

chloride in 2 mL of dry acetonitrile. The clear solution was kept at 22 °C for 40 min and then a solution of 3 mmol of diene 1a in 2.5 mL of dry acetonitrile added. The reaction flask was stoppered and the mixture heated at 70 °C. Workup as above yielded 3a-3b adduct ratios of 2.1 and 1.9 after 1- and 2-h reaction times, respectively.

Acknowledgment. F.F., F.P., and A.T. acknowledge

gratefully support for the work in Perugia by the Consiglio Nazionale delle Ricerche and A.T. and E.W. are indebted to NATO (Grant No. 257.81) for grant support.

Registry No. 1a, 106-99-0; 1b, 78-79-5; 1c, 2004-70-8; 2a, 930-30-3; 2b, 1120-73-6; 3a, 930-68-7; 3b, 1121-18-2; 4a, 1121-66-0; 4b, 35836-89-6; AlCl₃, 7446-70-0; AlBr₃, 7727-15-3; BF₃·Et₂O, 109-63-7; ZnCl₂, 7646-85-7; SnCl₄, 7646-78-8.

Solvent Effects upon the Thermal Cis-Trans Isomerization and Charge-Transfer Absorption of 4-(Diethylamino)-4'-nitroazobenzene

Kirk S. Schanze, T. Fleming Mattox, and David G. Whitten*

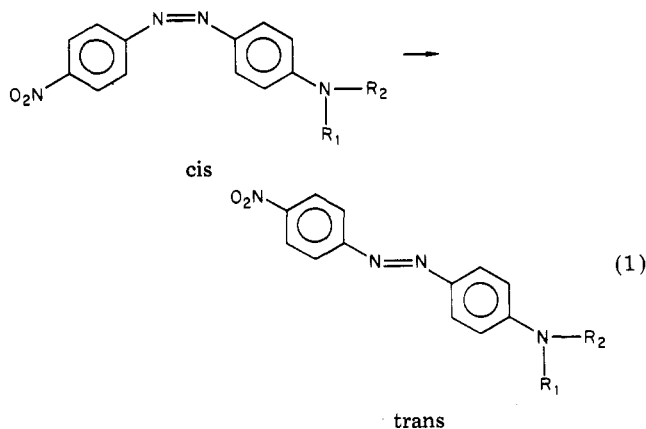
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Received March 8, 1983

A comprehensive study of the solvent effects on the rate of the thermal cis-trans isomerization and the position of the charge-transfer absorption of the trans isomer of 4-(diethylamino)-4'-nitroazobenzene (DENAB) is presented. The isomerization rates, the activation parameters, and the absorption maxima have been measured in a variety of protic and aprotic solvents. The data are analyzed and interpreted by using the Taft and Kamlet multiparameter approach and the pyrene fluorescence parameter P_y . The results of the correlations suggest that the isomerization reaction is accelerated in hydrogen-bonding solvents relative to aprotic solvents of similar polarity due to a hydrogen-bonding interaction between the solvent and the nitro group of the dye. Correlation of the absorption maxima with the Taft-Kamlet π^* parameter shows a similar dependence in protic and aprotic media. It is apparent that the absorption process is not affected by hydrogen bonding as strongly as the rate of isomerization. A linear correlation of the rate of isomerization with the position of the CT absorption in different solvents is suggestive of the fact that a similar degree of charge transfer exists in the transition state for the isomerization reaction and in the Frank-Condon excited state.

Introduction

The thermal cis-trans isomerization of azobenzenes was first noted by Hartley in 1937.^{1,2} Since Hartley's initial investigation, numerous groups have studied various aspects of the isomerization mechanism, including solvent, substituent, and temperature dependence effects upon the rate of the cis-trans reaction.³⁻⁸ In a previous investigation we reported that k_{ct} (eq 1) for the 4-(dialkylamino)-4'-



nitrobenzenes was extremely sensitive to solvent polarity.⁹ A general trend of increasing k_{ct} with increasing solvent dielectric constant was attributed to the transition state having considerable dipolar character.

In a recent paper¹⁰ it was shown that a quantitative correlation results when ΔG_{ct}^\ddagger (25 °C) for 4-(diethylamino)-4'-nitroazobenzene (DENAB) is plotted as a function of Kosower's Z value^{11,12} of solvent polarity for 14 solvents. It was noted that the correlation breaks up into two linear regions (aprotic solvents and protic solvents) and the effect is attributed to the presence of specific solvent-solute (hydrogen-bond) interactions in the protic solvent medium.

A substantial number of studies in the field of physical organic chemistry have addressed the problem of understanding the general phenomena of solvent effects upon the physical and chemical properties of solute molecules.¹³ Due to the failure of parameters based upon macroscopic properties of solvents (i.e., dielectric constant, refractive index, etc.) to correlate well with solute molecular properties, considerable effort has aimed at development of empirical scales that can be used to predict solvent effects on solute properties.¹⁴ Several groups have developed spectroscopic probes that serve to correlate remarkably well a variety of solvent effects on chemical reactivity and solvatochromism.^{11,14-17} However, as has been recently

(1) Hartley, G. S. *Nature (London)* **1937**, *140*, 281.
 (2) Hartley, G. S. *J. Chem. Soc.* **1938**, 633-642.
 (3) Haberfield, P.; Block, P. M.; Lux, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 5804-5806.
 (4) Nishimura, N.; Sueyoshi, T.; Yamanaka, H.; Imai, E.; Yamamoto, S.; Hasegawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1381-1387.
 (5) Zalukaev, L. P.; Voronkov, M. G.; Moiseeva, L. V.; Afanas'ev, S. V. *Dokl. Phys. Chem.* **1976**, *230*, 820-822.
 (6) Afanas'ev, S. V.; Moiseeva, L. V.; Zalukaev, L. P. *Russ. J. Phys. Chem.* **1978**, *52*, 1445-1447.
 (7) Asano, T. *J. Am. Chem. Soc.* **1980**, *102*, 1205-1207.
 (8) Asano, T.; Okada, T.; Shinkai, S.; Shigematsa, K.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161-5165.

