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The Thermal Isomerization of Azobenzenes. III.[1] Substituent, Solvent, and Pressure Effects on the Thermal Isomerization of Push-pull Azobenzenes

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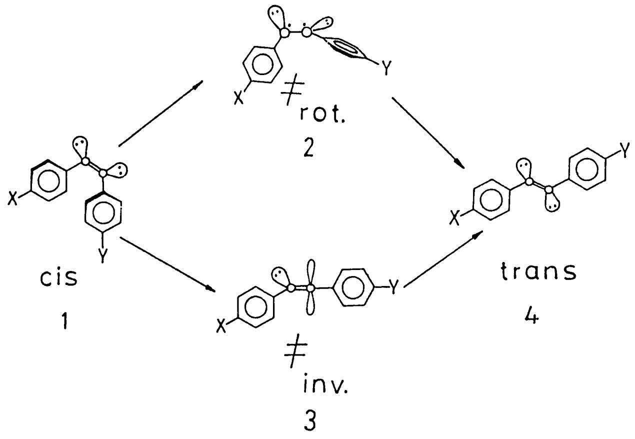
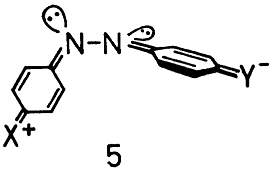
The substituent, solvent, and pressure effects on the rate of the thermal *cis*-to-*trans* isomerization of 4-dimethylamino-4′-nitroazobenzene(NDAAB) derivatives have been studied. 2-Methyl- and 2′-chloro-NDAAB isomerize faster than NDAAB, and 2′-methyl- and 2-chloro-NDAAB isomerize slower than NDAAB. For 2,2′-dimethyl- and 2,2′-dichloro-NDAAB, the rates are between those of the monosubstituted ones. These findings are very similar to those for 4-(dimethylamino)azobenzene (DAAB) derivatives, and no fundamental difference in the kinetic-substituent effects was observed between NDAAB and DAAB. The volume of activation, which is of a negative value, varies remarkably from solvent to solvent and from substituent to substituent; its magnitude increases generally with an increase in the solvent polarity. Even for DAAB and 4,4′-bis(diethylamino)azobenzene (BDEAAB), the rate is appreciably accelerated by external pressures in polar solvents. It is concluded that the observed results are more consistent with the inversion mechanism than with the rotational mechanism.

The mechanism of the thermal *cis*-to-*trans* isomerization of azobenzenes has attracted much attention for many years. Two mechanisms have been proposed. One involves rotation around the N=N double bond and includes the π-bond rupture. The other involves inversion on either or both of the azo-nitrogen atoms, the π-bond remaining intact.



Theoretical[2,3] and experimental[4–7] approaches favor the inversion mechanism for most cases. However, the rotational mechanism has been revived recently.[8–13] Nerbonne and Weiss[10] studied the isomerization of azobenzene in the cholesteric and isotropic phases and, observing that the Arrhenius plot in a liquid crystal did not yield a single straight-line slope, suggested the rotational mechanism. Whitten *et al.*[8,9] found a large solvent effect for push-pull-substituted azobenzenes and suggested a dipolar rotational transition state **5**.



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Asano *et al.*[11–13] reported that the isomerization rate of 4-dimethylamino-4′-nitroazobenzene (NDAAB) is considerably accelerated by external pressures in benzene and in polar solvents, but is little affected in hexane. According to them, this can be regarded as evidence for a change in the mechanism with the solvents for such push-pull azobenzenes, *i.e.*, from inversion in hexane to rotation in benzene. Indeed, such large pressure and solvent effects are consistent with the change in mechanism from solvent to solvent. However, it would be unnatural to expect such a drastic change in mechanism in nonpolar solvents. Therefore, it seems necessary to examine whether or not the proposed mechanism also accommodates other factors influencing the isomerization rate.

Several years ago, we reported on the kinetic data for the thermal isomerization of 36 kinds of azobenzene derivatives.[1,14] We found that the introduction of substituents almost invariably accelerates the rate, irrespective of the nature of the substituents. The substituent effect is of an additive nature, and the following Hammett-type equation holds approximately:

$$\log k/k_0 = \sum\sigma_{c-t}, \qquad (1)$$

where k_0 and k refer to the rate constant of a standard azobenzene derivative properly chosen and that of substituted derivatives with respect to the standard one respectively, and where σ_{c-t} denotes a substituent constant characteristic of the kind and the position of the substituent in question. We also found that the wavelength at the maximum absorption of the conjugation band of a *trans*-isomer is closely related to the rate constant. Another finding is that 2-methyl-4-(dimethylamino)azobenzene isomerizes about three times faster than 4-(dimethylamino)azobenzene (DAAB), whereas the 2′-methyl group rather retards the rate. We have interpreted these facts in terms of the resonance stabilization in the inversion-transition state. However, since the rotational mechanism has been newly proposed for NDAAB, we wish to examine which of the proposed mechanisms is more compatible with the experimental observations. Our views concerning the mechanistic implications will be described in some detail.

