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Synthesis and Crystal Structure of N′-[(2-Hydroxyphenyl) methylidene]-2-(2-nitrophenoxy) acetohydrazide

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The crystal structure of N′-[(2-hydroxyphenyl)methylidene]-2-(2-nitrophenoxy) acetohydrazide has been determined by single crystal X-ray diffraction method. The crystal belongs to orthorhombic system, space group P2(1)2(1)2(1) with unit cell constants $a = 7.3692$, $b = 7.5657$, $c = 26.0983$Å, $V = 1455.06$ Å^3, $Z = 4$, $D_c = 1.439$ g/cm^3, $\mu = 0.11$ mm^{-1}, $F(000) = 656$, R and wR are 0.0661 and 0.2655 respectively for 1502 unique reflections with 833 observed reflections ($I > 2\sigma(I)$). The molecules are interconnected into chains along the b axis by C_5-H_{5A} . . . O_5 and C_7-H_{7B} . . . O_4 intermolecular interactions.

Key Words: Synthesis, Crystal structure, Acetohydrazide.

INTRODUCTION

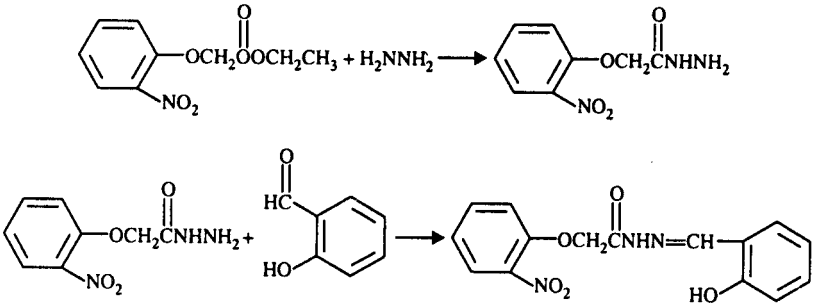
Recently, some compounds containing aryloxymethyl moiety are of considerable interest due to their strong biological activities[1]. As a matter of fact, salicylaldehyde Schiff base complexes present extremely antileucovirus activity[2, 3], antibacterial activity[4], good activity of auxins and on growth of root[5]. Meanwhile, much attention has been focussed on some compounds containing hydrazide moiety owing to its potential inhibitors for many enzymes[6, 7]. Thus, we synthesized and determined the X-ray crystal structure of the title compound in order to confirm its conformation and stereochemistry.

EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. ^{1}H NMR spectrum was recorded by Bruker AC-300 with TMS as an internal standard. IR spectrum was taken by Nicolet 510P FT-IR spectrometer (KBr). Elemental analysis was performed by Perkin-Elmer 240.

The title compound was prepared as follows: *o*-Nitro-phenoxyacetylhydrazine was obtained according to literature method.[8] To a warm solution of *o*-nitrophenoxyacetylhydrazine (10.55 g, 0.05 mol) and catalytic amount of acetic acid

in ethanol (80 mL), salicylaldehyde (6.11 g, 0.05 mol) was added dropwise with magnetic stirring and the mixture was refluxed for 2 h. The precipitate was collected by filtration, drying and recrystallization from ethanol. Yield: 81%. The filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, a crystalline solid appeared two weeks later and was separated by nitration. Anal.: Calcd. (%) for $C_{15}H_{13}N_3O_5$: C, 57.14; H, 4.13; N, 13.33. Found (%): C, 57.12; H, 4.11; N, 13.35. ^{1}H NMR (DMSO-d_6): δ 4.85 (s, 1H, CH=N), 5.30 (s, 2H, CH_2), 6.71–8.29 (m, 8H, Ar—H), 10.38 (s, 1H, N—H), 11.50 (s, 1H, OH). IR: 3300 (m, OH); 3152 (s, N—H), 3230 (s, N—H); 3045 (w, Ar—H); 1678 (s, C=O); 1340 (vs, NO_2); 1532 (vs, NO_2); 1250 (vs, Ar—O) cm^{-1}. The reaction equation for the synthesis of the title compound is as follows:



