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A new type of liquid crystal involving hydrogen bonding: single crystal X-ray structure characterization and properties of the liquid crystal

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A new liquid crystal involving hydrogen bonding between 4-hexyloxybenzoic acid and 4-octyloxylphenylethynylpyridine has been investigated by DSC, polarizing optical microscopy and X-ray diffraction. The mesogen shows a nematic phase and an unknown liquid crystalline phase. The liquid crystal crystallizes with a triclinic space group *P*-1 with the parameters: $a = 8.879(2)$ Å, $b = 10.137(2)$ Å, $c = 17.629(4)$ Å; $\alpha = 104.16(3)^\circ$, $\beta = 95.47(3)^\circ$, $\gamma = 101.48(3)^\circ$; $V = 1490.3(6)$ Å^3; $Z = 2$; $F(000) = 572$; $\mu = 0.076$ mm^{-1}; $\lambda_{(\mathrm{MoK}_\alpha)} = 0.71073$ Å; final $R_1 = 0.0435$. The complex is formed by strong intermolecular hydrogen bonding.

1. Introduction

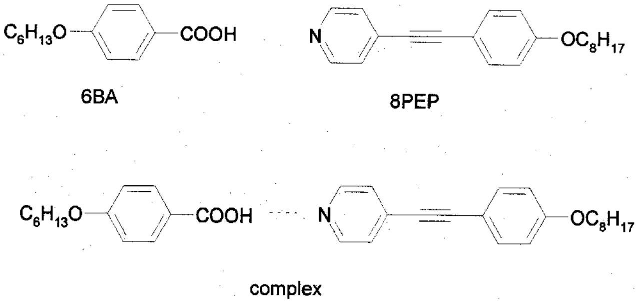
Hydrogen bonding plays important roles in molecular recognition and self-assembly [1]. In the last decade, a number of supramolecular mesogenic materials have been obtained by molecular self-assembly through hydrogen bonding [2]. In earlier years, Jones and co-workers found that hydrogen bonding in 4-substituted benzoic acids induced the liquid crystal phases formed, [3] but the components were of course identical. Kato enlarged the range of systems when he synthesized liquid crystals by mixing 4-alkoxybenzoic acids and pyridine derivatives [4]. There have also been many reports of hydrogen-bonded liquid crystals bearing ethynyl, ether and azo moieties in recent years [5].

High birefringence (Δn) liquid crystals are useful materials for application in reflective-type LCDs, spatial light modulators, compensation film reflectors and polarizers [6]. Liquid crystals containing acetylene groups also possess high birefringence, low viscosity and low melting points, but up to now there has been no report of aryl-acetylene liquid crystals induced by intermolecular hydrogen bonds. Crystal structure studies of liquid crystals, especially of liquid crystals induced by hydrogen bonds, can provide insight into and understanding of the intermolecular interactions controlling the mesophases [7]. However, there are only a few single crystal studies involving hydrogen-bonded mesogens because of the difficulty of growing good single crystals for X-ray analysis, and all the materials have been dimers of identical benzoic acid derivatives [8]. To the best of our knowledge, there has been no single crystal structural study of a hydrogen-bonded liquid crystal complex formed by two different components. Here we report the single crystal structure and properties of a hydrogen-bonded liquid crystal obtained from 4-*n*-hexyloxybenzoic acid (6BA) and 4-(4-octyloxyphenylethynyl)pyridine (8PEP) as shown in scheme 1.

2. Results and discussion

2.1. *Experimental*

6BA (hydrogen-bonding donor) and 8PEP (hydrogen-bonding acceptor) were synthesized by literature methods as shown in schemes 2 and 3 [9]. 6BA was recrystallized



Scheme 1.

