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Studies on UV/Vis Absorption Spectra of Azo Dyes. Part 26.* Electronic Absorption Spectra of 4,4′-Diaminoazobenzenes

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ABSTRACT

The electronic absorption spectra of twelve 4,4′-diaminoazobenzenes in n-*hexane at room temperature have been measured. With increasing electron-donating ability of the substituents, the absorption maxima are shifted bathochromically, the vibronic fine structure of the* $\pi_1 \rightarrow \pi_1^*$ *band is better resolved and the relative intensity of the vibronic* $0 \rightarrow 0$ *subband increases. HMO calculations show that with increasing electron donating ability of the substituents the π-bond order of the C—N(=) bonds increases, resulting in a hindrance of rotation and twisting of the phenyl rings, which simplifies the population of rotational states of the ground state and decreases torsional angles in the ground state. Reduction of rotation causes the well-resolved fine structure, and decreasing torsional angles lead to a higher intensity of the vibronic* $0 \rightarrow 0$ *subband.*

1 INTRODUCTION

The $\pi_1 \rightarrow \pi_1^*$ band of 4,4′-bis-*NN*-diethylaminoazobenzene exhibits a well-resolved vibrational fine structure with three subbands in *n*-hexane at room temperature.[1,2] The first subband is due to a vibronic transition from the vibrational ground state of the electronic ground state to the planar vibrational ground state of the electronic excited state. The second subband represents the N=N stretching vibronic transition between the ground state and a planar vibrational excited state of the electronic excited state and the

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* For part 25 see Ref. 1.

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third subband is attributed to torsional vibrations around the Ph—N(=) bonds in the electronic excited state.[1] In this connection the measurement of the electronic spectra of a number of different 4,4′-diaminoazobenzenes becomes of interest because of a possible relationship between the effects of substituents on the vibrational fine structure of the $\pi_1 \rightarrow \pi_1^*$ band.

Although substituent effects on the $\pi_1 \rightarrow \pi_1^*$ band of azobenzenes have been the subject of a considerable amount of work[3–15] there are no systematical investigations on the absorption spectra of 4,4′-diaminoazobenzenes. Therefore, this paper is concerned with the preparation of various 4,4′-diaminoazobenzenes and with the correlation of the electronic effects of the different amino substituents with the vibrational fine structure of the $\pi_1 \rightarrow \pi_1^*$ band.

2 RESULTS AND DISCUSSION

Comparison with the absorption maxima of various 4-aminoazobenzenes[16,17] reveals that the electron-donating ability decreases in the order pyrrolidino ≈ diethylamino > dimethylamino > piperidino > morpholino. These substituent effects arise from a combination of the different -I effect of the N-alkyl chains and alicyclic ring systems, respectively, and from steric factors. The inductive effect of the alkyl groups can be described by the Taft σ^*-values. The pK_a-values of tertiary amines give an excellent correlation with the sum of the σ^*-values of the alkyl groups and the cycloalkyl groups, respectively. The σ^*-values increase in the order[18] pyrrolidino

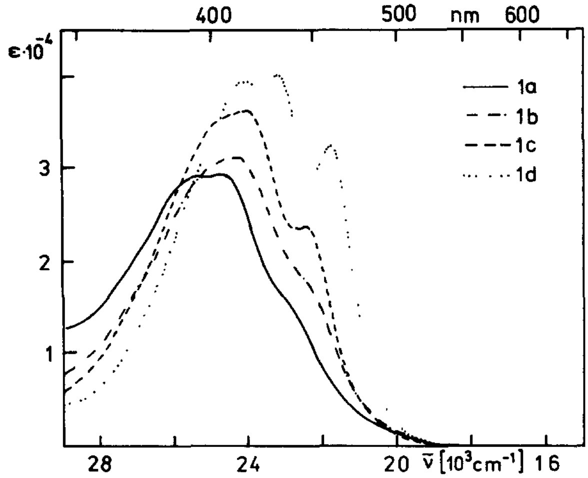
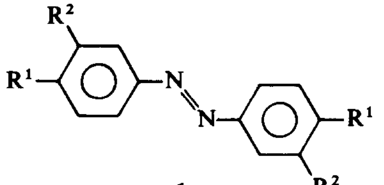


Fig. 1. Visible absorption bands of dye **1a** in cyclohexane and of dyes **1b**–**1d** in *n*-hexane.



