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Thermodynamic and Mesomorphic Properties of Some Phenylthiolbenzoate Derivatives

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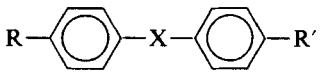
A homologous series of 4-*n*-alkylphenyl 4-*n*-alkoxythiolbenzoate and 4-*n*-alkoxyphenyl 4-*n*-alkoxythiolbenzoate were synthesized and their liquid crystal transition temperatures were determined. Among 26 compounds which synthesized, 17 are enantiotropic liquid crystals and 9 are monotropic. The nematic-to-isotropic transition temperatures decrease gradually with an increasing alkyl chain length of homologous series and exhibit an odd-even effect. The thermodynamic parameters of the mesophase transition were investigated by differential scanning calorimetry. The entropies of the nematic-to-isotropic transitions show an odd-even effect, and exhibit the erratic dependence on alkyl chain length of homologous series. The nematic-to-isotropic transition entropies of each homologous series remain nearly constant, being between 1.6 and 2.9 J/mole K.

INTRODUCTION

Liquid crystals have the mobility of liquids and the optical properties of solids owing to an orderness in the molecular arrangement. Most of the mesomorphic substances forming liquid crystals fall into the general formulas represented as



X: —CH=CH—, —N=N—, —N=N(→O)—, —C(=O)—O—

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where X represents a central linkage group, which should enhance the rigidity and linearity of the molecules associated with the *p*-substituted benzene rings.

The mesophase transition temperatures for a homologous series of liquid crystal compounds change with the central linkage group and *p*-substituted groups.[1–4] Van Meter and Klanderman[4] reported that the benzoate ester linkage provides liquid crystals which are chemically more stable than Schiff bases.

Recently, syntheses of low melting thermotropic liquid crystals have currently aroused considerable interest because of their potential uses in display devices. Compounds available for such uses should satisfy some basic requirements; they should possess a suitable mesomorphic range, and should be chemically, photochemically and electrochemically stable, colorless and safe to handle. Gray *et al.*[7] studied substituted biphenyl mesogens. Van der Veen[8] reported low melting azo and azoxy compounds, and Dave, Vora *et al.*[9] reported low melting *p*-substituted phenylbenzoates. Rheinbolt and Cilento[5] reported that 4-methylphenyl 4-methoxythiolbenzoate is an enantiotropic liquid crystal; this crystal melts to an anisotropic liquid at 65.5°C and to an isotropic liquid at 73.6°C.

In this investigation, we prepared a series of homologous phenylthiolbenzoate esters with *p*-substituents such as alkyl and alkoxy groups, and then studied the thermodynamic parameters of the pertinent mesophase transition by differential scanning calorimetry. The differential scanning calorimetry provides a relatively rapid means for measuring the energetics of the mesophase transitions for a large number of compounds. The enthalpy and entropy changes obtained in this way serve as a measure of the relative stability.[3]

EXPERIMENTAL

1 Syntheses

The phenylthiolbenzoate esters were prepared by the synthetic route depicted in Figure 1. The products were purified by recrystallization from suitable solvents. All of the new compounds had satisfactory spectral properties and elemental analysis data. Nuclear magnetic resonance spectra were run on a Hitach–Perkin Elmer NMR Spectrometer. Infrared spectra were recorded on a Hitachi Infrared Spectrometer.

Typical synthetic procedures are as follows;

4-n-Hexyloxybenzoyl chloride was synthesized from 4-*n*-hexyloxybenzoic acid and thionyl chloride according to the procedure of Kolosy and Claesen.[11] Yields ranged between 80–90%.

