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The Effects of Cyclic Terminal Groups in 4-Aminoazobenzene and Related Azo Dyes. Part 5. Electronic Absorption Spectra of Some Monoazo Dyes Derived from *N*-Phenylhexamethyleneimine and *N*-Phenylheptamethyleneimine*

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ABSTRACT

Monoazo dyes containing terminal seven- and eight-membered rings absorb bathochromically when compared with their six-membered counterparts due to the inherent flexibility of the hexa- and hepta-methyleneimine systems. The conjugative capacity of the hexamethyleneiminyl and heptamethyleneiminyl groups is similar to that of a pyrrolidinyl terminal ring.

1 INTRODUCTION

The effects of terminal three-, four,[1] five- and six-membered rings,[2,3] on the spectroscopic properties of monoazo dyes based on 4-aminoazobenzene have been examined in previous papers. Differences in spectroscopic behaviour can be related to differences in the conjugative capacity of the lone pair of electrons on the terminal nitrogen atom brought about by a change in size and content of the saturated heterocyclic ring. In this paper, a comparison is made between monoazo dyes derived from *N*-phenylpiperidine, **1** ($n = 5$), and those similarly obtained from *N*-phenylhexamethyleneimine, **1** ($n = 6$), and from *N*-phenylheptamethyleneimine, **1** ($n = 7$).

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* For Part 4, see Ref. 1.

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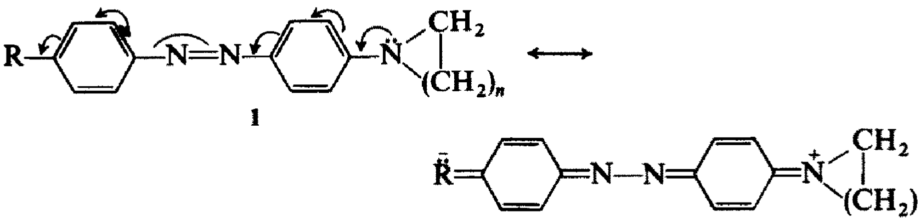
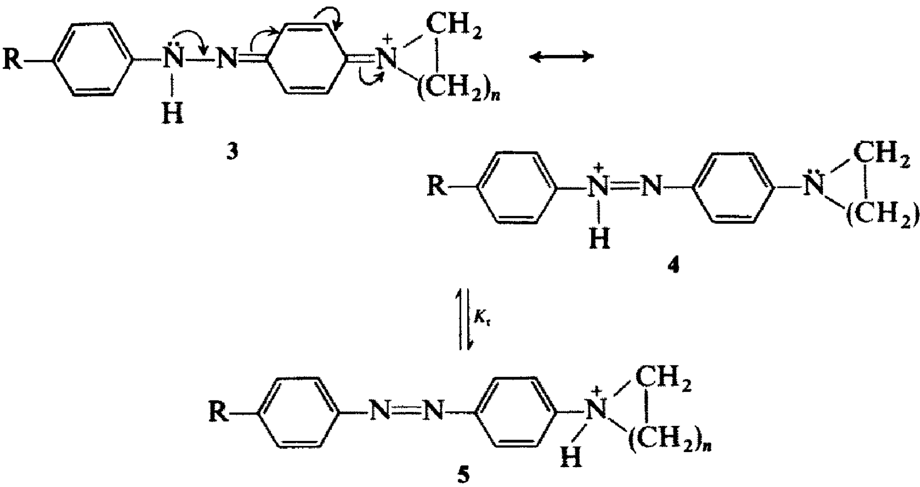


1 ↔ **2**

As pointed out previously,[1] the effects of *para*-substituents on the spectroscopic properties of 4-dialkylaminoazobenzene dyes can be accounted for qualitatively in terms of the valence-bond resonance approach.[4] Thus, the parent system can be regarded as a resonance hybrid of two extreme canonical structures, **1**↔**2**, of different energies. Structure **1** is a fairly close approximation to the ground state of the molecule, whereas the high-energy dipolar structure **2** can be taken as a reasonable approximation to the excited state. This qualitative interpretation is supported by PPP molecular orbital calculations.[5] When R is an electron-withdrawing group, the excited state is stabilised more than is the ground state, so that such substituents exert a bathochromic effect. The visible absorption band which arises from a migration of electron density from the terminal nitrogen atom towards the azo group, is shifted by an amount which is approximately proportional to the appropriate Hammett σ-constant.

