Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 74 (2007) 95–102
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Single crystal X-ray structure analysis of some heterocyclic monoazo disperse dyes

Kamaljit Singh [a,*], Aman Mahajan [a], Ward T. Robinson [b]

[a] *Department of Applied Chemical Sciences and Technology, Guru Nanak Dev University, Amritsar 143 005, India*
[b] *Department of Chemistry, University of Canterbury, Christchurch, New Zealand*

Received 6 September 2005; received in revised form 17 November 2005; accepted 6 January 2006
Available online 10 March 2006

Abstract

Single crystal X-ray structures of monoazo disperse dyes comprising thiadiazolyl based diazo component and *m*-aminoacetanilide based coupling component were analysed and compared with a thiazolyl based monoazo disperse dye. It has been found that contrary to the earlier findings intramolecular hydrogen bonding between the β-nitrogen of the azo linkage and *o*-acetylamino substituent on the coupler is not the exclusive factor for the observed brightness of such dyes. An unequivocal evidence of the non-existence of such interaction has been presented.

Keywords: Heterocyclic disperse dyes; X-ray; Crystal structure; Thiadiazolylazo; Thiazolylazo; Monoazo dyes

1. Introduction

The single crystal X-ray structure determination of disperse dyes is important, not because it reveals molecular conformation and intra- and intermolecular interactions in solid state but also the structural information gained from the analysis assists towards understanding the technical performance of the dyes [1–3]. The heterocyclic disperse dyes which are in use for polyester coloration and other high-tech applications, surprisingly are faced with the limitation of availability of insufficient structural data [4]. Furthermore, in the case of monoazo disperse dyes having hydrogen-bonding substituents on the coupling component at *o*-position to the azo linkage; the brightness has been associated with its intramolecular hydrogen bonding interactions with the β-azo nitrogen. Thus in the case of monoazo dyes derived from heterocyclic diazo components a similar intramolecular hydrogen bonding of the *o*-acetylamino substituent on the coupler with the azo linkage has been reasoned to enforce planarity [5], leading to narrow half-band widths of the absorption band in the visible spectrum of the dye. In the present investigation we demonstrate that an intramolecular hydrogen bonding between the β-nitrogen of the azo linkage and *o*-acetylamino substituent on the coupler is not the exclusive factor for the observed brightness of such dyes.

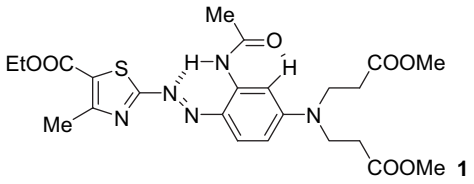
2. Experimental

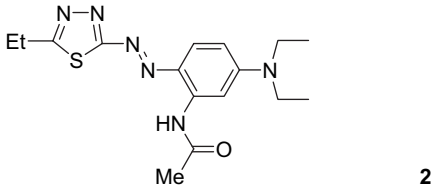
The synthesis and X-ray structure of 2-{2-acetylamino-4-[bis-(2-methoxycarbonylethyl)amino]phenylazo}-4-methylthiazole-5-carboxylic acid ethyl ester **1** has been reported earlier [6,7]. The dyes *N*-[5-diethylamino-2-(5-ethyl-[1,3,4]-thiadiazol-2-ylazophenyl]acetamide **2** and 3-{[3-acetylamino-4-(1,3,4-thiadiazol)phenyl]-(2-ethoxycarbonylethyl)amino}propionic acid ethyl ester **3** were synthesized analogously. The synthesis, characterization and color properties of these dyes will be reported elsewhere [8]. Suitable X-ray quality crystals of dyes **2** and **3** were grown by slow evaporation of the chloroform/hexane (9:1 v/v) solution.

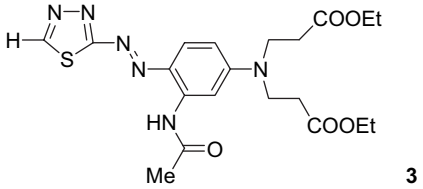
Relevant crystallographic data [9] and details of measurement are given in Table 1. X-ray crystallographic data were

* Corresponding author. Tel.: +91 183 258853; fax: +91 183 258819 20.
E-mail address: kamaljit19in@yahoo.co.in (K. Singh).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.01.018







collected from single crystal ($0.35 \times 0.30 \times 0.30$ mm^3). Unit cell dimensions were obtained using 25 centered reflections in θ range from 5.4700° to 10.8000° mounted on a Nonius MACH 3 diffractometer equipped with graphite monochromated Mo Kα radiation (0.71073 Å). The intensity data were collected by $\omega - 2\theta$ scan mode, and corrected by Lorentz polarization and absorption effects using Psi-scan (ψ-scan). Three standard reflections were monitored for every 200 reflection and three intensity control reflections were monitored every hour, and showed no significant changes (<3%). The structure was solved by direct methods using SHELXL-97 and refined by full-matrix least squares against F^2 using SHELXL-97 software [10]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Crystal data for dye **2**: $C_{16}H_{22}N_6OS$, $M = 346.46$, trigonal, space group R-3, $a = 30.0850(18)$ Å, $b = 30.085(2)$ Å, $c = 11.4510(12)$ Å, $\alpha = \beta = 90$ °, $\gamma = 120$ °, $U = 8975.8(12)$ Å^3, $D_c = 1.154$ Mg/m^3, $Z = 18$, $F(000) = 3312$, $\lambda = 0.71073$ Å, $\mu = 0.176$ mm^{-1}, total/unique reflections = 2407/2407 [$R_{int} = 0.0000$], $T = 293(2)$ K, θ range = 1.94°–24.98°, final $R[I > 2\sigma(I)]$. $R1 = 0.0926$, $wR2 = 0.2333$, R (all data): $R1 = 0.1627$, $wR2 = 0.2779$. Table 2 records the atomic coordinates and equivalent isotropic displacement parameters and Table 3 records bond lengths and angles for **2**, whereas the anisotropic displacement parameters are recorded in Table 4. Hydrogen coordinates and isotropic displacement parameters are given in Table 5 and torsion angles are given in Table 6.

