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FURTHER EVIDENCE OF INVERSION MECHANISM FOR THE CIS-TO-TRANS THERMAL ISOMERIZATION OF 4-DIMETHYLAMINOAZOBENZENE DERIVATIVES. ADDITIVITY RULE OF SUBSTITUENT CONSTANTS

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The thermal cis-to-trans isomerization of some substituted 4-dimethylaminoazobenzenes was studied. Substituent effects on the isomerization rate strongly support the view that the isomerization proceeds via inversion at either one of the azo-nitrogen atoms.

The mechanism of the thermal cis-to-trans isomerization of azobenzene and its derivatives has been the subject of much attention.[1-6] The isomerization was formerly considered to proceed by rotation about the N=N bond.[1-3] However, since the activation energies are too low to be compatible with the rotation mechanism, the inversion mechanism was suggested by Talaty and Fargo.[4] They found that all para-substituted azobenzenes isomerize faster than the parent compound, regardless of the nature of the substituents. This interesting feature has not been explained yet. Theoretical approach was also made,[7] using the CNDO/2 method, with a result in favor of inversion. Wildes et al.[6] suggested, however, that the rotation mechanism may be operative for para-donor/para-acceptor-substituted azobenzenes because of large solvent effects on the rate of isomerization.

The most reliable experimental evidence may be to study ortho effects on the rate, since a substituent in the o-position to the azo group would hinder the rotation as is the case in guanidinium salts[8] in which the lone pair electrons are fixed and no inversion is allowed. On the contrary, if inversion is involved, the steric hindrance would be less severe in the extended transition state than in the ground state, and hence the rate would be expected to increase by ortho substitution. This has been observed for imines. However, studies along this line do not seem to have been made for azobenzenes except the work of Gegiou et al.[9] who found that the thermal isomerization rates of 2,4,6-trimethyl- and 2,2',4,4',6,6'-hexamethylazobenzenes are closely similar to the rate of azobenzene.

In the present study, a clear acceleration effect by ortho substitution was observed. In Table 1, the rates of the thermal cis-to-trans isomerization are listed together with the molar extinction coefficients at the wavelength of maximum absorption of the conjugation bands.

Table 1. The molar extinction coefficients and the rate constants of the thermal cis-to-trans isomerization of 4-dimethylaminoazobenzene derivatives

No.	Substances	$\varepsilon_{max}(\lambda_{max}, nm)$	$k \times 10^{3*}$, min^{-1}
1	4-Dimethylaminoazobenzene	31200(390)	6.70
2	4'-Methyl-	31800(400)	9.90
3	4'-Chloro-	34100(410)	11.4
4	3'-Nitro-	31600(420)	8.38
5	2'-Methyl-	29900(394)	5.94
6	2-Methyl-	30200(405)	18.4
7	2',4'-Dimethyl-	31000(393)	9.90
8	2'-Methyl-4'-chloro-	32600(413)	11.6
9	2,4'-Dimethyl-	30500(405)	26.0
10	2-Methyl-4'-chloro-	32800(415)	39.8
11	2,2'-Dimethyl-5'-nitro-	29800(425)	23.3
12	2,2'-Dimethyl-	28800(400)	17.3
13	2,2',4'-Trimethyl-	29900(399)	28.8
14	2,2'-Dimethyl-4'-chloro-	31000(411)	51.7

*First-order rate constants at 35°C in cyclohexane.

Inspection of Table 1 shows that an introduction of 2-methyl group accelerates the rate by about three-fold(compare 1–6, 2–9, 3–10, 5–12, 7–13, and 8–14). On the other hand, such an obvious acceleration could not be said to exist for 2'-methyl group (compare 1–5, 2–7, 3–8, 6–12,9–13, and 10–14). Acceleration effect is generally observed whatever sort of groups are introduced into para (and possibly meta) positions.

Usual Hammett relationship does not hold. This is in agreement with the result of Talaty and Fargo[4], but is against the conclusion of Jaffé.[10] However, if dimethylaminoazobenzene is chosen as a standard substance, one can give a new substituent constant, σ_{c-t}, specific to the cis-to-trans isomerization of azobenzenes, such that

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

where k and k_o are the rate constants of substituted and unsubstituted 4-dimethylaminoazobenzenes. Table 2 shows the substituent constants determined using the data for the substances 1–6 in Table 1.

Table 2. Substituent constants calculated by eq. (1)

Substituents	σ_{c-t}
4'-Methyl	0.17
4'-Chloro	0.23
3'-Nitro	0.097
2'-Methyl	-0.052
2-Methyl	0.44

If there exists an additivity rule, eq. (2) should hold for multi-substituted dimethylaminoazobenzenes.

$$\log k/k_o = \Sigma\sigma_{c-t} \qquad (2)$$

In Fig. 1, $\log k/k_o$ are plotted against $\Sigma\sigma_{c-t}$ for 7–14, showing a fairly well correlation. Above finding shows that a linear free energy relationship exists with respect to these substituents.

