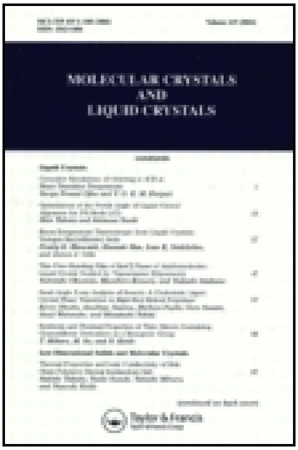

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Phase Rejection as a Factor in the Kinetics of Atropisomerization of 1,1′-Binaphthyl Conducted in Liquid Crystal and Solid Phases

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The atropisomerisation of 1,1′-binaphthyl has been studied through the phase transitions (twisted) nematic→ smectic *A*→ solid in a solvent consisting of a mixture of alkylcyanobiphenyls and an alkylcyanoterphenyl. Increases in rates with decreasing temperature and increasing apparent order of the solvent medium are observed. Enthalpy and entropy both decrease in value as the phase order increases. By studying in detail the thermograms of these and related systems, it is shown that phase rejection and consequent phase heterogeneity is an important factor in this anti-Arrhenius behavior.

Keywords: Liquid crystals; phase separation; kinetics; atropisomerization; 1,1′-binaphthyl

INTRODUCTION

A recurring theme in studies of reactions in liquid crystalline media is the influence of phase ordering on the kinetics. For unimolecular reactions, [1–9] factors leading to changes in reaction rate constants as one goes through phase transitions include: temperature, the nature of the molecular geometric changes as one passes through the transition state, changes in the microviscosity and dielectric constant of the medium, and any phase rejection of substrate that may occur. For higher order reactions, additional factors that may be involved include the diffusion constants and concentration changes associated with phase rejection.

In previous work from this laboratory, [9] the effect of the nematic-smectic *A*- reentrant nematic phase transitions on the kinetics of the thermal isomerization of cis-*N*, *N*′-diacetylindigo was reported. As one proceeds with decreasing temperature from less ordered to ordered and then to less ordered phase again, the reaction rate decreases in the smectic and increases in the reentrant phase. This interesting anti-Arrhenius behavior is rare in chemical systems; it has been observed in reactions in frozen solutions [10] and in certain electron-transfer reactions [11].

In an attempt to extend the knowledge of unimolecular systems, attention was focussed on another interesting unimolecular reaction that has been the subject of several investigations -- the atropisomerization of 1, 1′-binaphthyl (BN). In this system, too, temperature lowering leads to an increase in reaction rate as one goes through the transition from a nematic to a solid phase. The substrate BN exists in two optically active forms that can be resolved by heating-cooling-recrystallization cycles as proposed by Wilson and Pincock [12]. Thermal racemization of BN in six nematic solvents through the nematic-solid transition has been studied by Naciri *et al.* [8]. The authors compared the magnitude of the thermodynamic parameters for atropisomerization and correlated them with the degree of structural similarity between BN and the mesogen and with the degree of ordering in the mesophase. In their study, entering the solid phase of MBBA is accompanied by an increase in the rate of reaction as compared to the nematic phase. $\Delta H^{\neq}$ was found to be smaller and $\Delta S^{\neq}$ more negative in the solid phase. To account for the rate acceleration, it was proposed that the increase of the order of the solvent results in the compression of the angle between the naphthyl rings of BN, thus bringing the stable ground state conformation closer in structure and energy to the transition state for racemization. The study included the plastic crystalline phase of MBBA, which showed no significant effect as compared to the nematic phase.

In this work, a well-known mixture of 4-*n*-heptyl-4′-cyanobiphenyl (7CB), 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) and 4-*n*-pentyl-4′-cyanoterphenyl (5CT) in the ratio 73: 18: 9 by weight was employed as a solvent for the atropisomerization of BN. This solvent mixture will be denoted below as ACB. Attention was focussed on the observed acceleration of rate on cooling into both the smectic and solid phases, and the phases were examined closely for evidence of phase rejection.

EXPERIMENTAL SECTION

Materials and Methods

The liquid crystals 7CB, 5CB, 8OCB and 5CT were obtained from E.Merck under the commercial names of K21, K15, M24 and T15 respectively.

p- Nonyloxybenzoic acid, *p*-butylcyclohexylcarboxylic acid and 1, 1'-binaphthyl were purchased from Aldrich Chemical Company. All chemicals were used without further purification. A Nikon polarizing microscope equipped with a Mettler FP 82 hot stage was used for the optical observations of the textures, testing the homogeneity of the samples, and following the kinetics of R-(-)-1, 1' binaphthyl (RBN) atropisomerization by measuring the variation of the distance **d** between interference rings in droplets of twisted nematic material suspended in glycerol. DSC measurements were carried out on a TA Instruments Model DSC 2920 at a scan rate of 2°C/min. Crimped aluminum pans containing ~ 5–7 mg of sample were used.

