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Colour and Constitution of Some *N*-Phenylpyrrolidinylazo Dyes: Application of the PPP Molecular Orbital Method

Geoffrey Hallas and Richard Marsden

Department of Colour Chemistry, The University,
Leeds LS2 9JT, Great Britain

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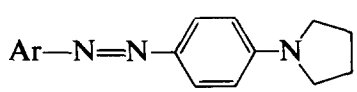
SUMMARY

Electronic absorption spectral data for a series of monoazo dyes derived from N*-phenylpyrrolidine have been calculated by the PPP molecular orbital method. In order to optimise the agreement between experimental and calculated results, certain parameters were reassessed by trial and error calculations. New parameters for some sulphur-containing heterocyclic systems permit the satisfactory prediction of* λ_{max} *values for the derived dyes. The relative intensities of the various heterocyclic azo dyes are also reasonably well accounted for by the PPP method.*

1. INTRODUCTION

Practical aspects of the Pariser–Parr–Pople (PPP) molecular orbital (MO) method in relation to colour prediction have been discussed by Griffiths.[1] The generalised parameter approach advocated by Griffiths, which enables reasonable predictions of visible spectra to be made for widely different chromogens, can usefully be refined when attention is focused within a particular dye class.[2] In the present paper, calculations are based on the *N*-phenylpyrrolidinylazo system (**1**) since the dyes can



(**1**)

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reasonably be assumed to have planar structures.[3] The effects of several sulphur-containing heterocyclic residues are examined, together with some *para*-substituted benzene derivatives.

2. CALCULATIONS

A standard PPP molecular orbital procedure was employed, within the fixed β approximation.[2] Two-centre electron repulsion integrals were determined by the Nishimoto–Mataga relationship,[4] and electronic

TABLE 1
PPP–MO Parameters for the Calculation of Electronic Absorption Spectral Data

Bond type (*X*—*Y*)	r_{X-Y}[a] (Å)	β_{X-Y}[b] (*eV*)	$VSIP_Y$[c] (*eV*)	A_Y[d] (*eV*)	Z_Y[e] (*eV*)
C—C aromatic	1·40	−2·39	11·16	0·03	1
C—NMe_2[f]	1·40	−2·75	18·00	8·00	2
C—NEt_2[f,g]	1·40	−2·75	17·50	7·50	2
C—OR	1·36	−2·60	32·90	11·43	2
Cl—C[h]	—	—	12·00	0·61	1
C—C } acetyl	1·45	−2·30	11·16	0·03	1
C=O } acetyl	1·22	−2·46	15·00	0·71	1
C—C } cyano	1·40	−2·30	11·19	0·10	1
C≡N } cyano	1·15	−2·67	14·18	3·50	1
C—N } nitro	1·49	−2·00	24·80	12·53	2
N—O[f] } nitro	1·21	−2·80	21·00	2·50	1
C—N } azo	1·40	−2·48	14·70	2·30	1
N=N } azo	1·23	−2·90	14·70	2·30	1
C—S[f,i] } heterocyclic	1·71	−1·00	20·00	10·00	2
C—N[f,j] } heterocyclic	1·38	−2·40	12·00	0·50	1
C=N[f] } heterocyclic	1·33	−2·00	12·00	0·50	1
R—N^+	1·35	−2·40	21·00	9·26	2

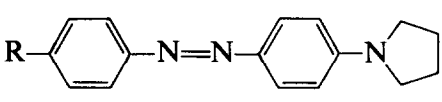
[a] Bond length.
[b] Bond resonance integral.
[c] Valence state ionisation potential of atom Y.
[d] Electron affinity of atom Y.
[e] Core charge of atom Y.
[f] Reoptimised parameter.
[g] Used for pyrrolidinyl.
[h] Modified to simulate inductive effect of Cl.
[i] N—S given same parameters.
[j] N—N given same parameters.

excitation energies were refined by a limited configuration interaction treatment involving the nine singly excited singlet configurations obtained by promoting an electron from the three highest occupied orbitals to the three lowest unoccupied orbitals; this treatment generally produced a bathochromic shift of the first band of about 5%. The calculated configuration vectors indicate that in most cases the contribution of the HOMO → LUMO electronic transition to the visible absorption band is about 95%. Thus, a description of the first excited states of these types of molecules in terms of orbital occupancies is quite sound.

