

## Synthesis of single azo disperse dye containing double ester and determination of crystal structure

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**Abstract**—The synthesis, crystal structure analysis and characterization of a monoazo dye, 4-((2,6-dichloro-4-nitro phenyl)azo)-N-(diacetyl oxygen ethyl)aniline, are reported. The dye crystallised in the triclinic system, space group P-1 with  $a=8.1663(3)$  Å,  $b=9.4222(3)$  Å,  $c=15.4694(5)$  Å,  $\alpha=78.9130(10)^\circ$ ,  $\beta=75.019(2)^\circ$ ,  $\gamma=70.787(2)^\circ$ ,  $V=1078.26(6)$  Å<sup>3</sup> and  $Z=2$ . There is only one molecule in the asymmetric unit. The dihedral angle between the two phenyl rings is 53.4 Å. In the crystal structure, intermolecular C-H...O hydrogen bonds link the molecules into centrosymmetric dimers, forming  $R_{22}(30)$  ring motifs, in which they may be effective in the stabilization of the structure. Between the phenyl rings, the  $\pi\cdots\pi$  stacking (interactions) may further stabilize the structure.

**Key words:** Crystal Structure, Monoazo Dye, Dihedral Angle, Hydrogen Bonds,  $\pi\cdots\pi$  Stacking

### INTRODUCTION

Azo dyes cover a wide variety of compounds whose main structural characteristic is the presence of an azo group (N=N) connecting to two phenyl rings (Ph-N=N-Ph). The whole of azo dyes contains at least one azo group (N=N), which links two sp<sup>2</sup>-hybridized C atoms in the structures. Azo dyes, including phenol groups, are particularly important for molecule groups due to their versatile application in various fields, such as dyeing of fibers or in pharmaceutical, food and cosmetic industries, acid-base, redox and metalochromic indicators [1-7]. In recent years, some azo dye compounds have been used in various areas of industry for optical storage media, optical actuators, photorefractive media, liquid crystalline display [LCDs] and non-linear optical devices (NLO). Azo dyes have also been used in photo-catalytic reactions as catalyzer exposed to ultraviolet light [8-13]. Moreover, in biological systems, some of these compounds could be used as inhibitors of tumor-growth [14,15].

Single crystal X-ray diffraction analysis has proven to be a powerful tool to give structural information in the solid state. Structural information obtained from single-crystal X-ray diffraction analysis including conformation, stereochemistry, and intra- and intermolecular interactions are in relation to the optical properties as well as to the technical properties of azo dyes and pigments [16-25]. Modern dyeing theory considers that the interactions between disperse dyes and synthesized fibers come from their supramolecular structures, whose characterization and evaluation are the emphasis and difficulty for dyeing theory researches. The analytic structure about single crystal of disperse dye with X-ray diffraction analysis supplies us the basic information for supramolecular studies mentioned above. The information provided is also fundamentally important for the use of crystal engineering methodology in the design of new products for improved performance [26]. Monoazo dyes derived from aro-

matic amines as coupling components and carbocyclic aromatic amines as diazo components constitute the types of greatest economic importance [27]. It is well known that a subtle change of the substituted groups of a given backbone and the coupling components will influence the structures of resulting azo dye molecules, thereby changing their solubility, stability, fastness, optical properties and so on. As X-ray diffraction analysis is a useful method to determine structural information and to provide templates for the design of new molecules, and the demand for the development of new functional dyes also requires additional information - including the structural conformations in molecular level, we report herein the synthesis and the crystal structure analysis of monoazo dye chemical compound. The comparison of the obtained results with those of the reported dyes having the similar 'push-pull' azo structures, the polarizability and space steric effects of the substituents were studied.

### EXPERIMENTAL

#### 1. Measurements

Automatic melting point apparatus was used for testing the melting point of compound; chemical shifts ( $\delta$ ) were measured in parts per million (ppm) from the internal standard. Elemental analyses were carried out on a Perkin Elmer (USA) 240C elemental analyzer with helium as a carrier gas. The wavelength of maximum absorption ( $\lambda_{max}$ ) was measured spectrophotometrically, using a 722S UV-vis spectrophotometer (Shanghai Analytical Instruments, China).

#### 2. Syntheses

The disperse dye was synthesized according to the following route; the synthetic route is shown in Fig. 1.

The product was filtered and washed with cold water, purified by recrystallization from ethanol and then dried (yield: 1.5 g, 92%, mp 393-395 K). The single crystals suitable for X-ray analysis were obtained by slow evaporation of an acetone solution in 15 days.

