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ORIGINAL PAPER

Experimental and Semi-Empirical and DFT Calculational Studies on (*E*)-2-[(2,4-Dichlorophenylimino) methyl]-*p*-cresol

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Abstract The molecular and crystal structure of the title compound, $C_{14}H_{11}Cl_2NO$, has been determined by X-ray single crystal diffraction technique. The compound crystallizes in the orthorhombic, space group *Pbca* with unit cell dimensions $a = 7.5537(10)$ Å, $b = 11.5518(13)$ Å, $c = 29.760(4)$ Å, $M_r = 280.14$, $V = 2596.8(6)$ Å^3, $Z = 8$, $R_1 = 0.065$ and $wR_2 = 0.191$. The title compound exists in the enol–imine tautomeric form with a strong intramolecular O–H···N hydrogen bond. The dihedral angle between the two benzene rings is 37.66(15)°. The asymmetric unit in the crystal structure contains only one neutral molecule. Calculational studies were performed by using AM1, PM3, PM6 semi-empirical and DFT methods. Geometry optimizations of compound have been carried out by using three semi-empirical methods and DFT method and bond lengths, bond and torsion angles of title compound have been determined. Dipole moments (Debye) and the energy parameters of compound (kcal/mol) were calculated by using above mentioned calculation methods. Atomic charge distribution has been obtained from AM1, PM3, PM6 and DFT. In order to determine conformational flexibility on the molecule, molecular energy profile of the title compound was obtained with respect to the selected torsion angle T(N1–C7–C1–C2), which is varied from −180° to +180° in every 10 via PM3 semi-empirical method.

Keywords Crystal structure · Schiff-base · AM1 · PM3 · PM6 · DFT

Introduction

Schiff-bases are N-substitute imines obtained by the reaction of ketone and aldehyde. They have been extensively used as ligands in the field of coordination chemistry [1, 2]. Schiff-bases are more stable if there is the alkyl group on the nitrogen instead of aryl group [3]. Schiff-base compounds can be classified by their photochromic and thermochromic characteristics [4–6]. In studies based on some thermochromic and Schiff-base compound, it has been proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar [5].

The Schiff-base compounds are studied widely because they have biological importance. Schiff-base complexes of amino acids play an important role in reactions of biological interest [7, 8]. Schiff-bases derived from amino acids show antitumor activities [9, 10]. Aromatic acid hydrazides and their Schiff-bases inhibit the growth of tuberculosis mycobacteria [11]. Some Schiff-base complexes show antifungal activity, which is increased by the presence of hydroxyl groups in the ligand [12]. Investigation of structural stability of compounds by both experimental techniques and theoretical methods has been of great interest. Functional material design, theoretical modeling of drug design and so on, has become possible as results of the development of the computational techniques. Many important properties such as molecular orbitals, electrostatic potentials, dipole

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moment, reaction pathways, vibrational frequencies can be predicted by various computational techniques [13].

In this paper, crystal structure of title compound, (*E*)-2-[(2,4-Dichlorophenylimino)methyl]-*p*-cresol ($C_{14}H_{11}Cl_2NO$), was obtained by single crystal X-ray diffraction technique. Calculations were performed by using AM1, PM3, PM6 semi-empirical and DFT methods. Total energy, binding energy, electronic energy, nuclear energy (kcal/mol) and dipole moments (Debye) were calculated by using three semi-empirical methods. Bond lengths, bond angles, torsion angles and atomic charge distributions were calculated by three semi-empirical methods and DFT method. In order to provide templates for molecular modeling studies, experimental results obtained from X-ray crystallography and those from AM1, PM3, PM6 semi-empirical methods and DFT method were compared. Investigation the conformational flexibility of title compound was defined as a function of the selected torsion angle T(N1–C7–C1–C2).

Experimental and Computational Methods

Synthesis of the Compound

The compound, (*E*)-2-[(2,4-Dichlorophenylimino) methyl] -*p*-cresol, was prepared by reflux a mixture of a solution containing 5-methylsalicylaldehyde (0.05 g 0.37 mmol) in 20 mL ethanol and a solution containing 2,4-dichloroaniline (0.059 g 0.37 mmol) in 20 mL ethanol. The reaction mixture was stirred for 1 h under heating at reflux. The crystals of (*E*)-2-[(2,4-Dichlorophenylimino) methyl]-*p*-cresol suitable for X-ray analysis were obtained from ethyl alcohol by slow evaporation (yield % 34; m.p. 403–405 K). Chemical diagram of the title compound is shown in Scheme 1.

