Dyes and Pigments **15** (1991) 129–137

Studies on the UV–Vis Absorption Spectra of Azo Dyes: Part 25.‡ Analysis of the Fine Structure of the $\pi_1 \rightarrow \pi_1^*$ Band of 4′-Donor-Substituted 4-*N*,*N*-Diethylaminoazobenzenes

Heinz Mustroph

Filmfabrik Wolfen AG, Direktorat Forschung und Entwicklung, Wolfen 4440, Germany

(Received 24 March 1990; accepted 30 April 1990)

ABSTRACT

*The electronic absorption spectra of 4′-donor-substituted 4-*N,N*-diethylaminoazobenzenes in *n*-hexane at room temperature have been measured. The* $\pi_1 \rightarrow \pi_1^*$ *band exhibits a vibrational fine structure. Systematic variation of the substituents allows assignments to be made for these sub-bands. The first sub-band is due to a vibronic transition from the ground state to the planar excited state. The intense second sub-band represents the N=N stretching vibronic transition between the ground state and a planar vibrational excited state. The third sub-band is attributed to torsional vibrations around the Ph—N(=) bonds in the excited state. Only this vibronic transition enables coupling to occur between the* n_s, π_1^* *singlet state and the* π_1, π_1^* *singlet state, resulting in the 'borrowing' of intensity by the* $n_s \rightarrow \pi_1^*$ *band from the* $\pi_1 \rightarrow \pi_1^*$ *band.*

1 INTRODUCTION

The absorption spectrum of azobenzene exhibits three regions of absorption. Jaffé *et al.*[1] made assignments for these bands on the basis of MO theory and, with some modifications, this is currently the principal accepted theory.[2–5] Both the highest occupied π-MO (π_1) and the lowest unoccupied π^*-MO (π_1^*) are delocalized across the whole molecule, and the intense 318 nm band is due to the $\pi_1 \rightarrow \pi_1^*$ transition. The other π-MOs (π_2–π_7) and π^*-MOs (π_2^*–π_7^*) are localized in the benzene rings. The bands in

---

‡ For Part 24 see Mustroph, H. & Gussmann, F., *J. Prakt. Chem.*, **332** (1990) 93.

Dyes and Pigments 0143-7208/91/$03·50

the region 210–290 nm are due to locally excited $\pi_i \rightarrow \pi_j^*$ transitions in the benzene rings (Jaffé *et al.* referred to these as $\phi \rightarrow \phi^*$ transitions).

Furthermore, there are two lone-pair orbitals on the two nitrogen atoms of the azo group. These lone-pair orbitals overlap, giving rise to splitting of the originally degenerate n orbitals. The higher-energy orbital is the symmetric combination (n_s) and the lower-energy orbital is the anti-symmetric combination (n_a). The weak band at 440 nm is due to the $n_s \rightarrow \pi_1^*$ transition. This transition is symmetry-forbidden but the intensity is unusually high. This was explained by vibronic interactions facilitating coupling between the n_s, π_1^* state and the π_1, π_1^* state, thus resulting in the 'borrowing' of intensity by the $n_s \rightarrow \pi_1^*$ transition from the $\pi_1 \rightarrow \pi_1^*$ transition.

For azobenzene and its alkyl, alkoxy and other acceptor-substituted derivatives, this interpretation is now accepted.[2–5] In these cases the three regions of absorption are well resolved. However, because of the strong electron-donating effect of a 4-dialkylamino or 4-amino group, the $\pi_1 \rightarrow \pi_1^*$ band undergoes a large bathochromic shift, and the exact position of the $n_s \rightarrow \pi_1^*$ band cannot be detected in the spectrum. Calculations using the extended PPP method, including the n-electrons,[6] predict that, for 4-*N*,*N*-dimethylaminoazobenzene, the $n_s \rightarrow \pi_1^*$ band is located at the same position as in azobenzene itself. The low-intensity shoulder on the long-wavelength side of the $\pi_1 \rightarrow \pi_1^*$ band (see Fig. 1) is often, therefore, interpreted as the $n_s \rightarrow \pi_1^*$ band.[6–8] This interpretation is supported by the $n_s \leftarrow \pi_1^*$ fluorescence of 4-aminoazobenzenes[7] and of sterically hindered azobenzenes.[9]

