I). As in the ZnTPP case no enhancement of intersystem crossing efficiency was observed in the aligned nematic. Thus the results regarding 2-PAQ compared to ZnTPP show more clearly that the enhancement of the T-T absorption intensity in the nematic phase is the result of increased absorption of the polarized laser light.

It was observed in the 2-PAQ/K18 system that upon flashing at high laser intensities at the same macroscopic temperature, the triplet lifetime decreased considerably. At 26 °C, the lifetime decreased from 55 μs for a 4.1% laser screen (~3.7 mJ/pulse) to 13 μs for a 29% laser screen (26.1 mJ/pulse). The decay process, however, remained first order (Figure 5a,b); hence, the decreased lifetime cannot be attributed to increased triplet-triplet annihilation. The transient absorption also does not return to the original base line at higher input intensities, leaving a positive optical density change at long time scales (>100 μs), Figure 5b. The optical density changes at these longer times were relatively constant in the wavelength region studied (Figure 4b). Similar experiments were carried out in the isotropic phase of K18, where it was observed that the triplet lifetime also decreases with increasing dose. At the highest laser dose used (~68 mJ/pulse) the lifetime was 10 μs compared to 45 μs observed at low dose (~4 mJ/pulse). Also at the higher doses considerable second-order contribution was observed in the decay kinetics. However, the transient absorption always decayed to the base line in contrast to the results in the nematic phase.

These results are interpreted as follows. At high laser energies, the total electronic energy degraded by the radiationless transitions of 2-PAQ is sufficient to locally melt the liquid crystal. The subsequent cooling of the isotropic phase to the nematic phase leads to a permanently scattering nonaligned texture as indicated by the decreased optical transmission at longer times. The decay of the transient absorption to the base line in the isotropic phase even at laser energies much higher than those used in the nematic phase study confirms the fact that the positive ΔOD changes observed in the nematic phase are due to a scattering texture and not due to a permanent product formation. Results similar to those in K18 were observed for K15. The shape of the curve of ΔOD vs. time will vary as a function of the relative values of the rates for triplet decay and cooling of the isotropic phase to the scattering phase. If the rates were comparable, a multiexponential decay would be observed. Our results in Figure 5 show that the triplet decays by a clean first-order process to a scattering phase, suggesting that the rate of cooling is at least an order of magnitude faster than that for triplet decay.

A laser dose dependence of the decay rate of the 2-PAQ triplet was observed in the nematic and isotropic phase. A similar dependence on excitation dose was also observed in benzene in an earlier pulse radiolysis study.[17] Therefore it is apparent that the excitation energy dependency of the triplet decay rate (shortening of the lifetime as the excitation energy increases) is inherent to the photophysics of 2-PAQ and does not depend specifically on a liquid crystalline phase.

We may note that the reversible melting/cooling by laser excitation of a dye/liquid crystal mixture, leaving behind a scattering texture, has important applications in the field of display devices.[18]

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Dynamics of Atropisomerization of 1,1′-Binaphthyl in Several Nematic Solvents. Rate Enhancement by a Solid Phase[1]

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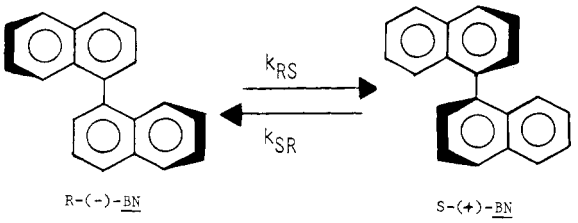
Abstract: The rates of atropisomerization of (*S*)-(+)-1,1′-binaphthyl (BN) are compared in six nematic phases and in the solid phase of *p*-methoxybenzylidene-*p*-*n*-butylaniline. The influence of each phase on the activation parameters for atropisomerization are correlated with the solvent molecular structures. The results in the nematic and solid phases are interpreted in terms of the degree to which the solvent matrices flatten the angle between the naphthyl rings of BN.

Since its spontaneous optical resolution by Wilson and Pincock,[2] 1,1′-binaphthyl (BN) has been employed extensively to investigate the factors which affect hindered rotation about σ-bonds.[3,4] Its low enthalpy of activation ($\Delta H^{\ddagger}$) for atropisomerization, ca. 22 kcal/mol in a wide variety of isotropic solvents,[5] allows the kinetics of naphthyl ring rotations in BN to be followed conveniently near room temperature (eq 1).



