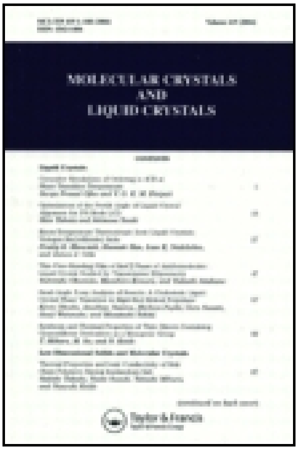

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Liquid Crystalline Solvents as Mechanistic Probes. VII. Investigation of a Photochromic Merocyanine to Indolinospiropyran Isomerization in the Isotropic and Smectic Phases of n-Butyl Stearate and in Polybutadiene Oligomers

Joseph P. Otruba III [a] & Richard G. Weiss [a]
[a] Department of Chemistry, Georgetown University, Washington, D.C., 20057

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Liquid Crystalline Solvents as Mechanistic Probes. VII. Investigation of a Photochromic Merocyanine to Indolinospiropyran Isomerization in the Isotropic and Smectic Phases of *n*-Butyl Stearate and in Polybutadiene Oligomers.[1]

JOSEPH P. OTRUBA III and RICHARD G. WEISS†
Department of Chemistry, Georgetown University, Washington, D.C. 20057

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The unimolecular isomerization of a merocyanine (**t** – **2a**) to an indolinospiropyran, 1′, 3′, 3′-trimethyl-6-nitrospiro [2H-benzopyran-2,2′-indoline] (**1a**), has been followed in the isotropic and smectic liquid crystalline phases of *n*-butyl stearate (*BS*) and in three polybutadiene oligomers (*PB*). The rate constants, k_{-t}, for isomerization in *PB* demonstrate that viscosity is not a factor as long as the solvent chains are mobile. The k_{-t} for all three *PB* fractions (η 13.1-506 cP) at 25°C range only from 1.0–3.6 min^{-1}. Comparison of the activation parameters in the two phases of *BS* ($E_a = 17.4$ kcal mole^{-1} and $\Delta S\ddagger = -9.3$ e.u. in the isotropic phase; $E_a = 38.2$ kcal mole^{-1} and $\Delta S\ddagger \simeq +55$ e.u. in the smectic phase) with each other and with other solvents reveals that polarity considerations, although important, are incapable of explaining the data completely. The effect of solvent order on the activation parameters must be included.

INTRODUCTION

The mechanism responsible for photochromism in indolinospiropyrans (1) such as 1′, 3′, 3′-trimethyl-6-nitrospiro [2H-benzopyran-2,2′-indoline] (**1a**, $R = CH_3$), has been investigated extensively[2] since the pioneering work of Hirshberg and Fischer.[3] It is generally accepted that colored merocyanines

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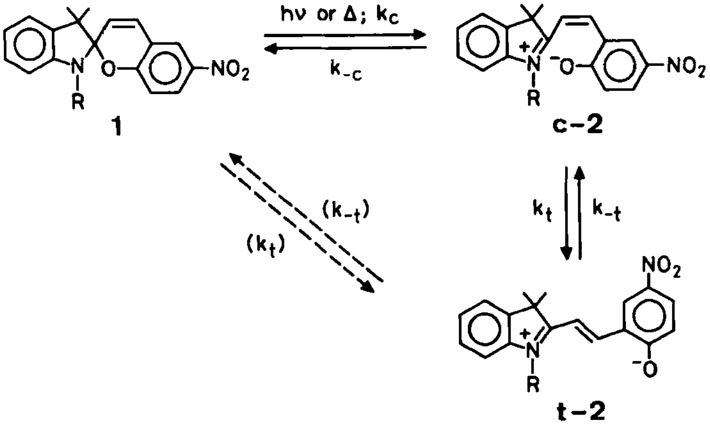
† To whom correspondence should be addressed.



SCHEME 1

(c — **2** and t — **2**) are formed upon irradiation or heating of **1**[2,4] (Scheme 1).[5] The rate of thermal fading of the coloration, indicative of the reversion of **2** to **1**, can frequently be separated into slow and fast first-order components. These are taken to represent the t — **2** → **1** and c — **2** → **1** processes, respectively.

Although the effect of solvent polarity and solute concentration on the rates for **2** → **1** are understood reasonably well, the dependence on solvent order and viscosity are still matters of controversy.[6,7] As a means of separating and examining these two variables, we have followed the **2a** → **1a** slow fading rate over a temperature range spanning the smectic and isotropic phase of a liquid-crystalline solvent, *n*-butyl stearate (*BS*)[8] and in three polybutadiene oligomers (*PB* 500, *PB* 1000, and *PB* 2500) of well-characterized molecular weights.

