Substituent and Solvent Effects on the Thermal Isomerisation of 7*H*-Pyrazolo[5,1-*c*]-1,2,4-triazole Azomethine Dyes

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Activation parameters for the thermal *syn–anti* isomerisation of 25 pyrazolotriazole azomethine dyes in ethanol have been obtained, and the effect of solvent on the rate of isomerisation examined for two of these compounds. Substituent and solvent variations have only a minor influence upon the rate constants, and steric crowding about the C=N bond is the major factor in determining the isomerisation rate. For substituent variations in the 3-position there is a reasonable Hammett correlation between rate constants and σ_p substituent constants and an isokinetic relationship, with an ill-defined isokinetic temperature, at *ca.* 520–1200 K. These data are discussed in terms of the inversion, rotation and biradical mechanisms for isomerisation.

Azomethine dyes are extensively used as the colour forming compounds in conventional colour photography,[1] and dyes derived from 1*H*-pyrazolo[5,1-*c*]-1,2,4-triazole couplers form a relatively new group of photographic dyes.[2] Photoinduced geometrical isomerisation about the carbon–nitrogen double bond is a characteristic reaction of azomethine dyes.[3–8] Our interest in this reaction arises for two main reasons. Firstly, the mechanism of *syn–anti* isomerisation about C=N bonds has been an area of active study for a considerable length of time, and the behaviour of azomethine dyes towards substituent and solvent changes appears somewhat unusual.[4,7,8] Secondly, knowledge of the energy barriers to isomerisation may provide information about ground state potential energy surfaces; this may be of some relevance to photodegradation mechanisms since the close approach of ground and excited states can provide an efficient deactivation route for photochemically excited states.[9]

There are three extreme mechanisms for isomerisation of azomethine dyes,[4–8,10] and these are shown in Fig. 1. One is a rotation about the carbon–nitrogen bond weakened by heterolytic cleavage, with formation of a dipolar transition state. The second mechanism is by inversion, in which the nitrogen atom can be formally considered to undergo rehybridisation from an sp^2 state to an sp state, with the lone pair of electrons being delocalised over the aminophenyl ring. These two mechanisms are those most commonly considered. However, there is a third mechanism involving a non-polar biradical species with rotation about the C=N bond following homolytic cleavage. Although the singlet biradical mechanism has generally been rejected on energetic grounds,[8] a biradical mechanism has been proposed for the isomerisation about C=C bonds in *N,N′*-diacetylindigo,[9] and a triplet biradical mechanism has been postulated for the isomerisation of some stilbene derivatives.[10] A triplet biradical mechanism would be expected to show low pre-exponential factors consistent with the need for a change in electron spin.[11] The low lying triplet states of azomethine dyes, and the observation of efficient triplet sensitised isomerisation,[6,12] suggest that a triplet biradical mechanism should be considered for these compounds.

The experimental evidence for isomerisation about C=N bonds has been well summarised by Asano *et al.*[8] In general, inversion is the favoured mechanism, although in some cases rotation appears to be indicated.[13,14] For some studies of substituent effects V-shaped Hammett plots have been interpreted as evidence for inversion with electron-withdrawing groups and rotation with electron-donating groups.[4,15,16] The arguments for interpreting these data in favour of the inversion mechanism have often been based on analogy to the isomerisation of azobenzene derivatives[17–25] For azobenzenes in which the possibility of rotation is removed by incorporation into ring structures the inversion mechanism exhibits only small solvent and pressure dependence effects, similar to those observed with the azomethine dyes. The rotation mechanism proceeds *via* a dipolar transition state and would be expected to show a marked rate acceleration as solvent polarity increases and a large negative volume of activation in polar solvents.[18–25]

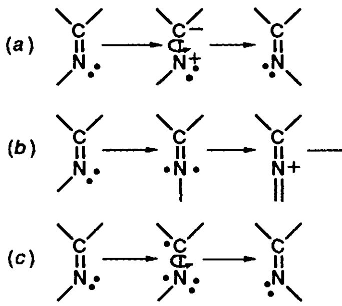

Fig. 1 Isomerisation mechanisms for azomethine dyes; (*a*) heterolytic cleavage and rotation, (rotation mechanism) (*b*) inversion, (*c*) homolytic cleavage and rotation, (biradical mechanism). (Note: the specific structures shown cannot be considered as 'intermediates' or 'transition states', they are simply convenient structures taken from along the reaction pathway to indicate the general mechanism.)

