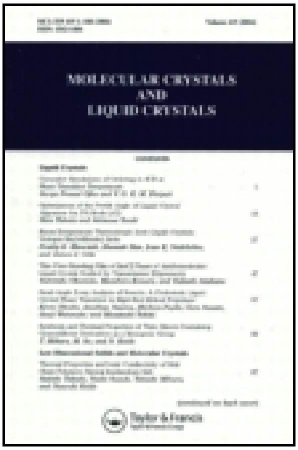

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Synthesis and Properties of Schiff's Bases Derived from 1,3,4-Thiadiazole as a Mesogenic Unit

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Synthesis and Properties of Schiff's Bases Derived from 1,3,4-Thiadiazole as a Mesogenic Unit

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Some new liquid crystalline 2,5-disubstituted 1,3,4-thiadiazole derivatives incorporating a central group (-CH=N-) have been synthesized by treating 2-amino-5-(4-alkoxyphenyl)-1,3,4-thiadiazole with corresponding p-alkoxybenzaldehyde. Their structures have been characterized with Elementary Analysis, IR, ^{1}HNMR and MS, and their properties were determined by using DSC and Texture. All 12 compounds are enantiotropic liquid crystals, and most of them exhibit nematic mesomorphism and broad smectic C mesomorphic ranges. Several compounds show only the smectic C mesophase. By introducing an -OH group into the phenyl ring the thermal stability of the mesophases increases due to the formation of a hydrogen bond.

Keywords: Schiff's Bases; liquid crystal; thiadiazoles; synthesis and properties

INTRODUCTION

Since the discovery of ferroelectricity in chiral smectic C phases by R. Meyer et al.[1] and its application in electro-optical displays proposed by Clark and Lagerwall[2], the search for new smectic C liquid crystals becomes important. Several liquid crystalline thiadiazole derivatives[3,4] have been reported during the past decade. These compounds exhibit broad smectic C ranges and possess moderate negative values of dielectric anisotropy. These materials are useful components for S_c host mixtures to give ferroelectric liquid crystalline mixtures after addition of chiral dopants. C. Tschierske et al. have synthesized 2,5-disubstituted 1,3,4-thiadiazole derivatives which belong to the general formulas A and B (Scheme 1).

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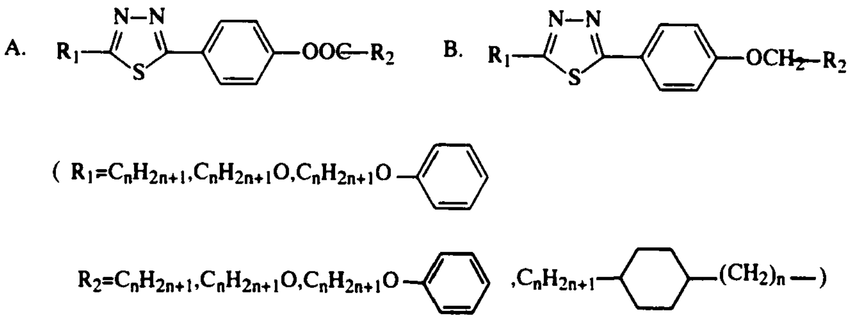
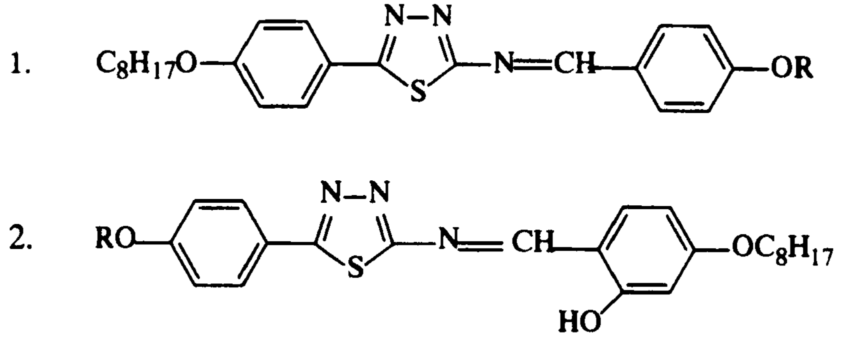
* Corresponding Author.