RESULTS AND DISCUSSION

Molecularity of the isomerization. Our efforts have been directed toward an understanding of the *unimolecular* isomerization of **2** → **1**. Conditions under which multimolecular processes do not contribute significantly were established experimentally since aggregation involving **1** and promoted by **2** does occur in even dilute saturated hydrocarbon solutions.[9] The complexation is not detected in very dilute solutions of slightly more polar solvents, like toluene,[10] and is unimportant in polar solvents at $<10^{-3}$ *M* solute concentrations.[4]

The data in Table I establish that the concentration dependence on the rate constant for color fading of t — **2a** in *BS* is very small. As expected, the rate plots indicate that two *consecutive* first-order decay components are present.

TABLE I

Run	Solvent	Temperature (°C)	[**1a**] *M*	k_{-t} (min^{-1})
1	Polybutadiene 500	25	1.59×10^{-5}	1.28
2		25	1.59×10^{-5}	1.23
3		25	0.92×10^{-5}	1.35
4		25	0.92×10^{-5}	1.41
1	Polybutadiene 1000	25	1.22×10^{-5}	3.15
2		25	1.22×10^{-5}	3.60
3		25	1.22×10^{-5}	3.52
4		25	1.14×10^{-5}	2.74
5		25	1.14×10^{-5}	2.69
1	Polybutadiene 2500	25	1.27×10^{-5}	1.10
2		25	1.27×10^{-5}	1.09
3		25	1.18×10^{-5}	1.04
4		25	1.18×10^{-5}	1.00
1	*n*-butyl stearate (isotropic)	30	1.06×10^{-5}	1.70
2		30	1.06×10^{-5}	1.72
3		30	1.17×10^{-3}	2.64
4		30	1.17×10^{-3}	2.77
5		30	2.69×10^{-3}	2.91
6		30	2.69×10^{-3}	3.18
7		30	5.48×10^{-3}	2.98
8		30	5.48×10^{-3}	3.23
9		30	1.05×10^{-2}	3.10
10		30	1.05×10^{-2}	3.21

[a] Hanovia 450 W medium-pressure Hg arc filtered through Pyrex and Corning filter #CS 754 ($\lambda = 300 - 410$ nm); ca. 10 sec. irradiation time.

Two *concurrent* processes of different molecularity do not appear to be responsible for the slow process since the data can be fit to first-order kinetic expressions over several half-lives. If the observed rate constants were pseudo n-order (i.e., $k_{-t} = k[\mathbf{1a}]^n$), the slope of a log-log plot of k_{-t} versus **1a** concentration would have a slope equal to n. The actual plot is not completely linear and, if forced, approximates an $n \simeq 0.1$. Both the magnitude of n and the lack of linearity indicate that this form of the rate constant is inappropriate.

This argument, alone, does not eliminate the possibility that complexes are involved. If the slow process represents the disappearance of a complex (or complexes) between **2a** and an unspecified number of **1a**, first-order kinetics are possible provided the mechanism in Scheme 2 applies, $k_1[\mathbf{2a}]$ and $k_n[\mathbf{1a}]^n[\mathbf{2a}]$ are much greater than $k_{cn}[C_n]$, and k_n and k_{cn} are approximately invariant with respect to the number of **1a** molecules present. Evidence against Scheme 2 for dilute *BS* solutions of **1a** is found in isomerization studies of **2** appended to polymethylmethacrylate chains.[6,11] Even though migration of **1** and **2** is prohibited beyond the motion of the polymer chains (and, therefore, aggregation after irradiation is unlikely), the rate constants for **2** → **1** are similar to those found in the smectic phase of *BS*.

A further complication introduced by large concentrations of **2a** or other photoproducts[12] has been avoided by irradiating **1a** for very short periods.

SCHEME 2

$$\mathbf{2} \xrightarrow{k_1} \mathbf{1} \qquad (1)$$

$$n\mathbf{1} + \mathbf{2} \xrightarrow{k_n} C_n \qquad (2)$$

$$C_n \xrightarrow{k_{cn}} (n+1)\mathbf{1} \qquad (3)$$

Scheme 2 does not describe the **2a** → **1a** isomerization in solutions of the polybutadiene oligomers, also. That the isomerization rate constants are independent of viscosity (Tables I and II) and, therefore, diffusion can be reconciled with Scheme 2 only if the k_n are extremely rapid with respect to (the approximately viscosity independent) k_1. Given the large range of viscosities spanned, this possibility is unlikely. The alternative, that complexation between **1a** molecules occur in the dark and C_n be formed upon irradiation, again predicts that the **2a** → **1a** isomerization will be pseudo first-order in **2a**. In this case, Eq. 2 is replaced by Eqs. 4 and 5. If C'_n complexes are formed, their presence has eluded our efforts to detect them: no new absorptions to the red of the accepted spectrum of monomeric **1a** ($\lesssim 10^{-3}$M) has been observed in *BS* or the polybutadiene oligomers.

$$n\mathbf{1} \xrightarrow{k'_n} C'_n \qquad (4)$$

$$C'_n \xrightarrow{h\nu} C_n \qquad (5)$$

For these reasons, we conclude that the dominant mechanism for the isomerizations reported here are unimolecular. Analyses of the data suppose this condition.

