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Synthesis of alkylphenanthrenes from naphthylalkylidenemalonodinitriles. A route to 1-methyl-, 2-methyl-, and 1,2-dimethylphenanthrene

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Abstract—The study has been carried out to evaluate the feasibility of synthesis of 1-methyl-, 2-methyl-, 1,2-dimethyl-, and 1-ethyl-2-methylphenanthrene through the annulation of the naphthalene system with the exploitation of the dicyanovinyl moiety of 2-naphthylalkylidenemalonodinitriles as an active electrophile in cold solutions of concentrated sulfuric acid. 2-(2-Naphthyl)propanal (**3**), 1-(2-naphthyl)propan-2-one (**9**), 3-(2-naphthyl)butan-2-one (**14**), and 3-(2-naphthyl)pentan-2-one (**19**) had been condensed with malonodinitrile to afford 2-naphthylalkylidenemalonodinitriles which were then cyclised to give 4-amino-1-methylphenanthrene-3-carbonitrile (**5**), 4-amino-2-methylphenanthrene-3-carbonitrile (**11**), 4-amino-1,2-dimethylphenanthrene-3-carbonitrile (**16**), and 4-amino-1-ethyl-2-metylphenanthrene-3-carbonitrile (**21**). The nitrile function has been removed from the aminonitriles, with the exception of **21**, through hydrolysis and decarboxylation in alkaline ethanolic solutions under elevated pressure (~3 MPa) and temperature 220–230°C to give the respective 4-amino-methylphenanthrenes. Diazotisation of the phenanthreneamines and the reaction with hypophosphorus acid has lead to the methylphenanthrenes in moderate yields (50–52%).

1. Introduction

As the importance of research related to the environmental problems is steadily increasing worldwide, there is continuous demand to design new synthetic methods which allow convenient and efficient preparation of reference samples of organic pollutants present in the biosphere. In connection with our environmental studies we were in need of reference samples of methylphenanthrenes and other alkylphenanthrenes. Herein we wish to report the results of our studies aimed at finding out whether naphthylalkylidenemalonodinitriles might be used as precursors in the synthesis of several methylphenanthrenes, and potentially other alkylphenanthrenes.

Phenyl- and tolyl-alkylidenemalonodinitriles have been employed in the synthesis of some dimethylnaphthalenes or their derivatives. The 'ylidenemalonodinitrile route' leading to these simple alkyl-aromatic hydrocarbons has been preliminarily explored.[1] The problems of regioselectivity in ring closure of tolyl-alkylidenemalonodinitriles or rearrangement of carbon framework in the course of cyclisations have also been encountered and investigated to the limited extent.[1,2] However, alkylnaphthalenes appear to be less important for the environmental studies than alkylphenanthrenes. Therefore it was of some interest to explore the extension of the aryl-alkylidenemalonodinitrile approach for the synthesis of aromatic systems possessing more than two condensed benzene rings.

Methylphenanthrenes belong to an important group of alkyl-aromatic hydrocarbons which are present in the natural environment. Methylphenanthrenes arise through the combustion of wood,[3] coal,[4] and are also emitted into the environment by the internal combustion engines,[5] in particular by Diesel engines.[6] These hydrocarbons are created in a variety of geochemical processes,[7] and their presence was also detected in soil, water, river and sea sediments,[8] sedimental rock,[9] and in crude oil.[10] Analysis of air, especially of subtle dust suspended in polluted air, entails evaluation of the total amount of phenanthrene derivatives, 1-methylphenanthrene and also isomeric methylphenanthrenes.[11]

There is a great variety of methods which are available for the synthesis of phenanthrene and its derivatives.[12] Perhaps the most extensively investigated method is the classical Haworth synthesis with its annulation of the naphthalene rings by a four carbon unit, and a stepwise aromatisation of the newly formed carbocyclic ring.[13] This method might be

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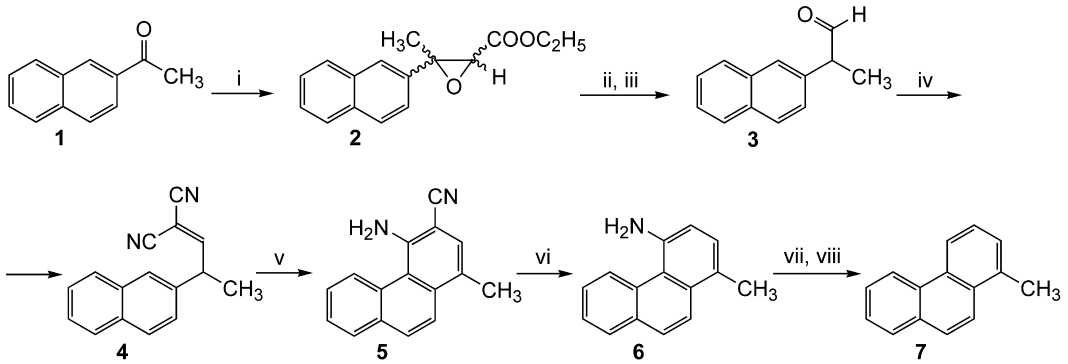
employed for the convenient introduction of alkyl group into the desired positions on the phenanthrene system. Other synthetic methods which lead to the phenanthrenes involve cyclisation of stilbenes,[14] cycloaromatisation of α-oxo-ketone dithioacetals,[15] rearrangement of certain carbocyclic spiranes,[16] or $PtCl_2$-catalysed cycloisomerisation of the *ortho*-alkynylated biphenyls.[17] This publication gives many references to reviews and recent reports on the synthesis of phenanthrenes which were published in the last years.

