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Synthesis of 4-Alkoxy-2-substituted-benzenethiols and Their Application to Thermotropic Liquid Crystals

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A new synthetic method of 4-alkoxy-2-X-benzenethiols (X = H, halogens, CH_3) has been established. In order to confirm the validity as a component of liquid crystal materials, some derivatives of *S*-(4-alkoxy-2-X-phenyl) 4-R-thiobenzoates (R = $C_nH_{2n+1}O$, CN, NO_2, X = halogens, CH_3) were prepared. Most of the thioesters exhibit a nematic phase, while the lateral substituents (X) tend to reduce the mesophase thermal stability as well as the melting point. The effect of lateral substituents on the mesomorphic properties is discussed.

Benzenethiols are one of the important components of liquid crystal (LC) molecules, and LC materials incorporating a thioester linkage have been developed.[1–6] The thioester linkage is also given much attention as the core of chiral LC materials.[7–9] Thioester compounds are known to have excellent mesomorphic properties compared with the corresponding ester ones, since the thioester linkage is superior in linearity and longitudinal length to the ester one.[10]

For example, 1,4-benzenebis(*S*-4-alkoxyphenyl carbothioate),[2] *S*-phenyl thiobenzoates,[2–6] and *S*-(4-biphenylyl) thiobenzoates[7] with alkyl and/or alkoxy groups at both terminal positions show a higher nematic–isotropic (N–I) transition temperature and a wider mesomorphic range than the corresponding ester compounds.

The introduction of a lateral substituent is one of the conventional methods for changing and improving the LC properties such as the dielectric constant, refractive index, and transition temperature. In the case of benzenethiol compounds, the introduction of a lateral substituent is not very easy because of high chemical reactivity around the sulfur moiety. As far as we know, therefore, thioester LC materials involving lateral substituents at the *S*-phenyl ring have not been developed.

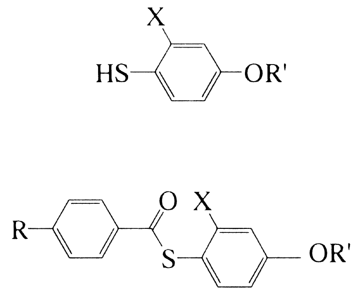
Recently, we successfully prepared LC materials having 3-fluoro- and 3-methyl-thiocyanatobenzenes.[11]

During the process, we found that thiocyanato compounds can be successfully converted to the corresponding thiols by the reaction of $LiAlH_4$ or $NaBH_4$ in high yield, suggesting that 4-thiocyanato-3-X-phenols are convenient intermediates for the synthesis of 4-alkoxy-2-X-benzenethiols.

In this paper we wish to show the synthesis of 4-alkoxy-2-X-benzenethiols (Fig. 1) and its application to LC materials. The LC properties are discussed in terms of the geometrical and electrostatic nature of the molecules.

Experimentals

Method. The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp 156.6 °C, 28.4 J/g). The DSC thermogram was operated at a heating or cooling rate of 5 °C/min. The mesophases were characterized by a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). ^{1}H NMR spectra were measured using a JEOL EX-270 spectrometer, where tetramethylsilane was used as an internal standard. IR spectra were recorded with a Horiba FT-200 infrared spectrometer. The purity was checked by HPLC and elementary analysis. Molecular parameters were estimated by a semi-empirical molecular orbital method (MOPAC 97).



R=CN, NO_2, Alkoxy group
R'=Alkyl group

Compounds	X
1	H
2	F
3	Cl
4	Br
5	CH_3

Fig. 1. Chemical structures of compounds **1**–**5**.

Materials. The synthetic scheme for **1**–**5** is shown in Fig. 2.

3-Fluoro-4-thiocyanatophenol: The thiocyanation of phenols was carried out according to a method described in our earlier paper.[11] After a solution of *N*-chlorosuccinimide (15.49 g, 116 mmol) and ammonium thiocyanate (8.8 g, 116 mmol) in methanol (150 mL) was stirred at 0 °C for 2 h, 3-fluorophenol (6.5 g, 57.8 mmol) in methanol (50 mL) was added dropwise, and the mixture

