Thermal *Cis*-to-*Trans* Isomerization of Substituted Azobenzenes II.[1] Substituent and Solvent Effects

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The thermal *cis*-to-*trans* isomerization rate of various azobenzenes was followed by means of spectrophotometric and flash photolysis techniques. For *para*-donor/*para'*-acceptor-substituted azobenzenes such as 4-nitro-4'-dimethylaminoazobenzene, the rate was distinctly accelerated, the activation energy decreasing with the increase in the polarity of solvents. Introduction of substituents in *para* positions with respect to azo group increased the rate irrespective of substituent. The effect is additive and a Hammett-type equation holds. For 4-dimethylamino- and 4-nitroazobenzenes, while the 2-methyl group accelerated the rate, the 2'-methyl group did not. The results suggest that the isomerization proceeds *via* inversion mechanism and the rate is controlled mainly by the resonance stabilization in the coplanar transition state. The inversion center for asymmetric azobenzenes is discussed.

The mechanism of *cis-trans* isomerization of azobenzenes and azomethines has attracted much attention from interest in its photochemistry. For their thermal *cis*-to-*trans* isomerization, two mechanisms have been proposed. One involves a rotation (torsion or twist) around the N=N double bond and includes a π-bond rupture. The other involves an inversion (in-plane lateral shift) through a linear state, the π-bond remaining intact.

The inversion mechanism has been assumed to hold for imines and azo compounds. However, recent accumulation of data of the isomerization has given rise to controversy on the mechanism.[2-9] Some authors explained their results in terms of different mechanisms,[6,7] and others suggested the possibility of a continuum of mechanisms between two limiting cases.[3] In addition to the study of activation parameters and solvent effects, a study of substituent effects on the rate of isomerization seemed to be the nearest way to solve the problem.

Recently, the present authors[1] presented a brief report on the *cis*-to-*trans* thermal isomerization of substituted 4-dimethylaminoazobenzenes as summarized below: (1) 2-Methyl group considerably accelerates the rate, while 2'-methyl group has virtually no effect on the rate. (2) All *para* substituents accelerate the rate, irrespective of the nature of the substituents. The effect is of an additive nature and an extended Hammett equation approximately holds:

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

where k and k_0 refer to the rate constants of *o*- and/or *p*-substituted and unsubstituted 4-dimethylaminoazobenzenes, respectively, and $\sum$ is the sum of the substituent constants for the substituents present in both benzene nuclei. (3) The logarithmic isomerization rate constants are roughly proportional to the molar extinction coefficients of the *trans*-isomers. The findings seemed to give us an useful suggestion regarding the rate-controlling factors for the isomerization.

This paper deals with the isomerization of various azobenzene derivatives for a better understanding of the isomerization mechanism and rate-controlling factors.

