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CRYSTAL STRUCTURE AND PROPERTIES OF (Z)-N′-((E)-2-(HYDROXYIMINO)-1-PHENYLETHYLIDENE) ISONICOTINOHYDRAZIDE

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Compound I contains in its molecule pyridyl, monoxime and hydrazone functions. A non-merohedral twin crystal of the compound with two reciprocal lattices differently oriented and giving rise to double diffraction spot sets with the 0.5:0.5 ratio of the twin components was studied. The hydrazone and oxime units are approximately planar. The dihedral angles between this plane and the planes of the pyridine and phenyl rings are 30.79(19)° and 18.43(13)°, respectively. Both the oxime and hydrazone units in I have an *E* configuration. The molecules of I are linked via C–H…O and O–H…N hydrogen bonds forming a 3D framework. The compound was also characterized by IR, ^{1}H NMR and elemental analyses.

Keywords: pyridine, oxime, hydrazone, twin crystal, isomerism.

INTRODUCTION

Oximes and hydrazones are interesting objects because of their wide application in medicine, industry and analytical chemistry. These compounds are used as analytical reagents for the detection and determination of some metal ions [1, 2]. Hydrazones have been utilized for the determination of carbonyl compounds [2, 3]. Hydrazones and hydrazone oximes exhibit biological activity. Hydrazone derivatives have been synthesized in order to investigate the relationship between structure and biological activity [4-6]. In this study, we present the crystal structure of the title compound, I, which is a product of the condensation reaction of isonicotinyl hydrazine and isonitrosoacetophenone.

RESULTS AND DISCUSSION

Spectroscopic characterization of 1. The structure of I was verified by means of IR (KBr), ^{1}H NMR (DMSO), UV-VIS spectral data and elemental analyses. In the IR spectrum of compound I characteristic bands are observed at 1690 cm^{-1}, 1607 cm^{-1}, 1536 cm^{-1}, 1509 cm^{-1} assigned to the ν(C=O), ν(C=N) hydrazone, ν(C=N)oxime and ν(N–H) vibrations, respectively. A strong band at 1007 cm^{-1} in the spectrum of I is mainly attributed to ν(N–O) vibration. The medium intensity band at 1040 cm^{-1} is ascribed to ν(N–N) vibration. In addition, the band 3136 cm^{-1} is asigned to overlapping oxime NOH and NH groups. In the ^{1}H NMR spectra of I the resonance of the NH protons appears as a singlet at 12.68 ppm. The characteristic oxime OH proton is observed at 13.16 ppm. The doublet around 8.82 ppm is assigned to the two protons of pyridine ring

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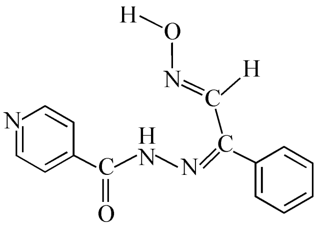

system (H10, H11). The other two protons of the pyridine ring appear at 7.80-7.46 ppm. A signal is also observed at 8.55 ppm for HC=N-group.

