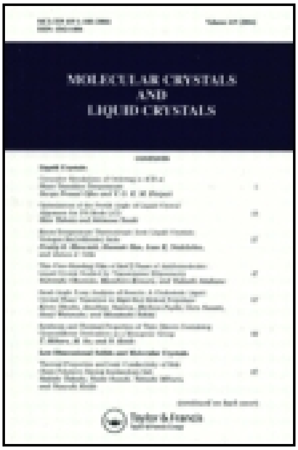

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Synthesis and Characterization of Liquid Crystalline Molecules Containing the Quinoline Unit

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Synthesis and Characterization of Liquid Crystalline Molecules Containing the Quinoline Unit

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A homologous series of heterocyclic liquid crystals containing the quinoline unit have been synthesized and characterized. These compounds show a smectic phase at low temperatures. The quinoline unit containing lone pair electrons introduces a significant dipole moment resulting in attractive forces to form a smectic phase. The heterocyclic structure may also break the centrosymmetry of the core of the molecule, which may be favored in the application of displays and nonlinear optics.

Keywords: heterocyclic liquid crystals, quinoline, nonlinear optics (NLO), second harmonic generation (SHG).

As is well known, liquid crystals with high (positive or negative) dielectric anisotropy ($\Delta\varepsilon$),[1] and even better with wide mesomorphic range at low temperatures[2] are useful for electro-optic devices. Therefore, in the case $\Delta\varepsilon < 0$, benzene-containing liquid crystalline (LC) molecules often contain lateral substituents with strong dipoles, such as a cyano group (see Fig. 1) to exhibit a large negative $\Delta\varepsilon$ and consequently to have low threshold voltages.[1a] However, to some extent, the lateral substituents may cause the disadvantage of the system broadening[1a,3] and in some cases depress the range of liquid crystalline phases.[1a] On the basis of this point of view, pyridine[1b,3] or pyridazine[4] derivatives are chosen as the rigid part of the target liquid crystalline molecules, because the lone pair electrons of the nitrogen atom in the core of the molecule generate a significant dipole moment to introduce attractive forces and thus to aid the formation of smectic phases.[1a,5] Nonetheless not many results have been reported on the preparation of the liquid crystalline molecules consisting of the quinoline unit[6] which also possesses lone pair electrons of nitrogen in the system. Accordingly, the lone pair electrons can introduce a dipole moment in the molecules and may also possess a high negative dielectric anisotropy as the pyridine derivatives behave. Moreover, heterocyclic compounds have also been noticed for

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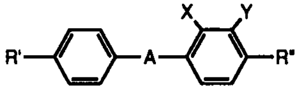
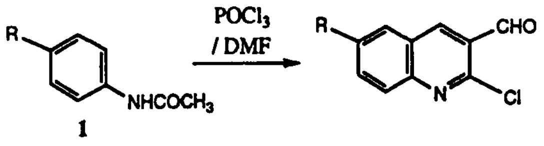
*Authors for correspondence.



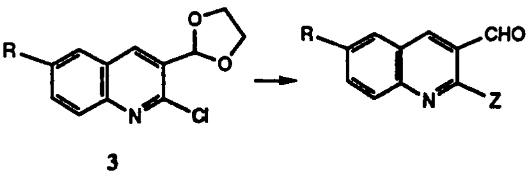
X, or Y = CN
A = linking group, R' and R" = terminal groups

FIGURE 1 Liquid crystalline structure containing lateral substituents with strong dipoles.



2a R = C_4H_9 (60%)
2b R = C=C-C-O (40%)
2c R = C_7H_{15} (42%)

SCHEME 1 The synthetic route for compounds **2a**–**2c**.



4a R = C_4H_9, Z = I (52%)
4b R = C_4H_9, Z = SCN (60%)
4c R = C_4H_9, Z = F (12%)
4d R = C_4H_9, Z = OEt (45%)
4e R = C_7H_{15}, Z = OEt (54%)

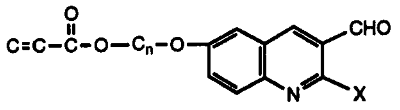
SCHEME 2 The synthetic route for compounds **4a**–**4e**.

the non-centrosymmetric chemical structure which may improve their liquid crystalline and nonlinear optical properties. For instance, the quinoline unit composed of the nitrogen atom in the core of the molecule breaks the inversion center of the symmetry, which may reduce LC phase transition temperatures and thus stabilize the highly disordered LC phases (S_A, S_C, etc.).[7] Herein, we wish to report our preliminary results of successful synthesis of heterocyclic liquid crystalline molecules containing the quinoline unit.

