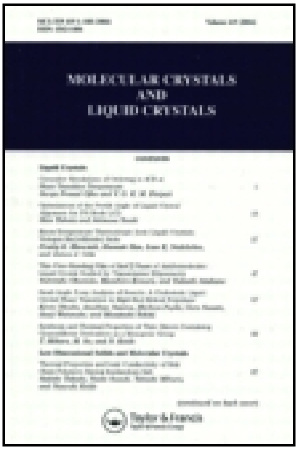

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2-(p-Cyanophenyl)-5-Alkyl-1,3-Dithianes in Liquid Crystal Mixtures

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2-(p-Cyanophenyl)-5-Alkyl-1,3-Dithianes in Liquid Crystal Mixtures

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The trans isomer of the 2-(p-cyanophenyl)-5-alkyl-1,3-dithianes, synthesized by the acid-catalyzed thioacetalization of p-cyanobenzaldehyde and dithiols, were separated by means of centrifugal liquid chromatography and recrystallization. Several properties of a liquid crystal mixture containing 2-(p-cyanophenyl)-5-alkyl-1,3-dithianes were measured. The values thus obtained were compared with those for mixtures containing other p-cyanophenyl compounds. The principal feature of the mixture containing 2-(p-cyanophenyl)-5-alkyl-1,3-dithianes is a low threshold voltage.

INTRODUCTION

In recent years, 2,5-disubstituted-1,3-dioxanes as novel types of liquid crystal materials were synthesized.[1] However, such compounds with sulfur atoms instead of the oxygen atoms in the 1,3-dioxane ring had not been encountered. Thereupon we reported the syntheses of several 1,3-dithiane and 1,3-oxathiane type liquid crystal compounds.[2,3,4,5] In this paper we wish to report several properties of 2-(p-cyanophenyl)-5-alkyl-1,3-dithianes as a dopant in mixtures of liquid crystal materials, in comparison with those of other cyanophenyl compounds.

RESULTS AND DISCUSSION

2-(p-Cyanophenyl)-5-alkyl-1,3-dithianes were synthesized via the following route.

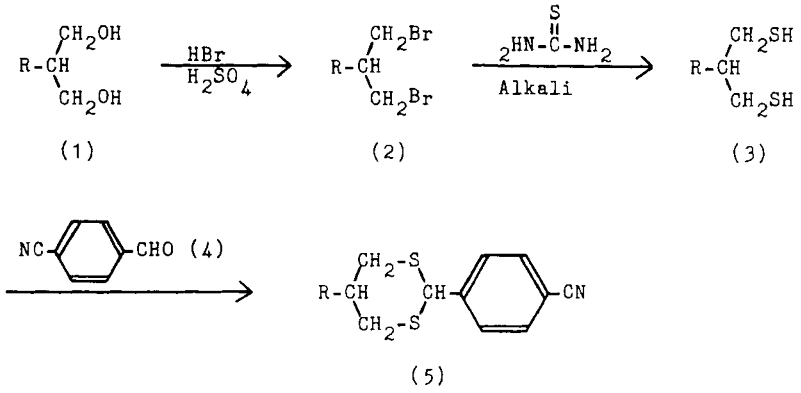


FIGURE 1

In step 1 → 2, the reaction temperature is kept within the range of 95–100°C to get 2 as the principal product. If the temperature is in the range of 70–75°C, monosubstituted bromide will become the main product. As compounds 3 is readily oxidized, the synthetic procedure must be done under a nitrogen atmosphere.

In step 3 → 5, both trans and cis isomers of 2-(p-cyanophenyl)-5-alkyl-1,3-dithianes are produced. The purification of trans isomers is made by centrifugal liquid chromatography and recrystallization. The identification of trans isomers was made by ^{1}H-NMR and ^{13}C-NMR data. In ^{13}C-NMR data of 5-alkyl-1,3-dithiane, the C5 carbon signal in the 1,3-dithiane ring of 5-equatorial isomer lies at lower fields than that of the 5-axial isomer,[6] thereby making the determination of trans isomers possible.