On the other hand, resonance Raman excitation profiles (REP) of acceptor-substituted 4-dialkylaminoazobenzenes definitely establish that the visible absorption spectrum of these dyes consists of at least two overlapping transitions with different geometries, which are each independently coupled to different regions of the visible absorption spectrum.[10–12] The REP data were interpreted as indicating that these transitions are due to an $n_s \rightarrow \pi_1^*$ transition at shorter wavelengths and an amine–ring charge-transfer transition at longer wavelengths (authors differ between a $\pi_1 \rightarrow \pi_1^*$ transition in azobenzene itself and an amine–ring charge-transfer transition in 4-aminoazobenzenes, but in both cases it is the $\pi_1 \rightarrow \pi_1^*$ transition[2–5] with different weights of CT configurations[13]).

Furthermore, 4,4′-bis-*N*,*N*-diethylaminoazobenzene exhibits an intense fluorescence in 2-methyltetrahydrofuran at 77 K.[14] The absorption and the fluorescence excitation spectra are identical, and the fluorescence and the fluorescence excitation spectra are mutually mirror-symmetrical. These results are typical of a $\pi \leftarrow \pi^*$ fluorescence. With decreasing temperature, the sub-bands in the absorption spectrum of this dye become sharp and an $n_s \rightarrow \pi_1^*$ band is not detectable. On the basis of these results, the first absorption band is interpreted as a pure $\pi_1 \rightarrow \pi_1^*$ transition.[14]

It is evident, therefore, that some experimental results can lead to different interpretations. To overcome this problem, new 4-aminoazobenzenes have been synthesized to investigate the absorption spectra of azobenzenes more systematically.

2 RESULTS AND DISCUSSION

The absorption spectrum of 4-*N*,*N*-diethylaminoazobenzene (**1a**) in *n*-hexane exhibits a vibrational fine structure (Fig. 1, Table 1). With increasing electron-donating ability of R (**1b**–**1d**) the intensity of the longest-wavelength shoulder at 430 nm increases considerably (Fig. 1).

The first sub-band is assigned as a 0 → 0 transition. From increasing intensity of the 0 → 0 transition it is possible to deduce that the displacement of the ground and first excited state Morse curves will slightly increase with increasing electron-donating ability of R, i.e. the excited state differs progressively less from the ground state in geometry.

In PPP calculations of azobenzenes it is assumed that azobenzene is planar and this simplification allows the prediction of absorption maxima.[15–18] However, Traetteberg *et al.*[19] have shown that gaseous azobenzene has a dihedral angle of 28° or 30° between the rings and there is also some question as to the degree of planarity of azobenzene in solution. Some evidence suggests that the phenyl rings are twisted in solution.[20] This is in accord with results of crystal structure studies.[21] Also, azobenzene shows no evidence of vibrational fine structure, even when its spectrum is measured in the vapour phase or at low temperature.[22] Quantum chemical

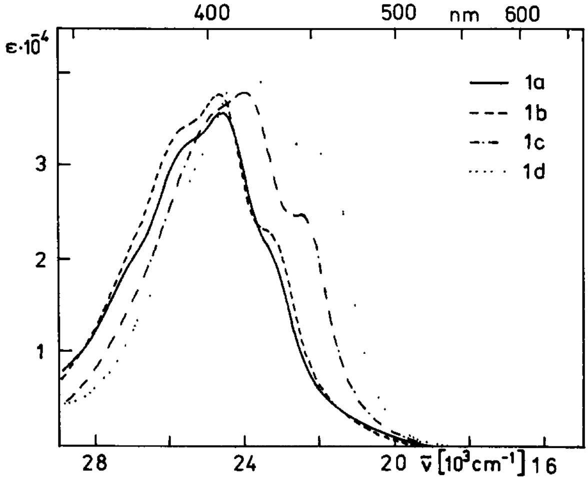


Fig. 1. Visible absorption bands of dyes **1a**–**1d** in *n*-hexane.

