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Colour and Constitution of Thiophene and Thiazole Azo Dyes: Application of CNDO/S and PPP Methods

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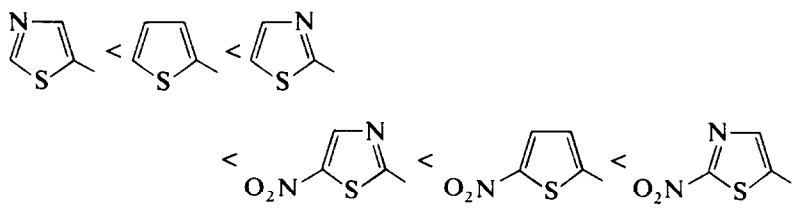
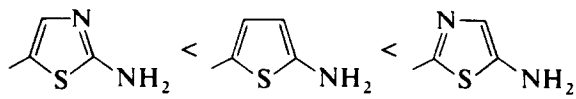
SUMMARY

*The electronic absorption spectra of a series of thiophene and thiazole azo dyes have been calculated by the CNDO/S method with inclusion of the 3*d *atomic orbitals on the sulphur atom and by the PPP method. The results calculated by the two methods consistently suggested that the orders of bathochromic effect of the diazo and coupling are as follows.*

Diazo component:



Coupling component:



*The CNDO/S calculations revealed that the bathochromicity of these dyes is not attributable to the 3*d *atomic orbitals on the sulphur atom.*

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1. INTRODUCTION

Thiophene and thiazole azo dyes, which belong to one of the most important groups of disperse dyes, absorb at much longer wavelengths than the corresponding phenyl azo dyes. It is of interest therefore to elucidate the relationship between the colour and constitution of these dyes, particularly the origin of the bathochromic effect.

Fabian and co-workers[1] have calculated the absorption spectra of various sulphur-heterocyclic dyes by the PPP method. The calculated results are in good agreement with experiments. Griffiths[2] has described how the PPP calculations predict a bathochromic effect of some thiophene and thiazole azo dyes but the magnitude of the shifts is less than that observed. On the other hand, in thiophene itself, the CNDO/S calculations with inclusion of 3*d* atomic orbitals (AO) on the sulphur atom have suggested that the 3*d* AOs may contribute to the first excitation energy.[3]

Thus it is interesting to examine the role of sulphur in thiophene and thiazole azo dyes by such a modified CNDO/S method. However, few examples of application of the CNDO/S method to azo dye systems have been published and the reliability of this method is still uncertain.

In this communication, for a series of thiophene and thiazole azo dyes the colour–structure relationships and the contribution of the 3*d* AOs on the sulphur atom are discussed on the basis of the modified CNDO/S and PPP calculations.

2. THE COMPUTATIONAL METHOD

The standard CNDO/INDO program[4] was modified according to the CNDO/S formalism[5] for the ground state wavefunctions and combined with the part for the excited state ones in the CNDO/S program.[6] The treatment of the sulphur atom followed the parameterization described by Schulte and Schweig:[3] the DBJ2 parameter set was employed.

The PPP method was the same as in a previous paper.[7]

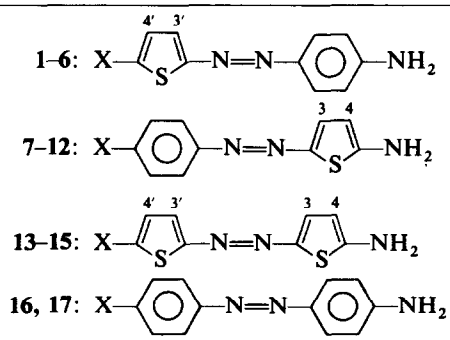
For simplicity, a planar structure was assumed for all the molecules studied.

3. RESULTS AND DISCUSSION

Table 1 shows the first excitation energies (ΔE_1) and the corresponding oscillator strengths (f_1) calculated by the CNDO/S and PPP methods. In Fig. 1, the CNDO/S ΔE_1 values are plotted against the PPP ΔE_1 values. The correlation between the CNDO/S and PPP ΔE_1 is not satisfactory

TABLE 1
First Excitation Energies (ΔE_1) and Oscillator Strengths (f_1) Calculated by CNDO/S and PPP Methods