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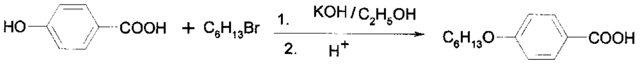
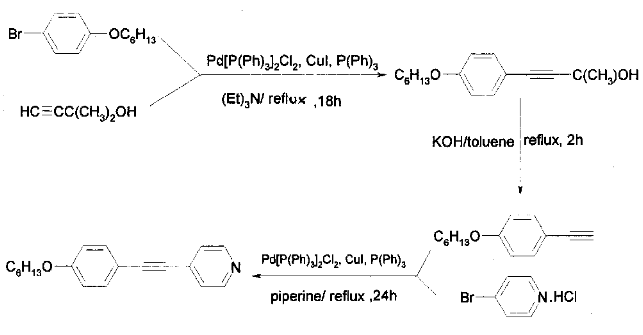


Scheme 2.



Scheme 3.

from ethanol and then from acetic acid. Elemental analysis: calc for $C_{13}H_{18}O_3$ C 70.24, H 8.16; found C 70.21, H 8.155%. 8PEP was purified by column chromatography on silica gel (petroleum: ethyl acetate = 1 : 1 as the eluent). Melting point 50.2–51.6°C. ^{1}H NMR (200 MHz) for 8PEP ($CDCl_3$, ppm): 8.56 (2H, d) and 7.36 (2H, d) (pyridyl), 7.50 (2H, d) and 6.90 (2H, d) (phenyl), 4.00 (2H, t) (OCH_2), 1.76–1.80 (2H, m) ($OCH_2\mathit{CH}_2$), 1.31–1.45 (10H, m), 0.89 (3H, t) (CH_3). M^+ *1/z*: 308. Elemental analysis: calc for $C_{21}H_{25}O_1N_1$ C 82.03, H 8.20, N 4.56; found C 82.19, H 8.262, N 4.491%. The hydrogen-bonded complex was obtained by evaporation from a THF solution containing equal amounts of the H-bonding donor and the H-bonding acceptor, followed by drying in vacuum at room temperature.

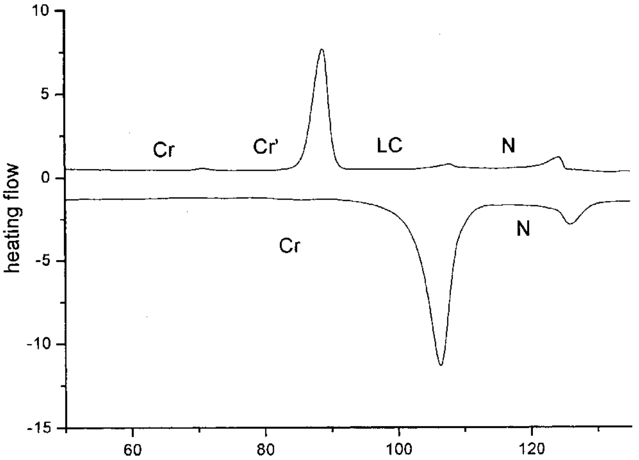


Figure 1. DSC curves of the complex.

