# STRUCTURE OF N-HYDROXY-4-PHENYLBUT-3-EN-2-IMINE

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The title compound, N-hydroxy-4-phenylbut-3-en-2-imine [$C_{10}H_{11}NO$], was synthesized by reacting benzylideneacetone 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 $Pbc2_1$ with unit-cell parameters: $a$= 5.591(6)Å, $b$=22.019(3)Å, $c$ = 14.742(2) Å, β = 90.0º, $Z$ = 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 N-H...N intermolecular H-bonds forming dimer. Molecules in the unit cell are packed together to form well defined layers.

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## Introduction

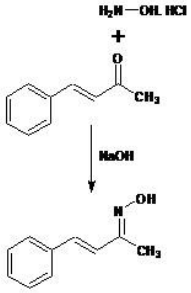
Oximes are highly crystalline compounds that find applications in the protection, purification and characterization of carbonyl compounds.[1] The synthetic applications of oximes include their conversion into amides *via* Beckmann rearrangement, nitriles, nitro compounds, nitrones, amines, and azaheterocycles.[2-7] In coordination chemistry, oximes are 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, benzothiazipines and thiazolidinone.[10] These heterocycles show various biological activities such as anti-cancer [11], anti-inflammatory[12], anti-allergics[13], anti-microbial[14] 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 oxime[10] is known, we got interested in synthesis and the crystal structure determination of N-hydroxy-4-phenylbut-3-en-2-imine.

## Experimental

### Synthesis

The synthetic route for the title compound is presented in Scheme 1. A mixture of a 4 benzylideneacetone (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 recystallized from DMF. The single crystals were grown from DMSO by slow evaporation method and yield of the compound was 56 %. (m.p. 390 K).




**Scheme 1.** Synthesis of the N-hydroxy-4-phenylbut-3-en-2-imine

### 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 Mo$K\alpha$ radiation (λ=0.71073 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 26.98º. 1535 reflections were treated as observed ($I$>2σ($I$)). 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 $U_{iso}$ = 1.2 $U_{eq}$(C), except for the methyl groups where $U_{iso}$(H) = 1.5$U_{eq}$(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.

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**Table 1.** Crystal data and other experimental details

| | |
|---|---|
| CCDC Number | 983555 |
| Crystal description | Block |
| Crystal size | 0.30 x 0.20 x 0.10 mm |
| Empirical formula | $C_{10}H_{11}NO$ |
| Formula weight | 322.40 |
| Radiation, Wavelength | Mo *K*α, 0.71073 Å |
| Unit cell dimensions | *a* = 5.591(6),<br>*b* = 22.019(3),<br>*c* = 14.742(2) Å,<br>α= 90.0º,<br>β = 90.0º,<br>γ= 90.0º |
| Crystal system, Space group | Orthorhombic,$Pbc2_1$ |
| Unit cell volume | 1814.9(4) $Å^3$ |
| No. of molecules per unit cell, *Z* | 4 |
| Absorption coefficient | 0.077 $mm^{-1}$ |
| *F*(000) | 688 |
| θ range for entire data collection | $3.95 < \theta < 26.98$ |
| Reflections collected / unique | 4425/ 2378 |
| Reflections observed I > 2σ(I)) | 1535 |
| Range of indices | *h*= -6 to 6,<br>*k*= -27 to 24,<br>*l*= -10 to 18 |
| No. of parameters refined | 276 |
| Final R-factor | 0.0557 |
| *wR*(*F2*) | 0.1442 |
| $R_{int}$ | 0.0402 |
| Rσ | 0.0452 |
| Goodness-of-fit | 1.078 |
| (Δ/σ)max | 0.001 |
| Final residual electron density | $-0.177 < \Delta\rho > 0.168$ $eÅ^{-3}$- |

## Results and Discussion

An ORTEP[17] view of the title compound with atomic labelling is shown in Figure 1. The geometry of the molecule was calculated using the PLATON[18] and PARST[19] 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.

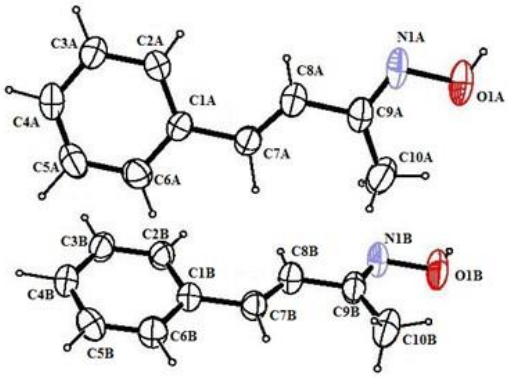


**Figure 1.** ORTEP view of the molecule with displacement ellipsoids drawn at the 40 % probability level. H atoms are shown as small sphere of arbitrary radii

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 oxime[10] 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 1.34Å.

