Conformational Studies of 9,10-Ditolylphenanthrenes: High Rotational Barriers for the *syn–anti* Interconversion *

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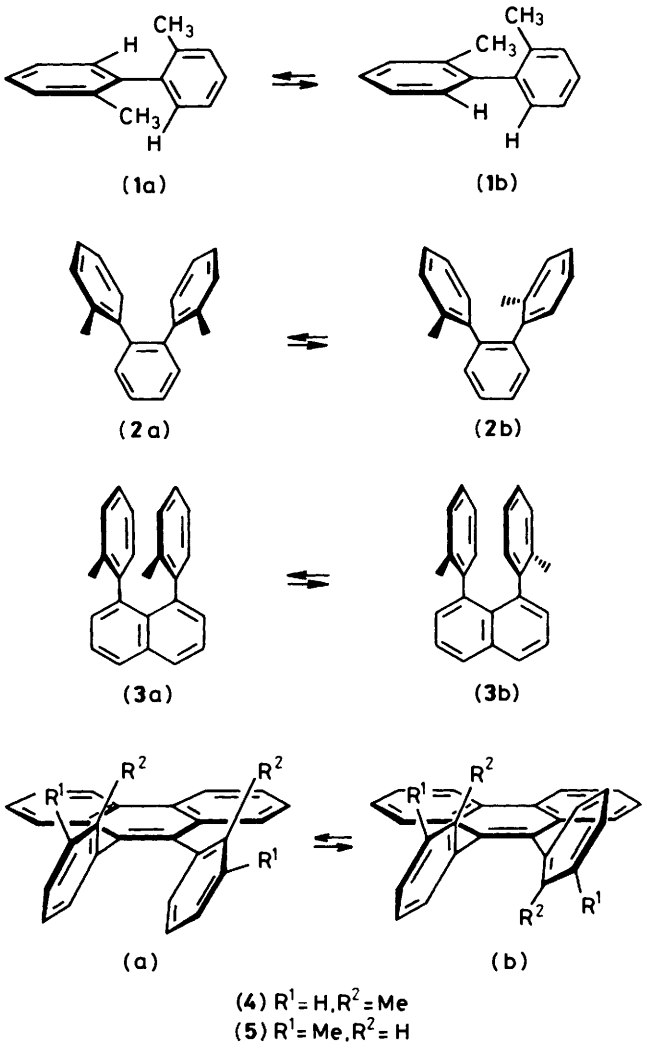
Both 9,10-di-*o*- and 9,10-di-*m*-tolylphenanthrene have been synthesized. The existence of the *syn* and *anti* isomers of the former is apparent from ^{1}H n.m.r. data and one of the isomers was obtained pure by fractional recrystallization. The chemical shifts for the methyl protons of isomers of the latter are almost identical in most solvents but they are clearly resolved in nitrobenzene. Conformational studies have revealed exceptionally high barriers to rotation ($\Delta G^{\ddagger} > 155$ kJ mol^{-1}) for the aryl rings in 9,10-di-*o*-tolylphenanthrene. At room temperature, restricted free rotation of the aryl rings was also observed in 9,10-di-*m*-tolylphenanthrene ($\Delta G_c^{\ddagger}$ 85 kJ mol^{-1}).

Molecular models, in particular CPK space-filling models, seem to indicate restricted rotation of sterically hindered groups in quite a large number of molecules, although their degree of conformational rigidity needs to be confirmed experimentally. They have in fact prompted a series of conformational studies of these compounds as they become synthetically available.[1] Many of these examples involve *ortho*-substituted benzene derivatives and significant efforts have been directed toward the isolation of *syn* and *anti* conformational isomers and/or the studies of their rotational barriers of interconversion. The presence of methyl groups in the *ortho-ortho'*-positions, as in (**1**), is believed to be sufficient to hinder free rotation in biphenyl systems.[2] The existence of *syn* and *anti* isomers of 2,2″-dimethyl-*o*-terphenyl (**2**) was clearly evident from ^{1}H n.m.r. studies reported by Mitchell *et al.*[3] with a barrier to rotation ($\Delta G_c^{\ddagger}$) of 62 kJ mol^{-1} [(**2a**) $\rightleftharpoons$ (**2b**)]. Roberts *et al.*,[4] however, have reported the successful separation of the *syn* and *anti* isomers of 1,8-di-*o*-tolylnaphthalene (**3a** and **b**) with an observed $\Delta G_{313}^{\ddagger}$ for rotation [(**3a**) $\rightleftharpoons$ (**3b**)] of 101 kJ mol^{-1}, although the half-life with respect to interconversion in solution is about one day at room temperature. Molecular models have indicated that both 9,10-di-*o*- (**4**) and 9,10-di-*m*-tolylphenanthrene (**5**), like (**2**) and (**3**), are able to exist as *syn* [(**4a**), (**5a**)] and *anti* [(**4b**), (**5b**)] isomers. It would thus be interesting to investigate whether the separate isomers could be isolated, especially for (**5a**) and (**5b**), since several attempts[5] to obtain separate isomers of 1,8-diarylnaphthalenes with substituent(s) at the *meta*-position(s) of the phenyl ring(s) have failed due to the low barriers of rotation at room temperature.