2. Results and discussion

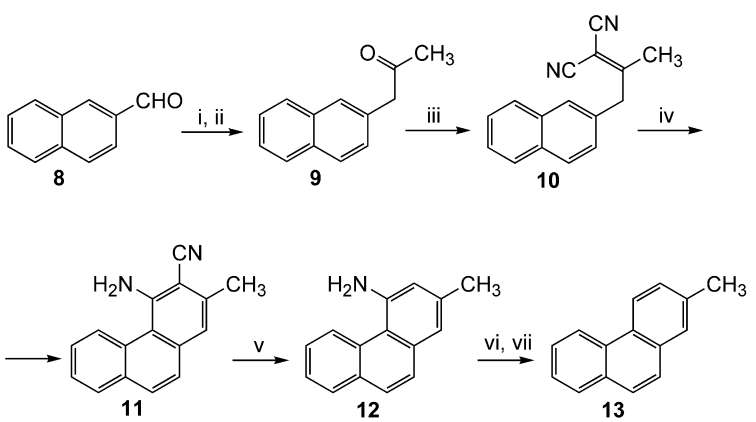
The approach reported here is a modification and extension of our method designed earlier for the synthesis of some dimethylnaphthalenes.[1,2] An aromatic aldehyde is converted to 1-arylpropan-2-one, usually through condensation with nitroethane and the reduction of obtained nitroalkenes. On the other hand 2-arylpropanals are synthesised from acetyl arenes using the Darzen's reaction. Condensation of arylpropanones and arylpropanals with malonodinitrile gives the dinitriles which are then cyclised to the phenanthrene aminonitriles. In our present synthesis cyclisation occurs in the α-position of the naphthalene system. Sequential removal of the nitrile and the amino groups from aminonitriles leads to methylphenanthrenes. Employing naphthylpropanones and naphthylpropanals allows the introduction of the methyl group in the 1- or 2-position of the phenanthrene system.

Synthesis of 1-methylphenanthrene from 2-acetylnaphthalene (**1**) is depicted in Scheme 1. 2-(2-Naphthyl)-propanal (**3**) was obtained from ketone **1** through a modified Darzen's condensation with ethyl chloroacetate in the presence of sodium hydride as a base.[18] Glycidic esters **2** (60% yield) were hydrolysed and decarboxylated to aldehyde **3** (70%). Condensation of **3** with malonodinitrile gave dinitrile **4** (57%) which on dissolving in cold sulfuric acid furnished aminonitrile **5** (50%). The aminonitrile was decyanated to amine **6** (71%) on heating under pressure (~3 MPa) with ethanolic sodium hydroxide solution. Diazotisation of **6** and then the reduction of the diazonium salt with hypophosphorous acid gave 1-methylphenanthrene (47%). The synthetic sequence leading from **1** to the known[19] hydrocarbon **7** is also a proof of the structure of aminonitrile **5** and amine **6**. Reservations about structure of aminonitrile **5** and in consequence of **6** and **7** are not completely unfounded. Our recent investigation revealed that some aryl-alkylidenemalonodinitriles might rearrange on cyclisation in sulfuric acid.[2] However, this was not the case in the outlined above reaction sequence leading from **4** to **7**.

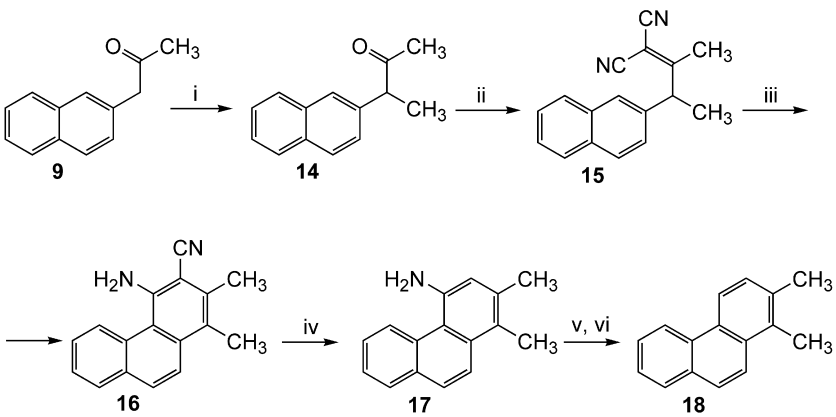
Ketone **9** was obtained in 61% yield from aldehyde **8** through condensation with nitroethane and then reduction of the mixture of nitropropenes. This method was used earlier for the preparation of tolylpropan-2-ones.[1] Ketone **9** afforded the dinitrile **10** (57%). Cyclisation of **10** in sulfuric acid gave aminonitrile **11** (60%) which was then decyanated to amine **12** under the same condition as aminonitrile **5**



Scheme 1. (i) $ClCH_2COOC_2H_5$, NaH, CH_3CN (60%); (ii) C_2H_5ONa, C_2H_5OH; (iii) 5% H_2SO_4 (70%); (iv) $CH_2(CN)_2$, CH_3COOH, CH_3COONH_4, benzene (57%); (v) H_2SO_4, 0°C (50%); (vi) NaOH, C_2H_5OH, 210°C, 3 MPa (71%); (vii) $NaNO_2$, HCl; 0–5°C, (viii) H_3PO_2 (47%).



Scheme 2. (i) $C_2H_5NO_2$, piperidine, toluene; (ii) Fe, HCl_{aq}, (61%); (iii) $CH_2(CN)_2$, CH_3COOH, CH_3COONH_4, benzene (57%); (iv) H_2SO_4, 0°C (60%); (v) NaOH, C_2H_5OH, 210°C, 3 MPa (85%); (vi) $NaNO_2$, HCl, 0–5°C; (vii) H_3PO_2 (41%).