The parameters used in the calculations are shown in Table 1. Standard bond lengths and angles were used in the computations wherever possible and literature values for β, the VSIP and the one-centre electron repulsion integral ($\gamma_{nm} = \mathrm{VSIP}_n - A_n$) were employed unless otherwise stated.[1,5,6]

3. RESULTS AND DISCUSSION

A comparison between experimental and calculated electronic absorption spectral data for the various monoazo dyes derived from *N*-phenylpyrrolidine (**2**–**8**) is shown in Table 2. In order to optimise the



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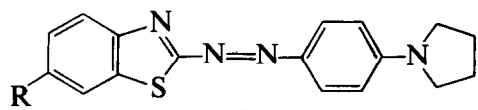

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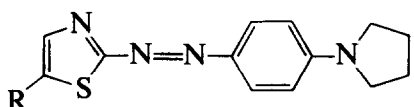

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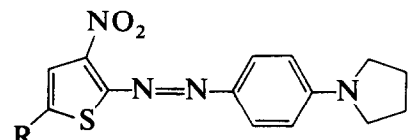

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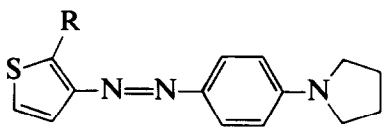

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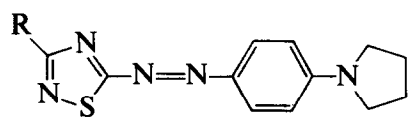

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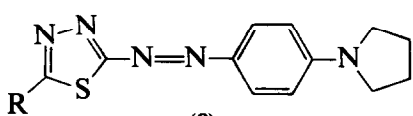

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TABLE 2
Comparison between Experimental and Calculated Electronic Absorption Spectral Data for Some Dyes Derived from *N*-Phenylpyrrolidine

Dye	*R*	λ_{max} (*nm*) (*calc.*)	f^a (*calc.*)	λ_{max} (*nm*)^b (*exp.*)	$10^{-4}\varepsilon$ (*exp.*)
2a	OMe	412	1·51	407	2·98[b]
2b	H	411	1·45	407	2·86[b]
2c	Cl	413	1·45	416	3·08[b]
2d	COMe	431	1·63	434	3·25[b]
2e	CN	439·5	1·66	438	3·52[b]
2f	NO_2	464	1·48	459	3·43[b]
3a	OEt	475·5	1·79	478	5·51[c]
3b	H	475	1·73	471	5·48[c]
3c	NO_2	509·5	1·85	505	6·48[c]
4a	H	466	1·52	452	3·93[c]
4b	NO_2	533	1·75	529	5·17[c]
5a	COMe	547·5	1·29	547	4·28[c]
5b	NO_2	556	1·47	589	5·94[c]
6a	COMe	448·5	1·31	440	2·73[c]
6b	CO_2Me	439	1·29	430	2·83[c]
7a	C_6H_5	466	1·58	472	4·86[c]
7b	SMe	471[d]	1·53[d]	474	4·60[c]
8	SEt	476[d]	1·57[d]	467	5·24[c]

[a] Oscillator strength.
[b] Solvent cyclohexane.
[c] Solvent ethanol.
[d] Calculated value is for methoxy analogue.