Experimental

Materials.—The dyes were prepared by oxidative coupling of the appropriate pyrazolotriazole (PT) coupler and diethylaminoanilinium developer. The majority of the PT couplers were obtained *via* the triazolothiadiazine sulphur extrusion route,[26] or by the method of Bailey.[2] Oxidation of 6-phenyl-3-thiomethyl PT with dichloromethane–*m*-chloroperbenzoic acid gave the 6-phenyl-3-methylsulphonyl PT in low yield.

The coupling reaction was typically carried out by adding 5 g of potassium persulphate to 0.01 mol of the PT and 0.012 mol of 4-diethylamino-2-methylanilinium chloride in a 50/50 mixture of ethanol/10% aqueous sodium carbonate. Stirring was continued for 1–2 h, and then 0.5 dm^3 of water was added.

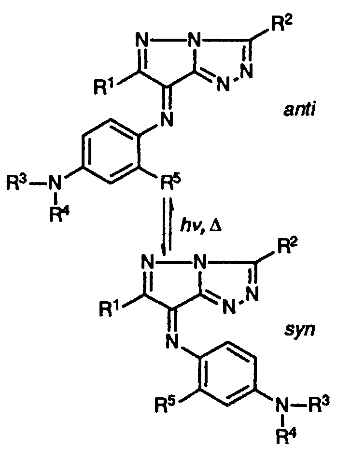

Fig. 2 Dye structures

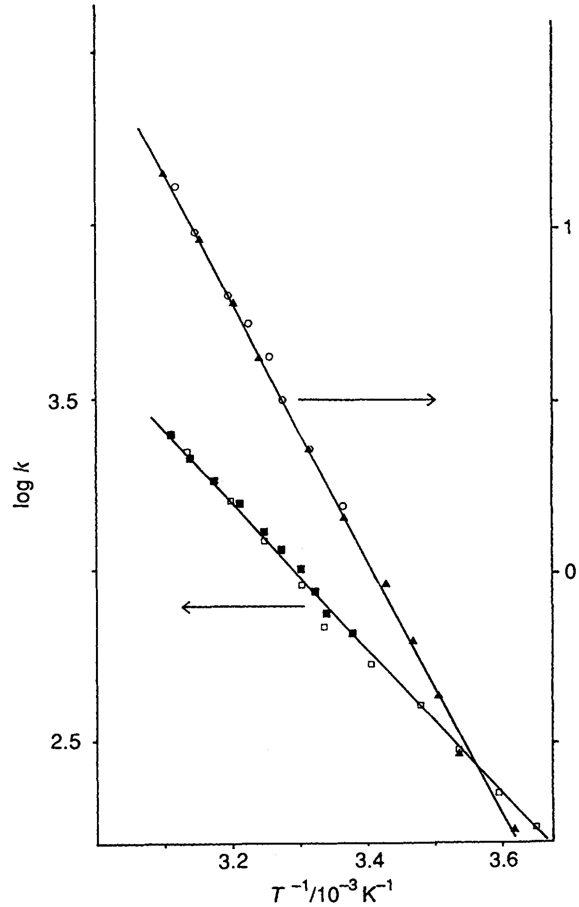

Fig. 3 Typical Arrhenius plots, using both heating methods; filled squares, dye **7** (hot air heating); open squares, dye **7** (thermostatted cell); triangles, dye **12** (thermostatted); circles, dye **12** (hot air heating)

The dye was collected by filtration, water-washed and dried. Column chromatography on Woelm silica gel with light petroleum (b.p. 60–80 °C) and ethyl acetate mixtures gave the purified dye. All dyes gave elemental analyses, and spectroscopic data, consistent with the assigned structures (Fig. 2).

Ethanol was BDH Aristar grade; hexane, BDH Spectrosol grade; methol, acetonitrile, benzene, acetone and dimethylformamide, BDH AnalaR grade and other solvents were BDH Reagent grade.

Methods.—Microsecond flash photolysis studies were carried out with a standard Applied Photophysics 200 J instrument (pulse duration 10 μs), with potassium nitrite filters to remove excitation light of wavelengths less than 400 nm. An excitation pulse of *ca.* 100 J electrical energy was used, with the *ca.* 30 cm³ photolysis solution in a 10 cm path length cell. The transient data were recorded on either a Gould OS 4020, or a Nicolet 2090, digital storage oscilloscope and analysed manually or transferred to a microcomputer (Acorn, BBC Masterclass) for kinetic analysis. The wavelength chosen for monitoring the isomer absorption was set at *ca.* 50 nm to the red of the room temperature absorption maximum, and for all dyes this lay in the 600–700 nm region. In all cases transient decays gave excellent first-order plots. The reproducibility of rate constants varied from dye to dye according to signal size and lifetime, but was typically *ca.* ±3–6%, except for the dye with R^1 = NHPh, where a small signal size and a high rate constant resulted in much poorer reproducibility (*ca.* ±20%).