(9) Wildes, P.; Pacifici, J. G.; Irick, G.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 2004-2008.
 (10) Schanze, K.; Mattox, T. F.; Whitten, D. G. *J. Am. Chem. Soc.* **1982**, *104*, 1733-1735.
 (11) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253-3260.
 (12) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3267-3270.
 (13) Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: New York, 1979, and references therein.
 (14) Reference 13, Chapter 7.
 (15) Brownstein, S. *Can. J. Chem.* **1960**, *38*, 1590-1596.

Table I. Rate Constants and Free Energies of Activation for Cis-Trans Isomerization and $E_{\max}(\pi, \pi^*)$ for DENAB in Various Solvents

no.	solvent	k_{ct} , ^a s ⁻¹	ΔG_{ct}^\ddagger , ^a kcal/mol	$E_{\max}(\pi, \pi^*)$, kcal/mol
1	cyclohexane	5.04×10^{-3}	20.6	
2	heptane	7.1×10^{-3}	20.4	63.3
3	CCl ₄	6.55×10^{-3}	20.4	61.0
4	diethyl ether	3.26×10^{-2}	19.5	61.1
5	benzene ^b	4.1×10^{-2}	19.4	59.6
6	1,4-dioxane	3.70×10^{-2}	19.4	59.9
7	CH ₂ Cl ₂			57.5
8	chloroform	1.0	17.5	57.9
9	THF	1.14	17.4	58.5
10	<i>o</i> -DCB ^b	2.2	17.0	
11	acetone	17.6	15.8	58.2
12	butyronitrile	21.6	15.6	
13	pyridine ^b	30.0	15.4	56.6
14	acetonitrile	58.0	15.1	58.2
15	DMF	138	14.6	56.8
16	nitrobenzene			56.2
17	Me ₂ SO	452	13.8	55.8
101	<i>tert</i> -butyl alcohol	5.12	16.5	58.8
102	1-heptanol	8.49	16.2	58.7
103	1-hexanol	10.0	16.1	58.6
104	1-pentanol	16.7	15.8	58.6
105	1-butanol	16.7	15.8	58.6
106	2-propanol	19.4	15.7	58.5
107	1-propanol	23.3	15.6	58.5
108	ethanol	38.7	15.3	58.6
109	methanol	90.0	14.8	58.4

^a Rate constants and calculated free energies of activation at 25 °C. Error in k_{ct} 5–10%. ^b Values from ref 9.

pointed out,^{18,19,22} these probes are sensitive not only to purely dielectric effects but also to specific probe dependent solvent-solute interactions. Often in correlating experimental data with an empirical solvent parameter, different linear correlations will emerge for families of solvents as in the present case. It is important to understand if this separation is apparent (i.e., caused by a probe molecule/solvent interaction), or if it is due to specific interactions present in the system under study (or some combination of these effects). Recent work by several groups has shown that a multiparameter approach can be used to separate out and quantify different interaction mechanisms present in a solute-solvent system.¹⁸⁻²² Thus, in order to better understand the separation of the rate data for DENAB into distinct protic and aprotic correlations, a multiparameter approach should be applied.

This paper presents the results of an extensive study of the solvent effects upon the activation parameters (ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger) for the cis-trans isomerization and upon $E_{\max}(\pi, \pi^*)$ for the visible absorption band of DENAB in a variety of solvents. An analysis of the rate data based upon the method of Kamlet and Taft^{19,20,22,23} along with the results of solvent isotope effects allows a quantitative evaluation of the role played by hydrogen bonding as it affects the cis-trans isomerization of DENAB. An examination of the results leads to interesting conclusions regarding the degree of charge transfer in the activated

Table II. Activation Parameters for Cis-Trans DENAB Isomerization in Various Solvents^a

solvent	ΔH_{ct}^\ddagger , kcal	ΔS_{ct}^\ddagger , eu
<i>n</i> -heptane	17.3 ± 0.2	-11.8 ± 0.5
benzene ^b	13 ± 1	-20 ± 3
<i>o</i> -dichlorobenzene ^b	9.7 ± 0.8	-24 ± 3
acetone ^b	9.8 ± 0.1	-19.6 ± 0.2
butyronitrile	9.8 ± 0.3	-20 ± 1
acetonitrile	9.7 ± 0.2	-18.0 ± 0.5
DMF	8.8 ± 0.1	-19.3 ± 0.1
Me ₂ SO	8.7 ± 0.2	-17.4 ± 0.7
1-heptanol	8.7 ± 0.1	-25.2 ± 0.2
1-hexanol	8.9 ± 0.1	-24.3 ± 0.8
1-butanol	9.0 ± 0.1	-23.0 ± 0.4
1-propanol	9.9 ± 0.1	-19.2 ± 0.4
ethanol	9.5 ± 0.9	-20 ± 3
methanol	9.7 ± 0.2	-17.0 ± 0.7

^a Based on four or five data points; 15 °C < T < 55 °C.

