Solvent and Substituent Effects on Thermal *cis–trans*-Isomerization of Some 4-Diethylaminoazobenzenes

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Thermal *cis–trans*-isomerization of some 4'-substituted 4-diethylaminoazobenzenes has been studied. Substitution in the 4'-position leads invariably to an acceleration of the reaction regardless of the nature of the substituent. Logarithms of kinetic constants in various solvents were found to be satisfactorily correlated by the π^* scale of solvent polarities both for 4'-nitro-4-diethylaminoazobenzene (I) and for 4'-methoxy-4-diethylaminoazobenzene (II), excluding amphiprotic solvents. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were also measured in *NN*-dimethylformamide. The results support an inversion mechanism rather than a rotational one; in the case of (I), the highly dipolar nature of the transition state can be justified by its stabilization through coplanar resonance structures (impossible in pure rotation).

The mechanism of the thermal *cis–trans*-isomerization of azobenzenes is still the subject of considerable debate in spite of several investigations carried out on the influence of substituents,[1,2] temperature,[3] pressure,[4] and solvent.[5,6]

Two basic mechanisms have been proposed, (a) rotation about the N=N bond through a π-bond rupture and (b) the inversion of one of the nitrogens through an *sp*-hybridized linear transition state as postulated for imines [7,8] (Figure 1). The most frequently cited argument in favour of the latter mechanism is probably the fact that activation energies for azobenzene isomerizations are in the order of 85 kJ mol^{-1} or less, while stilbenes, where inversion is not possible, require *ca.* 170 kJ mol^{-1} of activation energy to isomerize. As further support for inversion, some authors [1] found only minor solvent and substituent effects on a series of monosubstituted azobenzenes, a fact which clearly argues against involvement of a strongly dipolar transition state, such as the breaking of a π bond would require. Moreover, theoretical studies on azobenzene have supported an inversion mechanism for this compound.[9]

However, the rotation scheme cannot be ruled out. In fact several substituted olefins have now been found to have isomerization barriers of less than 85 kJ mol^{-1} [10,11] and large kinetic solvent [5] and pressure [4] effects were observed for 4-donor-4'-acceptor substituted azobenzenes.

Such a complex and, apparently, contradictory set of experimental data can probably be attributed to the extreme sensibility of the physical and chemical properties of this class of compounds to small changes in the substituents and in the environment. As a matter of fact, theoretical calculations for imine isomerizations have shown that very large changes in the energy barrier to torsion can occur in going from one compound to another.[12]

In this paper we report a detailed investigation on the

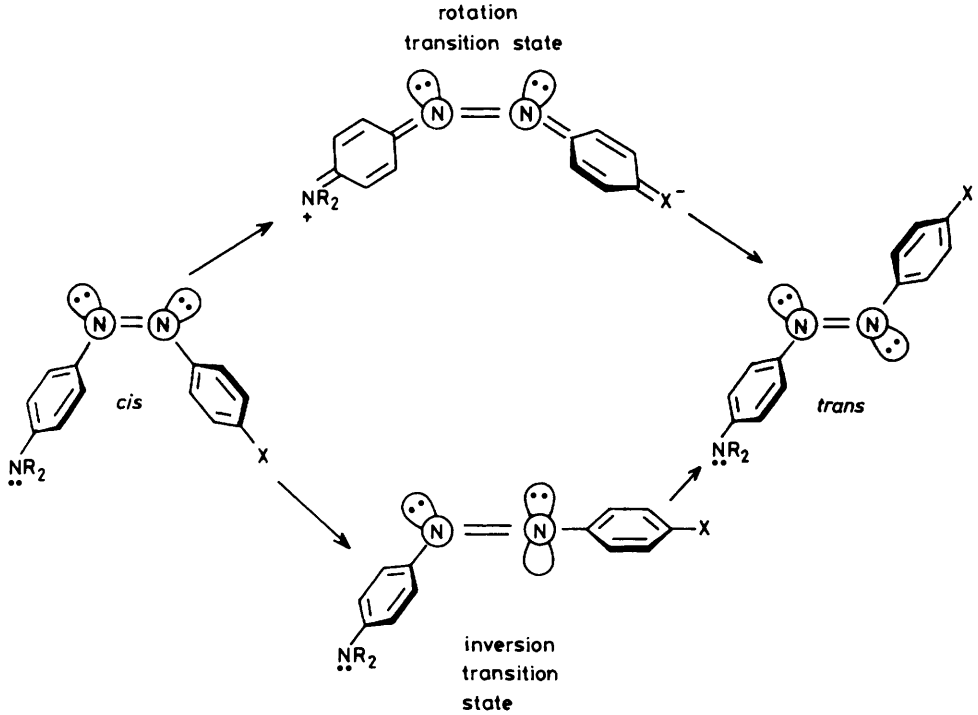


Figure 1.