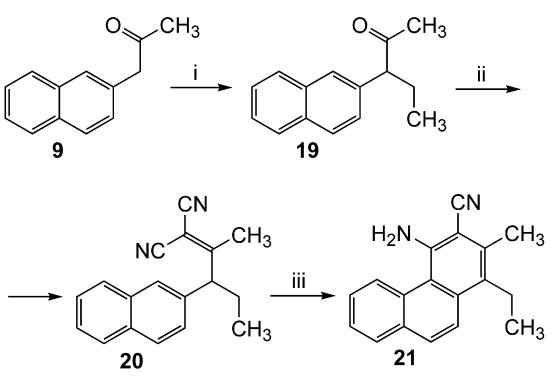


Scheme 3. (i) CH_3I, NaOH, TEBA (59%); (ii) $CH_2(CN)_2$, CH_3COOH, CH_3COONH_4, benzene (73%); (iii) H_2SO_4, 0°C (74%); (iv) NaOH, C_2H_5OH, 210°C, 3 MPa (92%); (v) $NaNO_2$, HCl, 0–5°C; (vi) H_3PO_2 (53%).

(Scheme 2). The structure of aminonitrile **11** was confirmed by spectroscopic measurements including HH COSY experiment. Amine **12** (85%) was diazotised and reduced in the presence of hypophosphorous acid to give known[15] hydrocarbon **13** (41%). As in the case of 1-methylphenanthrene, the synthetic pathway leading from aldehyde **8** to hydrocarbon **13** revealed that cyclisation of **10** to **11** occurred in the expected manner without the presence of any rearranged aminonitrile, an isomer of **11**.

Synthesis of 1,2-dimethylphenanthrene **18** was accomplished using ketone **9** as substrate (Scheme 3). Methylation of **9** with methyl iodide gave butanone **14** (59%). The following reaction sequence was similar to that presented in Scheme 3. Condensation of **14** with malonodinitrile gave **15** (73%) which on dissolving in sulfuric acid was cyclised smoothly to *o*-aminonitrile **16** (74%). Amine **17** was obtained in good yield (92%) from aminonitrile **16**. Elimination of the amino group from **17** afforded hydrocarbon **18** (53%).

This last reaction sequence leading to 1,2-dimethylnaphthalene might potentially be used to introduce alkyl groups of different sizes into '1' and '2' positions of phenanthrene. This possibility was explored in the case of 1-ethyl-2-methylphenanthrene (Scheme 4). Alkylation of **9** with ethyl iodide gave pentanone **19** in poor 30% yield. Condensation of **19** with malonodinitrile gave the dinitrile **20** (51%). Cyclisation of **20** in cold sulfuric acid afforded aminonitrile **21** in low yield (25%). Low yield of alkylating



Scheme 4. (i) CH_3CH_2I, NaOH, TEBA (30%); (ii) $CH_2(CN)_2$, CH_3COOH, CH_3COONH_4, benzene (51%); (iii) H_2SO_4, 0°C (25%).

ketone **9** with ethyl iodide under PTC conditions, low yields of condensation of ketone **19** with malonodinitrile and of cyclisation dinitrile **20** to aminonitrile **21**, discouraged us from completing the reaction sequence up to the preparation of 1-ethyl-2-methyl-phenanthrene. The difficulty in the introduction of ethyl group into the '1' position of phenanthrene aminonitrile **21** might be connected with steric hindrance at all three stages of synthesis leading to **21**.

3. Conclusion

The feasibility study presented in this report revealed that cyclisation of several 2-naphthylalkylidene malonodinitriles such as **4**, **10**, **15** or **20** might be smoothly accomplished in the α position of naphthalene to give phenanthrene aminonitriles in moderate yields (60–74%) in most cases. Ring closure leading to these phenanthrene derivatives is performed in a single step in sulfuric acid. Removal of the nitrile function from the aminonitriles furnishes aminophenanthrenes **6**, **12** or **17** in good yield (79–92%). Elimination of the amino group from the obtained amines leads in the final step to methylphenanthrenes **7**, **13** or **18** in relatively low yield (51–53%). A characteristic feature of the synthetic approach presented here is the introduction of the amino function in the '4' position of phenanthrene. Although this synthetic route has not been yet investigated, the obtained aminophenanthrenes might be useful substrates for the exchange of the amino function for other alkyl groups. In this way a variety of alkylphenanthrenes possessing a unique substitution pattern might be available for potential environmental studies and other applications.

4. Experimental

4.1. General

IR spectra were recorded on a Bruker IFS 48 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 500 spectrometer in the indicated solvent using TMS as internal standard. Elemental analyses were performed using an Euro EA 3000 instrument. Melting points were determined on a Boetius hot-stage microscope and are uncorrected.

4.2. Synthesis of 1-methylphenanthrene (7) from 2-acetylnaphthalene (1)

4.2.1. Ethyl 3-(2-naphthyl)-3-methyloxirane-2-carboxylate (2). In a 250 ml three-necked round-bottomed flask equipped with an efficient mechanical stirrer, a reflux condenser with protection from moisture and a thermometer, was placed dry acetonitrile (80 ml), 2-acethylnaphthalene (17.0 g, 0.10 mol) and ethyl chloroacetate (13.5 g, 0.11 mol). A solution was preheated to 60°C and sodium hydride (5.3 g, 0.11 mol) as 50% suspension in mineral oil was added in small portions over a period of 1 h to the well stirred mixture while the temperature was maintained at 60–65°C. The mixture was then stirred and heated for another 1 h. Acetonitrile was evaporated under reduced pressure, water (50 ml) was carefully added and the mixture was extracted with dichloromethane (3×100 ml). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated. The obtained dark oil was distilled under reduced pressure to give a *cis*/*trans* mixture (~1:1 ratio) of glycidic esters **2** as a pale yellow oil; yield 15.4 g (60%); bp 126–136°C/300 Pa (lit.[20] 175–180°C/700 Pa); IR (KBr) ν_{max} (cm^{-1}) 3075, 2993, 2945, 1738, 1618, 1598, 1290, 1234, 1083, 860, 797, 784; δ_H ($CDCl_3$) (a) 0.78 (t, 3H, J=7.1 Hz), 1.81 (s, 3H), 3.55 (s, 1H), 3.83 (q, 2H, J=7.1 Hz), 7.44–7.50 (m, 3H), 7.77–7.88 (m, 4H); (b) 1.33 (t, 3H, J=7.1 Hz), 1.87 (s, 3H), 3.75 (s, 1H), 4.30 (q, 2H, J=7.1 Hz), 7.44–7.50 (m, 3H), 7.77–7.88 (m, 4H); δ_C ($CDCl_3$) 13.6, 14.2, 17.1, 24.6, 60.8, 60.9, 61.4, 61.4 62.0, 63.7, 122.7, 124.0, 124.6, 125.5, 126.1, 126.2, 126.3, 126.4, 127.6, 127.7, 127.9, 128.3, 132.7, 132.8, 132.9, 132.9, 134.6, 137.6, 167.0, 167.5.