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 2).

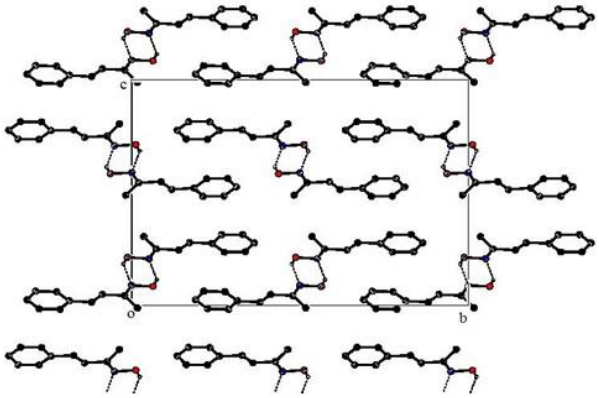


**Figure 2.** Packing diagram viewed down the a-axis

In the crystal packing, pairs of intermolecular hydrogen bonds (Table 3) link the molecules into dimmers (Figure 3) forming $R^2_2(6)$ ring motifs which are stacked along the *a* axis, forming a well defined layered structure (see Figure 2).

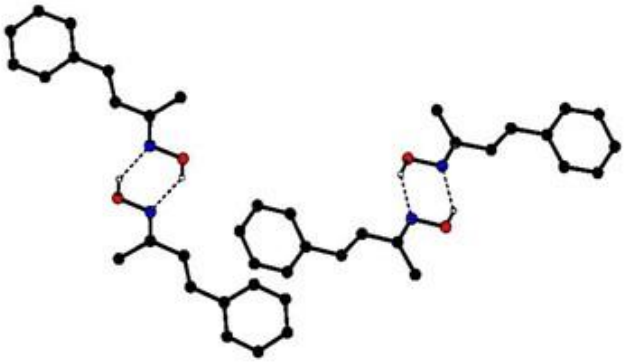

**Figure 3.** A plot of two molecules showing the formation of dimer by intermolecular N-H….N hydrogen bond (dashed lines).

**Table 2.** Selected bond lengths (Å) and bond angles (º) for non hydrogen atoms (e.s.d.'s are given in parentheses)

| **Bond distances, Å** | | **Bond angles, º** | | **Torsion angles, º** | |
|---|---|---|---|---|---|
| N1A-O1A | 1.410(5) | C8A-C9A-N1A | 114.2(5) | C2B-C1B-C7B-C8B | 179.4(5) |
| N1B-O1B | 1.413(5) | C8B-C9B-N1B | 113.4(5) | C2A-C1A-C7A-C8A | 177.6(5) |
| C7A-C8A | 1.308(7) | C9A-N1A-O1A | 113.6(4) | | |
| C7B-C8B | 1.308(7) | C9B-N1B-O1B | 113.1(4) | | |
| C9A-N1A | 1.268(6) | C2A-C1A-C7A | 119.6(4) | | |
| C9B-N1B | 1.276(6) | C2B-C1B-C7B | 119.1(4) | | |
| | | C8A-C9A-C10A | 121.8(5) | | |
| | | C8B-C9B-C10B | 122.2(5) | | |
| | | C10B-C9B-N1B | 124.3(5) | | |
| | | C10A-C9A-N1A | 124.0(5) | | |

**Table 3.** Geometry of intramolecular hydrogen bonds

| **D-H…A** | **D-H, Å** | **H…A, Å** | **D…A, Å** | **θ[DH…A,], º** |
|---|---|---|---|---|
| O(1A)-H(1)...N(1B)$^{i}$ | 0.820(4) | 2.061(5) | 2.787(7) | 147.3(3) |
| O(1B)-H(2)...N(1A)$^{ii}$ | 0.820(4) | 2.105(5) | 2.819(7) | 145.5(3) |

Symmetry codes:( i) -*x*+2, -*y*+1, +*z*+1/2 (ii) -*x*+2, -*y*+1, +*z*-1/2

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