The kinetic model. A number of simplifications of a kinetic model based upon Scheme 1 can be made. In nonhydroxylic solvents like *BS* and *PB*, $k_c \ll k_{-c}$ and $k_t \ll k_{-t}$ since very little merocyanine color is detectable at equilibrium in the dark.[4] Also, the appearance of slow and fast rates of formation of **1a** from **2a** is compatible with $k_{-c} \gg k_{-t}$. Using these conditions and Scheme 1, the thermal formation of **1a** can be represented by Eqs. 6 and 7.

$$c-\mathbf{2a} \xrightarrow{k_{-c}} \mathbf{1a} \qquad (6)$$

$$t-\mathbf{2a} \xrightarrow{k_{-t}} \mathbf{1a} \qquad (7)$$

Since the visible absorptions of c − **2a** and t − **2a** overlap, the disappearance of optical density (O.D.) results from contributions of Eqs. 6 and 7. At any time, therefore, the concentration of **1a** is given by Eq. 8 (where $\mathbf{1a}_\infty$ is the final concentration of **1a** and $[c-\mathbf{2a}]_0$ and $[t-\mathbf{2a}]_0$ are the initial concentrations of **2a**. From this expression, the rate of change in **1a** is given by Eq. 9. Since $k_{-c} \gg k_{-t}$ at late times (where the directly formed **c** — **2a** has been expended), Eq. 9 simplifies to Eq. 10 and, therefore, Eq. 11. The linear late-time slope of a plot of ln $[O.D._t - O.D._\infty]$ versus time yields $-k_{-t}$. Extrapolation of this slope to zero-time allows the components from Eqs. 6 and 7 to be separated and k_{-c} to be calculated. In some cases, the fast component decays too rapidly to be detected by our methods and only one linear slope is obtained. Even when detected, the fast component usually could not be determined very accurately. Only the later components (k_{-t}) are discussed here (Table I).

$$\mathbf{1a}_\infty - \mathbf{1a} = [\mathbf{c} - \mathbf{2a}]_0 e^{-k_{-c}t} + [\mathbf{t} - \mathbf{2a}]_0 e^{-k_{-t}t} \tag{8}$$

$$\frac{d(\ln[\mathbf{1a}_\infty - \mathbf{1a}])}{dt} = -\left\{\frac{[\mathbf{c} - \mathbf{2a}]_0 k_{-c} e^{-k_{-c}t} + [\mathbf{t} - \mathbf{2a}]_0 k_{-t} e^{-k_{-t}t}}{[\mathbf{c} - \mathbf{2a}]_0 e^{-k_{-c}t} + [\mathbf{t} - \mathbf{2a}]_0 e^{-k_{-t}t}}\right\} \tag{9}$$

$$\left\{\frac{d(\ln[\mathbf{1a}_\infty - \mathbf{1a}])}{dt}\right\}_{t=\text{late}} = -k_{-t} \tag{10}$$

$$\ln([\mathbf{t} - \mathbf{2a}]/[\mathbf{t} - \mathbf{2a}]_0) = -k_{-t}t \tag{11}$$

Reproducibility of the data associated with the late-time process (k_{-t}) was possible only when the samples were prepared under nitrogen (and then sometimes with difficulty; *vide infra*). Moisture appears to be the interfering species since bubbling dry oxygen through one *BS* solution of **1a** and dry nitrogen through another prior to irradiation led to indistinguishable kinetics for **2a** disappearance.[13] Representative rate plots of data are collected in Figures 1a and 1b. The k_{-t} from these were employed to calculate Arrhenius activation energies and pre-exponential factors in Table II and Figure 2.

Properties of solvents. The *PB* oligomers exhibit extremely narrow molecular weight distributions. Their dielectric constants are assumed to be approximately equal to an unconjugated alkene (1-pentene) with a similar olefinic to aliphatic proton ratio and to a higher molecular weight butadiene polymer (Table III). Solvent polarity is extremely important in determining the rates and mechanism of **2** → **1** isomerizations.[2,4] As mentioned previously, **2a**-containing aggregates form in saturated hydrocarbon solvents (hexane, isopentane, and methylcyclohexane; $\epsilon \sim 1.9$), but not in toluene ($\epsilon \sim 2.4$).[10] Based upon the similarity of the dielectric constants for these solvents, it was concluded that another solvent property, like polarizability, or **2a** interactions with individual unsaturated groups on solvent molecules must be responsible for the mechanistic difference.

