

IR, ^1H NMR, ^{13}C NMR and X-ray structure determination of 1-(2'-chloro-4'-nitrophenylazo)-2,4-benzenediol, intramolecular proton transfer between oxygen and nitrogen atoms, $\pi\cdots\pi$ interaction and H-bonds

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Abstract

A monoazo disperse dye, 1-(2'-chloro-4'-nitrophenylazo)-2,4-benzenediol ($\text{C}_{12}\text{H}_8\text{N}_3\text{ClO}_4$) was synthesized and characterized by X-ray diffraction, IR, ^1H NMR, ^{13}C NMR and elemental analysis. It is found that between the 2-OH and the central N atom intramolecular proton transfer exists with the hydrazone form being major component. The title molecule crystallizes in the monoclinic system space group $\text{P}2_1/c$ (#14), $a = 10.793(8)$, $b = 8.898(7)$, $c = 12.894(10)$ Å, $\beta = 95.789(10)^\circ$. The title molecule takes *trans* geometry about the azo linkage. The intramolecular hydrogen bond ring is essentially planar and coplanar with its adjacent phenyl ring, which stabilized the hydrazone form. In the crystal, molecules are interacted through $\pi\cdots\pi$ interaction, forming 'double chains' [1 $\bar{1}$ 0]. The 'double chains' are extended along [0 1 0] through H-bond $\text{O}(4)\cdots\text{H}(1)\text{--}\text{O}(3)$, forming double layers (0 0 1), which are in turn interacted by $\text{Cl}(1)\cdots\text{C}(8)\text{--}\text{H}(6)$ H-bond [0 0 1], forming crystals.

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Keywords: Azo dye; IR; ^1H and ^{13}C NMR; Proton transfer; $\pi\cdots\pi$ interaction; H-bond

1. Introduction

The azo (I)–hydrazone (II) tautomerism (Figs. 1 and 2) in disperse azo dyes [1] is one of the interesting research fields because it is very

important for their optical stability and usage. It is explained by the proton transfer between the O and imine N atoms [2], which also has potential use as the basis of optical data storage devices [3]. In this paper, the X-ray diffraction, IR, ^1H and ^{13}C NMR studies of the structure of 1-(2'-chloro-4'-nitrophenylazo)-2,4-benzenediol and its crystal packing are presented. A brief comparison between it and similar compounds is also reported.

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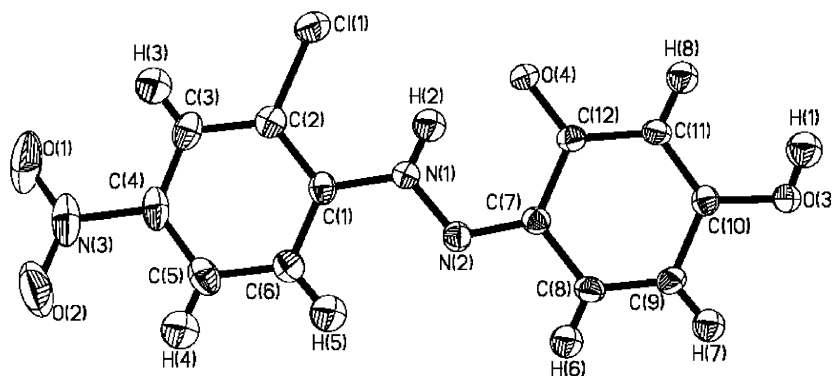


Fig. 1. Molecular structure of the title compound.

2. Experimental

2.1. Synthesis

A solution of NaNO_2 (0.7 g, 2 ml of water) was added dropwise into a mixture of 2-chloro-4-nitroaniline (1.72 g), HCl (36%, 3 ml) and water (10 ml) with vigorous stirring at 273–278 K. The suitable amount of NaNO_2 was determined by potassium iodide–starch paper. The solution was stirred for 30 min before the insoluble components were removed by filtration. The filtrate was added dropwise into a solution of 1,3-benzenediol (1.10 g) in a mixture of NaAc (16.40 g) and water (50 ml) at 273–278 K. The mixture was stirred for 1 h and its pH was adjusted to 3–4. The solution was filtrated to obtain the title compound, which was then washed with a lot of water and a little of ethyl alcohol, and the product was recrystallized five times from tetrahydrofuran. The red crystal was grown from tetrahydrofuran by slow evaporation at ambient temperature for a week. m.p.: 489 K.

