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Nematic phase formed by banana-shaped molecules

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Most mesogens formed by banana-shaped molecules exhibit liquid-like smectic phases. Here we present the synthesis and properties of homologous series of derivatives of resorcinol and 2,6-disubstituted pyridine. One of these classes of bent-core molecules displays the nematic phase.

1. Introduction

The thermotropic biaxial nematic phase is intensively sought among lath-like molecular systems with molecules with shape intermediate between rod-like and disc-like [1–3] or in mixtures [4] of these molecules. It should be noted that banana-shaped molecules might also form such a phase, as they are stiff and resemble the lath-like molecules. Although, these banana-shaped molecules easily give smectic, biaxial type phases, the appearance of the nematic phase is rather unusual [5–11]. Only one example of bent-shape molecules which exhibit the nematic phase has been found so far [12].

Here we present a series of V-shaped molecules that give the monotropic nematic phase at room temperature. These compounds are derivatives of resorcinol or pyridine. In the resorcinol series **1** (scheme 1) an additional lateral *n*-hexyl substituent has been attached at the 4-position of the phenyl ring. The related series **2** (scheme 1) without the alkyl substituent is also described. In series **3** (scheme 2), at the 2,6-positions of the pyridine ring, two ester branches are linked on by the extra methylene units. The resorcinol series give monotropic LC phases, while for the pyridine derivatives no mesophases were found.

2. Experimental

2.1. *Measurements*

Mesophase identification was based on microscopic examination of liquid crystalline textures. A Zeiss Jenapol-U polarizing microscope equipped with a Mettler FP82HT hot stage was used. To determine phase transition temperatures, calorimetric measurements were made using a Perkin Elmer DSC 7. Thermograms were taken at a routine scanning rate of 5 K min^{-1}. If necessary, other scanning rates were applied (heating or cooling) and thermal effects were recalculated at the standard rate. When it was possible, the microscopic phase identification was confirmed by X-ray studies using a DRON diffractometer. EPR investigations were performed in the X-band on a Radiopan spectrometer equipped with a nitrogen flow heater. The resulting spectra were analysed by a Bruker software package—Symfonia.

To confirm the molecular structure of the compounds synthesized, the following analyses were performed. Infrared (IR) spectra were obtained using a Nicolet Magna IR 500 spectrophotometer. NMR spectra were recorded by a Varian Unity Plus spectrometer operating at 200 MHz or 500 MHz for ^{1}H NMR and at 125 MHz for ^{13}C NMR. Tetramethylsilane was used as an internal standard. Chemical shifts are reported in ppm.

TLC analyses were performed on Merck 60 silica gel glass plates and visualized using iodine vapour. Column chromatography was carried out at atmospheric pressure using silica gel (100–200 mesh, Merck). Elemental analyses were also carried out.

2.2. *Synthesis*

To obtain the compounds of series **1** and **2**, similar synthetic procedures were applied as outlined in scheme 1. The pyridyl compounds of series **3** were obtained according to the route shown in scheme 2. For both reaction schemes a representative example for a given terminal chain length is described. The elemental analyses of the compounds synthesized confirmed the expected structures. The NMR and IR data obtained

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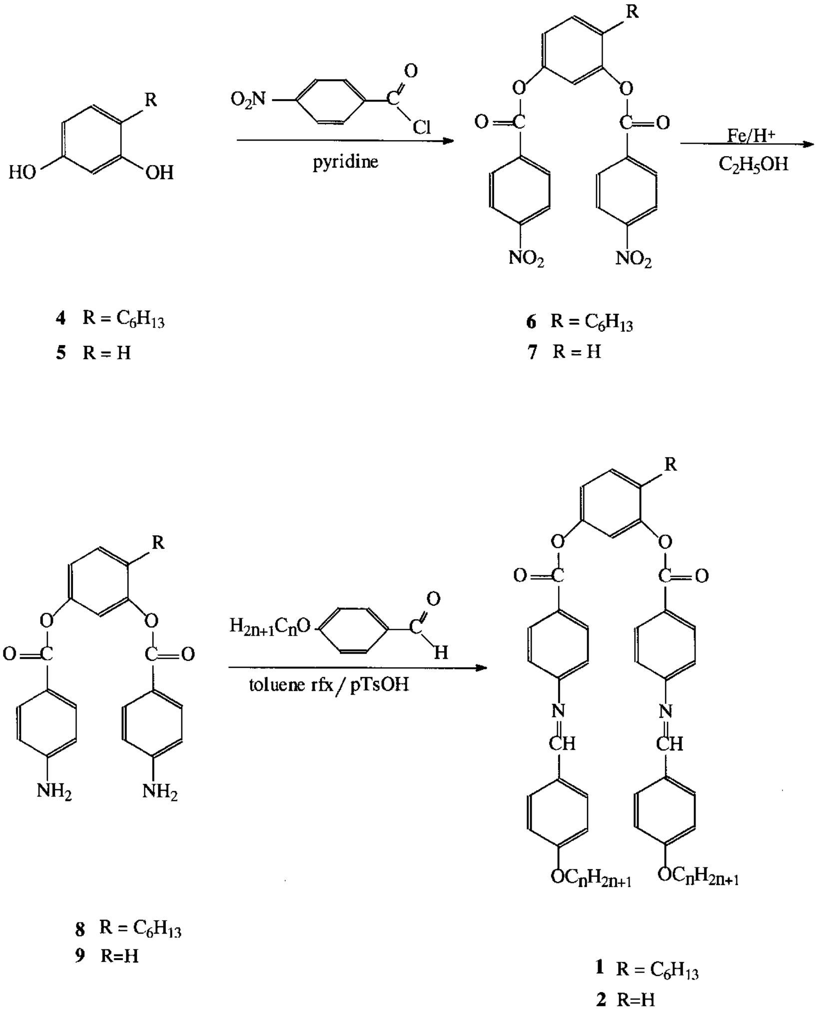


