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

A. A. Jarrahpour\textsuperscript{a*,} A. F. Jalbout\textsuperscript{b*}, S. Rezaei\textsuperscript{a} and B. Trzaskowski\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran
\textsuperscript{b}Department of Chemistry, University of Arizona, Tucson, AZ 85721 USA

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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 \textbf{1} (2.03 g, 1.8 mL, 15 mmol) and 2-methyl-1,3 phenylenediamine \textbf{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 \textbf{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\textsuperscript{-1}): 3244(OH) (B3LYP/6-31G*: 3217); 1604(C=N) (B3LYP/6-31G*: 1629), as well as NMR.

![Figure 1](http://www.mdpi.org/molbank/molbank2006/m455.htm)

\textbf{Figure 1.} (A). AM1 optimized geometry and (B) B3LYP/6-31G* optimized geometry with all bond lengths shown in angstroms (Å), and bond angles in degrees (°)

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 J mol⁻¹ K⁻¹), C_p (heat capacity at constant pressure in J mol⁻¹ K⁻¹), and ΔH=H°1-298.15 (enthalpy content, in kJ mol⁻¹) calculated AM1 frequencies. The fits were performed according to the equations implemented by the National Institute of Standards and Technology (NIST) [15].

<table>
<thead>
<tr>
<th></th>
<th>Fitted Thermodynamic Equation (T/1000=t)</th>
<th>100 K</th>
<th>298.15 K</th>
<th>1000 K</th>
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</thead>
<tbody>
<tr>
<td>AM1</td>
<td>C_p -32.60241+1.692.63626<em>t^-907.85165</em>t² + 150.38779<em>t³ +0.51679</em>t⁴</td>
<td>179.04</td>
<td>398.44</td>
<td>904.39</td>
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<tr>
<td></td>
<td></td>
<td>462.67</td>
<td>755.21</td>
<td>1541.55</td>
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<td></td>
<td>S 53.732 *ln(t) + 1197.55633 *t + 17.76292 *t²/2 -370.35669 <em>t³/3 - 5533.6327 /(2</em>t²) +153.29627</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>11.50</td>
<td>68.42</td>
<td>560.53</td>
</tr>
<tr>
<td></td>
<td>ΔH 465.16043 *t + 6885.20409 *t²/2 -13920.11871 *t³/3 + 7543.03025 *t⁴/4 - 7.77046/t +1756.97223</td>
<td></td>
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<tr>
<td>B3LYP/6-31G*</td>
<td>C_p -72.8544 + 1979.22049<em>t -1324.98024</em>t² + 333.74311<em>t³ +0.56512</em>t⁴</td>
<td>168.36</td>
<td>412.38</td>
<td>916.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>439.53</td>
<td>731.65</td>
<td>1540.23</td>
</tr>
<tr>
<td></td>
<td>S 35.62635 *ln(t) + 1302.38545 *t + 32.60854 *t²/2 -463.77548 <em>t³/3 + 2344.59164/(2</em>t²) + 159.49792</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>10.54</td>
<td>67.85</td>
<td>572.53</td>
</tr>
<tr>
<td></td>
<td>ΔH +101.60395<em>t + 6628.71227</em>t²/2 -13286.08662<em>t³/3 + 7109.30838</em>t⁴/4 + 14.26015/t +702.59222</td>
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</table>

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 J mol⁻¹ K⁻¹, S is the entropy in J mol⁻¹ K⁻¹, and ΔH is the standard enthalpy kJ mol⁻¹. These where fitted to the Shomate equations [15] which are implemented by the JANAF tables of the NIST databases. These equations converged to an R² 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=O).

¹H-NMR (250 MHz, CDCl₃): 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).

¹³C-NMR (62.9 MHz, CDCl₃): 11.56; 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.

Acknowledgment

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References:

Sample Availability: Available from MDPI

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