [s, 3H, CH_3]; 1,81 [br.s, OH]; 1.90–2.11 [m, 4H, H(8,8',9,9')]; 3.05 [m, 2H, H(10,10')]; 3.73 [s, 4H, H(4,4',5,5')]; 7.28 [d, 6.8, H(3)]; 7.46 [dd, 8.3, 6.8, H(2)]; 7.57 [s, H(6)]; 7.64 [d, 8.3, H(1)]. MS (250°C) *m/z* (%): 238 (28), 223 (100), 221 (20), 220 (49), 205 (83), 203 (19), 167 (41), 165 (31), 152 (21).

4,5,9,10-Tetrahydro-7-methylacephenanthrylene (17g)

Compound **16g** (190 mg) was dehydrated with *p*-TSA as described for the preparation of **1**. Column chromatography (silica; petroleum ether) and recrystallization (methanol) afforded **17g** (174 mg, 97%) as colourless plates, m.p. 94–95°C. ^{1}H NMR: δ 2.16 [m appearing as q, 3H, *J* 1.6, CH_3]; 2.34 [m, 2H, H(9,9')]; 3.09 [t, 2H, J 8.4, H(10,10')]; 3.38 [s, 4H, H(4,4',5,5')]; 5.94 [m, H(8)]; 7.21 [d, *J* 6.8, H(3)]; 7.32 [s, H(6)]; 7.44 [dd, *J* 8.4, 6.8, H(2)]; 7.69 [d, *J* 8.4, H(1)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 236 (0.79), 253sh (0.90), 260 (1.00), 284 (0.24), 297 (0.26), 308 (0.24), 324sh (0.078), 337 (0.062), 349sh (0.042), 357 (0.038). Exact mass calculated for $C_{17}H_{16}$: 220.1252 *m/z*, found 220.1258 *m/z*. MS (25°C) *m/z* (%): 220 (100), 219 (17), 218 (15), 205 (61), 204 (13), 203 (23), 202 (19), 189 (7).

7-Methylacephenanthrylene (1g)

Compound **17g** (170 mg, 0.77 mmol) was dehydrogenated with DDQ (420 mg, 1.85 mmol) in a similar manner as for **2f** (1 h., 60°C). Two-step column chromatography and recrystallization (methanol) yielded 1g (81 mg, 49%) as yellow plates, m.p. 120–121°C. ^{1}H NMR: δ 2.82 [s, 3H, CH_3]; 7.12 [d, *J* 5.3, H(5)]; 7.20 [d, *J* 5.3, H(4)]; 7.46 [d, *J* 7.1, H(8)]; 7.58 [dd, *J* 8.0, 7.1, H(9)]; 7.66 [m, 2H, H(2,3)]; 8.24 [s, H(6)]; 8.40 [dd, *J* 7.1, 1.7, H(1)]; 8.54 [d, *J* 8.0, H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 235 (0.94), 259sh (0.90), 263 (1.00), 291 (0.21), 303 (0.27), 326 (0.22), 340 (0.24), 357 (0.25), 376 (0.31). IR (KBr): 1590, 1528, 1449, 1375, 1170, 885, 780, 758, 710 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 *m/z*, found 216.0940 *m/z*. MS (25°C) *m/z* (%): 216 (100), 215 (43), 214 (8), 213 (13), 189 (3), 108 (3).

4,5,7,8,9,10-Hexahydroacephenanthrylene (HHAP) (18)

Compound **14** (1.66 g, 7.5 mmol) was reduced under Wolff–Kishner conditions in a similar way to that described for the preparation of **2**. Column chromatography (silica; petroleum ether) and recrystallization (methanol) yielded **18** (850 mg, 55%) as white plates, m.p. 87–88°C (lit.[41] 89–90°C). ^{1}H NMR: δ 1.83–1.98 [m, 4H, H(8,8',9,9')]; 2,91 [t, 2H, *J* 6.0, H(7,7')]; 3.03 [t, 2H, *J* 6.3, H(10,10')]; 3.29–3.39 [m, 4H, H(4,4',5,5')]; 7.02 [s, H(6)]; 7.23 [d, *J* 6.8, H(3)]; 7.43 [dd, *J* 8.4, 6.8, H(2)]; 7.60 [d, *J* 8.4 H(1)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 236 (1.00), 260 (0.060), 287 (0.107), 296 (0.115), 315sh (0.051), 329 (0.036). IR (KBr): 2940, 1658, 1449, 1338, 1240, 1180, 1140, 885, 860, 781, 763 cm^{-1}. Exact mass calculated for $C_{16}H_{16}$: 208.1252 *m/z*, found 208.1255 *m/z*. MS (25°C) *m/z* (%): 208 (100), 207 (17), 180 (26), 179 (9), 165 (12).

