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Polymesomorphism in a homologous series of 2-(4-alkoxyphenyl)-5-(4-methylphenyl)pyridines

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A new series of 2-(4-*n*-alkoxyphenyl)-5-(4-methylphenyl)pyridines ($CH_3C_6H_4C_5H_3NC_6H_4$-OC_nH_{2m+1}, $n = 1$–10) (APMPP), which are teraryl compounds containing a pyridine ring in the centre position of the rigid core, was synthesized and the phase transitions of the homologues were studied using DSC measurements, polarizing optical microscopy and miscibility tests with terephthalylidene-bis-4-*n*-pentylaniline (TBPA). Only a nematic phase was found for the shorter alkoxy homologues with $n < 4$. The longer alkoxy homologues with $n \geqslant 4$ showed the sequence of enantiotropic phase transitions CrG–SmF–SmC–SmA–N–I, while a monotropic CrH phase was observed for the $n = 5$–10 homologues. Interestingly, the polymesomorphisms appear when n is larger than 4.

1. Introduction

Since the early studies in liquid crystal (LC) science, many mesogenic nitrogen-heteroaromatic compounds have been devised [1–10]. Interesting fundamental results have been accumulated concerning the effects of the heteroaromatic ring in the rigid core part of a molecule on the mesomorphic phase transitions and the physical properties. Recently mesogenic compounds containing pyrimidine and pyridine rings in the N-heteroaromatic cores have earned much interest as components of LC-forming materials for electro-optic devices, because of their good miscibility with other mesogenic partners and the good thermal stability of the smectic C phases produced. Indeed, pure pyrimidine compounds exhibiting ferroelectric SmC* phases with good thermal stability have been reported [11, 12]. On the other hand, pyrimidine and pyridine compounds do tend to be polymesomorphic, and this may be occasionally problematic when they are used in LC devices, but they are of a great scientific interest.

In teraryl compounds including a N-heteroaromatic ring in the central position, the thermal stability of a mesophase is generally dependent on the position and number of nitrogen atoms in the heteroaromatic ring. For example, it is known that the thermal stability of 4,4″-dipentyl-*p*-terphenylene derivatives including N atoms in the centre ring falls in the order pyridazine, benzene, pyridine, pyrimidine, pyrazine, triazine and tetrazine [13–19]. The order may be derived from two effects, the conjugative interactions and the lateral intermolecular interactions.

The present work aims at investigating the phase transition behaviour in a series of 2-(4-*n*-alkoxyphenyl)-5-(4-methylphenyl)pyridines (APMPP) (see structure **7** in the scheme), which are LC teraryl compounds having a pyridine ring in the centre position (LCTR-pyridine) with the N atom deviating from the molecular long axis. Owing to the resulting dipole moment across the molecular long axis and the changed electronic distribution caused by introducing the pyridine moiety, LCTR-pyridine molecules can be expected to develop molecular packing modes different from those of the benzene analogue which would influence the mesomorphic properties. However, unexpectedly the mesomorphic phase transitions of LCTR-pyridine systems have hardly been studied, perhaps because of their synthetic unavailability [20, 21]. In this work, a homologous series of APMPP compounds was successfully prepared by applying the recently established method by Kagabu *et al.* [22, 23]; their polymorphic LC phase transitions are discussed as a function of the length of their alkoxy groups.

2. Experimental

2.1. *Materials*

A series of 2-(4-*n*-alkoxyphenyl)-5-(4-methylphenyl)-pyridines ($CH_3C_6H_4C_5H_3NC_6H_4OC_nH_{2n+1}$, $n = 1$–10)

