

## THE LOWEST TRIPLET STATE OF SUBSTITUTED AZOBENZENES: AN ENERGY TRANSFER INVESTIGATION<sup>†</sup>

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### Summary

The energy transfer process from aromatic hydrocarbons to some *para*-substituted azobenzenes was studied by flash kinetic spectrophotometry. The energies of the lowest triplet states of the azo derivatives investigated do not depend very much on the substituent and are in the range 30 - 35 kcal mol<sup>-1</sup> (125 - 145 kJ mol<sup>-1</sup>). Neither the donor nor the acceptor substituents produce inversion in the <sup>3</sup>( $\pi, \pi^*$ )–<sup>3</sup>( $n, \pi^*$ ) state order, so that the lowest triplet state has  $n, \pi^*$  character and appears to be distorted as in azobenzene. Inversion can be postulated for double substitution with strongly conjugated groups, *i.e.* in 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-NO<sub>2</sub>-azobenzene.

### 1. Introduction

Azobenzene (AB) and its derivatives form a class of compounds frequently used as commercial dyes [1]. Despite their widespread use, an understanding of their photoreactivity has been limited by the lack of information available about the properties of their excited states. The main characteristic of the photochemical behaviour of these compounds is a marked wavelength dependence [2, 3]. Efficient *trans*–*cis* isomerization occurs in the lowest excited singlet and triplet states only [4 - 6]. Less efficient *trans*–*cis* isomerization [4, 5] and photoreduction take place in the higher-lying excited states [3, 7]. Understanding of the singlet properties is limited by the non-fluorescent behaviour of most azo derivatives. Only amino or sterically hindered ABs exhibit fluorescence emission which can be detected using conventional apparatus [8]. The absence of triplet state data is mainly due to the lack of phosphorescence [8]. Evidence for a triplet state

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absorption with a lifetime in the nanosecond range has been reported for 4-dialkylaminoazobenzenes after laser excitation [9].

Energy transfer methods have been used to characterize the lowest triplet states of *trans*- and *cis*-AB. Both the energy and the geometrical distortion were determined by measuring the bimolecular rate parameters for the triplet energy transfer from aromatic compounds used as sensitizers of isomeric ABs [10].

The aim of the present work is to obtain information about the role of ring substituents in determining the properties of the lowest triplet states of AB derivatives. The influence of both donor and acceptor groups was investigated by energy transfer. A comparison of the behaviour of the AB derivatives with that of the parent compound was used to characterize the energy and geometrical distortion of their lowest triplet states.

## 2. Experimental details and results

The AB derivatives 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-AB, 4-NO<sub>2</sub>-AB, 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-NO<sub>2</sub>-AB, 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-OCH<sub>3</sub>-AB, all in the *trans* form, were synthesized by Aziende Colori Nazionali Affini, Italy, and were further purified by column chromatography [5, 7]. All the sensitizers were of the purest grade commercially available. Fluorometric grade benzene (RS, Carlo Erba) was used as received.

Benzene solutions of the sensitizer containing variable amounts of azo compounds were sealed under vacuum after repeated freeze-pump-thaw cycles. The concentration of the sensitizer was adjusted to give an absorbance of about 0.5 at 337 nm. Sample preparation was performed in red light to avoid the occurrence of photoreactions.

The rate constants for quenching of the triplet state of the sensitizer by azo compounds were obtained using a laser flash photolysis apparatus based on a Lambda Physik nitrogen laser (wavelength, 337.1 nm; full width at half-maximum, 3.5 ns; power, 1 MW). Further details are reported elsewhere [10]. Some of the triplet donors displayed mixed first- and second-order decay kinetics under the conditions used. In these cases the intensity of the excitation pulse was reduced. In all cases the addition of sufficient amounts of quencher caused the decays to become pseudo first order.

The first-order rate constant  $k$ , which was obtained by a best-fitting procedure based on the least-squares method, was found to depend on the concentration of the azo dye according to the equation

$$k = k^0 + k_q[\text{azo dye}] \quad (1)$$

where  $k^0$  is the first-order rate constant in the absence of the azo dye and  $k_q$  is the bimolecular rate constant for energy transfer. Values of  $k_q$  obtained from plots of  $k$  versus [azo dye] for various sensitizers are given in Table 1. Figure 1 shows the plots of  $\log k_q$  versus the triplet energy  $E_T^D$  of the donor. Curves a, b and c represent the fitting of the experimental data on the basis of the treatment described in Section 3. Curve d represents the schematized experimental energy transfer behaviour of *trans*-AB taken from ref. 10.

