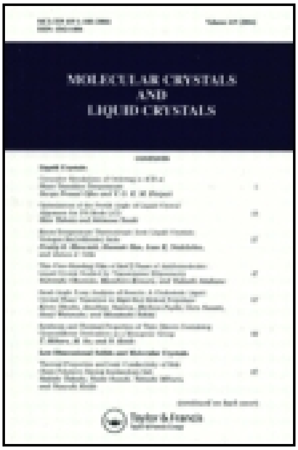

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

2-(p-Cyanophenyl)-5-Alkyl-1,3-Oxathianes in Liquid Crystal Mixture

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To cite this article: Y. Haramoto & H. Kamogawa (1985): 2-(p-Cyanophenyl)-5-Alkyl-1,3-Oxathianes in Liquid Crystal Mixture, Molecular Crystals and Liquid Crystals, 131:3-4, 201-207

To link to this article: http://dx.doi.org/10.1080/00268948508085042

Mol. Cryst. Liq. Cryst., 1985, Vol. 131, pp. 201–207
0026-8941/85/1314–0201/$15.00/0

Printed in the United States of America

2-(p-Cyanophenyl)-5-Alkyl-1,3-Oxathianes in Liquid Crystal Mixture

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(*Received June 18, 1985*)

The trans isomers of the 2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes (5) synthesized by the acid-catalyzed thioacetalization of p-cyanobenzaldehyde and 2-alkyl-3-mercapt-1-propanols and isolated by recrystallizations were added to a conventional liquid crystal composition. The principal features of the liquid crystal mixture containing 5 as compared with those containing other p-cyanophenyl type liquid crystal compounds are lower threshold voltage, smaller values of steepness factor, and smaller dependence on visual angle.

INTRODUCTION

In recent years, 2,5-disubstituted -1,3-dithianes and 2,5-disubstituted-1,3-oxathianes have been reported as new types of liquid-crystalline materials.1),2),3),4),5),6),7) In a previous paper,7) we reported several properties of a liquid crystal mixture containing 2-(p-cyanophenyl)-5-alkyl-1,3-dithianes.

In this paper, we wish to report several properties of 2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes as a dopant in mixtures of liquid crystal materials, in comparison with those with other p-cyanophenyl compounds.

RESULTS AND DISCUSSION

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

In step 1 → 2, the reaction temperature must be kept between 70

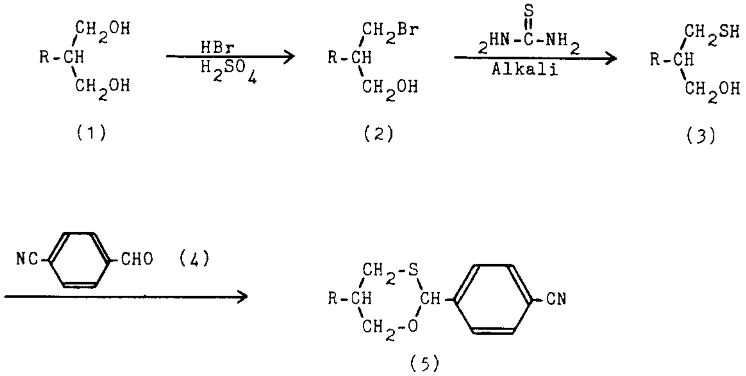


FIGURE 1

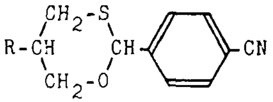
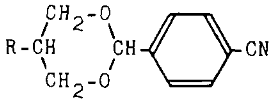
and 75°C. If the temperature is in the range of 90–100°C, the main product will be the disubstituted bromide contrary to the purpose. As compound 3 is susceptible to oxidation, the synthetic procedure must be done under a nitrogen atmosphere. In step 3 → 5, both trans and cis isomers differing at the C-5 position of the 1,3-oxathiane ring were produced. Five to seven times recrystallizations were required to get trans isomers.

