

## Short Communication

### Further evidence for rotation in the $\pi,\pi^*$ and inversion in the $n,\pi^*$ photoisomerization of azobenzenes

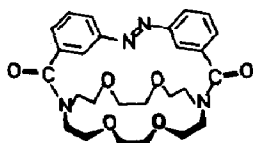
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We have proposed a hypothesis stating that normal non-cyclic azobenzenes should isomerize by a rotational mechanism when excited to the higher energy  $\pi,\pi^*$  states and by an inversion mechanism when excited to the lowest excited state which is of  $n,\pi^*$  type. This concept has been developed on the basis of the results of the *trans-cis* isomerization of two azobenzenophane molecules which cannot isomerize by rotation for structural reasons [1].

In this communication we present the results of isomerization experiments carried out with the azobenzene capped crown ether 1:



1

This compound was a gift from Professor Shinkai who has established that the thermal *cis-trans* isomerization must proceed via inversion because of steric conditions [2]. In 1 the azobenzene moiety is *meta* substituted; for comparison we have isomerized 3-nitroazobenzene and 4-acetylazobenzene (which have been prepared by standard procedures [3]) and 3,3'-dimethylazobenzene (prepared by the standard procedure given in ref. 4).

The isomerization experiments were performed with two independent sets of equipment.

(a) In our laboratory irradiation was carried out by means of a Philips HPK 125 W mercury lamp with Schott UV-PIL filters for 313 and 436 nm light and the absorption spectra were taken after transfer of the 1 cm cell to a Zeiss DMR 10 spectrophotometer.

(b) As a guest in Professor Gauglitz's laboratory at Tübingen we used his integrated microprocessor-directed irradiation-absorption system which consists of a Hanau St 75 mercury lamp, Schott interference filters, a

DMR 10 spectrophotometer and an on-line data processing unit. Irradiation was carried out at room temperature in stirred ethanol solutions, the concentrations were  $10^{-5}$  -  $10^{-4}$  M and oxygen was not excluded. The quantum flux of the lamps was determined by means of the azobenzene actinometer [5].

The data were evaluated in terms of the approach of the system to the photostationary state (PSS) [6]. The *trans*  $\rightarrow$  *cis* isomerization kinetics in terms of absorbance are given by

$$\ln \left\{ \frac{A_\infty - A(t)}{A_\infty - A(0)} \right\} = -1000I_0(\epsilon_t' \Phi_t' + \epsilon_c' \Phi_c') \int_0^t \frac{1 - 10^{-A'(t)}}{A'(t)} dt \quad (1)$$

where the primed quantities are those at the irradiation wavelength,  $A_\infty$  is the absorbance at the PSS and  $A(0)$  is the initial absorbance which need not be that of the pure isomer if the total concentration  $c_0$  is known. Plots of the left-hand side *versus* the integral (obtained by trapezoid integration) gave straight lines. As the 436 nm PSS is very rich in *trans* isomer this PSS is approached from the *cis* side by pre-irradiation with 366 or 313 nm light.

Evaluation of the quantum yields from the slope of eqn. (1) requires values for  $\epsilon_c'$ . We have separated the *cis* compound by thin layer chromatography and determined its absorption spectrum. However, we could not isolate enough of the material to weigh it. Thus we determined  $\epsilon_c'$  in an indirect way. The ratio of the  $\epsilon$  values at two arbitrary wavelengths 1 and 2 can be taken from the  $A$  spectrum:

$$\frac{\epsilon_{c,1}}{\epsilon_{c,2}} = \frac{A_1^c}{A_2^c} = K^c \quad (2)$$

With this information  $\epsilon_c$  can be obtained from two spectra at different extents  $\xi$  of reaction (or irradiation time  $t$ ):

$$\begin{aligned} \Delta A_1 &= A_1(\xi) - A_1(0) \\ &= \{(\epsilon_{t,1} - \epsilon_{c,1})c_t(\xi) - \epsilon_{c,1}c_0\} - \{(\epsilon_{t,1} - \epsilon_{c,1})c_t(0) - \epsilon_{c,1}c_0\} \\ &= (\epsilon_{t,1} - \epsilon_{c,1})\{c_t(\xi) - c_t(0)\} \end{aligned} \quad (3)$$

and

$$\frac{\Delta A_1}{\Delta A_2} = \frac{\epsilon_{t,1} - \epsilon_{c,1}}{\epsilon_{t,2} - \epsilon_{c,2}} \quad (4)$$