Table 1. Kinetic constants (k) of *cis–trans* isomerization reaction of $Et_2NC_6H_4N{=}NC_6H_4X$ in *NN*-dimethylformamide at various temperatures

X	T/K	k/s^{-1}
H	293.2	$(4.16 \pm 0.37) \times 10^{-5}$
CO_2H	293.2	$(1.49 \pm 0.15) \times 10^{-3}$ [a]
CN	293.2	$(2.63 \pm 0.21) \times 10^{-1}$
NO_2	293.2	$(1.28 \pm 0.07) \times 10^{2}$
	298.5	$(1.68 \pm 0.07) \times 10^{2}$
	302.0	$(2.19 \pm 0.05) \times 10^{2}$
	310.0	$(3.74 \pm 0.10) \times 10^{2}$
	312.4	$(4.27 \pm 0.15) \times 10^{2}$
OMe	293.2	$(2.30 \pm 0.05) \times 10^{-4}$
	298.2	$(4.12 \pm 0.08) \times 10^{-4}$
	303.2	$(7.30 \pm 0.15) \times 10^{-4}$
	308.2	$(1.17 \pm 0.11) \times 10^{-3}$
	315.2	$(2.24 \pm 0.18) \times 10^{-3}$
NH_2	293.2	$(5.1 \pm 0.4) \times 10^{-3}$

[a] Value extrapolated to zero concentration.

solvent and substituent effects on the rate of *cis–trans*-isomerization of some 4-diethylaminoazobenzenes in order to distinguish the factors affecting this reaction, as, in our previous papers on the same class of compounds,[13,14] this kind of analysis was found to be very useful in revealing and separating the various factors affecting the physicochemical properties.

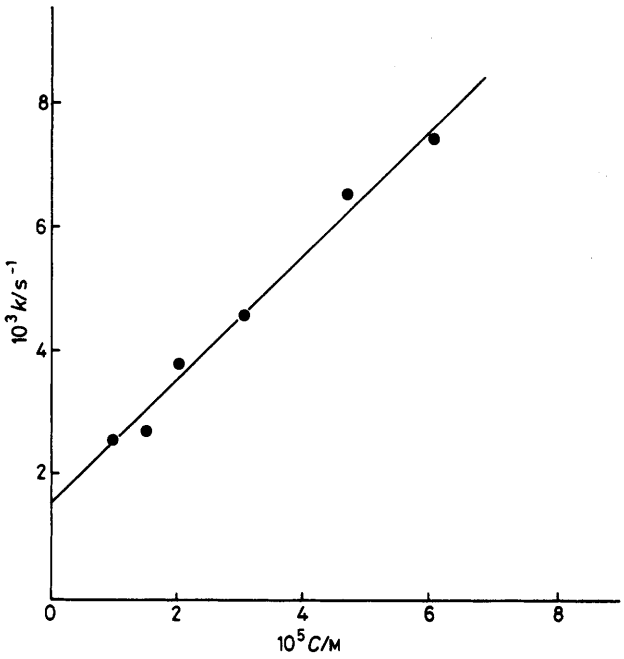


Figure 2. Kinetic constants (k) of *cis–trans*-isomerization of 4′-carboxy-4-diethylaminoazobenzene in *NN*-dimethylformamide as a function of stoicheiometric concentration of substrate (C) at 293.2 K

Experimental

Materials.—All the azobenzene derivatives were kindly supplied by A.C.N.A. S.p.A. and purified by repeated crystallizations from butan-1-ol. Spectrograde solvents were always used and purified by standard techniques.[15]

Measurements.—Solutions of dyes ranging from 1×10^{-5} to 5×10^{-5}M were prepared by diluting a stock 10^{-3}M solution in the desired solvent. All operations were carried out in the dark. For slow *cis–trans*-isomerization rates ($k < 10^{-2}$ s^{-1}) the solutions were exposed for 10 min in a quartz cell to 435 nm radiation, a time large enough to reach a photo-stationary state. The light source was an Italquartz (Milan) mercury arc lamp and the exciting wavelength was isolated by an Oriel interference filter. After irradiation the cell was quickly introduced in the thermostatted cell compartment of an Optica (Milan) model 10 spectrophotometer and the thermal return was monitored as the change in absorbance of the solution at a convenient wavelength.