agreement between experimental and calculated results over the range of dyes studied, certain parameters were reassessed by trial and error calculations. Thus, the resonance integral (β) for the N—O bonds of the nitro group was changed from $-3{\cdot}05$ to $-2{\cdot}80$ eV. This modification provided a bathochromic shift of the calculated λ_{max} values of 5–15 nm (Table 3). The VSIP and A values for the π-excessive sulphur atom of the heterocyclic ring systems were modified slightly, from 22·20 and 9·16 eV to 20·00 and 10·00 eV, respectively, in order to give the best fit for all the heterocycles. The most important change occurs in the parameters for the π-equivalent C=N bond(s) of the heterocyclic rings. Thus, the β value for the C=N bond is moved from $-2{\cdot}60$ to $-2{\cdot}00$ eV, producing a significant bathochromic shift of the first band. Reduction in the VSIP

TABLE 3
The Effect of Parameter Modification on the Calculated Electronic Absorption Spectral Data for Some *N*-Phenylpyrrolidinylazo Dyes

Dye	*R*	*Original parameters* $\lambda_{max}(nm)$ (f)	*Modified parameters* $\lambda_{max}(nm)$ (f)	*Experimental values* $\lambda_{max}(nm)$ $(10^{-4}\varepsilon)$[a]
2f	NO_2	452·5 (1·52)[b]	464 (1·48)[c]	459 (3·43)
3b	H	451 (1·69)[d]	442·5 (1·67)[e]	
			483·5 (1·73)[f]	
			475 (1·73)[e,f]	471 (5·48)
3c	NO_2	456 (1·81)[b,d]	471·5 (1·75)[c,e]	
			490·5 (1·92)[c,f]	
			509·5 (1·85)[c,e,f]	505 (6·48)
4a	H	453 (1·46)[d]	438·5 (1·51)[e]	
			480·5 (1·52)[f]	
			466 (1·52)[e,f]	452 (3·93)
4b	NO_2	478·5·(1·71)[b,d]	533 (1·75)[c,e,f]	529 (5·17)
7a	C_6H_5	432·5 (1·38)[d]	466 (1·58)[e,f]	472 (4·86)

[a] Solvent cyclohexane.
[b] $\beta_{N-O} = -3{\cdot}05$.
[c] $\beta_{N-O} = -2{\cdot}80$.
[d] Heterocyclic $VSIP_N = 16{\cdot}00$, $A_N = 2{\cdot}50$, $\beta_{C=N} = -2{\cdot}60$, $\beta_{C-N} = -2{\cdot}40$.
[e] As *d*, except $VSIP_N = 12{\cdot}00$, $A_N = 0{\cdot}50$.
[f] As *d*, except $\beta_{C=N} = -2{\cdot}00$.

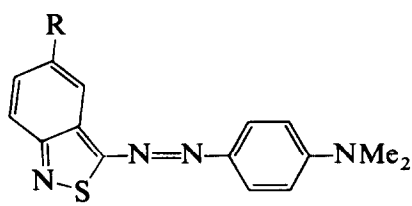
and *A* values from 16·00 and 2·50 to 12·00 and 0·50, respectively, permits separation of the originally similar λ_{max} values of the parent thiazole (**4a**) and benzothiazole (**3b**) azo dyes, and of the nitrobenzothiazole derivative (**3c**) (Table 3). The new parameters enable the absorption bands to be reasonably well predicted, free from other visible bands, and of high oscillator strength.

Examination of the data given in Table 2 reveals that in most cases the observed λ_{max} value of the dye is calculated to within about 5 nm. An obvious exception is the dinitrothiophene derivative (**5b**), for which the calculated wavelength is much too short; this discrepancy may be associated with the presence of an *o*-nitro group since λ_{max} for the corresponding acetyl dye (**5a**) is predicted very accurately. For the benzenoid dyes (**2a–2f**), the relative bathochromicities of the acceptor groups are well predicted, as is the small effect of a donor substituent;[7]

examination of the electron densities of the ground and excited states of the parent dye (**2b**) and its methoxy analogue (**2a**) reveals that oxygen lone pair electrons play a negligible part in the excitation process.[8] A similar situation obtains in the case of the heterocyclic dye **3a** (Table 2).

