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Hydrogen-bonding one-dimensional arrangement in the crystal of *N*-phenyl-2-hydroxyacetamide

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ABSTRACT

The *N*-phenyl-2-hydroxyacetamide was obtained in crystalline form by a direct reaction of aniline with glycolic acid. The whole molecule in the crystal is non-planar, but the planar 2-hydroxyacetamide group is inclined by 7.8(1)° to the plane of the phenyl ring that is cis located to the carbonyl oxygen atom. The hydroxyl group is in trans position to the carbonyl oxygen atom. The molecules are linked by the N—H···O and O—H···O hydrogen bonds into one-dimensional chains along the *a*-axis. Additionally, the C—H···π interactions interconnect the chains stabilizing the crystal structure. The X-ray geometry of the *N*-phenyl-2-hydroxyacetamide molecule has been compared with that obtained by the *ab-initio* molecular orbital calculated results that represents the geometry in the gas-phase.

1. Introduction

Crystal engineering has significant applications in the field of materials science, molecular biology and pharmaceutical science [1–3]. The directional interactions resulting from the multiple hydrogen bonds with the neighbours are the main key for organisation of molecules in solids [4,5]. Many different self-complementary hydrogen bonding groups can be used to control association in supramolecular chemistry to produce different and programmed arrangement, such as chains, sheets, ribbons, tapes, rosettes, etc. [6–9].

Besides the hydrogen bonds as directional non-covalent interactions responsible for organisation and design of the supramolecular architectures in solids, the π···π and C—H···π interactions are the molecular forces, whose nature is still a matter of discussion [10–13]. In general, the such π···π interaction integrates two aromatic rings arranged in a face-to-face orientation with a distance of 3.2–3.8 Å between the planes of the rings [14–16].

Continuing our investigations of the crystals with N—H···N, N—H···O and O—H···O hydrogen bonds and π···π or C—H···π interactions [17–19], in this paper we present the crystal structure of *N*-phenyl-2-hydroxyacetamide obtained by a direct reaction of aniline with glycolic acid. A search of the Cambridge Structural Database (Version 5.30, November, 2008) for structures containing *N*-substituted 2-hydroxyacetamide derivatives yielded only one compound of this class, i.e. *N*-(1′-ethyl-2′-hydroxyethyl)-2-hydroxyacetamide [20]. Thus the present compound is the second of this type, but the first of *N*-aryl substituted 2-hydroxyacetamide that has been structurally characterised. The X-ray geometry of *N*-phenyl-2-hydroxyacetamide molecule is compared to that obtained by an *ab-initio* molecular orbital calculated result that represents the geometry in the gas-phase.

2. Experimental

2.1. Preparation of N-phenyl-2-hydroxyacetamide

Aniline and glycolic acid (Aldrich, both reagents of purity of 99%) were added to hot water in a molar proportion of 1:1. When the solution became homogenous it was cooled slowly and kept at room temperature. After several days, transparent yellowish crystals were formed. Anal. Calculated for $C_8H_9NO_2$: C, 63.56%; H, 6.00%; N, 9.27% and O, 21.17%. Found: C. 63.64%, H, 5.97%; N, 9.12% and O, 22.27%.

2.2. X-ray data collection

X-ray intensity data for the crystal were collected using graphite monochromatic Mo$K\alpha$ radiation and a four-circle κ geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector. The ω-scan technique with $\Delta\omega = 1.0°$ for each image was used for data collection. The 760 images for six different runs covering over 95% of the Ewald sphere were performed. The unit cell parameters were refined by the least-squares methods on the basis of 565 reflections with intensity ($I_{(hkl)}$) greater than