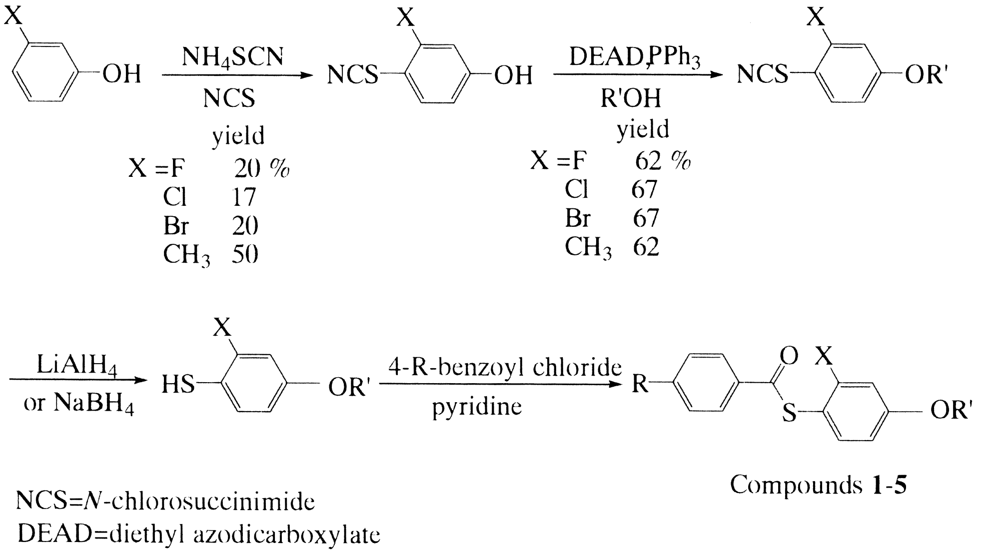


Fig. 2. Synthetic scheme of (*S*-4-alkoxy-2-X-phenyl) 4-R-thiobenzoates (**1**–**5**).

was stirred at 0 °C for 24 h. To the reaction mixture, a 20% aqueous solution of sodium hydrogencarbonate (200 mL) was added, and the precipitates were filtered off. Half of the solvent of the filtrate was evaporated in vacuo, and the residue was extracted twice with ether (50 mL). The combined ether layer was washed with water and dried over anhydrous sodium sulfate. After removing the solvent, the residue was purified by column chromatography on silica gel using chloroform as an eluent. The product was recrystallized from a mixed solvent of ether–hexane to give 3-fluoro-4-thiocyanatophenol as colorless needles; yield 20%; mp 66–68 °C; IR (KBr) 2171 (CN) and 3290 $\mathrm{cm^{-1}}$ (OH); ^{1}H NMR δ 6.38 (1H, br), 6.68–6.74 (2H, m), 7.45 (1H, t, J = 8.6 Hz).

3-Chloro-4-thiocyanatophenol: Colorless powder; yield 17%; mp 86–88 °C. ^{1}H NMR δ 6.16 (1H, br.), 6.82 (1H, dd, J = 8.6, 2.6 Hz), 7.01 (1H, d, J = 2.6 Hz), 7.54 (1H, d, J = 8.6 Hz).

3-Bromo-4-thiocyanatophenol: Pale yellow powder; yield 20%; mp 88–90 °C. ^{1}H NMR δ 6.21 (1H, br.), 6.87 (1H, dd, J = 8.9, 2.6 Hz), 7.18 (1H, d, J = 2.6 Hz), 7.56 (1H, d, J = 8.9 Hz).

3-Methyl-4-thiocyanatophenol: Colorless needles; yield 50%; mp 72–74 °C. ^{1}H NMR δ 2.47 (3H, s), 5.89 (1H, br.), 6.70 (1H, dd, J = 8.5, 3.0 Hz), 6.79 (1H, d, J = 3.0 Hz), 7.45 (1H, t, J = 8.5 Hz).