Experimental

Materials. The NDAAB derivatives were prepared by diazo coupling from the corresponding *N*,*N*-dimethylanilines and *p*-nitroanilines. The crude products were purified by column chromatography on silica gel and recrystallized from ethanol. The melting points, IR, NMR, and UV spectra were utilized for identification. For 2-methyl-NDAAB: mp 183—184 °C (lit,[15] 179—180.5 °C). For 2′-methyl-NDAAB: mp 159.5—160.5 °C (lit,[16] 161—163 °C). For 2,6-dimethyl-NDAAB: mp 169—170 °C. Found: C, 64.34; H, 6.21; N, 18.95%. Calcd for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.08; N, 18.78%. For 2,2′,6-trimethyl-NDAAB: mp 198—199 °C. Found: C, 65.45; H, 6.34; N, 17.86%. Calcd for $C_{17}H_{20}N_4O_2$: C, 65.37; H, 6.45; N, 17.94%. For 2-chloro-NDAAB: sublimed *ca.* 209 °C. Found: C, 55.35; H, 4.57; N, 18.55%. Calcd for $C_{14}H_{13}ClN_4O_2$: C, 55.18; H, 4.30; N, 18.39%. For 2′-chloro-NDAAB: mp 198—199 °C (lit,[17] 198—199 °C). For 2,2′-dichloro-NDAAB: mp 226—227 °C. Found: C, 49.36; H, 3.65; 16.41%. Calcd for $C_{14}H_{12}Cl_2N_4O_2$: C, 49.58; H, 3.57; N, 16.52%. The preparation of the other materials has been described elsewhere.[1] The solvents were purified and distilled in the usual manner.

Measurements. The pressure vessel,[18] with four optical windows, was made of SNCM-8 stainless steel and equipped with a water-circulating jacket. In this work, we used only two of the windows. High pressures were generated by means of a plunger pump and measured by means of a Heise Bourdon gauge. A turn mirror was installed between the pressure vessel and a monochrometor in order to switch the excitation light and the monitoring light. A 650-watt projector lamp was used for excitation. The light was passed through a 20-mm water layer and introduced into an inner cell. The cell was made of Teflon and consists of two compartments connected by a capillary tube (ϕ=1 mm). This made the uniform irradiation of the solution in the upper compartment possible, avoiding the mixing of the irradiated and unirradiated solutions. In order to avoid the adventitious contamination of acid which may affect the isomerization rate, small amounts of piperidine (0.3%) were added to the reaction solution. The solution was charged in the inner cell, and a desired pressure was applied to the solution through a liquid-separation piston. After a constant temperature and pressure had been attained, the solution was irradiated for *ca.* 1 min. Then the mirror was turned by 45 °, the absorption maximum of the *trans*-isomers was monitored by means of a Hitachi 139 spectrophotometer, and the absorbance was recorded. Satisfactory and reproducible first-order plots were obtained. The values of the rate constants listed in the tables are the average of several runs, the errors being within 2% in most cases. For 2,6-dimethyl- and 3-methyl-NDAAB in hexane, 2,6-dimethyl-NDAAB in CCl_4, 2,2′,6-trimethyl-NDAAB and 2′-chloro-NDAAB in toluene, and NDAAB in chloroform, the errors were within 5%.

Results

The wavelengths λ_{max} (nm) at the maximum absorption of the conjugation band of *trans*-NDAAB and other substances in various solvents are given in Table 1. It is noted that λ_{max} is quite sensitive to such solvent-polarity parameters as the E_T-values; *i.e.*, the band generally exhibits a bathochromic shift with an increase in the solvent polarity, with the exception of methanol, for which a specific solvent–solute interaction takes place, probably *via* hydrogen bonding. In Tables 2—4, the first-order rate constants in several

Table 1. Absorption maxima, λ_{max}(nm) of the conjugation band of *trans*-4-dimethylamino-4′-nitroazobenzene and others in solvents of different polarities

	Hexane	CCl_4	Toluene	Benzene	$CHCl_3$	Methanol
E_T/kcal†	30.9	32.5	33.9	34.5	39.1	55.5
Compound						
NDAAB[a)]	440	453	466	467	479	474
2-Me-NDAAB	450	462	477	476	490	488
2′-Me-NDAAB	440	451	462	463	470	469
2,2′-Me_2-NDAAB	449	460	471	471	480	481
2,6-Me_2-NDAAB	438	447	455	453	460	457
2,2′,6-Me_3-NDAAB	442	453	462	461	467	466
2-Cl-NDAAB	439	449	458	458	468	465
2′-Cl-NDAAB	459	474	488	488	500	493
2,2′-Cl_2-NDAAB	455	465	478	478	488	487
3-Me-NDAAB	407	420	427	427	433	420
DAAB[b)]	400[d)]		409		409	406
2-Me-DAAB	405[d)]		415		415	412
BDEAAB[c)]	431[d)]		448		463	470

a) 4-Dimethylamino-4′-nitroazobenzene. b) 4-(Dimethylamino)azobenzene. c) 4,4′-Bis(diethylamino)azobenzene. d) In cyclohexane. † 1 kcal=4.184 kJ.