4 R = C_6H_{13}
5 R = H

6 R = C_6H_{13}
7 R = H

8 R = C_6H_{13}
9 R=H

1 R = C_6H_{13}
2 R=H

Scheme. 1

for all the compounds were also fully consistent with the required structures, but only representative examples of the NMR and IR results are quoted.

2.2.1. *3-(4-Nitrobenzoyloxy)-4-hexylphenyl 4-nitrobenzoate (**6**)*

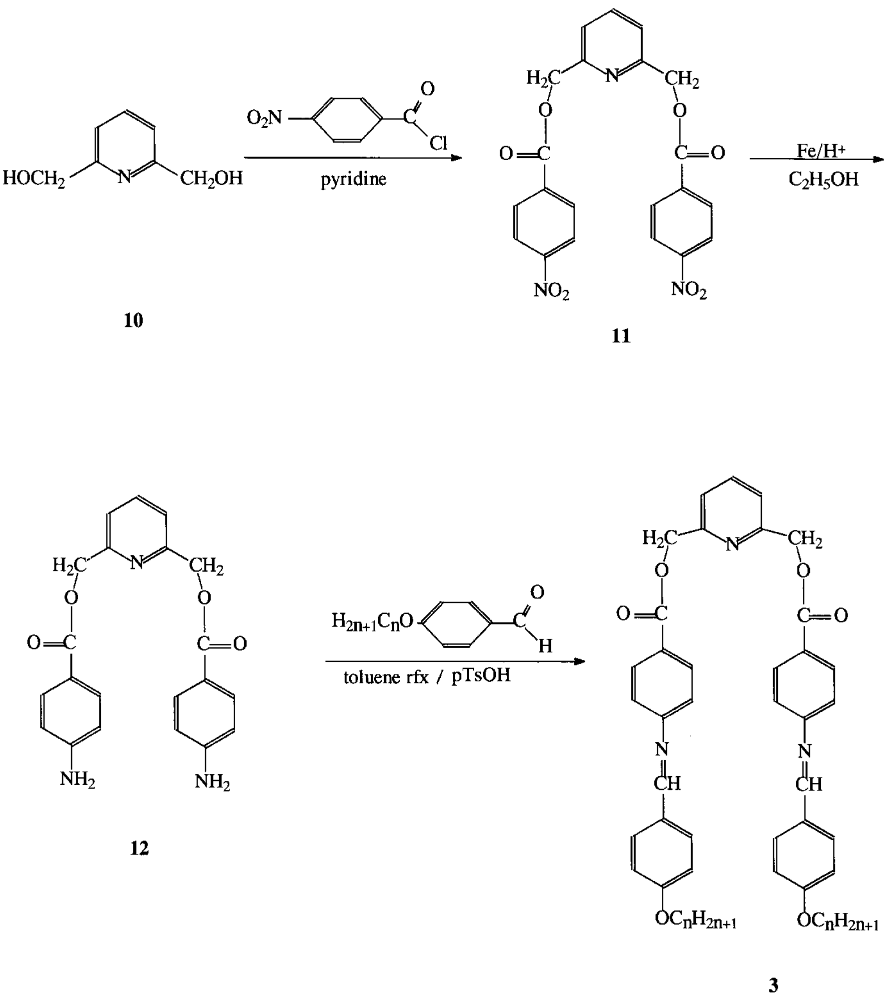
To a solution of 4-hexylresorcinol (6 g, 30.9 mmol) in toluene (200 cm^3) and pyridine (10 cm^3) *p*-nitrobenzoyl chloride (13 g, 70.1 mmol) in dry toluene (50 cm^3) was added all at once. The reaction mixture was heated on a water bath for 8 h; then the solvents were evaporated and the crude product was chromatographed on silica gel, eluting with toluene. The oily material slowly solidified under methanol to give the pure product **6** (11.3 g, 23 mmol). Yield 74.3%, m.p. = 75.9°C. ^{1}H NMR (200 MHz) (CDCl$_3$) δ 8.38 (d, 8H, $J = 5.8$ Hz), 7.19 (m, 2H), 7.16–7.14 (m, 1H), 2.61 (t, 2H, $J = 7.7$ Hz), 1.66–1.55 (m, 2H), 1.41–1.09 (m, 6H), 0.83 (t, 3H, $J = 5.8$ Hz). ^{13}C NMR (CDCl$_3$) δ 163.02, 162.91, 151.01, 150.92, 134.62, 134.44, 132.76, 131.27, 131.24, 130.98, 123.86, 123.73, 119.44, 115.71, 31.52, 29.99, 29.87, 28.96, 22.47, 13.98. IR (KBr) 2890, 1710, 1500 cm^{-1}. Elemental analysis for $C_{26}H_{24}O_8N_2$: calc. C 63.21, H 4.87, N 5.69; found C 63.29, H 5.01, N 5.35%.

