Synthesis and Diatropicity of *cis*-10b-Cyano-10c-methyl-10b,10c-dihydropyrene. The First Example of a Change in Stereochemical Preference from an *anti*-Dithia[3.3]metacyclophane to a *syn*-[2.2]Metacyclophane

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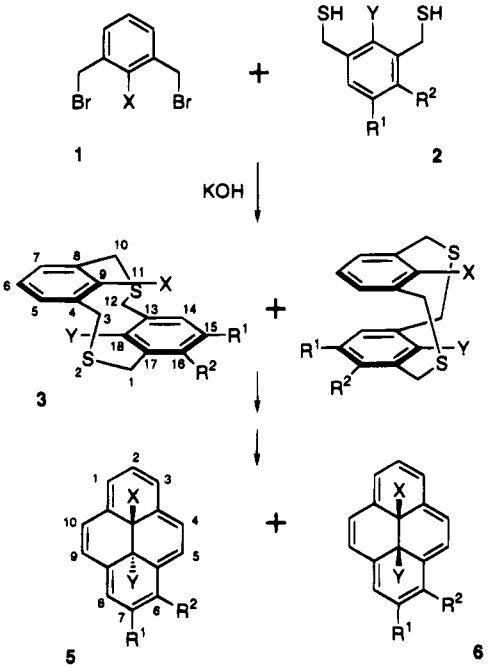
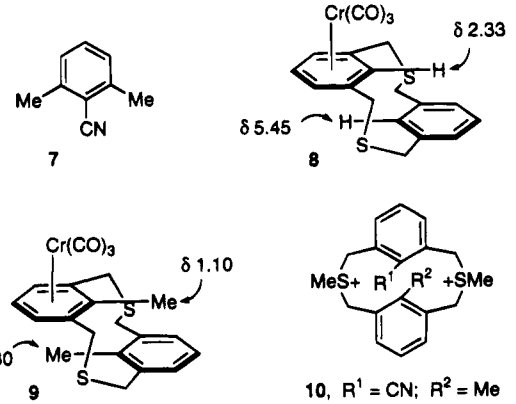
The *trans*-dimethyldihydropyrene **5a** and its derivatives have been proven to be among the best model systems for studies of the diatropicity of an annulene.[1,2] The chemistry of *cis*-dimethyldihydropyrene **6a**, however, is relatively less well explored as it is synthetically less accessible. Although the dithiacyclophane route (Scheme 1) to dihydropyrenes was well established,[3] *anti*-**3a** (**3a**:**4a** = 7:1)[3] and thus *trans*-**5a** were the major products isolated. It was later reported that the presence of electron-withdrawing group(s) on the benzene ring would increase the yield of the *syn*-dithiacyclophane.[4] Thus dithiacyclophanes **3b** and **4b**, **3c** and **4c** were obtained in ratios of 1:1[4] and 1:1.74,[5] respectively. We are interested[6] in the synthesis of derivatives of **5a** and **6a** that have an easily removable functional group at C10b. These model compounds may allow the studies of chemical reactions carried out within the π-cavity of an annulene. This paper reports the synthesis of *cis*-10b-cyano-10c-methyl-10b,10c-dihydropyrene **6e**, the first *cis*-dihydropyrene derivative with a C10b π-function within its macrocyclic, diatropic π-cloud.

Scheme 1



a, X = Y = Me; $R^1 = R^2 = H$
b, X = Y = Me; $R^1 = NO_2$; $R^2 = H$
c, X = Y = Me; $R^1 = R^2 = Cl$
d, X = Y = F; $R^1 = R^2 = H$
e, X = CN; Y = Me; $R^1 = R^2 = H$
f, X = H; Y = Me; $R^1 = R^2 = H$
g, X = F; Y = Me; $R^1 = R^2 = H$

By using the general procedure for a Sandmeyer reaction,[7] 2,6-dimethylbenzonitrile **7** was prepared from 2,6-dimethylaniline in 41% yield. Treatment of **7** with *N*-bromosuccimide gave the bis(bromomethyl) compound **1e** albeit in low yields (*ca.* 20%). Cyclization of **1e** with 2,6-bis(mercaptomethyl)toluene **2e**[3] under high dilution conditions[8] afforded a 57% yield of a mixture of dithiacyclophanes *anti*-**3e** and *syn*-**4e** in a 1.3:1 ratio, estimated on the basis of the integrated areas of their methyl signals in the ^{1}H NMR spectrum. The methyl signal of **3e** is less shielded at δ 1.48 compared to that (δ 1.30) of **3a**.[3] This could be due to a decrease in ring current in the cyano-substituted benzene ring resulting from the electron-withdrawing effect of the cyano group. Similar results were observed in the chromium-complexed cyclophanes **8** and **9** which indicate a reduced ring current in the complexed ring.[9,10] The methyl proton chemical shifts of **4a** (δ 2.51)[3] and **4e** (δ 2.59) are comparable, and the latter is likely to be slightly deshielded due to the anisotropic effect of the cyano group.