Likewise, crystals of the dye **3**, suitable for single crystal X-ray diffraction work could also be obtained by slow evaporation from chloroform/hexane (9:1 v/v) mixture. The structural analysis was performed using SMARTCCD area detector and 0.3° ϕ scans. The crystal with molecular formula $C_{20}H_{26}N_6O_5S$ and relative molecular mass 462.53 was triclinic with space group P-1 with $a = 5.6710(18)$, $b = 13.663(2)$,

Table 1
Crystal data and structure refinement of dye **2**

Identification code	**2** (CCDC no. 270791)
Empirical formula	$C_{16}H_{22}N_6OS$
Formula weight	346.46
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	R-3
Unit cell dimensions	$a = 30.0850(18)$ Å, $\alpha = 90°$ $b = 30.085(2)$ Å, $\beta = 90°$ $c = 11.4510(12)$ Å, $\lambda = 120.000°$
Volume, Z	8975.8(12) Å^3, 18
Density (calculated)	1.154 Mg/m^3
Absorption coefficient	0.176 mm^{-1}
$F(000)$	3312
Crystal size	$0.35 \times 0.30 \times 0.30$ mm
θ Range for data collection	1.94°–24.98°
Index ranges	$0 \le h \le 35$, $-29 \le k \le 0$, $-13 \le l \le 13$
Reflections collected/unique	2407/2407 [$R_{int} = 0.0000$]
Completeness to 2θ	24.98, 22.9%
Absorption correction	Psi-scan
Maximum and minimum transmission	0.9490 and 0.9408
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2407/0/225
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0926$, $wR2 = 0.2333$
R indices (all data)	$R1 = 0.1627$, $wR2 = 0.2779$
Largest diff. peak and hole	0.688 and −0.318 eÅ^{-3}

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) of dye **2**

	x	y	z	U(eq)
S(1)	3821(1)	1498(1)	7347(2)	63(1)
O(1)	5544(3)	3814(3)	8904(6)	87(2)
N(1)	4909(3)	3619(2)	12 787(5)	64(2)
N(2)	4873(3)	3000(3)	8873(6)	65(2)
N(3)	4021(2)	2126(2)	9357(5)	51(2)
N(4)	3589(2)	1718(2)	9538(5)	56(2)
N(5)	3002(3)	981(3)	8534(6)	71(2)
N(6)	2928(3)	712(2)	7496(6)	69(2)
C(1)	4370(5)	3775(5)	14 121(9	120(4)
C(2)	4701(4)	3558(3)	13 984(7)	76(3)
C(3)	5382(4)	4110(3)	12 554(8)	88(3)
C(4)	5855(5)	4062(4)	12 764(12)	133(5)
C(5)	5302(5)	3367(4)	7071(9)	116(4)
C(6)	5270(4)	3431(4)	8379(8)	70(3)
C(7)	4671(3)	2940(3)	10 014(7)	51(2)
C(8)	4909(3)	3320(3)	10 862(6)	53(2)
C(9)	4677(3)	3246(3)	11 970(6)	52(2)
C(10)	4219(3)	2782(3)	12 200(6)	50(2)
C(11)	4009(3)	2425(3)	11 374(6)	48(2)
C(12)	4214(3)	2473(3)	10 258(6)	45(2)
C(13)	3438(3)	1395(3)	8570(6)	52(2)
C(14)	3321(3)	930(3)	6818(7)	60(2)
C(15)	3354(4)	722(4)	5671(8)	90(3)
C(16)	2969(6)	203(5)	5445(10)	155(6)

U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

Table 3
Bond lengths (Å) and angles (deg) of dye **2**

S(1)–C(14)	1.726(8)	C(6)–N(2)–C(7)	128.2(8)
S(1)–C(13)	1.739(7)	C(6)–N(2)–H(2N)	113(7)
O(1)–C(6)	1.192(10)	C(7)–N(2)–H(2N)	119(7)
O(1)–C(9)	1.356(9)	N(4)–N(3)–C(12)	116.6(6)
N(1)–C(3)	1.475(11)	N(3)–N(4)–C(13)	111.2(6)
N(1)–C(2)	1.480(10)	C(13)–N(5)–N(6)	111.3(6)
N(2)–C(6)	1.370(11)	C(14)–N(6)–N(5)	112.3(6)
N(2)–C(7)	1.413(9)	C(2)–C(1)–H(1A)	109.5
N(2)–H(2N)	0.86(11)	C(2)–C(1)–H(1B)	109.5
N(3)–N(4)	1.281(7)	H(5A)–C(5)–H(5B)	109.5
N(3)–C(12)	1.372(8)	C(6)–C(5)–H(5C)	109.5
N(4)–C(13)	1.393(9)	H(1A)–C(1)–H(1B)	109.5
N(5)–C(13)	1.282(9)	C(2)–C(1)–H(1C)	109.5
N(5)–N(6)	1.392(9)	H(1A)–C(1)–H(1C)	109.5
N(6)–C(14)	1.286(10)	H(1B)–C(1)–H(1C)	109.5
C(1)–C(2)	1.445(13)	C(1)–C(2)–N(1)	113.0(8)
C(1)–H(1A)	0.9600	C(1)–C(2)–H(2A)	109.0
C(1)–H(1B)	0.9600	N(1)–C(2)–H(2A)	109.0
C(1)–H(1C)	0.9600	C(1)–C(2)–H(2B)	109.0
C(2)–H(2A)	0.9700	N(1)–C(2)–H(2B)	109.0
C(2)–H(2B)	0.9700	H(2A)–C(2)–H(2B)	107.8
C(3)–C(4)	1.518(15)	N(1)–C(3)–C(4)	110.9(8)
C(3)–H(3A)	0.9700	N(1)–C(3)–H(3A)	109.5
C(3)–H(3B)	0.9700	C(4)–C(3)–H(3A)	109.5
C(4)–H(4A)	0.9600	N(1)–C(3)–H(3B)	109.5
C(4)–H(4B)	0.9600	C(4)–C(3)–H(3B)	109.5
C(5)–C(6)	1.519(13)	H(3A)–C(3)–H(3B)	108.0
C(5)–H(5A)	0.9600	C(3)–C(4)–H(4A)	109.5
C(5)–H(5B)	0.9600	C(3)–C(4)–H(4B)	109.5
C(5)–H(5C)	0.9600	H(4A)–C(4)–H(4B)	109.5
C(7)–C(8)	1.394(10)	C(3)–C(4)–H(4C)	109.5
C(7)–C(12)	1.418(10)	H(4A)–C(4)–H(4C)	109.5
C(8)–C(9)	1.410(10)	H(4B)–C(4)–H(4C)	109.5
C(8)–H(8)	0.9300	C(6)–C(5)–H(5A)	109.5
C(9)–C(10)	1.412(10)	C(6)–C(5)–H(5B)	109.5
C(10)–C(11)	1.329(10)	H(5A)–C(5)–H(5B)	109.5
C(10)–H(10)	0.9300	C(6)–C(5)–H(5C)	109.5
C(11)–C(12)	1.395(10)	H(5A)–C(5)–H(5C)	109.5
C(11)–H(11)	0.9300	H(5B)–C(5)–H(5C)	109.5
C(14)–C(15)	1.479(11)	O(1)–C(6)–N(2)	124.1(8)
C(15)–C(16)	1.429(14)	O(1)–C(6)–C(5)	124.2(8)
C(15)–H(15A)	0.9700	N(2)–C(6)–C(5)	111.6(8)
C(15)–H(15B)	0.9700	C(8)–C(7)–N(2)	121.8(7)
C(16)–H(16A)	0.9600	C(8)–C(7)–C(12)	121.4(7)
C(16)–H(16B)	0.9600	N(2)–C(7)–C(12)	116.8(7)
C(16)–H(16C)	0.9600	C(7)–C(8)–C(9)	119.2(7)
C(14)–S(1)–C(13)	86.2(4)	C(7)–C(8)–H(8)	120.4
C(9)–N(1)–C(3)	122.9(7)	C(9)–C(8)–H(8)	120.4
C(9)–N(1)–C(2)	121.7(7)	N(1)–C(9)–C(8)	118.7(7)
C(3)–N(1)–C(2)	115.3(7)	N(1)–C(9)–C(10)	122.3(7)
C(8)–C(9)–C(10)	119.0(7)	N(6)–C(14)–S(1)	114.7(6)
C(11)–C(10)–C(9)	120.0(7)	C(15)–C(14)–S(1)	121.3(7)
C(11)–C(10)–H(10)	120.0	C(16)–C(15)–C(14)	115.7(9)
C(9)–C(10)–H(10)	120.0	C(16)–C(15)–H(15A)	108.4
C(9)–C(10)–H(10)	120.0	C(14)–C(15)–H(15A)	108.4
C(10)–C(11)–C(12)	124.2(7)	C(16)–C(15)–H(15B)	108.4
C(10)–C(11)–H(11)	117.9	C(14)–C(15)–H(15B)	108.4
C(12)–C(11)–H(11)	117.9	H(15A)–C(15)–H(15B)	107.4
N(3)–C(12)–C(11)	127.9(7)	C(15)–C(16)–H(16A)	109.5
N(3)–C(12)–C(7)	115.9(6)	C(15)–C(16)–H(16B)	109.5
C(11)–C(12)–C(7)	116.2(6)	H(16A)–C(16)–H(16B)	109.5
N(5)–C(13)–N(4)	121.5(7)	C(15)–C(16)–H(16C)	109.5
N(5)–C(13)–S(1)	114.4(6)	H(16A)–C(16)–H(16C)	109.5
N(4)–C(13)–S(1)	124.1(6)	H(16B)–C(16)–H(16C)	109.5
N(6)–C(14)–C(15)	124.0(8)		