#### 3. Crystallography

X-ray diffraction data was collected on an Enraf-Nonius (Neth-

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erlands) CAD-4 diffractometer equipped with Mo K $\alpha$  ( $\lambda=0.71073$  Å) radiation using  $w/2\theta$  scans. The intensity data were corrected for Lorentz polarization [28] and absorption [29] effects. The structure was analyzed using direct methods provided by the SHELXS-97 [30] computer program and was refined as full matrix least squares

against F $^2$  for all data by SHELXL-97; all non-hydrogen atoms were refined anisotropically. Crystal data and details of the structure determination are summarized in Table 1.

## RESULTS AND DISCUSSION

The crystal data and structure refinement details of the title com-

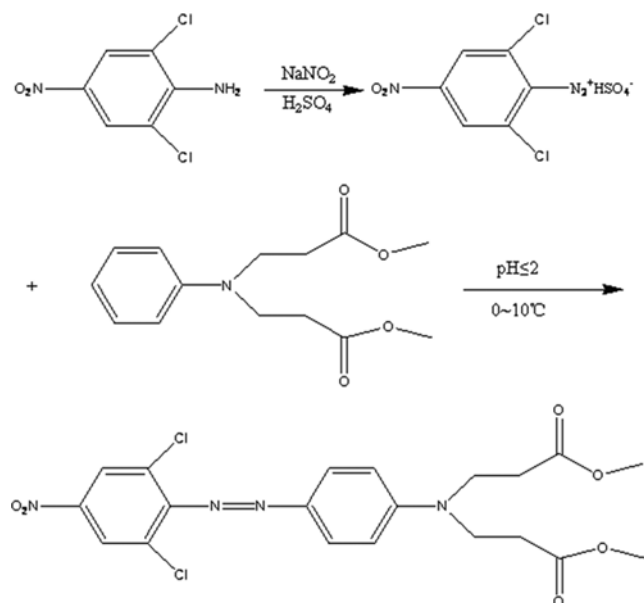


Fig. 1. The synthesis scheme of 4-((2,6-dichloro-4-nitro phenyl)azo)-N-(diacetyl oxygen ethyl)aniline.

Table 1. Crystal data and structure refinement for the title compound

Empirical formula	C <sub>20</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>6</sub>
Formula weight	483.3
Crystal dimensions (mm)	0.20 × 0.10 × 0.10
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	8.1663(3)
b (Å)	9.4222(3)
c (Å)	15.4694(5)
$\alpha$ (°)	78.9130(10)
$\beta$ (°)	75.019(2)
$\gamma$ (°)	70.787 (2)
Volume (Å <sup>3</sup> )	1078.26(6)
Z	2
$D_{calc}$ (g cm <sup>-3</sup> )	1.4886(1)
F(000)	500
2 $\theta$ max (°)	66.92
$\mu$ (mm <sup>-1</sup> )	3.117
No. of reflections measured	3782
No. of reflections observed [ $I > 2\sigma(I)$ ]	3481
R/Rw values	0.0576/0.1481
Goodness of fit (S)	1.005
Color/shape	Orange/polyhedron
Maximum shift in final cycles	0.000
Largest diffraction peak and hole (e Å <sup>-3</sup> )	0.346, -0.321

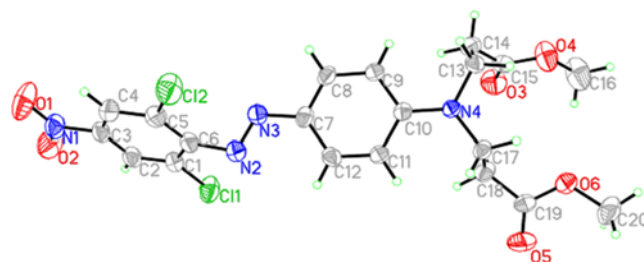


Fig. 2. X-ray structure of 4-((2,6-dichloro-4-nitro phenyl)azo)-N-(diacetyl oxygen ethyl)aniline.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