R-(-)-1,1'binaphthyl

Racemic 1, 1'binaphthyl (2.5 g) was resolved by heating, cooling, and crystallization cycles, [12] giving a yield of 1.7g of product with an optical purity of 65% after three such cycles (specific rotation $[\alpha]_D = -159°$ in benzene). This optical purity was sufficient for the kinetic studies.

Solvent

ACB shows a nematic phase between 65.6 and 26.9°C, a smectic *A* phase between 26.1 and 10.1°C and a reentrant nematic phase below 10.1°C. The incorporation of 1wt.% of RBN into ACB results in the suppression of the reentrant phase, and an increase in the temperature of the nematic-smectic transition (~ 2–3°C). If the same liquid crystal components are mixed in the proportion 83: 8: 9 by weight, only the nematic phase is observed. Addition of the same amount of RBN to this phase produced the expected twisted-nematic phase and also induced a smectic-*A* phase with a nematic-smectic transition temperature of 19°C. Both optical microscopic and differential scanning calorimetry (DSC) studies of the solution indicate that the smectic phase is a quite stable monotropic phase and the smectic-solid transition temperature is below 0°C, depending on the rate of cooling. The melting peak of the frozen solution is very broad as one enters the twisted-nematic phase (~ 25–35°C) and this will be discussed in detail later.

Kinetics

Kinetics can be accurately followed by measuring the variation of the distance **d** between interference rings in droplets of twisted nematic material suspended in glycerol (droplet method) [8]. The rate constant of atropisomerization ($\mathbf{k^a}$) is determined by applying eq. 1 (where $\mathbf{d_0}$ is the distance at time $\mathbf{t} = 0$)

$$\mathrm{Ln}(\mathbf{d_0}/\mathbf{d}) = -2\mathbf{k^a t} \qquad (1)$$

An important consideration in applying eq. 1 is that the droplet method requires a twisted nematic phase. For the solid and smectic phase, it is necessary to raise the temperature of each sample to enter the twisted nematic phase for each determination. The process requires between 3 to 5 minutes until the interference rings are observed. The effect of increasing the temperature on the rate constant is not important since for each temperature several aliquots are placed in a constant temperature bath. At a time $\mathbf{t_n}$ one removes a **n**-th sample, places it on a hot stage and increases the temperature for a constant period of time (~ 3–5 min) which is small compared to the half life of the reaction (~ 5 hrs.). A typical plot consists of 10–15 data points taken during 1.5–2 half-lives of the racemization, and shows a correlation coefficient of $r > 0.99$.

RESULTS AND DISCUSSION

Figure 1 is an Arrhenius plot for the atropisomerization of BN in the twisted nematic, smectic-*A*, and solid phases of the liquid crystal mixture ACB, showing that each increase in the order of the phase produces a concomitant increase in the reaction rate. The activation parameters in these phases along with known literature data on this reaction in the solid phase are shown in Table I. $\Delta H^{\neq}$ decreases as one proceeds from the twisted nematic to the solid phase, indicating a reduction in the isomerization barrier, while $\Delta S^{\neq}$ is more negative as the phase order increases.

The influence of the ACB solid phase on both the rate and thermodynamic parameters is less pronounced than the comparable influence of MBBA. Although the general tendency for activation parameters to decrease as one proceeds from liquid crystal to solid phase is consistent in both studies, the relative changes of these quantities in ACB are less than 15% of those observed in MBBA. This implies that the kinetic data obtained in the "solid phase" of ACB cannot be unambiguously interpreted as the kinetics of BN conversion in a solid crystalline medium. The assumption that all converting BN molecules are incorporated in the solid phase crystalline lattice of ACB seems even less likely when one compares the activation energy of this reaction in the solid phase of ACB (14 kcal/mol), or MBBA (8 kcal/mol) with that obtained by

