A New Group of Liquid Crystal Materials with Sulphur Atoms incorporated in the Principal Structure

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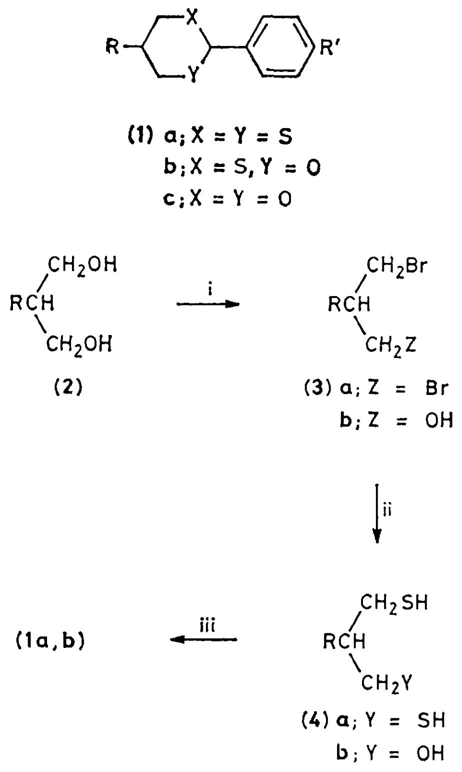
2-(*p*-Alkoxyphenyl)-5-alkyl-1,3-dithians and -1,3-oxathians, synthesized by the acetal-formation procedure, form mesomorphic phases with the lowest T_{C-N} at 37 °C and the highest T_{N-I} (but not for the same members of these series) at 81 °C; these compounds therefore constitute a new group of liquid crystal compounds with sulphur atoms incorporated in the principal structure.

In recent years, 2,5-disubstituted 1,3-dioxans have been reported as a novel type of liquid crystal system.[1] However, such systems with sulphur atoms instead of the oxygen atoms in the 1,3-dioxan ring have not been encountered to date. In this communication, we report the synthesis and properties of the 1,3-dithians and 1,3-oxathians (**1a**) and (**1b**). Several such



Scheme 1. i, HBr–H_2SO_4; ii, $H_2NC(:S)NH_2$ then alkali; iii, $R'C_6H_4CHO$, $BF_3 \cdot Et_2O$.

compounds were synthesised and their mesomorphic ranges are given in Table 1, together with those of some 1,3-dioxans (**1c**). Measurements of mesomorphic ranges and assignments of mesophase structure were carried out visually by both the capillary method and optical microscopy.

Compounds (**1a**, **b**) were synthesized as shown in Scheme 1. Compound (**2**) was obtained from diethyl malonate in a 2-step synthesis.[1,2] In step (**2**) → (**3**) the reaction temperature was crucial; the main products at 95—100 °C and at 70—75 °C were (**3a**) and (**3b**), respectively. Compound (**1**) was purified by repeated recrystallization from hexane (−20 °C) until only a single spot in t.l.c. (ether–hexane) was obtained. Compounds (**1a**) and (**1b**) are all colourless, odourless crystals, soluble in common organic solvents and gave satisfactory analytical data. A singlet ^1H n.m.r. signal at δ 5.1 (**1a**) or 5.65 (**1b**) (2-H of the 1,3-dithian or 1,3-oxathian ring) indicated that these compounds were isomer-free and were probably composed exclusively of the *trans* form.

The mesomorphic phase appears much less readily in (**1b**) than in (**1a**) (Table 1), probably because (**1b**) cannot assume the required cylindrical shape owing to a slight bend in the 1,3-oxathian ring arising from the difference in size between the S and O atoms. The principal features of the mesomorphic behaviour of compounds (**1a**) compared with the corresponding (**1c**) are (i) the appearance of enantiotropic nematic phases for all the compounds (**1a**) listed in Table 1, (ii) wider nematic ranges, and (iii) higher N–I transition temperatures. These facts suggest that the effect of the increased width of the 1,3-dithian molecule caused by the sulphur atoms is smaller than the effect of the increased attractive interactions between the molecules.

Table 1. Mesomorphic ranges for compounds (**1a**—**c**).

Compound	R	R′	Mesomorphic range/°C[a]
(**1a**)	Pr^n	OBu^n	$C \xrightarrow{38} N \xrightarrow{46} I$
	Bu^n	OMe	$C \xrightarrow{55} N \xrightarrow{81} I$
	Bu^n	OEt	$C \xrightarrow{56} N \xrightarrow{74} I$
	Bu^n	OPr^n	$C \xrightarrow{59} N \xrightarrow{65} I$
	Bu^n	OBu^n	$C \xrightarrow{58} N \xrightarrow{67} I$
	Bu^n	OC_6H_{13}	$C \xrightarrow{60} N \xrightarrow{66} I$
(**1b**)	Bu^n	OMe	$C \xrightarrow{48} I$
	Bu^n	OEt	$C \xrightarrow{68} I$
	Bu^n	OBu^n	$C \xrightarrow{37} N \xrightarrow{45} I$
	Bu^n	OC_6H_{13}	$C \xrightarrow{50} I$
(**1c**)	Bu^n	OMe	$C \xrightarrow{37} I^c$
	Bu^n	OPr^n	$C \xrightarrow{43} I^b$ $(N \xleftarrow{25} I)^b$
	Bu^n	OC_6H_{13}	$C \xrightarrow{51} I^b$ $(N \xleftarrow{43} I)^b$

[a] C = crystal; N = nematic; I = isotropic. [b] Cited from ref. 1. [c] Prepared *via* the same synthetic route as that mentioned in ref. 1.

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