Two different methods were used for temperature control. In some studies a stream of hot air was used to heat the sample together with the whole of the flash chamber. In other cases a thermostatted quartz sample cell with an outer circulating jacket and evacuated end-windows was used. Relative temperatures are accurate to ±0.25 °C, (which introduces a reproducibility of *ca.* 2% in the rate constant), while absolute temperatures are accurate to ±0.5 °C. Typically, results from experiments at eight temperatures were used for the Arrhenius plots, and typical errors (one standard deviation) for the data derived from Arrhenius plots are as follows: $\Delta G^{\ddagger} \leqslant 1.3\%$, $\Delta H^{\ddagger} \leqslant 6\%$, $\Delta S^{\ddagger} \leqslant 10$ J mol^{-1} K^{-1}.

Laser flash photolysis studies used 532 nm radiation from a frequency doubled Nd/YAG laser (Spectron Lasers) with an Applied Photophysics Laser Kinetic Spectrometer. Signal averaging of 16 transients were used to provide adequate signal-to-noise ratios. No thermostatting was used with this apparatus.

Results

The observed decay arises from four processes: the opposing thermal rates of the forward and back isomerisation, together with the photochemical forward and back isomerisations induced by the monitoring beam; however, the thermal back-isomerisation rate is much faster than the other processes. For most dyes the low quantum yields,[12] and relatively weak monitoring beam intensity allow us to neglect completely the photochemical reactions. The exceptions to this are those dyes with R^1 = H which have unusually high quantum yields and low isomerisation rates, and in these cases the normal monitoring beam caused a small but observable shift in the isomer equilibrium. A comparison of the observed rate constants with and without neutral density filters on the monitoring beam showed that for these dyes the systematic error of a few percent introduced by this photochemical isomerisation was of a similar magnitude to the random errors inherent in the experiment. The ratio of the forward and back thermal rates is small since for all dyes one isomer predominates at room temperature. The 250 MHz NMR spectra of compounds **8** or **12** consist of only one set of sharp peaks. For compound **8** the relaxation time for equilibration is on the millisecond time-scale and the single spectrum could be due to interconverting isomers.[27] For compound **12** the equilibration time is *ca.* 0.3 s at room temperature and it is very unlikely that the single ^{1}H NMR spectrum is due to a signal averaged over two configurations. Room temperature UV–VIS spectra show little evidence of the unstable isomer absorptions which are detected in the flash photolysis experiments.

For studies with R^1 = *tert*-butyl, CF_3 and 2-thienyl we could observe no isomerisation using microsecond flash photolysis. However, laser flash photolysis with R^1 = *tert*-butyl gave a

Table 1 Activation parameters for ethanol solutions at 30 °C

Dye[a]	$\Delta G^{\ddagger}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	k/s^{-1}
Group A				
R^2 = Ph, R^3 = R^4 = Et, R^5 = Me				
1 R^1 = Bu^t	36.5	—	—	3.2×10^6[b]
2 = CN	54.3	34	−68	2710
3 = NHPh	54.7	18	−128	2340
4 = Ph	54.8	47	−25	2240
5 = NHAc	55.4	55	−3	1750
6 = NHMe	56.5	46	−36	1130
7 = CO·OEt	57.0	39	−58	960
8 = Me	57.6	53	−17	760
9 = NH$_2$	58.1	47	−37	610
10 = CO·NH$_2$	58.1	57	−3	600
11 = PhCO	60.7	52	−30	216
12 = H	71.8	68	−13	2.69
Group B				
R^2 = Mesityl, R^3 = R^4 = Et, R^5 = Me				
13 R^1 = Me	57.0	50	−24	957
14 = H	71.3	61	−33	3.27
Group C				
R^1 = Ph, R^3 = R^4 = Et, R^5 = Me				
15 R^2 = SO$_2$Me	52.0	41	−36	6910
16 = CF$_3$	52.3	45	−23	5980
17 = H	54.0	46	−25	3100
18 = Thienyl	54.2	50	−15	2850
19 = NHAc	54.4	50	−13	2660
20 = Me	54.6	48	−21	2480
4 = Ph	54.8	47	−24	2240
21 = NHPh	56.4	51	−17	1210
Group D				
R^1 = Me, R^2 = Ph, R^5 = H				
22 R^3 = H, R^4 = Me	59.8	52	−26	300
23 R^3 = R^4 = H	60.1	51	−30	273
24 R^3 = R^4 = Et	60.4	56	−16	246
25 R^3 = R^4 = Me	61.2	55	−20	181

