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The Effects of Cyclic Terminal Groups in 4-Aminoazobenzene and Related Azo Dyes. Part 6. Electronic Absorption Spectra of some Monoazo Dyes Derived from *N*-Phenylisoindoline[1]

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ABSTRACT

Monoazo dyes containing a terminal isoindolinyl group absorb hypsochromically when compared with analogous compounds derived from N-*phenylpyrrolidine, due to the electronic influence of the benzene ring component of the heterocyclic substituent. The conjugative capacity of the isoindolinyl group is somewhat less than that of a pyrrolidinyl terminal ring. Copyright © 1996 Elsevier Science Ltd*

Keywords: Monoazo dyes, *N*-phenylisoindoline, synthesis, absorption spectra.

INTRODUCTION

The effects of cyclic terminal groups on the spectroscopic properties of monoazo dyes based on 4-aminoazobenzene have been examined in previous papers.[1–5] 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*-phenylisoindoline, **1**, and their *N*-phenylpyrrolidine analogues, **2**.

For monoazo dyes containing saturated heterocyclic terminal groups, it has been found that the nitrogen atom lone pair interacts most efficiently

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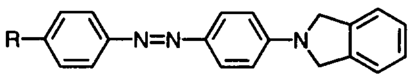
[1] For Part 5, see Ref. 4.



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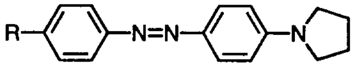

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with the rest of the molecule when incorporated into a five-membered ring.[5] Consequently, it seemed of interest to examine the effect of fusing a benzene ring on to the terminal five-membered heterocyclic system.

RESULTS AND DISCUSSION

A comparison between dyes derived from *N*-phenylisoindoline, **1**, and the corresponding compounds obtained from *N*-phenylpyrrolidine, **2**, is shown in Table 1. In neutral solution, the two groups of dyes are similar but, in every case, the isoindoline derivatives absorb hypsochromically when compared with their pyrrolidine counterparts. For both series, a progressive bathochromic shift of the visible absorption band is observed as the electron-withdrawing capacity of the *para*-substituent increases, in accordance with a gradual stabilisation of the excited state.[4] It is clear that the steric requirements of the two terminal groups are similar because the ε_{max} differences are small. Thus, the hypsochromic effect of the isoindolinyl group can only be

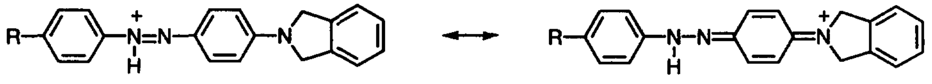
TABLE 1
Absorbtion Bands of some Dyes Derived from *N*-Phenylisoindoline and *N*-Phenylpyrrolidine in Ethanol

R	*Dye* **1**		*Dye* **2**		$\Delta\lambda$ (nm)
	λ_{max} (nm)	10^{-4} ε_{max}	λ_{max} (nm)	10^{-4} ε_{max}	*Dye* **2**–*Dye* **1**
OCH_3	406	3.53	411	2.98	5
CH_3	406	3.34	412	3.02	6
H	407	3.43	413	2.86	6
Br	417	3.68	425	3.32	8
CF_3	425	3.66	434	3.14	9
$COCH_3$	441	3.52	454	3.25	13
CN	442	3.73	460	3.52	18
NO_2	474	—*	488	3.43	14

*Incompletely soluble.

associated with the electronic influence of the aromatic component which brings about a decreased inductive effect compared with that of the pyrrolidinyl system.

Positive halochromism is shown by the *N*-phenylisoindoline dyes, **1**, in acid solution (Table 2) in accordance with previous findings.[5] The high values of ε_{max} indicate efficient conjugation between the terminal lone pair of electrons and the aromatic system. The protonated dyes, like their pyrrolidinyl counterparts,[1] exist almost entirely in the azonium form, **3** ↔ **4**.



3 **4**

The difference in absorption wavelength between a neutral dye and the corresponding azonium ion shows a linear increase as the donor strength of the *para*-substituent increases, as measured by appropriate Hammett σ-constants, in line with theory.[6] The values of $\lambda_{azonium}-\lambda_{neutral}$ are close to those observed for the corresponding *N*-phenylpyrrolidine dyes, reflecting the similar donor character of the two terminal groups.