Experimental

Materials. The usual azobenzene derivatives were prepared by the procedures described previously.[10,11] For 2,6-dimethyl-4-dimethylaminoazobenzene derivatives, *N,N*-dimethyl-*m*-xylidine was prepared *via* 2,4,6-trimethylpyridinium perchlorate by the method of Diels and Alder.[12] It was then coupled with diazonium salts to give the final substances. Ryan's method[13] was used for the coupling. The final products were purified by dissolving them in benzene, passing through an alumina column, and then crystallizing them from benzene. *p*-Nitroazobenzene was prepared by condensing *p*-nitronitrosobenzene with aniline, the former being obtained by oxidation of *p*-nitroaniline with Caro's acid. Other *p*-nitroazobenzene derivatives were prepared by similar procedures. Melting point, NMR and UV spectra were utilized for identification. Elemental analysis was made for the new compounds. Their names, melting points and values in literature (in parentheses) are as follows: 4-Dimethylaminoazobenzene, 118—119 °C (119—120 °C); 4-Methyl-4'-dimethylaminoazobenzene, 169—170 °C (169.5—170 °C); 4-Chloro-4'-dimethylaminoazobenzene, 158—159 °C (158—158.5 °C); 3-Nitro-4'-dimethylaminoazobenzene, 157.5—158 °C (157—158 °C); 2-Methyl-4'-dimethylaminoazobenzene, 73—74 °C (73.5—74 °C); 2-Methyl-4-dimethylaminoazobenzene, 67—67.5 °C (68—68.5 °C); 2,4-Dimethyl-4'-dimethylaminoazobenzene, 136—137 °C (137 °C); 2-Methyl-4-chloro-4'-dimethylaminoazobenzene, 114—115 °C (117 °C); 2,4'-Dimethyl-4-dimethylaminoazobenzene, 125—126 °C (121 °C); 2-Methyl-4'-chloro-4-dimethylaminoazobenzene, 98—99 °C (96 °C); 2,2'-Dimethyl-5'-nitro-4-dimethylaminoazobenzene, 148—149 °C (148—148.5 °C); 2,2'-Dimethyl-4-dimethylaminoazobenzene, 77—78 °C (79—80 °C); 2,2',4'-Trimethyl-4-dimethylaminoazobenzene, 118—119 °C (120—121 °C); 2,2'-Dimethyl-4'-chloro-4-dimethylaminoazobenzene, 114.5—115 °C (115—116 °C); 4-Diethylaminoazobenzene, 96—97 °C (98 °C); 4-Methoxyazobenzene, 55—56 °C (55.5 °C); 4,4'-Bis(dimethylamino)azobenzene, sublimes at *ca.* 235 °C. Found: C, 71.73; H, 7.29; N, 20.58%. Calcd for $C_{16}H_{20}N_4$: C, 71.61; H, 7.51; N, 20.88%; 4,4'-Bis(diethylamino)azobenzene, 176—177 °C (171 °C); 4,4'-Dimethoxyazobenzene, 163.5—164.5 °C (164 °C); 4,4'-Dichloroazobenzene, 185 °C(183—184 °C); 4,4'-Dimethylazobenzene, 144 °C (144 °C); 4,4'-Dinitroazobenzene, 215 °C (216 °C); 4-Pyrrolidinoazobenzene, 166—167 °C (166—167 °C); 4-Aminoazobenzene, 125.5 °C (125—126 °C); 4-Amino-4'-methylazobenzene, 147—148 °C. Found: C, 74.20; H, 6.48;

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE *cis*-TO-*trans* THERMAL ISOMERIZATION OF AZOBENZENES[a)]

No.	Substance	λ_{max}[b)] (nm)	ε_{max}[b)]	$10^2 k$, min^{-1} 25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C	70°C	75°C	E_a (kcal/mol)	ΔS^* (300K) (gibbs/mol)
1	4-Dimethylamino-azobenzene	390	31200	0.204	0.355	0.670	1.10								21.1	−10.7
2	4′-Methyl-DAAB[c)]	400	31800	0.319	0.562	0.990	1.57								20.1	−12.5
3	4′-Chloro-DAAB	410	34100	0.386	0.713	1.14	1.97								20.0	−12.5
4	3′-Nitro-DAAB	420	31600	0.291	0.517	0.838	1.47								18.8	−17.4
5	2′-Methyl-DAAB	394	29900			0.594	0.935	1.59							19.2	−16.5
6	2-Methyl-DAAB	405	30200			1.87	3.32	5.10							20.1	−11.0
7	2′,4′-Dimethyl-DAAB	393	31000			0.99		2.90	4.93						21.0	−9.75
8	2′-Methyl-4′-chloro-DAAB	413	32600			1.16	1.75	3.74	5.90						21.5	−7.46
9	2,4′-Dimethyl-DAAB	405	30500		1.54	2.60	4.69	7.95	11.6						19.7	−12.0
10	2-Methyl-4′-chloro-DAAB	415	32800			3.98	6.03	11.3							19.7	−11.0
11	2,2′-Dimethyl-5′-nitro-DAAB	425	29800	0.755	1.18	2.33	4.02								20.4	−9.75
12	2,2′-Dimethyl-DAAB	400	28800	0.567	1.02	1.73	2.91								20.6	−9.75
13	2,2′,4′-Trimethyl-DAAB	399	29900	1.01	1.59	2.88	4.38								18.3	−16.9
14	2,2′-Dimethyl-4′-chloro-DAAB	411	31000			5.17										
15	4-Diethylamino-azobenzene	407	32300			0.993										
16	4-Methoxy-AB[d)]	342	21350			0.194										
17	4,4′-Bis(dimethyl-amino)-AB	410	37000	1.61	2.81	4.69	7.49	11.1							19.2	−12.0
18	4,4′-Bis(diethyl-amino)-AB	431	39300	3.40	5.44	9.25	14.5								18.3	−13.9
19	4,4′-Dimethoxy-AB	353	26300			0.314										
20	4,4′-Dichloro-AB	331	26400			0.161										
21	4,4′-Dimethyl-AB	330	27000			0.173										
22	4,4′-Dinitro-AB	336	24600			2.40										
23	4-Pyrrolidino-AB	407	33000			0.865										
24	4-Amino-AB	363	29000			0.842										
25	4-Amino-4′-methyl-AB	363	28300			1.04										
26	4-Methyl-4′-pyrrolidino-AB	407	32800			1.15										
27	4-Chloro-4′-pyrrolidino-AB	417	35000			1.84										
28	4-Nitro-AB	330	25600			0.737										
29	2′-Methyl-4-nitro-AB	341	24100			0.491										
30	2-Methyl-4-nitro-AB	336	24600			1.16										
31	2,2′-Dimethyl-4-nitro-AB	345	21100			1.14										
32	2,2′,6′-Trimethyl-DAAB	377	26000						0.180	0.359	0.590	0.944	1.75		24.7	−4.71
33	2′,6′-Dimethyl-DAAB	389	23100								0.276	0.491	0.848	1.69	27.5	2.15
34	2,6-Dimethyl-DAAB	391	20000					0.480	0.914	1.40	2.84				24.5	−2.42
35	2,4′,6-Trimethyl-DAAB	395	24700				0.312	0.534	0.769	1.57	3.14				24.2	−2.88
36	2,2′,6-Trimethyl-DAAB	395	24800				0.850	1.34	2.03	3.44	5.30				19.2	−16.8

