Conformations and Structures of N,N'-Bis(2-methoxybenzylidene)-1,3-diamino-propanol and N,N'-Bis(3-methoxybenzylidene)-1,3-diamino-propanol

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N,N'-bis(2-methoxybenzylidene)-1,3-diamino-propanol ($C_{19}H_{22}N_2O_4$) **1** and N,N'-bis(3-methoxybenzylidene)-1,3-diamino-propanol ($C_{19}H_{22}N_2O_4$) **2** have been investigated by X-ray analysis and AM1 semi-empirical quantum mechanical method. **1** is in the monoclinic space group C2/c with $a = 33.694(6)$, $b = 6.735(1)$, $c = 17.681(3)$ Å, $\beta = 114.72(2)°$, $V = 3645(1)$ Å^3, $Z = 8$, $D_c = 1.248$ mg cm^{-3} and μ(Mo-K$_\alpha$) = 0.088 mm^{-1}. **2** is in the monoclinic space group C2/c with $a = 19.173(4)$, $b = 7.626(2)$, $c = 11.788(2)$ Å, $\beta = 91.72(2)°$, $V = 1722.8(6)$ Å^3, $Z = 4$, $D_c = 1.320$ mg cm^{-3} and μ(Mo-K$_\alpha$) = 0.093 mm^{-1}. The crystal structures of **1** and **2** were solved by direct methods and refined to $R = 0.053$ for **1** and $R = 0.041$ for **2**. Both molecules are not planar and **2** has twofold axes on C9 atom. Intramolecular hydrogen bonds occur between O1 and N1 [2.541(3) Å] and between O3 and N2 [2.573(4) Å] atoms for **1** and between O1 and N1 [2.631(2) Å] atoms for **2**. The optimized geometries of the crystal structures of **1** and **2** corresponding to non-planar conformation are the most stable conformation in all calculations. The results strongly indicate that the minimum energy conformation is primarily determined by non-bonded hydrogen-hydrogen and hydrogen-carbon repulsions.

Key words: X-Ray, Schiff Base, AM1, Photochromism, Thermochromism

Introduction

Schiff bases and their biologically active complexes have been studied during the past decade [1]. Schiff bases are of great interest because of their photochromic and thermochromic behaviour in the solid state, which may involve reversible proton transfer from the hydroxyl-oxygen atom to the imine nitrogen atom [2, 3]. Photochromism and thermochromism are produced by the intramolecular proton transfer associated with a change in π-electron configuration [4 – 6]. Photochromic compounds are of great interest due to their interest as the control and measurement of radiation intensity, optical computers and display systems [7, 8].

On the basis of structural studies on photochromic and thermochromic salicylaldimine derivatives, it was concluded that the significant difference lies in the manner of molecular packing in the lattice, and molecules exhibiting thermochromy are planar while those exhibiting photochromy are non-planar [9]. In other words, photochromic salicylideneanilines are packed rather loosely in the crystal, in which non-planar molecules may undergo some conformational changes, while thermochromic salicylideneanilines are packed tightly to form one-dimensional columns. With the aim of gaining a deep insight into the structural aspect responsible for the observed phenomenon in the solid state, conformational and crystallographic analysis of the non-planar title compounds have been carried out and the results are presented in this paper.

Experimental Section

The compounds **1** and **2** were synthesized according to well established methods [10].

Crystals of **1** and **2** were mounted on an Enraf-Nonius CAD-4 diffractometer with a graphite monochromatized Mo-K$_\alpha$ radiation. Experimental conditions are summarized in Table 1. Data reduction and corrections for absorption and

Table 1. Crystal data for **1** and **2**.

