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## Liquid Crystals

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# Liquid crystalline thiadiazole derivatives: new ferroelectric thiadiazole derivatives

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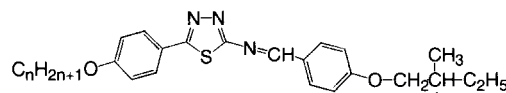
A series of optically active thiadiazole Schiff's bases were prepared and their liquid crystalline properties were studied. Chirality was achieved by introducing an asymmetric carbon atom into the alkoxy group. Thus, 2-(*p*-active-alkoxyphenyl-imine)-5-(*p*-*n*-alkoxy)phenyl-1,3,4-thiadiazoles were synthesized. Their structures were characterized using elemental analysis, and IR, <sup>1</sup>H NMR and mass spectroscopies their thermal properties were determined using DSC and polarized light microscopy. All the compounds are enantiotropic liquid crystals, and most of them exhibited both chiral smectic C\* and cholesteric mesophases. Only one of them did not show a smectic C\* phase.

## 1. Introduction

A great number of mesogenic compounds containing heterocyclic units have been synthesized, and interest in such structures continues to grow [1, 2]. The effect of heteroatoms can be to change considerably the polarity, polarizability and sometimes, the shape of the molecular, thereby influencing the type of mesophase, the phase transition temperatures, dielectric constants and other properties of the mesogens [3]. Heterocyclic compounds such as pyrimidine derivatives [4] and thiadiazole derivatives [5–8] are valuable liquid crystalline materials for technical applications.

The interest in ferroelectric liquid crystalline materials has recently increased because of their potential application in fast switching devices [9, 10]. Smectic liquid crystals which show a chiral smectic C\* phase, a high spontaneous polarization and broad mesogenic temperature ranges are required. Hence, the synthesis of new substances and the characterization of their physical properties are important activities in the development of new materials. In previous studies, 2,5-disubstituted 1,3,4-thiadiazole derivatives have been found to exhibit broad smectic C temperature ranges [11, 12]. In addition, chiral 2-methylcarboxylates and 2-alkoxypropionates incorporating a 1,3,4-thiadiazole structural unit having large values of spontaneous polarization have been described [13]. Here we report the synthesis and characterization of a number of novel chiral thiadiazole

derivatives (structure below) and compare these compounds with the analogous Schiff's bases we reported earlier.



## 2. Results and discussion

The transition temperatures and phase behaviour of the new materials are given in the table. Most of these compounds exhibit broad smectic C\* and cholesteric temperature ranges, and on increasing the length of the terminal alkyl chain, their clearing temperatures fall, the temperature range of the cholesteric phase decreases, but the stability of the smectic C\* phase increases. The temperature ranges of the phases are shown in figure 1.

Compound **1-1** shows different phase behaviour when compared with the other homologues. The DSC trace for compound **1-1** shows two peaks on heating at 120.10 and 180.10°C, which are attributed to the crystal–liquid crystal and liquid crystal–isotropic transitions, respectively. On cooling, a small peak is evident at 107.94°C in addition to peaks at 171.94 and 86.58°C, and corresponds to a transition between two liquid crystalline phases. The phases were identified using polarizing microscopy. An ‘oily streaks’ texture characteristic of the cholesteric phase [14] was observed at temperatures higher than the crystal–liquid crystal phase transition temperature. The optical texture does not change during the heating cycle. On cooling, a characteristic cholesteric fan texture

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Table. Transition temperatures ( $^{\circ}\text{C}$ ), and associated enthalpies of transition ( $\text{J g}^{-1}$ ) of the optical active Schiff's Bases.

Compound	$n$	Cr		SmC*		N*		I
1-1	4	•	120.10 (89.27)	(•	107.94 <sup>a</sup> (-4.82)	•	180.10 (1.82)	•
1-2	5	•	120.73 (48.95)	•	129.53 (5.11)	•	173.93 (1.87)	•
1-3	6	•	110.32 (40.89)	•	129.55 (3.82)	•	156.57 (2.10)	•
1-4	7	•	111.19 (41.43)	•	159.77 (4.21)	•	171.93 (2.96)	•
1-5	8	•	101.38 (43.20)	•	139.43 (5.91)	•	152.83 (3.45)	•
1-6	9	•	106.10 (43.51)	•	140.60 (4.62)	•	154.22 (2.65)	•
1-7	10	•	105.77 (65.88)	•	143.19 (4.60)	•	161.10 (2.81)	•

<sup>a</sup> Transition temperature in parentheses determined on cooling cycle using DSC.