Table 2. First-order rate constants (10^3k/s^{-1}) for the thermal *cis*-to-*trans* isomerization of NDAAB and its derivatives in hexane

Compound	25 °C	30 °C	35 °C	40 °C	45 °C
NDAAB	2.75	4.40	6.62	10.3	
2-Me-	4.38	6.87	11.5	18.3	
2′-Me-	2.05	3.50	5.65	8.65	
2,2′-Me_2-	3.95	6.28	9.77	15.3	
2,6-Me_2-	2.38	3.75	6.00	7.63	
2,2′,6-Me_3-	3.45	5.45	9.30	13.6	
2-Cl-		1.59	2.68	3.60	5.56
2′-Cl-	21.5	32.2	55.8	86.3	
2,2′-Cl_2-	5.97	7.85	12.9	23.2	33.8

solvents are listed. The activation parameters were estimated by using the least-squares method; their representative sets are given in Table 5. The isomerization rate was also followed under various pressures up to 1200 bar (1 bar$=10^5$ Pa) in various solvents; the rate constants for representative species in representative solvents are given in Tables 6—8. Plots of ln k_p/k_1 against the external pressure p for NDAAB in various solvents are shown in Fig. 1, where k_p and k_1 are the rate constants under the external pressure of p and 1 bar respectively. The solid lines in the figure represent the following quadratic regression equation:

TABLE 3. FIRST-ORDER RATE CONSTANTS ($10^3k/\mathrm{s}^{-1}$) FOR THE THERMAL ISOMERIZATION OF NDAAB DERIVATIVES IN CCl_4

Compound	20 °C	25 °C	30 °C	35 °C	40 °C
NDAAB	1.65	2.70	4.37	8.35	14.4
2-Me-	4.02	6.67	11.4	19.8	
2′-Me-	1.52	2.55	4.50	8.28	
2,2′-Me_2-	3.85	6.50	11.1	17.8	
2,6-Me_2-	2.47	4.35	7.10	13.9	
2,2′,6-Me_3-	4.92	7.73	11.8	22.0	
2-Cl-	0.475	0.678	1.16	2.07	3.42
2′-Cl-		38.5	62.2	95.3	160
2,2′-Cl_2-		7.82	13.4	23.0	37.8

TABLE 4. FIRST-ORDER RATE CONSTANTS ($10^3k/\mathrm{s}^{-1}$) FOR THE THERMAL ISOMERIZATION OF NDAAB DERIVATIVES IN TOLUENE

Compound	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
NDAAB	4.08	6.68	11.1	17.0	28.3	
2-Me-	24.5	40.0	61.8	84.0	137	
2′-Me-	3.35	5.73	9.72	14.0	25.0	
2,2′-Me_2-	18.0	31.7	49.3	63.8	107	
2,6-Me_2-	17.8	28.3	41.3	58.5	90.3	
2,2′,6-Me_3-	33.8	44.5	70.8	104	151	
2-Cl-			2.13	3.53	5.92	10.2
2′-Cl-	119	178	267	388		
2,2′-Cl_2-		32.3	56.2	84.0	119	

TABLE 5. ACTIVATION PARAMETERS FOR THE THERMAL ISOMERIZATION OF NDAAB AND ITS DERIVATIVES IN VARIOUS SOLVENTS

Compound	Solvent	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal K^{-1} mol^{-1}	$r^{a)}$
NDAAB	Hexane	15.7±0.2	−17.7±0.6	0.9997
	CCl_4	19.3±0.6	−5.5±1.8	0.9975
	Toluene	16.4±0.2	−12.5±0.6	0.9997
	$CHCl_3$	11.3±0.5	−24.3±1.8	0.9956
2-Me-NDAAB	Hexane	17.2±0.3	−11.6±0.9	0.9995
	CCl_4	18.5±0.3	−6.4±1.2	0.9993
	Toluene	14.2±0.4	−16.6±1.3	0.9978
2′-Me-NDAAB	Hexane	17.2±0.3	−13.0±1.0	0.9993
	CCl_4	19.7±0.5	−4.2±1.7	0.9987
	Toluene	16.8±0.4	−11.7±1.4	0.9981
	$CHCl_3$	10.3±0.5	−28.0±1.5	0.9960
2-Cl-NDAAB	Hexane	15.0±0.7	−22.0±2.3	0.9954
	CCl_4	17.9±0.7	−13.0±2.2	0.9958
	Toluene	18.6±0.2	−8.3±0.7	0.9997
	$CHCl_3$	13.0±0.1	−22.8±0.3	0.9999
2′-Cl-NDAAB	Hexane	16.8±0.5	−9.9±1.5	0.9983
	CCl_4	16.9±0.4	−8.5±1.2	0.9990
	Toluene	13.2±0.04	−17.2±0.1	0.9999
2,2′-Me_2-NDAAB	Hexane	16.2±0.1	−15.4±0.3	0.9999
	CCl_4	17.9±0.3	−8.7±0.5	0.9999
	Toluene	14.5±0.6	−16.2±2.0	0.9964
2,2′-Cl_2-NDAAB	Hexane	18.4±0.7	−7.3±2.0	0.9975
	CCl_4	19.0±0.1	−4.5±0.3	0.9999
	Toluene	14.9±0.7	−14.3±2.2	0.9957
3-Me-NDAAB	Toluene	19.6±0.6	−6.8±2.0	0.9979
	$CHCl_3$	12.6±0.3	−25.3±1.0	0.9985

a) Correlation coefficient for the plot of ln k *versus* $1/T$.