Dyes derived from 4-aminoazobenzene generally undergo a pronounced colour change on addition of acid (halochromism). The usual long-wavelength shift of the visible absorption band can be attributed to resonance stabilisation of the resulting cation.[6] Two absorption bands are normally shown by solutions of the mono-acid salts as a result of an equilibrium between two tautomeric forms. In the azonium cation, **3**↔**4**:



3 **4** **5**

the β-azo nitrogen atom is protonated, whereas it is the terminal nitrogen atom which is protonated in the ammonium ion **5**. In the latter species, protonation prevents mesomeric interaction of the terminal lone pair of electrons with the π-system, so that absorption occurs some 200 nm below that of the azonium ion. The tautomeric equilibrium constant K_{τ} is usually defined as [azonium]/[ammonium], because increasing acid concentration leads to an increase in [azonium].[7] The tautomeric equilibrium is dependent on steric effects, especially those which lead to deconjugation of the donor group.[2] The basicities of the β-azo and the terminal nitrogen atoms are largely determined by the extent of conjugation between the amino group and the rest of the molecule.[6]

Comparison with the neutral dye system **1**$\leftrightarrow$**2** shows that, for the azonium species **3**$\leftrightarrow$**4**, the ground and excited states are much closer together in energy terms, so that a bathochromic shift is observed on protonation (positive halochromism). The ground state of the azonium ion is best represented by the quinonoid structure **3**, so that the first absorption band is associated with a migration of electron density from the β-nitrogen atom towards the terminal nitrogen atom.[5] It follows that the positive halochromism tends to increase as the electron-donating capacity of R increases, as a result of preferential stabilisation of structure **4**. As a consequence of the opposite directions of charge migration associated with electronic excitation in the neutral dyes (**1**) and their azonium cations (**3**), the visible absorption bands of the two species converge with increasing electron-withdrawing capacity of R. An excellent linear correlation is observed between the wavelength shift (azonium − neutral), or more precisely the frequency difference, and the appropriate Hammett σ-constant, in agreement with theory.[8]

2 RESULTS AND DISCUSSION

A comparison between dyes derived from *N*-phenylhexamethyleneimine, **1** ($n = 6$), and their *N*-phenylheptamethyleneimine analogues, **1** ($n = 7$), is shown in Table 1. It is clear that, in neutral solution, the two groups of dyes are very similar, with the eight-membered ring derivatives absorbing slightly more bathochromically than their seven-membered ring counterparts. The marginally greater electron-donating capacity of the heptamethyleneiminyl group compared with that of the hexamethyleneiminyl group can be associated with a somewhat larger inductive effect. It is more instructive to relate the spectral results to those obtained from dyes containing five- and six-membered terminal ring systems.[2] Thus, the spectral data suggest that the electron-donor power of the terminal nitrogen atom decreases in

TABLE 1
Absorption Bands of Some Dyes Derived from *N*-Phenylhexamethyleneimine and *N*-Phenylheptamethyleneimine in Ethanol

R	*Dye 1 (n = 6)*		*Dye 1 (n = 7)*		Δλ *(nm)* *Dye 1 (n = 7) − Dye 1 (n = 6)*
	λ_{max} *(nm)*	*10*$^{-4}$ ε_{max}	λ_{max} *(nm)*	*10*$^{-4}$ ε_{max}	
OCH_3	413	3·39	—	—	—
CH_3	414	3·07	415	3·00	1
H	415	3·17	417	2·89	2
Br	428	2·92	429	3·46	1
CF_3	437	3·03	438	3·22	1
$COCH_3$	458	3·58	460	3·41	2
CN	462	3·72	463	3·40	1
NO_2	489	4·00	489	3·44	0

the order heptamethyleneiminyl > hexamethyleneiminyl > pyrrolidinyl > piperidinyl. This trend is supported by the respective maxima of the *p*-nitrophenyl derivatives of the parent amines in ethanol, which are 395, 394, 392 and 389 nm, respectively.

