Dimethyl [3-(*tert*-Butylacetoxy)-3-methyl-2-oxobutyl]-phosphonate (24). (General Procedure for Preparation of (Acyloxy)ketophosphonates from Siloxyketophosphonates.)[13] *tert*-Butylacetyl chloride (0.45 g, 3.7 mmol) was added dropwise to a stirred solution of siloxyphosphonate **22** (1 g, 3.08 mmol) and $FeCl_3$ (0.08 g, 5 mmol) in anhydrous CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred for 2 h at 0 °C and then allowed to warm slowly to room temperature. After being stirred overnight, the resulting mixture was diluted with $CHCl_3$ (50 mL), washed with 1 M HCl (3 × 30 mL), saturated $NaHCO_3$ (3 × 30 mL), and brine (30 mL), and then dried over $MgSO_4$. After concentration in vacuo, purification by flash chromatography (50% EtOAc, 50% hexane) afforded compound **24** (775 mg, 80%), identical with the material prepared above on the basis of TLC, GC, NMR, and MS comparisons.

2,2-Dimethyl-5-(1,1-dimethylethyl)-3(2*H*)-furanone (34).[6] **(General Procedure for Condensation Reaction.)** The (trimethylacetoxy)phosphonate **27** (260 mg, 0.885 mmol) in anhydrous DMF (5 mL) was added via syringe to a stirred suspension of potassium carbonate (175 mg, 1.25 mmol) in anhydrous DMF (15 mL). The mixture was stirred at room temperature for 1 h and then heated at 110 °C overnight. Quantitative conversion to the product was indicated by GC. The reaction mixture was diluted with 100 mL of water and extracted with pentane (3 × 25 mL). The organic layer was washed with water (50 mL) and brine (25 mL) and then dried ($MgSO_4$). Concentration in vacuo, followed by purification by flash chromatography (80% pentane, 20% Et_2O), afforded compound **34**[6] (98 mg, 65%) as needlelike crystals: mp 50–52 °C. (For spectral data, see Table I.)

Diethyl [3-(Triethylsiloxy)-1,3-dimethyl-2-oxobutyl]-phosphonate (30). A solution of LDA (56.8 mmol, generated from 7.95 mL of diisopropylamine and 35.4 mL of 1.60 M *n*-BuLi in 45 mL of anhydrous THF) was stirred at 0 °C for 10 min and then cooled to −78 °C. Diethyl ethylphosphonate (8.58 g, 51.70 mmol) was added, and the resulting solution was stirred at −78 °C for 1 h. The solution was then transferred via stainless steel canula to a solution of the silylated methyl ester **20** (3.0 g, 12.90 mmol) in THF (8 mL). After being stirred at −78 °C for 2 h, the solution was allowed to warm to room temperature. Following concentration in vacuo, and purification by flash chromatography (75% EtOAc, 25% hexane), compound **30** (2.94 g, 62.4%) was obtained as a colorless oil. (For spectral data, see Table I.)

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Registry No. **7**, 115-22-0; **11**, 93827-97-5; **12**, 93827-98-6; **12** (silyl ether), 102307-25-5; **13**, 93827-99-7; **14**, 93828-00-3; **15**, 93828-01-4; **16**, 93828-02-5; **17**, 102307-26-6; **18**, 10250-48-3; **19**, 2110-78-3; **20**, 102307-27-7; **21**, 756-79-6; **22**, 102307-28-8; **23**, 65378-72-5; **24**, 102307-29-9; **25**, 102307-31-3; **26**, 102307-32-4; **27**, 102307-33-5; **28**, 102307-34-6; **30**, 102307-30-2; **31**, 102307-35-7; **32**, 94815-47-1; **33**, 102307-36-8; **34**, 76777-48-5; **35**, 493-71-0; **36**, 102307-37-9; $(CH_3)_3CCH_2COCl$, 7065-46-5; $(CH_3)_2CHCH_2COCl$, 108-12-3; $C_9H_{19}COCl$, 112-13-0; $(CH_3)CCOCl$, 3282-30-2; C_6H_5COCl, 98-88-4; *N*-(*tert*-butylacetyl)imidazole, 4122-55-8.

Liquid-Crystalline Solvents as Mechanistic Probes. 17. Influence of Cholesteric and Smectic Mesophase Order on the Isomerization of Some *N,N'*-Diacylindigos[1]

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The rates and activation parameters for cis → trans thermal isomerization of four *N,N'*-diacylindigos have been compared in isotropic and liquid-crystalline phases. The results indicate that cholesteric solvent order has no perceptable influence on the isomerization of *N,N'*-diacetylindigo. The shape changes attendant upon isomerization of *N,N'*-diacylindigos are inhibited by smectic phase order when the acyl chains are incorporated into smectic layers: the indigoid portion of the molecule, per se, does not sense on a microscopic level the macroscopic order of the smectic phase. Thus, the activation parameters for isomerization of *cis*-*N*-acetyl-*N'*-stearoylindigo and *cis*-*N,N'*-distearoylindigo in the isotropic phase of *n*-butyl stearate (BS) are within experimental error of each other and are similar to the values obtained when benzene is solvent; in the smectic B phase of BS, the activation enthalpy and activation entropy of *N,N'*-distearoylindigo are, respectively, 7 kcal/mol larger and 18 eu more positive than the values of *N*-acetyl-*N'*-stearoylindigo.