Elemental analysis (Perkin–Elmer 240C elemental analyzer)—calcd. for $\text{C}_{12}\text{H}_8\text{N}_3\text{ClO}_4$ (%), C, 49.06, H, 2.93, N, 14.31; found: C, 48.90 H, 2.70, N, 14.05.

2.2. X-ray crystallography

A light red platelet crystal with dimensions 0.30 mm \times 0.50 mm \times 0.06 mm was mounted on a glass fiber and the data were collected in a Rigaku CCD diffractometer using graphite monochromated $\text{Mo-K}\alpha$ radiation under conditions of liquid nitrogen. The structure was solved by direct methods [4] and expanded using Fourier techniques [5]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference map and refined isotropically using the riding model. All calculations were performed using CrystalStructure [6,7] crystallographic software package. The details of the X-ray analysis are listed in Table 1.

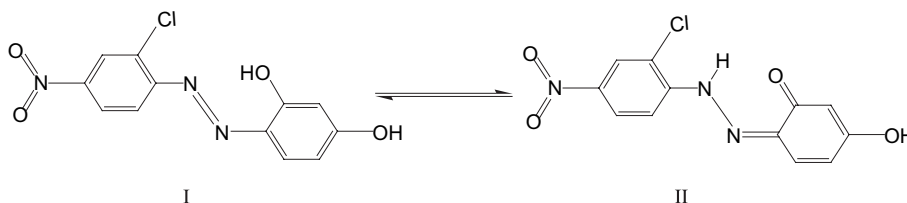


Fig. 2. The tautomerism between azobenzene form (I) and hydrazone form (II).

Table 1
Crystal data and structure refinement

Compound	C ₁₂ H ₈ N ₃ ClO ₄
Colour/shape	Light red/platelets
Formula wt.	293.67
Temp. (K)	193.1 ± 1
Wavelength (Å)	0.7107
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	10.793(8)
<i>b</i> (Å)	8.898(7)
<i>c</i> (Å)	12.894(10)
β (deg.)	95.789(10)
Cell volume (Å ³)	1231.9(16)
Formula units/unit cell	4
<i>D</i> _{calc} (g/cm ³)	1.583
<i>F</i> ₀₀₀	600.00
Crystal dimensions (mm)	0.30 × 0.50 × 0.06
2θ range for data collection (deg.)	7.0–55.0
Ranges of <i>h</i> , <i>k</i> , <i>l</i>	−14 ≤ <i>h</i> ≤ 13, −11 ≤ <i>k</i> ≤ 11, −16 ≤ <i>l</i> ≤ 16
Reflections collected	12 389
Absorption correction type	Multi-scan
Independent reflections	2789
Max. and min. transmission	1.000–0.981
Data/parameters	2053/189
Goodness-of-fit on <i>F</i> ²	1.07
<i>R</i> indices (all data)	0.031
Final <i>R</i> indices [<i>I</i> > 3σ(<i>I</i>)]	0.034, <i>wR</i> ₂ = 0.094
Largest peak and hole in final difference map (e [−] Å ³)	0.29 and −0.32

3. Results and discussion

3.1. IR and NMR spectra

IR (FT-IR spectrometer with KBr pellets, cm^{−1})
3109 (w, −OH/−NH), 3444 (m, −OH), 1586

(m, −C=O), 1504 (s, −NO₂), 1467, 1123 (s, Benz. ring), 1385 (m, N=N), 1339 (s, −NO₂, CN), 1218 (s, −OH, CO, Benz. ring). 3109 cm^{−1}: *ν* (O–H) overlaps with *ν* (N–H), an indicator of intra-molecular proton transferring between O(4) and N(1) atoms [8].