Dye no.	*Aza*	*X*	*CNDO/S*		*PPP*	
			ΔE_1 (*eV*)	f_1	ΔE_1 (*eV*)	f_1
1	—	H	3·72	1·13	3·26	1·10
2	3′	H	3·68	1·08	3·20	1·00
3	4′	H	3·76	1·10	3·34	1·04
4	—	NO_2	3·43	1·22	3·04	1·22
5	3′	NO_2	3·52	1·21	3·10	1·09
6	4′	NO_2	3·28	1·07	3·00	1·07
7	—	H	3·59	1·06	3·05	1·03
8	3	H	3·47	0·93	2·85	0·77
9	4	H	3·75	1·05	3·34	0·93
10	—	NO_2	3·40	1·17	2·89	1·16
11	3	NO_2	3·30	1·02	2·72	0·87
12	4	NO_2	3·56	1·18	3·18	1·03
13	—	NO_2	3·17	1·18	2·71	1·22
14	3′,4	NO_2	3·40	1·14	3·02	0·99
15	4′,3	NO_2	3·04	1·02	2·59	0·89
16	—	H	3·98	1·16	3·44	1·05
17	—	NO_2	3·74	1·24	3·27	1·15



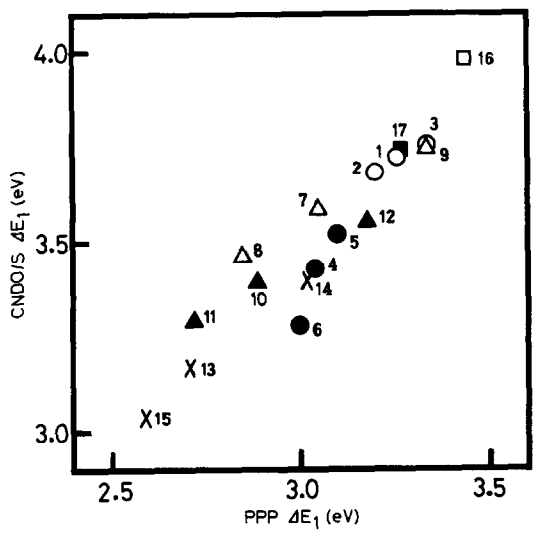
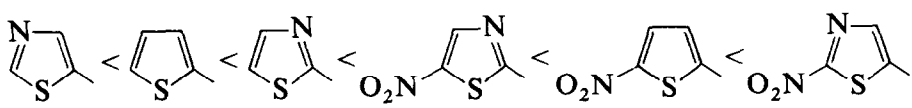


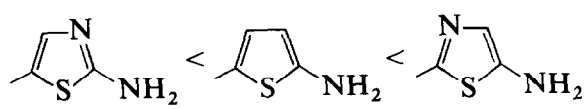
Fig. 1. Comparison between CNDO/S and PPP ΔE_1.

and the former values are always larger by ca. 0·3–0·6 eV than the latter. However, if the dyes are divided into the four groups, namely **1–6**, **7–9**, **10–12** and **13–15**, an excellent correlation between the CNDO/S and PPP ΔE_1 is found within each group, and hence it is suggested that the orders of bathochromic effect of the diazo and coupling components are as follows:

Diazo component



Coupling component



The replacement of =CH— by =N— at the 3′-position of thiophene azo dye **1** causes a bathochromic shift (**2**), and the replacement at the 4′-position gives rise to a hypsochromic shift (**3**). On the other hand, relative to 5′-nitrothiophene azo dyes **4**, 3′-aza dye **5** is hypsochromic and 4′-aza

dye **6** is bathochromic, showing that the 5′-nitro substitution reverses the effects of 3′- and 4′-aza substitutions on the absorption spectra.

This finding can be well interpreted by focusing attention on the energy levels of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) and their LCAO coefficients at the 3′- and 4′-positions shown in Fig. 2. It is apparent from Fig. 2 that the first excitation energy predominantly depends on the energy difference between the LUMO and HOMO. The LCAO coefficients in the HOMOs of both **1** and its 5′-nitro derivative **4** have larger values at the 3′-position than at the 4′-position. Hence, the HOMOs of both 3′-aza dyes **2** and **5** become lower in energy than those of 4′-aza dyes **3** and **6**, respectively, because nitrogen is more negative than carbon.

On the other hand, in the LUMOs of **1** and **4**, the position which has the larger value of the LCAO coefficient is the 3′-position for **1** and the 4′-position for **4**. Accordingly, the LUMO of 3′-aza dye **2** derived from **1** is much lower in energy than that of 4′-aza dye **3**, whereas the LUMO of 4′-aza dye **6** derived from 5′-nitro derivative **4** is lower than that of 3′-aza dye **5**. Thus, the 5′-nitro substitution reverses the effects of the 3′- and 4′-aza substitutions on the energy level of the LUMO, and consequently, on the first excitation energy.