Table 4
Anisotropic displacement parameters ($A^2 \times 10^3$) of dye **2**

	U11	U22	U33	U23	U13	U12
S(1)	64(1)	60(1)	52(1)	−7(1)	11(1)	22(1)
O(1)	99(5)	63(4)	77(5)	9(4)	32(4)	23(4)
N(1)	86(5)	51(4)	41(4)	−2(3)	6(3)	25(4)
N(2)	84(5)	49(4)	49(4)	4(4)	27(4)	23(4)
N(3)	64(4)	44(4)	42(4)	−1(3)	1(3)	26(4)
N(4)	60(4)	47(4)	46(4)	−3(3)	3(3)	16(4)
N(5)	74(5)	55(4)	57(5)	−11(4)	15(4)	12(4)
N(6)	68(5)	55(4)	59(5)	−15(4)	1(4)	11(4)
C(1)	187(13)	126(10)	90(8)	16(7)	38(8)	111(10)
C(2)	118(8)	60(6)	41(5)	−1(4)	1(5)	37(6)
C(3)	121(9)	51(6)	72(7)	−8(5)	−6(6)	28(6)
C(4)	109(10)	82(8)	154(13)	−9(8)	−26(9)	6(7)
C(5)	154(11)	95(8)	69(7)	11(6)	54(7)	39(7)
C(6)	93(7)	50(6)	64(6)	9(5)	26(5)	34(6)
C(7)	56(5)	42(5)	54(5)	8(4)	8(4)	25(4)
C(8)	63(5)	32(4)	53(5)	0(4)	4(4)	15(4)
C(9)	62(5)	47(5)	42(5)	−2(4)	−2(4)	23(4)
C(10)	57(5)	54(5)	32(4)	0(4)	−3(4)	23(4)
C(11)	55(5)	46(4)	41(5)	10(4)	10(4)	25(4)
C(12)	49(4)	43(4)	41(4)	−3(4)	2(3)	22(4)
C(13)	63(5)	47(5)	39(5)	−1(4)	2(4)	22(4)
C(14)	72(6)	53(5)	53(5)	3(4)	9(5)	29(5)
C(15)	122(8)	87(7)	52(6)	−18(5)	9(6)	45(7)
C(16)	230(16)	105(10)	95(10)	−34(8)	26(10)	58(11)

The anisotropic displacement factor exponent takes the form: $2\pi^2[h^2a^{*2}U \times 11 + \cdots + 2hka^*b^*U12]$.

$c = 15.003(3)$ Å, $v = 1116.4(5)$ Å^3, $z = 2$. A total of 8474 reflections are presented (Table 7).

