Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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

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Version of record first published: 17 Oct 2011.

To cite this article: H.-M. Vorbrodt , J. Vogel , H. Zaschke , G. Pelzl & D. Demus (1985): New Liquid Crystalline 2,5-Disubstituted 1,3-Dithians and 1,3-Dioxans, Molecular Crystals and Liquid Crystals, 123:1, 137-141

To link to this article: http://dx.doi.org/10.1080/00268948508074772

Mol. Cryst. Liq. Cryst., 1985, Vol. 123, pp. 137–141
0026-8941/85/1234–0137/$10.00/0

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

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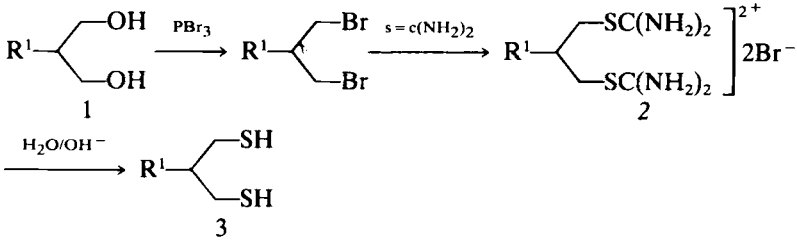
(*Received July 19, 1984*)

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

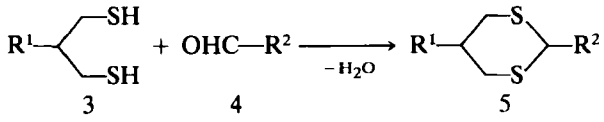
As a new class of substance with liquid crystal properties we have synthesized[1] 2,5-disubstituted 1,3-dithians (*5*). We obtained these compounds according to Scheme 1 by reaction of 2-alkyl-1,3-dimercaptopropanes (*3*) with aldehydes (*4*) in good yield. The dimercaptopropanes (*3*) can be obtained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

EXPERIMENTAL AND RESULTS



1 2 3

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

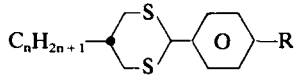


3 4 5

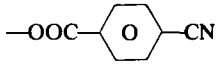
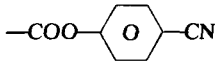
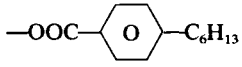
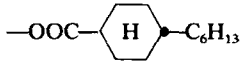
Scheme 1

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.

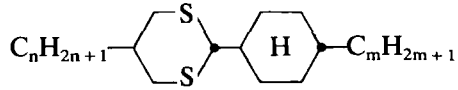
TABLE I



(5)

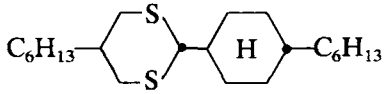
n	R	Cr	N	Is	No.
6	—CN	· 84	—	·	*5.1.*
7	—CN	· 99	—	·	*5.2.*
7		· 155	· 232	·	*5.3.*
7		· 128	· 217	·	*5.4.*
6		· 111	· 164	·	*5.5.*
6		· 140	· 184	·	*5.6.*

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-alkylcyclohexyl)-5-n-alkyl-1,3-dithians (6) exhibit the smectic B phase



(6)

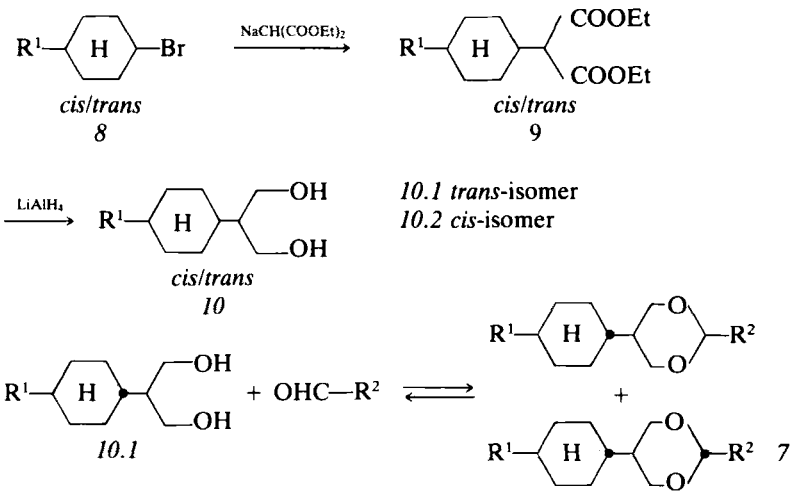
The melting points are relatively low and the clearing points are unexpectedly high:



Cr 57 S_B 146 Is

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

We have also synthesized[4] some novel cyclohexyl-substituted 1,3-dioxans (*7*). The synthetic route is given in Scheme 2.



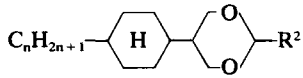
Scheme 2

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)

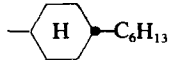
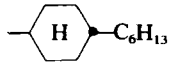
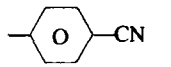
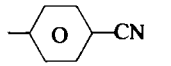
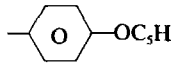
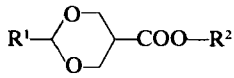
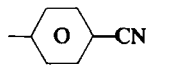
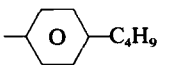
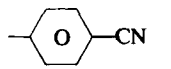
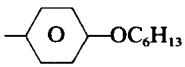
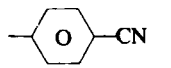
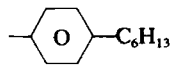
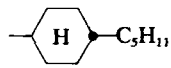
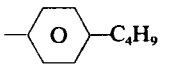
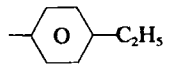
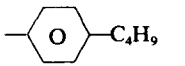
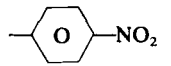
n	R^2	Cr	S_B	N	Is
6	$-C_6H_{13}$	· 34.5	· 109	—	· *7.1.*
2	$-C_6H_{13}$	· <25	· 89	—	· *7.2.*
6		· 55	· 229	—	· *7.3.*
2		· <25	· 194	—	· *7.4.*
5		· 84	—	· 220	· *7.5.*
6		· 95	—	· 214	· *7.6.*
6		· 45	· 203	—	· *7.7.*

TABLE III



(*11*)

R^1	R^2	Cr	S	N	Is
$-C_6H_{13}$		· 64	—	· (47.5)	·
		· 109	—	· 181	·
		· 96	—	· 193	·
$-C_6H_{13}$		· 39	· 74	—	·
$-C_4H_9$		· <20	· 89	—	·
		· 99	· 106	· 128	·
		· 125	—	· 132	·

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