Since the *PB* oligomers are conformationally labile, randomly oriented and of very similar dielectric constants, the major difference sensed by an isomerizing solute molecule of **2a** ought to be due to viscosity. The large range of viscosities spanned by the oligomers indicate that they should mediate *diffusional*

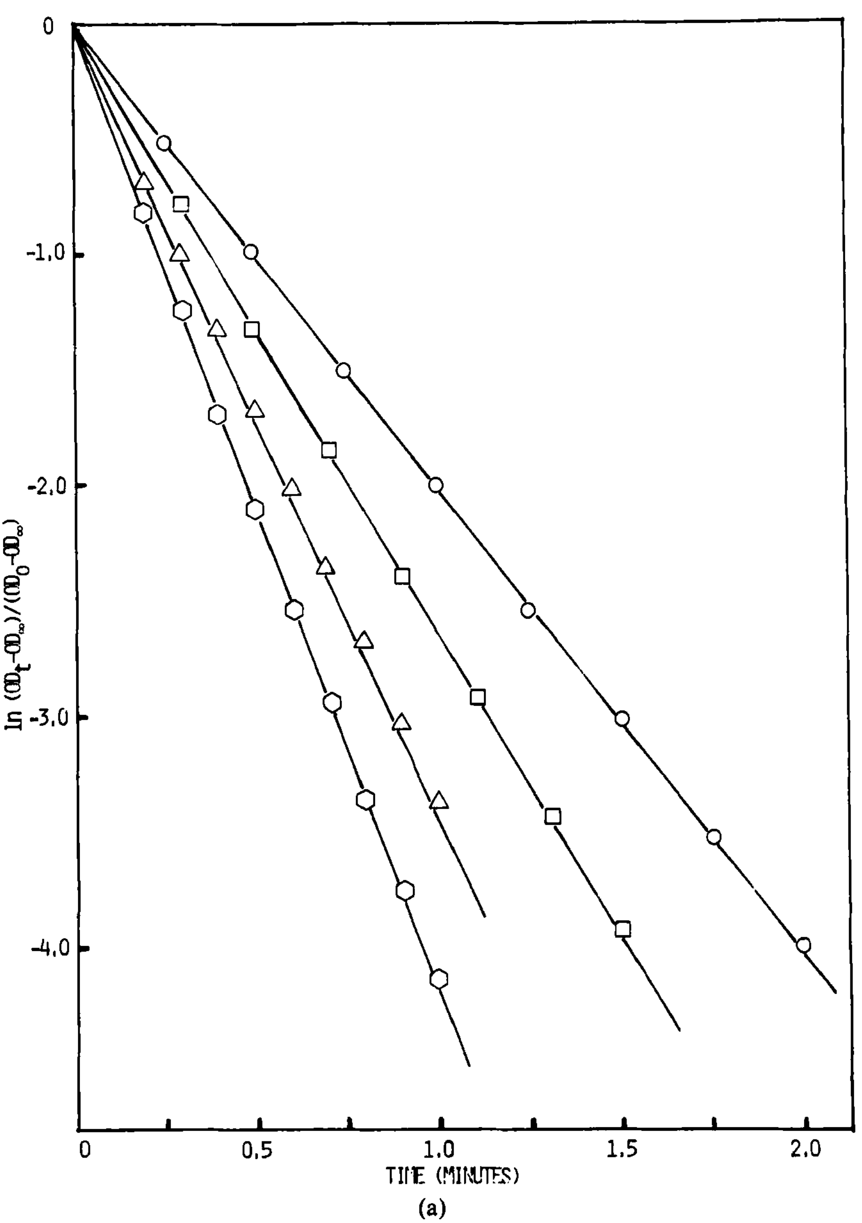
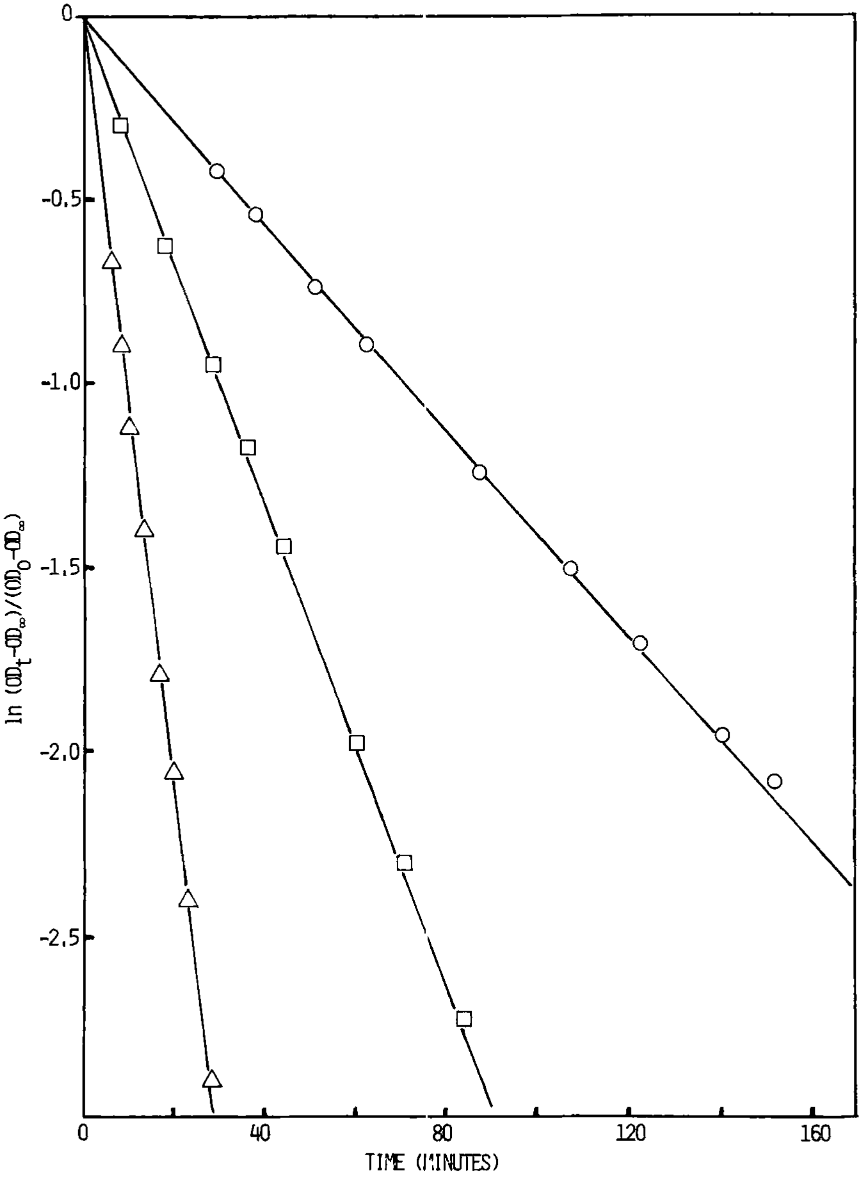