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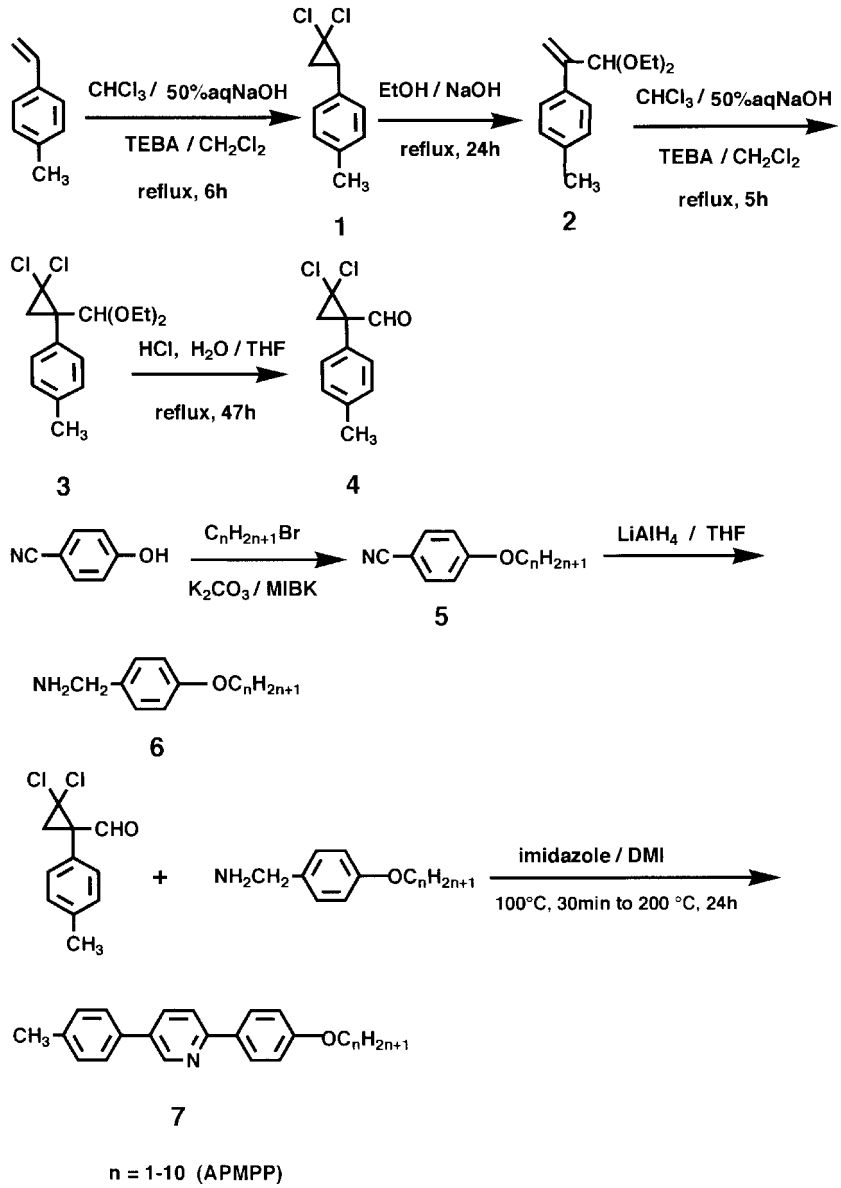

(APMPP) (structure **7** in the scheme) was synthesized from 2,2-dichloro-1-(4-methylphenyl)cyclopropanecarbaldehyde (compound **4**) and the 4-*n*-alkoxybenzylamine (structure **6**) as shown in the scheme. The representative synthetic procedures are described below for 2-(4-*n*-hexyloxyphenyl)-5-(4-methylphenyl)pyridine (the $n = 6$ homologue of structure **7**) [11, 12].

