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Effect of the Phase Transition of Smectic Liquid-Crystalline Solvent on the Thermal Isomerization of 5,5'-Dialkylthioindigo Compounds

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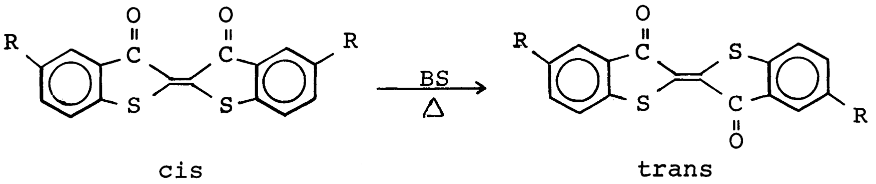
The rates and the activation parameters for the thermal cis-to-trans isomerization of 5,5'-dialkylthioindigo dyes embedded in a smectic mesophase of butyl stearate were affected by the transition of the liquid-crystalline to the isotropic phase, depending upon the alkyl length.

The photochromic behaviour of indigoid dyes in solutions,[1)] polymer films,[2)] multilayers,[3)] liquid crystal[4)] and when adsorbed on solid surfaces[5)] has been extensively investigated as mechanistic probes and photoresponsive media for information. In some cases mesophases do influence the dynamics of reactions of guest molecules.[6)] Studies by Ganapathy, Zimmermann, and Weiss[4)] on the thermal isomerization of N,N'-diacylindigo compounds showed that the large shape change to transform the cis- to the trans-isomer is impeded when acyl chains are incorporated into a smectic layer of butyl stearate (BS).[4)] The examination of the thermal isomerization of guest molecules within a layer and the adjacent layers is useful in exploring the mobility of host molecules. It is therefore of interest to study the kinetics of the isomeric behaviour of rod-like dialkylthioindigo dyes not accompanying so large shape change when embedded in a thermotropic liquid-crystalline phase of BS. BS exhibits an enantiotropic B phase in the temperature range 14 to 27 °C.[4)] In this communication we report some preliminary results on the regulation of the thermal cis-to-trans isomerization of thioindigo (1) and 5,5'-dialkylthioindigo dyes (2-4)[7)] by the use of the phase transition (Tc) from the smectic B phase to the isotropic phase of BS.[8)]

The cis-isomers were prepared by irradiating the isotropic or liquid-crystalline solution of the trans-isomers (3 x 10^{-5}M) with visible light



1 R=H
2 R=C_4H_9
3 R=C_8H_{17}
4 R=$C_{12}H_{25}$

(λ>540 nm). The rate constants of the thermal isomerization were determined spectrophotometrically after irradiation.

The λmax values of the trans- and the cis-isomers of 4 in the smectic phase of BS (25 °C) were 552 nm and 491 nm, respectively, and these values were nearly the same as those found for the other homologues (2 and 3), irrespective of the alkyl length. Similar λmax values were also obtained when these compounds (2–4) were solubilized in benzene.7)

Figure 1 shows the Arrhenius plots for the thermal isomerization of alkylthioindigo dyes (2 and 4) in BS. The reactions of 2 showed first-order kinetics over a temperature range examined (22–50 °C). When 4 with long alkyl chains was employed, the plots were observed to consist of two straight lines, showing a clear break at 27 °C which corresponds to the Tc value of BS.8) In contrast, the reactions carried out in benzene (isotropic phase) revealed no such a break in the Arrhenius plot.

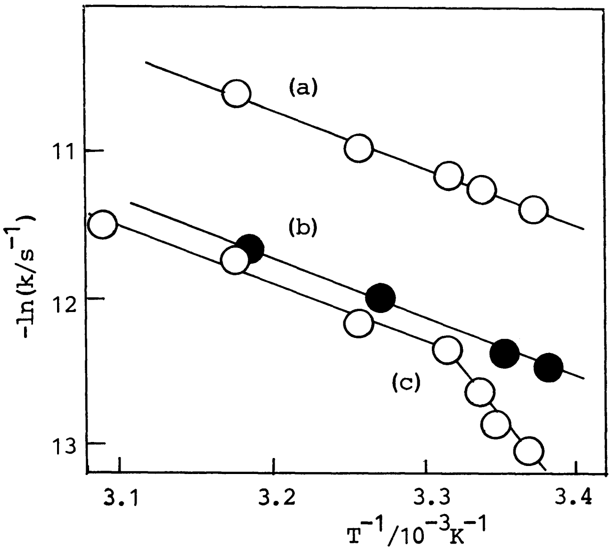


Fig. 1. Plots of -ln k vs. 1/T for thermal isomerization of 5,5'-dialkylthioindigo dyes. (a) 4 in benzene; (b) 2 in BS; (c) 4 in BS.

