tions: (1) the radical cation must add water to produce a hydroxycyclohexadienyl radical and (2) the hydroxycyclohexadienyl radical has no alternate pathways of decomposition.

Experimental Section

The experimental procedures have been described previously.[2,3] In the experiments at 80 °C, after 1 h about 20% of $S_2O_8^{2-}$ has decomposed, i.e., 4.5×10^{-4} mol, yielding, for example, in expt 6, Table II, 32×10^{-5} mol of phenols. The phenol, chlorophenols, and bromophenols were analyzed by gas chromatography using a 6-ft column of FFAP (5%) on Chromasorb W-AW-DMCS and a flow rate of 25 mL/min. This column was used at 220 °C for the analysis of *p*-chloro- and *p*-bromophenol (7.8 and 12.2 min, respectively) and at 180 °C for the analysis of *o*-chlorophenol, *o*-bromophenol, and phenol (4.5, 6.6, and 7.2 min. respectively). In the experiments with chlorobenzene and nitrobenzene, the *o*-chlorophenol appeared immediately after the big nitrobenzene peak when using the above column and conditions. We therefore used another column for these samples: 6 ft DEGS + 6 ft SF-96 (10% liquid phase on Chromosorb W-AW-DMCS) at 160 °C. Under these conditions the retention times were 5.0 min for *o*-chlorophenol, 5.5 min for nitrobenzene, and 7.8 min for phenol. The nitrophenols were analyzed after methylation with diazomethane on a 6 ft FFAP column at 200 °C as described.[26] The separation of the *m*- and *p*-chlorophenols and the *m*- and *p*-bromophenols was accomplished after silylation with BSA (Supelco, Inc.). The silylated derivatives could be separated on a 10-ft column of 5% SE-30 on 80/100 Supelcoport at 130 °C. Under these conditions the meta isomer appears before the para isomer.

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Registry No. Disodium persulfate, 7775-27-1; nitrobenzene, 98-95-3; hydroxy radical, 3352-57-6; fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1.

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Liquid Crystalline Solvents as Mechanistic Probes. 11. The Syn → Anti Thermal Isomerization Mechanism of Some Low-"Bipolarity" Azobenzenes[1]

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The effects of solvent order on the syn → anti isomerization rates of 15 azobenzenes have been investigated. The activation parameters determined in a cholesteric phase consisting of a 35/65 (w/w) mixture of cholesteryl chloride/cholesteryl nonanoate and in several other solvents are more consistent with an isomerization mechanism which proceeds via inversion (in plane) rather than rotation (out of plane). A correction of our previously reported data is given. The anomalous behavior of the isomerization mechanism of di-ortho-methylated azobenzenes is demonstrated by means of isokinetic plots.

The mechanism of the thermal syn → anti isomerization of azobenzene (1) has been investigated extensively for more than 40 years[2] and remains a subject of controversy. It is known to follow first-order kinetics which are slightly dependent upon solvent polarity in a wide variety of media[3] and phases: for instance, in the melt,[4] $E_a = 24.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5$ eu; in the vapor phase,[5] $E_a = 28$ kcal mol^{-1} and $\Delta S^{\ddagger} = +3$ eu. Unfortunately, none of these studies has been able to distinguish unambiguously between an inversional (in plane) motion and a rotational (out of plane) motion for the isomerization (Figure 1).

Theoretical calculations favoring the inversional process have been reported.[6] However, no treatment to date has included a wide selection of C–N rotamers in the transition states, and, of those which reproduce the experimental syn → anti isomer energy difference (9.9 kcal mol^{-1} [7]), none has been extended to calculate activation energies for isomerization.[8]

Recently, the isomerization of azobenzene has been reexamined by using some novel mechanistic tools. For instance, Rau and Lüddecke[9] measured the activation energy for syn,anti → anti,anti isomerization in a cyclic bichromophoric azobenzene in which a rotational mechanism can occur only with great difficulty. The fact that the observed activation energy is smaller than that found for syn → anti isomerization of **1** in the same solvent provides evidence for the inversional mechanism. Shinkai

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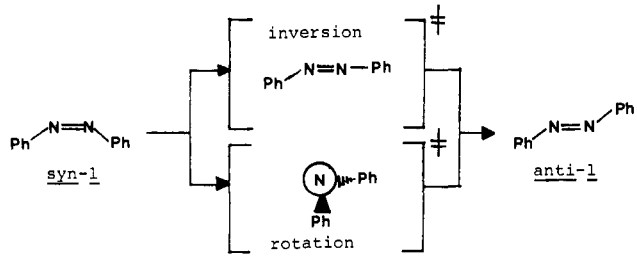

Figure 1. Proposed mechanisms for the thermal syn → anti isomerization of azobenzene (1).