SCHEME 1

Compounds A and B contain a thiadoazole ring and one or two phenyl rings, and the thiadiazole ring is connected with ph- or C_nH_{2n+1}- directly, without a central group. Here, we report several novel thiadiazole derivatives with a central group (-C=N-) (Scheme 2). The smectic C ranges of these new compounds are broader than compounds A and B.



SCHEME 2

RESULTS AND DISCUSSION

All synthesized compounds are mesogenic and most of them exhibit broad smectic C ranges. The transition temperatures and mesomorphic phases of these compounds are listed in Table I and II. Figure 1, 2, 3 and 4 are textures of some compounds.

TABLE I Transition Temperatures (°C), Enthalpies (J/g) of the Schiff's Bases 1

Comp.	*n*	*Cr*	S_B	*Sc*	*N*	*Is*
1.1	4	• 100.07 (72.63)	-	• 149.9 (2.49)	• 210.88 (2.66)	•
1.2	6	• 108.49 (72.72)	-	• 179.22 (5.59)	• 206.76 (3.43)	•
1.3	7	• 120.01 (81.28)	-	• 187.62 (7.02)	• 205.15 (4.07)	•
1.4	8	• 110.26 (75.26)	-	• 189.6 (7.81)	• 201.61 (4.66)	•
1.5	9	• 103.39 (59.99)	-	• 159.04 (15.08)	-	•
1.6	12	$Cr_1 \rightarrow Cr_2$ 96.0(19.91) $Cr_2 \rightarrow S_B$ 118.3(56.7)	• 189.66 (16.98)	• 193.66	-	•

TABLE II Transition Temperatures (°C), Enthalpies (J/g) of the Schiff's Bases 2

Comp.	*n*	*Cr*	*Sc*	*N*	*Is*
2.1	4	• 108.00 (56.51)	• 185.53 (5.52)	• 223.06 (4.67)	•
2.2	6	• 97.96 (44.05)	• 211.19 (8.64)	• 222.87 (5.52)	•
2.3	7	• 102.10 (47.79)	• 213.93 (9.21)	• 219.40 (6.14)	•
2.4	8	• 106.36 (49.52)	• 216.30 (11.49)	• 217.19 (5.55)	•
2.5	9	• 115.27 (29.14)	• 179.02 (14.70)	–	•
2.6	10	• 95.29 (47.11)	• 215.67 (17.49)	–	•

Within a certain chain length of alkyl substituents, the Sc phase is accompanied by the nematic mesophase at elevated temperatures and the nematic range of 1 decreases with increasing size of the substituent, while the smectic C range increases. For example, the nematic mesophase ranges decrease from 60.98°C, 27.54°C, 17.53°C to 12.01°C as n increases from 4, 6, 7 to 8, and finally, the

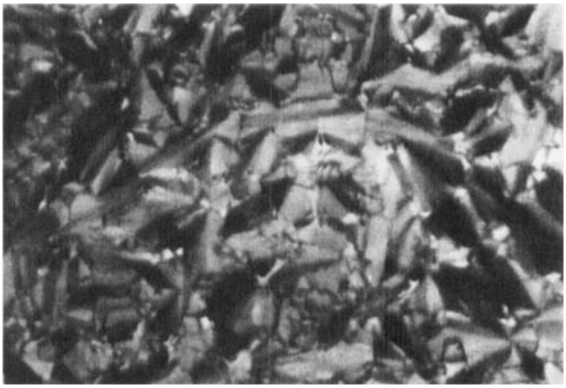


FIGURE 1 Texture of compound 1.5 (125°C, on cooling)

nematic phase disappears when n=9. As n reaches 12, the $S_B$phase appears below the smectic C phase. Comp. 1.6 exhibits a mosaic texture at 175°C (Figure 2). At 191°C, it exhibits a broken focal conic texture (Figure 3).