4,5,7,8,9,10-Hexahydro-1-, -3- and -6-acephenanthrylene carbaldehyde (19–21)

Compound **18** (475 mg, 2.3 mmol) was treated with dichloromethyl methyl ether (350 mg, 3.0 mmol) and tin(IV) chloride (1 ml) in a similar way to that described for **2**. Work-up yielded a mixture of three isomeric products: **19–21** in a ratio of 41:23:36 (total yield 534 mg, 98%) as a yellow crystalline mass. The isomers were separated and purified by means of two subsequent column chromatographic steps (silica; CH_2Cl_2/petroleum ether 1:1 and 1:2 respectively). The order of elution was **21**, **19** and **20**. Recrystallization (cyclohexane) furnished **19** as off-white crystals, m.p. 95–96°C (138 mg), **20** as white-yellow needles, m.p. 83–84°C (69 mg) and **21** as white needles, m.p. 159°C (86 mg).

19. ^{1}H NMR: δ 1.83–1.96 [m, 4H, H(8,8',9,9')]; 3.02 [t, 2H, *J* 6.2, H(7,7')]; 3.14 [t, 2H, *J* 5.8, H(10,10')]; 3.37 [s, 4H, H(4,4',5,5')]; 7.13 [s, H(6)]; 7.30 [d, *J* 7.3, H(3)]; 8.06 [d, *J* 7.3, H(2)]; 10.86 [s, CHO]. UV (cyclohexane), λ_{max} nm (relative ϵ): 235 (0.76), 259sh (0.98), 262 (1.00), 342br (0.35). IR (KBr): 2920 (CHO), 1666 (C = O), 1610, 1575, 1416, 1331, 1305, 1270, 1239, 1146, 890, 836, 783 cm^{-1}. Exact mass calculated for $C_{17}H_{16}O$: 236.1201 *m/z*, found 236.1203 *m/z*. MS (50°C)*m/z* (%): 236 (100), 235 (6), 208 (16), 207 (19), 180 (7), 179 (7), 165 (12).

20. ^{1}H NMR: δ 1.85–2.00 [m, 4H, H(8,8',9,9')]; 2,95 [t, 2H, *J* 6.0, H(7,7')]; 3.05 [t, 2H, *J* 6.3, H(10,10')]; 3.38 [t, 2H, *J* 5.9, H(5,5')]; 3.71 [t, 2H, *J* 5.9, H(4,4')]; 7.13 [s, H(6)]; 7.70 [d, *J* 8.6, H(1)]; 7.84 [d, *J* 8.6, H(2)]; 10.29 [s, CHO]. UV (cyclohexane), λ_{max} nm (relative ϵ): 256 (0.65), 264 (1.00), 294 (0.090), 302 (0.100), 314sh (0.074), 321sh

(0.058), 334 (0.044), 350 (0.074), 367 (0.102). IR (KBr): 2920 (CHO), 2720 (CHO), 1671 (C = O), 1612, 1583, 1418, 1351, 1240, 1152, 1000, 865, 803, 760, 750 cm^{-1}. Exact mass calculated for $C_{17}H_{16}O$: 236.1201 *m/z* found 236.1205 *m/z*. MS (50°C) *m/z* (%): 236 (100), 235 (8), 208 (14), 207 (17), 179 (11), 165 (11).

21. ^1H NMR: δ 1.89–1.98 [m, 4H, H(8,8',9,9')]; 3.07 [m, 2H, H(10,10')]; 3.33 [m, 2H, H(7,7')]; 3.42 [t, 2H, *J* 5.7, H(4,4')]; 3.70 [t, 2H, *J* 5.7, H(5,5')]; 7.35 [d, *J* 6.3, H(3)]; 7.61 [dd, *J* 8.3, 6.3, H(2)]; 7.65 [d, *J* 8.3, H(1)];10.65 [s, CHO]. UV (cyclohexane), λ_{max} nm (relative ϵ): 257 (0.76), 265 (1.00), 289 (0.13), 298 (0.14), 310 (0.091), 345sh (0.056), 361 (0.093), 379 (0.093). IR (KBr): 2930 (CHO), 2735 (CHO), 1676 (C = O), 1603, 1584, 1440, 1337, 1262, 1220, 1163, 992, 845, 782, 750 cm^{-1}. Exact mass calculated for $C_{17}H_{16}O$: 236.1201 *m/z*, found 236.1197 *m/z*. MS (50°C) *m/z* (%): 236 (100), 235 (7), 208 (10), 207 (22), 179 (7), 165 (12).

