J. Chem. Sci. Vol. 124, No. 3, May 2012, pp. 597–607.

Synthesis of dehydrobenzoannulenes with pyrene core

ANTONY JOSEPH, GANDIKOTA VENKATARAMANA
and SETHURAMAN SANKARARAMAN*
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India
e-mail: sanka@iitm.ac.in

MS received 9 January 2012; revised 11 February 2012; accepted 8 March 2012

Abstract. Synthesis of dehydrobenzoannulenes (DBAs) with pyrene core from 1,8-diethynylpyrene and 1,3,6,8-tetraethynylpyrene as building blocks is reported. A sequence involving Sonogashira coupling, Corey–Fuchs reaction and oxidative coupling (Eglinton coupling) is used for the synthesis of pyrene-based dehydrobenzoannulenes. Due to the presence of pyrenechromophore these DBAs and their precursors are highly fluorescent and emit in the visible region, due to extended conjugation of the acetylenic units with the pyrene core.

Keywords. Pyrene; dehydrobenzoannulene; acetylene; fluorescence.

1. Introduction

Dehydrobenzoannulenes (DBAs), also known as benzocyclynes have been known for a long time.[1] They are benzoannulenes in which the olefinic bonds are replaced by acetylenic bonds and hence the name dehydrobenzoannulenes. Initial interest in this class of compounds emerged from the stabilization of dehydroannulenes by fusing an aromatic ring and the study of tropicity (diamagnetic and paramagnetic) of the annulenes. Recently DBAs have attracted great deal of interest as a result of their applications as precursors for new forms of carbon allotropes,[2] as building blocks and model systems for 2D carbon networks[3] and their potential application as optoelectronic materials.[4] Interest in their aromatic/antiaromatic properties also continues as some of the DBAs serve as sensitive probes for the study of tropicity of the annulene ring.[5] The synthesis of DBAs has been made facile with the development of Pd(0) catalysed C–C bond forming reactions, especially those involving connection of sp^2-sp and sp-sp carbons.[6] DBAs of different π-topologies have been synthesized in an effort to understand the structure property relationships.[7] We have reported the syntheses and structures of cross-conjugated DBAs bearing Y-enediyne motifs.[8] Most of the DBAs known till date have a benzene or thiophene ring fused to the dehydroannulene ring. Reports of DBAs with fusion of higher polycyclic aromatic hydrocarbons are scarce. Synthesis and tropicity of dimethyldihydropyrene-DBA hybrids[9] and [2.2]paracyclophane-DBA hybrids have been reported.[10] Recently DBAs with triphenylene core have been reported.[11]

We report here the synthesis and spectroscopic properties of DBAs with a pyrene ring. Pyrene is a prototypical fluorescent polycyclic aromatic hydrocarbon.[12] We have studied the effect of acetylenic conjugation on the fluorescence emission of ethynylpyrenes.[13] For example 1,3,6,8-tetraethynylpyrene has been reported for the first time from our laboratory,[13] which can be used as a building block in acetylenic scaffolds of larger molecular systems.

2. Experimental

1,8-Diethynylpyrene (**2**)[14] and iodides **3a–c**[15] were synthesized by reported procedures and were characterized by spectroscopic techniques. Reactions were carried out under nitrogen atmosphere unless stated otherwise.

2.1 *General procedure for the preparation of **4a–c***

3a–c (2.4 mmol), [$PdCl_2(PPh_3)_2$] (0.06 eq, 0.14 mmol)), CuI (0.03 eq, 0.07 mmol), PPh_3 (0.06 eq, 0.14 mmol) were added to a degassed solution of diisopropylamine (25 mL) and THF (20 mL). The reaction mixture was heated at 50°C for 30 min. The reaction mixture was cooled to room temperature and then a solution of 1,8-ethynylpyrene (**2**) (1.0 mmol) dissolved in degassed

*For correspondence

THF was added drop-wise using a syringe. After complete addition, the mixture was heated at 50°C. Reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and poured into ice cold 2 N HCl (25 mL). The reaction mixture was extracted with CH_2Cl_2 (2 × 20 mL). The organic layer was further washed with brine solution and dried over anhydrous Na_2SO_4 and evaporated the solvent under reduced pressure. Column chromatographic purification of the crude product on silica gel with hexane/dichloromethane as eluent furnished pure **4a–c**.

2.1a *1,8-Bis-((4,5-bis(decyloxy)-2-((trimethylsilyl)-ethynyl)phenyl)ethynyl)pyrene (**4a**)*: Yield 22% (0.27 g, 0.20 mmol from 1.46 g, 2.40 mmol of **3a**), Waxy solid, IR (neat): 2961, 2922, 2853, 2372, 2339, 2147, 1507, 1465, 1260 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 440 (4.60), 420 (4.63), 365 (4.27), 341 (4.46), 327 (4.45), 275 (4.67), 251 (4.92) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.89 (s, 2H), 8.23 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.99 (s, 2H), 7.14 (s, 2H), 4.01 (m, 8H), 1.8 (m, 8H), 1.27 (m, 56H), 0.85 (m, 12H), 0.31 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 149.2, 149.1, 131.1, 130.9, 129.7, 127.5, 126.5, 124.6, 123.9, 118.8, 118.5, 118.3, 116.3, 115.7, 103.9, 96.6, 94.4, 90.7, 68.9, 31.6, 29.3, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 25.7, 25.6, 22.4, 13.8, 0.7; MALDI-TOF MS ($C_{82}H_{114}O_4Si_2$) : 1218 [M^+].

2.1b *1,8-Bis-((4,5-bis(dodecyloxy)-2-((trimethylsilyl)-ethynyl)phenyl)ethynyl)pyrene (**4b**)*: Yield 19% (0.25 g, 0.19 mmol from 1.60 g, 2.40 mmol of **3b**), waxy solid, IR (neat): 2960, 2922, 2853, 2372, 2340, 2147, 1594, 1507, 1465, 1260, 1021 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 440 (4.66), 420 (4.71), 366 (4.42), 342 (4.57), 327 (4.57), 275 (4.75), 242 (5.01) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.88 (s, 2H), 8.13 (q, J = 8.0 Hz, 4H), 8.06 (s, 2H), 7.13 (s, 2H), 7.04 (s, 2H), 4.03 (m, 8H), 1.80 (m, 8H), 1.27 (m, 72H), 0.85 (m, 12H), 0.28 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 149.0, 148.9, 131.4, 130.9, 129.8, 127.6, 126.5, 124.7, 124.0, 118.7, 118.5, 118.2, 116.2, 115.5, 103.8, 96.6, 94.3, 90.7, 68.8, 68.9, 316, 29.5, 29.4, 29.3, 29.1, 28.9, 28.8, 25.7, 22.4, 13.8, 0.7; MALDI-TOF MS ($C_{90}H_{130}O_4Si_2$) : 1330 [M^+].

2.1c *1,8-Bis-((4,5-bis(hexadecyloxy)-2-((trimethylsilyl)-ethynyl)phenyl)ethynyl)pyrene (**4c**)*: Yield 18% (0.25 g, 0.16 mmol from 1.87 g, 2.40 mmol of **3c**) waxy solid, IR (neat): 2959, 2922, 2853, 2373, 2340, 2275, 2147, 1595, 1507, 1465, 1260 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 440 (4.48), 422 (4.54), 365 (4.31), 341 (4.42), 328 (4.45), 295 (4.56), 275 (5.86) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.87 (s, 2H), 8.12 (q, J = 8.0 Hz, 4H), 8.05 (s, 2H), 7.13 (s, 2H), 7.04 (s, 2H), 4.02 (m, 8H), 1.83 (m, 8H), 1.24 (m, 104H), 0.85 (m, 12H), 0.28 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 149.1, 148.9, 131.4, 131.0, 127.6, 126.5, 124.7, 124.0, 118.8, 118.6, 118.2, 116.3, 115.6, 103.9, 69.6, 94.4, 90.7, 69.0, 68.9, 31.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 28.9, 28.8, 25.7, 25.6, 22.4, 13.8, 0.1; MALDI-TOF MS ($C_{106}H_{162}O_4Si_2$) : 1578 [M^++Na].