^b Data from ref 9.

complex and in the Frank-Condon excited state achieved via excitation of the trans isomer.

This system is rather unique as an example of a unimolecular thermally activated chemical reaction that exhibits dramatic solvent sensitivity. The kinetic data presented illustrate remarkably well the subtle but important role played by the solvent in controlling the rate of a chemical reaction that proceeds via a dipolar transition state.

Results

Rate Constants. Listed in Table I are the first-order rate constants, k_{ct} , and calculated ΔG_{ct}^\ddagger values for cis-trans DENAB isomerization monitored at 25 °C in 15 aprotic and 9 protic solvents. The solvents are listed in order of increasing k_{ct} for aprotic (solvents 1–17) and protic (solvents 101–109) media. In aprotic media the rate constant varies over the range $k_{ct}(\text{cyclohexane}) = 5.04 \times 10^{-3} \text{ s}^{-1}$ to $k_{ct}(\text{Me}_2\text{SO}) = 4.52 \times 10^2 \text{ s}^{-1}$, a factor of 10^5 . In protic media the rate constant varies from $k_{ct}(\text{tert-butyl alcohol}) = 5.12 \text{ s}^{-1}$ to $k_{ct}(\text{methanol}) = 90.0 \text{ s}^{-1}$, a factor of 2.0×10^1 .

(16) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* 1963, 661, 1–37.

(17) Brooker, L. G. S.; Craig, A. C.; Heseltine, D. W.; Jenkins, P. W.; Lincoln, L. L. *J. Am. Chem. Soc.* 1965, 87, 2443–2450.

(18) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* 1976, 98, 377–383.

(19) Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* 1976, 98, 2886–2894.

(20) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* 1977, 99, 6027–6038.

(21) Abboud, J. L.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* 1977, 99, 8325–8327.

(22) Koppel, I. A.; Palm, V. A. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Ed.; Plenum Press: New York, 1972; Chapter 5.

(23) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* 1979, 349–356.

Table III. Solvent Isotope Effect on k_{ct} in 10% Aqueous Dioxane

solvent mixture	$k_{ct},^a \text{ s}^{-1}$	k_H/k_D
10% H ₂ O/dioxane	4.19 ± 0.06	1.08 _s
10% D ₂ O/dioxane	3.86 ± 0.08	

^a k_{ct} averaged from six kinetic runs on different solutions; error is standard deviation from mean.

Solvatochromic Effect on the π, π^* Band. Also listed in Table I are the absorption maxima for DENAB in 14 aprotic and 6 protic solvents. As expected for a π, π^* transition with charge-transfer character the absorption band is observed to undergo a red shift concurrent with increasing solvent polarity. In aprotic solvents the band maximum shifts from E_{\max} (heptane) = 63.6 kcal to E_{\max} (Me₂SO) = 55.8 kcal (450 to 512 nm), a range of 7.8 kcal. The shift is somewhat less pronounced over the series of protic solvents, however, ranging from E_{\max} (*tert*-butyl alcohol) = 58.8 kcal to E_{\max} (methanol) = 58.4 kcal (486 to 490nm), a shift of 0.4 kcal through the series.

Temperature Dependence of Rate Constants. Table II presents the results of temperature-dependence studies for the rate of *cis*-*trans* DENAB isomerization in eight aprotic and six protic solvents. ΔH_{ct}^* and ΔS_{ct}^* were determined from the intercept and slope, respectively, of a least-squares fit of ΔG_{ct}^* vs. T at four or five temperatures over the range 15–55 °C. Throughout the series of aprotic solvents, ΔH_{ct}^* displays a regular decrease with increasing solvent polarity, varying from 17.3 kcal in heptane to 8.7 kcal in Me₂SO. Over the same series ΔS_{ct}^* varies little (within experimental error) and is clustered around -20 eu (except the data point for heptane, $\Delta S_{ct}^* = -11.8$ eu). For the range of protic solvents studied, ΔH_{ct}^* is observed to undergo a small but regular increase concomitant with increasing solvent polarity. The enthalpy term varies from 8.7 kcal in 1-heptanol to 9.7 kcal in methanol. ΔS_{ct}^* in protic solvents increases regularly as the solvent polarity increases, changing from -25.5 eu in 1-heptanol to -17.0 eu in methanol.

Solvent Isotope Effects. Table III gives the results of the solvent kinetic isotope effect observed in 10% aqueous/dioxane. The direction and magnitude of the kinetic isotope effect ($k_H/k_D = 1.08_s$, based upon six kinetic runs for each solvent mixture), are in accord with the other results presented as explained in the Discussion section. A measurable solvent isotope effect was not noted upon the position of $E_{\max}(\pi, \pi^*)$.

