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The Thermal *Cis*-to-*trans* Isomerization of *N,N'*-Diacylindigos. Kinetic Pressure, Solvent, and Substituent Effects

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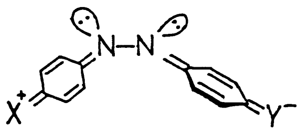
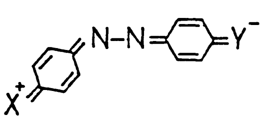
The kinetics of the thermal *cis*-to-*trans* isomerization of *N,N'*-diacylindigos(DAI) in various solvents and under high pressures has been studied. *N,N'*-Dibenzoylindigos(DBI) isomerize about 10 times slower than molecules not having a benzene ring in the acyl groups. The values of the activation volumes were about 8.0 $cm^3\ mol^{-1}$ for the former and about 3.0 $cm^3\ mol^{-1}$ for the latter. It was suggested that the thermal isomerization proceeds *via* the biradical mechanism. The positive values of the activation volume have been interpreted in terms of the increase in the intrinsic volume upon activation. The differences in the isomerization rates and the activation parameters between DBI and the others have been ascribed to an additional interaction between the two phenyl rings in the acyl groups in the *cis*-ground state.

Recently, reaction mechanisms have been actively discussed for the thermal *cis*-to-*trans* isomerization of push-pull azobenzenes. Whitten *et al.*1) reported that the rate of the thermal isomerization of 4-dialkylamino-4'-nitroazobenzenes is extremely sensitive to solvent polarity and that thermal isomerization proceeds *via* a dipolar rotational transition state (I).



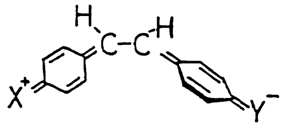
I

Asano *et al.*2) studied the kinetic-pressure effects for the thermal isomerization of 4-dimethylamino-4'-nitroazobenzene and advocated that the mechanism changes from inversion in hexane to rotation in benzene and polar solvents. They suggested a dipolar transition state (I) in benzene and polar solvents. According to our view, the substituent, solvent, and pressure effects are in favor of the inversion mechanism and a remarkable polarity change will occur on going from the *cis* to the inversion transition state (II).3)

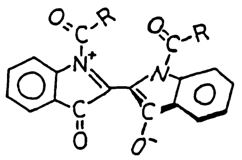


II

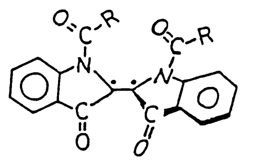
The thermal isomerizations of *N,N'*-diacylindigos (DAI) and push-pull stilbenes invariably proceed by the rotation mechanism around the carbon–carbon double bond. In analogy with the case of push-pull azobenzenes, charge-separated transition states (III and IV) are plausible for these compounds. However, according to Calvin and Alter,4) push-pull stilbenes thermally isomerize *via* a triplet state at 200—300 °C. Since push-pull stilbenes gradually decompose at high temperature, it is difficult to examine the solvent, substituent, and pressure effects. On the other hand, the thermal *cis*-to-*trans* isomerization of DAI readily takes place at room temperature.5) For the thermal isomerization of DAI, two routes are possible: the isomerization *via* a double bond breaking to produce either homopolar or dipolar transient species, as indicated by IV and V.



III



IV



V

In connection with the recent interest regarding the mechanism of the *cis*-to-*trans* isomerization of push-pull azobenzenes, we have undertaken the investigation of the thermal isomerization of DAI in order to clarify which of these routes is more consistent with experimental observations.

Experimental

Reagents. *N,N'*-Diacetylindigo (**1**), *N,N'*-dipropionylindigo (**2**), and *N,N'*-diisobutyrylindigo (**3**) were prepared by the method reported by Blanc and Ross.6) **1** and **2** were recrystallized from a hexane-chloroform mixture and **3** was recrystallized from hexane. **1**: mp 254—256 °C (lit,7)

256—257 °C), **2**: mp 211—212 °C (lit,[7] 211—213 °C), **3**: mp 230—231 °C (lit,[7] 229—230 °C). *N,N'*-Distearoylindigo(**4**) was prepared by the method reported by Omote *et al.*[5] and recrystallized from petroleum ether: mp 107.5—108 °C (lit,[5] 101—102 °C). *N,N'*-Bis(cyclohexylcarbonyl)indigo (**5**), *N,N'*-dibenzoylindigo (**6**), *N,N'*-bis(p-methylbenzoyl)indigo (**7**), *N,N'*-bis(p-chlorobenzoyl)indigo (**8**), and *N,N'*-di-2-naphthoylindigo (**9**) were prepared by the method reported by Posner.[8] **5** was recrystallized from a hexane-chloroform mixture: mp 244.5—245.5 °C. **6** and **9** were recrystallized from an acetone-water mixture and **7** and **8** were recrystallized from a hexane-chloroform mixture. **6**: mp 261—262 °C (lit,[7] 256—257 °C), **7**: mp 293—294 °C, **8**: mp 271—272 °C, **9**: mp 251—252 °C.