(**4**) R^1 = H, R^2 = Me
(**5**) R^1 = Me, R^2 = H

Results and Discussion

Syntheses.—Syntheses of (**4**) and (**5**) could be achieved by the route in the Scheme. Thus treatment of phenanthraquinone with *o*- and *m*-tolylmagnesium chloride gave the respective 1,2-diols (**6**) and (**7**) after hydrolysis. Both (**6**) and (**7**) could exist in the *meso* form and as a pair of enantiomers. As the addition of the two Grignard reagents is expected to be stepwise, steric consideration would suggest an *anti* addition to give the respective pairs of enantiomeric *trans*-diols (**6**) and (**7**). A similar observation was earlier reported for some related systems.[6] The presence of only one diastereoisomeric form was further confirmed by sharp m.p.s and ^{1}H n.m.r. spectra of (**6**) and (**7**) which showed sharp singlets at δ 2.70 and 2.23 respectively for the methyl protons. The ketones (**8**) and (**9**) were obtained *via* pinacol rearrangements of (**6**) and (**7**) respectively. The usual aryl pinacol rearrangement conditions (iodine in refluxing acetic acid) were ineffective in the transformation of (**6**) into (**8**) presumably due to steric hindrance of the *o*-methyl groups. Even the addition of sulphuric acid as a catalyst required rather a long reaction time. This rearrangement, however, was readily achieved in 88% yield of (**8**) in trifluoroacetic acid at room temperature (30—45 min). The ^{1}H n.m.r. spectrum of (**8**) showed two singlets (*ca.* 1:1) for the methyl protons, with a

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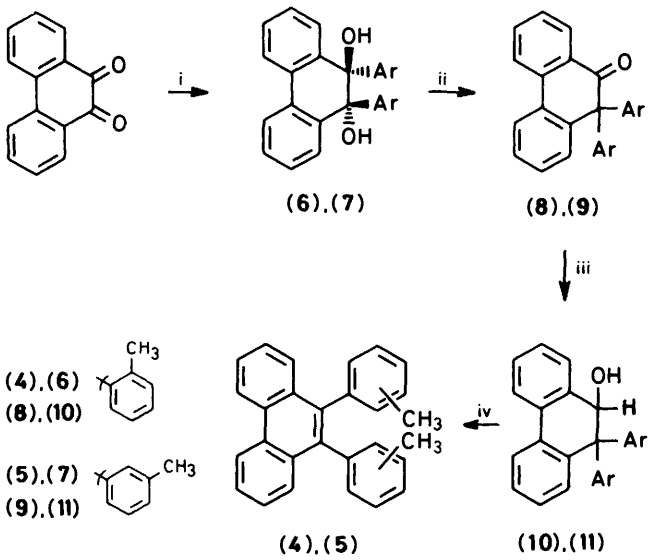
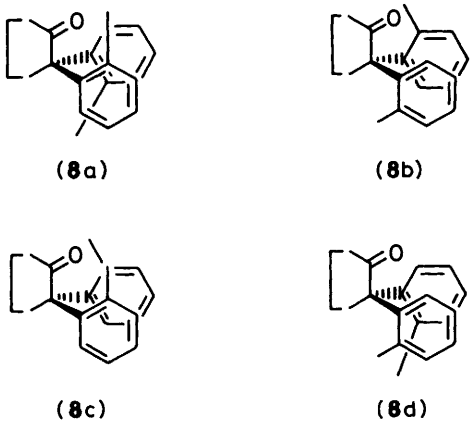


