A cyclophane route to acenaphthyleno[1,2-*e*]pyrene. Relative bathochromic shifts (colour changes) in a series of 1,2-diaryl-acenaphthylenes

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1,2-Bis(3-methylphenyl)acenaphthylene 16 has been synthesized from acenaphthenequinone and 3-chlorotoluene. Bromination of 16 followed by an intramolecular cyclization with sodium sulfide affords the *anti* thiacyclophanene 18. Ring contraction reactions of 18 lead to the isolation of acenaphthylenopyrene 9 directly, presumably *via* valence isomerization of cyclophanediene 22 followed by oxidation of dihydropyrene 23. Photochemical desulfurization of 18 results in the isolation of the acenaphthylenodihydropyrene 28 *via* valence isomerization of cyclophanene 26 followed by oxidation of tetrahydropyrene 27. An increase in the degree of conjugation in going from 24 to 16 to 18 is evidenced by a visual colour change from orange to orange–red to red and a significant bathochromic shift in the electronic absorption in the range 400–450 nm. A bathochromic shift is also observed in going from 28 to 9, consistent with a more extended conjugated system in the latter. Complete assignment of the protons in 9 and 28 is achieved on the basis of ^{1}H COSY and NOESY spectra. There is no observable through-space scalar coupling between H-1 and H-14 in 9 but a strong NOE between them is evident. A tilting of the dihydropyrene moiety in 28 due to the stereochemical demand of its ethylene bridge results in an upfield shift of its H-1 and H-14 signals relative to those in 9.

Introduction

Fluoranthene **1**[1] and its derivatives form an important family of nonalternant polycyclic aromatic hydrocarbons.[2] Some of these compounds have been shown to exhibit mutagenic and carcinogenic activities.[3] Among the many synthetic routes for the preparation of polycyclic aromatic compounds,[4] some are directed specifically towards fluoranthenes.[5] These compounds exhibit unique electronic behaviour[2e] and serve as good models for modelling and NMR spectroscopic studies.[6]

The synthesis and/or isolation of benzo- **2**[7] and **3**,[8] naphtho- **4**–**7**[9] and dibenzofluoranthene **8**[10] has been documented. Missing in the series before this work was the acenaphthylenopyrene **9** and thus its synthesis was of considerable interest. A general synthesis of substituted pyrenes using dithiacyclophanes as a precursor has been reported.[11] The pyrene moiety in **9** could thus be constructed *via* this cyclophane route.

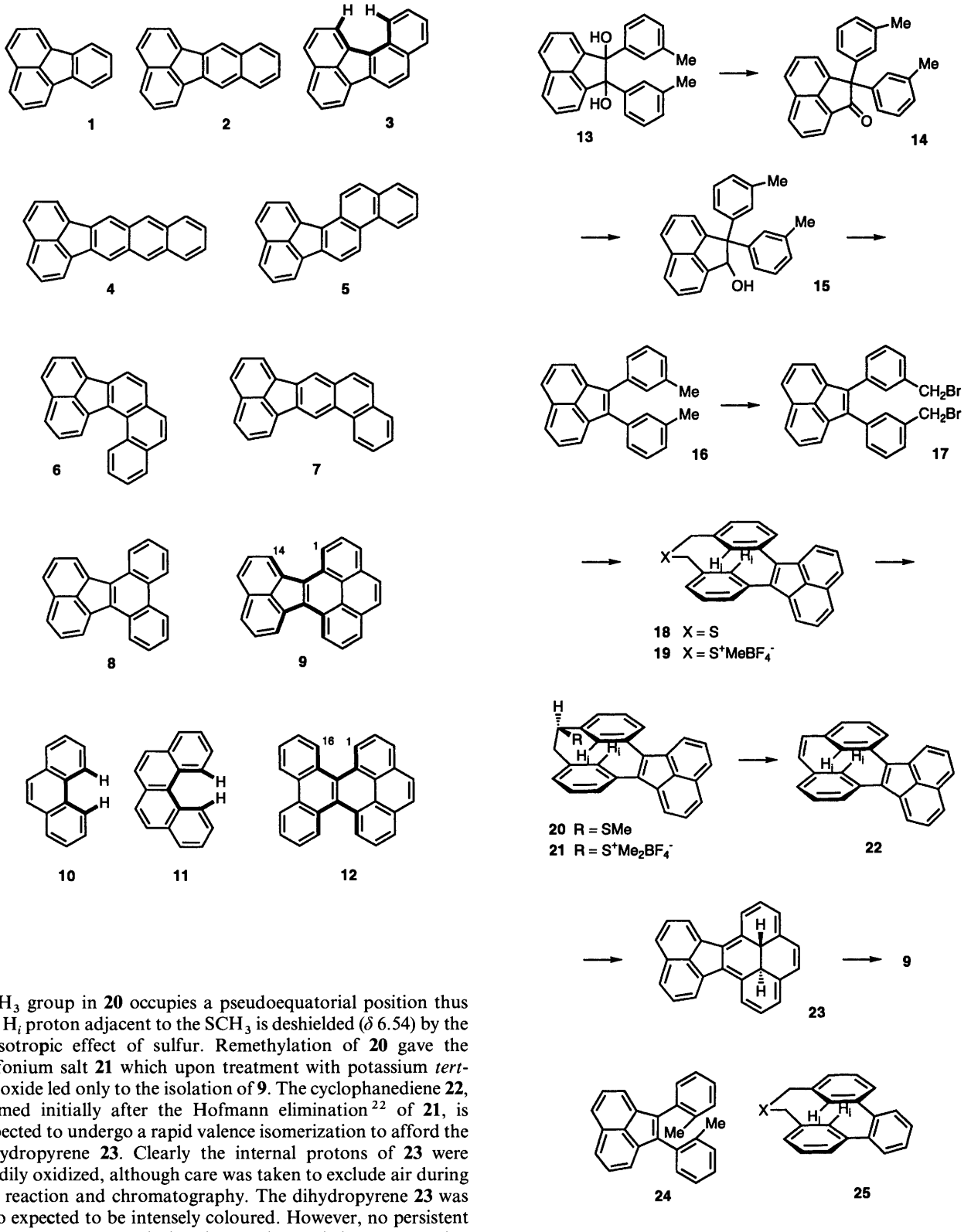
Two of the interesting aspects in ^{1}H NMR analysis of polycyclic aromatic hydrocarbons are the significant deshielding[11] of protons located in a bay region and their potential through-space long-range couplings.[12] These are dependent on a rigid molecular structure and close proximity of the protons concerned. Through-space couplings of the type in phenanthrene **10** and benzo[*c*]phenanthrene **11** are the most commonly observed.[12a–c] Such a coupling between H-1 and H-16 in **12**—an alternant polycyclic aromatic compound with a molecular structure similar to that of **9**—has in fact been reported.[13] The structure of benzo[*j*]fluoranthene **3** was found to be coplanar from completely-optimized molecular geometry calculations[14] indicating that the bay region interactions in **9** are likely to be less significant than those in **12**. A ^{1}H NMR analysis of **9** would thus be of considerable interest to determine whether a long range coupling of benzo[*j*]fluoranthene-type between H-1 and H-14 in **9** would be observed experimentally.