EXPERIMENTAL

N-Phenylisoindoline is readily available as a crystalline solid, m.p. 173°C, from the reaction between aniline and α,α-dibromo-*o*-xylene.[7] Conventional methods were used to diazotise the various amines.[8]

TABLE 2
Halochromism of some Dyes Derived from *N*-Phenylisoindoline

Dye **1** *R*	*Ethanol* λ_{max} (nm)	 $10^{-4}\ \varepsilon_{max}$	*Ethanol* + HCl λ_{max} (nm)	 $10^{-4}\ \varepsilon_{max}$	$\lambda_{azonium}$ - $\lambda_{neutral}$ (nm) *Dye* **2**–*Dye* **1**
OCH_3	406	3.53	547	6.39	141
CH_3	406	3.34	536	6.30	130
H	407	3.43	523	6.40	116
Br	417	3.68	529	6.44	112
CF_3	425	3.66	511	6.31	86
$COCH_3$	441	3.52	524	6.63	83
CN	442	3.73	517	6.92	75
NO_2	474	—*	517	—*	14

*Incompletely soluble.

Coupling to *N*-phenylisoindoline

N-Phenylisoindoline (0.02 mole) was dissolved in a mixture of acetone (200 cm^3) and acetic acid (10 cm^3) and then cooled to 35–40°C. The diazonium solution was then added at once and the mixture stirred at room temperature for a further 3 h, after which the crude dye was removed by filtration.

Dye purification

The crude dyes were purified by column chromatography on alumina, using toluene as solvent and eluent. Dyes **1** (R = OCH_3, CH_3 and H, respectively) were recrystallised from ethanol. Dyes **1** (R = Br and CF_3, respectively) were recrystallised twice from toluene and once from ethanol. Dyes **1** (R = CH_3CO, CN and NO_2, respectively) were boiled in acetic acid, filtered hot, washed with aqueous sodium hydroxide and then with water, dried and recrystallised twice from toluene. Yields, melting points and microanalytical data are summarised below; dye purity was confirmed by differential scanning calorimetry.

Dye characterisation

R = OCH$_3$
Yield, 4%; m.p. 243°C (yellow crystals). Analysis (%)—found: C, 76.7; H, 5.9; N, 12.5. $C_{21}H_{19}N_3O$ requires: C, 76.6; H, 5.8; N, 12.8.

R = CH$_3$
Yield, 9%; m.p. 161°C (yellow crystals). Analysis (%)—found: C, 80.2; H, 5.6 N, 13.6. $C_{21}H_{19}N_3$ requires: C, 80.5; H, 6.1, N, 13.4.

R = H
Yield, 17% m.p. 256°C (yellow crystals). Analysis (%)—found: C, 80.3; H, 5.7; N, 13.8. $C_{20}H_{17}N_3$ requires: C, 80.3; H, 5.7; N, 14.0.

R = Br
Yield, 45%; m.p. 280°C (yellow rhombs). Analysis (%)—found: C, 63.9; H, 4.2; N, 10.8; Br, 21.5. $C_{20}H_{16}BrN_3$ requires: C, 63.5; H, 4.2; N, 11.1; Br, 21.2.

R = CF$_3$
Yield, 31%; m.p. 171°C (yellow rhombs). Analysis (%)—found: C, 69.2; H, 4.5; N, 11.2; F, 15.9. $C_{21}H_{16}F_3N_3$ requires: C, 68.7; H, 4.4; N, 11.4; F, 15.5.

R = COCH$_3$
Yield, 53%; m.p. 283°C (reddish–orange crystals). Analysis (%)—found: C, 77.5; H, 5.4; N, 11.9. $C_{22}H_{19}N_3O$ requires: C, 77.4; H, 5.6; N, 12.3.

$R = CN$
Yield, 54%; m.p. 261°C (orange powder). Analysis (%)—found: C, 77.9; H, 4.9; N, 17.3 $C_{21}H_{16}N_4$ requires: C, 77.8; H, 4.9; N, 17.3.

$R = NO_2$
Yield, 67%; m.p. 280°C (maroon powder). Analysis (%)—found: C, 69.5; H, 4.6; N, 16.2. $C_{20}H_{16}N_4O_2$ requires: C, 69.8; H, 4.7; N, 16.3.

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