X-ray Structure Analysis Online

Crystal Structure of *N*-*n*-Propylalcohol-2-oxo-5-nitro-1-benzylidene-methylamine

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The title compound, $C_{10}H_{12}N_2O_4$, adopts the *keto*-amine tautomeric form and displays two intramolecular N–H···O hydrogen bonds. The *keto*-amine structure is favored by through-molecule conjugation between the hydroxyl O atom and the imine N atom. The title compound crystallizes in the monoclinic space group $P2_1/c$ with the following unit-cell parameters: a = 10.953(2)Å, b = 5.5272(6)Å, c = 18.754(4)Å, β = 108.306(16)° and V = 1077.9(3)Å^3. The crystal structure of this compound contains two molecules in an asymmetric unit, and each molecule exists as part of an O–H···O hydrogen-bonded centrosymmetric dimer.

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The extensive application of Schiff bases in industry and analytical determinations has attracted attention for decades. Schiff-base compounds display interesting photochromic and thermochromic features, and can be classified by them; these properties are caused by proton transfer from the hydroxy O atom to the imine N atom.[1] In general, Schiff bases display two possible tautomeric forms, the phenol-imine (N···H–O) and *keto*-amine (N–H···O) forms. It is claimed that phenol-imine tautomerism is dominant in salicylaldimine, while the *keto*-amine form is preferred in naphthaldimine Schiff bases, depending on the olvent polarities. However, in the solid state, it is spesicified that *keto*-amine tautomerism is pesent in naphthaldimine, while the phenol-imine form exists in salicylaldimine Schiff bases.[2] The title compound, *N*-*n*-propylalcohol-2-oxo-5-nitro-1-benzylidene-methylamine, is in the *keto*-amine tautomeric form (Fig. 1).

The compound *N*-*n*-propylalcohol-2-oxo-5-nitro-1-benzylidene-methylamine was prepared by refluxing a mixture of a solution containing 2-hydroxy-5-nitrobenzaldehyde (0.0574 g 0.34 mmol) in 20 ml of ethanol and a solution containing 3-amino-1-propanol (0.0423 g 0.34 mmol) in 20 ml of ethanol. The reaction mixture was stirred for 1 h under reflux. Crystals of *N*-*n*-propylalcohol-2-oxo-5-nitro-1-benzylidene-methylamine suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield %, 41; m.p., 445 - 446 K).

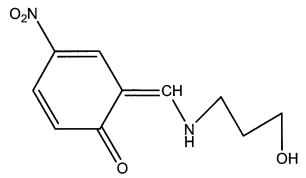

Fig. 1 Schematic diagram of the title compound.

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The structure was solved by direct methods using the program SHELXS-97; the refinement and all other calculations were carried out using SHELXL-97.[6] All H atoms were positioned geometrically and treated using a riding model, while fixing the aromatic C–H distances at 0.93 Å and the O–H distances at 0.82 Å, except for the H1 atom involved in the N–H···O hydrogen bond, which was found from a difference map of the electron density in the unit-cell, and was refined freely. The data-collection conditions and parameters of the refinement process are listed in Table 1. Selected inter-atomic parameters are given in Table 2.

Table 1 Crystal and experimental data

Formula: $C_{10}H_{12}N_2O_4$	
Formula weight: 224.22	
Crystal system: monoclinic	
Space group: $P2_1/c$	$Z = 4$
a = 10.953(2)Å	
b = 5.5272(6)Å	β = 108.306(16)°
c = 18.754(4)Å	
V = 1077.9(3)Å^3	
Density = 1.3817(4) g cm^{-1}	
T = 296(2)K	
Prism, yellow	
No. of reflections used = 15718	
$2\theta_{max}$ = 52.00° Mo K_α	
R = 0.0719	
$(\Delta/\sigma)_{max}$ = 0.0000	
$(\Delta\rho)_{max}$ = 0.127 e Å^{-3}	
$(\Delta\rho)_{min}$ = –0.153 e Å^{-3}	
Goodness-of-fit on F^2 = 1.084	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.072, $wR2$ = 0.111
R indices (all data)	$R1$ = 0.161, $wR2$ = 0.137
Measurement: STOE IPDS II	
Program system: STOE X-RED	
Structure determination: direct methods	
Refinement: full matrix	
CCDC number: CCDC 687467	

Table 2 Selected bond lengths (Å) and angles (°)