Scheme-1

Crystal data and structure determination

A colourless single crystal with approximate dimension of 0.30 mm × 0.28 mm × 0.24 mm was mounted on a glass fibre in a random orientation. The data were collected by Bruker Smart 1000 CCD diffractometer with graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å) using a scan mode in the range of $1.61 \le \theta \le 26.43°$ at temperature 293(2) K. A total of 4744 reflections were collected with 1502 unique ones (R_{int} = 0.0661), of which 833 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinements. Intensity data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods and expanded by using Fourier differential techniques with SHELXL-97[9]. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added according to the theoretical models. Full matrix least-squares refinement gave the final R = 0.0661 and wR = 0.2655, $\{W = 1/[\sigma^2(F_0)^2 + (0.1327P)^2 + 0.5336P]$ where $P = (F_0^2 + 2F_c^2)/3$. Fig. 1 shows the molecular structure of the compound.

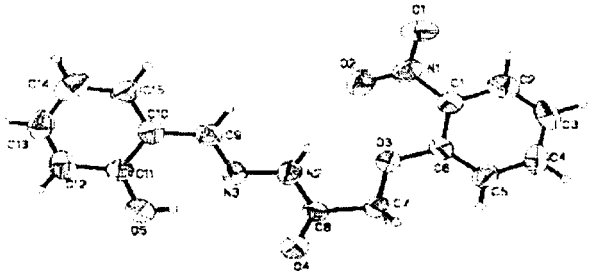


Fig. 1. The molecular structure of the title compound with the atomic numbering scheme

RESULTS AND DISCUSSION

The final atomic parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table-1. Selected bond lengths and bond angles are illustrated in Tables 2 and 3, respectively. The hydrogen bonding geometries are shown in Table-4.

TABLE-1
ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
O_1	3962(9)	9374(8)	58(7)	27(3)	C_5	5549(7)	8600(3)	1781(8)	23(9)
O_2	1770(5)	9570(4)	603(1)	28(5)	C_6	4275(5)	9083(1)	1427(7)	22(6)
O_3	2593(5)	9786(8)	1544(1)	18(7)	C_7	2175(7)	10133(0)	2066(9)	22(4)
O_4	–396(4)	11450(5)	2467(4)	21(6)	C_8	335(8)	11088(4)	2065(6)	21(7)
O_5	–4931(7)	13632(7)	1924(9)	20(7)	C_9	–2591(7)	12610(3)	1099(4)	21(9)
N_1	3368(5)	9272(9)	509(7)	20(9)	C_{10}	–4344(3)	13374(5)	1023(5)	22(4)
N_2	–296(1)	11481(7)	1597(2)	20(1)	C_{11}	–5439(2)	13849(6)	1439(0)	23(8)
N_3	–1962(9)	12287(1)	1554(9)	19(8)	C_{12}	–7179(3)	14596(5)	1336(9)	26(9)
C_1	4622(2)	8796(1)	909(4)	212(2)	C_{13}	–7736(2)	14795(0)	855(3)	28(9)
C_2	6299(3)	8106(6)	758(3)	29(5)	C_{14}	–6703(0)	14302(1)	437(4)	32(6)
C_3	7580(9)	7639(0)	1121(1)	28(1)	C_{15}	–5024(2)	13627(5)	538(5)	27(4)
C_4	7152(7)	7900(8)	1626(6)	27(5)					

The bond lengths and angles are within normal ranges[10], and are comparable with the corresponding structure[11], except for the N_2-N_3 (1.376(10) Å] shorter than that of 1.390(4) Å. The N_3-C_9 [1.299(11) Å] bond shows double-bond character, while N_2-C_8 [1.342(11) Å] bond has an intermediate character. Most bond lengths in the molecules are between the single and double bonds, which show high π-electron delocalized and a large conjugated system formed. The whole molecule is essentially planar, with the dihedral angle between two aromatic rings being 1.8(5)°, which is also mainly due to the conjugation.