Table I. Pitch Band Maxima (λ_p) in $(CCl/CN)_c$ at Various Temperatures

solvent	λ_p[a] 40 °C	54 °C	52 °C	59 °C
$(CCl/CN)_c$	745	770	795	850
$(CCl/CN)_c$ + 1[b] anti	755	785	820	870
syn + anti[d]	760	780	815	860
$(CCl/CN)_c$ + 15[c] anti	758	775	801	839
syn + anti[d]	762	777	803	839

[a] In nanometers. [b] 3.8×10^{-2} M. [c] 7.5×10^{-3} M. [d] Unknown amount of syn isomer after irradiation of the anti isomer for 5 min.

et al.,[10] employing a similar approach, have looked at the isomerization of an azobenzene covalently bound across a crown ether.

The enthalpies of transfer from cyclohexane to cyclohexanone for *syn*-1 and its isomerization transition state[11] and measurement of activation volumes for the syn → anti process[12] were used to argue for an inversional mechanism also. Both of these methods rely upon assumptions concerning the relative polarities of the reactants and their transition states. These, in turn, are dependent upon the *assumed* orientation of the phenyl rings of 1 with respect to the azo group during the reaction. While these assumptions may be valid, an experimental approach which relies solely upon shape changes of the reacting azobenzenes and not upon their coulombic or dipolar interactions with nearby solvent molecules would offer several advantages.

Earlier, in a preliminary paper, we described such an approach in which the effect of liquid-crystalline solvent order on the syn → anti isomerization rates is employed to distinguish between the inversional and rotational mechanisms.[13] On the basis of the data at hand, it was concluded that *syn*-1 isomerizes via a rotational motion. Here, we expand the number of phases and follow the isomerization of 14 other low-"bipolarity" azobenzene molecules.[14,15] It is concluded that *all* members of the series, including 1,[13b] isomerize via inversional motions.

Results

Solvent Properties. The enantiotropic, cholesteric phase of a 35/65 (w/w) mixture of cholesteryl chloride/cholesteryl nonanoate $(CCl/CN)_c$ persists from 37 to 77 °C. None of the azobenzenes employed exerted an appreciable effect on the helical pitch band[16] (λ_p) of $(CCl/CN)_c$ at 0.7% (by weight) loading. Some representative data are collected in Table I. The relatively slight variance of λ_p was fortuitous since quantitative, reproducible relationships between the optical densities of the syn absorption bands and isomer concentrations would have been very difficult to obtain if the pitch bands had been shifted into the spectral region used for sample interrogation. It is known that the syn isomers of azobenzenes produce a larger hypsochromic shift in a cholesteric pitch band than the anti isomers.[17] Sackmann has used pitch-band shifts to determine absolute concentrations of the two isomers of 1 in $(CCl/CN)_c$.[17c]

A compensated nematic point solvent $(CCl/CN)_n$ (pitch → ∞) was synthesized empirically by mixing various portions of CCl and CN[18] in the presence of 0.7% 1. The compensated nematic points of these varied from 60.9/39.1 (w/w) CCl/CN at 39 °C to 56.8/43.2 at 60 °C. For comparison purposes, several azobenzene isomerizations were conducted in the isotropic phase of the 35/65 CCl/CN mixture, $(CCl/CN)_i$.

Kinetic and Spectroscopic Considerations. The syn → anti isomerization rates in all solvents were followed spectrophotometrically. Irradiation of thermostated solutions containing the thermodynamically more stable *anti*-azobenzenes created an instantaneous concentration of syn isomer. The n → π* and/or π → π* absorptions of all of the syn isomers are hypsochromically shifted with respect to the anti isomers. Either the increase in anti absorption or decrease in syn absorption was monitored as a function of time. Concentrations of azobenzenes varied from ca. 10^{-5} M in isotropic solvents to ca. 10^{-2} M in liquid-crystalline ones.

Although all of the azobenzenes exhibit large shifts in their π → π* absorption bands upon irradiation, only the orthomethylated ones show a large change in the n → π* bands. For instance, the anti-syn shifts for **1**, **4**, and **7** are ≲6 nm, but those for **11**, **14**, and **15** are ≳13 nm. Since molecular models (CPK) indicate that *o*-methyl groups are capable of restricting the conformations of the phenyl rings in the syn isomers to a much greater extent than in the anti, we conclude that the magnitude of the n → π* shifts can be used as a qualitative measure of the degree to which a phenyl ring in the syn isomer is twisted out of conjugation with the π system of the azo group. Although correlations between phenyl twist and anti absorption maxima have been explored previously,[19] no relationship between *syn*-phenyl twisting and syn-anti absorption differences appears to have been noted.

