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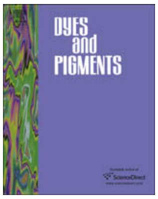

Single crystal X-ray structure analysis for two thiazolylazo indole dyes

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ABSTRACT

To determine the tautomeric form of the hetarylazo indole dye 3-(5-methylthiazol-2-yldiazenyl)-2-phenyl-1*H*-indole (**1**), 1-methyl-3-(thiazol-2-yldiazenyl)-2-phenyl-1*H*-indole (**2**) was synthesized as a model compound and both molecules were characterized by single crystal X-ray diffraction. (**1**) crystallized in the monoclinic system, space group $C2/c$, $a = 31.064(2)$, $b = 7.4051(5)$, $c = 27.7138(18)$ Å, $\beta = 97.617(1)^\circ$, $V = 6318.9(7)$ Å^3, $Z = 8$, while dye **2** crystallized in the monoclinic system, space group $P2_1/n$, $a = 11.4660(11)$, $b = 9.8223(9)$, $c = 14.2049(14)$ Å, $\beta = 97.418(2)^\circ$, $V = 1586.4(3)$ Å^3, $Z = 4$. The asymmetric unit of **1** contains two crystallographically independent molecules, in which geometries and conformations differ slightly, while there is only one molecule in the asymmetric unit for **2**. The intermolecular N–H···N hydrogen bonds in (**1**) link the molecules, via parallel, infinite sheets, along the *a* axis and stabilize the crystal structure; in **2**, there is no classical intermolecular hydrogen bond.

1. Introduction

Azo compounds are very important in the field of dyes, pigments and advanced materials [1]. It has been known for many years that the azo compounds are the most widely used class of dyes, due to their versatile applications in various fields such as the dyeing of textile fibers, the coloring of different materials, colored plastics and polymers, biological-medical studies and advanced applications in organic synthesis [2–6]. They are also used in the fields of nonlinear optics and optical data storage [5,7,8]. Their optical properties depend on not only the spectroscopic properties of the molecules but also their crystallographic arrangements [9,10].

Heterocyclic diazo components have also been extensively used in the preparation of disperse dyes. These dyes are also characterized by having generally excellent brightness and high extinction coefficients, relative to azo dyes derived from substituted anilines. Disperse monoazo dyes from enamine-type coupling components are known to exhibit azo-hydrazone tautomerism. Azo-hydrazone tautomerism is quite interesting in a theoretical viewpoint, it is also important from a practical standpoint because the two tautomers have different technical properties. Knowledge of the tautomeric form of the dyestuff in the solid phase is primarily important for dye-fiber interactions. The X-ray single crystal structure of disperse dyes has been important, not only because it provides details of the molecular conformation, including the intra- and inter-molecular interactions in the solid state but also because this information assists towards understanding the technical performance of the products [11–18].

Previously, the synthesis, crystal structures, spectroscopic and tautomeric properties of novel bis-hetarylazo indole dyes have been reported in solution and solid state [19–30]. In continuation of our work, we aimed to find new data for supporting the molecule structures of two new potential dyestuffs in solid state.

2. Experimental

2.1. Synthesis

The structures (Fig. 1) of 3-(5-methylthiazol-2-yldiazenyl)-2-phenyl-1*H*-indole (**1**) and 1-methyl-3-(thiazol-2-yldiazenyl)-2-phenyl-1*H*-indole (**2**) have been confirmed by FT-IR, ^{1}H NMR, elemental analysis and mass spectral data. The synthesis, characterization and spectroscopic properties of the dyes have been reported [30]. Suitable single crystals for X-ray analysis of dyes **1** and **2** were obtained by slow evaporation from ethanol.

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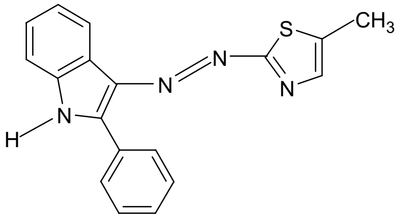
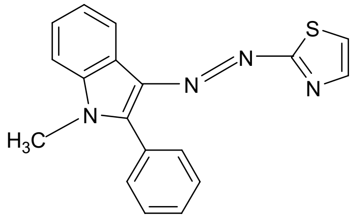


3-(5-methylthiazol-2-yldiazenyl)-2-phenyl-1H-indole (**1**)



1-methyl-3-(thiazol-2-yldiazenyl)-2-phenyl-1H-indole (**2**)

Fig. 1. Structures of dyes.

