Ester Linkages in the Nematic Phase: a Thermodynamic Study [1]

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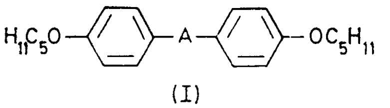
A study of the ester linkage in nematic liquid crystals has been made in which the criteria for intermolecular binding and ordering are the enthalpy ($\Delta H_{N\rightarrow I}$) and entropy ($\Delta S_{N\rightarrow I}$), respectively, of the nematic–isotropic transition. The data were obtained by calorimetric differential thermal analysis. The first objective was to examine analogous σ-bonded oxygen and σ-bonded sulphur esters. The thiolesters had consistently higher nematic–isotropic transition temperatures ($T_{N\rightarrow I}$) and usually higher transition heats and entropies. These results are explained in terms of geometrical effects of sulphur on liquid crystalline lattice interactions. The second study involved the position of the ester carbonyl in two sets of mesomorphs. These compounds are of the type R–COO–S and R–OOC–S. Those compounds in which conjugation of the terminal methoxy-substituents with the ester carbonyls is possible show increased $\Delta H_{N\rightarrow I}$ and $\Delta S_{N\rightarrow I}$ relative to the unconjugated analogues. Whether these thermodynamic properties are due to electronic or to geometrical effects is discussed. From the data and conclusions presented here for the nematic phase, some inferences can be drawn concerning earlier data obtained for cholesteric esters which were previously not well understood.

Many nematic liquid crystals consist of molecules in which benzene rings are linked by polar groups, these being of types which allow the linearity of the molecule to be perturbed as little as possible. Van Meter and Klanderman [2] reported a comparison of such central linkages, A, in compounds of type (I). The order for increasing thermal persistence of the mesophase for their series was found to be N=N→O > N=N > CH=N > O=C–O. These four central linkages are the ones most commonly used and the order agrees well with those reported by both Rondeau [3] and Young.[4] Recently Dewar and Riddle [5] have suggested that an important factor in such cases may be the width of the linking unit, the transition temperature being highest, other things being equal, for a linking unit which itself is of the same spatial size as the units being linked. Thus the transition temperatures for azoxy-compounds are higher than those of the corresponding azo-compounds.



(I)

Only recently have thiolesters been the subject of inquiry in liquid crystal investigations. Elser [6,7] and Ennulat [8] have studied the effect of σ-bonded sulphur in the ester linkage of steroidal compounds (cholesteric phase). Dewar and Riddle [5] have studied thiolesters (σ-bonded sulphur) in several nematic compounds. The results of these studies indicated that sulphur is quite often effective in raising the clearing points (compared to the oxygen analogues) of these compounds. Ennulat [8] has found, however, that thiolesters generally have

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[1] Taken in part from the Ph.D. dissertation of A. C. Griffin, University of Texas at Austin, 1975.

[2] J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liquid Cryst.*, 1973, **22**, 271.

[3] R. E. Rondeau, M. A. Berwick, R. N. Steppel, and M. P. Serve, *J. Amer. Chem. Soc.*, 1972, **94**, 1096.

[4] W. R. Young, I. Haller, and A. Aviram, *Mol. Cryst. Liquid Cryst.*, 1972, **15**, 311.

[5] M. J. S. Dewar and R. M. Riddle, *J. Amer. Chem. Soc.*, 1975, **97**, 6658.

[6] W. Elser, *Mol. Cryst. Liquid Cryst.*, 1969, **8**, 219.

[7] W. Elser, J. L. W. Pohlmann, and P. Boyd, *Mol. Cryst. Liquid Cryst.*, 1970, **11**, 279.

[8] R. D. Ennulat, *Mol. Cryst. Liquid Cryst.*, 1969, **8**, 247.

smaller heats of transition from the cholesteric phase to isotropic liquid than do the oxygen esters. Dewar and Riddle[5] suggested that the geometrical effects of sulphur substitution, *e.g.*, decreased C–S–C bond angle and increased C–S bond lengths, may be responsible for more favourable nematic arrangements, *e.g.*, relief of steric crowding and larger length : breadth ratio than those of the oxygen esters.