^{1}H NMR spectra were recorded on a Hitachi R-600 High Resolution NMR spectrometer (60 MHz) with TMS as an internal standard, and IR spectra on a JASCO IRA-I spectrophotometer. **4**: IR (nujol) 1680, 1670, 1600 cm^{-1} (lit,[5] IR (KBr) 1690, 1670, 1600 cm^{-1}); ^{1}H NMR (CDCl$_3$) δ=0.73—2.02 (m, 66H), 2.60—3.09 (m, 4H), 7.00—8.37 (m, 8H). Found: C, 78.32; H, 10.01; N, 3.51%. Calcd for $C_{52}H_{78}N_2O_4$: C, 78.54; H, 9.88; N, 3.52%. **5**: IR (nujol) 1710, 1680, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.35—2.30 (m, 20H), 2.70—3.34 (m, 2H), 7.00—8.37 (m, 8H). Found: C, 74.79; H, 6.30; N, 5.78%. Calcd for $C_{30}H_{30}N_2O_4$: C, 74.67; H, 6.27; N, 5.81%. **6**: IR (nujol) 1700, 1660, 1590 cm^{-1} (lit,[5] IR (KBr) 1700, 1660, 1590 cm^{-1}); ^{1}H NMR (CDCl$_3$) δ=6.95—8.10(m, 18H). Found: C, 76.30; H, 3.80; N, 5.76%. Calcd for $C_{30}H_{18}N_2O_4$: C, 76.58; H, 3.86; N, 5.96%. **7**: IR (nujol) 1700, 1670, 1600, 830 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.43 (s, 6H), 6.90—7.49 (m, 10H), 7.49—8.14 (m, 6H). Found: C, 77.03; H, 4.24; N, 5.45%. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.09; H, 4.45; N, 5.62%. **8**: IR (nujol) 1700, 1660, 1600, 830 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=6.90—7.80 (m, 8H), 7.44 (d, *J*=8Hz, 4H), 7.94 (d, *J*=8Hz, 4H). Found: C, 66.62; H, 2.86; N, 5.30%. Calcd for $C_{30}H_{16}N_2O_4Cl_2$: C, 66.80; H, 2.99; N, 5.19%. **9**: IR (nujol) 1700, 1675, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=6.50—8.65 (m, 22H). Found: C, 79.80; H, 3.77; N, 4.78%. Calcd for $C_{38}H_{22}N_2O_4$: C, 79.99, H, 3.89; N, 4.91%.

Solvents. Acetonitrile, acetone, and toluene of the reagent grade were purified by drying over calcium chloride, calcium sulfate, and sodium wire, respectively, and distillation.

Apparatus and Procedure. The high-pressure technique and the procedure for kinetic measurements were the same as those described elsewhere.[3] A solution containing an appropriate concentration of DAI (10^{-4} mol/l) in a pressure vessel was irradiated with a 650-W tungsten projection lamp through a filter of potassium dichromate solution to produce the *cis*-isomer. Then, the absorption maximum (λ_{max}=*ca.* 570 nm) of the *trans*-isomer was monitored by means of a Hitachi 100—50 spectrophotometer and the absorbance was recorded.

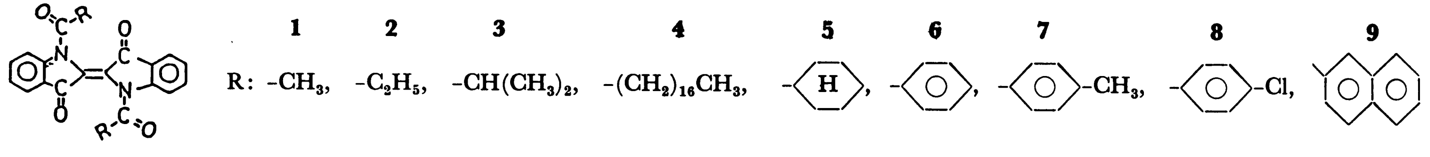
Results and Discussion

The thermal isomerization of DAI was carried out at various temperatures. It was found that the rate follows first-order kinetics. The rate constants are listed in Table 1, together with the activation pa-