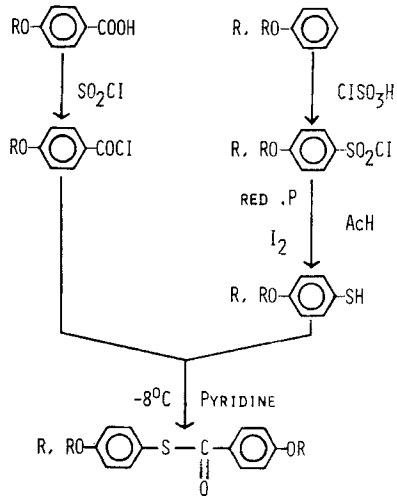


FIGURE 1 Reaction sequence used to synthesize the phenylthiolbenzoate ester.

4-Methoxybenzenesulfonyl chloride was prepared from the 4-methoxybenzene by treatment with chlorosulfonic acid in chloroform according to a procedure described elsewhere.[12] The product was purified by recrystallization from boiling hexane to give colorless crystals, mp. 41–42°C. Yields ranged between 70–80%.

4-Methoxythiophenol was prepared according to the procedure of Wagner.[13] A mixture of 75 g of red phosphorous 3.6 g of iodine and 60 g of acetic acid was heated to reflux in a round bottomed flask equipped with a magnetic stirrer, a heated dropping funnel and a reflux condenser with a calcium chloride drying tube. When the mixture began to boil, 20.7 g (0.1 mole) of 4-methoxybenzenesulfonyl chloride was carefully added dropwise and heated. After the mixture was boiled and iodine gas began to vaporize, the heating bath was removed, and 186.0 g (0.9 mole) of 4-methoxybenzenesulfonyl chloride was carefully added. When the addition was complete, the mixture was refluxed for 2–3 hours until the iodine gas was completely removed. Then, 60 ml of water was carefully added to the mixture, and heated to reflux for 1 hour. The mixture was steam-distilled. The product was transferred to a separatory funnel, and the organic layer was carefully separated from the aqueous layer, which was extracted with chloroform. The combined organic phase was dried over anhydrous sodium sulfate, filtered, and evaporated on a rotary evaporator. The residue was distilled in vacuo. Yield was in a range of 50–60%.

4-Methoxyphenyl 4-n-hexyloxythiolbenzoate was prepared according to the procedure of Miyaki.[14] A 50 ml three-necked flask equipped with a

mechanical stirrer, a dropping funnel and a thermometer was charged with 4.8 g (0.02 mole) of 4-*n*-hexyloxybenzoyl chloride, and 34 ml of pyridine. The mixture was stirred vigorously while the flask was partially immersed in an ice-salt bath to keep an internal temperature at −8°C. 4-Methoxythiophenol (2.8 g, 0.02 mole) was then added dropwise with stirring as rapidly as possible while keeping the reaction temperature at −5°C. When all of the prescribed amount of 4-methoxythiophenol had been added, the ice-salt bath was removed, and then the reaction mixture was heated at 50°C with continuous stirring. The reaction mixture was poured onto chopped ice, and then the crude white product was obtained by filtration. The product was recrystallized several times from ethanol until a constant melting point was obtained. Yield was in a range of 80–90%. Calculated for $C_{20}H_{24}O_3S$: C, 69.74; H, 7.02; S, 9.31%. Found: C, 69.92; H, 7.29; S, 9.27%.

2 Determination of transition temperatures

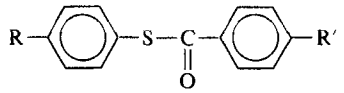
The mesophase were identified by standard techniques[6] using a Nikon polarizing microscope equipped with a heating stage. The mesophase transition temperatures were measured with both a Yamato melting point apparatus and a differential scanning calorimeter (Perkin-Elmer DSC-1B). In the former case, the mesophase transition temperature was measured in open capillary tubes. In the latter case, 4–7 mg of specimen was necessary for each run and was sealed in an aluminum cup, while the heating and cooling rates were 4°C/min. The heats of transition were obtained by comparing the peak areas by graphic integration with those of 99.999% pure indium supplied by the Perkin-Elmer Corp. The heat of fusion of indium is well established as 28.45 J/g. The instrument constant over a temperature range of 35–200°C was determined by calibrating with high purity NBS benzoic acid, benzyl and indium sample.