2.2 *General procedure for the preparation of dehydrobenzoannulenes **1a–c***

A solution of **4a–c** (0.13 mmol) dissolved in degassed THF (15 mL) was treated with n-Bu_4NF (0.1 eq.) and the resulting mixture was stirred at room temperature for 30 min. Progress of the reaction was monitored by TLC. After the reaction was complete the reaction mixture was transferred to another round bottom flask that contained $Cu(OAc)_2.H_2O$ (3 eq.) dissolved in 10 mL acetonitrile/pyridine (4:1) mixture. The reaction mixture was stirred at room temperature for 6–8 h. During this period a yellow precipitate appeared. The reaction mixture was neutralized with 5% aqueous HCl and extracted with dichloromethane (20 mL ×2). The organic layer was washed with water (15 mL × 2), dried over Na_2SO_4 and solvent was evaporated to dryness. Crude product was purified by column chromatography on silica gel using hexane and dichloromethane as eluent to yield **1a–c**.

2.2a *Dehydrobenzoannulene **1a***: Yield 20% (0.03 g, 0.03 mmol from 0.15 g, 0.13 mmol of **4a**), yellow colour solid, mp 67°C, IR (neat): 2923, 2852, 2373, 2339, 1591, 1506, 1466, 1249, 1206 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 450 (4.47), 425 (4.35), 410 (4.45), 370 (5.25), 307 (4.80), 295 (4.70) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 2H), 8.10 (AB, J = 8.0 Hz, 4H), 8.05 (s, 2H), 7.06 (s, 4H), 3.97 (t, J = 4.0 Hz, 4H), 3.87 (t, J = 4.0 Hz, 4H), 1.80 (m, 8H), 1.24 (m, 56H), 0.87 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): 149.4, 148.7, 132.0, 130.6, 127.7, 127.3, 126.5, 124.1, 122.8, 118.3, 110.1, 117.0, 115.3, 97.1, 91.7, 82.9, 78.3, 69.1, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 26.0, 22.7, 14.1; MALDI-TOF MS ($C_{76}H_{96}O_4$) : 1074 [M^+].

2.2b *Dehydrobenzoannulene **1b***: Yield 12% (0.02 g, 0.01 mmol from 0.16 g, 0.13 mmol of **4b**), yellow colour solid, mp 72–74°C, IR (neat): 2960, 2922,

2852, 2372, 2339, 1592, 1506, 1466, 1249, 1206 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 450 (4.40), 425 (4.30), 410 (4.39), 371 (5.16), 307 (4.73), 295 (4.63) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.61 (s, 2H), 8.32 (AB, J = 8.0 Hz, 4H), 8.26 (s, 2H), 4.09 (m, 8H), 1.90 (m, 8H), 1.25 (m, 72H), 0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 148.6, 148.2, 130.9, 130.3, 128.7, 126.8, 125.8, 123.9, 118.5, 117.6, 116.4, 115.8, 114.9, 93.4, 90.2, 82.2, 78.8, 68.3, 52.3, 30.9, 28.7, 28.6, 28.6, 28.5, 28.4, 28.3, 28.2, 28.1, 25.0, 21.6, 13.1; MALDI-TOF MS ($C_{84}H_{112}O_4$) : 1187 [M^+].

2.2c *Dehydrobenzoannulene **1c***: Yield 8% (0.02 g, 0.01 mmol from 0.19 g, 0.13 mmol of **4c**), yellow colour solid, mp 74–76°C, IR (neat): 2960, 2922, 2852, 2372, 2339, 1592, 1506, 1466, 1249, 1206 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 450 (4.25), 425 (4.16), 410 (4.25), 370 (5.01), 310 (4.55), 295 (4.49) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.59 (s, 2H), 8.27 (q, J = 8.0 Hz, 4H), 8.20 (s, 2H), 7.25 (s, 2H), 7.33 (s, 2H), 4.04 (m, 8H), 1.85 (m, 8H), 1.19 (m, 104H), 0.78 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 149.9, 149.1, 132.4, 131.0, 127.9, 127.5, 126.9, 124.6, 123.3, 118.8, 118.5, 118.4, 117.2, 115.7, 97.3, 91.9, 83.2, 78.4, 69.4, 32.1, 29.9, 29.8, 29.6, 29.5, 29.3, 29.2, 26.2, 22.8, 14.3; MALDI-TOF MS ($C_{100}H_{144}O_4$) : 1408 [M^+].

2.2d *1,8-Bis(2-formyl-5-t-butylphenylethynyl)pyrene (**6**)*: A Schlenk flask was charged with 2-bromo-4-*t*-butylbenzaldehyde (**5**) (2.2 g, 9.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.26 g, 0.37 mmol), PPh_3 (0.19 g, 0.8 mmol), CuI (0.14 g, 0.8 mmol) and degassed Et_3N (50 mL). The mixture was stirred at room temperature (rt) for 15 min and solid 1,8-diethynylpyrene (**2**) (1.0 g, 4.0 mmol) was added. Stirring was continued at 55°C for 3 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was neutralized with 5% aqueous HCl and extracted with CH_2Cl_2 (50 mL).The organic layer was washed with water (2 × 30 mL) and dried over Na_2SO_4 and then solvent was removed. The crude product was purified by column chromatography on silica gel using CH_2Cl_2-hexane (20:80 v/v) to yield **6** (1.92 g, 84%) as a yellow solid. Mp 228–230°C, IR (neat): ν 2195 (C≡C), 1693 (C=O) cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.81 (s, 2H), 8.80 (s, 2H), 8.28 (AB quartet, J = 8.0 Hz, 2H), 8.19 (AB quartet, J = 8.0 Hz, 2H), 8.12 (s, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 1.6 Hz, 2H), 7.57 (dd, J = 8.0, 1.6 Hz, 2H), 1.43 (s, 18H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 158.2, 133.9, 132.2, 132.0, 130.6, 128.7, 128.5, 128.0, 126.9, 126.8, 126.6, 125.6, 124.4, 118.1, 94.8, 92.1, 35.6, 31.3 ppm, MS (70 eV, EI): m/z (%) = 570 (100) [M^+], 277 (20).

2.2e *1,8-Bis((2-(2,2-dibromovinyl)-5-t-butylphenyl) ethynyl)pyrene (**7**)*: To a solution of PPh_3 (1.84 g, 7.0 mmol) in dry CH_2Cl_2 (35 mL) powdered zinc (0.5 g, 7.0 mmol) was added and cooled to 0°C. CBr_4 (2.33 g, 7.0 mmol) was added in small portions over 30 min. The reaction mixture was brought to rt and continued the stirring for 1 h. It was again cooled to 0°C and **6** (0.5 g, 0.9 mmol) was added in small portions over 30 min. Stirring was continued at rt for 8 h. The reaction mixture was filtered and solvent was evaporated to dryness. The crude product was purified by column chromatography on a silica gel using hexane to yield **7** (0.66 g, 85 %) as a pale yellow solid. Mp 165°C (dec), IR (neat): ν 2210 (C≡C) cm^{-1},^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.22 (AB quartet, J = 7.84 Hz, 2H), 8.14 (AB quartet, J = 8.08 Hz, 2H), 8.08 (s, 2H), 8.06 (s, 2H), 7.81 (d, J = 8.3, 2H), 7.74 (d, J = 2.0 Hz, 2H), 7.45 (dd, J = 8.3, 2.0 Hz, 2H), 1.4 (s, 18H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 135.9, 134.5, 131.9, 131.5, 130.6, 129.1, 128.1, 127.6, 126.8, 125.6, 124.9, 124.2, 122.6, 118.3, 94.0, 93.6, 91.1, 34.8, 31.1 ppm, MS (70 eV, EI): m/z (%) = 878 (13), 880 (52), 882 (80), 884 (52), 886 (13) [Br isotope peaks, M^+], 800 (20), 802 (60), 804 (60), 806 (20) [M+-Br], 720 (10), 722 (20), 724 (10) [M+-2Br].