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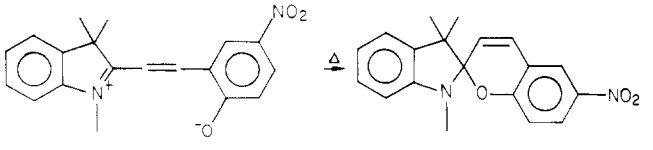
The relative concentrations of the syn isomers produced upon irradiation of the anti isomers were dependent upon the substituents and the irradiation conditions. As a result, the initial syn concentrations in kinetic runs were not constant. However, the rate constants for syn → anti isomerization were independent of the initial syn concentration: irradiation of an anti isomer for long or short periods led to the same half-life for syn disappearance.

Isomerization rate constants were obtained from the slopes of first-order plots of ln ($OD^t - OD^\infty$) vs. time and were linear for at least 2 half-lives. Although the isomerizations are thermally reversible, the reverse (anti → syn) reaction may be neglected kinetically since thermodynamic mixtures contain undetectable amounts of the syn isomers at the temperatures of our experiments. In all cases, the OD^∞ values matched the optical densities prior to irradiation, indicating the absence of processes other than syn ⇄ anti isomerization. Rate constants are believed to be accurate to ±3%. Activation parameters from the Eyring equation, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are based upon rate constants at a minimum of four temperatures in each phase (Table II and see supplementary material). Where comparisons are possible, our data are similar to those reported by others.[2-4,15]

Discussion

Solvent–Solute Interactions. The interpretation of the data in Table II is predicated upon the disturbing influences exerted by globular and cylindrical solutes on an ordered phase. It is assumed that a liquid–crystalline solvent is more disordered by a globular-shaped species than by a cylindrical one of similar functionality and mass and that, at least for the non-ortho-substituted azobenzenes, a rotational transition state is more globular than either a syn reactant or an inversional transition state. There is both static and dynamic evidence to support the former assumption. Martire et al.[20] have demonstrated that cholesteric and nematic phases are disturbed less by *n*-alkanes as dopants than by highly branched isomeric alkanes. For instance, the differences between the partial molar excess enthalpy and entropy for *n*-nonane and 3,3-diethylpentane in a β-cholesteric phase of 1.74/1 (w/w) cholesteryl chloride/cholesteryl myristate are, respectively, 3.4 kcal mol^{-1} and 11 eu.[20a]

Molecular models (CPK) support the latter assumption. In addition, we have recently found that the rate of the thermally induced merocyanine (plate-like structure) to spiropyran (globular structure) conversion of 1′, 3′, 3′-trimethyl-6-nitrospiro[2*H*-benzopyran-2,2′-indoline] (**16a** → **16b**) is decreased significantly by the *order* of smectic



16a 16b

n-butyl stearate:[21] the activation parameters are E_a = 38 kcal mol^{-1} and $\Delta S^\ddagger$ = +55 eu in the smectic phase and *Ea* = 17 kcal mol^{-1} and $\Delta S^\ddagger$ = −9 eu in the isotropic phase.

Table II. Activation Parameters for the Thermal Syn → Anti Isomerization of Azobenzenes in Various Media[a]