2.2.2. *3-(4-Nitrobenzoyloxy)phenyl 4-nitrobenzoate (**7**)*

This was prepared in a similar way to **6**. Yield 81%, m.p. = 184.1°C. ^{1}H NMR (500 MHz) (CDCl$_3$) δ 8.38 (d, 7H, $J = 1.5$ Hz), 7.54 (t, 1H, $J = 8.5$ Hz), 7.27–7.23 (m, 4H). IR (KBr): 2890, 1720, 1500 cm^{-1}. Elemental analysis for $C_{20}H_{12}N_2O_8$: calc. C 58.83, H 2.96, N 6.86; found C 58.72, H 3.05, N 6.71%.

2.2.3. *3-(4-Aminobenzoyloxy)-4-hexylphenyl 4-aminobenzoate (**8**)*

A mixture of dinitrocompound **6** (8.5 g, 17.2 mmol), ethanol (500 cm^3), iron dust (27 g, 0.5 mol) and conc. HCl (1 cm^3) was heated under reflux for 10 h. The



Scheme. 2

solvent was evaporated and the crude product was chromatographed on silica gel, eluting with ethylene dichloride. The product was twice recrystallized from ethylene dichloride to obtain the pure product **8** (3.6 g, 8.3 mmol). Yield 48.2%, m.p. = 143.6°C. ^{1}H NMR (200 MHz) ($CDCl_3$) δ 8.02–7.96 (m, 4H), 7.29 (s, 1H), 7.07–7.01 (m, 2H), 6.71–6.65 (m, 4H), 4.16 (broad s, 4H), 2.55 (t, 2H, $J = 7.5$ Hz), 1.68–1.51 (m, 2H), 1.40–1.11 (m, 6H), 0.83 (t, 3H, $J = 6.3$ Hz). ^{13}C NMR ($CDCl_3$) δ 165.04, 164.85, 151.54, 151.47, 149.47, 149.42, 132.35, 132.19, 130.23, 119.12, 118.66, 118.54, 116.45, 113.89, 113.84, 31.62, 30.04, 29.94, 29.04, 22.55, 14.05. IR (KBr) 3600, 2880, 1780, 1500 cm^{-1}. Elemental analysis for $C_{26}H_{28}N_2O_4$: calc. C 72.22, H 6.22, N 6.48; found C 72.01, H 6.62, N 6.25%.

2.2.4. *3-(4-Aminobenzoyloxy)phenyl 4-aminobenzoate (9)*

This was obtained in a similar way to **8**. Yield 41%, m.p. = 191.9°C. ^{1}H NMR (500 MHz) ($CDCl_3$) δ 8.17–8.15 (m, 4H), 8.00–7.98 (m, 4H), 7.44–7.40 (m, 4H), 4.05 (broad s, 4H). IR (KBr) 3600, 2900, 1710, 1600, 1500 cm^{-1}. Elemental analysis for $C_{20}H_{16}N_2O_4$: calc. C 68.96, H 4.63, N 8.04; found C 68.72, H 4.81, N 7.95%.