TABLE 1
Electronic Spectral Data of Dyes **1–5** in *n*-Hexane

Number	λ_{max} (*nm*)	ε_{max}	λ_{max} (*nm*)	ε_{max}	λ_{max} (*nm*)	ε_{max}
1a	391	32 100	407	35 500	430	19 300
1b	390	34 300	406	37 500	430	23 100
1c	403	35 100	417	37 500	443	24 500
1d	415	39 200	431	39 800	459	31 800
2	420	37 400	438	39 700	466	34 200
3	445	30 100	464	41 900	490	40 200
4	430	37 900	448	36 100	478	28 800
5	405	33 600	424	29 500	452	14 900

calculations, however, show that with increasing electron-donating ability of the substituents the π-bond orders of the C—N(=) bonds increase and, therefore, the planar or nearly planar conformation should be favoured. The well resolved vibrational fine structure of the $\pi_1 \rightarrow \pi_1$ band of **1d** supports the idea that the ground state of this dye is planar.[14] Thus, the $0 \rightarrow 0$ transition is due to a transition from the planar ground state to the planar conformation of the excited state.

It can be assumed that the intense second sub-band represents the N=N stretching vibrational–electronic (vibronic) transition between the ground state and a planar vibrational excited state. This interpretation is supported by the similarity of the resonance Raman vibrational frequencies of the N=N stretching vibration ($\tilde{\nu} \approx 1400\,\mathrm{cm}^{-1}$)[10–12,23] and the differences between the first two absorption maxima (Table 1).

Previous experimental results have led to different interpretations of the nature of the third sub-band. In these present investigations 4,4′-bis-*N*,*N*-diethylaminoazobenzene (**1d**) was chosen because it exhibits a well defined absorption spectrum (Fig. 1).

With lowering of temperature, the relative intensity of the $0 \rightarrow 0$ transition increases, whereas the intensity of the $0 \rightarrow 2$ transition decreases.[14] In a glassy solution at low temperature torsional vibrations should be hindered and a planar or nearly planar structure should be favoured.

A similar result is observed on increasing the polarity of the solvents (Fig. 2). In polar solvents, there are strong solvent–solute interactions; a rigid solvent cage is formed, resulting in a planar or nearly planar conformation of the dye. These interactions originate from the two diethylamino groups, which increase the basicity of the azo group.

Therefore, we can assume that the $0 \rightarrow 2$ vibronic transition is due to torsional vibrations. However, there are at least two possibilities, viz.

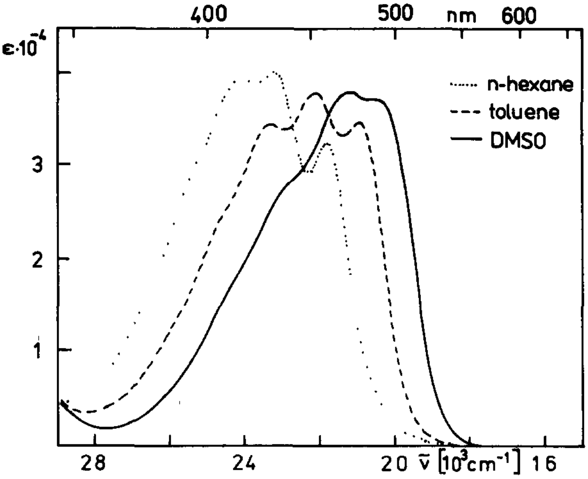


Fig. 2. Visible absorption bands of dye **1d** in *n*-hexane, toluene and DMSO.

torsional vibrations around the Ph—N(=) or around the Ph—NEt$_2$ bonds. In order to differentiate between these possibilities, dyes **2** and **3** were synthesized. In **2** both amino groups are fixed, and in **3** a phenyl ring is fixed via a hydrogen bond.[24] In comparison with **1d** the spectrum of **2** exhibits only the pure substituent effect (Fig. 3). The absorption maxima are shifted bathochromically and the intensity of the 0→0 transition is increased slightly (according to the expected substituent effects). Only where a phenyl ring is fixed in the plane of the azo group (**3**) does the relative intensity of the 0→2 transition decrease significantly (Fig. 3).

