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Preliminary communication

Synthesis and mesomorphic properties of four-ring liquid crystals containing cyclohexyl, phenyl and pyridyl units

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Two series of chiral and achiral 4-[(3-*n*-alkoxycarbonylpyridyl)-6-ethynyl]phenyl 4-(*trans*-4-*n*-alkylcyclohexyl)benzoate liquid crystals have been synthesized. Their mesomorphic properties were observed and measured by polarizing optical microscopy and DSC. A broad chiral smectic C phase was observed when terminal chains contained a chiral centre.

Mesogens containing the pyridyl unit group have been widely used. Because of the presence of one nitrogen atom, they are less symmetric and have lower melting points than similar mesogens containing a phenyl group [1–3]. On the other hand, they have a high birefringence and many other advantages [4–5], so they are often used as significant components of mixtures for ferroelectric liquid crystal displays (FLCDs). We have previously prepared three-ring liquid crystals containing cyclohexyl, phenyl and pyridyl units with a chiral terminal chain; but only a narrow chiral smectic C phase was obtained, and their clearing points were very low [6]. In order to meet the higher quality requirements for applied materials and to observe the relationship between structures and mesomorphic properties, we introduced another phenyl group to increase the clearing points and mesomorphic stability. In this paper, the synthesis and mesomorphic behaviours of a novel kind of four-ring mesogens containing cyclohexyl, two phenyl and pyridyl units are reported. Their mesomorphic properties are compared with similar compounds containing only one phenyl unit. Structures and synthesis route of target compounds are shown in the scheme.

The following are results of identification analyses of the target compounds.

4-[(3-((*S*)-1-Methylheptoxycarbonylpyridyl)-6-ethynyl]-phenyl 4-(*trans*-4-*n*-propylcyclohexyl)benzoate (**A3**). ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ H (ppm): 0.90 (t, 3H), 1.05–2.70 (m, 30H), 5.20 (m, 1H), 7.30 (d, 2H, $J = 9$ Hz), 7.35 (d, 2H, $J = 9$ Hz), 7.60 (d, 1H, $J = 9$ Hz), 7.65 (d, 2H, $J = 9$ Hz), 8.15 (d, 2H, $J = 9$ Hz), 8.30 (d, 1H, $J = 9$ Hz), 9.25 (s, 1H). MS (*m*/*z*, %): 579 (M^+, 0.30). Analysis for $C_{38}H_{45}O_4N$: calc. C 78.72, H 7.82, N 2.42; found C 78.71, H 8.00, N 2.18%. IR (KBr, ν_{max}, cm^{-1}): 2956, 2922, 2854, 2221, 1745, 1714, 1589, 1269, 1209, 1156, 1060, 1014, 877, 780.

4-[(3-((*S*)-1-Methylheptoxycarbonylpyridyl)-6-ethynyl]-phenyl 4-(*trans*-4-*n*-pentylcyclohexyl)benzoate (**A5**). ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ H (ppm): 0.90 (t, 3H), 1.05–2.70 (m, 34H), 5.20 (m, 1H), 7.30 (d, 2H, $J = 9$ Hz), 7.35 (d, 2H, $J = 9$ Hz), 7.60 (d, 1H, $J = 9$ Hz), 7.65 (d, 2H, $J = 9$ Hz), 8.15 (d, 2H, $J = 9$ Hz), 8.30 (d, 1H, $J = 9$ Hz), 9.25 (s, 1H). MS (*m*/*z*, %): 607 (M^+, 0.46). Analysis for $C_{40}H_{49}O_4N$: calc. C 79.04, H 8.13, N 2.30; found C 79.09, H 8.38, N 2.06%. IR (KBr, ν_{max}, cm^{-1}): 2922, 2854, 2220, 1746, 1714, 1589, 1508, 1377, 1268, 1209, 1122, 1062, 1014, 878, 780.

4-[(3-*n*-Octoxycarbonylpyridyl)-6-ethynyl]phenyl 4-(*trans*-4-*n*-propylcyclohexyl)benzoate (**B3**). ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ H (ppm): 0.90 (t, 3H), 1.05–2.70 (m, 29H), 4.35 (t, 2H, $J = 6$ Hz), 7.30 (d, 2H, $J = 9$ Hz), 7.35 (d, 2H, $J = 9$ Hz), 7.60 (d, 1H, $J = 9$ Hz), 7.65 (d, 2H, $J = 9$ Hz), 8.15 (d, 2H, $J = 9$ Hz), 8.30 (d, 1H, $J = 9$ Hz), 9.25 (s, 1H). MS (*m*/*z*, %): 579 (M^+, 0.26). Analysis for $C_{38}H_{45}O_4N$: calc. C 78.72, H 7.82, N 2.42; found C 78.46, H 8.00, N 2.21%. IR (KBr, ν_{max}, cm^{-1}): 2955, 2920, 2852, 2220, 1741, 1716, 1590, 1507, 1377, 1207, 1125, 1062, 1014, 879, 780.

Other target compounds and intermediates have satisfactory elementary analysis and appropriate ^{1}H and, IR and MS spectral data.

