

(E)-3-[(3-(Trifluoromethyl)phenylimino)methyl] benzene-1,2-diol: X-ray and DFT calculated structures

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Received 10.06.2009

The crystal structure of (E)-3-[(3-(Trifluoromethyl)phenylimino)-methyl]benzene-1,2-diol was determined using X-ray diffraction and the molecular structure was investigated with density functional theory (DFT). The X-ray study showed that the title compound has a strong intramolecular O-H...N hydrogen bond and 3-dimensional crystal networks are primarily determined by O-H...O intermolecular hydrogen bonds and weak van der Waals interactions. The strong O-H...N bond is evidence of the preference for the phenol-imine tautomeric form in the solid state. Optimized molecular geometry was calculated with DFT at the B3LYP/6-31G(d,p) level. The results from both experiment and theoretical calculations for the title compound are compared with each other in this study.

Key Words: Schiff bases, phenol-imine, X-ray crystal structure, IR, DFT.

Introduction

Schiff bases ($R^1HC=N-R^2$) are formed by reaction of a primary amine and an aldehyde, they are widely used as ligands in the field of coordination chemistry, and they play an important role in various fields of chemistry due to their activities. ¹*o*-Hydroxy Schiff bases derived from the reaction of *o*-hydroxy aldehydes with aniline have been examined extensively. ²⁻⁴ Some Schiff bases derived from salicylaldehyde have attracted the interest of chemists and physicists because they show thermochromism and photochromism in the solid state by H-atom transfer

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from the hydroxy O atom to the N atom.⁵ It has been proposed that molecules showing thermochromism are planar, while those showing photochromism are non-planar.⁶

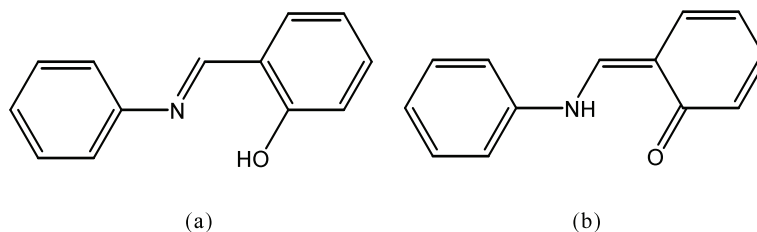


Figure 1. Phenol-imine (a) and keto-amine (b) tautomers of *o*-hydroxy Schiff bases.

In general, *o*-hydroxy Schiff bases exhibit 2 possible tautomeric forms; the phenol-imine (or benzenoid) and keto-amine (or quinoid) forms can be seen in Figure 1(a) and (b), respectively. Depending on the tautomers, 2 types of intra-molecular hydrogen bonds are possible: O-H...N in benzenoid and N-H...O in quinoid tautomers. *o*-Hydroxy Schiff bases have been previously observed in the keto form,⁷ in the enol form,⁸ or in enol/keto mixtures.^{9,10} Related to this phenomenon, we present here the crystal and molecular structures of the title compound.

Experimental

Synthesis

The compound (E)-3-[(3-(trifluoromethyl)phenylimino)methyl]benzene-1,2-diol

was prepared by reflux of a mixture of a solution containing 2,3-dihydroxybenzaldehyde (0.5 g 3.6 mmol) in 20 mL of ethanol and a solution containing 2-aminobenzotrifluoride (0.58 g 3.6 mmol) in 20 mL of ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (E)-3-[(3-(trifluoromethyl)phenylimino)methyl]benzene-1,2-diol suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield 76%; mp 387-389 K). The IR spectra of the compound were recorded on KBr discs with a Bruker 2000 FT-infrared spectrometer. IR (cm⁻¹): 1617.8 (C=N str.), 3311.0 (OH str.), 1391.9 (N=C-H bend.), 1144.2 (C-O str. aromatic), 1324.2 (O-H bend.), 1106.8 (C-F str.), 1507.68-1462.2 (C-C str. aromatic).

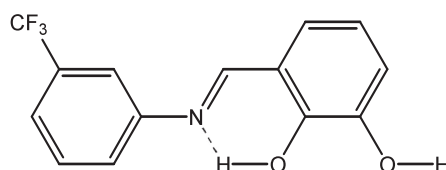


Figure 2. The chemical diagram of the title compound.