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8$\sigma(I)$. One image was used as a standard after every 40 images for monitoring the crystal stability and data collection. No correction on the relative intensity variations was necessary. Data collection were made using the CrysAlis CCD program [21]. Integration, scaling of the reflections, correction for Lorenz and polarisation effects and absorption corrections were performed using the CrysAlis Red program [21]. The structure was solved by the direct methods using SHELXS-97 and refined using SHELXL-97 programs [22]. The hydrogen atoms of the phenyl ring were located in their geometrical positions with the $U_{iso}(H) = 1.2U_{eq}(C)$ of the carbon atom directly joined the H atoms). The other H atoms (CH_2, NH and OH) were constrained: C—H = 0.97 Å with $U_{iso}(H) = 1.5U_{eq}(C)$; N—H = 0.86 Å with $U_{iso}(H) = 1.2U_{eq}(N)$ and O—H = 0.83 Å with $U_{iso}(H) = 1.5U_{eq}(O)$. The final difference Fourier map showed no peaks of chemical significance. The largest peaks on the final $\Delta\rho$ map were +0.135 and −0.136 eÅ^{-3}. The details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Visualisation of the structure was made with the Diamond 3.0 program [23].

2.3. Quantum calculations

Ab-initio molecular orbital calculations full geometry optimisation were performed with the Gaussian98 program package [24]. All calculations were performed by the density functional three-parameter hybrid (B3LYP) methods [25,26] with the 6-31+G* basis set starting from the X-ray geometry. As a convergence criterions the threshold limits of 0.00025 and 0.0012 a.u. were applied for the maximum force and the displacement, respectively.

Table 1
Crystallographic data for *N*-phenyl-2-hydroxyacetamide.

Empirical formula	$C_8H_9NO_2$
Formula weight (g mol^{-1})	151.16
Crystal system, space group	Monoclinic, *P* $2_1/n$
a (Å)	5.7300(11)
b (Å)	12.394(3)
c (Å)	10.489(2)
β (°)	94.02(1)
V (Å^3)	743.1(3)
Z	4
D_{calc}/D_{obs} (g cm^{-3})	1.351/1.35
μ (mm^{-1})	0.098
F(000)	320
Crystal size (mm)	0.32 × 0.24 × 0.21
Radiation type, wavelength, λ (Å)	Mo*K*α, 0.71073
Temperature (K)	295(2)
θ range (°)	3.29 ÷ 29.43
Absorption correction	Numerical, CrysAlis Red [21]
T_{min}/T_{max}	0.973/0.989
Reflections collected/unique/observed	9788/1924/1019
R_{int}	0.041
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0372
$wR(F^2$ all reflections)	0.0936
Goodness-of-fit, *S*	1.086
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.135, −0.136

$wR = \{\sum[w(F_o^2 - F_c^2)2]/\sum wF_o^4\}^{1/2}; w^{-1} = \sigma^2(F_o^2) + (0.0380P)^2$ where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

During reaction of aniline with glycolic acid in hot water solution, one proton of the NH_2 group of aniline molecule is transferred to the hydroxyl group of COOH of glycolic acid and finally the water molecule is eliminated. Elimination of water results in the formation of the N—C bonds between the reagents as illustrate the scheme 1.

The asymmetric unit of the crystal is illustrated in Fig. 1. The six-membered ring is planar, but shows slight distortions from the ideal hexagonal symmetry. The distortions result from the substitution effect of the 2-hydroxyacetamide group joined to the ring and the internal C6—C1—C2 and C3—C4—C5 angles to be smaller than 120°. These distortions are in agreement with those found in similar substituted benzene derivatives [27–32]. The non-H atoms of 2-hydroxyacetamide group are planar. This plane is inclined to the plane of the phenyl ring by 7.8(1)°. The phenyl ring is cis oriented to the carbonyl oxygen atom, whereas the hydroxyl group is in trans position the carbonyl oxygen (Fig. 1). The C—C bond lengths of the phenyl ring are in the range of 1.363(2)–1.385(2) Å. Both the C—C bonds involving the C1 atom are longer than the remaining four C—C bonds within the phenyl ring. The elongation of the C1—C2 and C1—C6 bonds is caused by the electron withdraw effect of the 2-hydroxyacetamide substituent that disturbs the delocalisation of the π electron in the ring.