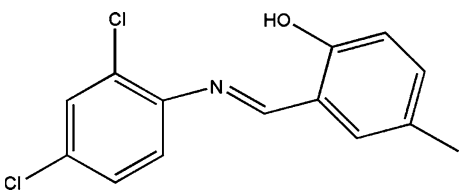
X-ray Single Crystal Structure Determination

A yellow crystal of the compound with dimensions of 0.67 mm × 0.28 mm × 0.08 mm was mounted on goniometer of a STOE IPDS II diffractometer. Measurements were performed at room temperature (296(2) K) using graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The systematic absences and intensity symmetries indicated the orthorhombic *Pbca* space group. A total of 8868 reflection (981 unique) within the θ range of [$1.8° < \theta < 26.0°$] were collected in the rotation mode with $R_{int} = 0.131$. Cell parameters were determined by using X-AREA software [14]. The intensities collected were corrected for Lorentz and polarization factors, absorption correction ($\mu = 0.49$ mm^{-1}) by integration method via X-RED32 software [14]. Extinction correction was not applied. The structure was solved by direct methods using SHELXS-97 [15]. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The scattering factors were taken from SHELXL-97 [15]. All H atoms were placed in calculated positions and constrained to ride on their parent atoms, with O–H = 0.82 Å, C–H = 0.93 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$, and C–H = 0.96 Å and $U_{iso}(H) = 1.5\ U_{eq}$ (methyl C).

Molecular graphic was drawn by using ORTEPIII for Windows [16]. WinGX software was used to prepare material for publication [17]. A summary of crystallographic data and details of the structure refinement is listed in Table 1.

Computational Methods

Calculations performed by using AM1, PM3 and DFT methods are carried out with the GAUSSIAN03 program package [18] and PM6 calculations were performed Win-MOPAC2007 (Version: 8.089W) program package (www.openmopac.net). The initial molecular structure obtained from the X-ray study was used for the calculations without any symmetry constraints. The geometry optimizations of the title compound leading to energy minima in vacuo was achieved by using AM1, PM3 and PM6 semi-empirical methods and DFT ab initio method. DFT calculations are performed using B3LYP level for geometry optimization. 6-31G basic set was used for the title compound. Molecular energy profile versus selected torsion angle T (N1–C7–C1–C2) was obtained by single point calculations on the computed potential energy surface. Torsion angle was varied from −180° to +180° in steps of 10° to clarify conformational flexibility of compound.



Scheme1 Chemical diagram of (*E*)-2-[(2,4-Dichlorophenylimino) methyl]-*p*-cresol ($C_{14}H_{11}Cl_2NO$)

Results and Discussion

Structure Description of the Compound

The title compound crystallizes in the orthorhombic *Pbca* space group in the unit cell. The displacement ellipsoid

Table 1 Crystallographic data for the title compound

Crystal data	
Chemical formula	$C_{14}H_{11}Cl_2NO$
Crystal shape/color	Prism/yellow
Formula weight	280.14
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell parameters	$a = 7.5537(10)$ Å
	$b = 11.5518(13)$ Å
	$c = 29.760(4)$ Å
Volume	2596.8(6) Å^3
Z	8
D_x (Mg cm^{-3})	1.433
μ (mm^{-1})	0.49
F_{000}	1152
Crystal size (mm^3)	0.67 × 0.28 × 0.08
Data collection	
Diffractometer/meas. meth	STOE IPDS II/*w*-scan
Absorption correction	Integration
T_{min}	0.903
T_{max}	0.966
No. of measured, independent and observed reflections	8868, 2506, 981
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.131
θ_{max}	26
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, wR, S	0.065, 0.191, 0.87
No. of reflection	2506
No. of parameters	164
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0843P)^2]$
	$P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.22