For the fast decay rates a flash spectroscopic technique was applied using a Nortech (Salisbury) model FPX-1 apparatus. The transient signals were recorded by means of a Tektronix model 5115 oscilloscope and a Polaroid camera.

Non-degassed solutions were used throughout the experiments. Excitation by unfiltered or monochromatic radiation at different wavelengths yielded substantially the same results.

The measured rate constants are reported in Tables 1 and 2; they all represent an average of at least ten measurements; standard deviations are quoted as uncertainties. The measured rate constants (k) were independent of concentration of substrate with the exception of 4′-carboxy-4-diethylaminoazobenzene for which a linear dependence of the kinetic constant on concentration was found. Such behaviour, reported in Figure 2, was not unexpected since azobenzene isomerization is known to undergo general acid catalysis; [16] in this case, the reported rate constants refer to values extrapolated to zero dye concentration.

Adventitious catalytic action by traces of acidic impurities in the solvent was eliminated by adding a small amount of diethylamine (*ca.* 0.5%) to the solutions under investigation when necessary. In this way reproducible data were obtained and the thermal return was always complete, under the irradiation conditions adopted.

Results and Discussion

The rates of return from *cis*- to *trans*-form after irradiation in the visible band of some 4-diethylaminoazobenzenes in several solvents and at different temperatures were measured. In each case and under all experimental conditions the reaction showed the expected first-order kinetics. Excitation with narrow band or unfiltered radiation and different times of exposure did not affect the results, within the experimental range of uncertainty.

As a first approach to the mechanistic problem, a Hammett-type correlation in *NN*-dimethylformamide (DMF) at 293.2 K was attempted.

The plot, shown in Figure 3, confirms the findings of Nishimura *et al.*[2] for some 4-diethylaminoazobenzenes that 4′-substitution leads invariably to an acceleration of the isomerization rate, regardless of the nature of the substituent.

The experimental plot consists of two linear portions; ln$k$ for 4′-electron-donor 4-diethylaminoazobenzenes, including unsubstituted 4-diethylaminoazobenzene, can be well correlated with the substituent parameters σ_p,[17] giving a good correlation coefficient (r 0.999) and a negative slope (ρ −3.15), while 4′-electron-acceptor derivatives are characterized by a good, positive correlation, which can be further improved using σ_p^- values [18] (r 0.990; ρ +10.2), stressing the importance of conjugative effects.

Unfortunately, such behaviour cannot be interpreted unambiguously. If the acceleration of the isomerization process with increasing electron-donor properties of the 4′-substituents seems difficult to explain in terms of a rotation mechanism, which requires a strongly dipolar transition state, nevertheless both rotation and inversion should be facilitated by increasing

Table 2. Kinetic constants of *cis–trans*-isomerization reaction of 4′-nitro-4-diethylaminoazobenzene (k_I) and of 4′-methoxy-4-diethylaminoazobenzene (k_{II}) in different solvents at 293.2 K

Solvent	π^* [a]	D [b]	k_I/s^{-1}	$10^4 k_{II}/s^{-1}$
n-Hexane	−0.081	7.3	0.0061 ± 0.0010	0.99 ± 0.06
Triethylamine	0.140		0.050 ± 0.002	
Toluene	0.535	8.9	0.27 ± 0.02	1.3 ± 0.1
Ethyl acetate	0.545	9.1	1.0 ± 0.1	1.52 ± 0.05
Benzene	0.590	9.2	0.82 ± 0.05	1.50 ± 0.05
Acetone	0.683	9.9	19.0 ± 0.3	1.82 ± 0.05
Anisole	0.734	9.7	1.02 ± 0.05	1.48 ± 0.06
Pyridine	0.867	10.7	22 ± 1	
NN-Dimethylformamide	0.875	11.8	128 ± 7	2.30 ± 0.05
Dimethyl sulphoxide	1.000	12.2	517 ± 10	2.51 ± 0.05

[a] Kamlet–Taft solvent polarity parameter.[20] [b] Solubility parameter.[22]

