Crystal Structure of *o*-Hydroxyacetophenone Anthranilhydrazone

Kalagouda B. GUDASI,*† Siddappa A. PATIL,* Ramesh S. VADAVI,* Rashmi V. SHENOY,*
Manjula S. PATIL,* and Munirathinam NETHAJI**

*P. G. Department of Chemistry, Karnatak University, Dharwad, 580 003, India

**Department of Inorganic and Physical Chemistry, Indian Institute of Science Bangalore, 560 012, India

The title compound $C_{15}H_{15}N_3O_2$ was synthesized and the structure was investigated by X-ray crystallography. It crystallizes in the orthorhombic space group $Pna2_1$ with cell parameters $a = 8.943(7)\text{\AA}$, $b = 5.674(5)\text{\AA}$, $c = 26.380(2)\text{\AA}$ and $Z = 4$. The final residual factor is 0.0388. The intermolecular hydrogen bonds of the type $N-H\cdots O$ were observed in the structure.

(Received April 8, 2005; Accepted August 5, 2005; Published on web September 30, 2005)

The preparation of heterocyclic compounds containing carbonyl ($>C=O$) and azomethine ($>C=N-$) group with potential ligating ability has drawn a lot of attention in recent years because of their use as chelating agents, analytical reagents, metal indicators in complexometric titrations and colorimetric reagents, in addition to biochemical research.¹ Various studies have shown that the azomethine ($>C=N$) group having a lone pair of electrons in either a π or sp^2 hybridized orbital on trigonally hybridized nitrogen has considerable biological importance.² The presence of a carbonyl ($>C=O$) group in the Schiff bases gives an additional donor site and introduces a wider range of properties in them. The ability of Schiff bases to form colors with different metal ions under different conditions and also their ability to form solid complexes with metal ions under varying conditions, are the key points when one considers them for use in analytical work. Because of their flexidentate and ambiprotic properties, they draw the attention from a structural point of view also.

Encouraged by these reports, we undertook the study of *o*-hydroxyacetophenone anthranilhydrazone (*o*-HAAH), a Schiff base containing carbonyl, azomethine and hydroxyl groups as potentially coordinating sites. The structure of the compound is confirmed by the spectral and single crystal X-ray analysis. Dinda *et al.* and Simeonov *et al.* have studied similar type of anthranilhydrazones.^{3,4} Ghosh *et al.* have studied divanadium (IV, V) complex of *o*-HAAH by single crystal X-ray diffraction.⁵

The title compound was prepared according to the literature method,⁵ by stirring *o*-aminobenzoylhydrazide (7.60 g; 50.33 mmol) and *o*-hydroxyacetophenone (6.80 g; 50 mmol) in ethanol (25 ml) for 2 h. The resulting yellowish white compound was filtered, then washed with ethanol. The solid was recrystallized from ethanol to get a pure compound. A crystal suitable for X-ray analysis was grown by the slow evaporation method using ethanol as the solvent. Yield 80%, m.p. 170 – 171°C. Anal. Calcd. for $C_{15}H_{15}N_3O_2$: C, 66.91; H, 5.58; N, 15.61. Found: C, 66.73; H, 5.53; N, 15.67%. IR (cm^{-1}) selected bands were: 3477(br), 3365(m), 3213(m), 1625(s), 1610(vs), 1547(vs). 1H NMR (DMSO- d_6): 13.4 (s, 1H), 7.64 – 6.57 (m, 8H), 2.46 (s, 3H).

A single crystal of the title compound of dimensions $0.51 \times 0.17 \times 0.12$ mm was chosen for X-ray diffraction studies. Data were collected at 293 K on a "BRUKER SMART APEX CCD"

diffractometer with Mo K_α radiation ($0.71073\text{\AA}$) and scan mode in the range of $3.09 < \theta < 27.09^\circ$. The structure was solved by direct methods (SHELXS-97)⁶ and refined by full-matrix least squares method with anisotropic temperature factors for the non-H atoms. All the H atoms were placed at chemically acceptable positions and were refined with isotropic temperature factors. The experimental crystallographic details are given in Table 1. The atomic coordinates for non-H atoms are listed in Table 2, and the bond distances and angles are listed in Table 3. The chemical structure and ORTEP diagram of title compound are shown in Figs. 1 and 2.

