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Electronic Supplementary Information

High birefringence bistolane liquid crystals: the synthesis and properties

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1 Preparative procedures

The purity of intermediates and the main compounds were determined by thin layer chromatography (TLC) and GC-MS(EI) (Agilent 6890N, Santa Clara, CA, USA) chromatography system. The structures of the final compounds were confirmed by ^{1}H and ^{1}C NMR spectroscopy (Bruker, Avance III HD, 500 Hz; $CDCl_3$, Billerica, MA, USA).

Experimental

4-iodo-2-methyl aniline

The suspension of 2-methylaniline (250g; 2.33mol), $NaHCO_3$ (391.4g; 4.66mol) in dichloromethane (1L) and water (1.4L) was mixed in room temperature. Then iodine was added partial wise. The reaction mixture was stirred at room temperature 1h. Then the reaction mixture was poured into $Na_2S_2O_5$ and then by water twice. Phases were separated. The crude product was crystallized from ethyl alcohol (0.5L)/water(1.5L).

Yield: 485g (89.2%); GC: 99.9%; MS: 233, 216, 204, 191, 176, 165.

1,4-diiodo-2-methylbenzene

To the suspension of 4-iodo-2-methyl aniline (485g; 2.08mol) in water (0.62L) hydrochloric acid (0.52mL) was added dropwise. The reaction mixture was cooled on carbon dioxide-acetone bath to -5°C and the solution of $NaNO_2$ (154.6g; 2.24mol) in water (0.7L) was added dropwise. Then the reaction mixture was stirred 1h at 5°C. Next, the solution of NaI (369.7g; 2.47mol) in water (0.4L) was added dropwise. Then to the reaction mixture CH_2Cl_2 (1L) was added and the reaction mixture was poured into $Na_2S_2O_5$ and by water twice. Phases were separated. The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude product was distilled under vacuum.

Yield: 395g (55.2%); bp: 108-109 (0.8mmHg); GC: 99.5%; MS: 344, 317, 291, 254, 217, 192, 172.

2-methyl-1,4-bis[(4-propylphenyl)ethynyl]benzene 3Me3

To the suspension of 1,4-diiodo-2-methylbenzene (17.2g; 0.05mol), triethylamine (13.84mL; 0.1mol), 1,8-diazabicyclo(5.4.0)undek-7-en (14.92mL; 0.1mol), $PdCl_2(PPh_3)_2$ cat. and CuI cat. in tetrahydrofurane (0.3L) the solution of 1-ethynyl-4-butylbenzen (18.63g; 0.1mol) in tetrahydrofurane (50mL) was added dropwise. The reaction mixture was stirred at room temperature 6h and then the solvent was evaporated. Then to the reaction mixture water (0.3L) and toluene (0.3L) were added and obtained emulsion was filtered off. Phases were separated. The inorganic phase was extracted with toluene (3×0.1L) and then the collected organic phases were poured into water (3×0.1L) and dried over $MgSO_4$. The solvent was evaporated. The crude product was crystallized from ethanol (1L)/acetone (0.5L). A yellow solid was purified on a column chromatography (SiO_2/hexane) and then recrystallized from ethanol (0.3L)/acetone (0.3L).

Yield: 15.3g (81.3%); GC: >99.9%; MS: 376, 360, 347, 331, 318, 302, 289, 276, 263, 250, 239, 226, 213, 202, 188, 173, 159.

^{1}H NMR ($CDCl_3$) δ 7.48-7.50 (*d*, 1H, Ar-H), 7.44 (*s*, 2H, Ar-H), 7.37 (*s*, 1H, Ar-H), 7.36 (*s*, 1H, Ar-H), 7.27 (*s*, 2H, A-H), 7.19-7.21 (*m*, 4H, Ar-H), 2.63-2.66 (*t*, 4H, Ar-CH_2-), 2.55 (*s*, 3H, Ar-CH_3) , 1.66-1.73 (*m*, 4H, -CH_2-), 0.97-1.00 (*t*, 6H, -CH_3). ^{1}C NMR ($CDCl_3$) δ 143.3, 140.1, 132.4, 131.7, 131.5, 128.8, 128.6, 123.2, 123.1, 120.6, 120.4, 95.3, 91.0, 88.8, 87.6, 38.0, 24.4, 24.3, 20.6, 13.8.

