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The crystal structure of 2′,6′-dichloro-4-dimethylaminoazobenzene

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Abstract

A monoazo dye, 2′,6′-dichloro-4-dimethylaminoazobenzene ($C_{14}H_{13}Cl_2N_3$) was synthesized and characterized by X-ray diffraction, IR, ^{1}H NMR, and elemental analysis. The title molecule crystallizes in the monoclinic system space group $P2_1/c$ (#14), $a = 10.782(1)$, $b = 8.9610(9)$, $c = 15.108(2)$ Å, $\beta = 103.008(5)^\circ$, $V = 1422.2(3)$ Å^3, $Z = 4$. The title molecule is not planar and takes *trans*-geometry and the two phenyl rings are twisted around the central linkage in opposite directions. In the crystal, molecules are interacted through π···π interaction, forming 'double chains' along [1 −1 0]. The 'double chains' are extended along [001] through H-Bond C11−H6···Cl2, C5−H3···Cl1 forming double layers (110), which are in turn interacted by C3−H1···Cl1 H-Bond [010], forming crystals. The molecular geometry has been calculated using the ab initio restricted Hartree−Fock and density functional method (B3LYP) with 6-311G** basis set. The optimized geometric parameters obtained by two methods are similar and in good agreement with the experimental values.

Keywords: Azobenzenes; π···π interaction; H-bond; Ab initio; Density functional theory

1. Introduction

Azobenzenes are used extensively as dyes in a variety of industries, including the cosmetics, food, leather, paper and textile industries. However, some azobenzenes manifest carcinogenicity through highly reactive metabolic intermediates that can interact covalently with DNA and cause mutations [1]. Methyl yellow (4-dimethylaminoazobenzene; MY, **1a** in Fig. 1) is a basic structure of those azo dyes which have been used as dyes in food, but the use of MY is now prohibited because of its carcinogenic activity in rodents [2]. It has been reported that in the study of halogenated MYs, the title compound (2′,6′-diCl MY, **1c** in Fig. 1) has the greatest enhancement of the ligand activity, and its AhR ligand activity is very close to that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). (AhR, also called the dioxin receptor, is a transcriptional factor that mediates the toxicity of a variety of compounds, most notably, of TCDD and structurally related polycyclic aromatic hydrocarbons (PAHs) and polyhalogenated PAHs.) [3–6]. Despite this, the studies of the properties of **1c** have not been communicated and no structure data are available.

In order to get more information about **1c**, we synthesized it and determined its crystal structure. Additionally, the extended MO calculations using density functional theory (DFT) and self-consistent field molecular orbital Hartree−Fock theory (RHF) were carried out, in order to compare the geometry of title compound with **1a** and 2′-Cl MY (**1b** in Fig. 1). These calculations are valuable for providing insight into the structure−activity correlation, and are useful for the

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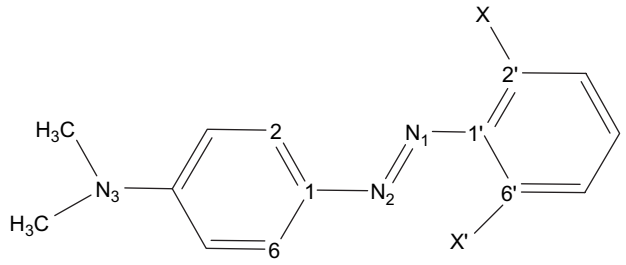

1a: X=X'=H **1b**: X=Cl, X'=H **1c**: X=X'=Cl

Fig. 1. Atomic labeling in molecules.

prediction of the toxicity of some structurally related compounds.