		in benzene		in *n*-butyl stearate		in $(CCl/CN)_c$		in $(CCl/CN)_i$		in $(CCl/CN)_n$	
compd	substituents	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
1		21.7 ± 0.4[b]	−12.0 ± 1.3[b]	20.3 ± 0.6[b]	−15.9 ± 1.5[b]	21.9 ± 1.3	−10.1 ± 4.1			21.7 ± 1.6	−10.2 ± 4.9
2	4-methoxy	22.9 ± 0.6	−6.3 ± 0.6	22.5 ± 0.6	−7.5 ± 2.0	19.2 ± 0.2	−16.7 ± 0.6				
3	4-carbomethoxy[b]	19.2 ± 0.5	−18.0 ± 1.7	20.9 ± 0.3	−12.5 ± 0.9	18.6 ± 0.3	−18.8 ± 0.9				
4	4-methyl	21.6 ± 0.5	−11.7 ± 1.4	20.0 ± 0.7	−16.1 ± 2.2	21.3 ± 0.7	−11.6 ± 2.2				
5	4-trifluoromethyl	24.8 ± 0.7	−2.1 ± 2.1	25.1 ± 0.5	−1.0 ± 1.6	22.4 ± 1.0	−8.2 ± 3.1				
6	4-chloro	20.6 ± 1.1	−14.6 ± 2.4	20.7 ± 0.6	−14.1 ± 1.9	21.2 ± 0.3	−12.1 ± 1.0				
7	4,4′-dimethyl	24.9 ± 0.6	−0.4 ± 1.9	23.1 ± 0.8	−5.3 ± 2.5	20.4 ± 0.6	−12.9 ± 2.0	21.9 ± 0.8	−8.6 ± 2.3		
8	4,4′-dimethoxy	21.1 ± 1.2	−9.1 ± 3.8	21.6 ± 1.1	−7.3 ± 3.6	20.8 ± 0.6	−9.2 ± 1.9				
9	4,4′-dichloro	24.2 ± 1.8	−2.4 ± 5.6	23.3 ± 0.9	−4.7 ± 2.8	19.6 ± 1.0	−15.6 ± 3.0				
10	4,4′-bis(trifluoromethyl)	22.5 ± 0.6	−9.2 ± 2.0	21.8 ± 1.2	−11.2 ± 3.7	17.6 ± 1.6	−22.8 ± 5.1				
11	2,4′,6-trimethyl	25.2 ± 0.6[c]	−4.4 ± 1.9[c]			23.4 ± 0.4	−9.0 ± 1.2	24.6 ± 2.1	−5.4 ± 5.8		
12	2,6-dimethyl-4′-methoxy	26.9 ± 0.6[c]	1.0 ± 1.8[c]			23.5 ± 0.9	−8.2 ± 2.8	23.8 ± 1.2	−7.4 ± 3.3		
13	2,6-dimethyl-4′-(trifluoromethyl)	25.0 ± 0.5[c]	−5.0 ± 1.6[c]			20.6 ± 1.0	−17.1 ± 3.1	21.4 ± 1.3	−14.4 ± 3.6	23.0 ± 0.8	−10.2 ± 2.4
14	2,2′,6,6′-tetramethyl	24.8 ± 0.5[c]	−2.5 ± 1.6[c]			23.4 ± 0.5	−6.1 ± 1.5				
15	2,2′,4,4′,6,6′-hexamethyl	24.1 ± 0.4[c]	−4.1 ± 1.2[c]			23.4 ± 0.2	−5.1 ± 1.2				

[a] $\Delta H^\ddagger$ in kcal mol^{-1}; $\Delta S^\ddagger$ in cal mol^{-1} K^{-1}. [b] Reference 13a. [c] In toluene.

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Thus, for a rotational syn → anti isomerization mechanism, of an azobenzene, a larger activation enthalpy and a more positive activation entropy in $(CCl/CN)_c$ are expected than in any of the other solvents employed.

Since the polar nature of individual solvent molecules does not change as bulk undergoes a phase transition, a liquid-crystalline medium like (CCl/CN) offers an especially attractive environment in which steric solute–solvent interactions (both local and long range) can be separated from polar interactions. Thus, the difference between the activation parameters in $(CCl/CN)_c$ and $(CCl/CN)_i$ represents the contribution of solvent order to the isomerization process.[22] This is true insofar as the reactant syn conformers and their transition-state geometries do not vary with CCl/CN phases. The syn conformers appear to meet this condition since we have been unable to detect differences between the absorption spectra of the azobenzenes in the isotropic and cholesteric phases. It is possible, although not likely, that the similarity of the activation parameters within the two phases results from a fortuitous balancing between the contributions to phase reorganization and solute changes. It would be remarkable if a fortuitous balancing were to occur for all of the azobenzenes in which comparisons are made. More likely, the transition-state geometries are phase independent and disturb the cholesteric phase to the extent that the syn conformers do.

Stilbene Photoisomerization as a Model? Balanced against these arguments are the known dependencies of stilbene isomerizations on bulk viscosity. Stilbene is isoelectronic with and structurally similar to azobenzene. Its cis ⇄ trans photoisomerization *must* be rotational. Yet, only the quantum efficiency of its trans → cis photoisomerization exhibits a marked dependence upon bulk medium viscosity. The quantum efficiencies for cis → trans photoisomerization of stilbene and several of its derivatives are unaffected by very large viscosity changes.[23] This may very well mean that viscous isotropic solvents cannot distinguish between *cis*-stilbene and its twisted excited states (which are, presumably, similar in shape to rotational azobenzene transition states) on the bases of size and shape. What complicates the use of stilbene photoisomerization as a model for the syn → anti isomerization of azobenzene is that twisted excited stilbene (^{1}p or ^{3}p) does not represent a transition-state geometry. In fact, it occurs at an energy minimum along the reaction coordinate and is formed from the planar excited species (^{1}c or ^{3}c) in a process which is exothermic.[23-25] As such, solute twisting is accompanied by a net transfer of vibrational energy *to* neighboring solvent molecules.[26] By contrast, *syn*-1 would be able to attain a twisted configuration (rotational transition state) only upon transfer of vibrational energy *from* neighboring solvent molecules. Thus, we believe that the energetics of twisting from planar excited *cis*-stilbene favor greater mobility of nearby solvent molecules while the energetics of motion of *syn*-1 to its transition state (rotational or inversional) do not. The coupling of solvent motions and solute shape changes are quite different for isomerization of stilbene and azobenzene. In fact, it is questionable whether transition-state theory should be applied to very fast isomerizations like *c → *p.[24b,27]