2-Fluoro-4-octyloxyphenyl Thiocyanate: 2-Fluoro-4-hydroxy-thiocyanatobenzene (0.88 g, 5.22 mmol), triphenylphosphine (1.78 g, 6.79 mmol), and octanol (0.82 g, 6.30 mmol) were dissolved in dry THF (10 mL), and diethyl azodicarboxylate (DEAD, 40% in toluene, 2.95 g, 6.78 mmol) was added to the solution at 0 °C under a nitrogen atmosphere. After the reaction mixture was brought to room temperature, stirring was continued for 12 h. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water and dried over anhydrous sodium sulfate. After removing the toluene, ether was added to the residue and diethyl hydrazodicarboxylate separated out was filtered off. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether–chloroform (2 : 1) as an eluent, giving 2-fluoro-4-octyloxyphenyl thiocyanate as a colorless oil; 0.91 g, yield 62%; IR (KBr) 2158 $\mathrm{cm^{-1}}$ (CN); ^{1}H NMR δ 0.91 (3H, t, J = 6.6 Hz), 1.30–1.44 (10H, m), 1.79 (2H, quin, J = 6.9 Hz), 3.96 (2H, t, J = 6.3 Hz), 6.71–6.78 (2H, m), 7.50 (1H, t, J = 8.6 Hz).

2-Fluoro-4-hexyloxyphenyl Thiocyanate: ^{1}H NMR δ 0.91 (3H, t, J = 6.6 Hz), 1.30–1.44 (6H, m), 1.79 (2H, quin., J = 6.9 Hz), 3.96 (2H, t, J = 6.3 Hz), 6.71–6.78 (2H, m), 7.50 (1H, t, J = 8.6 Hz).

2-Chloro-4-octyloxyphenyl Thiocyanate: Colorless oil; yield 67%. ^{1}H NMR δ 0.89 (3H, t, J = 6.9 Hz), 1.29–1.45 (10H, m), 1.79 (2H, quin., J = 7.0 Hz), 3.93 (2H, t, J = 6.6 Hz), 6.87 (1H, dd, J = 8.9, 2.6 Hz), 7.03 (1H, d, J = 2.6 Hz), 7.59 (1H, d, J = 8.9 Hz).

2-Bromo-4-octyloxyphenyl Thiocyanate: Colorless oil; yield 67%. ^{1}H NMR δ 0.89 (3H, t, J = 6.8 Hz), 1.29–1.46 (10H, m), 1.78 (2H, quin., J = 6.7 Hz), 3.95 (2H, t, J = 6.7 Hz), 6.92 (1H, dd, J = 8.9, 2.6 Hz), 7.15 (1H, d, J = 2.6 Hz), 7.61 (1H, d, J = 8.9 Hz).

2-Methyl-4-octyloxyphenyl Thiocyanate: Colorless oil; yield 62%. ^{1}H NMR δ 0.89 (3H, t, J = 6.6 Hz), 1.29–1.47 (10H, m), 1.78 (2H, quin., J = 6.8 Hz), 2.34 (3H, s), 3.95 (2H, t, J = 6.6 Hz), 6.76 (1H, dd, J = 8.6, 2.6 Hz), 6.84 (1H, d, J = 2.9 Hz), 7.52 (1H, d, J = 8.6 Hz).

4-Octyloxyphenyl Thiocyanate: Colorless oil; yield 35%. ^{1}H NMR δ 0.89 (3H, t, J = 6.8 Hz), 1.29–1.46 (10H, m), 1.79 (2H, quin., J = 6.9 Hz), 3.96 (2H, t, J = 6.7 Hz), 6.93 (2H, d, J = 8.9 Hz), 7.48 (2H, d, J = 8.9 Hz).

2-Fluoro-4-octyloxybenzenethiol: To a solution of 2-fluoro-4-octyloxy-thiocyanatobenzene (0.33 g, 1.17 mmol) in ethanol (5 mL), sodium borohydride (0.11 g, 2.91 mmol) was added dropwise at 0 °C. After stirring for 2 h, water (4 mL) was slowly added to the reaction mixture. The ethanol was removed by evaporation and the residue was extracted with ether twice. The combined ether layer was dried over anhydrous sodium sulfate. After removing ether, the product was obtained as a colorless oil. Because the oily material easily became dark under atmospheric conditions, it was reacted with the acids without further purification; yield 0.29 g (96%); IR (KBr) 2600 $\mathrm{cm^{-1}}$ (SH).

2-Chloro-4-octyloxy-, 2-bromo-4-octyloxy-, 2-methyl-4-octyloxybenzenethiols were obtained similarly.