X-ray diffraction analysis

A suitable sample was selected for the single crystal X-ray study. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated MoK α radiation and an STOE IPDS 2

diffractometer. Reflections were collected in the rotation mode and cell parameters were determined by using X-AREA software.¹¹ Absorption correction was achieved by the integration method via X-RED32 software.¹¹ The structure was solved by direct methods using SHELXS-97.¹² The refinement was carried out by full-matrix least-squares method using SHELXL-97 on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 221 crystallographic parameters.¹² All non-hydrogen atom parameters were refined anisotropically and all H atoms refined freely with C-H distances in the range 0.90(4)-0.98(3) Å and $U_{iso}(\text{H})$ values in the range 0.016(6)-0.057(11) Å². The data collection conditions and parameters of refinement process are listed in Table 1.

Table 1. Crystal data, data collection, and refinement details.

Chemical Formula	C ₁₄ H ₁₀ F ₃ NO ₂
Formula Weight	281.23
Crystal System	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4
Crystal Color	Orange
<i>a</i> , <i>b</i> , <i>c</i>	16.2181 (8), 4.7632 (2), 18.2882 (10) Å
β	121.748 (4)°
<i>V</i>	1201.37 (10) Å ³
<i>D_x</i>	1.555 Mg m ⁻³
Radiation, λ	MoK α , 0.71073 Å
μ	0.14 mm ⁻¹
<i>T</i>	293 K
<i>T_{min}</i> , <i>T_{max}</i>	0.927, 0.984
Scanning mode	ω
Scan range	-20 < <i>h</i> < 20, -5 < <i>k</i> < 5, -22 < <i>l</i> < 22
Crystal size	0.65 × 0.37 × 0.11 mm
θ_{min} , θ_{max}	1.5, 26.00°
Number of measured/independent reflections, <i>R_{int}</i>	5430/2316, 0.041
Number of reflections with 2 σ (<i>I</i>)	1876
Number of refined parameters	221
<i>S</i>	1.07
R[<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.059
wR(<i>F</i> ²)	0.156
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.82, -0.64 e Å ⁻³

Computational procedure

The geometry optimization of the molecule was carried out by using B3LYP hybrid exchange-correlation functional with 6-31G(d,p) basis set.^{13,14} The calculation was started from the crystallographically obtained

geometry of the molecule listed in Table 2 and carried out using the GAUSSIAN03W package.¹⁵ The optimized molecular geometry, total molecular energy, dipole moment, and Mulliken charges were obtained from the computational process.

Table 2. Fractional atomic coordinates and U_{eq} (\AA^2) for non-H atoms.

Atom	x	y	z	U_{eq}/U_{iso}^*
C1	0.25898 (17)	0.2197 (5)	0.25332 (15)	0.0200 (5)
C2	0.35663 (16)	0.1623 (5)	0.28136 (14)	0.0194 (5)
C3	0.37686 (16)	-0.0484	0.23952 (15)	0.0199 (5)
C4	0.30291 (18)	-0.1978	0.17251 (15)	0.0221 (5)
C5	0.20633 (18)	-0.1417	0.14510 (16)	0.0232 (5)
C6	0.18485 (17)	0.0654 (5)	0.18535 (15)	0.0227 (5)
C7	0.23549 (17)	0.4340 (5)	0.29623 (15)	0.0200 (5)
C8	0.28116 (17)	0.7832 (5)	0.40328 (15)	0.0203 (5)
C9	0.18794 (17)	0.8690 (5)	0.37926 (15)	0.0216 (5)
C10	0.17584 (17)	1.0751 (5)	0.42668 (15)	0.0226 (5)
C11	0.25545 (18)	1.1982 (5)	0.49773 (16)	0.0244 (5)
C12	0.34792 (19)	1.1134 (6)	0.52119 (16)	0.0263 (5)
C13	0.36030 (18)	0.9075 (5)	0.47432 (16)	0.0238 (5)
C14	0.07517 (18)	1.1629 (5)	0.39908 (17)	0.0267 (6)
N1	0.30220 (14)	0.5765 (4)	0.35980 (13)	0.0209 (4)
O1	0.43175 (12)	0.3019 (4)	0.34638 (11)	0.0253 (4)
O2	0.47316 (12)	-0.0913	0.26893 (12)	0.0242 (4)
F1	0.07073 (14)	1.3507 (5)	0.44976 (14)	0.0647 (7)
F2	0.03086 (13)	1.2922 (6)	0.32197 (13)	0.0646 (7)
F3	0.01862 (16)	0.9549 (4)	0.3893 (2)	0.0909 (11)

