



NOTE

Synthesis and Structural Characterization of (*E*)-1-(4-Chlorobenzylidene)semicarbazide

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The compound (*E*)-1-(4-chlorobenzylidene)semicarbazide ($C_8H_8N_3OCl$, $M_r = 197.62$) was synthesized and characterized by elemental analysis, IR spectra, 1H NMR spectra and single crystal X-ray diffraction. The crystal belongs to monoclinic, space group $P2_1/c$, with $a = 17.081(5)$, $b = 4.4508(13)$, $c = 11.896(4)$ Å, $\beta = 92.979(4)^\circ$, $V = 903.2(5)$ Å³, $Z = 4$, $D_c = 1.453$ g/cm³, $\lambda = 0.71073$ Å, $\mu(MoK\alpha) = 0.384$ mm⁻¹, $F(000) = 408$. The final refinement gave $R = 0.0379$, $wR(F^2) = 0.1000$ for 1,585 observed reflections with $I > 2\sigma(I)$. X-ray diffraction analysis reveals that the title compound molecule adopts an *E* configuration about the C=N double bond. The dihedral angles between the semicarbazide group and the benzene ring is $17.4(2)^\circ$. The crystal structure is stabilized by N-H...O hydrogen bonds.

Key Words: (*E*)-1-(4-chlorobenzylidene)semicarbazide, Synthesis, Structure characterization.

Schiff bases are used as substrates in the preparation of a number of industrial and biologically active compounds via ring closure, cycloaddition and replacement reactions¹. Schiff bases are known to have biological activities such as antimicrobial²⁻⁴, antitumor⁵, mesomorphic⁶ and herbicidal⁷ properties. They have also been widely used as versatile ligands involved in various metal chelation reactions to form metal complexes⁸⁻¹⁶, which are very interesting in many fields, such as biochemical activity¹¹⁻¹³, catalysis and enzymatic reactions^{14,15} and magnetism¹⁶. Recently, a few Schiff base compounds have been investigated^{13,4,17,18}. Investigation on the structure of the Schiff base compounds may be helpful to design and synthesise new metal complexes. In this paper, the synthesis and the structural characterization of (*E*)-1-(4-chlorobenzylidene)semicarbazide are reported.

All the reagents were of AR grade and used without further purification. IR spectra (400-4000 cm⁻¹), as KBr pellets, were recorded on a Nicolet FT-IR 510P spectrometer. 1H NMR spectra were measured with a Bruker ALP 80 nuclear magnetic resonance spectrometer (CD_3COCD_3 as solvent, TMS as internal standard).

Synthesis of (*E*)-1-(4-chlorobenzylidene)semicarbazide:

A mixture of 4-(diethylamino)benzaldehyde (1.77 g, 0.01 mol) and semicarbazide hydrochloride (1.12 g, 0.01 mol) in ethyl alcohol (20 mL) was refluxed for 1 h. After cooling, filtration and drying, the title compound was obtained. 10 mg of the title compound were dissolved in 15 mL ethylalcohol and the solution was kept at room temperature. The single crystal

suitable for X-ray determination was obtained by evaporation from ethylalcohol solution after a week. Elemental analysis: calcd. (%) for $C_8H_8N_3OCl$: C 48.61, H 4.05, N 21.27. Found (%): C 48.66, H 4.08, N 21.31. Selected IR data (cm⁻¹): 1686 (s, C=O), 1635 (s, C=N), 1420 and 1215 (s, C-N), 1091 cm⁻¹ (s, Ar-Cl). 1H NMR data (CD_3COCD_3 , ppm): $\delta = 8.12$ (s, 1H), 7.63 (d, 2H), 7.32 (d, 2H), 6.05 (d, 3H).

Data collection and structure determination: A selected crystal of the title compound was mounted on a SMART CCD diffractometer. The reflection data were measured at 298 K, using a graphite monochromator $MoK\alpha$ ($\lambda = 0.71073$ Å) radiation with an ω - 2θ scan mode. The total reflections were 3,539 with 1,585 independent ones ($R_{int} = 0.0259$), of which 119 were observed with $I > 2\sigma(I)$. Intensities were corrected for Lorentz and polarization effects and empirical absorption and all data were corrected using SADABB¹⁹ program.

The structure was solved by direct methods using SHELXS-97²⁰ program. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. All hydrogen atoms were placed in the geometrically calculated positions. The contributions of these hydrogen atoms were included in the structure factor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography²¹. The final least-square cycle gave $R = 0.0379$ and $wR = 0.1000$ ($w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 0.0700P]$, where $P = (F_o^2 + 2F_c^2)/3$). $S = 1.083$, $(\Delta\rho)_{min} = -0.198$ and $(\Delta\rho)_{max} = 0.164$ e/Å³. CIF file containing complete information on the

studied structure was deposited with CCDC, deposition number 849423 and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

The atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms in the title compound are given in Table-1. The selected bond distances and bond angles are given in Table-2. The hydrogen bond schemes are given in Table-3. A displacement ellipsoid plot with atomic numbering scheme is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell in Fig. 2.