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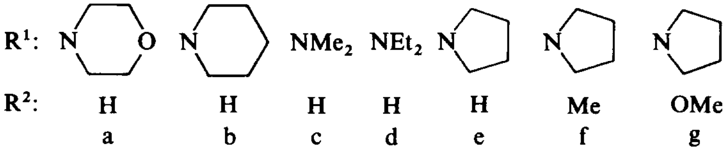

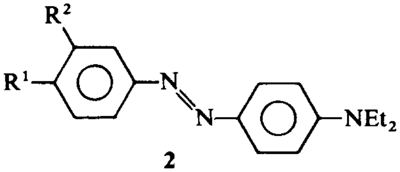

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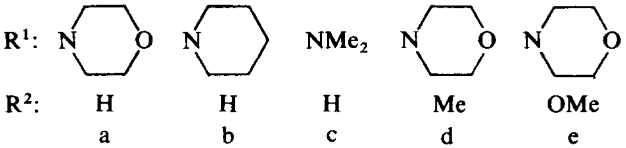

($\sigma^* = -0{\cdot}26$) < diethylamino ($\Sigma\sigma^* = -0{\cdot}20$) < piperidino ($\sigma^* = -0{\cdot}18$) < dimethylamino ($\Sigma\sigma^* = 0{\cdot}0$) < morpholino ($\sigma^* = 0{\cdot}67$).

The difference in absorption maxima between the piperidino and pyrrolidino dyes is due to steric effects.[16,17] It was shown that the steric requirements of the various six-membered rings are effectively constant,[17] and therefore the difference of the piperidino and morpholino dyes can be due to the -I effects of the alicyclic rings.

The sequence of absorption maxima of 4,4′-diaminoazobenzenes is the same as that deduced from an examination of the 4-aminoazobenzenes (Table 1). Furthermore, the sequence of absorption maxima is the same as that of the intensity of the 0 → 0 transition (Table 1, Fig. 1). With increasing electron-donating ability of substituents, the relative intensity of the 0 → 0 band increases, and the vibronic fine structure is better resolved (Fig. 1).

A methyl group ortho to a terminal amino group hinders this group and causes a hypsochromic shift and a reduction in intensity.[19] However, a methoxy group ortho to a terminal amino group produces a bathochromic shift.[20] Thus, there are other factors which can influence the electronic effect of dialkylamino groups. Absorption maxima, intensity of the 0 → 0 transition and vibronic fine structure of the $\pi_1 \rightarrow \pi_1^*$ band of the dyes **1e**–**1g** show that the expected effects are observed (Table 1, Fig. 2).

TABLE 1
Electronic Spectral Data of Dyes 1 and 2 in *n*-Hexane

No.	λ_{max} (*nm*)	ε_{max}	λ_{max} (*nm*)	ε_{max}	λ_{max} (*nm*)	ε_{max}
1a[a]	390	29 000	402	29 200	435	15 700
1b	396	29 400	410	30 900	442	17 500
1c	401	34 400	416	36 000	446	23 500
1d	415	39 200	431	39 800	459	31 800
1e	415	39 000	431	39 900	459	31 900
1f	393	28 800	406	29 200	438	15 800
1g	432	36 300	452	39 300	477	34 300
2a	403	35 100	417	37 500	443	24 500
2b	405	36 000	420	38 200	448	26 100
2c	410	38 400	426	39 100	453	29 200
2d	398	35 500	412	37 400	440	22 600
2e	407	35 700	422	37 800	449	27 000

[a] Measured in cyclohexane.

