Elucidation of the Thermal Isomerization Mechanism for Azobenzene in a Cholesteric Liquid Crystal Solvent

Sir:

As a result of their anisotropic interactions with solute molecules, liquid crystals have been shown capable of influencing the rates[1] and stereochemistries[2] of unimolecular[2a,b,c] and bimolecular[1,2d] reactions. In spite of this, they have received little attention as tools in the elucidation of reaction mechanisms. Previously, we[3] demonstrated how liquid crystals allow the preferred orientations of collisions leading to photodimerization of acenaphthylene, a bimolecular reaction, to be determined.

Here, we apply cholesteric liquid crystal solvents to the elucidation of the mechanism of the thermal isomerization of *syn*-azobenzene to its anti isomer, a unimolecular reaction, and show that the sensitivity of the cholesteric solvent to solute structural changes provides details of the reaction mechanism which are not readily available by other experimental techniques. Although this reaction has been the subject of numerous theoretical[4] and experimental[5] investigations, none has, heretofore, been able to eliminate unambiguously either the in-plane (inversion) or the out-of-plane (rotation) motions for isomerization (Scheme I). Both theoretical calculations[4] and experimental rate data[5] support the in-plane mechanism for isomerization.

We have measured rate constants for the syn-anti conversion of azobenzene in benzene (B), *n*-butyl stearate (S), and the isotropic phase of a 50/50 (w/w) mixture of 5α-cholestan-3β-yl acetate and 5α-cholestan-3β-yl nonanoate (ChA:ChN).[6] It was possible to measure isomerization rates in both the cholesteric (37–77 °C) and isotropic (>77 °C) phases of a 35:65 (w/w) mixture of cholesteryl chloride and cholesteryl nonanoate (CCl:CN) owing to the stable enantiotropic nature of the liquid crystalline phase. Reactions were conducted in thermostated cells and were followed spectroscopically.[7] Identical syn-to-anti rates were obtained from samples in which the syn was produced by irradiation of the anti dissolved in the cholesteric solvent and in which the pre-formed syn was dissolved in the ordered solvent.

The similarity among the activation parameters obtained in B, S, and the isotropic phase of ChA:ChN reveals that major changes in solvent viscosity influence the isomerization only slightly (Table I and Figure 1). A similar conclusion has been reached by Morawetz[8] who employed a completely different

Scheme I

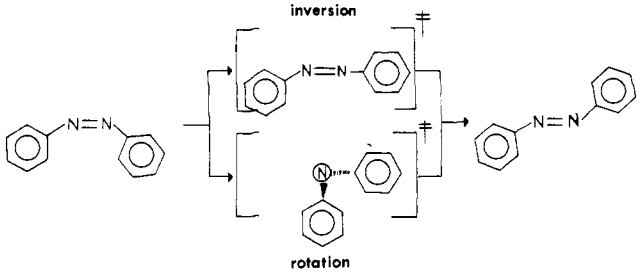

Table I. Activation Parameters for Syn–Anti Isomerization of Azobenzene

solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	E_a, kcal/mol
benzene	21.7 ± 0.4	−12.0 ± 1.3	22.4 ± 0.4
n-butyl stearate	20.3 ± 0.6	−15.9 ± 1.5	21.0 ± 0.6
ChA:ChN (isotropic)	21.1 ± 0.3	−13.5 ± 0.8	21.8 ± 0.3
CCl:CN (isotropic)	21.0 ± 0.6	−13.9 ± 1.6	21.8 ± 0.6
CCl:CN (cholesteric)	26.9 ± 0.6	4.8 ± 1.8	27.5 ± 0.5