Previously, we and others have used the microscopic ordering of thermotropic liquid-crystalline phases to investigate conformational[2-4] and configurational[5-12] changes in solutes. Only in some cases do mesophases influence the dynamics of guest molecule reactions. Examples of reactions requiring virtually no shape changes *or* very large shape changes to transform the reactants into products have been shown insensitive to solvent order. The factors

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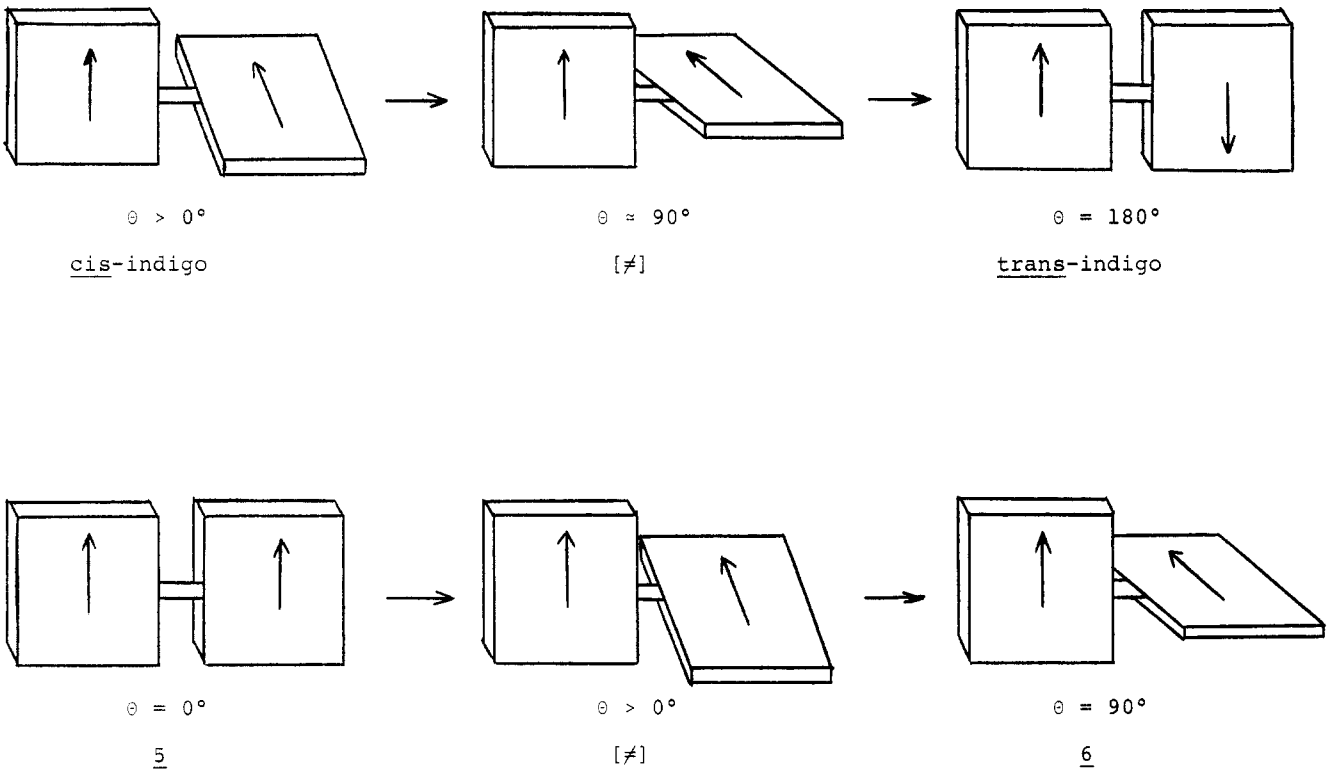
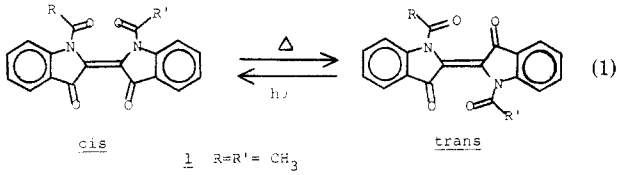


Figure 1. Representation of the rotational motions suffered during cis → trans isomerization of *N,N'*-diacylindigos and during ring closure of a merocyanine dye (**5**) to its indolinospiropyran (**6**).

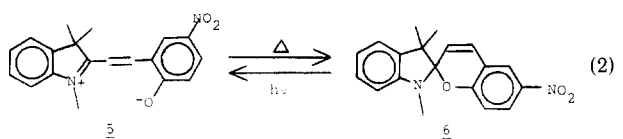
which allow the influence of solvent order to be manifested in solute dynamics are beginning to emerge from the data at hand but have not been identified in detail.

As a means of defining further the factors which are responsible, we have compared the rates and activation parameters for thermal cis → trans isomerization of four *N,N'*-diacylated indigos (**1–4**) in the isotropic and liquid-crystalline phases of *n*-butyl stearate (BS) and a 60/26/14 (w/w/w) mixture of cholesteryl oleate/cholesteryl nonanoate/5α-cholestan-3β-yl acetate (CE). CE exhibits an enantiotropic cholesteric phase from <17 °C to 61–62 °C and BS has an enantiotropic smectic B phase from 14–27 °C. Results from experiments in the isotropic phases of CE and BS were compared with those in which benzene or toluene was the solvent.



