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The Effects of Cyclic Terminal Groups in 4-Aminoazobenzene and Related Azo Dyes. Part 4—Electronic Absorption Spectra of some Monoazo Dyes Derived from *N*-Phenylaziridine and *N*-Phenylazetidine*

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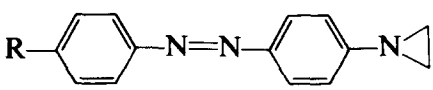
ABSTRACT

Monoazo dyes containing a terminal aziridinyl group absorb hypsochromically when compared with their azetidinyl counterparts. Geometrical and hybridisation factors prevent the aziridinyl lone pair of electrons from efficient conjugation with the adjacent aromatic ring system. In acid solution, the aziridinyl ring opens as a result of solvolysis whereas the azetidinyl ring is stable.

INTRODUCTION

Previous papers in this series[1,2] have examined the effects of terminal five- and six-membered rings on the spectroscopic properties of monoazo dyes based on 4-aminoazobenzene. 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*-phenylaziridine, **1**, and their *N*-phenylazetidine analogues, **2**:



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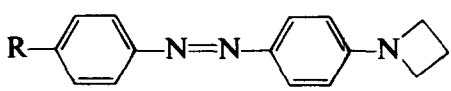

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* Part 3 was published in *J. Chem. Soc. Perkin Trans.*, **2** (1986) 123.[1]

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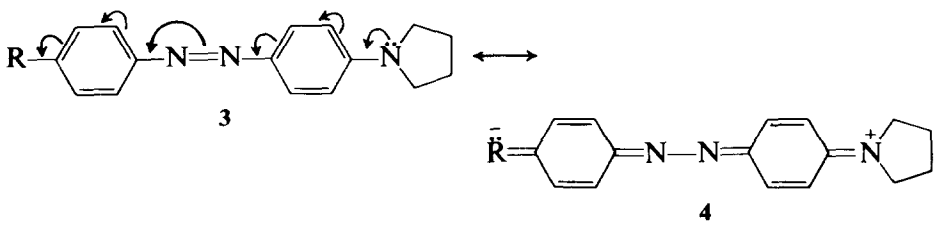
The effects of *para*-substituents on the spectroscopic properties of 4-dialkylaminoazobenzene dyes can be explained qualitatively in terms of the valence-bond resonance approach.[3] The situation is typified by dyes derived from *N*-phenylpyrrolidine, where the parent system can be regarded as a resonance hybrid of two extreme canonical structures, **3** ↔ **4**, of different energies:



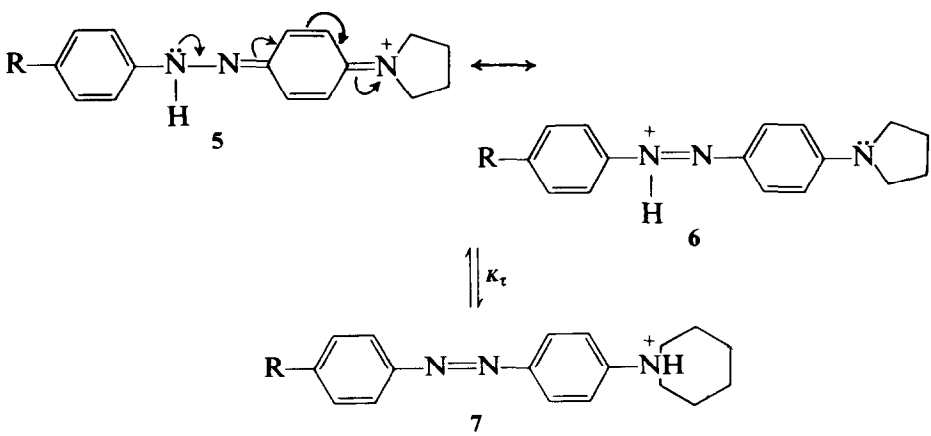
3 **4**

Dipole-moment studies[4,5] suggest that, for dyes of this type, structure **3** is a fairly close approximation to the ground state of the molecule. The high-energy dipolar structure **4** can be taken as a reasonable approximation to the excited state. This interpretation is supported by PPP molecular orbital calculations.[6] The excited state is stabilised more than the ground state when R is an electron-withdrawing group, so that such substituents exert a bathochromic effect, because ΔE becomes smaller. In general, 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 that is approximately proportional to the appropriate Hammett σ-constant.[7]