2,2-Dichloro-1-(4-methylphenyl)cyclopropane (compound **1**) was prepared by mixing 4-methylstyrene (189 g, 1·60 mol) in chloroform/dichloromethane 2/1 v/v (225 ml) with 50 wt % aqueous NaOH (150 ml) in the presence of triethylbenzylammonium chloride (TEBA) (6·00 g, 26·0 mmol) and maintaining at 40°C for 5 h. After washing the reaction mixture with water (300 ml), the organic phase was dried over $MgSO_4$, and the product was obtained by distilling under vacuum (b.p. 93–95°C/5 mmHg). 1-(4-Methylphenyl)acrolein diethyl acetal (compound **2**) was prepared by heating compound **1** (40 g, 0·20 mol) with NaOH (32 g, 0·80 mol) in boiling ethanol (320 ml) for 24 h. The mixture was diluted with water (360 ml) and shaken with hexane. After isolation, crude compound **2** was purified by vacuum distillation (b.p. 100–108°C/4 mmHg). 2,2-Dichloro-1-(4-methylphenyl)cyclopropanecarbaldehyde diethyl acetal (compound **3**) was prepared by stirring for 2 h a mixture of compound **2** (24 g, 0·11 mol), 53 wt % aqueous NaOH (50 ml) and TEBA (0·25 g, 1·1 mmol) in chloroform/dichloromethane 2/1 v/v (30 ml) at 40°C. After washing the reaction mixture with water (500 ml) and drying the organic phase over $MgSO_4$, the product

was obtained by distillation under vacuum (yield 70%) (b.p. 118–120°C/4 mmHg). Finally, 2,2-dichloro-1-(4-methylphenyl)cyclopropanecarbaldehyde (compound **4**) was obtained by hydrolysis of compound **3** (17 g, 0·057 mol) with 20 wt % aqueous HCl (55 ml) in THF (35 ml) and dried over $MgSO_4$. The product was distilled under vacuum (yield 77%) (b.p. 104–105°C/3 mmHg).

A solution of 4-hexyloxybenzonitrile (4·1 g, 20 mmol) (structure **5**, $n = 6$) in THF (30 ml) was added dropwise to $LiAlH_4$ (1·1 g, 26 mmol) in THF (30 ml) with cooling in ice. Then the mixture was stirred at 40–50°C for 3 h and then warmed under reflux for 1 h. The excess of $LiAlH_4$ was decomposed with 30% aqueous NaOH (30 ml). Extraction with isopropyl ether followed by evaporation of the organic solution to dryness gave the product (the $n = 6$ homologue of structure **6**) as yellow crystals (yield 79%). The other homologous alkoxybenzylamines were prepared in a similar manner.

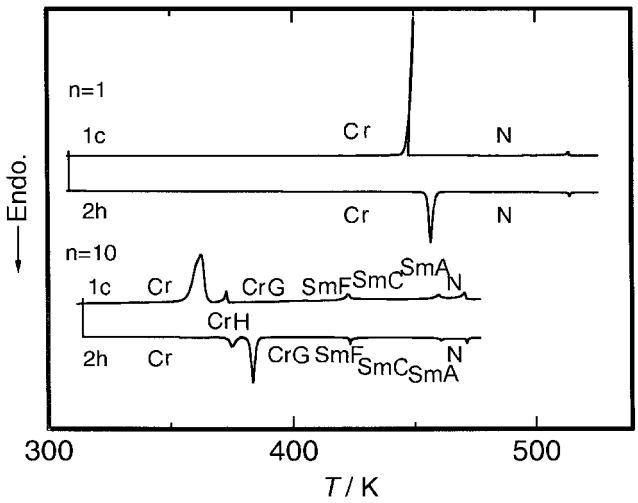

Figure 1. DSC thermograms for two APMPP homologues ($n = 1$ and 10). 1c: 1st cooling, 2h: 2nd heating.

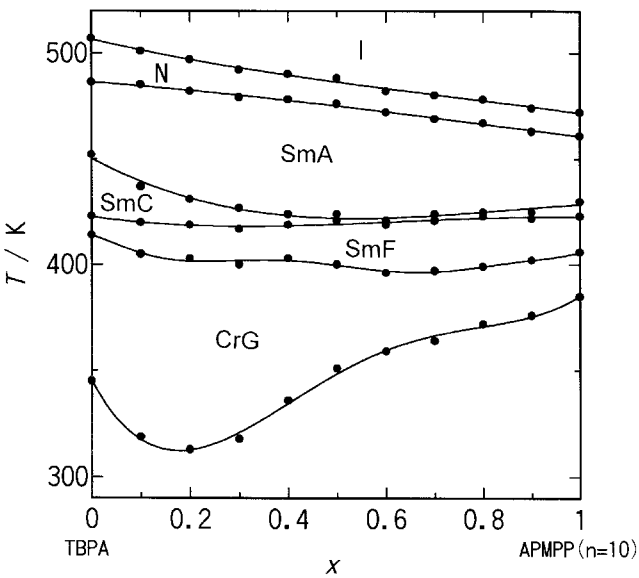

Figure 2. Miscibility diagram of state for APMPP ($n = 10$) with TBPA.