a) Substances **1**—**24**, **26**—**31** in cyclohexane, **25** in benzene and **32**—**36** in toluene. b) Wavelength and molar extinction coefficient at the maximum of the conjugation band in cyclohexane. c) DAAB: 4-Dimethylaminoazobenzene. d) AB: Azobenzene.

N, 19.45%. Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89%; 4-Methyl-4′-pyrrolidinoazobenzene, 187—188 °C (187—188 °C); 4-Chloro-4′-pyrrolidinoazobenzene, 197—198 °C (197—198 °C); 2,2′,6′-Trimethyl-4-dimethylaminoazobenzene, oil. Found: C, 76.33; H, 8.43; N, 15.28%. Calcd for $C_{17}H_{21}N_3$: C, 76.37; H, 7.92; N, 15.72%; 2,6-Dimethyl-4′-dimethylaminoazobenzene, 103.5—104.5 °C. Found: C, 75.87; H, 8.07; N, 16.81%. Calcd for $C_{16}H_{19}N_3$: C, 75.85; H, 7.56; N, 16.59%; 2,6-Dimethyl-4-dimethylaminoazobenzene, 91—92 °C. Found: C, 75.80; H, 8.03; N, 16.29%; 2,4′,6-Trimethyl-4-dimethylaminoazobenzene, 133—133.5 °C. Found: C, 76.24; H, 7.87; N, 15.99%. Calcd for $C_{17}H_{21}N_3$: C, 76.37; H, 7.92; N, 15.72%; 2,2′,6-Trimethyl-4-dimethylaminoazobenzene, 87.5—88 °C. Found: C, 76.24; H, 7.90; N, 15.59%; 4-Nitro-4′-dimethylaminoazobenzene, 228 °C (229—230 °C); 4-Nitro-4′-diethylaminoazobenzene, 151 °C (151 °C); 4-Nitro-3′-methyl-4′-dimethylaminoazobenzene, 121—122 °C (121—122 °C);4-Nitroazobenzene, 135—135.2 °C (135 °C); 2′-Methyl-4-nitroazobenzene, 81.5—82 °C. Found: C, 64.73; H, 4.58; N, 17.27%. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42%; 2-Methyl-4-nitroazobenzene, 98.5—99 °C (98—99 °C); 2,2′-Dimethyl-4-nitroazobenzene, 81.5—82 °C. Found: C, 66.26; H, 5.07; N, 16.20%. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46%.

Solvents. Benzene, toluene and acetone were purified, dried and distilled in the usual way. Cyclohexane was washed with a mixture of concentrated nitric acid and sulfuric acid. After repeated washing with distilled water, it was distilled over sodium wire. *N,N*-Dimethylformamide, dimethyl sulfoxide and pyridine of the reagent grade were used without further purification.

Measurements. An appropriate amount of the sample was dissolved in a solvent containing 0.2% piperidine* and allowed to stand overnight in the dark. The solution was transferred to a cylindrical cell (3 cm diam, 10 cm length) fitted with a glass window (3 mm thickness) at each end and equipped with a water jacket. Thermostated water was circulated. The solution was irradiated with a high pressure mercury lamp (Toshiba 400P) for 2 min. After irradiation, the absorbance at the peak of the conjugation band of *trans*-isomers was measured at appropriate time intervals with a Hitachi spectrophotometer Model 139. The rate constants were checked by duplicate runs, accuracy being within ±1%.