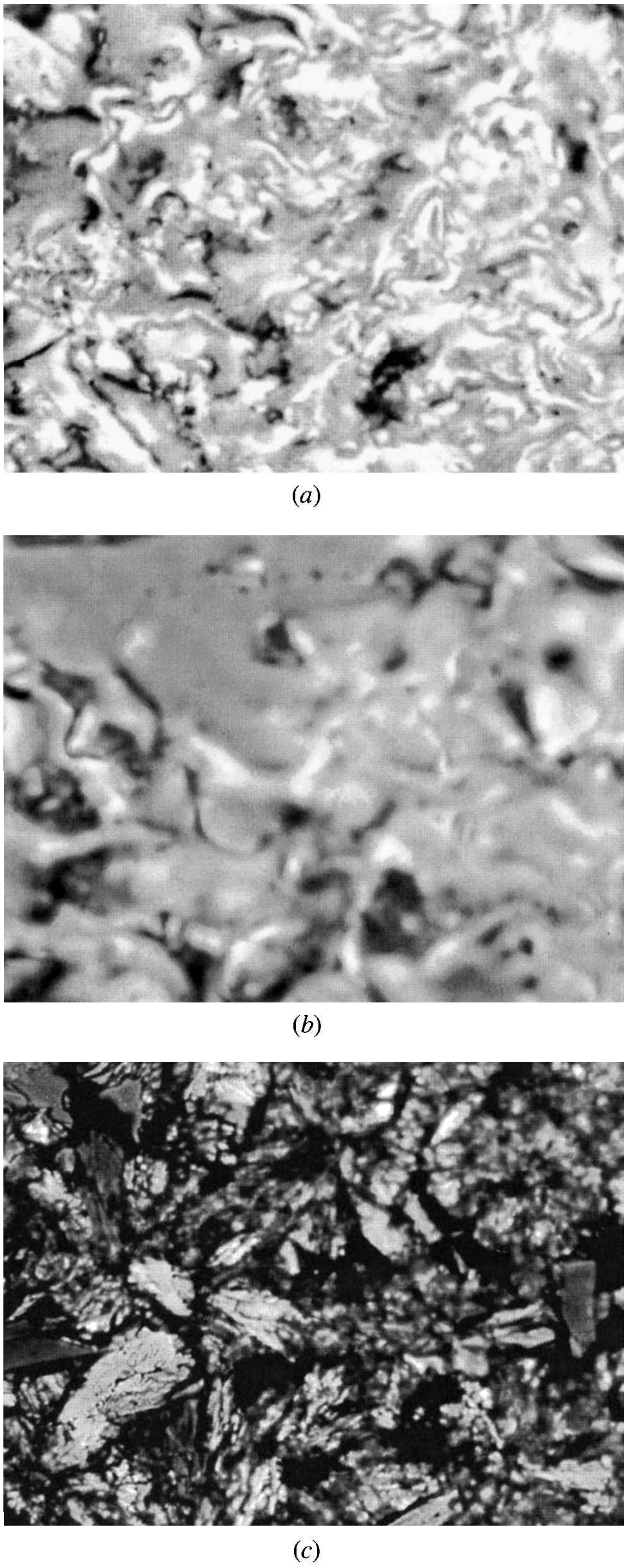


Figure 2. The microscopic textures of the complex. (*a*) 118°C (heating) nematic; (*b*) 119°C (cooling) nematic; (*c*) 81°C (cooling) crystal.

2.2. *FTIR*

The existence of intermolecular bonds can be identified by IR spectroscopy. The bands centred at 2450 and 1950 cm^{-1} show the formation of intermolecular bonds between the carboxylic acid and the pyridyl unit [10].

2.3. *Mesomorphic properties*

The mesomorphism of the complex was studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and variable temperature X-ray diffraction (XRD).

8PEP is not mesomorphic and melts directly to the isotropic liquid at 51°C; 6BA shows a nematic phase in the range 105–153°C. The DSC thermogram of the complex is shown in figure 1. The heating cycle thermogram clearly shows two endotherms at 106.64 and 126.07°C. In the subsequent cooling cycle, there were four exotherms at 124.27, 107.73, 88.71 and 70.62°C. POM studies suggested that the complex showed a nematic phase in the heating cycle (figure 2(*a*)), and a nematic (figure 2(*b*)), an unknown LC phase and two crystal phases in the subsequent cooling cycle. The nematic phase had a schlieren texture and the unknown LC phase appeared giving a textureless and completely homeotropic field of view.

Variable-temperature X-ray diffraction (XRD) studies were also used to identify the mesophases (figure 3). A weak, broad reflection in the wide angle and a weak, short reflection in the small angle region, corresponding to $d = 39.2$ and 4.4 Å, respectively were obtained at 118°C (heating and cooling) and are characteristic of a nematic phase. The calculated lengths of 6BA, 8PEP and the complex are 15.7, 21.8 and 39.1 Å, respectively. The length of the complex is in close agreement with $d = 39.2$ Å. Therefore the small angle reflection corresponds to the molecular length of the complex and the wide angle reflection corresponds to the intermolecular distance. There are no distinct changes between the XRD patterns at 118°C (cooling) and 98°C (cooling); therefore the liquid crystalline phase at 98°C remains unidentified.