TABLE-1
ATOMIC COORDINATES ($\times 10^4$) AND THERMAL
PARAMETERS ($\text{\AA}^2 \times 10^3$)

Atom	x	y	Z	U(eq)
C(1)	8815(1)	3424(5)	3101(2)	54(1)
C(2)	8339(1)	5319(5)	3652(2)	56(1)
C(3)	7679(1)	6456(5)	3083(2)	54(1)
C(4)	7496(1)	5691(4)	1969(1)	42(1)
C(5)	7996(1)	3785(5)	1431(2)	52(1)
C(6)	8656(1)	2661(5)	1993(2)	62(1)
C(7)	6798(1)	6995(4)	1399(1)	44(1)
C(8)	5508(1)	6606(4)	-963(1)	36(1)
Cl(1)	9646(1)	1973(2)	3813(1)	84(1)
N(1)	6546(1)	6147(3)	426(1)	39(1)
N(2)	5898(1)	7634(3)	-12(1)	42(1)
N(3)	5816(1)	4249(3)	-1466(1)	44(1)
O(1)	4909(1)	7923(3)	1327(1)	45(1)

TABLE-2
SELECTED BOND LENGTHS (\AA) AND BOND ANGLES ($^\circ$)

Bond	Length (\AA)	Bond	Angle ($^\circ$)
C(1)-Cl(1)	1.7386(19)	C(2)-C(1)-Cl(1)	119.16(15)
C(4)-C(7)	1.462(2)	N(1)-C(7)-C(4)	122.27(17)
C(7)-N(1)	1.270(2)	O(1)-C(8)-N(3)	123.80(15)
C(8)-O(1)	1.237(2)	O(1)-C(8)-N(2)	119.39(16)
C(8)-N(3)	1.330(2)	N(3)-C(8)-N(2)	116.79(15)
C(8)-N(2)	1.362(2)	C(7)-N(1)-N(2)	115.59(15)
N(1)-N(2)	1.3701(19)	C(8)-N(2)-N(1)	120.32(14)

TABLE-3
HYDROGEN BOND SCHEMES (\AA°)

D-H...A	D-H	H...A	D-A	D-H...A
N3-H3A...O1 ⁱ	0.86	2.06	2.905	167
N2-H2A...O1 ⁱⁱ	0.82	2.11	2.928	176

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

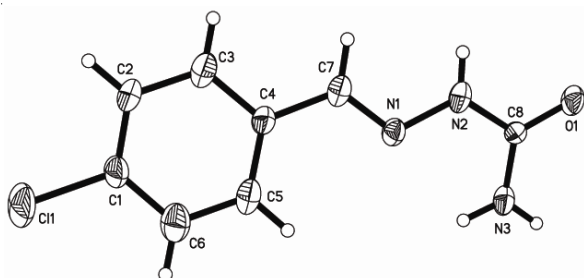


Fig. 1. Molecular structure with atomic numbering scheme

As seen from Fig. 1, (*E*)-1-(4-chlorobenzylidene)semicarbazide molecule adopts an *E* configuration about the C=N double bond. In the molecule, the C4-C7=N1-N2 and C7=N1-N2-C8 torsion angles between naphthalene ring and benzene

ring are $-178.25(15)^\circ$ and $-169.71(16)^\circ$, respectively. The dihedral angles between the semicarbazide group and the benzene ring is $17.4(2)^\circ$. The bond lengths and bond angles in the title compound are within normal ranges and comparable to those in the similar compound¹⁷. The C7=N1 with the bond length of $1.270(2) \text{\AA}$ conforms double bond. The bonds C8-N3 [$1.330(2) \text{\AA}$] and C8-N2 [$1.362(2) \text{\AA}$] in the title compound are found to have normal single bond length. They are shorter than that in the compound (*E*)-*N*-(4-(diethylamino)benzylidene)-naphthalen-1-amine¹⁷, this may be the reason of the effect of carbonyl group. As seen from Table-3 and Fig. 2, the molecules are interlinked, *via* the weak intermolecular N-H...O hydrogen bonds interactions, to form network.

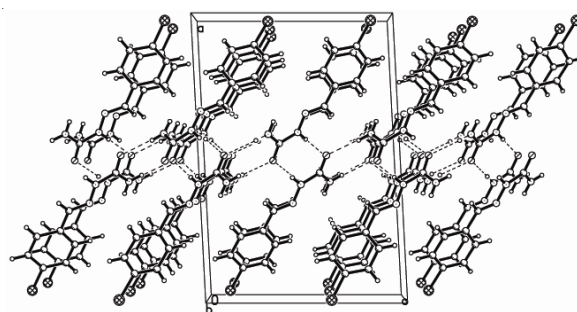


Fig. 2. View of crystal packing down the b-axis

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