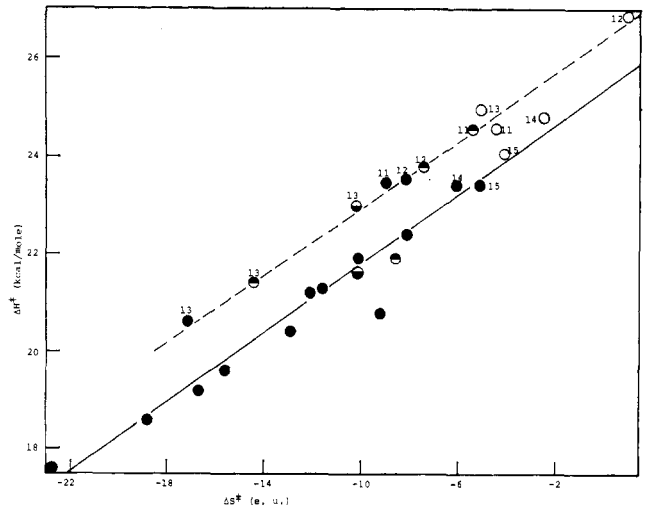

Figure 2. Isokinetic plot of syn → anti isomerizations of azobenzenes in CCl/CN: ●, in $(CCl/CN)_c$; ◓, in $(CCl/CN)_i$; ◒, in $(CCl/CN)_n$; ○, in benzene/toluene.

Activation Parameters. The activation parameters within a phase are simply the differences between the partial molar excesses of a transition state and its syn reactant. From the previously cited thermodynamic data of Martire[20] (and our own kinetic work[21]), it is clear that large shape changes in the azobenzenes during their syn → anti isomerization could have been detected were they occurring. That the activation enthalpies in $(CCl/CN)_c$ are within experimental error of those in benzene/toluene or $(CCl/CN)_i$ and $(CCl/CN)_n$ leads us to conclude that all of the *syn*-azobenzenes isomerize in these media via an inversional mechanism. In fact, although the activation entropies in $(CCl/CN)_c$ are within experimental error of those in $(CCl/CN)_i$, the average values of the former are consistently lower than the latter. At the very least, the entropies support the contention that the shape of the transition states appear no more globular to their local environments than do the syn isomers.

Isokinetic Relationships.[28] The constancy of mechanism among the solvents employed, including $(CCl/CN)_c$, is further evidenced by the excellent fit of the data to isokinetic relationships: $\Delta H^\ddagger = \beta\Delta S^\ddagger + C$ (where C is a constant in units of kcal mol^{-1}).[29] The data in Figure 2 include all of the azobenzenes investigated by us in all

(22) Another potential measure of solute–solvent interactions in ordered media, the Saupe order parameter, has been examined for *anti*-azobenzenes only due to the difficulties in maintaining a constant syn concentration while several absorption spectra are being recorded. For a recent review, see: Cox, R. J. *Mol. Cryst. Liq. Cryst.* **1979**, *55*, 1.

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(24) (a) Saltiel, J.; Chang, D. W. L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure. Appl. Chem.* **1975**, *41*, 559. (b) Hochstrasser, R. M. *Ibid.* **1980**, *52*, 2683.

(25) In benzene solution, ^{3}t and ^{3}p are about isoenergetic while ^{3}p is ~8 kcal mol^{-1} more stable than ^{3}c.[24a] Both ^{1}t and ^{1}c are several kilocalories per mole less stable than ^{1}p.[24b]

(26) (a) Were the activation barrier for twisting ^{1}c and ^{3}c large (i.e., near that for isomerization of *syn*-1), isomerization of *cis*-stilbene would still serve as a reasonable model. In fact, its activation barrier is smaller than that for solvent movement in a viscous medium; only in trans → cis isomerizations have measurable activation barriers for twisting been observed.[24b,26b] Saltiel, J.; D'Agostino, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 6445.

(27) See for instance: Lamola, A. A.; Flores, J. *J. Am. Chem. Soc.* **1982**, *104*, 2530.

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(29) The angle of inclination of the aromatic rings (with respect to the CNNC plane) should have little effect upon the azobenzene shape "seen" by nearby solvent molecules in $(CCl/CN)_c$. The van der Waals thickness of a benzene ring is ca. three-fourths its width. Thus, the shape of a rotating phenyl is better approximated by a cylinder than a plate: Kihara, T. *Acta Crystallogr., Sect. A* **1970**, *A26*, 315.