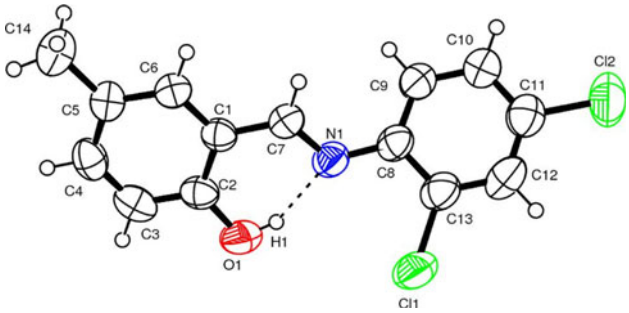


Fig. 1 The molecular structure of compound with the atom-numbering scheme, showing the intramolecular O–H···N hydrogen bond (*dashed line*). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as *small spheres* of arbitrary radii

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	x	y	z	U_{eq} [a]
C1	0.4118(6)	0.5948(3)	0.23174(17)	0.0523(11)
C2	0.3403(6)	0.4823(3)	0.2322(2)	0.0589(13)
C3	0.3016(6)	0.4319(4)	0.2733(2)	0.0689(15)
C4	0.3378(7)	0.4897(4)	0.3131(2)	0.0664(15)
C5	0.4108(6)	0.6006(4)	0.31323(17)	0.0580(12)
C6	0.4485(6)	0.6499(4)	0.27198(17)	0.0588(12)
C7	0.4506(6)	0.6509(4)	0.18961(17)	0.0556(12)
C8	0.4619(7)	0.6645(4)	0.11139(17)	0.0593(13)
C9	0.4327(8)	0.7828(4)	0.10604(18)	0.0699(14)
C10	0.4709(8)	0.8372(4)	0.06592(19)	0.0772(16)
C11	0.5378(8)	0.7745(5)	0.0306(2)	0.0763(16)
C12	0.5661(7)	0.6575(5)	0.03428(19)	0.0764(15)
C13	0.5247(7)	0.6026(4)	0.0743(2)	0.0712(15)
C14	0.4487(8)	0.6610(5)	0.35700(19)	0.0846(16)
Cl1	0.5555(3)	0.45487(11)	0.07856(5)	0.1027(7)
Cl2	0.5821(3)	0.84116(15)	−0.02021(6)	0.1105(7)
N1	0.4226(6)	0.6046(3)	0.15102(15)	0.0617(11)
O1	0.3085(5)	0.4216(3)	0.19407(13)	0.0766(11)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

plots with the numbering scheme for the title compound are shown in Fig. 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Hydrogen bond geometries, experimental and calculated bond lengths, bond and selected torsion angles are given Tables 3, 4, 5 and 6, respectively.

There are two possible types of intramoleculer hydrogen bonds in Schiff-bases, namely keto-amine (N–H···O) and enol–imine (N···H–O) tautomeric forms. The present X-ray investigation shows that the title compound prefers the enol–imine tautomeric form rather than the keto-amine tautomeric form. The C2–O1 (1.355(6) Å) and C7–N1 (1.284(6) Å) bond lengths given in Table 4 verify the enol–imine tautomeric form. These distances agree with literature (1.352(3) and 1.280(4) Å, respectively) which also shows the enol–imine tautomeric form [5]. In addition, C7–N1 bond length found as 1.284(6) Å is remarkably different from C–N bond lengths, which reflect their single bond character, obtained previous studies in the literature [19–21]. This value obviously indicates its double bond character. In the title compound with only one O–H···N type intramolecular hydrogen bond, the distance between donor and acceptor in O1–H1···N1 hydrogen bond is 2.618(5) Å and the angle of D–H···A is 142°. An intramolecular O–H···N hydrogen bond generates S(6) ring motif. C11–Cl2 and C13–Cl1 bond lengths are 1.730(6)

Table 3 Hydrogen-bond geometry (Å°)

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1···N1	0.82	1.92	2.618(5)	142

D donor, *A* acceptor

Table 4 Experimental and calculated bond lengths (Å)