The structure was solved by direct methods using SHELXL-93 and full matrix least-squares refinement based on F^2 data with anisotropic thermal parameters for all the

Table 5
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($A^2 \times 10^3$) of dye **2**

	x	y	z	U(eq)
H(1A)	4542	4121	13 834	144
H(1B)	4290	3774	14 933	144
H(1C)	4059	3573	13 689	144
H(2A)	4510	3196	14 176	91
H(2B)	4984	3723	14 530	91
H(3A)	5393	4374	13 059	105
H(3B)	5381	4212	11 751	105
H(4A)	5862	3970	13 564	160
H(4B)	6158	4384	12 598	160
H(4C)	5845	3802	12 262	160
H(5A)	5589	3670	6757	139
H(5B)	4992	3314	6706	139
H(5C)	5344	3076	6925	139
H(8)	5216	3618	10 700	64
H(10)	4064	2726	12 930	60
H(11)	3706	2125	11 552	57
H(15A)	3336	938	5065	108
H(15B)	3687	747	5613	108
H(16A)	3034	−24	5909	186
H(16B)	2974	128	4632	186
H(16C)	2638	156	5642	186
H(2N)	4750(4)	2740(4)	8420(9)	120(4)

Table 6
Torsion angles (deg) of dye **2**

C(12)–N(3)–N(4)–C(13)	−179.1(6)	N(4)–N(3)–C(12)–C(11)	3.3(11)
C(13)–N(5)–N(6)–C(14)	2.1(10)	N(4)–N(3)–C(12)–C(7)	−175.1(6)
C(9)–N(1)–C(2)–C(1)	−94.1(10)	C(10)–C(11)–C(12)–N(3)	−179.5(7)
C(3)–N(1)–C(2)–C(1)	85.8(11)	C(10)–C(11)–C(12)–C(7)	−1.1(11)
C(9)–N(1)–C(3)–C(4)	−86.8(11)	C(8)–C(7)–C(12)–N(3)	−179.1(7)
C(2)–N(1)–C(3)–C(4)	93.2(11)	N(2)–C(7)–C(12)–N(3)	0.8(10)
C(7)–N(2)–C(6)–O(1)	8.2(15)	C(8)–C(7)–C(12)–C(11)	2.3(10)
C(7)–N(2)–C(6)–C(5)	−169.2(9)	N(2)–C(7)–C(12)–C(11)	−177.8(6)
C(6)–N(2)–C(7)–C(8)	−8.2(13)	N(6)–N(5)–C(13)–N(4)	−179.6(7)
C(6)–N(2)–C(7)–C(12)	171.9(8)	N(6)–N(5)–C(13)–S(1)	−1.7(9)
N(2)–C(7)–C(8)–C(9)	177.3(7)	N(3)–N(4)–C(13)–N(5)	−175.4(7)
C(12)–C(7)–C(8)–C(9)	−2.8(11)	N(3)–N(4)–C(13)–S(1)	6.8(9)
C(3)–N(1)–C(9)–C(8)	2.9(12)	C(14)–S(1)–C(13)–N(5)	0.7(7)
C(2)–N(1)–C(9)–C(8)	−177.2(8)	C(14)–S(1)–C(13)–N(4)	178.6(7)
C(3)–N(1)–C(9)–C(10)	−178.8(8)	N(5)–N(6)–C(14)–C(15)	178.4(8)
C(2)–N(1)–C(9)–C(10)	1.1(12)	N(5)–N(6)–C(14)–S(1)	−1.6(9)
C(7)–C(8)–C(9)–N(1)	−179.6(7)	C(13)–S(1)–C(14)–N(6)	0.6(7)
C(7)–C(8)–C(9)–C(10)	2.0(11)	C(13)–S(1)–C(14)–C(15)	−179.4(8)
N(1)–C(9)–C(10)–C(11)	−179.2(7)	N(6)–C(14)–C(15)–C(16)	−13.1(15)
C(8)–C(9)–C(10)–C(11)	−0.8(11)	S(1)–C(14)–C(15)–C(16)	166.9(9)
C(9)–C(10)–C(11)–C(12)	0.4(11)		

non-hydrogen atoms that were carried out. All the hydrogens were fixed geometrically and made to ride on their respective atoms. A final refinement of 292 parameters with no restraints gave $R = 0.0333$ for observed reflections. Table 8 records the atomic coordinates and equivalent isotropic displacement parameters and Table 9 records bond lengths and angles of dye **3**, whereas the anisotropic displacement parameters are recorded in Table 10. Hydrogen coordinates and isotropic

Table 7
Crystal data and structure refinement of dye **3**

Identification code	**3** (CCDC no. 269429)
Empirical formula	$C_{20}H_{26}N_6O_5S$
Formula weight	462.53
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	$a = 5.6710(18)$ Å, $\alpha = 104.208(3)^\circ$ $b = 13.663(2)$ Å, $\beta = 92.204(3)^\circ$ $c = 15.003(3)$ Å, $\gamma = 96.774(3)^\circ$
Volume, *Z*	1116.4(5) Å^3, 2
Density (calculated)	1.376 Mg/m^3
Absorption coefficient	0.190 mm^{-1}
F(000)	488
Crystal size	2.0 × 2.0 × 1.5 mm
θ Range for data collection	2.34°–26.40°
Limiting indices	$-6 \le h \le 6$, $-15 \le k \le 17$, $-18 \le l \le 18$
Reflections collected/unique	8474/4437 [$R_{int} = 0.0473$]
Completeness to θ	26.40, 97.2%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4437/0/292
Goodness-of-fit on F^2	0.850
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0333$, $wR2 = 0.0663$
R indices (all data)	$R1 = 0.0591$, $wR2 = 0.0693$
Largest diff. peak and hole	0.275 and −0.245 eÅ^{-3}

Table 8
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) of dye **3**

	x	*y*	*z*	*U*(eq)
C(0)	−5728(3)	752(1)	3992(1)	18(1)
C(1)	722(3)	2297(1)	3099(1)	14(1)
C(2)	−1434(3)	1897(1)	3400(1)	14(1)
C(3)	−2781(3)	1042(1)	2862(1)	14(1)
C(4)	−2069(3)	547(1)	1986(1)	14(1)
C(5)	108(3)	933(1)	1704(1)	15(1)
C(6)	1478(3)	1766(1)	2241(1)	14(1)
C(7)	−8025(3)	102(1)	4042(1)	23(1)
C(8)	−8304(3)	−2439(1)	−533(1)	19(1)
C(9)	−4780(3)	−1451(1)	205(1)	14(1)
C(11)	1144(3)	3772(1)	4443(1)	16(1)
C(12)	1350(3)	3354(1)	5288(1)	18(1)
C(13)	3847(3)	3402(1)	5682(1)	17(1)
C(14)	6165(3)	2827(1)	6749(1)	23(1)
C(15)	5750(4)	2250(2)	7465(1)	43(1)
C(21)	4263(3)	3578(1)	3308(1)	16(1)
C(22)	3902(3)	4194(1)	2610(1)	15(1)
C(23)	6244(3)	4704(1)	2418(1)	16(1)
C(24)	8265(3)	5619(2)	1476(1)	29(1)
N(0)	−2948(2)	−748(1)	705(1)	16(1)
N(1)	2039(2)	3151(1)	3613(1)	14(1)
N(2)	−3654(2)	−238(1)	1466(1)	15(1)
N(3)	−4370(2)	−2153(1)	−512(1)	20(1)
N(4)	−6452(2)	−2740(1)	−944(1)	22(1)
N(5)	−4896(2)	602(1)	3138(1)	15(1)
O(0)	−4673(2)	1341(1)	4672(1)	29(1)
O(13)	5620(2)	3819(1)	5445(1)	20(1)
O(14)	3842(2)	2930(1)	6368(1)	21(1)
O(23)	8103(2)	4744(1)	2852(1)	20(1)
O(24)	6035(2)	5133(1)	1711(1)	20(1)
S(1)	−7762(1)	−1434(1)	418(1)	18(1)
C(25)	7818(4)	5882(2)	580(1)	45(1)

U(eq) is defined as one-third of the trace of the orthogonalized *Uij* tensor.

