Crystal Structure of *N*-Benzlidene-*N'*-(2-carboxyphenyl)hydrazine

Habibe TEZCAN,* Tuncay TUNÇ,** Ertan ŞAHİN,***† and Rahmi YAĞBASAN**

*Department of Chemistry Education, Gazi University, Beşevler, Ankara, Turkey

**Department of Physics Education, Gazi University, Beşevler, Ankara, Turkey

***Department of Engineering Physics, Hacettepe University, 06800 Beytepe, Ankara, Turkey

Molecules of the title compound (alternative name, benzaldehyde-2-carboxyphenylhydrazone), $C_{14}H_{12}N_2O_2$ adopt an *E* configuration about the azomethine $C=N$ double bond. The molecule is almost planar and the dihedral angle between the planes of phenyl and carboxy phenyl rings are only $4.9(1)^\circ$. The crystal structure is stabilized by the two intermolecular $O2-H\cdots O1$ hydrogen bonds between O atoms and the π - π interactions between the phenyl rings.

(Received April 6, 2004; Accepted July 9, 2004; Published on web October 1, 2004)

Hydrazones are of interest because of their importance in analytical chemistry, medicine and industry. Hydrazones have also been widely studied as chelating ligands for the spectrophotometric and fluorometric determination of trace metal ions.¹ Hydrazones are formed when hydrazines condense with aldehydes and ketones. These compounds can therefore be used to identify the aldehydes and ketones from which the hydrazones have been formed. The determination of the thermodynamic parameters and formation constants of charge-transfer complexes (CTC) between phenyl hydrazones and organics acceptors have been described.² It has also been pointed out that the possibility to obtain a charge-transfer (CT) interaction in solution is related to the presence of at least one atom bonded to a phenyl hydrazone skeleton.³ In our previous studies, the synthesis and characterization of aroylhydrazone compounds was achieved.⁴

We report on the crystal structure of the title compound (Fig.

Fig. 1 Chemical diagram of the title compound.

Fig. 2 Molecular structure of the title compound with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

1). A solution of 2-hydrazinobenzoic acid hydrochloride (5.65 g, 0.03 mol) in hot methanol (25 ml) was added dropwise to a solution of benzaldehyde (3.18 g, 0.03 mol) in hot methanol (25 ml) at 298 – 303 K. The resulting yellow solid was filtered off, dried and recrystallized after refluxing in hot methanol for 3 h. The obtained yellow crystals were filtered off and dried in air.

Molecules of the title compound adopt an *E* configuration about the azomethine $C=N$ double bond, with an $C9-C8-N2-N1$ torsion angle of $-179.5(3)^\circ$ (Fig. 2). Overall, the molecule is planar, the dihedral angle between the planes of the phenyl and carboxyphenyl rings is $4.9(1)^\circ$, and the phenyl and carboxyphenyl planes make dihedral angles with the central

Table 1 Crystal and experimental data

Formula:	$C_{14}H_{12}N_2O_2$
Formula weight:	240.26
Crystal system:	monoclinic
Space group:	$P21/n$
Z :	4
a :	13.4725(11) Å
b :	3.9749(5) Å
c :	22.6283(16) Å
V :	1211.7(2) Å ³
D_x :	1.317 g/cm ³
μ (Mo $K\alpha$):	0.090 cm ⁻¹
T :	293 K
Crystal color:	yellow
Crystal size:	0.40 × 0.25 × 0.20 mm
λ (Mo $K\alpha$):	0.71073 Å
R :	0.0552
wR :	0.1064
No. of reflections measured:	1965
No. of reflections used:	1891 [$I > 2\sigma(I)$]
No. of parameters:	163
Goodness-of-fit:	1.013
$(\Delta/\sigma)_{\max}$:	0.000
$(\Delta\rho)_{\max}$:	0.16 eÅ ⁻³
$(\Delta\rho)_{\min}$:	-0.20 eÅ ⁻³
$2\theta_{\max}$:	51.16°
Measurements:	Enraf-Nonius CAD-4 diffractometer
Program system:	CAD-4 EXPRESS Software
Structure determination:	SHELXS-97
Refinement:	full matrix
Hydrogen atoms:	geometrically located, but not refined

† To whom correspondence should be addressed.

E-mail : ertan@hacettepe.edu.tr

Fig. 3 Packing diagram showing the hydrogen bonding and π - π interactions (dotted lines) that link molecules.