2.2. *Crystallography*

The X-ray diffraction data collections were performed on a Bruker-AXS SMART CCD area-detector diffractometer equipped with Mo Kα ($\lambda = 0.71073$ Å) radiation using w-scans. The intensity data were corrected for Lorentz-polarization [31] and absorption [31] effects. The structures were analyzed using a combination of direct and difference Fourier methods provided by the SHELXS97 [32] and were refined as full matrix least squares against F^2 for all data by the SHELXL97 [32] computer programs; all non-hydrogen atoms were refined anisotropically. H1 and H24 atoms (for NH, in dye **1**) were located in difference synthesis and refined isotropically [N–H = 0.89(2) and 0.83(2) Å]. The remaining H atoms were positioned geometrically, with C–H=0.93 and 0.96 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for aromatic H, and $x = 1.5$ for methyl H atoms. Crystal data and details of the structure determinations for dyes **1** and **2** are summarized in Table 1.

Table 1
Crystal data and details of the structure determinations for dyes **1** and **2**.

Empirical formula	$C_{36}H_{28}N_8S_2$ (**1**)	$C_{18}H_{14}N_4S$ (**2**)
Formula weight	636.78	318.39
Crystal dimensions (mm)	0.75 × 0.25 × 0.08	0.72 × 0.63 × 0.41
Temperature (K)	297(2)	297(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2$_1$/*n*
a (Å)	31.064(2)	11.4660(11)
b (Å)	7.4051(5)	9.8223(9)
c (Å)	27.7138(18)	14.2049(14)
β (°)	97.617(1)	97.418(2)
Volume (Å^3)	6318.9(7)	1586.4(3)
Z	8	4
D_{calc} (g cm^{-3})	1.339	1.333
$2\theta_{max}$ (°)	52	56.42
μ (mm^{-1})	0.209	0.208
No. of reflections measured	17895	10361
No. of reflections observed[$I > 2\delta(I)$]	6203	3847
No. of variables	425	210
R/R_w values	0.0698/0.1311	0.0448/0.1286
Color/shape	Orange/plate	Red/block
Maximum shift in final cycles	0.000	0.000
Largest diffraction peak and hole (e Å^{-3})	0.467 and −0.183	0.344 and −0.318

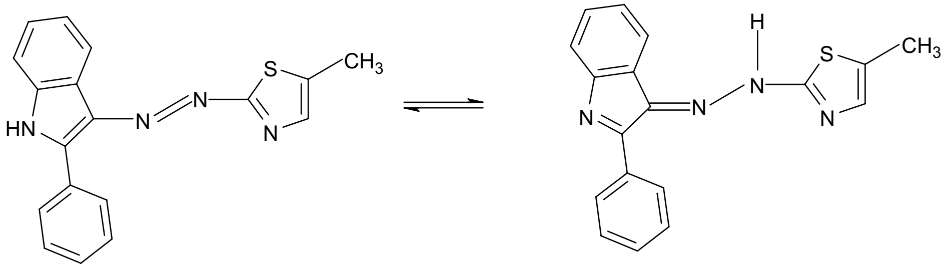
3. Results and discussion

Dye **1** may exist in azo-enamine form **A** or hydrazone-imine form **B**, in solid state and solution, as depicted in Fig. 2. In the case of dye **2**, the compound could only exist in azo-enamine form, and the structural results supported this idea. To determine the tautomeric forms of the dye (dye **1**) in solid state, X-ray data for dyes **1** and **2** were recorded (Table 1).