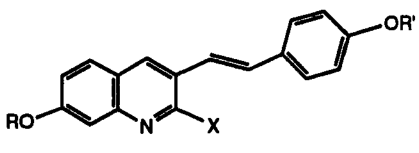
Compounds **2a**–**2c** were prepared according to the literature method,[8] and a typical procedure is shown as follows: The acetanilide **1**(20 mmole) was added to a solution of $POCl_3$ (140 mmole) and DMF (60 mmole) at 0°C, and the resulting mixture was sealed and then stirred at 80–85°C for 6–7 hours. The desired products **2a**–**2c** were obtained in moderate yields after normal work-up and recrystallization (see Scheme 1).[8]

Reaction of NaI with intermediate **3** which was prepared from compound **2a** and ethylene glycol in the presence of aqueous HCl produces compound **4a** in 52% overall yield (see Scheme 2).[9] Products **4b**–**4d** were prepared similarly.

The transition temperatures and corresponding enthalpy changes of compounds **2a**–**2c** and **4a**–**4e** are shown in Table I. Compound **4a** does not possess a liquid crystalline phase which may result from the broadening of the rigid part caused by iodide. Except for compounds **2b** and **4b**, compounds **2a**, **2c**, **4d** and **4e** possess a smectic phase at low temperatures which implies that these systems can be further studied and compounds such as analogous compound **5** will be potential liquid crystalline materials for polymerization in the practical uses. However, it is rather



5



6

TABLE I

Phase transition temperatures (°C)§ and corresponding enthalpy changes (J/g)*

Compound	Crystal		Smectic†		liquid
2a**	●	41.3(3.7)	●	77.5(65.3)	●
2b	●	118.0	●	120.8	●
2c‡	●	32.0(22.5)	●	63.0(78.0)	●
4a	(no liquid crystalline phase)				
4b	●	88.2	●	96.6	●
4c	(no liquid crystalline phase)				
4d	●	23.3	●	42.0	●
4e	●	38.5	●	43.2	●

§ Data obtained from the second DSC heating scan.

* Corresponding enthalpy changes are shown in the parentheses (blank for those overlapped phase transitions).

† Highly ordered smectic phases identified by polarizing microscope.

** The texture of **2a** is shown in Figure 3.

‡ The texture of **2c** is shown in Figure 4.

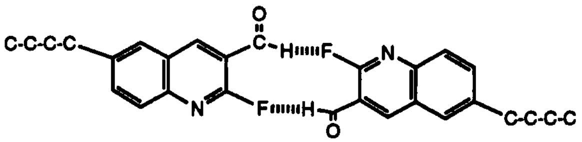


FIGURE 2 Possible molecular configuration of compound 4c.

surprising that compound **4c** does not show a smectic phase, which is quite abnormal.[1a] Possibly an internal hydrogen bonding between the aldehyde proton H and F arises, so the rigid part of the system is lengthened (see Fig. 2) and thus the liquid crystalline phase is depressed.

Another similar system **6** is also being investigated and found to show better liquid crystalline properties (broader range of S_A and S_C)[7] than those of the corresponding naphthalene system. As well as liquid crystalline properties, nonlinear optical (NLO) properties of system **6** has been investigated and it shows second harmonic generation (SHG) intensity 7 times larger than that of quartz in powder form. Further work of NLO experiments will give us more information in similar systems. Completed details will be published in the near future.[10]

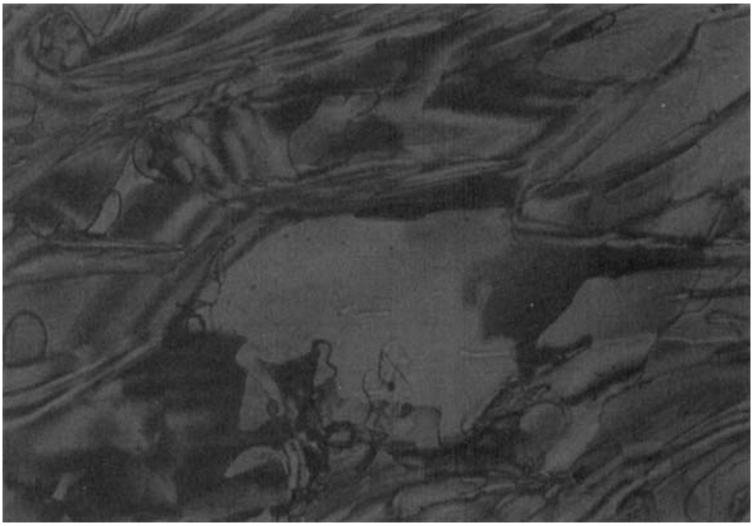


FIGURE 3 The highly ordered Smectic texture of **2a** identified by optical microscope. See Color Plate. XII.