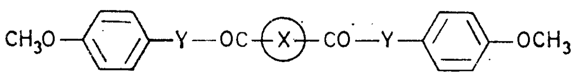
This paper reports a detailed study by differential thermal analysis (d.t.a.) of the thermodynamics of the nematic–isotropic transition for a number of esters and thiolesters. Our object was to compare the effectiveness of the ester and thiolester groups as linking groups in nematic mesophases and also to study the effect of inverting the ester linkage (R–COO–S→R–OOC–S).

EXPERIMENTAL

All m.p.s are corrected. They were determined using a temperature calibrated Stone differential thermal analyser model 202, with SH-11BR2 sample holder, platinel differential thermocouple, and aluminium sample containers. Heats of transition were obtained on the same instrument, calibrated for enthalpy measurements by the fusion thermograms of ultra-purity indium and lead reference standards. For calorimetric operation the samples were heated from ambient temperature to *ca.* 15° above the mesophase–isotropic temperature at a rate of 5° min^{-1}. An inert atmosphere (N_2) was used in the furnace. The reference against which the temperature of the sample was compared was reagent grade α-alumina which undergoes no transitions at or below the highest temperatures reached in this work. In order to include any thermal effects which are due to pretransition phenomena at temperatures immediately surrounding the transition temperature, the areas of peaks were obtained by integration (planimetry), the baseline having been extrapolated to the transition temperature from regions on both sides in which the heat capacity varies linearly with temperature.[9] In an effort to obtain more accurate values for the mesophase–isotropic enthalpy changes only enantiotropic liquid crystals were studied. This allowed the sensitivity of the instrument to be increased after the m.p. and before the clearing point. This increased sensitivity generates a larger area than would be otherwise seen for the endothermic mesophase–isotropic peak. From the enthalpy and temperature of the mesophase–isotropic transition the transition entropy was calculated from the relation $\Delta H = T\Delta S$.

TABLE 1

Thermodynamic properties of some thiolesters and analogous oxygen esters



No.	X	Y	$T^a_{C\to N}$/°C	$T^b_{N\to I}$/°C	$\Delta H^c_{N\to I}$/ kcal mol^{-1}	$\Delta S^d_{N\to I}$/ cal mol^{-1} K^{-1}
(1)	*p*-Phenylene[e]	S	216.7	320.2	0.356	0.599
(2)	*p*-Phenylene	O	210.6	287.6	0.232	0.414
(3)	Bicyclo[2.2.2]octane-1,4-diyl[f]	S	168.2	329.1	0.263	0.436
(4)	Bicyclo[2.2.2]octane-1,4-diyl	O	152.0	268.8	0.288	0.531
(5)	Cyclohexane-1,4-diyl	S	203.1	236.8	0.400	0.785
(6)	Cyclohexane-1,4-diyl	O	140.2	243.3	0.292	0.565
(7)	Thiophen-2,5-diyl	S	136.1	213.6	0.136	0.280
(8)	Thiophen-2,5-diyl	O				

[a] M.p. [b] N–I Transition temperature. [c] Heat of N–I transition. [d] Entropy of N–I transition. [e] Values of 210 and 311° have been reported.[5] [f] Values of 162 and >310° have been reported.[5]

The sample of bicyclo[2.2.2]octane-1,4-diyl bis-(*p*-methoxybenzoate) was provided by Dr. R. S. Goldberg. *p*-Phenylene bis-(*p*-methoxybenzoate) was supplied by Dr. J. P. Schroeder. Dr. R. M. Riddle provided samples of bis-(*p*-methoxyphenyl) terephthalate, *SS*-bis-(*p*-methoxyphenyl) dithioterephthalate, and *SS*-bis-(*p*-methoxyphenyl) bicyclo[2.2.2]octane-1,4-dithiocarboxylate. The other diacid chlorides and product diesters were prepared by the method of Riddle.[10] All compounds were recrystallized to give constant m.p. and dried under vacuum.

DISCUSSION

The role of σ-bonded sulphur in esters has been studied for steroidal (cholesteric) compounds.[6-8] It was found that the heat of transition to isotropic liquid ($\Delta H_{Ch\to I}$) was less for the thiolesters than for the analogous oxygen esters. The results reported here are the first thermodynamic data for nematic thiolesters. Table 1 shows our results for the nematic—isotropic (N–I) phase transitions of some thiolesters along with values for the analogous oxygen esters, for comparison.