2.2f *1,8-Bis((2-ethynyl-5-t-butylphenyl)ethynyl)pyrene (**8**)*: An oven dried Schlenk flask was charged with **7** (0.4 g, 0.45 mmol) and dry hexane/toluene (2:1 v/v, 30 mL) and cooled to −50°C. *n*-BuLi (1.6 M in hexane, 2.26 mL, 3.63 mmol) was added with stirring. After stirring at −50°C for 30 min the reaction was complete. It was quenched with saturated NH_4Cl at −50°C extracted with CH_2Cl_2 (30 mL). The organic layer was washed with water (2 × 40 mL), dried over Na_2SO_4 and then solvent was evaporated to dryness. The crude product was purified by column chromatography on silica gel using hexane to yield **8** (0.22 g, 85%) as a pale yellow solid. Mp 178–180°C (dec), IR (neat): ν 2200 (C≡C) cm^{-1}, UV-Vis (CH_2Cl_2): λ_{max} (log ε) 432 (4.72), 408 (4.72), 332 (4.89), 316 (4.72), 231 (5.01) nm, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (s, 2H), 8.23 (AB quartet, J = 8.0 Hz, 2H), 8.13 (AB quartet, J = 8.0 Hz, 2H), 8.05 (s, 2H), 7.66 (d, J = 2.4 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.0 (dd, J = 8.2, 2.0 Hz, 2H), 3.55 (s, 2H), 1.39 (s, 18H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 132.0, 131.7, 131.4, 129.9, 129.8, 127.9, 126.8, 126.1,

125.0, 124.1, 123.6, 118.6, 94.1, 92.0, 83.4, 80.8, 34.8, 31.0 ppm.

2.2g *Dehydrobenzoannulene* ***1d***: $Cu(OAc)_2.H_2O$ (0.14 g, 0.72 mmol) was dissolved in a mixture of acetonitrile and pyridine (4:1 v/v, 7.5 mL) and **8** (0.1 g, 0.2 mmol) was added. The reaction mixture was stirred at rt for 4 h. and then neutralized with 5% aqueous HCl followed by extraction with CH_2Cl_2 (20 mL). The organic layer was washed with water (30 mL), dried over Na_2SO_4 and solvent was evaporated to dryness. The crude product was purified by column chromatography on silica gel using hexane to yield **1d** (0.055 g, 55%) as a yellow solid. Mp >290°C, UV-Vis (CH_2Cl_2): λ_{max} (log ε) 440 (4.74), 414 (4.54), 401 (4.46), 353 (5.25), 304 (4.96) nm, IR (neat): ν 2180 (C≡C) cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 2H), 8.31 (AB quartet, J = 8.0 Hz, 2H), 8.24 (AB quartet, J = 8.0 Hz, 2H), 8.20 (s, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 1.9 Hz, 2H), 7.49 (dd, J = 8.4, 1.9 Hz, 2H), 1.43 (s, 18H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 135.5, 132.8, 131.3, 129.2, 128.1, 127.8, 127.2, 125.4, 125.1, 124.6, 123.4, 121.5, 118.4, 97.4, 92.7, 82.9, 79.1, 35.1, 31.1 ppm, MS (70 eV, EI): m/z (%) = 560 (100) [M^+], HRMS: Calcd. for $C_{44}H_{34}$ 560.25043; found 560.24924.

2.2h *1,3,6,8-Tetrakis((2-ethynylphenyl)ethynyl)pyrene* ***(14)***: A red solution of **13** (0.5 g, 0.5 mmol) in degassed THF (25 mL) was treated with n-Bu_4NF (0.013 g, 0.05 mmol) and the resulting mixture was stirred at rt for 15 min. The reaction mixture was then poured into ice cold water (100 mL) and the red colour solid was filtered and repeatedly washed with water (2 × 100 mL) and dried. Due to its poor solubility NMR of **14** could not be obtained. Yield: 0.33 g (95%), IR (neat): ν 2196 (C≡C) cm^{-1}, MALDI-TOF MS: m/z 698 [$C_{56}H_{26}$, M^+].

2.2i *Bis-dehydrobenzoannulene* ***9***: $Cu(OAc)_2.H_2O$ (0.23 g, 1.15 mmol) was dissolved in a mixture of pyridine and ether (3:1 v/v, 100 mL). Compound **14** (0.1 g, 0.15 mmol) was finely suspended in 20 mL of pyridine/ether (3:1 v/v) and added to the reaction mixture using a dropping funnel over 3 h with continuous stirring at rt. After complete addition, the reaction mixture was stirred at rt for 24 h. The red solid precipitated during course of the reaction was filtered and washed with dil HCl (50 mL). The solid obtained was completely insoluble and hence solution characterization could not be done. DBA **9** (0.10 g, 10%), IR (neat): ν 2185 (ν C≡C) cm-1, MALDI-TOF MS :m/z = 694 [M+, $C_{56}H_{22}$], 1388 ($2M^+$, π-dimer).

2.2j *1,3,6,8-Tetrakis(2-formyl-5-t-butylphenylethynyl) pyrene* ***(14)***: A mixture of **5** (0.40 g, 1.67 mmol), $Pd(PPh_3)_4$ (0.077 g, 0.067 mmol), CuI (0.025 g, 0.13 mmol) and Et_3N (8.0 mL) was stirred at room temperature for 15 min. 1,3,6,8-tetraethynylpyrene (**12**) (0.1 g, 0.33 mmol) was added and stirring was continued at 50°C for 4 h during which the reaction mixture turned orange red. Solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel and eluted with a mixture of CH_2Cl_2 and hexane (1:2 v/v) to yield tetraaldehyde **15** (0.25 g, 81%) as an orange red fluorescent solid. Mp 210°C (dec), IR (neat): ν 1683 (C=O), 2190 (C≡C) cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 10.77 (s, 4H), 8.78 (s, 4H), 8.52 (s, 2H), 7.92 (d, J = 8.4, 4H), 7.85 (d, J = 1.6 Hz, 4H), 7.56 (dd, J = 8.4, 1.6 Hz, 4H) 1.45 (s, 36 H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 158.0, 135.3, 134.2, 132.3, 130.0, 129.7, 128.5, 127.8, 126.6, 125.8, 118.8, 93.3, 92.9, 35.4, 31.0 ppm, MS (70 eV, EI): m/z (%) = 938 (35%) [M^+], 920 (40), 882 (95), 854 (100), 826 (90).

2.2k *1,3,6,8-Tetrakis((2-(2,2-dibromovinyl)-5-t-butylphenyl)ethynyl)pyrene* ***(16)***: A mixture of **15** (1.0 g, 1.0 mmol), CBr_4 (5.67 g, 17.0 mmol) and PPh_3 (4.5 g, 17.0 mmol) in 60 mL of benzene was refluxed for 8 h. The reaction mixture was brought to room temperature and filtered and the filtrate was passed through a short pad of silica gel using benzene as an eluent. Solvent was evaporated to dryness and the solid obtained was washed with excess of acetone to get pure **16** (0.9 g, 55%) as an orange red solid. Mp 262°C (dec), IR (neat): ν 2195 (C≡C) cm^{-1}, UV-Vis (CH_2Cl_2): λ_{max} (log ε) 482 (4.81), 453 (4.69), 353 (4.92) 250 (5.01) nm, ^1H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 4H), 8.47 (s, 2H), 8.07 (s, 4H), 7.80 (d, J = 8.3 Hz, 4H), 7.75 (d, J = 1.9 Hz, 4H), 7.47 (dd, J = 8.3, 1.9 Hz, 4H), 1.41 (s, 36H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 136.0, 134.9, 134.0, 132.7, 132.1, 129.4, 128.0, 127.5, 125.9, 122.5, 119.1, 94.9, 92.7, 91.4, 34.9, 31.2 ppm.