FIGURE 1 Representative plots for the thermal isomerization of **t** — **2a** in *n*-butyl stearate: a) isotropic phase at 27.25°C (○), 30.0°C (□), 32.25°C (Δ), and 34.5°C (⬡) and initial concentration of **1a** = $1.17 \times 10^{-3} M$; b) smectic phase at 16°C (○), 20°C (□), and 25°C (Δ) and initial concentration of **1a** = $1 \times 10^{-3} M$.


0
-0,5
-1,0
-1,5
-2,0
-2,5
ln (OD$_t$-OD$_\infty$)/(OD$_0$-OD$_\infty$)
0
40
80
120
160
TIME (MINUTES)

(b)

TABLE II

Solvent	[1]	E_a (kcal/mole)	A (sec^{-1})	$\Delta S\ddagger$ (e.u.)	Source
PB 500	10^{-5} *M*	17(±1)	$1(\pm1) \times 10^{11}$	−11(±2)	this work
polystyrene	2% (w/w)	17.6	1×10^{10}	−14.6	Ref. 11a
BS	10^{-3} *M*				
smectic phase		38(±2)	$2(\pm6) \times 10^{25}$	+55(±7)	this work
isotropic phase		17(±1)	$2(\pm2) \times 10^{13}$	−9(±2)	this work
polymethylmethacrylate	2% (w/w)	24.4	5×10^{14}	+3.9	Ref. 11a
polyisobutylmethacrylate					
copolymer	2.6% (w/w)				Ref. 11a
below glass-transition		15.1	5×10^{7}	−25.5	
above glass-transition		32.3	8×10^{18}	+25.8	
ethyl acetate		27.4	5×10^{14}		Ref. 2, p. 182

processes quite differently. The lack of significant change in the k_{-t} for the three fractions supports further a unimolecular mechanism for the isomerization.

The solvent properties of *BS* are phase dependent: a well-defined smectic phase obtains below 25.0°C and extends to 13.5°C; another, less well-defined phase has been reported to ca. 11°C.[8] The transition temperatures observed in the presence of 10^{-3} *M* **1a** are 25.0°, 14.0°, and ca. 12°C.

A smectic phase, in general, exhibits molecular order in which the long axes of the rod-like constituent molecules are aligned parallel to one another and approximately perpendicular to the plane of the layers.[14] On the basis of shape alone, a bulky solute like **1a** will disturb the smectic order to a much greater extent than the planar isomers **2a**. The **t — 2a**, especially, should fit reasonably well into the smectic phase since it can adopt an extended conformation similar in shape to the rod-like solvent molecules.

Thus, it is expected that two major effects-steric and electrostatic-will contribute to the overall (**2a** → **1a**) isomerization rates in the smectic phase of *BS* while the electrostatic effect will dominate in the isotropic phase. Recently, the **2a** → **1a** isomerization has been followed by Kobayashi[7] in a nematic liquid-crystalline phase of 4-cyano-4′-*n*-pentylbiphenyl. Based upon the similarity of the rates in this phase and in ethanol, it was concluded that the environments experienced by **2** are similar in the two solvents, and the rate of isomerization is determined by solvent polarity, alone.

