ANALYSIS OF N-H...O AND O-H...O HYDROGEN BONDING IN 4-(2-HYDROXY-PHENYLAMINO)-PENT-3-EN-2-ONE

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Abstract: The paper reports synthesis and crystal structure of 4-(2-hydroxy-phenylamino)-pent-3-en-2-one and the analysis of hydrogen bonding present in it. The crystal exists in orthorhombic symmetry with unit cell parameters a = 8.839(3), b = 10.517(2), c = 11.223(3) Å, Z=4 and space group is $P2_12_12_1$. The final reliability index is 0.0425 for 1079 observed reflections. The molecules are linked up by a combination of O-H...O intermolecular and N-H...O intramolecular interaction. The intramolecular N-H...O interaction is responsible for making carbonyl and amino group as a virtual six-membered ring whereas the intermolecular O-H...O interaction depicts a parallel two-dimensional array.
Keywords: Crystal Structure, torsion angles, intra and inter- hydrogen interactions

Introduction

N-Phenyl especially N-Benzyl amino acids find applications in peptide synthesis and are valuable building blocks for the synthesis of chiral compounds(1). The development of 4-(3′,5′-Dibromo-4′-hydroxyphenyl)amino-6,7-dimethoxy quinazoline has provided the basis for new treatment as well as prevention programs for allergic asthma(2). Owing to the medicinal properties of hydroxy-phenyl amino derivatives, the title compound has been investigated for its three-dimensional structure elucidation as a part of our on-going research work on the analysis of hydrogen bonded interactions in alkaloids(3-11).

Experimental

The synthesis of 4-(2-hydroxy-phenylamino)-pent-3-en-2-one has been carried out by using a solution of 2-amino phenol (1.09 gm, 0.01 mole) and acetyl acetone (1.00 gm, 0.01 mole) in methanol (20 ml) which was stirred for 12 hours in presence of few drops of pyridine at room temperature. The reaction mixture was allowed to stand at room temperature for 24 hours. The content was poured into the ice-cold water. The solid separated was filtered and washed with water and recrystallized from methanol. For $C_{11}H_{13}NO_2$, the calculated C, 69.09; H, 6.85; N, 7.32; O, 16.73 %, and obtained: C, 69.07; H, 6.87; N, 7.30; O, 16.75 %;Yield = 64%. IR KBr (cm^{-1}): 1685 (-$COCH_3$ str.), 3250 (-N-H str.), 3300 (-OH str.), 1375 (-CH str.), 1630 (-C=C str.). ^1H NMR (300 MHz, $CDCl_3$ + DMSO – d_6) δ ppm: 1.5 (s, 3H, -C-CH_3), 2.4 (s, 3H, -$COCH_3$), 7.4 (s, 1H, -C=CH), 8.2 (s, 1H, -NH), 7.3-7.6(m, 4H, Ar-H). Methanol was used as a solvent system to grow X-ray diffraction quality single crystals of 4-(2-hydroxy-phenylamino)-pent-3-en-2-one. The seed crystals were harvested from supersaturated solution through controlled evaporation. The chemical structure is shown in Figure-1.

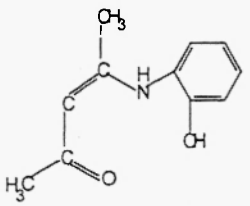

Figure-1: Chemical diagram of 4-(2-hydroxy-phenylamino)-pent-3-en-2-one

The three-dimensional intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. The reflection data were collected at 293K and ω/2θ scan mode was employed for data collection by using MoKα radiation (λ=0.71073Å). The structure has been elucidated by direct methods using SHELXS97(12). All non-hydrogen atoms of the molecule were located from the E-map. Isotropic refinement of the structure by least squares methods using SHELXL97(13) was followed by anisotropic refinement of all the non-hydrogen atoms. All the hydrogen atoms were fixed stereochemically. Atomic scattering factors were taken from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). Geometrical and other structural calculations were performed by using PARST(14) program.