Empirical formula	$C_{19} H_{22} N_2 O_4$	$C_{19} H_{22} N_2 O_4$
Formula weight	342.39	342.39
λ(Mo-K_α) (Å)	0.70730	0.70730
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
Unit cell	$a = 33.694(6)$	$a = 19.173(4)$
dimensions (Å, °)	$b = 6.735(1)$;	$b = 7.626(2)$;
	$\beta = 114.72(2)$	$\beta = 91.72(2)$;
	$c = 17.681(3)$	$c = 11.788(2)$
V (Å^3)	3645(1)	1723(1)
Z	8	4
D_x (calc.) (Mg/m^3)	1.248	1.320
M (mm^{-1})	0.088	0.093
$F(000)$	1456	728
Crystal size (mm)	$0.10 \times 0.15 \times 0.45$	$0.50 \times 0.40 \times 0.20$ mm
θ Range (°)	3.44 to 30.20	3.33 to 30.17 deg.
Index ranges	$-46 \leq h \leq 47$	$-26 \leq h \leq 22$
	$-9 \leq k \leq 8$	$-10 \leq k \leq 10$
	$-25 \leq l \leq 24$	$-15 \leq l \leq 16$
Refls collected	14261	6767
Independent refls	5046 [R(int) = 0.0845]	2376 [R(int) = 0.0513]
Data Completeness	0.926	0.923
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	5046 / 2 / 232	2376 / 0 / 117
GooF on F^2	0.736	0.733
Final R indices	$R1 = 0.053$	$R1 = 0.040$
	$wR2 = 0.099$	$wR2 = 0.074$
[$I > 2\sigma(I)$]		
Largest diff. Peak & hole (e·Å^{-3})	0.195 and -0.231	0.122 and -0.160

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of **1**. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

Atom	x	y	z	U(eq)
C1	3647(1)	794(6)	3607(2)	71(1)
C2	3367(1)	−912(5)	3442(2)	54(1)
C3	3112(1)	−1176(5)	3880(2)	53(1)
C4	2828(1)	−2785(5)	3701(2)	56(1)
C5	2803(1)	−4088(5)	3089(2)	66(1)
C6	3056(1)	−3810(6)	2654(2)	72(1)
C7	3339(1)	−2261(6)	2832(2)	65(1)
N1	3687(1)	2048(5)	4175(2)	80(1)
C8	3943(1)	3881(6)	4275(2)	96(1)
C9	4300(1)	3992(6)	5086(2)	89(1)
C10	4534(1)	6008(5)	5228(2)	80(1)
N2	4922(1)	5982(4)	6013(2)	70(1)
C11	5047(1)	7580(5)	6419(3)	69(1)
C12	5439(1)	7697(5)	7187(2)	60(1)
C13	5686(1)	6022(5)	7525(2)	60(1)
C14	6066(1)	6137(6)	8258(2)	64(1)
C15	6183(1)	7939(6)	8640(2)	73(1)
C16	5940(2)	9628(6)	8308(3)	84(1)
C17	5570(1)	9528(5)	7589(3)	80(1)
C18	2334(1)	−4611(5)	4067(2)	86(1)
C19	6688(1)	4506(5)	9245(2)	90(1)
O1	3125(1)	92(3)	4481(2)	73(1)
O2	2600(1)	−2910(3)	4176(1)	71(1)
O3	5575(1)	4221(4)	7160(1)	77(1)
O4	6287(1)	4412(4)	8528(2)	79(1)

decomposition were carried out using the Nonius Diffractometer Control Software [11]. The structures were solved by direct method using SHELX-97 [12] and refined with SHELXL-97 [13]. The positions of the H atoms (except hydroxyl H atom) bonded to C atoms were geometrically calculated and refined using a riding model. The H atom displacement parameters were restricted to 1.2 U_{eq} of the parent atom. The hydroxyl hydrogen atoms were found in difference Fourier maps calculated at the end of the refinement process as a small positive electron density (Fig. 2 and Fig. 4). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-211161 for **1** and CCDC-211162 for **2** [14].

Geometry optimization of **1** and **2** by the AM1 semi-empirical quantum mechanical method [15], implemented in the MOPAC package [16], running on a Pentium IV PC, was calculated starting from their crystallographic coordinates with hydrogen atoms placed at a distances of 1.08 Å from their target carbon atoms or 0.97 Å for oxygen atom. Geometry optimizations of the crystal structure of the title compound were carried out using the Fletcher-Powell-Davidson