(1)

In a previous study, we suggested that rate enhancements observed for atropisomerization of BN in cholesteric mesophase solvents can be attributed to solvent-induced compression of the angle (θ) between the two naphthyl rings.[3] In principle, the same factors should be operative in nematic mesophases; also, in many respects, cholesteric phases are only twisted nematics.[6]

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(1) This paper is part 25 in the Georgetown series, *Liquid-Crystalline Solvents as Mechanistic Probes*. For part 24, see: Lin, Y.-C.; Weiss, R. G. *Macromolecules* **1987**, *20*, 414.
(2) Wilson, K. R.; Pincock, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 1474.
(3) Ganapathy, S.; Weiss, R. G. In *Organic Phototransformations in Nonhomogeneous Media*; Fox, M. A., Ed.; American Chemical Society: Washington, DC, 1985; p 146.
(4) (a) Irie, M.; Yorozu, T.; Hayashi, K. *J. Am. Chem. Soc.* **1978**, *100*, 2236. (b) Yorozu, T.; Hayashi, K.; Irie, M. *J. Am. Chem. Soc.* **1981**, *103*, 5480.
(5) (a) Colter, A. K.; Clemens, L. M. *J. Phys. Chem.* **1964**, *68*, 651. (b) Cooke, A. S.; Harris, M. M. *J. Chem. Soc. C* **1967**, 988.
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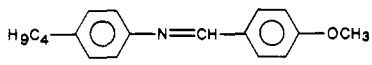
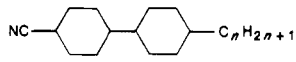
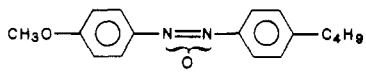
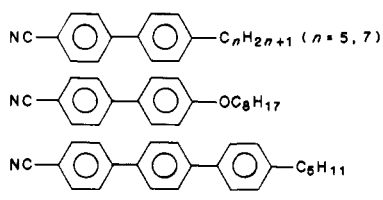
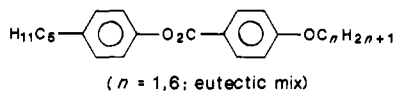
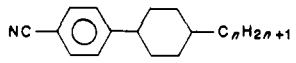
Table I. Structure and Properties of Nematic Solvents

liquid crystal	structure	supplier	transition temps[a] (°C)
MBBA		Aldrich	$k^{21}n^{43.0-43.5}i$
ZLI 1167	 (n = 3, 5, 7; eutectic mix)	Merck	$k^{25}s^{32}n^{83}i$
Phase IV	 (eutectic mix)	Merck	$k^{20}n^{74}i$
E7	 (eutectic mix)	BDH	$k^{-10}n^{60.5}i$
Phase 1052	 (n = 1,6; eutectic mix)	Merck	$k^{15}n^{48}i$
Phase 1083	 (n = 3, 5, 7; eutectic mix)	Merck	$k^{-3}n^{52}i$

[a] k = crystal; n = nematic; s = smectic; i = isotropic.

The degree to which an ordered solvent influences θ depends upon many factors. Among the most important of these are the following: (1) the intrinsic order of the undoped solvents; (2) the ordering of BN within the solvent matrix; (3) the ease with which solvent molecules in the cybotactic region yield to or help the internal BN motions which lead to its transition state; and (4) the relaxation times of the solvent molecules. A complete dissection of these factors is beyond our present understanding. By comparing the atropisomerization of BN in several different nematic phases and in several phases of one solvent, it should be possible to begin to identify the more important considerations. We report here the results of that study and show that structural differences among constituent solvent molecules alter the interactions between BN and the solvent matrix. Furthermore, we find *acceleration* of the rate of atropisomerization by a solid phase due to its more severe demands upon the structure of dissolved BN molecules.

The techniques for measuring these rate processes employ methods which require very small amounts of optically active materials and which are especially advantageous when the specific rotation of the solute is small. Only one of them has been used previously as a kinetic tool.[7,8]

Results and Discussion

Nature of the Ordered Solvent Phases.[9] Nematic mesophases are usually comprised of elongated molecules. Their long molecular axes are parallel to one another on average, but no other intermolecular order is necessary. Cholesteric mesophases are comprised of optically active molecules which exhibit nematic-like local order. Macroscopically, the molecules are twisted slightly so that they adopt a helical arrangement which can be detected by optical microscopy and other techniques.

Introduction of an optically active solute into a nematic solvent results in a cholesteric-like twist.[6] The helicity imparted by the chiral solutes to the twisted nematic can be related to the molecular structures[10] of the solvent and solute and depends upon the concentration of the solute.