4.2.2. 2-(2-Naphthyl)propanal (3). The mixture of diastereoisomeric glycidic esters **2** (15.0 g, 0.058 mol) was slowly syringed into a well stirred cold solution of sodium ethoxide. The solution was obtained by dissolving sodium (1.33 g, 0.058 mol) in 30 ml of ethanol. Subsequently water (1.0 ml) and diethyl ether (3.0 ml) were added. The mixture was extracted with water (300 ml). The water layer was acidified to pH=1 with hydrochloric acid. The mixture was gently heated for 30 min to complete the decarboxylation of the glicydic acids and was then extracted with toluene (3×30 ml). The combined extracts were dried over anhydrous magnesium sulfate. Toluene was evaporated and obtained oil was distilled under reduced pressure to give 7.5 g (70%) of **3** as an oil which solidified. Recrystallisation from diethyl ether gave colourless crystals; mp 57–58°C (lit.[20] mp 53°C); bp 120–126°C/100 Pa; IR (KBr) ν_{max} (cm^{-1}) 3063, 2980, 2922, 2723, 1724, 1610, 1361, 815, 748; δ_H ($CDCl_3$) 1.52 (d, 3H, J=7.0 Hz), 3.78 (q, 1H, J=7.0 Hz), 7.28–7.86 (m, 7H), 9.74 (br. s, 1H); δ_C ($CDCl_3$) 14.6, 53.0, 126.0, 126.1 126.4, 127.1, 127.7, 127.7, 128.8, 132.6, 133.6, 135.1, 200.9.

4.3. General procedure for condensation of aldehyde 3, and ketones 9, 14, and 19 with malonodinitrile

In a 50 ml flask equipped with a Dean–Stark water separator and a reflux condenser were placed acetic acid (1.20 g, 20 mmol), ammonium acetate (0.62 g, 8 mmol), malonodinitrile (1.78 g, 27 mmol), benzene (20 ml) and aldehyde **3** or ketones **9**, **14** or **19** (25 mmol). After heating at reflux for 4 h, the reaction progress was monitored by GC and, if necessary, additional portions of malonodinitrile (0.18 g, 2.7 mmol), ammonium acetate (0.21 g, 3 mmol) and acetic acid (0.42 g, 7 mmol) were added and heating was continued for the next 3–4 h. The solution was successively washed with water, saturated aqueous sodium hydrogen carbonate, water, and was dried over anhydrous magnesium sulfate. Benzene was removed and the obtained oil was distilled under reduced pressure or was purified by column chromatography using silica gel and toluene as eluent to give dinitriles **4**, **10**, **15** or **20**. Solid dinitrile **10** was recristallised from ethanol.

4.3.1. 3-(2-Naphthyl)-but-1-en-1,1-dicarbonitrile (4). Pale yellow oil; yield 3.3 g (57%); bp 132–136°C/20 Pa; IR (neat) ν_{max} (cm^{-1}) 3055, 2973, 2929, 2232, 1680, 1599; δ_H ($CDCl_3$) 1.65 (d, 3H, J=7.9 Hz), 4.30 (m, 1H), 7.32–7.96 (m, 8H); δ_C ($CDCl_3$) 19.5, 38.0, 88.3, 110.6, 111.9, 123.9, 124.6, 125.9, 126.1, 126.8, 127.7, 129.4, 132.9, 133.6, 135.5, 171.2. Anal. found: C 82.51, H 5.17, N 12.41%; calcd for $C_{16}H_{12}N_2$: C 82.73, H 5.21, N 12.06%.

4.4. General procedure for cyclisation of dinitriles 4, 10, 15 or 20 to 4-aminophenanthrene-3-carbonitriles

The oily dinitrile (10 mmol) was slowly dropped into stirred, ice-cold concentrated sulfuric acid (20 ml). The solid dinitrile **10** was added to sulfuric acid as a solution in 1.0 ml of acetone. The solution was kept in an ice-bath for 2 h and then was poured onto 300 g of crushed ice. The resulting pale yellow precipitate was filtered off, washed thoroughly with water, saturated aqueous sodium hydrogen carbonate, and finally with water. The aminonitriles **5**, **11**, **16** or **21** were chromatographed on silica gel with toluene or chloroform as eluent and recrystallised from an appropriate solvent. Analytical samples were sublimed under reduced pressure.