RESULTS AND DISCUSSION

The homologous series of phenylthiolbenzoate esters, 1 through 26, listed in Table I was prepared according to the synthetic route shown in Figure 1. The purified phenylthiolbenzoate esters were white crystalline solids at room temperature. Elemental analysis data for all 26 mesogens were within acceptable limits. All of the phenylthiolbenzoate esters exhibit strong C=O stretching absorption peaks at 1670 cm^{-1} in infrared spectra. The carbonyl stretching absorption band of thiónyl ester is observed in a lower frequency range than that of benzoate ester. This is well explained by Nyquist and

TABLE I

Measured transition temperatures and derived enthalpies entropies of phenylthiolbenzoate derivatives



No.	R	R′	Trans. Type	Trans. Temp.	ΔH kJ/mole	ΔS J/mole K
1	CH_3O	C_2H_5O	C–N	112.0	26.11	67.98
			N–I	127.0	0.82	2.05
2	CH_3O	C_3H_7O	C–N	88.0	21.51	61.62
			N–I	99.5	0.57	1.52
3	CH_3O	C_4H_9O	C–N	73.4	26.04	75.14
			N–I	105.5	0.62	1.66
4	CH_3O	$C_5H_{11}O$	C–N	80.5	33.45	94.56
			N–I	98.0	0.61	1.66
5	CH_3O	$C_6H_{13}O$	C–N	63.5	22.72	67.48
			N–I	99.0	0.73	1.97
6	CH_3O	$C_7H_{15}O$	C–N	64.0	16.91	50.11
			N–I	94.5	0.59	1.61
7	CH_3O	$C_8H_{17}O$	C–N	60.5	22.51	67.48
			N–I	97.5	0.68	1.84
8	C_2H_5O	C_4H_9O	C–N	77.5	36.43	120.64
			N–I	120.5	1.289	3.28
9	C_2H_5O	$C_5H_{11}O$	C–N	84.5	25.19	70.41
			N–I	110.0	0.90	2.36
10	C_2H_5O	$C_6H_{13}O$	C–N	86.0	28.10	78.15
			N–I	111.0	1.210	3.16
11	C_2H_5O	$C_7H_{15}O$	C–N	91.5	29.33	80.45
			N–I	106.0	0.82	2.16
12	C_2H_5O	$C_8H_{17}O$	C–N	80.5	28.66	81.04
			N–I	106.5	1.188	3.14
13	CH_3	C_2H_5O	C–I	99.5	23.11	61.99
			N–I	95.0	1.055	2.87
14	CH_3	C_3H_7O	C–I	96.0	30.71	83.18
			N–I	65.5	0.52	1.54
15	CH_3	C_4H_9O	C–I	80.0	35.27	99.88
			N–I	78.0	0.81	2.31
16	CH_3	$C_5H_{11}O$	C–I	75.5	29.07	83.39
			N–I	70.0	0.58	1.68
17	CH_3	$C_6H_{13}O$	C–N	62.0	24.29	72.46
			N–I	77.5	0.86	2.47
18	CH_3	$C_7H_{15}O$	C–N	60.5	29.52	88.49
			N–I	71.5	0.54	1.59
19	CH_3	$C_8H_{17}O$	C–N	57.0	29.53	89.45
			N–I	73.0	0.90	2.60
20	C_2H_5	C_2H_5O	C–N	71.0	21.83	63.42
			N–I	76.5	0.46	1.34
21	C_2H_5	C_3H_7O	C–I	70.5	26.18	76.19
			N–I	54.5	0.43	1.31
22	C_2H_5	C_4H_9O	C–I	83.0	31.69	89.09
			N–I	68.0	0.43	1.25
23	C_2H_5	$C_5H_{11}O$	C–I	67.0	27.22	80.04
			N–I	61.0	0.31	0.93
24	C_2H_5	$C_6H_{13}O$	C–I	69.5	21.11	93.93
			N–I	66.0	0.51	1.51
25	C_2H_5	$C_7H_{15}O$	C–I	70.0	32.37	94.35
			N–I	65.0	0.56	1.67
26	C_2H_5	$C_8H_{17}O$	C–N	63.5	28.42	84.43
			N–I	71.0	0.62	1.79