The kinetic parameters calculated from the plots are summarized in Table 1. The activation parameters of thioindigo dyes in benzene are nearly the same

Table 1. Activation parameters for the thermal cis-to-trans isomerization of 5,5'-dialkylthioindigo dyes

Indigo dyes	Solvent	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}
1	benzene	8.9	-52.5
	BS	9.6	-48.1
2	benzene	8.5	-53.3
	BS	7.9	-58.1
3	benzene	10.0	-50.8
	BS(isotropic phase)	12.3	-41.4
	BS(smectic phase)	34.2	30.0
4	benzene	7.1	-57.3
	BS(isotropic phase)	7.6	-57.8
	BS(smectic phase)	26.4	4.6

(about 10 kcal/mol for $\Delta H^{\ddagger}$ and about -50 cal/K mol for $\Delta S^{\ddagger}$). Even in the isotropic phase of BS, the activation parameters for isomerization cannot be distinguished. These data indicate that alkyl chain lengths play little role in thermal isomerization rates in isotropic solvents. These parameters of 1 and 2 in the smectic phase are in agreement with those in isotropic solvents. However, for thioindigo dyes with long alkyl chains, 3 and 4, there are distinct differences between their parameters in the smectic (26—34 kcal/ mol and 5—30 cal/K mol) and in the isotropic phases (7—12 kcal/mol and -41—-58 cal/ K mol). Such effects on their reactivity are interpreted as rising from the longer alkyl chain behaviour. Figure 2 shows a postulated model for possible solubilization sites of rod-like and ball-like dyes in the smectic liquid-crystalline. The estimated molecular length of 3 or 4, irrespective of the trans- and the cis-isomer, is longer than that of BS.$^{9)}$ The rod-like long chain of the cis-isomer of 3 or 4 can be extended over adjacent layers of smectic BS as a prop and followed by depression of a sliding motion between vicinal layers. Upon isomerization, the long alkyl chain will disturb the smectic order of BS molecules surrouding the dialkylthioindigo dye and will require the extra energy for translocation compared to that in the isotropic phase. As can be seen, the activation enthalpy is higher and the activation entropy is positive and larger in the smectic phase than in the isotropic phase. On the other hand, the isomerization behaviour of 1 and 2 does not influence the activation parameters, as being expected from the assumption that thioindigo dyes with short chains are embedded only in a single layer of the smectic phase. These results show that, although the reactivity in one layer of BS is not influenced owing to soft and labile fluidity of BS molecules, an interlayer cooperation of the BS mesophase influences the thermal isomerization drastically.

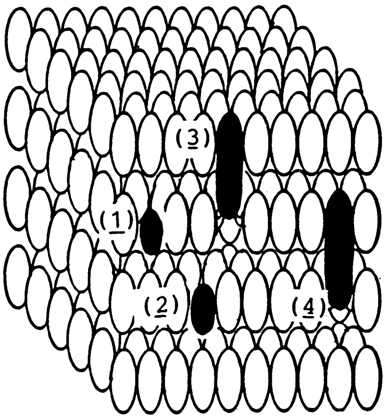


Fig. 2. The postulated model for the possible location of rod-like (3 and 4) and ball-like (1 and 2) thioindigo dyes incorporated into the smectic phase of BS.

In conclusion, it has been demonstrated that the thermotropic smectic B phase of BS functions as an effective medium for regulating the thermal cis-to-trans isomerization of long-chain alkylthioindigo dyes.

References

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7) 5,5'-Dialkylthioindigo dyes (2–4) were synthesized as described previously. See, for example, H. Heier and W. Lüttke, Liebigs Ann. Chem., 1981, 1303.
(2): mp 248–250 °C(233 °C Liebigs Ann. Chem., 1981, 1303); UV λmax (benzene) 556 nm (trans) and 494 nm(cis) ; ^{1}H-NMR(60MHz, $CDCl_3$) δ=1.93(t, 6H, 2×CH_3), 1.14-2.00 (m, 8H, 4×CH_2), 2.57(t, 4H, 2×CH_2-Ar), 6.90-7.83(m, 6H, the aromatic protons) ; HRMS for $C_{24}H_{24}O_2S_2$ m/z 408.1219, found 408.1206.
(3): mp 154-155 °C; UV λmax (benzene) 552 nm(trans) and 496 nm(cis); ^{1}H-NMR (60MHz, $CDCl_3$) δ=0.87(t, 6H, 2×CH_3), 1.05-1.09(m, 24H, 12×CH_2), 2.56(t, 4H, 2×CH_2-Ar), 6.54-7.85(m, 6H, the aromatic protons); HRMS for $C_{32}H_{40}O_2S_2$ m/z 520.2472, found 520.2459.
(4): mp 48-50 °C; UV λmax (benzene) 557 nm(trans) and 500 nm(cis) ; ^{1}H-NMR (60MHz, $CDCl_3$) δ=0.83(t, 6H, 2×CH_3), 0.19-1.87(m, 40H, 20×CH_2), 2.46(br, 4H, 2×CH_2-Ar), 7.20-7.60(m, 6H, the aromatic protons); Anal. Found: C,75.90; H, 8.60%. Calcd for $C_{40}H_{56}O_2S_2$: C, 75.90; H, 8.91%.

8) The smectic-isotropic phase transition-temperature (Tc) of BS was obtained as 26.5 °C by DSC analysis, which was almost identical with the reported value (Ref. 4). Thioindigo dyes (1–4, 3×10^{-5}M) could be added to BS without depression of the transition-temperature.

9) The X-ray determined layer thickness of smectic BS is 31.6 Å (D. Krishnamurti, K. S. Krishnamurthy, R. Shashidar, Mol. Cryst. Liq. Cryst., 8, 339 (1969)), indicating that the long axes of BS molecules are normal to the layer plane. According CPK molecular models, the molecular length of extended trans-1, trans-2, trans-3, trans-4, and a BS molecule was estimated to be 15 Å, 25 Å, 35 Å, 45 Å, and 31 Å, respectively, and similarly those for cis-1, cis-2, cis-3, and cis-4 were 16 Å, 25 Å, 34 Å, and 45 Å, respectively.

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