When a -OH is introduced into 2-position of the benzyl ring, an intramolecular hydrogen bond is formed with "N" of the central group and gives the molecules a rigid central core[5]. As a result, a reinforcement of the mesomorphic properties and an elevation of the clearing points for compounds 1 compared with those of compounds 2. Inspections of table I and II indicate that the clearing point (217.19°C) and the smectic C range (110°C) of compound 2.4 are higher and broader respectively than that of compound 1.4. When the chain length reaches n=10, the smectic C range (120°C) of compound 2.6 is even broader than that of compound 2.4, and the nematic phase disappears.

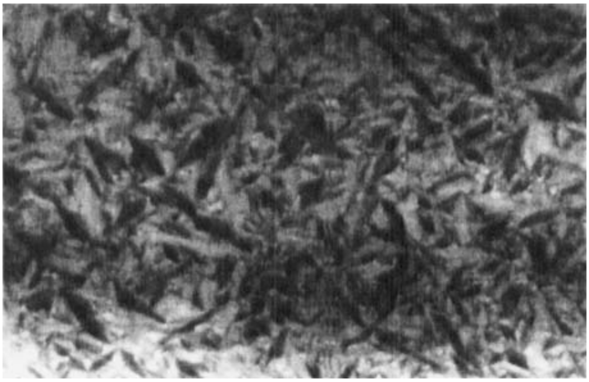


FIGURE 2 Texture of compound 1.6 (175°C, on cooling)

It is found that the melting enthalpy of compound 2.4 (49.52J/g) is much less than that of compound 1.4 (75.26J/g). The formation of the intramolecular hydrogen bond blocks the intramolecular rotation, thus the turbulence of the molecular is decreased and the melting enthalpy is also decreased.

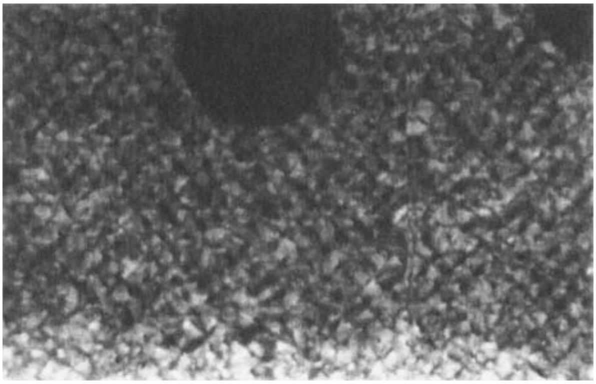


FIGURE 3 Texture of compound 1.6 (191°C, on cooling)

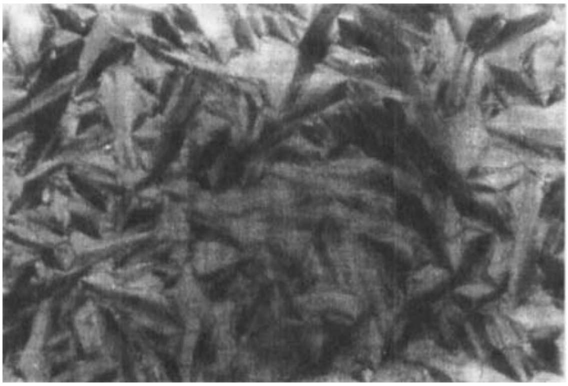
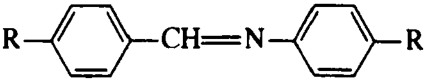


FIGURE 4 Texture of compound 2.6 (180°C, on heating)

It is notable that the clearing point of the simple Schiff's Base liquid crystal (Scheme 3) is not high. When R_1=R_2=$C_nH_{2n+1}O$-, the clearing point is 114°C, while the clearing point of compound 1.4 (n=8) is 201.61. Thus, it indicates that the clearing point is significantly influenced by the 1,3,4-thiadiazole ring. The introduction of a thiadiazole ring could lead to an obvious increase in the mesophase range.



SCHEME 3

EXPERIMENTAL

Instrument

Infrared (IR) spectra were recorded on Nicolet FT-IR 170s 5DX (KBr plates). Proton nuclear magnetic resonance spectra (^{1}HNMR) were recorded on a Bruker AM500 spectrometer in $CDCl_3$solvent. Mass spectrometry (MS) was carried out on VG-ZAB-HS(EI). Element Analysis was obtained on Perkin-Elmer 240C. Differential scanning calorimeter (DSC) was recorded on an ORTHOLUX II Perkin-Elmer DSC-7C. The heating rate was 10°C per min. A Leitz polarizing microscope equipped with a hot stage was used to identify the various mesophases. The heating rate was 2°C per min.