2.2.5. *3-[4-(4-Dodecyloxybenzylideneamino)benzoyloxy]-4-hexylphenyl 4-(4-dodecyloxybenzylideneamino)-benzoate (1, $n = 12$)*

To diamine **6** (2 g, 4.6 mmol) dissolved in toluene *p*-dodecyloxybenzaldehyde (3.5 g, 12 mmol) and *p*-toluenesulphonic acid (100 mg) were added. The reaction mixture was heated for 48 h with azeotropic removal of water. The solvent was then evaporated under reduced pressure and methanol was added to the remaining oil. The mixture was kept overnight when the product very slowly solidified. The precipitate was twice recrystallized from di-isopropyl ether and the pure product (**1**, $n = 12$) (1.81 g, 1.9 mmol) was obtained. Yield 40.2%. ^{1}H NMR (200 MHz) ($CDCl_3$) δ 8.38 (s, 2H), 8.24–8.18 (m, 4H), 7.82 (d, 4H, $J = 7.9$ Hz), 7.38–7.03 (m, 7H), 6.90 (d, 4H, $J = 7.9$ Hz), 4.03 (t, 4H, $J = 6.5$ Hz), 2.60 (t, 2H, $J = 7.5$ Hz), 1.95–1.20 (m, 48H), 0.88 (t, 9H, $J = 7.6$ Hz). ^{13}C NMR ($CDCl_3$) δ 164.75, 164.58, 162.39, 161.15, 161.18, 157.40, 157.29, 149.32, 149.27, 132.37, 131.51, 130.93, 130.46, 128.55, 126.12, 125.97, 121.04, 120.95, 119.26, 116.27, 114.80, 68.27, 31.93, 31.61, 30.06, 30.00, 29.65, 29.60, 29.36, 29.16,29.07, 26.01, 22.70, 22.55, 14.14, 14.07. IR (KBr) 2880, 1720, 1510 cm^{-1}. Elemental analysis for $C_{64}H_{84}N_2O_6$: calc. C 78.68, H 8.60, N 2.86; found C 78.50, H 8.85, N 2.71%.

The remaining compounds of series **1** and **2** were obtained by similar methods.

2.2.6. *3-[4-(4-Undecyloxybenzylideneamino)benzoyloxy]-4-hexylphenyl 4-(4-undecyloxybenzylideneamino)-benzoate (**1**, n = 11)*

Yield 31%. Elemental analysis for $C_{62}H_{80}N_2O_6$: calc. C 78.44, H 8.49, N 2.95; found C 78.25, H 8.55, N 2.78%.

2.2.7. *3-[4-(4-Tridecyloxybenzylideneamino)-benzoyloxy]-4-hexylphenyl 4-(4-tridecyloxy-benzylideneamino)benzoate (**1**, n = 13)*

Yield 36%. Elemental analysis for $C_{66}H_{88}N_2O_6$: calc. C 78.84, H 8.82, N 2.79; found C 78.63, H 8.99, N 2.62%.

2.2.8. *3-[4-(4-Tetradecyloxybenzylideneamino)-benzoyloxy]-4-hexylphenyl 4-(4-tetradecyloxy-benzylideneamino)benzoate (**1**, n = 14)*

Yield 45%. Elemental analysis for $C_{68}H_{92}N_2O_6$: calc. C 79.06, H 8.91, N 2.71; found C 79.11, H 9.02, N 2.61%.

2.2.9. *3-[4-(4-Pentadecyloxybenzylideneamino)-benzoyloxy]-4-hexylphenyl 4-(4-pentadecyloxy-benzylideneamino)benzoate (**1**, n = 15)*

Yield 28%. Elemental analysis for $C_{70}H_{96}N_2O_6$: calc. C 79.20, H 9.11, N 2.64; found C 79.01, H 9.25, N 2.47%.

2.2.10. *3-[4-(4-Hexadecyloxybenzylideneamino)-benzoyloxy]-4-hexylphenyl 4-(4-hexadecyloxy-benzylideneamino)benzoate (**1**, n = 16)*

Yield 42%. Elemental analysis for $C_{72}H_{100}O_6N_2$: calc. C 79.41, H 9.19, N 2.57; found C 79.62, H 9.29, N 2.69%.