The X-ray structure reveals that the molecule is planar. Plane I, comprising C9, C10, C11, C12, C13 and C14 atoms, makes a

Table 1 Crystal and experimental data

Formula	$C_{15}H_{15}N_3O_2$
Formula Weight	269.30
Temperature	293(2)K
Crystal size	$0.51 \times 0.17 \times 0.12\text{ mm}^3$
Crystal color	colorless
Crystal description	rectangular
Crystal system	orthorhombic
Space group	$Pna2_1$
Z	4
a	$8.943(7)\text{\AA}$
b	$5.674(5)\text{\AA}$
c	$26.380(2)\text{\AA}$
β	90.00
V	$1338.7(18)\text{\AA}^3$
Calculated density	1.336 Mg/m^3
Radiation	$0.71073\text{\AA}$ (Mo K_α)
Absorption correction	multi scan
$2\theta_{\text{max}}$	54.18°
R	0.0388[2461 reflections, $I > 2.0\sigma(I)$]
wR	0.0943
Goodness-of-fit	1.043
No. of reflections collected	9330
No. of independent reflections	2667
No. of parameters	241
Diffractometer	BRUKER SMART APEX CCD
Monochromator	graphite
Refinement	full-matrix least square on F^2

Table 2 Final atomic coordinates and equivalent thermal parameters

Atom	x	y	z	$U_{eq}(\text{\AA}^2)$
C1	0.56488(19)	0.3960(3)	-0.04595(7)	0.0445(4)
C2	0.6190(3)	0.3568(4)	-0.09520(8)	0.0569(5)
C3	0.7178(3)	0.5104(4)	-0.11791(8)	0.0598(5)
C4	0.7650(2)	0.7114(4)	-0.09276(8)	0.0542(5)
C5	0.71145(19)	0.7549(3)	-0.04474(7)	0.0448(4)
C6	0.61213(18)	0.6025(3)	-0.02038(7)	0.0388(4)
C7	0.55037(17)	0.6561(3)	0.03054(7)	0.0387(3)
C8	0.60511(16)	1.0314(3)	0.13419(6)	0.0398(4)
C9	0.54319(18)	1.0344(3)	0.18600(7)	0.0451(4)
C10	0.5854(3)	1.2105(4)	0.22026(8)	0.0629(6)
C11	0.5290(4)	1.2158(5)	0.26875(9)	0.0762(7)
C12	0.4306(3)	1.0463(6)	0.28472(10)	0.0798(8)
C13	0.3868(3)	0.8695(5)	0.25228(10)	0.0719(6)
C14	0.4417(2)	0.8614(4)	0.20301(8)	0.0520(5)
C15	0.7036(2)	1.2260(3)	0.11592(9)	0.0504(4)
N1	0.4701(2)	0.2354(3)	-0.02510(10)	0.0615(5)
N2	0.62216(17)	0.8210(3)	0.05902(6)	0.0417(3)
N3	0.56675(15)	0.8519(3)	0.10737(6)	0.0438(3)
O1	0.43606(13)	0.5590(2)	0.04713(5)	0.0491(3)
O2	0.39213(19)	0.6847(3)	0.17324(7)	0.0701(4)

$$[U_{eq} = (1/3)\sum_i \sum_j U_{ij}(a_i^* a_j^*)(a_i \cdot a_j)]$$

Table 3 Selected bond lengths (Å) and angles along with the torsion angles (°)