The Synthesis of Intermediates and Products

1) p-Alkoxybenzaldehydes

p-Hydroxy-benzaldehyde was treated with the respective alkyl bromide and anhydrous potassium carbonate in cyclohexanone by the known method.[6]

2) 4-Alkoxybenzaldehyde-3-Thiosemicarbazone

Equimolar quantities of a p-alkoxybenzaldehyde and finely powdered thiosemicarbazide were dissolved in 95% ethanol and refluxed for 30–60 min. The fine crystals were deposited after the reaction mixture cooled down to room temperature, filtered to get crystalline 4-alkoxybenzaldehyde-3-thiosemicarbazone(85–90%)

3) 2-Amino-5-(4-Alkoxyphenyl)-1,3,4-Thiadiazole

The standard route for 2-amino-5-aryl-1,3,4-thiadiazoles involved the acylation of a thiosemicarbazide followed by dehydration. The common dehydrating reagents for the cyclization were neat sulfuric acid, neat polyphosphoric acid or their mixtures. In contrast to these unhomogeneous procedures which were difficult to control, we used a convenient and homogeneous oxidative cyclization by ferric chloride.[7]

A mixture of finely powdered thiosemicarbazone(0.01mol) and ferric chloride hexahydrate(0.04mol) in 95% ethanol(90ml) was refluxed gently for 1.5–2 hr. Most of the ethanol was removed under reduced pressure, the residue was cooled in an ice-salt bath and then treated with concentrated hydrochloric acid (8ml). The acidic mixture was kept in the ice-salt bath for 2 hr, and the precipitated hydrochloride collected. The free base was liberated with aqueous ammonia and the mixture was heated in a water-bath for 15 min. The aminothiadiazole was extracted from the iron residues with boiling ethanol and then the ethanol solution was concentrated to get the crude amino compound (60%).

4) Schiff's Bases 1. Schiff's

Bases 1 were prepared by the condensation of equimolar quantities of 2-amino-5-(4-alkoxyphenyl)-1,3,4-thiadiazole and corresponding aldehydes in a minimum amount of anhydrous ethanol and 0.20ml of piperidine. The reaction mixtures were refluxed for 13–18 hours, cooled down, and then filtered under vacue. The crude products were crystalized from ethanol and dried to get pure product, yield 87%.

Comp. 1.1: ^{1}H-NMR (ppm): 9.88 (1H, s, -N=CH-), 7.96–6.85 (8H, m, 2×[Ar-H]$_4$), 4.10–3.96 (4H, m, CH$_2$-O), 1.95–0.78 (22H, m, CH-aliphat), IR(cm^{-1}): 2960 (m, C-H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1250, 1170 (s, C-O), Anal. Calcd for $C_{27}H_{35}N_3O_2S$: C, 69.68; H, 7.53; N, 9.03. Found: C, 69.57; H, 7.69; N, 9.10. m/z: 465 (M$^+$, 20.4%), 464 (100), 408 (24.7), 296 (9.84), 57 (27.34).

Comp. 1.2: ^{1}H-NMR (ppm): 9.88 (1H, s, -N=CH-), 7.94–6.98 (8H, m, 2×[Ar-H]$_4$), 4.04 (4H, m, CH$_2$-O), 1.81–0.91 (26H, m, CH-aliphat), IR(cm^{-1}): 2950 (m, C-H), 1610, 1515 (s, Ar), 1560 (s, N=C), 1250, 1170 (s, C-O), Anal. Calcd for $C_{29}H_{39}N_3O_2S$: C, 70.59; H, 7.91; N, 8.52. Found: C, 70.54; H, 7.95; N, 8.59. m/z: 493 (M$^+$, 38.7%), 492 (100), 408 (19.18), 296 (9.53), 43 (20.84).