All dyes **1a**–**1g** are symmetrically substituted, and it is possible that there is a 'symmetry effect' on spectra. Therefore in addition, the unsymmetrical 4,4′-diaminoazobenzenes **2a**–**2c** were investigated. The trend of increasing bathochromicity, increasing intensity of the $0 \rightarrow 0$ transition and better resolved fine structure with increasing electron-donating ability of the amino groups which is observed with the symmetrically substituted dyes, is maintained when a different amino group is present in the second phenyl ring (**2a**–**2c**, Table 1). Substitution by a 3-methoxy group (**2e**) results also in effects observed from symmetrical 4,4′-diaminoazobenzenes. The 3-methyl

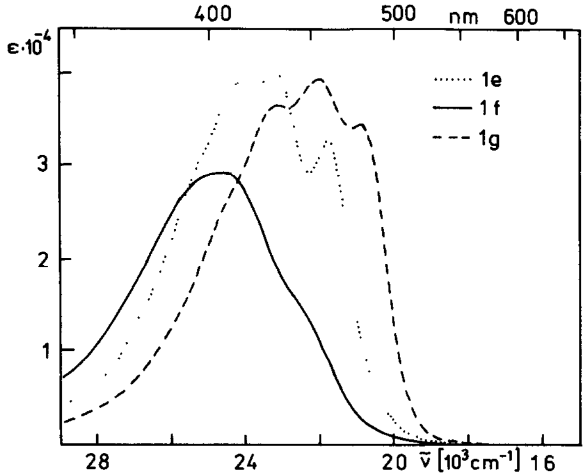

Fig. 2. Visible absorption bands of dyes **1e**–**1g** in *n*-hexane.

derivative (**2d**) absorbs at shorter wavelengths with lower intensity than dye **2a** and the $\pi_1 \rightarrow \pi_1^*$ band does not exhibit a well-resolved fine structure. These results demonstrate that the shape and the absorption maximum of the $\pi_1 \rightarrow \pi_1^*$ band are affected only by electronic effects.

With regard to the $\pi_1 \rightarrow \pi_1^*$ band of azobenzene it is possible to explain the observed effects. In contrast to 4,4'-bis-*NN*-diethylaminoazobenzene, the $\pi_1 \rightarrow \pi_1^*$ band of azobenzene exhibits no well-resolved fine structure in hydrocarbon solvents at room temperature, but only two inflections[21] (λ = 346 nm; ε = 9600; λ = 329 nm; ε = 20 200) behind the absorption maximum (λ = 316 nm; ε = 22 900). On lowering the temperature, the absorption bands develop a fine structure with three subbands nearly at the positions of the inflections.[22] This is due to the hindrance of rotational transitions in a glassy solution.

HMO calculations show that with increasing electron-donating ability of the substituents in symmetrical substituted dyes the π-bond order of the C—N(=) bonds increases (Fig. 3). Also, this effect should hinder rotation of the phenyl rings around the Ph—N(=) bonds in the ground state, leading to a