The NMR data (Bruker AV-400 NMR spectrometer, *d*₆-DMSO as solvent, ¹H (399.97 MHz), ¹³C (100.57 MHz) NMR, ambient temperature) of the title compound are listed in Table 2 [9,10].

3.2. Description of the crystal structure

The fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 3. The selected bond lengths and angles are listed in Table 4.

The title molecule has *trans* geometry about the azo linkage and the torsion angle C(1)–N(1)–N(2)–C(7) is 179.2(2)°. The molecular skeleton is almost planar (see Table 7 for dihedral angles). There is a strong intramolecular H-bond O(4)⋯H(2)–N(1) [2.537 (3)Å, 141.6(2)°] (Table 5), forming a six-membered ring. The relevant bond lengths and angles are changed significantly (see below), which indicates that the H-bond is significantly strengthened through the resonance [11,12] (I=II, Fig. 2) and, therefore, the title molecule mainly exists in the hydrazone form as shown in Fig. 1.

Crystal packing analysis was done using OPEC [13] program, which was locally modified with additional calculation routines added. Given a reference molecule (FM) and the intermolecular interactions being limited within 15 Å, approximately 60–150 surrounding molecules (SM) consist of the

Table 2
¹H and ¹³C chemical shifts in the title compound in *d*₆-DMSO (Hz)

H	δ (¹ H)	H	δ (¹ H)	C	δ (¹³ C)	C	δ (¹³ C)
H(1)	11.150	H(7)	6.579–6.602	C(1)	147.0	C(7)	123.8
H(2)	13.185	H(8)	6.372	C(2)	134.3	C(8)	131.7
H(3)	8.058–8.081			C(3)	125.9	C(9)	111.9
H(4)	8.311–8.334			C(4)	149.9	C(10)	160.2
H(5)	8.522			C(5)	130.6	C(11)	103.2
H(6)	7.717–7.740			C(6)	118.1	C(12)	166.4

For atomic labeling, see Fig. 1.

Table 3
Atomic coordinates and thermal parameters

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} (Å ²)
Cl(1)	0.26680(5)	0.04633(5)	0.30292(3)	3.059(11)
O(1)	0.4808(2)	−0.3556(2)	0.5569(2)	6.08(5)
O(2)	0.4620(2)	−0.2808(2)	0.7137(2)	5.96(5)
O(3)	−0.01691(12)	0.90423(13)	0.38102(9)	2.34(3)
O(4)	0.12548(11)	0.41492(13)	0.30660(8)	2.24(3)
N(1)	0.22898(13)	0.2719(2)	0.46264(10)	1.98(3)
N(2)	0.21189(13)	0.3870(2)	0.52329(10)	1.94(3)
N(3)	0.4492(2)	−0.2637(2)	0.6188(2)	3.69(4)
C(1)	0.2843(2)	0.1407(2)	0.50377(13)	1.92(3)
C(2)	0.3068(2)	0.0236(2)	0.43562(13)	2.10(3)
C(3)	0.3619(2)	−0.1092(2)	0.4719(2)	2.45(4)
C(4)	0.3921(2)	−0.1227(2)	0.5782(2)	2.57(4)
C(5)	0.3710(2)	−0.0102(2)	0.6478(2)	2.66(4)
C(6)	0.3181(2)	0.1229(2)	0.6103(1)	2.42(4)
C(7)	0.1572(2)	0.5092(2)	0.48013(12)	1.74(3)
C(8)	0.1398(2)	0.6315(2)	0.54932(12)	1.94(3)
C(9)	0.0837(2)	0.7598(2)	0.51485(12)	1.93(3)
C(10)	0.0396(2)	0.7746(2)	0.40672(12)	1.82(3)
C(11)	0.0545(2)	0.6612(2)	0.33642(12)	1.88(3)
C(12)	0.1122(2)	0.5248(2)	0.36887(12)	1.72(3)

