Structural Studies on Phenanthro[9,10-*e*]pyrene and its 9,10-Dihydro-Derivative: Dependence of Chemical Shift on Degree of Planarity of and Buttressing Effect in the Polycyclic Aromatic Compounds

Yee-Hing Lai,* Slau-Gek Ang, Hwee-Chze Li and Siew-Ying Wong
Department of Chemistry, National University of Singapore, Kent Ridge, Republic of Singapore 0511

The first example of a transannular reaction of a *syn*-[2.2]metacyclophane derivative *via* photochemical iodination has been employed in the preparation of 9,10-dihydrophenanthro[9,10-*e*]-pyrene (**2**). The structural studies of **2** and the phenanthropyrene **1** were carried out by 1D and 2D NMR spectroscopic analyses. Qualitative correlation between tilting of the fused moieties and the change in deshielding effect was observed by probing the chemical shifts of H3 and H1′ (H6 and H8′). Buttressing effects resulting from the steric interaction of H3 and H1′ (H6 and H8′), although differing in magnitudes for the two groups of protons (H3→H2→H1→H10 and H1′→H2′→H3′→H4′), seem to transmit evenly among those on the same moiety according to a simple additivity rule.

Theoretical and experimental studies[1,2] of polycyclic aromatic compounds (PACs) have shown no signs of decreasing after many years of investigation. As far as the structural study on PACs is concerned, spectral data[3,4] are available for many of the reported systems. The structural assignments are, however, not always easy as the spectra are basically similar for each class of PAC. The use of 1D ^{1}H NMR spectroscopy in the structural study[5,7] of the higher benzenoids is usually complicated by the 'near equivalence' of all the aromatic protons and the complexity of the spectrum arising from multiple couplings among different types of protons. A 2D ^{1}H NMR study would in principal be expected to simplify significantly the assignments of aromatic protons. There is, however, no extensive documentation of 2D ^{1}H NMR spectroscopic data of PACs to allow correlation studies.

A synthetic route to specifically-substituted pyrenes was earlier reported.[6] This was modified and led successfully to the synthesis of the phenanthropyrene **1**[9] and the structural study of this model PAC by 2D ^{1}H NMR spectroscopy is of special interest. We were also interested in its 9,10-dihydro derivative **2** for the following reasons.* Molecular models of **1** and **2** show that the degree of planarity differs appreciably going from **1** to **2** (see later discussion). Among all the aromatic protons in **1** and **2**, the interaction between H3 and H1′ (or H6 and H8′) is expected to be most dependent on a change in the geometry of the molecule. Probing the chemical shifts of these protons in ^{1}H NMR spectra would provide useful information in the structural studies of other related PACs and their dihydro- or polyhydro-derivatives, the structures of which tend to deviate from planarity owing to the saturated bridges.

Results and Discussion

Synthesis of **2**.—Earlier reports showed that tetrahydropyrene (**5**) could be prepared from transannular reactions of *anti*-[2.2]metacyclophane (**4**) *via* electrophilic nitration,[10] free-radical bromination[11] or photochemical iodination.[12] A more convenient method[13,14] using pyridinium hydrobromide perbromide (py·HBr_3) was recently employed in the synthesis of a series of di- and poly-hydropyrene derivatives, such as **7** from **6**. All the [2.2]metacyclophane systems studied so far, however, have the *anti* conformation. *syn*-[2.2]Metacyclo(9,10)phenanthrenophane (**3**)[9] was the only known system which does not isomerize readily to the *anti* conformer. It was thus synthetically challenging to study whether similar reagents could be employed to achieve transannular reactions in a *syn*-[2.2]metacyclophane derivative resulting in the ring closure in **3** to afford **2**.