2. Experimental

2.1. Synthesis

A solution was formed by dissolving 1.62 g 2,6-dichloroaniline in 20 ml water and 3 ml concentrated hydrochloric acid at 80–90 °C in a three-necked flask equipped with an efficient stirrer, a dropping funnel, and a thermometer. Then cooled to 0 °C, another 3 ml of concentrated hydrochloric acid was added, and the temperature of the mixture was maintained below 5 °C by means of an ice-salt bath. To the stirred mixture, a solution of 0.7 g of sodium nitrite in 2 ml of water was added slowly, drop-wise. After completion of addition, the stirring was continued for 15 min. The solution of the diazonium salt was filtrated to a mixture of 1.21 g *N*,*N*-dimethylaniline and 3 ml concentrated hydrochloric acid, the above diazonium salt was added slowly. The stirring was continued for 1 h. Then, the mixture was heated below 40 °C, and made neutral by the addition of hydrated sodium acetate. The solution was filtrated to title compound, washed with a lot of water and a little of ethyl alcohol, and the product was recrystallized five times from ethanol/water (10:1). The red crystal was grown from acetone by slow evaporation at ambient temperature for a week. Melting point (m.p.), 396–397 K. Elemental analysis (Perkin Elmer 240C elemental analyzer): Calcd. for $C_{14}H_{13}Cl_2N_3$ (%), C, 57.14; H, 4.42; N, 14.30. Found: C, 56.95; H, 4.35; N, 14.30.

2.2. X-ray crystallography

A red chunk crystal with dimensions of $0.69 \times 0.40 \times 0.25$ mm was selected for X-ray diffraction. Data were collected at -80 ± 1 °C with a Rigaku Mercury CCD area detector with graphite monochromated Mo–Kα radiation ($\lambda = 0.71070$ Å). A total of 3158 unique ($R_{int} = 0.036$) reflections were collected in the range of $7.2° < 2\theta < 55°$ with ω scans mode and used in the refinement. The structure was solved by direct methods [7] and expanded using Fourier techniques [8]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically using the riding model. All calculations were performed using the Crystal Structure Analysis Package [9,10], SHELTX-86 and SHELTX-93 programs [11,12]. The details of the X-ray analysis are listed in Table 1. The molecular structure and crystal packing are shown in Figs. 2 and 3.

Table 1
Crystal data and structure refinement

Compound	$C_{14}H_{13}Cl_2N_3$
Color/shape	Red/chunk
Formula weight	294.18
Temperature (K)	193.1 ± 1
Wavelength (Å)	0.7107
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.782(1)
b (Å)	8.9610(9)
c (Å)	15.108(2)
β (°)	103.008(5)
Cell volume (Å^3)	1422.2(3)
Formula units/unit cell	4
D_{calc} (g/cm^3)	1.374
F_{000}	608.00
Crystal dimensions (mm)	$0.69 \times 0.40 \times 0.25$
2θ range for data collection (°)	7.2–55.0
Ranges of h, k, l	$-13 \le h \le 13$ $-11 \le k \le 11$ $-19 \le l \le 19$
Reflections collected	14 042
Absorption correction type	Multi-scan
Independent reflections	3158
Maximum and minimum transmission	1.000–0.895
Data/parameters	2602/185
Goodness-of-fit on F^2	1.05
R indices (all data)	0.036
Final R indices [$I > 3\sigma(I)$]	0.046, $wR_2 = 0.140$
Largest peak and hole in final difference map (e Å^{-3})	0.48 and −0.38

2.3. Method of calculation

Initial molecular geometry was optimized using MM+ molecular modeling and semi-empirical AM1

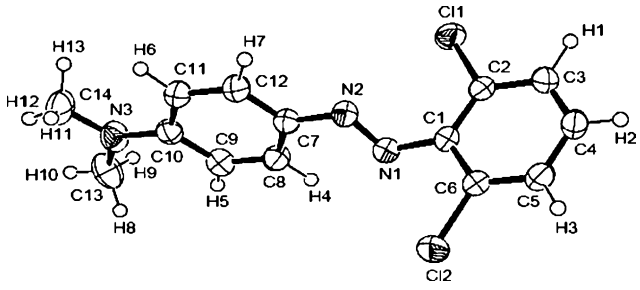

Fig. 2. Molecular structure of the title compound.