2.2l *1,3,6,8-Tetrakis((2,6-bis(2,2-dibromovinyl)-4-t-butylphenyl)ethynyl)pyrene(****19****)*: To a solution of PPh_3 (2.4 g, 9.14 mmol) in dry CH_2Cl_2 (50 mL) powdered zinc (0.6 g, 9.14 mmol) was added and the mixture was cooled to 0°C. CBr_4 (3.03 g, 9.14 mmol) was added portion-wise over 30 min. The reaction mixture was

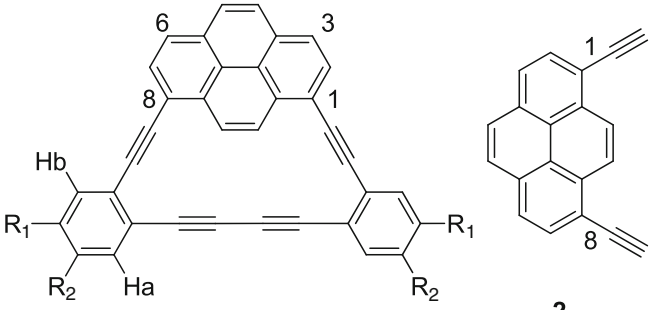
brought to rt and stirring was continued for 1 h. It was cooled to 0°C and **18** (0.3 g, 0.3 mmol) was added portion-wise over 30 min. Stirring was continued at rt for 12 h. Reaction mixture was filtered and then solvent was evaporated to dryness. The crude product was purified by column chromatography on silica gel using THF/hexane (5:95, v/v) as eluent to yield **19** as a red solid. Yield 60%; Mp: 245°C (decomp), IR (neat): ν 2220 (C≡C) cm^{-1}, UV-Vis (CH_2Cl_2): λ_{max} (log ε) 460 (4.94), 360 (5.10), 254 (5.44) nm, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 4H), 8.48 (s, 2H), 8.07 (s, 8H), 7.85 (s, 8H), 1.40 (s, 36H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 137.6, 136.1, 134.1, 131.9, 128.0, 127.5, 125.9, 124.0, 118.8, 98.3, 92.6, 92.2, 35.2, 31.0 ppm.

3. Results and discussion

The structures of the DBAs (**1a–d**) with pyrene core, derived from 1,8-diethynylpyrene (**2**), are shown in scheme 1. DBAs **1a–c** with long alkoxy chains were expected to exhibit discotic liquid crystalline behaviour[16] and hence were investigated.

3.1 *Synthesis of DBA 1a–c*

Synthesis of DBAs (**1a–c**) bearing dialkoxy groups was accomplished by the Sonogashira coupling of **2** with **3a–c** to yield **4a–c**. Iodides **3a–c** were sluggish to undergo Sonogashira coupling and under the reaction conditions **2** polymerized to yield an insoluble red polymer which reduced the yields of the desired product **4a–c**. *In situ* deprotection of the silyl group in **4a–c** followed by oxidative coupling of the resulting terminal acetylenes using $Cu(OAc)_2$ and pyridine was carried out in one-pot to yield DBAs **1a–c** (scheme 2).



$R_1 = R_2 = OC_{10}H_{21}$ **1a**
$R_1 = R_2 = OC_{12}H_{25}$ **1b**
$R_1 = R_2 = OC_{16}H_{33}$ **1c**
R_1 = t-Bu, R_2 = H **1d**

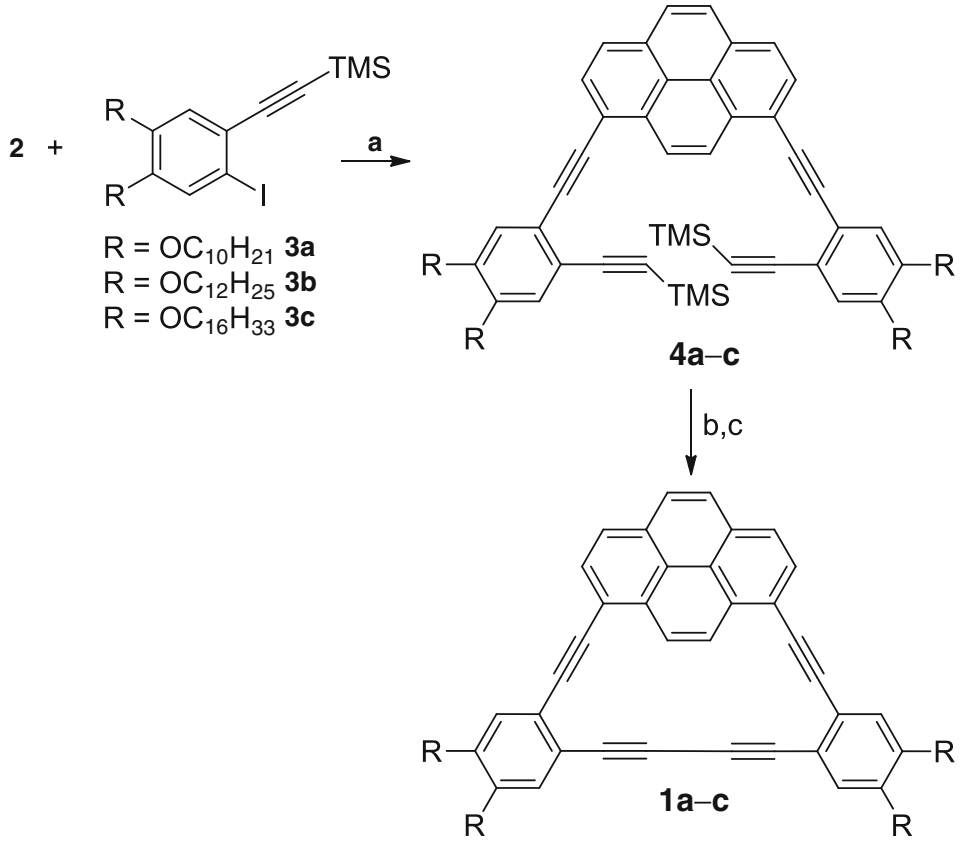
Scheme 1. Structure of DBAs (**1a–d**) synthesized from 1,8-diethynylpyrene (**2**)(systematic numbering of the pyrene ring is shown).

3.2 *Synthesis of DBA 1d*

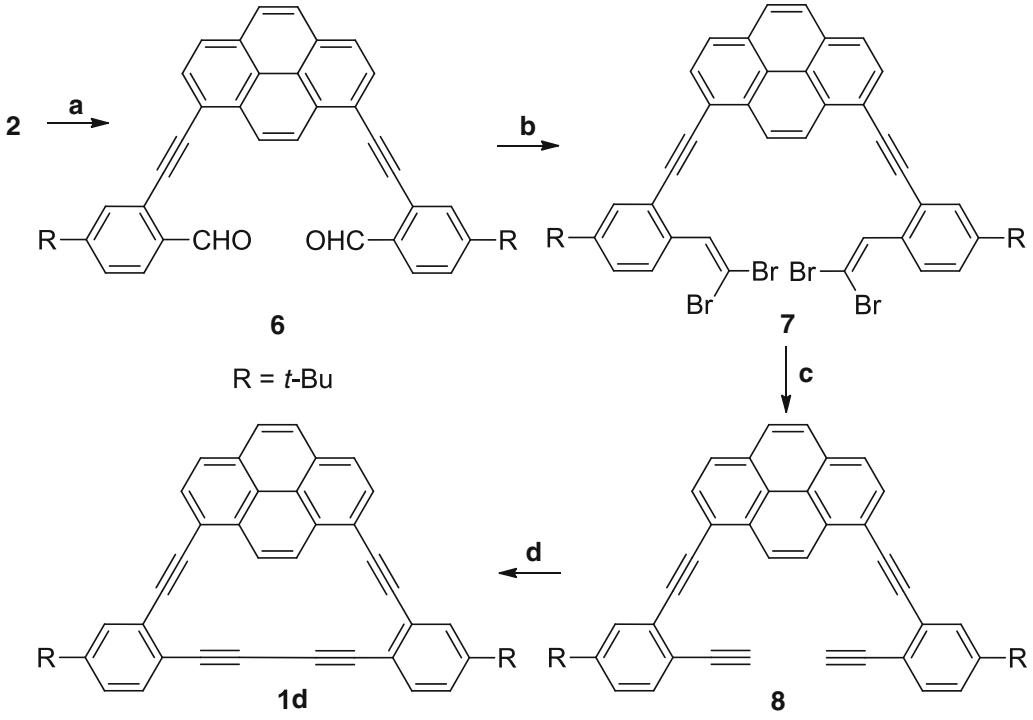
Synthesis of **1d** bearing *tert*-butyl group was accomplished following a slightly different route. Sonogashira coupling of diyne **2** with 2-bromo-4-*t*-butylbenzaldehyde (**5**) under standard conditions proceeded smoothly and gave the desired dialdeyhde **6** in 84% yield as an yellow fluorescent solid (scheme 3). In comparison to **3a–c** bromoaldehyde **5** underwent coupling in a facile manner and polymerization of **2** under these conditions was minimum and the desired coupling product was obtained in good yield. The aldehyde protons in **6** appeared as a singlet at δ 10.81 ppm in the ^{1}H NMR spectrum. Dialdehyde **6** was converted to *bis*-dibromovinyl derivative **7** by treating with CBr_4, Ph_3P and Zn in DCM in 85% yield. The vinylic protons in **7** appeared as a singlet at δ 8.06 ppm in the ^{1}H NMR spectrum. Treatment of **7** with LDA in THF yielded the desired terminal acetylene **8** only in 10% yield. However, treatment of **7** directly with *n*-BuLi in a mixture of hexane and toluene at −50°C yielded diacetylene **8** in 85% as a pale yellow solid. The acetylenic protons appeared as a singlet at δ 3.55 ppm in the ^{1}H NMR spectrum of **8**. Oxidative cyclization of **8** using $Cu(OAc)_2$ and pyridine gave DBA **1d** in good yield as a yellow solid (scheme 3).