The asymmetric unit of dye **1**, containing two crystallographically independent molecules, in which geometries and conformations of them are slightly different (Fig. 3), while there was only one molecule in the asymmetric unit for dye **2** (Fig. 5). The selected bond lengths and angles and hydrogen-bond geometry for the dyes **1** and/or **2** are given in Tables 2–4. The results of X-ray analysis indicate that the dye **1** is in azo-enamine form. An examination of the deviations from the least-square planes through the individual rings showed that all of the rings are planar in the dyes **1** and **2**. The indole ring systems were planar, with dihedral angles of 1.44(2)° and 1.22(3)° between the rings: A (N1/C2–C5) and B (C4–C9), A′(N24/C25–C28) and B′(C27–C32) in dye **1**, and 1.26(3)° between rings A (N1/C2–C5) and B (C4–C9) in dye **2**. In the closely related compounds, 2-phenyl-3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole **3** [21], 3-(4-chlorophenyldiazenyl)-1-methyl-2-phenyl-1*H*-indole **4** [22], *N*-{4-[(2-phenyl-1*H*-indol-3-yl)diazenyl]phenyl}acetamide **5** [23], ethyl[2-(2-phenyl-1*H*-indol-3-yldiazenyl)-1,3-thiazol-4-yl]acetate **6** [24], ethyl 2-{[(2-phenyl-1*H*-indol-3-yl)diazenyl]thiazol-4-yl}acetate **7** [25], 1-methyl-2-phenyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole**8** [26], 1,2-dimethyl-3-(thiazol-2-yldiazenyl)-1*H*-indole **9** [27], 3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1-methyl-2-phenyl-1*H*-indole **10** [28] and 3-(6-methoxybenzothiazol-2-yldiazenyl)-1-methyl-2-phenyl-1*H*-indole **11** [29], the observed A/B and/or A′/B′ dihedral angles were 2.28(9)° and 1.32(11)° in **3**, 1.56(11)° and 0.77(12)° in **4**, 1.63(14)° in **5**, 0.99(10)° in **6**, 0.59(7)° in **7**, 4.26(7)° in **8**, 2.07(9)° and 2.04(9)° in **9**, 0.59(12)° in **10** and 1.16(7)° in **11**. The orientations of rings C (S19/N22/C18/C20/C21), D (C10–C15) and C′ (S42/N45/C41/C43/C44), D′ (C33–C38) (in dye **1**) and C (S20/N23/C19/C21/C22) and D (C11–C16) (in dye **2**) with respect to the indole ring systems might be described by the dihedral angles of 7.97(3)°, 23.35(3)°, 3.94(2)° and 24.14(2)° (for dye **1**) and 7.99(3)° and 51.11(2)° (for dye **2**), respectively.

The phenyl rings are rotated around the C2–C10 and C25–C33 (in dye **1**) and C2–C11 (in dye **2**) bonds with the corresponding torsion angles of N1–C2–C10–C15 [156.2(2)°] and N24–C25–C33–C38 [−157.5(4)°] (for dye **1**) and N1–C2–C11–C16 [−132.6(2)°] (for dye **2**). The molecules of dye **1** are in the azo-enamine forms and they have apparent delocalisation of electron densities along the chains of the connected atoms through the N atoms. The molecules of the dyes **1** and **2** have *trans* geometries about the azo linkages and the torsion angles of the central –C–N=N–C– are −177.78(18)° [C3–N16–N17–C18] and 177.74(19)° [C26–N39–N40–C41] (for dye **1**) and 176.72(11)° [C3–N17–N18–C19] (for dye **2**).

In dye **1** (Fig. 3), intermolecular N–H···N hydrogen bonds (Table 4) link the molecules, into parallel infinite sheets along the *a* axis (Fig. 4), in which they seem to be effective in the stabilization of the crystal structure. In dye **2** (Fig. 5), there is no classical intermolecular hydrogen bond. In the crystal structure, the molecules are aligned in the [100] and [010] directions differently with respect to that of [001], in such a way that neighbouring indole planes face in anti-parallel fashion (Fig. 6). In dyes **1** and **2**, dipole–dipole and van der Waals interactions were effective in the molecular packing. The single crystal X-ray diffraction study on dye **1** clearly indicates that the present compound exists in azo-enamine form rather than in hydrazone-imine form in the solid state and this is in good agreement in our previous studies [19–30].



(A)
(azo-enamine)

(B)
(hydrazone-imine)

Fig. 2. Tautomeric forms of dye **1**.