CCl/CN phases. The lack of solvent effect, especially solvent order, is demonstrated by (1) the lack of aberrant placement of the nematic and isotropic points with respect to their corresponding cholesteric points and (2) the fact that the temperatures for all of the solvents are within experimental error of a common value: β(cholesteric) = 347 ± 33 K; β(butyl stearate) = 317 ± 56 K; β(benzene/toluene) = 366 ± 31 K.

An approximate "best-fit" line is drawn through the $(CCl/CN)_c$ points. Although most of the points are very close to the line, the 2,6-dimethylated azobenzenes (**11–13**) fall consistently above it and seem to describe a separate, nearly parallel slope. An equally good fit to the new line is obtained when the toluene, $(CCl/CN)_i$, and $(CCl/CN)_n$ points for **11–13** are included. Surprisingly, the $(CCl/CN)_c$ and toluene points for the 2,2′,6,6′-tetramethylated azobenzenes (**14** and **15**) fall very near the line described by the non-ortho-substituted azobenzenes.

Not all azobenzenes follow these trends. When the data of Nishimura et al.[15a] for the syn → anti isomerization of mono-, di-, and tri-ortho-methylated 4-(dimethylamino)-azobenzenes in cyclohexane and toluene are plotted on Figure 2 (not shown), 12 of the 13 points, each from a different compound, lie far *below* the full line. While this may be an indication that these (dimethylamino)azobenzenes isomerize via a different mechanism from that followed by **1–15**, it does not help to explain why **11–13** behave differently from the others.

The difference in the intercepts of the two slopes, ca. 1 kcal mol^{-1}, is compatible with at least three interpretations: (1) all of our azobenzenes isomerize through a more-or-less common transition-state geometry but proceed from different syn conformers; (2) the syn conformers remain similar throughout the series, and the transition state geometry changes; (3) ortho methylation alters the syn connformations and the transition-state geometry in a manner that they are not energetically compensated. Certainly, the effect of ortho substitution on the conformations of phenyl rings of *anti*-azobenzenes has been documented.[19] Our spectroscopic observations (vide ante) and molecular models indicate that ortho methylation has an ever larger steric influence on the syn conformations. Thus, the second interpretation seems unreasonable. The third one, in which all of our azobenzenes isomerize via variants of an inversional transition state, seems intuitively most likely. Unfortunately, neither our experimental data, molecular models, nor the available theoretical calculations allow for an assessment of the energy profile associated with rotation (about a C–N bond) of an ortho-methylated phenyl in an inversional azobenzene transition state.[29] Until such calculations become available, we do not foresee a means of distinguishing between the first and third interpretations or of explaining why **14** and **15** behave kinetically like **1–10** instead of **11–13**.

Conclusions

The activation parameters for syn → anti isomerization of 15 low-"bipolarity" azobenzenes show no dependence upon solvent order, indicating that the syn isomers and their transition states present a similar steric appearance to the solvent environment. From this, it is concluded that the isomerizations proceed via an inversional mechanism.

Experimental Section

NMR spectra were obtained on either a 60-MHz Varian A-60 spectrometer or a Bruker HFX-10 90-MHz Fourier transform spectrometer. IR spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. UV–vis spectra were recorded on a Cary Model 14 or a Perkin-Elmer 552 spectrophotometer by using matched 1.0-cm quartz cuvettes or 1-in. diameter quartz plates whose optical path was varied by Teflon spacers. Irradiations were performed with a Hanovia 450-W medium-pressure Hg lamp (Model 679A36) housed in a Pyrex or quartz water-jacketed well. Melting points were taken on either a Kofler hot-stage microscope equipped with polarizing lenses or a Gallenkamp melting point apparatus and are corrected. Elemental analyses were performed by Guelph Chemical Laboratories, Ltd., Guelph, Canada.

Benzene (Baker, reagent grade) was purified by the method of Saltiel[30] (bp 80 °C). Toluene (Baker chromatographic grade) was used as received. Hexane (Baker, reagent grade) was purified by the method of Murray and Keller[31] (bp 69 °C) and displayed no discernible absorption above 220 nm. Cholesteryl chloride (Sigma or PCR) was recrystallized at least twice from acetone; mp 95–96 °C (lit.[32] mp 95.7 °C). Cholesteryl nonanoate (Aldrich or RPC) was recrystallized twice from 95% ethanol and exhibited an enantiotropic liquid crystalline phase from 77.5 to 91.5 °C (lit.[33] 77.5–92 °C). *n*-Butyl stearate was synthesized by the method of Nerbonne:[34] 78% yield; bp 158–162 °C (0.03 torr) [lit.[35] bp 223 °C (25 torr)].