	Experimental	AM1	PM3	PM6	DFT
C1–C2	1.407(6)	1.4086	1.4158	1.4069	1.4258
C1–C7	1.441(6)	1.4639	1.4582	1.4413	1.4426
C2–O1	1.355(6)	1.3651	1.3537	1.3550	1.3618
C2–C3	1.388(8)	1.4153	1.4098	1.3877	1.4022
C3–C4	1.385(8)	1.3824	1.3816	1.3854	1.3913
C3–H3	0.9300	1.1003	1.0961	0.9300	1.0833
C4–C5	1.394(7)	1.4059	1.4022	1.3944	1.4139
C4–H4	0.9300	1.1013	1.0965	0.9300	1.0862
C5–C6	1.383(7)	1.3903	1.3875	1.3830	1.3936
C5–C14	1.506(7)	1.4808	1.4861	1.5056	1.5140
C6–H6	0.9300	1.1021	1.0975	0.9300	1.0881
C7–N1	1.284(6)	1.2926	1.3015	1.2843	1.3063
C7–H7	0.9300	1.1163	1.1031	0.9300	1.0963
C8–C9	1.394(6)	1.4124	1.4007	1.3943	1.4110
C9–C10	1.379(7)	1.3895	1.3883	1.3795	1.3954
C9–H9	0.9300	1.1018	1.0971	0.9300	1.0844
C10–C11	1.373(7)	1.3977	1.3937	1.3727	1.3931
C10–H10	0.9300	1.1011	1.0960	0.9300	1.0827
C11–C12	1.373(7)	1.3964	1.3917	1.3727	1.3937
C11–Cl2	1.730(6)	1.6980	1.6835	1.7295	1.8213
C12–C13	1.386(7)	1.3961	1.3925	1.3856	1.3919
C12–H12	0.9300	1.1024	1.0918	0.9300	1.0815
C13–Cl1	1.727(5)	1.6979	1.6804	1.7268	1.8149
C14–H14A	0.9600	1.1175	1.0981	0.9600	1.0973
C14–H14B	0.9600	1.1188	1.0984	0.9600	1.0945
C14–H14C	0.9600	1.1186	1.0985	0.9600	1.0974
O1–H1	0.8200	0.9720	0.9675	0.8200	1.0111

and 1.727(5) Å, respectively. These values agree with C–Cl bond lengths reported in the literature [22]. In the title compound, the benzene rings are not coplanar with the dihedral angle of 37.66(15)° between them (Fig. 2).

Optimized Geometry

Geometry optimization for title compound was performed by using AM1, PM3, PM6 semi-empirical methods and DFT method. The structural parameters were determined for title compound and then these values are tabulated in Tables 4, 5 and 6. Dipole moments and energy parameters of the optimized title compound calculated by AM1, PM3 and PM6 semi-empirical methods are listed in Table 7.

Table 5 Experimental and calculated bond angles (°)

	Experimental	AM1	PM3	PM6	DFT
C2–C1–C7	120.1(5)	125.1	123.0	120.1	121.0
O1–C2–C1	122.6(5)	126.0	124.0	122.6	121.8
C3–C2–C1	118.5(5)	120.1	120.0	118.5	119.3
C4–C3–C2	120.6(4)	120.2	119.8	120.6	120.1
C2–C3–H3	119.7	118.5	119.7	119.7	118.2
C3–C4–C5	121.6(5)	120.6	120.7	121.6	122.0
C3–C4–H4	119.2	119.8	119.7	119.2	119.1
C6–C5–C4	117.2(5)	119.1	119.6	117.2	117.6
C4–C5–C14	120.3(5)	120.6	120.6	120.3	121.1
C5–C6–H6	118.8	119.1	119.4	118.8	119.6
N1–C7–C1	123.9(4)	123.6	119.4	123.9	122.0
C1–C7–H7	118.1	113.6	117.4	118.1	117.0
C10–C9–C8	120.8(5)	121.2	120.0	120.8	121.5
C8–C9–H9	119.6	119.7	120.5	119.6	119.1
C11–C10–C9	120.0(5)	119.8	119.7	120.0	118.8
C9–C10–H10	120.0	120.0	120.5	120.0	120.7
C12–C11–C10	121.1(5)	120.4	121.1	121.0	121.7
C10–C11–Cl2	120.4(4)	119.9	119.5	120.4	119.4
C11–C12–C13	118.9(5)	119.8	119.3	118.9	118.4
C11–C12–H12	120.5	120.3	120.5	120.5	121.1
C12–C13–Cl1	119.0(4)	118.3	119.0	119.0	118.1
C5–C14–H14A	109.5	111.2	112.2	109.5	111.1
C5–C14–H14B	109.5	110.3	110.9	109.5	111.6
C5–C14–H14C	109.5	110.5	111.0	109.5	111.7
C2–O1–H1	109.5	110.3	108.1	109.5	109.3

Table 6 Experimental and calculated torsion angles (°)