Our efforts to separate dithiacyclophanes **3e** and **4e** by recrystallization and column chromatography failed to afford any pure sample of either conformer. ^{1}H NMR spectroscopic studies of a mixture of **3e** and **4e** however allow the assignments of the respective protons (Table 1). The shielded aromatic protons of **4e** are consistent with those expected from the stacking of two near-parallel benzene rings.[3,11] The methylene protons in each of **3e** and **4e** appear as two AB quartets which are readily correlated in a COSY spectrum. Irradiation at the

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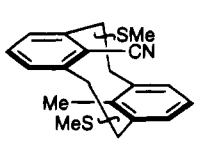
Table 1. Chemical Shifts (δ; $CDCl_3$) of Aromatic and Methylene Protons in Dithiacyclophanes 3e and 4e

phane	H5,7	H6	H14,16	H15	$H3,10_{ax}$	$H3,10_{eq}$	$H1,12_{ax}$	$H1,12_{eq}$
3e		7.42–7.48		7.27	3.96	3.73	3.74	3.84
4e	7.06–7.13		6.93	6.66	4.34	3.78	4.36	3.70

methyl signal in separate NOE experiments readily assigned the respective H1,12 axial protons in **3e** and **4e**.

Methylation of a mixture of **3e** and **4e** with dimethoxycarbonium fluoroborate[12] followed by a Stevens rearrangement[13] of their bis(sulfonium) salts **10** gave a mixture of **11** and **12** in 93% yield. In a similar



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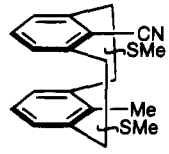

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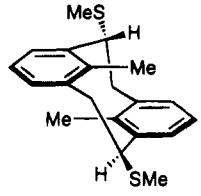

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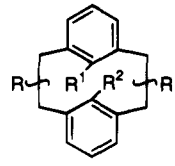
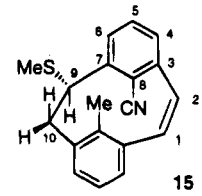


14, R = $SMe_2^+BF_4^-$; R^1 = CN; R^2 = Me

rearrangement reaction of a mixture of **3a** and **4a**,[3] the major isomer isolated pure from the product mixture was the *anti*-[2.2]cyclophane **13**. The internal methyl protons in **13** are located in the shielding zones of the respective benzene rings and thus significantly shielded at δ 0.64 in its ^1H NMR spectrum. The ^1H NMR analysis of a mixture of **11** and **12** are complicated by the fact that there are various regio- and stereoisomers. A set of shielded singlets at δ 0.53–0.58, however, should correspond to the internal methyl protons of isomers of *anti*-**11**. The internal methyl protons of isomers of *anti*-**12** and the SMe protons are observed as a set of overlapping singlets in the expected range of δ 2.02–2.48. On the basis of the integration of the methyl signals, the ^1H NMR spectrum of the product mixture unexpectedly indicates an *anti*-**11**/*syn*-**12** ratio of *ca.* 1:6. This clearly suggests that the Stevens rearrangement of **10** resulted in net isomerization from an *anti* to a *syn* conformation. Direct ring contraction of a mixture of **3e** and **4e** via a Wittig rearrangement[14] gave a 74% yield of a mixture of **11** and **12**. Integration of the methyl signals shows an *anti*-**11**/*syn*-**12** ratio of *ca.* 1:3.5. The mechanism of either the Stevens or the Wittig rearrangement of a dithia[3.3]cyclophane is likely to involve a ring opening step.[15] For **3a–c** and **4a–c**,[3–5] and several of their dialkyl derivatives,[1] the observed isomerization in the rearrangement processes were always from *syn* to *anti*. Going from *anti*-**3e** or *anti*-**10** to *syn*-**12** in our work represents the first example of a significant *anti* to *syn* isomerization in this series. The reason for the greater thermodynamic stability of the *syn* conformer may be a result of the unfavorable π–π interaction involved in placing the cyano group over the opposite benzene ring in the more rigid *anti*-[2.2]metacyclophane structure. The relatively electron poor benzonitrile and electron rich toluene rings in *syn*-**12** may however be stabilized by transannular charge interactions.[10]