In the case of dyes **7**–**12**, such a reversal of the effects of the 3- and 4-aza substitutions does not appear because the nitro group is too far away to influence the LCAO coefficients for the heterocyclic ring in both the HOMO and LUMO.

Table 2 shows the LCAO coefficients for the $3p_z$, $3d_{xz}$ and $3d_{yz}$ AOs on the sulphur atom in the HOMO and LUMO, and the total π-electron density changes (ΔP_π) on the sulphur atom accompanying the first electronic excitation: the HOMO and LUMO are π-type molecular orbitals and expressed in terms of the $2p_z$ AOs for carbon and nitrogen atoms and the $3p_z$, $3d_{xz}$ and $3d_{yz}$ AOs for the sulphur atom.

A relatively large absolute value of the LCAO coefficient is obtained for the $3p_z$ AO of the three π-type AOs on the sulphur atom. For example, the maximum value is calculated to be 0·215 for the $3p_z$ AO in the LUMO of **5**. However, the value is still smaller than those for the $2p_z$ AOs on carbon atoms in the heterocyclic ring (see Fig. 2). The coefficient values for the $3d_{xz}$ and $3d_{yz}$ AOs are below only 0·1 and much smaller than those for the $2p_z$ AOs, suggesting that the contribution of the $3d$ AOs to the first electronic excitation is negligible.