A solution of 4-hexyloxybenzylamine (1·0 g, 5·0 mmol), compound **4** (1·1 g, 5·0 mmol) and imidazole (0·65 g, 10 mmol) in the presence of hydroquinone (*c.* 10 mg) in 1,3-dimethyl-2-imidazolidinone (DMI) (30 ml) was heated at 100°C for 30 min and then at 200°C for 24 h. After the solvent was evaporated, the residue was successively washed with 1% aqueous HCl, 1% aqueous NaOH and saturated brine, and column chromatographed (SiO_2, $CHCl_3$). The analytically pure sample was obtained by repeated recrystallization of the crude product from ethanol (yield 40%). ^{1}H NMR (400 MHz, $CDCl_3$); δ 8·91 (s, 1H), 8·05 (m, 3H), 7·79 (d, 8·1 Hz, 1H), 7·54 (m, 2H), 7·31 (m, 2H), 7·04 (m, 2H), 4·03 (t, 6·6 Hz, 2H), 1·83 (m, 2H), 1·34–55 (m, 6H), 0·92 (t, 7·1 Hz, 3H). EI-MS (70 eV); *m/z* 261 (100), 345 (M^+, 61). FTIR (KBr) 1607, 1592, 1583, 1514, 1475, 1248, 1037. Elemental analysis, found: C 83·69, H 8·07, N 4·08%; calc. for $C_{24}H_{27}NO$: C 83·44, H 7·88, N 4·08%. The other APMPP homologues were synthesized essentially by the same procedure as that described above for the $n = 6$ homologue.

2.2. *Analytical techniques and instruments*

The ^{1}H NMR spectra were measured using $CDCl_3$ solutions with an internal standard of TMS and a JEOL JNM-A400 spectrometer. The thermal data were recorded by differential scanning calorimetry (Seiko Instruments DSC 210) at a heating/cooling rate of 5 K min^{-1} in the temperature range from 300 K to above the clearing points. The textures of the liquid crystalline phases were observed with a polarizing microscope, Nikon Optiphoto-pol XTP-11, equipped with a Mettler hot stage FP-82, at a heating/cooling rate of 5 K min^{-1} and using crossed polarizers. The miscibility tests for APMPP with terephthalylidene-bis-4-*n*-dipentylaniline (TBPA) were performed by use of either DSC or polarizing microscope observations during cooling from the isotropic liquid state. The IR spectra were measured (KBr disks) using a Perkin Elmer FTIR 1600 spectrometer. Mass spectra were recorded (EI method at 70 eV) using a Shimazu QP 1000 mass spectrometer.

3. Results and discussion

Figure 1 shows DSC thermograms for two APMPP homologues ($n = 1$ and 10). In the first cooling for the $n = 1$ homologue, two exothermic peaks were observed at 514 and 444 K, while two endothermic peaks were observed at 444 and 513 K in the second heating. This phase transition behaviour was also observed for the second cooling and third heating processes. In polarizing microscope observations using crossed polarizers, a