The origin of the bathochromic shift associated with the presence of sulphur-containing heterocyclic systems in monoazo dyes has been the subject of some speculation.[2] The present results show that these long-wavelength shifts can be accounted for without involving the sulphur 3*d* atomic orbitals in the calculations. The same conclusion has been reached very recently by Kogo[9] on the basis of the CNDO/S method. It seems likely that the various heterocyclic residues are more polarisable than the benzene ring so that the electronic effects of appropriate substituents are transmitted more efficiently to the rest of the chromogen.[10] The relative intensities of the heterocyclic azo dyes are also reasonably well accounted for by the PPP method, with an approximate correlation between *f* and ε_{max} (Table 2).

As a further test of the applicability of the modified parameters, calculations were carried out on some known benzoisothiazole (**9**) and isothiazole (**10**) dyes.[11] The exceptionally bathochromic properties of these dyes are reproduced (Table 4). In particular, λ_{max} of the blue nitrobenzoisothiazole dye (**9b**) is estimated accurately and the parent dye (**9a**) is found to be almost as bathochromic as the nitroisothiazole dye (**10b**).



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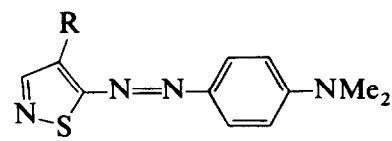


(**10**)

The ground state of the parent dye **2b** shows a significant loss of electron density at the terminal nitrogen atom, the main electron-rich centres being the *ortho* and *para* carbon atoms of the donor ring, together with the β-azo nitrogen atom and, to a lesser extent, the α-azo nitrogen atom (Table 5). The polarity of the ground state is reflected in the dipole moment of the dye (3·76 D),[12] which is somewhat greater than that of the corresponding diethylamino compound (3·40 D).[13] Electronic excitation results in even more conjugation by the terminal nitrogen lone pair

TABLE 4

Comparison between Experimental and Calculated Electronic Absorption Spectral Data for Some Heterocyclic Azo Dyes

Dye	*R*	λ_{max} (*nm*) (*calc.*)	*f* (*calc.*)	λ_{max} (*nm*)[a] (*exp.*)
9a	H	521·5	1·71	548
9b	NO_2	599	1·15	598
10a	H	445	1·44	482·5[b]
10b	NO_2	536	0·91	558[b]

[a] From ref. 11.
[b] 3′-Methyl derivative.

TABLE 5

Calculated π-Electron Densities and Bond Orders for 4-Phenylazo-*N*-phenylpyrrolidine (Fig. 1)

Atom	*π-Electron density*		*Bond*	*Bond order*	
	Ground state	*Excited state*		*Ground state*	*Excited state*
1	1·64	1·32	1–2	0·58	0·63
2	0·99	1·02	2–3	0·53	0·49
3	1·12	0·99	3–4	0·72	0·75
4	0·96	1·03	4–5	0·58	0·52
5	1·04	0·89	5–6	0·43	0·52
6	1·08	1·35	6–7	0·82	0·57
7	1·14	1·29	7–8	0·37	0·48
8	0·97	0·98	8–9	0·62	0·55
9	0·99	1·03	9–10	0·68	0·70
10	1·01	1·01	10–11	0·66	0·64
11	1·00	1·05			

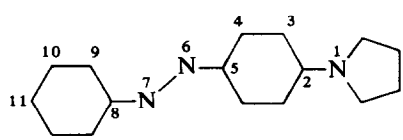


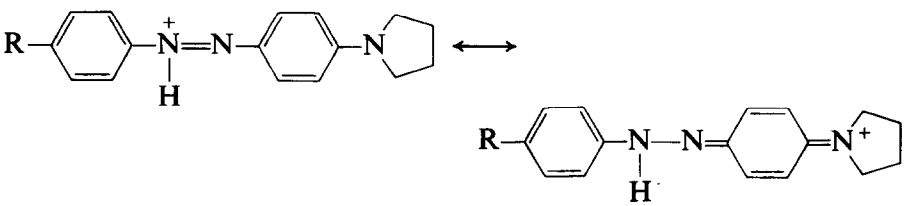
Fig. 1. Numbering of atoms and bonds listed in Table 5 for 4-phenylazo-*N*-phenylpyrrolidine.

