

Structure of N-Hydroxy-4-Phenylbut-3-En-2-Imine

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Abstract— The title compound, N-Hydroxy-4-phenylbut-3-en-2-imine [C₁₀H₁₁NO], was synthesized by reacting benzylidene acetone with hydroxylamine hydrochloride in the presence of base. The structure of the compound was characterized by single crystal XRD data. It crystallizes in the orthorhombic space group Pbc21 with unit-cell parameters: $a = 5.591(6)\text{Å}$, $b = 22.019(3)\text{Å}$, $c = 14.742(2)\text{Å}$, $\beta = 90.0^\circ$, $Z = 4$. The crystal structure has been elucidated by direct methods and refined to a final R-value of 0.056 for 1535 observed reflections. In the crystal molecules are linked by two O-H...N intermolecular H-bonds forming dimer. Molecules in the unit cell are packed together to form well defined layers.

Keywords— Oximes; Intermolecular hydrogen bond; Crystal structure; Direct methods.

I. INTRODUCTION

Oximes are highly crystalline compounds that find applications in the protection, purification and characterization of carbonyl compounds.¹ The synthetic applications of oximes include their conversion into amides *via* Beckmann rearrangement, nitriles, nitro compounds, nitrones, amines, and azaheterocycles.²⁻⁷ In coordination chemistry, oximes act as a versatile ligand.⁸ Moreover, oximes are also used as therapeutic agents in organophosphorus poisoning.⁹ Oximes are important intermediates for the preparation of primary amines by reduction. The primary amine generated can be used for the preparation of many heterocycles like quinoline, azetidinone, 1,2,4-triazole and 1,3,4-thiadiazole, benzothiazepines and thiazolidinone.¹⁰ These heterocycles show various biological activities such as anti-cancer¹¹, anti-inflammatory¹², anti-allergics¹³, anti-microbial¹⁴ and anthelmintic.¹⁵ In view of the importance of oximes and the fact that the crystal structure of the reduced form of the title compound *viz.* (E)-4-phenylbutan-2-one oxime¹⁰ is known, we got interested in synthesis and the crystal structure determination of N-Hydroxy-4-phenylbut-3-en-2-imine.

II. EXPERIMENTAL

Synthesis

The synthetic route for the title compound (Figure 1) is presented in Scheme 1. A mixture of 4 benzylidene acetone (1.46 g, 0.01 mole) and hydroxylamine hydrochloride (0.69 g, 0.01 mole) in 50 mL ethanolic sodium hydroxide was refluxed for 3 h, then cooled to room temperature. The precipitate that appeared was filtered off and recrystallized from DMF. The single crystals were grown from DMSO by slow evaporation method and yield of the compound was 56 %. (m.p. 390K).

X-Ray Structure determination

X-ray intensity data of 4425 reflections (of which 2378 unique) were collected at 293(2) K on X'calibur CCD area-detector diffractometer equipped with graphite monochromated MoK α radiation ($\lambda = 0.71073\text{Å}$). The crystal used for data collection was of dimensions 0.30 X 0.20 X 0.10

mm. The intensities were measured by ω scan mode for θ ranges 3.95 to 26.98°. 1535 reflections were treated as observed ($I > 2\sigma(I)$). Data were corrected for Lorentz-polarization and absorption factors. The structure was solved by direct methods using SHELXS97.¹⁶

All non-hydrogen atoms of the molecule were located in the best E-map. All the hydrogen atoms (except O1A, O1B, C10A and C10B H atoms) were geometrically fixed and allowed to ride on the corresponding non-H atoms with C-H = 0.93-0.98 Å and $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$, except for the methyl groups where $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$. The final refinement cycles converged to an $R = 0.056$ and $wR (F^2) = 0.144$ for the observed 1535 reflections. Residual electron densities ranged from -0.177 to 0.168 eÅ⁻³. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1.

