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ORIGINAL PAPER

Crystallographic and Conformational Analysis of [(*Z*)-2-ethoxy-6-[(2-hydroxyphenylamino)methylene]cyclohexa-2,4-dienone]

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Abstract The single crystal X-ray diffraction analysis of the title compound, $C_{15}H_{15}NO_3$, shows that the structure is adopted to its NH tautomeric form and crystallizes in the orthorhombic space group *P bcn* with $a = 21.2424(15)$ Å, $b = 12.7696(9)$ Å, $c = 9.3605(10)$ Å, $Z = 8$, $V = 2539.1(4)$ Å^3, $D_c = 1.346$ g/cm^3. The molecular conformation in the crystal is stabilized by an intramolecular H-bond and the crystal structure is stabilized by the bifurcated O–H···O type intermolecular H-bonds. In order to understand the effects on conformational flexibility of the title molecule, molecular energy profile was calculated as a function of the selected torsion angle by means of AM1 semi-empirical method.

Keywords Crystal structure · Schiff base · AM1 · Conformational analysis · Bifurcated hydrogen bond

Introduction

Schiff bases and their complexes are of great interest in many fields of chemistry and biochemistry because of their versatile metal binding ability and striking antitumour activities [1, 2]. Intramolecular hydrogen transfer from *o*-hydroxy group to imine-N is of particular interest in understanding of their thermochromic and photochromic properties [3]. Schiff bases exist in two possible tautomeric forms known as phenol-imine (OH) and keto-amine (NH). Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O–H···N in phenol-imine [4, 5] and N–H···O in keto-amine [6–9] tautomers. Another form of the Schiff base compounds is also known as zwitterion having an ionic intramolecular hydrogen bond (N^+–H···O^-) and this form is rarely seen in the solid state [10–12]. NH form of Schiff bases in solid state can be regarded as a resonance hybrid of two canonical structures, the keto-amine and zwitterionic forms. While OH and NH form may co-exist in the same crystal structure [13], both characters may also be in the same molecular structure [14].

Here we report, the molecular and crystal structure of (*Z*)-2-ethoxy-6-[(2-hydroxyphenylamino)methylene]cyclohexa-2,4-dienone (Fig. 1), determined by single crystal X-ray diffraction study, and the conformational analysis of the title molecule with respect to the selected torsion angle performed by AM1 semi-empirical quantum chemical method. The results obtained from both methods are compared.

Experimental

Synthesis of the Title Compound

The compound [(*Z*)-2-ethoxy-6-[(2-hydroxyphenylamino)methylene]cyclohexa-2,4-dienone] was prepared by reflux a mixture of a solution containing 3-ethoxysalicylaldehyde (0.5 g 3 mmol) in 20 mL ethanol and a solution containing 2-hydroxyaniline (0.33 g 3 mmol) in 20 mL ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of [(*Z*)-2-ethoxy-6-[(2-hydroxyphenylamino) methylene] cyclohexa-2,4-dienone] suitable for

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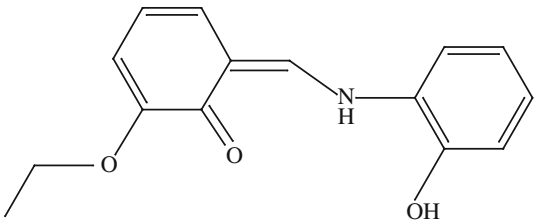

Fig. 1 Chemical diagram of the title compound $C_{15}H_{15}NO_3$

X-ray analysis were obtained from acetone by slow evaporation (yield % 70; m.p. 454–456 K).

X-ray Crystallography

A red coloured plate-shaped crystal sample with dimensions of 0.56 × 0.32 × 0.04 mm was chosen for the crystallographic study. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated MoK_α radiation on a STOE IPDS 2 diffractometer. The systematic absences and intensity symmetries indicated the orthorhombic *P bcn* space group. A total of 13571 reflections with $[1.86° < \theta < 26°]$ were collected in the ω scan mode and cell parameters were determined by using X-AREA software [15]. Absorption correction ($\mu = 0.094$ mm^{-1}) was obtained by the integration method via X-RED software [15].

