

Crystallographic and Conformational Analysis of [(*E*)-2-[(3-Chlorophenylimino)methyl]-4-methoxyphenol]

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Abstract The crystal structure of $C_{14}H_{12}ClNO_2$ was determined by X-ray analysis. It crystallizes in the triclinic space group Pc with $a = 12.5346(10)$ Å, $b = 4.5101(3)$ Å, $c = 12.0534(11)$ Å, $\alpha = 90.00^\circ$, $\beta = 113.669(6)^\circ$, $\gamma = 90.00^\circ$, $Z = 2$, $D_x = 1.393$ mg/m³, μ (MoK α) = 0.298 mm⁻¹. The title compound is photochromic and molecule is non-planar. It adopts a phenol–imine tautomeric form with a strong intramolecular O–H \cdots N hydrogen bond and a strong intermolecular C–H \cdots O hydrogen bond. Minimum energy conformations AM1 were calculated as a function of the three torsion angles θ_1 (C10–C9–N1–C8), θ_2 (C9–N1–C8–C1) and θ_3 (N1–C8–C1–C6), varied every 10°. As in the X-ray experiment results, molecule has an angle that makes it non-planar between two aromatic rings in AM1 optimized geometry.

Keywords Crystal structure · Schiff base · Phenol–imine · AM1 · Conformational analysis

Introduction

Most Schiff bases have antibacterial, anticancer, anti-inflammatory and antitoxic properties [1]. In addition to that, Schiff bases have been used widely as ligands in the field of coordination chemistry [2]. There are two characteristic

properties of Schiff bases which are photochromism and thermochromism [3, 4]. These properties are caused by proton transfer from hydroxyl O atom to the imine N atom [5, 6]. It has been proposed that molecules showing thermochromism are planar, while those showing photochromism are non-planar [7]. In general, o-hydroxy Schiff bases exhibit two possible tautomeric forms, the phenol–imine (or benzenoid) and keto–amine (or quinoid) forms. Depending on the tautomers, two types of intra-molecular hydrogen bonds are possible: O–H \cdots N in benzenoid and N–H \cdots O in quinoid tautomers. o-hydroxy Schiff bases have been previously observed in the keto form [8], in the phenol form [9] or in phenol/keto mixtures [10, 11].

Here we report the molecular and crystal structure of (*E*)-2-[(3-chlorophenylimino)methyl]-4-methoxyphenol (Fig. 1), determined by single crystal X-ray diffraction study, and the conformational analysis of the title molecule with respect to the selected torsion angles are achieved by AM1 semi-empirical quantum mechanical model.

Experimental

Synthesis of the Title Compound

The compound (*E*)-2-[(3-chlorophenylimino)methyl]-4-methoxyphenol was prepared by reflux a mixture of a solution containing 5-methoxysalicylaldehyde (0.5 g 3.3 mmol) in 20 mL ethanol and a solution containing 3-chloraniline (0.420 g 3.3 mmol) in 20 mL ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (*E*)-2-[(3-chlorophenylimino)methyl]-4-methoxyphenol suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield 82%; m.p. 346–347 K).

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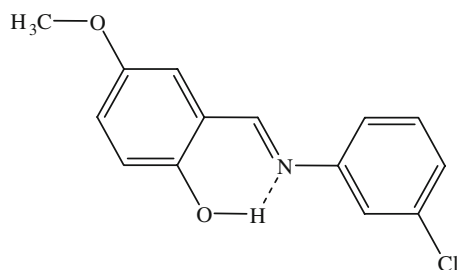


Fig. 1 Chemical diagram of the phenol-imine form for the title compound

X-ray Crystallography

A suitable sample of size $0.67 \times 0.43 \times 0.16$ mm was selected for the crystallographic study. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated MoK_α radiation and an STOE IPDS 2 diffractometer. A total of 8,238 reflections with $[3.39^\circ < \theta < 27.49^\circ]$ were collected in the rotation mode and cell parameters were determined by using X-AREA software [12]. Absorption correction ($\mu = 0.298 \text{ mm}^{-1}$) was achieved by the integration method via X-RED software [12]. The structure was solved by direct methods using SHELXS-97 [13]. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 212 crystallographic parameters. All non-hydrogen atom parameters were refined anisotropically and all H atom parameters were freely refined. The C–H distances are in the range $0.88(3)$ – $1.05(2)$ Å and Uiso(H) values are in the range $0.052(6)$ – $0.115(13)$ Å² [2].