With the exception of the bicyclo-octyl esters (3) and (4), the sulphur-containing compounds have larger heats of transition than their oxygen counterparts. This at first seems rather surprising because sulphur is thought to be less able to undergo a mesomeric interaction with carbonyl than is oxygen.[11] Thiolesters should therefore be less polar than their oxygen analogues. The arguments of Dewar and Riddle[5] seem to account quite nicely for this increased $\Delta H_{N\to I}$ however. The effect on the geometry of such esters when the ether-type oxygen is replaced by sulphur is quite pronounced, due to the decreased C–S–C bond angle[12] (104 *vs.* 110°) and the increased C–S bond length[12] (1.81 *vs.* 1.43 Å). The increased bond length tends to make the thiolester more

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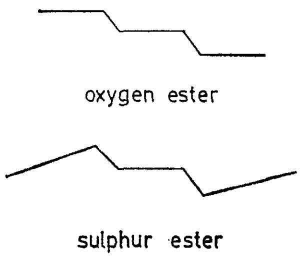
[9] W. R. Young, I. Haller, and A. Aviram, *Mol. Cryst. Liquid Cryst.*, 1971, **13**, 357.

[10] R. M. Riddle, Ph.D. Dissertation, University of Texas at Austin, 1971.

[11] C. C. Price, and S. Oae, 'Sulfur Bonding,' Ronald Press, New York, 1952, p.12.

[12] S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 407.

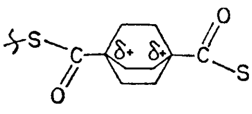
nearly planar by reducing unfavourable steric interactions (*i.e.* non-bonded repulsions between ring hydrogens and lone pair electrons on the carbonyl oxygen). The decreased bond angle permits a more efficient packing in the nematic lattice (Scheme 1).



SCHEME 1

The more nearly planar structure, and more efficient lattice packing, in the thiolester should promote intermolecular attractions. The adjacent molecules are able to approach one another more closely and to interact more strongly. This argument explains why $\Delta H_{N\rightarrow I}$ is greater for (1) and (5) than for the analogous compounds (2) and (6).

The bicyclo-octyl compounds (3) and (4) are an interesting pair. The oxygen ester (4) has the larger $\Delta H_{N\rightarrow I}$. This is out of line with respect to the two pairs of esters described above. The relative increase in packing efficiency should be approximately the same for (3) as for the other thiolesters (1) and (5); the decrease in $\Delta H_{N\rightarrow I}$ for (3), compared with (4), is therefore rather unexpected. A possible explanation for this decrease may lie in the fact that the polarity of the carbonyl group in a thiolester is not increased significantly by mesomeric interactions with sulphur. In the case of (3) the strongly polarized carbons α to the carbonyl carbons (*i.e.* the bridgehead atoms) are partially positively charged and repel each other through space (field effect) as indicated in (II).

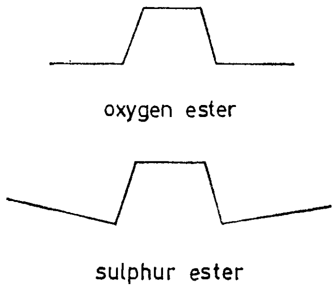


(II)

Since the interacting carbon atoms are closer than the analogous carbons in the cyclohexane compound (5), this repulsive interaction will be correspondingly greater. There will therefore be a tendency for the polarization ($\overset{\delta+}{C}=\overset{\delta-}{O}$) of the carbonyl groups to decrease, in order to reduce the positive charges on the proximal carbon atoms. This in turn should tend to reduce intermolecular attractions and so offset the geometrical advantages of the thiolesters.

The entropies of the N–I transitions can also be explained in a similar way. The fact that the entropy changes are larger in the thiolesters (1) and (5) than in the oxygen analogues (2) and (6) is due to the greater ordering of the mesophase in a thiolester than in the corresponding esters. The more constricted intermolecular structure is brought about by the smaller C–S–C bond angle. The empty 'pockets' of space in the nematic lattice of the oxygen esters are reduced in size in the thiolesters, allowing closer packing and leading to increased values for both $\Delta H_{N\rightarrow I}$ and $\Delta S_{N\rightarrow I}$. In the isotropic phase, where internal rotation occurs freely and the molecules are arranged randomly, these effects are much reduced. In the pair of bicyclo-octyl esters (3) and (4) one finds a larger $\Delta S_{N\rightarrow I}$ for the oxygen ester (4). This may be due to a decreased order in the mesophase of (3), resulting from the weakened lateral attractions.