*4,5,7,8,9,10-Hexahydro-1-methylacephenanthrylene (**18a**)*

Compound **19** (135 mg, 0.58 mmol) was deoxygenated under Wolff–Kishner reduction conditions as described for **2**. Column chromatography (silica; CH_2Cl_2/petroleum ether, 1:9) gave **18a** (108 mg, 84%) as a white solid. Recrystallization (methanol) furnished **18a** as white crystals, m.p. 115–116°C. ^1H NMR: δ 1.76–1.91 [m, 4H, H(8,8',9,9')]; 2.86 [s, 3H, CH_3]; 2.92 [t, 2H, *J* 5.9, H(7,7')]; 3.27 [s, 4H, H(4,4',5,5')]; 3.40 [t, 2H, *J* 5.8, H(10,10')]; 6.98 [s, H(6)]; 7.06 [d, *J* 7.1, H(3)]; 7.16 [d, *J* 7.1, H(2)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 237 (1.00), 289 (0.116), 298 (0.127), 320 (0.061), 334 (0.059). Exact mass calculated for $C_{17}H_{18}$: 222.1408 *m/z*, found 222.1409 *m/z*. MS (25°C) *m/z* (%): 222 (100), 221 (11), 207 (14), 194 (21), 179 (13), 165 (9).

*1-Methylacephenanthrylene (**1a**)*

Compound **18a** (105 mg, 0.47 mmol) was dehydrogenated with DDQ (320 mg, 1.40 mmol) in dry toluene in a similar manner to that described for **2f**. The reaction mixture was stirred for 1 h at room temperature and 30 min at 60°C. Two-step column chromatography and recrystallization (methanol) gave **1a** (43 mg, 42%) as yellow crystals, m.p. 72–73°C. ^1H NMR: δ 3.17 [s, 3H, CH_3]; 7.03 [d, *J* 5.3, H(5)]; 7.16 [d, *J* 5.3, H(4)]; 7.45 [d, *J* 7.1, H(2)]; 7.56 [d, *J* 7.1, H(3)]; 7.61 [m, H(8)]; 7.69 [m, H(9)]; 8.00 [s, H(6)]; 8.04 [d, *J* 7.8, H(7)]; 8.88 [d, *J* 8.5, H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 236 (0.73), 245 (0.71), 257 (0.88), 263 (1.00), 272 (0.51), 293 (0.17), 304 (0.24), 319 (0.23), 331 (0.24), 348 (0.21), 366 (0.22). IR (KBr): 1444, 1359, 1302, 1109, 892, 829, 765, 750, 710, 661, 626 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 *m/z*, found 216.0935 *m/z*. MS (25°C) *m/z* (%): 216 (100), 215 (67), 214 (9), 213 (22), 189 (5), 108 (10).

*4,5,7,8,9,10-Hexahydro-3-methylacephenanthrylene (**18c**)*

Compound **20** (67 mg, 0.29 mmol) was reduced under Wolff–Kishner conditions as described for the preparation of **2**. Compound **18c** (51 mg, 79%) was isolated after column chromatography (silica; CH_2Cl_2/petroleum ether, 1:9) and recrystallization (methanol) as white crystals, m.p. 89–90°C. ^1H NMR: δ 1.82–1.97 [m, 4H, H(8,8'9,9')]; 2.38 [s, 3H, CH_3)]; 2.89 [t, 2H, *J* 6.2, H(7,7')]; 3.02 [t, 2H, *J* 6.3, H(10,10')]; 3.22–3.33 [m, 4H, H(4,4',5,5')]; 6.98 [s, H(6)]; 7.27 [d, *J* 8.3, H(2)]; 7.53 [d, *J* 8.3, H(1)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 237 (1.00), 288 (0.094), 298 (0.086), 318 (0.040), 333 (0.048). Exact mass calculated for $C_{17}H_{18}$: 222.1408 *m/z*, found 222.1410 *m/z*. MS (25°C) *m/z* (%): 222 (100), 221 (10), 207 (9), 194 (24), 179 (9), 165 (5).

*3-Methylacephenanthrylene (**1c**)*

The dehydrogenation of **18c** (47 mg, 0.21 mmol) with DDQ (140 mg, 0.61 mmol) in toluene (1 h room temperature; 30 min, 60°C) was performed in the same manner as that of **2f**. **1c** (16 mg, 35%) was purified by two-step column chromatography and recrystallization (methanol). **1c** was isolated as yellow crystals, m.p. 83–84°C. ^1H NMR: δ 2.69 [s, 3H, CH_3]; 7.08 [d, *J* 5.3, H(5)]; 7.30 [d, *J* 5.3, H(4)]; 7.46 [d, *J* 8.2, H(2)]; 7.57 [m, H(8)]; 7.67 [m, H(9)]; 7.99 [s, H(6)]; 8.00 [d, *J* 7.9, H(7)]; 8.30 [d, *J* 8.2, H(1)]; 8.61 [d, *J* 8.1, H(10)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 235 (1.00), 261 (0.93), 290 (0.19), 302 (0.24), 320 (0.21), 336 (0.22), 354 (0.21), 373 (0.24). IR (KBr): 1600, 1446, 1370, 1212, 1173, 1150, 947, 911, 895, 823, 750, 714 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 *m/z*, found 216.0937 *m/z*. MS (25°C) *m/z* (%): 216 (100), 215 (64), 214 (7), 213 (17), 189 (3), 108 (11).