***S*-(4-Octyloxyphenyl) 4-Butoxythiobenzoate (1b):** **1b** was obtained by the reaction of 4-butoxybenzoyl chloride and 4-octyloxybenzenethiol according to the conventional method. IR (KBr) 1670 cm^{-1} (C=O); ^{1}H NMR δ 0.89 (3H, t, J = 6.6 Hz), 0.98 (3H, t, J = 7.0 Hz), 1.29–1.54 (12H, m), 1.74–1.86 (4H, m), 3.97 (2H, t, J = 6.6 Hz), 4.02 (2H, t, J = 6.6 Hz), 6.92 (2H, d, J = 8.8 Hz), 6.96 (2H, d, J = 8.9 Hz), 7.38 (2H, d, J = 8.8 Hz), 7.98 (2H, d, J = 8.9 Hz). Found: C, 72.43; H, 8.27%. Calcd for $C_{25}H_{34}O_3S$: C, 72.21; H, 8.09%.

Compounds **1c**–**5b** were prepared by the similar manner.

***S*-(4-Octyloxyphenyl) 4-Hexyloxythiobenzoate (1c):** ^{1}H NMR δ 0.89 (6H, t, J = 6.6 Hz), 1.29–1.50 (16H, m), 1.74–1.86 (4H, m), 3.98 (2H, t, J = 6.7 Hz), 4.02 (2H, t, J = 6.6 Hz), 6.92 (2H, d, J = 8.8 Hz), 6.96 (2H, d, J = 8.9 Hz), 7.38 (2H, d, J = 8.8 Hz), 7.98 (2H, d, J = 8.9 Hz).

***S*-(4-Octyloxyphenyl) 4-Octyloxythiobenzoate (1d):** ^{1}H NMR δ 0.89 (6H, t, J = 6.6 Hz), 1.29–1.50 (20H, m), 1.74–1.84 (4H, m), 3.98 (2H, t, J = 6.6 Hz), 4.02 (2H, t, J = 6.6 Hz), 6.92 (2H, d, J = 8.8 Hz), 6.96 (2H, d, J = 8.9 Hz), 7.38 (2H, d, J = 8.8 Hz), 7.98 (2H, d, J = 8.9 Hz).

***S*-(2-Fluoro-4-hexyloxyphenyl) 4-Ethoxythiobenzoate (2a):** ^{1}H NMR δ 0.89 (3H, t, J = 6.6 Hz), 1.24–1.40 (6H, m), 1.45 (3H, t, J = 6.6 Hz), 1.74–1.85 (4H, m), 3.95 (2H, t, J = 6.6 Hz), 4.10 (2H, q, J = 6.8 Hz), 6.72–6.78 (2H, m), 6.92 (2H, d, J = 8.9 Hz), 7.34 (1H, t, J = 7.7 Hz), 7.99 (2H, d, J = 8.9 Hz).

***S*-(2-Fluoro-4-hexyloxyphenyl) 4-Hexyoxythiobenzoate (2b):** ^{1}H NMR δ 0.89 (6H, t, J = 6.6 Hz), 1.29–1.52 (12H, m), 1.74–1.86 (4H, m), 3.95 (2H, t, J = 6.6 Hz), 4.02 (2H, t, J = 6.6 Hz), 6.72–6.78 (2H, m), 6.92 (2H, d, J = 8.8 Hz), 7.34 (1H, t, J = 8.0 Hz), and 7.97 (2H, d, J = 8.9 Hz).

***S*-(2-Fluoro-4-hexyloxyphenyl) 4-Cyanothiobenzoate (2c):** ^{1}H NMR δ 0.90 (3H, t, J = 6.6 Hz), 1.29–1.49 (6H, m), 1.81 (2H, quin., J = 6.9 Hz), 3.99 (2H, t, J = 6.6 Hz), 6.78 (2H, d, J = 8.6 Hz), 7.34 (1H, t, J = 8.1 Hz), 7.81 (2H, d, J = 8.9 Hz), 8.10 (2H, d, J = 7.7 Hz).

***S*-(2-Fluoro-4-octyloxyphenyl) 4-Ethoxythiobenzoate (2d):** ^{1}H NMR δ 0.89 (3H, t, J = 6.5 Hz), 1.24–1.40 (10H, m), 1.45 (3H, t, J = 6.7 Hz), 1.74–1.85 (4H, m), 3.95 (2H, t, J = 6.6 Hz), 4.10 (2H, q, J = 6.9 Hz), 6.72–6.78 (2H, m), 6.92 (2H, d, J = 8.8 Hz), 7.34 (1H, t, J = 7.6 Hz), 7.99 (2H, d, J = 8.9 Hz).