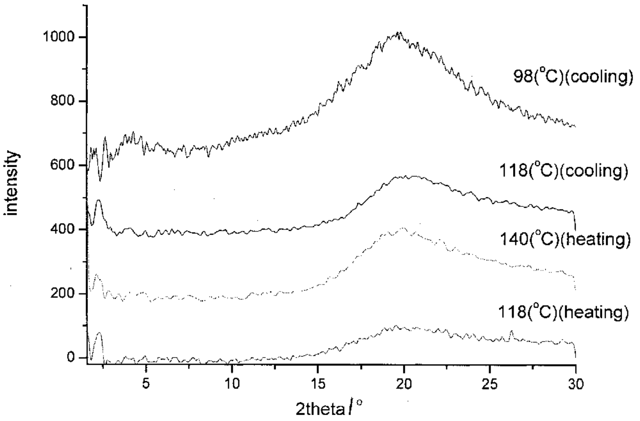


Figure 3. X-ray diffractograms for the complex at different temperatures: 118°C (heating) nematic; 140°C (heating) isotropic; 118°C (cooling) nematic; 98°C (cooling) unknown LC phase.

Table 1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for test. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
O(1)	8531(1)	9188(1)	912(1)	34(1)	C(16)	13324(2)	7288(2)	−811(1)	24(1)
O(2)	7859(1)	6889(1)	317(1)	31(1)	C(17)	12230(2)	6019(2)	−997(1)	28(1)
O(3)	1758(1)	7195(1)	1787(1)	29(1)	C(18)	10852(2)	5967(2)	−695(1)	28(1)
O(4)	20814(1)	6112(1)	−3068(1)	32(1)	C(19)	14762(2)	7333(2)	−1129(1)	27(1)
N(1)	10497(2)	7083(1)	−227(1)	27(1)	C(20)	15908(2)	7242(2)	−1433(1)	27(1)
C(1)	7606(2)	8061(2)	750(1)	23(1)	C(21)	17205(2)	7013(2)	−1839(1)	25(1)
C(2)	6070(2)	7874(2)	1041(1)	22(1)	C(22)	18588(2)	8018(2)	−1704(1)	26(1)
C(3)	5098(2)	6540(2)	873(1)	23(1)	C(23)	19823(2)	7771(2)	−2103(1)	26(1)
C(4)	3670(2)	6361(2)	1132(1)	24(1)	C(24)	19673(2)	6486(2)	−2645(1)	25(1)
C(5)	3189(2)	7502(2)	1563(1)	23(1)	C(25)	18304(2)	5470(2)	−2790(1)	28(1)
C(6)	4144(2)	8842(2)	1743(1)	26(1)	C(26)	17082(2)	5727(2)	−2394(1)	28(1)
C(7)	5579(2)	9007(2)	1476(1)	25(1)	C(27)	22223(2)	7144(2)	−2989(1)	28(1)
C(8)	1174(2)	8286(2)	2274(1)	28(1)	C(28)	23243(2)	6467(2)	−3526(1)	31(1)
C(9)	−377(2)	7579(2)	2440(1)	26(1)	C(29)	24728(2)	7482(2)	−3562(1)	29(1)
C(10)	−1136(2)	8578(2)	2988(1)	28(1)	C(30)	25726(2)	6799(2)	−4130(1)	29(1)
C(11)	−2701(2)	7851(2)	3152(1)	28(1)	C(31)	27260(2)	7757(2)	−4149(1)	29(1)
C(12)	−3476(2)	8822(2)	3701(1)	36(1)	C(32)	28254(2)	7032(2)	−4701(1)	30(1)
C(13)	−5055(2)	8116(2)	3843(1)	43(1)	C(33)	29763(2)	7969(2)	−4758(1)	35(1)
C(14)	11538(2)	8313(2)	−59(1)	27(1)	C(34)	30729(2)	7220(3)	−5319(1)	45(1)
C(15)	12950(2)	8455(2)	−335(1)	26(1)					

Table 2. Bond lengths (Å) and angles (°). Symmetry transformations used to generate equivalent atoms.