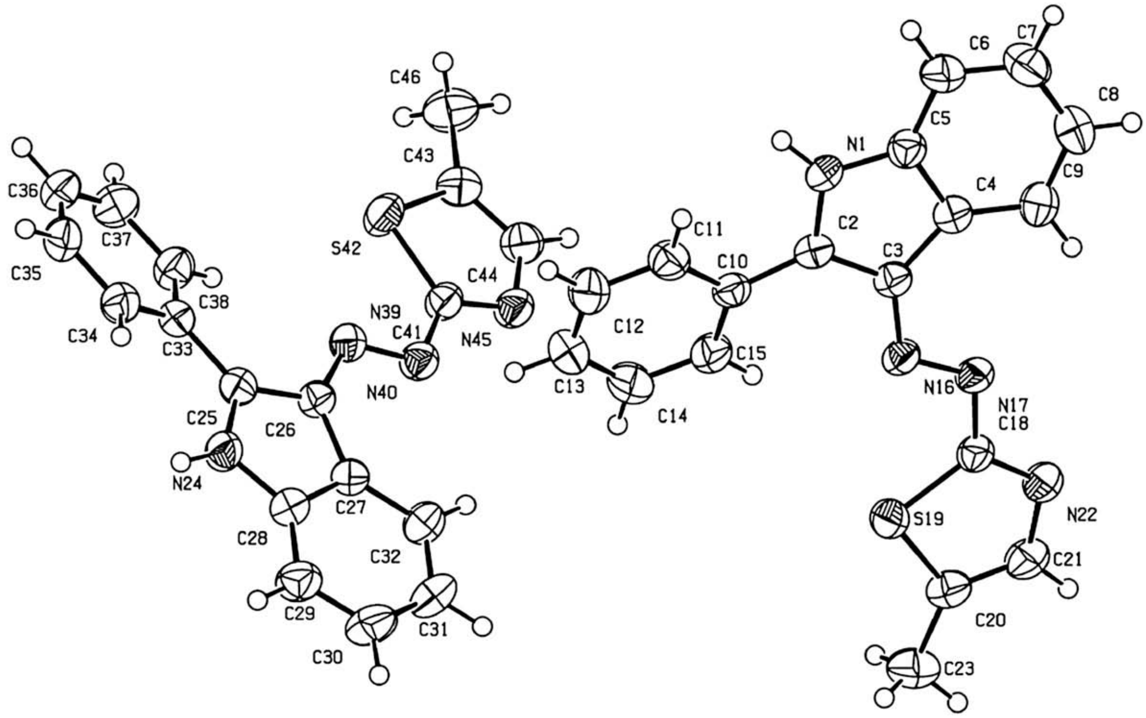


Fig. 3. The molecular structure of dye **1**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level [33].

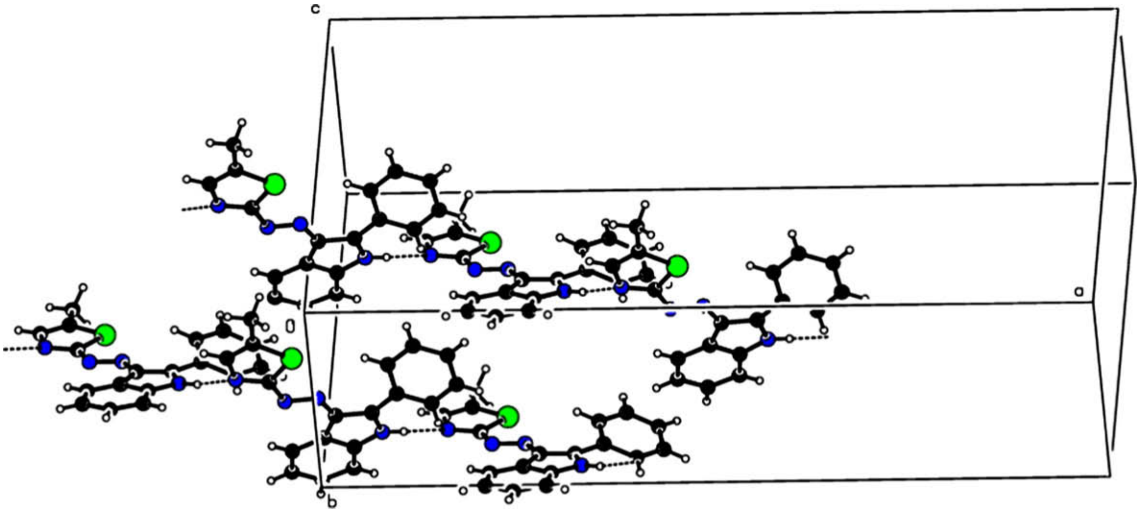


Fig. 4. A partial packing diagram of dye **1**, hydrogen bonds are shown as dashed lines [34].