***S*-(2-Fluoro-4-octyloxyphenyl) 4-Butoxythiobenzoate (2e):** ^{1}H NMR δ 0.89 (3H, t, J = 6.5 Hz), 0.98 (3H, t, J = 7.2 Hz), 1.29–1.54 (12H, m), 1.74–1.86 (4H, m), 3.97 (2H, t, J = 6.6 Hz), 4.03 (2H, t, J = 6.6 Hz), 6.72–6.78 (2H, m), 6.92 (2H, d, J = 8.9 Hz), 7.34 (1H, t, J = 7.9 Hz), 7.97 (2H, d, J = 8.9 Hz).

***S*-(2-Fluoro-4-octyloxyphenyl) 4-Hexyloxythiobenzoate (2f):** ^{1}H NMR δ 0.89 (6H, t, J = 6.6 Hz), 1.29–1.50 (16H, m), 1.74–1.86 (4H, m), 3.95 (2H, t, J = 6.7 Hz), 4.03 (2H, t, J = 6.6 Hz), 6.72–6.78 (2H, m), 6.92 (2H, d, J = 8.9 Hz), 7.34 (1H, t, J = 7.9 Hz), 7.97 (2H, d, J = 8.9 Hz).

***S*-(2-Fluoro-4-octyloxyphenyl) 4-Octyloxythiobenzoate (2g):** ^{1}H NMR δ 0.89 (6H, t, J = 6.6 Hz), 1.29–1.54 (20H, m), 1.74–1.86 (4H, m), 3.94 (2H, t, J = 6.6 Hz), 4.02 (2H, t, J = 6.6 Hz), 6.72–6.78 (2H, m), 6.92 (2H, d, J = 8.9 Hz), 7.34 (1H, t, J = 7.9 Hz), 7.97 (2H, d, J = 8.9 Hz).

***S*-(2-Fluoro-4-octyloxyphenyl) 4-Decyloxythiobenzoate (2h):** ^{1}H NMR δ 0.89 (6H, t, J = 6.6 Hz), 1.29–1.54 (24H, m), 1.74–1.86 (4H, m), 3.94 (2H, t, J = 6.6 Hz), 4.02 (2H, t, J = 6.6 Hz), 6.72–6.78 (2H, m), 6.92 (2H, d, J = 8.9 Hz), 7.34 (1H, t, J = 7.9 Hz), 7.97 (2H, d, J = 8.8 Hz).

***S*-(2-Fluoro-4-octyloxyphenyl) 4-Cyanothiobenzoate (2i):** ^{1}H NMR δ 0.90 (3H, t, J = 6.5 Hz), 1.30–1.48 (10H, m), 1.81 (2H, quin., J = 6.9 Hz), 3.99 (2H, t, J = 6.6 Hz), 6.78 (2H, d, J = 8.7 Hz), 7.34 (1H, t, J = 8.2 Hz), 7.81 (2H, d, J = 8.6 Hz), 8.10 (2H, d, J = 8.6 Hz).

***S*-(2-Fluoro-4-octyloxyphenyl) 4-Nitrothiobenzoate (2j):** ^{1}H NMR δ 0.90 (3H, t, J = 6.3 Hz), 1.30–1.55 (10H, m), 1.79 (2H, quin., J = 6.8 Hz), 3.99 (2H, t, J = 6.5 Hz), 6.78 (2H, d, J = 8.8 Hz), 7.35 (1H, t, J = 7.7 Hz), 8.20 (2H, d, J = 8.9 Hz), 8.34 (2H, d, J = 8.9 Hz).

***S*-(2-Chloro-4-octyloxyphenyl) 4-Butoxythiobenzoate (3a):** ^{1}H NMR δ 0.89 (3H, t, J = 6.6 Hz), 0.98 (3H, t, J = 7.0 Hz), 1.29–1.54 (12H, m), 1.74–1.86 (4H, m), 3.97 (2H, t, J = 6.6 Hz), 4.03 (2H, t, J = 6.6 Hz), 6.86 (1H, dd, J = 8.9, 2.6 Hz), 6.93 (2H, d, J = 8.9 Hz), 7.09 (1H, d, J = 2.6 Hz), 7.44 (1H, d, J = 8.9 Hz), 8.00 (2H, d, J = 8.8 Hz).