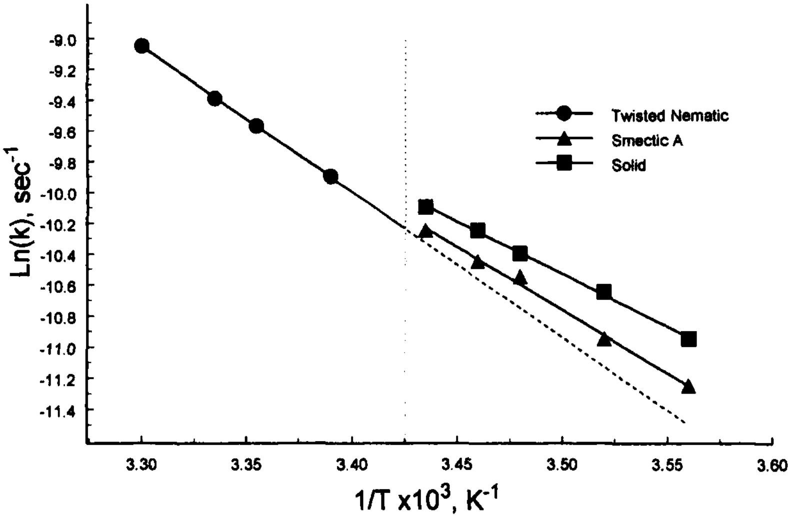

FIGURE 1 Arrhenius plot of the atropisomerization of R-(-)-1, 1'-binaphthyl in 7CB/8OCB/5CT, 83 : 18 : 9 wt %. The dotted vertical line indicates the phase transition.

TABLE I Thermodynamic Parameters for the Atropisomerization of BN in Several Solvents

Solvent	*Phase*	$\Delta H^{\neq}$ *Kcal/mol*	$\Delta S^{\neq}$ *e.u.*
	T Nematic	18.8 ± 0.9	− 14.0 ± 1.5
ACB	Smectic-A	16.2 ± 1.1	− 21.0 ± 2.2
	Solid	13.6 ± 1.0	− 30.0 ± 2.5
MBBA[a]	Nematic (and plastic)	23.5 ± 0.4	− 8.9 ± 1.4
	Solid	8.0 ± 0.7	− 63.2 ± 5.4
Polycrystalline BN[b]		~ 60.0	–

[a]from ref. 8. [b]from ref. 13.

Wilson and Pincock [13] in polycrystalline samples of BN (~ 60 kcal/mol). It is much more likely that phase rejection and consequent inhomogeneity will occur at a liquid crystal-solid phase transition.

There are indeed many known cases of rate acceleration in the solid phase upon freezing a solution -- the classical cases of "puddle effects" [10]. This effect, in bimolecular and higher order reactions, can be explained by the concentration of reactants into puddles of solutions in an otherwise solid matrix. When the concentration of reagents increases, there can be a very strong enhancement of the reaction rate. Since such "puddles" have never been observed via optical microscopy in frozen solutions or the solid phases of liquid crystals, presumably because their size is inappropriate for observation with this resolution, another method needs to be employed to furnish supporting evidence for their existence.

Precision DSC measurements were therefore undertaken to provide evidence of phase rejection in the solid phase of the mesogenic solvents. The validity of this approach was tested on a binary system of *p*-nonyloxybenzoic acid (A) and *p*-butylcyclohexylcarboxylic acid (B). Although fairly miscible in the nematic phase, this system undergoes phase separation in the solid phase. In the range of low concentration ($\sim 1-7$ wt.%) of either component (A in B or B in A) phase separation manifests itself either by the appearance of additional endothermic peaks in the DSC thermograms (A in B) or by distortion of the shape of the major component melting peak (B in A). In the latter case, taking the first derivative of the $\Delta H \sim T$ curves made it possible to detect the position of the additional peak and its enthalpy. In both cases the enthalpy of the additional peaks was found to be proportional to the rejected component concentration.

Addition of 1 wt.% of BN to the initially nematic mixture ACB induced a monotropic smectic-*A* phase with a nematic-smectic transition temperature of 19°C and a very broad melting peak at 25–30°C, indicating that the solute creates considerable disorder in the crystalline lattice of ACB. Since the broad melting peak of the employed ternary mixture did not lend itself to an unambiguous interpretation in the sense of phase rejection, thermograms of the major component (83 wt.%) of the employed ternary mixture - 7CB and its very close homolog-5CB were studied instead (Fig. 2).

Figure 2, a)-**1** and b)-**1** present DSC data on the pure solvents, and show peaks associated with the transitions from solid to nematic and from nematic to isotropic phases. Addition of BN causes the temperatures of the two transitions to lower and new exothermic peaks to appear on the thermograms (Fig. 2, a)-**2** and b)-**2**), their intensities increasing with BN concentration.