FIGURE 4 The highly ordered Smetic texture of **2c** identified by optical microscope. See Color Plate. XIII.

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References

1. a) D. Coates, 1990, *Liquid Crystals-Application and uses* **1**, edited by B. Birendra, (World Scientific), Chapter 3, and references cited therein.
   b) A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, M. F. Grebyonkin and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, **209**, 155 (1991) and references cited therein.
2. a) J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 85 (1973).
   b) M. F. Schiekel and K. Fahrenschon, *Appl. Phys. Lett.*, **19**, 391 (1971).
3. M. P. Burrow, G. W. Gray, D. Lacey and K. J. Toyne, *Liq. Cryst.*, **3**, 1643 (1988).
4. M. P. Burrow, G. W. Gray, D. Lacey and K. J. Toyne, *Z. Chem.*, **94**, 139, (1986).
5. H. Schubert and H. Zaschke, *J. Prakt. Chem.*, **312**, 494 (1970).
6. a) A. K. Agrawal and S. A. Jenekhe, *Macromolecules*, **26**(5), 895 (1993).
   b) J. Bartulin, C. Zuniga, M Parra, B. Ros and J. L. Serrano, *Bol. Soc. Chil. Quim.*, **37**(3), 241 (1992).
   c) C. Zuniga, J. Bartulin, H. J. Muller, E. Schumacher and T. R. Taylor, *Mol. Cryst. Liq. Cryst.*, **206**, 131 (1991).
   d) R. Leardini, D. Nanni, G. F. Pedulli, A. Tundo and G. Zanardi, *Liq. Cryst.*, **2**(5), 625 (1987).
7. H. C. Lin, L. -L. Lai, W. P. Hsieh, R. C. Chen and L. Tsai, *Pacifichem Conference* (1995).
8. O. Mech-Cohn, B. Narine and B. Tarnowski, *Tetrahedron Lett.*, **33**, 3111 (1979).
9. Products with liquid crystalline phase *i.e.* **2a-2c**, **4b**, **4d** and **4e** were identified as the required materials and judged to be pure by elementary ^{1}H-and^{13}C-NMR spectroscopy as well as mass and high mass spectroscopy. Elementary analytical results for C, N, and H agreed with the calculated values within 0.3 percent. Products **4a** and **4c** were characterized by ^{1}H-and ^{13}C-NMR spectroscopy as well as mass and high mass spectroscopy. Selected physical data are as follows: **2a** ^{1}H-NMR: δ(CDCl$_3$) 0.96 (*t*, 3H, Me), 1.34 – 1.45(*m*, 2H, CH$_2$), 1.66 – 1.74(*m*, 2H, CH$_2$), 2.82(*t*, 2H, CH$_2$), 7.71 – 7.76(*m*, 2H, 2 × Ar-H), 7.98(d, 1H, $J = 9.2$ Hz, Ar-H), 8.69(s, 1H, Ar-H), 10.55(s, 1H, CHO). ^{13}C-NMR: δ(CDCl$_3$) 13.81(Me), 22.26, 33.00, 35.37(3 × CH$_2$), 126.20, 126.45, 127.65, 128.18, 135.07, 139.44, 143.10, 148.20, 149.07 (C of Ar), 188.89(CHO). **2b** ^{1}H-NMR: δ(CDCl$_3$) 4.65–4.69(*m*, 2H, CH$_2$), 5.34–5.53(*m*, 2H, 2 × =CH), 6.04–6.17(*m*, H, = CH), 7.17(d, 1H, $J = 2.7$ Hz, Ar-H), 7.51(2d, 1H, $J = 2.8$ and 6.8 Hz, Ar-H), 7.94 (d, 1H, $J = 9.3$ Hz, Ar-H), 8.58(s, 1H, Ar–H), 10.51(s, 1H, CHO). ^{13}C-NMR: δ(CDCl$_3$)69.39(CH$_2$), 107.82, 118.53, 126.54, 126.76, 127.73, 