*4,5,7,8,9,10-Hexahydro-6-methylacephenanthrylene (**18f**)*

Compound **21** (80 mg, 0.34 mmol) was reduced under Wolff–Kishner conditions, as described for **2**. Column chromatography (silica; CH_2Cl_2/petroleum ether 1:9) and recrystallization (methanol) yielded **18f** (58 mg, 77%) as white crystals, m.p. 88–89°C. ^1H NMR: δ 1.89–1.93 [m, 4H, H(8,8'9,9')]; 2.28 [s, 3H, CH_3]; 2.79 [m, 2H, H(7,7')]; 3.07 [m, 2H H(10,10')]; 3.28–3.41 [m, 4H, H(4,4',5,5')]; 7.21 [d, 6.8, H(3)]; 7.38 [dd, 8.3, 6.8, H(2)]; 7.59 [d, 8.3, H(1)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 237 (1.00), 288 (0.085), 297 (0.094), 311sh (0.060), 327 (0.017). Exact mass calculated for $C_{17}H_{18}O$: 222.1408 *m/z*, found 222.1408 *m/z*. MS (25°C) *m/z* (%): 222 (100), 221 (8), 207 (25), 194 (21), 179 (11), 165 (7).

*6-Methylacephenanthrylene (**1f**)*

The dehydrogenation of **18f** (56 mg, 0.25 mmol) with DDQ (175 mg, 0.77 mmol) in dry toluene (1 hour, 60°C) was performed in a similar event to that of **2f**. Two-step column chromatography gave **1f** (20 mg, 36%).

*Oxidation of **18** with DDQ in acetic acid / water*

Compound **18** (416 mg, 2.0 mmol) was dissolved in acetic acid (80 ml) and water (15 ml) was added under stirring, followed by DDQ (900 mg, 4.0 mmol). The solution was refluxed for 1 h and then allowed to cool to room temperature. Water was added and the reaction mixture was extracted twice with CH_2Cl_2. The combined organic layers were subsequently washed with Na_2CO_3 solution, Na_2SO_3 solution, and water. Drying over $MgSO_4$ and evaporation of the solvent yielded a brown solid. Purification by means of column chromatography (silica; CH_2Cl_2/petroleum ether 3:1) yielded a mixture of 5,7,8,9-tetrahydro-10(4*H*)-acephenanthrylenone (**22**) and 7,8,9,10-tetrahydro-5(4*H*)-acephenanthrylenone (**23**) (ratio 4:5) as a light-brown solid (137 mg, 31%).

22. ^1H NMR: δ 2.13–2.21 [m, 2H, H(8,8')]; 2.76 [t, 2H, *J* 6.3, H(9,9')]; 3.11 [t, 2H, *J* 6.1, H(7,7')]; 3.31–3.41 [m, 4H, H(4,4',5,5')]; 7.13 [s, H(6)]; 7.32 [d, *j* 7.0, H(3)]; 7.60 [dd, *J* 8.5, 7.0, H(2)]; 9.05 [d, *J* 8.5, H(1)]. MS (250°C) *m/z* (%): 222 (87), 194 (100), 179 (20), 166 (64), 165 (76), 152 (13).

23. ^1H NMR: δ 1.87–2.03 [m, 4H, H(8,8',9,9')]; 3.03 [t, 2H, *J* 6.0, H(7,7')]; 3.21 [t, 2H, *J* 6.2, H(10,10')]; 3.78 [s, 2H, H(4,4')], 7.39 [d, *J* 6.8, H(3)]; 7.57 [dd, *J* 8.6, 6.8, H(2)]; 7.70 [s, H(6)]; 783 [d, *J* 8.6, H(1)]. MS (250°C) *m/z* (%): 22 (84), 194 (100), 179 (58), 166 (25), 165 (61), 152 (18).

*4,5,7,8,9,10-Hexahydro-10-methyl-1-acephenanthrylenol (**24j**)*

A mixture of **22** and **23** (160 mg, 0.72 mmol, ratio 4:5) was treated with MeLi in the same way as described for **9**. Purification and separation were achieved by means of column chromatography (silica; CH_2Cl_2). **24j** Eluted first and was collected as a yellow oil (50 mg, 66% based on **22**). 4,5,7,8,9,10-Hexa-hydro-5-methyl-acephenanthrylenol (**25e**) eluted as the second fraction and was collected as a yellow oil (28 mg, 29% based on **23**).