To account for the exothermic peaks, one may assume that BN behaves in the following manner in a cyanobiphenyl type solvent: (1) molecules of BN form stable associates with molecules of cyanobiphenyl [8]; (2) these associates are rejected from the bulk of the solvent on cooling because of their low solubility; (3) during the crystallization of the supercooled solvent the microregions of the rejected guest-host associates still preserve their liquid crystalline phase, since they crystallize slower than the solvent; (4) on heating, these thermodynamically unstable regions crystallize, giving rise to the exothermic peaks appearing before the solvent melting peak.

This behavior can be reasonably assumed to occur as well in the ACB mixture. Thus, when working with the "solid" phase of ACB, one might really be performing the reaction in a supercooled smectic phase which is probably more ordered than the conventional smectic *A* phase.

The evidence indicating phase rejection of 1,1'-binaphthyl from the solid phases of cyanobiphenyls motivated us to reinvestigate its solubility in another liquid crystal, MBBA, which has also been employed as a medium for BN atropisomerization. A significant acceleration of this reaction in the solid phase of MBBA has been explained as being solely due to the solid matrix effect on the BN transition state [8]. We have studied a 1 wt.% solution of BN in MBBA utilizing the DSC technique. Although the heat flow curves of the

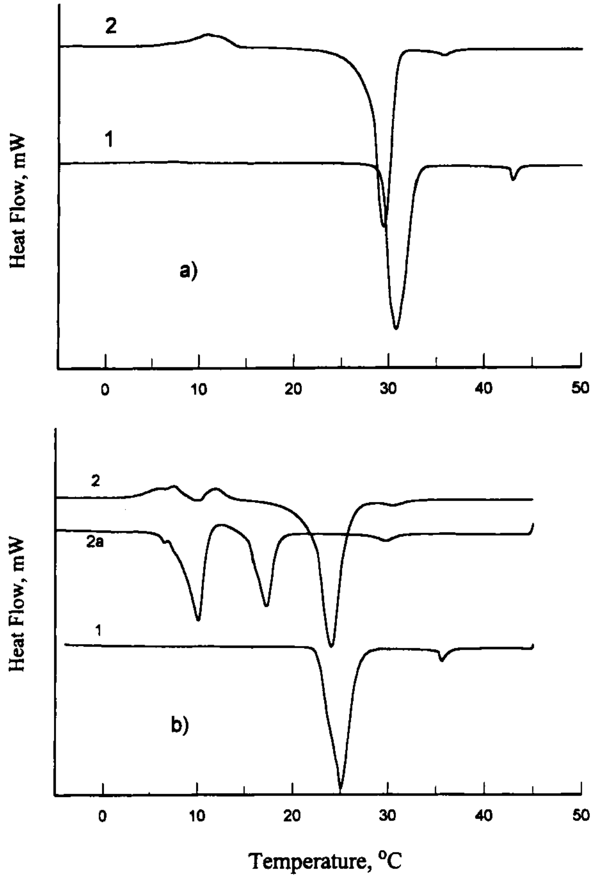

FIGURE 2 DSC thermograms obtained by heating 7CB (a) and 5CB (b). 1- pure liquid crystal solvents; 2, 2a - doped with 2.5 wt % of BN.

solution did not show any obvious manifestations of additional thermodynamic events, as compared with pure MBBA (Fig. 3, solid lines), a careful analysis of the thermograms allows one to discern another endothermic process accompanying melting of MBBA. The existence of this endothermic event is clearly seen in the first derivative curve (Fig. 3, dashed lines), and lends further credence to the idea of phase separation.

The interpretation presented here associating the observed kinetic effects with phase separation is consistent with the other recent studies of unimolecular reactions [14–19]. For example, studies of the solubility of aromatic ketones in trans, trans-4′-butylbicyclohexyl-4-carbonitrile (CCH-4) [14,15] confirm that most aromatic molecules have very low solubilities (~ 0.2–2.0 mol%) in the crystal phase of the mesogens of this type. Employing the NMR