From eqns. (4) and (2) we calculate for the irradiation wavelength ( $\epsilon_{c,2} = \epsilon_c'$ )

$$\epsilon_c' = \left( \epsilon_{t,1} - \epsilon_t' \frac{\Delta A_1}{\Delta A'} \right) / \left( K^c - \frac{\Delta A_1}{\Delta A'} \right) \quad (5)$$

If we use the absorbance of the PSS,  $A(\xi_\infty) = (\epsilon_t - \epsilon_c)c_{t\infty} - \epsilon_c c_0 = A_\infty$ , we find  $c_{t\infty}$  and  $c_{c\infty}$ . With the well-known PSS relation  $\epsilon_t' \Phi_t' / \epsilon_c' \Phi_c' = c_{c\infty} / c_{t\infty}$  the slope of eqn. (1) is

TABLE 1

Isomerization quantum yields of azobenzene derivatives

Compound	313 nm excitation		436 nm excitation	
	$\Phi_{t \rightarrow c}^a$	$\Phi_{c \rightarrow t}^a$	$\Phi_{t \rightarrow c}^b$	$\Phi_{c \rightarrow t}^b$
Azobenzene	0.12	0.31	0.24	0.53
4-acetylazobenzene	0.10	0.46	0.18	0.56
Crown ether 1	0.29	0.53	0.29	0.56
3-nitroazobenzene	0.18	0.61	0.33	0.53
3,3'-dimethylazobenzene	0.24	0.38	0.35	0.57

<sup>a</sup> ±15%.<sup>b</sup> ±25%.

$$m = -1000I_0 \left( 1 + \frac{c_{t\infty}}{c_{c\infty}} \right) \epsilon_t' \Phi_t' \quad (6)$$

which gives  $\Phi_t'$ . From the PSS condition  $\Phi_c'$  is computed.

We have also tried to sensitize the isomerization of 1 with eosin, Rose Bengal and benzil [7]. Unfortunately the crown ether reacts with the sensitizers.

The results of the direct photoisomerization are compiled in Table 1. The high error margin of ±25% for  $n \rightarrow \pi^*$  excitation stems from the fact that the 436 nm PSS contains more than 85% of the *trans* isomer. It is evident that the crown ether which is unable to rotate has the same *trans* → *cis* quantum yields for the excitation to the  $n, \pi^*$  and  $\pi, \pi^*$  states. As is usual for normal azo compounds the other molecules show significantly lower isomerization yields on high energy excitation. We note that the *meta*-substituted azobenzenes seem to have higher isomerization quantum yields than the *para*-substituted azobenzenes for which roughly 0.10 has been found on 313 nm irradiation and 0.15 - 0.25 on 436 nm irradiation [8].

The photoisomerization experiments with azobenzene and its normal derivatives indicate a violation of Kasha's rule that molecules excited to higher states should relax thermally to the lowest excited state in each multiplicity.† Excitation to the  $^1(\pi, \pi^*)$  state of *trans*-azobenzene is followed by the competition of (a) internal conversion (IC) to the *trans*  $^1(n, \pi^*)$  state, (b) IC to the ground state, (c) intersystem crossing (ISC) to a  $^3(\pi, \pi^*)$  (or the  $^3(n, \pi^*)$ ) state and (d) a change in geometry. The radiative lifetime of the  $^1(\pi, \pi^*)$  state of azobenzene at  $31\,500\text{ cm}^{-1}$  (and 1 is very similar) calculated from the integrated absorption [9] is about  $2 \times 10^{-9}$  s. Taking into account the emission quantum yield of less than  $10^{-4}$  the relevant lifetime of the  $^1(\pi, \pi^*)$  state is computed to be less than  $2 \times 10^{-13}$  s. IC to the ground state can be ruled out as the experiments are not carried out in rarefied gases [10]

†I thank a referee for encouragement to discuss this.