The structures of the solvents employed in this study are listed with their mesomorphic temperature ranges in Table I. Each solvent consists of two six-membered rings which are linked either directly or indirectly and which contain substituents at the 4 and 4' (or para and para') positions of the rings. The rigidity of the central cores increases with increasing ring unsaturation and decreasing separation between the rings.

p-Methoxybenzylidene-*p*-*n*-butylaniline (MBBA) presents a special case in which the phases obtained are dependent upon sample history.[11,12] Spectroscopic studies indicate that a plastic crystalline phase exists in the temperature range between the nematic and solid phases (ca. 15–21 °C).[13] Individual molecules in the plastic phase are able to rotate nearly freely within a unit cell but do not diffuse from it. Considering the cylindrical shape of MBBA molecules, it is likely that rotation occurs along their long molecular axes. X-ray data suggest, further, that the intermolecular ordering of molecules within this phase is more smectic-like than nematic-like.[11] Plastic crystallinity may be a general property of molecules like those in Table I.[14]

A detailed X-ray structural analysis of MBBA in its solid phase has not been performed. The packing of the crystalline ethoxy analogue, EBBA, has been reported;[15] there is no reason to believe

(7) (a) Ruxer, J.-M.; Solladie, G.; Candau, S. *J. Chem. Res. (S)* **1978**, 82. (b) Seuron, P. Thesis, Universite Strasbourg, 1979. (c) Hibert, M. Thesis, Universite Strasbourg, 1980. (d) Solladie, G.; Zimmerman, R. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348.

(8) Other studies which follow pitch changes of cholesteric phases in order to establish the rates of solute reactions in which no racemization occurs have been performed: (a) Park, J. W.; Labes, M. M. *Mol. Cryst. Liq. Cryst.* **1976**, *34*, 25. (b) Okamoto, K.-I.; Labes, M. M. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 9.

(9) See, for instance: Demus, D.; Diele, S.; Grande, S.; Sackmann, H. In *Advances in Liquid Crystals*; Brown, G. H., Ed.; Academic Press: New York, 1983; Vol. 6, Chapter 1.

(10) Gottarelli, G.; Spada, G. P. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 377.

(11) Lydon, J. E.; Kessler, J. O. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 153.

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(13) Arumugam, S.; Bhat, S. V.; Kumar, N.; Ramanathan, K. V.; Srinivasan, R. *Mol. Cryst. Liq. Cryst.* **1985**, *126*, 161.

(14) (a) Fung, B. M.; Gargoda, M. *J. Am. Chem. Soc.* **1985**, *107*, 3395. (b) Hayamizu, K.; Yanagisawa, M.; Yamamoto, O. *Chem. Phys. Lett.* **1986**, *127*, 566.

(15) Howard, J. A. K.; Leadbetter, A. J.; Sherwood, M. *Mol. Cryst. Liq. Cryst.* **1980**, *56*, 271.

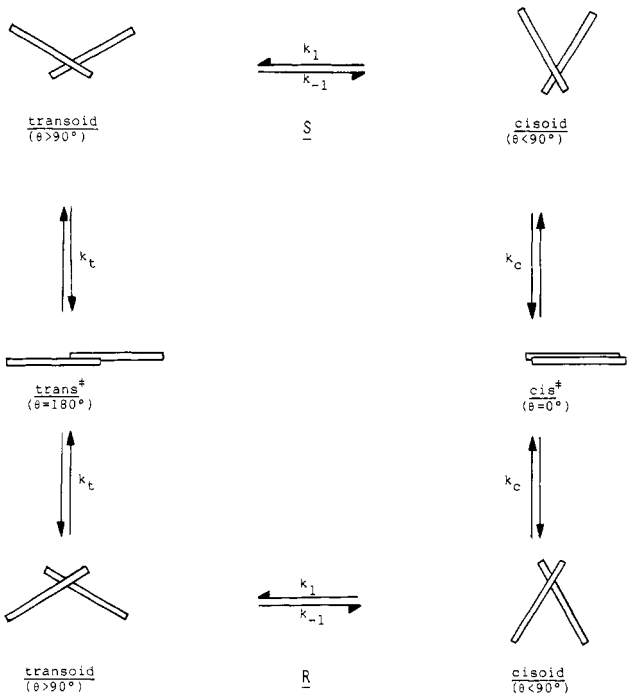

Figure 1. Cartoon mechanistic scheme for interconversion of BN atropisomers.