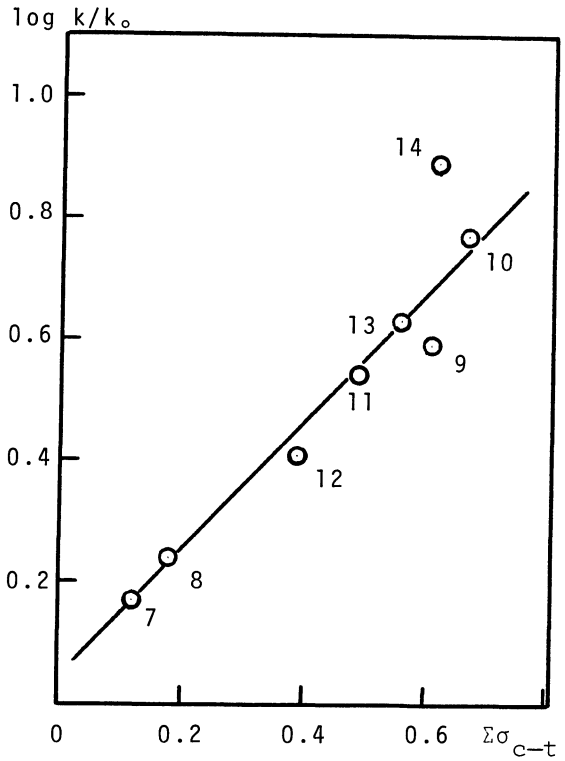

Fig. 1. Examination of additivity rule.

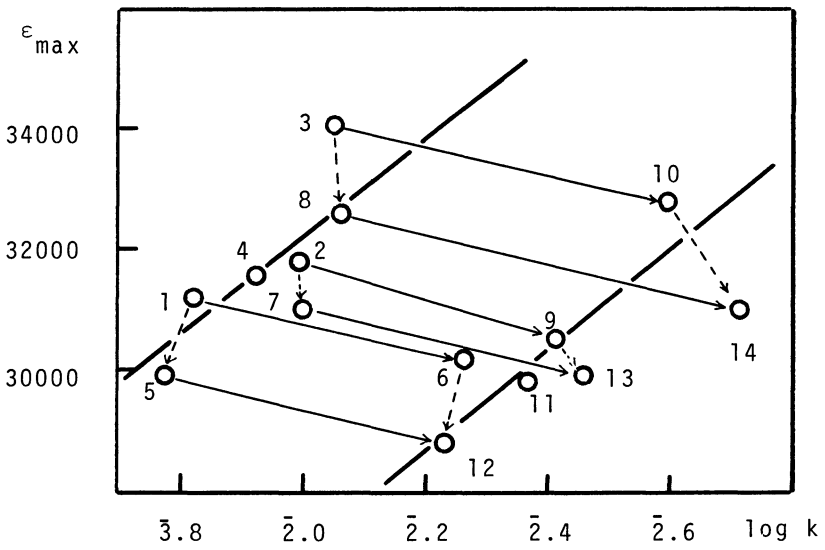

Fig. 2. Correlation of ε_{max} with log k. Effects of 2- and 2'-methyl groups are shown by arrows.

The large difference in the effect between 2-methyl and 2'-methyl group indicates that the inversion takes place exclusively at either one of the nitrogen atoms.

On the other hand, as far as rotation mechanism is concerned, one cannot, at

least to a zeroth-order approximation, distinguish 2-methyl group from 2'-methyl group through rotation. Hence above finding is in contradiction to the rotation mechanism.

In Fig. 2, the molar extinction coefficients of trans dimethylaminoazobenzenes, in which approximate coplanar structures are accepted, are plotted against log k. It is interesting to note that this correlation is much better than those between log k and pK_a, ν_{max}, or any kind of σ's, possibly suggesting that the rate is mainly governed by the resonance stabilization in the transition state. As shown in Fig. 2 (vector representation), 2-methyl group decreases ε_{max} to about the same extent as does 2'-methyl group, but the effects of the two groups on the rate of isomerization are quite different, probably due to the difference in the steric hindrance between the p-orbital and the methyl groups in the transition state.

It can be shown that a coplanar structure is impossible through rotation. A large solvent effect for para-acceptor/para-donor-substituted azobenzenes[6] does not rule out the inversion mechanism, but rather support it, because a dipolar resonance contribution in the transition state may be larger in the inversion mechanism than in the rotation mechanism.

A more detailed discussion will be made shortly.

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