The positive solvatochromism shown by numerous analogues of 4-aminoazobenzene can also be explained in terms of resonance canonicals. Thus, an increase in solvent polarity will tend to stabilise the dipolar excited state more than the neutral ground state, resulting in a bathochromic shift of the first absorption band.

Many dyes derived from 4-aminoazobenzene undergo a pronounced colour change on addition of acid (halochromism), the generally observed shift of the absorption band to longer wavelength being attributed to resonance stabilisation of the resulting cation.[8] Two absorption bands are usually shown by solutions of the mono-acid salts as a result of an equilibrium between two tautomeric forms. In the azonium cation, **5** ↔ **6**, the β-azo nitrogen atom is protonated whereas it is the terminal nitrogen atom which is protonated in the ammonium ion **7**.

In the latter species, protonation prevents mesomeric interaction of the terminal lone pair of electrons with the π-system, so that absorption occurs at about 320 nm, some 200 nm below that of the azonium ion. The tautomeric equilibrium constant K_T is usually defined as [azonium]/[ammonium], as increasing acid concentration leads to an increase in



[azonium].[9] 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 terminal nitrogen atoms are largely determined by the extent of conjugation between the amino group and the rest of the molecule.[8]

Comparison with the neutral dye system **3** ↔ **4** shows that for the azonium species **5** ↔ **6** the ground and excited states are much closer together in energy terms, so that a bathochromic shift is observed on protonation (positive halochromism). Although the azonium ion can be regarded as a charge-resonance system, it is best represented in the ground state by the quinonoid structure **5**, so that the first absorption band is associated with a migration of electron density from the β-nitrogen atom towards the terminal nitrogen atom.[6] Consequently, the positive halochromism tends to increase as the electron-donating capacity of R increases, as a result of preferential stabilisation of structure **6**. As a consequence of the opposite directions of charge migration associated with electronic excitation in the neutral dyes and their azonium cations, the visible absorption bands of the two species converge with increasing electron-withdrawing capacity of R (**3** and **5**). An excellent linear correlation is observed between the wavelength shift ($\lambda_{azonium} - \lambda_{neutral}$), or more precisely the frequency difference, and the appropriate Hammett σ-constant[2] in agreement with theory.[10]

RESULTS AND DISCUSSION

A comparison between dyes derived from *N*-phenylaziridine, **1**, and their *N*-phenylazetidine counterparts, **2**, is shown in Table 1. It is clear that, in neutral solution, the dyes derived from *N*-phenylaziridine **1** are much more hypsochromic than their counterparts obtained from *N*-phenylazetidine **2**.

TABLE 1
Solvatochromism of Some Dyes Derived from *N*-Phenylaziridine and *N*-Phenylazetidine

Dye	*Cyclohexane*		*Ethanol*		$\Delta\lambda$ (*nm*)
	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	
1; R = OCH_3	361	2·65	360	2·14	−1
1; R = CH_3	356	2·60	353	1·82	−3
1; R = H	355	1·82	350	1·63	−5
1; R = Br	363	2·76	357	2·14	−6
1; R = CF_3	366	2·35	358	1·84	−8
1; R = $COCH_3$	373	2·70	368	1·87	−5
1; R = CN	376	2·67	369	1·97	−7
1; R = NO_2	387	[a]	385	2·04	−2
2; R = OCH_3	390	2·64	398	1·91	8
2; R = CH_3	390	3·10	398	1·91	8
2; R = H	391	3·16	399	1·72	8
2; R = Br	404	3·81	412	2·11	8
2; R = CF_3	409	3·10	420	1·96	11
2; R = $COCH_3$	418	3·19	436	1·85	18
2; R = CN	422	3·34	441	2·17	19
2; R = NO_2	442	2·15	469	2·19	27

[a] Sparingly soluble.