algorithm [17, 18] implemented in the package and the PRE-CISE option to improve the convergence criteria. To determine the conformational energy profiles, the optimized geometries of **1** and **2** were kept fixed, and values of the AM1 total energies were calculated as a function of two torsion angles θ_1(C8-N1-C1-C2) and θ_2(C9-C8-N1-C1) from $-180°$ to $180°$, varied every $10°$. The molecular energies were calculated as function of each θ, keeping the other θ's constant. From the X-ray structure determinations, θ_1(C8-N1-C1-C2) and θ_2(C9-C8-N1-C1) values are found to be 174.0(3)°, 175.1(2)° for **1** and $-120.0(4)°$, $-115.4(2)°$ for **2**, respectively. The optimized values of the θ_1(C8-N1-C7-C6) and θ_2(C9-C8-N1-C7) torsion angles to cis conformation for **1** and **2** in turn in order are $-178.8°$, $178.7°$ and $-111.9°$, $125.5°$, respectively. In all theoretical calculations, it was found that the non-planar optimized conformation of X-ray structures were the most stable conformation.

Results and Discussion

Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms for both molecules are given in Table 2 and Table 4. Bond distances and bond angles for **1** and **2** are listed in Table 3 and Table 5. ORTEP view of the molecular structure of **1** and **2** are given in Fig. 1 and Fig. 3 [19].

Table 3. Bond distances (Å) and bond angles (°) with e. s. d. s in parenthese of **1**.

C1-C2	1.438(4)	C1-N1	1.276(4)
C7-C6	1.360(4)	C3-C2	1.388(4)
C4-C3	1.391(4)	C5-C4	1.367(4)
C6-C5	1.379(4)	C7-C2	1.385(4)
N1-C8	1.475(4)	C9-C10	1.537(4)
C4-O2	1.358(3)	C3-O1	1.349(3)
N2-C11	1.265(4)	C8-C9	1.437(4)
C10-N2	1.454(4)	C11-C12	1.447(4)
C12-C13	1.380(4)	C12-C17	1.399(4)
C13-C14	1.392(4)	C14-C15	1.365(4)
C13-O3	1.351(4)	C14-O4	1.354(4)
C15-C16	1.382(4)	C16-C17	1.360(4)
O2-C18	1.418(3)	O4-C19	1.417(3)
C6-C7-C2	119.6(3)	C4-C5-C6	120.3(3)
C7-C6-C5	121.0(3)	O2-C4-C5	125.8(3)
O2-C4-C3	114.8(3)	O1-C3-C2	122.3(3)
C2-C3-C4	119.9(3)	C7-C2-C1	120.4(3)
N1-C1-C2	122.1(3)	C1-N1-C8	120.8(3)
C9-C8-N1	111.6(3)	C8-C9-C10	111.5(3)
N2-C10-C9	109.9(3)	C11-N2-C10	119.0(3)
N2-C11-C12	122.4(3)	C13-C12-C17	119.7(4)
C17-C12-C11	119.7(4)	O3-C13-C14	117.2(4)
C13-C12-C11	120.6(3)	O3-C13-C12	122.1(4)
C12-C13-C14	120.7(4)	O4-C14-C15	125.8(4)
C15-C14-C13	118.3(4)	C17-C16-C15	120.4(4)
O4-C14-C13	115.9(4)	C5-C4-C3	119.4(3)
O1-C3-C4	117.8(3)	C7-C2-C3	119.7(3)
C3-C2-C1	119.8(3)	C14-C15-C16	121.6(4)
C16-C17-C12	119.4(4)	C4-O2-C18	117.1(3)
C14-O4-C19	117.1(3)		

Table 5. Bond distances (Å) and bond angles (°) with e. s. d. s in parenthese of **2**.

C1-C2	1.438(2)	C1-N1	1.278(2)
C3-C2	1.404(3)	C4-C3	1.385(2)
C3-O1	1.347(2)	C5-C4	1.377(2)
C7-C6	1.357(2)	C7-C2	1.393(2)
C6-C5	1.401(2)	C5-O2	1.362(2)
C8-C9	1.517(2)	N1-C8	1.463(2)
O2-C10	1.424(2)	C9-C8*	1.517(2)
C6-C7-C2	122.1(2)	124.7(2)	C1-N1-C8
C4-C5-C6	120.8(2)	O1-C3-C4	118.1(2)
C4-C3-C2	120.8(2)	C7-C2-C1	120.4(2)
N1-C1-C2	123.7(2)	C7-C6-C5	119.1(2)
O2-C5-C6	114.5(2)	C5-C4-C3	119.3(2)
N1-C8-C9	109.8(1)	C8-C9-C8*	114.2(2)
O1-C3-C2	121.1(2)	C7-C2-C3	117.9(2)
C3-C2-C1	121.7(2)	C1-N1-C8	117.6(2)
C5-O2-C10	118.3(2)		

Symmetry transformations used to generate equivalent atoms:
$^* -x+1, y, -z+5/2$.