4.4.1. 4-Amino-1-methylphenanthrene-3-carbonitrile (5). Pale yellow needles (from ethanol); yield 1.16 g (50%); mp 131–132°C; IR (KBr) ν_{max} (cm^{-1}) 3425, 3337, 3049, 2923, 2208, 1674, 1630, 1599; δ_H ($CDCl_3$) 2.59 (s, 3H), 5.16 (s, 2H), 7.36 (s, 1H), 7.60–7.67 (m, 2H), 7.77–7.85 (m, 2H), 7.93 (d, 1H, J=7.1 Hz), 9.12 (d, 1H, J=8.2 Hz); δ_C ($CDCl_3$) 19.3, 94.2, 118.7, 119.1, 122.8, 125.1, 125.2, 126.4, 127.0, 128.4, 129.0, 130.1, 130.2, 132.6, 135.6, 148.0. Anal. found: C 82.81, H 5.34, N 12.12%; calcd for $C_{16}H_{12}N_2$: C 82.73, H 5.21, N 12.06%.

4.5. General procedure for elimination of the nitrile group from aminonitriles 5, 11 or 16. Synthesis of phenanthrene amines 6, 12, and 17

Aminonitrile (1.5 mmol) and sodium hydroxide (1.0 g, 25 mmol) were dissolved in ethanol (100 ml). The solution was heated in a 300 ml autoclave at 240°C (~3.0 MPa) for 4 h. The mixture was diluted with water (50 ml) and ethanol was removed on a rotary evaporator. After cooling, the light brown precipitate was filtered off and washed with water. Crude amines were purified by column chromatography or TLC (SiO_2/toluene), sublimation under reduced pressure, and recrystallisation from an appropriate solvent.

4.5.1. 4-Amino-1-methylphenanthrene (6). Light-brown prisms (from hexane); yield 223 mg (71%); mp 114–116°C; IR (KBr) ν_{max} (cm^{-1}) 3454, 3374, 2926, 2846, 1619, 1595, 1415, 1325, 824, 746; δ_H ($CDCl_3$) 2.65 (s, 3H), 4.13 (s, 2H), 6.93 (d, 1H, *J*=7.7 Hz), 7.25–7.27 (m, 1H), 7.54–7.62 (m, 2H), 7.72 (d, 1H, *J*=9.0 Hz), 7.87 (d, 1H, *J*=9.1 Hz), 7.90 (d, 1H, *J*=7.7 Hz), 9.32 (d, 1H, *J*=7.7 Hz); δ_C ($CDCl_3$) 19.6, 114.9, 120.1, 123.5, 125.5, 125.6, 125.8, 126.0, 126.9, 128.0, 128.5, 131.2, 132.5, 132.5, 143.3. Anal. found: C 87.11, H 6.04, N 6.52%; calcd for $C_{15}H_{13}N$: C 86.92, H 6.32, N 6.76%.

4.6. General procedure for elimination of the amino function from phenanthrene amines 6, 12 or 17. Synthesis of methylphenanthrenes 7, 13, and 18

The aminophenanthrene (0.95 mmol) was suspended in 7.0 ml of 50% hypophosphorous acid. The suspension was cooled in an ice-bath and diazotised with sodium nitrite (100 mg, 1.45 mmol) dissolved in a small amount of water. The diazonium solution was left at +5°C for 48 h and the mixture was then diluted with 20 ml of water. The solid product was filtered off, washed with water and sublimed in vacuo. Recrystallisation from ethanol gave colourless crystals.

4.6.1. 1-Methylphenanthrene (7). Yield 86 mg (47%); mp 120–122°C (lit.[19] mp 122–122.5°C); IR (KBr) ν_{max} (cm^{-1}) 3054, 3021, 1601, 822, 806, 745; δ_H ($CDCl_3$) 2.73 (s, 3H), 7.45 (d, 1H, *J*=6.3 Hz), 7.53–7.64 (m, 3H), 7.78 (d, 1H, *J*=8.8 Hz), 7.90 (d, 1H, *J*=6.3 Hz), 7.96 (d, 1H, *J*=8.9 Hz), 8.59 (d, 1H, *J*=7.9 Hz), 8.70 (d, 1H, *J*=7.8 Hz); δ_C ($CDCl_3$) 19.9, 120.7, 122.9, 126.1, 126.4, 126.5, 126.7, 127.8, 128.5, 130.4, 130.7, 130.8, 131.7, 134.9.

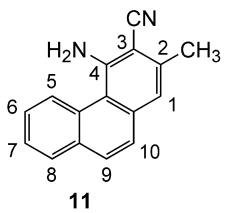
4.7. Synthesis of 2-methylphenanthrene (13) from 2-naphthaldehyde (8)

4.7.1. 1-(2-Naphthyl)propan-2-one (9). In a 250 ml flask equipped with a Dean–Stark water trap and a reflux condenser were placed nitroethane (4.8 g, 0.064 mol), piperidine (1.4 ml), 2-naphthaldehyde (10.0 g, 0.064 mol) and toluene (50 ml). The mixture was heated at reflux for 10 h and additional portions of nitroethane (4.8 g, 0.064 mol) and piperidine (1.4 ml) were added. After heating at reflux for the next 10 h the solution was transfered to a three-necked flask equipped with a reflux condenser, a mechanical stirrer, a dropping funnel and a thermometer. Iron dust (17 g, 0.304 mol) was added and the mixture was preheated to 80°C. Concentrated hydrochloric acid (30 ml) was added dropwise to the solution over a period of 1 h and the reaction was heated at 85–95°C for the next 1 h. After cooling, the mixture was distilled with steam. The distilate was extracted with toluene (4×50 ml). The combined organic layers were dried over anhydrous magnesium sulfate and toluene was evaporated. The residual dark oil was fractionated under reduced pressure to give ketone **9** which solidified to colourless crystals; yield 7.18 g (61%); mp 35–37°C (lit.[21] mp 37–37.5°C); IR (KBr) ν_{max} (cm^{-1}) 3055, 2923, 2854, 1711, 1509, 1361, 1164, 811, 753, 482; δ_H ($CDCl_3$) 2.17 (s, 3H), 3.84 (s, 2H), 7.32–7.30 (m, 1H), 7.49–7.43 (m, 2H), 7.66 (s, 1H), 7.82–7.78 (m, 3H).