For rapid isomerization, flash technique was applied. A glass sample cell (1.5 cm diam, 10 cm length) was put into a flash box and a xenon flash lamp was fired at 100J (2 μF, 10 KV). After the flash, steady monitoring light beam from a tungsten projective lamp was passed through the cell perpendicular to the direction of the flash. After being passed through a Shimadzu prism monochromator, the transmitted light was received by a photomultiplier (Hamamatsu R 106) and transient signals were recorded on a dry-plate with the aid of an Iwasaki oscilloscope and a polaroid camera.

* Influence of adventitious catalytic action: When a solution of *trans*-isomers was irradiated by UV light in a quartz cell the solution was irreversibly photo-bleached. The rate of thermal isomerization was found to depend strongly on the time of irradiation. The factors affecting the rate have been studied by some authors.[14-16] When a small quantity of piperidine was added to the azobenzene solution and all light of $\lambda<310$ nm was cut by a glass filter, most azobenzenes restored the color almost completely after being kept in the dark. Reproducible data were obtained under the above conditions. However, some abnormal behavior was observed for azobenzene, 4-chloroazobenzene, 2,2′-dichloroazobenzene, and 2,2′-dibromoazobenzene. Since these substances did not reversibly return to the *trans*-form after visible light irradiation, they should have been partly decomposed. Therefore, the data for these substances were omitted.

Results

The thermal *cis*-to-*trans* isomerization of various kinds of azobenzene derivatives was carried out at various temperatures. The rate constants, estimated from excellent first-order plots, are listed in Tables 1—3 together with the activation parameters. Some of the rate constants (Tables 1 and 2) can be compared with those in literature (Table 4). The values of Schulte-Frohlinde[16] and Le Fèbre and Northcott[18] were estimated by interpolating the Arrhenius plot. It is to be noted that Schulte-Frohlinde, and Talaty and Fargo[17] used pure *cis*-isomers, while others used *trans*-isomers as the starting materials. In spite of the fact that the data were obtained under different conditions, the agreement is fair except for 4,4′-dinitro- and 4-nitroazobenzenes.

Table 2. Thermal isomerization rate constants for *para*-donor/*para*′-acceptor-substituted azobenzenes at 25 °C in various solvents

Solvent	k, min^{-1}		
	37[a]	38[b]	39[c]
Cyclohexane	2.4	3.6	1.8
Benzene	2.4	3.0	1.8
Pyridine	180	420	12
Acetone	150	240	8.4
DMF	3000	5100	120
DMSO	7200	11400	600

a) 4-Nitro-4′-dimethylaminoazobenzene, ε_{max}=33500, λ_{max}=445 nm. b) 4-Nitro-4′-diethylaminoazobenzene, ε_{max}=37200, λ_{max}=458 nm. c) 4-Nitro-3′-methyl-4′-dimethylaminoazobenzene, ε_{max}=22700, λ_{max}=410 nm.

Discussion

Linear Free Energy Relationship. A general linear enthalpy-entropy relationship has been discussed in relation to the simple interaction mechanism.[19-25] ΔS^* tends to increase with increase in E_a, although there exists a considerable scatter (Fig. 1). Leffler[23] has shown that such a case is a result of more than two interactions whose vectors move independently on the E_a *vs.* ΔS^* plane. It is difficult to interpret the scatter, but a tentative explanation is as follows: The rate is mainly governed by the electronic effect of substituents, small perturbations due to solvation and steric effects being involved. The Arrhenius parameters fall in a reasonable range as compared with those reported.[16,18,22]

According to Schulte-Frohlinde,[16] the observation of preexponential factors as large as 10^{11-12} precludes the intervention of a triplet exited state involving a rupture of the N=N π-bond. The barrier to rotation around the N=N double bond was calculated to be 55—84 kcal/mol,[26-28] whereas the activation energy for the *cis*-to-