TABLE 1

Measured rate constants for energy transfer to substituted azobenzenes in benzene solution at 22 °C

Donor	$E_T^D$ (kcal mol <sup>-1</sup> )	$k_q^a$ (M <sup>-1</sup> s <sup>-1</sup> ) for the following compounds			
		4-NO <sub>2</sub> -AB	4-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> -AB	4-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> -4'-OCH <sub>3</sub> -AB	4-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> -4'-NO <sub>2</sub> -AB
Chrysenes	56.6	5.7 × 10 <sup>9</sup>	5.5 × 10 <sup>9</sup>	—	6.0 × 10 <sup>9</sup>
Acridine	45.3	4.1 × 10 <sup>9</sup>	4.8 × 10 <sup>9</sup>	5.2 × 10 <sup>9</sup>	4.8 × 10 <sup>9</sup>
Anthracene	42.6	—	3.5 × 10 <sup>9</sup>	3.5 × 10 <sup>9</sup>	4.4 × 10 <sup>9</sup>
9,10-dibromoanthracene	40.2	1.6 × 10 <sup>9</sup>	2.0 × 10 <sup>9</sup>	1.4 × 10 <sup>9</sup>	4.3 × 10 <sup>9</sup>
Perylene <sup>b</sup>	36.0	3.2 × 10 <sup>8</sup>	2.0 × 10 <sup>8</sup>	—	2.1 × 10 <sup>9</sup>
3,4,8,9-dibenzopyrene	34.4	7.9 × 10 <sup>7</sup>	8.7 × 10 <sup>7</sup>	1.2 × 10 <sup>8</sup>	1.5 × 10 <sup>9</sup>
Anthanthrene	33.8	—	—	—	1.1 × 10 <sup>9</sup>
Tetracene	29.6	—	—	—	≤ 1.0 × 10 <sup>8</sup>

<sup>a</sup>The  $k_q$  values were measured with a precision of about 15%.<sup>b</sup>Sensitized by benzophenone.

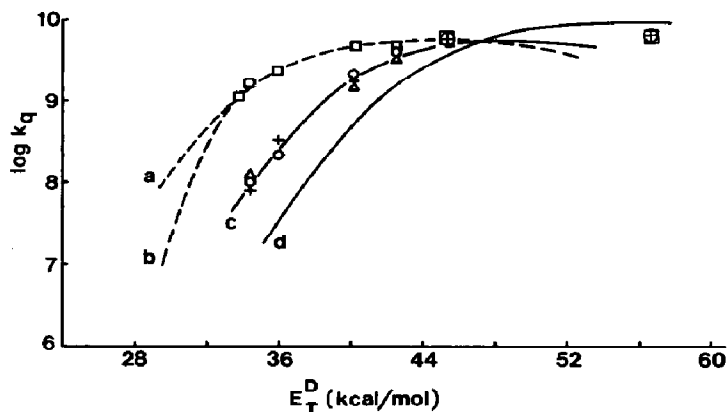
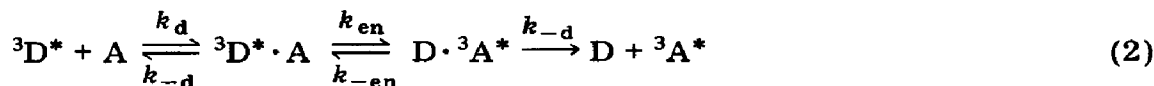


Fig. 1. Plots of  $\log k_q$  vs.  $E_T^D$  for the energy transfer process from aromatic triplets to substituted ABs ( $\square$ , 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-NO<sub>2</sub>-AB;  $\circ$ , 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-AB;  $\triangle$ , 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-OCH<sub>3</sub>-AB; +, 4-NO<sub>2</sub>-AB): curve a, calculated according to eqn. (3) for an acceptor triplet energy of 28 kcal mol<sup>-1</sup>; curve b, calculated according to eqn. (3) for an acceptor triplet energy of 33 kcal mol<sup>-1</sup>; curve c, calculated according to eqn. (3) for an acceptor triplet energy of 34 kcal mol<sup>-1</sup>; curve d, schematized energy transfer behaviour of *trans*-AB taken from ref. 10. The calculated curves show a decrease at high donor energies owing to the decrease in the Franck-Condon factors. The model takes into account only the lowest triplet state of the acceptor, whereas higher electronic triplet states take over the energy transfer process experimentally.