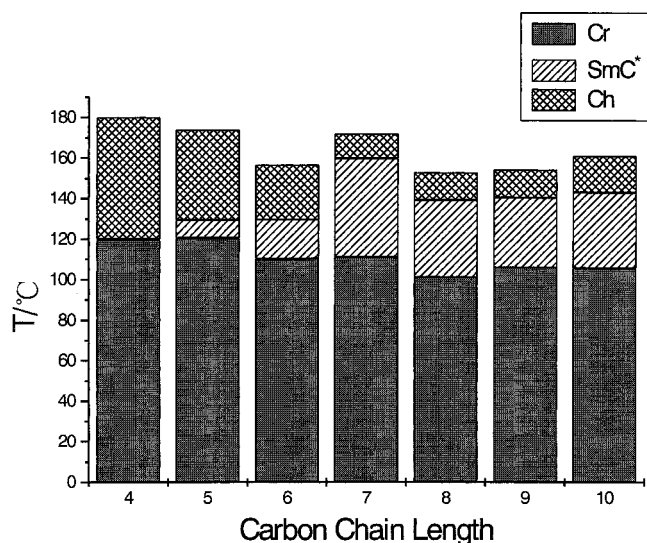


Figure 1. Temperature ranges of the phases as a function of terminal chain length.

in coexistence with the Grandjean texture containing 'oily streaks' was obtained. On further cooling, the texture changed to give a filament texture which has not been observed in the other derivatives (see figure 2). The filament texture is not a characteristic texture of the SmC\* phase, but to some extent resembles the filament texture of the twisted grain boundary (TGB) phase [15]. This phase has been denoted SmX\* and the phase sequence is summarized in scheme 1.

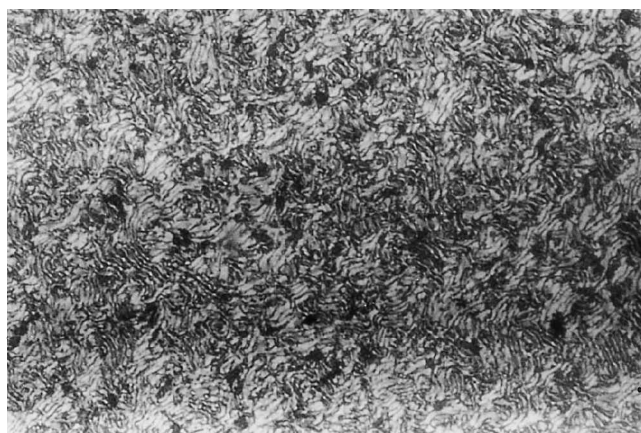
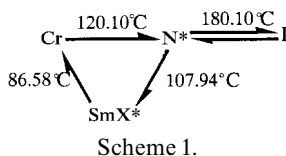
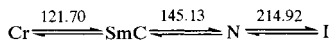
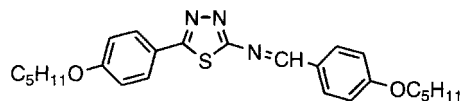


Figure 2. The filament texture shown by compound 1-1 ( $106^{\circ}\text{C}$ , on cooling).

The higher members of the series ( $n \geq 5$ ) show characteristic textures for enantiotropic cholesteric and smectic C\* phases. There are three peaks in the DSC traces obtained of 1-5 on both heating and cooling. On cooling, the cholesteric phase separated from the isotropic liquid in the form of oily streaks. Further cooling gives a transition to a smectic C\* phase. This phase exhibited a banded fan-shaped texture which is one of the characteristic textures of the SmC\* phase. A cholesteric focal-conic fan texture was obtained for compound 1-6 which on cooling further changed to give coexisting regions of banded, focal-conic fan and iridescent texture characteristic of the smectic C\* phase. The striations on the focal-conic domains in the smectic C\* phase, which mirror the positions of the molecular layers, are due to pitch bands and dechiralization lines [16].

For comparative purposes, we synthesized an analogous achiral Schiff's base, compound 2 (scheme 2). Compound



Scheme 2.

**2** has the same number of carbon atoms and a similar structure to compound **1-2**, but shows a wider mesomogenic temperature range than **1-2**. Presumably, the lower mesophase stabilities of compound **1** are due to the presence of the methyl branch which produces an additional deviation from linearity and disturbs the formation of stable mesophases.

