

Synthesis and Physical Characterization of 2-((E)-1-(3-((E)-1-(2-hydroxyphenyl)ethylideneamino)-2-methylphenylimino)ethyl)phenol

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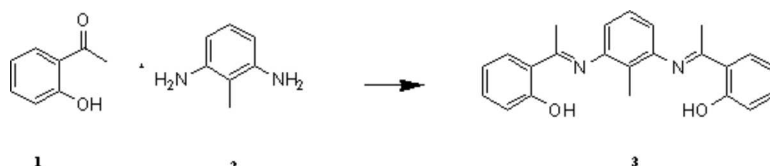
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Abstract: In this paper we propose the synthesis of 2-((E)-1-(3-((E)-1-(2-hydroxyphenyl) ethylideneamino)-2-methylphenylimino) ethyl) phenol. In addition to its synthesis we present AM1 and B3LYP/6-31G* calculations to characterize the physical properties of the molecule.

Keywords: 2-Hydroxyacetophenone, 2-methyl-1,3-phenylenediamine, Schiff base, AM1, B3LYP

Introduction:

Schiff bases are important intermediates for the synthesis of various bioactive compounds [1-2]. Furthermore, they are reported to show a variety of biological activities including antibacterial [3], antifungal [4], anti mouse hepatitis virus (MHV) [5], inhibition of herpes simplex virus type 1 (HSV-1) and adenovirus type 5 (Ad 5) [6], anti cancer [7], anti mosquito larvae [8] and herbicidal activities [9]. The complexes containing the nontoxic 2-hydroxyacetophenone have been used in selective membrane electrodes [10]. Choudhuri et al have synthesized a copper complex of 2-hydroxyacetophenone and they have evaluated it as an anticancer agent [11]. Some Co(III) complexes of 2-hydroxyacetophenone have been synthesized by John and his coworkers [12]. Grunule group have synthesized and characterized four copolymer derived from 2-hydroxyacetophenone. In view of these facts we decided to synthesize a new Schiff base from the nontoxic 2-hydroxyacetophenone as potential biological and complexometric agent. Its biological activities and analytical works are under study.



Results and Discussion:

2-Hydroxyacetophenone **1** (2.03 g, 1.8 mL, 15 mmol) and 2-methyl-1, 3 phenylenediamine **2** (0.61 g, 5 mmol) were dissolved in 20 ml of warm ethanol. The reaction mixture was refluxed for 8h at 85 °C, and allowed to stand. The solid crystals were filtered off and washed with ethanol. The pure Schiff base **3** was isolated as a light yellow crystalline solid (yield 68%). We next performed theoretical calculations to present a viable structure for the product. All calculations in this work were carried out with the AM1 level of theory using the GAUSSIAN 03 [13] suite of programs. More information about these methods is available elsewhere [14]. Figure 1 presents the optimized structure of the molecule with bond lengths and bond angles shown. We obtained a melting point (mp) value 184-186 °C, and IR (KBr, cm⁻¹): 3244(OH) (B3LYP/6-31G*: 3217); 1604(C=N) (B3LYP/6-31G*: 1629), as well as NMR.

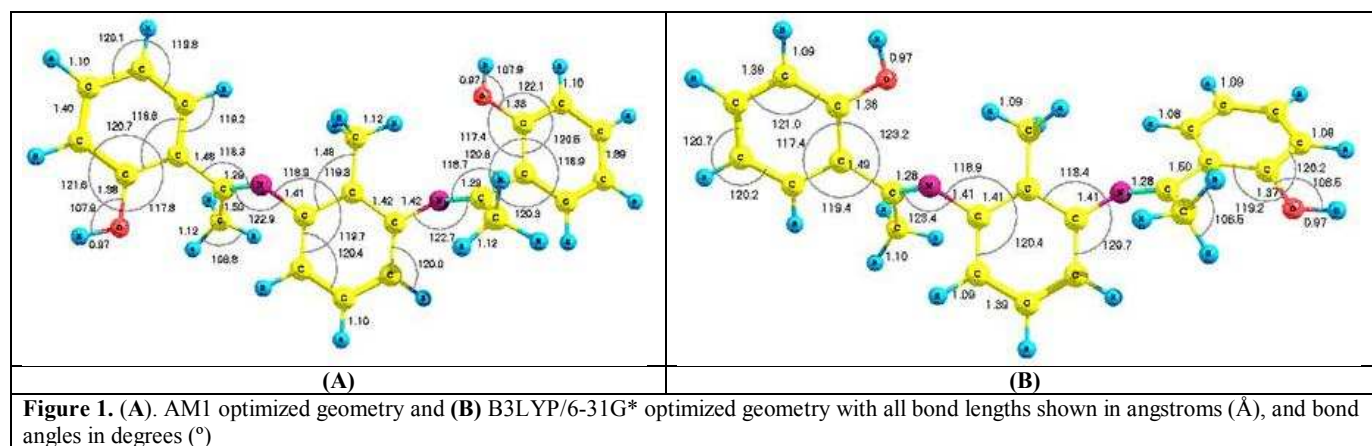


Figure 2 shows the theoretical IR vibrational spectrum for this molecule.