Fig. 2. Resonance canonicals associated with the excited state of 4-phenylazo-*N*-phenylpyrrolidine.

electrons and a reduction in electron density at the *ortho* and *para* positions of the donor ring (Table 5). A build-up of electron density occurs at the azo link, especially at the α-nitrogen atom,[14] and in the acceptor ring. These changes do not accord all that well with qualitative resonance representations, which imply an increase in electron density at the β-nitrogen atom in particular (Fig. 2). However, bond order calculations do suggest a movement towards a more quinonoid structure in the excited state as witnessed by the increased bond order for the 1–2, 3–4, 5–6, 7–8 and 9–10 bonds and the marked decrease at the 6–7 (azo) link (Table 5).

It has already been mentioned that the introduction of a methoxy group at the *para* position of the parent dye has little effect on the absorption characteristics of the dye. Replacement of this substituent by an electron-withdrawing group such as nitro, however, causes a reduction in the build-up of electron density at the β-azo nitrogen atom, leading to an overall loss on excitation.[8] The terminal nitrogen lone pair electrons show increased conjugation in both ground and excited states, and a significant increase in electron density occurs at the *para* substituent in the excited state. Calculated π-electron dipole moments for the various dyes reveal that the excited state is more polar than the ground state,[8] and this situation is reflected in the positive solvatochromism shown by the benzenoid derivatives (**2**).[3]

The ground-state electron density at the terminal nitrogen atom is greater than that at the β-azo nitrogen atom for all the pyrrolidinylazo



(**11**)

Fig. 3. Resonance stabilisation of the azonium tautomer of 4-phenylazo-*N*-phenylpyrrolidine.

TABLE 6

Comparison between Experimental and Calculated Electronic Absorption Spectral Data for Some Protonated Dyes Derived from *N*-Phenylpyrrolidine

Dye	*R*	λ_{max} (*nm*) (*calc.*)	f^a (*calc.*)	λ_{max} (*nm*)^b (*exp.*)	$10^{-4}\varepsilon$ (*exp.*)
11a	OMe	502	2·02	559	5·90
11b	H	478	2·01	519	5·77
11c	Cl	479	2·02	524	5·88
11d	COMe	490	2·20	520	6·34
11e	CN	488	2·26	512	6·19
11f	NO_2	483	2·18	512	6·82

[a] Oscillator strength.

[b] Solvent ethanol.

dyes. Nevertheless, in the case of the benzene series (**2**),[3] protonation occurs almost exclusively at the β-azo nitrogen atom (azonium tautomer), due to factors such as the resonance stabilisation of the resulting cation (Fig. 3). The protonated dyes generally absorb at longer wavelengths and with increased intensities than their neutral precursors (positive halochromism) and PPP calculations are in line with this fact (Table 6). Thus, the relatively small wavelength shifts caused by electron-withdrawing groups are reproduced and the methoxy derivative is correctly predicted to be the most bathochromic member of the series. The general discrepancy between the observed and calculated λ_{max} values can be related to the need to carry out spectral measurements in a polar solvent. In the case of the benzothiazole (**3**) and the thiazole (**4**) dyes, protonation takes place at the heterocyclic nitrogen atom to generate a diazahemicyanine cation, leading to an extended conjugated system (Fig. 4)[15] and resulting in an enhanced bathochromic effect which is predicted by PPP calculations. Thus, for example, the parent dye **4a** has λ_{max} at 589 nm in ethanolic hydrogen chloride compared with a calculated value of 542 nm.