(1)

1 R=R'= CH_3
2 R=R'= Ph
3 R= CH_3; R'= n-$C_{17}H_{35}$
4 R=R'= n-$C_{17}H_{35}$



(2)

5 **6**

cis-N,N'-Diacylindigos are nonplanar about their central double bonds ($\theta > 0°$; see Figure 1) and their isomerization transition states ($\theta \simeq 90°$) are only slightly more voluminous.[13] The motions which connect the cis isomers and their transition states may be considered as an extension of the process in which the merocyanine dye (**5**) ($\theta = 0°$) rotates to its transition state ($0° < \theta < 90°$) for indolinopiropyran (**6**) formation ($\theta = 90°$).[5] Since our experiments probe the motions connecting a reactant and its transition state, the results reported here for **1–4** and those from **5** → **6** allow us to compare the effects of a selection of geometric changes. They also have allowed us to uncover a novel influence on solute reactivity in ordered media: the migration of stearoyl chains of **4**, although not directly involved in the indigoid isomerization, dominate the rate of reaction in smectic BS. This effect should be observable whenever solute chains are intertwined with ordered solvent molecules and must translocate during reaction.

Results

Sample Preparation. In our experience, reproducible, low rate constants for thermal isomerization of the cis indigos can be achieved only if extreme care is taken to exclude moisture from the samples, to clean all glassware carefully, to perform transfers in dim light, and to employ pure reagents which are free of (especially) acidic impurities.[14-16]

In spite of our extreme precautions, some kinetic runs gave spurious results. Our pragmatic protocol excluded from consideration those experiments in which curved (non-first-order) kinetic plots or irreproducibly high rate constants were found.

Kinetic Considerations. The cis isomers were prepared in situ by irradiating isotropic or liquid-crystalline solutions of the trans rather than doping the pure cis[17] into the various solvents. This method is expedient and convenient. More importantly, the rates of isomerization in

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Table I. Wavelength Maxima (λ_{max}) and Molar Extinction Coefficients (ϵ) Corresponding to the Longest Wavelength Visible Absorption Bands of Several *N,N'*-Diacylindigos

compd	solvent	λ_{max}, nm (ϵ) trans	cis	ref
1	benzene	562 (7000)	438 (4500)	14
	toluene	562 (7470)	435 (4520)	14
	benzene	560 (6500)	430 (3930)[a]	this work
	BS (32 °C)	555	420	this work
2	benzene	574 (7700)	460 (3900)	14
	benzene	577 (7900)		this work
	CE	574		this work
3	benzene	564 (6550)	418 (5350)[a]	this work
	BS (32 °C)	560 (5680)	440 (4120)[a]	this work
4	benzene	567 (7100)	435 (3900)	14
	benzene	569 (7300)	412 (3950)[a]	this work
	BS (32 °C)	560 (6300)	425 (4830)[a]	this work

[a] Calculated assuming that only the trans isomer absorbs in the 560–660-nm region.

our experiments are independent of the initial cis/trans ratio.

The high molar extinction coefficients of the cis and trans isomers of 1–4 permitted experiments to be conducted on very dilute solutions. Initial concentrations were usually 2×10^{-4} M or less and never exceeded 10^{-3} M. No differences in the transition temperatures of doped mesophase samples and neat mesophases could be detected by optical microscopy.

The percentage of cis produced upon irradiation can be approximated from the relative intensities of the wavelength maxima characteristic of each isomer (Table I) and knowledge that the contribution of each isomer to the absorption band of the other is very small.[17] Generally, irradiations of the trans ($\lambda > 490$ nm) were continued until an initial conversion of 20–80% of trans to cis isomer had been achieved. After allowing the irradiated samples to reequilibrate thermally, the kinetics of isomerization of the cis to the trans isomer were followed spectrophotometrically. Both the increases in the absorption maxima of the trans isomers and the decreases in the maxima of the shorter wavelength band of the cis isomers were monitored.

Optical densities of the trans isomer before irradiation and after 9 half-lives of the cis isomer were always the same within experimental error except when CE was solvent. In some runs in the cholesteric solvent, the final values were 1–9% lower than the initial ones. The reproducibility of the rate data obtained with different samples and irradiation times in CE leads us to believe that photobleaching occurred *during* irradiation and does not affect the thermal isomerizations. Eventual reversion of cis to trans is complete since the trans isomers of *N,N'*-diacylindigos are known to be several kcal/mol more stable than the cis.[16,18]

Isomerization rate constants (k), obtained from the slopes of first-order plots (eq 3), are collected in Tables II–V. Where comparisons are possible, our rate constants are the lowest reported to date.

$$\ln [OD_\infty - OD_t] = \ln [OD_\infty - OD_0] - kt \qquad (3)$$

In order to avoid photochemical conversion of trans to cis or cis to trans during the monitoring process, the spectrophotometer was programmed to wait at 750 nm (where neither isomer absorbs) or its light path to the sample was blocked between periodic measurements. Representative rate plots for 4 in smectic BS, the most difficult rate experiments attempted, are shown in Figure 2.

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Table II. Rate Constants for the Thermal Cis to Trans Isomerizations of 1 in Various Solvents

solvent	T[a] (°C)	$k \times 10^3$[b] (min^{-1})
benzene	35.2	2.46 ± 0.01
	35.2	2.53 ± 0.07
	40.0	4.51 ± 0.01
	40.0	5.06 ± 0.02
	47.0	12.2 ± 0.1
	47.5	13.2 ± 0.1
	47.5	13.8 ± 0.1
	48.0	13.5 ± 0.1
	48.0	15.5 ± 0.1
	51.0	16.5 ± 0.1
	51.0	17.9 ± 0.1
	55.8	30.0 ± 0.1
	55.8	32.7 ± 0.2
isotropic BS	40.8	4.24 ± 0.04
	40.8	4.15 ± 0.03
	41.2	4.68 ± 0.04
	41.3	4.48 ± 0.05
mixture CE	40.0	2.81 ± 0.02
(cholesteric phase)	44.3	5.44 ± 0.03
	44.3	5.18 ± 0.07
	44.3	6.40 ± 0.08
	49.3	8.69 ± 0.08
	49.8	10.2 ± 0.1
	54.8	16.5 ± 0.1
	54.8	19.2 ± 0.1
	58.0	23.2 ± 0.1
(isotropic phase)	64.0	68 ± 5

[a] ±0.5 °C. [b] Errors are 1 standard deviation.