With the recent discovery of new mesophase types, for example, the TGB phase [17, 18] and the anti-ferroelectric and ferroelectric phases [19], chirality in liquid crystals has grown to become a topical subject in liquid crystal research. Some optically active liquid crystalline 1,3,4-thiadiazole derivatives incorporating differently substituted allenic moieties exhibit a complex SmC\* polymorphism [20]. In addition to ferroelectric phases, the occurrence of an antiferroelectric and ferroelectric phases was proposed [21]. In compounds **1** no additional phase transitions have been detected within the SmC\* phase region by DSC, and the optical textures show no significant changes in the SmC\* phase range. Therefore, the 1,3,4-thiadiazole derivatives described here are ferroelectric liquid crystals. Further investigations of the liquid crystalline phases and the preparation of other 1,3,4-thiadiazole derivatives are now in progress.

### 3. Experimental

#### 3.1. Characterization

Infrared (IR) spectra (KBr plates) were recorded on an IDP-440 spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AM500 NMR spectrometer in CDCl<sub>3</sub>. Mass spectrometry (MS) (EI) was performed using a VG-ZAB-HS mass spectrometer. Elemental analyses were obtained using a Perkin-Elmer 240C instrument. Differential scanning calorimetry (DSC) was performed using an Ortholux II Perkin-Elmer DSC-7C. The heating rate was 10°C min<sup>-1</sup>. A Leitz polarizing microscope equipped with a hot stage was used to identify the various mesophases. The heating rate was 2°C min<sup>-1</sup>.

#### 3.2. The synthesis of intermediates and products

##### 3.2.1. (S)-(+)-1-Bromo-2-methylbutane

(S)-(-)-2-Methylbutanol ( $[\alpha]_D^{20} = -5.72^\circ$ ) was purchased from Aldrich and treated with phosphorus tribromide to give (S)-(+)-1-bromo-2-methylbutane ( $[\alpha]_D^{20} = +3.9^\circ$ ) [22].

##### 3.2.2. Optically active p-(2-methyl)butoxybenzaldehyde

p-Hydroxybenzaldehyde was treated with (S)-(+)-1-bromo-2-methylbutane and anhydrous potassium carbonate in cyclohexanone using a method described elsewhere [23].

##### 3.2.3. 2-Amino-5-(4-alkoxyphenyl)-1,3,4-thiadiazole

This series was prepared according to the procedure described elsewhere [24].

##### 3.2.4. Optically active Schiff's bases

Equimolar quantities of optically active p-(2-methyl)butoxybenzaldehyde and the appropriate 2-amino-5-(4-alkoxyphenyl)-1,3,4-thiadiazole were dissolved in a minimum amount of anhydrous ethanol and 0.20 ml of piperidine. The reaction mixture was heated at reflux for 22–25 h, and allowed to cool to room temperature. The product was separated by filtration, recrystallized from ethanol and dried.

**1-1**: <sup>1</sup>H NMR (ppm): 8.86 (1H, s, -N=CH-), 7.98–6.93 (8H, m, 2 × [Ar-H]<sub>4</sub>), 4.06–3.84 (4H, m, CH<sub>2</sub>-O), 1.91–0.91 (16H, m, CH-aliphatic). IR (cm<sup>-1</sup>): 2910 (m, C-H), 1610, 1510 (s, Ar), 1550 (s, N=C), 1240, 1160 (s, C-O). Anal: calc. for C<sub>24</sub>H<sub>29</sub>N<sub>3</sub>O<sub>2</sub>S C 68.09, H 6.86, N 9.93; found C 68.28, H 6.83, N 9.84%. *m/z*: 422.8 (M<sup>+</sup>, 57.55%), 421.9 (100), 351.8 (40.48), 295.8 (15.05), 136.9 (30.57), 57 (4.40), 43 (23.53).

**1-2**: <sup>1</sup>H NMR (ppm): 8.83 (1H, s, -N=CH-), 7.95–6.62 (8H, m, 2 × [Ar-H]<sub>4</sub>), 4.01–3.80 (4H, m, CH<sub>2</sub>-O), 1.90–0.97 (18H, m, CH-aliphatic). IR (cm<sup>-1</sup>): 2910 (m, C-H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1250, 1160 (s, C-O). Anal: calc. for C<sub>25</sub>H<sub>31</sub>N<sub>3</sub>O<sub>2</sub>S C 68.65, H 7.09, N 9.61; found C 68.51, H 7.08, N 9.75%. *m/z*: 436.7 (M<sup>+</sup>, 58.15%), 435.7 (100), 365.7 (36.38), 295.8 (13.76), 136.9 (30.57), 71 (2.98), 43 (31.41).