Table 9
Bond lengths (Å) and angles (deg) of dye **3**

C(0)–O(0)	1.2184(19)	C(23)–O(24)	1.340(2)
C(0)–N(5)	1.3590(19)	C(24)–O(24)	1.4542(18)
C(0)–C(7)	1.503(2)	C(24)–C(25)	1.494(3)
C(1)–N(1)	1.3500(19)	C(24)–H(24A)	0.9700
C(1)–C(2)	1.415(2)	C(24)–H(24B)	0.9700
C(1)–C(6)	1.423(2)	N(0)–N(2)	1.2879(17)
C(2)–C(3)	1.371(2)	N(3)–N(4)	1.3858(18)
C(2)–H(2)	0.9300	N(5)–H(51)	0.8600
C(3)–N(5)	1.4007(18)	C(25)–H(25A)	0.9600
C(3)–C(4)	1.419(2)	C(25)–H(25B)	0.9600
C(4)–N(2)	1.3700(19)	C(25)–H(25C)	0.9600
C(4)–C(5)	1.406(2)	O(0)–C(0)–N(5)	123.15(15)
C(5)–C(6)	1.356(2)	O(0)–C(0)–C(7)	122.13(15)
C(5)–H(5)	0.9300	N(5)–C(0)–C(7)	114.69(14)
C(6)–H(6)	0.9300	N(1)–C(1)–C(2)	121.11(14)
C(7)–H(7A)	0.9600	N(1)–C(1)–C(6)	120.85(13)
C(7)–H(7B)	0.9600	C(2)–C(1)–C(6)	118.03(14)
C(7)–H(7C)	0.9600	C(3)–C(2)–C(1)	120.54(14)
C(8)–N(4)	1.2957(19)	C(3)–C(2)–H(2)	119.7
C(8)–S(1)	1.7093(17)	C(1)–C(2)–H(2)	119.7
C(8)–H(8)	0.9300	C(2)–C(3)–N(5)	122.77(14)
C(9)–N(3)	1.303(2)	C(2)–C(3)–C(4)	120.94(14)
C(9)–N(0)	1.3839(19)	N(5)–C(3)–C(4)	116.28(14)
C(9)–S(1)	1.7347(15)	N(2)–C(4)–C(5)	125.55(14)
C(11)–N(1)	1.4689(19)	N(2)–C(4)–C(3)	116.24(13)
C(11)–C(12)	1.520(2)	C(5)–C(4)–C(3)	118.10(14)
C(11)–H(11A)	0.9700	C(6)–C(5)–C(4)	121.35(15)
C(11)–H(11B)	0.9700	C(6)–C(5)–H(5)	119.3
C(12)–C(13)	1.501(2)	C(4)–C(5)–H(5)	119.3
C(12)–H(12A)	0.9700	C(5)–C(6)–C(1)	120.93(14)
C(12)–H(12B)	0.9700	C(5)–C(6)–H(6)	119.5
C(13)–O(13)	1.2059(18)	C(1)–C(6)–H(6)	119.5
C(13)–O(14)	1.3420(19)	C(0)–C(7)–H(7A)	109.5
C(14)–O(14)	1.4518(19)	C(0)–C(7)–H(7B)	109.5
C(14)–C(15)	1.492(3)	H(7A)–C(7)–H(7B)	109.5
C(14)–H(14A)	0.9700	C(0)–C(7)–H(7C)	109.5
C(14)–H(14B)	0.9700	H(7A)–C(7)–H(7C)	109.5
C(15)–H(15A)	0.9600	H(7B)–C(7)–H(7C)	109.5
C(15)–H(15B)	0.9600	N(4)–C(8)–S(1)	116.13(12)
C(15)–H(15C)	0.9600	N(4)–C(8)–H(8)	121.9
C(21)–N(1)	1.4643(18)	S(1)–C(8)–H(8)	121.9
C(21)–C(22)	1.518(2)	N(3)–C(9)–N(0	114.67(12)
C(21)–H(21A)	0.9700	N(0)–C(9)–S(1)	124.20(12)
C(21)–H(21B)	0.9700	N(1)–C(11)–C(12)	114.24(13)
C(22)–C(23)	1.497(2)	N(1)–C(11)–H(11A)	108.7
C(22)–H(22A)	0.9700	C(12)–C(11)–H(11A)	108.7
C(22)–H(22B)	0.9700	N (1)–C(11)–H(11B)	108.7
C(23)–O(23)	1.2066(18)	C(12)–C(11)–H(11B)	108.7
H(11A)–C(11)–H(11B)	107.6	C(23)–C(22)–H(22B)	109.6
C(13)–C(12)–C(11)	114.98 (13)	C(21)–C(22)–H(22B)	109.6
C(13)–C(12)–H(12A)	108.5	H(22A)–C(22)H(22B)	108.1
C(11)–C(12)–H(12A)	108.5	O(23)–C(23)–O(24)	123.43(14)
C(13)–C(12)–H(12B)	108.5	O(23)–C(23)–C(22)	124.58(16)
C(11)–C(12)–H(12B)	108.5	O(24)–C(23)–C(22)	111.98(13)
H(12A)–C(12)–H(12B)	107.5	O(24)–C(24)–C(25)	107.93(15)
O(13)–C(13)–O(14)	123.80 (15)	O(24)–C(24)–H(24A)	110.1
O(13)–C(13)–C(12)	126.13(16)	C(25)–C(24)–H(24A)	110.1
O(14)–C(13)–C(12)	110.05 (13)	O(24)–C(24)–H(24B)	110.1
O(14)–C(14)–C(15)	106.94(14)	C(25)–C(24)–H(24B)	110.1
O(14)–C(14)–H(14A)	110.3	H(24A)–C(24)H(24B)	108.4
C(15)–C(14)–H(14A)	110.3	N(2)–N(0)–C(9)	110.98(12)
O(14)–C(14)–H(14B)	110.3	C(1)–N(1)–C(21)	121.74(13)
C(15)–C(14)–H(14B)	110.3	C(1)–N(1)–C(11)	121.27(12)
H(14A)–C(14)H(14B)	108.6	C(21)–N(1)–C(11)	116.47(12)
C(14)–C(15)–H(15A)	109.5	N(0)–N(2)–C(4)	116.77(12)
C(14)–C(15)–H(15B)	109.5	C(9)–N(3)–N(4)	111.87(12)
H(15A)–C(15)H(15B)	109.5	C(8)–N(4)–N(3)	111.47(14)
C(14)–C(15)–H(15C)	109.5	C(0)–N(5)–C(3)	129.24(14)
H(15A)–C(15)H(15C)	109.5	C(0)–N(5)–H(51)	115.4
H(15B)–C(15)H(15C)	109.5	C(3)–N(5)–H(51)	115.4
N(1)–C(21)–C(22)	113.70 (12)	C(13)–O(14)–C(14)	115.81(12)
N(1)–C(21)–H(21A)	108.8	C(23)–O(24)–C(24)	114.49(12)
C(22)–C(21)–H(21A)	108.8	C(8)–S(1)–C(9)	85.84(8)
N(1)–C(21)–H(21B)	108.8	C(24)–C(25)–H(25A)	109.5
C(22)–C(21)–H(21B)	108.8	C(24)–C(25)–H(25B)	109.5
H(21A)–C(21)H(21B)	107.7	H(25A)–C(25)H(25B)	109.5
C(23)–C(22)–C(21)	110.38 (13)	C(24)–C(25)–H(25C)	109.5
C(23)–C(22)–H(22A)	109.6	H(25A)–C(25)H(25C)	109.5
C(21)–C(22)–H(22A)	109.6	H(25B)–C(25)H(25C)	109.5
C(23)–C(22)–H(22B)	109.6		