Table 6. First-order rate constants ($10^2k/\mathrm{s}^{-1}$) at various pressures for the isomerization of azobenzene derivatives in hexane

Compound	Temp/°C	P/bar				
		1	300	600	900	1200
NDAAB	50	2.33	2.57	2.73	2.97	3.17
2-Me-NDAAB	40	1.55	1.78	2.00	2.22	2.38
2′-Me-NDAAB	50	2.40	2.55	2.65	2.77	3.03
2,2′-Me$_2$-NDAAB	40	1.55	1.75	1.92	2.08	2.18
2-Cl-NDAAB	50	0.753	0.805	0.835	0.878	0.882
2′-Cl-NDAAB	25	2.07	2.32	2.51	2.77	3.00
2,2′-Cl$_2$-NDAAB	35	1.30	1.46	1.65	1.77	1.92

Table 7. First-order rate constants ($10^2k/\mathrm{s}^{-1}$) at various pressures for the isomerization of azobenzene in CCl_4

Compound	Temp/°C	P/bar				
		1	300	600	900	1200
NDAAB	40	1.22	1.36	1.52	1.59	1.73
2-Me-NDAAB	40	2.93	3.35	3.83	4.50	5.05
2′-Me-NDAAB	40	1.32	1.41	1.53	1.65	1.75
2,2′-Me$_2$-NDAAB	40	2.81	3.12	3.47	3.82	4.25
2,6-Me$_2$-NDAAB	40	1.82	2.42	2.90	3.47	3.95
2,2′,6-Me$_3$-NDAAB	25	0.775	0.928	1.13	1.32	1.48
2-Cl-NDAAB	50	0.962	1.05	1.15	1.23	1.32
2′-Cl-NDAAB	25	3.75	4.20	4.70	5.25	5.82
2,2′-Cl$_2$-NDAAB	40	3.93	4.47	5.08	5.51	6.05

Table 8. First-order rate constants ($10^2k/\mathrm{s}^{-1}$) at various pressures for the isomerization of azobenzene derivatives in toluene

Compound	Temp/°C	P/bar				
		1	300	600	900	1200
NDAAB	25	1.11	1.45	1.78	2.12	2.48
2-Me-NDAAB	16	2.52	3.40	4.47	5.78	
2′-Me-NDAAB	25	0.952	1.09	1.26	1.47	1.64
2,2′-Me$_2$-NDAAB	25	4.35	5.75	7.33	9.00	10.7
2-Cl-NDAAB	50	2.55	2.90	3.38	3.85	4.47
2′-Cl-NDAAB	15	11.4	14.2	17.8	22.5	28.2
2,2′-Cl$_2$-NDAAB	25	5.25	6.75	8.61	10.4	12.6
NAAB	70	0.585	0.592	0.585	0.590	0.595
2-Me-DAAB	70	1.45	1.51	1.56	1.60	1.63
BDEAAB	50	3.00	3.18	3.35	3.47	3.58

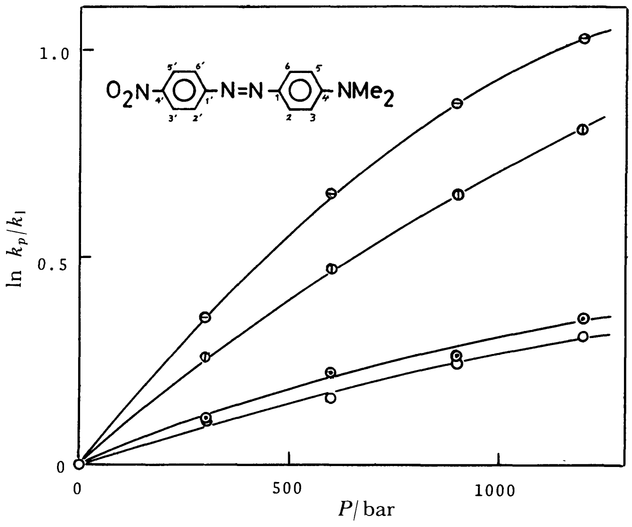


Fig. 1. Pressure effects on the first-order rate constants for the thermal *cis*-to-*trans* isomerization of 4-dimethylamino-4′-nitroazobenzene (NDAAB): (○) hexane; (⊙) CCl_4; (⦶) toluene; (⊖) chloroform.

$$\ln k_p/k_1 = a + bp + cp^2. \tag{2}$$

The activation volumes at 1 bar were estimated according to Eq. 3; the values are given in Table 9:

$$\Delta V^{\ne} \approx -bRT. \tag{3}$$

Discussion

General Survey of Rate-controlling Factors. Large differences in the activation energy between azobenzenes and the corresponding iso-π-electronic stilbenes have been considered as indirect evidence of the inversion mechanism for azobenzenes.[5] Enthalpy considerations[19,20] and theoretical approaches[2,3] are compatible with this view. However, for 4-amino-4′-nitrostilbene, both the activation energy and the frequency factor drop a great deal compared with those of unsubstituted stilbene. According to Calvin and Alter,[21] the *cis*-isomer of this substance is thermally isomerized *via* a triplet state, as characterized by the very low frequency factor ($A \approx 10^5\ \mathrm{s}^{-1}$). Hence, our data

Table 9. Activation volumes ($\Delta V^{\neq}$/cm^3 mol^{-1}) for the thermal *cis*-to-*trans* isomerization of azobenzene derivatives in various solvents (temp/°C)