Results and discussion

Synthesis

The synthesis of 1,2-bis(3-methylphenyl)acenaphthylene **16** from acenaphthenequinone and 3-chlorotoluene was achieved by a route, *via* **13**–**15**, similar to that reported for the synthesis of 1,2-bis(2-methylphenyl)acenaphthylene **24**.[15] The optimized overall yield of **16** was about 52%. Acid catalysed dehydration of **13** afforded the ketone **14**, mp 154–156 °C—some 7 °C higher than the reported value.[16] The structure of **14** was, however, confirmed by spectroscopic analyses and a correct elemental analysis. The diarylacenaphthylene **16** was isolated as an orange–red oil. Its ^{1}H NMR spectrum showed only one singlet at δ 2.25 at room temperature. Dynamic ^{1}H NMR studies showed no resolution of methyl signals down to a temperature of −80 °C. This is consistent with an unrestricted rotation of the aryl rings in **16** presumably due to a relatively low conformational barrier compared to that of **24** which exists in its *anti* and *syn* conformers at room temperature.[15] A less likely assumption is that the methyl protons of the *anti* and *syn* conformers of **16** have identical chemical shifts.[17]

Bromination of **16** with NBS gave the dibromide **17** isolated as yellow crystals. An intramolecular cyclization of **17** with sodium sulfide under high dilution conditions[18] afforded the thiacyclophanene **18**. The *anti* stereochemistry of **18** was confirmed by its internal H_i protons which appeared at δ 6.31 as a singlet shielded by the opposite benzene rings in its ^{1}H NMR spectrum. The reported chemical shift of the internal H_i protons of *anti* **25** is δ 6.08.[19] Treatment of **18** with dimethoxycarbonium fluoroborate[20] gave the sulfonium salt **19**. A Stevens rearrangement[21] of **19** by treating it with potassium *tert*-butoxide afforded orange crystals of **20**. Its ^{1}H NMR spectrum shows two shielded singlets at δ 6.54 and 5.94, respectively, for the H_i protons, consistent with the *anti* stereochemistry. The large chemical shift difference, however, indicates that the



SCH_3 group in **20** occupies a pseudoequatorial position thus the H_i proton adjacent to the SCH_3 is deshielded (δ 6.54) by the anisotropic effect of sulfur. Remethylation of **20** gave the sulfonium salt **21** which upon treatment with potassium *tert*-butoxide led only to the isolation of **9**. The cyclophanediene **22**, formed initially after the Hofmann elimination[22] of **21**, is expected to undergo a rapid valence isomerization to afford the dihydropyrene **23**. Clearly the internal protons of **23** were readily oxidized, although care was taken to exclude air during the reaction and chromatography. The dihydropyrene **23** was also expected to be intensely coloured. However, no persistent colour was observed during the reaction and chromatography. This is clearly consistent with a high reactivity (oxidation) of the internal protons in a dihydropyrene system as observed in previous work.[23]

An attempt was made to prepare the cyclophanene **26** from desulfurization of **18**. Irradiation of a solution of **18** in trimethylphosphite with UV light at 254 nm resulted in both desulfurization and oxidation to afford acenaphthylenodihydropyrene **28**. It is clear that desulfurization of **18** to afford **26** was followed by photochemical conversion to the tetrahydropyrene **27**. The internal methine protons of **27** were then readily oxidized to form the aromatic system **28**. As expected, further oxidation of **28** with DDQ afforded the polycyclic benzenoid system **9**.