Table 1. Phase transition temperatures (T/K) and liquid crystalline phase transition enthalpies (ΔH/kJ mol^{-1}) for a series of 2-(4-alkoxyphenyl)-5-(4-methylphenyl)pyridines(APMPP) ($C_nH_{2n+1}C_6H_4C_5H_3NC_6H_4CH_3$, $n=1$–10) obtained by DSC in the second heating process.[a]

n	K	•	CrH	•	CrG	•	SmF	•	SmC	•	SmA	•	N	•	I
1		—		—		—		—				458/14		513/0·5	
2		—		—		—		—				456/17		521/0·7	
3		—		—		—		—				444/16		503/0·6	
4		—		425/6·2		429/—		431/2·8		433/—		434/1·2		503/1·7	
5		(380/8·6)		406/17		421/—		431/1·9		441/—		443/0·5		493/0·6	
6		(373/11)		398/22		403/—		427/1·9		441/—		447/0·5		491/1·5	
7		(361/12)		392/23		413/—		430/2·3		437/—		455/0·9		484/1·1	
8		(362/15)		389/20		415/—		427/2·0		434/—		457/0·8		480/1·5	
9		(363/38)		386/41		408/—		426/2·3		435/—		460/1·2		475/1·6	
10		(366/37)		384/27		406/—		424/1·7		429/—		461/1·1		472/1·8	

[a] Parentheses indicate the values for a monotropic phase transition.

typical nematic schlieren texture exhibiting disclinations with $s=\pm1$ and $s=\pm1/2$ [24] were observed between 514 and 444 K in the cooling processes. The phase transition behaviour for the $n=2$ and 3 homologues was similar to that for the $n=1$, showing only the nematic phase. Therefore, the shorter alkoxy homologues with $n<4$ exhibit only enantiotropic nematic phases.

In the first cooling process for the $n=10$ homologue, seven exothermic peaks were observed at 472, 461, 429, 424, 406, 384 and 366 K. Using polarizing microscopy with crossed polarizers, there were observed schlieren disclinations with $s=\pm1$ and $s=\pm1/2$ between 472 and 461 K, a fan texture between 461 and 429 K, and a broken-fan texture with simultaneous schlieren disclinations with $s=\pm1$ between 429 and 424 K, which were assigned to nematic, smectic A and smectic C phases, respectively [24]. The two lower temperature phases below 424 K appeared to be more highly ordered smectic or crystal phases, since the textures showed schlieren mosaic and mosaic textures on cooling from higher temperatures. These two phases were identified as SmF and CrG by miscibility tests with terephthalylidene-bis-4-*n*-dipentylaniline (TBPA) as mentioned later. The series of the longer alkoxy chain APMPP homologues with $n\geqslant4$ showed essentially similar thermal behaviours. Another monotropic phase was observed between 374 and 366 K in the DSC thermograms for the $n=10$ homologue, figure 1. This phase was seen for all the longer homologues ($n\geqslant5$) but not for $n=4$. Miscibility tests with terephthalylidene-bis-4-*n*-dipentylaniline (TBPA) were performed to identify the nature of this phase; TBPA has the polymorphic phase sequence Cr–(345 K)–CrG–(424 K)–SmF–(423 K)–SmC–(452 K)–SmA–(486 K)–N–(507 K)–I, with a monotropic CrH phase between 322 and 335 K [25]. One typical example of a miscibility test is shown for the APMPP ($n=10$)-TBPA system in figure 2. All the phases except the monotropic CrH phase, of APMPP ($n=10$) are immiscible over the entire composition range with those of TBPA, indicating that APMPP ($n=10$) shows the successive phase transitions Cr–CrG–SmF–SmC–SmA–I. The mixing test for the CrH phase could not be performed over all mixing ratios by DSC, because the CrH phase is monotropic, but we assigned the monotropic mesophase in APMPP to CrH, since it showed a mosaic texture similar to the mosaic CrH texture of TBPA in polarizing microscopic observations.