Crystallography. The molecular structure of I is shown in Fig. 1. Compound I comprises three functional groups: pyridine, monoxime and hydrazone. The crystal is monoclinic, space group $P2_1/c$ with $a = 8.5235(5)$ Å, $b = 7.7619(5)$ Å, $c = 20.7354(13)$ Å, $\beta = 109.089(5)°$, $V = 12.9639(15)$ Å^3, $Z = 4$ (Table 1). The hydrazone and oxime units are approximately co-planar. The dihedral angles between this plane and the planes of the pyridine and phenyl rings are 30.79(19) and 18.43(13)°, respectively. The bond lengths and angles of the oxime and hydrazone are given in Table 2. Both the oxime and hydrazone units in I have an *E* configuration (Dihedral angles O1–N3=C8–C7 = 176.1(2)° and N2–N1=C7–C1 = 178.3(2)°). The N1–N2 bond distance of 1.372(3) Å is appreciably shorter than a typical N–N single bond, such as that found in free 2,4-dinitrophenylhydrazone, 1.405(6) Å [7]; this suggests the existence of a delocalized double bond. The N3=C8 and N1=C7 distances of 1.276(3) Å and 1.291(3) Å, respectively, are typical of a double bond. The C=N and N–O distances of the free oximes are close to those commonly found in oxime derivatives [C=N = 1.292(13) Å and N–O = 1.396(3) Å] [8]. The molecules of I are linked *via* C–H…O and O–H…N hydrogen bonds (Table 3) forming a 3D framework. Atoms C13 at (x, y, z) and $(1-x, 1-y, -z)$ H-bond to atoms O1 at $(x, 1/2-y, -1/2+z)$ and $(2-x, 1/2+y, 1/2-z)$ producing two C(11) chains [9] running parallel to the $[00\bar{1}]$, [001] direction. Atoms generated by *c*-glide plane at $y = 1/4$ and screw axis at $z = 1/4$ at (x, y, z) and $(1-x, -y, -z)$ act as donors to atoms N4 (Fig. 2) generating centrosymmetric $R_2^2(24)$ rings centred at (1, 0, 0) and (1, 1/2, 1/2). These rings are linked to each other by H atoms of the C13 atoms. The $R_2^2(24)$ rings formed by hydrogen bonds are centred at $[1, 0, n]$ and $[1, 1/2, n+1/2]$ (*n* is zero or integer). Besides, C–H…π and π–π interactions are also observed in the crystal. Crystals of I were found to be twinned in approximate 0.5:0.5 ratio; the twinned cell can be obtained by the unit-cell transformation a_{twin}vector = $-a$vector, b_{twin}vector = $-b$vector, c_{twin}vector = $c$vector, indicating a two-fold twinning axis along [001] direction.

EXPERIMENTAL

Preparation of I. Isonicotinic acid hydrazide (0.67 g, 5 mmol) was dissolved in hot anhydrous ethanol (40 ml). To this solution was added dropwise isonitrosoacetephenone (0.75 g, 5 mmol) in anhydrous ethanol (30 ml) and few drops of glacial acetic acid. The reaction mixture was refluxed for 7 h. A white product formed was separated by filtration and washed

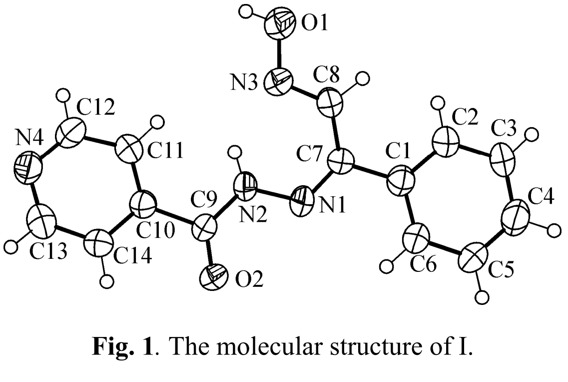

Fig. 1. The molecular structure of I.

TABLE 1. Crystallographic and Experimental Data for I

Formula	$C_{14}H_{12}N_4O_2$
M	268.28
Temperature (K)	296
λ, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, deg)	$a = 8.5235(5)$, $b = 7.7619(5)$, $c = 20.7354(13)$, $\beta = 109.089(5)$
V, Å^3	1296.39(14)
Z	4
D_{calc}, g/cm^3	1.375
$T_{\min}$, $T_{\max}$	0.9563, 0.9903
Crystal size, mm	0.77×0.42×0.10
μ, mm^{-1}	0.10
$\theta_{\max}$, deg	26.00
Index ranges	$h = -10 \rightarrow 10$, $k = -9 \rightarrow 9$, $l = -26 \rightarrow 26$
Measured reflections	12087
Independent reflections	1307
Observed reflections ($I > 2\sigma(I)$)	1028
GOOF	1.06
R ($I > 2\sigma(I)$)	0.039
wR ($I > 2\sigma(I)$)	0.093
CCDC deposition N	713706

TABLE 2. Selected Geometric Parameters for I (Å, deg)