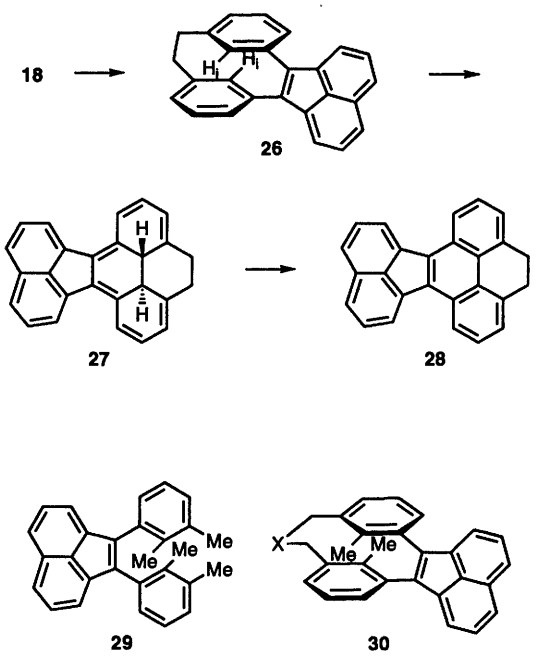
Electronic behaviour in acenaphthylene derivatives

Going from the parent acenaphthylene[24] to 1,2-diarylacenaphthylenes **16**, **24**, **29** to *anti* thiacyclophanene **18**, an interesting visual observation is that the colour of the compound changes from yellow to orange to red seemingly corresponding to an increase in conjugation. In the electronic spectra of these compounds, a common absorption is a strong band at about 230 nm. Their absorptions between 400 and 500 nm—the spectral range chiefly responsible for the observed chromatic colours in these compounds—indeed show a bathochromic shift in that order (Table 1). The two aryl rings in **24** and **29**, due to the steric demand of the *ortho* methyl groups, are expected to be tilted at a large angle with respect to the molecular plane of

Table 1 Major UV–VIS absorption (300–500 nm range) of acenaphthylene and several of its 3,4-diaryl derivatives ([cpd] = 1.5×10^{-4} mol dm^{-3}; spectra taken in cyclohexane)

Compound	Colour	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	Dihedral angle[b]/°
Acenaphthylene[a]	Pale yellow	323	10 800	—
16	Orange–red	422	9 900	41.6/42.0
24	Orange	412	9 100	55.5
29	Orange	414	10 700	53.4/53.9
18	Red	443	8 800	35.0/45.4
30	Orange–red	438	9 900	44.6/50.2

[a] Spectrum taken in hexane; see ref. 10(*a*). [b] Based on the optimized structure derived from MM2 calculations.



the acenaphthylene moiety resulting in minimum conjugation between the benzene and acenaphthylene rings. When the methyl groups are relocated at the *meta* positions in **16**, the two benzene rings could now tilt at a smaller angle allowing a higher degree of conjugation. With the introduction of the bridge in **18**, the molecule is 'locked' in a stepwise conformation allowing better interaction (due to molecular rigidity) between the π-systems in the benzene and acenaphthylene rings. Interestingly, the thiacyclophanene **18** is red in colour but its dimethyl derivative **30**[25] is orange–red with a relatively shorter λ_{max} (Table 1). The spatially larger methyl groups in **30** are expected to result in an inward sliding[26] of their stepped benzene rings. This change in molecular geometry would slightly increase the tilting angle between the benzene and acenaphthylene rings consistent with a shift to shorter absorption wavelength in going from **18** to **30**.

In order to support the above qualitative correlation between the electronic spectra and the degree of conjugation, MM2[27] calculations were performed to determine the dihedral angle between a benzene ring and the acenaphthylene moiety in the energy-minimized structure of the molecules concerned (Table 1). The optimized structures for **16**, **24** and **29** are symmetrical while those of **18** and **30** have the two benzene rings in each molecule tilted at significantly different dihedral angles with respect to the acenaphthylene unit. Going from **24**(**29**) to **16** to **18** results in a decrease in the dihedral angle(s) (an increase in conjugation) and is consistent with the observed bathochromic shifts in that order. Although the calculated dihedral angles in **16** are smaller than those in **30**, the former is expected to undergo unrestricted rotation in solution. The rigid stereochemistry of the π-systems in **30** should account for its absorption at longer wavelength.

Unlike the series of reported fluoranthene derivatives[5,7–10] which are yellow or orange in colour, both **9** and **28** form bright red crystals. This is reflected in their almost identical absorptions in the range 300–500 nm (Fig. 1) which are shifted significantly from those in the range 250–400 nm for fluoranthene.[28] The shift is a result of both conjugation and annelation effects.[29] The electronic spectra of **9** and **28** in the range 300–450 nm, however, are similar to those of several acenaphthofluoranthenes.[2e] A significant red shift (*e.g.* 326 nm→346 nm) is observed going from **28** to **9** (Fig. 1). This is likely a result of the relatively greater extended conjugation in **9**. Another contributing factor could be a more significant puckering of the acenaphthylene and dihydropyrene moieties in **28** due to the stereochemical demand of the ethylene bridge, thus resulting in less conjugation between the two aromatic π-systems.