displacement parameters are given in Table 11 and torsion angles are given in Table 12.

3. Results and discussion

We have recently reported [7] on the single crystal X-ray structure determination of a monoazo disperse dye **1**, similar

Table 10
Anisotropic displacement parameters ($A^2 \times 10^3$) of dye **3**

	*U*11	*U*22	*U*33	*U*23	*U*13	*U*12
C(0)	23(1)	14(1)	17(1)	3(1)	5(1)	6(1)
C(1)	15(1)	13(1)	14(1)	6(1)	−1(1)	3(1)
C(2)	16(1)	16(1)	12(1)	3(1)	1(1)	6(1)
C(3)	14(1)	14(1)	16(1)	6(1)	2(1)	5(1)
C(4)	15(1)	12(1)	15(1)	5(1)	−1(1)	3(1)
C(5)	19(1)	16(1)	13(1)	4(1)	3(1)	7(1)
C(6)	12(1)	16(1)	16(1)	6(1)	2(1)	3(1)
C(7)	24(1)	26(1)	22(1)	9(1)	10(1)	5(1)
C(8)	19(1)	20(1)	17(1)	6(1)	−3(1)	1(1)
C(9)	15(1)	16(1)	14(1)	5(1)	3(1)	3(1)
C(11)	14(1)	14(1)	18(1)	0(1)	2(1)	1(1)
C(12)	19(1)	18(1)	13(1)	1(1)	3(1)	−1(1)
C(13)	25(1)	11(1)	12(1)	−3(1)	2(1)	2(1)
C(14)	32(1)	18(1)	20(1)	5(1)	−3(1)	6(1)
C(15)	56(1)	51(2)	36(1)	26(1)	14(1)	28(1)
C(21)	14(1)	16(1)	16(1)	3(1)	0(1)	0(1)
C(22)	16(1)	13(1)	15(1)	2(1)	1(1)	3(1)
C(23)	22(1)	12(1)	12(1)	−3(1)	3(1)	3(1)
C(24)	28(1)	31(1)	29(1)	13(1)	7(1)	−7(1)
N(0)	17(1)	16(1)	15(1)	13(1)	2(1)	2(1)
N(1)	14(1)	15(1)	13(1)	2(1)	2(1)	2(1)
N(2)	17(1)	15(1)	13(1)	4(1)	1(1)	4(1)
N(3)	20(1)	20(1)	17(1)	−1(1)	3(1)	1(1)
N(4)	22(1)	21(1)	20(1)	2(1)	1(1)	0(1)
N(5)	13(1)	19(1)	12(1)	3(1)	1(1)	−2(1)
O(0)	39(1)	26(1)	16(1)	0(1)	9(1)	−7(1)
O(13)	18(1)	22(1)	19(1)	7(1)	0(1)	−2(1)
O(14)	25(1)	23(1)	16(1)	9(1)	3(1)	5(1)
O(23)	15(1)	24(1)	19(1)	3(1)	1(1)	0(1)
O(24)	21(1)	22(1)	18(1)	10(1)	4(1)	−1(1)
S(1)	14(1)	21(1)	18(1)	2(1)	2(1)	3(1)
C(25)	46(1)	57(2)	40(1)	29(1)	10(1)	−5(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U \times 11 + \cdots + 2hka^*b^*U12]$.

Table 11
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($A^2 \times 10^3$) of dye **3**

	x	*y*	*z*	*U*(eq)
H(2)	−1941	2217	3968	17
H(5)	618	611	1137	18
H(6)	2932	1992	2045	17
H(7A)	−7701	−452	4297	35
H(7B)	−8791	−164	3434	35
H(7C)	−9050	506	4427	35
H(8)	−9839	−2752	−743	22
H(11A)	−516	3829	4312	19
H(11B)	2018	4452	4582	19
H(12A)	451	3731	5762	21
H(12B)	619	2649	5127	21
H(14A)	7050	3493	7021	28
H(14B)	7068	2463	6269	28
H(15A)	4940	2638	7954	64
H(15B)	7250	2131	7709	64
H(15C)	4792	1610	7195	64
H(21A)	5148	3025	3037	19
H(21B)	5217	4010	3841	19
H(22A)	3130	3749	2042	18
H(22B)	2877	4705	2847	18
H(24A)	9462	5160	1420	35
H(24B)	8834	6230	1954	35
H(51)	−5797	177	2705	18
H(25A)	7277	5271	110	68
H(25B)	9265	6211	414	68
H(25C)	6623	6332	641	68