Table II. Activation Parameters for Atropisomerization of BN

solvent	phase	$\Delta H^{\ddagger}$ [b] (kcal/mol)	$\Delta S^{\ddagger}$ [b] (eu)
E7	nematic	15.5 ± 1.0	−26 ± 3.4
Phase 1083	nematic	16.5 ± 0.4	−22 ± 1.4
Phase IV	nematic	17.3 ± 0.7	−21 ± 2
ZLI 1167	nematic	17.7 ± 1.6	−18 ± 5
Phase 1052	nematic	19.7 ± 1.0	−13 ± 3.5
MBBA	nematic (+plastic)	23.5 ± 0.4	−8.9 ± 1.4
	solid	8.0 ± 0.7	−63.2 ± 5.4
benzene[a]	isotropic	22.2	−5.8
dimethylformamide[a]	isotropic	21.5	−6.5
cyclohexane[a]	isotropic	21.9	−7.1

[a] From ref 5. [b] Errors are one standard deviation.

that MBBA and EBBA do not share very similar crystalline features. EBBA is in a fully extended conformation and arranged as two sets of anti-parallel skewed molecules per unit cell. The twist angle between phenyl rings is 57.6°. In their nematic phases, the two molecules share very similar conformations for their common core; the butyl chain of nematic MBBA may be less extended than that of EBBA.[16]

BN Mechanism of Atropisomerization. Two distinct mechanisms for BN atropisomerization are possible. As shown in Figure 1, planarity of the two naphthyl rings can be achieved in a cis or trans transition state. Severe steric interactions which occur especially between H_8 and $H_{8'}$ in the cis transition state have led to the qualitative conclusion that the trans transition state is preferred. A quantitative measure of the trans preference has been obtained from molecular mechanics calculations which predict $\Delta H^{\ddagger} > 35$ kcal/mol for a cis transition state mechanism and only 20.2 kcal/mol for the trans.[17] The similarity between the $\Delta H^{\ddagger}$ (trans) calculation and the observed $\Delta H^{\ddagger}$ in a wide variety of isotropic solvents[5] (Table II) provides compelling evidence for the trans transition state.

Since atropisomerization occurs preferentially from the transoid conformation, it is important to explore the cisoid ⇌ transoid equilibrium. The circular dichroism spectra of unbridged BN analogues with small substiuents in the 2 and 2′ positions in isotropic solvents are similar in shape and intensity to those of bridged derivatives,[18] indicating that the two naphthyl rings prefer a cisoid conformation. From analysis of the circular dichroism spectra, a dihedral angle $\theta < 100°$ was proposed, even though there is uncertainty about the value of θ depending on the type of calculation.[18] Binaphthyl derivatives with larger substituents (CH_2Br, $CHBr_2$) show inversion in the diagnostic regions of the CD spectrum, indicating predominance of the transoid conformation.[19] These conclusions were confirmed by measurements of helical twisting powers β in nematic liquid crystals.[19]

The circular dichroism spectrum of BN[18,20] is in agreement with the expected cisoid conformation. In E7, β is positive and larger than the value observed for other 2,2′-disubstituted binaphthyls. Positive values of β for the S-configuration indicate a preferred cisoid conformation.[19] Thus, a cisoid conformation is more favored by BN than by its 2,2′-disubstituted derivatives. On the other hand, the values of β determined for conformationally locked binaphthyls are much larger and very sensitive to variations of the liquid–crystalline matrix.[21] In total, these data indicate that in BN both cisoid and transoid conformations are likely to be present, the former being the more populated one.

Pitch as a Means of Following the Progress of BN Atropisomerization. The parameter upon which our kinetic measurements are based is the helical twisting power β of a chiral solute in an achiral, nematic solvent. As defined in eq 2 (where p is the pitch in μm, c is the concentration of solute in moles/moles, and r is the enantiomeric purity of the solute), β is a *quantitative* measure of the chirality that an optically active solute imparts *macroscopically* to a host nematic phase.[22] It arises as a consequence of structural asymmetry of the solute and its recognition by the solvent.[10] As such, solutes with high optical rotations in isotropic solvents may exhibit very small β values (and vice versa).[23] Equation 2 is valid for solute concentrations which do not disturb significantly the mesophase order (usually <10% by weight[7d]). The solute concentrations employed here (1% by weight) are far below that limit. We find, for instance, that the nematic → isotropic phase transition of MBBA is depressed 5–6° by 1% of BN, and the solid (plastic) → nematic transition remains unchanged.