Scheme 1.
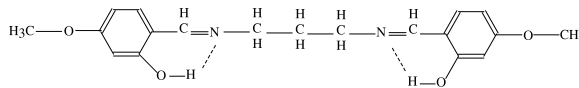
Scheme 2.

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

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x10^3) of **2**. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

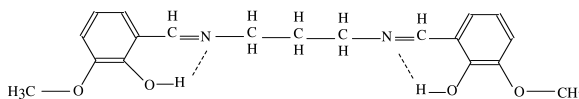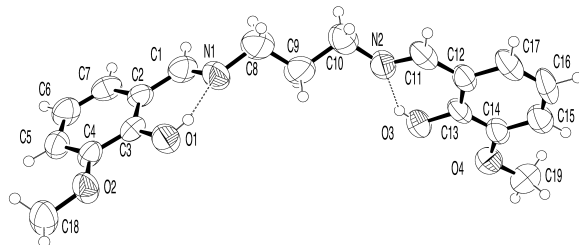| Atom	x	y	z	U(eq)
C1	3697(1)	1809(3)	10615(2)	48(1)
C2	3554(1)	2014(2)	9417(2)	40(1)
C3	4017(1)	2898(2)	8716(2)	43(1)
C4	3881(1)	3028(2)	7558(2)	44(1)
C5	3281(1)	2294(2)	7097(2)	44(1)
C6	2809(1)	1417(3)	7783(2)	50(1)
C7	2955(1)	1283(3)	8913(2)	50(1)
C8	4341(1)	2005(3)	12335(2)	60(1)
C9	5000	924(4)	12500	66(1)
C10	3576(1)	3035(3)	5199(2)	67(1)
N1	4235(1)	2440(2)	11133(1)	50(1)
O1	4604(1)	3644(2)	9147(1)	59(1)
O2	3095(1)	2320(2)	5973(1)	56(1)

Thermochromic and photochromic properties of the salicylideneanilines are a function of the crystal and molecular structure [2]. Ab-initio calculations on benzylideneaniline and related molecules have shown that, rotations about the Ph-N bond of up to 45° from a planar conformation are stabiliz-ing, while rotations about the Ph-C bond are destabi-lizing, and the most stable free-molecule conforma-tion is non-planar [1]. In agreement with the above conclusion, the title molecules are not planar. The metohyxbenzaldehyde-parts **A** (C1, C2, C3, C4, C5, C6, C7, C18, O1, O2,) and **B** (C11, C12, C13, C14, C15 C16, C17, C19, O1, O2) in **1** and **2** are rotated relative to the 1,3-diaminopropane bridge and the an-gles between the methoxybezaldehyde-parts of **A** and **B** are 87.96(4) and 61.38(4)°, respectively. When the

Fig. 2. Difference Fourier map (bold contours show positive electron densities) of **1**.