Pyrene protons, namely H-4/5 and H-9/10 appeared as singlets in **4a–c**, **8** and **1a–d**. Peripheral protons H-4/5 in DBAs **1a–d** were deshielded by about 0.15 to 0.22 ppm when compared to the corresponding open precursors **4a–c** and **8**, respectively. Intraannular protons H-9/10 in **1a–d** were shielded by about 0.13 to 0.26 ppm when compared to that in **4a–c** and **8**, respectively. Similarly, peripheral protons on the phenyl rings, namely Ha and Hb (scheme 1), were deshielded in DBAs **1a–d** compared to those in open precursors **4a–c** and **8**. (table 1). These observations are consistent with **1a–d** being a closed loop of π−electrons in comparison to **4a–c** and **8**. Compounds **1a–d** can be considered either as a dehydrobenzo[22]annulene or a dehydrobenzo[18]- annulene, depending upon how the π-electrons are counted on the pyrene ring.

While **1d** is a high melting solid, compounds **1a–c** are low melting due to the presence of long flexible alkoxy chains. In fact, **1b** and **1c** are waxy solids. Structures **1a–c** are isosceles trapezoid shaped that possess a planar pyrene ring that is part of the rigid DBA ring bearing long alkoxy chains. It was expected that



Scheme 2. Synthesis of DBAs **1a–c**. Reagents and reaction conditions: (**a**) $Pd(PPh_3)_2Cl_2$, Ph_3P, CuI, *i*-Pr_3N, 50°C, 4–6 h, **4a** 22%, **4b** 19%, **4c** 18%; (**b**) TBAF, THF, rt, 1h; (**c**) $Cu(OAc)_2$, py, CH_3CN, rt, 12 h, **1a** 10%, **1b** 8%, **1c** 8%.



Scheme 3. Synthesis of DBA **1d**. Reagents and reaction conditions: (**a**) 2-bromo-4-*t*-butylbenzaldehyde (5), $Pd(PPh_3)_2Cl_2$, Ph_3P, CuI, Et_3N, 55°C, 3 h, 84%; (**b**) CBr_4, Ph_3P, Zn, CH_2Cl_2, rt, 8 h, 85%; (**c**) *n*-BuLi, hexane/toluene, –50°C, 30 min, 85%; (**d**) $Cu(OAc)_2$, py, CH_3CN, rt, 4 h, 55%.

Table 1. Comparison of chemical shift (δ_H) values of various protons of DBAs (**1a–d**) with their open precursors (**4a–c** and **8**).

	1a	**4a**	**1b**	**4b**	**1c**	**4c**	**1d**	**8**
H4/5	8.06	8.02	8.26	8.06	8.28	8.06	8.20	8.05
H9/10	8.28	8.93	8.62	8.88	8.66	8.87	8.87	9.0
Ha	7.06	7.09	7.30	7.05	7.32	7.04	7.88	7.65
Hb	7.07	7.17	7.37	7.14	7.40	7.13	7.86	7.66

such structural elements might impart discotic liquid crystalline properties to **1a–c**. For example triphenylene derivatives bearing multiple long alkoxy chains are known to exhibit discotic liquid crystalline behaviour.[14] However, examination of **1a–c** using a polarizing optical microscope under both heating and cooling cycles did not exhibit any liquid crystalline state. These low melting solids melted to a clear liquid state on heating and turned to a cloudy pasty mass on cooling.

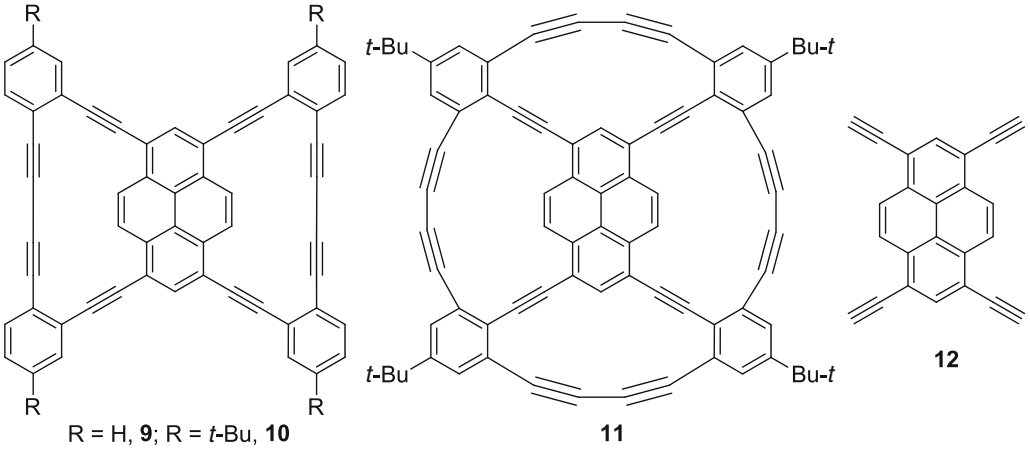
3.3 *Attempted synthesis of multiply bridged dehydrobenzoannulenes with pyrene core*

Having accomplished the synthesis of DBAs **1a–d** we investigated the synthesis of multiply bridged DBAs **9–11** (scheme 4). It was envisaged that 1,3,6,8-tetraethynylpyrene (**12**) could serve as the building block for the synthesis of DBAs **9–11**.