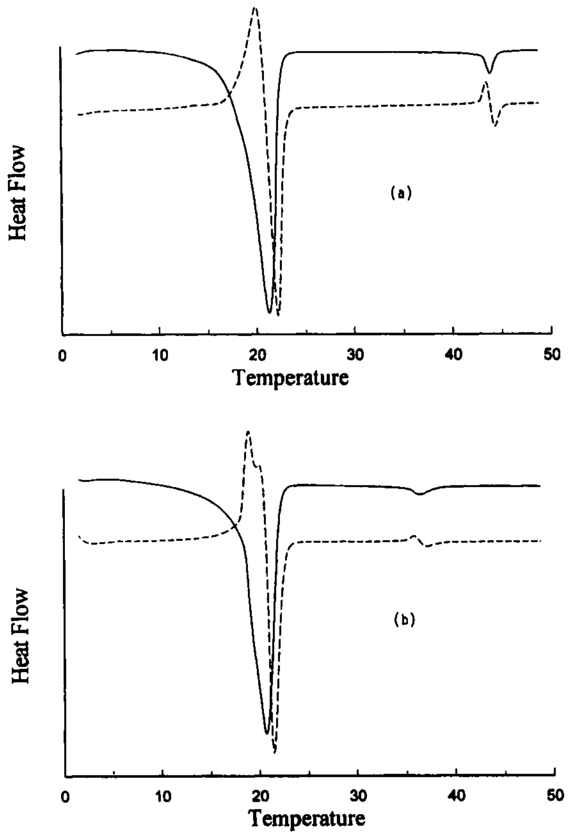

FIGURE 3 Heating DSC thermograms for MBBA (a) and a 1 wt.% solution of BN in MBBA (b). Solid lines represent heat flow; dashed lines - first derivative of the heat flow.

method, the authors observed, in mixtures of aromatic solutes with CCH-4, the formation of a smectic/isotropic biphasic system below the temperature of the nematic-smectic transition. Thus, a nematic phase transforms to both an isotropic phase (an exothermic process) and a smectic phase (an endothermic process), and under certain conditions a net zero change in the system enthalpy might mask the phase separation event. On further cooling, the coexistence of crystal smectic and crystal isotropic biphasic systems is observed. The authors conclude that their data require a reinterpretation of the previously reported investigation of solute behavior in this liquid crystal.

In another example [16], the kinetic behavior of the *p*-dimethylaminobenzenesulfonate (ASE) rearrangement in the liquid crystal OS35 (E. Merck) is interpreted by a complicated mechanism involving partitioning of the reactant molecule ASE between coexisting smectic, nematic and/or isotropic phases, followed by elimination of the product from the smectic phase. In a third example, formation of biphasic smectic B-nematic and smectic B-isotropic systems were also recognized in the photoreaction of E-ethyl-4-methoxycinnamate in CCH-4 [17].

Another complicating factor in interpreting the kinetics of chemical reactions in the solid phase of alkyl- and alkoxy-cyanobiphenyl solvents is the possibility of the coexistence of several crystalline phases in these compounds which can show significant differences in their molecular mobility [20]. It is known that there are 3 types of low temperature solid phases in 5CB, having melting points at 14, 18 and 24°C respectively. Thus the type of solid phase formed will be dependent on the history of the sample. In fact, it was observed that there is a somewhat random formation of the various solid phases during the heating-cooling cycles in the BN-5CB guest- host system (curve **2** or **2a**, Fig. 2, b). As one can see from curve **2a**, instead of the melting peak at ~ 24°C, there appear two melting endothermic peaks at ~ 11°C and ~ 18°C. Between these two peaks, there is also observed one exothermic peak presumably related to the crystallization of the supercooled puddles of rejected solute.

CONCLUSIONS

The atropisomerization of BN in ACB shows increases in rate as one goes from the (twisted) nematic to the smectic *A* to the solid phase. $\Delta H^{\neq}$ decreases, indicating a reduction in the isomerization barrier, and $\Delta S^{\neq}$ is also more negative as the phase order increases.

DSC thermograms of alkylcyanobiphenyl liquid crystal mixtures display new endo- and exothermic peaks upon the addition of BN. Thus the solid phase of the ACB- BN system is most unlikely to be a true solid solution. Rather, it is undoubtedly a heterogeneous medium, containing liquid crystalline regions of the rejected reagent. Further evidence that this is the case is the observed change in the activation parameters of the atropisomerization upon going from the smectic *A* to solid phase, which is of the same order of magnitude as the change observed in going from the isotropic to nematic phase.

For a first order unimolecular reaction, an increase in the reagent concentration in puddles should *not* result in an acceleration of the reaction rate. Thus, other factors associated with the properties of puddles should be considered. In particular, the BN microenvironment and the solvent-solute interactions in puddles are clearly quite different than that of a homogeneous phase.

Acknowledgment

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