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Liquid Crystal Materials with Sulfur Atoms Incorporated in the Principal Structure III. Trans and Cis Isomers of New Liquid Crystal Material: 2-(*p*-Substituted phenyl)-5-alkyl-1,3-dithianes

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Trans and cis isomers of 2,5-disubstituted 1,3-dithianes were synthesized by the acid-catalyzed thioacetalization of *p*-substituted benzaldehydes and dithiols. The results of identifications of trans and cis isomers made by means of ^{13}C-NMR chemical shifts indicate that the isomerism occurred at the 5 position in the 1,3-dithiane ring. Benzaldehydes with electrondonating *p*-substituents produced less cis isomers than that with the cyano group, which seems to indicate the establishment of an equilibrium in the formation reaction between trans and cis isomers. Several electro-optic properties of *trans*- and *cis*-2-(*p*-cyanophenyl)-5-alkyl-1,3-dithianes were determined by using them as a dopant of mixture of liquid crystals. Mixture added with trans isomers was superior to that added with cis isomers in several points.

In recent years, we have synthesized 2,5-disubstituted 1,3-dithianes and 1,3-oxathianes[2,3,4] as novel analogs of the 1,3-dioxanes now in practical uses.[1] These compounds were produced in both trans and cis isomers. Then we analyzed these two isomers by means of ^{13}C-NMR to determine which isomer was trans and at what position the isomerism occurred in the 1,3-dithiane ring.

In addition to this, we compared several physical properties of trans and cis 2-(*p*-cyanophenyl)-5-alkyl-1,3-dithianes by using them as a dopant of liquid crystal mixtures.

Results and Discussion

2,5-Disubstituted 1,3-dithianes were synthesized *via* the following route.

In step **3**→**5**, the ^{1}H-NMR of the product indicated a splitting of the singlet due to the C-2 proton of the 1,3-dithiane ring, which was caused by the presence of two isomers, both trans and cis. In compound R′=CN, separation of trans and cis isomers was successfully carried out either by recrystallizations from hexane or by centrifugal liquid chromatography (CLC).

In compounds R′=OR, or CH_3, separation of trans and cis isomers was done by recrystallizations (5—7 times) from hexane to get pure one isomer. The mother liquors were collected and several recrystallizations were further effected to isolate some of the other isomer. In ^{1}H-NMR, these two isomers have different signal patterns of CH_2–S: isomer A with a broad rugged singlet proton signal at δ=2.5—2.9 and isomer B with a broad quintet signal at δ=2.4—3.5 (Table 1).

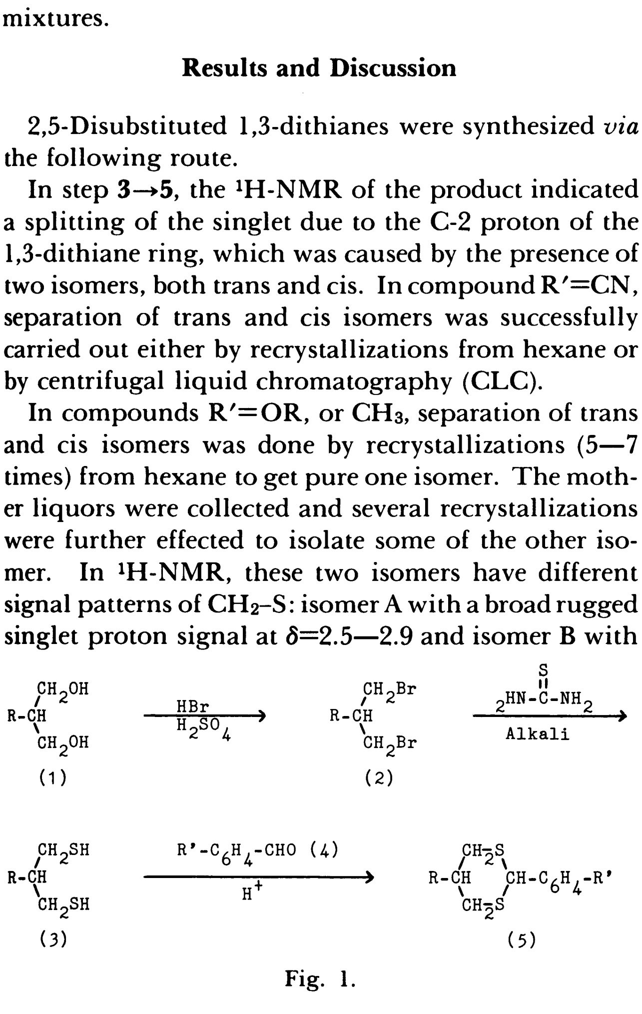


Fig. 1.