O(1)–C(1)	1.2174(18)	O(1)–C(1)–(C(2)	122.62(14)
O(2)–C(1)	1.3195(19)	O(2)–C(1)–C(2)	113.34(13)
O(3)–C(5)	1.3663(18)	C(7)–C(2)–C(3)	118.82(14)
O(3)–C(8)	1.4407(19)	C(7)–C(2)–C(1)	121.25(14)
O(4)–C(24)	1.3725(18)	C(3)–C(2)–C(1)	119.93(14)
O(4)–C(27)	1.433(2)	C(4)–C(3)–C(2)	120.26(15)
N(1)–C(18)	1.340(2)	C(3)–C(4)–C(5)	120.36(14)
N(1)–C(14)	1.343(2)	O(3)–C(5)–C(4)	115.05(13)
C(1)–C(2)	1.495(2)	O(3)–C(5)–C(6)	124.50(14)
C(2)–C(7)	1.390(2)	C(4)–C(5)–C(6)	120.45(14)
C(2)–C(3)	1.397(2)	C(7)–C(6)–C(5)	118.53(15)
C(3)–C(4)	1.382(2)	C(2)–C(7)–C(6)	121.58(15)
C(4)–C(5)	1.388(2)	O(3)–C(8)–C(9)	106.04(13)
C(5)–C(6)	1.394(2)	C(8)–C(9)–C(10)	113.25(14)
C(6)–C(7)	1.393(2)	C(9)–C(10)–C(11)	112.74(14)
C(8)–C(9)	1.511(2)	C(12)–C(11)–C(10)	113.76(14)
C(9)–C(10)	1.526(2)	C(13)–C(12)–C(11)	113.94(16)
C(10)–C(11)	1.527(2)	N(1)–C(14)–C(15)	122.70(15)
C(11)–C(12)	1.519(2)	C(14)–C(15)–C(16)	119.41(15)
C(12)–C(13)	1.515(2)	C(15)–C(16)–C(17)	117.83(14)
C(14)–C(15)	1.381(2)	C(15)–C(16)–C(19)	123.49(14)
C(15)–C(16)	1.392(2)	C(17)–C(16)–C(19)	118.67(14)
C(16)–C(17)	1.393(2)	C(18)–C(17)–C(16)	119.04(15)
C(16)–C(19)	1.441(2)	N(1)–C(18)–C(17)	123.31(15)
C(17)–C(18)	1.377(2)	C(20)–C(19)–C(16)	173.92(17)
C(19)–C(20)	1.203(2)	C(19)–C(20)–C(21)	174.93(17)
C(20)–C(21)	1.440(2)	C(22)–C(21)–C(26)	118.12(15)
C(21)–C(22)	1.389(2)	C(22)–C(21)–C(20)	122.66(15)
C(21)–C(26)	1.403(2)	C(26)–C(21)–C(20)	119.22(14)
C(22)–C(23)	1.390(2)	C(21)–C(22)–C(23)	121.55(15)
C(23)–C(24)	1.388(2)	C(24)–C(23)–C(22)	119.10(15)
C(24)–C(25)	1.385(2)	O(4)–C(24)–C(25)	115.17(14)
C(25)–C(26)	1.378(2)	O(4)–C(24)–C(23)	124.54(14)
C(27)–C(28)	1.511(2)	C(25)–C(24)–C(23)	120.28(14)
C(28)–C(29)	1.520(2)	C(26)–C(25)–C(24)	120.21(15)
C(29)–C(30)	1.530(2)	C(25)–C(26)–C(21)	120.73(15)
C(30)–C(31)	1.516(2)	O(4)–C(27)–C(28)	106.98(13)
C(31)–C(32)	1.529(2)	C(27)–C(28)–C(29)	112.94(14)
C(32)–C(33)	1.508(2)	C(28)–C(29)–C(30)	112.55(14)
C(33)–C(34)	1.531(3)	C(31)–C(30)–C(29)	114.16(14)
C(5)–O(3)–C(8)	119.98(12)	C(30)–C(31)–C(32)	112.94(14)
C(24)–O(4)–C(27)	118.20(12)	C(33)–C(32)–C(31)	114.37(15)
C(18)–N(1)–C(14)	117.69(14)	C(32)–C(33)–C(34)	113.30(16)
O(1)–C(1)–O(2)	124.02(14)		

