The Photo and Thermal *cis–trans*-Isomerisation of 1,1′-Dimethoxy-4,4′-bis(phenylazo)-2,2′-binaphthyl in Chloroform. Kinetics and Mechanism

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The photo and reverse thermal *cis–trans*-isomerisation of the title compound in chloroform has been investigated kinetically, giving the rate constants and thermodynamic parameters of the thermal isomerisation and confirming the mechanism of the isomerisation.

Recently, the *cis–trans* photoisomerisation of azobenzenes has attracted particular interest in connection with chemical and biochemical functions; *e.g.* photoresponsive crown ether isomerisation.[1] This phenomenon has been known for a long time,[2,3] and the existence of *cis*- and *trans*-isomers confirmed.[2—9] In many cases the *cis*-isomer is too unstable to be isolated, and has been detected only by spectroscopic techniques. For molecules containing two azo-groups, since the isomerisation of each azo-group occurs independently, *trans–trans*-, *trans–cis*-, and *cis–cis*-isomers are possible. The unstable *trans–cis*- and *cis–cis*-isomers of (4-phenylazo)azobenzene and 4,4′-bis(phenylazo)biphenyl have been identified,[4,5] and a number of methyl ethers of azophenols (2,4- and 2,6-dimethoxyazobenzene, 1-methoxy-4-phenylazo- and 1-*ortho*-substituted phenylazo-2-methoxynaphthalene, and 1-*ortho*-substituted naphthylazo-2-methoxynaphthalene) are comparatively stable in the *cis*-form.[4,5] We have investigated the photoisomerisation of 1,1′-dimethoxy-4,4′-bis(phenylazo)-2,2′-binaphthyl (**1**),† which was prepared by the methylation of 4,4′-bis(phenylazo)-2,2′-binaphthyl-1,1′-diol[10] with diazomethane

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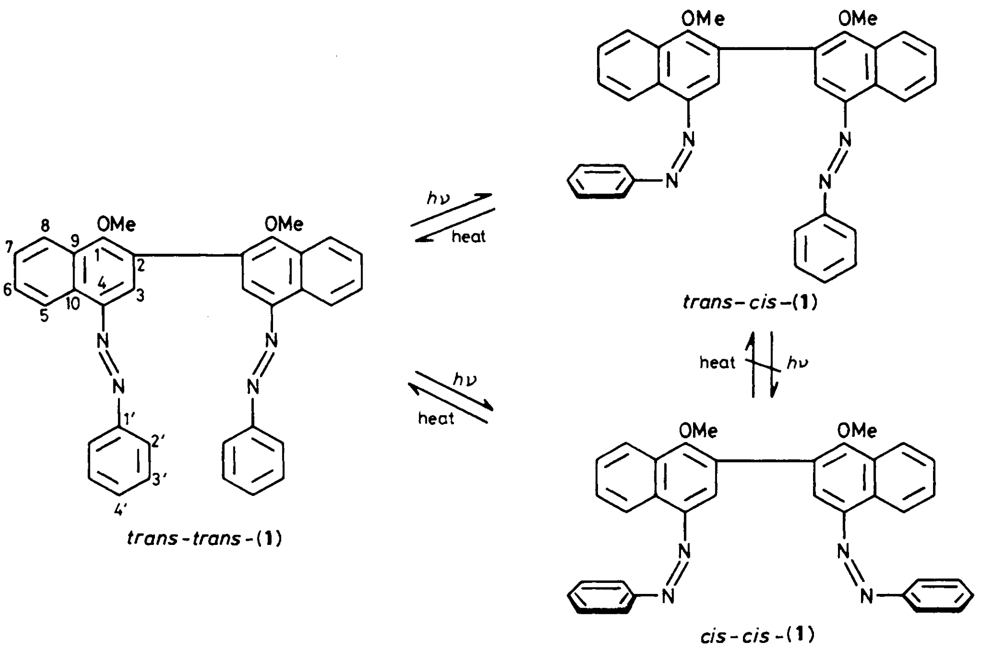
† Satisfactory elemental analyses were obtained; m.p. 238—240 °C; i.r. (KBr) $\nu_{max.}$ 2930, 2840, 1460, and 1355 cm^{-1}; ^{13}C n.m.r.: δ_C ($CDCl_3$) 157.2(C-1), 129.3(C-2), 116.2(C-3), 144.2(C-4), 124.1(C-5), 127.0(C-6), 127.8(C-7), 123.3(C-8), 126.8(C-9), 133.0(C-10), 158.9(C-1′), 123.4(C-2′), 129.4(C-3′), 131.1(C-4′), and 62.1(Me); *m/z* 522(M^+), 507, 417, 387, 282, 105, and 77.



Scheme 1

Table 1. Irradiation time required to reach the photostationary state in the photoisomerisation of (1) in chloroform at 25 and 40 °C.

Temp./°C	Time/min	% of isomer *t–t*	*t–c*	*c–c*
25	0.5	52.60	37.13	10.27
	1.0	40.90	44.36	14.73
	2.0	38.27	45.80	15.93
	3.0	36.12	46.69	17.19
	5.0	36.36	46.55	17.10
	20.0	36.06	46.85	17.09
40	0.5	52.60	37.13	10.27
	1.0	42.82	43.50	13.69
	2.0	35.75	47.06	17.18
	3.0	35.69	47.04	17.27
	5.0	36.34	46.98	16.68
	20.0	37.69	46.42	15.89

Table 2. Rate constants and thermodynamic parameters for the thermal isomerisation in the dark of (1) in chloroform at different temperatures.