to the ones studied in the current investigation. We evidenced the presence of an intramolecular H-bonding between amide hydrogen (H2A) and azo nitrogen (N4) with amide nitrogen···N4 distance being 2.687(1) Å, H2A···N4 distance 2.0 Å and the azo bond length link was 1.285 Å, longer than the similar reported systems [4,11–13]. This clearly indicates the effect of the *o*-acetylamino substituent on the bond length of the azo linkage. This enlargement of azo bond length indirectly proved the presence of strong intramolecular hydrogen bonding, which aided in forcing a part of the molecule to lie in a plane. Fig. 1A shows the ORTEP diagram of the structure of dye **2** as well as the numbering scheme used. Most of the bond lengths and bond angles are normal. The bond length of the azo link, i.e. N3═N4 is 1.281 Å and is similar to the one observed for dye **1**. Surprisingly there is no evidence of any hydrogen bonding of the acetylamino group with the azo β-nitrogen N4. Since the molecular framework is non-coplanar no centroid-to-centroid distance could be located, however, the azo link maintains *trans* geometry as indicated by the angles N4–N3–C12 (116.6°) and N3–N4–C13 (111.2°). The torsion angles C2–N1–C9–C8 (−177°), C3–N1–C9–C10 (−178.8°) and C2–N1–C9–C10 (1.1°), C3–N1–C9–C8 (2.9°) indicate the *syn* and *anti* dispositions of the ethyl chains attached to a coupler side chain and that these chains are only slightly non-coplanar (Fig. 1B) with the chromophore skeleton unlike the side chains of the coupler moiety of the related dye **1**. More surprising is the observed unusual increase in the bond length of the amide CO (C6–O1) that is found to be 1.92 Å. A possible reason for this observation could be linked to the existence of a unique O1–C9 (bond length = 1.356 Å) contact. This is the only contact, the acetylamino group is found to make with any other part of the molecule. Thus from these findings, it can be argued that there is no intramolecular interaction between the acetylamino substituent and the azo linkage, which has earlier been held responsible for the observed brightness of the dyeings of such dyes.

Table 12
Torsion angles (deg) of dye **3**

N(1)–C(1)–C(2)–C(3)	178.58(15)	C(22)–C(21)–N(1)–C(1)	79.82(18)
C(6)–C(1)–C(2)–C(3)	−2.1(2)	C(22)–C(21)–N(1)–C(11)	−91.96(16)
C(1)–C(2)–C(3)–N(5)	178.39(14)	C(12)–C(11)–N(1)–C(1)	79.27(18)
C(1)–C(2)–C(3)–C(4)	−1.0(2)	C(12)–C(11)–N(1)–C(21)	−108.91(15)
C(2)–C(3)–C(4)–N(2)	−173.73(14)	C(9)–N(0)–N(2)–C(4)	−174.19(13)
N(5)–C(3)–C(4)–N(2)	6.9(2)	C(5)–C(4)–N(2)–N(0)	9.6(2)
C(2)–C(3)–C(4)–C(5)	2.7(2)	C(3)–C(4)–N(2)–N(0)	−174.34(14)
N(5)–C(3)–C(4)–C(5)	−176.73(14)	N(0)–C(9)–N(3)–N(4)	−176.54(14)
N(2)–C(4)–C(5)–C(6)	174.81(15)	S(1)–C(9)–N(3)–N(4)	−0.24(18)
C(3)–C(4)–C(5)–C(6)	−1.2(2)	S(1)–C(8)–N(4)–N(3)	−0.61(19)
C(4)–C(5)–C(6)–C(1)	−1.9(2)	C(9)–N(3)–N(4)–C(8)	0.5(2)
N(1)–C(1)–C(6)–C(5)	−177.11(15)	O(0)–C(0)–N(5)–C(3)	1.0(3)
C(2)–C(1)–C(6)–C(5)	3.6(2)	C(7)–C(0)–N(5)–C(3)	−176.78(15)
N(1)–C(11)–C(12)–C(13)	69.20(18)	C(2)–C(3)–N(5)–C(0)	−16.0(3)
C(11)–C(12)–C(13)–O(13)	7.4(2)	C(4)–C(3)–N(5)–C(0)	163.41(15)
C(11)–C(12)–C(13)–O(14)	−174.24(13)	O(13)–C(13)–O(14)–C(14)	−7.7(2)
N(1)–C(21)–C(22)–C(23)	173.32(12)	C(12)–C(13)–O(14)–C(14)	173.92(13)
C(21)–C(22)–C(23)–O(23)	−10.2(2)	C(15)–C(14)–O(14)–C(13)	−177.73(14)
C(21)–C(22)–C(23)–O(24)	171.03(13)	O(23)–C(23)–O(24)–C(24)	2.7(2)
N(3)–C(9)–N(0)–N(2)	−168.97(15)	C(22)–C(23)–O(24)–C(24)	−178.51(13)
S(1)–C(9)–N(0)–N(2)	15.1(2)	C(25)–C(24)–O(24)–C(23)	169.46(15)
C(2)–C(1)–N(1)–C(21)	−179.54(14)	N(4)–C(8)–S(1)–C(9)	0.40(14)
C(6)–C(1)–N(1)–C(21)	1.2(2)	N(3)–C(9)–S(1)–C(8)	−0.07(13)
C(2)–C(1)–N(1)–C(11)	−8.1(2)	N(0)–C(9)–S(1)–C(8)	176.09(15)
C(6)–C(1)–N(1)–C(11)	172.59(14)		

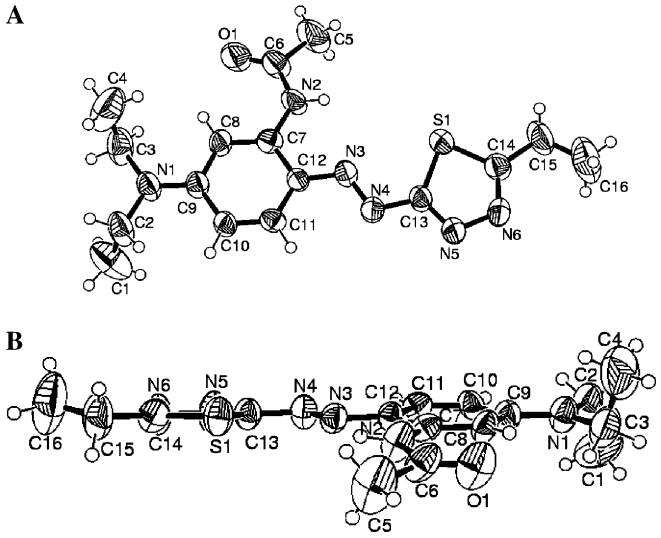


Fig. 1. X-ray structure and crystallographic numbering of atoms of dye **2**: (A) top side view, (B) view from the plane of the molecule, showing the planarity of the donor–acceptor part.