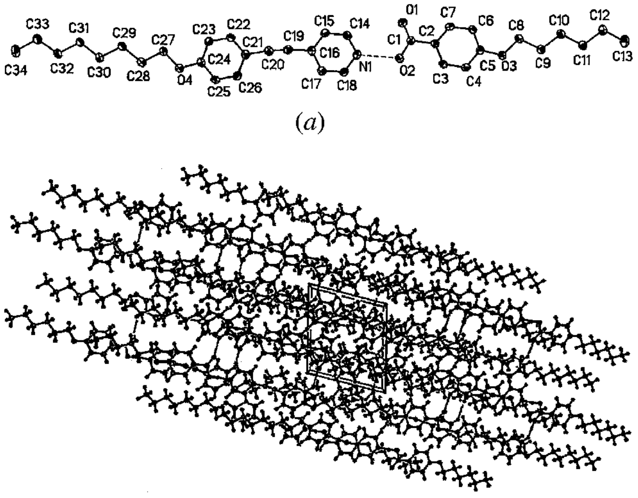
3. Single crystal structure of the complex

Colourless chips of single crystals of the complex were obtained by slow evaporation from a THF solution. A $0.40 \times 0.40 \times 0.20\,\mathrm{mm}^3$ single crystal was selected and mounted on the goniometer of Rigaku R-AXIS PAPID imaging plate diffractometer. Diffraction data were collected at 173 K with graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) operating at 50 Kv and 40 mA. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program (Sheldrick, G. M., 1997). The structure was solved by the direct method and successive difference maps (SHELX-97), and refined by full-matrix least-squares on F2 using all unique data (SHELXL-97).

The crystal is triclinic, space group P-1, $a = 8.879(2)$, $b = 10.137(2)$, $c = 17.629(4)$ Å, $\alpha = 104.16(3)^\circ$, $\beta = 95.47(3)^\circ$, $\gamma = 101.48(3)^\circ$, $V = 1490.3(6)\,\text{Å}^3$, formula $C_{34}H_{43}NO_4$, $M = 529.69$, $Z = 2$, $D_c = 1.180\,\mathrm{g\,cm^{-3}}$, $\mu = 0.076\,\mathrm{mm^{-1}}$. A total of 6461 reflections were read from which 3843 unique reflections were used for the structural determination. The structure was refined against 525 parameters. $R_1 = 0.0435$ and $wR_2 = 0.0970$ for 3843 $[I > 2\sigma(I)]$. In the final difference map, $\Delta\rho_{\max} = 0.303\,\mathrm{e}\text{Å}^{-3}$, $\Delta\rho_{\min} = -0.211\,\mathrm{e}\text{Å}^{-3}$ and goodness-of-fit = 0.892. The position

Table 3. Hydrogen bond distances (Å) and angle (°) for the complex.

D–H ... A	*d*(D–H)	*d*(H ... A)	*d*(D ... A)	<(DHA)
O(2)–H(1) ... N(1)	1.109(2)	1.502(2)	2.604(2)	172.8(18)



(*a*)

(*b*)

Figure 4. (*a*) Numbering of atoms in the molecular complex, hydrogen atoms being omitted for clarity; (*b*) a packing diagram of the nematic-like structure

and displacement parameters (without H atoms) are given in table 1. Bond lengths and angles are shown in table 2.