Scheme. *Reagents:* i, $CH_3C_6H_4MgCl$; ii, CF_3CO_2H; iii, $LiAlH_4$; iv, I_2–AcOH

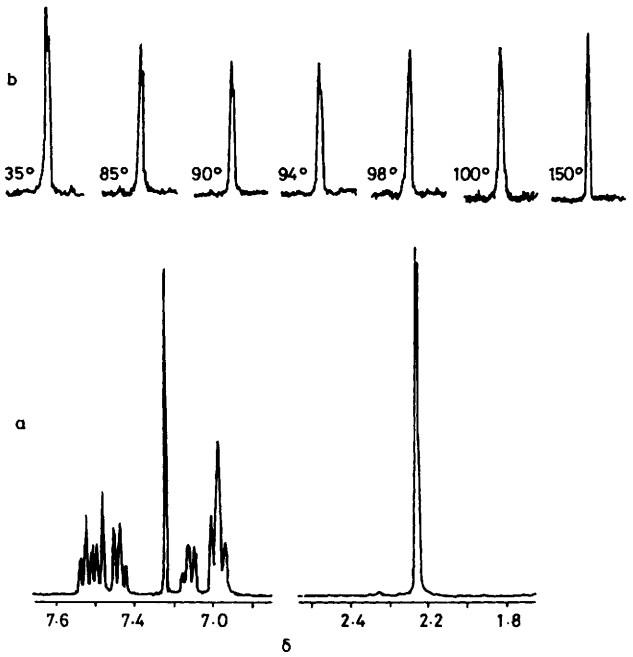


large difference in chemical shifts (Δν 30 Hz), at δ 1.75 and 2.08, respectively. This is obviously not consistent with a fast equilibrium among all the four conformers of (**8**), namely *anti* (**8a**), *anti* (**8b**), *syn* (**8c**), and *syn* (**8d**), which would only lead to an averaged signal for the methyl protons. Although the presence of a non-interconverting mixture of *syn* (**8c** and **d**) would show two different methyl signals, the likelihood of two non-identical isomers having a 1:1 population distribution in such a crowded molecule seems rather remote. A more promising possibility is that the 1:1 doublet for (**8**) arises from a single structure (**8a**) [and its enantiomer (**8b**)] where the two methyl groups occupy different environments, and with interconversion of enantiomers which is slow on the n.m.r. timescale. The methyl group in close proximity to the carbonyl function would thus be deshielded due to the anisotropic effect and appear relatively downfield at δ 1.75. The ^1H n.m.r. spectrum of (**9**), however, showed only one sharp singlet at δ 2.22 expected of interconverting *syn* and *anti* isomers of (**9**) due to much lower conformational barriers with the methyl protons at the *meta*-positions. Reduction of the ketones (**8**) and (**9**) with $LiAlH_4$ followed by further acid-catalysed rearrangements then afforded the respective 9,10-ditolylphenanthrenes (**4**) and (**5**).

Conformational Analyses.—The ^1H n.m.r. spectrum of the product mixture of (**4**) isolated from the reaction showed two sharp singlets for the methyl protons at δ 1.94 and 2.04, respectively, in the ratio of 1.0:2.7. T.l.c. studies of the mixture showed two components with very similar R_F values but attempts using column chromatography failed to separate them. A g.c.m.s. analysis, however, showed complete separation and clearly supported the presence of the two isomers (**4a** and **b**) with the molecular ion at *m/z* 358 as the base peak, thus confirming the general structure of (**4**). Fractional recrystallization from carbon tetrachloride successfully separated only the less soluble isomer, m.p. >250 °C (decomp.), with the methyl protons appearing at δ 2.04 in its ^1H n.m.r. spectrum. Unambiguous assignments of *syn* (**4a**) and *anti* (**4b**) could possibly be achieved only with *X*-ray crystallographic determination. We have, however, assigned the ^1H n.m.r. signals at δ 2.04 and 1.94 to methyl protons of *syn* (**4a**) and *anti* (**4b**) respectively based on the following observation. Suitable molecular models have indicated that the *anti*-methyl groups in (**4b**) are expected to be slightly more shielded by the opposite aryl rings; the *anti* (**3b**) compound reported by Roberts[4] also showed a more upfield methyl signal than the corresponding *syn* (**3a**). The chemical shifts of the methyl protons of 9,10-di-*m*-tolylphenanthrenes (**5a** and **b**) (see below), with their methyl groups in an environment more similar to those in (**4a**) than (**4b**), are similar to that of the methyl signal of *syn* (**4a**) and appear further downfield.

