

CRYSTAL AND MOLECULAR STRUCTURE OF 4-METHOXY-2-*{(E)[(2-HYDROXYPHENYL) IMINO]METHYL}*PHENOL STUDIED BY X-RAY, B3LYP AND PM3 CALCULATIONS

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Abstract: 4-methoxy-2-*{(E)[(2-hydroxyphenyl)imino]methyl}*phenol (C₁₄H₁₃NO₃) has been synthesized and characterized by elemental analysis, X-ray, IR and ¹H-NMR spectroscopy and by B3LYP/6-31G(d,p) and PM3 calculations. The X-ray diffraction measurements, and B3LYP/6-31G and PM3 levels of theory, calculation results were compared. The crystals are monoclinic having the space group P2₁/c, with a = 9.8118(2), b = 9.2865(2), c = 12.6850(3) Å, β = 92.520(2)°, Z=4, R_w=0.037. The whole molecule is slightly out of plane with bending around imide bond. Each molecule contains a weak intramolecular hydrogen bond. On both sides of the molecule, there is highly negatively charged oxygen containing corners and these come face to face with van der Waals contacts with the next layers. From the *ab initio* calculations of different levels of theory, it was found that there is a good agreement between the structures determined experimentally and computationally. The molecular structure is discussed in view of these findings

Key words: Schiff Base, X-ray, B3LYP and PM3 calculations.

INTRODUCTION

Schiff bases have been used for various aims. Numerous Schiff bases and their complexes have been studied because of their interesting and important properties, such as, their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins [2] and transfer of an amino group [3], photochromic properties [4] and complexing ability towards certain toxic metals [5].

Schiff bases have been also under investigation during last years because of their potential applicability in optical communications and many of them have non-linear optical (NLO) behaviour [6]. Effects of electron donor-acceptor substituents on the conjugated systems and consequently changes in the aromaticity of phenolic rings have received a great deal attention in recent years [7,8].

It is well known that the N...O distance in the N...H-O hydrogen bonded group depends on the both number of hydrogen atoms at the O atom and formal charge on the donor and acceptor functional groups [9,10].

It is of interest to consider the factors that influence the properties of intramolecular hydrogen bonds in Schiff Bases. In the present study, we investigate the structure of 4-methoxy-2-*(E)*[(2-hydroxyphenyl)imino]methyl}phenol ($C_{14}H_{13}NO_3$) by X-ray diffraction, IR and 1H -NMR spectroscopy, elemental analysis and the isolated molecules by the B3LYP/6-31G and PM3 levels of theory. On the basis of these methods, the effects of hydrogen bonding, changes in the aromaticity of phenolic rings and electrostatic interactions on the molecular levels were discussed.

EXPERIMENTAL

Preparation: A Schiff base, 4-methoxy-2-*(E)*[(2-hydroxyphenyl)imino]methyl}phenol, (m.p. 154 °C) was prepared by condensation reaction of 2-aminophenol (185 mg; 1.7 mmol) with 2-hydroxy-5-methoxy benzaldehyde (259 mg; 1.7 mmol) in ethanol. The crystals of 4-methoxy-2-*(E)*[(2-hydroxyphenyl)imino]methyl}phenol were obtained from ethanol solution at room temperature. The yield of the red crystals was 350 mg; 85%. M.p. 154 °C. Elemental analysis results obtained from Thermo Finnigan Flash EA 1112 analyser are calculated for $C_{14}H_{13}NO_3$: C 69.12, H 5.39, N 5.76 %; found C 69.21, H 5.14, N 5.55 %. 1H -NMR spectra were recorded with a Varian Unity Inova 500 NMR spectrometer (CD_3OD as solvent and internal standard).