Bond distances			
C1-O1	1.266(4)	C4-N2	1.447(4)
C7-N1	1.288(4)	N2-O2	1.220(3)
C8-N1	1.468(4)	N2-O3	1.224(4)
C10-O4	1.406(4)		
Bond angles			
O1-C1-C2	122.9(3)	O4-C10-C9	109.1(3)
O1-C1-C6	121.6(3)	C7-N1-C8	125.9(3)
C5-C4-N2	119.7(3)	O2-N2-O3	122.4(3)
C3-C4-N2	119.6(3)	O2-N2-C4	119.3(4)
N1-C7-C6	125.5(3)	O3-N2-C4	118.4(3)
N1-C8-C9	111.6(3)		

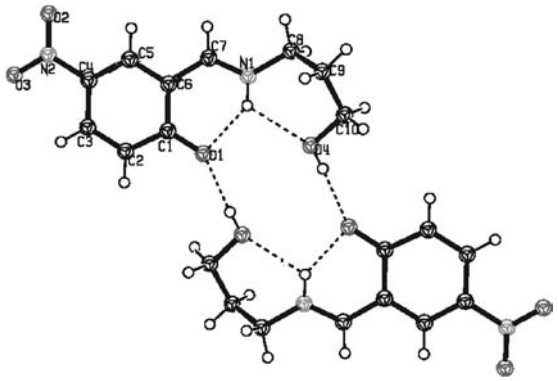

Fig. 2 Molecular structure of (I), showing the atom-numbering scheme. The dashed lines indicate hydrogen bonds.

The molecular structure is shown in Fig. 2, with the atom-numbering scheme. The compound exists in the *keto*-amine tautomeric form with strong intra-molecular N1–H1···O1 and N1–H1···O4 bifurcated hydrogen bonds [N···O = 2.649(4) and 2.767(4)Å, respectively]. These types of strong intra-molecular hydrogen bonds are a common feature of *o*-hydroxysalicylidene systems. The N1–H1···O1 hydrogen-bonded ring is planar with an adjacent ring, with an N1–C7–C6–C1 torsion angle of 0.6(5)°. The C1=O1 bond length is 1.266(4)Å and consistent with another C=O double bond [1.274 Å] in 1-[*N*-(2-pyridyl)amino-methylidene]-2(1*H*)-naphthalenone.[3] The *keto*-amine form of the title compound is supported by the bond length of the N1–C7 bond [1.288(4)Å], this value is in agreement with another C–N bond length [1.288(4)Å] in the literature.[4] The N2–O2 and N2–O3 bond lengths are as expected for a nitro group (Table 3). Similar to this compound, a very related structure was reported in the literature.[5] For both molecules, the bond lengths and angles are very close; but in the other structure,[5] due to the fact that one CH2 chain length is missing, the inter-molecular hydrogen bond is inhibited. The asymmetric unit of the title compound contains two crystalographically independent molecules, and each molecules exist as an O4–H4···O1 hydrogen-bonded centrosymmetric dimer with an $R_2^6(8)$ ring. There are also two inter-molecular C–H···O hydrogen bonds, the details of which are given in Table 3. The crystal packing is stabilized by inter-molecular C–H···O hydrogen bonds.

Table 3 Hydrogen-bond geometry (Å)

D-H···A	D-H	H···A	D···A	D-H···A
N1-H1…O1	0.88(4)	1.92(4)	2.649(4)	139(3)
N1-H1…O4	0.88(4)	2.23(4)	2.767(4)	120(3)
O4-H4…O1 ^{i}	0.82	1.90	2.705(3)	165
C7-H7…O2 ^{ii}	0.93	2.40	3.296(5)	163
C10-H10A…O3 ^{iii}	0.97	2.57	3.521(5)	167

Symmetry code: (i) –*x*, –*y*, 1–*z*, (ii) 1–*x*, 2–*y*, 1–*z*, (iii) –1+*x*, 1/2–*y*, –1/2+*z*

References

1. E. Hadjoudis, M. Vitterakis, and I. M. Maviridis, *Tetrahedron*, **1987**, *43*, 1345.
2. B. Kaitner and G. Pavlovic, *Acta Cryst.*, **1996**, *C52*, 2573.
3. T. Hökelek, Z. Kılıç, M. Işıklan, and M. Toy, *J. Mol. Struct.*, **2000**, *523*, 61.
4. B. Koşar, O. Büyükgüngör, Ç. Albayrak, and M. Odabaşoğlu, *Acta Cryst.*, **2004**, *C60*, o458.
5. Yu. M. Chumakov, V. I. Tsapkov, Z. A. Starikova, I. I. Vorontsov, A. A. Korlyukov, B. Ya. Antosyak, and M. Perrin, *J. Mol. Struct.*, **2003**, *647*, 269.
6. G. M. Sheldrick, SHELXS97 and SHELXL97, **1997**, University of Göttingen, Germany.