Azobenzene (**1**, Eastman) was recrystallized from 95% ethanol; mp 68–69 °C (lit.[2] mp 68 °C). 4-Methoxyazobenzene (**2**) (Eastern Chemical Co.) was recrystallized from 95% ethanol; mp 55.5–56 °C (lit.[36] mp 52–53.5 °C). 4,4′-Dichloroazobenzene (**9**, Aldrich) was recrystallized from acetone; mp 187.5–188.5 °C (lit.[19b] mp 185 °C).

The following azobenzenes were synthesized by standard techniques: 4-methylazobenzene (**4**), mp 70–72 °C (lit.[37] mp 70–71.5°C); 4-(trifluoromethyl)azobenzene (**5**), mp 98.5–99 °C (lit.[38] mp 98–99 °C); 4-chloroazobenzene (**6**), mp 87–88.5 °C (lit. mp 90–90.5 °C,[39a] 87–88.5 °C[39b]); 4,4′-dimethylazobenzene (**7**), mp 144–145 °C (lit.[40] mp 143–143.5 °C); 4,4′-dimethoxyazobenzene (**8**), mp 166.5–167 °C (lit.[40] mp 162 °C); 4,4′-bis(trifluoromethyl)azobenzene (**10**), mp 103–104 °C (lit.[41] mp 101–102 °C); 2,4′-,6-trimethylazobenzene (**11**), as a red oil whose NMR ($CDCl_3$) was δ 7.28 (d, *J* = 8 Hz, 2 H), 7.29 (d, *J* = 8 Hz, 2 H), 7.1 (s, 3 H) 2.4 (s), and 2.32 (s, 9 H); 2,2′,6,6′-tetramethylazobenzene (**14**), mp 49–49.5 °C (lit. mp 48 °C,[42a] 46-47 °C[42b]); 2,2′,4,4′,6,6′-hexamethylazobenzene (**15**), mp 73–74 °C (lit.[43] mp 74 °C).

2,6-Dimethyl-4′-methoxyazobenzene (12) was synthesized in 8% yield by the method of Talaty.[3a] A red solid (mp 37.2–40.3 °C) was obtained after the initial oil was allowed to stand for 1 day at room temperature: NMR (neat oil) δ 7.87 (d, *J* = 8.5 Hz, 2 H), 7.00 (s) and 6.83 (d, *J* = 8.5 Hz, 5 H), 3.48 (s, 3 H), 2.40 (s, 6 H); IR (KBr) 1600, 1581, 1504, 1460, 1440, 1416, 1255, 1143, 1032, 837, 767 cm^{-1}; UV–vis (95% ethanol) 435 nm (ε 1090), 326 (12 700), 235 (8470). Anal. Calcd for $C_{15}H_{16}N_2O$: C, 75.0; H, 6.7; N, 11.7. Found: C, 73.0; H, 6.7; N, 11.7.

2,6-Dimethyl-4′-(trifluoromethyl)azobenzene (13) was synthesized in 1.5% yield as a red oil by the method of Talaty also:[3a] NMR (CCl_4) δ 7.8 (dd, *J* = 8 Hz, 4 H), 7.2 (s, 3 H), 2.38 (s, 6 H); UV–vis (*n*-hexane) 457 nm (ε 609), 319 (15 700); IR (neat) 2960, 2920, 2855, 1610, 1590, 1468, 1413, 1380, 1325 (s), 1170, 1131,

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1102, 1070, 850, 775 cm^{-1}. Anal. Calcd for $C_{15}H_{13}F_3N_2$: C, 64.7; H, 4.68; N, 10.1. Found: C, 64.6; H, 4.92; N, 10.3.

Coated Quartz Disks. Four quartz disks (1.0 cm in diameter) were cleansed sequentially with distilled water, methanol, acetone, sulfuric acid, and distilled water and then air-dried. The disks were then soaked for 5 min in a 1% aqueous solution of [(3-methylamino)propyl]methoxysilane (MAP).[44] The disks were removed, washed with distilled water, dried under a stream of nitrogen, and placed in an oven overnight at 110 °C.

Helical Pitch Measurements. The pitch bands of the cholesteric liquid crystals were measured on a Cary 14 spectrophotometer. Samples containing ≤0.7% (by weight) azobenzene were prepared and applied to the MAP coated disks, which were separated by a 0.025-nm Teflon spacer. Samples were heated in an aluminum thermostating block until they cleared and were then allowed to cool to an appropriate temperature. Pitches with λ_{max} of the reflectance band from 230 to 2600 nm were observable.