	Experimental	AM1	PM3	PM6	DFT
C7–C1–C2–C3	−178.8(4)	179.6	−179.6	−178.8	−179.7
C1–C2–C3–C4	−1.9(7)	−0.2	−0.4	−1.9	−0.1
C2–C3–C4–C5	1.1(8)	0.02	−0.013	1.1	−0.1
C3–C4–C5–C6	−1.0(7)	0.2	0.2	−1.0	−0.1
C3–C4–C5–C14	180.0(5)	−179.6	−179.7	−180.0	−179.8
C2–C1–C7–N1	0.5(7)	0.2	0.5	0.5	0.1
C8–C9–C10–C11	0.2(9)	−0.5	−0.1	0.2	0.2
C9–C10–C11–C12	0.7(9)	0.2	0.6	0.7	0.4
C10–C11–C12–C13	178.7(5)	−179.9	−179.5	178.7	−0.2
C11–C12–C13–Cl1	0.5(9)	0.1	−0.2	0.5	0.5
C11–C12–C13–Cl1	178.5(4)	−179.6	179.7	178.5	−179.8

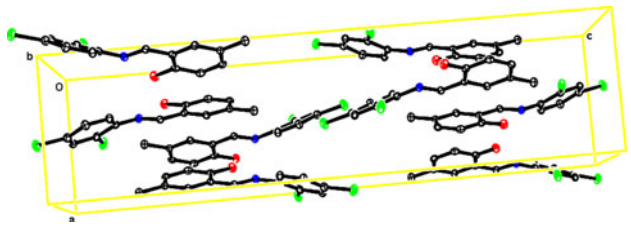


Fig. 2 Packing diagram of the title compound. Hydrogen atoms were omitted for clarity

The experimental and calculated bond lengths, bond and torsion angles have been compared by four theoretical methods (Tables 4, 5 and 6). Most of the calculated bond lengths are slightly longer than experimental bond lengths due to the fact that experimental results are based on the molecules in the solid state while theoretical calculations are based on the isolated molecules in the gaseous phase [23]. As seen in Table 4, the values calculated by PM6 method are more realistic than those of the others. The biggest deviations of calculated values are 0.1863 Å (C7–H7) for AM1 method, 0.1731 Å (C7–H7) for PM3 method, −0.0005 Å (C11–Cl2) for PM6 method and 0.1911 Å (O1–H1) for DFT method. The smallest deviations of calculated values are 0.0016 Å (C1–C2) for AM1 method, −0.0013 Å (C2–O1) for PM3 method, 0.0000 Å (C2–O1, C3–H3, C4–H4, C5–C6, C6–H6, C7–H7, C9–H9, C10–H10, C12–H12, C14–H14A, C14–H14B, C14–H14C and O1–H1) for PM6 method and 0.0016 Å (C1–C7) for DFT methods. As seen in Table 4, the values calculated by PM6 method are fairly closer to experimental bond lengths and also 13 of values are equal.

Compared to experimental and calculated bond angles, the biggest deviations are 5.0° (C2–C1–C7) for AM1, −4.5° (N1–C7–C1) for PM3 and 2.2° (C5–C14–H14C) for DFT methods. As seen in Table 5, values calculated by PM6 method are equal to experimental values. The smallest deviations of calculated values are 0.0° (C9–C10–H10) for AM1, 0.0° (C12–C13–Cl1) for PM3 and −0.1° (C3–C4–H4) for DFT method. It can be seen from Table 5, that the values calculated by PM6 method quite agree with experimental bond angles (with 0.1 error bar).

The best agreement between experimental and theoretical values was obtained by PM6 method (Table 6). Calculated torsion angles by PM6 are agree perfectly with experimental values.

Table 7 shows energy parameters and dipole moments of the optimized title compound obtained by three semi-empirical methods. Total energy of the system expresses all of probable interactions between whole electrons and nucleus in the system and it is negative. As seen in Table 7, total energy is sum of electronic energy and nuclear energy.

The title compound was optimized by AM1, PM3, PM6 and DFT. As can be seen in Tables 4, 5 and 6, the best approximation was obtained by PM6 method. The diagram of the title compound obtained by optimized geometry from PM3 is given Fig. 3 because such a diagram was not obtained from PM6 method.