The values of the latter series fall between those of the corresponding *N*-phenylpyrrolidine **3** and *N*-phenylpiperidine dyes.[2] Thus, the spectral data suggest that the electron-donor power of the terminal nitrogen atom decreases in the order pyrrolidinyl > azetidinyl ≫ aziridinyl. Thus, for example, the respective λ_{max} values of the *p*-nitro derivatives in ethanol are 488, 469 and 385 nm. This trend is supported by other experimental data. Thus, the absorption maxima of the *p*-nitro derivatives of the parent amines follow the same sequence.[11] Values of the exaltation in molar refraction (ΔR_D) decrease for the series *N*-phenylpyrrolidine > *N*-phenylazetidine > *N*-phenylaziridine in accordance with decreasing resonance interaction.[12] Measurements of pK_a for the corresponding *p*-nitro derivatives[13] suggest that the amine nitrogen atom in the aziridine ring is near sp^3 hybridised, whereas in the larger rings the hybridisation is nearer sp^2. Photoelectron spectroscopy of various *N*-phenyl cyclic amines has shown that, in the gas phase, *N*-phenylaziridine, *N*-phenylazetidine and *N*-phenylpyrrolidine each achieve a conjugated conformation.[14]

In *N*-phenylazetidine, to minimise non-bonded interactions, the azetidine ring is puckered and the phenyl group occupies an equatorial site.[15] Interaction between the nitrogen lone pair and the opposite proton in the azetidine ring tends to diminish conjugation with the aromatic system,

leading to an increase in electronic transition energy.[16] This increase in energy should be reflected in a hypsochromic shift by comparison with less strained systems, as is found to be the case when the *N*-phenylazetidine dyes **2** are compared with their *N*-phenylpyrrolidine analogues **3**.

The preferred conformation of *N*-phenylaziridine has the axis of the nitrogen lone pair perpendicular to the plane of the aromatic ring.[17] This arrangement is supported by electron-diffraction studies in the gas phase,[18] dipole moment and Kerr constant measurements in solution[19] and by photoelectron spectroscopy.[14] Investigations by means of ^{13}C nuclear magnetic resonance (NMR),[12,20] ^{15}N NMR,[17] ^{19}F NMR,[21] IR intensities[22] and UV spectroscopy[11,23] all suggest that *N*-phenylaziridine is the least conjugated of the series of *N*-phenyl cyclic amines. The spectral characteristics of the *N*-phenylaziridine dyes **1** (Tables 1 and 2) are in accordance with these findings. Thus, the various aziridinyl dyes absorb at much shorter wavelengths than their azetidinyl analogues. In fact, all the aziridinyl compounds listed in Table 1 are yellow, as, in each case, λ_{max} appears below 400 nm.

An X-ray study of *N*-phenylaziridine has shown that the nitrogen atom is pyramidal.[24] Near sp^3 hybridisation of the terminal nitrogen atom provides a less strained structure than that resulting from sp^2 hybridisation at this atom. Consequently, mesomeric interaction with the aromatic system will be less likely than in the case of larger ring systems. The peculiar nature of the three-membered aziridine ring can be associated with the concept of σ-aromaticity.[25] The σ-aromatic nature of the aziridine ring would account for its ease of formation despite severe angle distortion.[20] In the *N*-phenylaziridine dyes **1**, any mesomeric interaction between the terminal nitrogen lone pair and the three-membered ring would have a marked

TABLE 2
Absorption Bands of Some Dyes Derived from *N*-Phenylaziridine and *N*-Phenylazetidine in Ethanol