IR and 1H -NMR spectra: The vibrational bands for the title compound are observed in the 400-4000 cm^{-1} . Absorption bands at 3072 and 3045 (ν_{C-H} , Ar-H), 1450-1600 ($\nu_{C=C}$), 2983 (ν_{C-H_3}), 3453 (ν_{O-H}), 1259 (ν_{C-O}), 743 and 812 (ν_{C-H} , Ar-H, oop) cm^{-1} are observed. The absorption band assignable to the stretching of C=N

bond is observed at 1628 and 1532 cm^{-1} . On the other hand, the broad bands between the 2500 and 3500 cm^{-1} is due to the intramolecular neutral hydrogen bonding (N...H-O).

In the 1H -NMR spectrum of the title compound, a singlet observed at $\delta = 8.84$ is assigned to azomethyn ($CH=N$) proton. The OH group protons could not be detected probably due to increasing of their acidic character in CD_3OD . The 1H -NMR data are as follows (CD_3OD); δ ppm, 8.84 (s, 1H, CH=N), 7.29 (d-d, $J=1.5$ and 7.8, 1H, H4), 7.13 (m, 1H, H3), 7.07 (d, $J=2.9$, 1H, H8), 7.01 (d-d, $J=2.9$ and 8.8, 1H, H7), 6.94 (m, 1H, H2), 6.91 (d-d, $J=1.5$ and 7.3, 1H, H1), 6.88 (d, $J=8.8$, 1H, H6), 3.81 (s, 3H, OCH_3).

X-ray measurements: Diffraction measurements were carried out at $20 \pm 1^\circ C$ on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K α radiation, at the 127.40 mm distance between the crystal and the detector.

For the structure solution, 34695 reflections were collected, 3582 were unique ($R_w = 0.037$); equivalent reflections were merged. The linear absorption coefficient, μ , for Mo-K α radiation is 0.9109 cm^{-1} . An empirical absorption correction was applied which resulted in transmission factors ranging from 0.91 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods [11] and expanded using Fourier techniques [12]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least squares refinement on F was based on 3274 observed reflections ($I > 3.00\sigma(I)$) and 182 variable parameters and converged with weighted R factor equal to 0.037. All calculations were performed using the CrystalStructure [13,14] crystallographic software package. The crystal data and details of data processing are given in Table 1 and the final fractional atomic coordinates are given in Table 2.

Table 1. Crystal data and structure refinement for 4-methoxy-2- $\{(E)[(2\text{-hydroxyphenyl})\text{imino}]\text{methyl}\}$ phenol

Empirical Formula	C ₁₄ H ₁₃ NO ₃
Formula Weight	243.26
Temperature	293(1) K
Radiation	MoK α ($\lambda = 0.7107 \text{ \AA}$) graphite monochromated
Crystal System	Monoclinic
Space Group	P2 ₁ /c
Unit cell dimensions	a = 9.8118(2) \AA b = 9.2865(2) \AA c = 2.6850(3) \AA $\beta = 92.520(2)^\circ$
Volume	1154.70(4) \AA^3
Z value	4
Calculated density	1.399 g/cm ³
Crystal size	0.60 \times 0.50 \times 0.20 mm
Linear absorption coefficient, μ	0.9109 cm ⁻¹
F(000)	512.00
Diffractometer	Rigaku RAXIS Rapid
No. of Reflections Measured	Total 34695 Unique 3582 ($R_{\text{int}} = 0.031$)
Corrections	Lorentz polarization
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w(F_o - F_c)^2$
Goodness of Fit Indicator on F	1.061
Least Squares Weights	Chebyshev polynomial with 3 parameters 5.7330 -4.3698 3.6501
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00 \sigma(I)$)	3274
No. Variables	182
Reflection/Parameter Ratio	18.60
Residuals R_w ($I > 3.00 \sigma(I)$)	0.037
Maximum peak in Final Diff. Map	0.47 e ⁻ / \AA^3
Minimum peak in Final Diff. Map	-0.28 e ⁻ / \AA^3