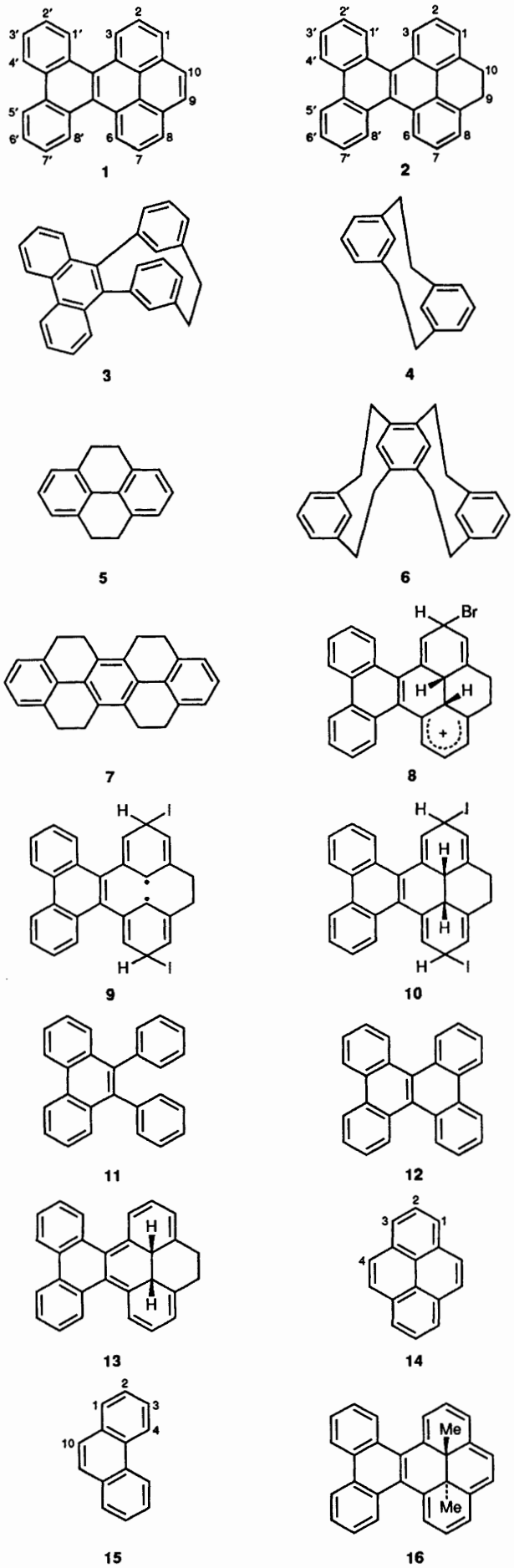
Treatment of **3** with py·HBr_3 under reported conditions[13,14] led to recovery of the starting material only. Under even more drastic conditions, there was no noticeable consumption of **3** nor detectable evolution of hydrogen bromide. The 'near parallel' arrangement of the benzene rings in the *syn* conformation is apparently less favourable than the stepped stereochemistry in the *anti* conformation to allow intramolecular electrophilic ring closure; thus, **3** failed to undergo the electrophilic transannular reaction to afford **8**. Irradiation of a solution of **3** and iodine in cyclohexane with light at 210 nm, however, achieved the cyclization affording **2** in good yields (60–70%). ^{1}H NMR and mass spectroscopic analyses showed that the isolated product contained trace amounts of **1**. The formation of the latter in the reaction was not unexpected because iodine present could also oxidise **2** to **1**. Attempts to remove completely the latter by column chromatography or recrystallization proved to be unsuccessful. The presence of trace amounts of **1**, however, did not affect the structural analysis of **2** (see later discussion).

Tetraphenylethene is converted photochemically to 9,10-diphenylphenanthrene (**11**) in the presence of an oxidant but the second cyclization to form dibenzotriphenylene (**12**) does not occur even on prolonged irradiation,[15] obviously for steric reasons. Irradiation of a solution of **5** in the absence of iodine but without the exclusion of oxygen indicated no photochromic behaviour nor the formation of **2**, consistent with the observation described for **11**. Thus, the formation of **2** in our attempt was not a result of the oxidation of **13** by iodine. Instead it is consistent with the formation[12] of iodinated diradicals **9** which perhaps is the driving force for the cyclization process to afford **10** followed by dehydroiodination–aromatization to give **2**.

Structural Studies on **1** *and* **2**.—The electronic spectra of **1** and **2** are presented in Fig. 1. A significant blue-shift is observed going from **1** to **2**. This could be due to a slightly more extended conjugated system in **1**. However, another contributing factor could be due to more significant puckering of the phenanthrene and dihydropyrene moieties in **2** resulting in even less conjugation. More evidence of this could be found in the following NMR spectroscopic study.

The presence of a C_2 symmetry in **1** clearly simplifies the

* The numbering system in compound **2** is not IUPAC systematic numbering but is employed for clarity.