Conceptually, the pitch (p) represents the distance along the helical axis of a twisted nematic necessary to attain 2π rotation of the constituent molecules.[24] It is available from absorption or reflectance measurements since the handedness of the mesophase helicity reflects selectively one component of circularly polarized light: $\lambda = np$ where n is the refractive index, and λ is the wavelength maximum of the reflectance band.[25]

The distance, d, between interference rings in droplets of twisted nematics suspended in a noninteracting medium like glycerol (droplet method)[26] can be viewed microscopically between plane

(16) Yosuniwa, M.; Taki, S.; Takemura, T. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 111.
(17) Carter, R. E.; Liljefors, T. *Tetrahedron* **1976**, *32*, 2915.
(18) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671.
(19) Gottarelli, G.; Spada, G. P.; Bartsch, R.; Solladie, G.; Zimmermann, R. G. *J. Org. Chem.* **1986**, *51*, 589.
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(21) Gottarelli, G.; Hibert, M.; Samori, B.; Solladie, G.; Spada, G. P.; Zimmermann, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318.
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(23) The magnitude of optical rotations are dependent upon differences among the polarizabilities of groups about a chiral center. See, for instance: (a) Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5475, 5483, 5493. (b) Richter, W. J.; Richter, B.; Ruch, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 30. (c) Ruch, E. *Acc. Chem. Res.* **1972**, *5*, 49. (d) Brewster, J. H. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1967; Vol. 2, p 1.
(24) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Weinheim, 1980, pp 301ff. (b) Gibson, H. W. In *Liquid Crystals, the Fourth State of Matter*; Saeva, F. D., Ed.; Marcel Dekker: New York, 1979; pp 106ff.
(25) deVries, H. L. *Acta Crystallogr.* **1951**, *4*, 219.
(26) Robinson, C.; Ward, J. C.; Beevers, R. B. *Disc. Faraday Soc.* **1958**, *25*, 29.

light polarizers. Pryce and Franck[26] have shown conceptually that $p = 2d$. Thus, by rearrangement of eq 2 and substitution for p, eq 3 is obtained. The pitch can also be determined with the

$$\beta = (pcr)^{-1} \tag{2}$$

$$r = (2dc\beta)^{-1} \tag{3}$$

$$p = r_d/R(n - \tfrac{1}{2}) \qquad (n = 1, 2, 3...) \tag{4}$$

Grandjean–Cano method[27] by observing the radius r_d of the disclination circles which appear in aligned thin samples between a flat plate and a plano-convex lens of radius R (eq 4).[28]

Kinetics of BN Atropisomerization in Ordered Solvents. The kinetics of atropisomerization are complicated by the presence of a cisoid ⇄ transoid equilibrium since only the transoid can lead to racemization. By using the designations of Figure 1, the rate expression for atropisomerization is given by eq 5. If the slow

$$\frac{d[R]}{dt} = \frac{k_1}{k_{-1}}k_t[\text{cisoid } S] - \frac{k_1}{k_{-1}}k_t[\text{cisoid } R] \tag{5}$$

step along the isomerization pathway were conformer equilibration of one atropisomer (i.e., k_{-1} and $k_1 \ll k_t$), the rate expression would be much more complicated (eq 6). Equation 5 predicts that the racemization rates will decrease nonexponentially with time. That they do obey single exponential kinetic treatments in all of our ordered solvents means that conformational equilibration within one atropisomer occurs rapidly or that only one conformer is present. In either case, eq 7 holds.

$$\frac{d[R]}{dt} = k_1[\text{cisoid } S] + k_t[\text{transoid } S] - k_1[\text{cisoid } R] - k_t[\text{transoid } R] \tag{6}$$

$$\frac{d[R]}{dt} = k_a([\text{cisoid } S] + [\text{transoid } S]) - k_a([\text{cisoid } R] + [\text{transoid } R]) \tag{7}$$

We have employed both the droplet and Grandjean circle methods to follow the time dependence of d and therefore to measure the rates of racemization of BN. There appear to be no other reported applications of the Grandjean circle method to follow reaction rates in spite of its simplicity and the extremely small amounts of chiral material required: 0.5 mg of *S*-(+)-BN was sufficient to complete six kinetic runs.

The link between d and k_a, the rate constant for atropisomerization, is presented in eq 8 (where d_0 is the half-pitch at time = 0). As racemization proceeds, the pitch increases and approaches infinity. Thus, the distance between rings increases progressively with time. Six tables of rate constants derived from treatment of data by using eq 8 are available as Supplementary Material. Both methods allowed at least 1.5 half-lives to be followed, and correlation coefficients were always ≥0.99 except for two nematic phase-temperature runs of MBBA (>0.98). Treatment of the rate constants using the Eyring equation allowed calculation of the activation parameters collected in Table II.

$$\ln (d_0/d) = -2k_a t \tag{8}$$

A Conceptual Link between Solvent Molecular Structure, Helical Twisting Power, and BN Activation Parameters. A cursory examination of $\Delta G^{\ddagger}$, the free energy of activation, at 37 °C (where all of the mesophases are nematic) indicates very little influence of solvent order on atropisomerization. All of the $\Delta G^{\ddagger}$ except for MBBA are very similar and are within 1 kcal/mol of the values in normal isotropic solvents. However, careful scrutiny of the dissected free-energy data in Table II reveals several interesting trends. The nematic phase molecules in which the two six-membered rings are linked directly influence the atropisomerization most. The nematic molecules in which the two six-membered rings are separated by two linking atoms affect the racemization of BN least. The only exception occurs with Phase IV, a very polar nematic phase whose constituent molecules may interact with BN specifically through the very polar azoxy group.[29] Within the solvents whose rings are linked directly, the solvent influence is greatest (i.e., $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are most different from the values found in normal isotropic solvents for the most rigid core; the rigidity and influence on BN racemization follow the trend of E7 > Phase 1083 > ZLI-1167).