The sterical hindered dyes **4** and **5** support this result. With increasing

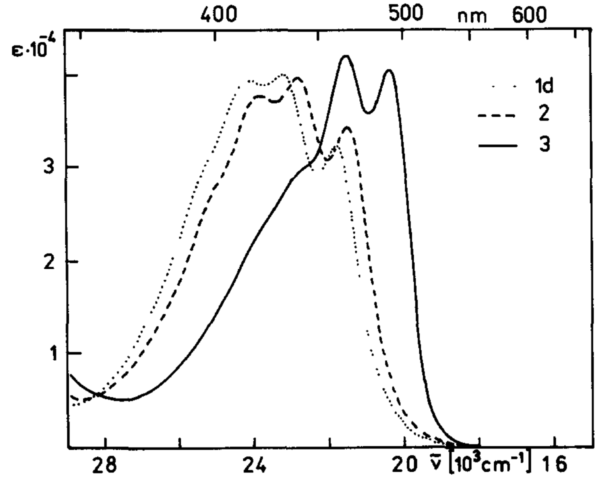
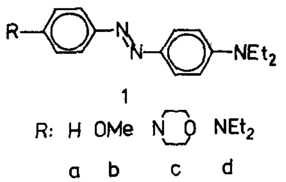
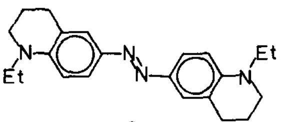


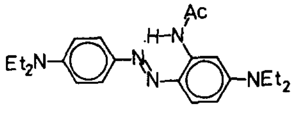
Fig. 3. Visible absorption bands of dyes **1d**, **2** and **3** in *n*-hexane.



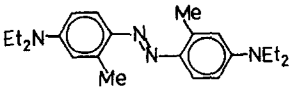
1



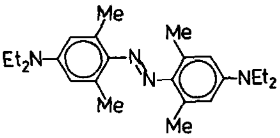
2



3



4



5

steric hindrance of the phenyl rings the relative intensity of the 0→0 and 0→1 vibronic transitions decreases (Fig. 4). Substituent effects on the absorption maxima are in accord with those reported for *o*-alkylazobenzenes,[9,20] namely a bathochromic shift for 2,2′-dimethyl substitution and a hypsochromic shift for 2,2′,6,6′-tetramethyl substitution.

Therefore, the 0→2 vibronic transition is due to torsional vibrations around the Ph—N(=) bonds in the first excited singlet state. Only this vibronic transition enables coupling to occur between the n_s, π_1^* singlet state and the π_1, π_1^* singlet state, resulting in the 'borrowing' of intensity by the

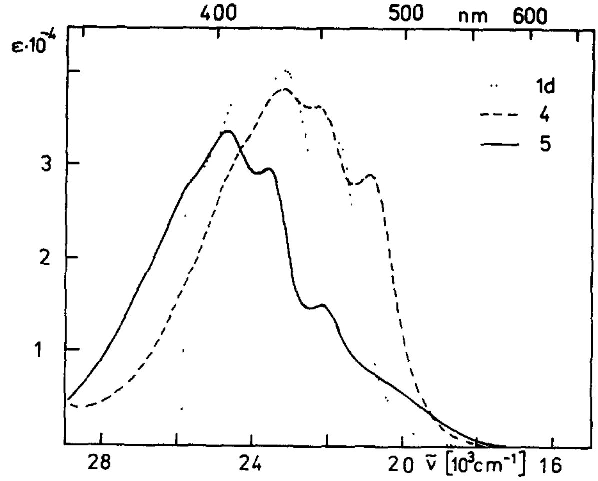


Fig. 4. Visible absorption bands of dyes **1d**, **4** and **5** in *n*-hexane.

$n_s \rightarrow \pi_1^*$ band from the $\pi_1 \rightarrow \pi_1^*$ band. This transition is, however, not the $n_s \rightarrow \pi_1^*$ transition itself, as was concluded from results of resonance Raman excitation profiles;[10−12] it mixes with the n_s, π_1^* state and, if the n_s, π_1^* state participates in the π_1, π_1^* state, the π_1, π_1^* state has to participate also in the n_s, π_1^* state. Thus, the vibronic 0 → 2 transition should be a mixture of both states.