Comp. 1.3: ^{1}H-NMR (ppm): 9.88 (1H, s, -N=CH-), 7.97–6.91 (8H, m, 2×[Ar-H]$_4$), 4.05–3.97 (4H, m, CH$_2$-O), 1.83–0.90 (28H, m, CH-aliphat), IR(cm^{-1}): 2940 (m, C-H), 1605, 1510 (s, Ar), 1550 (s, N=C), 1240, 1150 (s, C-O), Anal. Calcd for $C_{30}H_{41}N_3O_2S$: C, 71.01; H, 8.09; N, 8.28. Found: C, 71.22; H, 8.20; N, 8.25. m/z: 507 (M$^+$, 45.90%), 506 (100), 408 (21.09), 296 (10.84), 137(27.40), 43 (34.84). Comp. 1.4: ^{1}H-NMR (ppm): 9.87 (1H, s, -N=CH-), 7.84–6.70 (8H, m, 2×[Ar-H]$_4$), 4.05–3.78 (4H, m, CH$_2$-O), 1.83–0.89 (30H, m, CH-aliphat), IR(cm^{-1}): 2920 (m, C-H), 1605, 1510 (s, Ar), 1550 (s, N=C), 1240, 1155 (s, C-O), Anal. Calcd for $C_{31}H_{43}N_3O_2S$: C, 71.40; H, 8.25; N, 8.06. Found: C, 71.30; H, 8.30; N, 8.07. m/z: 521 (M$^+$, 62.96%), 520 (100), 408 (24.89), 296 (9.74), 137 (20.65), 43(19.21).

Comp. 1.5: ^{1}H-NMR (ppm): 9.88 (1H, s, -N=CH-), 7.95–6.89 (8H, m, 2×[Ar-H]$_4$), 4.11–3.95 (4H, m, CH$_2$-O), 1.95–0.78 (32H, m, CH-aliphat), IR(cm^{-1}): 2940 (m, C-H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1250, 1160 (s, C-O), Anal. Calcd for $C_{32}H_{45}N_3O_2S$: C, 71.78; H, 8.41; N, 7.85. Found: C, 71.83; H, 8.48; N, 7.73. m/z: 535 (M$^+$, 67.41%), 534 (100), 408 (27.64), 296 (9.36), 57 (16.52).

Comp. 1.6: ^{1}H-NMR (ppm): 9.80 (1H, s, -N=CH-), 7.95–6.85 (8H, m, 2×[Ar-H]$_4$), 4.15–3.95 (4H, m, CH$_2$-O), 1.95–0.83 (38H, m, CH-aliphat), IR(cm^{-1}): 2940 (m, C-H), 1610, 1510 (s, Ar), 1560 (s, N=C), 1260, 1160 (s, C-O), Anal. Calcd for $C_{35}H_{51}N_3O_2S$: C, 72.79; H, 8.84; N, 7.28. Found: C, 72.95; H, 8.71; N, 7.23. m/z: 577 (M$^+$, 73.95%), 576 (100), 408 (30.87), 296 (9.21), 137 (17.58), 43 (30.78).

5) 4-Alkoxy-2-Hydroxybenzaldehyde

Was treated with the respective alkyl bromide and potassium hydroxide in methanol by the known method.[8]

6) Schiff's Bases 2

Schiff's Bases 2 were prepared by the condensation of equimolar quantities of 2-amino-5-(4-alkoxyphenyl)-1,3,4-thiadiazole and 2-octyloxy-4-hydroxybenzaldehydes in a minimum amount of anhydrous ethanol. The mixtures were refluxed for 7 hours and cooled to give yellow needlelike crystals (94%). Comp. 2.1: ^{1}H-NMR (ppm): 12.36 (1H, s, OH), 9.00 (1H, s, N=CH-), 7.87–6.41 (7H, m, Ar-H), 4.03–3.98 (4H, m, CH$_2$-O), 1.82–0.88 (22H, m, CH-aliphat), IR(cm^{-1}): 3440 (O-H), 2960 (m, C-H), 1610, 1510 (s, Ar), 1570 (s, N=C), 1250, 1170 (s, C-O), Anal. Calcd for $C_{27}H_{35}N_3O_3S$: C, 67.36; H, 7.28; N, 8.73. Found: C, 67.47; H, 7.35; N, 8.69.