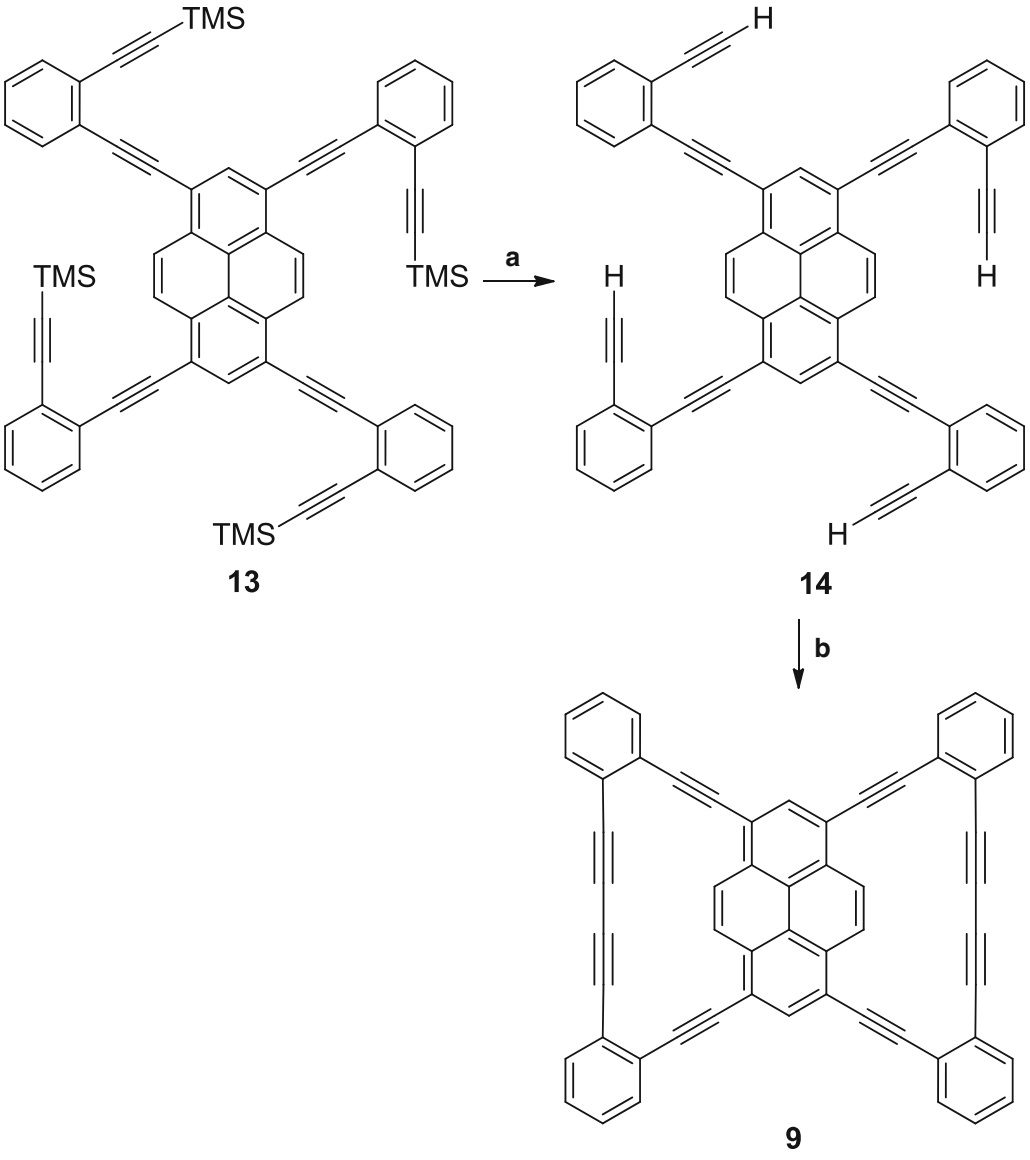
3.4 *Synthesis of DBAs **9-11***

Precursor **13**, whose synthesis has been described from our laboratory,[17] was used for the synthesis of **9**. Treatment of **13** with n-Bu_4NF in THF yielded octaacetylene **14** in near quantitative yield as a red insoluble solid (scheme 5). It was characterized by MALDI-TOF MS which showed the molecular ion peak (M^+) at m/z 698. It was immediately subjected to oxidative cyclization under high dilution conditions using $Cu(OAc)_2$ and pyridine in ether gave **9** as a red solid, albeit in poor yield. The solid was completely insoluble in all the common organic solvents which hampered its characterization in solution. However, MALDI-TOF MS clearly showed the molecular ion peak at m/z 694 along with another peak at m/z 1388, presumably due to the π-dimer of **9**.

In an effort to make a more soluble derivative of **9**, target **10** was chosen with tertiarybutyl groups substituted around the periphery. Sonogashira coupling of 2-bromo-4-t-butylbenzaldehyde **5** with 1,3,6,8-tetraethynylpyrene (**12**) gave the corresponding tetra coupled product **15** in 81% yield as an orange red fluorescent solid (scheme 6). The aldehyde protons appeared as a singlet at δ 10.77 ppm and the pyrene protons appeared as two singlet at δ 8.78 ppm (H-4/5/9/10) and 8.52 ppm (H-2/7) in the integration ratio of 2:2:1, respectively, which is consistent with the symmetry of the 1,3,6,8-tetra substituted derivative of pyrene. We have demonstrated earlier the successful utilization of Corey–Fuchs reaction for the conversion of polyaldehydes to the corresponding terminal alkynes in the



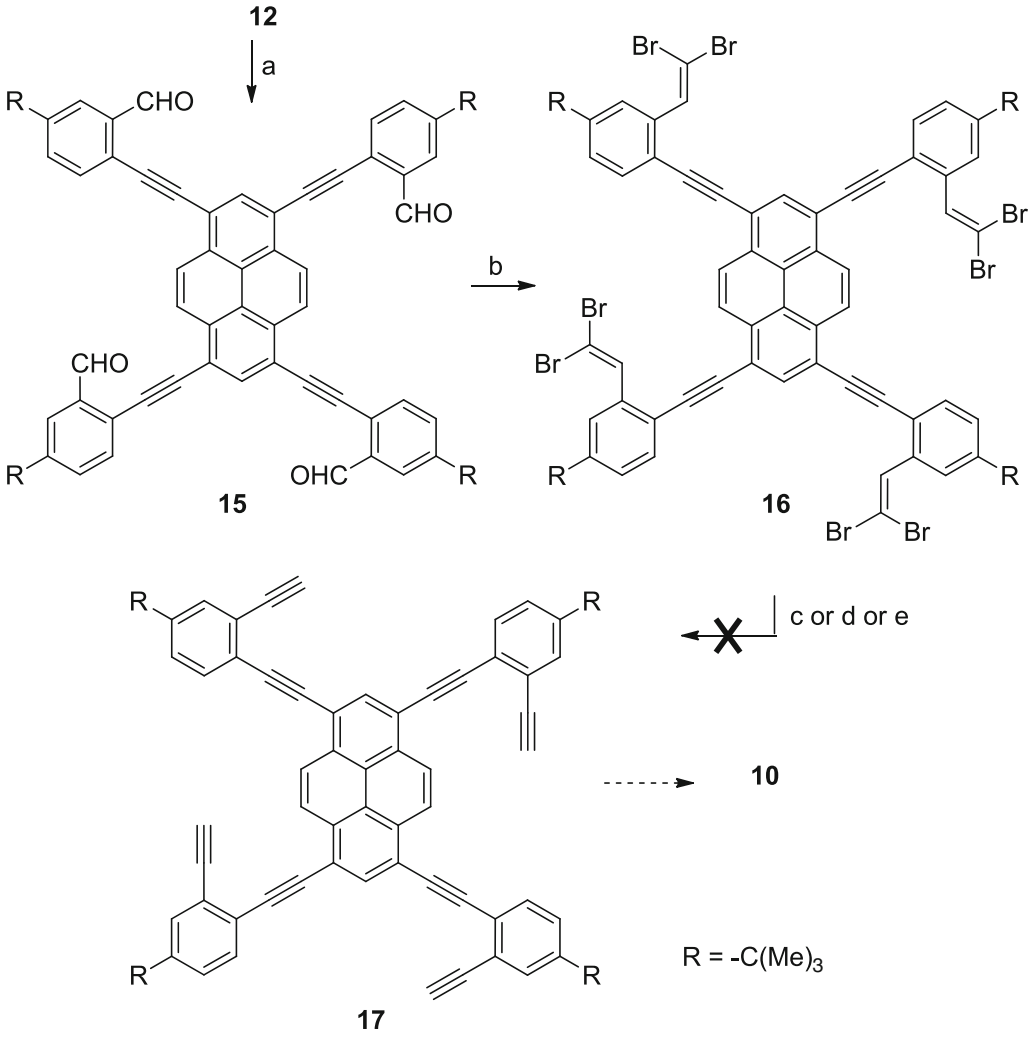
Scheme 4. Structure of multiply bridged DBAs **9–11** and 1,3,6,8-tetraethynylpyrene **12**.