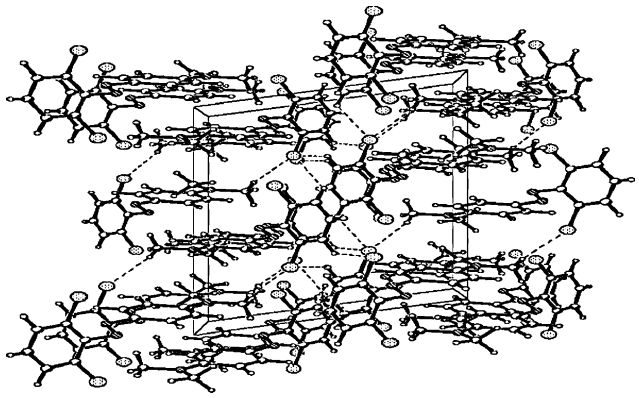

Fig. 3. Packing diagram viewed down the axis *a*.

methods (HYPERCHEM 5.0, Hypercube, Ontario, Canada). In the next step, the DFT and ab initio RHF calculations were performed with the GAUSSIAN 98 software package [13]. A hybrid functional B3LYP (Becke's Three parameter Hybrid Functional Using the LYP Correlation Functional) were selected in DFT calculation. All calculations employed 6-311G** basis set.

Table 2
Atomic coordinates and B_{iso}/B_{eq}

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq} (Å^2)
Cl1	0.6454(5)	0.11658(5)	0.24443(3)	3.825(12)
Cl2	0.7027(6)	0.03905(6)	0.60649(3)	4.45(1)
N1	0.7594(2)	−0.0280(2)	0.42848(10)	3.14(3)
N2	0.7149(1)	−0.1396(2)	0.38188(10)	3.04(3)
N3	1.0394(2)	−0.6203(2)	0.36611(13)	3.85(4)
C1	0.6652(2)	0.0859(2)	0.42568(11)	2.76(3)
C2	0.6086(2)	0.1633(2)	0.34718(11)	2.93(3)
C3	0.5268(2)	0.2830(2)	0.34784(13)	3.42(4)
H1	0.4876(2)	0.3411(2)	0.28611(13)	3.89(9)
C4	0.4996(2)	0.3246(2)	0.42953(13)	3.67(4)
H2	0.4550(2)	0.4150(2)	0.42786(13)	4.24(9)
C5	0.5524(2)	0.2490(2)	0.50928(13)	3.54(4)
H3	0.5246(2)	0.2670(2)	0.56660(13)	4.16(9)
C6	0.6354(2)	0.1322(2)	0.50677(12)	3.11(3)
C7	0.8040(2)	−0.2534(2)	0.37830(11)	2.92(3)
C8	0.9357(2)	−0.2415(2)	0.41016(12)	3.28(4)
H4	0.9722(2)	−0.1452(2)	0.43566(12)	3.93(9)
C9	1.0145(2)	−0.3609(2)	0.40561(13)	3.30(4)
H5	1.1019(2)	−0.3466(2)	0.42558(13)	3.97(9)
C10	0.9641(2)	−0.4997(2)	0.37001(11)	2.96(3)
C11	0.8300(2)	−0.5102(2)	0.33759(13)	3.36(4)
H6	0.7880(2)	−0.6086(2)	0.30997(13)	3.94(9)
C12	0.7534(2)	−0.3878(2)	0.34089(13)	3.38(4)
H7	0.6549(2)	−0.3935(2)	0.31789(13)	4.00(9)
C13	1.1769(2)	−0.6106(3)	0.3955(2)	4.65(5)
H8	1.2041(2)	−0.5736(3)	0.4613(2)	5.74(10)
H9	1.2031(2)	−0.5396(3)	0.3603(2)	5.71(10)
H10	1.2131(2)	−0.6986(3)	0.3943(2)	5.72(10)
C14	0.9849(2)	−0.7647(3)	0.3351(2)	5.03(5)
H11	0.9136(2)	−0.7988(3)	0.3758(2)	5.92(10)
H12	1.0586(2)	−0.8278(3)	0.3398(2)	5.94(10)
H13	0.9216(2)	−0.7678(3)	0.2728(2)	5.93(10)

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$.

3. Results and discussion

3.1. IR and NMR spectra

IR (FT-IR spectrometer with KBr pellets, cm^{-1}): 2915 (w, N−CH_3), 1602, 1523 (s, benzene ring C−C), 1410 (s, N=N), 1372, 1143 (s, benzene ring, C−H), 820 (s, di-substituted benzene ring) cm^{-1}, 774 (m, C−Cl).