The structure was solved by direct methods using SHELXS-97 [16]. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic thermal parameters of the non-hydrogen atoms, or equivalently corresponding to 233 crystallographic parameters. All non-hydrogen atoms were refined anisotropically and the positions of H atoms were obtained from difference-Fourier map of electron density in the unit cell. The structure was refined to $R_1 = 0.0491$ for observed 1290 reflections prescribed by the condition of $I > 2\sigma$ (I) and to $R_1 = 0.1088$ for all 2500 reflections used in refinement process. The maximum peaks and deepest hole observed in the final $\Delta\rho$ map were 0.14 and −0.15 eÅ^{-3}, respectively. The scattering factors were taken from SHELXL-97 [16]. The data collection conditions and parameters of refinement process are listed in Table 1.

Computational Procedures

The geometry optimization of the molecule was performed starting from the crystallographic coordinates by using AM1 self-consistent field molecular orbital method [17] at the restricted Hartree-Fock (RHF) level [18] with the aid of WinMopac 7.21 package [19]. Non-Linear Least Squares (NLLSQ) gradient minimization routine was used in the optimization procedure with very precise GNorm of 0.01.

Table 1 Crystallographic data for the title compound

CCDC deposit no.	CCDC 641445
Color/shape	Red/Plate
Chemical formula	$C_{15}H_{15}NO_3$
Formula weight	257.28
Temperature	296 K
Crystal system	Orthorhombic
Space group	*P bcn*
Unit cell parameters	a = 21.2424(15) Å
	b = 12.7696(9) Å
	c = 9.3605(10) Å
Volume	2539.1(4) Å^3
Z	8
Density	1.346 g/cm^3
Absorption coefficient	0.094 mm^{-1}
T_{min}, T_{max}	0.9579, 0.9931
Diffractometer/meas. meth.	STOE IPDS 2/ϖ-scan
θ range for data collection	1.86–26.05°
Unique reflections measured	2500
Independent/observed reflections	2500/1290
Data/restraints/parameters	1290/0/233
Extinction coefficient	0.0045(7)
Goodness of fit on F^2	0.977
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0491$, $wR_1 = 0.0980$
R indices (all data)	$R_2 = 0.1088$, $wR_2 = 0.1172$

In order to describe conformational flexibility of the title molecule, the selected torsion angle, T(C7–N1–C8–C13), was varied from −180 to 180° in every 10° and the molecular energy profile as a function of the selected torsional degree of freedom is obtained by performing single point calculations on the calculated potential energy surface.

Results and Discussion

An ORTEP-3 view [20] with the atom-numbering scheme of the molecular structure and crystal packing drawing [20] with the bifurcated hydrogen bonds of the title compound are shown in Figs. 2 and 3, respectively. The selected geometrical parameters obtained by both crystallographic and theoretical study are listed in Table 2.

X-ray crystallographic study reveals that the compound is in NH form with a strong intramolecular N–H···O hydrogen bond. The C2–O1 [1.291(2) Å] and C7–N1 [1.307(3) Å] bonds are the most sensitive indicators of the tautomeric type of the title molecule. These bond distances are comparable with those of compounds previously reported as keto-amine [6–9]. Although these bond distances have intermediate values between single and double

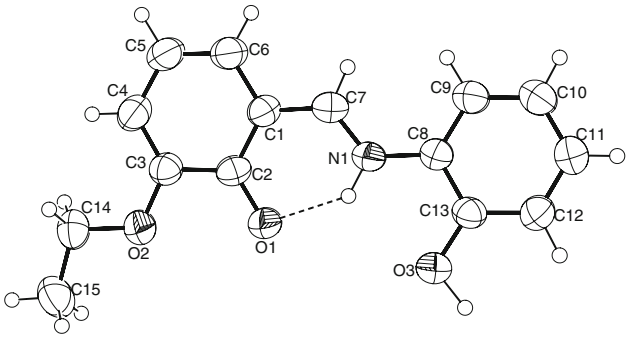

Fig. 2 An ORTEP-3 view of the title molecule with the atomic numbering scheme showing intramolecular hydrogen bond depicted by dashed lines. Displacement ellipsoids are shown at the 50% probability level

Table 2 Comparative results of the selected geometrical parameters (Å, °) both crystallographic and quantum chemical calculations

