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X-ray crystal structure of C.I. Disperse Brown 1

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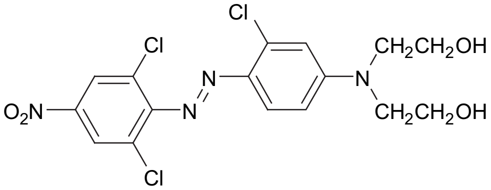
Abstract

Crystals of C.I. Disperse Brown 1, an aminoazobenzene derivative, were grown from an ethanol solution and the crystal structure was determined by single crystal X-ray diffraction analysis. The dye molecule crystallizes in the orthorhombic *Fdd*2 space group with the unit cell dimensions: $a = 30.6593(17)$ Å, $b = 32.2928(18)$ Å, $c = 7.3738(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7300.6(7)$ Å^3. Results showed that the 4-nitro-4′-aminoazobenzene skeleton is non-planar, with a dihedral angle of 45.53° between the phenyl rings presumably to minimize the repulsive force between Cl atoms in each ring. Several types of intra- and intermolecular hydrogen bonds, together with anti-parallel interlayer $\pi-\pi$ stacking interaction also stabilize the molecular conformation. In particular, two aminoalcohol chains form a pseudo-cycle by strong O−H⋯O intramolecular hydrogen bond.

Keywords: C.I. Disperse Brown 1; X-ray crystal structure; Hydrogen bond

1. Introduction

The structural investigation of the disperse dyes in solid state [1–13] is one of the promising research field because the absorption behavior is believed to be dependent not only on the conformation of the solid dyestuff but also on the interactions between the dye molecule and substrate surface in molecular level [14]. Accordingly, the technical performance and functionality of the disperse dyes have strong relationship with their particle size, morphology as well as crystal structure arrangement [15]. As part of long-term program for the investigation of structure/function relationships for the dye molecules, our group has reported the crystal structures of some disperse dyes such as monoazo [11], methine [12] and anthraquinone [13] dyes. Recently we were successful to prepare the single crystals of C.I. Disperse Brown 1 (C.I. number 11152) [16], which is one of the most important group of aminoazobenzene dyes. Herein we report its molecular structure characterized by single crystal X-ray diffraction.



C.I. Disperse Brown 1

2. Experimental

The C.I. Disperse Brown 1 was extracted with dichloromethane to separate the colorant from diluents. Crystallization of this dye from dichloromethane, ethyl acetate,

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Table 1
Crystallographic data and intensity collection for C.I. Disperse Brown 1

Empirical formula	$C_{16}H_{15}Cl_3N_4O_4$
Formula weight	433.67
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Fdd*2 (no. 43)
a (Å)	30.6593(17)
b (Å)	32.2928(18)
c (Å)	7.3738(4)
Volume ($Å^3$)	7300.6(7)
Z	16
D_{calc} (g/cm^3)	1.578
μ (mm^{-1})	0.534
$F(000)$	3552
Crystal dimensions (mm)	0.40 × 0.20 × 0.20
Color of crystal	Red-brown
Shape of crystal	Block
$2\theta_{max}$ (°)	56.56
No. of reflections measured	11 404
No. of reflections observed [$I > 2\sigma(I)$]	3527
No. of variables	245
R	0.0485
R_w	0.1061
Largest diff. peak and hole (e $Å^{-3}$)	0.459 and −0.398
Maximum shift in final cycles	< 0.001

methanol and acetone afforded an amorphous solid. The single crystals suitable for the X-ray analysis were obtained by slow evaporation of ethanol solution of the purified dye. The suitable crystal was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated MoKα ($\lambda = 0.71073$ Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 10 s. The frame data were processed to give structure factors using the program SAINT [17]. The intensity data were corrected for Lorentz and polarization effects. The structures were solved by a combination of direct and difference Fourier methods provided by the program package SHELXTL [18] and refined using a full matrix least square against F^2 for all data. All non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. Crystallographic data are summarized in Table 1. CCDC reference number 273234.

3. Results and discussion

Acceptable red-brown crystals were produced by slow evaporation of the ethanol solution of the purified dye. The crystal used exists in the orthorhombic space group *Fdd*2. The atomic coordinates, bond lengths and angles, and torsion angles are reported in Tables 2 and 3. The molecular structure and the atomic numbering are given in Fig. 1.