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL ISOMERIZATION OF DAI (PROBABLE ERRORS IN PARENTHESES)

Compd No.	Solvent	λ_{max}^{trans}	$10^4\,k/s^{-1}$					E_a	$\Delta S^{*}_{323\,K}$
		nm	30 °C	40 °C	50 °C	60 °C	70 °C	kJ mol^{-1}	J K^{-1} mol^{-1}
1	Acetonitrile	551		0.914(0.011)	2.85(0.01)	6.75(0.02)	17.7(0.2)	86.6(1.7)	−53.6(5.0)
1	Acetone	552	0.556(0.006)	1.58(0.02)	3.49(0.02)			74.9(3.3)	−87.9(10.0)
1	Toluene	561	0.204(0.006)	0.842(0.034)	1.67(0.02)			85.8(10.5)	−59.4(33.9)
2	Toluene	568		0.926(0.008)	2.59(0.02)	6.24(0.03)		82.8(1.7)	−66.5(4.6)
3	Toluene	577		0.550(0.006)	1.69(0.01)	4.20(0.01)		88.3(2.5)	−53.6(7.9)
4	Toluene	570		1.03(0.03)	3.17(0.02)	7.76(0.10)		87.4(2.9)	−50.2(8.8)
5	Toluene	580		0.898(0.008)	2.64(0.01)	6.90(0.07)	26.8(0.7)	99.2(4.2)	−15.1(13.0)
6	Toluene	574			0.200(0.004)	0.764(0.010)	1.80(0.01)	101(7)	−29.3(22.2)
7	Acetone[a)]	575	0.0452(0.0003)	0.137(0.013)	0.533(0.007)			100(5)	−25.1(16.3)
8	Acetone[a)]	578	0.0658(0.0004)	0.225(0.004)	0.533(0.011)			85.4(4.6)	−70.3(15.5)
9	Toluene	580			0.472(0.003)	1.35(0.02)	2.66(0.05)	80.0(5.9)	−89.2(17.2)

a) **7** and **8** are sparingly soluble in toluene.



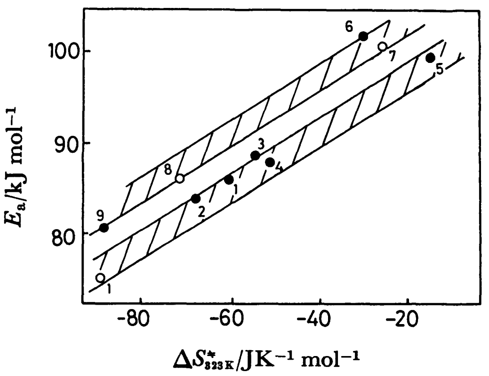
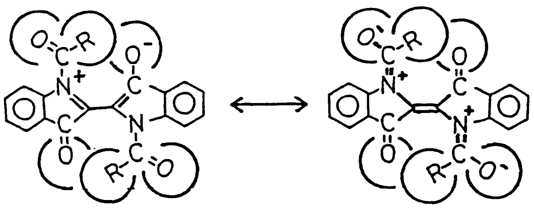


Fig. 1. Ea—$\Delta S^{*}_{323\,K}$ relationship for the thermal isomerization of DAI. ●: in toluene, ○: in acetone.

rameters. Figure 1 shows the relationship between the activation energy and entropy. It may be seen that the activation energy tends to increase with an increase in the activation entropy as a whole. From the figure, we notice the following point: the plots for **6**—**9** shift upward compared with the others. According to Leffler,[9] a linear enthalpy-entropy relationship suggests the simple interaction mechanism. If the activation enthalpy-entropy plots are scattered, more than two interactions must be operating. Shinkai and co-workers[2] showed that the activation enthalpy-entropy plots for the isomerization of azobenzenes give parallel straight lines and accounted the root of the parallel straight lines as the change in mechanism. In opposition to this idea, we have explained[3] that the shift is not due to a mechanism change but, rather, to the extra free-energy change. We consider that the same is true in the present case (see below).