Table III. Rate Constants for the Thermal Cis to Trans Isomerizations of 3 in Various Solvents

solvent	T[a] (°C)	$k \times 10^3$[b] (min^{-1})
toluene	52.0	1.69 ± 0.01
	52.0	1.75 ± 0.01
	56.0	2.81 ± 0.02
	56.0	2.74 ± 0.02
	63.0	6.30 ± 0.05
	63.0	6.30 ± 0.04
	68.0	10.7 ± 0.1
	68.3	10.5 ± 0.1
	68.5	11.1 ± 0.1
	71.2	17.3 ± 0.2
	72.5	19.4 ± 0.1
	72.5	19.0 ± 0.1
mixture CE	55.2	10 ± 2
(cholesteric phase)	56.2	11 ± 2
(isotropic phase)	67.4	28.4 ± 0.5

[a] ±0.5°. [b] Errors are 1 standard deviation.

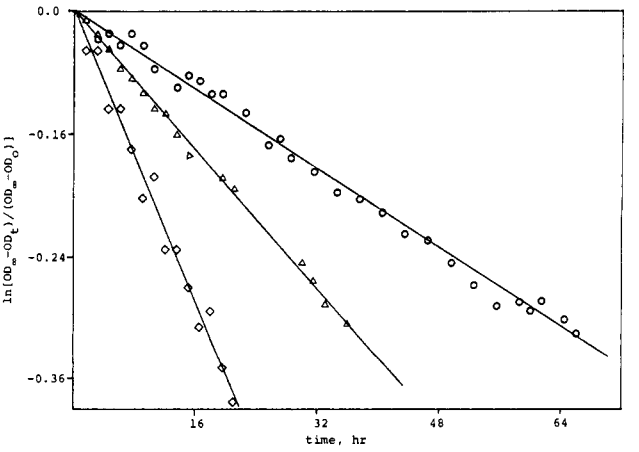

Figure 2. Some rate plots for the thermal isomerization of *cis*-**4** in smectic BS at 17.9 °C (○), 21.0 °C (△), and 24.0 °C (◇). Optical density changes were monitored at 561 nm.

Table IV. Rate Constants for the Thermal Cis to Trans Isomerizations of 3 in Various Solvents

solvent	T^a (°C)	$k \times 10^{3\,b}$ (min^{-1})
benzene	25.4	0.82 ± 0.04
	29.2	1.45 ± 0.01
	29.2	1.49 ± 0.02
	30.3	1.76 ± 0.01
	30.3	1.79 ± 0.03
	36.7	3.65 ± 0.03
	36.7	3.83 ± 0.04
	39.6	5.45 ± 0.04
	39.7	5.69 ± 0.07
	37.7	6.69 ± 0.06
	42.1	7.88 ± 0.04
	42.1	7.94 ± 0.07
	48.7	17.3 ± 0.2
	48.7	17.2 ± 0.2
	49.0	16.0 ± 0.3
	49.0	16.3 ± 0.2
BS	29.8	3.6 ± 0.4
(isotropic phase)	30.0	3.5 ± 0.1
	35.5	8.7 ± 0.2
	35.8	7.6 ± 0.2
	35.8	8.1 ± 0.2
	40.8	12.6 ± 0.2
	40.9	12.7 ± 0.3
	44.4	20.6 ± 0.2
	44.5	18.4 ± 0.5
	44.6	16.3 ± 0.1
	51.6	47.6 ± 0.3
	51.9	42.5 ± 0.8
	52.0	42.4 ± 0.2
(smectic phase)	13.2	0.71 ± 0.02
	14.7	0.91 ± 0.02
	15.4	0.96 ± 0.02
	18.1	1.17 ± 0.04
	19.9	1.78 ± 0.07
	19.9	2.00 ± 0.02
	22.0	2.67 ± 0.05
	22.2	2.52 ± 0.07
	22.7	2.43 ± 0.11
	22.7	2.96 ± 0.07

[a] ±0.5°. [b] Errors are 1 standard deviation.

Due to the exceedingly slow isomerization of *cis*-4 in smectic BS ($\tau_{1/2} \simeq 45$ h at 24 °C and 140 h at 18 °C), the kinetics were monitored for 24–72 h (more than one-half of the first half-life). To obtain OD_∞, the samples were heated to 41 °C (an isotropic temperature), left there until no more cis isomer could be detected, and then returned to the original smectic temperature where the absorption spectra were again recorded. Infinity values of the trans isomer obtained in this way were always within experimental error of the initial optical densities before irradiation. Rate constants calculated by using OD_∞ or by the method of Swinbourne,[19] which does not require OD_∞ but for which a reaction order must be assumed, led to the same results.

Unfortunately, rates of isomerization of *cis*-1 in smectic BS could not be measured. Extremely dilute samples of 1 (2×10^{-4} M) could be dissolved and maintained in isotropic BS. Once cooled to smectic temperatures, optical microscopy gave evidence for the slow development of microcrystals of 1.