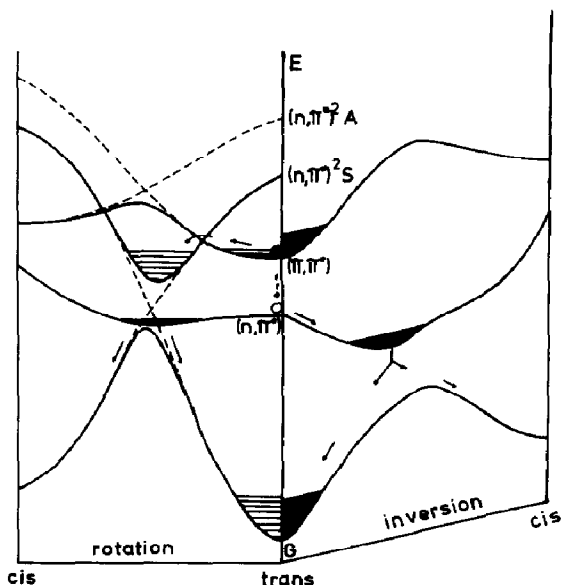


Fig. 1. Qualitative potential energy surface diagram.

but in solution and because excess energy within a specific band does not influence the quantum yield of isomerization [11]. Turro [12] gives limits of ISC rates  $10^{11} \text{ s}^{-1} > k_{\text{isc}} > 10^5 \text{ s}^{-1}$  which are considerably lower than the rate of deactivation of the  $^1(\pi, \pi^*)$  state. This leaves IC to the  $^1(n, \pi^*)$  state and nuclear displacement. The *trans*  $^1(n, \pi^*)$  state, however, is not reached in normal azobenzenes as is seen from the deviation of the isomerization quantum yields of  $\pi \rightarrow \pi$  and  $n \rightarrow \pi^*$  excitations. The *trans*  $^1(n, \pi^*)$  state is, in contrast, reached in azobenzenes that cannot rotate.

Hence "bypassing" of the  $^1(n, \pi^*)$  state must be due to some rotational feature. We have constructed the qualitative potential energy surface diagram of Fig. 1 on the basis of one-electron orbitals, their correlations and state correlations derived therefrom [13, 14]. Energy considerations and the spectroscopic and thermochemical data of azobenzene have been included. From the above considerations and with those of Bortolus and Monti [15] we conclude that triplet states play a secondary role in direct isomerization. The diagram turned out to be in reasonable agreement with calculations; in fact it is a combination of azomethane [16 - 18] and stilbene diagrams [19, 20]. Orlandi and Palmeri [21], however, predict not a depression but a hill at the  $90^\circ$  twist position of the  $n, \pi^*$  state.

This diagram allows that inversion should be preferred on  $n \rightarrow \pi^*$  excitation but precluded on  $\pi \rightarrow \pi^*$  excitation. It indicates that the  $^1(\pi, \pi^*)$  state finds a minimum in rotation at the  $90^\circ$  twisted configuration and that this minimum is coupled dynamically to the ground state which in turn at this geometry is degenerate with the twisted  $^1(n, \pi^*)$  state. This situation is favourable for a "bypass" which otherwise is difficult to conceive in condensed media. The bifurcation of the reaction to the *cis* and *trans* ground states may take place here or at the *trans*  $^1(\pi, \pi^*)$  position. However, one

problem remains: the fast start of rotation immediately after excitation to the *trans*  $^1(\pi, \pi^*)$  state. Taking the sharpness of the vibrational structure of the absorption band as a crude measure of the lifetime of the corresponding state we may compare azobenzene with stilbene [22, 23] and derive a much shorter lifetime of the  $^1(\pi, \pi^*)$  state of azobenzene from the more diffuse band contours.

I present this potential energy diagram although it does not meet all requirements. The simple fact that  $\Phi_{t \rightarrow c} + \Phi_{c \rightarrow t} \neq 1$  indicates processes that are not included in Fig. 1. The diagram, however, should stimulate new discussion, reassessment of results and, perhaps, new experiments.

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