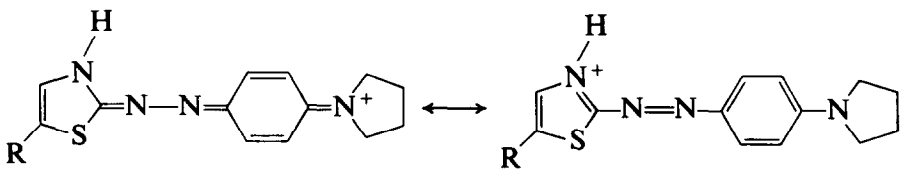


Fig. 4. Diazahemicyanine system resulting from protonation in the thiazole ring of dye **4**.

4. EXPERIMENTAL

The physical characteristics of the benzenoid dyes (**2**) have already been described.[3] Several methods were used to diazotise the various heterocyclic amines and these are described below. In each case, except for 5-amino-3-phenyl-1,2,4-thiadiazole, the diazonium solution was then added gradually to a well-stirred dispersion of *N*-phenylpyrrolidine in aqueous acetic acid containing sodium acetate and kept at 0 °C for 3 h; the coupling reaction was completed by stirring the mixture overnight before basification.

The crude dyes were purified by column chromatography on alumina or silica, using dichloromethane or toluene as solvent and eluant, followed by recrystallisation from toluene. In the case of dye **6a**, a column treatment was followed by preparatory layer chromatography on silica, before recrystallisation, using toluene throughout. Yields of purified dye, melting points, appearance and microanalytical data are summarised below.

Diazotisation of 2-aminothiazole

Finely powdered sodium nitrite (1·14 g, 0·02 mol) was added portionwise with stirring at below 20 °C to concentrated sulphuric acid (15 ml) at a rate such that no brown fumes were evolved. After stirring for 10 min, the suspension was heated to a maximum of 65 °C to give a clear solution which was then cooled to 0 °C. To this reagent was added, at a temperature below 15 °C, 10 ml of a 1:5 mixture of propionic acid and acetic acid. The resulting cloudy mixture was cooled to 0 °C and 2-aminothiazole (2·0 g, 0·02 mol) was added gradually in small portions. The mixture was stirred for 2 h at 0 °C to give the diazonium species as a dark orange-brown viscous solution.

This method was also used for 2-amino-5-nitrothiazole, 5-acetyl-2-amino-3-nitrothiophene, 2-amino-3,5-dinitrothiophene, 2-acetyl-3-aminothiophene, 3-amino-2-methoxycarbonylthiophene and 2-amino-5-ethylthio-1,3,4-thiadiazole.

Diazotisation of 2-aminobenzothiazole

2-Aminobenzothiazole (2·7 g, 0·018 mol) was dissolved in a mixture of concentrated sulphuric acid (28 ml) and water (50 ml) and cooled to 0 °C.

A solution of sodium nitrite (1·3 g, 0·018 mol) in concentrated sulphuric acid (5 ml) was added dropwise at 0 °C and the mixture was stirred for 2 h to give the diazonium species as an orange viscous solution.

This method was also used for 2-amino-6-ethoxybenzothiazole.

Diazotisation of 2-amino-6-nitrobenzothiazole

Nitrosylsulphuric acid (0·02 mol), prepared as above, was added to a solution of 2-amino-6-nitrobenzothiazole (3·5 g, 0·018 mol) in a mixture of phosphoric acid (30 ml) and acetic acid (9 ml) at 0 °C. The mixture was stirred for 4 h to produce a dark brown viscous solution of the diazotised amine.

Nitrosation of 5-amino-3-phenyl-1,2,4-thiadiazole

5-Amino-3-phenyl-1,2,4-thiadiazole (3·55 g, 0·02 mol) was added to formic acid (90%, 20 ml) and the mixture was stirred for 15 min at room temperature. The milky suspension was cooled to 0 °C and finely powdered sodium nitrite (1·4 g, 0·02 mol) was added in small portions at 0–5 °C, after which stirring was continued for 1 h.