Activation Parameters. Activation enthalpies and entropies in Table VI were calculated from the Eyring equation. Two or more independently measured values of k at each temperature were used in the calculations. The errors are largest for smectic BS since the temperature range over which rate data can be obtained is limited to ca. 13°. In spite of this, differences among the activation parameters and rates for 1–4 are apparent.

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Table V. Rate Constants for the Thermal Cis to Trans Isomerizations of 4 in Various Solvents

solvent	T^a (°C)	$k \times 10^{3\,b}$ (min^{-1})
benzene	34.0	3.93 ± 0.1
	34.0	3.87 ± 0.01
	38.0	6.05 ± 0.01
	42.0	11.1 ± 0.1
	42.0	10.5 ± 0.1
	42.0	11.4 ± 0.1
	46.8	17.5 ± 0.1
	46.8	17.5 ± 0.1
	48.0	18.6 ± 0.1
	48.0	20.0 ± 0.1
	52.0	31.0 ± 0.1
	52.0	31.0 ± 0.1
toluene	48.0	15.7 ± 0.1
mixture CE	47.3	10.2 ± 0.1
(cholesteric phase)	48.0	10.9 ± 0.1
BS	32.0	1.83 ± 0.01
(isotropic)	32.0	1.78 ± 0.01
	37.0	3.02 ± 0.01
	37.0	3.03 ± 0.01
	41.0	4.92 ± 0.03
	41.0	5.11 ± 0.02
	41.0	5.19 ± 0.04
	41.0	5.24 ± 0.03
	41.0	5.38 ± 0.07
	41.0	5.26 ± 0.03
	46.0	9.02 ± 0.05
(smectic)	17.9	0.081 ± 0.001
	18.0	0.102 ± 0.002
	20.8	0.114 ± 0.001
	20.8	0.155 ± 0.002
	21.0	0.147 ± 0.002
	21.0	0.141 ± 0.002
	23.2	0.230 ± 0.002
	23.8	0.252 ± 0.009
	24.0	0.295 ± 0.009

[a] ±0.5°. [b] Errors are 1 standard deviation.

Table VI. Activation Parameters for the Thermal Cis to Trans Isomerization of *N,N'*-Diacylindigos in Several Solvents

indigo	solvent	$\Delta H^{\ddagger\,a}$ (kcal/mol)	$\Delta S^{\ddagger\,a}$ (eu)
1	benzene	23.8 ± 0.7	−1 ± 2
		(18.8)[b]	(−14.8)[b]
	CE (cholesteric phase)	23.2 ± 0.8	−4 ± 3
2	toluene	25.3 ± 0.4	−2 ± 1
		(22.4)[b]	(−6.6)[b]
		(24.2)[c]	(−7.0)[c]
3	benzene	23.5 ± 0.3	−2 ± 1
	BS (isotropic phase)	21.0 ± 0.8	−8 ± 3
	(smectic phase)	24.0 ± 1.6	+3 ± 11
4	benzene	22.2 ± 0.5	−6 ± 1
		(19.2)[b]	(−12.9)[b]
	BS (isotropic phase)	21.7 ± 0.6	−8 ± 2
	(smectic phase)	31 ± 3	+21 ± 11

[a] Errors are 1 standard deviation. [b] Reference 14. [c] Reference 13.

Discussion

Solute Order in Cholesteric CE and Smectic BS. Liquid-crystalline and isotropic solvents differ in several microscopic features. Among the most interesting of these is the long-range order of mesophases.[20] In cholesteric phases, solvent molecules are arranged conceptually in nematic-like "layers" and each layer is twisted slightly with respect to its neighbors so that the macrostructure is

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helical. Since the angle of twist, as determined from pitch band studies,[21] is much less than 1°, the layering concept is useful only as a mathematical construct. In smectic B phases like that exhibited by BS, individual molecules are fully extended on average and arranged in layers. The X-ray determined layer thickness of smectic BS is 32 Å,[22] indicating that the long axes of the solvent molecules are normal to the layer plane. Within each layer, the BS molecules are hexagonally packed. Thermochemical and spectroscopic data indicate that solvent order in smectic phases (especially the more ordered types like smectic B) is greater than that in cholesteric phases.[20]

Thermodynamic[23] and spectroscopic[24] studies have shown that rod-like or planar guest molecules can be incorporated into liquid-crystalline matrices with much greater facility than can more globular species. Previous experiments[3,5,6,10] indicate that the conformational and configurational mobility of solutes is dependent upon the degree to which they are ordered initially in the liquid-crystalline lattice: those which disturb their local environment make nearby solvent molecules appear more isotropic and less hostile to subsequent shape change.

Additionally, initially bulky solutes which proceed to bulky transition states may undergo important intramolecular structural changes which are not detected by nearby solvent molecules. For instance, Leigh et al.[8] reported recently that the activation energy and activation entropy for cis → trans isomerization of 1,2-bis(4-cyanophenyl)-1,2-diphenylethene (**7**) are only 1–2 kcal/mol greater and ca. 1 eu more positive, respectively, in several cholesteric phases than those in the corresponding isotropic phases or in benzene. X-ray crystallographic data show that **7** is far from planar, the phenyl rings being skewed in a propeller-like orientation and the ethene double bond being twisted from planarity by ca. 8°.[25] Gross disturbances to the cholesteric phases were caused by **7** since addition of even 0.2% of solute depressed the temperatures of the optically detected solvent phase transitions.