Kinetic studies (first-order kinetics is assumed) of the conformational interconversion (**4a**) $\rightleftharpoons$ (**4b**) were carried out starting with a sample of *syn* (**4a**). The change in concentration of (**4a**) was followed by ^1H n.m.r. A solution of (**4a**) in $CDCl_3$ at room temperature showed no conversion of (**4a**) into (**4b**) after several days. Variable-temperature ^1H n.m.r. studies (hexachlorobutadiene as solvent) further revealed that the conversion (**4a**) ⟶ (**4b**) is extremely slow even at 150 °C as was evident by no appreciable concentration of (**4b**) observed (indicated by no appearance of the methyl peak at δ 1.94) in the temperature range studied. Significant changes were observed when the interconversion was studied at 196 °C. The equilibrium of the conformational interconversion (**4a**) $\rightleftharpoons$ (**4b**) at this temperature was, however, observed only after >20 h. In these studies, a solution of (**4a**) in hexachlorobutadiene in an n.m.r. tube was immersed in refluxing ethylene glycol (b.p. 196—197 °C). The n.m.r tube was then removed and plunged into ice–water to freeze the interconversion processes at suitable time intervals before the equilibrium. The relative concentrations of (**4a** and **b**) were then estimated from the integration of the signals at δ 2.04 and 1.94, respectively, in the ^1H n.m.r. spectra. Taking (**4a**) $\rightleftharpoons$ (**4b**) as an example of opposing first-order reactions, the equilibrium constant, [(**4b**)]/[(**4a**)], was found to be 0.52 which corresponds to a free energy difference between the isomers of 2.59 kJ mol^{-1}. The rate constant of the conversion (**4a**) ⟶ (**4b**) was found to be 2.42×10^{-5} s^{-1} [that of (**4b**) ⟶ (**4a**) was 4.70×10^{-5} s^{-1}]. The barrier to rotation ($\Delta G^{\ddagger}$) for (**4a**) ⟶ (**4b**) was thus calculated to be 158.1 kJ mol^{-1} [that of (**4b**) ⟶ (**4a**) was 155.5 kJ mol^{-1}].

Our results have unexpectedly indicated that the *syn* (**4a**) is the more stable isomer, in contrast to that observed for 1,8-di-*o*-tolylnaphthalenes where the *anti* (**3b**) is more stable than the *syn* isomer (**3a**).[4] The more interesting result is the much higher barriers of rotation observed for the conformational interconversion (**4a**) $\rightleftharpoons$ (**4b**) compared with those reported for the interconversion processes (**2a**) $\rightleftharpoons$ (**2b**)[3] and (**3a**) $\rightleftharpoons$ (**3b**).[4] We believe that this is due to the additional steric interaction caused by the protons on C(1) and C(8) of the phenanthrene nucleus when free rotation of the aryl rings is required to achieve the interconversion (**4a**) $\rightleftharpoons$ (**4b**). The large activation energies observed would also suggest that the barriers to rotation in the interconversion of the *meta* isomers (**5a**) $\rightleftharpoons$ (**5b**) should be much higher than those reported for *meta*-substituted 1,8-diarylnaphthalenes.[5]



a, ^{1}H N.m.r. spectrum of 9,10-di-*m*-tolylphenanthrene (**5**) ($CDCl_3$; 250 MHz). The double doublet at δ 8.795 for 4,5-H is not shown. b, ^{1}H N.m.r. spectra of the methyl protons of 9,10-di-*m*-tolylphenanthrene (**5**) at different temperatures ([$^2H_5$]nitrobenzene; 90 MHz)