Scheme 5. Synthesis of DBA **9**. Reagents and reaction conditions: (**a**) *n*-Bu_4NF, THF, rt, 15 min, 95%; (**b**) $Cu(OAc)_2$, py, ether, rt, 24 h, 10%.

synthesis of polyalkynes.[18] In our experience the use of Bestmann–Ohira reagent, namely dimethyl (1-azo-2-oxopropyl)phosphonate, for the conversion of polyaldehydes to polyalkynes gave only poor yields. Therefore, we used Corey–Fuchs methodology in the present study for the conversion of polyaldehyde precursors to poly terminal alkynes. Tetraaldehyde **15** was readily converted to the corresponding tetrakis(dibromovinyl) derivative **16** using CBr_4, and Ph_3P in 55% yield. The vinylic protons appeared as a singlet at δ 8.07 along with two singlets due to the pyrene protons at 8.79 and 8.47 ppm in the ^{1}H NMR spectrum of **16**. Efforts to convert the octabromo derivative **16** to the corresponding tetraalkyne **17** failed. Part of the problem was the poor solubility of **16**, especially at low temperatures. The reaction was tried with LDA and *n*-BuLi using various solvents and reaction conditions. All these attempts gave a fairly complicated mixture of products along with **17** due to incomplete elimination. Isolation of pure **17** from the mixture proved impractical.

In a similar manner we attempted the synthesis of the precursor to **20** from the readily available octaaldehyde derivative **18** which could be easily prepared in good yields from the Sonogashira coupling of **12** and 2-bromo-5-*t*-butylisophthalaldehyde (**21**), as described by our group earlier.[15] The octakis(dibromovinyl) derivative **19** was obtained from octaaldehyde **18** in 60% yield as a red solid using CBr_4 (scheme 7). The symmetrical tetra substitution pattern on the pyrene was confirmed by the observation of two singlets for the pyrene protons at δ 8.79 and 8.47 ppm in the 2:1 ratio in the ^{1}H NMR spectrum of **19**. Once again, attempts to

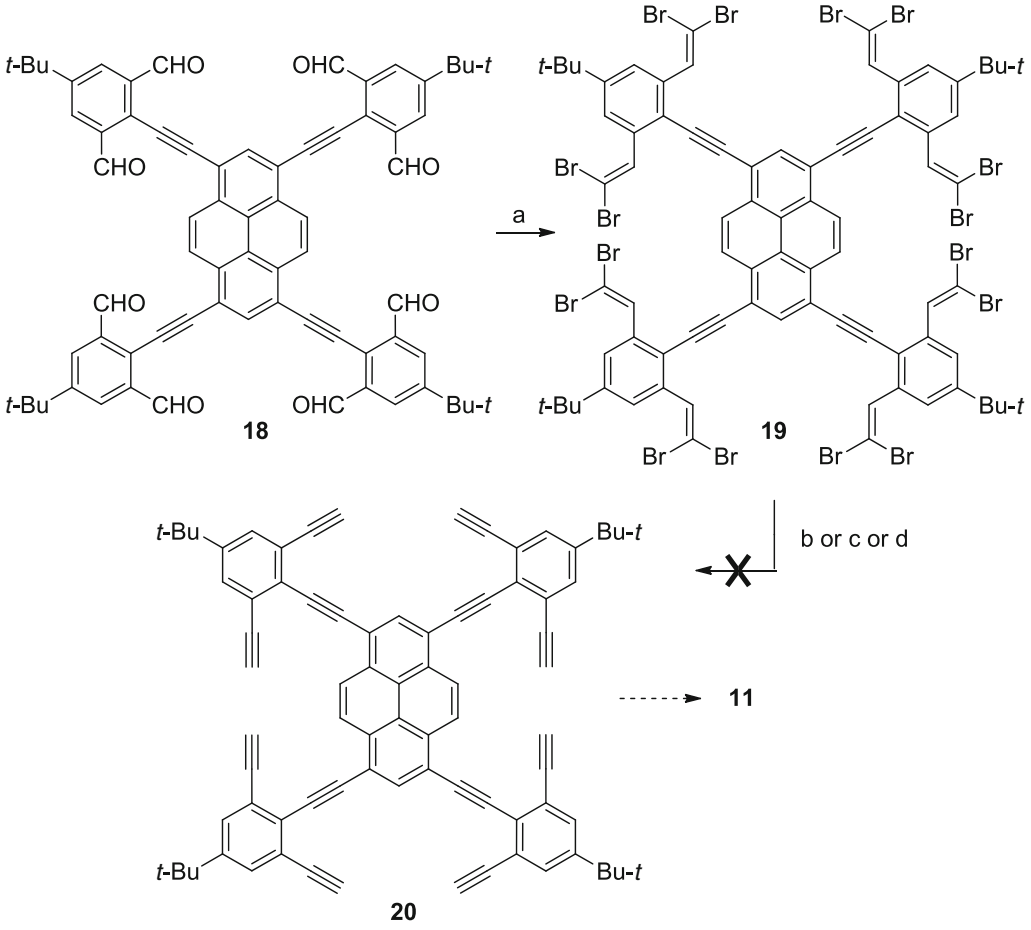


Scheme 6. Attempted synthesis of precursor **17** to DBA **10**. Reagents and reaction conditions: (**a**) 2-bromo-4-*t*-butylbenzaldehyde (**5**), $Pd(PPh_3)_4$, CuI, Et_3N, 50°C, 4 h, 81%; (**b**) CBr_4, Ph_3P, benzene, reflux, 18 h, 55%; (**c**) *n*-BuLi, hexane/toluene, –50°C, 1 h; (**d**) LDA, THF –78°C, 30 min; (**e**) LDA, toluene/hexane, –50°C, 1 h.

convert **19** to **20** under various conditions failed. Therefore, the synthesis of targets **10** and **11** could not be accomplished using the present approach. DBA **11** is not a planar molecule. It must be emphasized that the challenge in the synthesis of target **11** is due to highly strained bowl-shaped structure of this molecule. Nevertheless, an attempt has been made to synthesize **11** that is described in this report.

3.5 *Absorption and fluorescence emission spectra of DBAs and their precursors*

Absorption spectrum of **2** showed vibrational fine structure that is typical of substituted pyrene derivatives and absorption is confined to the UV region. Extension of conjugation in **8** and **1d** resulted in bathochromic shift by nearly 50 nm into the visible region. However, in **8** the vibrational fine structure is lost in comparison to **2** and the lowest energy absorption bands of **8** appeared broad. In comparison to **8**, the absorption bands of **1d** are further red shifted by about 10 nm and the bands are also sharper (figure 1). This might be due to the rigid nature of the dehydrobenzoannulene skeleton. Extension of conjugation of pyrene chromophore with alkynyl groups results in the shifting of the fluorescence emission to visible region.[13,17] A comparison of the absorption and fluorescence spectra of **1d**, **2** and **8** clearly reveals that the absorption and emission maxima are shifted to longer wavelengths with increasing conjugation. Otherwise the features of the absorption and emission spectra in figures 1 and 2 are reminiscent of the spectra of ethynylpyrene derivatives reported earlier.[13,17] Absorption and fluorescence emission spectra of **4a–c** and **1a–c** were similar to that of **8** and **1d**, respectively.



Scheme 7. Attempted synthesis of precursor **20** to DBA **11**. Reagents and reaction conditions: (**a**) CBr_4, Ph_3P, Zn, CH_2Cl_2, rt, 12 h, 60%; (**b**) *n*-BuLi, hexane/toluene, –50°C, 1 h; (**c**) LDA, THF –78°C, 30 min; (**d**) LDA, toluene/hexane, −50°C, 1 h.