III. RESULTS AND DISCUSSION

An ORTEP¹⁷ view of the title compound with atomic labelling is shown in Figure 2. The geometry of the molecule was calculated using the PLATON¹⁸ and PARST¹⁹ software. Selected bond lengths, bond angles and torsion angles are given in Table 2. Geometry of inter-molecular hydrogen bonds is given in Table 3.

The structure consists of two molecules in the asymmetric unit. Bond distances and bond angles are comparable with the reported structure (E)-4-phenylbutan-2-one oxime¹⁰ except the bond distances C1A=C7A and C1B=C7B. The other geometrical parameters are comparable with some analogous structures.²⁰ The double bonds N1A=C9A and N1B=C9B are confirmed by their respective distances of 1.268(6) Å and 1.276(6) Å. The C7A=C8A (1.308 Å) and C7B=C8B (1.308 Å) bond distances are smaller than the standard value of 1.34 Å. The variation in bond angles around the atom C9A and C9B is primarily due to the existence of intermolecular hydrogen bond O-H...N. These O-H...N (O1A-H1...N1B and O1B-H2...N1A) intermolecular hydrogen bond are responsible for the formation of hydrogen bonded network thus, providing more stability to the molecules in the unit cell. The best

packing view has been obtained down a-axis i.e. bc plane (Figure 3). In the crystal packing, pairs of intermolecular hydrogen bonds (Table 3) link the molecules into dimmers (Figure 4) forming $R^2_2(6)$ ring motifs which are stacked along the *a* axis, forming a well defined layered structure (see Figure 3).

IV. REFERENCES

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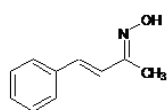
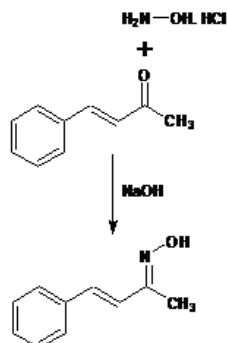


Figure 1. Structure of title compound



Scheme 1

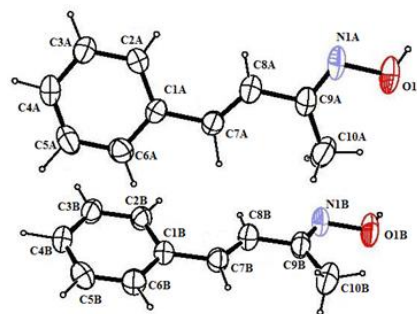


Figure 2. ORTEP view of the molecule with displacement ellipsoids drawn at the 40 % probability level. H-atoms are shown as small sphere of arbitrary radii.

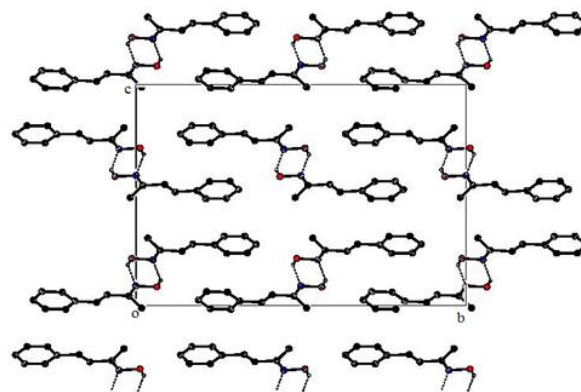


Figure 3. Packing diagram viewed down the a-axis

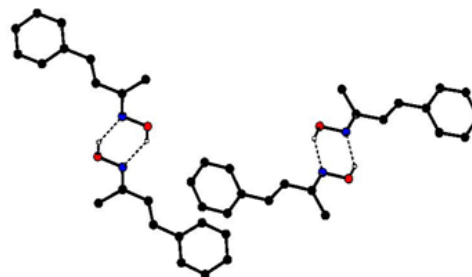


Figure 4. A plot of two molecules showing the formation of dimer by intermolecular N-H...N hydrogen bond (dashed lines)