A 1:6 mixture of **11** and **12** was remethylated with dimethoxycarbonium fluoroborate[12] to give a mixture of the dark brown bis(sulfonium) salts **14** in 75% yield. Results from the Hofmann elimination of **14** were dependent largely on the solvent system. A mixture of *tert*-butyl alcohol and THF (1:1) proved to be most appropriate and the reaction afforded a mixture of *syn*-**6e** (23%), pyrene (28%), and *anti*-cyclophanene **15** (4%). There was, however, no indication of the presence of *anti*-**5e** in the product mixture. The dihydropyrenes **5f**[16] and **5g**[17] have been found to readily eliminate methane and fluoromethane, respectively, to form pyrene. A similar elimination with loss of acetonitrile from *anti*-**5e** is thus expected. Its *cis* isomer **6e** was also found to decompose thermally and form pyrene (see later discussion). Whether there was a preferential decomposition of *anti*-**5e** over *syn*-**6e** is uncertain since the percentage of **5e** (from **11**) was undoubtedly lower than that of **6e** (from **12**) in the product mixture.



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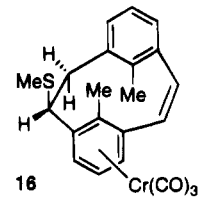

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The *anti* stereochemistry of **15** is confirmed by the strongly shielded methyl signal at δ 0.70. The methylthio group is evidently in a pseudoequatorial position adjacent to the benzonitrile ring supported by the coupling constants of H9, $H10_{ax}$, and $H10_{eq}$ (see Experimental Section) and results from NOE experiments. It is interesting to note that the only other related systems reported are **16**[10] with the methylthio group in a pseudoaxial position adjacent to the relatively electron poor aromatic ring and **17**[17] with the methylthio group in a pseudoequatorial position but adjacent to the relatively electron rich aromatic ring. The formation of **15** is probably due to the electron-withdrawing effect of the cyano group which helps stabilize the anion formation at C9 thus somewhat discouraging the subsequent elimination process.

Very few *cis*-10b,10c-dihydropyrene derivatives are known. The only reported examples before our work were **6a**,[3] **6b**,[4] **6c**,[5] and **6d**.[18] The derivative **6e**, however, is the first example with an internal π-functional group. It forms dark green crystals but slowly decomposes to afford pyrene even when kept at −10 to 0 °C. The

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Table 2. A Comparison of the Electronic Spectra (cyclohexane) of 6a and 6e

compd	λ/nm (ε/dm³ mol⁻¹ cm⁻¹)
6a[3,18]	310 (5 300), 328 (22 400) 335 (15 800), 355 (11 600), 396 (1 130), 420 (1 740), 439 (3 800), 506 (26), 564 (62), 581 (66), 602 (70)
6e	311 (6 600), 328 (23 000), 334 (18 300), 356 (14 200), 392 (1 600), 418 (2 100), 438 (3 700), 514 (38), 566 (54), 614 (173)

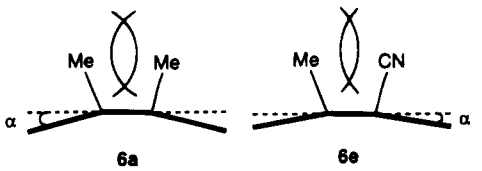
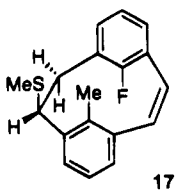


Figure 1. Representations to illustrate a decrease in steric demand of the internal substituent resulting in a more planar molecular periphery for **6e**.

electronic spectrum of **6e** is very similar to that of **6a**[3,19] (Table 2) which may suggest that there is no appreciable electronic interaction between the cyano π-function and the 14π aromatic periphery.