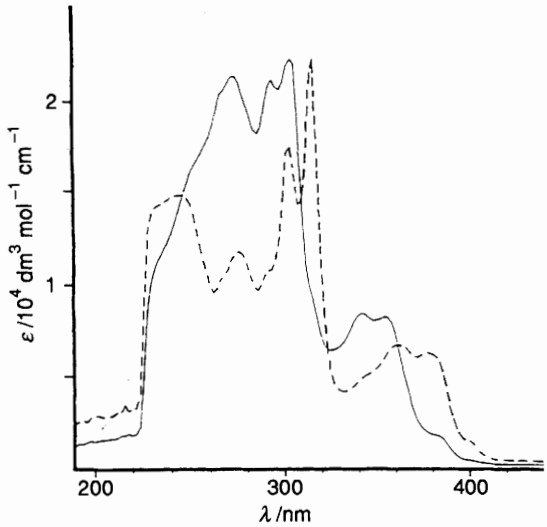


Fig. 1 UV absorption spectra of PACs **1** [– – – –] and **2** [——] ([PAC] = 1.41 × 10^{-4} mol dm^{-3} in dichloromethane)

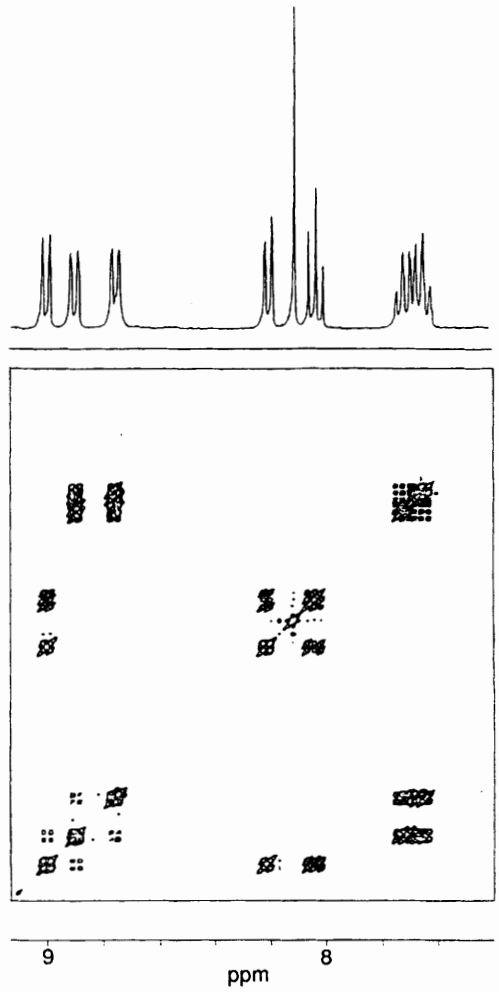


Fig. 2 1D and COSY ^{1}H NMR spectra ($CDCl_3$; 300 MHz) of the phenanthropyrene **2**

^{1}H NMR studies and the following discussion will only centre on protons of one-half of the molecule. The 1D and selected 2D ^{1}H NMR spectra of **1** are presented in Fig. 2. H10 could be readily assigned to the singlet at δ 8.12. Based on the argument of significant steric crowding which leads to a deshielding effect, the signals between δ 8.7 and 9.1 should correspond to H3, H1′ and H4′. The ABX system in the molecule is H2-H1-H3; thus the doublet of doublets at δ 8.22 and the triplet at δ 8.05 could be

Table 1 A comparison of proton chemical shifts in **1**, **2**, **14** and **15**

Compound	δ(ppm)							
1	H1 8.22	H2 8.05	H3 9.02	H10 8.12	H1′ 8.92	H2′ 7.66	H3′ 7.73	H4′ 8.77
2	H1 7.46	H2 7.56	H3 8.55	H10 3.30	H1′ 8.75	H2′ 7.62	H3′ 7.67	H4′ 8.70
14	H1 7.90	H2 7.75	H1 7.90	H4 7.80	—	—	—	—
15	H3 7.61	H2 7.57	H1 7.86	—	H1 7.86	H2 7.57	H3 7.61	H4 8.65
Δδ(A)[a]	0.32	0.30	1.12	0.32	—	—	—	—
Δδ(B)[a]	—	—	—	—	1.06	0.09	0.12	0.12
Δδ(C)[a]	−0.15	−0.01	0.69	—	0.89	0.05	0.06	0.05
Δδ(D)[a]	0.76	0.49 (0.31)[b]	0.47 (0.43)[b]	—	0.17	0.04	0.06	0.07

[a] The chemical shift difference between the pair of corresponding protons in (A), **1** and **14**; (B), **1** and **15**; (C), **2** and **15**; and (D), **1** and **2**. Minus values indicate upfield shift. [b] Corrected values, taking into account the shifts of these protons going from a pyrene to a phenanthrene moiety.