2-methyl-1,4-bis[(4-butylphenyl)ethynyl]benzene 4Me4

Yield: 15.2g (75.0%); GC: 99.6%; MS: 404, 389, 361, 345, 318, 302, 276, 250, 226, 202, 181, 159.

2-methyl-1,4-bis[(4-pentylphenyl)ethynyl]benzene 5Me5

Yield: 13.1g (60.7%); GC: >99.9%; MS: 432, 417, 402, 389, 375, 362, 345, 331, 318, 302, 289, 276, 263, 239, 216, 202, 189, 176, 159.

2-methyl-1,4-bis[(4-hexylphenyl)ethynyl]benzene 6Me6

Yield: 16.8g (72.9%); GC: >99.9%; MS: 460, 438, 416, 389, 364, 345, 318, 289, 263, 245, 226, 202, 178, 159.

2-methyl-1,4-bis[(4-heptylphenyl)ethynyl]benzene 7Me7

Yield: 16.9g (69.2%); GC: >99.9%; MS: 488, 458, 430, 403, 373, 345, 318, 289, 263, 226, 202, 159, 115, 91, 67, 43, 20.

4-[(4-heptylphenyl)ethynyl]-2-methyl-1-[(4-butylphenyl)ethynyl]benzene 7Me4

Yield: 3.8g (45%); GC: 98.7%; MS: 446, 418, 403, 376, 361, 345, 318, 302, 276, 252, 226, 202, 181, 159.

4-[(4-heptylphenyl)ethynyl]-2-methyl-1-[(4-pentylphenyl)ethynyl]benzene 7Me5

Yield: 3.5 (42%); GC: 97.7%; MS: 460, 444, 417, 403, 389, 375, 361, 346, 332, 318, 302, 276, 252, 226, 202, 187, 173, 159.

1,4-bis[(4-pentyloxyphenyl)ethynyl]-2-methylbenzene 5OMeO5

Yield: 4.2g (55%); GC: 99.4%; MS: 464, 435, 418, 393, 377, 350, 324, 294, 276, 252, 231, 202, 178, 162.

1-[(4-pentylphenyl)ethynyl]-2-methyl-4-{[4-(ethylsulfanyl)phenyl]ethynyl}benzene 2SMe5

Yield: 3.4g (65%); GC: 99.9%; MS: 422, 393, 365, 336, 182.

2-methyl-1,4-bis{[4-(pentylsulfanyl)phenyl]ethynyl}benzene 5SMeS5

Yield: 7.1 (47%); GC: 99.4%; MS: 496, 466, 443, 425, 393, 374, 355, 321, 289, 269, 248, 213, 178, 160.

2-ethyl-1,4-bis[(4-ethylphenyl)ethynyl]benzene 2Et2

Yield: 15g (55%); GC: 99.5%; MS: 362, 317, 289, 166.

^{1}H NMR ($CDCl_3$) δ 7.48-7.50 (*d*, 1H, Ar-H), 7.44 (*s*, 2H, Ar-H), 7.37 (*s*, 1H, Ar-H), 7.35 (*s*, 1H, Ar-H), 7.27 (*s*, 2H, A-H), 7.21-7.24 (*m*, 4H, Ar-H), 2.89-2.94 (*q*, 2H, Ar-CH_2-), 2.68-2.73 (*q*, 4H, Ar-CH_2-) , 1.34-1.37 (*t*, 3H, -CH_3), 1.27-1.30 (*t*, 6H, -CH_3). ^{1}C NMR ($CDCl_3$) δ 146.1, 144.8, 136.6, 132.0, 131.5, 131.0, 128.8, 128.0, 123.2, 122.5, 120.6, 120.4, 94.7, 90.9, 88.9, 87.3, 28.9, 27.7, 15.3, 14.6.