Proton NMR analysis

The presence of a C_2 symmetry in the structure of acenaphthyleno[1,2-*e*]pyrene **9** should in principle simplify the assignment of its protons in the ^{1}H NMR spectrum (Table 2). Both the H-1, 2, 3 and H-12, 13, 14 protons, however, appear as a set of AB_2 system (Fig. 2). The triplet at δ 8.09 is assigned to H-2 based on the following argument. The H-2 (δ 7.75)[30] in pyrene is considerably more deshielded than H-4 (δ 7.48)[31] in acenaphthylene. H-1 and H-14 in the bay region of **9** are expected to be the most deshielded. Using H-4 (a singlet at δ 8.07) as a reference, there was no NOE [Fig. 2(*b*)] observed between H-4 and the doublet at δ 7.89 which was correlated to the triplet at δ 7.70 [Fig. 2(*a*)]. Lastly, the H-1–H-4 protons in **9** have very similar chemical shifts ($\Delta\delta \leqslant 0.05$ ppm) to the corresponding protons in **12**.[13]

A through-space scalar (spin–spin) coupling between H-1 and H-16 in **12** was clearly observed in its ^{1}H COSY spectrum.[13] A similar long-range coupling between H-1 and H-14 in **9** was, however, not evident [Fig. 2(*a*)] confirming qualitatively that the bay region steric interactions in **9** are far less significant than those in **12**. The through-space distance between H-1 and H-14 in **9** is still expected to be $\leqslant 5$ Å since a significant NOE between these protons was observed in their ^{1}H NOESY spectrum [Fig. 2(*b*)].

The chemical shifts of H-12 and H-13 remain practically unchanged in going from **9** to **28** while the changes in H-2 and H-3 are consistent with a decrease in the effect of deshielding in going from a pyrene to a dihydropyrene system. H-1 of pyrene[30] and that of phenanthrene[32] have almost identical chemical shifts. Going from **9** to **28**, there is, however, an upfield shift of H-1 ($\Delta\delta$ = 0.35 ppm) and H-14 ($\Delta\delta$ = 0.11 ppm). This, we believe, is the result of a tilting of the dihydropyrene system in **28** due to the stereochemical demand of its ethylene bridge as mentioned earlier. Such a change in molecular geometry would further release the steric interactions in the bay region in **28** and place the H-1 and H-14 in locations of relatively less significant deshielding effects of the acenapthylene and dihydropyrene systems, respectively.

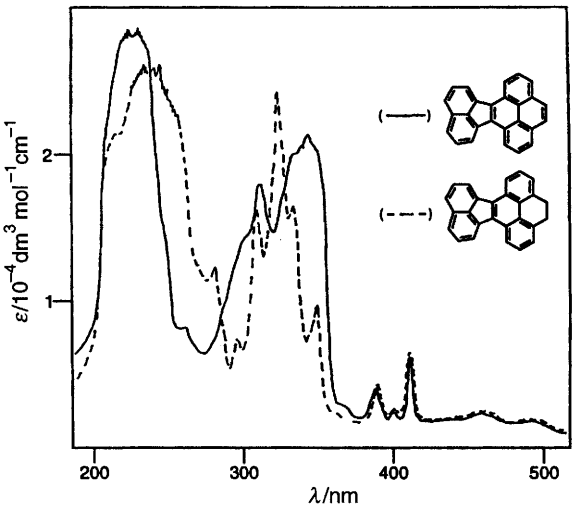


Fig. 1 Electronic spectra of **9** (——) and **28** (- - - -) ([cpd] = 1 × 10^{-5} mol dm^{-3} in cyclohexane)

Table 2 Proton chemical shifts (δ) in **9** and **28**

Compound	H-1	H-2	H-3	H-4	H-12	H-13	H-14
9	9.07	8.09	8.18	8.07	7.89	7.70	8.65
28	8.72	7.66	7.45	3.34	7.88	7.70	8.54

Experimental

All melting points were determined by using a Sybron-Thermolyne MP-12615 melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined in $CDCl_3$ on a JEOL FX90Q (90 MHz) or a Bruker WM250 (250 MHz) Fourier Transform spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer. UV–VIS spectra were determined in cyclohexane on a Shimadzu UV240 Graphicord spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV using electron impact methods. Relative intensities are given in parentheses. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

1,2-Bis(3-methylphenyl)acenaphthene-1,2-diol 13[33]

This was isolated, after recrystallization from benzene–hexane, as colourless crystals (56%), mp 152–154 °C (lit.,[16] 152.3–153.3 °C) (Found: C, 85.2; H, 6.0%. $C_{26}H_{22}O_2$ requires C, 85.2; H, 6.05%); δ_H 6.9–8.0 (14 H, m, ArH), 2.32 (6 H, s, CH_3), 2.19 (2 H, br s, OH); λ_{max}(KBr) 3530 (O–H), 1600, 1480, 1325, 1230, 1180, 1130, 1110, 1085, 1040, 990, 930, 860, 795, 780, 750, 700, 680, 675 cm^{-1}; *m*/*z* 366 (M^+, 18%), 348 (100), 305 (39), 289 (23), 247 (40), 246 (27), 245 (82), 229 (46), 119 (35).