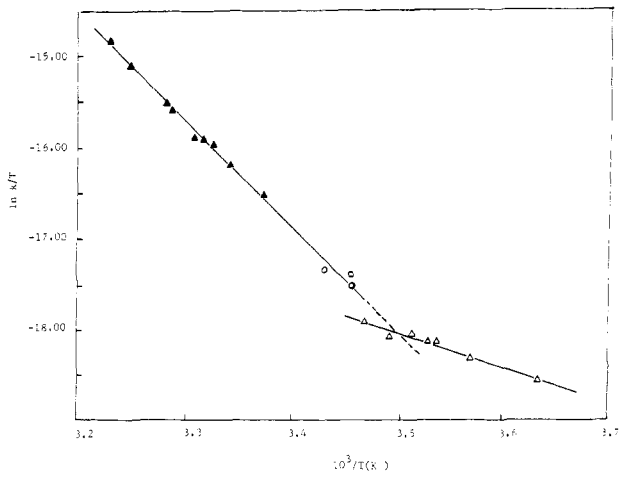

Figure 2. Arrhenius plot for atropisomerization of BN in MBBA: solid (△), plastic (○), and nematic (▲) phase-data points. See text for transition temperatures.

These observations are consistent with and support the general features of the interaction model advanced by Solladie, Gottarelli, et al.[21] to explain β. The importance of shape matching between a reactant and the molecules of a solvent mesophase to the dynamics of solute reactivity has been demonstrated also by us[30] and others.[31] It should be mentioned that other factors (such as electronic interactions) can contribute significantly to both structural and dynamic influences of ordered solvents or solutes. The relatively nonpolar nature of BN and most of the nematic solvents employed allow us to concentrate here on steric aspects of the solvent–solute interactions.

Atropisomerization of BN in MBBA Phases. The phases mentioned previously for MBBA present the possibility to compare the influence of three arrangements of one solvent on BN atropisomerization. The rate constant obtained at each temperature (spanning the solid, plastic, and nematic phases) obeyed first-order kinetics. They are presented according to the Eyring equation in Figure 2.

Both the nematic- and plastic-phase data are accommodated by the same straight line. The paucity of data in the plastic phase does not permit activation parameters in it to be calculated independently. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for MBBA in Table II combine

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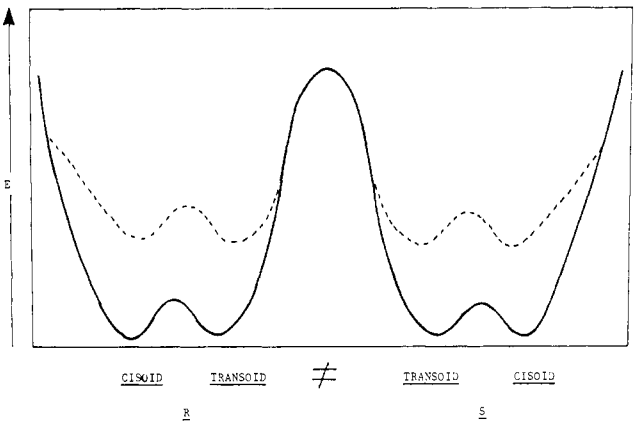

Figure 3. Qualitative potential (free) energy surface for atropisomerization of BN in isotropic (—) and ordered solvents (– – –) (like solid MBBA) which tend to flatten BN.

the nematic and plastic phase data. The values are within experimental error of those obtained in normal isotropic solvents.[5] In fact, the MBBA nematic phase is the least recognized (of any employed) by BN as an organized medium.

The solid-phase rate data are fit to a separate line. It intersects the nematic line at 12 °C, very near the macroscopically observed plastic-solid phase-transition temperature. The 3° difference is reasonable considering that the *microscopic* disturbance to solvent order near a BN solute can depress local phase transitions.[30,32]

The extremely low $\Delta H^{\ddagger}$ demonstrates that solid MBBA forces BN to adopt a conformation closer to its transition state than in any of the nematic phases. The very negative $\Delta S^{\ddagger}$ implicates significant reorganization of MBBA solvent molecules in the cybotactic region: the isotropic data in nonpolar solvents show that BN reorganization along its reaction coordinate can account for no more than 5–10 negative entropy units.[5] We believe that the remaining negative ~50 entropy units arise as the nearby solvent molecules "relax" to positions and conformations closer to those of the unperturbed crystal matrix when BN moves to its transition state.