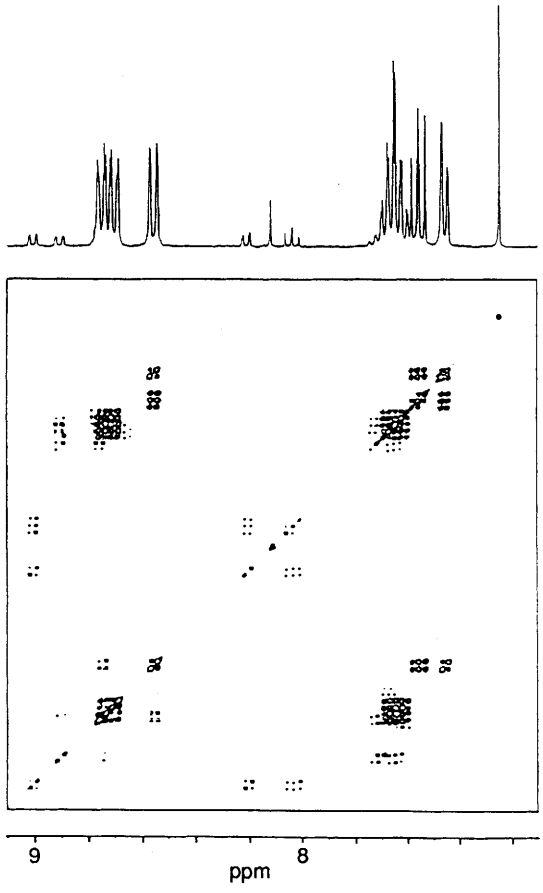
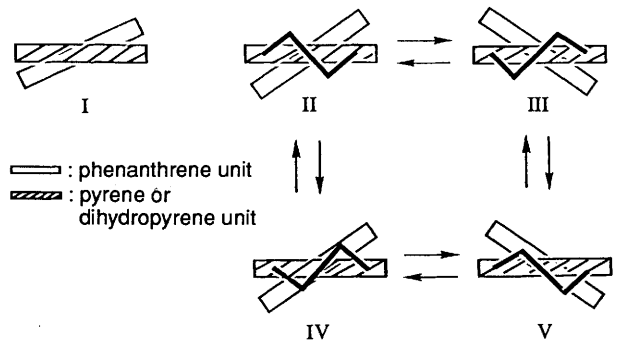


Fig. 3 ID and COSY ^{1}H NMR spectra ($CDCl_3$; 300 MHz) of the dihydrophenanthropyrene **2** (trace amount of **1** was present)

assigned to H1 and H2, respectively. The two sets of doublets of triplets centred at δ 7.73 and 7.66 should correspond to H2′ and H3′ although respective assignments were not possible in the 1D spectrum. From the COSY spectrum, the signal at δ 9.02 was assigned to H3 due to a strong coupling observed between this signal and that of H2. A through-space scalar (spin–spin) coupling expected between H3 and H1′ owing to their close proximity in turn confirmed the doublet at δ 8.92 as H1′. This is consistent with the fact that the steric interaction betwen H3 and H1′ is expected to be more severe than that between H4′ and H5′, and the doublet of doublets at δ 8.77 was then assigned to H4′. Although couplings among H1′, H2′, H3′ and H4′ were all evident, the COSY spectrum could not distinguish H2′ and H3′. An NOE experiment carried out with irradiation at H1′ to confirm the through-space interaction of H1′ and H3, however, also led to enhancement of the doublet of triplets at δ 7.66 which should then correspond to H2′. With H3′ observed as the signal centred at δ 7.73, all protons in **1** were then successfully assigned (Table 1). The 1D and 2D ^{1}H NMR spectra of **2** are presented in Fig. 3. Similar arguments as used above could be employed to assign all the protons in **2** (Table 1). The only major difference was that the two sets of doublets of triplets expected of H2′ and H3′ overlapped to appear as a doublet of quintets. H10 was observed at δ 3.30, a significant downfield shift compared to normal benzylic methylene protons obviously due to additional deshielding of H10 by the adjacent benzene ring. The observed singlet suggests a rapid conformational equilibrium between all four twisted conformers **II**–**V**. Molecular models of 'bowed'



conformers of **2** with both H1′ and H8′ on the same side with respect to the dihydropyrene unit indicate high angle and steric strains and thus preference for these conformations is considered unlikely. Another interesting feature is that the largest upfield shift [Δδ(D); Table 1] is observed for H1 going from **1** to **2** due to reduction of the 9,10-bond in **2** eliminating the deshielding effect of the ring concerned on H1.