The ^{13}C-NMR characteristics of isomeric 2-(*p*-substituted phenyl)-5-alkyl-1,3-dithianes were investigated by means of the ^{1}H-complete decoupling (COM), ^{1}H-off resonance decoupling (OFR), and ^{1}H-selective decoupling (SEL) procedures. As C-2 and C-4, C-6 protons in the 1,3-dithiane ring show peculiar chemical shifts in ^{1}H-NMR, the ^{1}H-selective decoupling method was useful to determine the assignment in ^{13}C-NMR. In compounds R=C_2H_5, R′=CN, the difference in the ^{13}C-NMR chemical shift for the 1,3-dithiane ring carbons between isomers A and B (δ isomer A—δ isomer B) are 0.76 (C2), 1.79 (C4, C6), and 6.39 (C5) (Table 1).

These values indicate that the isomerism occurs at C5 with a large difference ($\Delta\delta$=6.39), and not at C2 ($\Delta\delta$=0.76).

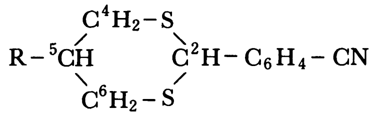
In the ^{13}C-NMR data of 5-alkyl-1,3-dithiane, the C5 signal for 5-equatorial isomer lies at a lower magnetic field than that for 5-axial isomer.[5] Therefore, it is concluded that isomer A is 5-equatorial (trans) and B is 5-axial (cis).

With increasing purity, several trans isomers of this class began to exhibit the monotropic liquid crystal phase under a polarization microscope.[3] As two isomers (cis and trans) are white powder as produced, whereas two raw material compounds (**3**, **4**) are liquid, mixcd isomers are obtained in pure state after about two recrystallizations. At this point the mixture contains about 10% of cis isomer. This mixed isomer did not exhibit any liquid crystal phases. It is generally known that when two different liquid crystalline compounds with the same phase were mixed, the mixture exhibits the liquid crystal phase.[6] Therefore, cis isomer is considered to have no nematic liquid crystalline properties. In addition to this, some separable cis isomers (for example R=C_7H_{15}, R′=OC_2H_5; trans isomer of this compound exhibits the monotropic nematic liquid crystal phase: I 57 N 48 C) also did not exhibit any liquid crystal phases.

This fact supports that the cis isomers generally do not exhibit liquid crystal phases.

TABLE 1. ^{1}H AND ^{13}C-NMR CHEMICAL SHIFTS OF ISOMERIC 2-(*p*-SUBSTITUTED PHENYL)-5-ALKYL-1,3-DITHIANES. ^{13}C-NMR ($CDCl_3$)

Carbon No. (1,3-dithiane ring)	$R=C_2H_5$ Trans	R'=CN Cis	δ trans—δ cis	$R=C_3H_7$ Trans	R'=CN cis	δ trans—δ cis
2	50.77	50.01	0.76	50.77	50.06	0.71
4,6	37.06	35.27	1.79	37.38	35.60	1.78
5	37.22	30.83	6.39	35.22	28.88	6.34
Carbon No. (1,3-dithiane ring)	$R=C_4H_9$ Trans	R'=CN Cis	δ trans—δ cis	$R=C_5H_{11}$ Trans	R'=CN Cis	δ trans—δ cis
2	50.66	49.96	0.70	50.82	50.01	0.81
4,6	37.33	35.60	1.73	37.38	35.49	1.89
5	36.14	29.80	6.34	36.36	30.12	6.34



^{1}H-NMR ($CDCl_3$, δ)