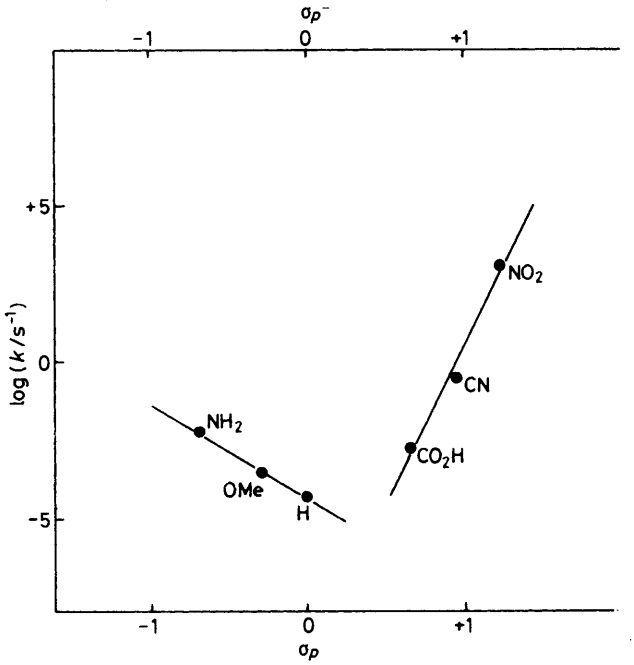
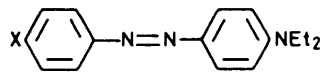


Figure 3. log k *versus* substituent constants (σ_p and σ_p^-) for *cis–trans* isomerization reaction of some 4′-substituted 4-diethylaminoazobenzenes in *NN*-dimethylformamide at 293.2 K



(I) X = NO_2
(II) X = OMe

electron-withdrawing power of the 4′-group. In fact, in the rotational path (Figure 1), electron-acceptor substituents would decrease the barrier to isomerization by reducing the double-bond character of the azo-group, while, in the lateral shift mechanism, the same effect would be obtained by conjugative delocalization of the nitrogen lone pair involved in the rehybridization process.[19] In conclusion, simple electronic effects cannot be used to make a choice between the two mechanisms.

On the other hand, the transition states for the two proposed pathways differ strongly in geometry and electronic distribution, so that they should interact with the solvent in quite different ways. Therefore, we have carried out a series of kinetic measurements in different solvents on 4′-nitro-4-diethylaminoazobenzene (I) and on 4′-methoxy-4-diethylaminoazobenzene (II) chosen as typical representatives of the two classes of compounds considered above. We limited our attention to aprotic solvents to avoid complications connected to the formation of hydrogen bonds; as a matter of fact, some preliminary experiments carried out in alcohols showed a pattern of behaviour completely different from aprotic solvents.

As pointed out previously,[14] regarding the solvent effect on the electronic spectra of some 4-diethylaminoazobenzenes, spectral data can be very well correlated with the Kamlet–Taft π^* scale of solvent dipolarity–polarizability,[20] but only if one deals separately with different classes of solvents, namely solvents which are neither hydrogen-bonding donors nor acceptors (NHB), amphiprotic solvents (HBD/A), and hydrogen-bond acceptor solvents (HBA). The differences in behaviour of the 4-diethylaminoazobenzenes in those three groups of solvents show that dipole–dipole dipole-induced dipole interactions play a predominant role in the solvatochromism of these dyes in all cases, but in HBD/A and HBA solvents more specific interactions exist that can modify strongly their physical and chemical properties.

Actually, the isomerization rates of 4′-methoxy- and 4′-nitro-4-diethylaminoazobenzene are apparently influenced by the solvent in a markedly different way: the rate of return from *cis* to *trans* for (I) is strongly solvent dependent, while for (II) it is relatively insensitive to the medium, as clearly shown by the kinetic constants (k), measured at 293.2 K, in different solvents, reported in Table 2. However, a plot of ln k_I *versus* ln k_{II} gives a very good positive correlation (r 0.996), suggesting fundamental similarity in the two cases. In order to check this hypothesis, a more detailed analysis has been carried out; as for spectral data, in both cases a satisfactory correlation of ln k with the π^* polarity parameter could be found.