O1–N3	1.370(3)	C7–N1–N2	117.3(2)	C7–N1–N2–C9	–176.2(2)
O2–C9	1.211(3)	C9–N2–N1	119.7(2)	N2–N1–C7–C8	3.1(4)
N1–C7	1.291(3)	C8–N3–O1	112.5(2)	N2–N1–C7–C1	178.3(2)
N1–N2	1.372(2)	N1–C7–C8	127.1(2)	N1–C7–C8–N3	–4.2(4)
N2–C9	1.356(3)	N1–C7–C1	115.1(2)	N1–N2–C9–O2	2.7(4)
N3–C8	1.275(3)	N3–C8–C7	123.9(3)	N1–N2–C9–C10	–177.9(2)
N4–C13	1.321(3)	O2–C9–N2	124.9(2)	C13–N4–C12–C11	–1.7(4)
N4–C12	1.325(3)	O2–C9–C10	121.3(3)	C10–C11–C12–N4	2.3(4)
C1–C7	1.488(3)	N2–C9–C10	113.7(2)	C12–N4–C13–C14	–1.3(4)
C7–C8	1.448(3)	N4–C13–C14	124.1(3)		
C9–C10	1.511(3)				

TABLE 3. Hydrogen Bonds Geometry of I (Å, deg)

D–H…A	D–H	H…A	D…A	
N2–H2A…N3	0.86	1.97	2.641(3)	134
O1–H1…N4 ^{i}	0.82	1.87	2.692(3)	176
C13–H13…O1 ^{ii}	0.93	2.56	3.473(3)	169

Symmetry codes: ^{i} $-x+2$, $-y$, $-z$, ^{ii} x, $-y-1/2$, $z-3/2$.

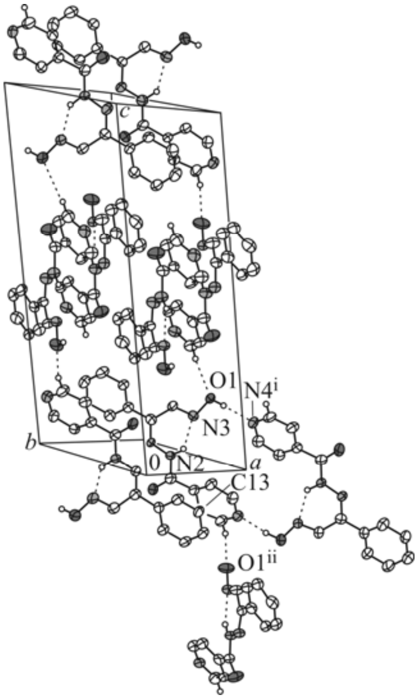

Fig. 2. Crystal packing in I.

with ethanol. The solid product was recrystallized from hot ethanol to give crystals of the title compound. Yield 40%. *Anal.* Calcd. for $C_{14}H_{12}N_4O_2$: C 62.68, H 4.51, N 20.88%. Found: C 62.63, H 4.58, N 20.81%.

Materials and measurements. Elemental analyses were performed using standard methods at TÜBI˙TAK (The Turkish Scientific Research Centre). The IR spectrum was recorded on a Vertex 80v sample Compartment RT-DLaTGS spectrophotometer operating within 4000-500 cm^{-1}. ^1H NMR spectra were recorded on BRUKER DPX-400, 400 MHz High Performance Digital FT-NMR spectrometer utilizing deuterated dimethylsulfoxide as a solvent.

Crystallographic analysis. Data collection was performed on a STOE IPDSII image plate detector using MoK_α radiation. Details of the crystal structure are given in Table 1. Data collection: Stoe X-AREA [10]. Cell refinement: Stoe X-AREA [10]. Data reduction: Stoe X-RED [10]. The structure was solved by direct methods using SHELXS-97 [11]. Anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2. H atoms were placed in calculated positions and constrained to ride on their parents atoms, with C–H = 0.93 Å, O–H = 0.82 Å, and N–H = 0.86 Å. $U_{iso}(H) = 1.2U_{eq}(C, N)$, $U_{iso}(H) = 1.5U_{eq}(O)$. The crystal was twinned and the reflection data were measured for the two twin domains, scaled and combined together. Overlapping reflections could not be satisfactorily measured and were discarded, leading to a data completeness of only 57%. Molecular drawing was obtained using ORTEP-III [12]. Full crystallographic data were deposited with Cambridge Crystallographic Database; CCDC deposition number 713706.

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