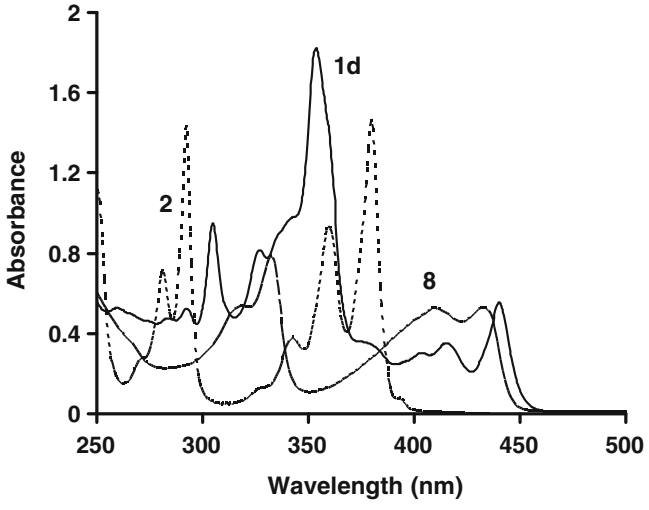


Figure 1. Absorption spectra (10^{-5} M) of **2**, **8** and **1d** in CH_2Cl_2.

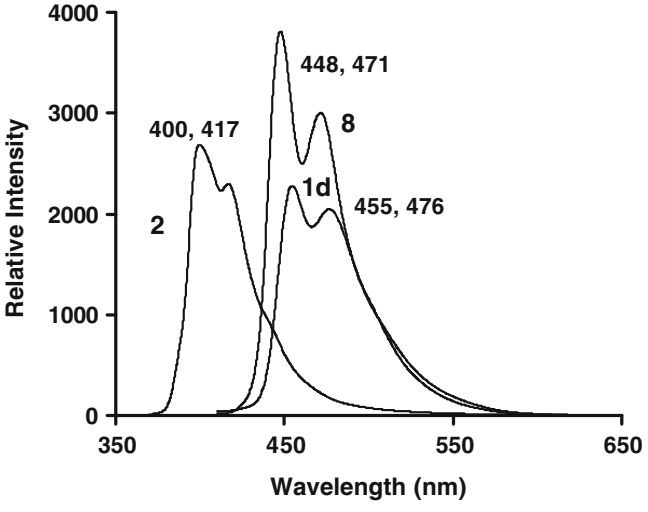


Figure 2. Fluorescence emission spectra (10^{-5} M) of **2** (λ_{ex} 360 nm), **8** (λ_{ex} 409 nm) and **1d** (λ_{ex} 405 nm) in CH_2Cl_2.

4. Conclusion

DBAs **1a–d** with a pyrenecore have been synthesized for the first time using a sequence of Sonogashira coupling, Corey–Fuchs reaction and Eglinton coupling. A comparison of the chemical shift values of various pyrene protons of DBAs with that of their open precursors clearly showed that the peripheral protons H-4/5 were deshielded and the internal protons H-9/10 were shielded in the DBAs, consistent with the closed loop of π–electrons. DBAs **1a–c**, bearing long alkoxy groups did not exhibit any liquid crystalline behaviour. In comparison to **2** the absorption and emission spectra of **1a–d**, **4a–c** and **8** were red shifted due to extension of conjugation. DBA **9** was synthesized and characterized by only mass spectrometry. MALDI-MS data showed molecular ion peak corresponding to **9** along with a peak with double the m/z value of the molecular ion, presumably due to the corresponding π-dimer. Solution phase characterization could not be done due to its insoluble nature in most common organic solvents. Synthesis of polyacetylene precursors **17** and **20** for DBAs **10** and **11**, respectively, was hampered due to incomplete elimination of **16** and **19** under a variety of conditions and also presumably due to the instability of polyacetylenic derivatives **17** and **20** under reaction and ambient conditions.

Acknowledgements

We thank the Department of Science and Technology (DST) and the Council of Scientific and Industrial Research (CSIR), New Delhi for financial support. We also thank the Department of Chemistry and SAIF, Indian Institute of Technology Madras for spectral data.

References

1. (a) Staab H A and Graf F 1966 *Tetrahedron Lett.* 751; (b) Campbell J D, Eglinton G, Henderson W and Raphael R A 1966 *J. Chem. Soc. Chem. Commun.* 87; (c) Darby N, Cresp T M and Sondheimer F 1977 *J. Org. Chem.* **42** 1960; for a recent review Spitler E L, Johnson II C A and Haley M M 2006 *Chem. Rev.* **106** 5344
2. (a) Boese R, Matzger A J and Vollhardt K P C 1997 *J. Am. Chem. Soc.* **119** 2052; for reviews (b) Diederich F and Rubin Y 1992 *Angew. Chem. Int. Ed. Engl.* **31** 1101; (c) Diederich F 1994 *Nature* **368** 199
3. For reviews (a) Haley M M 1998 *Synlett* 557; (b) Marsden J A, Palmer G J and Haley M M 2003 *Eur. J. Org. Chem.* 2355; (c) Bunz U H F, Rubin Y and Tobe Y 1999 *Chem. Soc. Rev.* **28** 107
4. (a) Baughman R H, Eckhardt H and Kertesz M 1987 *J. Chem. Phys.* **87** 6687; (b) Marsden J A and Haley M M 2005 *J. Org. Chem.* **70** 10213; (c) Sarkar A, Pak J J, Rayfield G W and Haley M M 2001 *J. Mater. Chem.* **11** 2943
5. (a) For a review, Mitchell R H 2001 *Chem. Rev.* **101** 1301; (b) Laskoski M, Steffen W, Smith M D and Bunz U H F 2001 *Chem. Commun.* 691; (c) Boydson A J, Haley M M, Williams R V and Armantrout J R 2002 *J. Org. Chem.* **67** 8812; (d) Boydson A J and Haley M M 2001 *Org. Lett.* **3** 3599
6. (a) Brandsma L, Vasilevsky S F and Verkruijsse H D 1999 *Application of transition metal catalysts in organic synthesis* (eds) A de Meijere and F Diederich, Berlin: Springer, **67**, 179; (b) de Meijere A and Diederich F 2004 *Metal-catalyzed cross-coupling reactions*, Weinheim: Wiley-VCH
7. (a) For a recent review, Tobe Y and Sonoda M 2004 *Modern cyclophane chemistry* **1** 1 R Gleiter and H Hopf, (Eds), Weinheim: Wiley-VCH; (b) Haley M M, Brand S C and Pak J J 1997 *Angew. Chem. Int. Ed. Engl.* **36** 836; (c) Wan W B and Haley M M 2001 *J. Org. Chem.* **66** 3893
8. Bandyopadhyay A, Varghese B, Hopf H and Sankararaman S 2007 *Chem. Eur. J.* **13** 3813
9. (a) Kimball D B, Haley M M, Mitchell R H and Ward T R 2001 *Org. Lett.* **3** 1709; (b) Kimball D B, Haley M M, Mitchell R H, Ward T R, Bandyopadhyay S, Williams R V and Armantrout J R 2002 *J. Org. Chem.* **67** 8798
10. (a) Boydston A J, Bondarenko L, Dix I, Weakley T J R, Hopf H and Haley M M 2001 *Angew. Chem. Int. Ed.* **40** 2986; (b) Heinrichs H, Fischer A K, Jones P G, Hopf H and Haley M M 2005 *Org. Lett.* **7** 3793
11. Takeda T, Fix A G and Haley M M 2010 *Org. Lett.* **12** 3824
12. Winnik F M 1993 *Chem. Rev.* **93** 587
13. Venkataramana G and Sankararaman S 2005 *Eur. J. Org. Chem.* 4162
14. Leroy-Lhez S and Fages F 2005 *Eur. J. Org. Chem.* 2684
15. Johnson II C A, Lu Y and Haley M M 2007 *Org. Lett.* **9** 3725
16. (a) Chandrasekar S and Raganath G S 1990 *Rep. Prog. Phys.* **53** 57; (b) Boden N, Bushby R J, Cammidge A N, El-Mansoury A, Martin P S and Lu Z 1999 *J. Mater. Chem.* **9** 1391
17. Venkataramana G and Sankararaman S 2006 *Org. Lett.* **8** 2739
18. Narayanan V, Sankararaman S and Hopf H 2005 *Eur. J. Org. Chem.* 2740