The π^* scale was derived from solvent effects on the p–π^* and π–π^* electronic spectral transitions of a variety of nitroaromatic compounds, averaging measurements on *ca.* 40 indicators; the indicators were chosen so that π^* should represent only solvent polarity–polarizability interactions. π^* Values, for the solvents used in this work, are reported in Table 2. When hydrogen-bonding effects are excluded, as in our case, the general form of the linear solvation energy relationship for reaction rates is (1) where s is a measure of the

$$\ln k = \ln k_0 + s(\pi^* + d\delta) \qquad (1)$$

response of ln k to solvent dipolarity and, therefore, is related to the difference in electronic distribution between initial and

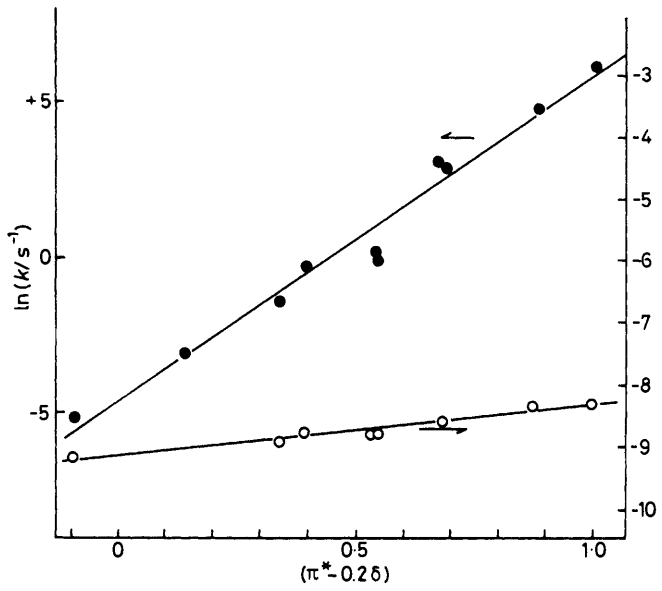
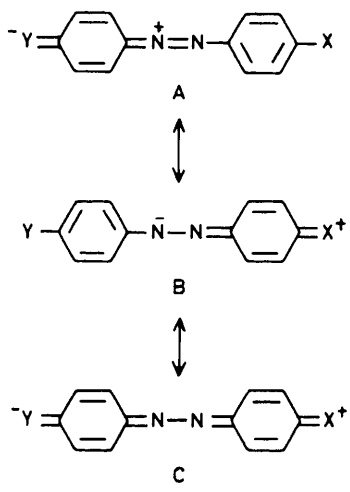


Figure 4. Natural logarithms of kinetic constants of *cis–trans*-isomerization of 4′-nitro-4-diethylaminoazobenzene (ln k_I, ●) and 4′-methoxy-4-diethylaminoazobenzene (ln k_{II}, ○) as a function of $(\pi^* - 0.2\delta)$ [20] at 293.2 K



Scheme.

transition state, δ is a ' polarizability correction term ', equal to 0.0 for non-chlorinated aliphatic solvents, 0.5 for poly-chlorinated aliphatics, and 1.0 for aromatic solvents, and d is interpreted as an indicator of the change in direction of the molecular dipole moment in going from initial to transition state.[21]

When only aliphatic solvents are considered, the regression equations fitting the experimental data for (I) and (II) are (2) and (3), respectively, and the respective correlation co-

$$\ln k_I = -4.56 + 10.53\pi^* \quad (2)$$

$$\ln k_{II} = -9.18 + 0.87\pi^* \quad (3)$$

efficients are 0.991 and 0.990. In both cases the positive value of s shows a transition state more charge-concentrated than the initial one; but, for (I), the difference between the two states is much stronger.

When aromatic solvents are also considered and the general equation (1) is used, the least-squares procedure, applied to return rates of 4′-nitro-4-diethylaminoazobenzene, leads to (4)

$$\ln k_I = -4.67 + 10.6(\pi^* - 0.2\delta) \quad (4)$$

with r 0.985. The parameter d (−0.2) was calculated through the equation $d = 2[\ln k(\text{aryl}) - \ln k(\text{alkyl})]/[s(\text{aryl}) + s(\text{alkyl})]$ where s(aryl) and s(alkyl) are the slopes of the aromatic and aliphatic solvent regression equations and [ln k (aryl) − ln k(alkyl)] refers to π^* 0.7.[21]

For 4′-methoxy-4-diethylaminoazobenzene in aromatic solvents, the adoption of the same value of d leads to an acceptable linear correlation (r 0.981), given by equation (5).

$$\ln k_{II} = -9.20 + 0.88\,(\pi^* - 0.2\delta) \quad (5)$$

From these equations (the plots are shown in Figure 4) some preliminary information can be deduced; the transition states of the isomerization reactions of the two dyes under investigation differ strongly in polarity, dipole–dipole interactions being dominant for (I). Nevertheless, the parallel behaviour of these two compounds, shown by the reciprocal correlation and by the equality of d, suggests that the same type of process takes place in going from the initial to the activated state.