R	R'	Trans	Cis
n-C_5H_{11}	$OC_4H_9^n$	0.7—2.1 (m, R-CH, OCH_2-C_nH_{2n+1}), 2.6—2.9 (m, 4H, CH_2-S), 3.9 (t, 2H, OCH_2), 5.06 (s, 1H, $\begin{smallmatrix}S\\S\end{smallmatrix}\!>$CH-), 6.65—7.5 (q, 4H, ArH)	0.7—2.1 (m, R-CH, OCH_2-C_nH_{2n+1}), 2.5—3.5 (m, 4H, CH_2-S), 3.9 (t, 2H, OCH_2), 5.03(s, 1H, $\begin{smallmatrix}S\\S\end{smallmatrix}\!>$CH-), 6.65—7.5 (m, 4H, ArH)
n-C_7H_{15}	OC_2H_5		
C_2H_5	CN	0.7—2.0 (m, R—CH), 2.6—2.9 (m, 4H, CH_2-S), 5.10 (s, 1H, $\begin{smallmatrix}S\\S\end{smallmatrix}\!>$CH-), 7.60 (s, 4H, ArH)	0.7—2.0 (m, R—CH), 2.4—3.5 (m, 4H, CH_2-S), 5.08 (s, 1H, $\begin{smallmatrix}S\\S\end{smallmatrix}\!>$CH-), 7.65 (s, 4H, ArH)
n-C_3H_7	CN		
n-C_4H_9	CN		
n-C_5H_{11}	CN		

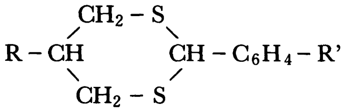


TABLE 2. CONTENTS OF TRANS AND CIS ISOMERS IN THE 2,5-DISUBSTITUTED 1,3-DITHIANES (5) SYNTHESIZED[a]

R	R'	Trans (%)	Cis (%)
n-C_3H_7	CN	51	49
n-C_3H_7	CH_3	78	22
n-C_3H_7	$OC_4H_9^n$	80	20
n-C_5H_{11}	CN	64	36
n-C_5H_{11}	CH_3	78	22
n-C_5H_{11}	$OC_4H_9^n$	83	17

a) Determined gas-chromatographically Column: OV 17, 3m; Oven temp 250°C.

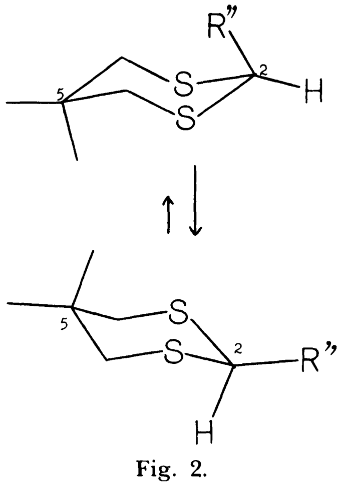


Fig. 2.

The production ratio of cis to trans isomers, as determined by means of gas chromatography (Table 2), seems to depend upon the kind of *p*-substituent (R′) of compounds **5**. In step **3**→**5**, benzaldehyde **4** having the electron-donating substituent (R′), such as the alkyl and alkoxyl groups, produced much more C-5 equatorial isomer (trans) than C-5 axial isomer (cis). On the contrary, **4** with the electron-withdrawing substituent, such as the cyano group, produced both isomers in a nearly equal ratio.

This result is explainable as follows. In step **3**→**5**, possible configurations around C-5 and C-2 are as follows: C-5 Eq C-2 Ax, C-5 Eq C-2 Eq, C-5 Ax C-2 Ax, and C-5 Ax C-2 Eq. (Eq: equatorial, Ax: axial) As the C-2 substituent is the steric hindered *p*-substituted phenyl group, C-2 Ax should be converted to the more stable state C-2 Eq through the next equilibration (Fig. 2).