The N1—C1 bond with a distance of 1.413(2) Å between the *N*-amide and the C atoms of the phenyl ring is longer than the N1—C8 bond (1.339(2) Å) in the 2-hydroxyacetate group (Table 2). This can be explained by the partial delocalisation of the π electron of the double C8—O2 bond over the N1—C8 bond, since the fragment is planar. In addition the lone-pair of electron on the N1 atom is localised on the p orbital, which is perpendicular to the plane of 2-hydroxyacetamide group similarly as the p orbitals of C and O atoms that form the double C—O bond. Thus the partial delcocalisation of

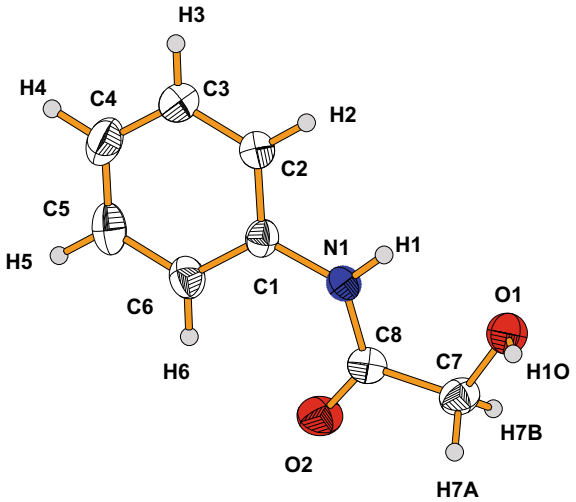
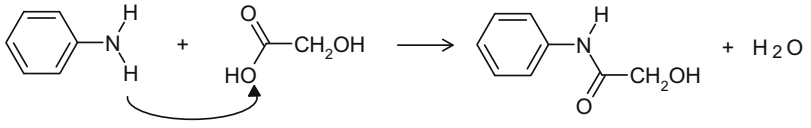


Fig. 1. A view of *N*-phenyl-2-hydroxyacetamide molecule showing displacement ellipsoids at the 50% probability level and H atoms as a sphere of arbitrary radii.



Scheme 1.

Table 2
Bond lengths (Å) and angles (°) for *N*-phenyl-2-hydroxyacetamide.

C1—C6	1.382(2)
C2—C3	1.373(2)
C5—C6	1.382(2)
O2—C8	1.226(2)
C1—C2	1.385(2)
C3—C4	1.375(2)
O1—C7	1.407(2)
C7—C8	1.506(2)
C1—N1	1.413(2)
C4—C5	1.363(2)
N1—C8	1.339(2)
C6—C1—N1	123.31(12)
C8—N1—C1	128.85(11)
O2—C8—N1	125.27(13)
N1—C8—C7	116.01(11)
C3—C2—C1	120.15(14)
C3—C4—C5	118.99(14)
C5—C6—C1	119.82(14)
C2—C1—N1	117.68(11)
O1—C7—C8	113.60(11)
O2—C8—C7	118.72(12)
C6—C1—C2	119.00(13)
C2—C3—C4	120.89(15)
C4—C5—C6	121.14(14)

the π electrons of the double C8—O2 bond over these three atoms (N, C and O) is possible due to the symmetry of the p orbitals. The interaction of the π-electrons of the phenyl ring and the lone-pair of electron on the O2 atom makes the respective angles (C6—C1—N1, C1—N1—C8 and N1—C8—O2) significantly greater than 120°, as expected for the sp^2 hybridisation, since according to the valence-shell electron pair repulsion model, VSEPR [33], the lone-pair of electrons occupies a wider region as the bonding pair. Additionally, both angles, N1—C8—C7 and C8—C7—O1, are significantly smaller than 120° due to the attractive interaction between the lone-pair of electron on O1 atom with the H1 atom of amide group into the intramolecular hydrogen bond N1—H1···O1 with a D···A distance of 2.658(2) Å.