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
O1	0.62295(15)	0.1775(7)	-0.00009(9)	0.0607(8)
O2	0.50386(17)	0.1539(7)	-0.06721(9)	0.0554(8)
N1	0.5384(2)	0.4431(8)	-0.17175(11)	0.0482(9)
N2	0.5145(2)	0.5188(7)	-0.22870(11)	0.0420(8)
C1	0.6308(2)	0.5142(9)	-0.15020(14)	0.0362(9)
C2	0.7016(3)	0.6807(10)	-0.18512(14)	0.0437(10)
C3	0.7942(3)	0.7474(9)	-0.16416(15)	0.0490(10)
C4	0.8208(3)	0.6534(10)	-0.10737(15)	0.0490(10)
C5	0.7527(2)	0.4944(9)	-0.07227(14)	0.0422(10)
C6	0.6569(2)	0.4190(9)	-0.09220(13)	0.0381(9)
C7	0.5883(3)	0.2411(9)	-0.05318(13)	0.0412(10)
C8	0.4293(3)	0.4230(9)	-0.24586(13)	0.0416(10)
C9	0.3935(3)	0.4820(9)	-0.30534(15)	0.0401(9)
C10	0.2996(3)	0.3672(10)	-0.32076(16)	0.0527(11)
C11	0.2637(3)	0.4124(10)	-0.37716(18)	0.0658(13)
C12	0.3210(3)	0.5702(11)	-0.41873(18)	0.0673(13)
C13	0.4133(3)	0.6850(10)	-0.40446(15)	0.0618(12)
C14	0.4499(3)	0.6447(10)	-0.34838(15)	0.0486(10)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

Table 3 Selected bond distances (Å) and angles along with the torsion angles (°).

O1 C7	1.310(3)	C6 C7	1.465(4)
C8 N2	1.268(4)	N1 C1	1.364(4)
C8 C9	1.446(4)	N1 N2	1.360(3)
O2 C7	1.229(3)		
N2 N1 C1	120.1(3)	O1 C7 C6	115.1(3)
N2 C8 C9	122.1(3)	O2 C7 C6	124.6(3)
C8 N2 N1	115.5(3)	O2 C7 O1	120.3(3)
N1 C1 C6	119.9(3)	C14 C9 C8	123.0(3)
N1 C1 C2	121.2(3)	C10 C9 C8	118.5(3)
C9 C8 N2 N1	-179.5(3)		
C1 N1 N2 C8	175.4(3)		
N2 N1 C1 C6	-176.6(3)		
N2 N1 C1 C2	3.1(5)		
C5 C6 C7 O2	-177.6(4)		
C1 C6 C7 O2	1.4(6)		
C5 C6 C7 O1	2.7(5)		
C1 C6 C7 O1	-178.4(3)		
C7 C6 C1 N1	0.5(5)		

hydrazone bridge (N1/N2/C8) of 1.9(2) and 3.6(2)°, respectively. The N1-N2 [1.359(3)Å] and N2-C8 [1.268(4)Å] bond distances (Table 1) are comparable to those in our previous studies and related compounds, *p*-methoxybenzaldehyde isonicotinoylhydrazone monohydrate and *p*-methoxybenzaldehyde nicotinoylhydrazonedihydrate.⁵

For a π -stacked arrangement, planarity of the whole molecule is one of the prerequisites. In Fig. 3, a packing diagram of the molecule is shown. A stacking of H-bonding dimers formed by two O2-H...O1ⁱ hydrogen bonding [symmetry code: (*i*) $-x, 1-y, 1-z$] and π - π interactions between the phenyl rings along *b* axis can be seen. The interplanar distance between overlapping phenyl rings is 3.513Å. The centroid-to-centroid distance is 3.975 Å. These values can be compared with those in the literature.⁶ Intermolecular π - π interactions play an important role in controlling the crystal packing of the aromatic compound.

Acknowledgements

The authors wish to acknowledge the purchase of the CAD-4 diffractometer and the financial support of this work under grants DPT/TBAG1 and TBAG-1693 of The Scientific and Technical Research Council of Turkey and Hacettepe University, Scientific Research Unit (grant number 02 02 602 002).

References

1. A. Galiano-Roth and D. B. Collum, *J. Am. Chem. Soc.*, **1988**, *110*, 3546.
2. P. Bruni, L. Cardellini, and G. Tosi, *Gazz. Chim. Ital.*, **1981**, *111*, 67.
3. G. Tosi, L. Cardellini, and G. Bocelli, *Acta Cryst.*, **1988**, *B44*, 55.
4. T. Tunç, D. M. Sarı, R. Yağbasan, H. Tezcan, and E. Şahin, *Acta Cryst.*, **2003**, *C59*, 192.
5. H.-K. Fun, K. Sivakumar, Z.-L. Lu, C.-Y. Duan, Y.-P. Tian, and X.-Y. You, *Acta Cryst.*, **1996**, *C52*, 986.
6. N. R. Sangeetha, S. Pal, C. E. Anson, and A. K. Powell, *Inorg. Chem. Commun.*, **2000**, *3*, 415.