Atom	x	y	z	U (eq)
Cl1	0.44438	0.20775	0.44702	0.0648
Cl2	0.47771	0.77484	0.31443	0.0653
O1	-0.02975	0.81138	0.59541	0.0901
O2	-0.03461	0.58767	0.65422	0.0787
O3	0.90845	0.05211	-0.20119	0.0716
O4	1.06884	0.17960	-0.30355	0.0695
O5	1.47784	-0.17540	-0.03873	0.0738
O6	1.45458	-0.07087	-0.17754	0.0542
N1	0.02582	0.67342	0.59706	0.0538
N2	0.58884	0.42609	0.31525	0.0454
N3	0.55830	0.48292	0.23786	0.0400
N4	1.04202	0.29788	-0.07608	0.0309
C1	0.36837	0.40059	0.45135	0.0424
C2	0.23092	0.45703	0.52183	0.0443
C3	0.17180	0.61142	0.52290	0.0422
C4	0.24316	0.70985	0.45932	0.0463
C5	0.38078	0.64957	0.38998	0.0443
C6	0.44383	0.49465	0.38325	0.0409
C7	0.68883	0.42920	0.16404	0.0349
C8	0.65021	0.49762	0.08095	0.0358
C9	0.76495	0.45524	0.00158	0.0338
C10	0.92767	0.34032	0.00228	0.0286
C11	0.96718	0.27169	0.08750	0.0341
C12	0.85132	0.31474	0.16589	0.0371
C13	0.99628	0.37058	-0.16240	0.0347
C14	0.86360	0.31266	-0.18883	0.0452
C15	0.94492	0.16761	-0.22994	0.0431
C16	1.16322	0.04377	-0.34576	0.0915
C17	1.21741	0.18747	-0.07792	0.0322
C18	1.21453	0.02287	-0.06244	0.0397
C19	1.39604	-0.08493	-0.08917	0.0371
C20	1.62757	-0.16919	-0.21239	0.0669

**Table 3. Hydrogen bond lengths (Å) and angles (°) for the geometry**

D-H...A	D-H	H...A	D...A	D-H...A
C13-H13A...O4	0.9700	2.5300	2.9151	104.00
C16-H16B...O1	0.9600	2.5500	3.4473	156.00
C17-H17A...O5	0.9700	2.5000	3.3939	153.00

pound,  $C_{20}H_{20}Cl_2N_4O_6$  are provided in Table 1. The asymmetric unit of the chemical compound contains only one molecule (Fig. 2). The atomic coordinates, selected bond lengths and angles and hydrogen-bond geometry for the dye are given in Tables 2-4. The C6-N2 [1.4283(7) Å], N2=N3 [1.2657(7) Å] and C7-N3 [1.3908(7) Å] bonds (Table 4) indicate the azo form and the mentioned C-N bonds are longer than the expected values of the corresponding C-N single bonds (1.36-1.39 Å) [31], but they are in good agreement with the corresponding values in 4-nitro-4'-aminoazobenzenes, in which the corresponding C-N single bonds range from 1.387 to 1.440 Å.

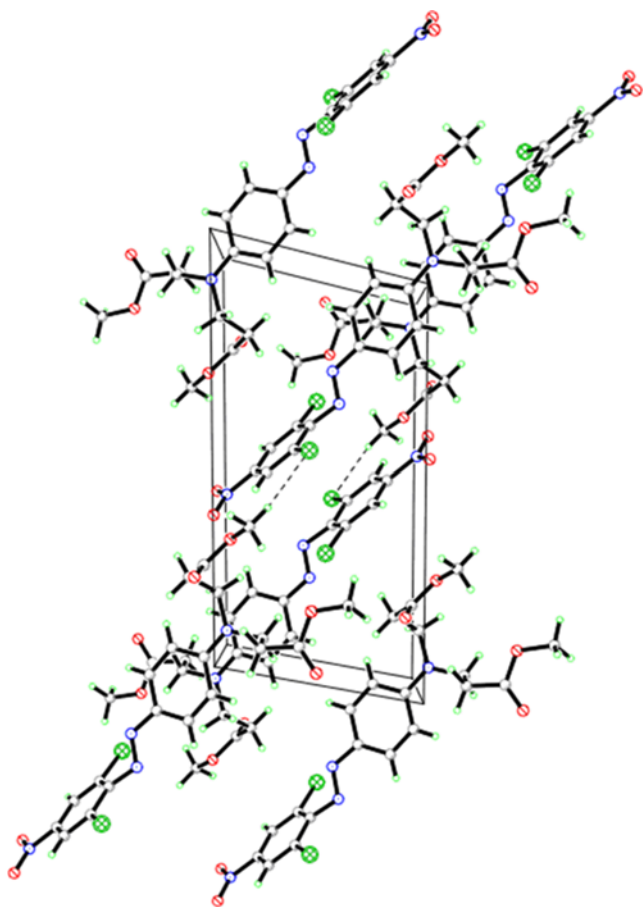
In the molecule the C6-N2-N3-C7 torsion angle is 179.15°, almost in the same plane. But the two phenyl rings are not planar (as shown in Fig. 3); atom N1 is almost coplanar with ring A (C1-C6) with a deviation, while phenyl ring B (C7-C12), C10, N3, N4 and C7 atoms are almost on the same plane. In the crystal structure, intermolecular C-H...O hydrogen bonds (Table 3) link the molecules into centrosymmetric dimers (Fig. 3), in which they may be effective in the stabilization of the structure. The  $\pi\cdots\pi$  stacking or interactions between the phenyl rings may further stabilize the structure.