Comp. 2.2: ^{1}H-NMR (ppm): 12.35 (1H, s, OH), 9.00 (1H, s, N=CH-), 7.86–6.41 (7H, m, Ar-H), 4.03–3.98 (4H, m, CH$_2$-O), 1.80–0.90 (26H, m, CH-aliphat), IR(cm^{-1}): 3430 (O-H), 2950 (m, C-H), 1610, 1515 (s, Ar), 1570 (s, N=C), 1250, 1170 (s, C-O), Anal. Calcd for $C_{29}H_{39}N_3O_3S$: C, 68.37; H, 7.66; N, 8.25. Found: C, 68.26; H, 7.70; N, 8.14.

Comp. 2.3: ^{1}H-NMR (ppm): 12.37 (1H, s, OH), 9.01 (1H, s, N=CH-), 7.88–6.41 (7H, m, Ar-H), 4.03–3.99 (4H, m, CH$_2$-O), 1.81–0.89 (28H, m, CH-aliphat), IR(cm^{-1}): 3400 (O-H), 2940 (m, C-H), 1605, 1510 (s, Ar), 1560 (s, N=C), 1240, 1150 (s, C-O), Anal. Calcd for $C_{30}H_{41}N_3O_3S$: C, 68.83; H, 7.84; N, 8.03. Found: C, 68.95; H, 7.89; N, 7.97.

Comp. 2.4: ^{1}H-NMR (ppm): 12.37 (1H, s, OH), 9.01 (1H, s, N=CH-), 7.88–6.41 (7H, m, Ar-H), 4.13–3.98 (4H, m, CH$_2$-O), 1.97–0.88 (30H, m, CH-aliphat), IR(cm^{-1}): 3400 (O-H), 2910 (m, C-H), 1605, 1510 (s, Ar), 1565 (s, N=C), 1240, 1155 (s, C-O), Anal. Calcd for $C_{31}H_{43}N_3O_3S$: C, 69.27; H, 8.01; N, 7.82. Found: C, 69.48; H, 8.24; N, 7.74. m/z: 537 (M^+, 5.50%), 520 (7.36), 239 (89.35), 225 (100), 119 (17.48), 73 (43.95), 43 (9.52).

Comp. 2.5: ^{1}H-NMR (ppm): 12.36 (1H, s, OH), 8.99 (1H, s, N=CH-), 7.87–6.40 (7H, m, Ar-H), 4.08–3.99 (4H, m, CH_2-O), 1.81–0.78 (32H, m, CH-aliphat), IR(cm^{-1}): 3420 (O-H), 2940 (m, C-H), 1610, 1510 (s, Ar), 1570 (s, N=C), 1250, 1160 (s, C-O), Anal. Calcd for $C_{32}H_{45}N_3O_3S$: C, 69.69; H, 8.17; N, 7.62. Found: C, 69.61; H, 8.23; N, 7.54.

Comp. 2.6: ^{1}H-NMR (ppm): 12.36 (1H, s, OH), 9.01 (1H, s, N=CH-), 7.88–6.41 (7H, m, Ar-H), 4.03–3.99 (4H, m, CH_2-O), 1.92–0.87 (34H, m, CH-aliphat), IR(cm^{-1}): 3400 (O-H), 2920 (m, C-H), 1610, 1515 (s, Ar), 1580 (s, N=C), 1260, 1170 (s, C-O), Anal. Calcd for $C_{33}H_{47}N_3O_3S$: C, 70.09; H, 8.32; N, 7.43. Found: C, 70.25; H, 8.23; N, 7.38.

CONCLUSION

Twelve Schiff's Bases derived from 1,3,4-thiadiazole as a mesogenic unit were synthesised. These liquid crystal Schiff's Bases all had high clearing points and showed enantiotropic nematic and smectic C mesophases. Only compound *1.6* was found to exist as a smectic B mesophase. When $n \geq 9$, the nematic phase disappeared. The hydrogen bond between the hydroxyl group in the ortho-position and the nitrogen of the central group in compounds 2 gives the molecules a rigid central core and influences the nature of the mesomorphism and the clearing points of these compounds.

Acknowledgements

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