Correlations with Empirical Parameters. In Figure 1 the isomerization rate data are analyzed by using the Kamlet and Taft sequential analysis method.²⁵ Figure 1 (top) shows ΔG_{ct}^* plotted vs. the π^* polarity parameter for nine aprotic and six protic solvents. A least-squares analysis is drawn for ΔG_{ct}^* vs. π^* , using only the aprotic solvents as a data basis. (Data for the halocarbons and benzene was not utilized for the aprotic least-squares fit to eliminate polarizability effects.²¹) Equation 2 is the least-squares fit for ΔG_{ct}^* vs. π^* with the aprotic solvents.

$$\Delta G_{ct}^* = -6.33\pi^* + 20.77 \text{ kcal} \quad r = 0.935 \quad (2)$$

As Figure 1 illustrates, the data for the protic solvents falls below the line for the aprotic fit. Figure 1 (bottom) has $\Delta\Delta G_{ct}^*$ ²⁶ plotted vs. the Kamlet-Taft α parameter of

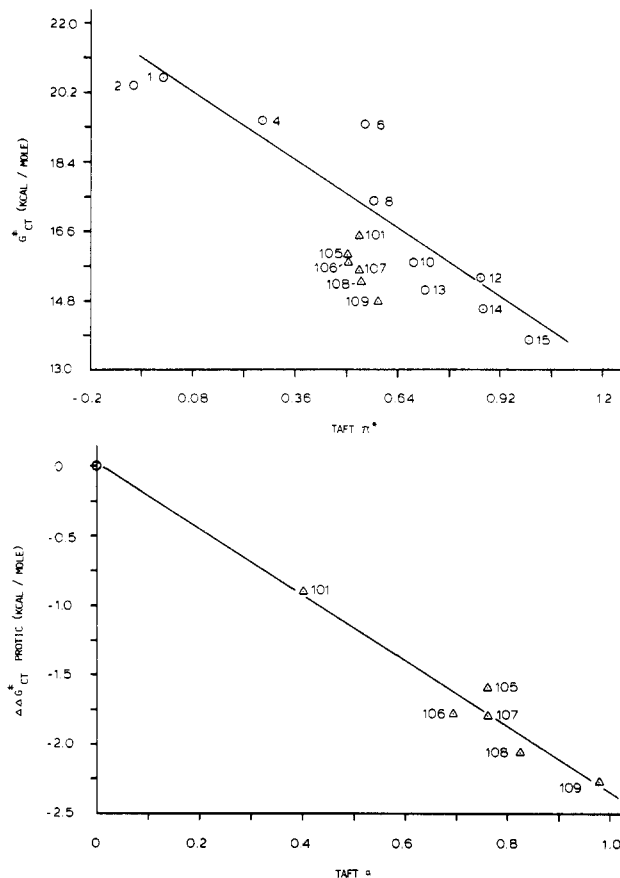


Figure 1. ΔG_{ct}^* vs. Taft π^* ; (O) aprotic solvents, (Δ) protic solvents. Best fit line through aprotic solvents. Bottom: $\Delta\Delta G_{ct}^*$ vs. Taft α , protic solvents.

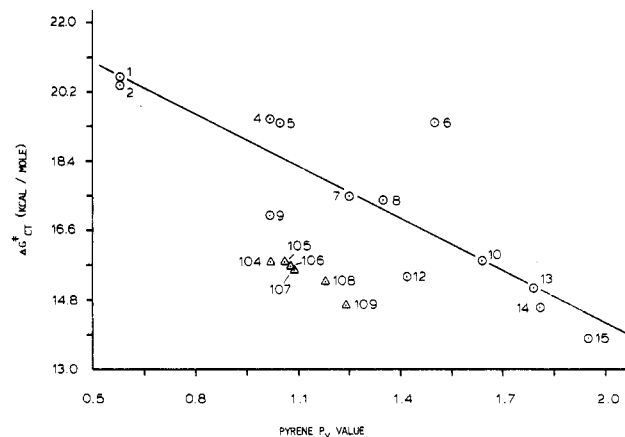


Figure 2. ΔG_{ct}^* vs. pyrene P_y ; (O) aprotic solvents, (Δ) protic solvents. Best fit line through aprotic solvents.

solvent hydrogen bond donor ability^{19,24} for the protic solvents. Equation 3 describes the best fit of the $\Delta\Delta G_{ct}^*$ vs. α data.

$$\Delta\Delta G_{ct}^* = -2.38\alpha + 0.03 \quad r = 0.965 \quad (3)$$

Figure 2 shows ΔG_{ct}^* plotted vs. Winnick's P_y scale of solvent polarity²⁷ for 13 aprotic and 6 protic solvents. The best fit line from a least-squares analysis is shown ($r = 0.870$) with the aprotic solvents as a data base. For ΔG_{ct}^* vs. P_y the data for the protic solvents is clustered below the best fit line for the aprotic solvents, analogous to the plot of ΔG_{ct}^* vs. π^* .

Figure 3 illustrates the correlation obtained when $E_{\max}(\pi, \pi^*)$ DENAB is plotted vs. Taft's π^* for 14 aprotic and 6 protic solvents. The line drawn shows the best fit

(24) Taft, R. W.; Kamlet, M. J. *J. Chem. Soc., Perkin Trans. 2* 1979, 1723-1729.

(25) Kamlet, M. J.; Jones, M. E.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* 1979, 342-348.

(26) $\Delta\Delta X = \Delta X_{\text{obsd}} - \Delta X_{\text{calc}}$ (calculated from 11s correlation for aprotic data).