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å × 10^3) for C.I. Disperse Brown 1

	x	y	z	U (eq)
Cl(1)	181(1)	−589(1)	6320(2)	34(1)
Cl(2)	891(1)	−900(1)	12 909(2)	36(1)
Cl(3)	993(1)	447(1)	6165(1)	30(1)
O(1)	668(1)	−2123(1)	6467(5)	46(1)
O(2)	875(1)	−2271(1)	9204(6)	48(1)
O(3)	192(1)	2159(1)	8628(4)	29(1)
O(4)	−61(1)	2111(1)	12 086(4)	32(1)
N(1)	741(1)	−2030(1)	8033(6)	35(1)
N(2)	526(1)	−355(1)	10 165(5)	24(1)
N(3)	690(1)	−108(1)	9041(4)	22(1)
N(4)	711(1)	1584(1)	10 841(4)	21(1)
C(1)	669(1)	−1594(1)	8597(6)	27(1)
C(2)	487(1)	−1327(1)	7358(6)	26(1)
C(3)	434(1)	−919(1)	7848(6)	23(1)
C(4)	566(1)	−775(1)	9552(5)	21(1)
C(5)	736(1)	−1063(1)	10 766(5)	23(1)
C(6)	791(1)	−1478(1)	10 295(6)	27(1)
C(7)	674(1)	310(1)	9548(6)	21(1)
C(8)	821(1)	605(1)	8311(5)	20(1)
C(9)	834(1)	1022(1)	8704(6)	22(1)
C(10)	692(1)	1167(1)	10 405(5)	19(1)
C(11)	538(1)	870(1)	11 669(5)	25(1)
C(12)	528(1)	456(1)	11 243(6)	24(1)
C(13)	893(1)	1883(1)	9568(6)	24(1)
C(14)	596(1)	1995(1)	8007(6)	28(1)
C(15)	613(1)	1722(1)	12 689(6)	26(1)
C(16)	128(1)	1778(1)	13 081(6)	26(1)

Table 3
Selected bond lengths (Å), bond angles, and torsion angles (°) for C.I. Disperse Brown 1

Cl(1)−C(3)	1.734(4)	N(1)−C(1)	1.484(4)
Cl(2)−C(5)	1.732(4)	N(2)−N(3)	1.257(4)
Cl(3)−C(8)	1.745(3)	N(2)−C(4)	1.434(4)
O(1)−N(1)	1.213(5)	N(3)−C(7)	1.402(4)
O(2)−N(1)	1.233(5)	N(4)−C(10)	1.386(4)
O(3)−C(14)	1.423(4)	N(4)−C(13)	1.457(5)
O(4)−C(16)	1.425(4)	N(4)−C(15)	1.464(5)
O(1)−N(1)−O(2)	124.9(3)	C(4)−C(5)−Cl(2)	119.1(3)
O(1)−N(1)−C(1)	118.3(4)	C(6)−C(5)−Cl(2)	119.1(3)
O(2)−N(1)−C(1)	116.8(4)	C(8)−C(7)−N(3)	118.2(3)
N(3)−N(2−)−C(4)	111.0(3)	N(3)−C(7)−C(12)	124.8(3)
N(2)−N(3)−C(7)	114.9(3)	C(9)−C(8)−Cl(3)	117.9(3)
C(10)−N(4)−C(13)	120.6(3)	C(7)−C(8)−Cl(3)	119.4(3)
C(10)−N(4)−C(15)	120.1(3)	N(4)−C(10)−C(9)	121.1(3)
C(13)−N(4)−C(15)	118.6(3)	N(4)−C(10)−C(11)	121.3(3)
C(6)−C(1)−N(1)	118.7(4)	N(4)−C(13)−C(14)	114.6(3)
C(2)−C(1)−N(1)	118.0(4)	O(3)−C(14)−C(13)	111.7(3)
C(5)−C(4)−N(2)	117.5(3)	N(4)−C(15)−C(16)	114.3(3)
C(3)−C(4)−N(2)	124.9(3)	O(4)−C(16)−C(15)	112.8(3)
O(1)−N(1)−C(1)−C(2)	5.8(5)	C(4)−N(2)−N(3)−C(7)	−178.7(3)
O(2)−N(1)−C(1)−C(6)	5.8(5)	N(3)−C(7)−C(8)−Cl(3)	3.0(4)
Cl(1)−C(3)−C(4)−N(2)	−2.7(4)	N(4)−C(13)−C(14)−O(3)	57.8(4)
Cl(2)−C(5)−C(4)−N(2)	−0.5(4)	N(4)−C(15)−C(16)−O(4)	−67.1(4)