Table 2. Atomic coordinates and equivalent isotropic displacement parameters $B_{\text{iso}}/B_{\text{eq}}$ ($\text{\AA}^3 \times 10^3$) for 4-methoxy-2- $\{(E)[(2\text{-hydroxyphenyl})\text{imino}]\text{methyl}\}$ phenol

Atom	x	y	z	B_{eq}
O(1)	0.92267(12)	0.07457(13)	0.29678(8)	3.59(2)
O(2)	1.12143(12)	0.38189(12)	0.34900(8)	3.42(2)
N(1)	0.97971(12)	0.22843(12)	0.47065(8)	2.60(2)
C(13)	1.0394(2)	0.2947(2)	0.55073(10)	2.70(3)
C(2)	0.87633(13)	0.1238(1)	0.47447(10)	2.38(2)
O(3)	1.3731(2)	0.6140(2)	0.70783(10)	5.51(3)
C(7)	1.2094(2)	0.4609(2)	0.62658(11)	3.17(3)
C(10)	1.2881(2)	0.5389(2)	0.42674(12)	3.32(3)
C(9)	1.1822(1)	0.4372(2)	0.43351(10)	2.62(2)
C(1)	0.8476(1)	0.0466(2)	0.38087(10)	2.59(2)
C(3)	0.8035(2)	0.0953(2)	0.56423(11)	2.97(3)
C(8)	1.1442(1)	0.3989(1)	0.53707(10)	2.50(2)
C(6)	0.7446(2)	-0.0564(2)	0.37899(11)	3.12(3)
C(14)	1.4665(2)	0.7274(2)	0.7008(2)	4.17(4)
C(4)	0.7020(2)	-0.0078(2)	0.56109(12)	3.47(3)
C(11)	1.3524(2)	0.5979(2)	0.51535(12)	3.37(3)
C(5)	0.6725(2)	-0.0828(2)	0.46874(13)	3.52(3)
C(12)	1.3134(2)	0.5597(2)	0.61615(12)	3.37(3)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

B3LYP and PM3 levels of theory calculations: The PM3 semi empirical method and DFT calculations were used as implement in the GAUSSIAN-03 program package [15]. The calculations employed the Becke three-parameter Lee–Yang–Parr (B3LYP) exchange–correlation functional, which combines the hybrid exchange functional of Becke [16,17] with the gradient correlation functional of Lee, Yang and Parr [18] and the split-valence polarized 6-31G(d,p) basis set [19]. The X-ray geometry was used as the starting input file in calculations for both levels of theory.

RESULTS AND DISCUSSION

Crystal Structure: The chemical diagram of the title compound is shown in Figure 1. The ORTEP III diagram of 4-methoxy-2- $\{(E)[(2\text{-hydroxyphenyl})\text{imino}]\text{methyl}\}$ phenol is depicted in Figure 2. The bond lengths, bond and torsion angles, are listed in Table 3. The hydroxyl group of 4-methoxyphenol is negatively charged and formed an intramolecular hydrogen bond with the nitrogen of imino group as shown in Figure 2. The H(13)...N(1) distance is 2.1754 Å and O(2)...H(13)...N(1) angle is

108.46°. The intramolecular hydrogen bonds keep the molecule in almost planar structure. Intramolecular

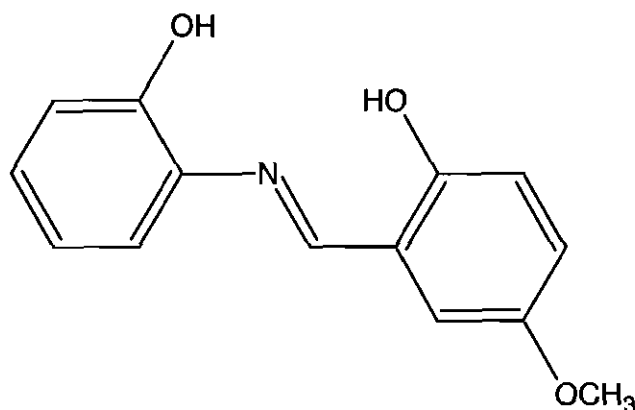


Figure 1. Chemical diagram of the title compound: 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol, $C_{14}H_{13}NO_3$.

hydrogen bond length shows that it is in the range of weak hydrogen bonds. 2-(Hydroxyphenyl) and 4-methoxyphenol rings have almost ideal aromatic ring conformations.