2.2.11. *3-[4-(4-Octyloxybenzylideneamino)benzoyloxy]-phenyl 4-(4-octyloxybenzylideneamino)-benzoate (**2**, n = 8)*

Yield 35%. ^{1}H NMR (500 MHz) ($CDCl_3$) δ 8.43 (s, 2H), 8.21–8.20 (m, 4H), 7.99–7.97 (m, 4H), 7.49–7.43 (m, 2H), 7.40–7.36 (m, 4H), 7.20–7.16 (m, 2H), 7.00–6.98 (m, 4H), 4.03 (t, 4H, $J = 6.5$ Hz), 1.83–1.79 (m, 4H), 1.49–1.44 (m, 4H), 1.41–1.20 (m, 16H), 0.89 (t, 6H, $J = 7.0$ Hz). IR (KBr) 2920, 2880, 1720, 1600, 1500 cm^{-1}. Elemental analysis for $C_{50}H_{56}N_2O_6$: calc. C 76.92, H 7.18, N 3.59; found C 76.79, H 7.02, N 3.71%.

2.2.12. *3-[4-(4-Tridecyloxybenzylideneamino)benzoyloxy]-phenyl 4-(4-tridecyloxybenzylideneamino)-benzoate (**2**, n = 13)*

Yield 38%. Elemental analysis for $C_{60}H_{76}N_2O_6$: calc. C 78.22, H 8.31, N 3.04; found: C 78.02, H 8.50, N 2.86%.

2.2.13. *3-[4-(4-Tetradecyloxybenzylideneamino) benzoyloxy]phenyl 4-(4-tetradecyloxy-benzylideneamino)benzoate (**2**, n = 14)*

Yield 43%. Elemental analysis for $C_{62}H_{80}N_2O_6$: calc. C 78.44, H 8.49, N 2.95; found C 8.26, H 8.55, N 2.92%.

2.2.14. *3-[4-(4-Pentadecyloxybenzylideneamino) benzoyloxy]phenyl 4-(4-pentadecyloxy-benzylideneamino)benzoate (**2**, n = 15)*

Yield 42%. Elemental analysis for $C_{64}H_{84}N_2O_6$: calc. C 78.65, H 8.66, N 2.87; found C 78.51, H 8.76, N 2.69%.

2.2.15. *3-[4-(4-Hexadecyloxybenzylideneamino) benzoyloxy]phenyl 4-(4-hexadecyloxy-benzylideneamino)benzoate (**2**, n = 16)*

Yield 48%. Elemental analysis for $C_{66}H_{88}N_2O_6$: calc. C 78.84, H 8.82, N 2.79; found C 78.69, H 8.99, N 2.65%.

2.2.16. *6-(4-Nitrobenzoyloxymethyl)pyridine-2-methyl 4-nitrobenzoate (**11**)*

p-Nitrobenzoyl chloride (38 g, 0.2 mol) in toluene (250 cm^3) was added to 6-(hydroxymethyl)-2-pyridyl-methanol (**10**) (14 g, 0.1 mol) suspended in toluene (200 cm^3) and pyridine (30 cm^3). The reaction mixture was heated for 48 h on a water bath, and then the solvents were evaporated. The crude product was purified by column chromatography on silica gel, eluting with 2% methanol in chloroform. The product solidified slowly under methanol to give the pure product **11** (31 g, 71 mmol). Yield 70.4%, m.p. = 160.4°C. ^{1}H NMR (200 MHz) ($CDCl_3$) δ 8.29 (s, 8H), 7.82 (t, 1H, $J = 8.0$ Hz), 7.43 (d, 2H, $J = 7.6$ Hz), 5.53 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 164.37, 155.22, 137.87, 135.16, 130.15, 123.65, 121.29, 67.79. IR (KBr) 2880, 1720, 1500 cm^{-1}. Elemental analysis for $C_{21}H_{15}N_3O_8$: calc. C 57.67, H 3.46, N 9.61; found C 57.48, H 3.66, N 9.38%.

2.2.17. *6-(4-Aminobenzoyloxymethyl)pyridine-2-methyl 4-aminobenzoate (**12**)*

To dinitro compound **11** (30 g, 68.6 mmol), iron dust (100 g), ethanol (700 cm^3) and conc. HCl (1 cm^3) were added. The reaction mixture was heated at reflux for 48 h. The inorganic salts were removed on a celite pad by filtration and the red filtrate was evaporated to dryness. The product crystallized from ethylene dichloride–tetrahydrofuran (2:1) mixture to give the pure compound **12** (11.5 g, 30.5 mmol). Yield 44%, m.p. = 193.9°C. ^{1}H NMR (200 MHz) ($CDCl_3$) δ 7.92–7.89 (m, 4H), 7.30–7.25 (m, 3H), 6.67–6.62 (m, 4H), 5.44 (s, 4H), 4.05 (broad s, 4H). IR (KBr): 3600, 2990, 2880, 1710, 1600, 1500 cm^{-1}. Elemental analysis for $C_{21}H_{19}N_3O_4$: calc. C 66.83, H 5.07, N 11.13; found C 66.71, H 5.25, N 11.01%.