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

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

Atom	Atom	Distance	Atom	Angle
Cl(1)	C(2)	1.734(2)	N(2)–N(1)–C(1)	120.5(1)
O(1)	N(3)	1.216(3)	N(1)–N(2)–C(7)	118.1(1)
O(2)	N(3)	1.227(3)	O(1)–N(3)–O(2)	124.1(2)
O(3)	C(10)	1.331(2)	O(1)–N(3)–C(4)	118.3(2)
O(4)	C(12)	1.282(2)	O(2)–N(3)–C(4)	117.6(2)
N(1)	N(2)	1.313(2)	N(1)–C(1)–C(2)	118.7(2)
N(1)	C(1)	1.392(2)	N(1)–C(1)–C(6)	122.0(2)
N(2)	C(7)	1.332(2)	Cl(1)–C(2)–C(1)	119.38(13)
N(3)	C(4)	1.470(2)	Cl(1)–C(2)–C(3)	119.3(1)
C(1)	C(2)	1.400(2)	N(3)–C(4)–C(3)	118.5(2)
C(1)	C(6)	1.394(2)	N(3)–C(4)–C(5)	118.5(2)
C(2)	C(3)	1.382(3)	C(3)–C(4)–C(5)	123.0(2)
C(3)	C(4)	1.381(3)	N(2)–C(7)–C(8)	116.1(1)
C(4)	C(5)	1.380(3)	N(2)–C(7)–C(12)	124.9(2)
C(5)	C(6)	1.381(3)	C(8)–C(7)–C(12)	119.0(2)
C(7)	C(8)	1.431(2)	O(3)–C(10)–C(9)	114.9(1)
C(7)	C(12)	1.474(2)	O(3)–C(10)–C(11)	123.5(1)
C(8)	C(9)	1.346(2)	C(9)–C(10)–C(11)	121.6(2)
C(9)	C(10)	1.433(2)	O(4)–C(12)–C(7)	119.4(2)
C(10)	C(11)	1.377(2)	O(4)–C(12)–C(11)	123.0(2)
C(11)	C(12)	1.409(2)	C(2)–C(1)–C(6)	119.3(2)

Table 5
H-bond geometries (Å, °)

D	H	A	D–H	H⋯A	D⋯A	D–H⋯A	Symmetry code
O(3)	H(1)	O(4)	0.843(4)	1.735(4)	2.574(4)	173.1(2)	$-x+1, y-1/2, -z+1/2$
C(8)	H(6)	Cl(1)	0.936(4)	2.886(4)	3.755(4)	155.0(2)	$x, -y+1/2, z-1/2$
N(1)	H(2)	O(4)	0.910(3)	1.760(3)	2.537(3)	141.6(2)	x, y, z
N(1)	H(2)	Cl(1)	0.910(3)	2.552(3)	2.929(3)	105.4(2)	x, y, z

crystal model. The molecules, which are most strongly interacted with the FM are listed in Tables 5 and 6. As shown by the tables, molecules are interacted through $\pi\cdots\pi$ [14] interaction, forming ‘double chains’ [1–10]. The ‘double chains’ are interacted through O(4)⋯H(1)–O(3) (2.574 (4) Å, 173.1(2)°, $-x+1, y-1/2, -z+1/2$) H-bond, forming double layers (0 0 1), which are in turn interacted by Cl(1)⋯C(8)–H(6) (3.755(4) Å, 155.0(2)°, $x, -y+1/2, z-1/2$) H-bond, forming crystals (Fig. 3).

For comparison reason, the crystal structural data of 2-hydroxy-substituted azobenzenes and similar compounds were retrieved from Cambridge Structural Database (CSD) [15]. Their relevant bond lengths are listed in Table 8. As shown by Table 8, in the title molecule the bond lengths for N(1)–N(2) [1.313 (2)Å], C(7)–C(12) and that for C(7)–C(8) are significantly lengthened and N(2)–C(7), O(4)–C(12) and N(1)–C(1) are significantly shortened when compared with the statistical mean values [16]. The bond lengths in the resorcinol ring (Table 4) are also changed regularly. The molecule is essentially planar

(dihedral angles, Table 7 and D_m , Table 8). The above changes in bond lengths can well be explained by the resonance I–II in Fig. 2. [17]. These are in agreement with the above IR and NMR data.