Fig. 2 shows the ORTEP diagram [9] and the numbering scheme of the structure of dye **3**. The structure consists of well-separated monomeric molecules. The shortest intermolecular distances of 3.2 Å from S and N atoms indicate that there is no intermolecular hydrogen bonding. The main feature of note is an apparent delocalization of electron density along the chain of connected atoms from N2 to N4. This is evident from the covalent bond lengths described in Table 9. The bond length of the azo link N0–N2 in this molecule is 1.2879 Å, similar to the one observed for dyes **1** and **2**. Again there is no evidence for intramolecular hydrogen bonding of the *N*-acetylamino group in this molecule. However, the *trans* disposition of the azo linkage is supported by the angles N0–N2–C4 (116.77°) and N2–N0–C9 (110.98°). The torsion angles C11–N1–C1–C2 (−8.1°), C21–N1–C1–C6 (1.2°), C11–N1–C1–C6 (172.59°) and C21–N1–C1–C2 (−179.54°) describe the orientation of the side chains of the coupler aligning perpendicular to the plane of the aromatic ring unlike dye **2** where the two ethyl chains are in the plane of the chromophore. This can be ascribed to the relatively small size of the ethyl side chains.

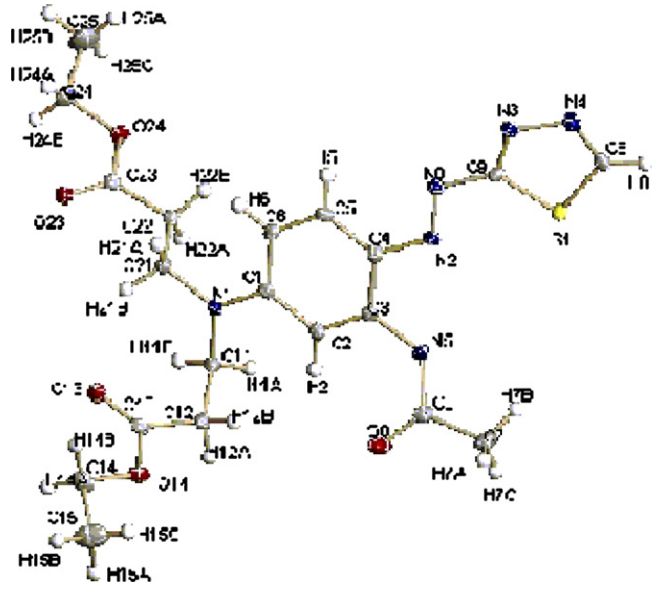


Fig. 2. X-ray structure and crystallographic numbering of atoms of dye **3** (top view showing the planarity of the donor–acceptor part and *trans* disposition of azo linkage).

In contrast to the structure of dye **2**, the amide carbonyl bond length C0–O0 is normal (1.2184 Å) and the orientation of the amide group is away from the chromophoric skeleton and no hydrogen bonding contact of the NH is observed with any other atom in the structure.

Thus from this investigation, it has been found that in none of the two thiadiazole based dyes **2** and **3**, the intramolecular hydrogen bonding of the *N*-acetylamino group of the coupler with the azo β-nitrogen is observed. However, in the thiazole dye **1**, a moderate to strong interaction between the NH of the amide group and the azo β-nitrogen was observed. Since the dyes **1** and **3** have same coupling component, different from the dye **2**, the driving force in enforcing the planarity in the chromophore doesn't seem to be the intramolecular hydrogen bonding of the *N*-acetylamino group with the azo β-nitrogen, but the diazo component (thiazolyl in dye **1** and thiadiazolyl in dyes **2** and **3**) appears to play an important role. On the other hand, unlike dye **3**, the bulky ester substituent at C5 of thiazole in dye **1**, might orient the azo linkage to assist the development of intramolecular hydrogen bonding with the *N*-acetylamino group of the coupler. Thus the observed bathochromism and brightness of the dyeings (vide infra) of the thiazolyl dyes used in this investigation may be attributed to the electronic factors (inductive and more importantly mesomeric effect) rather than the enforcement of rigidity in the chromophore through the intramolecular hydrogen bonding of the acetylamino substituent with the azo β-nitrogen.

4. Conclusions

The single crystal X-ray structures of the three heterocyclic monoazo dyes have been compared and it has been unequivocally evidenced that the presence of an *o*-acetylamino substituent on the coupler does not ensure intramolecular hydrogen bonding with the azo linkage and that the observed brightness of the dyeings of these dyes may at large originate from the electronic factors.

Acknowledgements

KS is grateful to National Single Crystal X-ray Diffraction Facility, IIT Powai, Bombay (India) for crystallographic work of dye **3**.

References

[1] Dawson JF. JSDC 1983;99:183.
[2] Annen O, Egli R, Hasler B, Jakob H, Matzinger P. Rev Prog Color 1987;17:72.
[3] Leadbetter PW, Leaver AT. Rev Prog Color 1989;19:33.
[4] Temel A, Ozbey S, Ertan N. Dyes Pigments 1996;32:237.
[5] Gordon PF, Gregory P. Organic chemistry in colour. Berlin: Springer; 1983. p. 129.
[6] Singh K, Singh S, Taylor JA. Dyes Pigments 2002;54:189.
[7] Singh K, Singh S, Garg PK, Hundal MS. Color Technol 2004;120:72.
[8] Singh K, Mahajan A. Unpublished results.
[9] Crystallographic data for the dyes **2** and **3** have been deposited at Cambridge Crystallographic Data Centre [CCDC no. 270791 (dye **2**) and 269429 (dye **3**)]. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK.
[10] Sheldrick GM. SHELXTL-PC version 5.03. Madison, WI: Siemens Analytical Instruments Inc.; 1995.
[11] Park K-M, Yoon I, Lee SS, Choi G, Lee JS. Dyes Pigments 2002;54:155.
[12] Kavounis CA, Rentzeperis PJ. Acta Crystallogr Sect C Cryst Struct Commun 1984;40:1434.
[13] Butler RN, Evans AM, Gillian AM, James JP, McNeela EM, Cunningham D, et al. J Chem Soc Perkin Trans 1 1990:2537.