2,2-Bis(3-methylphenyl)acenaphthen-1-one 14[33]

Recrystallization of a chromatographed sample from benzene–hexane afforded colourless crystals (97%) of **15**, mp 154–156 °C (lit.,[16] 147.5–148.5 °C) (Found: C, 89.4; H, 5.6%. $C_{26}H_{20}O_2$ requires C, 89.6; H, 5.8%); δ_H 7.0–8.1 (14 H, m, ArH), 2.21 (6 H, s, CH_3); λ_{max}(KBr) 1720 (C=O), 1595, 1480, 1450, 1420, 1355, 1335, 1250, 1210, 1160, 1110, 1090, 990, 970, 920, 830, 775, 750, 730, 695 cm^{-1}; *m*/*z* 348 (M^+, 100%), 318 (27), 305 (67), 292 (38), 229 (67), 144 (23).

2,2-Bis(3-methylphenyl)acenaphthen-1-ol 15[33]

Compound **15** was isolated as a colourless oil (99%) after chromatography on silica gel (Found: M^+, 350.1685. $C_{26}H_{22}O$ requires *M*, 350.1671); δ_H 6.8–7.8 (14 H, m, ArH), 6.11 (1 H, s, OH), 2.19, 2.23 (total 6 H, s, CH_3); λ_{max}(KBr) 3300 (O–H), 1595, 1480, 1165, 1110, 1050, 960, 820, 780, 735, 700 cm^{-1}; *m*/*z* 350 (M^+, 95%), 332 (100), 320 (23), 301 (20), 245 (85), 228 (33), 215 (26).

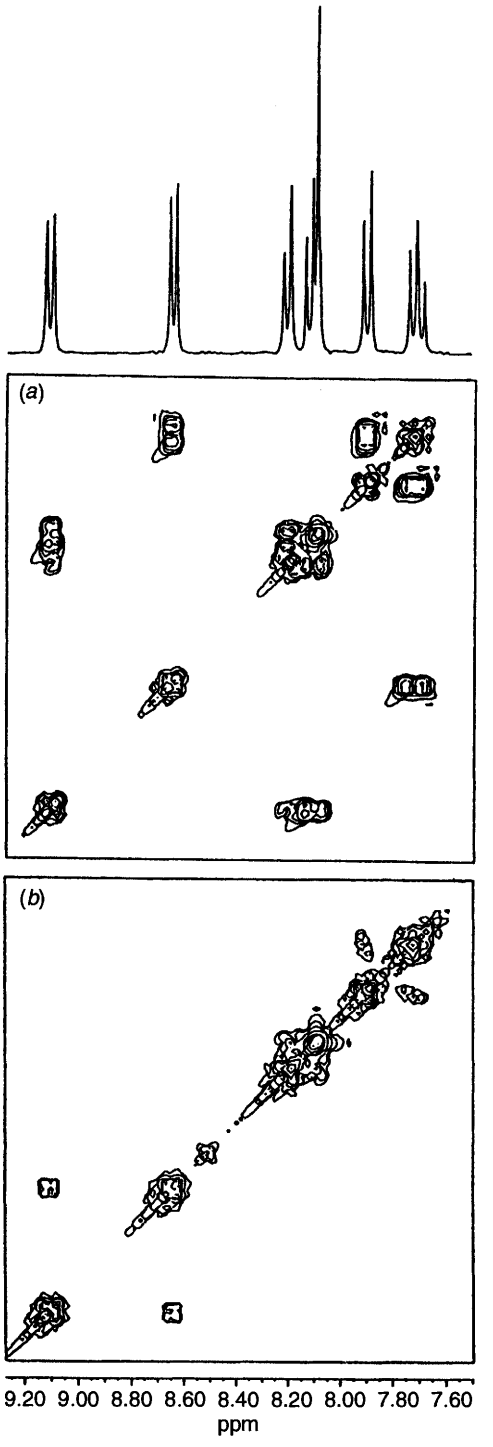


Fig. 2 (*a*) ^{1}H COSY and (*b*) ^{1}H NOESY spectrum of **9**

1,2-Bis(3-methylphenyl)acenaphthylene 16[33]

The reaction product mixture was chromatographed on silica gel to give **16** as an orange–red oil (98%) (Found: M^+, 332.1547. $C_{26}H_{20}$ requires *M*, 332.1565); δ_H 7.0–7.4 (14 H, m, ArH), 2.25 (6 H, s, CH_3); λ_{max}(KBr) 1590, 1460, 1420, 1210, 1080, 1025, 900, 875, 815, 785, 760, 695 cm^{-1}; *m*/*z* 332 (M^+, 100%), 317 (12), 316 (19), 302 (20), 152 (20), 150 (10).