In the crystal structure, there is a twin by inversion (racemic twin), as suggested by the value of the Flack (1983) parameter of $0.46(17)$. The structure was refined to $R_1 = 0.035$ for observed reflections which obeyed to the condition of $2,480 I > 2\sigma(I)$ and to $R_1 = 0.0970$ for all 2,848 data used in refinement process. The maximum peaks and deepest hole observed in the final $\Delta\rho$ map were 0.163 and -0.201 eÅ^{-3} , respectively. The scattering factors were taken from SHELXL-97 [13]. The data collection conditions and parameters of refinement process are listed in Table 1.

Computational Procedure

The geometry optimization of the molecule leading to energy minima was achieved by using AM1 semi-empirical quantum mechanical method [14] at the restricted Hartree-Fock (RHF) level [15] with the aid of WinMopac 7.21 package [16]. Calculation was started from the crystallographic coordinates of molecule. Non-Linear least

Table 1 Crystallographic data for the title compound

Color/shape	Brown/prism
Chemical formula	$\text{C}_{14}\text{H}_{12}\text{ClNO}_2$
Formula weight	261.70 akb
Temperature	296 K
Crystal system	Monoclinic
Space group	Pc
Unit cell parameters	$a = 12.5346(10)$ Å $b = 4.5101(3)$ Å $c = 12.0534(11)$ Å $\alpha = 90.00^\circ$ $\beta = 113.669(6)^\circ$ $\gamma = 90.00^\circ$
Volume	$624.09(9)$ Å ³
Z	2
Density	1.393 Mg m^{-3}
Absorption coefficient	0.298 mm^{-1}
T_{\min} , T_{\max}	0.8367, 0.9516
Diffractometer/meas. meth.	STOE IPDS 2/ ω -scan
θ range for data collection	3.39 , 27.49°
Reflections read	8,238
Unique reflections	5,464
Data in refinement/restraints/parameters	2,848/2/212
Data with $I > 2\sigma(I)$	2,848
Goodness of fit on F^2	1.041
R factor	0.0350
Weighted R factor	0.0970
Flack parameter	$0.46(17)$

squares (NLLSQ) gradient minimization routine was used in the optimization procedure. To elucidate conformational flexibility of the title molecule, the selected torsion angles $\theta_1(\text{C}10\text{--C}9\text{--N}1\text{--C}8)$, $\theta_2(\text{C}9\text{--N}1\text{--C}8\text{--C}1)$ and $\theta_3(\text{N}1\text{--C}8\text{--C}1\text{--C}6)$ are varied from 0° to 360° in every 10° and the molecular energies were calculated as a function of each θ , keeping the other θ values constant thus molecular energy profiles are obtained by performing single point calculations on the calculated potential energy surface. It is well known that the AM1 and similar calculations underestimate like inter- and intramolecular hydrogen bond interactions. That is why, somewhat differences were observed between X-ray experimental study and AM1 semi-empirical calculation results of bond distance, angle and torsion angle values.

Results and Discussion

An ORTEP-3 plot [17] with the atom-numbering scheme of the title compound is shown in Fig. 2. Comparative results obtained from the X-ray crystallographic and

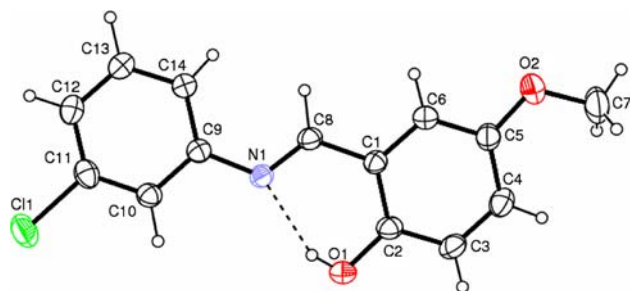


Fig. 2 An ORTEP view of the title compound with the atomic numbering scheme. Dashed line shows intramolecular hydrogen bond. Displacement ellipsoids are shown at the 30% probability level

computational studies of bond distances, angles and torsion angles are presented in Table 2.

In the title compound, the phenol–imine tautomer is favoured over the keto–amine form, as indicated by the C2–O1, C8–N1, C1–C8 and C1–C2 bond lengths (Fig. 2 and Table 2). A similar work was observed for N-(2,5-methylphenyl)salicylalimine (C–O = 1.346(3) Å, C–N = 1.276(2) Å) [18]. The H atom in the title compound is located on atom O1, thus confirming a preference for the phenol–imine tautomer in the solid state. The C2–O1 bond length indicate single-bond character, whereas the C8–N1 bond length is indicative of significant double-bond character.