4.7.2. 3-(2-Naphthyl)-2-methylprop-1-en-1,1-dicarbonitrile (10). Condensation of ketone **9** with malonodinitrile was carried out according to the general procedure described under Section 4.3. Pale yellow needles (from ethanol); yield 3.3 g (57%); mp 144–146°C; IR (KBr) ν_{max} (cm^{-1}) 3049, 3011, 2942, 2226, 1599, 1509, 827, 761, 473; δ_H ($CDCl_3$) 2.20 (s, 3H), 4.02 (s, 2H), 7.30–7.25 (m, 1H), 7.55–7.49 (m, 2H), 7.67 (s, 1H), 7.86–7.81 (m, 3H); δ_C ($CDCl_3$) 22.2, 43.8, 86.5, 111.7, 112.0, 126.3, 126.5, 126.8, 127.6, 127.8, 128.0, 129.2, 131.7, 132.8, 133.5, 179.4. Anal. found: C 82.70, H 5.31, N 11.98%; calcd for $C_{16}H_{12}N_2$: C 82.73, H 5.21, N 12.06%.

4.7.3. 4-Amino-2-methylphenanthrene-3-carbonitrile (11). Cyclisation of dinitrile **10** to aminonitrile **11** was carried out according to the general procedure described under Section 4.4. Pale yellow needles (from ethanol); yield 1.39 g (60%); mp 161–162°C; IR (KBr) ν_{max} (cm^{-1}) 3431, 3356, 3249, 2923, 2201, 1657, 1616, 1402, 868, 811, 745, 613, 564, 531; δ_H ($CDCl_3$) 2.56 (s, 3H), 5.23 (s, 2H), 7.06 (s, 1H), 7.47 (d, 1H, *J*=8.7 Hz), 7.56 (dd, 1H, *J*=7.8, 7.2 Hz), 7.62 (dd, 1H, *J*=8.4, 7.2 Hz), 7.71 (d, 1H, *J*=8.7 Hz), 7.87

Table 1. Correlations in ^1H ^1H COSY spectrum of **11**



11

	Chemical shift and coupling constant	Correlated signals
H_3C	2.56 (s, 3H)	7.06 (s, 1H) HC-1
H_2N	5.23 (s, 2H)	–
HC-1	7.06 (s, 1H)	2.56 (s, 3H) H_3C
HC-10	7.47 (d, 1H, *J*=8.7 Hz)	7.71 (d, 1H, *J*=8.7 Hz) HC-9
HC-7	7.56 (dd, 1H, *J*=7.8, 7.2 Hz)	7.87 (d, 1H, *J*=7.8 Hz) HC-8; 7.62 (dd, 1H, *J*=8.4, 7.2 Hz) HC-6
HC-6	7.62 (dd, 1H, *J*=8.4, 7.2 Hz)	8.93 (d, 1H, *J*=8.4 Hz) HC-5; 7.56 (dd, 1H, *J*=7.8, 7.2 Hz) HC-7
HC-9	7.71 (d, 1H, *J*=8.7 Hz)	7.47 (d, 1H, *J*=8.7 Hz) HC-10
HC-8	7.87 (d, 1H, *J*=7.8 Hz)	7.56 (dd, 1H, *J*=7.8, 7.2 Hz) HC-7
HC-5	8.93 (d, 1H, *J*=8.4 Hz)	7.62 (dd, 1H, *J*=8.4, 7.2 Hz) HC-6

(d, 1H, J=7.8 Hz), 8.93 (d, 1H, J=8.4 Hz); δ_C ($CDCl_3$) 20.7, 96.4, 116.4, 117.8, 119.6, 124.4, 126.0, 126.7, 127.1, 129.2, 130.0, 130.2, 132.6, 136.4, 137.6, 149.8. Anal. found: C 82.89, H 5.43, N 11.98%; calcd for $C_{16}H_{12}N_2$: C 82.73, H 5.21, N 12.06% (Table 1).

4.7.4. 4-Amino-2-methylphenanthrene (12). Elimination of the nitrile group from **11** was performed as described in the general procedure under Section 4.5. Light brown prisms (from ethanol); yield 264 mg (85%); mp 110–112°C; IR (KBr) ν_{max} (cm^{-1}) 3449, 3376, 2935, 2845, 1613, 1599, 1338, 824, 745; δ_H ($CDCl_3$) 2.45 (s, 3H), 4.34 (s, 2H), 6.82 (s, 1H), 7.16 (s, 1H), 7.49–7.63 (m, 4H), 7.85 (d, 1H, J=7.8 Hz), 9.16 (d, 1H, J=8.4 Hz); δ_C ($CDCl_3$) 21.2, 117.0, 117.6, 120.3, 125.0, 125.4, 125.9, 127.2, 127.5, 128.7, 130.9, 132.5, 134.6, 136.6, 144.9. Anal. found: C 86.65, H 6.64, N 6.59%; calcd for $C_{15}H_{13}N$: C 86.92, H 6.32, N 6.76%.

4.7.5. 2-Methylphenanthrene (13). 2-Methylphenanthrene was obtained from amine **12** according to the general procedure given under Section 4.6. Yield 75 mg (41%); mp 55–57°C (lit.[15] mp 56–57°C); IR (KBr) ν_{max} (cm^{-1}) 3046, 3026, 1598, 823, 806, 746; δ_H ($CDCl_3$) 2.55 (s, 3H), 7.44–7.50 (m, 1H), 7.53–7.67 (m, 4H), 7.70 (m, 1H), 7.86 (m, 1H) 8.56 (d, 1H, J=8.4 Hz), 8.64 (d, 1H, J=8.3 Hz); δ_C ($CDCl_3$) 19.9, 120.9, 122.8, 122.9, 126.1, 126.4, 126.5, 126.7, 127.8, 128.5, 130.0, 130.7, 130.8, 131.7, 134.9.