[a] Dye structures shown in Fig. 2. [b] Measured at 20 °C.

weak transient signal, which we assign to isomerisation on the basis of the transient spectrum and insensitivity to oxygen.

We considered the possibility that dyes with R^1 = H (**12**, **14**) might exist in a different ground state conformation as compared to dyes bearing other R^1 substituents. This is known to be the case for the pyrazolone azomethine dyes, where the conformation can be determined from the chemical shifts of the protons *ortho* to the C=N bond.[29] However, the NMR spectra of dyes **8** and **12** show little difference in the position of the absorbances due to this proton and we have been unable to reach any conclusions about relative conformations.

Activation Parameters.—Typical Arrhenius plots are shown in Fig. 3, and Table 1 collects data for studies in ethanol. Arrhenius plots have been interpreted using the thermodynamic formulation of transition state theory with a transmission coefficient of 1.[28] The change of electron spin required by the triplet biradical mechanism is expected to lead to a reduced transmission coefficient and if this mechanism is operative the true values of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ will be less than those calculated, but the value of $\Delta H^{\ddagger}$ will remain as shown.

Although the activation energies range from 20–70 kJ mol^{-1}, and pre-exponential factors range from 10^6–10^{13} s^{-1}, for most compounds the rate constants at 30 °C are reasonably constant at *ca.* 5–50 × 10^2 s^{-1}, and substituent effects on $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ compensate for one another to give a reasonably constant $\Delta G^{\ddagger}$. The R^1 = H dyes (**12**, **14**) and the R^1 = *tert*-butyl dye (**1**) are exceptions to this.

Isokinetic Relationships.—Compensation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ will arise if there is an isokinetic relationship in the data,[30–32] and we have used the methods recommended by Exner[31] in order to examine our data for such relationships (data for dye **3** have not been included in these analyses because of the large errors associated with the Arrhenius data for this dye). Fig. 4 shows a plot of the logarithms of the rate constants at two temperatures as recommended by Exner. The interesting feature of this plot is that it is the dyes with low pre-exponential factors (**2**, **3**, **7**) which appear anomalous, rather than those with low rate constants. Statistical analyses of a number of groupings of dyes: Group A; A minus **12**; A minus **2**, **7**; A + B + D; A + B + C + D: A + B + C + D minus **12**, **14**; and A + B + C + D minus **3**, **7**, give little support to the presence of a physically significant isokinetic temperature.[32] However, in the case of the dye set where R^2 is varied (group C) the analysis shows that an isokinetic relationship must be accepted unconditionally, although the isokinetic temperature is not well defined (Fig. 5).

Hammett Correlations.—For substituent variations in R^1 (Group A) we could find no obvious correlation between any of the kinetic parameters and Hammett *m* or *p* substituent constants. For the variation in the R^2 substituent (Group C) there is a reasonable correlation between Hammett σ_p constants[33] and log k as shown in Fig. 6. The slope of +0.6 suggests that partial removal of charge from the pyrazolotriazole moiety reduces $\Delta G^{\ddagger}$.

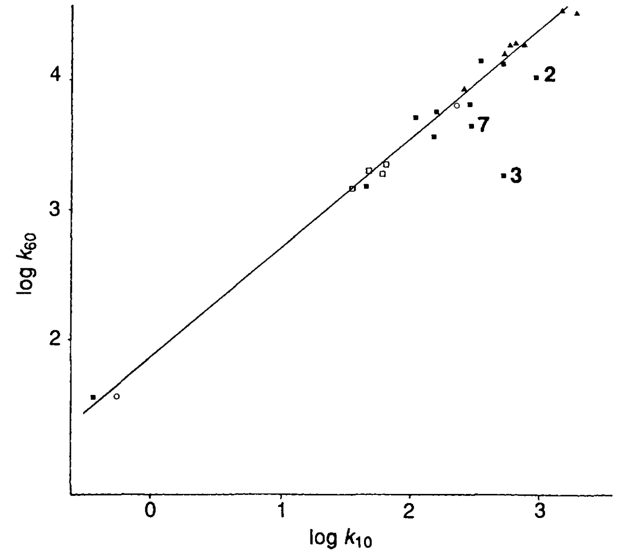

Fig. 4 Plot of log k at 60 °C *vs.* log k at 10 °C. Filled squares, Group A; open circles, Group B; filled triangles, Group C; open squares, Group D.