The dihedral angle between the C1–C6 and C9–C14 rings is 6.14(1)°. Against this background we can say that the compound is non-planar and displays photochromic

Table 2 Comparative results of the selected bond lengths (Å), bond and torsion angles (°)

	X-ray	AM1
Bond lengths		
C8–N1	1.278(2)	1.292
C2–O1	1.351(2)	1.368
C1–C8	1.451(2)	1.466
C1–C2	1.405(2)	1.408
N1–C9	1.414(2)	1.4106
C5–O2	1.361(3)	1.385
Bond angles		
C6–C5–O2	115.69(18)	114.851
C6–C1–C8	118.84(15)	116.139
C9–N1–C8	120.51(13)	121.685
C14–C9–N1	124.55(16)	123.373
N1–C8–C1	122.70(14)	123.804
C1–C2–O1	121.39(17)	125.819
Torsion angles		
C10–C9–N1–C8	−173.45(15)°	−148.696°
C9–N1–C8–C1	−179.20(17)°	−179.091°
N1–C8–C1–C6	178.12(17)°	−177.946°

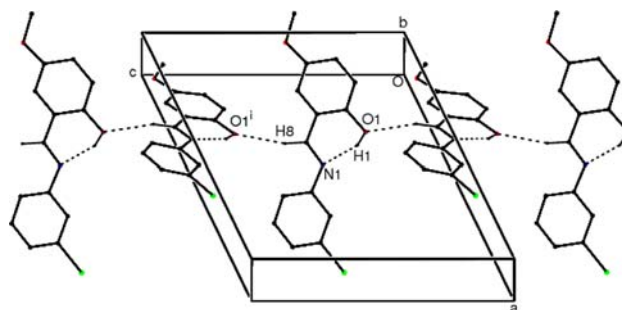


Fig. 3 A partial packing view of the title compound shows the formation of the C(5) chain through C–H...O hydrogen bonds. H atoms are represented as small spheres of arbitrary radii and H atoms not involved in hydrogen bonding have been omitted for clarity [symmetry code: (i) $x, 1-y, z + 1/2$]

Table 3 Hydrogen bonding geometry (Å, °) for the title compound

D–H...A	D–H	H...A	D...A	D–H...A
O1–H1...N1	0.75 (4)	1.95 (4)	2.633 (2)	152 (4)
C8–H8...O1 ⁱ	1.01 (2)	2.494 (2)	3.382 (3)	145.98 (2)

Note: D donor, A acceptor. Symmetry code: (i) $x, 1-y, z + 1/2$

features. As is a common feature of o-hydroxysalicylidene systems, title compound displays a strong intramolecular hydrogen bond between atoms N1 and O1 [19, 20], and this O1–H1...N1 hydrogen bond generates an S(6) ring motif [21]. The crystal structure has a strong intermolecular C–H...O hydrogen bond. The occurrence of C–H...O hydrogen bond results in the formation of C(5) chains developing parallel to the c axis [22] (Fig. 3). Geometrical parameters of the intra- and inter-molecular H-bonds are listed in Table 3.

In order to define the conformational flexibility of compound, semi-empirical calculations using the AM1

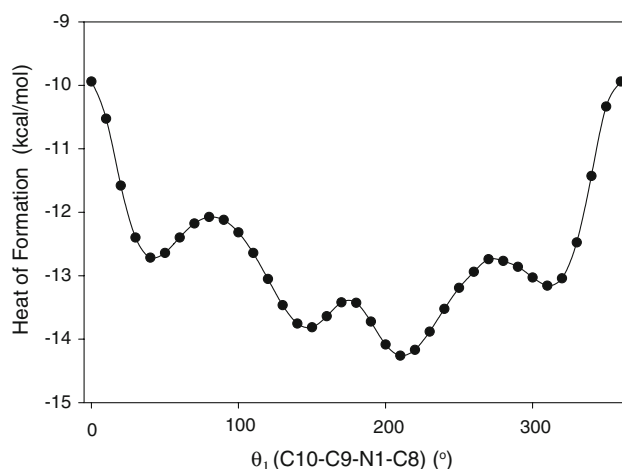


Fig. 4 Molecular energy profile against the selected torsional degree θ_1 of freedom