Results and discussion

An ORTEP-3 plot showing the atom-numbering scheme of the title compound is shown in Figure 3.¹⁶ It is clear that the structure reported here adopts a phenol-imine tautomeric form. The bond lengths with this form were 1.288(3) Å for the N1=C7 double bond and 1.347(2) for the O1-C2 single bond. These distances are in agreement with those observed in N-(2-methyl-5-chlorophenyl)salicylalimine (1.281(3), 1.354(3) Å), which is also a phenol-imine tautomer.¹⁷ The same bond distances can be compared with the corresponding distances in 4-[(4-Methylphenyl)diazenyl]-6-methoxy-2-[[tris(hydroxymethyl)methyl]aminomethylene]cyclohexa-3,5-dien-1(2H)-one (1.296(5), 1.279(5)), which is a keto-amin tautomer.¹⁸

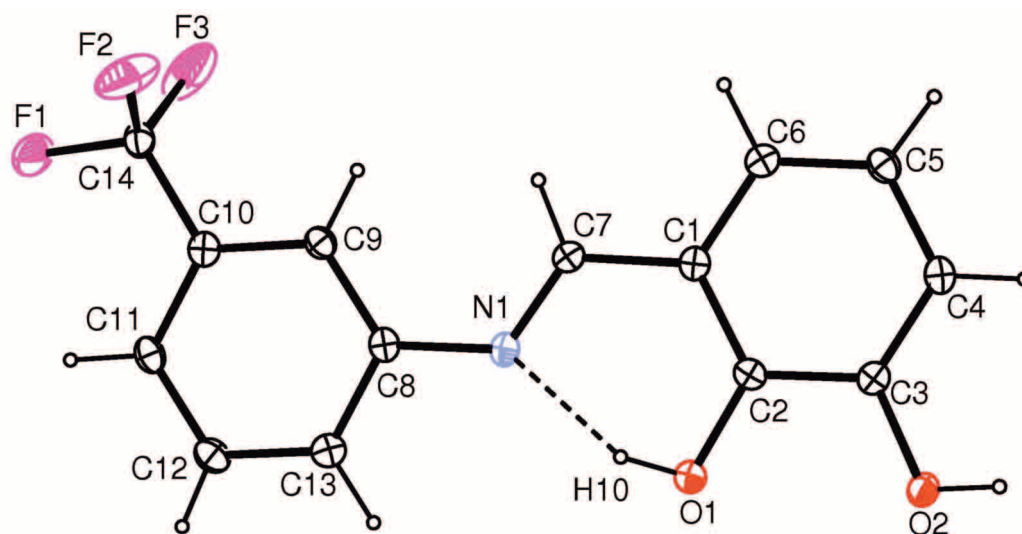


Figure 3. An ORTEP-3 view of the title compound with the atomic numbering scheme. The dashed line shows the intramolecular hydrogen bond. Displacement ellipsoids are shown at the 30% probability level.

In a phenol-imine tautomeric form, both rings of the title compound must be aromatic. In order to make another verification for the phenol-imine form and investigate the aromaticity of rings, HOMA (harmonic oscillator model of aromaticity) indices were calculated.^{19,20} The HOMA index is equal to 1 for aromatic systems and 0 for non-aromatics. The indices are 0.970 and 0.940 for the fluoro-attached ring and the other one, respectively. The dihedral angle between 2 aromatic rings of the molecule is $4.43(2)^\circ$. Against this background we can conclude that the compound is almost planar and displays thermochromic features.

The title compound displays a strong intramolecular hydrogen bond between atoms O1 and N1 as a common feature of o-hydroxysalicylidene systems.^{21,22} The crystal structure is stabilized by weak van der Waals interactions and O-H...O bonds in a 3-dimensional network. Geometrical parameters of the intra- and intermolecular H-bonds are listed in Table 3.