Compound	Hexane	CCl_4	Toluene	$CHCl_3$	MeOH
NDAAB	−7.7(50)	−10.3(40)	−22.0(25)	−30.4(15)	
2-Me-NDAAB	−13.0(40)	−12.1(40)	−24.0(16)		
2′-Me-NDAAB	−3.2(50)	−7.1(40)	−12.0(25)	−22.1(16)	
2,2′-Me_2-NDAAB	−11.2(40)	−8.8(40)	−24.3(25)		
2,6-Me_2-NDAAB	−16.9(50)	−17.8(40)	−23.6(15)		
2,2′,6-Me_3-NDAAB	−13.7(40)	−17.6(25)	−21.9(15)		
2-Cl-NDAAB	−6.4(50)	−8.2(50)	−12.0(50)		
2′-Cl-NDAAB	−8.8(25)	−9.6(25)	−17.6(15)		
2,2′-Cl_2-NDAAB	−11.3(35)	−12.0(40)	−21.9(25)		
3-Me-NDAAB	−8.6(50)		−11.8(50)	−30.8(25)	
DAAB			−0.1(70)	−1.9(57)	−3.6(50)
2-Me-DAAB			−4.2(70)	−3.7(70)[a]	
BDEAAB	−2.9(50)		−5.7(50)	−6.8(40)	−5.0(15)

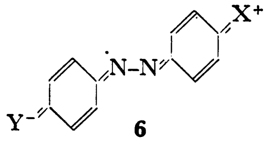
a) In chlorobenzene.

(Table 5) must preclude the intervention of the triplet state involving the rupture of the N=N π-bond.

Previously, we pointed out that the stabilization by means of the delocalization of the π-electrons in the transition state is an important rate-controlling factor. This inference has arisen from the following reasoning: if the conformation of the transition state of the species in question is similar to that of the *trans*-isomer in the sense that the phenyl rings are coplanar, the solvent and substituent effects on the isomerization rate would reflect the nature of the *trans*-isomer. As may be seen in Table 1, the conjugation band shifts to a longer wavelength almost invariably upon the introduction of the substituent, irrespective of their nature, and as the solvent polarity increases. It follows from an inspection of Tables 1—4 that, as the conjugation band of the *trans*-isomers of NDAAB derivatives shifts to a longer wavelength, the rate as a whole increases. This correlation has already been observed for DAAB derivatives.[1,14] The introduction of strong push-pull groups remarkably affects the rate and the position of the conjugation band. Because of the additive nature of the substituent effects on the rate, greatly accelerated rates are observed for NDAAB derivatives.

Very recently, Whitten and his co-workers[9,22] showed that the $\Delta G^{\neq}$ value for the isomerization of NDAAB is linearly related to Kosower's *Z*-values or other solvent polarity parameters, and suggested that **5** is responsible for the transition state. This conformation has also been supported by Asano *et al.* on the basis of the kinetic pressure effects.[11–13] However, we have a different idea of the conformation and the electronic structure of the activated complex, as will be discussed below.

Solvent Effects. The thermal isomerization of most azobenzenes exhibits few solvent effects. For push-pull azobenzenes such as NDAAB, however, a significant solvent effect has been observed. According to Whitten *et al*, [8,9] this favors a dipolar transition state **5**. Asano *et al.* also consider that **2** and **3** greatly differ in their polarities, and that in **2** (=**5**), the original π-electrons are transferred toward the pulling group and the newly formed positive charge center is stabilized by the pushing group. It should be noted that, in **5**, the N=N π-bond is completely ruptured. If such a charge-separated species is stabilized by solvation at the expense of the N=N π-bond rupture, the same logic must be admitted for the *cis*- and *trans*-isomers, too. Then the *trans*-isomer may have an electronic structure of the following type:



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where the original N=N π-bond is completely broken and where charges are localized on the push and pull groups. If this were true, the dipole moment of the *trans*-isomer must be as large as 50 Debye, but this is not the case (see below). We admit that **6** is one of the canonical resonance forms, but it is not an *entity* (*cf.* **7**, **10**, and **11**).

The free energy of activation for the isomerization in the gas phase may be compensated for by solvation in a condensed medium. Laidler and Landskroener[23] gave expressions for the rate constant for reactions involving ions and dipoles. These are based on the treatment of Kirkwood, who gave general expressions for the free-energy change when a sphere with a radius *r* containing a distribution of charges is transferred from a medium of the unit dielectric constant to one of the dielectric constant ε. If azobenzenes are regarded as dipoles with no net charges, the rate constant for the thermal isomerization may be given by:

$$\ln k = \ln k_0 + \frac{3}{8kT}\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu^2}{r^3}\right)\left(\frac{\varepsilon-1}{\varepsilon+1}\right), \tag{4}$$

where k_0 is the hypothetical rate constant in a condensed medium of $\varepsilon=1$, and where μ and $\mu_{\neq}$ denote the dipole moments in the *cis* and transition states. We may expect that the plot of ln *k versus* $(\varepsilon-1)/(\varepsilon+1)$ makes a straight line.

In order to examine Eq. 4, the isomerization rate was followed for three representative azobenzenes in various solvents; the results are listed in Table 10. In Fig. 2, ln *k* is plotted against $(\varepsilon-1)/(\varepsilon+1)$. From the slope and assuming that $r \approx r_{\neq} = 0.5$ nm, $T = 300$ K, and $\mu = 3$ D (1 Debye$=3.3\times10^{-30}$ m C), we tentatively estimated $\mu_{\neq} \approx 12$

TABLE 10. RATE CONSTANTS FOR THE THERMAL *cis*-to-*trans* ISOMERIZATION OF DAAB, NDAAB, AND BDEAAB IN VARIOUS SOLVENTS AT 25 °C

Solvent	ε	$\ln k/\mathrm{s}^{-1}$		
		DAAB	NDAAB	BDEAAB
Hexane	1.90	−10.3	−5.90	−7.47
Dioxane	2.21		−4.16	
CCl_4	2.23		−5.91	
Benzene	2.27	−10.16	−4.47	
Toluene	2.38		−4.50	
$CHCl_3$	4.70		−4.02	−4.71
Chlorobenzene	5.61	−9.54	−1.73	−5.40
1,2-Dichloroethane	10.37			−4.92
Acetone	20.5	−9.88	0.92[a]	−5.13
Methanol	32.6			−3.17
DMF	36.7		3.91[a]	
DMSO	48.9		4.79[a]	

a) Cited from Ref. 1.