In another example,[4] liquid-crystalline order was purported to retard dimethylamino rotation in 4-(dimethylamino)pyrimidine. However, the difference in activation enthalpy from experiments in the mesophase and in normal isotropic solvents is small and activation entropies vary erratically from solvent to solvent. We prefer to interpret these data differently from the authors: the liquid-crystalline environment, being comprised of molecules which are larger than the solute, does not detect the small shape changes that accompany rotation about the dimethylamino group. In this regard, it is important to realize that the van der Waals diameter and thickness of an aromatic ring are similar.[26] This and the previous example provide cases in which the rates of shape changes of relatively large and small solutes are virtually unaffected by solvent order.

By contrast, we have found that the thermal ring closure of the planar **5** to its thermodynamically favored (globular) indolinospiropyran **6** is impeded enormously by the smectic B order of BS:[5] the activation energy is 20 kcal/mol higher and activation entropy is 64 eu more positive in the mesophase than in the isotropic phase! The initially planar **5** may be incorporated efficiently into the smectic solvent matrix. As rotation of the two halves take **5** to its transition state for closure (Figure 1), the order of nearby solvent molecules will be disturbed increasingly, causing a substantial entropy increase. A partial measure of the resistance by the solvent molecules to being disturbed is the increase in the activation energy.

Thermal Isomerization of *N,N'*-Diacylindigos. Evidence for twisting about the central double bond of *cis*-*N,N'*-diacylindigos is circumstantial but compelling. Unfortunately, X-ray crystallographic structures for cis indigos are not listed in the Cambridge Crystallographic Date File.[27] However, the higher electronic absorption energies[28] and carbonyl stretching frequencies[28a] of the cis isomers (with respect to the trans) have been interpreted as consequences of considerable twisting about the central double bond.[28a,d] CPK space-filling models indicate that if the cis isomers were planar, their acyl groups and carbonyl oxygens would approach one another to a distance which is much less than the sum of their van der Waals radii.

Studies by Whitten[29] on the isomerization of some thioindigos in monolayer films and multilayer assemblies present further evidence for twisting about the central double bond in the cis isomers: 6,6'-bis(hexyloxy)thioindigo photoisomerized very efficiently from cis to trans; no trans to cis isomerization could be observed except in isotropic media. It was suggested that the twisted photointermediate which decays normally to yield both cis and trans isomers may be *less* bulky than the cis isomer. Thus, photoisomerization of cis → trans allows a continuous ordering increase of the monolayer while trans → cis would have required a continuous decrease in monolayer order. The experiments of Sueishi, Ohtani, and Nishimura[13] demonstrate that the transition state for thermal isomerization of our *N,N'*-diacylindigos is slightly bulkier than the cis isomers.

The facile photoisomerization of trans-*N,N'*-diacylindigos to their cis isomers in cholesteric CE and smectic BS is not surprising. N-Substitution results in indigo molecules which are intrinsically bulkier than the thioindigos examined by Whitten. The presence of substituents at the 6 and 6' positions of thioindigo makes the molecule appear much more rod-like in both its cis and trans forms than the *N,N'*-diacylindigos. Additionally, our liquid-crystalline phases should be less ordered and more easily disturbed than monolayer assemblies. A combination of factors—the bulkiness of the trans isomers of the indigos and a looser solvent matrix—help explain why trans → cis photoisomerization occurs in our systems.

Isomerization of *N,N'*-Diacylindigos in the Cholesteric Phases of CE. The data in Tables II and VI indicate that isomerization of *cis*-**1** is subjected to no special influence by the order of cholesteric CE: the activation parameters in benzene and cholesteric CE agree with each other within experimental error; rate constants measured in isotropic CE fall on the line predicted by the Eyring equation for cholesteric CE data. This is especially

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surprising since the much greater (macroscopic) viscosity of the cholesteric solvent[30] should lead to a microscopically manifested drag on isomerizing **1**. Destruction of local solvent order near *cis*-**1** may well decrease the viscosity "seen" by the solute. In fact, the twofold greater rates for isomerization of *cis*-**1** and *cis*-**4** in benzene are probably without mechanistic significance since *cis*-**2** isomerizes 4 times faster in cholesteric (*or* isotropic) CE.

In essence, we find no evidence to suggest that cholesteric order influences the thermal isomerizations of the *N,N'*-diacylindigos.

Isomerization of 3 and 4 in the Isotropic and Smectic B Phases of BS. The possible solvation sites for a solute in a smectic B phase are more distinct than in a cholesteric phase. In general, a solute may reside at or near a layer interface or imbedded within a layer. The molecule dimensions of **3** and **4** as well as the attraction of BS chains for the stearoyl chains of the indigos make the overwhelmingly probable site for the reactive chromophore at or near a layer interface. Once a stearoyl chain is imbedded in a layer of BS, the indigo moiety will be forced to reside near the solvent chain ends. Experiments with other long *n*-alkylated species in smectic BS had led us to similar conclusions.[31] While the specific consequences of this type of solubilization on reactivity will vary from solute to solute, it is clear that all will experience a somewhat disordered environment. NMR and IR studies indicate that methylene groups near the ends of a hydrocarbon chain in ordered phases,[22,32] including the smectic B phase of BS,[33] rotate more freely than those near the center of the chain.

On this basis and given the lack of effect of cholesteric order on the isomerizations of *N,N'*-diacylindigos, we expected that cis isomers of both **3** and **4** would exhibit phase-independent activation parameters for isomerization. The much higher activation enthalpy and much more positive activation entropy for **4** in the smectic B phases of BS were, therefore, unanticipated. They suggest that the activation parameters are dependent on factors in addition to the shape changes which accompany isomerization of the indigo moiety.