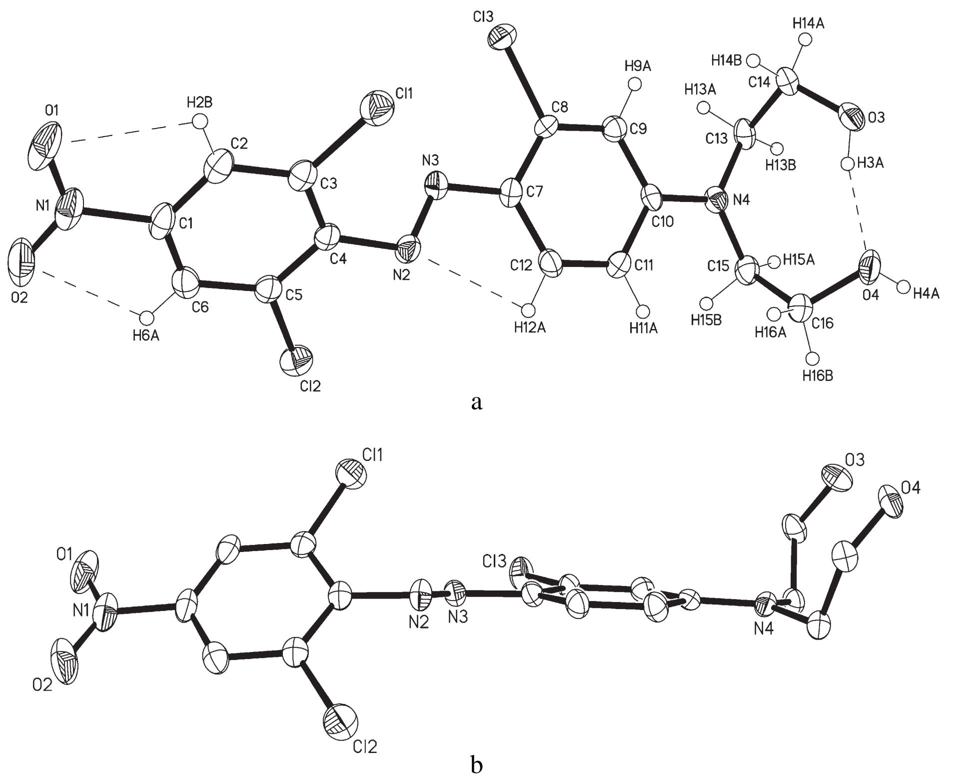

Fig. 1. ORTEP views of molecular structure of C.I. Disperse Brown 1 with intramolecular hydrogen bonds (dashed lines); (a) top view and (b) side view.

First of all, the 4-nitro-4′-aminoazobenzene skeleton is not planar because of the relatively large dihedral angle of 45.5(1)° between two phenyl rings. The 4-nitro group is almost coplanar with the phenyl ring A (C1–C6) as indicated by the dihedral angle of 6.6(3)°, which is due to the formation of hydrogen bonds of two nitro O atoms with adjacent aromatic CH atoms [O1···H–C2; 2.420 Å, O2···H–C6; 2.403 Å]. Phenyl ring B (C7–C12), N2, N3 and N4 atoms are almost on the same plane with the following deviations from the aromatic ring: N2 −0.028(2) Å, N3 0.052(2) Å, and N4 0.022(2) Å. Therefore the large dihedral angle between two phenyl rings is due to the repulsive forces of Cl1 and Cl3 which may induce the C4–N2 free rotation.