2.2.18. *6-[Dodecyloxybenzylideneamino)benzoyloxy-methyl]pyridine-2-methyl 4-(4-dodecyloxy-benzylideneamino)benzoate (3, n = 12)*

To diamine **12** (1 g, 2.7 mmol), *p*-dodecyloxybenzaldehyde (2 g, 6.9 mmol), *p*-toluenesulphonic acid (0.1 g) and toluene (300 cm^3) were added. The reaction mixture was heated for 48 h with azeotropic removal of water; the solvent was then evaporated under reduced pressure and the resulting solid was twice recrystallized from a tetrahydrofuran–di-isopropyl ether (1 : 1) mixture to give the product (**3**, $n = 12$) (1.1 g, 1.2 mmol). Yield 45%. ^{1}H NMR (200 MHz) (CDCl$_3$) δ 8.35 (s, 2H), 8.14 (d, 4H, $J = 8.5$ Hz), 7.84 (d, 4H, $J = 8.5$ Hz), 7.42–7.37 (m, 3H), 7.20 (d, 4H, $J = 8.5$ Hz), 6.97 (d, 4H, $J = 8.5$ Hz), 5.05 (s, 4H), 4.02 (t, 4H, $J = 6.5$ Hz), 1.84–1.78 (m, 4H), 1.49–1.44 (m, 4H), 1.40–1.21 (m, 32H), 0.88 (t, 6H, $J = 6.8$ Hz). IR (KBr, cm^{-1}): 2930, 2880, 1720, 1505 cm^{-1}. Elemental analysis for $C_{59}H_{75}N_3O_6$: calc. C 76.84, H 8.20, N 4.56; found C 76.77, H 8.25, N 4.23%.

The other compounds of group **3** were obtained in similar way.

2.2.19. *6-[Tetradecyloxybenzylideneamino)benzoyloxy-methyl]pyridine-2-methyl 4-(4-tetradecyloxy-benzylideneamino)benzoate (3, n = 14)*

Yield 51%. Elemental analysis for $C_{63}H_{83}N_3O_6$: calc. C 77.34, H 8.55, N 4.26; found C 77.14, H 8.65, N 4.11%.

2.2.20. *6-[Pentadecyloxybenzylideneamino)benzoyloxy-methyl]pyridine-2-methyl 4-(4-pentadecyloxy-benzylideneamino)benzoate (3, n = 15)*

Yield 42%. Elemental analysis for $C_{65}H_{87}N_3O_6$: calc. C 77.57, H 8.71, N 4.18; found C 77.39, H 8.95, N 4.01%.

2.2.21. *6-[Hexadecyloxybenzylideneamino)benzoyloxy-methyl]pyridine-2-methyl 4-(4-hexadecyloxy-benzylideneamino)benzoate (3, n = 16)*

Yield 48%. Elemental analysis for $C_{67}H_{91}N_3O_6$: calc. C 77.79, H 8.87, N 4.06; found C 77.58, H 8.95, N 4.01%.

3. Results and discussion

The compounds of series **1** exhibit monotropic nematic phase about 20°C below the clearing temperatures (see the table). The mesophase can be easily supercooled and is stable at room temperature for several hours. A weak odd–even effect can be observed along the nematic–isotropic phase transition line. At these points DSC gives enthalpy changes of *c.* 0.7 J g^{-1}.

The microscopic phase identification was confirmed by X-ray studies. A diffractogram obtained for the nematic phase of the compound with $n = 12$ of series **1** shows two broad lorentzian signals related to the averaged longitudinal and transverse dimensions of the molecule. These reflections are typical for nematics with a short correlation length and a liquid-like translational order of the molecules.

In the microscopic studies of the nematic phase's schlieren texture a large number of $s = \pm 1/2$ defects was found and $s = \pm 1$ disclinations were much less numerous than the centres with two brushes (figure 1) [12]. In a unixial nematic, defects of strength ± 1 are preferred due to the escape of the director orientation in the third dimension and formation of a continuous structure of low energy [13]; this is not the case for our compounds. In a biaxial nematic phase, the escape in the third dimension does not make the phase structure smooth and cannot relax the defect energy. The microscopic textures suggest that the nematic phase observed might be biaxial. However, we were not able to verify this possibility by conoscopic studies because attempts to obtain a homeotropic texture on a surfactant support were unsuccessful.

Table. Phase sequences, phase transition temperatures (°C) and enthalpies (in parenthesis, J g^{-1}) for compounds of series **1**, **2** and **3**.