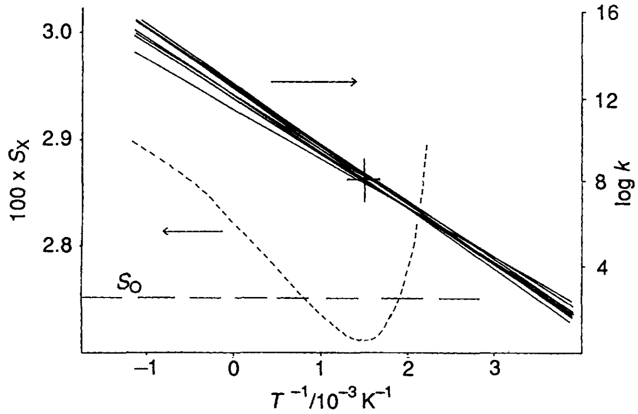

Fig. 5 Statistical analysis of Arrhenius data for Group B. Solid lines are experimental Arrhenius plots. S_x is shown as the dashed line, and is the optimum standard deviation if Arrhenius plots are constrained to pass through a common point at a given temperature. S_o is the standard deviation for the data if the Arrhenius plots are not constrained to pass through a common point. The isokinetic temperature is at the minimum of the S_x plot, and the associated log k indicated by the cross.

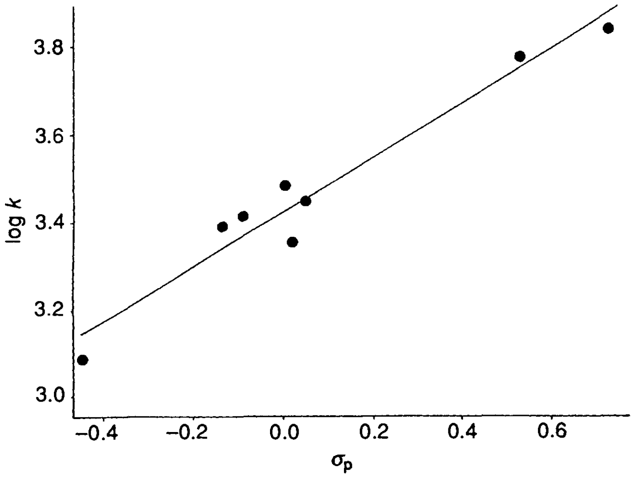

Fig. 6 Hammett plot for the isomerisation rate constant of Group C (8 points, correlation coefficient = 0.96, slope = 0.61)

Solvent Effects.—As Tables 2 and 3 show, solvent effects on rate constants and activation parameters are small. For dyes **8** and **12** the rate constants decrease slightly with solvent polarity, and there is a reasonable negative correlation between $\Delta G^{\ddagger}$ and solvent E_T^N values[34] for non-H-bonding solvents. Alcohols give somewhat higher rate constants than expected from this relationship, but H-bonding solvents do not have a dramatic effect on rate.

Table 2 Solvent effects on rate constants (k/s^{-1}) at 30 °C

		Compound		
Solvent	$E_T^{N\,a}$	**8**	**12**	**15**
Hexane	0.009	1060	2.21	
Diethyl ether	0.117	800	2.47	5600
Ethanol	0.654	757	2.69	6900
Methanol	0.762	718	2.59	
Benzene	0.111	658	1.85	
Ethyl acetate	0.228	614	—	
DMF	0.404	590	—	
Pyridine	0.302	580	1.33	
Acetone	0.355	574	1.76	6600
DMSO	0.444	480	1.25	
Acetonitrile	0.460	411		

[a] From ref. 34.