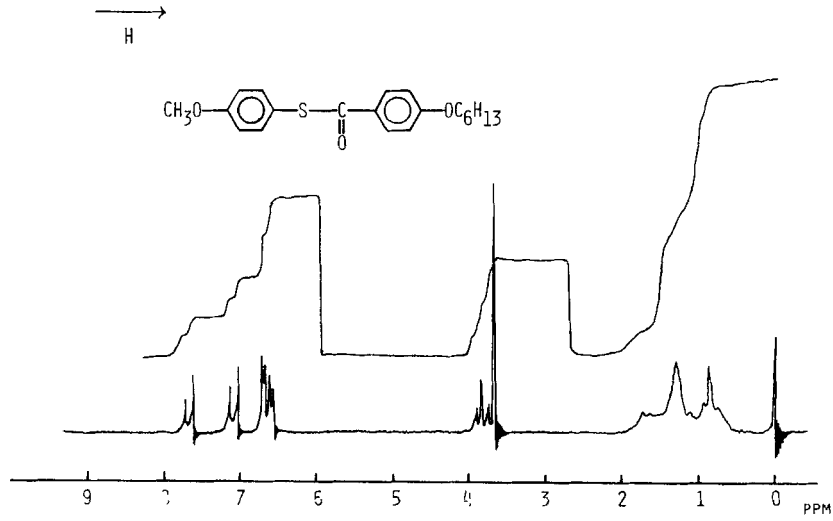


FIGURE 2 NMR spectrum of 4-methoxyphenyl 4-*n*-hexyloxythiolbenzoate.

co-worker[10] to have resulted from the inductive and resonance effect. The nuclear magnetic resonance (NMR) spectrum of 4-methoxyphenyl 4-*n*-hexyloxythiolbenzoate is shown in Figure 2. The aromatic proton resonances are in the region between 6.65 and 7.71 ppm; 6.65 ppm for 4-methoxyphenyl protons and 7.05 and 7.71 ppm for 4-*n*-hexyloxythiolbenzoate protons. This is virtually the same for the entire series of phenylthiolbenzoate esters investigated. The methoxy group is a sharp singlet at 3.65 ppm, while the hexyloxy chain, which includes a triplet at 3.68 ppm, comprises the remainder of the spectrum.

These phenylthiolbenzoate esters exhibit liquid crystal properties. Among 26 compounds prepared in this work, 17 are enantiotropic liquid crystals and 9 are monotropic. The phase transition temperatures and thermodynamic properties of these compounds are recorded in Table I.

In order to get a better understanding of the effects of molecular structure on the mesomorphic behavior, the mesophase transition temperatures were plotted as a function of carbon number of the alkyl chain in the homologous series. The mesomorphic character as a function of chain length has been encountered frequently, although the precise demarcations between the groupings are somewhat variable. Figures 3–6 show the changes in mesophase transition temperatures with an increase in the number of carbon atoms in the alkyl chain at a terminal position of the molecule. The mesomorphic thermal properties of *p*-substituted phenylthiolbenzoate esters agree well with the trends reported by other workers[6,15] for homologous series of other liquid crystalline compounds.