TABLE-2
SELECTED BOND LENGTHS (Å)

Bond	Dist.	Bond	Dist.	Bond	Dist.
O_1-N_1	1.258(11)	O_2-N_1	1.223(10)	O_3-C_6	1.383(11)
O_4-C_8	1.211(10)	O_5-C_{11}	1.332(10)	N_1-C_1	1.439(11)
N_2-N_3	1.376(10)	N_3-C_9	1.299(11)	C_1-C_6	1.393(12)
C_2-C_3	1.383(14)	C_3-C_4	1.371(14)	C_4-C_5	1.356(13)
C_7-C_8	1.537(12)	C_9-C_{10}	1.429(13)	C_{10}-C_{15}	1.375(13)
C_{11}-C_{12}	1.426(13)	C_{12}-C_{13}	1.331(15)	C_{13}-C_{14}	1.381(16)
O_3-C_7	1.423(10)	N_2-C_8	1.342(11)	C_1-C_2	1.398(13)
C_5-C_6	1.367(12)	C_{10}-C_{11}	1.399(12)	C_{14}-C_{15}	1.364(15)

TABLE-3
SELECTED BOND ANGLES (°)

Angle	(°)	Angle	(°)	Angle	(°)
C_6-O_3-C_7	118.4(7)	O_2-N_1-O_1	120.7(9)	O_2-N_1-C_1	121.3(9)
O_1-N_1-C_1	118.0(9)	C_8-N_2-N_3	118.8(8)	C_9-N_3-N_2	118.4(8)
C_6-C_1-C_2	119.6(9)	C_6-C_1-N_1	123.1(8)	C_2-C_1-N_1	117.2(9)
C_5-C_6-O_3	124.8(8)	O_3-C_6-C_1	116.0(8)	O_3-C_7-C_8	106.0(7)
O_4-C_8-N_9	125.8(9)	O_4-C_8-C_7	119.9(8)	N_3-C_8-C_7	114.4(7)
C_3-N_9-C_{10}	121.7(9)	O_5-C_{11}-C_{12}	118.6(9)		

TABLE-4
THE HYDROGEN BOND LENGTHS (Å) AND BOND ANGLE (°)
FOR THE TITLE COMPOUND

Donor-H . . . Acceptor	D-H	H . . . A	D . . . A	D-H . . . A
N_2-H_{2A} . . . O_2	0.8602	2.5089	3.338(11)	162.03
N_2-H_{2A} . . . O_3	0.8602	2.0746	2.490(10)	108.89
O_5-H_{5B} . . . N_3	0.8205	1.8754	2.599(10)	146.48
C_5-H_{5A} . . . O_5	0.9289	2.4867	3.405(12)	169.91
C_7-H_{7B} . . . O_4	0.9699	2.4321	3.311(12)	150.44

The O_1 . . . N_1 separation of 2.599(10) Å, which is much shorter than that of the related compound [2.669(8) Å][11], suggests a possible intramolecular hydrogen bond, *via* O_5-H_{5B} . . . N_3, forming a six-membered ring. There is also another intramolecular interation, *viz.*, N_3-H_{2A} . . . O_3, forming a five-membered $N_2/C_8/C_7/O_3/H_{2A}$ ring. The molecules are interconnected into chains along the axis by C_5-H_{5A} . . . O_5 and C_7-H_{7B} . . . O_4 intermolecular interactions. The packing is further stabilized by van der Waals forces. Packing diagram of the title compound in a unit cell is shown in Fig. 2.

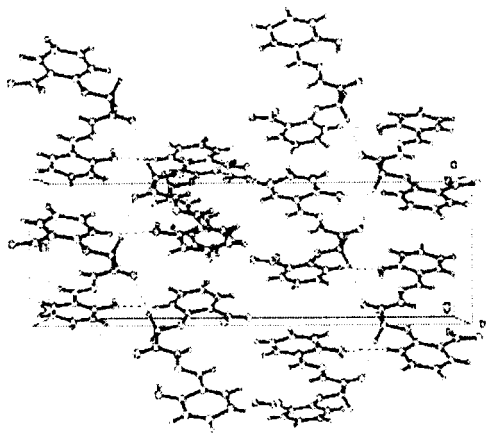


Fig. 2. A view of the crystal packing for the title compound

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