As for (II), a good linear correlation (r 0.980) can also be obtained by plotting ln k as a function of D, the square root of the cohesive energy density, defined by equation (6) where

$$D = \left(\frac{\Delta U}{V_m}\right)^{\frac{1}{2}} = \left(\frac{\Delta H - RT}{M_r/\rho}\right)^{\frac{1}{2}} \quad (6)$$

ΔU and ΔH are, respectively, the energy and the latent heat of vaporization of the solvent, V_m is the molar volume, M_r the molecular mass, and ρ the density of the solvent. The linear regression equation is (7).

$$\ln k_{II} = -10.5 + 0.19D \quad (7)$$

The so-called ' solubility parameter ' D, the use of which, as a solvent parameter, was suggested by Herbrandson and Neufeld,[22] depends only on the physical properties of the solvent and is related to the energy required to form a solvent cavity to accommodate a solute molecule. When reactants and activated complexes are barely polar and dipole–dipole interactions can be neglected, as in the *cis–trans*-isomerization of (II), a linear correlation of the logarithms of the kinetic constants of a reaction in different solvents with D is expected and a simple physical meaning can be attributed to the slope of this plot: a positive slope means that $D^{\ddagger}$, the solubility parameter of the activated complex, is larger than D of the reactants, while a negative slope should be found when the reverse is true. In conclusion, the cohesive energy density of solvents should influence the reaction rates of non-polar reactions in the same direction as external pressure and the small positive slope of equation (7) can be interpreted in terms of a small negative volume of activation, $\Delta V^{\ddagger}$, as predicted by an apolar inversion mechanism.[4] Even if there is a correlation with D for 4′-nitro-4-diethylaminoazobenzene (r 0.960), in this case any simple interpretation of this fact is obscured by the presence of much stronger dipole–dipole interactions.

Therefore, all the data here reported for (II) are more in agreement with an inversion mechanism than with a rotational one and, on the basis of the Hammett plot of Figure 3, this conclusion should also apply to other 4′-donor 4-diethyl-

aminoazobenzenes. As to 4′-nitro-4-diethylaminoazobenzene, a definite choice of one of the two possible models is more difficult. However, the differences with (II) seem to be more quantitative than qualitative in nature, supporting an inversion mechanism in this case as well. The high polarity of the transition state of 4′-acceptor-4-donor derivatives is not in contradiction with the proposed pathway, if resonance structures such as A—C are taken into account for extra stabilization of the activated complex.

Moreover, the negative activation entropies obtained in both cases for *NN*-dimethylformamide ($\Delta S^{\ddagger}_{I}$ −47; $\Delta S^{\ddagger}_{II}$ −50 J K^{-1} mol^{-1}) are an indication of loss of much molecular freedom in going to the transition state, which would not apply to the torsion mechanism. In the same solvent, the corresponding activation enthalpies are $\Delta H^{\ddagger}_{I}$ 46.1 and $\Delta H^{\ddagger}_{II}$ 77.5 kJ mol^{-1}. This marked difference is partly justified by the conjugation stabilization of the activated complex of (I) with respect to the non-planar initial *cis*-form, but also by the different strength of specific solute–solvent interaction. In the inversion process one of the azo-nitrogen lone pairs is converted into a *p* orbital on the *sp*-hybridized nitrogen, and, consequently, energy is required to overcome the local solvation interactions between this lone pair dipole and the carbonyl group of *NN*-dimethylformamide.

This type of specific interaction is much stronger for (II) than for (I), as shown by an investigation of solvent effect on spectral data carried out previously.[14] This demonstrated that the solvatochromism of (I) is ruled essentially by polarity–polarizability effects and the dipolar nature of this compound strongly reduces the magnitude of all other possible specific interactions with all the investigated classes of solvents. On the other hand, specific interactions play a major role in the solvatochromism of (II), especially in carbonyl HBA solvents. These interactions, therefore, contribute to the energy of activation of the isomerization reaction more for 4′-methoxy-4-diethylaminoazobenzene than for 4′-nitro-4-diethylaminoazobenzene, even if, due to the lack of planarity of the *cis*-isomer, this effect is probably energetically smaller in *cis*- than in *trans*-isomers.

Finally, the increase in isomerization rates with increasing electron-donating properties of 4′-substituents may find a reasonable explanation in the increasing possibility of both azo-nitrogens acting as inversion centres and in the correspondingly increased stabilization of the transition state. This fact may also lead to the greater ability of compound (II), relative to (I), to withstand changes in polarity of the solvent, thus showing a certain insensitivity of the inversion process to the medium.

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