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Tautomeric properties, conformations and structure of *N*-(2-hydroxyphenyl)-4-amino-3-penten-2-on

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Abstract

N-(2-hydroxyphenyl)-4-amino-3-penten-2-on ($C_{11}H_{13}NO_2$) has been studied by X-ray analysis. It crystallizes the orthorhombic space group P2₁2₁2₁ with a = 8.834(1), b = 10.508(2), c = 11.212(2) Å, V = 1040.8(3) Å³, Z = 4, $D_c = 1.22$ g cm⁻³ and $\mu(MoK_{\alpha}) = 0.084$ mm⁻¹. The structure was solved by direct methods and refined to R = 0.038 for 1373 reflections ($I > 2\sigma(I)$). The title compound is photochromic and the molecule is not planar. Intramolecular hydrogen bonds occur between the pairs of atoms N(1) and O(1) [2.631(2) Å], and N(1) and O(2) [2.641(2) Å], the H atom essentially being bonded to the N atom. There is also a strong intermolecular O–H…O hydrogen bonding [2.647(2) Å] between neighbouring molecules. Tautomeric properties and conformations of the title compound were investigated by semi-empirical quantum mechanical AM1 calculations and the results are compared with the X-ray results. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: X-ray; Schiff base; AM1; Photochromic; Tautomerism

1. Introduction

Schiff bases and their biologically active complexes have been studied during the past decade [1]. Schiff bases undergo photochromism and thermochromism in the solid state by proton transfer [2]. Intramolecular hydrogen bonds (either N–H···O or N···H–O) can exist in aldimine compounds derived from the aromatic aldehydes having a hydroxyl group in position 2 to the aldehyde group [3]. The existence of the enol (or predominantly enol) tautomer has been established in all crystal structures of *N*-substituted salicylaldimine listed so far in the Cambridge Structure Database [3].

In this paper we investigated the structure of the

Schiff base, including the non-aromatic aldehyde, in order to reveal the presence of either the enol or keto form (or the predominant presence of one of them) in the crystalline state.

2. Experimental

The suitable crystals were obtained directly from the synthesis of the compound. A solution of 0.003 mol of 2-aminophenol in 100 ml pure ethanol was prepared and heated to boiling temperature. Acetylacetone (0.003 mol) was dissolved in 50 ml of hot ethanol. The mixture of the two solutions was then refluxed for 3 h. Yellow needle crystals were formed during the refluxions.

A crystal of dimensions $0.40 \times 0.30 \times 0.25$ mm was mounted on an Enraf–Nonius CAD-4

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diffractometer equipped with a graphite monochromator. Cell constants were determined by leastsquares refinement of diffractometer angles for 20 reflections collected in the range $3.15^{\circ} < \theta < 7.25^{\circ}$. Three standard reflections were monitored every 120 min, but no considerable intensity variations were recorded. A total of 1884 reflections were recorded, with Miller indices $h_{\min} = -9$, $h_{\max} = 9$, $k_{\min} = -1, k_{\max} = 11, l_{\min} = -1, l_{\max} = 12$. The structure was solved by direct methods using SHELXS86 [4]. The E-map computed from the phase set with the best combined figure of merit revealed the positions of all non-hydrogen atoms. Full-matrix least-square refinement of the fractional coordinates of the non-hydrogen atoms with anisotropic atomic displacement parameters was performed SHELX97 [5]. Positions of H atoms (except hydroxyl and amine H atoms) were generated from the assumed geometries checked in Fourier maps and refined isotropically. The hydroxyl and amine H atoms were found in the difference Fourier maps calculated at the end of the refinement process as a small positive electron density. Final R(F) and $wR(F^2)$ factors were 0.038 and 0.109 for 134 parameters using the I values of 1373 $(I > 2\sigma(I))$ reflections. A weighting scheme was used during the refinement as $w = 1/[\sqrt{\sigma^2(F_0^2)} + (0.0807P)^2 + 0.2220P],$ where $P = [F_0^2 + 2F_c^2)/3$. The highest and the lowest peaks in the final difference map were 0.21 and $-0.15 \text{ e} \text{ Å}^{-3}$. Scattering factors were taken from SHELX97.

Crystal data for (*I*), $C_{11}H_{13}NO_2$, $M_r = 191.2 \text{ g mol}^{-1}$, orthorhombic $P2_12_12_1$, a = 8.834(1), b = 10.508(2), c = 11.212(2) Å, V = 1040.8(3) Å³, Z = 4, $D_c = 1.22 \text{ gcm}^{-3}$, $\mu(MoK_{\alpha}) = 0.084 \text{ mm}^{-1}$, F(000) = 408, T = 292 K, R(F) = 0.038 and $wR(F^2) = 0.109$ for 1373 observed reflections. Flack parameter is found to be zero in the refinement [6]. A list of structure factors, H atom fractional atomic coordinates and anisotropic atomic displacement parameters for non-hydrogen atoms has been deposited with the B.L.L.D. as Supplementary Publications No. SUP26605 (10 pages).