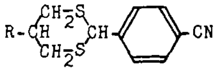
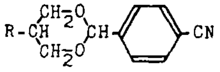
The compositions of the liquid crystal mixtures used were given in Table 1. The measurements of liquid crystal properties were carried out by using 9.4 μm twisted nematic cells to ensure good guiding of the plane of polarization. Threshold voltage (Vth); rising time (Tr), decay time (Td), birefringence (Δn), dielectric anisotrophy (Δε), steepness factor (β), temperature dependence, and viscosity (η) were measured in mixture A, B, C, and D respectively. The steepness factor (β) and temperature dependence are defined below.

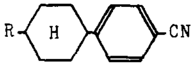
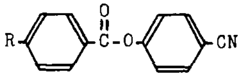
$$\beta = \frac{\mathrm{Vsat}}{\mathrm{Vth}}, \quad \text{Temperature dependence} = -\frac{1}{\mathrm{Vth}}\left(\frac{d\mathrm{Vth}}{dT}\right)$$

Vth: threshold voltage (voltage of exhibiting 10% contrast)
Vsat: saturated voltage (voltage of exhibiting 90% contrast)

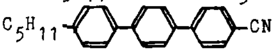
TABLE I

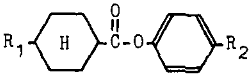
Compositions of each liquid crystal mixture.

	Mixture A	Mixture B
		
	mol %	mol %
Base mixture	80	80
R= C_2H_5	8	8
R= C_4H_9	8	8
R= C_7H_{15}	4	4

	Mixture C	Mixture D
		
	mol %	mol %
Base mixture	80	80
R= C_2H_5	8	8
R= C_4H_9	8	8
R= C_7H_{15}	4	4

Composition of base liquid crystal mixture (Base mixture)

R_1	R_2	mol %
C_3H_7	OC_2H_5	9.9
C_3H_7	OC_4H_9	23.5
C_4H_9	OCH_3	20.1
C_4H_9	OC_2H_5	19.3
C_5H_{11}	OCH_3	21.0
		6.2



The data obtained by the measurements of electro-optic and other relevant properties are indicated in Table 2.

Threshold voltage (Vth) of mixture C is larger than those of other mixtures. Generally Vth is proportional to the square root of $K/\Delta\varepsilon$,[7] so that it must originate in smaller $\Delta\varepsilon$ of mixture C.

Decay time (Td) of mixture A is larger than those of other mixtures. Decay time is proportional to η/K.[8] Compounds 5, contained in mixture A, have larger differences in shape, size, and polarizability against the base liquid crystal molecules. The addition of these compounds may weaken the interactions among base liquid crystal molecules largely, and this seems to make K small. Therefore the decay time of mixture A having larger η and smaller K is longer than those of other mixtures.

The rising time (Tr) of mixture C is the longest. Generally, rising time is proportional to $\eta/(\Delta\varepsilon V^2 - K\pi^2)$.[8] Viscosity ($\eta$) of mixture C is somewhat smaller than those of other mixtures, so that, in this respect, rising time of mixture C must be shorter than those of other mixtures. But the dielectric anisotrophy ($\Delta\varepsilon$) of mixture C is also smallest, and the elastic constant (K) of mixture C seems to be larger than that of the mixture A mentioned above. Therefore, this value of rising time for mixture C must imply that differences in $\Delta\varepsilon$ and K had larger influences on rising time than difference in η.

Birefringence (Δn) of mixture A is smaller than those of other mixtures, so that mixture A must use a somewhat thick cell to gain sufficient contrast.

The values of T(N-I) are in the decreasing order: D (69.0°C), C (66.5°C), B (64.0°C), A (59.8°C). When a compound is contained in a liquid crystal mixture, the extent of the lowering of $T_{N\text{-}I}$ seems to relate to the degrees of the similarities in basic chemical structure and polarizability to the base liquid crystal molecules.[9] That is, the larger the difference in these points, the larger the extent of the lowering of $T_{N\text{-}I}$ is ($T_{N\text{-}I}$ of the base liquid crystal group is 78°C). Therefore, the order of $T_{N\text{-}I}$ given above seems to be reasonable.

Mixture B and D exhibit somewhat smaller values of steepness factor.