^{1}H NMR data (Bruker AV-400 NMR spectrometer, DMSO-d_6 as solvent, ^{1}H (399.97 MHz), ambient temperature, ppm): 3.145 (S, 6H, −N(CH_3)$_2$), 6.988−7.000 (d, H5, H6), 7.124−7.164 (m, H2), 7.387−7.397 (d, H1, H3), 7.951−7.973 (d, H7, H4) [14].

3.2. Description of the crystal structure

The fractional coordinates and equivalent isotropic thermal parameters for atoms are given in Table 2. The selected bond lengths and angles are listed in Table 3.

The title molecule has *trans*-geometry about the azo linkage and the torsion angle C1−N1−N2−C7 is 177.3(1)°. A dihedral angle of 74.5° exists between chlorine-substituted aniline ring (plane 1) and *N*,*N*-dimethyl substituted aniline ring (plane 2), which are oppositely twisted around the central linkage with 62.9° and 11.7° for plane 1 and plane 2, respectively.

Crystal packing analysis was done using OPEC [15] program, which was locally modified with additional calculation routines added. Given a reference molecule (FM) and the intermolecular interactions being limited

Table 3
Selected bond lengths and bond angles (Å, °)

Atoms		Distance	Atoms			Angle
C11	C2	1.737(2)	N2	N1	C1	111.9(1)
N1	N2	1.254(2)	N1	N2	C7	114.9(2)
N2	C7	1.410(2)	C10	N3	C13	121.2(2)
N3	C13	1.451(3)	C10	N3	C14	121.2(2)
C1	C2	1.391(2)	C13	N3	C14	117.6(2)
C7	C8	1.398(3)	N1	C1	C2	123.5(2)
C10	C11	1.421(3)	N1	C1	C6	119.1(2)
Cl2	C6	1.732(2)	C2	C1	C6	117.2(2)
N1	C1	1.433(2)	Cl1	C2	C1	119.84(13)
N3	C10	1.361(2)	Cl1	C2	C3	117.7(1)
N3	C14	1.455(3)	C1	C2	C3	122.4(2)
C1	C6	1.397(2)	Cl2	C6	C1	119.06(13)
C5	C6	1.384(2)	Cl2	C6	C5	119.2(1)
C7	C12	1.389(2)	C1	C6	C5	121.7(2)
C9	C10	1.414(3)	N2	C7	C8	125.4(2)
			N2	C7	C12	115.8(2)
			C8	C7	C12	118.8(2)
			N3	C10	C9	122.2(2)
			N3	C10	C11	120.2(2)
			C9	C10	C11	117.6(2)

Table 4
Hydrogen bond geometries (Å, °)

D	H	A	D–H	H···A	D···A	D–H···A	Sym. cod.
C5	H3	Cl1	0.991(3)	2.903(3)	3.671(3)	134.9(1)	$x, -y+1/2, z+1/2$
C3	H1	Cl1	1.069(3)	2.840(3)	3.628(3)	130.6(1)	$-x+1, y+1/2, -z+1/2$
C11	H6	Cl2	1.035(3)	3.068(3)	3.462(3)	103.7(1)	$x, -y-1/2, z-1/2$
C13	H9	Cl1	0.914(3)	2.880(3)	3.756(3)	161.1(1)	$-x+2$, y $-1/2, -z+1/2$

Table 5
π···π interaction[a] (Å)

E (SM) sym. cod. (%)[b]	Interaction	Dplane	Dcenter	
17.6	$-x+2, -y-1, -z+1$	Plane 2-2	3.52	4.64
12.2	$-x+1, -y, -z+1$	Plane 1-1	3.69	4.82

Plane 1: C1–C6.
Plane 2: C7–C12, Fig. 2.
[a] Two parallel phenyl rings or π systems are stacked closely, which makes most of the atoms involved closely. The parameters followed are respectively the distances between the ring planes and their centers.
[b] The percentage of intermolecular interaction energy in the total packing energy.

within 15 Å, approximately 60–150 surrounding molecules (SM) consist of the crystal model. The molecules, which are most strongly interacted with the FM, are listed in Tables 4 and 5. As shown in the tables, molecules are interacted through π···π [16] interaction, forming 'double chains' along [1 −1 0]. The 'double chains' are interacted through C–H···Cl H-bonds (3.671(3) Å, 134.9(1)°, x, $-y+1/2$, $z+1/2$; 3.462(3) Å, 103.7(1)°, x, $-y-1/2$, $z-1/2$), forming double layers (110), which are in turn interacted by C3–H1···Cl1 H-Bond (3.628(3) Å, 130.6(1)°, $-x+1$, $y+1/2$, $-z+1/2$), forming chunk crystals (Fig. 3).