Unlike the piperidinyl group, which takes up a relatively rigid chair conformation and exerts a significant steric effect when attached to a benzene ring system,[2,9] the hexamethyleneiminyl and heptamethyleneiminyl groups are conformationally mobile. By analogy with cycloheptane[10] and cyclooctane,[11] respectively, the hexamethyleneimine and heptamethyleneimine rings can adopt flexible arrangements, whereby nonbonded interactions are more easily minimised. The terminal nitrogen atoms of the seven- and eight-membered ring systems can be accommodated in an sp^3 arrangement with negligible angle strain, as indicated by molecular models (Dreiding). Mesomeric interaction with the phenyl ring will, however, increase the sp^2 character of the atom and will, in conjunction with pseudorotation within the flexible systems, tend to obviate steric crowding between the *ortho*-positions of the phenyl ring and the α-methylene protons of the seven- and eight-membered rings. Consequently, the various hexamethyleneiminyl and heptamethyleneiminyl dyes (Table 1) absorb more intensely and at significantly longer wavelengths than their piperidinyl analogues.[2] The dyes containing seven- and eight-membered terminal rings are also somewhat more bathochromic than the corresponding five-membered ring derivatives.[2] For example, as the terminal ring size decreases stepwise from eight to five, the absorption maxima of the corresponding *p*-cyano derivatives in ethanol are 463, 462, 442 and 460 nm.

In neutral solution, both series of dyes, **1** ($n = 6$ and $n = 7$), show bathochromic shifts as the electron-withdrawong capacity of R is increased (Table 1). Positive halochromism is shown by both series of dyes in acid solution (Table 2) in accordance with previous findings.[2] The difference in absorption wavelength between the neutral dye and the corresponding azonium ion, **3**↔**4**, shows a progressive increase as the donor strength of the *para*-substituent increases. The values of $\lambda_{azonium} - \lambda_{neutral}$ for the present series of dyes are close to those observed for the corresponding *N*-phenylpyrrolidine dyes,[2] in accordance with the similar donor character of the three terminal groups. As in the case of the analogous derivatives of *N*-phenylpyrrolidine, the dyes obtained from *N*-phenylhexamethyleneimine and from *N*-phenylheptamethyleneimine exist almost entirely in the azonium form, reflecting efficient conjugation between the terminal lone pair of electrons and the aromatic system. In contrast, dyes derived from *N*-phenylpiperidine are present very largely as the ammonium form in acid solution,[2] due to diminution of conjugation brought about by steric factors. These findings are in line with earlier work in which it was suggested that an *exo* double bond will destabilise a six-membered ring, but favour five-, seven- and eight-membered rings.[12]

TABLE 2
Halochromism of some Dyes Derived from *N*-Phenylhexamethyleneimine and *N*-Phenylheptamethyleneimine

Dye 1	*Ethanol*		*Ethanol + HCl*		$\lambda_{azonium} - \lambda_{neutral}$ *(nm)*
	λ_{max} *(nm)*	$10^{-4}\,\varepsilon_{max}$	λ_{max} *(nm)*	$10^{-4}\,\varepsilon_{max}$	
$n = 6$; R=OCH_3	413	3·39	562	5·96	149
$n = 6$; R=CH_3	414	3·07	547	5·79	133
$n = 6$; R=H	415	3·17	535	6·07	120
$n = 6$; R=Br	428	2·92	542	5·52	114
$n = 6$; R=CF_3	437	3·03	522	5·79	85
$n = 6$; R=$COCH_3$	458	3·58	536	6·83	78
$n = 6$; R=CN	462	3·72	527	6·82	65
$n = 6$; R=NO_2	489	4·00	528	7·93	39
$n = 7$; R=CH_3	415	3·00	548	5·87	133
$n = 7$; R=H	417	2·89	534	5·65	117
$n = 7$; R=Br	429	3·46	542	6·63	113
$n = 7$; R=CF_3	438	3·22	524	6·94	86
$n = 7$; R=$COCH_3$	460	3·41	540	6·69	80
$n = 7$; R=CN	463	3·40	528	6·43	65
$n = 7$; R=NO_2	489	3·44	528	6·85	39