As anticipated from the above, the ΔP_π values of all the dyes in Table 2

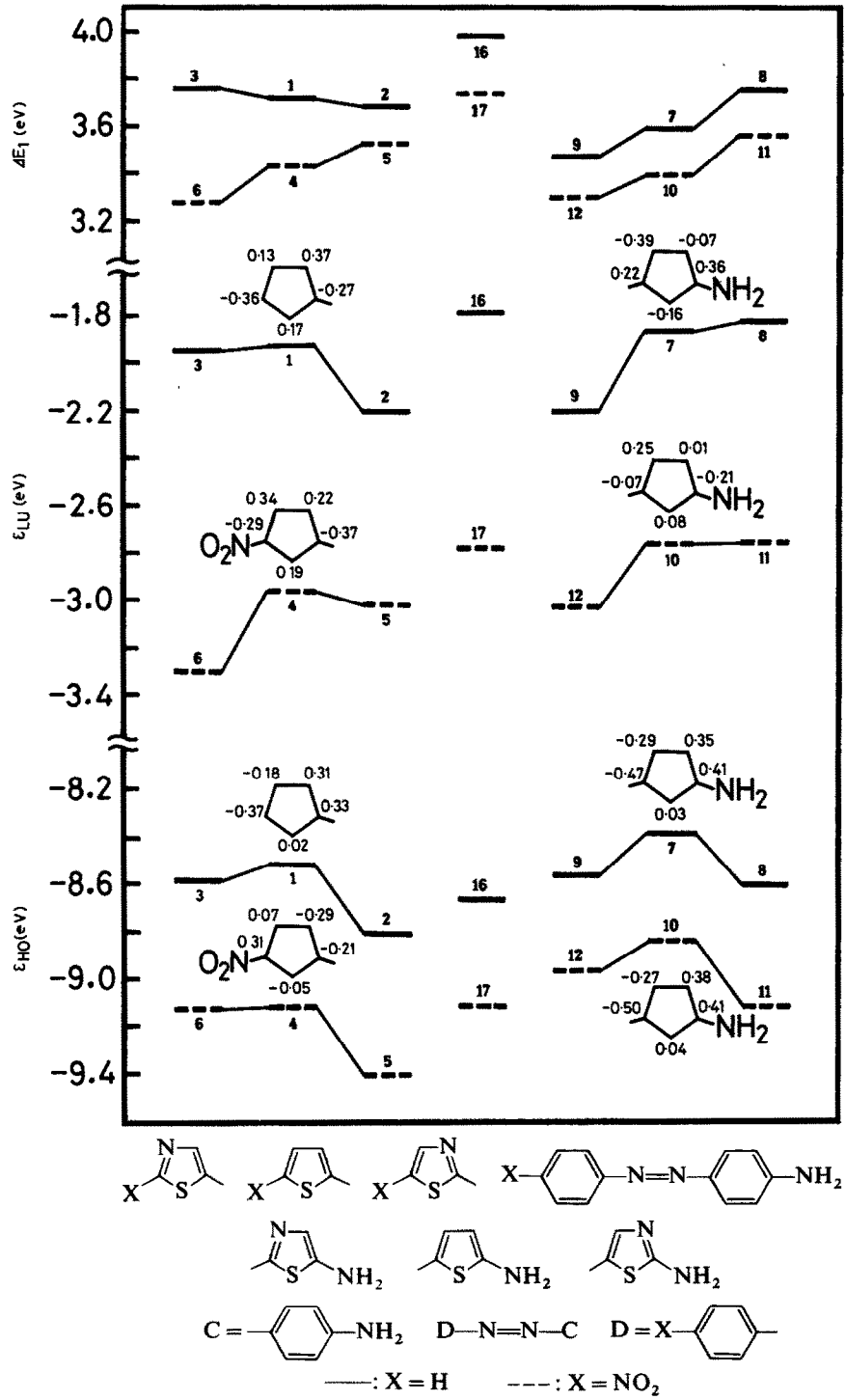


Fig. 2. Energy levels of the HOMO (ε_{HO}) and LUMO (ε_{LU}), the first excitation energy ΔE_1, and the LCAO coefficients at key positions.

TABLE 2

LCAO Coefficients of $3p_z$,$3d_{xz}$, $3d_{yz}$ AOs on the Sulphur Atom in HOMO and LUMO and Total π-Electron Density Changes (ΔP_π) on the Sulphur Atom Accompanying the First Electronic Excitation

Dye no.		*LCAO coefficient* HOMO	LUMO	$(\Delta P_z)^a$ Δp_π	*Dye no.*		*LCAO coefficient* HOMO	LUMO	$(\Delta P_z)^a$ ΔP_π
	$3p_z$	0·024	0·174	(0·030)		$3p_z$	0·029	−0·155	(0·023)
1	$3d_{xz}$	0·072	0·022		**7**	$3d_{xz}$	−0·089	−0·026	
	$3d_{yz}$	0·015	−0·070			$3d_{yz}$	−0·026	0·065	
				0·029					0·020
	$3p_z$	−0·015	−0·197	(0·039)		$3p_z$	0·047	−0·175	(0·028)
2	$3d_{xz}$	0·059	−0·035		**8**	$3d_{xz}$	0·091	−0·006	
	$3d_{yz}$	0·021	0·080			$3d_{yz}$	0·007	0·074	
				0·041					0·025
	$3p_z$	−0·111	−0·187	(0·023)		$3p_z$	−0·089	0·160	(0·018)
3	$3d_{xz}$	−0·070	−0·002		**9**	$3d_{xz}$	0·074	0·033	
	$3d_{yz}$	0·002	0·076			$3d_{yz}$	0·038	−0·068	
				0·023					0·015
	$3p_z$	−0·046	0·187	(0·033)		$3p_z$	0·041	0·082	(0·005)
4	$3d_{xz}$	−0·053	0·001		**10**	$3d_{xz}$	−0·093	0·020	
	$3d_{yz}$	−0·007	−0·073			$3d_{yz}$	−0·028	−0·026	
				0·031					−0·002
	$3p_z$	0·023	0·215	(0·046)		$3p_z$	0·035	−0·119	(0·013)
5	$3d_{xz}$	0·047	0·019		**11**	$3d_{xz}$	0·094	−0·009	
	$3d_{yz}$	0·011	−0·077			$3d_{yz}$	0·010	0·043	
				0·048					0·005
	$3p_z$	−0·113	−0·199	(0·027)		$3p_z$	−0·120	0·071	(−0·009)
6	$3d_{xz}$	−0·042	0·011		**12**	$3d_{xz}$	0·078	0·019	
	$3d_{yz}$	0·007	0·081			$3d_{yz}$	0·041	−0·022	
				0·026					−0·015

[a] The electron density change in the $3p_z$ AO on the sulphur atom accompanying the promotion of an electron from the HOMO to LUMO.

are small and nearly equal to the ΔP_z values, where ΔP_z is the electron density change in the $3p_z$ AO on the sulphur atom accompanying the promotion of an electron from the HOMO to LUMO.

In addition, the CNDO/S calculations without inclusion of the 3*d* AOs on the sulphur atom give ΔE_1 values of 3·68 eV for **1** and 3·53 eV for **7**. These values are smaller than those calculated with inclusion of 3*d* AOs (3·72 eV for **1** and 3·59 eV for **7**). Furthermore, the CNDO/S ΔE_1 value for the analogous furan azo dye is calculated to be 3·59 eV by assuming the same geometry as that of the thiophene azo dye **1**, which is much smaller than the value for **1**.

Thus, it can be concluded that the bathochromicity of the thiophene and thiazole azo dyes studied here is not attributable to the 3*d* AOs on the sulphur atom in the heterocyclic ring.

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