Namely, C-5 Eq C-2 Ax and C-5 Ax C-2 Ax are converted to C-5 Ax C-2 Eq and C-5 Eq C-2 Eq, respectively. Therefore, C-2 configuration becomes all Eq. and the ratio of trans (C-5 Eq C-2 Eq) to cis (C-5 Ax C-2 Eq) should become nearly equal to unity. Nevertheless, in the 1,3-dithianes with the *p*-electron-donating phenyl group, trans isomers are produced more than cis isomers. In the 1,3-dithianes with the p-electron-donating phenyl group, the backward reaction of cis to trans may occur more readily owing to the reversible nature of the 1,3-dithiane ring formation and the stabilization of the carbocation at C-2 due to

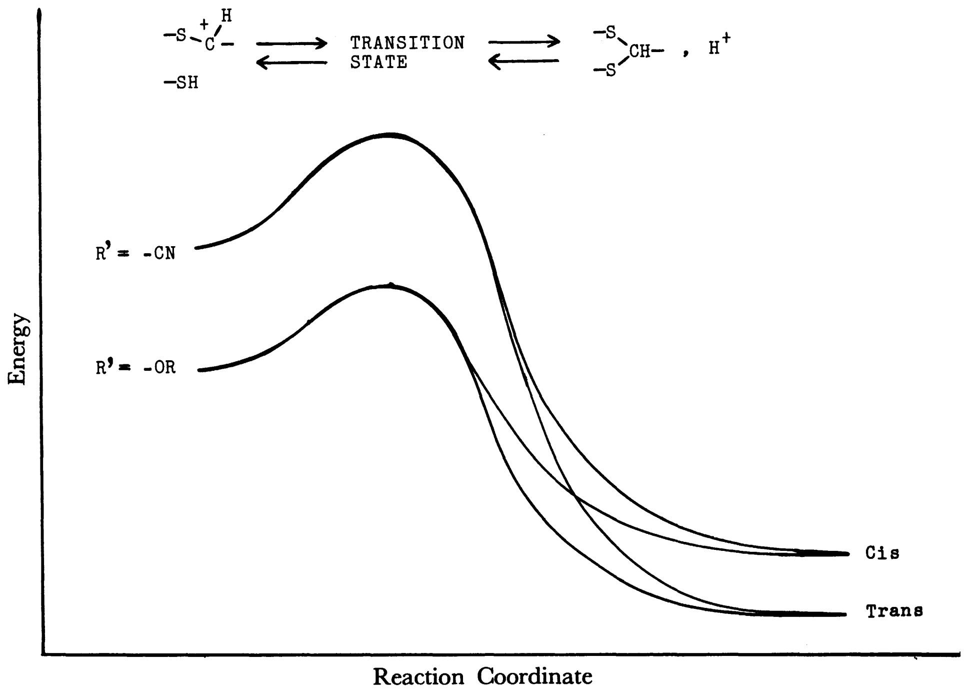
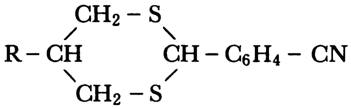


Fig. 3.

TABLE 3. COMPOSITION OF LIQUID CRYSTAL MIXTURE

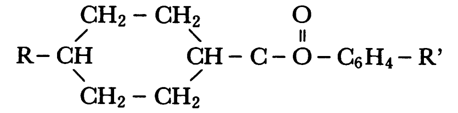


$$R-CH(CH_2-S)_2CH-C_6H_4-CN$$

	Mixture T (trans) mol/%	Mixture C (cis) mol/%
[a]Base mixture	90	90
$R=C_2H_5$	5	5
$R=n\text{-}C_4H_9$	5	5

a) Composition of base liquid crystal mixture (Base mixture)

R	R'	mol/%
$n\text{-}C_3H_7$	OC_2H_5	8.8
$n\text{-}C_3H_7$	$OC_4H_9^n$	20.9
$n\text{-}C_4H_9$	OCH_3	17.9
$n\text{-}C_4H_9$	OC_2H_5	17.2
$n\text{-}C_5H_{11}$	OCH_3	18.7
$C_2H_5-C_6H_4-COO-C_6H_4-CN$		5.5
$C_4H_9^n-C_6H_4-COO-C_6H_4-CN$		5.5
$C_5H_{11}^n-C_6H_4-C_6H_4-C_6H_4-CN$		5.5



$$R-CH(CH_2-CH_2)_2CH-C(=O)-O-C_6H_4-R'$$

the electron -donation by R′ (Fig. 3). Thus, this backward reaction (cis to trans) is equilibrium controlled,[7] energetically more favorable trans isomer will be produced in a higher ratio than cis isomer. In 1,3-dithiane with the *p*-cyanophenyl group, the electron-withdrawing substituent (CN) destabilizes the carbcation at C2, so that the activating energy of the backward reaction is too large to make the reaction thermodynamically-controlled.