## CONCLUSIONS

The asymmetric unit of Chemical compound contains only one molecule. In the dye, the 4-nitro-4'-aminoazobenzene skeleton is not planar. In the crystal structure, intermolecular C-H...O hydrogen bonds link the molecules into centrosymmetric dimers, forming  $R_{22}(30)$  ring motifs, in which they may be effective in the stabilization of the structure. The weak  $\pi\cdots\pi$  stacking (interactions)

**Table 4. Selected bond lengths (Å), bond angles and torsion angles (°)**

Bond lengths (Å)		Bond angles (°)		Torsion angles (°)	
C11-C1	1.7246	C15-O4-C16	116.41	C16-O4-C15-C14	176.53
C12-C5	1.7296	C19-O6-C20	117.11	C16-O4-C15-O3	-2.33
O1-N1	1.2253	O1-N1-O2	123.65	C20-O6-C19-C18	-179.50
O2-N1	1.2001	O1-N1-C3	117.41	C20-O6-C19-O5	-1.26
O3-C15	1.1956	O2-N1-C3	118.92	O1-N1-C3-C2	-177.44
O4-C15	1.3280	N3-N2-C6	110.11	O1-N1-C3-C4	3.38
O4-C16	1.4388	N2-N3-C7	117.11	O2-N1-C3-C4	-178.25
O5-C19	1.1918	C10-N4-C13	119.97	O2-N1-C3-C2	0.93
O6-C19	1.3225	C10-N4-C17	122.39	C6-N2-N3-C7	179.15
O6-C20	1.4428	C13-N4-C17	117.52	N3-N2-C6-C1	127.90
N1-C3	1.4733	C11-C1-C2	118.68	N3-N2-C6-C5	-57.12
N2-N3	1.2657	C11-C1-C6	119.09	N2-N3-C7-C12	1.63
N2-C6	1.4283	C2-C1-C6	122.21	N2-N3-C7-C8	-178.66
N3-C7	1.3908	C1-C2-C3	117.35	C13-N4-C10-C9	-0.55
N4-C10	1.3626	N1-C3-C2	118.13	C17-N4-C10-C11	-4.51
N4-C13	1.4593	N1-C3-C4	118.50	C13-N4-C10-C11	179.69
N4-C17	1.4643	C2-C3-C4	123.36	C13-N4-C17-C18	-101.43
C1-C2	1.3889	C3-C4-C5	117.77	C10-N4-C13-C14	-78.03
C1-C6	1.3927	C12-C5-C4	116.90	C17-N4-C10-C9	175.25
C2-C3	1.3756	C12-C5-C6	121.13	C17-N4-C13-C14	105.97
C3-C4	1.3696	C4-C5-C6	121.91	C10-N4-C17-C18	82.68
C4-C5	1.3883	N2-C6-C1	118.24	C2-C1-C6-C5	2.48
C5-C6	1.3938	N2-C6-C5	124.24	C11-C1-C6-C5	-178.96
C7-C8	1.3871	C1-C6-C5	117.34	C6-C1-C2-C3	-0.72
C7-C12	1.4109	N3-C7-C8	114.71	C2-C1-C6-N2	177.82
C8-C9	1.3757	N3-C7-C12	126.91	C11-C1-C6-N2	-3.63
C9-C10	1.4121	C8-C7-C12	118.38	C11-C1-C2-C3	-179.28
C10-C11	1.4196	C7-C8-C9	121.63	C1-C2-C3-N1	179.89
C11-C12	1.3688	C8-C9-C10	120.69	C1-C2-C3-C4	-0.98
C13-C14	1.5307	N4-C10-C9	121.00	C2-C3-C4-C5	0.77
C14-C15	1.4939	N4-C10-C11	121.58	N1-C3-C4-C5	179.90
C17-C18	1.5303	C9-C10-C11	117.42	C3-C4-C5-C12	-176.17
C18-C19	1.5012	C10-C11-C12	121.19	C3-C4-C5-C6	1.15



**Fig. 3.** Intermolecular C-H...O hydrogen bonds link the molecules into centrosymmetric.

between the nitrophenyl rings may further stabilize the structure.