DAI has electron-donating and -attracting groups. Therefore, there are two possible routes for the thermal isomerization (see IV and V). If a reaction starts from a nonpolar state and proceeds *via* a polar transition state (*e.g.*, IV), the reaction rate will be substantially accelerated in polar solvents. However, it was not the case (Table 1). We reported that the wavelengths(λ^{trans}_{max}) at the maximum absorption of the *trans*-isomer of push-pull azobenbenes are sensitive to the solvent polarity and are closely related to the rate of isomerization.[3] In the case of DAI, we observed that the absorption band shifts to a shorter wavelength as the solvent polarity increases (for example, **1** in Table 1). It appears, therefore, that the *trans*-ground state is somewhat more polar than the excited one. However, as far as our data are concerned, no correlation between λ^{trans}_{max} and the rate constant seems to exist. *Trans*-DAI is twisted around the central C=C double bond and the C-N bond of the acyl group and the extent of the twist may depend on the bulkiness of substituents (R). Since the twist causes a reduction in the resonance contribution (VI), the polarity of the *trans*-ground state will be diminished by the introduction of bulky substituents. Since the *trans*-ground state may be more polar than the excited one, as described above, the decrease in the polarity of the ground state due to the bulkiness of substituent gives rise to a longer wavelength shift. This is in accord with the experimental observations (Table 1). On the other hand, *cis*-DAI is originally extremely twisted around the C=C double bond, and this might be responsible for the small substituent effect on the rate. However, it is of great interest to note that the rate constants for the isomerization of **6**—**9** are about 10 times smaller than those of **1**—**5**. A plausible reason will be given later.



VI

Pressure Effects. Table 2 shows the pressure effects on the thermal isomerization in some solvents. The reactions are slightly retarded by external pressures. By using the data in Table 2, the activation volumes ($\Delta V^{\ddagger}$) at p=1 atm were estimated according to Eq 2.

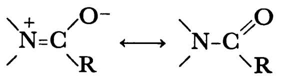
$$\ln k = a + bp \tag{1}$$

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial p}\right)_{T,\,p=1} = -bRT \tag{2}$$

The activation volume ($\Delta V^{\ddagger}$) is usually divided into two terms:

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{\mathrm{i}} + \Delta V^{\ddagger}_{\mathrm{el}} \tag{3}$$

where $\Delta V^{\ddagger}_{\mathrm{i}}$ is the difference in the intrinsic volume of reacting molecules between the initial and the transition state and $\Delta V^{\ddagger}_{\mathrm{el}}$ due to solvation or electrostriction. The values of the activation volume decrease slightly with an increase in the solvent polarity: from $\Delta V^{\ddagger}$(acetonitrile)=3.6 cm^3 mol^{-1} to $\Delta V^{\ddagger}$ (toluene)=1.9 cm^3 mol^{-1} in **1**, from $\Delta V^{\ddagger}$(acetonitrile)= 3.3 cm^3 mol^{-1} to $\Delta V^{\ddagger}$(toluene)=−0.6 cm^3 mol^{-1} in **5** (Table 2). The above solvent dependency indicates that the transition state is slightly more polar than the *cis*-state. In the transition state, the crowdedness between the two acyl groups would be relaxed compared to the *cis*-ground state. Then, a resonance contribution, such as


VII

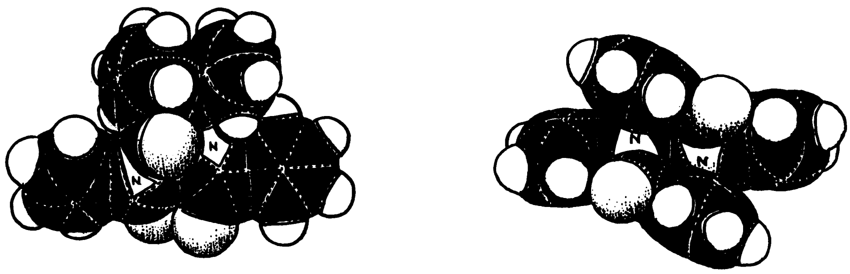
becomes greater in the transition state than in the *cis*-state. This accounts for the above observations. The volume of activation is, as a whole, small and positive. The positive values of activation volume may be explained in terms of the increase in the intrinsic volume. Since the bond character of the central carbon–carbon bond varies from the C=C double bond to the C–C single bond in the activation process, the bond length must become longer. On the assumption that the central C–C distance increment is 0.21 Å (difference in the distance between the C–C single bond and the C=C double bond) and the thickness of the molecule 3.4 Å, the increase in the van der Waals volume ($\Delta V_{\mathrm{W}}^{\neq}$) is calculated to be about 1.5 cm^3 mol^{-1}. Hitherto, the intrinsic volume change upon activation has often been ascribed to the van der Waals volume change. Very recently, however, Yoshimura *et al.*[10] pointed out that there is a large gap between $\Delta V^{\neq}$ and $\Delta V_{\mathrm{W}}^{\neq}$, and between ΔV and ΔV_{W} for 1,3-dipolar cycloaddition reactions. Indeed, the molar volumes of normal alkanes of short chain are about twice of their van der Waals volumes. Therefore, $\Delta V^{\neq}$ may be $\approx$3 cm^3 mol^{-1}, which agrees with the experimental values. Alternatively, the change in the void volume[11] around the van der Waals volume might be responsible for the gap between $\Delta V^{\neq}$ and $\Delta V_{\mathrm{W}}^{\neq}$.