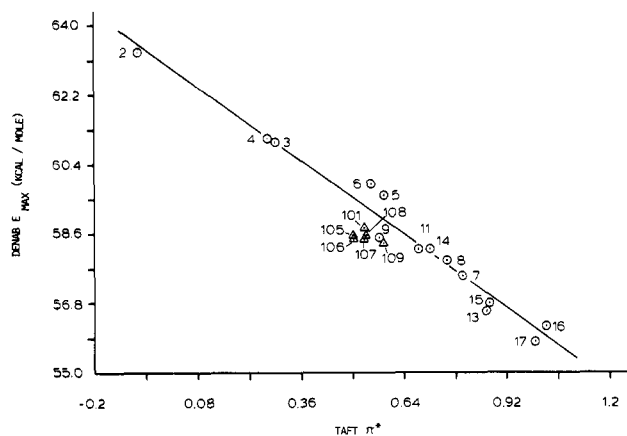
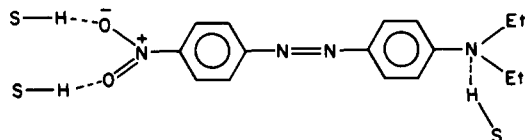


Figure 3. E_{\max} vs. Taft π^* ; (O) aprotic solvents, (Δ) protic solvents. Best fit line through aprotic solvents.

Chart I



for a least-squares analysis with the aprotic solvents as a data base. Equation 4 gives the numerical results for the linear least-squares fit. The data points for the protic

$$E_{\max}(\pi, \pi^*) = -6.88\pi^* + 63.00 \text{ kcal } r = 0.986 \quad (4)$$

solvents are clustered just below the line for the aprotic solvents. A further analysis of the data by plotting $\Delta\Delta E_{\max}(\pi, \pi^*)$ ²⁶ for the protic solvents vs. Taft's α does not lead to a useful correlation. The error in the measured E_{\max} values is ± 0.25 kcal, which is larger than the differences between the individual values. Thus a linear correlation of $E_{\max}(\pi, \pi^*)$ (which is based upon small differences in E_{\max} values) to α inherently involves a large degree of uncertainty.

Finally, Figure 4 depicts a plot of ΔG_{ct}^* vs. $E_{\max}(\pi, \pi^*)$ for DENAB in 12 aprotic and 9 protic solvents. The least-squares fit again is run for only the aprotic solvents. The equation describing the best fit for a linear correlation is given by eq 5. Analogous to the other correlations (vide

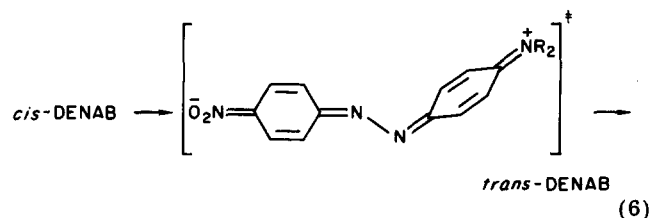
$$\Delta G_{ct}^* = 1.01E_{\max}(\pi, \pi^*) - 41.82 \text{ kcal } r = 0.908 \quad (5)$$

supra) the data points for the protic solvents are clustered below the best fit line through the aprotic solvent data.

Discussion

Hydrogen-Bonding Effects on Isomerization Rates.

The mechanism of the cis-trans thermal isomerization of DENAB and related azo dyes has been postulated to proceed via a rotation around the N-N bond axis that is facilitated by an intramolecular charge-transfer interaction (eq 6).⁷⁻¹⁰ Clearly an increase in solvent polarity should



cause rate enhancement for such a process; however it is not as easy to predict how specific solvation effects such as hydrogen bonding will affect the reaction rate. There

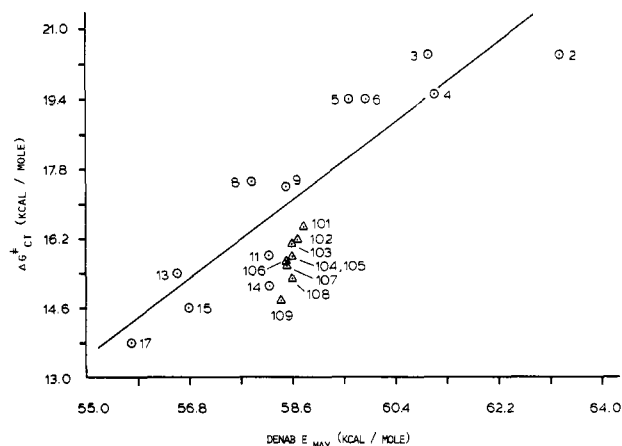


Figure 4. ΔG_{ct}^* vs. E_{\max} ; (O) aprotic solvents, (Δ) protic solvents. Best fit line through aprotic solvents

are several possible sites at which DENAB could act as a hydrogen-bond acceptor in a HBD (hydrogen-bond donor) type solvent (Chart I). DENAB can act as an acceptor at the two oxygens of the nitro group and at the amino nitrogen atom. Hydrogen bonding at the amino nitrogen would be expected to raise the activation barrier to isomerization by making the amino nitrogen a poorer donor. Conversely, hydrogen bonding at the oxygens of the nitro group would be expected to lower the activation barrier by enhancing the ability of the nitro group to act as an acceptor.

A plot of ΔG_{ct}^* vs. Kosower's Z was presented in a recent paper.¹⁰ These results suggest that the rate of isomerization is slower in protic solvents than in aprotic solvents (when comparing solvents with similar Z values). However, the compound used as a basis for the Z scale, 1-ethyl-4-carbomethoxypyridinium iodide (1), has been shown to be fairly sensitive to the ability of protic solvents to act as HBDs.¹⁹ Thus it is possible that the separation of the plot of ΔG_{ct}^* (DENAB) vs. Z into two correlations may only be an apparent phenomena due to the specific interactions between 1 and protic solvents.