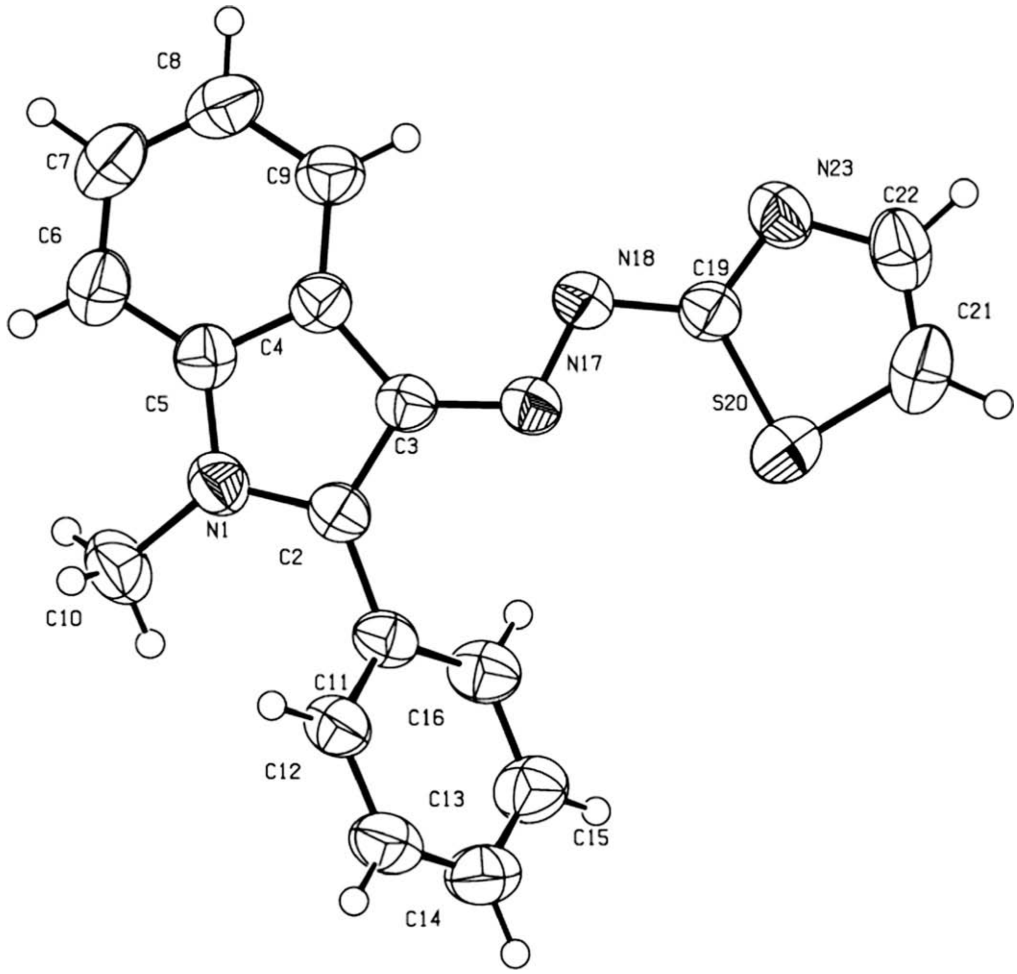


Fig. 5. The molecular structure of dye **2**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level [33].

Table 2
Selected bond lengths (Å) and angles (°) for dye **1**.

S19–C20	1.725(2)	C41–S42	1.739(2)
S19–C18	1.730(2)	S42–C43	1.722(2)
N1–C2	1.354(3)	N24–C25	1.352(3)
N1–C5	1.383(3)	N24–C28	1.385(3)
N16–N17	1.281(2)	N39–N40	1.283(2)
N17–C18	1.389(3)	N40–C41	1.390(3)
C18–N22	1.302(3)	N40–C41	1.390(3)
N17–C18	1.389(3)	N39–N40	1.283(2)
C20–S19–C18	89.37(11)	C43–S42–C41	89.21(11)
C18–N22–C21	109.8(2)	C41–N45–C44	110.13(19)
N17–N16–C3	115.34(18)	N40–N39–C26	115.83(18)
N16–N17–C18	110.78(17)	N39–N40–C41	111.40(18)
N22–C18–N17	121.1(2)	N45–C41–N40	121.80(19)
N22–C18–S19	114.74(17)	N45–C41–S42	114.63(16)
N17–C18–S19	124.12(15)	N40–C41–S42	123.53(16)
C20–C21–N22	117.3(2)	C43–C44–N45	116.9(2)

Table 3
Selected bond lengths (Å) and angles (°) for dye **2**.