Kinetic Procedures. The syn isomer of each azobenzene was obtained by irradiation of the anti isomer in the reaction cells for ca. 5 min. Irradiation wavelengths were dictated by the absorption spectrum of the anti isomers but generally were 300–400 nm (Pyrex and Corning CS-754 filters). The change in optical density (OD) was monitored on either a Beckman Model DU or a Perkin-Elmer Model 552 recording spectrophotometer. When the Beckman DU was used for isotropic liquids, a cuvette was employed as the reaction cell. It was irradiated outside the sample compartment, placed in the cell compartment, and allowed to equilibrate thermally for 10–20 min. The OD was recorded as a function of time at a single wavelength at or near the λ_{max} of either the n → π* or π → π* transition of the anti isomer for at least 2 half-lives. The liquid–crystalline samples examined with the Beckman DU were housed in an aluminum cell holder containing spaces for both sample and reference. The whole thermostatted cell compartment was removed and irradiated as above to obtain the syn isomer. The cell compartment was replaced and thermally equilibrated (10–20 min), and the change in OD was monitored as before.

When the Perkin-Elmer 552 was used, sample cells were housed in specially made thermostated cell holders. The cell holders were removed from the cell compartment, irradiated, and replaced to obtain the syn isomer. Thermal equilibration required 10–20 min. The change in OD was monitored at a single wavelength as before.

Temperature measurements were made by using a calibrated thermistor and immersing its tip into the benzene or toluene sample. Since it was not possible to measure the temperature of the liquid crystal directly due to the design of the cell holder, the temperature was recorded by placing the thermistor tip agaiinst the cell window.

Concentrations of the various azobenzenes varied from 5×10^{-5} to 1×10^{-3} M in benzene, *n*-butyl stearate and toluene, depending on which absorption band was followed. Sample concentrations in of cholesteryl chloride/cholesteryl nonanoate (35/65 w/w) were <1% (w/w; $\lesssim 10^{-2}$ M) and depended on the azobenzene substituents, the spectroscopic properties, and the thickness of the spacer (usually 0.025 or 0.05 mm). Kinetic runs were performed at temperatures between 40 and 65 °C in benzene and *n*-butyl stearate, 55–80 °C in toluene, 40–70 °C in $(CCl/CN)_c$, and 76–90 °C in $(CCl/CN)_i$. At least 20 points were taken for each run, and correlation coefficients were always better than 0.99. The rate constants, temperatures, concentrations, etc. are included as supplementary material.

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Registry No. *syn*-**1**, 1080-16-6; *syn*-**2**, 15516-72-0; *syn*-**3**, 86885-32-7; *syn*-**4**, 6720-28-1; *syn*-**5**, 86885-33-8; *syn*-**6**, 6530-97-8; *syn*-**7**, 30926-02-4; *syn*-**8**, 82570-64-7; *syn*-**9**, 30926-04-6; *syn*-**10**, 86885-34-9; *syn*-**11**, 86885-35-0; *syn*-**12**, 86885-36-1; *syn*-**13**, 86885-37-2; *syn*-**14**, 86885-38-3; *syn*-**15**, 20488-60-2.

Supplementary Material Available: Tables of rate constants for syn → anti isomerizations in various solvents and at various temperatures (15 pages). Ordering information is given on any current masthead page.

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Structures and Relative Energies of Silabenzene Isomers

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Ab initio molecular orbital calculations with the 3-21G(*) basis set (a split-valence basis which includes d functions on silicon) were carried out on silabenzene (**1**), Dewar silabenzene (**2**), 1-silacyclohexadienylidene (**3**), 2-silacyclohexadienylidene (**4**), and 4-silacyclohexadienylidene (**5**). Geometries optimized at the STO-3G level were used for **1**–**3** and **5**, while the MNDO geometry was employed for **4**. Planar **1** is the most stable isomer with an aromatic stabilization of ca. 20 kcal/mol. Isomers **3** and **4** are estimated to be only 20–25 kcal/mol higher in energy and may be suitable precursors for the synthesis of **1**. The calculated relative energy of 38 kcal/mol for **2** represents an upper bound; inclusion of electron correlation is expected to reduce this value. The least stable isomer considered, **5**, is the only structure indicated to have a triplet ground state. The reasons for the differences in the relative energies of C_6H_6 and C_5SiH_6 isomers are analyzed. On the basis of the calculated electronic structures and charge distributions, substituents which might be suitable for stabilizing the different isomers preferentially are suggested.

The recent matrix isolation and IR, UV, and PE spectral characterization of silabenzene (**1**) and silatoluene have heightened interest in group 4 heterobenzene molecules.[2-6] The possibility of valence isomerization in **1** assumes im-

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