Table 3 Solvent effects on activation parameters for dyes at 30 °C

Solvent	$\Delta G^{\ddagger}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
Compound **8**			
Ethanol	57.6	53	−17
Acetone	58.2	54	−15
Compound **12**			
Ethanol	71.8	68	−13
DMSO	73.7	64	−34
Benzene	72.7	68	−14

Discussion

A comparison of these data for compounds **1**, **8** and **12** indicates that steric effects are very important at position R^1, a view supported by the generally lower rate constants observed for dyes without the *ortho* methyl developer substituent (**22**–**25**). Electronic substituent effects are more influential on rate at position R^2 than R^1, however, the most remarkable feature of this data overall is the general insensitivity of the rate to substituent and solvent variations.

The solvent effects are similar to those reported by Anao *et al.* for the pyrazolone azomethine dyes,[8] and indicate a slight decrease in the relative solvation of the transition state in polar solvents. The room temperature partition coefficient between hexane and dimethyl sulphoxide for compound **12** is 38 ± 10 and the difference in free energy of solvation is *ca.* 9 kJ mol^{-1}. This is greater than the difference in free energy of activation for these two solvents. If both isomers are solvated to similar degrees then reactant and transition state are highly solvated in DMSO as compared with hexane. There is no evidence of the marked change in solvation between reactant and transition state which might be expected for the rotational mechanism with heterolytic cleavage of the C=N bond.

Given the solvent effects, the enhanced rate observed with electron withdrawing R^2 groups is surprising. Such stabilisation by electron-withdrawing groups would be expected if the heterolytic rotation mechanism was operative but it is difficult to rationalise this effect in terms of the inversion mechanism.

The triplet biradical mechanism would be expected to show only small solvent effects, and perhaps substituent effects of

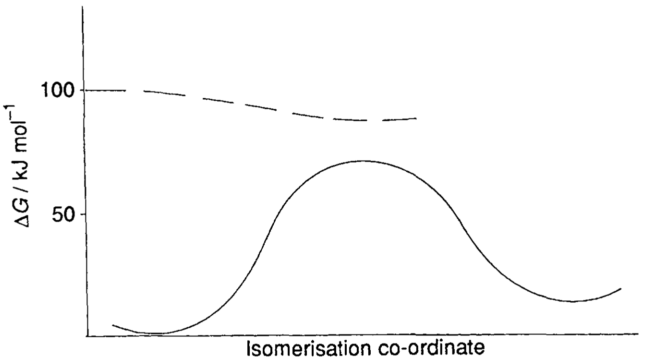

Fig. 7 Proposed potential energy surfaces for the triplet (dashed line) and ground state (solid line) of dye **7**. The energies for the minima and maxima of the curves are discussed in the text.

the magnitude seen here. Fig. 7 shows the ground state and proposed triplet state free energy surface for dye **7**. Energy transfer experiments suggest a triplet energy of *ca.* 100 kJ mol^{-1} for this dye in ethanol.[35] $\Delta G^{\ddagger}$ is 57 kJ mol^{-1} (or perhaps somewhat lower than this if the transmission coefficient is less than 1), and the free energy difference between *syn* and *anti* isomers must be greater than *ca.* 12 kJ mol^{-1} for one isomer to predominate at room temperature. These figures place the transition state less than 30 kJ mol^{-1} lower than the unrelaxed triplet. The question arises as to whether the depth of the triplet energy well and any possible increase in the energy difference between isomers could account for the remaining *ca.* 30 kJ mol^{-1} and these potential energy surfaces meet. The change from what is believed to be a singlet dipolar mechanism to the biradical triplet mechanism in the isomerisation of substituted stilbenes is accompanied by a reduction in the pre-exponential factor from 6×10^{12} s^{-1} in stilbene to 1×10^{8} s^{-1} in *p*-amino-*p*′-nitrostilbene.[11] By analogy to the stilbenes, then, we might argue that those dyes which have low pre-exponential factors (**2**, **3**, **7**) isomerise by a triplet biradical mechanism, while the others isomerise *via* a singlet state mechanism.

Conclusion

Isomerisation rate constants in these dyestuffs are remarkably independent of either solvent changes or electronic substituent effects and by far the major influence on rate is steric hindrance about the C=N bond. The failure to observe either clear Hammett or isokinetic relationships with variation in R^1 is an indication that there is not just one interaction mechanism for substituents at this position. By way of contrast the isokinetic and Hammett relationships observed for the R^2 substituent set indicates a relatively simple electronic interaction.

For the majority of dyes the high pre-exponential factors suggest a singlet state mechanism, and since there is little change in solvation upon activation this may well be *via* inversion. However, electron withdrawing substituents at R^2 lead to rate enhancement, and for some dyes low pre-exponential factors suggest a triplet biradical mechanism.

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