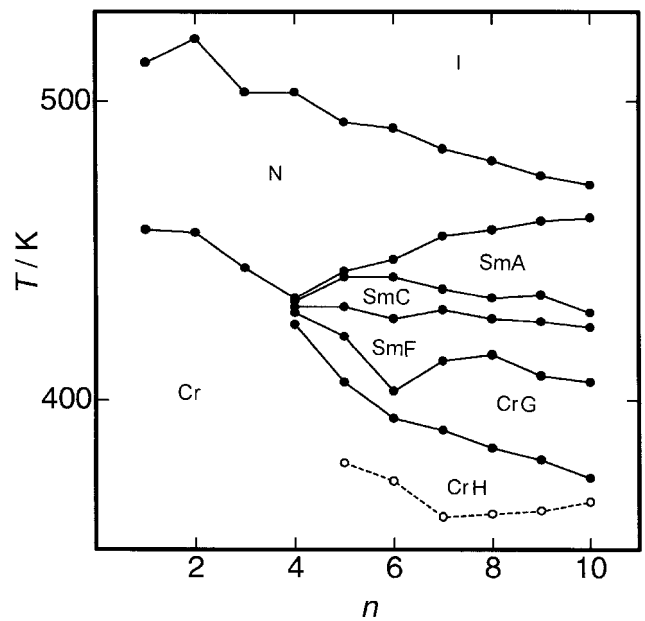

Figure 3. Phase transition temperatures versus length of the alkoxy group (n) for the APMPP homologues.

The thermal parameters are listed for all the APMPP homologues in the table. Endothermic peaks corresponding to the CrG–SmF and SmC–SmA phase transitions were not observed by DSC for most homologues due to the extremely small enthalpy changes

involved. In these cases, the type of phase in the table and the transition temperatures were determined by texture observations using crossed polarizers. The phase transition temperatures are plotted against the length of alkoxy group (n) in the APMPP compounds in figure 3. The APMPP series shows only a nematic phase when $n<4$, but a rich LC polymorphism when $n\geqslant 4$. As n increases, the N–I phase transition temperature gradually decreases with an even–odd effect. As noted, the LC polymorphism appears suddenly at $n=4$, and with increasing n the overall smectic temperature range becomes wider, and the nematic temperature range decreases.

In the present work, we have synthesized the APMPP compounds according to Kagabu's synthetic procedure and shown that the homologues show LC polymorphism when $n\geqslant 4$. It is rather uncommon that LC polymorphism appears so suddenly at $n=4$. For example, in the 5-(4-alkoxyphenyl)-2-(4-alkylphenyl)pyrimidines (C_nH_{2n+1}-C_6H_4-$C_4N_2H_2$-C_6H_4-OC_nH_{2n+1}) having the pyrimidine ring at the centre position in the three ring core [26, 27], only a nematic phase exists when the lengths of both alkyl and alkoxy groups (n) are 1. As n increases, a SmA phase appears from $n=2$, and from $n=4$ SmC and CrG phases appear while the nematic phase disappears. From $n=5$, the SmF phase appears, resulting in the phase transition sequence Cr–CrG–SmF–SmC–SmA–I when n is between 5 and 9. The two nitrogen atoms of the pyrimidine ring are symmetrical about the long rigid core axis, but the nitrogen atom in the pyridine ring of the APMPP series is asymmetrically positioned. As is well known, the appearance and type of smectic phase may be closely connected with the lateral intermolecular interactions which become larger as the terminal groups are lengthened. The present work clearly shows that the central rigid core profoundly affects the smectic phases which appear, and especially that the position and number of nitrogen atoms are important in relation to the appearance of LC polymorphism.

In conclusion, the new homologous series of APMPP compounds ($n=1$–10) has been synthesized. The APMPP homologues show a nematic phase in the shorter chain homologues with $n<4$, while an enantiotropic LC polymorphism (Cr–CrG–SmF–SmC–SmA–N–I) occurs for the longer chain homologues with $n\geqslant 4$; also, a monotropic CrH phase was observed for the $n=5$–10 homologues. These teraryl compounds containing a pyridine ring with a dipole moment oriented across the molecular long axis are of interest because they generate a characteristic polymorphism. Studies are progressing on the mesogenicity of p-quaterphenylene compounds containing one pyridine ring, and the results from our laboratories will be published elsewhere.

References

[1] Shubert, H., and Zaschke, H., 1973, *J. pract., Chem.*, **315,** 1113.

[2] Gray, G. W., 1976, *Advances in Liquid Crystals*, Vol. 2, edited by G. H. Brown (New York: Academic Press), p. 17.