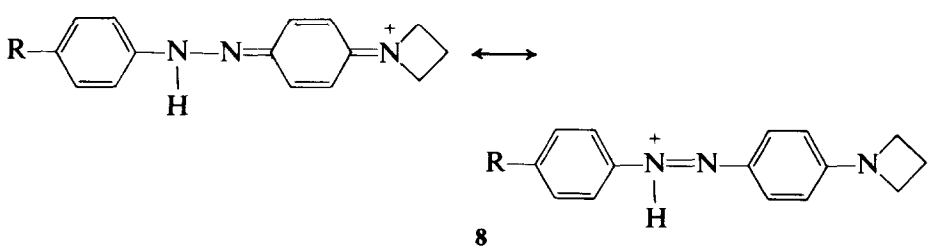
R	*Dye 1*		*Dye 2*		$\Delta\lambda$ (*nm*) *Dye 2 − Dye 1*
	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	
OCH_3	360	2·14	398	1·91	38
CH_3	353	1·82	398	1·91	45
H	350	1·63	399	1·72	49
Br	357	2·14	412	2·11	55
CF_3	358	1·84	420	1·96	62
$COCH_3$	368	1·87	436	1·85	68
CN	369	1·97	441	2·17	72
NO_2	385	2·04	469	2·19	84

hypsochromic effect compared with the less strained *N*-phenylazetidine dyes **2**, as is observed (Table 2). In particular, the energy of the excited state will be raised relative to that of the azetidines, owing to an increase in the sp^2 character of the terminal nitrogen atom leading to increased angle distortion. To some extent, this destabilisation might be offset by resonance interaction between the σ-aromatic ring and the exocyclic conjugative benzene ring.[20]

The *N*-phenylazetidine dyes **2** exhibit positive solvatochromism with an increase in solvent polarity, as expected, owing to greater stabilisation of the dipolar excited state than of the neutral ground state (Table 1). The positive solvatochromism increases gradually as the electron-withdrawing capacity of the *para*-substituent increases, as a result of a progressive stabilisation of the excited state by the polar solvent. The *N*-phenylaziridine dyes **1**, on the other hand, show negative solvatochromism (Table 1). This effect can be accounted for by a general stabilisation of the ground state by hydrogen bonding between the hydroxylic solvent and the sp^3-hybridised aziridinyl nitrogen atom. Such an interaction is much less effective at an sp^2-hybridised atom and has been advanced as an explanation for the anomalously low basicity of *N*-phenylaziridine.[13]

In neutral solution, both series of dyes show bathochromic shifts as the electron-withdrawing capacity of R is increased, but the extent of the shift is much less for the aziridines **1** (Table 2). For example, 4-(4-nitrophenylazo)-*N*-phenylazetidine (**2**; $R = NO_2$) is 70 nm more bathochromic than the parent dye (**2**; R = H). The corresponding aziridines **1** show a difference of only 35 nm, a reflection of the resistance to conjugation by the aziridinyl group.

Positive halochromism is shown by the *N*-phenylazetidine dyes **2** in acid solution (Table 3) in accordance with previous findings.[2] The difference in absorption wavelength between the neutral dye and the corresponding azonium ion **8** shows a progressive increase as the donor strength of the *para*-substituent increases:



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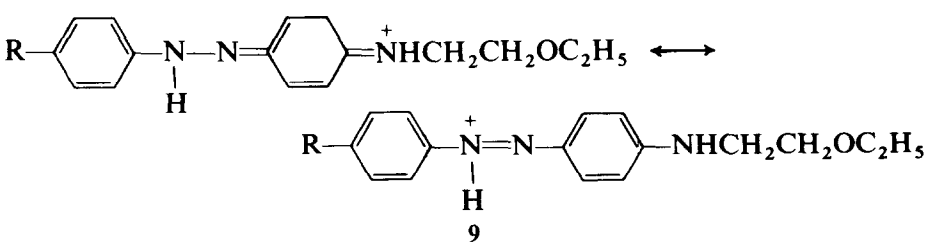
The values of $\lambda_{azonium} - \lambda_{ammonium}$ for the azetidines are somewhat greater than those observed for the corresponding *N*-phenylpyrrolidine dyes **3**, in accordance with the weaker donor character of the azetidinyl group.