The ^{1}H n.m.r. spectrum (90 MHz) of (**5**) (isolated from the reaction) in [^{2}H]chloroform at room temperature showed a rather broad signal (half-height linewidth 2.5 Hz) for the methyl protons at δ 2.24. In addition, only a singlet at δ 21.3 p.p.m. was observed for the methyl carbons in the ^{13}C n.m.r. spectrum (22.5 MHz) of (**5**). An obvious possible explanation would be the result of a fast equilibrium (**5a**) ⇌ (**5b**) with very low barriers of rotation at room temperature similar to the results observed for *meta*-substituted 1,8-diarylnaphthalenes.[5] Low-temperature ^{1}H n.m.r. studies ([$^2H_2$]dichloromethane as solvent) indicated no further broadening of the methyl signal even at −60 °C. High-temperature ^{1}H n.m.r. studies (hexachlorobutadiene as solvent), however, showed a relatively much sharper singlet at δ 2.24 for the methyl protons at 150 °C. The latter observation is consistent with the possibility that the methyl groups of (**5a** and **b**) have very similar chemical shifts and the broad signal observed at room temperature was due to the presence of a non-interconverting mixture of the two isomers. This seemed to be further supported by a rather broad m.p. (225—230 °C) observed for (**5**). Confirmation of the existence of the two isomers, however, came from a ^{1}H n.m.r. spectrum of (**5**) determined in [^{2}H]chloroform at 250 MHz. The methyl signals were resolved at δ 2.259 and 2.252 respectively with a relative intensity of 1.5:1.4 (Figure, a). ^{1}H N.m.r. spectra (90 MHz) of (**5**) were then recorded using a series of solvents to investigate whether solvent shifts would separate the component signals for the methyl protons. While all the spectra determined in [$^2H_2$]dichloromethane, [$^2H_6$]benzene, [$^2H_6$]acetone, hexachlorobutadiene, and [$^2H_5$]pyridine only showed a broad signal (half-height linewidth 2.0—3.5 Hz) for the methyl protons at δ *ca.* 2.2, the solubility of (**5**) in more polar solvents such as [$^2H_4$]methanol and [$^2H_6$]dimethyl sulphoxide was too low to give satisfactory ^{1}H n.m.r. spectra. However, two clearly resolved (relative peak height *ca.* 1.0:1.2) methyl signals at δ 2.22 and 2.25 respectively were observed at 35 °C using [$^2H_5$]nitrobenzene as solvent (Figure, b). Variable-temperature ^{1}H n.m.r. (90 MHz) studies using the same solvent have clearly shown that the two methyl peaks at δ 2.22 and 2.25 collapse to a single peak at their average position at higher temperatures (Figure, b). This is indicative of a true fluxional process, consistent with (**5a**) ⇌ (**5b**), rather than one conformer going to a different conformer. When the sample was cooled to 35 °C after the high-temperature studies, the methyl signals were again resolved and the original spectrum at 35 °C was observed. Application of the Gutowsky–Holm equation (coalescence temperature method)[7] to the separation of the methyl groups (Δν 2.7 Hz; T_c 371 K) gave $\Delta G_c^{\ddagger}$ (the transition-state free energy at coalescence) 85 kJ mol^{-1} as the barrier to rotation of the aryl rings in (**5**) (*syn* ⇌ *anti*). This is clearly a much higher barrier compared with those observed for several *meta*-substituted 1,8-diarylnaphthalenes.[5] ^{1}H N.m.r. studies of these molecules indicated that $\Delta G^{\ddagger}$ for rotation is *ca.* 65 kJ mol^{-1}, which corresponds to rather rapid rotation in solution at room temperature.[5]

Despite considerable efforts, we failed to separate the two isomers of (**5**) using various chromatographic methods and fractional recrystallization. Although direct isolation of the isomers in our hands was not successful, the results from the conformational studies have undoubtedly given the evidence that restricted free rotation of the aryl rings in 9,10-di-*m*-tolylphenanthrene (**5**) was observed at room temperature.

Experimental

All m.p.s were determined using a Sybron–Thermolyne MP-12615 apparatus and are uncorrected. ^{1}H N.m.r. spectra were determined in $CDCl_3$ (unless otherwise stated) on a Perkin-Elmer R32 (90 MHz) or a Bruker WM-250 (250 MHz) spectrometer. Variable-temperature ^{1}H n.m.r. studies were carried out on a Perkin-Elmer R32 (90 MHz) spectrometer. ^{13}C N.m.r. spectra were recorded on a JEOL FX90Q 22.5 MHz spectrometer. All chemical shifts are reported in p.p.m. downfield from tetramethylsilane used as internal standard. I.r. spectra were recorded on a Pye–Unicam SP1000 or a Perkin-Elmer 1310 spectrometer. Mass spectra were determined on a VG Micromass 7035 spectrometer at 70 eV using elecron impact. Relative intensities are given in parentheses. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