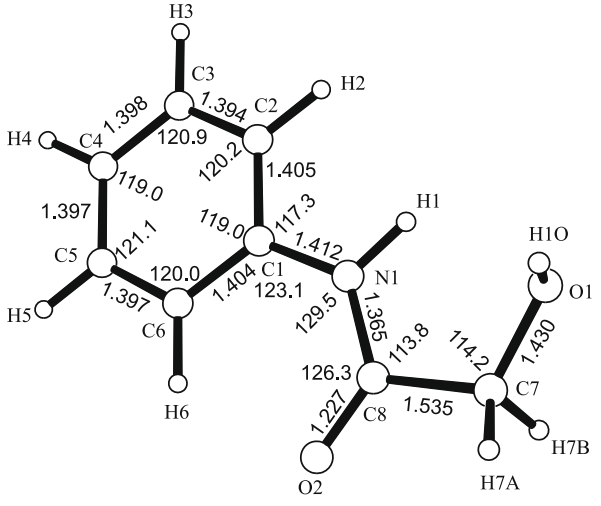
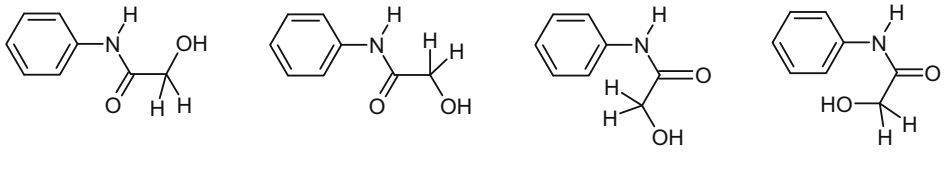


Fig. 2. Results of the optimized molecular orbital calculations (B3LYP/6-31+G*) for isolated *N*-phenyl-2-hydroxyacetamide molecule (Å, °).

Ab-initio full-optimised molecular orbital calculation performed for an isolated molecule of *N*-phenyl-2-hydroxyacetamide shows quite similar correlation between the bond lengths and angles as found in the crystal (Fig. 2, Table 2). However, the conformation of the optimised molecule is slightly different than that in the crystal. For example the planar 2-hydroxyacetamide group is inclined by 4.3° to the plane of the phenyl ring. The inclination is smaller than in the crystal due to the intramolecular interaction between the carbonyl oxygen O2 atom and the hydrogen H6 atom in orto position in relation to the 2-hydroxyacetamide substituent with O2···H6 distance of 2.280 Å. The conformation of the molecule, in which the phenyl ring and the hydroxyl group are, respectively, in cis and trans position to the carbonyl oxygen atom is the most stable conformation of the *N*-phenyl-2-hydroxyacetamide molecule within the other possible conformers (cis–trans conformation I, see Scheme 2), according to our conformational analysis. The MO calculations on I–IV conformers were performed with constrained torsion angles C1—N1—C8—O2 and O2—C8—C7—O1 to the values 0 or 180° defining the possible conformers (Scheme 2). After optimisation routines, the cis/cis conformer (II), in which the phenyl ring and the hydroxyl group are in cis position in relation to carbonyl oxygen, and the trans/cis conformer (III), in which the phenyl ring and the hydroxyl group are, respectively, in trans and in cis position in relation to carbonyl oxygen, have higher single-point energy by ∼7.2 and ∼24.8 kcal/mol, respectively, in comparison to the lowest energy conformation cis–trans (I). The trans–trans conformer IV is rather unstable, since the optimisation does not converge. The energy differences between the conformers are about 25% (7.2 kcal/mol) and 75% (24.8 kcal/mol) of the strong hydrogen bond energy [34,35]. Concluding, the geometry of *N*-phenyl-2-hydroxyacetamide molecule resulting from X-ray study is mainly determined by the electronic structure, while the greater rotation of the 2-hydroxyacetamide group in relation to the phenyl rings is caused by the intermolecular hydrogen bonding system and the crystal packing forces.

In the crystal the molecules related by a translation along the a-axis interact via the O—H···O hydrogen bonds between the hydroxyl group (donor) and the carbonyl oxygen (acceptor) forming one-dimensional chains along [100] direction (Fig. 3). Two neighbouring chains are interconnected by the N—H···O hydrogen bonds between the imine (NH) groups and the hydroxyl group (Table 3) into a double chains extending along the *a*-axis (Fig. 4). The double chains interact with each other by a weak C—H···π interaction of a distance of ∼3.52 Å formed between the donor CH_2 and centroid of the π-aromatic ring. The C—H···π interactions between the C—H and the aromatic ring are much weaker (E = 2 ÷ 4 kcal/mol) [36] than the N—H···O or O—H···O hydrogen bonds (E = 25 ÷ 35 kcal/mol) [34,35]. This type of intermolecular interactions have been recently recognised as equally important



Scheme 2.