24j. ^1H NMR: δ 1.80 [s, 3H, CH_3]; 1.83–2.19 [m, 4H, H(8,8',9,9')]; 2,82–3.04 [m, 2H, H(7,7')]; 3.26–3.38 [m, 4H, H(4,4',5,5')]; 6.98 [s, H(6)]; 7.23 [d, *J* 6.8, H(3)]; 7.42 [dd, *j* 8.6, 6.8, H(2)]; 8.44 (d, *J* 8.6, H(1)]. MS (250°C).

25e. ^1H NMR: δ 1.74 [s, 3H, CH_3]; 1.85–2.00 [m, 4H, H(8,8',9,9')]; 2.97 [t, 2H, *J* 6.0, H(7,7')]; 3.09 [t, 2H, *J* 7.2, H(10,10')]; 3.46 [d, *J* 16.5, H(4 or 4')]; 3.54 [d, *J* 16.5, H(4 or 4')]; 7.20 [s, H(6)]; 7.25 [d, *j* 6.9, H(3)]; 7.50 [dd, *J* 8.4, 6.9, H(2); 7.68 [d, *J* 8.4, H(1)]. MS (250°C) *m/z* (%): 238 (27), 223 (100), 205 (18), 195 (12), 181 (17), 165 (17, 152 (10).

*4,5,7,8-Tetrahydro-10-methylacephenanthrylene (**26j**)*

Compound **24j** (48 mg, 0.20 mmol) was dehydrated with *p*-TSA as described for the preparation of **1**. Column chromatography (silica; CH_2Cl_2/petroleum ether (1:9)) furnished **26j** (38 mg, 83%) as a light yellow oil. ^1H NMR: δ 2.05 [m, 2H, H(8,8')]; 2.46 [m appearing as q, 3H, *J* 1.6, CH_3]; 2.80 [dd, 2H, *J* 7.9, 5.9, H(7,7')]; 3.30–3.40 [m, 4H, H(4,4',5,5')]; 6.03 [m, H(9)]; 7.17 [s, H(6)]; 7.21 [d, *J* 6.8, H(3)]; 7.39 [dd, *J* 8.6, 6.8, H(2)]; 8.01 [d, *J* 8.6, H(1)]. UV (cyclohexane), λ_{max} nm (relative ϵ): 244 (1.00), 321sh (0.20), 328 (0.21), 344 (0.18). Exact mass calculated for $C_{17}H_{16}$: 220.1252 *m/z*, found 220.1252 *m/z*. MS (25 C) *m/z* (%): 220 (100), 219 (23), 218 (75), 217 (11), 205 (52), 204 (12), 203 (41), 202 (37), 193 (20), 191 (11), 190 (10), 189 (16), 183 (19), 165 (10).

10-Methylacephenanthrylene (1j)

Dehydrogenation of **26j** (36 mg, 0.16 mmol) with DDQ (87 mg, 0.38 mmol) in toluene (1 h, 70°C) was carried out in a similar way to that of **2f**. Two-step chromatography and recrystallization (methanol) yielded **1j** (18 mg, 51%) as yellow plates, m.p. 138–139°C. ^{1}H NMR: δ 3.17 [s, 3H, CH_3]; 7.09 [d, *J* 5.3, H(5)]; 7.23 [d, *J* 5.3, H(4)]; 7.52 [m, 2H, H(8,9)]; 7.67 [dd, *J* 8.0, 7.0, H(2); 7.71 [d, *J* 7.0, H(3)]; 7.92 [m, H(7)]; 8.03 [s, H(6)]; 8.71 [d, *J* 8.0, H(1)]. UV (cyclohexane), λ_{max} nm (relative ε): 243 (0.65), 259 (1.00), 273sh (0.33), 291 (0.15), 302 (0.19), 323 (0.20), 334 (0.21), 350 (0.19), 368 (0.23). IR (KBr): 1590, 1433, 1380, 1073, 905, 881, 824, 746, 712 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 *m/z*, found 216.0941 *m/z*. MS (25°C) *m/z* (%): 216 (100), 215 (48), 214 (8), 213 (17), 189 (8), 108 (8).

1,2-Dihydro-α- and -β-methyl-γ-oxo-5-acenaphthylene-butanoic acid (15h, 15i)

Under a nitrogen atmosphere, $AlCl_3$ (15.0, 112.5 mmol) was added to a cooled (−10°C) and stirred solution of acenaphthene (7.5 g, 48.6 mmol) in dry CH_2Cl_2 (300 ml). Methylsuccinic anhydr de (6.0 g, 52.6 mmol) was added in portions at such a rate that the temperature of the reaction mixture remained constant. Stirring was continued for 1 h whereupon the cooling bath was removed. After additional stirring at room temperature for 3 h, the reaction mixture was poured out on crushed ice. 3N HCl was added and the mixture was extracted twice with CH_2Cl_2. The solvent was evaporated and the brown residue was taken up in a $NaHCO_3$ solution. Insoluble substances were removed by filtration over a Büchner funnel. The solution was acidified with concentrated HCl and the mixture of acids was filtered over a Büchner funnel. Drying under vacuum yielded a mixture of **15h** and **15i** (12.0 g, 92%) as a beige solid. The ratio was 1:2, as determined by ^{1}H NMR.