S20–C21	1.714(2) N17–N18 1.2786(15)
S19–C20	1.7326(14) N18–C19 1.3897(17)
N1–C2	1.3574(17) C19–N23 1.3027(18)
N1–C5	1.3894(18) N17–C3 1.3597(17)
C21–S20–C19	88.03(8) N23–C19–N18 121.34(12)
C19–N23–C22	109.86(14) N23–C19–S20 114.74(17)
N17–N18–C3	115.32(11) N18–C19–S20 123.63(10)
N17–N18–C19	111.62(11) C21–C22–N23 116.21(16)

Table 4
Hydrogen bond geometry (Å, °) for dye **1**.

D–H···A	D–H	H···A	D···A	D–H···A
N24–H24···N22^{i}	0.83(2)	2.08(3)	2.882(3)	163(2)
N1–H1···N45^{ii}	0.89(2)	2.05(3)	2.920(3)	167(2)

Symmetry code: (i) $3/2 - x$, $y - 1/2$, $1/2 - z$, (ii) $1 - x$, $1 + y$, $1/2 - z$.

4. Conclusions

The results of X-ray analysis indicate that the dye **1** prefers to be in the azo-enamine form in solid state. The asymmetric unit of dye **1** contains two crystallographically independent molecules, while there is only one molecule in the asymmetric unit for dye **2**. In dye **1**, intermolecular N–H···N hydrogen bonds link the molecules, into parallel infinite sheets along the *a* axis, in which they seem to be effective in the stabilization of the crystal structure. In dye **2**, there is no classical intermolecular hydrogen bond. In the crystal structure, the molecules are aligned in the [100] and [010] directions differently with respect to that of [001], in such a way that neighbouring indole planes face in anti-parallel fashion.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic data Centre as the supplementary publication nos, CCDC 694566 and 694567. Copies of

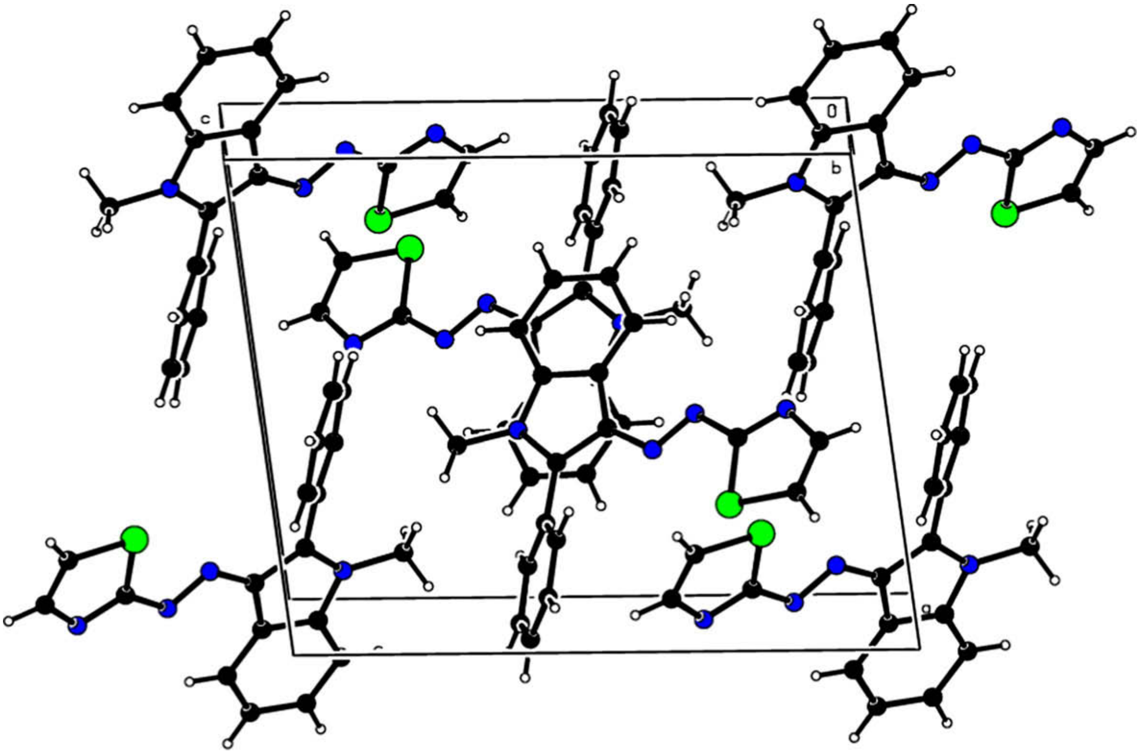


Fig. 6. A packing diagram of dye **2** [34].

the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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