The ΔG_{ct}^* data has been fit to a two-parameter regression analysis of the form,¹⁹ $\Delta G_{ct}^* = s\pi^* + a\alpha + \Delta G_{ct}^{*0}$. π^* is a parameter that reportedly measures the intrinsic polarity of a solvent (separated from specific solute/solvent interactions such as hydrogen bonding). α measures the ability of a protic solvent to act as a HBD. The regression coefficients s and a determine the extent that ΔG_{ct}^* is sensitive to dipolar and hydrogen-bonding effects, respectively. The results of the regression analysis yield (eq 2 and 3) $s = -6.33$ kcal and $a = -2.38$ kcal. The $\Delta\Delta G_{ct}^*$ vs. α correlation has an intercept of 0 as expected; a non-HBD solvent ($\alpha = 0$) should have $\Delta\Delta G_{ct}^* = 0$ (ΔG_{ct}^* in this case should fall on correlation for aprotic solvents). It is clear that the correlation of $\Delta\Delta G_{ct}^*$ with α is significant and reflects a HBD-solvent/dye interaction upon the molecular level. This correlation shows that the rate of the cis-trans thermal isomerization is increased by good HBD solvents. Comparison of the magnitude of s and a shows that for the series of alcohols studied, 27% of the decrease in ΔG_{ct}^* in going from *tert*-butyl alcohol to methanol is due to enhanced HBD ability and 73% is due to increase in solvent polarity.

The results of the aforementioned multiparameter analysis lead to two possible conclusions regarding the hydrogen bonding present in the DENAB/HBD solvent systems. Hydrogen bonding may occur only at the oxygen atoms of the nitro group, increasing k_{ct} in solvents with enhanced HBD ability. However, it could be possible that

hydrogen bonding occurs at both the amino and nitro groups, but the interaction at the nitro group is stronger and a net rate enhancement is observed in better HBD solvents. It seems clear, however, that regardless of whether hydrogen bonding is occurring at the amino nitrogen, the dominating interaction is between the HBD solvent and the nitro group of DENAB.

Figure 2 shows the plot of ΔG_{ct}^{\ddagger} for DENAB as a function of P_y . The solvent parameter P_y is based upon the intensity of the 0-0 band (band 1) compared to band 3 of the fluorescence of pyrene ($I_1/I_3 = P_y$). The intensity of the 0-0 band is sensitive to solvent polarity, while band 3 remains relatively unaffected.²⁷ Winnik has suggested quite reasonably that the pyrene probe should show little sensitivity to specific HBD or HBA properties of a solvent. In support of his premise, a plot of P_y vs. the Kamlet-Taft π^* polarity parameter for 13 aprotic and 6 protic solvents shows that the protic points deviate very little from the best fit line for the aprotic solvents.

The correlation of ΔG_{ct}^{\ddagger} as a function of P_y supports the tenet that a specific DENAB/HBD solvent interaction causes an increase in k_{ct} . Figure 2 shows that ΔG_{ct}^{\ddagger} is smaller in the HBD solvents relative to aprotic solvents with similar P_y values. This evidence lends additional support to the conclusion that hydrogen bonding at the nitro group is responsible for rate enhancement in the cis-trans isomerization reaction.

The observed solvent-induced rate changes (k_{ct} increases with solvent polarity and HBD ability) could be induced through two mechanisms: (1) a solvent effect upon the transition-state energy or (2) a solvent effect upon the cis isomer energy. It is apparent that the transition state is more dipolar than the cis isomer; hence it is reasonable to assume that solvent interactions with the transition state should be stronger. Accordingly, the observed solvent effects are primarily due to mechanism 1 above; the more polar and better HBD solvents lower ΔG_{ct}^{\ddagger} through stabilization of the transition state.

Activation Parameters and Kinetic Isotope Effects. The trends displayed by the activation parameters ΔH_{ct}^{\ddagger} and ΔS_{ct}^{\ddagger} (Table II) show that the nature of the solvent plays an important role in determining whether the cis-trans reaction rate is controlled by the entropy or enthalpy term. In aprotic solvents ΔH_{ct}^{\ddagger} decreases with increasing solvent polarity. A plot of ΔG_{ct}^{\ddagger} (aprotic) vs. ΔH_{ct}^{\ddagger} (aprotic) is approximately linear ($r = 0.918$) and the slope is 0.7 ± 0.1 , thus the reaction rate is controlled to a great extent by the enthalpy term in an aprotic medium. It seems that the aprotic solvent acts effectively as a dielectric continuum,²⁸ an increase in the solvent polarity enhances the rate through stabilization of the dipolar transition state.

In protic solvents ΔH_{ct}^{\ddagger} and ΔS_{ct}^{\ddagger} increase with increasing solvent polarity. It is apparent that the protic solvents act in a more complicated fashion than a simple dielectric continuum; solvent-solute and solvent-solvent hydrogen-bonding interactions certainly have an effect upon the relative energies of the reactant molecule and the transition state. The increase of ΔS_{ct}^{\ddagger} (protic) with increasing solvent polarity can be explained through an understanding of a model of the cybotactic region around a reacting dye molecule for two cases: a relatively nonpolar solvent (e.g., heptanol) and a polar solvent (e.g., methanol). In the nonpolar medium the solvent molecules in the cybotactic region of the dye are relatively unstructured; as the dye molecule reacts, however, the increase in dipole

moment tends to organize the solvent molecules in the region. Thus the entropy of the system will be decreased overall and ΔS_{ct}^{\ddagger} (nonpolar protic) $\ll 0$. Alternatively, in the polar medium the solvent molecules in the cybotactic region are already relatively structured (methanol tends to form a structured dynamic lattice of solvent-solvent hydrogen bonds²⁹). As the dissolved dye reacts, the increased dipole moment of the transition state will not inflict as great an increase upon the structure of the solvent shell as in the nonpolar case; hence ΔS_{ct}^{\ddagger} (polar protic) $> \Delta S_{ct}^{\ddagger}$ (nonpolar protic). This general effect has been observed in other chemical reactions that proceed through a dipolar transition state.^{30,31}