The Isomerization in Ordered and Viscous Media. The isomerization of **t — 2** to **1** involves a very large reorganization of atoms and electrons. Regardless of the conformation adopted by **t — 2**, reformation of the spiropyran ring (directly or through **c — 2**) requires that the nitrophenoxy rotate out of the plane defined by the indolino group as **t — 2** → **c — 2** (or **t — 2** → **1** directly) and

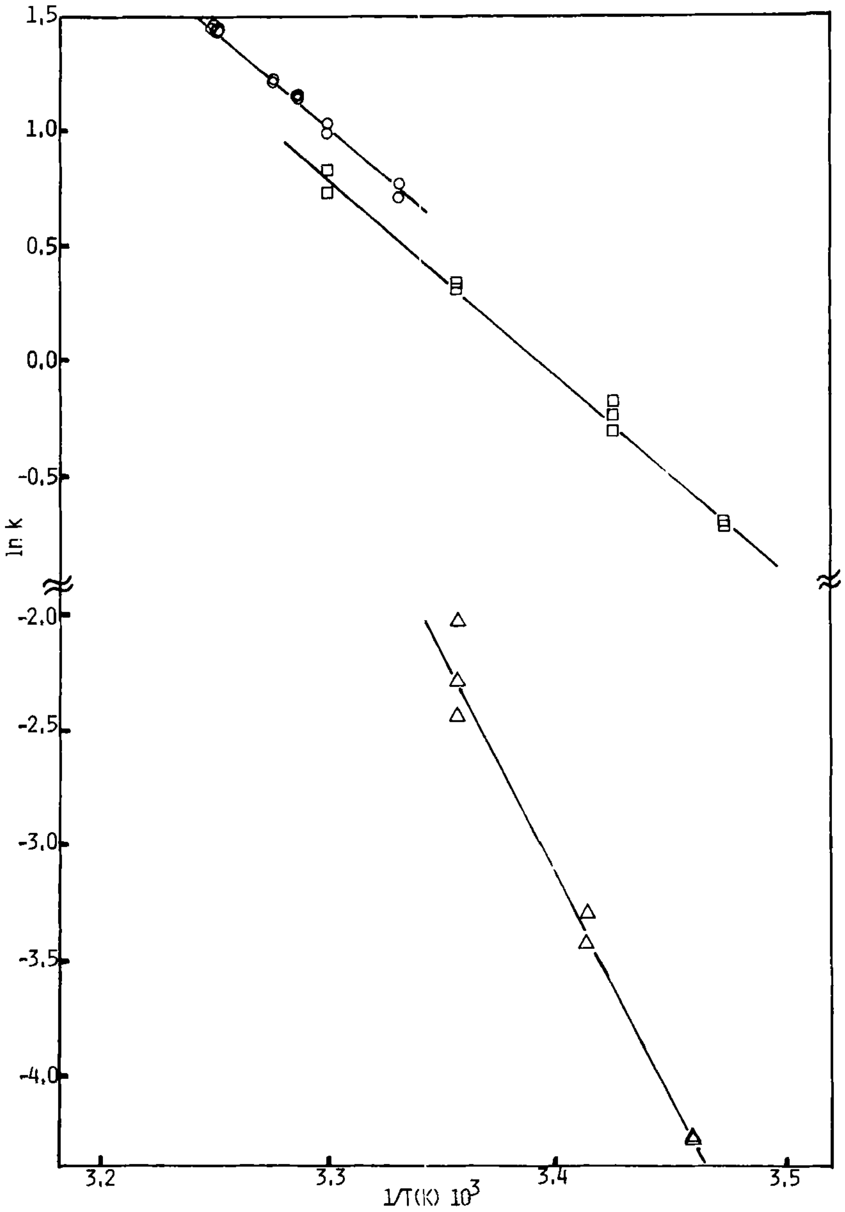


FIGURE 2 Arrhenius plots for the thermal isomerization of **t** — **2a** in *PB* 500 (□), isotropic *BS* (○), and smectic *BS* (△).

TABLE III

	viscosity[a] η(cp)(°C)	proton ratio[b] aliphatic/olefinic	dielectric constant ϵ(°C)	density (°C) ρ(g/ml)
PB 500	13.1 (25°)	2.4/1		0.82 (25°)
PB 1000	87.5 (25°)	2.3/1		0.91 (25°)
PB 2500	506 (25°)	2.1/1		0.92 (25°)
1-pentene		2.3/1	2.10 (20°)[c]	
1,4-transpolybutadiene			2.51 (25°)[d]	
BS	8.0 (27°)			
	7.3 (30°)		3.11 (30°)[e]	0.855 (30°)
	6.4 (34.7°)			

[a] Dodecane (η = 1.35 cp[23]) as standard. Less precise values employing undried glycerin (η = 954 cp[23]) as reference are 14.8, 98.3, and 569 cp for the polybutadienes and 9.0, 8.2, and 7.2 cp for *BS* at the 3 temperatures.

[b] From proton magnetic resonance spectra ($CDCl_3$): olefinic region 4.7–6.2 δ; aliphatic region 0.5–2.7 δ.

[c] M. V. Dover, *Ind. Eng. Chem.*, **27**, 455 (1935).