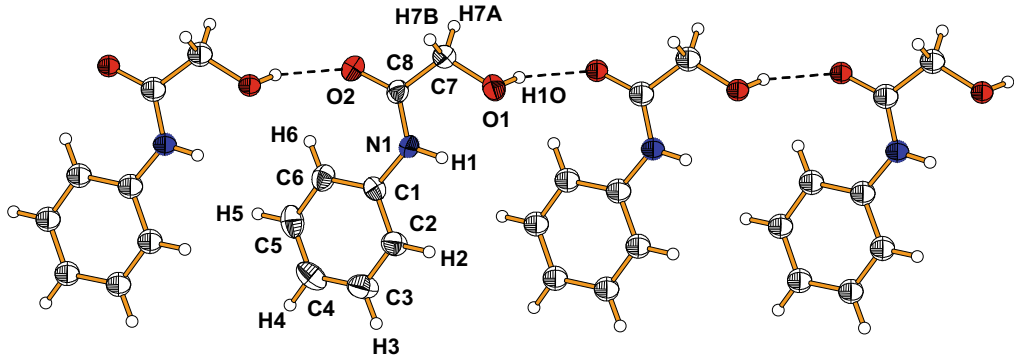


Fig. 3. View of the O—H···O hydrogen bonded chain of *N*-phenyl-2-hydroxyacetamide molecules.

factors determining the arrangement of molecules in crystals and have found a broad application in crystal engineering for design of new functional materials [37–41]. The closest contact between the hydrogen atom of CH_2 of 2-hydroxyacetate group and the π-aromatic phenyl ring points to the presence of week C—H···π interactions that stabilise the three-dimensional structure. The reaction of glycolic acid with amine group of aniline with elimination of water molecule yielding the *N*-phenyl-2-hydroxyacetamide can be useful in crystal engineering as a method for obtaining crystals of different compounds using different aromatic or aliphatic amines, Ar—NH_2 or R—NH_2.

Table 3
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O2^{i}	0.83	1.99	2.777(2)	160
N1—H1···O1	0.86	2.20	2.658(2)	113
N1—H1···O1^{ii}	0.86	2.32	3.032(2)	141
C7—H1···π(C1—C6)^{iii}	0.97	2.77	3.523(3)	139

Symmetry code: $i = 1 + x, y, z$; $ii = -x + 2, -y + 1, -z$; $iii = 1 - x, 1 - y, -z$.

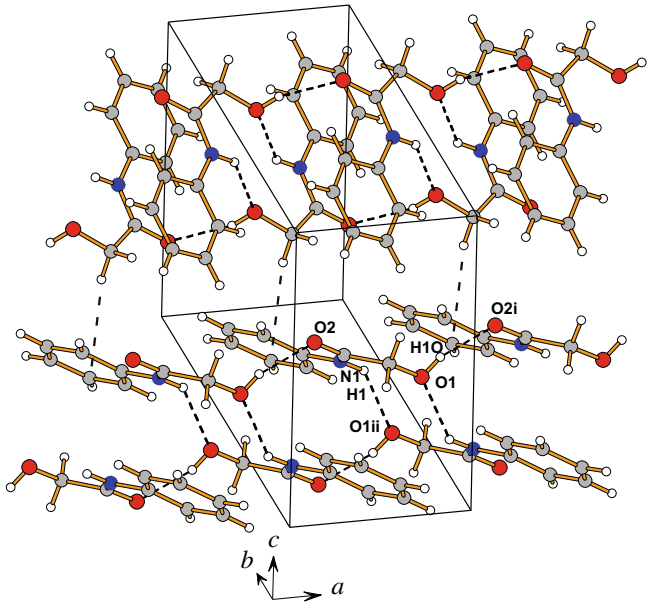


Fig. 4. View of the crystal packing of *N*-phenyl-2-hydroxyacetamide. Dashed lines represent the N—H···O and O—H···O hydrogen bonding as well as the C—H···π interactions that stabilise the 3D structure.

4. Supplementary material

Additional material comprising full details of the X-ray data collection and final refinement parameters including anisotropic thermal parameters and full list of the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Center in the CIF format as supplementary publications no. CCDC 721009. Copies of the data can be obtained free of charge on the application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK, (Fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk).

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