Temp. /°C	Rate constant $k_{c,c\rightarrow t,t}$ $\times 10^{-4}$/s^{-1}	$k_{t,c\rightarrow t,t}$ $\times 10^{-4}$/s^{-1}
25	0.956	0.340
30	1.818	0.697
35	3.330[a]	1.244[b]
40	6.863	2.560

[a] $\Delta H^{\ddagger}$ 23.6 kcal mol^{-1}; $\Delta S^{\ddagger}$ 2.1 cal mol^{-1} K^{-1}. [b] $\Delta H^{\ddagger}$ 24.0 kcal mol^{-1}; $\Delta S^{\ddagger}$ 1.6 cal mol^{-1} K^{-1}. 1 cal = 4.184 J

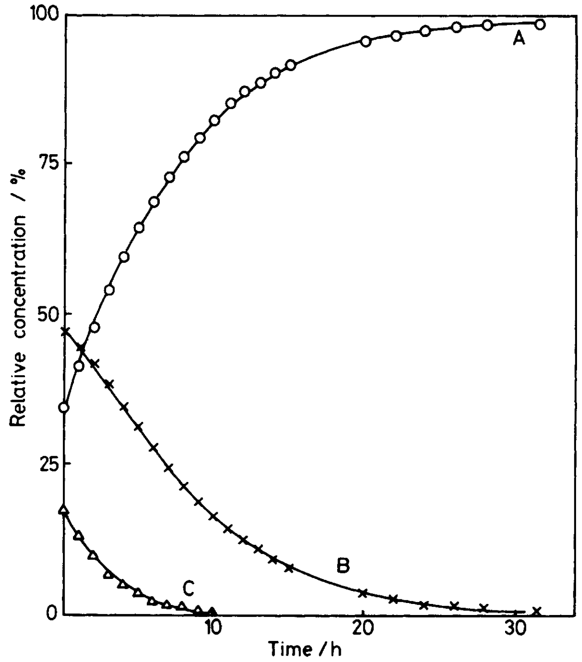


Figure 1. Relative concentration (%) *vs.* time for the thermal isomerisation in the dark of compound (1) in chloroform at 25 ± 0.05 °C: A, *trans–trans*; B, *trans–cis-*; C, *cis–cis*-isomer.

in diethyl ether, and now report the kinetics and mechanism of the photo and thermal isomerisation of (**1**). The photoisomerisation of (**1**) was carried out using a 400 W high-pressure mercury lamp with a Pyrex filter in chloroform at 25 ± 5 °C; the photostationary state was reached after only 5 min irradiation, and three peaks (t_R 2.5, 3.4, and 6.2 min) appeared on the h.p.l.c. chromatograms simultaneously after 1 min. The absorption spectra of the compounds giving rise to these peaks were measured by a Spectra Multi Channel Photo Detector (Union Giken MCPD-350PC) equipped with a data processor (ShimazuC-R3A Chromatopac). These three peaks changed gradually with time in the dark at 25 ± 0.05 °C. The band at *ca.* 280 nm due to the π,π* band of the *trans–trans*-isomer (peak 1) shifted more to shorter wavelength than peaks 2 and 3, and the intensity of the π,π* maximum at *ca.* 385 nm decreased as peaks 2 and 3 were blue-shifted. Hence, these peaks correspond to the *trans–trans-* (peak 1), *trans–cis-* (peak 2, and *cis–cis*-isomer (peak 3) respectively. It was estimated from h.p.l.c. data that in the photostationary state at 25 °C the mixture consists of 36.36% of the *trans–trans*-form, 46.75% of the *trans–cis*, and 16.89% of the *cis–cis* (Table 1). The kinetics and mechanisms of the reactions of azobenzene and azobenzene-bridged crown ethers have been investigated, and have revealed the effect of substituents and solvents,[11] and steric courses,[12] but few kinetic investigations[13] of the *cis–trans*-isomerisation of compounds containing two phenylazo-groups in one molecule such as (**1**) have been reported. Moreover, it has been estimated that the *cis–cis* into *trans–cis* conversion is the rate-limiting step in the thermal isomerisation of the *cis–cis* to the *trans–trans*-form, and that the *trans–cis*-structure is destabilised. Now this study has made it clear that the thermal isomerisation was noticeably dependent on temperature, whereas the photoisomerisation was only slightly affected by temperature in reaching the photostationary state (Tables 1 and 2). The kinetic results are shown in Tables 1 and 2 and Figure 1. If the mechanism of the thermal isomerisation involved consecutive steps, *e.g. cis–cis* → *trans–cis* → *trans–trans*, the plots of the relative concentration of each component *vs.* time should show a uniformly exponential decreasing curve for the *cis–cis*-isomer, a fairly sharply increasing curve reaching a maximum for the *trans–cis*-isomer, and a linear increasing curve having a short induction period for the *trans–trans*-isomer. However, it is obvious from Figure 1 that the plots of the *cis–cis-* and *trans–cis*-isomer show a uniform decrease in their relative concentration, while the plot for the *trans–trans*-isomer shows a uniform increase. This result indicates that the thermal isomerisations of *cis–cis* to *trans–trans* and *trans–cis* to *trans–trans* both proceed simultanteously. These findings confirm that the mechanism of the thermal isomerisation involves simultaneous (parallel) rather than consecutive reactions, as shown in Scheme 1. The mechanism of the photoisomerisation may be considered to be similar.

Received, 3rd March 1986; Com. 275

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