Series **1**			Series **2**			Series **3**	
n	Cr–I	N–I	*n*	Cr–I	Sm–I	*n*	Cr–I
11	77.3 (55.6)	33.8 (0.5)	8	128.0 (43.9)	—	12	138.2 (99.4)
12	74.0 (43.4)	43.6 (0.7)	13	112.7 (82.6)	110.5 (12.3)	14	137.4 (103.3)
13	65.0 (54.6)	42.8 (0.7)	14	111.7 (78.2)	108.8 (6.4)	15	136.2 (110.2)
14	63.2 (50.7)	46.7 (0.8)	15	112.3 (84.7)	—	16	135.6 (105.7)
15	74.8 (90.6)	44.0 (0.8)	16	115.1 (74.5)	113.7 (17.2)		
16	63.2 (49.8)	46.6 (0.8)					

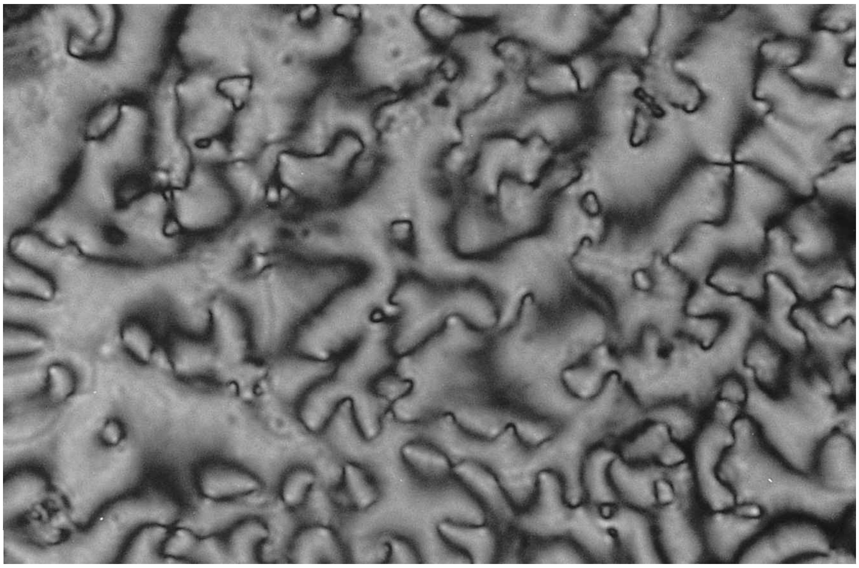


Figure 1. Texture of the nematic phase for the compound of series **1**, with $n = 12$.

To study the orientational order of the mesophase, the EPR spin prove method was used [14]. The compound of series **1** with $n = 12$ was doped by the paramagnetic bis(dimethyldithiocarbamato)copper(II) complex, $(dmdtc)_2Cu$, (see inset in figure 2). In the dopant, the isotope ^{63}Cu was introduced to reduce the EPR line broadening due to the presence of the second natural isotope. The length of the paramagnetic molecule used is chosen to be comparable to the length of the branches of the banana-shaped molecule in order to study the alignment of the branch groups in the mesomorphic matrix. The EPR spectrum obtained for the nematic phase is not typical. It is biaxial and resembles the spectrum of the glassy solid state, figure 2(*a*),