It is noteworthy that hydrogen atom H(12) attached to O(1) does not participate in hydrogen bonding. The C(2)-N(1)-C(13)-C(8) moiety has *cis* conformation with torsion angle of 179.6° and N(1)-C(2)-C(1)-O(1) and N(1)-C(13)-C(8)-C(9) have conformations with torsion angles of 2.0° and 2.6° respectively. The structure in the crystal is organized in the sandwich like mode; with the infinite layers composed of lamellas parallel to the x and z axis. Inside the layers, negative and positive charged points appear to come face to face on both ends having only Van der Waals contacts with the next layers. The spectroscopic view of the unit cell down y-axis is drawn in Figure 3. The crystals of title compounds consists of negatively charged phenoxy oxygen atoms on either side of C=N bond. A network of Van der Waals and crystal forces holds the molecules together in crystal. The molecule is slightly bent around imine bond in the X-ray structure whereas the whole molecule is found to be planar in the optimized structures with B3LYP and PM3.

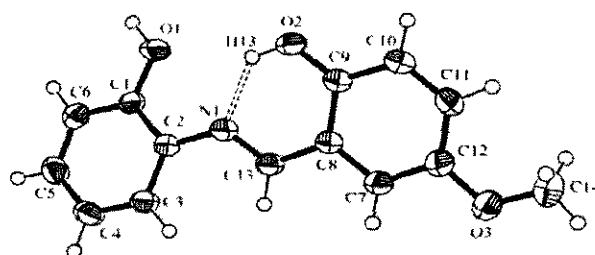


Figure 2. ORTEP [20] diagram of 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol with the atomic numbering showing 50% probability displacements.

B3LYP/6-21G(d,p) calculations of isolated 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol: In B3LYP optimized structure of 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol O(2)-H(13)...N(1) intramolecular hydrogen bond is observed and the distance between H(13)...N(1) (1.5720 Å) is shorter than in the crystal (2.1752 Å). N(1)-C(13)-C(8)-C(7) torsion angles for X-ray and B3LYP are -176.7 and -179.6° respectively. The dipole moment is 3.36 D.

PM3 calculations of isolated 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol: As shown in Figure 4, the structure of 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol optimized by PM3 level of theory is quite different from those in X-ray and B3LYP level of theory. As a comparison, the calculated and measured bond lengths; bond and torsion angles are all listed in Table 3. The dipole moment is 3.06 D.

Comparison of the structures of 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol: The crystal and isolated structures of the title compound are compared with the analogous compounds, such as, 3,5-dimethoxy-2-((phenylimino)methyl)phenol and 4-methoxy-2-((phenylimino)methyl)phenol. As a measure of delocalisation, changes in bond lengths, HOMA (Harmonic Oscillator Model of Aromaticity) index value, are calculated for 4-methoxy-2-((E)((2-hydroxyphenyl)imino)methyl)phenol and HOMA values of two analogous compounds, i.e., 3,5-dimethoxy-2-((phenylimino)methyl)phenol and 4-methoxy-2-((phenylimino)methyl)phenol are taken from literature [21,22].