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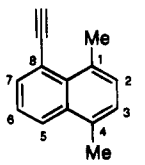

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The *cis*-dihydropyrene **6a** (δ Me at −2.06)[3,19] is significantly less diatropic than its *trans* isomer **5a** (δ Me at −4.25)[3] due to a deviation from planarity in its molecular periphery[1] (Figure 1). The internal methyl proton signal of **6e** (δ −1.64) is found to shift further downfield. This however is believed to result from the deshielding effect of the cyano function. An appropriate example of a significant triple-bond deshielding effect is that the methyl protons at C1 in **18** are shifted about 0.5 ppm downfield compared to those at C4.[20] Thus the chemical shift of the internal methyl protons in **6e** does not serve as a good probe for the diatropicity of the macro ring. A comparison of the chemical shifts of the peripheral H5,6,7,8,9 in **6e** and those in **6a** (Table 3) in fact indicates that the former series is relatively more deshielded by an average of 0.16 ppm. This is in fact consistent with a relatively stronger ring current in **6e**. A decrease in steric demand[21] going from a conical methyl group in **6a** to a cylindrical cyano group in **6e** is expected to result in a more planar periphery (smaller angle α; Figure 1) for **6e** which could explain why it is relatively more diatropic than **6a**.

The two groups of peripheral protons in **6e**, namely H1,2,3 and H6,7,8 are readily correlated in a COSY spectrum. An NOE experiment carried out with irradiation at the methyl signal (δ −1.64) led to enhancement of the doublet at δ 8.43 which should corresponding to H6,8. Irradiation at H6,8 resulted in enhancement of the doublet at δ 8.87 which is then assigned to H5,9. The proton signals of H1,3, H2 and H4,10 are clearly shifted downfield compared to the respective H6,8, H7 and H5,9 (Table 3). This is believed to be a result of an appreciable deshielding of the aromatic protons by the transannular anisotropic effect of the internal cyano function. Measurements estimated on the basis of Dreiding stereomodels of **6e** suggest an increasing order in the distance between the centre of the cyano function and H2, H1,3, and H4,10. This is consistent with an observed decreasing order in Δδ value (Table 3) supporting qualitatively a linear mapping of the anisotropic effect (deshielding zone) of the cyano group.[22]

Experimental Section

Melting points were determined with a GALEN III Hot Stage Microscope and are uncorrected. The ^{1}H NMR spectra were determined using $CDCl_3$ (unless otherwise stated) on a Bruker ACF-300 (300 MHz) or an AMX-500 (500 MHz) spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard. Mass spectra were determined on a VG Micromass 7035 spectrometer at 70 eV, electron impact being used. Relative intensities are given in parentheses. Microanalysis was performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

1,3-Dimethylbenzene-2-carbonitrile (7). This was prepared by a procedure similar to that reported in the literature.[7] Compound **7** was isolated as colorless crystals (41%), mp 89−90 °C (lit.[23] 90−91 °C): ^{1}H NMR δ 7.34 (t, J = 7.7 Hz, 1H, H5), 7.12 (d, J = 7.7 Hz, 2H, H4,6), 2.53 (s, 6 H, CH_3); IR (KBr) 2202 (C≡N) cm^{-1}; MS (M·$^+$) m/z 131 (95), 116 (100), 103 (20).

1,3-Bis(bromomethyl)benzene-2-carbonitrile (1e). A solution of compound **7** (1.31 g, 10 mmol) and catalytic amount of benzoyl peroxide in carbon tetrachloride (200 mL) was heated to solvent refluxing temperature with irradiation from a 200 W lamp. *N*-Bromosuccinimide (3.56 g, 20 mmol) was added in portions. The mixture was kept at solvent refluxing temperature until all *N*-bromosuccinimide reacted. After cooling to room temperature, the reaction mixture was filtered. The filtrate was washed with 10% aqueous $NaHCO_3$ solution and water, dried, and evaporated. The residue was chromatographed on silica gel using a mixture of hexane−dichloromethane (2:1) as eluent to give colorless crystals of compound **1e** (0.66 g, 23%): mp 72−75 °C; ^{1}H NMR δ 7.49−7.58 (m, 3 H, ArH), 4.65 (s, 4 H, CH_2); IR (KBr) 2210 (C≡N) cm^{-1}; MS (M·$^+$) m/z 291 (10), 289 (20), 287 (10), 210 (100), 208 (100). Anal. Calcd for $C_9H_7Br_2N$: C, 37.69; H, 2.34; N, 4.74; Br, 55.14. Found: C, 37.42; H, 2.42; N, 4.85; Br, 55.32.