3.3. Computational study

The experimental and optimized geometric parameters (bond lengths, bond angles and torsion angles) of **1a**, **1b** and **1c** by RHF and DFT (B3LYP) with 6-311G** basis set are listed in Table 6. The optimized geometric parameters obtained by two methods are similar and in good agreement with the experimental values. All three molecules have *trans*-geometry about the azo linkage.

The major difference among these three molecules is their molecular planarity. The optimized structure of **1a** is found to be planar, but **1b** and **1c** are nonplanar. As shown by torsion angle of N2–N1–1′-2′, in **1a**, it is close to 0°, but in **1b** and **1c** the angles are 54° and 65°, respectively (the average of two methods). It indicates that the molecular planarity of these compounds is **1a** > **1b** > **1c**. On the other hand, the AhR ligand activity is **1c** > **1b** > **1a** [6]. So it is thought that the enhancement of AhR ligand activity of **1c** might be due to its nonplanarity. However, there are other factors to affect the AhR ligand activity, e.g. electronic effect. Further structure determination and theoretical calculation on more *ortho*-haloganated MYs are needed to better understand the relationship between these two factors.

Table 6
Optimized and experimental geometries of MY, 2′-Cl MY and 2′,6′-diCl MY

Parameters	X-ray analysis			RHF/6-311G**			B3LYP/6-311G**		
	1a*	**1b**	**1c**	**1a**	**1b**	**1c**	**1a**	**1b**	**1c**
Bond lengths									
N1-1′	1.412(2)	/	1.433(2)	1.4214	1.4218	1.4213	1.4169	1.4142	1.4122
N1-N2	1.261(0)	/	1.254(2)	1.2461	1.2453	1.2440	1.2578	1.2581	1.2578
N2-1	1.417(1)	/	1.410(2)	1.4127	1.4123	1.4150	1.4032	1.4029	1.4013
X-2′	/	/	1.737(2)	1.0720	1.7436	1.7407	1.0817	1.7575	1.7359
X-6′	/	/	1.732(2)	1.0745	1.0744	1.7410	1.0836	1.0834	1.7365
1′-2′	1.383(2)	/	1.391(2)	1.3917	1.3894	1.3896	1.4036	1.4085	1.4063
1′-6′	1.391(1)	/	1.397(2)	1.3843	1.3890	1.3896	1.3991	1.4038	1.4076
Bond angles (°)									
N1-1′-2′	124.2(2)	/	123.5(2)	124.42	125.69	123.28	124.79	127.81	125.20
1′-N1-N2	113.9(7)	/	113.9(1)	115.72	114.87	114.09	114.95	115.66	114.93
N1-N2-1	115.4(0)	/	114.9(2)	116.32	116.39	116.21	115.74	115.54	115.54
N2-1-2	117.8(7)	/	115.8(2)	116.61	116.37	116.15	116.47	116.19	116.18
N2-1-6	125.1(4)	/	125.4(2)	125.04	125.05	124.81	125.28	125.39	125.24
Torsion angle (°)									
1′-N1-N2-1	−178.2(5)	/	177.3(1)	−179.99	179.41	179.88	−180.00	179.07	177.91
N2-N1-1′-2′	0.3(5)	/	−65.1(2)	0.02	−51.95	−67.23	0.011	−57.20	−62.61
N2-N1-1′-6′	178.6(1)	/	120.6(2)	179.98	131.38	117.60	179.99	126.40	123.53
N1-N2-1-2	5.5(1)	/	−9.8(3)	0.38	1.69	−1.46	−0.025	3.45	−1.53
N1-N2-1-6	−175.9(8)	/	169.1(2)	−179.94	−178.11	178.63	179.99	−176.89	178.34

*The X-ray data of MY were retrieved from CSD (version 5.25, November 2003) [17,18].

Acknowledgements

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