**1-3**: <sup>1</sup>H NMR (ppm): 8.85 (1H, s, -N=CH-), 7.95–6.60 (8H, m, 2 × [Ar-H]<sub>4</sub>), 4.04–3.80 (4H, m, CH<sub>2</sub>-O), 1.90–0.97 (20H, m, CH-aliphatic). IR (cm<sup>-1</sup>): 2910 (m, C-H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1240, 1160 (s, C-O). Anal: calc. for C<sub>26</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>S C 69.18, H 7.32, N 9.31; found C 68.93, H 7.27, N 9.68%. *m/z*: 450.7 (M<sup>+</sup>, 53.50%), 449.7 (100), 397.7 (24.38), 295.8 (7.80), 136.9 (19.58), 71 (2.40), 43 (24.63).

**1-4**: <sup>1</sup>H NMR (ppm): 8.84 (1H, s, -N=CH-), 7.93–6.62 (8H, m, 2 × [Ar-H]<sub>4</sub>), 4.04–3.83 (4H, m, CH<sub>2</sub>-O), 1.89–0.91 (22H, m, CH-aliphatic). IR (cm<sup>-1</sup>): 2920 (m, C-H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1250, 1160 (s, C-O). Anal: calc. for C<sub>27</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub>S C 69.68, H 7.53, N 9.03; found C 69.43, H 7.47, N 9.51%. *m/z*: 464.7 (M<sup>+</sup>, 59.27%), 463.7 (100), 393.6 (26.78), 295.7 (13.01), 136.8 (19.28), 71 (2.04), 43 (19.35).

**1-5**: <sup>1</sup>H NMR (ppm): 8.83 (1H, s, -N=CH-), 7.95–6.62 (8H, m, 2 × [Ar-H]<sub>4</sub>), 4.01–3.83 (4H, m, CH<sub>2</sub>-O),

1.90–0.89 (24H, m, CH-aliphatic). IR ( $\text{cm}^{-1}$ ): 2910 (m, C–H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1250, 1160 (s, C–O). Anal: calc. for  $\text{C}_{28}\text{H}_{37}\text{N}_3\text{O}_2\text{S}$  C 70.15, H 7.72, N 8.77; found C 70.09, H 7.50, N 8.64%.  $m/z$ : 479.1 ( $\text{M}^+$ , 4.21%), 478.0 (7.64), 305.0 (49.70), 192.9 (100), 120.0 (31.26), 71 (4.36), 43 (25.95).

**1-6:**  $^1\text{H}$  NMR (ppm): 8.85 (1H, s,  $-\text{N}=\text{CH}-$ ), 7.94–6.62 (8H, m,  $2 \times [\text{Ar}-\text{H}]_4$ ), 4.01–3.81 (4H, m,  $\text{CH}_2-\text{O}$ ), 1.90–0.88 (26H, m, CH-aliphatic). IR ( $\text{cm}^{-1}$ ): 2950 (m, C–H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1250, 1170 (s, C–O). Anal: calc. for  $\text{C}_{29}\text{H}_{39}\text{N}_3\text{O}_2\text{S}$  C 70.59, H 7.91, N 8.52; found C 70.44, H 7.36, N 8.75%.  $m/z$ : 493.0 ( $\text{M}^+$ , 66.02%), 492.0 (100), 421.9 (19.63), 295.9 (15.15), 136.9 (15.83), 71 (9.02), 43 (34.19).

**1-7:**  $^1\text{H}$  NMR (ppm): 8.84 (1H, s,  $-\text{N}=\text{CH}-$ ), 7.95–6.60 (8H, m,  $2 \times [\text{Ar}-\text{H}]_4$ ), 4.04–3.82 (4H, m,  $\text{CH}_2-\text{O}$ ), 1.90–0.87 (28H, m, CH-aliphatic). IR ( $\text{cm}^{-1}$ ): 2910 (m, C–H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1260, 1170 (s, C–O). Anal: calc. for  $\text{C}_{30}\text{H}_{41}\text{N}_3\text{O}_2\text{S}$  C 71.01, H 8.09, N 8.28; found C 71.04, H 8.19, N 8.20%.  $m/z$ : 507.2 ( $\text{M}^+$ , 61.84%), 506.1 (100), 436.1 (23.88), 296.0 (13.33), 137.0 (19.52), 71 (4.11), 43 (27.28).

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