Table 3. Bond lengths (Å), bond and torsion angles ($^{\circ}$) for 4-methoxy-2-((E)[(2-hydroxyphenyl)imino]methyl)phenol

	X-ray	B3LYP	PM3
Bond lengths			
O(1)-C(1)	1.350(2)	1.381	1.364
N(1)-C(13)	1.304(2)	1.302	1.302
C(13)-C(8)	1.426(2)	1.441	1.459
C(2)-C(3)	1.395(2)	1.401	1.400
O(3)-C(12)	1.378(2)	1.408	1.394
C(7)-C(12)	1.377(2)	1.382	1.393
C(10)-C(11)	1.379(2)	1.383	1.381
C(1)-C(6)	1.395(2)	1.394	1.404
C(6)-C(5)	1.385(2)	1.394	1.388
C(11)-C(12)	1.399(2)	1.408	1.405
O(2)-C(9)	1.312(2)	1.347	1.354
N(1)-C(2)	1.408(2)	1.404	1.429
C(2)-C(1)	1.400(2)	1.415	1.413
O(3)-C(14)	1.401(2)	1.472	1.409
C(7)-C(8)	1.405(2)	1.409	1.402
C(10)-C(9)	1.400(2)	1.409	1.411
C(9)-C(8)	1.426(2)	1.429	1.412
C(3)-C(4)	1.381(2)	1.393	1.387
C(4)-C(5)	1.384(2)	1.397	1.392
Bond angles			
C(13)-N(1)-C(2)	126.8(1)	126.1	122.4
C(1)-C(2)-C(3)	120.1(1)	118.7	118.9
C(3)-C(2)-N(1)	123.5(1)	125.8	122.5
C(8)-C(7)-C(12)	120.4(1)	120.9	119.9
C(8)-C(9)-O(2)	121.7(1)	122.3	124.0
O(2)-C(9)-C(10)	121.6(1)	119.7	115.7
C(6)-C(1)-C(2)	119.0(1)	119.9	119.9
C(4)-C(3)-C(2)	120.1(1)	121.2	120.7
C(13)-C(8)-C(9)	120.0(1)	119.4	122.7
C(5)-C(6)-C(1)	120.1(1)	120.6	119.9
C(12)-C(11)-C(10)	120.6(2)	121.0	119.6
O(3)-C(12)-C(7)	116.8(1)	119.9	117.8
C(7)-C(12)-C(11)	119.6(1)	119.2	121.1
C(8)-C(13)-N(1)	121.7(1)	120.3	119.4
C(1)-C(2)-N(1)	116.3(1)	115.5	118.6
C(14)-O(3)-C(12)	118.7(1)	113.9	113.7
C(9)-C(10)-C(11)	121.9(1)	121.0	120.0
C(8)-C(9)-C(10)	116.6(1)	118.0	120.3
C(6)-C(1)-O(1)	122.8(1)	123.7	122.1
O(1)-C(1)-C(2)	118.1(1)	116.4	117.9