[d] M. Pegoraro and K. Mitoraj, *Makromol. Chem.*, **61**, 132 (1963).

[e] Ref. 23, pp. E-57 and -58.

then adopt a fixed position perpendicular to the plane upon formation of the C-O spiro linkage. Even the most economical motion from **t** − **2** to **1** would create severe constraints upon an ordered or glass-like solvent. Manifestations of this shape change have been detected by comparing the **2a** → **1a** rates in polystyrene and polyisobutylene[13] with those in saturated hydrocarbon solvents and from pressure curves in monolayers doped with an indolinospiropyran.[15]

However, our results in *PB* solutions demonstrate that the solvent matrix must be very rigid in order to detect this effect: from the lack of significant variation in k_{-t} over the large span of viscosities encompassed by the *PB* oligomers, we conclude that torsional drag along the **t** − **2a** → **1a** reaction coordinate is not important as long as the individual polymer chains are fluid. Only when chain motion near the isomerizing solute is frozen, as in the case of polymeric glasses, will the isomerization rates be affected. This point can be demonstrated by comparing the rate constants at 30°C for isomerization of **2b** to **1b** [$R = (CH_2)_2O_2CCH(CH_3)_2$] in rigid polymethylmethacrylate (ca. 0.02 min^{-1})[11a] and the more fluid smectic phase of *BS* (ca. 0.14 min^{-1}).[16] Of course, changes in other phase-dependent parameters (e.g., specific volumes and specific heats) will affect the isomerization to a certain extent as well. The data, *in toto*, indicate that chain mobility is the major factor.

A cursory examination of parameters in Table II and rate constants in Table I is sufficient to convince one that neither polarity nor viscosity, alone, can explain the rate trends. As mentioned previously, the **t** − **2a** to **1a** isomerization proceeds at almost the same rate in all three *PB* oligomers. Whereas *BS* has a higher E_a and more positive $\Delta S\ddagger$ for **2** → **1** in its (more viscous) smectic phase than in its isotropic phase, a **2c**[$R = -(CH_2)_2NHCOC(CH_3) = CH_2$]-polyisobutylmethacrylate copolymer exhibits the higher activation energy and more positive activation entropy in its *less* viscous phase.[11a] High E_a and $\Delta S\ddagger$ are found typically in isotropic solvents of high polarity, while lower E_a and more negative $\Delta S\ddagger$ are associated with nonpolar media.[4] In fact, the activation parameters listed in Table II for **2b** in polystyrene[11a] and **2a** in *PB* 500 are very close to those reported for benzene and carbon tetrachloride.[4] The activation parameters in the more polar carboxy-containing solvents in Table II do not follow a clean polarity trend. Although ethyl acetate and polymethylmethacrylate seem like polar solvents, the isotropic phase of *BS* does not. Instead it behaves similarly to a non-polar solvent or a polar one in which the functional groups have difficulty in interacting with the centers of merocyanine charge.[17] The negative entropy of activation in this case can be ascribed to solute structural changes; the atoms in the transition state are expected to be more ordered than in **t** − **2a**. If, as has been suggested, carboxy-**2** interactions are responsible for the large E_a and very positive $\Delta S\ddagger$ above the glass transition temperature of polyisobutylmethacrylate,[11a,17] we would have expected a similar phenomenon with isotropic *BS*. That the activation parameters are very different suggests that the carboxy groups experience difficulty in interacting with **t** − **2a**: the long alkyl chains may prohibit strong solvation from occurring. If carboxy groups were tightly held about the centers of charge in **t** − **2a**, their partial release on passing to the less polar transition state for isomerization to **1** (or **c** − **2a**) would add a positive component to $\Delta S\ddagger$.

Interpretation of results in smectic *BS* must be done with caution. Although $\Delta S\ddagger$ is clearly large and positive, it has not been determined as accurately as the other activation entropies in this work. Different batches of *BS*, prepared and purified according to seemingly identical recipes, yielded Arrhenius plots with very similar slopes (and therefore E_a) but widely differing intercepts. The $\Delta S\ddagger$ in Table II are from the batch of solvent which yielded the *fastest* rates: since polar groups retard the **t** − **2a** → **1a** rate,[2,4,11a] it is assumed that the purest *BS* is that for which the solvent is least polar and the isomerization most rapid.[18]

The very high E_a and very positive $\Delta S\ddagger$ in smectic *BS* indicate that the smectic order retards isomerization and that disorder in the system increases as **t** − **2a** passes to its rate-limiting transition state. From the results in isotropic *BS*, it is unlikely that the smectic activation parameters can be reconciled with a model in which carboxy solvation of **t** − **2a** is important *unless* the *BS* conformations in the smectic phase hold the carboxy groups exposed for interaction with **t** − **2a**.