### 3. Discussion

A comparison of the dependence of the quenching rate constants on  $E_T^D$  for the substituted ABs with that for AB suggests that the same mechanism, *i.e.* energy transfer, operates in all cases. The process can be schematized as follows [11, 12]:



The quenching rate constant is then given by

$$k_q = \frac{k_d}{1 + k_{-d}/k_{en} + \exp(\Delta\bar{G}/RT)} \quad (3)$$

where  $\Delta\bar{G}$  is the change in the free energy of the energy transfer step (in most cases  $\Delta\bar{G}$  can be assumed to be equal to the triplet energy difference  $\Delta\bar{E}_T$  between the acceptor and the donor). The term  $k_{-d}/k_{en}$  accounts for the so-called "non-classical" behaviour exhibited by molecules with strongly distorted excited states. Typical examples are metallocenes [13],  $\alpha$ -diketones [14], olefins [15] and the isomeric ABs [10]. Equation (3) has been successfully applied to the description of energy transfer quenching rates in all the above cases [10 - 12].

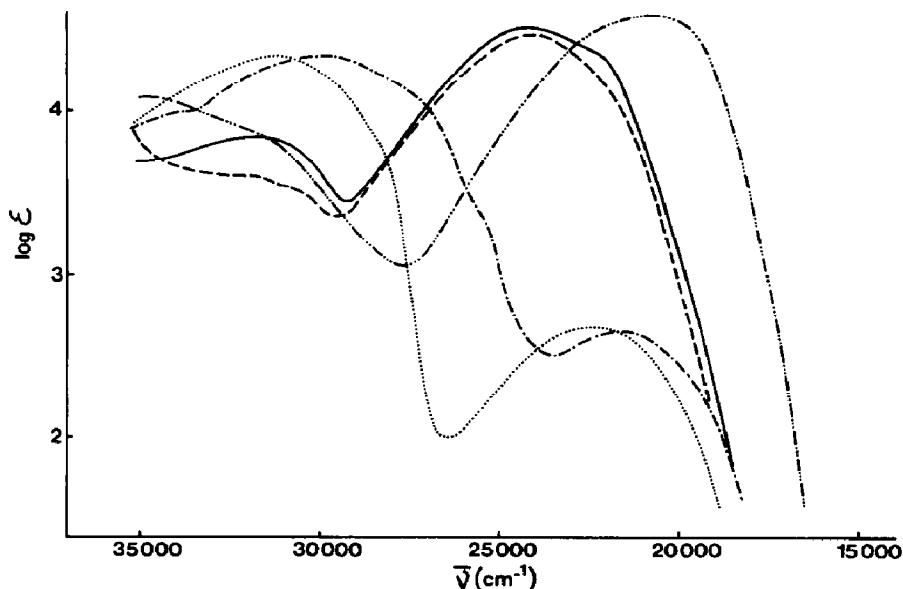


Fig. 2. Absorption spectra of the substituted ABs in benzene solution: ·····, *trans*-AB; -·-·-·, 4-NO<sub>2</sub>-AB; ---, 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-AB; —, 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-OCH<sub>3</sub>-AB; - - - - , 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-NO<sub>2</sub>-AB.

$k_{\text{en}}$  can be calculated using a quantum mechanical approach [10, 12] derived from the Ulstrup-Jortner theory of electron transfer [16]. The energy transfer process is described as a non-radiative decay of a supermolecule consisting of the donor and the acceptor. From the above model,  $k_{\text{en}}$  is given by

$$k_{\text{en}} = V^2 N \quad (4)$$

where  $V$  is the electron exchange interaction between D\* and A in the encounter and  $N$  is the Franck-Condon factor for the energy transfer step. If the relevant information, *i.e.* the spectral properties of both the donor and the acceptor molecules, is available, the factor  $N$  can easily be calculated and eqn. (4) gives a good description of the energy transfer process [12].

The spectroscopic data for AB are poor. However, the model was satisfactorily applied by using the results of theoretical calculations [17] and the energies of the lowest triplet state of the *trans* and *cis* isomers were determined [10].

To apply the same method to the AB derivatives investigated here the electronic nature of their lowest triplets must be hypothesized. Information is available only for singlet states. On the basis of fluorescence properties the lowest excited singlet states of the 4-dialkylamino derivatives have been reported to have  $n, \pi^*$  character [18]. The electronic spectrum of 4-NO<sub>2</sub>-AB clearly shows the  $^1(n, \pi^*)$  band as the lowest energy transition (Fig. 2). Therefore we assumed as a working hypothesis that the lowest triplet in all the compounds has  $n, \pi^*$  character as in AB.