Thus, solid MBBA *accelerates* BN atropisomerization when the nematic progression of rates is extrapolated to solid-phase temperatures. This occurs in spite of the much higher viscosity which must be present in the solid phase.[33] In fact, we had previously found that a 40-fold increase in viscosity has no measurable effect upon the rate of *BN* atropisomerization.[3] Qualitative potential (free) energy surfaces for the two limiting cases of atropisomerization—in the nematic and solid phases of MBBA—are shown in Figure 3. The potential energy curves in the other nematic solvents fall between these; the ordered media flatten the naphthyl rings of BN to varying extents.[3]

In essence, we believe that the transition-state energy is similar in both ordered phases of MBBA and that the major differences occur in solvation of the transoid conformation. Both the nematic and solid phases should accept more easily a platelike solute (the transition state) than a globular one (the transoid conformation).[34] The harder solid matrix must resist incorporation of the transoid conformation to a greater extent than the nematic matrix. Thus, curves like Figure 3 which follow the influence of BN conformations only on *solvent* energy are expected to display minima when BN is at its transition state.[30a,30c,35]

Conclusions

The intimacy of interaction between the optical active solute, (*S*)-(+)-1,1′-binaphthyl, and nearby solvent molecules of a nematic phase depends upon their structural compatibility. Those solvents which contain directly linked six-membered rings sense the chirality of BN and its derivatives (as indicated by β) to a greater extent than those in which the six-membered rings are separated by two or more atoms. The most ordered solid phase of MBBA exhibits the greatest influence upon the BN atropisomerization. The results, in toto, are consistent with a model in which the ordered phases tend to flatten the naphthyl rings of BN (i.e., making it appear more planar in shape and, therefore, less disruptive to local solvent order).

The methods employed to follow the kinetics of atropisomerization rely upon the pitch changes in solvent which attend racemization. They require very small amounts of solute. Although relatively unexploited in dynamic studies, the methods are simple and hold promise of much wider applicability than has been appreciated.

Experimental Section

Racemic BN was synthesized from the Grignard reagent of 1-bromonaphthalene and anhydrous $CuCl_2$ according to the method of Sakellarios and Kyrimis.[36] It was sublimed twice under reduced pressure and recrystallized from benzene: mp 143.5–144 °C (lit.[2] mp 144.5–145 °C). BN was resolved in the solid state according to the heating–cooling–recrystallization cycles suggested by Wilson and Pincock[2] to yield $[\alpha]^{29}_{D}$ +160°, benzene (lit.[2] $[\alpha]^{25}_{D}$ +245°, benzene), corresponding to ca. 65% optical purity of the (*S*)-(+)-atropisomer. Some of the optically active BN ($[\alpha]^{29}_{D}$ +220°, benzene) was available from a previous study.[3]

The liquid crystals were used as received. A summary of their undoped phase transition temperatures and structures is given in Table I.

Thermal Racemization of (*S*)-(+)-BN in MBBA by the Droplet Method.[37] A solution of 2 mg of (*S*)-(+)-BN, 200 mg of MBBA, and a minimum amount of anhydrous ether was prepared in a small vial. Most of the ether was removed rapidly under reduced pressure at room temperature. A current of nitrogen gas was then passed through the solution for several minutes to remove the remainder. A series of vials, each containing one or two drops of the mixture, was placed in a thermostated water bath. Single vials were removed periodically from the bath and quenched at dry ice temperatures. A few drops of glycerol were mixed thoroughly with the vial contents, and an aliquot was placed rapidly upon a cover glass and observed under polarized light through a microscope. The optical pattern of the suspended MBBA droplets consisted of concentric rings. A photographic transparency of each image at the same microscope power (100×) was taken as rapidly as possible. Since the half-life of BN at room temperature is ca. 12 h and the time to prepare the droplets and photograph them was less than 10 min, no correction for racemization subsequent to temperature quenching was made. The relative pitch was calculated from the distances between rings when the transparencies were projected onto a planar surface. Several ring separations for each pattern were averaged.