The fact that ΔH_{ct}^{\ddagger} (protic) increases with increasing solvent polarity is also attributable to the more structured nature of the polar protic solvents. As the dye molecule reacts and the solvent molecules rearrange in order to stabilize the increased dipole, more hydrogen bonds will be disrupted in the more highly structured polar protic solvent. Hence, more energy will be required for the transition state to be reached in the polar medium and ΔH_{ct}^{\ddagger} (polar protic) $> \Delta H_{ct}^{\ddagger}$ (nonpolar protic). It is also interesting to note that even though ΔH_{ct}^{\ddagger} (protic) increases from *n*-heptanol to methanol, ΔG_{ct}^{\ddagger} (protic) decreases along the same series. Hence, in the protic solvents the rate of cis-trans isomerization is controlled by the entropy term.

The kinetic isotope effect observed in 10% aqueous/dioxane is attributable to the fact that D₂O forms stronger hydrogen bonds than H₂O.³² In the solution doped with heavy water, more energy is required to reorganize the solvent molecules around the dipolar transition state than in the light water solution. Thus, k_{ct} is faster in the H₂O/dioxane solvent.

CT Absorption and Its Relationship to Cis-Trans Isomerization. A plot of $E_{max}(\pi, \pi^*)$ for the absorption of *trans*-DENAB correlates remarkably well with the π^* solvent parameter (Figure 3). The data points for the protic solvents are clustered just slightly below the best fit line for the aprotic solvents. It is apparent that although there is a small specific solvent effect on $E_{max}(\pi, \pi^*)$ occurring in the protic solvents, hydrogen bonding does not play as important a role as in the isomerization reaction.

Light absorption by the *trans* dye molecule leads to a Frank-Condon excited state that is not in equilibrium with its cybotactic environment.³³ If the ground-state molecule was not hydrogen bound prior to excitation (due to the timescale of the transition), the Frank-Condon state also will not be hydrogen bonded and specific protic solvent effects will not be observed. Therefore, in light of the experimental results it seems probable that *trans*-DENAB is not subject to strong hydrogen-bond association with the solvent molecules. However, due to the slower timescale of the cis transition state reorganization, the cybotactic region of the transition state is at equilibrium; thus hydrogen bonds could form between the solvent and the reacting dye molecule as charge separation occurs (even if the ground-state cis isomer is not hydrogen bonded).

The fact that a correlation of ΔG_{ct}^{\ddagger} vs. $E_{max}(\pi, \pi^*)$ has a slope of 1.0 (Figure 4) suggests that there is a similar degree of charge transfer in the Frank-Condon excited state and in the transition state of the isomerization re-

(29) Reference 13, p 13.

(30) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* 1965, 4, 29-40.(31) Pearson, R. G. *J. Chem. Phys.* 1952, 20, 1478-1480.

(32) Arnett, E. M.; McKelvey, D. R. In "Solute Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Ed.; Marcel Dekker: New York, 1969; Vol. 1, Chapter 6.

(33) Reference 13, p 196.

(27) Dong, D. C.; Winnik, M. A. *Photochem. Photobiol.* 1982, 35, 17-21.

(28) Reference 22, p 209.

action. It is possible to calculate the approximate dipole moment for the transition state from the kinetic data with use of 7.^{30,31,34} In eq 7 k is the rate constant for the

$$\ln k = \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \left(\frac{1}{k_B T} \right) \left(\frac{\mu_{c\text{-DENAB}}^2}{r_{c\text{-DENAB}}^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \right) + \ln k_0 \quad (7)$$

reaction in a solvent of dielectric constant ϵ , k_0 is the rate in a solvent of dielectric constant 1, k_B is the Boltzman constant, T is absolute temperature, μ is the dipole moment of the molecule or transition state, and r is the mean radius of the solvent shell surrounding the molecule or transition state. The results from this calculation can be compared to the experimentally determined dipole moments for the ground and excited states of 4-(dimethylamino)-4'-nitroazobenzene (2; determined by dielectric and electrochromic methods, respectively), $\mu_g = 8.0$ D and $\mu_e = 25$ D.³⁵ A fit of the rate data to eq 7 (plot $\ln k$ vs. $(\epsilon - 1)/(2\epsilon + 1)$) for 10 aprotic solvents has a slope of 33.9 ($r = 0.945$). With use of $\mu_{c\text{-DENAB}} = 6.0$ D, $r_{c\text{-DENAB}} = 4.0$ Å, and $r_{\ddagger} = 6.0$ Å,³⁶ a value for $\mu_{\ddagger} = 20.5$ D is calculated. Although the calculated dipole moment has a large degree of uncertainty, it is in good agreement with the dipole moment for the excited state of 2. A dipole moment of 25 D corresponds to a positive and a negative point charge q ($q =$ charge on an electron) separated by 5.2 Å. This separation is somewhat smaller than would be expected if the charges are located on the aromatic rings; thus complete charge separation probably is not occurring.