C1 N1	1.361(3)	C8 C9	1.475(3)
C1 C2	1.404(3)	C8 C15	1.492(3)
C1 C6	1.417(3)	C9 C10	1.399(3)
C2 C3	1.378(3)	C9 C14	1.410(3)
C3 C4	1.385(3)	C10 C11	1.376(4)
C4 C5	1.377(3)	C11 C12	1.370(5)
C5 C6	1.396(3)	C12 C13	1.376(4)
C6 C7	1.484(3)	C13 C14	1.390(3)
C7 O1	1.241(2)	C14 O2	1.349(3)
C7 N2	1.361(2)	N2 N3	1.380(2)
C8 N3	1.287(2)		
N1 C1 C2	118.87(19)	N3 C8 C15	124.42(18)
N1 C1 C6	123.19(19)	C9 C8 C15	120.82(16)
C2 C1 C6	117.94(17)	C10 C9 C14	117.7(2)
C3 C2 C1	121.54(19)	C10 C9 C8	120.37(18)
C2 C3 C4	120.5(2)	C14 C9 C8	121.91(17)
C5 C4 C3	118.8(2)	C11 C10 C9	121.2(3)
C4 C5 C6	122.24(17)	C12 C11 C10	120.4(3)
C5 C6 C1	118.89(17)	C11 C12 C13	120.3(2)
C5 C6 C7	121.75(16)	C12 C13 C14	120.3(3)
C1 C6 C7	119.32(16)	O2 C14 C13	116.9(2)
O1 C7 N2	119.94(16)	O2 C14 C9	122.95(19)
O1 C7 C6	122.32(15)	C13 C14 C9	120.1(2)
N2 C7 C6	117.73(14)	C7 N2 N3	115.37(14)
N3 C8 C9	114.76(15)	C8 N3 N2	120.89(15)
N1 C1 C6 C5	179.08(19)	C15 C8 N3 N2	3.28(27)
C5 C6 C7 O1	161.12(18)	C8 C9 C14 O2	1.23(31)
O1 C7 N2 N3	5.56(25)		

dihedral angle of $5.47(7)^\circ$ with plane II, comprising C1, C2, C3, C4, C5 and C6. The C–C bond distances in both phenyl rings are in the normal range of 1.37 to 1.41 Å, which is characteristic of delocalized phenyl rings. The C–C–C bond angles are around 120° , with the variation being less than 2° , which is characteristic of sp^2 -hybridized carbons. The torsion angles along C1–C6 [N1–C1–C6–C5 = $179.08(19)^\circ$] and C6–C7 [C5–C6–C7–O1 = $161.12(18)^\circ$] clearly indicates that the atoms N1 and O1 are in *trans* position with respect to C5 and N1 and O1 are *cis* to each other. Three other torsion angles across C7–N2 [O1–C7–N2–N3 = $5.56(25)^\circ$], N3–C8 [C15–C8–N3–N2 = $3.28(27)^\circ$] and C9–C14 [C8–C9–C14–O2 = $1.23(31)^\circ$] reveal that O2 and O1 occupy a meridional³ plane. The title compound shows two intramolecular [O2–H···N3 = $2.522(3)\text{\AA}$ and N1–H···O1 = $2.664(3)\text{\AA}$] hydrogen bond and one intermolecular [N2H···O1 = $2.905(3)\text{\AA}$] hydrogen bond. The molecular

Fig. 1 Chemical structure of title compound

Fig. 2 ORTEP diagram of the title compound with atom labeling

packing diagram shows two layers of molecules, which are independently arranged in the unit cell. Molecules forming each layer are connected through the intermolecular hydrogen bonding formed between N2H and O1. In each layer the molecules are alternatively parallel. When both the layers are taken together, the first molecule of one layer makes an angle about 102° to the second molecule of the adjacent layer. This arrangement continues and forms a tree-like structure.

Supplementary Material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 259674 for $C_{15}H_{15}N_3O_2$.

Acknowledgements

The authors thank the CCD-X-Ray facility under DST IRPHA program, Department of Inorganic and Physical Chemistry and Sophisticated Instrumentation Facility, Indian Institute of Science, Bangalore, India, for the X-ray data collection and ^1H NMR spectra. Thanks are also due to University Sophisticated Instrumentation Center, Karnatak University Dharwad, for carrying out elemental analysis. One of the authors (SAP) is grateful to Karnatak University for the award of a University Research fellowship.

References

1. K. Dey, *J. Sci. Ind. Res.*, **1974**, 33, 76.
2. S. Patai, "The chemistry of carbon-nitrogen double bond," **1970**, Interscience publishers Inc., New York.
3. R. Dinda, P. Sengupta, S. Ghosh, H. M. Figge, and W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, **2002**, 4434.
4. M. F. Simeonov, F. Fulop, R. Sillanpaa, and K. Pihlaja, *J. Org. Chem.*, **1997**, 62, 5089.
5. R. Dind, P. Sengupta, S. Ghosh, and T. C. W. Mak, *Inorg. Chem.*, **2002**, 41, 1684.
6. G. M. Sheldrick, SHELXS97, *Program for the Solution of Crystal Structures*, **1997**, University of Gottingen.