2-ethyl-1,4-bis[(4-propylphenyl)ethynyl]benzene 3Et3

Yield: 18g (65%); GC: 99.7%; MS: 392, 317, 166.

4-[(4-propylphenyl)ethynyl]-2-ethyl-1-[(4-pentylphenyl)ethynyl]benzene 3Et5

Yield: 5g (59%); GC: 99.5%; MS: 418, 389, 361, 317, 166.

2-ethyl-1,4-bis[(4-butylphenyl)ethynyl]benzene 4Et4

Yield: 11g (67%); GC: 99.8%; MS: 418, 375, 317, 166.

4-[(4-butylphenyl)ethynyl]-2-ethyl-1-[(4-ethylphenyl)ethynyl]benzene 4Et2

Yield: 12g (62%); GC: 99.3%; MS: 390, 347, 317, 166.

4-[(4-butylphenyl)ethynyl]-2-ethyl-1-[(4-propylphenyl)ethynyl]benzene 4Et3

Yield: 6.8g (54%); GC: 99.6%; MS: 404, 375, 331, 166.

2-ethyl-1,4-bis[(4-pentylphenyl)ethynyl]benzene 5Et5

Yield: 12g (55%); GC: 99.0%; MS: 446, 431, 389, 166.

4-[(4-pentylphenyl)ethynyl]-2-ethyl-1-[(4-propylphenyl)ethynyl]benzene 5Et3

Yield: 12g (62%); GC: 99.5%; MS: 418, 389, 361, 317, 166.

2-ethyl-1,4-bis{[4-(pentylsulfanyl)phenyl]ethynyl}benzene 5SEtS5

Yield: 5.6g (49%); GC: 99.5%; MS: 510, 439, 302, 255, 185.

Table 1. The melting temperatures [°C] (upper row; onset point) and the enthalpies [kJ/mol] (lower row) of the members of the homologous series **nXRXm** from DSC measurements determined during heating cycles.

Acronym	R	n	m	Cr	T_{mp} [°C]	N	T_c [°C]	Iso
3Me3	CH_3	3	3	•	125.3 *19.16*	•	208.3 1.08	•
4Me4	CH_3	4	4	•	87.7 *27.38*	•	178.9 0.88	•
5Me5	CH_3	5	5	•	80.5 *20.60*	•	176.1 1.44	•
6Me6	CH_3	6	6	•	73.4 *27.29*	•	151.5 1.02	•
7Me7	CH_3	7	7	•	72.7 *26.94*	•	147.4 1.27	•
7Me4	CH_3	7	4	•	45.5 *11.99*	•	158.9 1.22	•
7Me5	CH_3	7	5	•	53.3 *15.90*	•	160.7 1.56	•
5OMeO5	CH_3	5	5	•	120.8 *36.97*	•	217.9 0.22	•
2SMe5	CH_3	2	5	•	110.9 *27.04*	•	186.3 1.20	•
5SMeS5	CH_3	5	5	•	120.0 *50.32*	•	126.4 0.67	•
5SMe5	CH_3	5	5	•	94.1 *34.57*	•	150.2 0.96	•
2Et2	C_2H_5	2	2	•	84.6 *20.70*	•	131.7 0.96	•
3Et3	C_2H_5	3	3	•	48.2 *14.48*	•	151.9 1.65	•
3Et5	C_2H_5	3	5	•	59.4 *16.37*	•	137.4 1.59	•
4Et4	C_2H_5	4	4	•	29.5 *16.70*	•	121.0 1.37	•
4Et2	C_2H_5	4	2	•	58.7 *26.03*	•	123.5 1.08	•
4Et3	C_2H_5	4	3	•	36.4 *22.27*	•	131.8 1.45	•
5Et5	C_2H_5	5	5	•	3.9 *5.88*	•	120.7 1.58	•
5Et3	C_2H_5	5	3	•	26.8 *9.11*	•	136.1 1.87	•
5SEtS5	C_2H_5	5	5	•	86.5 *48.58*	-	-	•