1,2-Bis(3-bromomethylphenyl)acenaphthylene 17

N-Bromosuccinimide (0.68 g, 3.82 mmol) and a catalytic amount of benzoyl peroxide were added to a solution of **16** (0.50 g, 1.50 mmol) in carbon tetrachloride (100 cm^3). The mixture was brought to reflux under the irradiation of a 200 W tungsten lamp for 2.5 h. The reaction mixture was filtered, and the filtrate was washed successively with aqueous $NaHCO_3$ and water, dried and evaporated. The residue was chromatographed on silica gel using hexane–dichloromethane (3:1) as eluent to yield **17** (0.52 g, 67%). Recrystallization from benzene–hexane gave bright yellow crystals of **17**, mp 160–162 °C (Found: C, 63.4; H, 3.8%. $C_{26}H_{18}Br_2$ requires C, 63.7; H, 3.7%); δ_H 7.4–7.9 (14 H, m, ArH), 4.45 (4 H, s, CH_2); λ_{max}(KBr) 1595, 1575, 1475, 1460, 1420, 1225, 1205, 1180, 1110, 1080, 1035, 905, 815, 800, 760, 700, 680 cm^{-1}; *m/z* 488 (50%), 411 (15), 409 (16), 330 (49), 329 (48), 316 (38), 315 (37), 314 (27), 313 (31), 157 (41).

***anti*-Acenaphthyleno[1,2-*a*]-10-thia[2.3]metacyclophan-1-ene 18**

A solution of **17** (0.90 g, 1.84 mmol) in benzene (200 cm^3) and a solution of 95% sodium sulfide nonahydrate (0.47 g, 1.84 mmol) in water (30 cm^3) and ethanol (170 cm^3) were prepared. These solutions, in separate rotaflow dropping funnels, were added at the same rate into vigorously stirred 95% ethanol (1 dm^3) under nitrogen at room temperature. After the addition, the mixture was stirred for another 15 h. The bulk of the solvent was removed under reduced pressure and the product was extracted into dichloromethane. The organic layer was washed, dried and evaporated. The residue was chromatographed on silica gel using hexane–dichloromethane (2:1) as eluent to give the cyclophanene **18** (0.35 g, 52%). Recrystallization from benzene–hexane gave bright red crystals of **18**, mp 220–222 °C (Found: C, 86.2; H, 4.8%. $C_{26}H_{16}S$ requires C, 86.15; H, 5.0%); δ_H 7.4–8.0 (12 H, m, ArH), 6.31 (2 H, s, 8-, 17-H), 3.63 (4 H, s, CH_2); λ_{max}(KBr) 1590, 1470, 1450, 1420, 1210, 1175, 1150, 1105, 920, 810, 800, 760, 695 cm^{-1}; *m/z* 362 (M^+, 100%), 329 (18), 328 (40), 327 (37), 314 (34), 313 (35), 156 (24).

***anti*-Acenaphthyleno[1,2-*a*]-9-methylsulfanyl[2.3]metacyclophan-1-ene 20**

A solution of **18** (50 mg, 0.14 mmol) in dichloromethane (5 cm^3) was added to a stirred suspension of dimethoxycarbonium fluoroborate (48 mg, 0.30 mmol) in dichloromethane (5 cm^3) at −30 °C under nitrogen. The mixture was then stirred without cooling for 2 h. Ethyl acetate (10 cm^3) was then added and the mixture stirred for another 2 h. The yellow solids were filtered to give **19**: 49 mg (75%). This salt was then directly suspended in dry THF (10 cm^3) under nitrogen and potassium *tert*-butoxide (17 mg, 0.15 mmol) was added. The reaction mixture was then stirred at room temperature for 1 h. HCl (1 mol dm^{-3}) was added and the mixture was extracted with dichloromethane, washed, dried and evaporated. The crude product was chromatographed on silica gel using dichloromethane–hexane (1:3) as eluent to yield orange crystals of **20** (22 mg, 39%), mp 201–203 °C (Found: M^+, 376.1284. $C_{27}H_{20}S$ requires *M*, 376.1286); δ_H 7.1–8.7 (12 H, m, ArH), 6.54, 6.94 (total 2 H, s, 8-, 16-H), 4.42 (1 H, dd, *J* 3.4, 3.7, 1-H), 3.31 (1 H, dd, *J* 3.4, 3.2, 2-H), 2.59 (1 H, dd, *J* 3.7, 3.2, 2′-H), 1.97 (3 H, s, SCH_3); λ_{max}(KBr) 3020, 2895, 1420, 812, 790, 760, 718, 706 cm^{-1}; *m/z* 372 (M^+, 12%), 329 (26), 328 (76), 327 (89), 326 (100), 163 (36), 162 (30).