4.8. Synthesis of 1,2-dimethylphenanthrene (18) from 1-(2-naphthyl)propan-2-one (9)

4.8.1. General procedure for alkylation of 1-(2-naphthyl)propan-2-one (9) with methyl or ethyl iodide. Synthesis of 3-(2-naphthyl)butan-2-one (14) and 3-(2-naphthyl)pentan-2-one (19). In a 50 ml, three-necked flask equipped with magnetic stirrer, a dropping funnel and a thermometer were placed 50% sodium hydroxide solution (15 ml) and TEBA (0.20 g, 0.90 mmol). The mixture was preheated to 40°C and a solution of 1-(2-naphthyl)propan-2-one (**9**) (4.7 g, 25 mmol) in toluene (10 ml) was added. The mixture was stirred vigorously and methyl or ethyl iodide (33 mmol) was slowly added in the course of 45 min while the temperature of the reaction mixture was maintained at 40–45°C. After the addition of alkyl iodide had been complete, the stirring was continued for additional 2 h. The mixture was diluted with water (100 ml) and the product was extracted with toluene (3×50 ml). The combined extracts were dried over anhydrous magnesium sulfate. Toluene was distilled off and oily ketones were distilled under reduced pressure.

4.8.2. 3-(2-Naphthyl)butan-2-one (14). Colourless oil; yield 2.98 g (59%); bp 95–100°C/20 Pa; (lit.[22] no bp is given); IR (neat) ν_{max} (cm^{-1}) 3052, 2979, 1709, 1634, 1601, 1504, 952, 898, 856, 823, 751; δ_H ($CDCl_3$) 1.47 (d, 3H, J=7.0 Hz), 2.05 (s, 3H), 3.88 (q, 1H, J=6.9 Hz), 7.30 (d, 1H, J=8.5 Hz), 7.44 (t, 1H, J=6.8 Hz), 7.47 (t, 1H, J=6.7 Hz), 7.67 (s, 1H), 7.77–7.81 (m, 3H); δ_C ($CDCl_3$) 17.2, 25.5, 53.7, 125.7, 125.8, 126.2, 126.5, 127.6, 128.6, 132.5, 133.6, 138.0, 208.5.

4.8.3. 3-(2-Naphthyl)-2-methylbut-1-ene-1,1-dicarbonitrile (15). Condensation of ketone **14** (1.50 g, 7.5 mmol) with malonodinitrile was carried out according to the general procedure described under Section 4.3. Orange oil, after chromatography; yield 1.35 g (73%); IR (KBr) ν_{max} (cm^{-1}) 3052, 2979, 2884, 2226, 1634, 1592, 1504, 948, 898, 856, 823, 756; δ_H ($CDCl_3$) 1.63 (d, 3H, J=7.1 Hz), 2.02 (s, 3H), 4.62 (q, 1H, J=7.1 Hz), 7.27 (d, 1H, J=8.5 Hz), 7.48 (t, 1H, J=6.8 Hz), 7.51 (t, 1H, J=6.9 Hz), 7.70 (s, 1H), 7.81–7.84 (m, 3H); δ_C ($CDCl_3$) 16.6, 18.3, 45.3, 85.4, 111.8, 111.9, 125.1, 125.8, 126.4, 126.6, 127.6, 127.8, 128.8, 132.7, 133.3, 135.9, 184.0. Anal. found: C 82.78, H 5.72, N 11.44%; calcd for $C_{17}H_{14}N_2$: C 82.93, H 5.69, N 11.38%.

4.8.4. 4-Amino-1,2-dimethylphenanthrene-3-carbonitrile (16). Cyclisation of dinitrile **15** (1.0 g, 4 mmol) to aminonitrile **16** was carried out as described in Section 4.4. Pale yellow needles (from ethanol); yield 0.74 g (74%); mp 135–136°C; IR (KBr) ν_{max} (cm^{-1}) 3437, 3369, 3049, 2998, 2923, 2195, 1639, 1580, 814, 764, 664; δ_H ($CDCl_3$) 2.53 (s, 3H), 2.63 (s, 3H), 5.18 (s, 2H), 7.58 (t, 1H, J=7.0 Hz), 7.63 (t, 1H, J=7.0 Hz), 7.80 (d, 1H, J=9.1 Hz), 7.87 (d, 1H, J=9.2 Hz), 7.91 (d, 1H, J=7.7 Hz), 9.09 (d, 1H, J=8.7 Hz); δ_C ($CDCl_3$) 14.9, 19.2, 97.1, 117.2, 118.5, 122.8, 124.9, 126.0, 126.2, 126.8, 128.8, 129.9, 130.2, 132.0, 134.7, 135.3, 147.6. Anal. found: C 83.15, H 5.79, N 11.12%; calcd for $C_{17}H_{14}N_2$: C 82.93, H 5.69, N 11.38%.

4.8.5. 4-Amino-1,2-dimethylphenanthrene (17). Elimination of the nitrile function from 0.40 g (1.6 mmol) of aminonitrile **16** was performed as described in Section 4.5. Pale yellow prisms after sublimation; yield 0.33 g (92%); mp 88–90°C; IR (KBr) ν_{max} (cm^{-1}) 3393, 3325, 3061, 2923, 2860, 1618, 814, 751, 626; δ_H ($CDCl_3$) 2.44 (s, 3H), 2.54 (s, 3H), 4.24 (s, 2H), 6.85 (s, 1H), 7.51 (t, 1H, J=7.9 Hz), 7.57 (t, 1H, J=6.9 Hz), 7.67 (d, 1H, J=9.2 Hz), 7.86 (d, 1H, J=7.7 Hz), 7.91 (d, 1H, J=9.2 Hz), 9.25 (d, 1H, J=8.4 Hz); δ_C ($CDCl_3$) 14.7, 20.8, 117.7, 117.9, 118.4, 123.3, 123.5, 125.1, 125.7, 126.9, 128.3, 131.2, 131.9, 132.8, 134.7, 142.4. Anal. found: C 86.67, H 6.91, N 6.27%; calcd for $C_{16}H_{15}N$: C 86.84, H 6.83, N 6.33%.