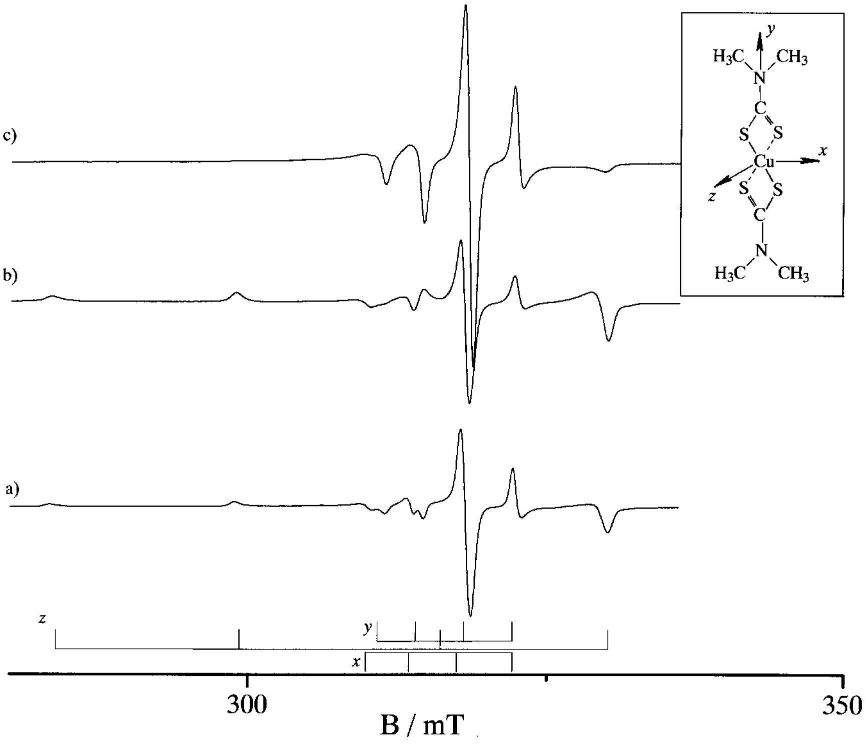


Figure 2. EPR spectra of the probe, $(dmdtc)_2Cu$ (see the inset) dispersed in the host matrix of the compound of series **1**, with $n = 12$: glassy state of the crystalline phase (*a*), the aligned sample in the nematic phase, with the director oriented perpendicular (*b*) and parallel (*c*) to the external magnetic field.

with its characteristic signals and magnetic parameters ($g_{xx} = 2.024$, $g_{yy} = 2.019$, $g_{zz} = 2.087$, $A_{xx} = 4.25$ mT, $A_{yy} = 3.65$ mT, $A_{xx} = 15.5$ mT). A similar spectrum is observed for the isotropic phase at temperatures above the clearing point. When the temperature is increased to ~150°C the EPR spectrum does become isotropic. The visible biaxiallity of the nematic and isotropic phases is due to the strong restriction of molecular movement in the sample on the EPR time scale. In the nematic phase, the high field signal related to the z component of the copper ion is 0.2 mT broader than that in the glassy state. Thus, an evaluated frequency of molecular reorientation [15] is of the order 3×10^9 Hz and is not significantly changed at the clearing point. The slow molecular rotation is probably associated with the very high viscosity of the compounds studied in both the liquid crystalline and isotropic phases.

When the sample is slowly cooled (during an hour) in a magnetic field of 1 T from the isotropic (at 150°C) to the nematic phase, the latter becomes partially oriented. In the EPR spectrum obtained for such a sample, figure 2(*c*), the signals related to the molecular long axis of the probe (y signals of co-ordinated Cu ions) are the more intense, whereas the signals connected with the transverse probe axis (z and x signals of Cu ions) are suppressed. When the oriented sample is rotated around an axis perpendicular to the applied magnetic field the intensities of the EPR signals are steadily changed—the small peaks grow and the large decrease. After rotation by 90°, the lines belonging to the z and x axes of the probe are the highest in the spectrum, figure 2(*b*). However, the positions of the EPR features are almost stable during the sample rotation. These results unambiguously show that the probe molecules are aligned along the magnetic field.

The matrix molecules in the liquid-like phase introduced into the strong magnetic field are aligned due to their diamagnetic anisotropy. The diamagnetic anisotropy of the phenyl rings directs the banana branches parallel to the field. As a result, we can suppose that the whole bent molecule is aligned with its long axis parallel to the field, the long axis being defined as a line connecting the molecular extremes. In the uniaxial nematic phase, even if the molecular rotation around the long axis were strongly slowed down, but not restricted in angle, the probe molecules would feel the cylindrical molecular potential, and on average would be aligned along the nematic director, and thus the magnetic field. On the other hand in the biaxial nematic matrix, where the rotation of the molecules around the long axis would be restricted, the appropriately adjusted probes would interact mainly with the banana branches. Thus the probe molecules would be inclined to the field. This is not the situation observed experimentally. In our experiment, the probes are parallel to the magnetic field. This shows that the molecules of the host matrix, which order the probes, exhibit a uniaxial symmetry.

The related compounds of series **2** were also studied. The absence of the lateral hexyl chain gives typical banana-shaped molecules for which a monotropic smectic phase was detected. The natural texture obtained for a thin sample upon cooling from the isotropic phase is schlieren-like, resembling the nematic phase texture. However, the high clearing enthalpy and weakly birefringent fan-like texture observed under an applied electric field show that the phase exhibits smectic order. The structure of the smectic phase could not however be studied in detail since the materials easily recrystallize.

The compounds of group **3**, in which the central phenyl ring is replaced by a pyridine ring and a three-atom linking group is used, do not form any liquid crystalline phases.

4. Conclusions

Summarizing, new series of bent-shaped molecules have been synthesized. The lateral chain introduced at the 4-position into the central resorcinol ring promotes formation of the nematic phase. The nematic phase, although formed by biaxial molecules, seems to be uniaxial.

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