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#### REFERENCES

1. H. B. Scher, M. Rodson and K. S. Lee, *Pestic. Sci.*, **54**, 394 (1998).
2. T. H. Kim, Y. S. Ko and Y. K. Kwon, *J. Nanosci. Nanotechnol.*, **11**, 3450 (2006).
3. O. Yaroshchuk, T. Sergan, J. Lindau, S. N. Leve, J. Kelly and L. C. Chien, *J. Chem. Phys.*, **114**, 5330 (2001).
4. T. Nakamura and T. Shibusawa, *Text. Res. J.*, **70**, 801 (2000).
5. S. Sakthivel, B. Neppolian, M. V. Shankar, B. Arabindo, M. Palani-chamy and V. Murugesam, *Sol. Energy Mater. Sol. Cells*, **77**, 65 (2003).
6. M. Muruganandham and M. Swaminathan, *Sol. Energy Mater. Sol. Cell.*, **84**, 439 (2004).
7. M. Muruganandham, N. Shabana and M. Swaminathan, *J. Mol. Catal. A: Chem.*, **246**, 154 (2006).
8. Y. Qian, G. Wang, G. Xiao, B. Lin and Y. Cui, *Dyes Pigm.*, **75**, 460 (2007).
9. F. Qiu, Y. Cao, H. Xu, Y. Jiang, Y. Zhou and J. Liu, *Dyes Pigm.*, **75**, 454 (2007).
10. B. K. So, H. J. Kim, S. M. Lee, H. H. Song and J. H. Park, *Dyes Pigm.*, **70**, 38 (2006).
11. R. Gimenez, M. Millaruelo, M. Pinol, J. L. Serrano, A. Vinuales, R. Rosenhauer, T. Fischer and J. Stumpe, *Polymer*, **46**, 9230 (2005).
12. A. Ghanadzadeh, M. A. Shahzamanian, S. Shoarinejad, M. S. Zakerhamidi and M. Moghadam, *J. Mol. Liq.*, **136**, 22 (2007).
13. N. K. Viswamathan, D. Y. Kim, S. Bian, J. Williams, W. Liu, L. Liu, L. Samuelson and J. Kumar, *J. Mater. Chem.*, **9**, 1941 (1999).
14. A. Wang, C. Tao, Y. Cui, L. i. Duan, Y. Yang and J. Li, *J. Colloid Interface Sci.*, **332**, 271 (2009).
15. L. Yuan, G. Liang, J. Xie, L. Li and J. Guo, *Polymer*, **47**, 5338 (2006).
16. W. Yang, X. L. You, Y. Zhong and D.-C. Zhang, *Dyes Pigm.*, **73**, 317 (2007).
17. J. Seo, W. J. Jo, G. Choi, K.-M. Park, S. S. Lee and J. S. Lee, *Dyes Pigm.*, **72**, 328 (2007).
18. Z. Seferoğlu, N. Ertan, G. Kickelbick and T. Hökelek, *Dyes Pigm.*, **82**, 20 (2009).
19. K. Singh, A. Mahajan and W. T. Robinson, *Dyes Pigm.*, **74**, 95 (2007).
20. J. E. Lee, H. J. Kim, M. R. Han, S. Y. Lee, W. J. Jo, S. S. Lee and J. S. Lee, *Dyes Pigm.*, **80**, 181 (2009).
21. W. Jiang, J. Tang, Q. Qi, W. Wu, Y. Sun and D. Fu, *Dyes and v*, **80**, 11 (2009).
22. K. Singh, S. Singh, P. K. Garg and M. S. Hundal, *Dyes Pigm.*, **54**, 72 (2004).
23. Jagadeesh B, Bodapati and Huriye Icil, *Dyes Pigm.*, **79**, 224 (2008).
24. S. Özbey, A. Karayel, G. Kavak, Z. Seferoğlu and N. Ertan, *Color Technol.*, **123**, 358 (2007).
25. K. Singh, S. Singh, P. K. Garg and M. S. Hundal, *Color Technol.*, **120**, 72 (2004).
26. C.-H. Chang, R. M. Christie and G. M. Rosair, *Dyes Pigm.*, **82**, 147 (2009).
27. Mojgan Zandi, Seyed Ali Hashemi, Payam Aminayi and Farzad Hosseinali, *J. Appl. Polym. Sci.*, **119**, 586 (2011).
28. K. Harms and S. Wocadlo, XCAD4, University of Marburg, Germany (1995).
29. A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr.*, **A24**, 351 (1968).
30. G. M. Sheldrick, *Acta Crystallogr.*, **A64**, 112 (2008).
31. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans.*, **2**, 1 (1987).