The activation parameters of **1**, **3**, and **4** in benzene are nearly identical, as expected if acyl chain length plays little or no role in the isomerization rates in isotropic media. Even in isotropic BS, the activation parameters for isomerization of **3** and **4** cannot be distinguished. Seely and Shaw[15] had suggested on the basis of rate constants for cis → trans isomerization of *cis-N,N'*-dimyristoylindigo in several isotropic solvents that acyl chain conformations influence the reaction rates. Our data indicate that long chains have no influence on the rates of isomerization in isotropic solvents of low polarity.

However, differences between the activation parameters of **4** in the smectic and isotropic phases of BS can be interpreted as arising from stearoyl chain behavior. Stearoyl chains in *cis*-**4** can be inbedded in either the same or in vicinal layers of smectic BS. In either case, the indigoid part of the molecule will reside at a layer interface. Upon isomerization, the stearoyl groups will be translocated in a manner which will be resisted by nearby BS molecules. Since the single stearoyl group of *cis*-**3** need not be moved during isomerization of the indigo, its activation parameters in BS represent only the influence of smectic order on an *N,N'*-diacylindigo which isomerizes near a layer boundary. As can be seen, the smectic activation parameters for *cis*-**3** are slightly higher than those in the isotropic phase but they do not approach the values obtained with *cis*-**4**.

We conclude that movement of stearoyl chains, remote from the reactive site, and not shape changes of the isomerizing indigoid moiety, are responsible for the large increases in the activation parameters measured in smectic BS. This anchoring effect suggests a new synthetic strategy which we are exploiting at present in other systems.[34]

Experimental Section

Ultraviolet absorption (UV) spectra were recorded on a Cary Model 14 or a Perkin-Elmer Model 551 spectrophotometer. Most kinetic measurements were performed on the latter instrument; in a few cases, a Beckman DU spectrophotometer was employed. High performance liquid chromatography (HPLC) was conducted on a Waters Associates liquid chromatograph with UV (254 nm) and refractive index detectors. A Water Associates Rad-Pak B silica gel column (10 × 0.8 cm; 10 μm particles) and a 80/20 (v/v) THF/water mixture as eluent for **1** or a Rad-Pak C18 column (10 × 0.8 cm; 10 μm particles) 1/99 (v/v) ethyl acetate/CH_2Cl_2 mixture as eluent for **2–4** were used for analytical purposes. Melting points and transition temperatures were obtained on a Kofler micro hot-stage microscope fitted with polarizing lenses and are corrected. Elemental analyses were performed by Guelph Laboratories of Guelph, Ontario or Galbraith Laboratories of Knoxville, TN.

All column chromatography was by the flash method[35] on silica gel. Irradiations to produce cis indigos employed a Hanovia 450-W medium pressure Hg arc whose output was filtered through water, Pyrex, and a Corning CS 3-70 filter ($\lambda > 490$ nm).

Benzene (Burdick and Jackson or Baker reagent, purified by the method of Saltiel[36]) was distilled from sodium and benzophenone immediately prior to its use. Toluene (Baker "instraanalyzed" reagent) was distilled from sodium. Methylene chloride (Baker reagent or Burdick and Jackson) was used as received. Petroleum ether (50–110 °C, Baker reagent) was distilled and the 66–98 °C fraction collected. Xylenes and diethyl ether (Baker reagents) were distilled prior to use.

n-Butyl stearate (BS) was synthesized by our previously published procedure[37] to yield material exhibiting

$$k \overset{14\ °C}{\text{------}} s_B \overset{27\ °C}{\text{------}} i \quad [\text{lit.}^{22}\ k \overset{15\ °C}{\text{------}} s_B \overset{26.1\ °C}{\text{-------}} i]$$

Cholesteryl oleate (Aldrich) was purified by irradiating a solution of 7 g in 46 mL of *n*-heptane under nitrogen for 29 h using a Hanovia 450-W medium pressure Hg lamp (Pyrex filter). After evaporation of the solvent, the residue was chromatographed (benzene as eluent) and recrystallized twice from diethyl ether–ethanol to yield 3.2 g of material which exhibited no absorption above 300 nm. Its transition temperatures were

$$s \overset{41.2\ °C}{\text{--------}} c \overset{55\ °C}{\text{------}} i \quad [\text{lit.}^{38}\ s \overset{40\ °C}{\text{------}} c \overset{50.5\ °C}{\text{--------}} i]$$

The purified material was stored under a dry nitrogen atmosphere in the dark at −30 °C until its use. 5α-Cholestan-3β-yl acetate, mp 110–111 °C [lit. mp 109 °C[39]], was synthesized as described previously.[40] Cholesteryl nonanoate (Aldrich) was purified by

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chromatography (benzene as eluent) followed by recrystallization form 2-butanone/95% ethanol to yield the following transition temperatures:

k 78.5–80.0 °C c 92.5 °C i [lit.[41] k 77.5 °C c 92 °C i]

N,N'-Diacylindigos. General Synthetic Considerations. Indigos were synthesized initially in their trans configurations. Preparatory procedures and intermediate purifications were performed in very diffuse white or red light. The purified materials were stored under nitrogen in the dark at or below 0 °C. HPLC analyses showed all of the indigos thus prepared to be >99% pure.

N,N'-Diacetylindigo (1) was synthesized in 63% yield by the method of Blanc and Ross.[28c] After being recrystallized 5 times from benzene and being dried in the dark at room temperature and ca. 30 torr for 6 days, material of mp 268–269 °C dec [lit. mp 256–257 °C[14]; 263–264 °C[28c]] was obtained.