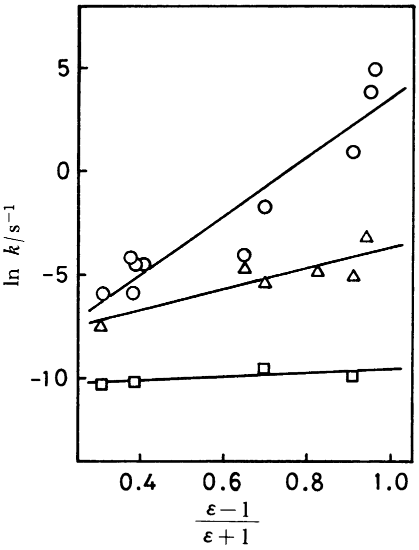


Fig. 2. Plots of ln k against $(\varepsilon-1)/(\varepsilon+1)$, according to Eq. 4: (○) NDAAB; (△) BDEAAB; (□) DAAB.

Debye for NDAAB. This may be an acceptable order of magnitude, since μ=7.91 D for *trans*-NDAAB.[24] There are very few solvent effects on DAAB, but it is notable that BDEAAB exhibits considerably greater solvent effects than DAAB, indicating a substantial polarity change upon activation. Therefore, we admit a polar *inversion* transition state for this kind of species, too (see **8** and **9** below), since a rotational dipolar structure such as **5** is quite unlikely. (Relevant discussion will be undertaken in the section on pressure effects.) The considerable scatter of the plots in Fig. 2 may indicate very complicated solvent effects on the rate, which has been often observed in Menschutkin reactions. The magnitude of the slope could then be regarded as a measure of the change in charge distribution upon activation.

Substituent Effects. As Talaty and Fargo[5] first pointed out, the introduction of substituents almost invariably accelerates the rate, regardless of the nature of the substituents. Therefore, the Hammett plot becomes V-shaped, with a mimimum near σ=0. Hall *et al.*,[25] and Herkstroeter[26] also reported similar observations for the isomerization of *N*-(hexafluoroisopropylidene)anilines and pyrazolone azomethines. They explained these observations in terms of a change in the mechanism. However, we question this and made a brief comment on it previously.[1] It has been found that the introduction of bulky substituents into *ortho* positions with respect to azomethine nitrogen always accelerates the rate. According to Kessler and his coworkers, the steric hindrance of bulky *ortho* substituents becomes less severe in the inversion-transition state than in the ground state, thus accounting for the acceleration in terms of the inversion mechanism.[27—30]

In this respect, we considered that, if we introduce substituents on *ortho* positions with respect to the azo group, and then examine the kinetic effects, it would shed light on the mechanism. Two sorts of substituents were chosen: Cl- and Me-groups. Let us regard NDAAB as the standard of the push-pull azobenzenes, since interest is focused on this species. When we examine the data in Tables 2—4, we notice some interesting points: (1) 2-Me- accelerates the rate, while 2′-Me- slightly retards it. (2) This effect tends to become more remarkable as the polarity of the solvent increases. (3) On the other hand, 2-Cl- retards the rate, while 2′-Cl- accelerates it. These kinetic substituent and solvent effects are more remarkable than those of the Me-group. (4) For 2,2′-disubstituted NDAAB, the rates fall between those of the 2- and 2′-groups. (5) The kinetic effect of 6-Me- is notable: 2-Me->2,6-dimethyl, and 2,2′-dimethyl<2,2′,6-trimethyl in most solvents.

We previously reported that Eq. 1 approximately holds for DAAB derivatives for a specified solvent. The above findings indicate that Eq. 1 is valid for NDAAB derivatives and in other solvents, too. However, the rule is not valid for the 6-Me-group. A plausible reason for this may be the additional steric hindrance: 2-Me-<2,6-dimethyl in the transition state and 2,2′-dimethyl<2,2′,6-trimethyl in the *cis* ground state.

As is shown in Table 1, λ_{max} is sensitive to substituents: 2-Me- and 2′-Cl- shift the conjugation band to a longer wavelength, while 2′-Me- and 2-Cl- shift it to a shorter one. Fig. 3 shows the relationship between the ln k/k_0 and $\tilde{\nu}_{\mathrm{max}}$ values of the *trans*-isomers. In benzene as well as in hexane, good parallelograms can be observed. These observations suggest that the delo-