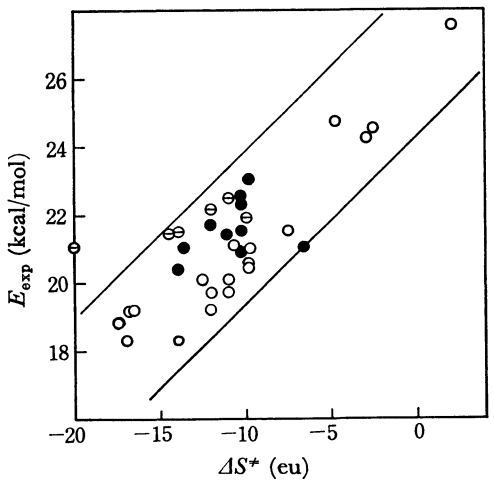


Fig. 1. Activation energy *vs.* entropy for the thermal *cis*-to-*trans* isomerization of azobenzenes.
○: This work; ●: Schulte-Frohlinde;[16] ◑: Brown and Granneman.[22]

trans thermal isomerization of azobenzene *via* inversion was calculated to be 32.9 kcal/mol by Ljunggren and Wettermark[28] by means of the CNDO/2 method, and improved to be 23.0 kcal/mol by Brown and Grannemann.[22]

On the other hand, Bineboym *et al.*[29] and Talaty and Fargo[17] suggested from the value of experimental activation energy that E_a of *ca.* 20 kcal/mol is too low to be compatible with the singlet transition state, because the corresponding isomerization of stilbenes considered to involve the rotation mechanism is followed by E_a of 34—37 kcal/mol in the liquid phase. They suggested therefore a transition state in which one or both azo-nitrogen atoms undergo a change in hybridization from sp^2- to sp-state. Thus it is likely that the lower activation energies support the inversion mechanism (Table 1).

However, recent evidence[30–32] has shown that there are some olefins and guanidinium salts which have activation energies of *ca.* 20 kcal/mol or even less, where only torsion is allowed. This has caused again much discussion on the mechanism of the *cis*-to-*trans* thermal isomerization of azomethines.[2–9] It was pointed out[4,7] that the lower activation energies cannot necessarily be regarded as a criteria of the inversion mechanism.

Solvent Effects. Although there are trials to relate the kinetic data to the properties of solvents such as dipole moment and dielectric constant, solvent effects in this field are generally ambiguous, and the rate varies only by a factor of a few times for most azobenzenes from solvent to solvent.[17,18] Wildes *et al.*,[9] however, observed a large solvent effect on the rate and activation energy for the thermal isomerization of *para*-donor/*para'*-acceptor-substituted azobenzenes. The isomerization rate of 4-diethylamino-4'-nitroazobenzene is about 10^5 times faster in *N*-methylformamide than in hexane. This seemed to contradict the former observation that the rate is not much affected by solvent.

Table 3. Activation parameters for the isomerization of **37** in various solvents

Solvent	E_a (kcal/mol)	ΔS^*(300K) (gibbs/mol)
Benzene	14	−14
Acetone	11	−20
DMF	10	−21
DMSO	9	−24

For the sake of confirmation, we followed the rate by means of the flash photolysis method, the results being given in Table 2. For 4-nitro-4'-dimethylaminoazobenzene, the activation parameters in various solvents are given in Table 3. The results are virtually in line with those of Wildes *et al.*[9] They suggested the rotation mechanism since the double bond character of the N=N bond and consequently the barrier to rotation would decrease with substituent.

Our view is as follows: Using a simple structure model, one can show that azobenzenes in no way take a coplanar

Table 4. Comparison of rate constants at 35°C

Azobenzene	$10^2 k$, min^{-1}				
	S-F[a]	T-F[b]	F-N[c]	W-P-I-W[d]	This work[e]
4-Dimethylamino-	0.98				0.670
4-Methoxy-	0.138	0.103	0.166		0.194
4,4'-Dimethoxy-	0.339				0.314
4-Chloro-	0.078	0.0556	0.067		
4-Nitro-	0.912	0.933	0.00021		0.74
Unsubstituted		0.0358	0.0416		
3-Nitro-	0.0371	0.0316			
4,4'-Dichloro-	0.324				0.161
4-Methyl-		0.0559	0.126		
4,4'-Dinitro-	0.252				2.40[f]
4,4'-Dimethyl-	0.098				0.173
4-Nitro-4'-dimethylamino-				120	240 (25 °C)
4-Nitro-4'-diethylamino-				180	360 (25 °C)

a) Shulte-Frohlinde;[16] in benzene; *k* at 35°C calcd by the Arrhenius equation. b) Talaty and Fargo;[17] in benzene. c) Le Fèvre and Northcott;[18] in benzene; *k* at 35°C calcd by the Arrhenius equation. d) Wildes, Pacifici, Irick and Whitten;[9] in benzene; temperature not specified. e) In cyclohexane containing 0.2% piperidine. f) In benzene containing 0.2% piperidine.