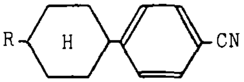
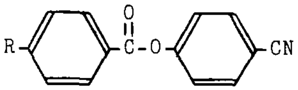
The identification of trans isomers was made by ^{1}H-NMR and ^{13}C-NMR data. As trans and cis isomers exhibit C-2 proton signals of the 1,3-oxathiane ring in ^{1}H-NMR at $\delta = 5.75$ and 5.80, respectively, the presence of cis isomer can be detected by the examination of proton signals at $\delta = 5.80$. The presence of 1,3-dithiane can be detected by the examination of proton signals at $\delta = 5.10$. Absorption of C2, C4, and C6 carbons of the 1,3-oxathiane ring in ^{13}C-NMR spectra, as determined by ^{1}H-complete decoupling (COM), ^{1}H-off resonance decoupling (OFR), and ^{1}H-selective decoupling (SEL) procedures, are located at $\delta = 83.22$, 34.84, and 75.53, respectively ($R = C_8H_{17}$). The compositions of the liquid crystal mixtures used were given in Table I. The measurements of liquid crystal properties were carried out using 10.2 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 anisotropy ($\Delta\epsilon$), steepness factor (β), temperature dependence, dependence on visual angle (α), and viscosity (η) were measured in mixture A, B, C, and D respectively. The steepness factor (β) and temperature dependence are defined below.

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

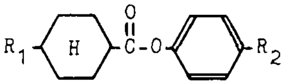
TABLE I

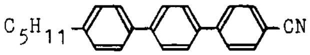
Composition of each liquid crystal mixture.

	Mixture A	Mixture B
		
	mol %	mol %
Base mixture	80	80
$R=C_4H_9$	7	7
$R=C_5H_{11}$	7	7
$R=C_7H_{15}$	6	6

	Mixture C	Mixture D
		
	mol %	mol %
Base mixture	80	80
$R=C_4H_9$	7	7
$R=C_5H_{11}$	7	7
$R=C_7H_{15}$	6	6

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

Vth: threshold voltage (voltage exhibiting 10% contrast)

Vsat: saturated voltage (voltage exhibiting 90% contrast)

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

Threshold voltage (Vth) of mixture C is larger than those of other mixtures. Since Vth is generally proportional to the square root of $K/\Delta\epsilon$,[8] the larger value should originate in smaller $\Delta\epsilon$ of mixture C. Decay time (Td) of mixture A is larger than those of other mixtures. This result is somewhat different from that obtained for 1,3-dithianes.[7] Whereas, in the case of 1,3-dithianes, the decay time of mixture A (containing 1,3-dithiane compounds) is 22ms smaller than that of mixture D, in the case of 1,3-oxathianes in this report, the difference becomes very small: Td of mixture A − Td of mixture D = 4ms. It is known that decay time is proportional to η/K.9) The result seems to originate in η of mixture A which is not so high as in the case of 1,3-dithianes and close to those of other mixtures.

The difference of Tr between mixture A and C is small in comparison with the case of 1,3-dithianes. Thus, in the case of 1,3-dithianes, this difference is 16 ms (16ms corresponds to 18% against Tr of mixture C), whereas, in the case of 1,3-oxathianes, the difference is 9ms (9ms corresponds to 7% against Tr of mixture C). This fact may originate in a greater value (+4.88) of $\Delta\epsilon$ for mixture A containing 1,3-oxathianes as compared with that (+4.55) for mixture C, because this relation was reversed for 1,3-dithianes in the previous paper[7](+4.49 versus +4.58).

Birefringence (Δn) of mixture A is somewhat improved in comparison with 1,3-dithianes: Δn of mixture A containing 1,3-oxathianes is larger than those of mixtures B and C, whereas Δn of a mixture containing 1,3-dithianes was smaller than those of other mixtures.

Steepness factor (β) of mixture A is as small as those of other mixtures. Therefore, this factor is improved in comparison with the case of 1,3-dithianes in the previous paper.[7]

Temperature dependences of mixture A and B are somewhat larger than those for mixture C and D. This result also supports the hypothesis presented in the previous paper,[7] that the presence of hetero atoms in the principal molecular structure provides a larger temperature dependence.

A good value of dependence on visual angle (α) is obtained for mixture A.