Results and Discussions

The crystal data of the title compound are given in Table-1. The atomic coordinates of non-hydrogen atoms are listed in Table-2. The bond lengths and the bond angles are presented in Table-3. An ORTEP drawing of the compound with atom numbering scheme is shown in Figure-2(15).

Table-1: Crystal data and experimental data.

Formula	$C_{11}H_{13}NO_2$
Relative formula weight	192.23
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions	a = 8.839(3) Å
	b = 10.517(2)Å
	c = 11.223(3)Å
Z	4
Volume	1043.4(5)Å^3
Temperature	293(2) K
Density	1.224 Mg/m^3
Absorption coefficient (μ)	0.084 mm^{-1}
θ range	2.65 to 24.95°
Radiation (Mo Kα)	λ=0.71073 Å
Crystal Size	0.3 x 0.2 x 0.3 mm
F (000)	412
Total no. of reflections	1095
No. of independent reflections	1078
No. of observed reflections	942
No. of parameters	128
R- factor [Fo>4σ (Fo)]	0.0425
Weighted R	0.1211
Refinement method	Full- matrix least- squares on F^2
Goodness-of-fit on F^2	1.043
$(\Delta/\sigma)_{max}$	0.005
$(\Delta\rho)_{max}$	0.204 e. Å^{-3}
$(\Delta\rho)_{min}$	–0.179 e. Å^{-3}
Measurement (data collection):	ENRAF-NONIUS Detector Program
Program system:	ENRAF-NONIUS Program
Structure determination:	SHELXS97
Refinement:	SHELXL97
Structure drawing:	ORTEP III

Table-2: Atomic coordinates (x 10^4) and equivalent isotropic thermal parameters ($Å^2$ x 10^3) for non-hydrogen atoms

Atom	X	Y	Z	U_{eq}^*
O1	4531(2)	6847(2)	8517(2)	55(1)
O2	0807(2)	7068(2)	9604(2)	54(1)
N1	1977(3)	5782(2)	7819(2)	40(1)
C1	-0309(4)	4410(3)	7765(3)	57(1)
C2	-1712(4)	4127(3)	8227(4)	70(1)
C3	-2280(4)	4813(3)	9156(3)	65(1)
C4	-1468(3)	5800(3)	9641(3)	55(1)
C5	-0072(3)	6120(2)	9177(2)	41(1)
C6	0517(3)	5424(3)	8216(2)	41(1)
C7	2593(3)	5780(3)	6732(2)	42(1)
C8	4032(3)	6224(3)	6552(2)	46(1)
C9	4953(4)	6765(3)	7444(3)	44(1)
C10	6472(4)	7294(4)	7122(3)	68(1)
C11	1679(4)	5332(4)	5685(3)	66(1)

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

Table -3: Bond lengths (Å) and bond angles (°) for non-hydrogen atoms

Bond Lenghts (Å)

O1-C9	1.263(3)	C3-C4	1.375(5)
O2-C5	1.352(3)	C4-C5	1.381(4)
N1-C7	1.336(3)	C5-C6	1.403(4)
N1-C6	1.416(4)	C7-C8	1.370(4)
C1-C2	1.377(5)	C7-C11	1.502(4)
C1-C6	1.389(4)	C8-C9	1.410(4)
C2-C3	1.363(5)	C9-C10	1.498(5)

Bond Angles (°)

C7-N1-C6	131.2(2)	C1-C6-N1	124.7(3)
C2-C1-C6	120.1(3)	C5-C6-N1	116.2(2)
C3-C2-C1	120.4(3)	N1-C7-C8	120.9(2)
C2-C3-C4	120.7(3)	N1-C7-C11	119.7(3)
C3-C4-C5	120.1(3)	C8-C7-C11	119.4(3)
O2-C5-C4	124.0(3)	C7-C8-C9	124.6(3)
O2-C5-C6	116.4(2)	O1-C9-C8	122.3(3)
C4-C5-C6	119.6(3)	O1-C9-C10	118.0(3)
C1-C6-C5	119.1(3)	C8-C9-C10	119.7(3)