The mesomorphic properties of the new compounds were studied by thermal polarizing optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a temperature control unit (FP-82); also by differential scanning calorimetry (DSC, Shimadzu-50 calorimeter with a data system,

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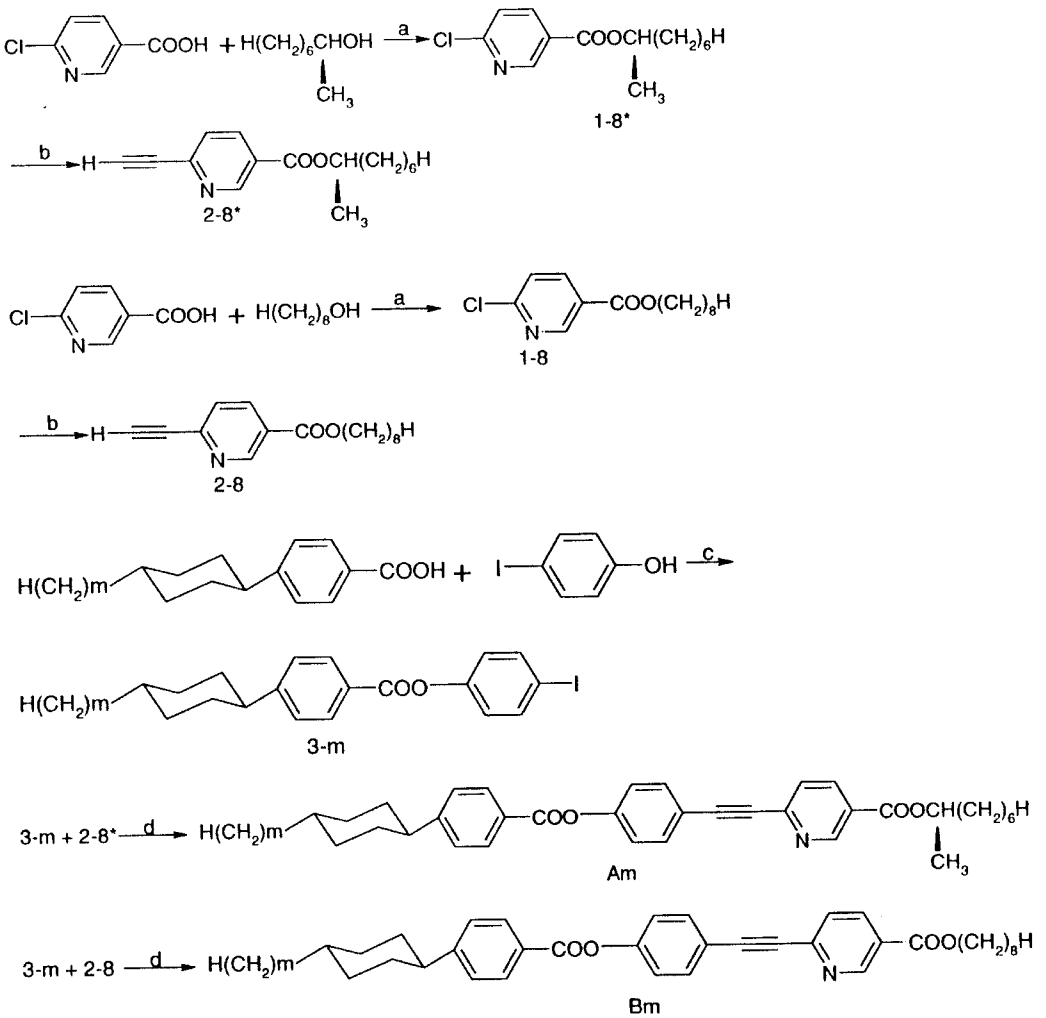
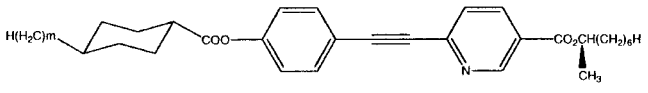


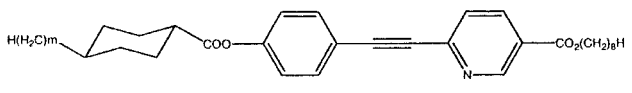
Reagents and conditions: (a) DCC, cat. DMAP, THF; (b) 1. trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; 2. TBAF, THF; (c) DCC, cat. DMAP, THF; (d) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N.

Scheme. Synthesis route.

heating and cooling rate 5°C min^{-1}). Phase identification was made by comparing the observed textures with those reported in the literatures [7, 8]. Their transition temperatures are summarized below (°C), together with those for the comparison compounds **A′*m***, **B′*m***, whose structures are shown here.



A′m



B′m

A3: Cr 122.2 SmC* 226.0 N 233.7 I 232.9 N 225.3 SmC* 106.4 Recr

A5: Cr 126.5 SmC* 218.5 I 217.4 SmC* 107.5 Recr

B3: Cr 122.2 SmA 236.2 N 264.7 I 273.5 N 235.2 SmA 114.7 Recr

A′3: Cr 92.3 SmC* 113.3 I 112.5 SmC* 73.9 Recr

A′5: Cr 90.2 SmC* 121.4 I 120.6 SmC* 79.3 SmE 74.7 Recr

B′3: Cr 89.5 SmA 125.0 N 170.6 I 170.2 N 125.7 SmA 78.1 Recr.

From the observation of the mesomorphic properties of the target compounds, we see that all are mesogens. Comparing series **A*m*** and **B*m*** with series **A′*m*** and **B′*m***, it can be seen that melting points increase by about 30–36°C, but clearing points increase by about 90–120°C, the mesophase range thus increases 60–90°C. The new phenyl ring increases the molecular conjugation, making the molecules more rigid and increasing the width to length ratio; the stability of the mesophases is therefore much increased.

On the other hand, a narrow nematic phase is exhibited by **A3**, with a broad chiral smectic C phase; but in **A′3**, only a narrow chiral smectic C phase is seen. Thus the new phenyl group is advantageous to the formation of both nematic and smectic phases in series **A*m***. But in the **B*m*** series the situation is different; the nematic phase range was reduced, but the smectic phase range was increased.

In conclusion, the increase of the rigid liquid crystalline core stabilizes the mesophases, and the chiral smectic C phase broadens.

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