N,N'-Dibenzoylindigo (2) was synthesized by the method of Posner.[42] After 3 recrystallizations from xylene, a 22% yield of mp 260–262 °C dec [lit.[14] mp 256–257 °C] was obtained.

N-Acetylindigo.[43] A 2.8 g-portion of 1 was heated at 80–100 °C in 30 mL of a 20/80 (v/v) water/pyridine mixture for 2 h. After evaporation of the solvent under aspirator vacuum, the crude product was purified by column chromatography (1% acetone in CH_2Cl_2 as eluent) to yield 1.3 g (55%) of mp 187–189 °C dec [lit. mp[43] 185–186 °C].

N-Acetyl-N'-stearoylindigo (3). A solution of 340 mg of *N*-acetylindigo, 775 mg of freshly distilled stearoyl chloride (bp 165 °C (0.8 torr)), 20 mL of CH_2Cl_2, and 3 mL of pyridine were refluxed overnight under nitrogen. The solvent was removed under reduced pressure, the residue was chromatographed (1% acetone in CH_2Cl_2 as eluent), and the main fraction was recrystallized from hot hexane to yield 430 mg (68%) of **3**. After repeated recrystallizations from hexane or hexane/ethyl acetate under nitrogen, material of mp 98–101 °C dec was obtained: NMR ($CDCl_3$; 60 MHz) 0.9–2.0 ppm (m, 33 H), 2.60 (s, 3 H, CH_3O), 2.85 (t, J = 6 Hz, 2 H, $-CH_2O-$), 7.1–8.6 (m, 8 H, Ar); IR (KBr pellet) 2920, 2900, 2800, 1700, 1680, 1598 cm^{-1}. Anal. Calcd for $C_{36}H_{46}N_2O_4$: C, 75.76; H, 8.12. Found: C, 76.01; H, 8.25.

N,N'-Distearoylindigo (4). A mixture of 2 g of indigo, 20 mL of dry pyridine (distilled from P_2O_5), and 15 g of freshly distilled stearoyl chloride was refluxed under a dry atmosphere for 25 min. It was poured with stirring into 10% aqueous HCl and filtered while warm. The dark precipitate was boiled in 200 mL of absolute ethanol for 20 min and filtered. The residue was recrystallized from petroleum ether to give 1.5 g (32%) of crude **4**. After being chromatographed (benzene) twice and recrystallized twice from petroleum ether, material of mp 111–112 °C [lit. mp[14] 101–102 °C] was obtained.

Preparation of Kinetic Samples. Due to the sensitivity of the indigos to visible light, their solutions were prepared and handled in very diffuse white or red light. Cells and all glassware in contact with the solutions were cleaned thoroughly by washing with soapy water, water, ethanol, acetone, and finally distilled water. The glassware was dried at 120 °C and stored in a dessicator until being used.

Solutions of (1–2) × 10^{-4} M *trans-N,N'*-diacylindigos in benzene or toluene were deoxygenated in 1.0-cm quartz cuvettes by bubbling dry N_2 through for several minutes. The cuvettes were closed tightly with Teflon stoppers and were thermostated in the cell compartment of the spectrophotometer.

Solutions in CE were prepared by placing measured aliquots of the indigos dissolved in CH_2Cl_2 (passed through a silica column and distilled immediately prior to use) into ampules containing preweighted amounts of homogeneous CE. The CH_2Cl_2 was removed slowly under vacuum to avoid bumping. A heat–swirl–cool sequence was repeated. The samples were brought to 1 atm under nitrogen and sandwiched between two quartz plates separated by a 0.2-mm Teflon spacer which was thermostated in the cell compartment of the spectrophotometer.

Solutions in BS were prepared directly under nitrogen by heating the indigo and solvent to an isotropic temperature (>30 °C) and swirling. For isotropic and some smectic B phase experiments, the nitrogen saturated solutions were placed in capped 1-mm quartz cells and thermostated. In other smectic B phase experiments, the solutions were degassed at 0.1 torr in the isotropic phase, cooled, and flame-sealed in 0.4-mm cells made from Kimax flattened capillaries (Vitro Dynamics).

Kinetic Procedures. The samples were temperature equilibrated for 1–2 h and then irradiated to obtain 20–80% of the cis isomer. Temperatures were measured several times during each run with a calibrated thermister.

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Registry No. *trans*-1, 2533-03-1; *trans*-2, 72738-57-9; *trans*-3, 102396-59-8; *trans*-4, 72751-95-2; *trans-N*-acetylindigo, 102396-60-1; indigo, 482-89-3.

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Liquid-Crystalline Solvents as Mechanistic Probes. 20. Crystalline and Smectic B Solvent Control over the Selectivity of Photodimerization of *n*-Alkyl Cinnamates[1]

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The photodimerizations of *n*-octadecyl, *n*-hexadecyl, and *n*-tetradecyl esters of *trans*-cinnamic acid have been investigated in the crystalline, smectic B, and isotropic phases of *n*-butyl stearate. A strong preference for head-to-tail dimerization is found in the ordered solvent phases. Dipole–dipole-induced interactions between cinnamates and solvent-mediated solute alignments are the factors that combine to control the regioselectivity of photodimerization. The ability of cinnamate esters to be incorporated into the ordered solvent phases is extremely dependent upon the length of the *n*-alkyl solute chains. However, ease of incorporation has little influence upon regioselectivity.

Photodimerization of crystalline cinnamic acid,[2] substituted cinnamic acids,[3] and *n*-octadecyl *trans*-cinnamate,[4] of glassy ethyl cinnamate,[5] and of solid poly(vinyl cinnamate)[6] have been investigated as empirical methods to

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