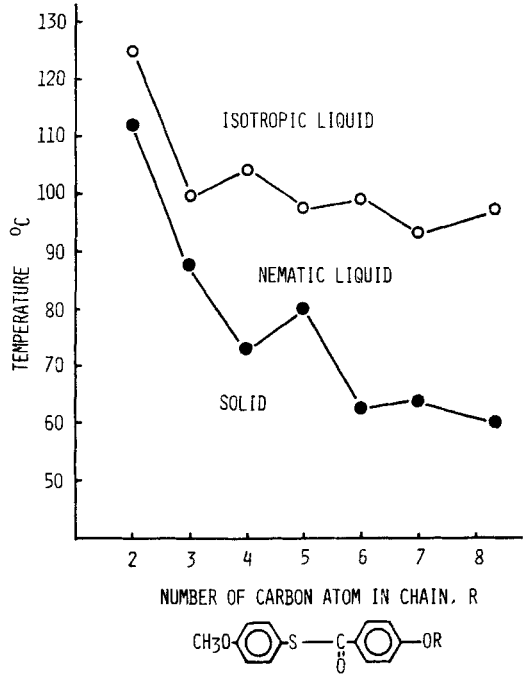


FIGURE 3 Phase transition plot for the 4-methoxyphenyl 4-*n*-alkoxythiolbenzoates: ●; Crystal–Nematic, ○; Nematic–Isotropic.

As shown in the Figures 3–5, the nematic-to-isotropic (N–I) transition temperatures decrease gradually with an increasing carbon chain length and exhibit the odd-even effect. It has been well established that the nematic-to-isotropic transition temperatures *versus* the length of alkyl chain usually form smooth curves for even and odd numbers of a homologous series,[5] although the shapes of curves vary substantially from series to series.[4,6,16]

In the present case, it is difficult to explain the detailed nature of these liquid crystalline compounds, for the reason that the series are quite short and that some involve monotropic transitions. However, the concept of lateral *versus* terminal cohesive forces is qualitatively useful for interpretation of the mesophase transition. In general, the molecules in the nematic states are held at their parallel orientation by residual terminal and lateral interactions between the molecules, and the trends in the mesophase transition properties of homologous series could be explained in terms of a balance between the lateral and terminal cohesive forces.[6] As seen from Figures 3–5, the decreasing trend of the N–I transition temperatures with an increasing alkyl chain length is due to a decrease in strength of terminal intermolecular

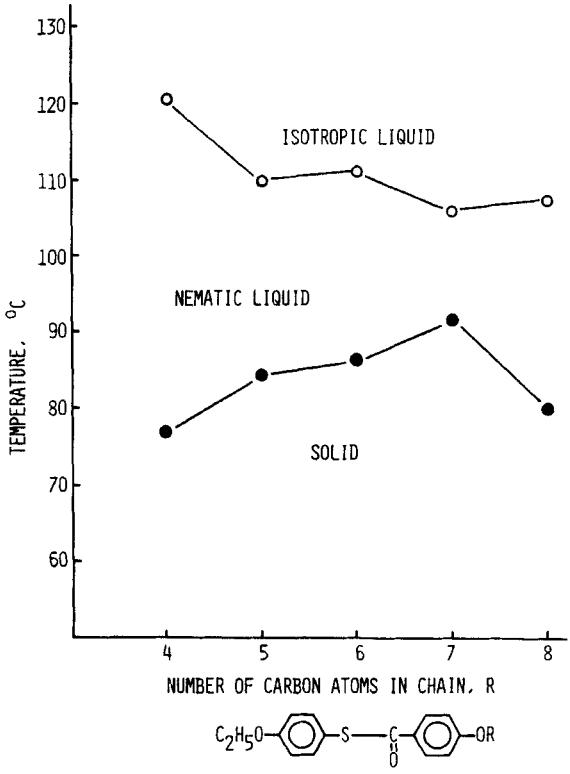


FIGURE 4 Phase transition plot for the 4-ethoxyphenyl 4-*n*-alkoxythiolbenzoates: ●; Crystal–Nematic, ○; Nematic–Isotropic.

cohesive forces. It may be noted that other series show a similar trend in their transition–chain length plots.[17]