3 EXPERIMENTAL

3.1 General

N-Phenylhexamethyleneimine[13] was prepared in three stages from hexamethyleneimine and *p*-nitrochlorobenzene.[14] The resulting nitro-compound was then reduced by means of catalytic hydrogenation. Deamination was achieved by diazotisation and treatment with hypophosphorous acid.[15]

N-Phenylheptamethyleneimine was obtained by a similar reaction sequence from *p*-nitrofluorobenzene and heptamethyleneimine. The two series of dyes were obtained by conventional coupling procedures;[2] conventional methods were used to diazotise the various amines.[16] The crude dyes obtained from *N*-phenylhexamethyleneimine were purified by column chromatography on alumina, using either toluene or dichloromethane as solvent and eluent, followed by recrystallisation from ethanol. The same procedure was used for some of the analogues derived from *N*-phenylheptamethyleneimine. However, the acetyl-, cyano- and nitro-dyes **1** ($n = 7$; $R = COCH_3$, CN and NO_2, respectively) were purified chromatographically using toluene–dichloromethane (9:1) initially as solvent, and then gradually increasing the proportion of dichloromethane in the eluent. The parent dye **1** ($n = 7$; $R = H$) and its methyl derivative, **1** ($n = 7$; $R = CH_3$), were isolated as liquids. Purification was achieved by column chromatography on alumina, using cyclohexane–toluene (9:1), followed by preparative thin-layer chromatography in toluene solution on silica, and recrystallisation from cyclohexane. Yields, melting points and microanalytical data are summarised below; dye purity was confirmed by differential scanning calorimetry.

3.2 Reaction of *p*-halogenonitrobenzene with cyclic imine

A mixture of the cyclic imine (0·2 mol) was heated under reflux with *p*-halogenonitrobenzene (0·1 mol) in butan-1-ol (100 cm^3) for 20 h. The cooled reaction mixture was diluted with ethanol (50 cm^3) to precipitate the yellow nitro-compound in almost quantitative yield. Recrystallisation of the precipitate gave pure material, having melting points in accord with literature values.[14]

3.3 Reduction of *p*-nitrophenyl derivatives

The *p*-nitrophenyl derivative (0·06 mol) was dissolved in a mixture of ethanol (95 cm^3) and acetic acid (5 cm^3) in a 250 cm^3 conical flask. Palladium (0·5 g) was added to the solution, and the flask was attached to a hydrogenation apparatus. The mixture was stirred magnetically, and hydrogen gas was allowed to pass into the flask until the yellow solution became colourless. The filtrate obtained after removal of the catalyst was poured into water ($100\,cm^3$) containing hydrochloric acid ($15\,cm^3$).

3.4 Deamination of *p*-aminophenyl derivatives

Sodium nitrite (0·065 mol) in water ($20\,cm^3$) was added gradually at 0 to 5°C (−15°C in the case of the heptamethyleneimine derivative) to the solution of the amine. After stirring the mixture for a further 30 min at 0 to 5°C, the solution was added gradually to 30% hypophosphorous acid ($52{\cdot}5\,cm^3$) at 0 to 5°C, and the mixture was then stirred at this temperature for 2 h. The solution was kept in a refrigerator for 18 h and then at room temperature for 24 h before basifying to pH 7 to 8, using sodium carbonate; the organic layer was extracted with dichloromethane. Removal of solvent from the dried (Na_2SO_4) solution gave a product, which was distilled under vacuum. *N*-Phenylhexamethyleneimine was thus obtained as a colourless liquid (8·9 g; 51%), b.p. 130°C at 0·3 mm Hg. (Found: C, 82·2; H, 9·6; N, 8·2. $C_{12}H_{17}N$ requires: C, 82·3; H, 9·7; N, 8·0%).

N-Phenylheptamethyleneimine was similarly isolated as a colourless liquid (4·1 g; 22%), b.p. 100–102°C at 0·3 mm Hg. (Found: C, 82·6; H, 10·0; N, 7·3. $C_{13}H_{19}N$ requires: C, 82·5; H, 10·0; N, 7·4%.)