***S*-(2-Chloro-4-octyloxyphenyl) 4-Octyloxythiobenzoate (3b):** ^{1}H NMR δ 0.90 (6H, t, J = 6.6 Hz), 1.29–1.49 (20H, m), 1.72–1.86 (4H, m), 3.97 (2H, t, J = 6.6 Hz), 4.02 (2H, t, J = 6.6 Hz), 6.86 (1H, dd, J = 8.9, 2.6 Hz), 6.93 (2H, d, J = 8.8 Hz), 7.09 (1H, d, J = 2.6 Hz), 7.44 (1H, d, J = 8.9 Hz), 8.00 (2H, d, J = 8.8 Hz).

***S*-(2-Bromo-4-octyloxyphenyl) 4-Butoxythiobenzoate (4a):** ^{1}H NMR δ 0.89 (3H, t, J = 6.6 Hz), 0.98 (3H, t, J = 7.1 Hz), 1.29–1.57 (12H, m), 1.74–1.86 (4H, m), 3.97 (2H, t, J = 6.6 Hz), 4.03 (2H, t, J = 6.6 Hz), 6.90 (1H, dd, J = 8.8, 2.6 Hz), 6.95 (2H, d, J = 8.9 Hz), 7.27 (1H, d, J = 2.6 Hz), 7.47 (1H, d, J = 8.8 Hz), and 8.00 (2H, d, J = 8.9 Hz).

***S*-(2-Bromo-4-octyloxyphenyl) 4-Octyloxythiobenzoate (4b):** ^{1}H NMR δ 0.90 (6H, t, J = 6.6 Hz), 1.29–1.50 (20H, m), 1.74–1.86 (4H, m), 3.97 (2H, t, J = 6.6 Hz), 4.04 (2H, t, J = 6.6 Hz), 6.90 (1H, dd, J = 8.8, 2.6 Hz), 6.95 (2H, d, J = 8.9 Hz), 7.27 (1H, d, J = 2.6 Hz), 7.47 (1H, d, J = 8.9 Hz), 8.00 (2H, d, J = 8.9 Hz).

S-(2-Methyl-4-octyloxyphenyl) 4-Butoxythiobenzoate (5a): ^{1}H NMR δ 0.89 (3H, t, J = 6.6 Hz), 0.98 (3H, t, J = 6.6 Hz), 1.29–1.49 (12H, m), 1.74–1.84 (4H, m), 3.97 (2H, t, J = 6.6 Hz), 4.04 (2H, t, J = 6.6 Hz), 6.76 (1H, dd, J = 8.9, 2.6 Hz), 6.89 (1H, d, J = 2.6 Hz), 6.93 (2H, d, J = 8.8 Hz), 7.34 (1H, d, J = 8.9 Hz), 8.01 (2H, d, J = 8.8 Hz).

S-(2-Methyl-4-octyloxyphenyl) 4-Octyloxythiobenzoate (5b): ^{1}H NMR δ 0.90 (6H, t, J = 6.6 Hz), 1.29–1.47 (20H, m), 1.74–1.84 (4H, m), 2.34 (3H, s), 3.95 (2H, t, J = 6.6 Hz), 4.03 (2H, t, J = 6.6 Hz), 6.76 (1H, dd, J = 8.9, 2.6 Hz), 6.89 (1H, d, J = 2.6 Hz), 6.93 (2H, d, J = 8.8 Hz), 7.34 (1H, d, J = 8.9 Hz), 8.01 (2H, d, J = 8.8 Hz).

Results and Discussion

Syntheses. 4-Alkoxybenzenethiols have been prepared through several steps from phenols.[2] These synthetic methods are not necessarily convenient for the preparation of substituted benzenethiols, since the scheme involves drastic reaction conditions. Therefore, we attempted to prepare 4-alkoxy-2-X-benzenethiols according to the scheme in Fig. 2. Usually, the thiocyanation of phenol has been achieved by the reaction of chlorine and lead(II) thiocyanate.[12]

We found that the reaction of 3-substituted (X) phenols with *N*-chlorosuccinimide and ammonium thiocyanate gives 3-X-4-thiocyanatophenols. Under such conditions, thiocyanation selectively occurs only at the 4 position of the phenols. The thiocyanation appears to be sensitive to the electrostatic nature of the substituents, X. That is, an electron-donating substituent, such as a methyl group gives a better yield than the electron-withdrawing ones, such as halogens.