Conversely, Figure 6 exhibits a tendency in which the N–I transition temperatures as the alkyl chain length increases, and a typical odd-even effect. This behavior is generally found for the series having low transition temperatures, which could be classified into three types. The first type includes compounds such as substituted N(4-*n*-alkoxybenzylidene)-4-aminobiphenyls,[6] where the lateral substituents prevent a close packing of molecules in the mesophase. This behavior is explained by the decreasing ratio of lateral to terminal interactions owing to the steric effect.[6] The molecules of the second type possess a terminal carbonyl group conjugated with an aromatic system.[18,19] Castellano and McCaffrey[18] suggested that the acetyl group produces strong terminal attraction and results in a low ratio of lateral to terminal cohesions. The third type of compounds includes N(4-*n*-alkoxybenzylidene)-4-alkylanilines. Dietrich and Steiger[20] attributed the

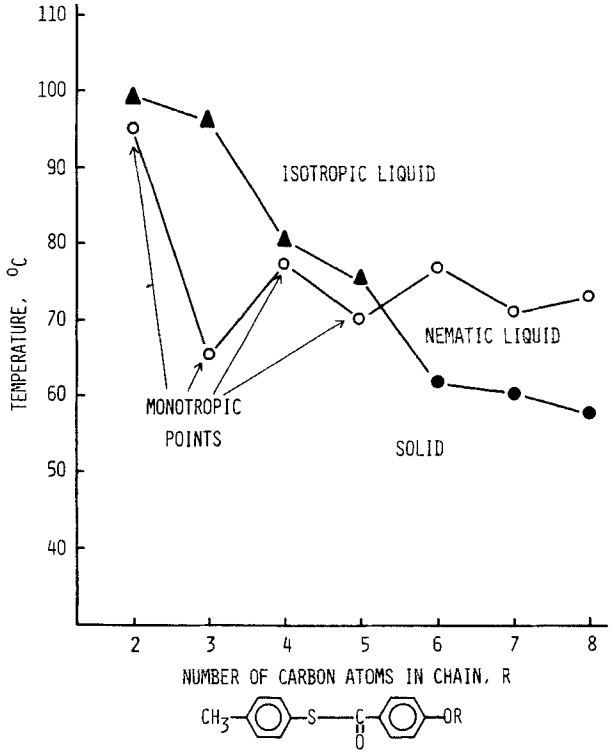


FIGURE 5 Phase transition plot for the 4-methylphenyl 4-*n*-alkoxythiolbenzoates: ●; Crystal–Nematic, ▲; Crystal–Isotropic, ○; Nematic–Isotropic.

behavior of these compounds to a weak intermolecular cohesive force. We speculate, in accordance with earlier suggestions, that the increasing trend of N–I transition temperatures with an increasing alkyl chain length is due to the decrease in the ratio of lateral to terminal interaction, because the dipolar interaction associated with the alkoxy group remains unchanged, while the overall polarizability and therefore the terminal interaction increase, as the length of alkoxy group increases.

The smectic mesophase was not found in any numbers of the homologous series studied in this work. This implies that the lack of dipolar interaction operating across the long axis of molecule at the central linkage group does not provide the molecules with lateral cohesive forces enough to induce smectic formation.

The second distinguishing feature noticeable in Figures 3–6 is a regular alternation from even to odd values of the carbon atom of alkyl chain in N–I transition temperatures. This feature has been considered by Gray[6] and other worker[10] in terms of the analyses of the conformation of terminal