For the remaining compounds in Table 8, the above regular changes are also observed, showing that the tautomerism also exists in these cases, but to a lesser extent (except NBZANO11), for the substituent groups also affect the tautomerism. The electron withdrawing substituents such as NO₂ on phenyl ring originating from diazonium salt increase the hydrazone form component (NBZANO11, Table 8), and electron donating hydroxy group in position 4 of the passive component has nearly the same effect [10]. Because of these both substituents the title molecule exists mostly in the hydrazone form.

Table 6
 $\pi\cdots\pi$ interaction^a (Å)

$E(\text{SM})$ %	Symmetry code	Interaction	D_{plane}	D_{center}
18.3	$-x, -y+1, -z+1$	Plane 2–2	3.28	3.78
16.7	$-x+1, -y, -z+1$	Plane 1–1	3.35	3.74

^a Two parallel phenyl rings or π systems are stacked closely, which makes most of the involved atom very closely. The parameters followed are, respectively, the distances between the ring planes and their centers. For plane definitions, see Table 7.

^b The percentage of intermolecular interaction energy in the total packing energy.

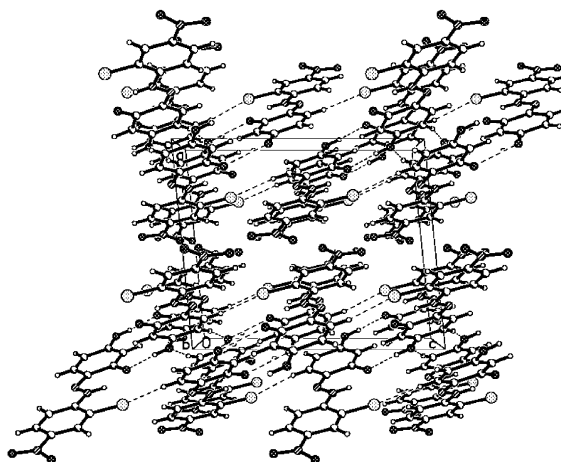


Fig. 3. Packing diagram viewed down the b axis.

Table 7

Dihedral angles in 2-OH substituted azobenzenes and related compounds (°)

No.	Refcode	A ₁₂	A ₁₃	A ₁₄	A ₂₃	A ₂₄	A ₃₄
1	This study	4.6	3.8	4.8	1.5	0.9	1.1
2	JEBMAE	86.2	87.8	87	4.0	2.3	1.7
3	LIWDUQ	1.6	1.3	1.9	0.4	0.5	0.8
4	NUBDET	0.0	0.0	0.0	0.0	0.0	0.0
5	NUTROJ	5.8	1.8	3.2	4.0	2.8	1.4
6	TITNUF	10.3	4.1	7.3	6.2	0.3	3.2
7	WIHYAN	0.0	1.5	0.9	1.5	0.9	1.5
8	WOBPOS	2.7	0.1	1.5	2.6	2.2	1.4
9	JARPIB	1.7	3.6	2.7	2.1	1.7	1.3
10	JARPIB01	1.8	3.6	2.6	2.0	1.4	1.3
11	NBZANO11	2.7	1.5	0.4	3.5	3.1	1.3
12	ACLMSA	4.9	4.9	5.1	0.1	0.2	0.3
13	BCNPPN10	5.5	4.7	4.9	0.8	0.7	0.4
14	CEMSPB10	11.1	7.8	8.9	5.0	4.1	1.2
15	CEMSPC10	3.4	2.0	3.6	3.0	2.1	1.9

Plane 1: the phenyl ring with R' (Fig. 4).

Plane 2: the phenyl ring with R (Fig. 4).

Plane 3: the central C–N=N–C.

Plane 4: the six-membered ring formed by the intramolecular H-bond.

