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New Liquid Crystalline 2,5-Disubstituted 1,3-Dithians and 1,3-Dioxans

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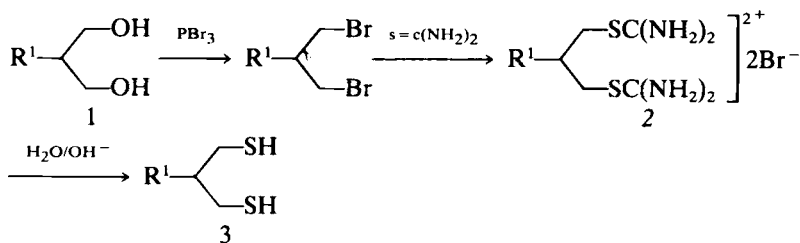
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This paper describes the synthesis of new classes of liquid crystal materials based upon 2,5-disubstituted 1,3-dioxans and 1,3-dithians.

INTRODUCTION

As a new class of substance with liquid crystal properties we have synthesized¹ 2,5-disubstituted 1,3-dithians (5). We obtained these compounds according to Scheme 1 by reaction of 2-alkyl-1,3-dimercaptopropanes (3) with aldehydes (4) in good yield. The dimercaptopropanes (3) can be obtained from the corresponding diols (1) in two steps without isolation of the thiuronium salts (2).

EXPERIMENTAL AND RESULTS



†Presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

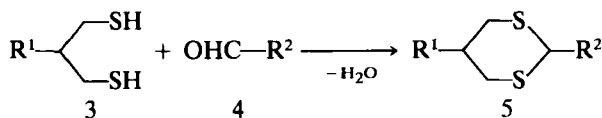




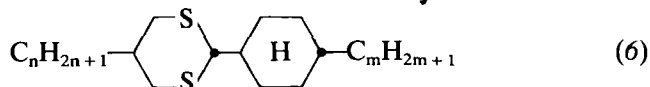
**Scheme 1**

Table I shows some examples of substituted 2-phenyl-1,3-dithians (5). Most of the compounds are nematic with high melting and clearing temperatures.

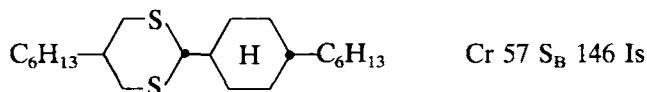
TABLE I

$ \begin{array}{c} \text{C}_n\text{H}_{2n+1} - \text{CH}_2 - \text{S} \\ \quad \quad \\ \text{CH}_2 - \text{S} - \text{C}_6\text{H}_4 - \text{R} \\ \text{(5)} \end{array} $					
n	R	Cr	N	Is	No.
6	—CN	• 84	—	•	5.1.
7	—CN	• 99	—	•	5.2.
7	—OOC—  —CN	• 155	• 232	•	5.3.
7	—COO—  —CN	• 128	• 217	•	5.4.
6	—OOC—  —C ₆ H ₁₃	• 111	• 164	•	5.5.
6	—OOC—  —C ₆ H ₁₃	• 140	• 184	•	5.6.

The CN-substituted compounds of Table I possess high dielectric anisotropies. Compared with analogous dioxan derivatives^{2,3} the substituted dithians prefer to form nematic phases and they have a tendency to have higher melting and clearing temperatures. 2-(4-n-alkyl-cyclohexyl)-5-n-alkyl-1,3-dithians (6) exhibit the smectic B phase

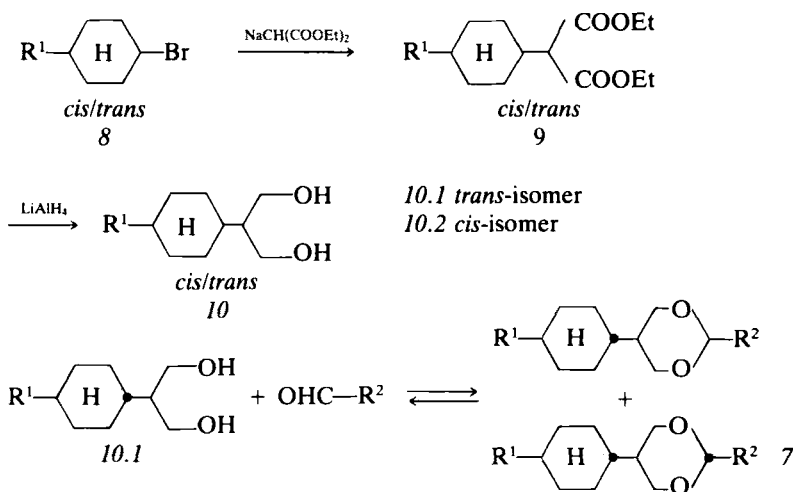


The melting points are relatively low and the clearing points are unexpectedly high:



At certain concentrations, they are miscible with nematic compounds giving nematic mixtures.

We have also synthesized⁴ some novel cyclohexyl-substituted 1,3-dioxans (7). The synthetic route is given in Scheme 2.



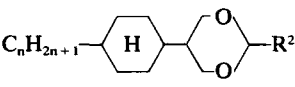
Scheme 2

Starting from a *cis/trans* mixture of 4-alkylcyclohexyl bromides (8) and the sodium salt of diethyl malonate, a *cis/trans* mixture of the 4-alkylcyclohexyl diethyl malonates (9) was obtained. After reduction with LiAlH_4 we obtained the cyclohexyl substituted propane-1,3-diols (10).⁴ Recrystallisation from hexane gave the pure *trans*-diols (10.1). Surprisingly, these diols possess smectic phases.⁶ Reaction of (10.1) with aldehydes yielded the dioxans (7). Most of these compounds are purely smectic (see Table II), but especially the 2(4-*n*-alkylcyclohexyl)-5-(4-*n*-alkylcyclohexyl)-1,3-dioxans (7.3) and (7.4) are well suited as additives for nematic mixtures, because they enhance clearing points remarkably without enlarging the viscosities. 2-(4-cyanophenyl)-5-(4-*n*-alkylcyclohexyl)-1,3-dioxanes (7.5) and (7.6) are nematic and possess high dielectric anisotropies of about $\Delta\epsilon \approx +15$. Therefore they are valuable compounds for nematic mixtures for application in electro-optical displays.

Examples of *trans*-2-substituted 1,3-dioxan-5-carboxylates (11) are listed in Table III. The CN-substituted compounds possess high positive dielectric anisotropies and are well suited for mixtures for LCD's.⁵

A more detailed description of this new class of liquid crystals will be given later.

TABLE II

(7)

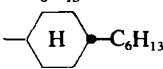
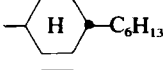
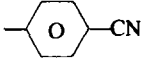
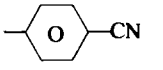
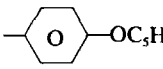
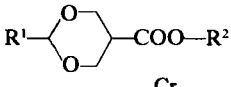
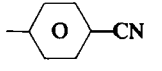
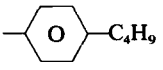
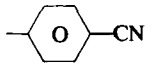
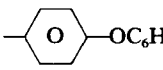
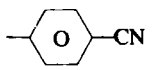
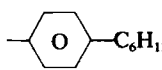
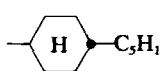
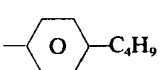
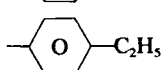
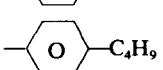
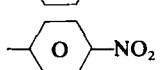
n	R ²	Cr	S _B	N	Is
6	—C ₆ H ₁₃	• 34.5	• 109	—	• 7.1.
2	—C ₆ H ₁₃	• <25	• 89	—	• 7.2.
6		• 55	• 229	—	• 7.3.
2		• <25	• 194	—	• 7.4.
5		• 84	—	• 220	• 7.5.
6		• 95	—	• 214	• 7.6.
6		• 45	• 203	—	• 7.7.

TABLE III

(II)

R ¹	R ²	Cr	S	N	Is
—C ₆ H ₁₃		• 64	—	• (47.5)	•
		• 109	—	• 181	•
		• 96	—	• 193	•
—C ₆ H ₁₃		• 39	• 74	—	•
—C ₄ H ₉		• <20	• 89	—	•
		• 99	• 106	• 128	•
		• 125	—	• 132	•

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