Coupling procedure

To the above nitrosamine slurry was added a solution of *N*-phenylpyrrolidine (2·94 g, 0·02 mol) in formic acid (90%, 30 ml) at 0 °C. After stirring for 30 min, the mixture was heated to 70 °C and maintained at 70–75 °C for 3 h. Water (200 ml) was then added to the dark red solution and the mixture was cooled to room temperature. The required dye (**7a**) was obtained by neutralisation of the mixture with aqueous sodium hydroxide.

Characterisation of the azo dyes

3a Yield, 34%; m.p. 246–249 °C (maroon leaflets). Analysis (%), Found: C, 64·45; H, 5·45; N, 16·15; S, 9·35; $C_{19}H_{20}N_4OS$ requires: C, 64·85; H, 5·7; N, 15·9; S, 9·35.

3b Yield, 39%; m.p. 252–254 °C (maroon needles). Analysis (%), Found: C, 66·3; H, 5·2; N, 18·2; S, 10·8; $C_{17}H_{16}N_4S$ requires: C, 66·2; H, 5·2; N, 18·2; S, 10·4.

3c Yield, 19%; m.p. 238–240°C (dark blue crystals). Analysis (%), Found: C, 58·3; H, 4·3; N, 19·8; S, 8·9; $C_{17}H_{15}N_5O_2S$ requires: C, 57·8; H, 4·25; N, 19·8; S, 9·1.

4a Yield, 27%; m.p. 195–197°C (dark red crystals). Analysis (%), Found: C, 60·76; H, 5·2; N, 21·5; S, 12·45; $C_{13}H_{14}N_4S$ requires: C, 60·5; H, 5·4; N, 21·7; S, 12·4.

4b Yield, 8%; m.p. 238–240°C (blue-black crystals). Analysis (%), Found: C, 51·6; H, 4·35; N, 22·65; S, 10·8; $C_{13}H_{13}N_5O_2S$ requires: C, 51·5; H, 4·3; N, 23·1; S, 10·6.

5a Yield, 27%; m.p. 201–202°C (green needles). Analysis (%), Found: C, 56·3; H, 4·65; N, 16·15; S, 9·4; $C_{16}H_{16}N_4O_3S$ requires: C, 55·8; H, 4·65; N, 16·3; S, 9·3.

5b Yield, 13%; m.p. 184–186°C (green-black crystals). Analysis (%), Found: C, 48·95; H, 3·95; N, 19·9; S, 9·1; $C_{14}H_{13}N_5O_4S$ requires: C, 48·4; H, 3·75; N, 20·2; S, 9·2.

6a Yield, trace; m.p. 155–157°C (dark red crystals). M^+, 299·1088; $C_{16}H_{17}N_3OS$ requires: M, 299·1092.

6b Yield, 2%; m.p. 174–176°C (red crystals) Analysis (%), Found: C, 60·8; H, 5·5; N, 13·1; S, 10·1; $C_{16}H_{17}N_3O_2S$ requires: C, 60·95; H, 5·4; N, 13·3; S, 10·2.

7a Yield, 13%; m.p. 218–220°C (violet leaflets). Analysis (%), Found: C, 64·8; H, 5·2; N, 20·7; S, 9·6; $C_{18}H_{17}N_5S$ requires: C, 64·5; H, 5·1; N, 20·9; S, 9·55.

7b Yield, 13%; m.p. 218–219°C (violet leaflets). Analysis (%), Found: C, 51·55; H, 4·9; N, 23·05; S, 21·0; $C_{13}H_{15}N_5S_2$ requires: C, 51·15; H, 4·9; N, 22·95; S, 21·0.

8 Yield, 26%; m.p. 223–225°C (purple leaflets). Analysis (%), Found: C, 52·8; H, 5·3; N, 21·75; S, 19·95; $C_{14}H_{17}N_5S_2$ requires: C, 52·7; H, 5·3; N, 21·9; S, 20·1.

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