Table 3. continued

	X ray	B3LYP	PM3
Bond angles			
C(13)-C(8)-C(7)	119 0(1)	120 6	118 2
C(7)-C(8)-C(9)	120 9(1)	120 0	119 1
C(5)-C(4)-C(3)	119 8(1)	119 7	120 1
C(6)-C(5)-C(4)	120 7(1)	120 0	120 4
O(3)-C(12)-C(11)	123 6(2)	120 9	120 8
Torsion angles			
C(2)-N(1)-C(13)-C(8)	179 6(1)	180 0	179 9
C(13)-N(1)-C(2)-C(3)	13 0(2)	-1 0	0 3
N(1)-C(13)-C(8)-C(9)	2 6(2)	0 3	0 5
N(1)-C(2)-C(1)-C(6)	-178 8(1)	180 0	-179 9
C(3)-C(2)-C(1)-C(6)	1 0(2)	0 0	0 0
C(1)-C(2)-C(3)-C(4)	-0 7(2)	0 0	0 0
C(14)-O(3)-C(12)-C(11)	8 4(3)	117 8	-71 6
C(12)-C(7)-C(8)-C(9)	-0 7(2)	0 8	0 3
C(8)-C(7)-C(12)-C(11)	0 4(2)	-0 6	0 1
C(11)-C(10)-C(9)-C(8)	0 3(2)	0 1	0 0
O(2)-C(9)-C(8)-C(13)	1 6(2)	-0 2	-0 4
C(10)-C(9)-C(8)-C(13)	178 9(1)	179 6	179 6
O(1)-C(1)-C(6)-C(5)	178 7(1)	180 0	180 0
C(2)-C(3)-C(4)-C(5)	-0 1(2)	-0 1	180 0
C(3)-C(4)-C(5)-C(6)	0 5(2)	0 0	0 0
C(10)-C(11)-C(12)-C(7)	0 3(2)	0 2	-0 4
C(13)-N(1)-C(2)-C(1)	-167 3(1)	179 0	179 8
N(1)-C(13)-C(8)-C(7)	-176 7(1)	-179 6	179 6
N(1)-C(2)-C(1)-O(1)	2 0(2)	0 0	0 1
C(3)-C(2)-C(1)-O(1)	178 2(1)	-180 0	-180 0
N(1)-C(2)-C(3)-C(4)	179 0(1)	180 0	179 9
C(14)-O(3)-C(12)-C(7)	-172 0(2)	104 0	113 7
C(12)-C(7)-C(8)-C(13)	-178 6(1)	-179 3	-179 6
C(8)-C(7)-C(12)-O(3)	-179 2(2)	178 0	174 8
C(11)-C(10)-C(9)-O(2)	179 9(1)	179 9	180 0
C(9)-C(10)-C(11)-C(12)	-0 7(3)	0 1	0 3
O(2)-C(9)-C(8)-C(7)	179 1(1)	179 7	179 6
C(10)-C(9)-C(8)-C(7)	0 4(2)	-0 5	-0 4
C(2)-C(1)-C(6)-C(5)	-0 5(2)	0 0	0 0
C(1)-C(6)-C(5)-C(4)	-0 2(2)	0 0	0 0
C(10)-C(11)-C(12)-O(3)	179 9(2)	-178 4	8 9

The bond lengths are given in Table 3. It is interesting to note that interatomic neutral bond length ($H-N = 2.1754 \text{ \AA}$) in Schiff base according to the X-ray crystal results seems to be longer than the typical interatomic hydrogen bonds which are equal to 1.809 \AA [23]. It has a similar donor-acceptor distance (2.5544 \AA)

to those of neutral bonds ($2.5625(5) \text{ \AA}$) [21]. Considering the bonds from the donor and acceptor atoms to their nearest neighbours, the $C(9)-O(2)$ length (1.3122 \AA) is characteristic of a single bond (ca. 1.40 \AA) in title compound, whereas $C(13)-N(1)$ length being 1.3040 \AA is slightly longer than the typical $C=N$ bond

(ca. 1.27 Å) but still much shorter than a single bond (ca. 1.45 Å) [24].

The structural effects of intramolecular hydrogen bonding and π electron delocalisation can be further quantified by measuring the bond length changes in both phenol rings of the either side of C=N bond. The effect of bond length changes can be expressed by means of mean square of bond length deviations from the average bond length in phenyl rings as A parameter [9];

$$A = \frac{\sum_i (d_i - d)^2}{6} \times 10^6$$

A values and bond lengths used in calculations are listed in Table 4. Bond variations in 3-methoxyphenol increases drastically due to the π electron delocalisation attached to the Schiff base. The difference between precursor chemicals and product Schiff base reflects the bond length variations in the direction of imine bond. Average C-C, C=N, C=O distances decreases with the increasing substitutions [25]. Comparison with an analogous series of methoxy-substituted phenols reveals the same increase in π electron delocalisation and corresponding increases in bond lengths relative to phenol. A parameter of 4-methoxy phenol precursor is about 18 but, when it is in Schiff base form, then A parameter increases to about 300 (see Table 4).