	X-ray	AM1		X-ray	AM1
Bond lengths					
C1–C7	1.402(3)	1.38	C1–C2	1.426(3)	1.46
C7–N1	1.307(3)	1.36	C2–C3	1.439(3)	1.49
C2–O1	1.291(2)	1.25	C3–C4	1.362(3)	1.36
N1–C8	1.409(3)	1.41	C4–C5	1.411(4)	1.43
C3–O2	1.364(3)	1.38	C5–C6	1.350(4)	1.35
O2–C14	1.435(3)	1.43	C6–C1	1.416(3)	1.44
C13–O3	1.356(3)	1.38	C14–C15	1.499(4)	1.51
Bond angles					
C1–C7–N1	125.2(2)	126.35	N1–C8–C13	117.6(2)	119.95
C7–N1–C8	126.2(2)	123.50	C3–C2–O1	121.5(2)	121.10
C1–C2–O1	122.3(2)	123.42	C3–O2–C14	116.6(2)	115.73
Torsion angles					
C1–C7–N1–C8	179.6(2)	−178.86			
C6–C1–C7–N1	179.9(2)	−179.40			
C7–N1–C8–C13	169.4(2)	153.88			
C3–O2–C14–C15	179.0(3)	−179.98			
C2–C3–O2–C14	−178.8(2)	−179.90			

C–O (1.362 and 1.222 Å, respectively) and C–N (1.339 and 1.279 Å, respectively) bond distances [21], it can be stated that the molecular structure of the compound is shifted slightly to the expected values for canonical NH (keto-amine) tautomer, when other geometrical parameters are considered as a whole. C1–C7 [1.402(3) Å], C3–C4 [1.362(3) Å] and C5–C6 [1.350(4) Å] bonds are of double bond character, whereas the C1–C2 [1.426(3) Å], C1–C6 [1.416(3) Å], C2–C3 [1.439(3) Å] and C4–C5 [1.411(4) Å] are of single bond character as are in canonical keto-amin tautomers. Similar tendencies are observed for other keto-amin tautomers [6–9]. The N1–H1 [0.93(2) Å] bond is somewhat longer than the distance observed in neutral N–H bonds (0.87 Å). These deformations in covalent topology of the compound can be explained by a possible through-resonance effect between canonical NH and zwitterionic forms of the compound [14, 22, 23]. The chelate ring atoms O1, C2, C1, C7, N1 and H1 are in the same plane and O2, C14 and C15 atoms in the ethoxy group are nearly coplanar with their parent ring. The molecule is not planar and the

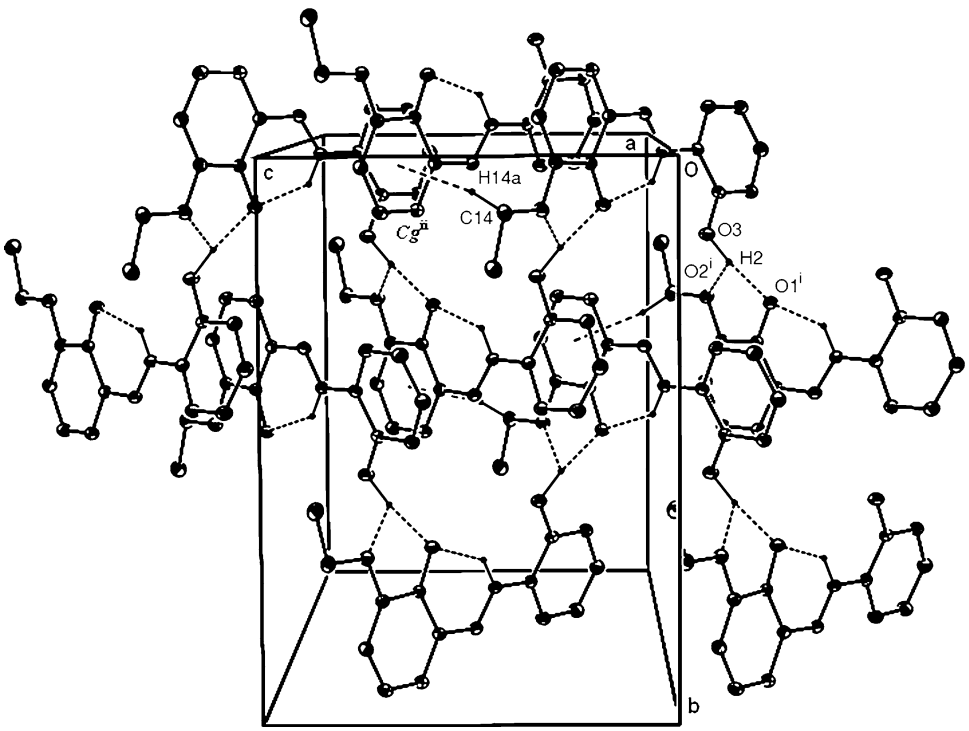

Fig. 3 Bifurcated H-bonds and weak C–H···π interaction in the unit cell. H atoms not involved in hydrogen bonds have been omitted for clarity