The alkylation of phenol is usually achieved by Williamson synthesis with alkyl halides under the presence of anhydrous potassium carbonate. In the cases of 3-X-4-thiocyanatophe-

Table 1. Thermal Properties for Compounds **1–5**

Compounds				Transition temperatures /°C					Latent heats /kJ mol^{-1}	
No	X	R	R′	C		N		I	C–N	N–I
1a[*1]	H	C_2H_5O	C_8H_{17}	•	81	•	107	•		
1b	H	C_4H_9O	C_8H_{17}	•	60	•	105	•	40.1	1.7
1c	H	$C_6H_{13}O$	C_8H_{17}	•	58	•	105	•	35.4	1.7
1d	H	$C_8H_{17}O$	C_8H_{17}	•	59[*2]	•	102	•	40.5	2.6
1e	H	$C_{10}H_{21}O$	C_8H_{17}	•	64[*3]	•	99	•		
2a	F	C_2H_5O	C_6H_{13}	•	78	•	79	•	45.2	1.7
2b	F	$C_6H_{13}O$	C_6H_{13}	•	57	•	74	•	38.0	1.7
2c	F	NC	C_6H_{13}	•	101	(•	74)	•	36.3	1.0
2d	F	C_2H_5O	C_8H_{17}	•	78	(•	75)	•	47.7	1.7
2e	F	C_4H_9O	C_8H_{17}	•	48	•	72	•	43.1	1.6
2f	F	$C_6H_{13}O$	C_8H_{17}	•	42	•	72	•	32.7	1.6
2g	F	$C_8H_{17}O$	C_8H_{17}	•	44	•	74	•	44.6	1.9
2h	F	$C_{10}H_{21}O$	C_8H_{17}	•	62	•	73	•	45.6	2.0
2i	F	NC	C_8H_{17}	•	79	(•	72)	•	40.4	0.9
2j	F	O_2N	C_8H_{17}	•	71	—		•	35.1	—
3a	Cl	C_4H_9O	C_8H_{17}	•	55	(•	40)	•	43.2	2.2
3b	Cl	$C_8H_{17}O$	C_8H_{17}	•	43	•	44	•	50.6	2.6
4a	Br	C_4H_9O	C_8H_{17}	•	53	(•	29)	•	42.8	1.8
4b	Br	$C_8H_{17}O$	C_8H_{17}	•	34	•	35	•	46.2	2.0
5a	CH_3	C_4H_9O	C_8H_{17}	•	53	(•	49)	•	42.0	1.7
5b	CH_3	$C_8H_{17}O$	C_8H_{17}	•	29	•	49	•	39.9	1.8

C, N, and I indicate crystal, nematic, and isotropic liquid phases, respectively. Values in parentheses indicate a monotropic transition temperature.

[*1] Transition temperatures of **1a** were cited from Ref. 5.

[*2] A transition at 59 °C is a C–Sm C transition. An Sm C–N transition was observed at 68.2 °C ($\Delta H = 0.8$ kJ mol^{-1}).

[*3] Transition temperatures of **1e** were cited from Ref. 2. Our observation indicated that a transition at 59 °C is a C–Smectic C transition, and this compound undergoes an Sm C–N transition at 74 °C.

nols, a similar reaction causes of decomposition of the thiocyanato group. Because a ^{1}H NMR examination of the crude products suggested the presence of two alkyl groups, we assumed that the decomposition of the thiocyanato group and S-alkylation occurred simultaneously under the conditions.

In this work, therefore, alkylation of the hydroxy group was achieved by the Mitsunobu reaction,[13] and the objective materials were obtained by mild conditions. For the reaction, the synthetic yield seems to be almost independent of the electrostatic nature of the substituent.

The thiocyanatobenzene compounds were quantitatively converted to the corresponding benzenethiols by the reaction of $LiAlH_4$. We confirmed that this reaction also occurs by $NaBH_4$. Because the benzenethiols were less stable under an atmospheric condition, these were reacted with the benzoyl chloride without further purification.