The unit correlation of ΔG_{ct}^{\ddagger} vs. E_{\max} shows that the CT absorption band and the thermal cis-trans isomerization reaction are subject to the same solvent effects. The visible absorption band of *trans*-DENAB is due to an intramolecular charge transfer (or electron transfer). This correlation therefore suggests that the rate-determining step in the thermal cis-trans isomerization of DENAB is, in fact, a thermal, intramolecular electron transfer that leads to a zwitterionic transition state. Further, the unit-slope relationship of ΔG_{ct}^{\ddagger} and E_{\max} of DENAB in the solvents investigated suggests the possibility that the thermal and photochemical isomerization reactions occur via a common intermediate that is accessible via light-induced or thermal excitation of the ground-state dye.

Conclusion

Through the analysis of the rate data at 25 °C and of the temperature dependence of the rates in different solvents it is clear that (i) the rate is enhanced in polar aprotic solvents due to stabilization of the dipolar transition state via a nonspecific dielectric effect and (ii) protic solvents stabilize the transition state through a nonspecific dielectric effect and also via a specific hydrogen-bonding interaction between the HBD solvent and the nitro group of the dye. The charge-transfer absorption band of *trans*-DENAB is shifted to lower energy with increased solvent polarity and it appears that the shift is mostly attributable to a nonspecific stabilization (hydrogen-

bonding effects are not important) of the dipolar Frank-Condon excited state relative to the ground state.

The isomerization rate data for DENAB have been analyzed with Kosower's Z value,¹⁰ the Taft-Kamlet multiple regression method, and the pyrene P_v parameter. These correlations show that interpretation based on the results of a single correlation at a molecular level should not be accepted with confidence. However, analysis of data using a variety of methods leads to correlations that are less subject to bias due to specific probe dependent solute-solvent interactions and interpretation of such results based upon theories of molecular interactions can be done with greater confidence.

Experimental Section

Materials. The *p*-(diethylamino)-*p'*-nitroazobenzene sample was supplied courtesy of G. Irick. 1,4-Dioxane (Fisher) and THF (Aldrich) were distilled from LiAlH_4 . Acetonitrile (Baker) and butyronitrile (Aldrich) were passed through activated alumina; the alcohols (Aldrich, Fisher) were dried over anhydrous Na_2SO_4 . All other solvents were used as received. Water was triply distilled, once from permanganate and once from sulfuric acid. Deuterium oxide (Aldrich, 99.8% D) was used as received.

Procedures. Dye solutions were 1×10^{-5} M for flash photolysis, 5×10^{-6} M for rates measured by a Perkin-Elmer 576 UV-vis spectrophotometer, and 5×10^{-5} M for visible absorption spectra. Solutions were prepared by pipetting 1.0-mL aliquots of CH_2Cl_2 stock solutions (1×10^{-4} M for flash and 5×10^{-4} M for UV-vis measurements) into 10-mL volumetric flasks; the CH_2Cl_2 was then evaporated by a slow stream of N_2 . The flasks were then diluted to the mark with the appropriate solvent and agitated to dissolve the dye.

Rate constants $> 1.0 \text{ s}^{-1}$ were measured by flash photolysis. The flash spectrophotometer has been previously described.^{38,39} The kinetics were monitored by observing the decay of the transient bleaching of the *trans*-DENAB absorption at 509 nm. The monitoring lamp was filtered through a 509-nm interference filter (10-nm bandpass) prior to passing through the sample to minimize effects due to continuous photolysis of the sample. The flash discharge was filtered by Corning 3-73 filters to cut off UV excitation. The samples were contained in a thermostated cylindrical cell (2 cm diameter \times 4 cm path length); temperatures were maintained by a Forma-Temp Jr. bath circulator (Forma Scientific Co.).

Rate constants $< 1.0 \text{ s}^{-1}$ were measured by photolyzing the solutions contained in a 1-cm square cell within the thermostated cell compartment of the Perkin Elmer UV-vis spectrophotometer using an unfiltered 100-W tungsten filament lamp for 5 min; the decay of the bleaching of the *trans*-DENAB was then monitored at the absorption max by the spectrophotometer.

The rate constants were calculated by fitting the decays to a first-order kinetic analysis. The first-order plots were generally linear (correlations > 0.99) for at least 3 lifetimes.

Visible absorption maxima were measured with the Perkin-Elmer spectrophotometer. Absorption maxima values reported are accurate to approximately ± 1 nm.

Acknowledgment. We thank Professor Mitchell Winnik for a helpful discussion. We are grateful to the National Science Foundation (Grant No. CHE8121140) for support of this work.

Registry No. D_2O , 7789-20-0; DENAB, 3025-52-3; deuterium, 7782-39-0.

(34) Kirkwood, J. *J. Chem. Phys.* 1934, 2, 351-361.

(35) Liptay, W. M. In "Excited States"; Lim, E. C., Ed.; Academic Press: New York, 1974; Vol. 1, pp 129-229.

(36) $\mu_{c\text{-DENAB}}$ has not been determined experimentally, so this value represents an educated guess. $r_{c\text{-DENAB}}$ and r likewise are not determined experimentally; however these figures are in line with r 's used in similar calculations (ref 37).

(37) Pasman, P.; Rob, F.; Verhoeven, J. W. *J. Am. Chem. Soc.* 1982, 104, 5127-5133.

(38) Young, R. C. Ph. D. Dissertation, University of North Carolina, Chapel Hill, NC, 1977.

(39) Nagle, J. K. Ph. D. Dissertation, University of North Carolina, Chapel Hill, NC, 1979.