structure during rotation. On the other hand, if the inversion mechanism is accepted, a coplanar configuration is possible in the transition state (see **B–F** below). The dipole moment of this configurational structure may be as large as that for the *trans*-isomers (for example $\mu=$ 7.63D for **37**[10]). A considerable lowering in the free energy of activation and hence the increase in the rate for these species can be attributed to the large interaction with polar solvents. From a large decrease in the molar extinction coefficient (Table 2), the introduction of a methyl group in the *ortho* position with respect to the dimethylamino group would cause a considerable decrease in the dipole moment. This might be responsible for a much smaller solvent effect for **39** as compared with that for **37**. It should be noted that similarly substituted stilbenes, for which inversion is impossible, do not undergo facile thermal and photochemical isomerization in polar solvents.[33]

Table 5. Estimated substituent constants according to equation (1)

Substituent	σ_{c-t} [a]			
	This work	Talaty	S-F	Le Fèvre
2-CH_3	0.46*			
2'-CH_3	−0.01*			
4 (or 4')-Cl	0.33*	0.20	0.34	0.28
4 (or 4')-CH_3	0.19*	0.20		0.45
3 (or 3')-NO_2	0.11*	−0.05	0.02	
4-$N(CH_3)_2$	1.27		1.44	
4-$N(C_2H_5)_2$	1.44			
4-OCH_3	0.73	0.46		0.67
4-Pyrrolidino	1.38			
4-NH_2	1.37			
4-I			0.21	
4-NO_2		1.42	1.41	
4-$COCH_3$		0.52		
4-C_2H_5		0.19		
4-$CH(CH_3)_2$		0.35		
4-$C(CH_3)_3$		0.25		

*) DAAB is chosen as standard and σ-values are estimated from the possible combinations of the *k*-values of **1**—**14**. For σ-values with no asterisk, Talaty's *k*-value for azobenzene is chosen as a standard. a) *k*-values at 35 °C are used.

Substituent Effects. *para*-Substitutions invariably accelerate the isomerization rate, regardless of the nature of the substituents (Tables 1 and 2). This was first pointed out by Talaty and Fargo.[17] It was pointed out that this acceleration is of the additive nature and Eq. 1 is approximately valid for 4-dimethylaminoazobenzene derivatives.[1] From the data in Tables 1 and 2, the substituent constant, σ_{c-t} for various kinds of substituents has been estimated (Table 5). The first five σ_{c-t} values with an asterisk are obtained from the data of **1**—**14** in Table 1. Using these values, log k/k_0 are again plotted against σ_{c-t} according to Eq. 1 (Fig. 2). The correlation coefficient is calculated to be 0.987.

Using σ_{c-t}-values listed in the second column in Table 5, the same plots were made for substances **17**—**31** and **37**—**38** (Fig. 3) Although the correlation

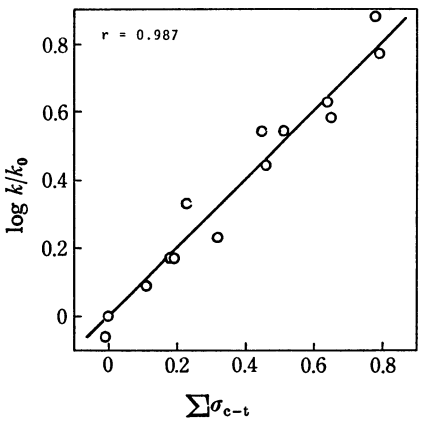


Fig. 2. Log k/k_0 *vs.* $\sum\sigma_{c-t}$ according to Eq. 1.

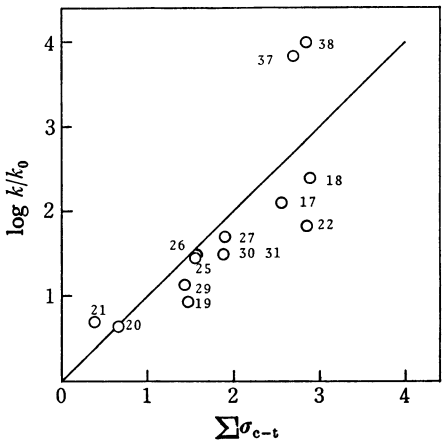


Fig. 3. Log k/k_0 against $\sum\sigma_{c-t}$ plot according to Eq. 1. Key is shown in Tables 1 and 2.