Theoretical calculations were performed with the semi-empirical quantum-mechanical program AM1 [7], which is part of the MOPAC package [8]. The models of keto and enol forms of the title compound were built and taken the values from Allen et al. [9].

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² × 10³). U_{eq} is defined as one third of the trace of orthogonalized U_{ii} tensor

	x	у	z	$U_{ m eq}$
C(1)	6472(2)	2298(2)	2877(2)	77(1)
C(2)	4945(2)	1766(2)	2555(1)	52(1)
C(3)	4031(2)	1224(2)	3440(1)	54(1)
C(4)	2590(2)	779(2)	3264(1)	49(1)
C(5)	1678(2)	328(2)	4312(2)	76(1)
C(6)	513(2)	424(2)	1783(1)	49(1)
C(7)	-71(2)	1118(1)	822(1)	50(1)
C(8)	-1470(2)	798(2)	356(2)	64(1)
C(9)	-2279(2)	-187(2)	842(2)	72(1)
C(10)	-1708(2)	-871(2)	1766(2)	79(1)
C(11)	-304(2)	-589(2)	2231(2)	65(1)
O(1)	804(1)	2068(1)	394(1)	62(1)
O(2)	4532(1)	1846(1)	1486(1)	63(1)
N(1)	1972(1)	781(1)	2183(1)	49(1)

Table 2

Bond distances (Å) and angles (°) of X-ray, optimized X-ray, keto and enol forms of molecule with esd's in parentheses

	X-ray	X-opt.	Keto	Enol
C(1)-C(2)	1.504(3)	1.500	1.500	1.491
C(2) - C(3)	1.401(2)	1.448	1.449	1.356
C(3) - C(4)	1.370(2)	1.375	1.374	1.461
C(4) - C(5)	1.501(2)	1.503	1.502	1.503
C(4) - N(1)	1.330(2)	1.374	1.377	1.300
N(1) - C(6)	1.415(2)	1.403	1.403	1.403
C(6) - C(7)	1.400(2)	1.425	1.427	1.427
C(7) - C(8)	1.384(2)	1.398	1.400	1.401
C(8)–C(9)	1.371(3)	1.392	1.391	1.393
C(9)-C(10)	1.359(3)	1.394	1.391	1.394
C(10) - C(11)	1.377(3)	1.391	1.392	1.391
C(7)–O(1)	1.351(2)	1.379	1.377	1.378
C(2)–O(2)	1.256(2)	1.246	1.245	1.362
C(3)-C(2)-C(1)	119.9(2)	114.8	114.8	121.8
C(4) - C(3) - C(2)	124.9(2)	126.6	126.7	128.1
C(5)-C(4)-C(3)	119.6(1)	116.1	116.9	113.4
N(1)-C(4)-C(3)	120.8(1)	122.6	122.3	120.0
C(6) - N(1) - C(4)	131.5(1)	125.8	125.7	124.6
C(7)-C(6)-N(1)	116.2(1)	120.6	120.1	119.5
C(8) - C(7) - C(6)	119.6(2)	121.2	120.5	121.3
C(9) - C(8) - C(7)	119.9(2)	119.8	120.1	120.2
C(10)-C(9)-C(8)	120.6(2)	120.1	120.1	119.3
C(11)-C(10)-C(9)	120.6(2)	120.3	120.5	121.0
C(10) - C(11) - C(6)	120.0(2)	121.4	120.9	121.4
C(11)-C(6)-C(7)	119.3(2)	117.2	117.9	116.8
C(11)-C(6)-N(1)	124.5(2)	122.1	121.9	123.5
O(1)-C(7)-C(8)	124.0(2)	121.7	122.0	121.1
O(1) - C(7) - C(6)	116.6(1)	117.1	117.5	117.6
O(2)-C(2)-C(1)	117.7(2)	120.5	120.6	110.9



Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

The X-ray, keto and enol geometries were optimized by using an AM1 method. To determine the conformational energy profiles, the optimized geometries were kept fixed and values of energies were calculated as a function of the torsion angle $\theta(C(4)-N(1)-C(6)-C(11))$ from 0 to 360°, varied every 10°. The zero values of the torsion angle $\theta(C(4)-N(1)-C(6)-C(11))$ is 3.99° for optimized X-ray, -7.39° for keto and -7.99° for enol structures. The results are illustrated in Fig. 4.

3. Results and discussion

Fractional atomic coordinates and equivalent isotropical thermal parameters for non-hydrogen atoms are given in Table 1. Bond distances and bond angles for X-ray, keto and enol tautomer structures are listed in Table 2. The ORTEP [10] view of the molecular structure of the title compound is given in Fig. 1 and the crystal packing diagram in Fig. 2 [11].



Fig. 2. Crystal packing diagram for the title compound.