It may be anticipated that the intensity of the $n_s \rightarrow \pi_1^*$ band would depend on the intensity of the 0 → 2 vibronic $\pi_1 \rightarrow \pi_1^*$ transition. With increasing relative intensity of the latter, the intensity of the $n_s \rightarrow \pi_1^*$ transition should also increase. All substituents which reduce the planarity also increase the intensity of the $n_s \rightarrow \pi_1^*$ band. This is confirmed experimentally in sterically hindered alkyl-substituted azobenzenes.[9,20] In contrast to dyes **1d** and **4**, the absorption spectrum of the sterically hindered dye **5** exhibits a long-wavelength shoulder at 480 nm (Fig. 4). This could be due to the $n_s \rightarrow \pi_1^*$ transition. Conversely, substituents which favour planarity should lower the intensity of the $n_s \rightarrow \pi_1^*$ band. It appears, however, that only in 4,4′-diaminoazobenzenes at low temperatures is the major form in solution the planar form. In these dyes it is not possible to detect directly the $n_s \rightarrow \pi_1^*$ band, but the $\pi_1 \leftarrow \pi_1^*$ fluorescence of **1d** proves indirectly the low intensity of the $n_s \rightarrow \pi_1^*$ band. In 2-methyltetrahydrofuran at room temperature the intensity of the 0 → 2 transition is comparable with the intensity of the 0 → 0 transition and no fluorescence is detected. On lowering the temperature, the intensity of the 0 → 2 transition decreases considerably (the intensity of the $n_s \rightarrow \pi_1^*$ transition should then be near zero) and at 77 K a strong fluorescence is observed.[14]

3 CONCLUSIONS

The $\pi_1 \rightarrow \pi_1^*$ band of 4′-donor-substituted 4-*N*,*N*-diethylaminoazobenzenes exhibits a vibrational fine structure with three sub-bands in *n*-hexane at room temperature.

The 0 → 0 transition is due to a vibronic transition from the ground state to the planar excited state, the 0 → 1 transition represents the N=N stretching vibronic transition between the ground state and a planar vibrational excited state, and the 0 → 2 transition is attributed to torsional vibrations around the Ph—N(=) bonds in the excited state. Only the last vibronic transition enables the coupling to occur between the n_s, π_1^* singlet state and the π_1, π_1^* singlet state, resulting in the 'borrowing' of intensity by the $n_s \rightarrow \pi_1^*$ band from the $\pi_1 \rightarrow \pi_1^*$ band.

Structural variations favouring the planar form increase the relative intensity of the 0 → 0 band and decrease the relative intensity of the 0 → 2 band; conversely, variations which reduce the planarity lower the relative intensity of the 0→0 band.

Factors which hinder the torsional vibrations and favour the planar or nearly planar structure include electron-donor substituents which increase proportionally to their electron-donating ability the π-bond orders of the C—N(═) bonds, *ortho*-substituents which are capable of hydrogen bonding to the azo linkage, polar solvents which form a rigid solvent cage and the lowering of the temperature. Spherical substituents (e.g. Me) *ortho* to the azo linkage, leading to steric crowding, favour the torsional vibrations.

4 EXPERIMENTAL

The preparation and physical constants for dyes **1a**, **1b** and **1d** have been previously described.[8] Dyes **2**, **4** and **5** were prepared by the method of Vorländer & Wolferts.[25]

Dye **2** was purified by column chromatography on silica gel, applying the dye from solution in toluene and eluting with toluene. Recrystallization from toluene yielded red crystals, m.p. 195–198°C.

Dye **4** was recrystallized from EtOH in dark red crystals, m.p. 144–147°C.

The crude dye **5** was freed from amines by steam distillation and the residue was chromatographed in silica gel using toluene as eluant. Recrystallization from EtOH yielded red crystals, m.p. 136–139°C.

4.1 4′-Morpholino-4-*N*,*N*-diethylaminoazobenzene, 1c

4-Morpholinobenzenediazonium tetrafluoroborate (2·77 g, 10 mmol) was dissolved in a mixture of CH_2Cl_2 (50 ml) and MeOH (50 ml). The solution was stirred and cooled to below 5°C. A solution of *N*,*N*-diethylaniline (3 g) in MeOH (10 ml) was then added with stirring. After 3 h, water (20 ml) was added and the solution was stirred for 1 h. The product was filtered, washed with warm water and dried. Recrystallization from EtOH gave yellow crystals. Yield: 0·56 g (16%), m.p. 221–222°C.