15h. H NMR: δ 1.33 [d, 3H, *J* 7.0, CH_3]; 3.12–3.23 [m, 2H, H(α,β)]; 3.40 [s, 4H, H(1,1′,2,2′)]; 3.58 [m, H(β′)]; 7.29 [d, *J* 7.3, H(3)]; 7.35 [d, *J* 7.0, H(8)]; 7.57 [dd, *J* 8.5, 7.0, H(7)]; 8.07 [d, *J* 7.3, H(4)]; 8.66 [d, *J* 8.5, H(6)].

15i. ^{1}H NMR: δ 1.24 [d, 3H, *J* 7.2, CH_3]; 2.52 [dd, *J* 17.0, 5.6, H(α)]; 3.03 [dd, *J* 17.0, 8.3, H(α′)]; 3.40 [s, 4H, H(1,1′,2,2′)]; 4.00 [m, *J* 8.3, 7.2, 5.6, H(β)]; 7.30 [d, *J* 7.3, H(3)]; 7.35 [d, *J* 7.0, H(8)]; 7.56 [dd, *J* 8.5, 7.0, H(7)]; 8.06 [d, *J* 7.3, H(4)]; 8.48 [d, *J* 8.5, H(6)].

MS (125°C) of mixture of isomers: *m/z* (%): 268 (26), 250 (4), 236 (4), 182 (18), 181 (100), 153 (32), 152 (49).

1,2-Dihydro-α- and -β-methyl-5-acenaphthylenebutanoic acid (27h, 27i)

The Wolff–Kishner reduction of a mixture of **15h** and **15i** (7.6 g, 28.3 mmol) was performed in the same way as described for the preparation of **2**. After the reaction mixture had cooled to room temperature it was diluted with water and acidified with 3N HCl. Extraction was performed twice with diethyl ether. The combined organic layers were washed with water and dried over $MgSO_4$. Evaporation of the solvent yielded a mixture of **27h** and **27i** as a brown sticky oil (5.8 g, 81%). Purification by means of column chromatography (silica; diethyl ether/petroleum ether 3:1) gave **27h** and **27i** (3.4 g, 48%) as a beige solid. The isomeric ratio was the same as that of **15h** and **15i**.

27h. ^{1}H NMR: δ 1.27 [d, 3H, 7.0, CH_3]; 1.84 [m, H(β)]; 2.16 [m, H(β′)]; 2.59 [m, H(α)]; 3.02 [m, H(γ)]; 3.31–3.40 [m, 5H, H(1,1′,2,2′,γ′)]; 7.19 [d, *J* 7.0, H(3)]; 7.23 [d, *J* 7.0, H(4)]; 7.27 [d, *J* 6.8, H(8)]; 7.46 [dd, *J* 8.4, 6.8, H(7)]; 7.70 [d, *J* 8.4, H(6)].

27i. ^{1}H NMR: δ 1.01 [d, 3H, *J* 6.6, CH_3]; 2.27 [dd, *J* 16.8, 9.6, H(α)]; 2.43 [dd, *J* 16.8, 5.8, H(α′)]; 2.46 [m, H(β)]; 2.86 [dd, *J* 13.6, 7.4, H(γ)]; 3.06 [dd, *J* 13.6, 6.5, H(γ′)]; 3.31–3.40 [m, 4H, H(1,1′,2,2′)]; 7.19 [d, *J* 7.0, H(3)]; 7.23 [d, *J* 7.0, H(4)]; 7.28 [d, *J* 6 8, H(8)]; 7.46 [dd, *J* 8.4, 6.8, H(7)]; 7.72 [d, *j* 8.4, H(6)].

MS (125°C) of the mixture of isomers: *m/z* (%): 254 (42), 198 (43), 180 (17), 168 (21), 167 (100), 165 (38), 153 (57), 152 (69).