[3] Boller, A., Cereghetti, M., and Sherrer, H., 1978, *Z. Naturforsch. B*, **33,** 433.

[4] Zaschke, H., 1979, *Advances in Liquid Crystal Research and Applications*, edited by L. Bata (Oxford: Pergamon Press), p. 1059.

[5] Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals* (Weinheim: Verlag Chemie), p. 70.

[6] Kraus, G., and Zaschke, H., 1981, *J. pract., Chem.*, **323,** 199.

[7] Karamysheva, L. A., Kovshev, E. I., Pavlchenko, A. I., Roitman, K. V., Titov, V. V., Torgova, S. I., and Grebenkin, M. F., 1981, *Mol. Cryst. liq. Cryst.*, **67,** 241.

[8] (*a*) Beguin, A., Dubois, J. C., Le Barney, P., Billard, J., Bonamy, F., Buisine, J. M., and Cuvelier, P., 1984, *Mol. Cryst. liq. Cryst.*, **115,** 138; (*b*) **115,** 282.

[9] Grebyonkin, M. F., Petrov, V. F., Belyaev, V. V., Pavlchenko, A. I., Smirnova, N. I., Lovshev, E. I., Titov, V. V., and Ivashchenko, A. V., 1985, *Mol. Cryst. liq. Cryst.*, **129,** 245.

[10] Heppke, G., Loetzsch, D., Demus, D., Diele, S., Jahn, K., and Zaschke, H., 1991, *Mol. Cryst. liq. Cryst.*, **208,** 9.

[11] Boemelburg, J., and Heppke, G., 1989, *Z. Naturforsch. B*, **44,** 1127.

[12] Sekine, C., Tani, T., Ueda, K., Fujisawa, K., Higashi, T., Kurimoto, I., Toda, S., Takano, N., Fujimoto, Y., and Minai, M., 1993, *Ferroelectrics*, **148,** 203.

[13] Weygand, C., and Lanzendorf, W., 1938, *J. pract., Chem.*, **151,** 221.

[14] Shubert, H., Hacker, R., and Kindermann, K., 1968, *J. pract. Chem.*, **37,** 112.

[15] Shubert, H., and Zaschke, H., 1970. *J. pract. Chem.*, **312,** 494.

[16] Demus, D., Diele, S., Klapperstueck, M., Link, V., and Zaschke, H., 1971, *Mol. Cryst. liq. Cryst.*, **15,** 161.

[17] Demus, D., Koez, K. H., and Zackemann, H., 1972, *Z. phys. Chem.*, **249,** 217.

[18] Nash, J. A., and Gray, G. W., 1974, *Mol. Cryst. liq. Cryst.*, **25,** 299.

[19] Zaschke, H., Nitsche, K., and Shubert, H., 1977, *J. pract. Chem.*, **319,** 475.

[20] Demus, D., 1975, *Z. phys. Chem.*, **15,** 1.

[21] Shubert, H., 1970, *Wiss. Z. Martin-Luther-Univ., Halle-Wittenberg, Math., Naturwiss., Reihe*, **19,** 1.

[22] Kagabu, S., and Mizoguchi, S., *Synthesis*, **1966,** 372.

[23] Kagabu, S., Naruse, S., Tagami, Y., and Watanabe, Y., 1989, *J. org. Chem.*, **54,** 4275.

[24] Demus, D., and Richter, D., 1978, *Textures of Liquid Crystals* (Weinheim: Verlag Chemie), p. 32.

[25] Neubert, M. E., and Maurer, L. J., 1977, *Mol. Cryst. liq. Cryst.*, **43,** 313.

[26] Biering, A., Demus, D., Richter, L., Sackmann, H., Wiegleben, A., and Zaschke, H., 1980, *Mol. Cryst. liq. Cryst.*, **62,** 1.

[27] Wiegleben, A., Richter, L., Deresch, J., and Demus, D., 1980, *Mol. Cryst. liq. Cryst.*, **59,** 329.