TABLE 2. RATE CONSTANTS AND ACTIVATION VOLUMES FOR THE THERMAL ISOMERIZATION OF DAI AT 50 °C (PROBABLE ERRORS IN PARENTHESES)

Compd No.	Solvent	$10^4\,k$/s^{-1}				$\Delta V^{\neq}$
	p/kg cm^{-2} a)	1	400	800	1200	cm^3 mol^{-1}
1	Acetonitrile	2.85(0.01)	2.65(0.02)	2.53(0.02)	2.43(0.01)	3.6(0.2)
1	Acetone	3.49(0.01)	3.41(0.01)	3.19(0.11)	3.21(0.05)	2.2(0.4)
1	Toluene	1.67(0.02)	1.63(0.04)	1.58(0.04)	1.54(0.02)	1.9(0.1)
2	Toluene	2.59(0.02)	2.43(0.01)	2.33(0.02)	2.26(0.05)	3.1(0.2)
3	Toluene	1.69(0.01)	1.60(0.01)	1.53(0.01)	1.45(0.01)	3.5(0.1)
4	Toluene	3.17(0.02)	3.04(0.02)	2.93(0.02)	2.78(0.02)	3.0(0.1)
5	Acetonitrile	3.62(0.03)	3.49(0.05)	3.25(0.05)	3.15(0.01)	3.3(0.3)
5	Toluene	2.64(0.01)	2.67(0.01)	2.64(0.03)	2.73(0.02)	−0.6(0.3)
6	Acetone	0.366(0.007)	0.328(0.005)	0.273(0.004)	0.248(0.002)	9.3(0.5)
6	Toluene	0.200(0.004)	0.178(0.002)	0.155(0.001)	0.142(0.002)	8.0(0.3)
7	Acetone	0.533(0.007)	0.488(0.007)	0.452(0.007)	0.396(0.005)	6.6(0.4)
8	Acetone	0.533(0.011)	0.478(0.007)	0.430(0.005)	0.376(0.005)	7.9(0.2)
9	Toluene	1.35(0.02) b)	1.21(0.03) b)	1.10(0.01) b)	1.03(0.01) b)	6.4(0.3) b)

a) 1 kg cm^{-2}=0.9807 bar. b) at 60 °C.

It is noted that in **1**—**5** and **6**—**9**, significant differences between the activation volumes as well as the rate constants were observed. Cristol and Lewis[12] showed the significant differences of ultraviolet spectra in janusene which has face-to-face rings close enough to interact. Ingraham[13] suggested that if two benzene rings are brought face-to-face (3 Å apart), the VB and LCAO methods predict that there is 4 kcal more resonance energy than for two infinitely separated benzene rings. On the other hand, Cram and Goldstein[14] reported that in the solvolysis of [9]paracyclophanyl tosylate, the interaction between the phenyl ring and a carbonium ion takes place. In the case of *cis*-DBI, the molecular structure has not been established yet. As plausible models, the following conformations may be proposed (Fig. 2). Then, the interactions just described must exist for each conformation: (a) The interaction between the two phenyl rings in the acyl groups which are held face-to-face and (b) the interaction between the phenyl ring in the acyl group and >N– group are important. It is difficult to decide which of the two conformations is more favorable. As far as $\Delta V^{\neq}$ is concerned, the face-to-face conformation appears more plausible. It appears that the volume change on going from conformation (b) to the activated state may be similar to those observed for **1**—**5** since the situation around the benzene rings in solution to the surrounding solvent molecules will not change between (b) and activated complex. Meanwhile, in the face-to-face conformation, the independent mo-



(a) (b)

Fig. 2. Plausible geometical models of *cis-N,N'*-dibenzoylindigo: (a) phenyl-phenyl interaction and (b) phenyl- $\rangle$N- interaction.

tion of the two benzene rings will be partly restricted, resulting in a smaller exclusion of solvent molecules. This may be responsible for the values of $\Delta V^{\neq}$ for **6**—**9** compared with those for **1**—**5**. We tentatively consider that the *cis*-isomer of **6**—**9** is stabilized by the additional interaction, which is responsible for the significant differences in the rates (Table 1) and the $\Delta V^{\neq}$-values (Table 2), and the upward shift of the activation energy-entropy relationship (Fig. 1).

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