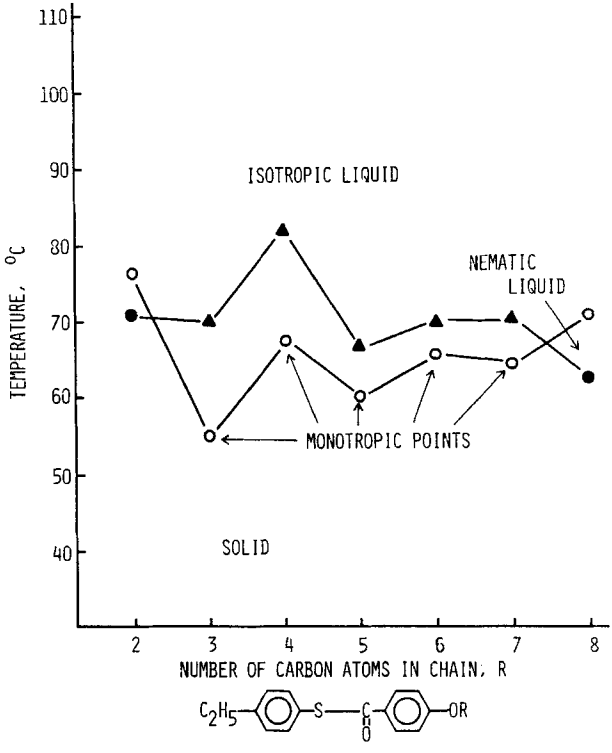


FIGURE 6 Phase transition plot for the 4-ethylphenyl 4-*n*-alkoxythiolbenzoates: ●; Crystal–Nematic, ▲; Crystal–Isotropic, ○; Nematic–Isotropic.

substituents and the anisotropy of polarizability of molecules. Each successive methylene unit makes a different contribution to the axial polarizability dependent upon whether the extension in chain length is odd or even. The axial polarizability on changing from an odd to an even carbon chain in the alkoxy series increases more extensively than that on changing from even to odd.[6] This is supported by the fact that the N–I transition temperature curve for the homologue containing even numbers of carbon atoms lies above a curve of the N–I transition temperature for the odd members of the series.

The amplitude of the alternation of the N–I transition temperatures always decreases as the alkyl chain grows longer. This can be explained in terms of the change in sensitivities of the terminal attraction and the effect of different molecular conformations in the nematic mesophase.[4] The sensitivity of the terminal attraction to the spatial distribution of the terminal methyl group is expected to grow less and, therefore, the amplitude of the

alternation always decreases, with an increasing alkyl chain length of the homologous series.

In this homologous series, the crystal-to-isotropic (C–I) and crystal-to-nematic (C–N) transition temperatures do not exhibit a regular pattern *versus* the length of the alkyl chain. It is well known that the melting behavior is closely related to the crystal structure but, only in a secondary way, to the molecular structure. Also, Ubbelohde[21] emphasized a difficulty of predicting melting points based on the similarity of molecular structures. The random nature of the C–N transition temperatures and the C–I transition temperatures for the homologous series could be attributed to wide varieties of possible crystal structures. Therefore, X-ray diffraction studies[22] on the liquid crystalline compounds would help to clarify this difference.

The N–I transition entropies are shown graphically in Figures 7 and 8. The N–I transition entropies for 4-ethylphenyl 4-*n*-alkoxythiolbenzoates do not show any noticeable trend when they are plotted against the alkyl

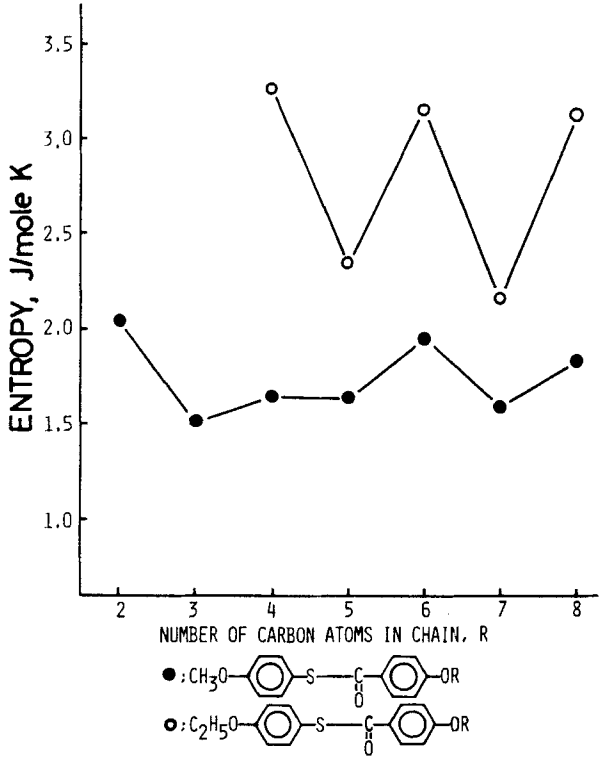


FIGURE 7 Entropy–chain length relationships for the 4-methoxyphenyl 4-*n*-alkoxythiolbenzoate and 4-ethoxyphenyl 4-*n*-alkoxythiolbenzoate.