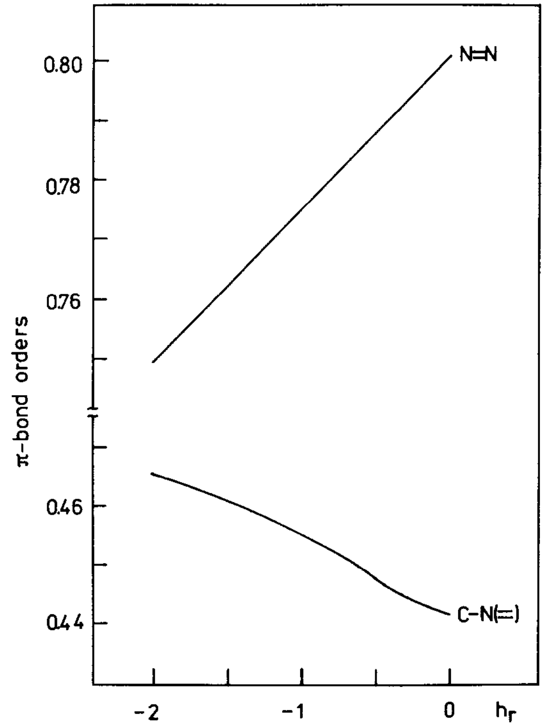

Fig. 3. The effect of electron-donor substituents in symmetrical 4,4'-disubstituted azobenzenes on HMO π-bond orders. The substituent effect is considered by the Coulomb integral (h_r) of the substituent-bearing carbon atom.

reduction of the population of rotational states of the ground state and the vibrational subbands become sharper.

Furthermore, with increasing C—N(=) π-bond order, the torsional angles of the Ph—N(=) bonds should decrease, resulting in a more planar geometry in the ground state. The more planar the geometry in the ground state, the smaller is the change of the equilibrium bond lengths associated with an electronic transition, i.e. Morse curves displacement of ground and excited state is lower and the intensity of the $0 \rightarrow 0$ vibronic transition increases.

3 CONCLUSIONS

With increasing electron-donating ability of the substituents in 4,4'-diaminoazobenzenes (i) the absorption maxima are shifted bathochromically, (ii) the vibronic fine structure of the $\pi_1 \rightarrow \pi_1^*$ band is better resolved (there are at least three vibronic transitions) and (iii) the relative intensity of the $0 \rightarrow 0$ subband increases.

The experimental observations can be explained by the results of simple HMO calculations which show that with increasing electron-donating ability of the substituents, the energy difference between HOMO and LUMO decreases, explaining the bathochromic effect, and the π-bond order of the C—N(=) bonds increases, resulting in a hindrance of rotation and twisting of the phenyl rings. The former effect simplifies the population of rotational states of the ground state, leading to the reduction of rotational transitions which causes a well-resolved vibrational fine structure. The last effect causes a decrease in the torsional angles of the Ph—N(=) bonds. With decreasing torsional angles, the difference between equilibrium bond lengths in the ground and excited state is lower, and therefore the Morse curves displacement is lower, resulting in higher intensity of the $0 \rightarrow 0$ subband.

4 EXPERIMENTAL

The synthesis of dye **1d** has been previously described.[1] All dyes **1** were prepared by the method of Vorländer and Wolferts.[23] Dyes **1e** and **1f** were purified by column chromatography on silica gel using toluene as solvent and eluant, followed by recrystallization from toluene. The other dyes were subsequently recrystallized to constant melting point from toluene: **1a** (m.p. 323–325°C), **1b** (m.p. 271–272°C), **1c** (m.p. 280–281°C), **1e** (m.p. > 360°C), **1f** (m.p. 180–181°C), **1g** (m.p. 213–214°C).

The synthesis of dye **2a** has been previously described.[1] Dyes **2d** and **2e** were prepared similarly to **2a**. Dye **2d** was recrystallized from EtOH (m.p. 181–182°C) and **2e** from toluene (m.p. 213–214°C). Dye **2c** was prepared and purified according to Kameo *et al.*[24]

4′-Piperidino-4-*NN*-diethylaminoazobenzene 2b

2·75 g (10 mmol) 4-piperidinobenzenediazoniumtetrafluoroborate was suspended in 60 ml MeOH and the suspension stirred and cooled to below 5°C. A solution of 1·49 g (10 mmol) *NN*-diethylaniline in 10 ml MeOH was then added with stirring. After 1 h a solution of 1 g sodium acetate in 10 ml water was added and after a further 2 h a solution of 2 g sodium acetate in 20 ml water was added. The liquor was stirred for 2 h, then the product filtered and washed with warm water. It was purified by column chromatography on silica gel using toluene:EtOH = 20:1 as solvent and eluant and finally recrystallized from EtOH to give 90 mg of pure dye (m.p. 184–186°C).

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

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