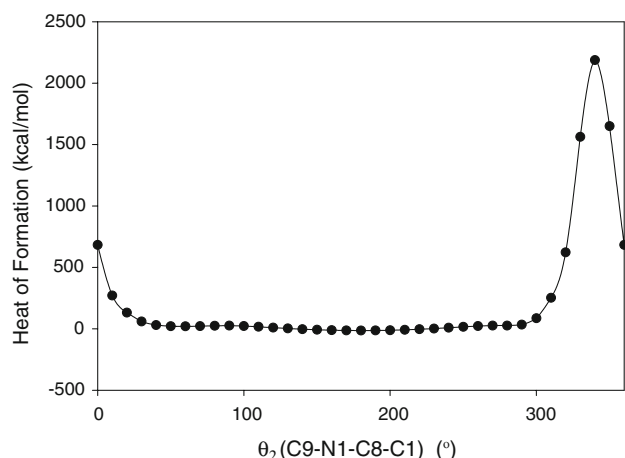


Fig. 5 Molecular energy profile against the selected torsional degree θ_2 of freedom

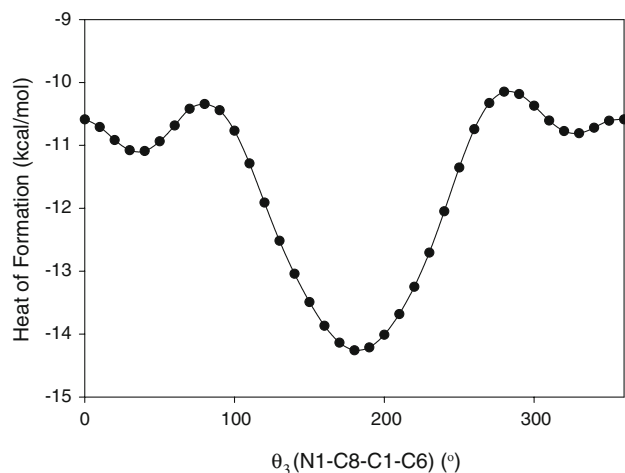


Fig. 6 Molecular energy profile against the selected torsional degree θ_3 of freedom

molecular orbital method were carried out. The calculated molecular energy profiles of the molecule against the selected torsional degrees of freedom are shown in Figs. 4–6. The energy profiles show that the most stable conformation is determined by non-bonded hydrogen-hydrogen repulsions. Some discrepancies between the molecular conformations of the AM1 optimized structure (its heat of formation is -14.263 kcal/mol) and the X-ray structure are observed. According to X-ray crystallographic study $\theta_1(\text{C}10\text{--C}9\text{--N}1\text{--C}8)$, $\theta_2(\text{C}9\text{--N}1\text{--C}8\text{--C}1)$ and $\theta_3(\text{N}1\text{--C}8\text{--C}1\text{--C}6)$ torsion angles are $-173.45(15)^\circ$, $-179.20(17)^\circ$ and $178.12(17)^\circ$, same torsion angles are obtained as -148.696° , -179.091° and -177.946° in the AM1 optimized geometry of the title compound, respectively.

The energy profile as a function of $\theta_1(\text{C}10\text{--C}9\text{--N}1\text{--C}8)$ shows two maxima at 0° and 360° and a minima at near 210° (Fig. 4). The energy profile as a function of

$\theta_2(\text{C}9\text{--N}1\text{--C}8\text{--C}1)$ has an energy barrier at near 340° because of steric interaction between $\text{H}(\text{C}14)$ and $\text{H}(\text{O}1)$. There is a considerable energy difference (approximately $2,200$ kcal/mol) between heat of formation values of the most favorable and unfavorable conformer of the title compound according to Fig. 5. This energy profile shows that the *cis*-isomer around the $\text{N}1\text{--C}8$ double bond is required great amount of energy, and corresponding to unfavorable conformer. The energy profile as a function of $\theta_3(\text{N}1\text{--C}8\text{--C}1\text{--C}6)$ shows two maxima at 80° and 280° and a minima at near 180° (see Fig. 6).

The planarity of molecule is controlled by θ_1 , θ_2 and θ_3 torsion angles. The AM1 optimized geometry of the crystal structure of title compound corresponding to non-planar conformation is the most stable conformation which agrees with the result obtained from X-ray investigation. According to Bürgi and Dunitz [23] the non-planarity of *N*-benzylideneaniline and related compounds caused by two principal factors: (a) the interaction of the ortho hydrogen on the aniline ring and the hydrogen on the bridge carbon is repulsive in the planar conformation but reduced with increasing nonplanarity, (b) the π -electron system, itself divisible into two components, including, on the one hand, delocalisation between the --HC=N-- double bond and the aniline phenyl ring and, on the other hand, delocalisation of the nitrogen lone pair electron of electrons into the aniline ring which is essentially zero for the planar conformation but increases with increasing non-planarity. Consequently, the most stable conformation is primarily determined by non-bonded hydrogen–hydrogen repulsions.