Table 3. Hydrogen bonding geometry (\AA , $^\circ$).

D-H...A	D-H	H...A	D...A	\angle D-H...A
O1—H10...N1	0.83 (4)	1.83 (4)	2.594 (3)	153 (4)
O2—H11...O2 ⁱ	0.87 (4)	1.89 (4)	2.7466 (16)	167 (3)

Symmetry code: (i) $-x + 1, y - 1/2, -z + 1/2$.

In the DFT/B3LYP calculations, the total energy of optimized geometry and dipole moment of molecule were -1044.25 a.u. and 2.6857 debye, respectively. According to the calculated results for Mulliken atomic charge analysis, atoms N1, O1, and O2 have larger negative charges relative to other atoms as expected. The charges were calculated as -0.597 , -0.557 , and -0.544 e, respectively.

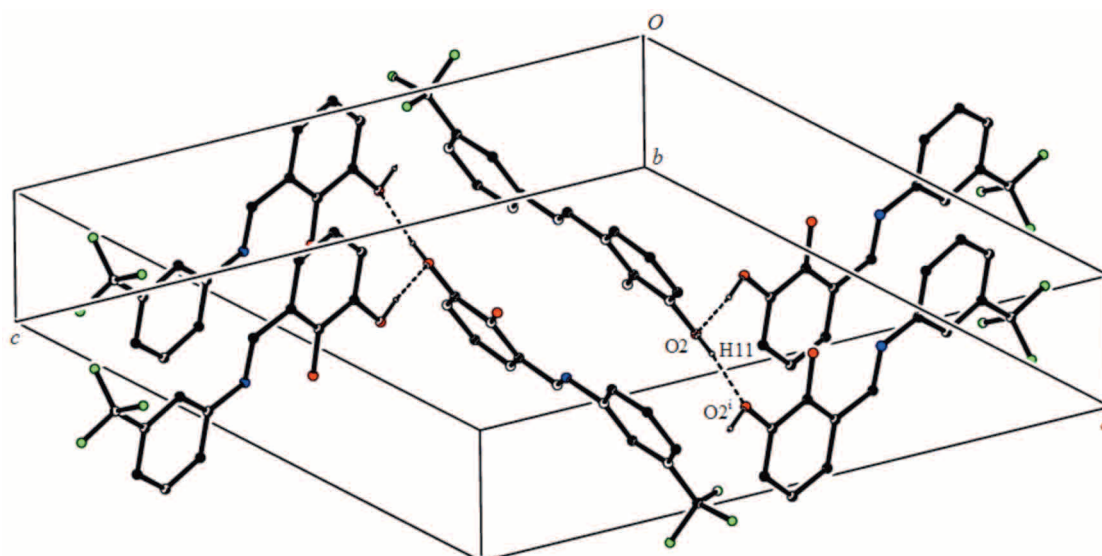


Figure 4. A packing diagram of the title compound. Dashed lines indicate the O-H...O intermolecular hydrogen bonds. For clarity, only H atoms involved in hydrogen bonding are included.

Table 4. Selected bond lengths (Å), angles (°), and torsion angles (°) respectively.

	X-Ray	DFT/B3LYP
Bond lengths (Å)		
C8-N1	1.416 (3)	1.406
N1-C7	1.288 (3)	1.290
C7-C1	1.455 (3)	1.447
C2-O1	1.347 (3)	1.337
Bond angles (°)		
C8-N1-C7	122.5 (2)	121.2
N1-C7-C1	121.5 (2)	122.5
Torsion angles (°)		
C13-C8-N1-C7	175.8 (2)	146.4
C8-N1-C7-C1	179.1 (2)	177.3
N1-C7-C1-C6	178.9 (2)	179.5

Comparative results obtained from the X-ray crystallographic and computational studies of bond distances, angles, and torsion angles are presented in Table 4. It is well known that the DFT and similar calculations underestimate interactions like inter- and intramolecular hydrogen bonds and handle molecules in the gaseous phase (in vacuo). For that reason some differences were observed between the X-ray experimental study and DFT/B3LYP calculation results of bond distance, angle, and torsion angle values.

Supplementary data

CCDC 727236 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 emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgments

The authors wish to thank the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the STOE IPDS 2 diffractometer (purchased under grant F.279 of the University Research Fund).

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