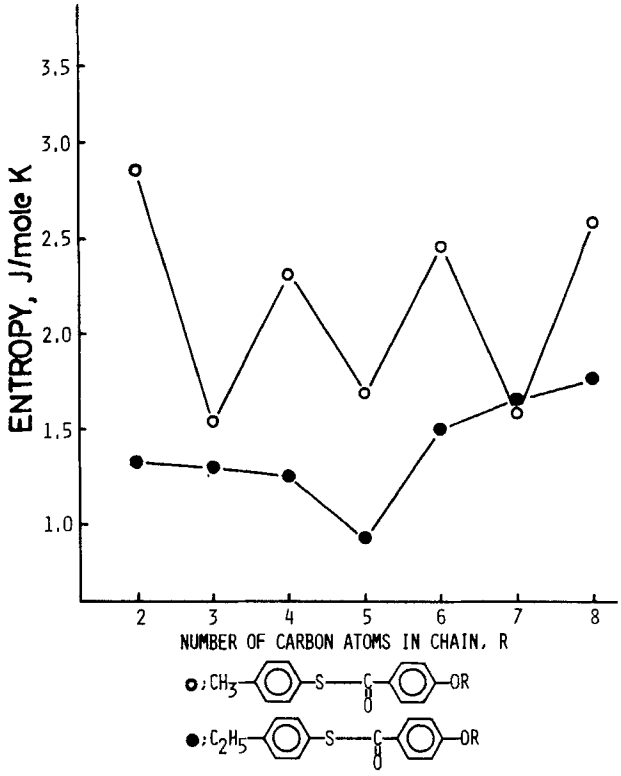


FIGURE 8 Entropy–chain length relationship for the 4-methylphenyl 4-*n*-alkoxythiolbenzoate and 4-ethylphenyl 4-*n*-alkoxythiolbenzoate.

chain length as illustrated in Figure 8. The N–I transition entropies of the other homologous series, as seen in Figures 7–8, exhibit usual erratic dependences on alkyl chain length, and show an odd-even effect, where the branch for even chain lengths carries higher values. Similar behaviors were reported for *p-p'*-dialkoxyazoxybenzenes by Arnold[23] and for the cholesteryl ω-phenylalkanoates by Ennulat.[24] The odd-even effect could be ascribed to a difference in molecular conformations, because the extension of the alkyl chain by a methylene unit does not appreciably cause the change in polarizability and size of molecules.[24]

The values of the N–I transition entropy of each homologous series remain nearly constant, being in a range between 1.6 and 2.9 J/mole K. This indicates that the energy difference between alkyl chain conformational isomers and the potential barrier to internal rotation change very little between the nematic and isotropic states,[3] and also reflects that the orderliness involved in the nematic state depends scarcely on the alkyl chain length.

CONCLUSION

The results of the present investigation lead us to the following conclusions. All of the phenylthiolbenzoate esters prepared in this work form nematic mesophases on either heating or cooling. In this series, the relationship between the N–I transition temperature and the alkyl chain length is similar to those of the other liquid crystalline materials.[4,13,19] The smectic mesophase for the phenylthiolbenzoate esters was not found over the range covered. This is due to a lack of a lateral cohesive force at the central linkage of the molecule. The value of the N–I transition entropy of each homologous series remains nearly constant like other homologous series of liquid crystals. This suggests that the orderliness involved in the nematic mesophase depends scarecely on alkyl chain length.

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