Fig. 3. The difference Fourier map for the least squares plane through the chelate atoms O(2), C(2), C(3), C(4) and N(1) showing the position of the H(1N) atom and revealing the presence of intramolecular N-H···O hydrogen bonding. Contours are drawn from -0.17 to 0.34 e Å⁻³ at intervals of 0.01 e Å⁻³ [16].

Thermochromic and photochromic properties of the salicylideneanilines are a function of the crystal and molecular structure [2]. From some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromy are planar, while those exhibiting photochromy are non-planar [12]. In agreement with the above conclusions, the title compound is photochromic [13] and the molecule is not planar; moieties A(C(1)-(5), O(2)) and B(N(1), C(6)-(11), O(1))[both planar with a maximum deviation of -0.020(2) Å] are inclined at an angle of $32.8(1)^{\circ}$ reflecting mainly the twist about N(1)-C(6) [C(11)- $C(6)-N(1)-C(4) = -37.1(3)^{\circ}$]. The distortion can be seen in the crystal packing diagram (Fig. 2).

The crystal structure is stabilized by intermolecular hydrogen bonds. The crystal structure determination indicates the existence of both $N(1)-H(1N)\cdots O(1)$ and $N(1)-H(1N)\cdots O(2)$ the bifurcated intramolecular hydrogen bonds as follows: $N(1)\cdots O(1)$ 2.631(2) Å and $N(1)\cdots O(2)$ 2.641(2) Å. These distances are significantly shorter than the sum, 3.07 Å of the van der Waals' radii for nitrogen and oxygen [14]. The atom H(1N) was located from a difference Fourier

map as a well designed small electron density maximum of 0.21 e Å⁻³ (Fig. 3). The N(1)-H(1N), $O(1)\cdots H(1N)$ and $O(2)\cdots H(1N)$ distances are 0.80(2), 2.31(2) and 2.00(2) Å, respectively. The angles $N(1)-H(1N)\cdots O(1)$ bond and N(1)- $H(1N)\cdots O(2)$ are $105(1)^{\circ}$ and $138(2)^{\circ}$, respectively. The C(2) = O(2) bond [1.256(2) Å] was determined to be of bond order 1.5 from the values of the single and double C-O bonds [9]. This along with the very short C(3) = C(4) bond [1.370(2) Å] suggests the presence of a significant keto tautomer (Scheme 1). Clearly, the keto tautomer is favoured over the enol form.



Scheme 1.



Fig. 4. AM1 calculated conformation energies for X-ray, keto and enol structures vs the $\theta(C(4)-N(1)-C(6)-C(11))$ torsion angle.

There is also a strong intermolecular hydrogen bond between O(1) and O(2)ⁱⁱ [2.647(2) Å] [symmetry code(ii): x - 1/2, -y + 1/2, -z] atoms of neighbouring molecules (Fig. 2). The O(1)–H(1O) distance is 0.90(2) Å.

The optimized bond distances and angles of X-ray structure and keto tautomer are in good agreement, but enol form shows some differences (Table 2). The conformations of the optimized X-ray geometry are in good agreement with the keto tautomer. The X-ray structure and keto tautomer are more stable than the enol tautomer as seen in Fig. 4. The non-planar conformations corresponding to zero values of $\theta(C(4)-N(1)-C(6)-C(11))$ are the most stable conformation for X-ray, keto and enol structures. The energies corresponding to this non-planar conformations are -47.95 kcal/mol for X-ray, -48.24 kcal/mol for keto and - 40.66 kcal/mol for enol structures. The energy profile as a function of $\theta(C(4)-N(1)-C(6)-C(11))$ shows one maximum at 34.0° for X-ray, 37.4° for keto and 28.0° for enol structures. This energy barrier arises from the steric interactions between the hydroxyl substituent and the

methyl group. Burgi and Dunitz carried out an extensive theoretical and experimental study on the non-planar conformation of the N-benzylideneaniline and related compounds [15]. Their explanation for the non-planarity of N-benzylideneaniline involves a competition between two principal factors: (a) the interaction of the ortho hydrogen on the aniline ring and the hydrogen on the 'bridge' carbon which is repulsive in the planar conformation but is reduced with the increasing non-planarity; and (b) the π -electron systems itself divisible into two components, including, on the one hand, delocalization between the -CH=N- double bond and the aniline phenyl ring, which is maximized for a planar conformation, and, on the other hand, delocalization of the nitrogen lone pair electrons into the aniline ring which is essentially zero for the planar conformation but increases with increasing non-planarity (where the lone pair density on the nitrogen may interact with the π -system of the ring).

In summary, semi-empirical AM1 calculations show a good agreement between X-ray and keto structures. The AM1 optimized geometries of X-ray, keto and enol structures of the title compound corresponding to non-planar conformation is the most stable conformation. The results strongly indicate that the minimum energy conformation is primarily determined by non-bonded hydrogen-hydrogen repulsions. Although non-bonded repulsions are largely responsible for the conformational differences of the title compound, interaction between the N-lone pair and the π -electrons of the rotated phenyl ring might also contribute to the conformational energy of the title compound.

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