Table 3 Hydrogen bonding and weak C–H···π interaction geometries (Å, °) for the title compound

D–H···A	D–H	H···A	D···A	∠D–H···A
N1–H1···O1	0.93(2)	1.90(2)	2.649(2)	135.9(18)
O3–H2···O1^{i}	1.05(3)	1.63(3)	2.664(2)	166(3)
O3–H2···O2^{i}	1.05(3)	2.49(4)	3.106(2)	117(2)
C14–H14a···Cg^{ii}	1.03(3)	2.785	3.72	150.87

Note: D: donor, A: acceptor. Symmetry transformation used to generate equivalent atoms: (i) $-x + 3/2$, $-y + 1/2$, $z - 1/2$; (ii) x, $-y$, $z + 1/2$

dihedral angle between the mean planes through its six-membered rings is 11.2(1)°.

There are two noteworthy hydrogen bonds in the structure, one of which is relatively weak. Geometrical details of them are listed in Table 3. O3 atom acts as a donor to the bifurcated O–H···O type intermolecular H-bond formed by O3–H2···O1^{i} and O3–H2···O2^{i}. Bite angle of the bifurcation, O1^{i}–H2–O2^{i}, is 77.47°. The bifurcated intermolecular hydrogen bonds and intramolecular hydrogen bonds generate edgefussed $R_1^2(5)\,S(6)$ motif [24] (Fig. 3). In addition to hydrogen bonds, weak C14–H14a···π interaction involving the centroid of C1/C6 ring (Table 3) contributes to establish crystal packing arrangement.

The r.m.s. fit of the bond distances of the optimized geometry to its crystallographically observed counterpart is moderate and their r.m.s. deviation is 1.2602 Å. This result indicates that the molecular geometry in solid state cannot be regarded as canonical NH form of the title compound properly. Some conformational discrepancies are observed in Table 2. Both optimized and X-ray crystal structure of the compound is non-planar. While the dihedral angle between the rings is 11.2(1)° in crystal structure, it is 25.53° in the optimized geometry. Torsion angle C7–N1–C8–C13 [169.4(2)°] of the crystal structure is calculated as 153.88° in the optimized geometry (its heat of formation is −51.042 kcal/mol). The calculated molecular energy profile as a function of the selected torsional degree of freedom, T(C7–N1–C8–C13), is shown in Fig. 4. Molecular energy profile has a remarkable maximum at 0° besides two local maxima at −90° and +90° for the selected torsion angle, corresponding to perpendicular orientations of the rings. This behavior can be essentially based on the relative orientations of the rings in the molecule. The reason for that two local maxima have smaller potential barrier than that observed at 0̊ is also that steric hindrances between the substituted groups become less augmentative at −90° and +90° than the former.

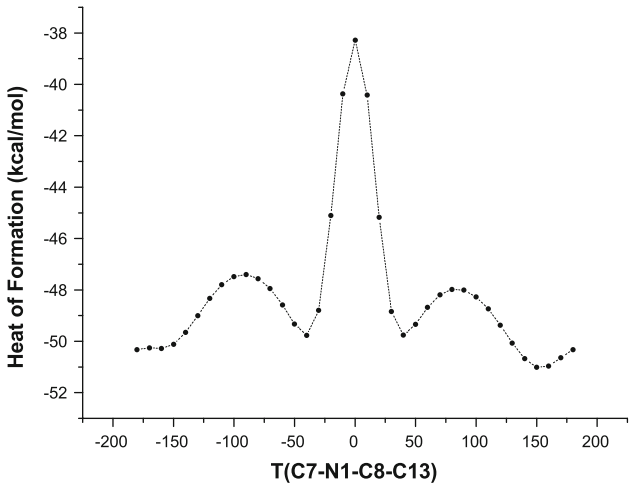

Fig. 4 Molecular energy profile against the selected torsional degree of freedom

In conclusion, although the title Schiff base compound has NH form, its crystallographically observed geometric parameters do not correspond to exact canonical keto-amin tautomer. This inference is in agreement with the statement that canonical keto-amin (or quinoidal) form of Salicylideneaniline derivatives cannot be observed exactly in solid state [23]. In addition, the selected torsion angle in the crystal structure of the compound is near to its value in the global minimum (optimized geometry) and the differences between them arise from inter- and intramolecular H-bonds and crystal packing interactions prescribed by the space group symmetry relations.

Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 641445. Copies of the data can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK (Fax: (+44) 1223 336–033; e-mail: data_request@ccdc.cam.ac.uk).

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