The values of T(N-I) are in the decreasing order: D (71.0°C), C (70.8°C), B (68.8°C), and A (66.9°C). When a compound is added to a liquid crystal mixture, the extent of the lowering of Tn-i seems

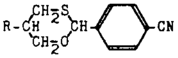
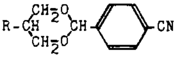
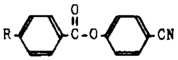
TABLE II

Electro-optic and other relevant properties

	Mixture A	Mixture B	Mixture C	Mixture D
Threshold voltage (Vth)	2.11 V	2.22 V	2.54 V	2.05 V
Rising time (Tr)	144 ms	135 ms	178 ms	118 ms [a]
Decay time (Td)	72 ms	59 ms	45 ms	68 ms [a]
Birefringence (Δn)	0.102	0.100	0.100	0.112
Dielectric anisotropy ($\Delta\varepsilon$)	+ 4.88	+ 4.55	+ 3.34	+ 5.82
Steepness factor (β)	1.32	1.32	1.33	1.32
Temperature dependence	0.39 %/°C	0.39 %/°C	0.35 %/°C	0.32 %/°C
Dependence on visual angle (α)	1.22	1.21	1.21	1.25
Viscosity (η) (25°C)	20 cp	18 cp	17 cp	20 cp [b]
(5°C)	65 cp	58 cp	54 cp	64 cp [b]
T (N - I)	66.9°C	68.8°C	70.8°C	71.0°C

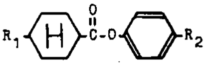
a) Von = 4 volt, Voff = 0 volt.

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%	5 mol%	5 mol%
Mixture B'		90 mol%	5 mol%	5 mol%
Mixture C'		90 mol%	5 mol%	5 mol%
Mixture D'		90 mol%	5 mol%	5 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



to relate to the degrees of the similarities in basic chemical structure and polarizability to the base liquid crystal molecules.[10] Namely, the larger the differences in these points, the larger the extent of the lowering of Tn-i is (Tn-i of base liquid crystal group is 78°C). Therefore, the order of Tn-i given above seems to be reasonable. Tn-i of a mixture containing 1,3-dithianes is 4.2°C lower than that containing 1,3-dioxanes,[7] whereas in the case of 1,3-oxathianes, this corresponding difference of Tn-i becomes small (Tn-i of mixture B − Tn-i of mixture A = 1.9°C). This must imply that the degree of similarity to the base liquid crystal molecules decreases in the next order: 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane.

Some of compounds 5 exhibit monotropic nematic liquid crystal phase: C 74 I 19 N 11 C ($R = C_5H_{11}$), C 73 I 17 N 6 C ($R = C_6H_{13}$), C 78 I 30 N 15 C ($R = C_7H_{15}$), C 70 I 26 N 15 C ($R = C_8H_{17}$), where C, I, and N represent crystal, isotropic, and nematic, respectively. ΔH of melting are 5.42 Kcal/mol ($R = C_5H_{11}$), 5.97 Kcal/mol ($R = C_6H_{13}$), 7.26 Kcal/mol ($R = C_7H_{15}$), and 6.25 Kcal/mol ($R = C_8H_{17}$), respectively.

In summary, the pricipal features of mixture A containing 2-(p-cyanophenyl)-5-alkyl-1,3-oxathiane compounds are lower threshold voltage, small steepness factor and dependence on visual angle, and somewhat larger dielectric anisotropy. These features seem to originate in the basic molecular structure of compounds 5 containing an oxathiane ring.

EXPERIMENTAL

IR, ^1H-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 RMG-6 MG spectrometer, respectively. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Transition temperature were determined by means of both a Mitamura Riken micro melting point apparatus equipped with polarizers and Rigaku Denki D.S.C. CN8059L1, CN 8208A2. The viscosity (η), dielecric anisotropy ($\Delta\epsilon$), and birefringence (Δn) of liquid crystal mixture were measured using a Tokyo Keiki E type rotating cone viscometer, a Yokokawa Hewlett Packard 4274A multi frequency LCR meter, and a Hitachi 30 spectrometer, respectively. The measurements of liquid crystal properties are carried out by using 10.2 μm twisted nematic cells to ensure good guiding of the plane of polarization.

Threshold voltage (Vth), rising time (Tr), decay time (Td), steepness factor (β), and dependence on visual angle (α) were measured at 25°C.

Syntheses and detailed analytical data of compounds 1, 2, 3, and 5 were described in a previous paper.[6]

Acknowledgment

The authors wish to express their gratitude to Suwa Seikosha Co., Ltd. for extensive assistance in the measurement of liquid crystal properties.

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