9,10-*Bis*-(2-*methylphenyl*)-9,10-*dihydroxy*-9,10-*dihydrophenanthrene* (**6**).—*o*-Tolylmagnesium chloride was first prepared by treating *o*-chlorotoluene (18.99 g, 150 mmol) with magnesium (4.01 g, 150 mmol) in dry THF (200 ml) using 1,2-dibromoethane as an initiator. The mixture was heated at reflux under nitrogen until a homogeneous solution was obtained. The Grignard reagent was cooled and 9,10-phenanthraquinone (8.33 g, 40 mmol) was then added in batches. The mixture was heated under reflux for 12 h, cooled in an ice–water bath, and hydrolysed with dilute HCl. The mixture was extracted with methylene dichloride, and the extract washed with water and aqueous $NaHCO_3$ solution, dried, and evaporated to dryness. Recrystallization from chloroform yielded crystals of (**6**) (3.99 g, 26%), m.p. 158—159 °C (Found: C, 86.0; H, 6.4. $C_{28}H_{24}O_2$ requires C, 85.7; H, 6.2%); $\nu_{max.}$ 3 500 (OH), 1 600, 1 490, 1 452, 1 440, 1 335, 1 295, 1 270, 1 162, 1 110, 1 058, 1 046, 910, 845, 760, 742, 730, and 650 cm^{-1}; δ_H (90 MHz) 2.70 (6 H, s, Me), 6.6—7.5 (14 H, m, Ar), and 7.94 (2 H, br d, *J* 8 Hz, 4-, 5-H); *m/z* 392 (M^+, 6%), 377 (13), 271 (70), 181 (11), and 119 (100).

9,10-*Bis*-(3-*methylphenyl*)-9,10-*dihydroxy*-9,10-*dihydrophenanthrene* (**7**).—This was prepared by the reaction between *m*-tolylmagnesium chloride and phenanthraquinone using the method described for (**6**). Recrystallization of the crude product from chloroform yielded crystals of (**7**) (3.72 g, 24%), m.p. 169—170 °C (Found: C, 85.8; H, 6.3%); $\nu_{max.}$ 3 550 (OH),

1 602, 1 486, 1 450, 1 320, 1 224, 1 180, 1 140, 1 062, 1 050, 936, 808, 778, 750, and 705 cm^{-1}; δ_H (90 MHz) 2.23 (6 H, s, Me), 6.9—7.6 (14 H, m, Ar), and 7.87 (2 H, br d, *J* 8 Hz, 4-, 5-H); *m/z* 392 (M^+, 13%), 271 (68), 181 (13), 149 (10), and 119 (100).

9,9-*Bis*-(2-*methylphenyl*)-9,10-*dihydrophenanthren*-10-*one* (**8**).—A sample of (**6**) (3.54 g, 9 mmol) was dissolved in trifluoroacetic acid (15 ml) and the solution stirred at room temperature for 45 min. Saturated aqueous $NaHCO_3$ solution was added gradually until no effervescence was observed. The mixture was extracted with methylene dichloride, washed, and evaporated. Recrystallization of the crude product from chloroform gave crystals of (**8**) (2.97 g, 88%), m.p. 195—199 °C (Found: C, 89.9; H, 6.2. $C_{28}H_{22}O$ requires C, 89.8; H, 5.9%); $\nu_{max.}$ 1 698 (CO), 1 600, 1 482, 1 450, 1 265, 875, 850, 780, 770, 752, 740, 725, and 648 cm^{-1}; δ_H (90 MHz) 1.75, 2.08 (total 6 H, s, Me), and 6.4—8.0 (16 H, m, Ar); *m/z* 374 (M^+, 72%), 356 (100), 331 (24), 269 (22), 266 (47), 255 (56), 254 (20), 253 (39), 252 (29), and 239 (34).

9,9-*Bis*-(2-*methylphenyl*)-9,10-*dihydrophenanthren*-10-*one* (**9**).—This was prepared by the rearrangement of diol (**7**) using the method described for (**8**). Recrystallization of the crude product from chloroform yielded crystals of (**9**) (2.69 g, 80%), m.p. 204—209 °C (Found: C, 90.0; H, 6.2%); $\nu_{max.}$ 1 682 (CO), 1 600, 1 490, 1 455, 1 270, 788, 775, 760, 735, and 710 cm^{-1}; δ_H (90 MHz) 2.22 (6 H, s, Me) and 6.6—8.1 (16 H, m, Ar); *m/z* 374 (M^+, 100%), 359 (24), 346 (95), 331 (45), 255 (87), and 239 (47).