Atomic Charge Analysis

The calculated Mülliken atom charges by using AM1, PM3, PM6 and DFT methods for the compound are given in Table 8. As considering the atomic charges in compound given in Table 8 it is revealed that atomic charge redistribution occurs on all of the atoms. The optimized geometries given in Tables 4, 5 and 6 indicate that the best approximation with the crystal structure was obtained by PM6 method. For this reason, the atomic charges calculated by PM6 were considered for analysis of the atomic charge distributions. The termination of the hydroxyl (net charge is −0.0937) and the chloro-groups (−0.0449 and −0.0758) of the compound show negative electronic character. The methyl group (net charge is 0.0122) shows positive character. The dipole moment calculated by PM6 of compound is 4.105 Debye.

Conformational Analysis

Conformational analysis of the title compound was carried out as a function of the selected torsion T (N1–C7–C1–C2) by using PM3 method. The most unfavorable and favourable conformer were determined. The calculated energy profiles from PM3 versus the torsion angle T (N1–C7–C1–C2) is given in Fig. 4. According to X-ray study, torsion angle T

Table 7 The optimized calculated parameters of title compound

	AM1	PM3	PM6
Total energy (kcal/mol)	−74207.883	−67268.070	−65564.315
Binding energy (kcal/mol)	−3187.290	−3196.106	–
Electronic energy (kcal/mol)	−414118.410	−406690.688	−408445.685
Core–core interaction (kcal/mol)	339910.527	339422.625	342881.000
Molecular point group	C1	C1	C1
Total dipole (debye)	3.202	4.012	4.107

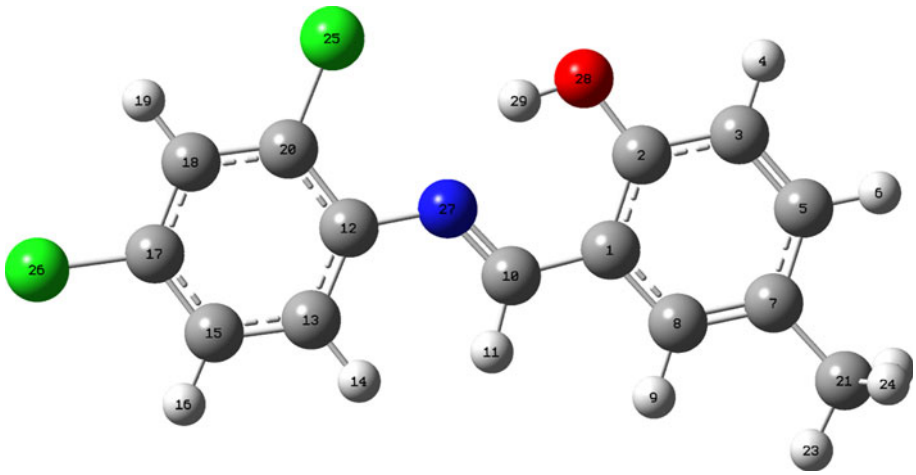


Fig. 3 The diagram of the title compound obtained by optimized geometry from PM3

(N1–C7–C1–C2) is obtained as 0.5°. This torsion angle is calculated as 0.5° from both PM3 and PM6. In Fig. 4, variation of heat of formation versus torsion angle has two maximum and one minimum value. The minimum value of the heat of formation values is corresponding to torsion angle in vicinity of 0° and this value agrees well with results obtained by experimental value. Two maximum values are in vicinity of −100° and 90°, respectively. It can be stated that these maxima arise due to a strong intramolecular O–H···N hydrogen bond containing the compound. Because, there is no remarkable steric hindrance during the rotations around the selected torsion angle T(N1–C7–C1–C2). The heats of formation are 0.00910 Hartree for −100°, 0.00023 Hartree for 0° and 0.00893 Hartree for 90°. The energy differences between maximum and minimum values are 0.00887 and 0.00870 Hartree, respectively. These values are approximately 40 times of minimum energy value. This result is evident that the title compound contains a strong intramolecular O–H···N hydrogen bond.