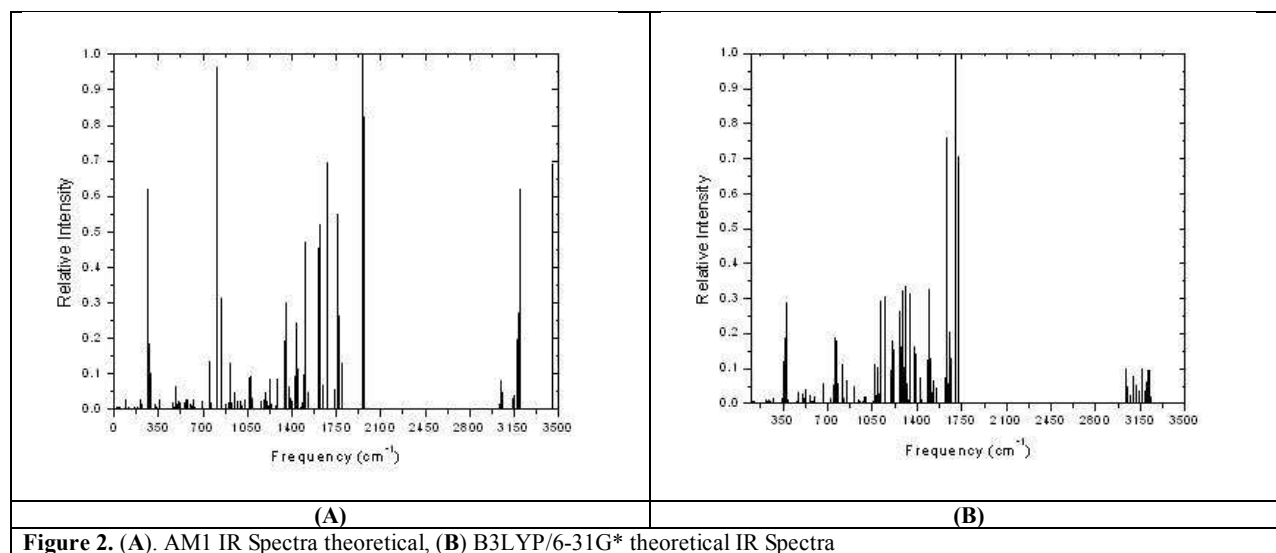


Table 1 shows the thermodynamic properties for the complex in figure 1 where T (temperature in K), S (entropy in $\text{J mol}^{-1} \text{K}^{-1}$), C_p (heat capacity at constant pressure in $\text{kJ mol}^{-1} \text{K}^{-1}$), and $\Delta H = H^\circ - H^\circ_{298.15}$ (enthalpy content, in kJ mol^{-1}), $T_1=100 \text{ K}$, $T_2=298.15 \text{ K}$, and $T_3=1000 \text{ K}$ calculated AM1 frequencies. The fits were performed according to the equations implemented by the National Institute of Standards and Technology (NIST) [15].

		<i>Fitted Thermodynamic Equation ($T/1000=t$)</i>	<i>100 K</i>	<i>298.15K</i>	<i>1000 K</i>
AM1	C_p	$-32.60241 + 1692.63626*t - 907.85165*t^2 + 150.38779*t^3 + 0.51679*t^2$	179.04	398.44	904.39
	S	$53.732 * \ln(t) + 1197.55633 * t + 17.76292 * t^2/2 - 370.35669 * t^3/3 - 5533.6327 / (2*t^2) + 153.29627$	462.67	755.21	1541.55
	ΔH	$465.16043 * t + 6885.20409 * t^2/2 - 13920.11871 * t^3/3 + 7543.03025 * t^4/4 - 7.7704 / t - 1756.97223$	11.50	68.42	560.53
B3LYP/6-31G*	C_p	$-72.8544 + 1979.22049*t - 1324.98024*t^2 + 333.74311*t^3 + 0.56512*t^2$	168.36	412.38	916.56
	S	$35.62635 * \ln(t) + 1302.38545*t + 32.60854*t^2/2 - 463.77548*t^3/3 + 2344.59164 / (2*t^2) + 159.49792$	439.53	731.65	1540.23
	ΔH	$-101.60395*t + 6628.71227*t^2/2 - 13286.08662*t^3/3 + 7109.30838*t^4/4 + 14.26015/t + 702.59222$	10.54	67.85	572.53

Table 1. Thermodynamic properties of the molecule in Figure 1, calculated at the AM1 level and B3LYP/6-31G* level of theory, where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, S is the entropy in $\text{J mol}^{-1} \text{K}^{-1}$, and ΔH is the standard enthalpy kJ mol^{-1} . These were fitted to the Shomate equations [15] which are implemented by the JANAF tables of the NIST databases. These equations converged to an R^2 value of 0.999 on average.

These equations have been very good at predicting physical properties of various molecules, as we have tested in the past [16-19]. Overall, there is some relative correlation between the AM1 and B3LYP/6-31G* values, however, the density functional theory values should be much more reliable.

Melting Point: 184-186 °C

IR (KBr, cm^{-1}): 3244(OH); 1604(C=N).

$^1\text{H-NMR}$ (250 MHz, CDCl_3): 1.65(6H, s, ArCH₃), 2.26(3H, s, ArCH₃), 6.21(2H, d, Ar), 6.24(2H, d, Ar), 6.88-7.64(5H, m, Ar), 7.94(2H, d, Ar), 14.57(2H, s, OH).

$^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 11.516; 17.133; 30.944; 111.21; 111.71; 113.20; 118.02; 118.22; 119.63; 126.66; 128.88; 132.95; 145.55; 145.60; 146.60; 162.15; 171.23.

MS (m/z): 358.47, 225, 132, 106, 77.

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