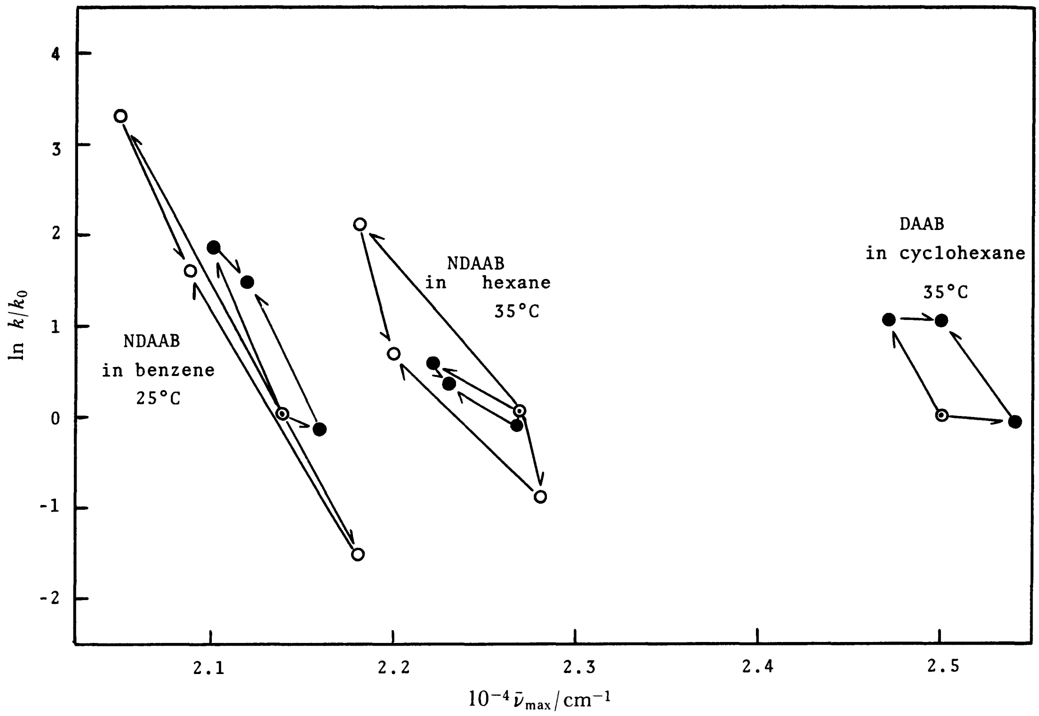
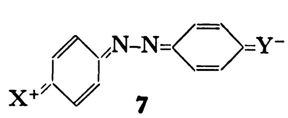


Fig. 3. Correlation between ln k/k_0 and $\tilde{\nu}_{max}$ for Me-substituted (●), and Cl-substituted (○) azobenzene derivatives. Data for DAAB are cited from Ref 1.

calization of the π-electrons, and hence the mesomeric effect, are important rate-controlling factors. Therefore, the two phenyl rings must be coplanar; this supports the inversion mechanism. If **5** is assumed, the correlation shown in Fig. 3 could not be expected, since the benzene rings are twisted in relation to each other.

From the above observations, one could say that there is no indication of the mechanism change for any kind of azobenzene in any solvent. The idea that NDAAB and its homologues isomerize *via* a route to rotation in solvents other than hexane, while other azobenzenes do so *via* a route to inversion or inversion-rotation competition paths, is thus questionable.

The substantial contribution of the canonical resonance form **7**:



7

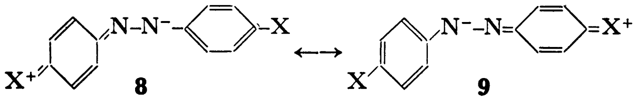
which is possible for push-pull azobenzenes alone, may be responsible for the enhanced rate, especially in polar solvents. This resonance contribution must be strongly forbidden in the *cis*-isomer, for which two phenyl rings are twisted by 56 ° out of the C-N-N-C plane,[31] as well as in the rotational transition state (compare **7** with **5**). Therefore, we can reasoably assume that, for push-pull azobenzenes, a remarkable polarity change occurs on going from the *cis* to the inversion transition state, a change which accommodates the substantial substituent and solvent effects. From the theoretical approaches,[2,3] it is known that the energy required for the hybrid change from sp^2 to sp is much less than the energy needed for the π-bond rupture. Even if the latter energy were compensated for partially by solvation in the rotational dipolar transition state, it is unlikely that *cis* push-pull azobenzene prefers a route *via* rotation to a route *via* inversion in benzene, and *vice versa* in hexane.

Linear Free-energy Relationship. According to Leffler and others,[32—36] a linear enthalpy-entropy relationship should hold for the simple interaction mechanism. If the $\Delta H^{\neq}$ *versus* $\Delta S^{\neq}$ plot is scattered, more than two interactions must be involved. Shinkai and his co-workers[7,12] have shown that the $\Delta H^{\neq}$ *versus* $\Delta S^{\neq}$ plots for various kinds of azobenzenes, but not NDAAB, constitute a straight line, while the same plots for NDAAB in various solvents, including hexane, give other straight line shifted downward, thus accounting for the change in the mechanism. Nevertheless, they opined that the mechanism change for NDAAB depends on the solvents, on the basis of the kinetic pressure effect; this is inconsistent.

If the data in Table 5 are inspected, it may be seen that $\Delta H^{\neq}$ tends to increase with the increase in $\Delta S^{\neq}$. It may also be noted that the sets of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in hexane for NDAAB derivatives fall in the region in which other sets are involved, and we cannot see any indication of special behavior in hexane. We consider that the downward shift is not due to the mechanism change, but to the remarkable free-energy depression attributable to the extra mesomeric contribution **7** and the accompanying solvation.