The chemical shifts of aromatic protons observed obviously would depend on several factors, such as the sp characters of the carbon atoms to which the protons are bonded, the local anisotropy of each 'benzene' ring and steric repulsion among adjacent protons and those in close proximity. The ^{1}H NMR spectrum of **12** was reported[6] but not completely resolved and analysed; thus, chemical shifts of protons in pyrene (**14**)[3] and phenanthrene (**15**)[3] are used for a qualitative comparison with those observed in **1** and **2**. The 4,5- and 9,10-bonds of pyrene and phenanthrene are known to exhibit high double-bond character. Fusion of the two moieties in **1** would result in a slightly twisted 'double bond' but the sp characters of the other carbon atoms are expected to be similar to those in **1** and **2**, respectively. The study of diatropicity of the macro ring in **16**[16] indicates that effects of benzannelation and/or conjugation of the phenanthrene moiety result in a significant decrease in ring current of the macro ring. Similarly, effects of benzannelation and/or conjugation would be expected to reduce the 'local aromaticity' in each benzene ring of both moieties in **1** resulting in upfield shifts of the aromatic protons compared with those in **14** or **15**. Data from Δδ(A) and Δδ(B) in Table 1, however, indicate that all protons in **1** are deshielded compared with

those in **14** or **15**. Except for H1′ and H3 which are in closer proximity and thus deshielded most significantly, the other protons on the pyrene and phenanthrene moieties in **1** are consistently shifted downfield to *ca.* 0.3 and 0.1 ppm, respectively. A reasonable explanation for these results observed in **1** is that of a novel buttressing effect. Severe steric interaction between H3 and H1′ causes secondary crowding between H3 and H2 (H1′ and H2′), and so on. This 'propagation' is less effective (0.1 ppm deshielding) in the phenanthrene moiety owing to an opposing effect resulting from steric interaction between H4′ and H5′. On the other hand, the steric interaction between H1 and H10 is less severe and the buttressing effect could be experienced more significantly in the pyrene moiety leading to stronger deshielding (0.3 ppm). Our argument is further supported by the data summarized in $\Delta\delta$(C), Table 1. The further puckering of the two moieties going from **1** to **2** (going from **I** to **II**/**III**) certainly reduces the buttressing effect (steric interaction/deshielding) significantly. The deshielding (*ca* 0.05 ppm) of protons on the phenanthrene moiety in **2** from those in phenanthrene **15** still shows a moderate steric interaction but that of H2 on the dihydropyrene moiety (H1 is no longer a good probe) indicates a negligible effect. The latter is probably a result of further release of steric strain due to absence of H1–H10 interaction.

Using the chemical shifts of H3 and H1′ in **1** and **2** as the probes [$\Delta\delta$(D); Table 1], corrected values have to be used in the correlation. The dihydropyrene moiety in **2** resembles that of phenanthrene and it is known[3] that a large shift (0.18 ppm) is observed for H2 going from pyrene to phenanthrene. From our analysis (Table 1), deshielding of H3 [1.12 ppm; $\Delta\delta$(A)] and H1′ [1.06 ppm; $\Delta\delta$(B)] in **1** are comparable when compared with chemical shifts of reference protons in **14** and **15**. There is, however, a significant difference observed in **2** [0.69 ppm for H3, 0.89 ppm for H1′; $\Delta\delta$(C)]. In fact the change for H3 is much larger than that for H1′. This is reflected more directly in the comparison of $\Delta\delta$(D) values (0.43 ppm for H3, 0.17 ppm for H1′). In addition, H2 also shows a much larger $\Delta\delta$(D) value (0.31 ppm) than those (*ca.* 0.06 ppm) of H2′, H3′ and H4′. The above is consistent with our argument that although the protons on the pyrene moiety in **1** experience a more significant buttressing effect, the corresponding protons on the dihydropyrene moiety in **2** in turn are expected to show a more significant decrease in steric deshielding due to greater tilting of the two fused moieties and the absence of the H1–H10 interaction.