Acenaphthyleno[1,2-*l*]-4,5-dihydropyrene 28

A solution of **18** (0.14 g, 0.39 mmol) in trimethylphosphite (80 cm^3) placed in a quartz cell was irradiated with light at 254 nm for 12 h. The reaction mixture was washed with 1 mol dm^{-3} HCl and the product was extracted into hexane. The organic layer was washed, dried and evaporated. The residue was chromatographed on silica gel using hexane–dichloromethane (4:1) as eluent to give **28** (32 mg, 28%). Recrystallization from hexane gave red crystals of **28**, mp 198–200 °C (Found: C, 94.8; H, 4.8%. $C_{26}H_{16}$ requires C, 95.1; H, 4.9%); δ_H 8.72 (2 H, d, *J* 8.5, 1-, 8-H), 8.54 (2 H, d, *J* 7.0, 9-, 14-H), 7.88 (2 H, d, *J* 8.1, 11-, 12-H), 7.70 (2 H, dd, *J* 7.0, 8.1, 10-, 13-H), 7.66 (2 H, d, *J* 7.1, 3-, 6-H), 7.45 (2 H, dd, *J* 7.1, 8.5, 2-, 7-H), 3.34 (4 H, s, CH_2); δ_C 138.2, 136.5, 134.0, 129.5, 129.0, 128.8, 128.0, 127.5, 127.0, 125.0, 124.9, 122.7, 30.0; λ_{max}(KBr) 1460, 1420, 1270, 1160, 1120, 810, 780, 755 cm^{-1}; *m/z* 328 (M^+, 100%), 327 (40), 326 (64), 324 (22), 164 (15), 163 (28), 161 (10).

Acenaphthyleno[1,2-*e*]pyrene 9

(*a*) Remethylation of **20** (30 mg, 0.08 mmol) was achieved as described for **19**. The salt **21** obtained was treated with potassium *tert*-butoxide and stirred for 1 h at room temperature. HCl (1 mol dm^{-3}) was added and the mixture was extracted with dichloromethane. The crude product was chromatographed on silica gel using cyclohexane as eluent. Recrystallization from hexane gave red crystals of **9** (6 mg, 23%), mp 243–245 °C (Found: C, 95.5; H, 4.3%. $C_{26}H_{14}$ requires C, 95.7; H, 4.3%); δ_H 9.07 (2 H, d, *J* 8.5, 1-, 8-H), 8.65 (2 H, d, *J* 7.0, 9-, 14-H), 8.18 (2 H, d, *J* 7.4, 3-,6-H), 8.09 (2 H, dd, *J* 8.5, 7.4, 2-, 7-H), 8.07 (2 H, s, 4-, 5-H), 7.89 (2 H, d, *J* 8.1, 11-, 12-H), 7.70 (2 H, dd, *J* 7.0, 8.1, 10-, 13-H); δ_C 138.1, 134.4, 132.2, 132.0, 129.5, 129.0, 128.0, 127.8, 127.6, 126.3, 125.3, 125.0, 122.1; λ_{max}(KBr) 3020, 2920, 1440, 1290, 1220, 1160, 1030, 820, 710 cm^{-1}; *m/z* 326 (M^+, 100%), 323 (25), 163 (33), 161 (30).

(*b*) DDQ (136 mg, 0.60 mmol) was added to a solution of **28** (100 mg, 0.30 mmol) in benzene (20 cm^3) under nitrogen. The reaction mixture was then brought to reflux for 2 h and cooled to room temperature. The product was extracted into dichloromethane, washed, dried and evaporated. Recrystallization from hexane gave red crystals of **9** (51 mg, 51%), identical to the previously obtained sample.

Acknowledgements

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References

1 T. Sasaki, K. Kanematsu and T. Hiramatsu, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1213.

2 (*a*) E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London, 1964, vols. 1 and 2; (*b*) J. R. Dias, *Handbook of Polycyclic Hydrocarbons*, Elsevier, Amsterdam, 1988; (*c*) W. C. Herndon, *Tetrahedron*, 1982, **38**, 1389; (*d*) D. Plavsic, S. Nikolic and N. Trinajstic, *J. Mol. Struct.*, 1992, **96**, 213; (*e*) B. F. Plummer, L. K. Steffen, T. L. Braley, W. G. Reese, K. Zych, G. Van Dyke and B. Tulley, *J. Am. Chem. Soc.*, 1993, **115**, 11542; (*f*) I. Murata, *Pure Appl. Chem.*, 1993, **65**, 97; (*g*) M. Zander, *Polycyclische Aromaten-Kohlenwasserstoffe und Fullerene*, Teubner, Stuttgart, 1995 (in German).

3 (*a*) W. F. Busby, Jr., M. E. Goldman, P. M. Newberne and G. N. Wogan, *Carcinogenesis*, 1984, **5**, 1311; (*b*) J. E. Rice, T. J. Hosted, Jr., M. C. DeFloria, E. J. LaVoie, D. L. Fischer and J. C. Wiley, Jr., *Carcinogenesis*, 1986, **7**, 1761.

4 (*a*) M. Yamaguchi, K. Hasebe, H. Higashi, M. Uchida, A. Irie and T. Minami, *J. Org. Chem.*, 1990, **55**, 1611; (*b*) J. A. Robl, *Tetrahedron Lett.*, 1990, **31**, 3421; (*c*) R. L. Danheiser, R. G. Brisbois, J. J. Kowalczyk and R. F. Miller, *J. Am. Chem. Soc.*, 1990, **112**, 3093; (*d*) N. Smyth, D. Vanengen and R. A. Pascal, *J. Org. Chem.*, 1990, **55**, 1937; (*e*) R. G. Harvey, J. Pataki, C. Cortez, P. Diraddo and C. X. Yang, *J. Org. Chem.*, 1991, **56**, 1210; (*f*) C. X. Yang and R. G. Harvey, *J. Org. Chem.*, 1993, **58**, 4155.