***anti*- and *syn*-18-Methyl-2,11-dithia[3.3]metacyclophane-9-carbonitrile (3e and 4e).** A solution of 2,6-bis(mercaptomethyl)toluene (**2e**)[3] (0.32 g, 1.7 mmol) and compound **1e** (0.50 g, 1.7 mmol) in benzene (100 mL) was added dropwise with stirring under nitrogen atmosphere to a solution of KOH (0.25 g, 4.4 mmol) in 95% ethanol (500 mL). The mixture was stirred at room temperature for 24 h and the bulk of the solvent was removed under reduced pressure. The residue was extracted with dichloromethane. The organic layer was dried and evaporated. The residue was chromatographed on silica gel using hexane−dichloromethane (1:1) as eluent to give a mixture of *anti*-**3e** and *syn*-**4e** (0.31 g, 57%): mp 128−140 °C; ^{1}H NMR (**3e**) δ 7.42−7.48 (m, 5H, H5, H6, H7, H14, H16), 7.27 (t, J = 7.7 Hz, 1H, H15), 3.96 (d, J = 14.4 Hz, 2H, $H3_{ax}$, $H10_{ax}$), 3.84 (d, J = 14.0 Hz, 2H, $H1_{eq}$, $H12_{eq}$), 3.74 (d, J = 14.0 Hz, 2H, $H1_{ax}$, $H12_{ax}$), 3.73 (d, J = 14.4 Hz, 2H, $H3_{eq}$, $H10_{eq}$), 1.48 (s, 3H, CH_3); ^{1}H NMR (**4e**) δ 7.06−7.13 (m, 3H, H5, H6, H7), 6.93 (d, J = 7.6 Hz,

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Table 3. A Comparison of Proton Chemical Shifts (δ; $CDCl_3$) of 6a and 6e

compd	CH_3	H2	H7	H1,3	H6,8	H4,10	H5,9
6e	−1.64	7.98	7.76	8.59	8.43	8.94	8.87
6a[3]	−2.06	7.50		8.24		8.74	
$\Delta\delta$ (δ **6e** − δ **6a**)	0.42	0.48	0.16	0.35	0.19	0.20	0.13

2H, H14, H16), 6.66 (t, J = 7.6 Hz, 1H, H15), 4.36 (d, J = 15.0 Hz, 2H, $H1_{ax}$, $H12_{ax}$), 4.34 (d, J = 15.2 Hz, 2H, $H3_{ax}$, $H10_{ax}$), 3.78 (d, J = 15.2 Hz, 2H, $H3_{eq}$, $H10_{eq}$), 3.70 (d, J = 15.0 Hz, 2H, $H1_{eq}$, $H12_{eq}$), 2.59 (s, 3H, CH_3); the ratio of the signals at δ 1.48 and 2.59 is 1.3:1; IR (KBr) 2230 (br; C≡N) cm^{-1}; MS ($M^{\bullet+}$) m/z 311 (35), 278 (10), 192 (50), 149 (100), 134 (20), 118 (50). Anal. Calcd for $C_{18}H_{17}NS_2$: C, 69.45; H, 5.46; N, 4.50; S, 20.60. Found: C, 69.42; H, 5.35;, N, 4.42; S, 20.84.

Stevens Rearrangement of 3e and 4e To Give 11 and 12. A solution of a mixture of **3e** and **4e** (0.15 g, 0.47 mmol) in dichloromethane (10 mL) was added slowly to a suspension of dimethoxycarbonium fluoroborate[12] (0.47 g, 2.9 mmol) in dichloromethane (10 mL) kept at −30 °C under nitrogen atmosphere. When the addition was complete, the mixture was allowed to warm to room temperature and stirred for another 7 h. Ethyl acetate was added to dissolve the excess reagent and the salt **10** was obtained as a white solid (0.24 g, 100%) after filtration. The salt **10** was hygroscopic and was used directly without further purification.

To a suspension of the salt **10** (0.24 g, 0.47 mmol) in dry tetrahydrofuran (20 mL) under nitrogen atmosphere was added potassium *tert*-butoxide (0.16 g, 1.41 mmol). The mixture was stirred for 14 h and the bulk of the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and acidified by dilute HCl. The organic layer was separated, washed with water, dried, and evaporated. The residue was chromatographed on silica gel to give a mixture of isomers of **11** and **12** as a yellow oil (0.15 g, 93%): ^1H NMR δ 6.08−8.00 (m, ArH), 2.50−5.10 (m, CH and CH_2), 2.02−2.48 (m, SCH_3 and *syn*-CH_3), 0.53−0.58 (m, *anti*-CH_3); the overall ratio of the two multiplets at δ 2.02−2.48 and 0.53−0.58 is *ca.* 1:20; MS ($M^{\bullet+}$) m/z 339 (100), 324 (10), 292 (40), 276 (55), 244 (80). M_r calcd for $C_{20}H_{21}NS_2$ 339.1121, found (MS) 339.1115.