in this case is not so good as in Fig. 2, some interesting features may be noted. For 4-amino and 4-pyrrolidino derivatives, the deviation from the theoretical line is comparatively small. This means that the nature of these groups is virtually the same as that of dimethylamino group. For symmetrically substituted azobenzenes, the rate is usually not so accelerated as expected by the additivity rule. For *para*-donor/*para'*-acceptor-substituted azobenzenes, the rate is much more

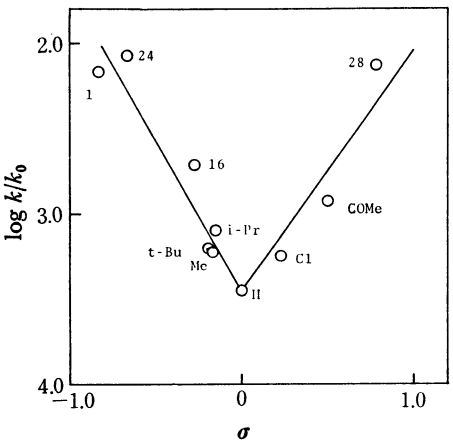
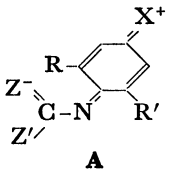


Fig. 4. The Hammett relationship. Key is shown in Table 1.

accelerated than expected from the rule. Hence the additivity rule, though it is useful to presume the effect of substituent on the rate of isomerization, has limited applicability.

In this connection, it may be worthwhile examining the Hammett relationship. The rate constants expressed in logarithmic scale, were plotted against σ for 4-monosubstituted azobenzenes. The plots are V-shaped with the minimum near σ equal to zero (Fig. 4).

Similar examples were reported recently by Hall *et al.*[6] and Herkstroeter[7] who found that the plots are all V-shaped for the isomerization of *N*-hexafluoroisopropylideneanilines, benzoylacetanilides, and pyrazolone azomethines. They explained the results in terms of the resonance stabilization in the transition state: If Z and Z′ in **A** are electron-accepting group, the rotation mechanism is



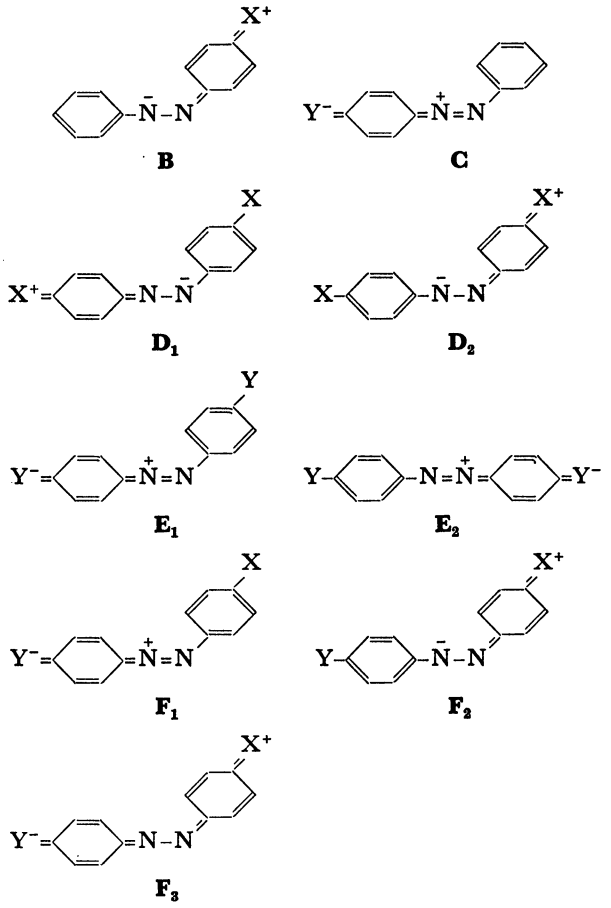
A

facilitated as the electron-donating strength of X increases as depicted, whereas growing electron-accepting capacity of X facilitates the isomerization by inversion, thus accounting for the V-plots. It is noted, however, that such a single bond character should substantiate only in the transition state through coplanar resonance structures. Such a coplanar structure is impossible through pure rotation. It does not seem plausible to assume such a drastic change in mechanism in going from electron-donating groups to electron-accepting groups. Further, the introduction of bulky substituent(s) to *ortho* position(s) with respect to azomethine nitrogen invariably accelerates the rate.[2,7,34–36] This cannot reasonably be explained in terms of the rotation mechanism, because the steric hindrance of R and R′ in **A** should destabilize the transition state a great deal. For the inversion mechanism, on the contrary, the steric effect may be less severe in the transition state than in the ground state for azomethines as has been explained successfully by Kessler *et al.* and others.[34–36]

The facilitated rate by *para*-substituents in azobenzenes, irrespective of their nature, may be explained in terms of a similar mesomeric effect, as depicted by resonance structures in the transition state **B**–**F**. If σ_{c-t} (or absolute Hammett σ) is regarded as a crude measure of the contribution of the resonance stabilization in the transition state, the deviation from the additivity rule may indicate that the contribution of the above resonance structures is not always additive (Fig. 3). As an example, an extra stabilization effect may arise from the resonance contribution depicted by $\mathbf{F}_3$, thus accounting for the upward deviation.