Table 8 Mülliken atom charges of the compound

	AM1	PM3	PM6	DFT
1C	−0.1693	−0.2093	−0.2825	0.0796
2C	0.1516	0.1922	0.4012	0.2391
3C	−0.1754	−0.1702	−0.3033	−0.1092
4H	0.1549	0.1249	0.1854	0.1480
5C	0.0702	−0.0338	−0.0560	−0.1487
6H	0.1377	0.1033	0.1488	0.1308
7C	−0.1186	−0.1396	−0.0214	0.1059
8C	−0.0711	−0.0289	−0.0843	−0.2015
9H	0.1312	0.1018	0.1450	0.1276
10C	0.0299	0.0251	0.1449	0.0900
11H	0.1097	0.0969	0.1311	0.1463
12C	0.0068	−0.0498	0.1180	0.2386
13C	−0.1412	−0.1033	−0.1904	−0.0961
14H	0.1421	0.1133	0.1665	0.1502
15C	−0.1144	−0.0938	−0.1504	−0.1118
16H	0.1521	0.1202	0.1734	0.1681
17C	−0.1175	−0.1168	0.0456	−0.2262
18C	−0.0597	−0.1052	−0.1845	−0.0908
19H	0.1641	0.1315	0.1905	0.1892
20C	−0.0382	−0.1000	0.0214	−0.2591
21C	−0.1728	−0.0542	−0.4735	−0.4805
22H	0.0823	0.0445	0.1600	0.1459
23H	0.0830	0.0406	0.1628	0.1533
24H	0.0836	0.0449	0.1629	0.1548
25Cl	0.0121	0.1095	−0.0449	0.1289
26Cl	−0.0029	0.0799	−0.0758	0.0877
27N	−0.1977	−0.1130	−0.3966	−0.5679
28O	0.2613	−0.2607	−0.4716	−0.6191
29H	−0.2533	0.2501	0.3779	0.4270

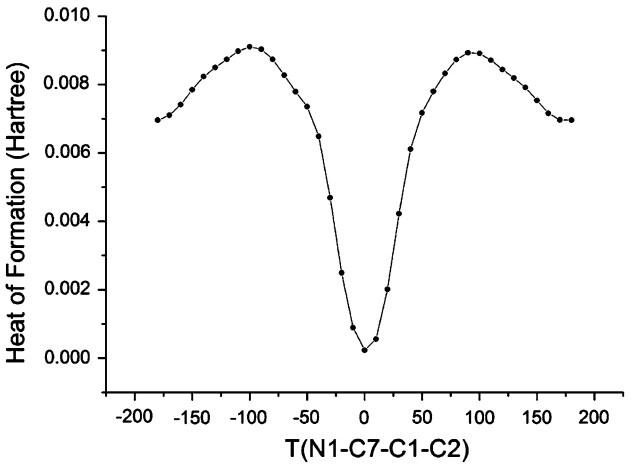


Fig. 4 Variation of heat of formation versus the selected torsion angle. (Calculated or molecular energy profile from PM3 of the title compound versus the torsion angle T(N1–C7–C1–C2))

Conclusions

In this study, the compound, (*E*)-2-[(2,4-Dichlorophenylimino)methyl]-*p*-cresol, has been synthesized and molecular and crystal structure of the title compound, $C_{14}H_{11}CI_2NO$, has been determined by X-ray single crystal diffraction technique. The compound crystallizes in the orthorhombic *Pbca* space group in the unit cell. The present X-ray investigation shows that the title compound prefers the enol–imine tautomeric form rather than the keto–amine tautomeric form. The C2–O1 and C7–N1 bond lengths, 1.355(6) Å and 1.284(6) Å, verify the enol–imine tautomeric form. The title compound, exists as an enol–imine tautomer, in which a strong intramolecular O–H···N hydrogen bond is formed. The dihedral angle between the two benzene rings is 37.66(15)°. The theoretical calculations performed by semi-empirical (AM1, PM3, PM6) and ab initio (DFT) methods on the title compound agree with experimental values. The calculational studies indicate that the most suitable method for the geometry optimization is PM6. In order to determine conformational flexibility on the molecule, molecular energy profile of the title compound was obtained with respect to the selected torsion angle, which is varied from −180° to +180° in every 10 via PM3 semi-empirical method. By the conformational analysis, the most unfavourable and favourable conformer were determined. The minimum value of the heat of formation corresponding to torsion angle in vicinity of 0° is 0.00023 Hartree. This energy value indicates the most favourable conformer. The torsion angle of 0° is consistence with torsion angle of 0.5° obtained from experimental and calculational studies in Table 5. The energy values corresponding to the most unfavourable conformers are approximately 40 times of the energy value corresponding to the most favourable conformer. The energy barrier between unfavourable and favourable conformer for title compound arises due to a strong intramolecular O–H···N hydrogen bond.

Supplementary Data

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 685633. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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