As illustrated in Fig. 1a, the molecular conformation is mainly stabilized by the formation of several hydrogen bonds such as C–H···O, C–H···N and O–H···O types [19,20], which have bond length of ca. 1.8–2.5 Å. The structural parameters for the hydrogen bonds are summarized in Table 4. In particular, two alcohol chains, which direct towards same side form strong O3–H···O4 hydrogen bond. For the idealized position of the hydrogen atom, the H···O4 distance is 1.861 Å, the O3···O4 distance is 2.699(4) Å, and O3–H···O4 angle is 161.01°. Accordingly, an eight-membered pseudo-cycle is formed by the hydrogen bond between two alcohol chains. The alcohol chains also prevent the formation of a regular stacking arrangement of the molecules, but they include the anti-parallel ABAB-type stacking (Fig. 2). The interplanar (A···B) separation is approximately 3.73 Å, which means weak π–π stacking interaction [21]. In addition, the intermolecular hydrogen bonds, which stabilize the molecular packing are also observed.

Consequently, the single crystals of C.I. Disperse Brown 1 were grown from the ethanol solution and its molecular structure was characterized by X-ray analysis. In view of the single molecule, the non-planar structure is stabilized by the multiple intramolecular hydrogen bonds together with the repulsive forces between Cl atoms. The close packing of the molecules, which is due to the intermolecular hydrogen bonds and weak arene–arene stacking interaction also promote the stabilization of the crystal structure.

Table 4
Intra- and intermolecular hydrogen bonds geometry (Å, °) for C.I. Disperse Brown 1

D–H···A	D–H	H···A	D···A	D–H···A
O3–H3A···O4	0.84	1.86	2.669(4)	161.0
C2–H2B···O1	0.95	2.42	2.712(4)	97.5
C6–H6A···O2	0.95	2.40	2.698(5)	97.6
C12–H12A···N2	0.95	2.48	2.739(4)	95.3
C13–H13B^{ii}···O1	0.99	2.71	3.570(5)	145.4
C15–H15A^{ii}···O2	0.99	2.60	3.532(5)	157.2
O4–H4A^{ii}···O3^{i}	0.84	1.83	2.649(4)	163.4
C13^{i}–H13A^{i}···Cl2^{iii}	0.99	3.07	3.880(4)	140.1
C6–H6A^{iii}···Cl3^{i}	0.95	2.89	3.799(4)	160.2

Symmetry transformations used to generate equivalent atoms: (i) −*x*, −*y*, *z*; (ii) *x*, *y* − 1/2, *z* − 1/2; (iii) *x* − 1/4, −*y* − 1/4, *z* − 3/4.

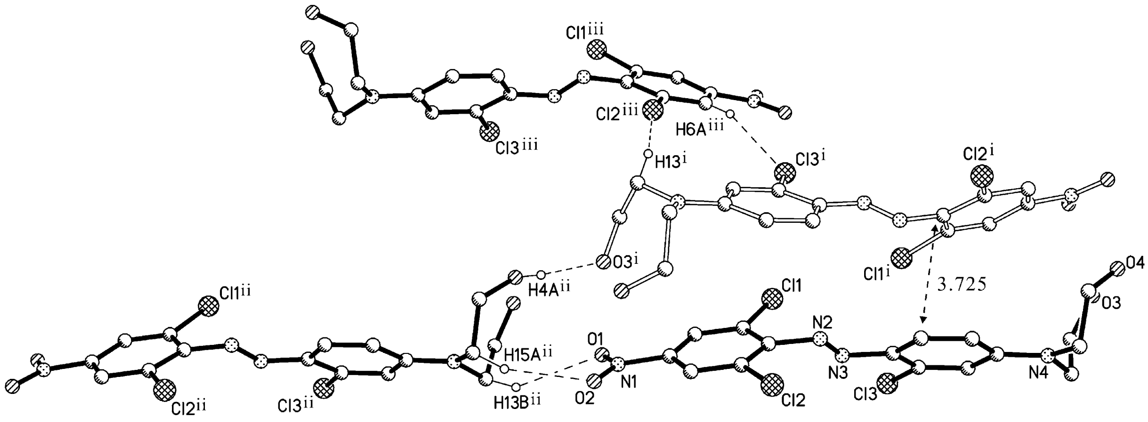

Fig. 2. Representation of intermolecular hydrogen bonds (dashed lines) and interlayer π–π stacking (dashed arrow, Å) [symmetry codes: (i) $-x$, $-y$, z; (ii) x, $y - 1/2$, $z - 1/2$; (iii) $x - 1/4$, $-y - 1/4$, $z - 3/4$].

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