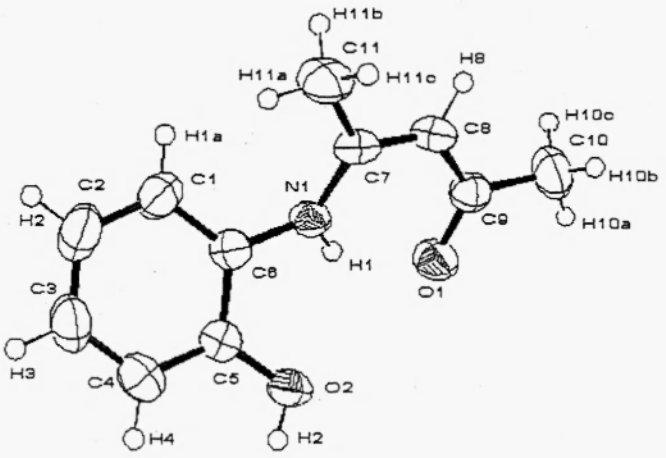

Figure-2: ORTEP view of 4-(2-hydroxy-phenylamino)-pent-3-en-2-one drawn at 50% probability level with atomic numbering scheme.

The bond distances and angles in the phenyl ring have normal values. The bond distances O1-C9 and N1-C7 are shorter than the normal expected values and variation of this kind in the values of bond distances has been observed in case of some analogous structures(3,16-17). The small value of N1-C7 [1.336(3)Å] in comparison to N1-C6 [1.416(4)Å] results into significant variation in C7-N1-C6 bond angle [131.2(2)°]. The difference in C-N bond distances could be due to the presence of carbonyl group located at C9 position. Shortening of C7-N1 bond length and a large value of the C-N-C bond angle leads to the existence of N1-H1...O1 intramolecular hydrogen-bond(18).

The crystal structure is stabilized by an intramolecular N1(amino)-H1...O1(one) and intermolecular O2-H2...O1 hydrogen bond which falls in the range of "intermediate hydrogen bonds" as proposed by Desiraju and Steiner(18). Both kinds of interactions are depicted in the unit cell-packing diagram [Figure-3] in which the molecules are held together through a hydrogen-bonded network.

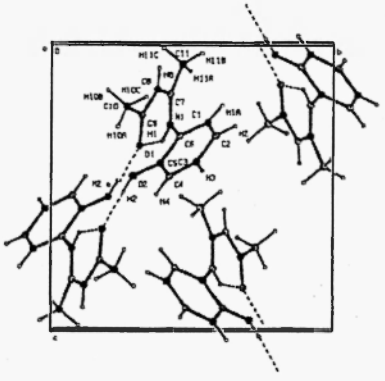

Figure-3: Packing diagram 4-(2-hydroxy-phenylamino)-pent-3-en-2-one showing the hydrogen-bonding network.

The intramolecular bond results into the formation of a virtual six-membered ring; thus making the present molecule look like a two-ring structure. The molecules exhibit typical orthorhombic symmetry. In both the interactions, O1 acts as a bifurcated acceptor atom whereas O2 and N1 acts as donors. The details of hydrogen bonding are presented in Table 4.Using compiled data for a large number of O-H...O and N-H...O contacts, Desiraju and Steiner(18) find significant statistical directionality and conclude that these are legitimately viewed as "intermediate" hydrogen bonds, with a greater contribution to packing forces than simple van der Waals interactions.

Table-4: Geometry of intra- and intermolecular hydrogen interactions.

X-H...A	H...A(Å)	X...A(Å)	X-H...A(°)
N1-H1...O1	1.934(1)	2.639(3)	138.4(1)
O2-H2...O1$^{(i)}$	1.831(2)	2.650(1)	176.5(2)

Equivalent symmetry position: (i) -x-1/2, -y+3/2, -z+2

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