5,8,9,10-Tetrahydro-8- and -9-methyl-7(4H)-acephenanthrylenone (14h, 14i)

A mixture of acids **27h** and **27i** (1.1 g, 4.3 mmol) was cyclized with P_2O_5 in methanesulphonic acid according to a literature procedure[15]. The crude reaction product was purified by means of column chromatography (silica; CH_2Cl_2/petroleum-ether 3:1). The first fraction contained mainly the 8-methyl isomer **14h** (220 mg) (relative yield from **27h** 88%) and the second fraction mainly the 9-methyl isomer **14i** (250 mg) (relative yield from **27i** 45%). Both **14h** and **14i** were column-chromatographed again (silica; CH_2Cl_2/petroleum-ether 3:2) and recrystallized (CH_2Cl_2/cyclohexane). Compound **14h** (160 mg) gave beige needles, m.p. 110–111°C and **14i** (170 mg) gave beige needles, m.p. 146.0–146.5°C.

14h. H NMR: δ 1.32 [d, 3H, *J* 6.8, CH_3]; 1.99 [m, *J* 13.3, 11.9, 10.8, 4.5, H(9)]; 2.36 [m, *J* 13.3, 5.0, 4.7, 4.5, H(9′)]; 2.70 [m, *J* 11.9, 6.8, 4.5, H(8)]; 3.21 [ddd, *J* 17.3, 10.8, 5.0, H(10)]; 3.36–3.42 [m, 4H, H(4,4′,5,5′)]; 3.48 [ddd appearing as dt, *J* 17.3, 4.7, H(10′)]; 7.42 [d, *J* 6.9, H(3)]; 7.54 [dd, *J* 8.3, 6.9, H(2)]; 7.79 [d, *J* 8.3, H(1)]; 7.92 [s, H(6)]. UV (cyclohexane), λ_{max} (relative ε): 250 (0.76), 258 (1.00), 284 (0.109), 294 (0.131), 305 (0.101), 326sh (0.025), 341 (0.059), 358 (0.065). IR (KBr): 2920, 1647 (C = O), 1447, 1398, 1370, 1230, 1176, 878, 772, 763 cm^{-1}. Exact mass calculated for $C_{17}H_{16}O$: 236.1201 *m/z*, found 236.1213 *m/z*. MS (50°C) *m/z* (%): 236 (100), 221 (6), 207 (13), 194 (37), 166 (42), 165 (31).

14i. ^{1}H NMR: δ 1.26 [d, 3H, *J* 6.2, CH_3]; 2.37–2.50 [m, 2H, H(8,9)]; 2.76–2.87 [m, 2H, H(8′,10)]; 3.35–3.45 [m, 4H, H(4,4′,5,5′)]; 3.52 [m, H(10′)]; 7.43 [d, *J* 6.9, H(3)]; 7.54 [dd, *J* 8.3, 6.9, H(2)]; 7.81 [d, *J* 8.3, H(1)]; 7.92 [s, H(6)]. UV (cyclohexane), λ_{max} nm (relative ε): 250 (0.76), 258 (1.00), 284 (0.108), 294 (0.131), 306 (0.101), 329 (0.031), 342 (0.061), 359 (0.071). IR (KBr): 2925, 1667 (C = O), 1452, 1400, 1375, 1308, 1235, 1204, 1150, 938, 899, 881, 865, 779, 760 cm^{-1}. Exact mass calculated for $C_{17}H_{16}O$: 236.1201 *m/z*, found 236.1200 *m/z*. MS (50°C) *m/z* (%): 236 (100), 221 (5), 194 (18), 166 (33), 165 (28).

4,5,9,10-Tetrahydro-8-methylacephenanthrylene (17h)

Compound **14h** (160 mg, 0.68 mmol) was reduced with $NaBH_4$ (100 mg, 3.5 mmol) and the ensuing alcohol was dehydrated with *p*-TSA as described for the preparation of **1**. **17h** Was collected after column chromatography (silica; CH_2cl_2/petroleum-ether 1:9) as a light-yellow solid (120 mg, 86%). Recrystallization (methanol) gave **17h** as light-yellow needles, m.p. 97.0–97.5°C. ^{1}H NMR: δ 1.95 [d, 3H, *J* 1.6, CH_3]; 2.35 [t, 2H, *J* 8.8, H(9,9′)]; 3.13 [t, 2H, *J* 8.8, H(10,10′)]; 3.29–3.37 [s, 4H, H(4,4′,5,5′)]; 6.32 [q, *J* 1.6, H(7)]; 7.00 [s, H(6)]; 7.18 [d, *J* 6.8, H(3)]; 7.43 [dd, *J* 8.4, 6.8, H(2)]; 7.64 [d, *J* 8.4, H(1);. UV (cyclohexane), λ_{max} nm (relative ε): 248sh (0.65), 261 (1.00), 269 (1.00), 312 (0.15), 324 (0.16), 341sh (0.10). Exact mass calculated for $C_{17}H_{16}$: 220.1252 *m/z*, found: 220.1255 *m/z*. MS (25°C): 220 (100), 219 (22), 218 (18), 205 (67), 204 (18), 203 (30), 202 (30), 191 (13), 189 (19) 178 (9), 165 (9).