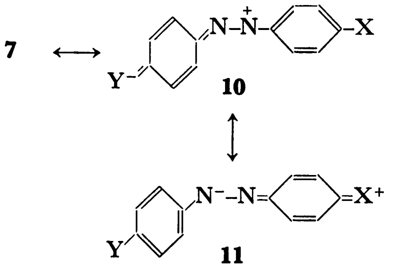
Pressure Effects. We now wish to examine the pressure effects on the isomerization of various kinds of azobenzenes in various solvents with different polarities. From an inspection of Tables 6—9, we see some interesting points: (1) First of all, an appreciable acceleration in the rate by external pressures for NDAAB and its homologues can be observed, even in hexane. The values of $\Delta V^{\neq}$ are similar to those reported by Asano *et al.*, except for that of NDAAB in hexane. (2) The pressure effect and, hence the activation volume $|\Delta V^{\neq}|$, tend to increase as the solvent polarity increases, but there is a distinction between CCl_4 and toluene. (3) When ln k_p is plotted against p for substituted NDAAB, we can see that the patterns of the kinetic pressure effect for 2-Me- and 2′-Cl- , 2′-Me- and 2-Cl-, and 2,2′-dimethyl and 2,2′-dichloro-NDAAB are very similar to each other. We have already pointed out that these sets of substituents exert similar effects on the rate as well as the position of $\bar{\nu}_{\max}$. (4) Astonishingly, BDEAAB and DAAB also exhibit appreciable pressure effects in toluene, chloroform, and methanol (Table 9).

The above findings indicate very complex kenetic pressure effects, and it is very difficult to give a clear-cut explanation of them. It is well known, though, that if a reaction starts from a nonpolar ground state and proceeds *via* a polar transition state, a more negative activation volume is to be expected for a less polar solvent, as observed in Menschutkin reactions.[37—40] The above findings are just the reverse; therefore, they could be explained in terms of two competing reaction paths for push-pull azobenzenes for which $|\Delta V^{\neq}|$(inversion)$\approx$0, and $|\Delta V^{\neq}|$(rotation)=20—30 cm^3 mol^{-1}.[13] However, the (4) observation excludes this, since a dipolar structure for the rotational transition state is least likely for a bis-substituted azobenzene such as BDEAAB. At the same time, it is possible to write the dipolar inversion transition state for push-push azobenzenes as follows:



8 **9**

The partial charge on the molecule would cause the polarization of the surrounding solvent molecules, thus accounting for the substantial pressure and solvent effects for these kinds of azobenzenes. The red shift of the conjugation band of *trans*-BDEAAB, which is nominally a nonpolar molecule, could thus be explained (Table 1). For push-pull azobenzenes, there must be a substantial contribution of the following dipolar canonical resonance forms to the stabilization of the inversion transition state:



7 **10** **11**

The solvent dependencies of $\Delta V^{\neq}$ for reactions in which a polarity change between a reactant and the activated complex takes place have hitherto been interpreted as follows: if Eq. 4 is differentiated with respect to the pressure, it follows that:

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^{\neq}}{RT} = \frac{3}{4kT}\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu^2}{r^3}\right)\frac{(\partial\varepsilon/\partial p)_T}{(\varepsilon+1)^2}. \quad (5)$$

The $(\partial\varepsilon/\partial p)_T/(\varepsilon+1)^2$ term generally decreases as the polarity of a solvent increases, in agreement with the trend observed in Menschutkin reactions. However, this is nothing but a qualitative explanation. For example, $\Delta V^{\neq}$(benzene)/$\Delta V^{\neq}$(nitrobenzene)$\approx$1.6(obsd) and 10(calcd) for a reaction between pyridine and methyl iodide. This large discrepancy, together with the considerable scatter in Fig. 2, may be ascribed to the neglect of specific solute-solvent interactions in the Kirkwood model. Such interactions will give rise to a polarization enhanced by polar solvents. In our case, the dipole moment in the transition state may be more susceptible to the solvent polarity, compared with the case of the Menschutkin reactions, since the transition state of substituted azobenzenes are *soft* in the sense that the π-electrons are labile(see **7**—**11**). Thus, if the effect of solvent polarity on the μ-term overwhelms the effect on the ε-term in Eq. 5, $\Delta V^{\neq}$ will increase with the increase in solvent polarity, and *vice versa*, the preference depending on the type of reactions. It seems that the investigation and the interpretation along these lines have not yet been well-established, and so we must suspend a straightforward conclusion.

The above assumption requires that the plot of Fig. 2 be curved concavely upward. Probably, a quadratic regression equation for NDAAB will support it, but the plots are too scattered, and therefore more sophisticated investigations are necessary. Further, the freedom to rotate around the C–N bond in the *cis* and transition states may be deeply related to the nature of the solvents as well as to the bulkiness and positions of substituents. The above findings (1)—(4), together with the solvent and substituent effects, show very complicated aspects of the isomerization of azobenzenes.

Conclusion

We have compared the kinetic substituent, solvent, and pressure effects for the thermal *cis*-to-*trans* isomerization of push-pull azobenzenes with those for other kinds of azobenzenes for which the inversion mechanism has been accepted, and have seen that there are no essential differences in kinetic behavior between them. Rather, we have observed very similar *ortho* effects between NDAAB and DAAB derivatives. Further, we have found substantial kinetic-pressure and solvent effects for symmetrically substituted azobenzene. The above findings argue in favor of the inversion mechanism and against the rotational one.

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