TABLE 3
Halochromism of Some Dyes Derived from *N*-Phenylaziridine and *N*-Phenylazetidine

Dye	*Ethanol*		*Ethanol + HCl*		$\lambda_{azonium} - \lambda_{neutral}$ (*nm*)
	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	
1; R = OCH_3	360	2·14	544	5·21	184
1; R = CH_3	353	1·82	526	4·86	173
1; R = H	350	1·63	515	4·71	165
1; R = Br	357	2·14	518	6·01	161
1; R = CF_3	358	1·84	504	5·83	146
1; R = $COCH_3$	368	1·87	514	5·59	146
1; R = CN	369	1·97	510	6·25	141
1; R = NO_2	385	2·04	522	7·40	137
2; R = OCH_3	398	1·91	550	3·96	152
2; R = CH_3	398	1·91	532	5·34	134
2; R = H	399	1·72	523	4·71	124
2; R = Br	412	2·11	524	5·37	112
2; R = CF_3	420	1·96	510	5·52	90
2; R = $COCH_3$	436	1·85	522	5·67	86
2; R = CN	441	2·17	514	6·09	73
2; R = NO_2	469	2·19	512	6·96	43

Although the *N*-phenylaziridine dyes **1** exhibit a marked positive halochromism in acid solution (Table 3), the species formed, **9**, is that resulting from solvolysis at the terminal ring; it is known that the aziridinyl ring in *N*-phenylaziridine opens readily on protonation.[26] This finding was confirmed by an examination of several related hydroxyethyl dyes in acid solution; the λ_{max} values of the azonium cations were found to be very similar. Typically, dye **9** (R = OCH_3) absorbs at 544 nm whereas the analogous hydroxyethyl compound absorbs at 543 nm:



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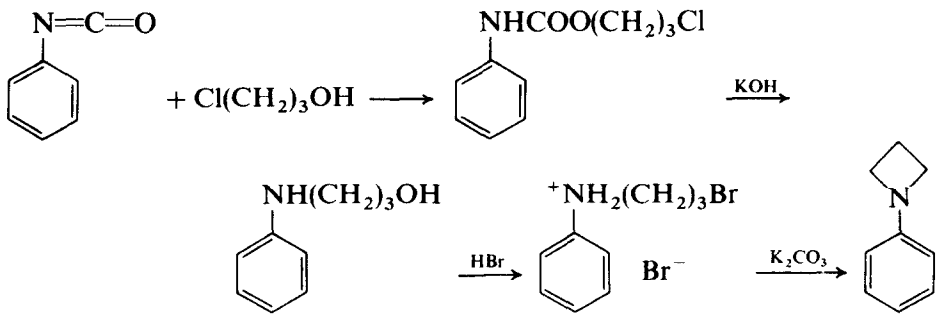
EXPERIMENTAL

N-Phenylazetidine[27] was prepared in high yield by cyclisation of *N*-(3-bromopropyl)aniline using potassium carbonate in aqueous ethanol.



Scheme 1. Synthesis of *N*-phenylazetidine.

The amine precursor was obtained in three steps from phenylisocyanate (Scheme 1). The azetidine dyes **2** were obtained by conventional coupling procedures;[2] conventional methods were used to diazotise the various amines.[28] The crude dyes were purified by column chromatography on alumina using either toluene or dichloromethane as solvent and eluant followed by recrystallisation from ethanol. Yields, melting points and microanalytical data are summarised below; dye purity was confirmed by differential scanning calorimetry.