5 (*a*) B. P. Cho and R. G. Harvey, *J. Org. Chem.*, 1987, **52**, 5668; (*b*) B. P. Cho and R. G. Harvey, *Tetrahedron Lett.*, 1987, **28**, 861.

6 (*a*) J. D. Memory and N. K. Wilson, *NMR of Aromatic Compounds*, Wiley, New York, 1982; (*b*) B. P. Cho and R. G. Harvey, *J. Org. Chem.*, 1987, **52**, 5679; (*c*) B. F. Plummer, *Poly. Arom. Cpd.*, 1994, **4**, 25.

7 H. Whitlock, *J. Org. Chem.*, 1964, **29**, 3129.
8 (*a*) M. Crawford and V. R. Supanekar, *J. Chem. Soc.*, 1964, 2380; (*b*) T. K. Dobbs, D. V. Hertzler, G. W. Keen, E. J. Eisenbraun, R. Fink, M. B. Hossain and D. Van der Helm, *J. Org. Chem.*, 1980, **45**, 4769.
9 (*a*) N. Campbell, A. Marks and D. H. Reid, *J. Chem. Soc.*, 1950, 3466; (*b*) W. Schmidt, G. Grimmer, J. Jacob and K. W. Naujack, *Fresenius Z. Anal. Chem.*, 1987, **326**, 401; (*c*) A. Minsky and M. Rabinovitz, *Synthesis*, 1983, 497.
10 E. Buchta, *Chem. Ber.*, 1962, **95**, 1826.
11 R. H. Martin, N. Defay, F. Geerts-Ervard and S. Delavarenne, *Tetrahedron*, 1964, **20**, 897.
12 (*a*) S. Sternhell, *Pure Appl. Chem.*, 1964, **14**, 15; (*b*) K. D. Bartle, D. W. Jones and R. S. Matthews, *Pure Appl. Chem.*, 1969, **19**, 191; (*c*) M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.*, 1969, **91**, 6352; (*d*) M. W. Jarvis and A. G. Mortiz, *Aust. J. Chem.*, 1971, **24**, 89.
13 Y.-H. Lai, S.-G. Ang, H.-C. Li and S.-Y. Wong, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1315.
14 K. Gustav and C. Seydenschwanz, *J. Mol. Struct.*, 1986, **136**, 275.
15 Y.-H. Lai and P. Chen, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1665.
16 W. E. Bachmann and E. J.-H. Chu, *J. Am. Chem. Soc.*, 1936, **58**, 1118.
17 Y.-H. Lai, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1667.
18 (*a*) L. Rossa and F. Vögtle, *Top. Curr. Chem.*, 1983, **113**, 1; (*b*) P. Knops, N. Sendhoff, H.-B. Mekelburger and F. Vögtle, *Top. Curr. Chem.*, 1991, **161**, 1; (*c*) A. Ostrowicki, E. Koepp and F. Vögtle, *Top. Curr. Chem.*, 1991, **161**, 37.
19 E. Hammerschmidt and F. Vögtle, *Chem. Ber.*, 1980, **113**, 1125.
20 R. F. Borch, *J. Org. Chem.*, 1969, **34**, 627.
21 R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1970, 1197.
22 R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1547.
23 (*a*) H. Blaschke, C. E. Ramey, I. Calder and V. Boekelheide, *J. Am. Chem. Soc.*, 1970, **92**, 3675; (*b*) R. H. Mitchell, *Adv. Theor. Interesting Mol.*, 1989, **1**, 135.
24 (*a*) *UV Atlas of Organic Compounds*, Verlag Chemie, Weinheim, 1967, vol. III, E6/12; (*b*) *Handbook of Data on Organic Compounds*, 2nd edn., eds. R. C. Weast and J. G. Grasselli, CRC Press, Boca Raton, Florida, 1985, vol. 1, p. 2.
25 P. Chen, *Ph.D. Dissertation*, National University of Singapore: Singapore, 1992.
26 R. H. Mitchell, J. S. H. Yan and T. W. Dingle, *J. Am. Chem. Soc.*, 1982, **104**, 2551.
27 *CSC Chem3D Molecular Modeling and Analysis*, Version 3.1, Cambridge Scientific Computing, Inc, Cambridge, Massachusetts, 1986–1993.
28 *Spectral Atlas of Polycyclic Aromatic Compounds*, eds. W. Karcher, R. J. Fordham, J. Dubois, P. G. J. Glaude and J. A. M. Lighthart, D. Reidel Publishing, Dordrecht, Holland, 1985, vol. 1, pp. 72–75.
29 E. Clar, *The Aromatic Sextet*, Wiley, London, 1972, pp. 96–102.
30 Ref. 28, pp. 92–105.
31 *Spectral Atlas of Polycyclic Aromatic Compounds*, eds. W. Karcher, S. Ellison, M. Ewald, P. Garrigues, E. Gevers and J. Jacob, Kluwer Academic, Dordrecht, Holland, 1988, vol. 2, pp. 74–83.
32 Ref. 28, pp. 52–65.
33 The synthesis of **16** from acenaphthenequinone and 3-chlorotoluene followed a similar sequence reported for **24**; see ref. 15.

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