As mentioned previously, **t** − **2a**, especially, should be able to adopt extended conformations which make it similar in shape to the constituent molecules of the smectic phase. Once "incorporated" into the smectic matrix, **t − 2a** would be retarded from closing to the more globular **1a** since the order of nearby solvent molecules would be severely disturbed. A late transition state, especially, ought to result in large increases in the solvent's contribution to ΔS‡. The energy required for an isomerizing **t − 2a** to move nearby *BS* molecules from their preferred locations is not known. However, it is unreasonable that this energy should be sufficient to explain the difference between the E_a's in the smectic and isotropic phases. If, as suggested, the smectic *BS* conformations are appropriate for interaction with **t − 2a**, their release upon isomerization would also contribute to the large E_a and positive ΔS‡. Although the arguments presented are largely qualitative, it is clear that perturbation of solvent order is manifested in the activation parameters for the **t − 2a → 1a** isomerization and polarity arguments alone are insufficient to explain the rates of isomerization in smectic *BS*.[19]

EXPERIMENTAL

Ultraviolet-visible spectra were recorded on a Perkin-Elmer 552 spectrophotometer. Melting points were obtained on a Kofler hot-stage apparatus and are corrected.

1′,3′,3′-Trimethylspiro-6-nitro-[2H-benzopyran-2,2′-indoline] was synthesized by the method of Hinnen, Audic and Gautron[20] in 62% yield, recrystallized from absolute ethanol, mp 178.5 −179°C (lit.:[20] 180°C). *n*-Butyl stearate was synthesized and purified as described previously,[21] bp 161°C/0.07 mm (lit.:[22] 223°C/25 mm). It exhibits an enantiotropic smectic phase 13.5 −25°C (lit.:[8] 15 −26.1°C). The polybutadiene oligomers (Pressure Chemical Co.) were kept refrigerated in the dark and chromatographed on alumina (Baker) before use. Their physical properties are listed in Table IV. Densities were measured by weighing solvents in volumetric flasks. Viscosities were determined with a micro Ostwald viscometer (volume ca. 1 ml) immersed in a thermostatting bath (±0.1°C) using dodecane ($\eta^{25°C} = 1.35$ cp[23]) and glycerin ($\eta^{25°C} = 954$ cp[23]) as reference materials. An average of at least two determinations were made for each compound.

Kinetics. Samples were prepared by dissolving a known amount of **1a** in dry diethyl ether and pipetting an aliquot into a 1 ml ampoule. After evaporating the ether carefully under vacuum, polybutadiene or *n*-butyl stearate was added under dry nitrogen to obtain the correct concentration. Thermostatted cell holders maintained the temperature (±0.3°C) of isotropic solutions in 1 cm quartz cuvettes and smectic solutions held between 2.5 cm diameter coated quartz discs[21] separated by a 0.050 mm Teflon spacer. Irradiations were performed using a 450 watt Hanovia medium-pressure Hg lamp in a quartz water-jacketed well. Pyrex and Corning CS 754 filters were used to iso-

TABLE IV

Physical constants of polybutadiene oligomers[a]

	M_n[b]	M_w/M_n[c]	$[\eta]$,[d] (dl/g)
PB 500	420	1.17	0.0296
PB 1000	960	1.07	0.0517
PB 2500	2350	1.13	0.1013

[a] Data supplied by Pressure Chemical Co.
[b] Number-average molecular weight by vapor pressure osmometry.
[c] Heterogeneity Index where M_w is weight-average molecular weight.
[d] Specific viscosity in toluene at 30°C.

late light from ca. 300–410 nm. The isotropic samples were irradiated for ca. 15 seconds and the smectic samples for ca. 75 seconds. Decoloration of the irradiated solutions was followed at 600 nm (polybutadiene) and 570 nm (*n*-butyl stearate).

CONCLUSIONS

The unimolecular rate of **t** — **2a** → **1a** is independent of solvent viscosity in a non-polar, isotropic set of *PB* oligomers. Although polarity is an extremely important factor in these isomerizations, it, alone, cannot explain the magnitudes of the activation parameters observed in ordered and immobile solvents. The ability of the solutes to fit within the solvent matrix must be considered, also.

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5. Other zwitterionic and valence bond resonance structures contribute to an accurate electronic picture of **2**. Regardless of which dominates, **2** is much more polar than **1** and exhibits the dipolar characteristics expected from the forms displayed in Scheme 1.

   An alternate mechanism for **t** — **2** → **1** circumvents **c** — **2**. Were this to occur, k_t and k_{-t} would refer to a direct **t** — **2** → **1** interconversion. The discussion which follows in this paper applies regardless of the mechanism followed. Scheme 1 is assumed.

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19. The macroscopic orders of smectic and nematic phases are similar in many respects.[14] The major difference is that the constituent smectic molecules lie, on average, parallel to each other and in layers while the nematic molecules lie along the same axis but are not ordered further with respect to one another. Therefore, we doubt that, as has been proposed,[7] the rate of **t** – **2a** → **1a** isomerization in the nematic phase of 4-cyano-4'-*n*-pentylbiphenyl can be explained on the basis of solvent polarity, alone.
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