The aziridine dyes **1** could not be obtained by conventional coupling to *N*-phenylaziridine. The parent amine polymerises rapidly when emulsified with water or when exposed to air.[29] Consequently, the aziridine ring has to be created as the final step of the dye synthesis. Thus, a series of precursor dyes was obtained by coupling to *N*-(2-bromoethyl)aniline hydrobromide.[30] The resulting dyes were then cyclised under basic conditions. Hydrolysis also occurs to some extent in aqueous media, and by-products include derivatives of *N,N'*-diphenylpiperazine. Separation of the aziridine dyes from their hydroxyethyl analogues was achieved by column chromatography.

3-Chloropropyl *N*-phenylcarbamate[31]

A mixture of 3-chloropropan-1-ol (9·45 g) and freshly distilled phenylisocyanate (11·9 g) was heated to 150°C in an oil-bath for 3 h. The product was distilled under vacuum and the fraction boiling at 160–170°C (5 mm Hg) was collected. The distillate readily solidified and was recrystallised from ethanol to give the carbamate as colourless crystals (19·0 g; 89%), m.p. 38°C. (Found: C, 56·25; H, 5·65; Cl, 16·5; N, 6·5. $C_{10}H_{12}ClNO_2$ requires: C, 56·2; H, 5·6; Cl, 16·6; N, 6·6%.)

N-(3-Hydroxypropyl)aniline[32]

The chloropropyl carbamate (7·9 g) was heated with potassium hydroxide (8·3 g; 4 equiv.) dissolved in ethanol (25 cm^3) on a steam-bath for 2 h. The

cooled mixture was filtered to remove inorganic salts, and the ethanol was evaporated. The crude amine was extracted with dilute hydrochloric acid. After basification, the oily layer was extracted with ether. Removal of solvent from the dried organic layer gave a crude product which was distilled under vacuum to yield the required amine as a colourless liquid (5.5 g; 92%), b.p. 146–149°C at 2 mm Hg. (Found: C, 71·7; H, 8·65; N, 9·3. $C_9H_{13}NO$ requires: C, 71·5; H, 8·6; N, 9·3%.)

N-(3-Bromoethyl)aniline hydrobromide

N-(3-Hydroxypropyl)aniline (11·0 g) was cooled to 0°C before precooled 48% hydrobromic acid (31 cm^3) was added dropwise with stirring and cooling. The mixture was then distilled using an efficient fractionating column until a constant boiling distillate was reached. The residue was cooled somewhat and poured into an open dish to solidify. The resulting product was crystallised from ethanol to give colourless crystals of the hydrobromide (15·2 g; 71%), m.p. 132°C. (Found: C, 36·7; H, 4·5; Br, 54·0; N, 4·6. $C_9H_{13}Br_2N$ requires: C, 36·6; H, 4·4; Br, 54·2; N, 4·7%.)

N-Phenylazetidine

N-(3-Bromoethyl)aniline hydrobromide (2·95 g) in aqueous ethanol (110 cm^3; 60%) was treated with potassium carbonate (12 cm^3; 2M) at 55°C. After 12 h, saturated brine (200 cm^3) was added. Extraction of the amine with dichloromethane afforded a crude product which was purified by distillation under vacuum to give *N*-phenylazetidine as a colourless liquid (1·15 g; 86%), b.p. 86–88°C at 5·5 mm Hg. (Found: C, 80·9; H, 7·7; N, 11·2. $C_9H_{11}N$ requires: C, 81·2; H, 8·3; N, 10·5%.)

Characterisation of the aziridine dyes (1)

R = OCH_3 Yield, 16%; m.p. 119°C (yellow crystals). Analysis (%)—found: C, 70·9; H, 5·9; N, 16·6. $C_{15}H_{15}N_3O$ requires: C, 71·1; H, 5·9; N, 16·6.

R = CH_3 Yield, 18%; m.p. 90°C (yellow flakes). Analysis (%)—found: C, 75·6; H, 6·4; N, 16·7. $C_{15}H_{15}N_3$ requires: C, 75·9; H, 6·3; N, 17·2.