Steric Effects and Inversion Center. Complication arises for asymmetrical azobenzenes in which there are two distinct centers capable of inversion. In this case the empirical rate constant can be given by

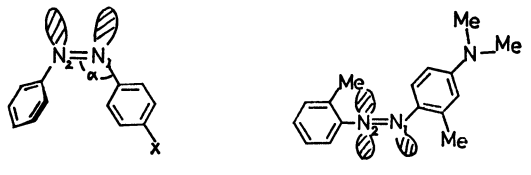
$$k = k_1 + k_2 = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT} \qquad (2)$$



B **C** **D**$_1$ **D**$_2$ **E**$_1$ **E**$_2$ **F**$_1$ **F**$_2$ **F**$_3$

where the suffixes 1 and 2 denote the two rate processes.[22] The rate constants in Tables 1, 2 and 4 correspond to k in Eq. 2.

It is of interest to distinguish the two centers. According to Brown and Granneman,[22] the difference in the activation energies for the two distinct inversion routes is calculated to be 1—2 kcal/mol by the CNDO/2 method. They predicted that the amount of curvature in the Arrhenius plots would be quite small. In the present study, the Arrhenius plots failed to distinguish the two routes. The CNDO/2 calculations predict that the isomerization is aided by the electron-withdrawal by the ring adjacent to the rehybridizing nitrogen. We also have a similar idea summarized as follows: Due to the steric hindrance the ground *cis*-state may have a folded conformation as depicted by **G**.



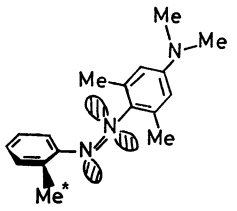
G **H**

If X is an electron-accepting group, the repulsive force among paired electrons on N_1 atom will be lowered, resulting in the increase in the s-character in the C–N_1 bond and the increase in the bond angle α. This should cause the inversion on N_1 atom more easily than on N_2. With X, as an electron donor, the reverse effect is expected.

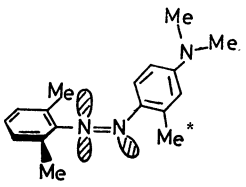
A large difference in the effect of 2- and 2′-methyl groups on the rate for 4-dimethylaminoazobenzenes seems to indicate that the main inversion center is N_2 as will be understood by the conformation **H**. If the above view is valid, it is expected that the 2′-methyl group should facilitate the rate, but not the 2-methyl in the case of 4-nitroazobenzenes. As seen in Table 1 (**28**—**31**), the 2-methyl group accelerates the rate, but the 2′-methyl group retards it, contrary to expectation.

As an alternative, one may postulate that if X is a strong electron donor or electron acceptor, the approximately planar X–  –N_1=N_2– moiety can take a "stiff" conformation through conjugation in the ground *cis*-isomer. If this is the case, the inversion center should be N_2. The distinctly different *ortho* effects between 2- and 2′-methyl groups on the isomerization rate could be interpreted tentatively by this assumption.

A study was made using 2,6- and 2′,6′-dimethylated 4-dimethylaminoazobenzene derivatives. The steric effects may become so severe for these substances that at least one of the benzene rings may be considerably twisted with respect to the C–N=N–C plane in the transition state as in the ground *trans*-isomer,* and this may be responsible for the considerable decrease in rate. The most favorable conformation will be determined by the compromise between the energy stabilization through conjugation and the steric hindrance. Thus, although it is by no means decisive, favorable conformations in the transition state of 2,6- and 2′,6′-dimethyl-4-dimethylaminoazobenzenes will be given by **I** and **J**, respectively.



I



J

These conformations may be responsible for the acceleration effect due to the methyl group with an asterisk.

* A considerable decrease in the molar extinction coefficient of the conjugation band for **32**—**36** may be ascribed to the twist. For detail *cf.* Ref. 10.

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