130.02, 132.39, 138.66, 145.80, 147.74, 157.80(C of Ar), 189.31 (CHO). **2c** ^{1}H-NMR: δ(CDCl$_3$) 0.88(*t*, 3H, Me), 1.26–1.35(*m*, 8H, 4 × CH$_2$), 1.69–1.74(*m*, 2H, CH$_2$), 2.81 (*t*, 2H, CH$_2$), 7.71–7.74(*m*, 2H, 2 × Ar–H), 7.98(*d*, 1H, $J = 9.2$ Hz, Ar-H), 8.68(*s*, 1H, Ar-H), 10.55 (*s*, 1H, CHO). ^{13}C-NMR: δ(CDCl$_3$) 13.98(Me), 22.56, 29.04, 29.12, 30.93, 31.69, 35.73(6 × CH$_2$), 126.28, 126.56, 127.72, 128.26, 135.20, 139.61, 143.26, 148.37, 149.19(C of Ar), 189.16(CHO). **4a** ^{1}H-NMR: δ (CDCl$_3$) 0.96(*t*, 3H, Me), 1.36–1.43(*m*, 2H, CH$_2$), 1.65–1.72(*m*, 2H, CH$_2$), 2.80(*t*, 2H, CH$_2$), 7.68–7.71(*m*, 2H, 2 × Ar-H), 7.99(*d*, 1H, $J = 6.2$ Hz, Ar-H), 8.45(*s*, 1H, ArH), 10.25(*s*, 1H, CHO). ^{13}C-NMR: δ(CDCl$_3$) 13.95(Me), 22.34, 33.02, 35.54(3 × CH$_2$), 119.31, 126.50, 127.73, 128.57, 134.98, 138.08, 143.42, 150.43 (C of Ar), 194.49(CHO). **4b** ^{1}H-NMR: δ(CDCl$_3$) 0.97(*t*, 3H, Me), 1.36–1.47(*m*, 2H, CH$_2$), 1.69–1.76(*m*, 2H, CH$_2$), 2.85(*t*, 2H, CH$_2$), 7.75–7.82(*m*, 2H, 2 × ArH), 8.10(*d*, 1H, $J = 8.4$ Hz, Ar–H), 8.59 (*s*, 1H, Ar–H), 10.12(*s*, 1H, CHO). ^{13}C-NMR: δ(CDCl$_3$) 13.89(Me), 22.34, 33.05, 35.46 (3 × CH$_2$), 108.97(CN), 125.80, 127.28, 128.62, 135.96, 143.72, 145.09, 147.11, 148.12, (C of Ar), 190.29 (CHO). **4c** ^{1}H-NMR: δ(CDCl$_3$) 0.96 (*t*, 3H, Me), 1.37–1.44(*m*, 2H, CH$_2$), 1.67–1.73(*m*, 2H, CH$_2$), 2.82(*t*, 2H, CH$_2$), 7.70–7.74(*m*, 2H, 2 × ArH), 7.90(*d*, 1H, $J = 5.7$ Hz, Ar-H), 8.74(*d*, 1H, $J = 6.3$ Hz, Ar-H), 10.38(*s*, 1H, CHO).^{13}C-NMR: δ(CDCl$_3$)13.75 (Me), 22.17, 33.08 35.25 (3 × CH$_2$), 117.96, 118.83, 126.47, 127.78, 135.21, 141.81, 141.90, 142.26, 146.35, 146.61, 157.82, 161.08 (C of Ar), 186.23(CHO). **4d** ^{1}HN MR: δ(CDCl$_3$) 0.95(*t*, 3H, Me), 1.26–1.53(*m*, 5H, CH$_2$ + Me), 1.62–1.90 (*m*, 2H, CH$_2$), 2.75(*t*, 2H, CH$_2$), 4.63(*q*, 2H, OCH$_2$), 7.54–7.58(*m*, 2H × Ar-H), 7.75(*d*, 1H, $J = 8.4$ Hz, Ar-H), 8.51(*s*, 1H, Ar-H), 10.49(*s*, 1H, CHO). ^{13}C-NMR: (CDCl$_3$) 13.89, 14.48(2 × Me), 22.26, 33.36, 35.22(3 × CH$_2$), 62.20(O-C), 119.85, 124.23, 126.98, 127.99, 133.97, 139.14, 139.55, 147.67, 160.67(C of Ar), 189.59(CHO). **4e** ^{1}H-NMR: δ(CDCl$_3$) 0.74(*t*, 3H, Me), 108–1.33(*m*, 9H, 3 × CH$_2$ + Me), 1.49(*t*, 3H, Me), 1.63–1.77(*m*, 2H, CH$_2$), 2.73(*t*, 2H, CH$_2$), 4.65(*q*, 2H, OCH$_2$), 7.53–7.56(*m*, 2H, 2 × Ar-H), 7.74(*d*, 1H, $J = 8.6$ Hz, Ar-H), 8.49(*s*, 1H, Ar-H), 10.47(*s*, 1H, CHO). ^{13}C-NMR: δ(CDCl$_3$)14.01, 14.45(2 × Me), 22.60, 29.12, 29.67, 31.20, 31.76, 35.53(6 × CH$_2$), 62.17(O-C), 119.87, 124.24, 126.99, 127.95, 133.91, 139.09, 139.57, 147.67, 160.66(C of Ar), 189.48(CHO).
10. H. C. Lin, L. -L. Lai, W. P. Hsieh, and W. Y. Huang, *J. Chem Soc., Chem. Commun.*, in preparation.