R = H Yield, 19%; m.p. 70°C (yellow flakes). Analysis (%)—found: C, 76·2; H, 6·1; N, 19·0. $C_{14}H_{13}N_3$ requires: C, 76·3; H, 5·8; N, 18·8.

R = Br Yield, 37%; m.p. 155°C (orange flakes). Analysis (%)—found: C, 55·7; H, 3·9; Br, 26·2; N, 13·6. $C_{14}H_{12}BrN_3$ requires: C, 55·6; H, 4·0; Br, 26·5; N, 13·9.

R = CF_3 Yield, 42%; m.p. 164°C (orange flakes). Analysis (%)—found: C, 61·6; H, 4·1; F, 19·1; N, 14·1. $C_{15}H_{12}F_3N_3$ requires: C, 61·9; H, 4·1; F, 19·6; N, 14·4.

R = $COCH_3$ Yield, 38%; m.p. 136°C (orange flakes). Analysis (%)—found: C, 72·45; H, 5·7; N, 15·7. $C_{16}H_{15}N_3O$ requires: C, 72·45; H, 5·7; N, 15·85.

R = CN Yield, 35%; m.p. 189°C (orange flakes). Analysis (%)—found: C, 72·8; H, 4·9; N, 22·5. $C_{15}H_{12}N_4$ requires: C, 72·6; H, 4·8; N, 22·6.

R = NO_2 Yield, 41%; m.p. 159°C (red–brown flakes). Analysis (%)—found: C, 62·5; H, 4·5; N, 20·8. $C_{14}H_{12}N_4O_2$ requires: C, 62·7; H, 4·5; N, 20·9.

Characterisation of the azetidine dyes (2)

R = OCH_3 Yield, 60%; m.p. 162°C (yellow–orange flakes). Analysis (%)—found: C, 71·8; H, 6·4; N, 15·9. $C_{16}H_{17}N_3O$ requires: C, 71·9; H, 6·4; N, 15·7.

R = CH_3 Yield, 75%; m.p. 187°C (yellow crystals). Analysis (%)—found: C, 76·4; H, 6·6; N, 16·5. $C_{16}H_{17}N_3$ requires: C, 76·5; H, 6·8; N, 16·7.

R = H Yield, 83%; m.p. 121°C (yellow crystals). Analysis (%)—found: C, 75·8; H, 6·3; N, 17·6. $C_{15}H_{15}N_3$ requires: C, 76·0; H, 6·3; N, 17·7.

R = Br Yield, 85%; m.p. 161°C (orange crystals). Analysis (%)—found: C, 56·7; H, 4·3; Br, 25·6; N, 12·6. $C_{15}H_{14}BrN_3$ requires: C, 57·0; H, 4·4; Br, 25·3; N, 13·3.

R = CF_3 Yield, 91%; m.p. 164°C (reddish orange flakes). Analysis (%)—found: C, 63·2; H, 4·5; F, 18·6; N, 13·4. $C_{16}H_{14}F_3N_3$ requires: C, 63·0; H, 4·6; F, 18·7; N, 13·8.

R = $COCH_3$ Yield, 79%; m.p. 227°C (crimson powder). Analysis (%)—found: C, 73·2; H, 6·0; N, 14·5. $C_{17}H_{17}N_3O$ requires: C, 73·1; H, 6·1; N, 15·0.

R = CN Yield, 79%; m.p. 178°C (reddish orange flakes). Analysis (%)—found: C, 73·2; H, 5·4; N, 21·4. $C_{16}H_{14}N_4$ requires: C, 73·3; H, 5·3; N, 21·4.

R = NO_2 Yield, 98%; m.p. 207°C (bluish red flakes). Analysis (%)—found: C, 63·6; H, 5·0; N, 20·1. $C_{15}H_{14}N_4O_2$ requires: C, 63·8; H, 5·0; N, 19·9.

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