8-Methylacephenanthrylene (1h)

Compound **17h** (60 mg, 0.27 mmol) was dehydrogenated with DDQ (150 mg, 0.67 mmol) in dry toluene (40°C, 3 h) in the same way as **2f**. Two-step column chromatography and recrystallization (methanol) gave **1h** (21 mg, 35%) as yellow crystals, m.p. 111–112°C. ^{1}H NMR: δ 2.58 [s, 3H, CH_3]; 7.09 [d, *J* 5.3, H(5)]; 7.19 [d, *J* 5.3, H(4)]; 7.51 [dd, *J* 8.2, 1.9, H(9)]; 7.63 [m, 2H, H(2,3)]; 7.79 [br.s, H(7)]; 7.92 [s, H(6)]; 8.35 [dd, *J* 6.4, 2.4, H(1)]; 8.52 [d, *J* 8.2, H(10)]. UV (cyclohexane), λ_{max} nm (relative ε): 235 (1.00), 260 (0.91), 266 (0.94), 289 (0.23), 300 (0.27), 320sh (0.22), 333 (0.24), 350 (0.22), 368 (0.23). IR (KBr): 2905, 2840, 1721, 1600, 1459, 1380, 1270, 1157, 1119, 1070, 916, 901, 801, 752, 712 cm^{-1}. Exact mass calculated for $C_{17}H_{12}$: 216.0939 *m/z*, found 216.0939 *m/z*. MS (25°C) *m/z* (%): 216 (100), 215 (42), 214 (10), 213 (17), 189 (6), 108 (9).

4,5,9,10-Tetrahydro-9-methylacephenanthrylene (17i)

The reduction of **14i** (150 mg, 0.64 mmol) with $NaBH_4$ and subsequent dehydration of the alcohol with p-TSA gave, after column chromatography (silica; CH_2Cl_2/petroleum-ether 1:9), **17i** (133 mg, 95%) as a light-yellow solid. Recrystallization furnished **17i** as light-yellow needles, m.p. 92.5–93°C. ^{1}H NMR: δ 1.17 [d, 3H, *J* 6.8, CH_3]; 2.67 [m, H(9)]; 2.78 [dd, *J* 15.3, 10.2, H(10)]; 3.24 [dd, *J* 15.3, 6.8, H(10′)]; 3.30–3.39 [s, 4H, H (4,4′, 5,5′)]; 5.96 [dd] 9.5, 3.4 H(8)]; 6.53 [dd J 9.5, 2.0, H(7)]; 7.06 [s, H(6)]; 7.22 [d, *J* 6.8, H(3)]; 7.45 [dd, *J* 8.4, 6.8, H(2)]; 7.69 [d, *J* 8.4, H(1)]. UV (cyclohexane), λ_{max} nm (relative ε): 243sh (0.64), 259 (1.00), 267 (0.99), 311 (0.15), 323 (0.16), 335 (0.11), 352 (0.048). Exact mass calculated for $C_{17}H_{16}$: 220.1252 *m/z*, found 220.1259 *m/z* MS (25°C) *m/z* (%): 220 (78), 219 (11), 205 (100), 204 (16), 203 (31), 202 (31), 191 (11), 190 (11), 189 (18), 178 (12), 165 (10).

9-Methylacephenanthrylene (1i)

Compound **17i** (85 mg, 0.39 mmol) was dehydrogenated with DDQ (220 mg, 0.97 mmol) in dry toluene (40°C, 3 h) similarly as **2f**. Two-step column chromatography and recrystallization (methanol) yielded **1i** (44 mg, 52%) as yellow crystals, m.p. 91–92°C. ^{1}H NMR: δ 2.63 [s, 3H, CH_3]; 7.09 [d, *J* 5.3, H(5)]; 7.18 [d, *J* 5.3, H(4)]; 7.43 [dd, *J* 8.1, 1.9, H(8)]; 7.66 [m, 2H, H(2,3)]; 7.89 [d, *J* 8.1, H(7)]; 7.95 [s, H(6)]; 8.37 [dd, *J* 7.3, 1.5, H(1)]; 8.43 [br.s, H(10)]. UV (cyclohexane),

λ_{max} nm (relative ϵ): 234 (1.00), 266 (0.89), 293 (0.24), 304 (0.30), 322 (0.20), 333 (0.26), 350 (0.28), 369 (0.32). IR (KBr): 1600, 1438, 1380, 1163, 1082, 955, 914, 897, 881, 811, 752, 710 cm. Exact mass calculated for $C_{17}H_{12}$: 216.0939 m/z, found 216.0928 m/z. MS (25°C) m/z (%): 216 (100), 215 (40), 214 (7), 213 (17), 189 (6), 108 (8).

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