Table 8

Intramolecular H-bond in 2-OH substituted azobenzenes and related compounds (Å)

No.	R'	R	R (%)	D _{CO}	D _{NO}	D _{CN}	D _{NN}	D _{NC}	D _m	
1	2'-Cl, 4'-NO ₂	4-OH	3.4	1.281	2.537	1.332	1.313	1.392	−0.0057	
2	2',6'-Br, 4'-CH ₃	4-N(CH ₃) ₂	6.7	1.340	2.566	1.363	1.278	1.438	0.0091	
3	4'-CH ₃	5-CH ₃	5.4	1.344	2.562	1.404	1.266	1.418	0.0067	
4		5-OCH ₃ , 3- <i>t</i> Bu	4.4	1.348	2.534	1.401	1.274	1.418	0.0058	
5	2'-Cl	5-OCH ₃ , 3- <i>t</i> Bu	5.5	1.345	2.548	1.405	1.266	1.417	0.0236	
6	4'-CH ₃	3-OCH ₃ ,5-C ₂ H ₃ =CH ₂	7.8	1.349	2.557	1.413	1.272	1.423	0.0180	
7	2'-OH		4.3	1.347	2.606	1.403	1.274	1.403	0.0114	
8	4'-OCH ₃	5-Ph	4.8	1.360	2.580	1.410	1.275	1.423	−0.0151	
9	4'-N(CH ₃) ₂		3.6	1.337	2.523	1.392	1.286	1.404	−0.0102	
10	4'-N(CH ₃) ₂		3.9	1.343	2.526	1.398	1.275	1.400	−0.0115	
11	4'-NO ₂		9.0	1.269	2.563	1.310	1.361	1.357	0.0097	
No.	R'	R ₁	R		D _{CN'}	D _{NN'}	D _{CN}	D _{NN}	D _{NC}	D _m
12	2'-Cl, 4'-SO ₂ CH ₃	−C ₂ H ₅	4-N(C ₂ H ₅) ₂	7.7	1.399	2.657	1.367	1.276	1.409	0.0246
13	2'-Cl, 4'-SO ₂ CH ₃	−CH ₃	4-N(C ₂ H ₅) ₂	6.5	1.395	2.663	1.394	1.278	1.423	0.0074
14	2'-Br, 4'-NO ₂ , 6'-CN	−C ₂ H ₅	4-N(C ₂ H ₅) ₂	4.8	1.398	3.978	1.369	1.294	1.393	0.0043
15	2'-Br, 4'-NO ₂ , 6'-CN	−CH ₃	4-N(C ₂ H ₅) ₂	6.5	1.392	3.966	1.384	1.281	1.387	0.0169
Mean					1.350	2.758	1.383	1.284	1.407	
Mean'					1.362	2.755	1.468	1.225	1.468	

D_{CO}, D_{NO}, D_{CN}, D_{NN}, D_{NC}, D_{CN'}, D_{NN'}: see Fig. 4.D_m: The maximum deviation from the ring plane for the ring atoms.R', R, R₁: see Fig. 4.

Mean: average bond lengths from this table.

Mean': statistical average values [16].

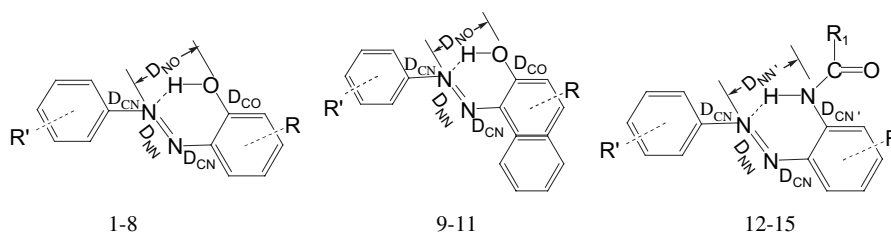


Fig. 4. The schematic structures of 2-hydroxy-substituted azobenzenes and similar compounds.

Acknowledgements

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Appendix A

A search was done at the early stage of this work on the CSD [15] using the following criteria: (1) the structure sought consists of one and only one fragment shown in Fig. 4; (2) there is no cyclic link between the central N atoms; (3) organometallic, polymeric, erroneous structures are excluded and R is less than 0.09. The search resulted in our database, consisting of 14 structures. Table 8 lists their refcodes and substituted groups.

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