9,9-*Bis*-(2-*methylphenyl*)-9,10-*dihydrophenanthren*-10-*ol* (**10**).—A solution of (**8**) (3.30 g, 8.8 mmol) in dry THF was added to a suspension of $LiAlH_4$ (589 mg, 15.5 mmol) in dry THF (75 ml). The mixture was heated under reflux for 1.5 h under N_2. The mixture was then decomposed by ethyl acetate, followed by addition of dilute HCl. The hydrolysed mixture was extracted with methylene dichloride, and the extract was washed, dried, and evaporated to yield the alcohol (**10**) (3.12 g, 94%), m.p. 113—119 °C (from cyclohexane) (Found: C, 89.8; H, 6.6. $C_{28}H_{24}O$ requires C, 89.3; H, 6.4%); $\nu_{max.}$ 3 500 (OH), 1 600, 1 490, 1 450, 1 380, 1 075, 1 020, 910, and 745 cm^{-1}; δ_H (90 MHz) 1.51, 1.90 (total 6 H, s, Me), 5.70 (1 H, s, 10-H), and 6.5—8.7 (16 H, m, Ar); *m/z* 376 (M^+, 11%), 358 (80), 265 (20), and 181 (100).

9,9-*Bis*-(3-*methylphenyl*)-9,10-*dihydrophenanthren*-10-*ol* (**11**).—This was prepared by the reduction of (**9**) using the method described for (**10**). Recrystallization of the crude product from cyclohexane gave the alcohol (**11**) (2.68 g, 90%), m.p. 101—106 °C (Found: C, 89.8; H, 6.6%); $\nu_{max.}$ 3 520 (OH), 1 595, 1 476, 1 440, 1 180, 1 090, 1 062, 760, 732, and 700 cm^{-1}; δ_H (90 MHz) 2.14, 2.30 (total 6 H, s, Me), 5.74 (1 H, s, 10-H), and 6.8—7.9 (16 H, m, Ar); *m/z* 376 (M^+, 22%), 358 (100), and 181 (95).

9,10-*Di*-o-*tolylphenanthrene* (**4**).—The alcohol (**10**) (3.20 g, 8.5 mmol) was dissolved in a 0.3% acetic acid solution of iodine (125 ml) and heated under reflux for 1.5 h. The mixture was cooled, and then decomposed by an ethanolic solution of sodium hydrogensulphite. The crystalline precipitate was collected by filtration to yield (**4**) (2.48 g, 81%). Repeated recrystallization from carbon tetrachloride yielded *syn* (**4a**) as the less soluble isomer, m.p. >250 °C (decomp.) (Found: C, 93.8; H, 6.2. $C_{28}H_{22}$ requires C, 93.8; H, 6.2%); $\nu_{max.}$ 1 480, 1 442, 1 415, 1 375, 1 108, 1 040, 758, 748, 724, and 626 cm^{-1}; δ_H (90 MHz) 2.04 (6 H, s, Me), 6.9—7.8 (14 H, m, Ar), and 8.82 (2 H, br d, *J* 8 Hz, 4-, 5-H); *m/z* 358 (M^+, 100%), 343 (18), 267 (31), 265 (50), and 252 (20).

9,10-*Di*-m-*tolylphenanthrene* (**5**).—This was prepared by the acid-catalysed rearrangement of (**11**) using the method described for (**4**). Chromatography on silica gel with methylene dichloride–hexane (1 : 1) as eluant yielded (**5**) (2.69 g, 88%), m.p. 225—230 °C (Found: C, 93.9; H, 6.2%); $\nu_{max.}$ 1 490, 1 450, 1 420, 1 092, 1 075, 1 040, 1 000, 824, 795, 765, 730, and 710 cm^{-1}; δ_H (90 MHz) 2.24 (6 H, s, Me), 6.9—7.8 (14 H, m, Ar), and 8.76 (2 H, dd, *J* 2 and 8 Hz, 4-, 5-H); δ_H (250 MHz) 2.252, 2.259 (total 6 H, s, Me), 6.93—7.68 (14 H, m, Ar), and 8.795 (2 H, dd, *J* 2 and 8 Hz, 4-, 5-H); *m/z* 358 (M^+, 100%), 343 (29), 328 (16), 327 (20), 326 (19), 258 (18), 257 (13), 256 (13), and 252 (21).

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