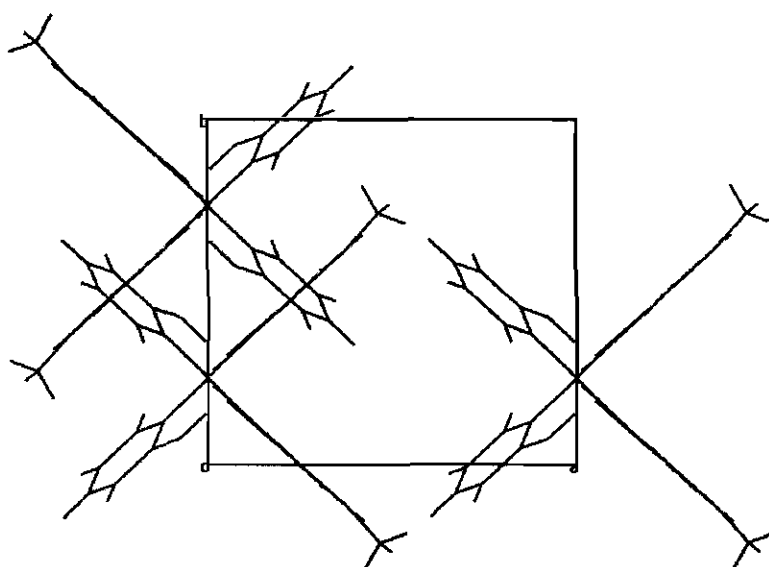


Figure 3. Packing diagram of 4-methoxy-2-((E)[(2-hydroxyphenyl)imino]methyl)-phenol down the z-axis

Additionally, same calculations were performed for B3LYP and PM3 levels of theory optimized structures and the A parameters and bond lengths are given in Table 3 and 4 as a comparison. Same trends were observed in line with the findings from X-ray determined structure in the crystal.

Variations in π electron delocalisation can be more elaborately measured by HOMA index and from its extended form given below [8].

$$\text{HOMA} = 1 - [\alpha (R_{\text{opt}} - R_{\text{av}})^2 - \frac{\alpha}{n} \sum (R_{\text{av}} - R_i)^2]$$

The extended form of HOMA [21] gives information about the nature of π electron delocalisation. If π electron delocalisation is due to an increase of bond

alternation, then the GEO (dearomatization term due to bond length alternations) index is large; if π electron delocalisation is due to bond elongation, then the EN term (energetic term, bond elongation) is large. HOMA is 1 for a system with all bond equal to an optimum value ($R_{\text{opt}} = 1.388$). HOMA is zero for a modal nonaromatic system. R_i stands for a running bond length. In the extended form of HOMA index, the formula extends to

$$\text{HOMA} = 1 - \text{EN} - \text{GEO}$$

where n is the number of bonds taken into the summation; α is a normalization constant fixed to give HOMA = 0 for a model non-aromatic system and HOMA = 1 for the system with all bonds equal to the optimal value R_{opt} . All data discussed were obtained

from X-ray diffraction, PM3 and DFT levels of theory computations at B3LYP/6-311+G(d,p) level taken from literature.

In view of these results it seems that the most important factor affecting the π -electron delocalisation in the spacer is the substituent effect from substituents attached to the ring of which the bond is the part of the spacer. In the case of compound 3,5-dimethoxy-2-[(phenylimino)methyl]phenol, two electron-donating methoxy groups are in positions *ortho* and *para* to the

C=N substituent and hence a substantial mesomeric effects may appear. In the case of compound 4-methoxy-2-[(phenylimino)methyl]phenol, the methoxy group is in the *meta*-position to the C=N group, and hence the mesomeric effect is much smaller and in consequence there is a much stronger bond alternation in the ring with a HOMA about 0.25 [22]. Values calculated from structures of X-ray determined and computed from other levels of theories are listed in Table 4.

Table 4. HOMA indices and A values of structures determined by X-ray, different levels of theories and reference compounds.