The molecular structure of the complex is shown in figure 4 (*a*) where it is seen that the H-donor and H-acceptor molecules are strongly bound into a complex through a well defined hydrogen bond. Information about the intermolecular hydrogen-bonded unit is given in table 3.

The deviation from the plane containing the pyridine ring, the benzene ring and the acetylene group of 8PEP is 0.0601 Å. All non-hydrogen atoms in the 8PEP component are in plane A with a deviation of 0.0878 Å. The benzene ring and the carboxyl group of 6BA are coplanar to within 0.0207 Å and all non-hydrogen atoms in component 6BA are in plane B with a deviation of 0.0604 Å. The angle between ring plane A and the plane B is 4.9°. The coplanarity of the complex will favour the formation of the LC phase, as will the fully extended tail carbon chains. Figure 4 (*b*) shows how the complex molecules are arranged head-to-tail along the long axis of the complex molecule and their alignment in an anti-parallel way. The crystal packing shows that the molecules of the complex pack in a nematic-like arrangement, consistent with the formation of the nematic liquid crystal phase and with the variable-temperature XRD spectra and the microscopic texture.

4. Conclusion

In conclusion, the hydrogen-bonded liquid crystal containing the aryl-acetylene group shows a low viscosity nematic phase substantiated by the single crystal structure studied which demonstrates the liquid crystal packing mode.

References

[1] Lehan, J. M., 1988, *Angew. Chem. int. Ed. Eng.*, **27,** 89.

[2] Constantinos, M. P., and Dimitris, T., 2001, *Liq. Cryst.*, **28,** 1127.

[3] (*a*) Bradfield, A. E., and Jones, B., 1929, *J. chem. Soc.*, 2660; (*b*) Gray, G. W., and Jones, B., 1953, *J. chem. Soc.*, 4179.

[4] Kato, T., and Jean, M. J. F., 1989, *J. Am. chem. Soc.*, **111,** 8533.

[5] (*a*) Gündogan, B., and Binnemans, K., 2000, *Liq. Cryst.*, **27,** 851; (*b*) Lin, H. C., and Ko, C. W., 1999, *Liq. Cryst.*, **26,** 613.

[6] (*a*) Sekine, C., Iwakura, K., Minai, M., and Fujisawa, K., 2001, *Liq. Cryst.*, **28,** 1505; (*b*) Wu, S. T., 1995, *Mol. Cryst. liq. Cryst.*, **261,** 79; (*c*) Takatsu, H., Takeuchi, K., Tanaka, Y., and Sasaki, M., 1986, *Mol. Cryst. liq. Cryst.*, **141,** 279; (*d*) Wu, S. T., Finkenzeller, U., and Reiffenrath, V., 1989, *J. appl. Phys.*, **65,** 4372.

[7] (*a*) Prasad, J. S., Sridhar, M. A., and Surendranath, V., 1999, *Liq. Cryst.*, **26,** 1707; (*b*) Gallardo, H., Magnago, R., and Bortoluzzi, A. J., 2001, *Liq. Cryst.*, **28,** 1343; (*c*) Allouchi, H., Cotrait, M., and Malthete, J., 2001, *Mol. Cryst. liq. Cryst.*, **362,** 101.

[8] (*a*) Lokanath, N. K., Sridhar, M. A., Revannasiddaiah, D., and Prasad, J. S., 2000, *Liq. Cryst.*, **27,** 767; (*b*) Lokanath, N. K., Sridhar, M. A., Revannasiddaiah, D., and Prasad, J. S., 2000, *Mol. Cryst. liq. Cryst.*, **348,** 7.

[9] (*a*) Jones, B., 1953, *J. chem. Soc.*, 1874; (*b*) Yam, V. W. W., Yang, Y., Yang, H. P., and Cheung, K. K., 1999, *Organometallics*, **18,** 5252.

[10] Tian, Y. Q., Su, F. Y., Zhao, Y. Y., Luo, X. Y., Tang, X., Zhao, X. G., and Zhou, E., 1995, *Liq. Cryst.*, **19,** 743.