4.2 2-Acetylamido-4,4′-bis-*N*,*N*-diethylaminoazobenzene, 3

3-(*N*,*N*-Diethylamino)acetanilide (2·06 g, 10 mmol) was dissolved in MeOH (100 ml) and the solution was stirred and cooled to below 5°C. 4-*N*,*N*-Diethylaminobenzenediazonium tetrafluoroborate (2·63 g, 10 mmol) was then added with stirring and a solution of sodium acetate (2 g) in water (20 ml) was added dropwise with stirring. After 3 h, the product was filtered and recrystallized from MeOH as dark red crystals. Yield: 1·9 g (49%), m.p. 127–128°C.

Purity of the dyes was checked by TLC. Electronic absorption spectra were recorded with a Specord UV–VIS.

REFERENCES

1. Jaffé, H. H., Yeh, S.-J. & Gardner, R. W., *J. Mol. Spectrosc.*, **2** (1958) 120.
2. Griffiths, J., *Colour and Constitution of Organic Molecules.* Academic Press, London, New York and San Francisco, 1976.
3. Fabian, J. & Hartmann, H., *Light Absorption of Organic Colorants.* Springer-Verlag, Berlin, 1980.
4. Gordon, P. F. & Gregory, P., *Organic Chemistry in Colour.* Springer-Verlag, Berlin, Heidelberg and New York, 1983.
5. Zollinger, H., *Color Chemistry.* VCH Verlagsgesellschaft, Weinheim, 1987.
6. Hohlneicher, G. & Sänger, W., *The Jerusalem Symposia on Quantum Chemistry and Biochemistry,* Jerusalem, 1970, p. 193.
7. Bisle, H., Römer, M. & Rau, H., *Ber. Bunsenges. Phys. Chem.*, **80** (1976) 301.
8. Haessner, C. & Mustroph, H., *J. Prakt. Chem.*, **328** (1986) 113.
9. Bisle, H. & Rau, H., *Chem. Phys. Lett.*, **31** (1975) 264.
10. Cataliotti, R. S., Murgia, S. M., Paliani, G., Poletti, A. & Zgierski, M. Z., *J. Raman Spectrosc.*, **16** (1985) 251, 258.
11. Rava, R. P., *J. Chem. Phys.*, **87** (1987) 3758.
12. Morresi, A., Paliani, G., Santini, S. & Cataliotti, R. S., *Can. J. Spectrosc.*, **33** (1988) 69.
13. Fabian, J., *Chimia*, **32** (1978) 323.
14. Nepras, M., Lunak, S., Hrdina, R. & Fabian, J., *Chem. Phys. Lett.*, **159** (1989) 366.
15. Kogo, Y. & Kikuchi, H., *Nippon Kagaku Kaishi*, **11** (1979) 1524.
16. Mustroph, H. & Epperlein, J., *Z. Phys. Chem., Leipzig*, **261** (1980) 158.
17. Griffiths, J., *Dyes and Pigments*, **3** (1982) 211.
18. Hallas, G. & Marsden, R., *Dyes and Pigments*, **6** (1985) 463.
19. Traetteberg, M., Hilmo, I. & Hagen, K., *J. Mol. Struct.*, **39** (1977) 231.
20. Forber, C. L., Kelusky, E. C., Bunce, N. J. & Zerner, M. C., *J. Am. Chem. Soc.*, **107** (1985) 5884.
21. Brown, C. J., *Acta Crystallogr.*, **21** (1966) 146.
22. Rau, H. & Kortüm, G., *Ber. Bunsenges. Phys. Chem.*, **71** (1967) 664.
23. Kyziol, J. B. & Frej, H., *Chem. Papers*, **42** (1988) 781.
24. Gregory, P. & Thorp, D., *J. Chem. Soc., Perkin Trans. I* (1979) 1990.
25. Vorländer, D. & Wolferts, E., *Ber. Dtsch. Chem. Ges.*, **56** (1923) 1229.