Several electro-optic properties of *trans*-and *cis*-2-(*p*-cyanophenyl)-5-alkyl-1,3-dithianes by using them as a dopant of a mixture of liquid crystals were given in Table 4. And the compositions of mixture T (trans) and mixture C (cis) were given in Table 3. Threshold

TABLE 4. ELECTRO-OPTIC AND OTHER RELEVANT PROPERTIES

	Mixture T (trans)	Mixture C (cis)
Threshold voltage (Vth)	1.82 V	1.69 V
Rising time (T_r)	100 m s	84 m s [c]
Decay time (T_d)	70 m s	89 m s
Birefringence (Δn)	0.103	0.090
Dielectric anisotropy ($\Delta\varepsilon$)	+5.37	+4.56
Steepness factor[a]	1.34	1.36
Temperature dependence[b]	0.35%/°C	0.53%/°C

a) Steepness factor=$Vsat/Vth$. b) Temperature dependence=$-1/Vth(dVth/dT)$ Vth: threshold voltage, $Vsat$: saturated voltage c) Von=4 volt, Voff=0 volt.

voltage (Vth), rising time (T_r), decay time (T_d), birefringence (Δn), dielectric anisotropy ($\Delta\varepsilon$), steepness factor and temperature dependence of Vth were measured in mixture T and mixture C respectively.

Threshold voltage (Vth) of mixture C (cis) is smaller than that of mixture T (trans). Generally, Vth is proportional to the square root of $K/\Delta\varepsilon$.[8] (K: elastic constant). In mixture C, axial alkyl chain should weaken the interactions among liquid crystal molecules, so that K of mixture C seems to be smaller than that of mixture T. But $\Delta\varepsilon$ of mixture T is somewhat larger than that of mixture C. The result obtained for Vth must imply that K had larger influence than $\Delta\varepsilon$.

Rising time (T_r) of mixture T is longer than that of mixture C.

Generally, T_r is proportional to $\eta/(\Delta\varepsilon V^2 - K\pi^2)$.[9] Viscosity ($\eta$) of mixture containing 2 mol% of trans isomers (R=C_2H_5, C_4H_9) is 11 cp (25 °C), and that of cis isomers (R=C_2H_5, C_4H_9) is 13 cp. So η of mixture T is somewhat smaller than that of mixture C. Therefore values of viscosity (η) and $\Delta\varepsilon$ are support reverse result of T_r. But K of mixture C seems to be smaller than that of mixture T as written above. The result obtained for T_r must imply that difference of K had larger influence to T_r than differences of $\Delta\varepsilon$ and η. Since decay time (T_d) is proportional to η/K,[9] it is reasonable that the T_d of mixture T having larger K and smaller η is shorter than that of mixture C. In birefrigence (Δn), the value for mixture C is smaller than that for mixture T, so that mixture C must use a somewhat thick cell to gain a sufficient contrast. The facts that $\Delta\varepsilon$ of mixture T is somewhat larger, steepness factor is also superior, and temperature dependence is smaller, indicate that mixture T is superior to mixture C.

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 analyses were carried out with a Perkin-Elmer 250 instrument. Centrifugal liquid chromatography was made with a Hitachi CLC-5 apparatus. Transition temperature and mesomorphic phases 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) and dielectric anisotropy ($\Delta\varepsilon$), and birefringence (Δn) of liquid crystal mixtures were measured using a Tokyo Keiki E type rotating cone viscometer, a Yokokawa Hewlett Packard 4274A multi frequency LCR meter, and a Hitachi 340 spectrometer, respectively.

The measurement of liquid crystal properties are carried out by using 9.4 μm twisted nematic cells to ensure good guiding of the plane of polarization. Syntheses and detailed analytical data of compounds **1**, **2**, **3**, and **5** were written in a previous paper.[3] ^{1}H-NMR and ^{13}C-NMR data of separable cis and trans isomers are in Table 1.

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