The  $S_0 \rightarrow T_1$  absorption band of the acceptor is characterized by low frequency modes only ( $\hbar\omega_A < kT$ ). This reflects the absence of any structure even in a dilute mixed crystal at very low temperatures [19]. These modes, which are assumed to be harmonic and undistorted, can be described cumulatively by a reorganization parameter  $E_s$ . The  $T_1 \rightarrow S_0$  emission band of the donor is described by only one high frequency vibration ( $\hbar\omega_D > kT$ ), *i.e.* the totally symmetric stretching of the C=C bond. This vibration is assumed to be harmonic and undistorted with a displacement parameter  $\gamma_D$ . A gaussian lineshape defined by the parameter  $\Delta$  is attributed to each vibronic band to account for all the other low frequency modes and for the inhomogeneous broadening of the vibrational structure.

When the above model is assumed (for further details see refs. 10 and 12), the factor  $N$  can be calculated using the expression

$$N = \left\{ \frac{\pi\beta}{\hbar^2(E_s + \Delta)} \right\}^{1/2} \exp(-\gamma_D) \sum_{v_D=0}^{\infty} (v_D!)^{-1} \gamma_D^{v_D} \exp(-\beta v_D \hbar\omega_D) \times \\ \times \exp \left[ - \left\{ \frac{\beta}{4(E_s + \Delta)} \right\} \{ -\overline{\Delta E_T} - (E_s + \Delta - v_D \hbar\omega_D) \}^2 \right] \quad (5)$$

where  $\overline{\Delta E_T}$  is the triplet energy difference between the acceptor and the donor,  $v_D$  is the vibrational quantum number and  $\beta = 1/kT$ . As in ref. 10 the quantities appearing in eqns. (3) - (5) have been assumed to be as follows:  $k_a = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{-a} = 1.2k_a$ ;  $V = 8 \text{ cm}^{-1}$ ;  $\hbar\omega_D = 1400 \text{ cm}^{-1}$ ;  $\gamma_D = 1.2$ ;  $\Delta = 150 \text{ cm}^{-1}$ .

The lowest  $^3(n,\pi^*)$  state for *trans*-AB [10] was very distorted ( $E_s = 4700 \text{ cm}^{-1}$ ) with  $E_T = 35 \text{ kcal mol}^{-1}$ . Equation (3) fits the experimental rate constants for 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-AB, 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-OCH<sub>3</sub>-AB and 4-NO<sub>2</sub>-AB (Fig. 1, curve c) when the values  $E_T = 34 \text{ kcal mol}^{-1}$  and  $E_s = 4000 \text{ cm}^{-1}$  are attributed to their triplet states. The results obtained are very similar to those for the lowest  $^3(n,\pi^*)$  state of *trans*-AB. As already discussed in ref. 10, there is a correlation between  $E_T$  and  $E_s$  so that the value found for  $E_T$  is only reliable for a good estimate of  $E_s$  from the spectra. Since neither the energy nor the shape of the potential energy surface of an  $n,\pi^*$  state is expected to be much affected by ring substitution in the *para* position, the results obtained for the above azo derivatives appear to be reliable.

The result for 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-NO<sub>2</sub>-AB is somewhat different. The quenching rate parameters retain nearly the values for diffusion control for donors with  $E_T^D$  in the range 33 - 36 kcal mol<sup>-1</sup>. Unfortunately, with tetracene ( $E_T^D = 29.6 \text{ kcal mol}^{-1}$ ) as donor no reliable values for  $k_q$  can be given because the strong absorption of the dye in the wavelength range useful for the detection of tetracene triplet-triplet absorption prevents sufficient amounts of quencher from being used. On the basis of the experiments carried out, we can only assign an upper limit of  $10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the value of  $k_q$ .

If the true value for  $k_q$  is  $10^8 \text{ M}^{-1} \text{ s}^{-1}$ , the triplet state energy of the dye decreases to  $28 \text{ kcal mol}^{-1}$  and the distortion parameter remains  $4000 \text{ cm}^{-1}$  (Fig. 1, curve a). The situation is very similar to that of the monosubstituted compounds, the lowering of the state energy probably being due to the introduction of strongly conjugated groups.