Thermal Properties. *S*-Phenyl thiobenzoates having alkyl and alkoxy groups at both terminal positions are reported to exhibit nematic (N), smectic A and C phases (Sm A and C, respectively), and for some members also to exhibit smectic phases having a higher order of the molecular arrangement.[2] Compounds **1d** and **1e** also show an Sm C phase having a broken focal conic fan and schlieren textures under homogeneous and homeotropic alignments, respectively. Most of the materials having a lateral substituent show an N phase exhibiting a usual schlieren texture. The transition temperatures and latent heats are summarized in Table 1. The average N–I transition temperature for the hydrogen compounds (**1a**–**1e**) is 104 °C, which is slightly higher than that for the corresponding ester compounds (91 °C).[14] The introduction of a lateral fluorine atom reduces the N–I transition temperature, 73 °C on average for **2d**–**2h**. Generally, the effect of the lateral substituent on the mesomorphic properties has been interpreted in both geometrical and electrostatic terms. The substitution of a fluorine atom at the lateral position, for example, slightly increases the breadth around the substituent, since the C–F bond (1.36 Å) is longer than the C–H one (1.10 Å), and the van der Waals radius for fluorine is larger than hydrogen. The effective order for the N–I transition temperature decreases by the order of H > F > Cl = CH_3 > Br. The N–I transition temperatures for some members are plotted against the breadths calculated by MOPAC in Fig. 3. The breadths are the distance between the longitudinal axis of the phenyl ring and the center of the atom or the group. The N–I transition temperatures for *S*-(4-pentylphenyl) 4-decyloxy-2-X-thiobenzoates (X = H, F, or Cl) are also plotted in the Figure.[15] Both compounds show a similar feature. The features quite resemble that for 4-octyloxy-3-X-biphenyl-4′-carboxylic acids (X = H, F, Cl, Br, I, CH_3, and NO_2).[16]

Generally, the reduction of the N–I transition temperature

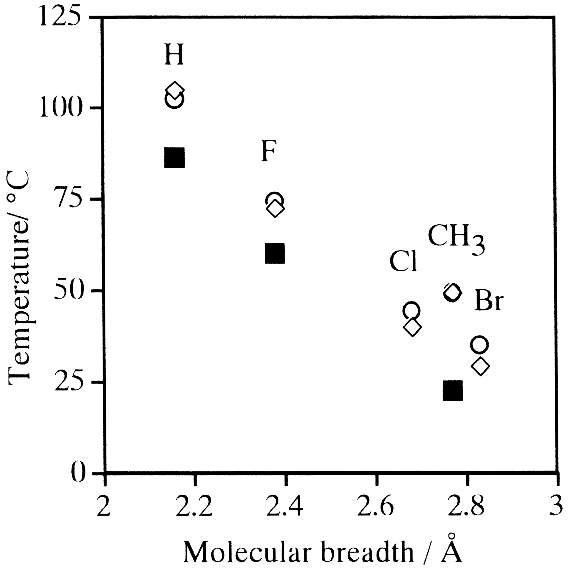


Fig. 3. Plots of N–I transition temperatures vs molecular breadth*1 around the substituent estimated by a semi-empirical molecular orbital calculation (see text). (◇) *S*-(4-butoxy-2-X-phenyl) 4-octyloxythiobenzoates (X = H, F, Cl, Br, CH_3), (○) *S*-(4-octyloxy-2-X-phenyl) 4-octyloxythiobenzoates (X = H, F, Cl, Br, CH_3), (■) *S*-(4-pentylphenyl) 4-decyloxy-2-X-thiobenzoates (X = H, F, Cl).
*1 see text.

has been interpreted in terms of an increased molecular breadth around the substituent. In the present compounds the increase in the torsional angle between two phenyl rings due to a steric hindrance between the substituent and the carbonyl oxygen of the benzoate ring must be taken into consideration.

For the effect of lateral substituents on the mesomorphic properties, the relative importance of the dipole has also been pointed out.[17] In 6-alkoxy-5-X-naphthalene-2-carboxylic acid systems, for example, the substituents, such as halogens, are known to enhance the N–I transition temperature.[18,19] For the phenomena, it has been postulated that the increased dipole arising from the substituent causes an enhancement of the N–I transition temperature.[17] In the present cases, the change in the molecular geometry rather than the dipole is responsible for the reduction of the N–I transition temperature.

Conclusion

A new synthetic pathway of 4-alkoxy-2-X-benzenethiols was established; the materials incorporating this moiety show LC properties, and the lateral substituent slightly lowers the N–I transition temperature. These compounds are expected to be useful for LC devices.

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