The heteroaromatic compound (7) is very interesting. The values for both $\Delta H_{N\rightarrow I}$ and $\Delta S_{N\rightarrow I}$ are much less than those for the analogous carbocyclic compound (1). The substitution pattern in the thiophen ring is undoubtedly responsible for this. Since the 2- and 5-positions are not even close to collinearity, the diester (7) has a rather unusual bulge in the middle of the molecule. The oxygen analogue (8) is not mesomorphic; only the thiolester is. This suggests that the sulphur atoms serve to allow the ends of the molecule to kink back inward to produce an arrangement in which the deleterious effect of the heteroaromatic ring is compensated to some degree (Scheme 2). The sulphur compound forms a mesophase, but it has little stability (small $\Delta H_{N\rightarrow I}$). The molecule has a structure which prohibits close approach (association) between adjacent molecules. The resulting decrease in packing efficiency of (7), compared to (1), is also reflected in a small $\Delta S_{N\rightarrow I}$.



SCHEME 2

The cholesteric compounds of Elser and Ennulat seem to follow a similar pattern. In these steroid derivatives, the smaller bond angle of sulphur in the thiolesters confers no real geometrical advantage in the corresponding mesophases. Moreover the sulphur decreases the polarity of the carbonyl. The heat and entropy changes for the Ch–I transition for these thiolesters are thus usually lower than for the analogous oxygen compounds.

Inversion of Carbonyl Groups in Nematic Esters.—Riddle [10] concluded from a comparison of N–I transition temperatures that inversion of the ester function has relatively little effect on the mesophase stability of similarly constituted σ-bonded thiolesters and oxygen esters. This was in contrast to the conclusions drawn by Dewar and Goldberg [13] which indicated that the mutual conjugation between a terminal *para*-substituent on an aromatic ring and the carbonyl carbon was import-

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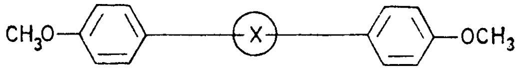
[13] M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, 1970, **35**, 2711.

Table 2

Thermodynamic properties of some isomeric diesters



No.	X	$T^a_{C \rightarrow N}$/°C	$T^b_{N \rightarrow I}$/°C	$\Delta H^c_{N \rightarrow I}$/ kcal mol^{-1}	$\Delta S^d_{N \rightarrow I}$/ cal mol^{-1} K^{-1}
(2)	Terephthaloyl	210.6	287.6	0.232	0.414
(9)	*p*-Phenylenebis(oxycarbonyl)	217.0	301.0	0.408	0.711
(4)	Bicyclo[2.2.2]octane-1,4-bis(carbonyloxy)	152.0	268.8	0.288	0.531
(10)	Bicyclo[2.2.2]octane-1,4-bis(oxycarbonyl)	191.9 [e]	279.7 [e]	0.443	0.801

[a] M.p. [b] N–I Transition temperature. [c] Heat of N–I transition. [d] Entropy of N–I transition. [e] Values of 185 and 269° have been reported (M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, 1970, **92**, 1582).

ant in this regard. Thus the higher $T_{N \rightarrow I}$ for (9) than for (2) was attributed by them to the increased polarity of the molecule, especially that of the carbonyl oxygen. Table 2 contains thermodynamic data for two pairs of compounds in which the carbonyl group of the ester linkage is inverted.

The esters in which the terminal methoxy-group can conjugate with the ester carbonyl, compounds (9) and (10), have larger heats and entropies of the N–I transition than the ' inverted ' analogues (2) and (4). This is probably due to one or both of two factors: (a) increased lateral attractions in the mesophase due to increased carbonyl polarity; or (b) increased attractions due primarily to more efficient lattice arrangement.[5] It is rather difficult to distinguish between the two possibilities. However it is clear that location inversion of the ester group can have a large effect on both $\Delta H_{N \rightarrow I}$ and $\Delta S_{N \rightarrow I}$.

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