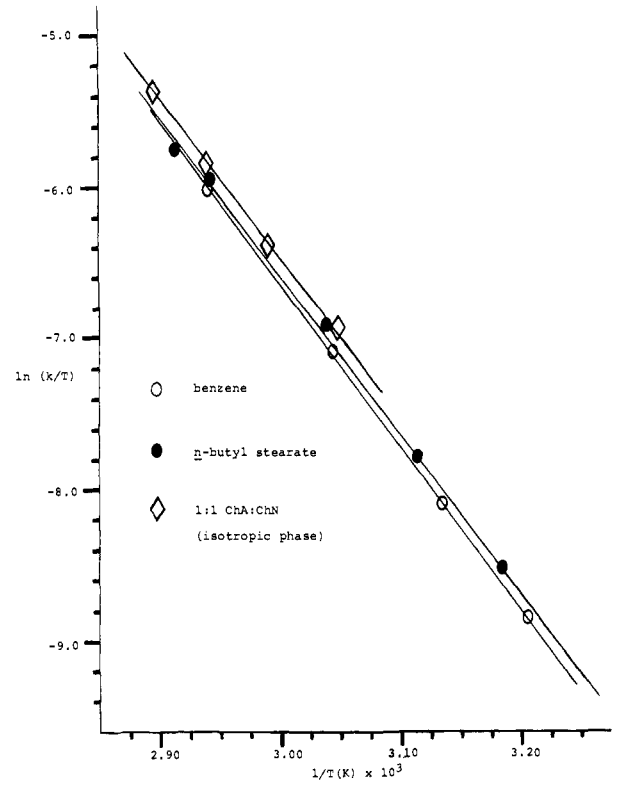

Figure 1. Plot of ln (k/T) vs. $1/T$ for thermal isomerization of *syn*-azobenzene in benzene, *n*-butyl stearate, and the isotropic phase of ChA:ChN.

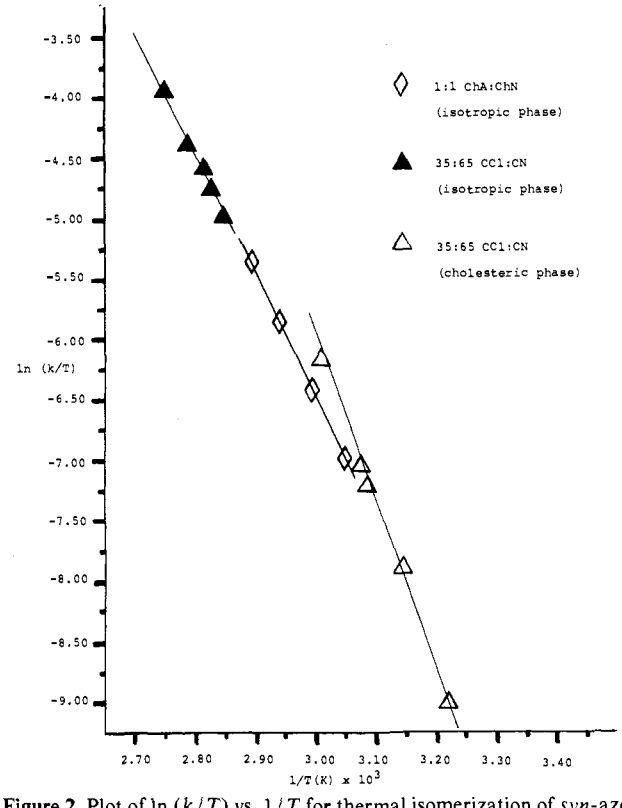

Figure 2. Plot of ln (k/T) vs. $1/T$ for thermal isomerization of *syn*-azobenzene in the isotropic phase of ChA:ChN and the isotropic and cholesteric phases of CCl:CN.

experimental approach. The data obtained in CCl:CN, however, differ dramatically. As can be seen in Figure 2, a plot of ln (k/T) vs. $1/T$ does not yield a single straight-line slope for the cholesteric and isotropic phases.[9] In the isotropic phase of

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CCl:CN, the activation parameters are nearly identical with those obtained in B, S, and ChA:ChN. Comparison of these results with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the cholesteric phase of CCl:CN reveals that solvent order exerts a substantial influence on the reaction mechanism. The large increases in both parameters (Table I) in the cholesteric phase support the out-of-plane mechanism for isomerization, but not the in-plane mechanism.

In a cholesteric mesophase, solvent molecules are arranged in stacked layers in which the constituent molecules display unidirectional alignment of their long axes within an individual layer. Displacement of one layer with respect to its neighbors results in a "twisted" nematic macrostructure.[11] Solute molecules, when dissolved in a cholesteric (or nematic) mesophase, align in the best packing arrangement based upon steric considerations. For example, planar molecules orient their long axis parallel to the long axis of the liquid crystal.[12] Theoretical calculations[13] indicate that anti-azobenzene is planar,[14] whereas the syn isomer is slightly distorted from planarity (the two phenyl rings being twisted ~30° out of the plane of the nitrogen-nitrogen double bond). Therefore, steric factors should orient both azobenzene isomers parallel to the long axis of our liquid crystal. Optical studies performed on solutions of *syn*- and *anti*-azobenzene in compensated nematic liquid crystals are consistent with this hypothesis.[15]