Conclusions

We have shown that 2D ^{1}H NMR spectroscopy allows a more direct analysis/assignments of the aromatic protons in higher PACs. Probing the chemical shifts of protons experiencing the most significant steric interaction in the PACs and their dihydro- or polyhydro-derivatives may, in addition to indicating qualitatively the degree of tilting of the fused moieties, also reflect the change in steric crowding in each moiety. From the centres of the most significant steric interaction, the buttressing effects [refer to $\Delta\delta$(A) and $\Delta\delta$(B) values] propagate along the two moieties at different magnitudes which result, however, in seemingly very similar deshielding of all protons in each moiety. This simple additivity rule may be valuable in future structural studies on other related or higher PACs.

Experimental

The ^{1}H NMR spectra were determined using $CDCl_3$ on a Bruker ACF-300 spectrometer. All the chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard. The 1D and 2D spectra were collected with 16 K and 1 K × 1 K data points, respectively. *J* Values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1310 spectrometer. UV–VIS spectra were determined in dichloromethane on a Hewlett Packard 8052A Diode-array spectrometer. Mass spectra were determined on a VG Micromass 7035 spectrometer at 70 eV, electron impact ionization being used.

Phenanthro[9,10-e]*pyrene** (**1**).—This compound was prepared according to literature procedure.[9] δ_H 9.02 (2 H, d, *J* 7.9, 3- and 6-H), 8.92 (2 H, d, *J* 8.0, 1′- and 8′-H), 8.78 (2 H, dd, *J* 7.8, 1.3, 4′- and 5′-H), 8.22 (2 H, dd, *J* 7.6, 0.6, 1- and 8-H), 8.12 (2 H, s, 9- and 10-H), 8.05 (2 H, t, *J* 7.8, 2- and 7-H), 7.73 (2 H, dt, *J* 7.5, 1.3, 3′- and 6′-H), 7.66 (2 H, dt, *J* 7.6, 1.3, 2′- and 7′-H). Other spectral data of **1** have been reported.[9,17]

9,10-*Dihydrophenanthro*[9,10-e]*pyrene** (**2**).—A mixture of **5**[9] (90 mg, 0.25 mmol), iodine crystals (67 mg, 0.26 mmol) and excess $NaHCO_3$ (0.70 g) in cyclohexane (40 cm^3) was irradiated on a Rayonet photochemical reactor (Model RPR-100) at 254 nm for 24 h. The mixture was washed with dilute aqueous $Na_2S_2O_3$ solution and extracted with diethyl ether, dried and evaporated. The crude product was chromatographed on silica gel with hexane as eluent to afford pale yellow solids of **2** (60 mg, 67%; with trace amount of **1**). Recrystallization from ethanol–dichloromethane gave pale yellow crystals of **2** (with trace amount of **1**), m.p. 265–268 °C (Found: M^+, 354.1421. $C_{28}H_{18}$ requires *M*, 354.1409). λ_{max}/nm (dichloromethane) 272 (ε 21 600 $dm^3\ mol^{-1}\ cm^{-1}$), 294 (ε 21 400), 304 (ε 22 600), 342 (ε 8470), 354 (ε 8250) and 382 (ε 1640); δ_H 8.75 (2 H, dd, *J* 7.7, 1.3, 1′- and 8′-H), 8.70 (2 H, dd, *J* 7.6, 1.7, 4′- and 5′-H), 8.55 (2 H, d, *J* 8.3, 3- and 6-H), 7.67 (2 H, dt, *J* 7.3, 1.6, 3′- and 6′-H), 7.62 (2 H, dt, *J* 7.4, 1.6, 2′- and 7′-H), 7.56 (2 H, t, *J* 8.0, 2- and 7-H), 7.46 (2 H, d, *J* 7.9, 1- and 8-H) and 3.30 (4 H, s, CH_2); *m*/*z* 354 (100%), 353 (28), 252 (26), 351 (22), 350 (19), 175 (18), 174 (16), 169 (17), 168 (17) and 162 (11).

Acknowledgements

This work was supported by the National University of Singapore (RP 860606).

* Refer to footnote, p. 1315, for comment on the numbering system used here.

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Paper 2/00987K
Received 25*th February* 1992
Accepted 6*th April* 1992