However, let us suppose that the value of  $k_q$  is much lower than  $10^8 \text{ M}^{-1} \text{ s}^{-1}$ , e.g.  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ . The triplet state energy is almost unchanged, i.e.  $33 \text{ kcal mol}^{-1}$ , but the distortion parameter  $E_s$  is reduced to  $1850 \text{ cm}^{-1}$  (Fig. 1, curve b). This is not consistent with  $n, \pi^*$  character for the triplet state and suggests a  $\pi, \pi^*$  electronic configuration. In this hypothesis, the factor  $N$  is calculated by attributing a high frequency vibration [12] to the acceptor  $S_0 \rightarrow T_1$  transition. The prominent feature of the  $\pi, \pi^*$  band is in fact the N=N stretching mode ( $\hbar\omega_A = 1340 \text{ cm}^{-1}$  [19]). As in ref. 12 for the corresponding stilbene transition, the typical value  $\gamma_A = 2$  was assumed, which is justified by the close similarity of the two band profiles [19]. The data were then fitted with the same energy value ( $33 \text{ kcal mol}^{-1}$ ) but with a smaller distortion parameter of  $700 \text{ cm}^{-1}$ . The magnitude of  $E_s$  was then in agreement with the expected features for a  $^3(\pi, \pi^*)$  potential energy surface. The difference with the value found for *trans*-stilbene ( $E_s = 300 \text{ cm}^{-1}$ ) [12] is due to the different contribution of the low energy modes, as is clearly evident from a comparison of the stilbene and azobenzene  $^1(\pi, \pi^*)$  absorption bands [19].

It is interesting to note that 4-dialkylamino-4'-nitroazobenzenes are the only azo dyes which exhibit  $T_n \leftarrow T_1$  absorption. This behaviour has been attributed to  $\pi, \pi^*$  character of their lowest triplet state [9]. Moreover, preliminary complete neglect of differential overlap/spectroscopic calculations show an inversion of the order of the  $^3(\pi, \pi^*)$  and  $^3(n, \pi^*)$  states in 4-NH<sub>2</sub>-4'-NO<sub>2</sub>-AB with respect to AB and 4-NH<sub>2</sub>-AB [20]. This is due to a substantial lowering of the  $\pi, \pi^*$  triplet energy owing to the intramolecular charge transfer interaction between the strongly conjugated substituents.

On the basis of the experimental and theoretical results presented here we are inclined to assign  $\pi, \pi^*$  character to the lowest triplet state of 4-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-4'-NO<sub>2</sub>-AB with an energy of about  $33 \text{ kcal mol}^{-1}$  and a low degree of geometrical distortion.

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## References

- 1 J. Fabian and H. Hartmann, *Light Absorption of Organic Colorants*, Springer, Berlin, 1980, Chap. 7.

- 2 G. Zimmermann, L. Y. Chow and U. J. Paik, *J. Am. Chem. Soc.*, **80** (1958) 3528.
- 3 G. Irick, Jr., and G. Pacifici, *Tetrahedron Lett.*, (17) (1969) 1303.
- 4 P. Bortolus and S. Monti, *J. Phys. Chem.*, **83** (1979) 648, and references cited therein.
- 5 A. Albin, E. Fasani and S. Pietra, *J. Chem. Soc., Perkin Trans. II*, (1983) 1021.
- 6 P. D. Wildes, J. C. Pacifici, G. Irick, Jr., and D. G. Whitten, *J. Am. Chem. Soc.*, **93** (1971) 2004.
- 7 A. Albin, E. Fasani and S. Pietra, *J. Chem. Soc., Perkin Trans. II*, (1982) 1393.
- 8 H. Rau, *Angew. Chem., Int. Edn. Engl.*, **12** (1973) 224.
- 9 H. Görner, H. Gruen and D. Schulte-Frohlinde, *J. Phys. Chem.*, **84** (1980) 3031.
- 10 S. Monti, E. Gardini, P. Bortolus and E. Amouyal, *Chem. Phys. Lett.*, **77** (1981) 115.
- 11 V. Balzani, F. Bolletta and V. Scandola, *J. Am. Chem. Soc.*, **102** (1980) 2152.
- 12 G. Orlandi, S. Monti, F. Barigelletti and V. Balzani, *Chem. Phys.*, **52** (1980) 313.
- 13 W. G. Herkstroeter, *J. Am. Chem. Soc.*, **97** (1975) 4161.  
A. Farmilo and F. Wilkinson, *Chem. Phys. Lett.*, **34** (1975) 575.  
A. P. Chapple, J. P. Vikesland and F. Wilkinson, *Chem. Phys. Lett.*, **50** (1977) 81.
- 14 K. Sandros, *Acta Chem. Scand.*, **27** (1973) 3021.
- 15 W. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88** (1966) 4769.
- 16 J. Ulstrup and J. Jortner, *J. Chem. Phys.*, **63** (1975) 4358.
- 17 S. Monti, G. Orlandi and P. Palmieri, *Chem. Phys.*, **71** (1982) 87.
- 18 H. Bisle, M. Römer and H. Rau, *Ber. Bunsenges. Phys. Chem.*, **80** (1976) 301.
- 19 R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36** (1962) 2326.
- 20 G. Marconi and S. Monti, unpublished results.