Supplementary Material

CCDC 653301 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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References

1. Williams DR (1972) Chem Rev 72:203. doi:[10.1021/cr60277a001](https://doi.org/10.1021/cr60277a001)
2. Calligaris M, Nardin GMJ, Randaccio C (1972) Coord Chem 7:385. doi:[10.1016/S0010-8545\(00\)80018-1](https://doi.org/10.1016/S0010-8545(00)80018-1)
3. Cohen MD, Schmidt GMJ, Flavian J (1964) J Chem Soc 2041. doi:[10.1039/jr9640002041](https://doi.org/10.1039/jr9640002041)

4. Moustakali-Mavridis I, Hadjous E, Mavridis A (1978) *Acta Crystallogr B* 34:3709
5. Hadjoudis E, Vitterakis M, Mavridis IM (1987) *Tetrahedron* 43:1345. doi:[10.1016/S0040-4020\(01\)90255-8](https://doi.org/10.1016/S0040-4020(01)90255-8)
6. Xu X-X, You X-Z, Sun Z-F, Wang X, Liu H-X (1994) *Acta Crystallogr C* 50:1169
7. Moustakali-Mavridis I, Hadjoudis E, Mavridis A (1980) *Acta Crystallogr B* 36:1126
8. Koşar B, Albayrak Ç, Odabaşoğlu M, Büyükgüngör O (2005) *Acta Crystallogr E* 61:o1097
9. Karadayı N, Gözüyeşil S, Güzel B, Kazak C, Büyükgüngör O (2005) *Acta Crystallogr E* 59:o851
10. Nazır H, Yıldız M, Yılmaz H, Tahir MN, Ülkü D (2000) *J Mol Struct* 524:241. doi:[10.1016/S0022-2860\(00\)00393-8](https://doi.org/10.1016/S0022-2860(00)00393-8)
11. Antanov L, Fabian WMF, Nedeltcheva D, Kamounah FS (2000) *J Chem Soc Perkin Trans 2*:1173. doi:[10.1039/b000798f](https://doi.org/10.1039/b000798f)
12. Stoe & Cie X-Area (Version 1.18) and X-RED32 (Version 1.04), Darmstadt, Germany, 2002
13. Sheldrick GM (1997) SHELXS 97 and SHELXL 97, program for crystal structure solution and refinement. University of Göttingen, Germany
14. Dewar MJS, Dieter KM (1986) *J Am Chem Soc* 108:8075. doi:[10.1021/ja00285a033](https://doi.org/10.1021/ja00285a033)
15. Roothaan CC (1951) *J Rev Mod Phys* 23:69. doi:[10.1103/RevModPhys.23.69](https://doi.org/10.1103/RevModPhys.23.69)
16. Shchepin R, Litvinov D (1998) WinMopac 7.21, Program for semi-empirical calculations. Perm State University, Perm, Russia
17. Farrugia LJ (1998) ORTEP-3 for Windows. Dept. of Chemistry, University of Glasgow, UK
18. Elmalı A, Elerman Y, Zeyrek CT (1998) *J Mol Struct* 443:123. doi:[10.1016/S0022-2860\(97\)00382-7](https://doi.org/10.1016/S0022-2860(97)00382-7)
19. Filarowski A, Koll A, Glowiake T (2003) *J Mol Struct* 644:187. doi:[10.1016/S0022-2860\(02\)00489-1](https://doi.org/10.1016/S0022-2860(02)00489-1)
20. Kabak M, Elmalı A, Elerman Y, Svoboda I (2003) *Z Naturforsch* 58b:1141
21. Temel E, Albayrak Ç, Büyükgüngör O, Odabaşoğlu M (2006) *Acta Crystallogr E* 62:o4484
22. Özek A, Albayrak Ç, Odabaşoğlu M, Büyükgüngör O (2007) *Acta Crystallogr C* 63:o177
23. Bürgi HB, Dunitz JD (1971) *Helv Chim Acta* 54:1255. doi:[10.1002/hlca.19710540504](https://doi.org/10.1002/hlca.19710540504)