The isomers of azobenzene should perturb the order of a cholesteric liquid crystal similarly since both solutes are of comparable size and shape. It follows that interconversion of the azobenzene isomers via motions within the plane defined by a solvent layer (i.e., the inversion mechanism) will cause a minimal perturbation on the cholesteric structure. Should the interconversion process include severe distortion from planarity (such as those expected if the rotation mechanism is operative), the solvent layers immediately above and below the reacting solute will be disturbed. These hypotheses suggest that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the inversion mechanism should be similar in isotropic and cholesteric phases.[16] However, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the rotation mechanism should both be more positive in a cholesteric phase than in an isotropic phase: rotation will be hindered by the solvent layers directly above and below the solute; the layers will be more disorganized in the transition state than in the ground state. Our results, employing CCl:CN as solvent, are clearly more consistent with the rotation mechanism than the previously preferred inversion mechanism for isomerization.

The experimental approach outlined here demonstrates the utility of cholesteric liquid crystal solvents in the elucidation of reaction mechanisms. We are investigating currently the effects of substituents on the thermal and photochemical pathways for isomerization of other azobenzenes and will report on these in future publications.

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(6) Experiments were performed only in the isotropic phase of ChA:ChN, since its monotropic cholesteric phase (below 54 °C) could not be maintained for long periods.
(7) Details of the experimental procedure will be given in a full paper.
(8) (a) D. Tabak and H. Morawetz, *Macromolecules*, **3**, 403 (1970); (b) C. S. Paik and H. Morawetz, *ibid.*, **5**, 171 (1972).
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(16) A referee has suggested that our data are compatible with an inversion motion in which one phenyl ring becomes orthogonal to the plane described by the other phenyl and the azo group. While we cannot eliminate this possibility unequivocally, the magnitude of the increase in $\Delta S^{\ddagger}$ upon changing from the isotropic to the cholesteric phase seems more consistent with the torsion motion. The spectroscopic data of Sackmann[15] indicate that the ground-state conformations of azobenzene in liquid crystals and isotropic solvents are similar. Assuming, then, that a phenyl ring of *syn*-azobenzene in the liquid crystal is twisted out of plane by ~30°,[13] movement to a perpendicular transition state involves a small change in molecular geometry (and in solvent–solute interactions). Models indicate that movement to the torsion transition state from the same ground state results in a significant change in molecular geometry (and in solute–solvent interactions). It is known that the partial molar excess entropy of nonmesomorphic solutes in liquid crystals, $\bar{S}$, are dependent on solute shape.[17] The $\bar{S}$ are most different for the normal and most globularly shaped isomers of an alkane series: $\Delta\bar{S}$ between *n*-nonane and 3,3-diethylpentane is ≃ 11 eu. If, as we believe, our $\Delta\Delta S^{\ddagger} \simeq 19$ eu (isotropic to cholesteric phase) arises primarily from interactions like those responsible for ΔS, the geometry of the transition state for azobenzene need be *much* different from that of the syn conformation.
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An Isotope Effect Maximum for Proton Transfer between Normal Acids and Bases

Sir:

We wish to report that we have observed a maximum in the dependence of the kinetic isotope effect, on proton transfer between "normal" [1] acids and bases, upon the acid strength of the proton donor. Although a number of such isotope effect maxima are now known for proton transfer to or from carbon,[2] the present case and that described in the accompanying paper[3] are the only known examples for proton transfer limited to oxygen and nitrogen acids and bases.[4] The nature of these maxima has an important bearing on the detailed mechanism of proton transfer between normal acids and bases, and it also offers a ready explanation for the general absence of large isotope effects on these reactions.

Proton transfer between normal acids and bases is usually a very fast reaction.[1] There are systems, however, in which it occurs after an unfavorable equilibrium as part of a complex reaction scheme, and when, in such cases, it is the rate-determining step, it can be studied by classical (slow) kinetic techniques. The reaction between *p*-methoxybenzaldehyde and methoxylamine in the presence of acidic catalysts (eq 1) has been shown to be such a process: under certain conditions of *pH* and catalyst concentration, proton transfer from the catalyst to the alkoxide oxygen of the first-formed zwitterionic intermediate, **1**, is rate determining, eq 2.[7]

$$p\text{-}CH_3OC_6H_4CHO + CH_3ONH_2 \xrightarrow{HA} p\text{-}CH_3OC_6H_4CH{=}NOCH_3 \quad (1)$$

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