4.8.6. 1,2-Dimethylphenanthrene (18). Elimination of the amino group from 270 mg (1.22 mmol) of **17** was carried out as described in Section 4.6. Yield 130 mg (53%); mp 144–145°C; (lit.[23] mp 142–143°C); IR (KBr) ν_{max} (cm^{-1}) 3048, 2997, 2922, 1636, 1575, 808, 745, 682; δ_H ($CDCl_3$) 2.51 (s, 3H), 2.63 (s, 3H), 7.44 (d, 1H, J=8.4 Hz), 7.55 (t, 1H, J=8.0 Hz), 7.60 (t, 1H, J=7.0 Hz), 7.73 (dd, 1H, J=9.2, 6.1 Hz), 7.85 (d, 1H, J=7.3 Hz), 8.01 (d, 1H, J=8.7 Hz), 8.46 (d, 1H, J=8.5 Hz), 8.65 (d, 1H, J=8.3 Hz). δ_C ($CDCl_3$) 15.1, 21.0, 122.7, 122.9, 126.1, 126.4, 126.6, 128.3, 128.7, 129.1, 130.7, 130.9, 131.1, 132.3, 134.4.

4.9. Synthesis of 4-amino-1-ethyl-2-methylnaphthalene-3-carbonitrile (21) from 1-naphthylpropan-2-one (9)

4.9.1. 3-(2-Naphthyl)pentan-2-one (19). Ketone **9** (3.68 g, 20 mmol) was alkylated with ethyl iodide as described in Section 4.8.1. Light brown oil; yield 1.15 g (30%); bp 105–106°C/10 Pa; IR (neat) ν_{max} (cm^{-1}) 3052, 2958, 1714, 1634, 1597, 1504, 818, 747; δ_H ($CDCl_3$) 0.86 (t, 3H, J=7.4 Hz), 1.78–1.84 (m, 2H), 2.07 (s, 3H), 3.70 (t, 1H, J=7.4 Hz), 7.32 (d, 1H, J=8.3 Hz), 7.45 (t, 1H, J=6.8 Hz), 7.48 (t, 1H,

J=6.7 Hz), 7.68 (s, 1H), 7.80–7.82 (m, 3H); δ_C ($CDCl_3$) 12.0, 24.9, 29.1, 61.6, 125.8, 126.0, 126.2, 127.2, 127.6, 127.6, 128.6, 132.6, 133.6, 136.4, 208.5. Anal. found: C 85.02, H 6.97%; calcd for $C_{15}H_{16}O$: C 84.88, H 7.58%.

4.9.2. 3-(2-Naphthyl)-2-methylpent-1-ene-1,1-dicarbonitrile (20). Condensation of ketone **19** (500 mg, 2.36 mmol) with malonodinitrile was performed according to the general procedure described in Section 4.3. Pale yellow oil; yield 315 mg (51%); IR (neat) ν_{max} (cm^{-1}) 3052, 2958, 2884, 2226, 1634, 1588, 856, 823, 756; δ_H ($CDCl_3$) 1.03 (t, 3H, J=7.3 Hz), 2.00–2.04 (m, 1H), 2.07 (s, 3H), 2.16–2.20 (m, 1H), 4.37 (t, 1H, J=7.7 Hz), 7.31 (d, 1H, J=8.5 Hz), 7.49 (t, 1H, J=6.8 Hz), 7.52 (t, 1H, J=6.8 Hz), 7.80–7.85 (m, 3H), 7.72 (s, 1H); δ_C ($CDCl_3$) 11.9, 18.2, 24.3, 53.4, 86.0, 111.8, 112.1, 125.4, 126.5, 126.6, 126.6, 127.6, 127.8, 128.9, 132.8, 133.4, 135.2, 182.9. Anal. found: C 83.29, H 6.06, N 10.92%; calcd for $C_{18}H_{16}N_2$: C 83.08, H 6.15, N 10.77%.

4.9.3. 4-Amino-1-ethyl-2-methylphenanthrene-3-carbonitrile (21). Cyclisation of dinitrile **20** (100 mg, 0.38 mmol) to aminonitrile **21** was performed as described in Section 4.4. Pale yellow crystals (from methanol); yield 25 mg (25%); mp 145°C; IR (KBr) ν_{max} (cm^{-1}) 3437, 3369, 3055, 2961, 2866, 2195, 1611, 1580, 827, 758; δ_H ($CDCl_3$) δ (ppm) 1.22 (t, 3H, J=7.6 Hz), 2.62 (s, 3H), 3.00 (q, 2H, J=7.6 Hz), 5.16 (s, 2H) 7.56 (t, 1H, J=6.9 Hz), 7.60 (t, 1H, J=7.0 Hz), 7.78 (d, 1H, J=9.2 Hz), 7.85 (d, 1H, J=9.2 Hz), 7.88 (d, 1H, J=7.5 Hz), 9.06 (d, 1H, J=8.3 Hz); δ_C ($CDCl_3$) 14.5, 18.3, 21.9, 97.2, 117.5, 118.5, 122.6, 124.9, 126.1, 128.7. 128.8, 129.2, 130.1, 130.4, 132.0, 134.3, 134.6, 147.8. Anal. found: C 82.96, H 6.10, N 10.56%; calcd for $C_{18}H_{16}N_2$: C 83.08, H 6.15, N 10.77%.

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