Wittig Rearrangement of 3e and 4e To Give 11 and 12. A solution of lithium diisopropylamide (5.3 mmol) was prepared from *n*-butyllithium and diisopropylamine and kept at 0 °C. A solution of a mixture of **3e** and **4e** (0.15 g, 0.48 mmol) was then added to the base. The mixture was stirred at 0 °C for 30 min and quenched with excess methyl iodide. The bulk of the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, washed, dried, and evaporated. The residue was chromatographed on silica gel using dichloromethane/hexane (1:1) as eluent to give a mixture of isomers of **11** and **12** as a yellow oil (0.12 g, 74%): ^1H NMR δ 6.04−8.02 (m, ArH), 2.60−4.80 (m, CH and CH_2), 2.01−2.53 (m, SCH_3 and *syn*-CH_3), 0.48−0.58 (m, *anti*-CH_3); the overall ratio of the two multiplets at δ 2.01−2.53 and 0.48−0.58 is *ca.* 1:12; the mass spectrum is similar to that of product mixture obtained in the Stevens rearrangement.

***cis*-10b-Cyano-10c-methyl-10b,10c-dihydropyrene (6e) and *anti*-8-Cyano-10-methyl-9-methylthio[2.2](1,3)cyclophane (15).** The salt **14** (0.15 g, 78%) was prepared by a similar method as described for **10**. To a suspension of the salt **14** (0.15 g, 0.28 mmol) in tetrahydrofuran (20 mL) and *t*-BuOH (20 mL) under nitrogen atmosphere was slowly added potassium *tert*-butoxide (0.40 g, 3.52 mmol). The mixture was stirred for 50 min at room temperature. Benzene and dilute HCl were added and the organic layer was separated, washed, dried, and evaporated. The residue was immediately preadsorbed on silica gel and chromatographed using benzene/cyclohexane (2:1) as eluent. The first fraction collected was pyrene (50 mg, 28%), which was identical in all respects with an authetic sample. Eluted next was compound **6e** obtained as green crystals (64 mg, 23%) which decomposed slowly to pyrene even when kept at 0 °C: ^1H NMR δ 8.94 (d, J = 8.6 Hz, 2H, H4, H10), 8.87 (d, J = 8.6 Hz, 2H, H5, H9), 8.59 (d, J = 7.7 Hz, 2H, H1, H3), 8.43 (d, J = 7.7 Hz, 2H, H6, H8), 7.98 (t, J = 7.7 Hz, 1H, H2), 7.76 (t, J = 7.7 Hz, 1H, H7), −1.64 (s, 3 H, CH_3); IR ($CHCl_3$) 2253 (C≡N) cm^{-1}; MS ($M^{\bullet+}$) m/z 243 (10), 227 (90), 202 (100); UV λ_{max} 328 (ϵ 23 000), 356 (14 100), 418 (2 100), 438 (3 600), 614 (170); M_r calcd for $C_{18}H_{13}N$ 243.1052, found (MS) 243.1055. Eluted last was compound **15** (10 mg, 4%) obtained as a pale yellow oil: ^1H NMR δ 7.85 (d, J = 7.7 Hz, 1H, H6), 7.43 (t, J = 7.7 Hz, 1H, H5), 7.29 (d, J = 7.7 Hz, 1H, H4), 7.21 (d, J = 7.5 Hz, 1H, H14), 7.18 (d, J = 7.5 Hz, 1H, H12), 7.11 (t, J = 7.5 Hz, 1H, H13), 6.96 9d, J = 11.2 Hz, 1H, H2), 6.66 (d, J = 11.2 Hz, 1H, H1), 3.84 (dd, J = 11.0, 3.2 Hz, 1H, H9), 3.22 9dd, J = 12.4, 3.2 Hz, 1H, $H10_{eq}$), 2.48 (dd, J = 12.4, 11.0 Hz, 1H, $H10_{ax}$), 2.16 (s, 3H, SCH_3), 0.70 (s, 3H, $ArCH_3$); MS ($M^{\bullet+}$) m/z 291 (40), 276 (10), 243 (30), 228 (100), 216 (30), 202 (50); M_r calcd for $C_{19}H_{17}NS$ 291.1086, found (MS) 291.1089.

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