Compound	HOMA	A values
X-ray Title compound	0.617	301
B3LYP/6-21G(d,p) Title compound	0.426	264
PM3 Title compound	0.315	128
X-ray Reference compound I	0.506	-
X-rayReference compound II	0.268	-

Title compound: 4-methoxy-2-[(E)[(2-hydroxyphenyl)imino]methyl]phenol

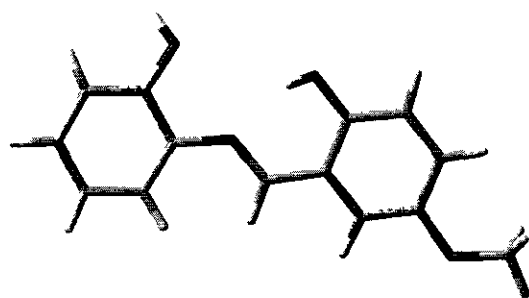
Reference compound I: 3,5-dimethoxy-2[(phenylimino)methyl]phenol

Reference compound II: 4-methoxy-2-[(phenylimino)methyl]phenol

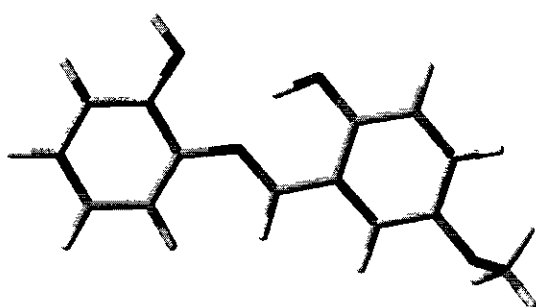
In view of these results, HOMA value for the title compound is 0.617 and HOMA value for a similar compound, i.e., 4-methoxy-2-[(phenylimino)methyl]phenol, is found to be 0.25 [22]. Since the 4-methoxy substituent in the phenol ring is located in *meta* position relative to C=N group, hence mesomeric effect should be smaller but a rather large HOMA index value is observed here of title compound. In view of the above discussion, this increase in HOMA

value could be due to the OH group attached to the ring in *ortho* position where N is a part of the phenol. This could be simply again mesomeric effect of the second OH group in *ortho* position relative C=N imine bond.

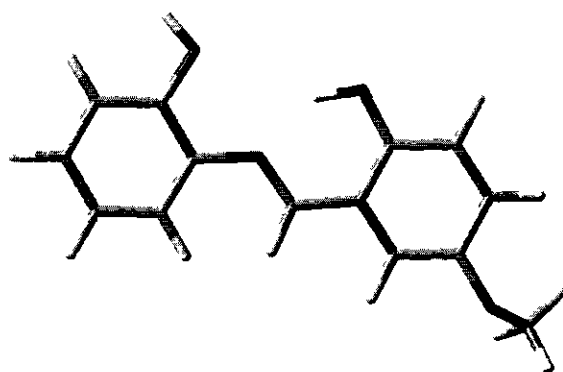
Thus Krygowski's [22] conclusion about π -electron delocalisation is valid for the title compound too. More general conclusion might be stated that substituents in both sides of C=N bond exerts an effect on π -electron delocalisation if substituents may interact mesomerically with the oxygen atom or with the C=N group or both.



X-ray



DFT



PM3

Figure 4. Comparison of X-ray structure of 4-methoxy-2-((E)[(2-hydroxyphenyl)imino]methyl)phenol with that calculated by the B3LYP/6-21G(d,p) and PM3 level of theory

CONCLUSIONS

In the crystals of 4-methoxy-2-((E)[(2-hydroxyphenyl)imino]methyl)phenol negatively charged oxygen containing phenol groups around phenyl

moieties extend the molecule around imine bonds. Intramolecular H-bond bend the molecule around the imine group and π electron system is also affected by the substituents attached phenyl rings.

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