Thermal Racemization of (*S*)-(+)-BN in Nematic Phases by the Grandjean Circle Method.[27,28] The solutions of ca. 0.5 mg of (*S*)-(+)-BN in 50 mg of liquid–crystalline solvent were prepared by mixing the two components in a small vial, heating for several seconds above the isotropic transition temperature, and stirring for ca. 30 min at room temperature. One drop of the solution was placed on a glass plate which had been rubbed in one direction with tissue paper. The plate was placed on the thermostated stage of a Zeiss polarizing microscope. A plano-convex lens (curvature radius ca. 40 mm) which had been rubbed previously with tissue paper was placed atop the drop so that the rubbing directions were parallel. Both the lens and the plate were coated with a thin film of polyvinyl alcohol in order facilitate alignment of the droplets. The distance between the concentric circles, as they appeared through the microscope, was measured as a function of time.

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Supplementary Material Available: Tables III-VIII of rate constants for atropisomerization of (*S*)-(+)-BN in nematic solvents (2 pages). Ordering information is given on any current masthead page.

The ^{18}O Isotope Shift in ^{15}N NMR Spectroscopy. 3. Effects of Structure and Solvent

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Abstract: Various ^{15}N,^{18}O-labeled compounds were synthesized and the ^{18}O-induced isotope shifts on their ^{15}N NMR spectra were measured in order to examine the effects of structural changes on the magnitudes of the shifts. The measured shifts vary greatly, ranging from 0.027 ppm for a nitrile oxide to 0.159 ppm for an isoxazole. The large isotope shifts of isoxazoles compared to oximes and isoxazoline are attributed to the aromatic nature and shorter N–O bond lengths of the isoxazoles. The nature of substituents in the para position of some aromatic aldehyde and ketone oximes affects the magnitude of the ^{18}O-induced shift. Intramolecular hydrogen bonding significantly decreases the magnitude of the isotope shift in oximes. A study of the effect of solvents on the isotope shifts of three oximes is made. A significant decrease in the isotope shift is observed in solvents having an electron donor atom such as oxygen or nitrogen. This decrease in the magnitude of the isotope shift is ascribed to the formation of hydrogen bonds between the oxime hydroxyl proton and the oxygen or nitrogen of the solvent. Possible applications of the ^{18}O isotope shift in ^{15}N NMR are briefly discussed.

Effects of isotopic substitution on nuclear magnetic resonance signals have been known for some time. Ramsay and Purcell[1] first predicted an isotope effect on nuclear magnetic resonance signals, and this was soon followed by reports of a ^{2}H isotope induced shift on ^{1}H and ^{19}F NMR spectra.[2-4] Since then, isotope-induced shifts on NMR spectra of other nuclei have been increasingly studied and utilized. The advent of high-field Fourier transform NMR instruments with increased sensitivity and resolution has facilitated the measurement of many of the new isotope effects, including those due to oxygen. It was known that when oxygen-18 was substituted for an oxygen-16, an upfield shift occurred in the NMR signals of ^{1}H, ^{55}Mn, and ^{95}Mo.[5-7] Particularly following reports of ^{18}O isotope shifts on ^{31}P and ^{13}C NMR,[8,9] interest in the area has increased. Hansen has reviewed the isotope effects of all nuclei through 1981, and Forsyth has recently surveyed the isotope effects on ^{13}C NMR chemical shifts and coupling constants.[10,11] These isotope shifts are being extensively utilized to understand mechanisms of reactions and to elucidate biosynthetic pathways.[12-17]

The existence of the ^{18}O isotope shift on ^{15}N NMR was first demonstrated by Van Etten and Risley in studies with ^{15}N,^{18}O-labeled samples of sodium nitrite, silver nitrite, and sodium nitrate.[18] The ^{18}O shift on ^{15}N NMR was then employed to study the kinetics of the acid-catalyzed oxygen-exchange reaction between sodium nitrite and water. Subsequently it has been utilized to establish the source of oxygen in the oxidation of ammonium ion to nitrite ion by a *Nitrosomonas* species,[19,20] the conversion of nitrite ion to nitrate ion by *Nitrobacter agilis*,[21] and in the biosynthesis of 3-nitropropionic acid from L-aspartic acid by cultures of *Penicillium atrovenetum*.[22] This rapid utilization is due in part to the fact that NMR spectroscopy is a direct method with distinct experimental advantages over many conventional mass spectroscopic methods, particularly those that require a conversion to volatile compounds for analysis.

In the limited number of cases that have been studied so far, the magnitudes of the ^{18}O isotope induced shifts made it relatively easy to employ ^{15}N NMR spectroscopy as a tool to study the particular pathways. Because the ^{18}O isotope induced shift on ^{15}N NMR is a relatively new addition to the library of isotope effects on NMR signals, it is important to define the characteristics of the spectral shifts. Most fundamental among these would be an examination of the relationship between structure and magnitude of the shift. Recently we reported the synthesis of a key

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