3.5 Characterisation of the hexamethyleneimine dyes (1; *n* = 6)

R=OCH$_3$
Yield, 20%; m.p. 118°C (yellow plates). Analysis (%)—found: C, 73·85; H, 7·45; N, 13·45. $C_{19}H_{23}N_3O$ requires: C, 73·8; H, 7·4; N, 13·6.

R=CH$_3$
Yield, 31%; m.p. 113°C (yellow-orange crystals). Analysis (%)—found: C, 77·5; H, 7·5; N, 14·0. $C_{19}H_{23}N_3$ requires: C, 77·8; H, 7·85; N, 14·3.

R=H
Yield, 44%; m.p. 95°C (orange flakes). Analysis (%)—found: C, 77·45; H, 7·5; N, 15·1. $C_{18}H_{21}N_3$ requires: C, 77·4; H, 7·5; N, 15·05.

R=Br
Yield, 62%; m.p. 138°C (brown crystals). Analysis (%)—found: C, 60·6; H, 5·4; Br, 22·65; N, 10·9. $C_{18}H_{20}BrN_3$ requires: C, 60·3; H, 5·6; Br, 22·3; N, 11·7

R=CF$_3$
Yield, 43%; m.p. 132°C (brick-red crystals). Analysis (%)—found: C, 65·4; H, 5·8; F, 16·45; N, 11·9. $C_{19}H_{20}F_3N_3$ requires: C, 65·7; H, 5·8; F, 16·4; N, 12·1.

R=COCH$_3$
Yield, 55%; m.p. 151°C (red plates). Analysis (%)—found: C, 74·75; H, 7·3; N, 13·2. $C_{20}H_{23}N_3O$ requires: C, 74·8; H, 7·2; N, 13·1.

R=CN
Yield, 68%; m.p. 153°C (orange–red leaflets). Analysis (%)—found: C, 74·85; H, 6·55; N, 18·2. $C_{19}H_{20}N_4$ requires: C, 75·0; H, 6·5; N, 18·4.

R=NO$_2$
Yield, 64%; m.p. 172°C (brownish-red powder). Analysis (%)—found: C, 66·35; H, 6·2; N, 17·0. $C_{18}H_{20}N_4O_2$ requires: C, 66·7; H, 6·2; N, 17·3.

3.6 Characterisation of the heptamethyleneimine dyes (1; *n* = 7)

R=CH$_3$
Yield, 3%; m.p. 99°C (orange flakes). Analysis (%)—found: C, 77·4; H, 8·3; N, 12·5. $C_{20}H_{25}N_3$ requires: C, 78·2; H, 8·1, N, 13·7.

R=H
Yield, 4%; m.p. 108°C (brownish-yellow crystals). Analysis (%)—found: C, 77·8; H, 7·85; N, 14·3. $C_{19}H_{23}N_3$ requires: C, 77·8; H, 7·85; N, 14·3.

R=Br
Yield, 47%; m.p. 142°C (orange–red crystals). Analysis (%)—found: C, 61·05; H, 5·8; Br, 21·35; N, 11·0. $C_{19}H_{22}BrN_3$ requires: C, 61·3; H, 5·9; Br, 21·5; N, 11·3.

R=CF$_3$
Yield, 44%; m.p. 116°C (red powder). Analysis (%)—found: C, 66·5; H, 6·05; F, 15·9; N, 11·5. $C_{20}H_{22}F_3N_3$ requires: C, 66·5; H, 6·1; F, 15·8; N, 11·6.

R=COCH$_3$
Yield, 55%; m.p. 127°C (brick-red powder). Analysis (%)—found: C, 75·2; H, 7·45; N, 12·25. $C_{21}H_{25}N_3O$ requires: C, 75·2; H, 7·5; N, 12·5.

R=CN
Yield, 59%; m.p. 138°C (brown crystals). Analysis (%)—found: C, 75·5; H, 6·95; N, 17·6. $C_{20}H_{22}N_4$ requires: C, 75·5; H, 6·9; N, 17·6.

R=NO_2
Yield, 53%; m.p. 155°C (bluish-red leaflets). Analysis (%)—found: C, 67·3; H, 6·5; N, 16·35. $C_{19}H_{22}N_4O_2$ requires: C, 67·45; H, 6·5; N, 16·6.

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