Temperature dependences of mixtures A and B are somewhat larger than those for mixture C and D. This seems to be related with basic molecular structure, that is, the former contain hetero atoms in their principal structures. Although compounds 5 do not exhibit any liquid crystal phases by themselves, they can drive liquid crystal mixtures by using them as a dopant having positive dielectric anisotropy.

Melting point of compounds 5 are 130°C ($R = C_2H_5$), 88°C ($R = C_4H_9$), and 98°C ($R = C_7H_{15}$), and ΔH of melting are 5.68 Kcal/mol,

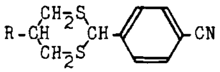
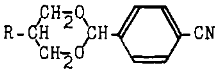
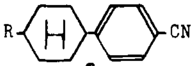
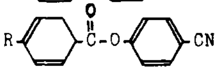
TABLE II

Electro-optic and other relevant properties.

	Mixture A	Mixture B	Mixture C	Mixture D	
Threshold voltage (Vth)	1.87 V	2.00 V	2.34 V	1.90 V	
Rising time (Tr)	103 ms	87 ms	121 ms	84 ms	a
Decay time (Td)	85 ms	57 ms	45 ms	63 ms	
Birefringence (Δn)	0.095	0.097	0.098	0.111	
Dielectric anisotropy ($\Delta\varepsilon$)	+ 4.49	+ 4.58	+ 3.32	+ 5.96	
Steepness factor (β)	1.37	1.34	1.36	1.34	
Temperature dependence	0.45 %/°C	0.43 %/°C	0.37 %/°C	0.32 %/°C	
Viscosity (η) (25 °C)	22 cp	18 cp	17 cp	20 cp	b
(5 °C)	53 cp	58 cp	54 cp	64 cp	
T (N - I)	59.8 °C	64.0 °C	66.5 °C	69.0 °C	

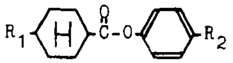
a) Von = 4 volt, Voff = 0 volt.

b) The measurement of viscosity (η) was carried out for the following liquid crystal compositions.

		(Base mixture)'	R = C_4H_9	R = C_7H_{15}
Mixture A'		90 mol%	10 mol%	10 mol%
Mixture B'		90 mol%	10 mol%	10 mol%
Mixture C'		90 mol%	10 mol%	10 mol%
Mixture D'		90 mol%	10 mol%	10 mol%

Composition of (Base mixture)'

R_1	R_2	mol %
n-C_3H_7	OC_2H_5	10.5
n-C_3H_7	$OC_4H_9{}^n$	25.1
n-C_4H_9	OCH_3	21.5
n-C_4H_9	OC_2H_5	20.5
n-C_5H_{11}	OCH_3	22.4



5.38 Kcal/mol, and 7.54 Kcal/mol, respectively. These ΔH values of compounds 5 are as large as those of other common liquid-crystal materials.[10]

In this way, the principal features of mixture A containing compounds 5 are 1, lower threshold voltage; 2, longer decay time; 3, lower nematic-isotropic transition temperature. These features seem to originate in the principal molecular structure of compounds 5 which have two large sulfur atoms.

EXPERIMENTAL

IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, a JNM-FX 90Q FT-NMR spectrometer, and a Hitachi RMU-6 MG spectrometer, respectively. Elemental anaylses were carried out with a Perkin-Elmer 250 instrument. Centrifugal liquid chromatography was made with a Hitachi CLC-5 apparatus. Transition temperatures were determined by means of both a Mitamura Riken micro melting point apparatus equipped with polarizers and Rigaku Denki D.S.C. CN8059L1, CN8208A2. The viscosity (η), dielectric anisotrophy ($\Delta\varepsilon$), and birefringence (Δn) of liquid crystal mixture were measured using a Tokyo Keiki E type rotating cone viscometer, Yokokawa Hewlett Packard 4274A multi frequency LCR meter, and Hitachi 340 spectrometer, respectively. The measurements of liquid crystal properties are carried out by using 9.4 μm twisted nematic cells to ensure good guiding of plane of polarization. Threshold voltage (Vth), rising time (Tr), decay time (Td), and steepness factor (β) were measured at 25°C.

Syntheses and detailed analytical data of compounds 1, 2, 3, and 5 were given in a previous paper.[3]

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