Fig. 3. The molecular structure of the title compound **2**. Displacement ellipsoids are plotted at the 50 % probability level.
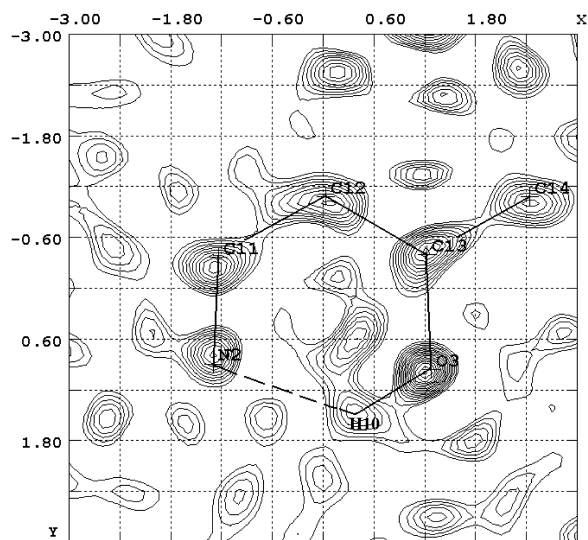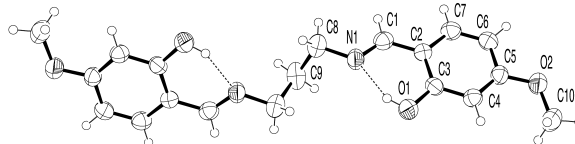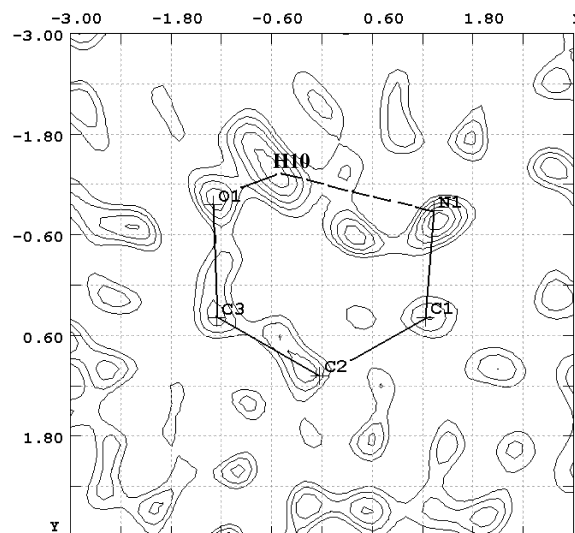

Fig. 4. Difference Fourier map (bold contours show positive electron densities) of **2**.

molecules packed along the **c** axis and have no inter-molecular approximation were photochromic [3]. The conformation of the free ligand in the solid state is of particular interest in relation to that required in a metal complex [20]. Clearly, this conformation is not suitable for direct coordination to a metal ion.

Two types of intra molecular hydrogen bond (either N-H...O or N...H-O) can occur in Schiff bases [1]. The Schiff bases derived from salicylaldehyde always from the N...H-O type of hydrogen bonding regardless of N-substituent (alkyl or aryl) [21]. In the title molecules, intramolecular hydrogen bonds occur between O1 and N1 [2.541(3) Å] and between O3 and N2 [2.573(4) Å] atoms for **1** and between O1 and N1 [2.631(2) Å] atoms for **2**. Clearly, the enolimine tautomer is favoured over the ketamine form. This is evident from the observed O1-C3 and O3-C13 bond distances of 1.349(3) and 1.351(4) Å for **1** and O1-C3 1.347(2) Å for **2**, respectively, which are consistent with the O-C single bonds; similarly the N1-C1 and N2–C11 distances of 1.276(4) and 1.265(4) Å for **1** and N1-C1 1.278(2) Å for **2** are consistent with N=C double bonding.

In order to define the conformational flexibility of the title molecule, semi-empirical calculations using the AM1 molecular orbital method were carried out. The AM1 optimized geometry and conformations of **1** and **2** are in agreement with those crystallographically observed. The molecular energy can be devided into

bonded and non-bonded contributions. The bonded energy is considered to be independent of torsional angle changes and therefore vanishes when relative conformer energies are calculated as in our calculations. The non-bonded energy (E_N) is then further separated into torsional (E_T), steric (E_S) and electrostatic (E_{ES}) contribitions

$$E_N = E_T + E_S + E_{ES}, \qquad (1)$$

where the torsional energy (E_T) is that part of the torsional energy which does not arrive form the steric or electrostatic form. Due to non-bonded hydrogen-hydrogen interactions the energy profile of θ_1(C8-N1-C1-C2) show maximum near $-10°$ and $50°$ for **1** (H(C1)...H(O1) = 0.269 Å and H(O1)...H(C9) = 0.814 Å, respectively) and near $0°$ for **2** (H(C8)...H(O1) = 0.216 Å). But, the energy profile of θ_2(C9-C8-N1-C1) due to the non-bonded hydrogen carbon interactions show maximum near $10°$ and $130°$ for **1** (H(C8)...C9 = 0.401 Å and H(C8)...C9 = 0.435 Å) and near $0°$ and $-110°$ for **2** (H(C8)...C9 =
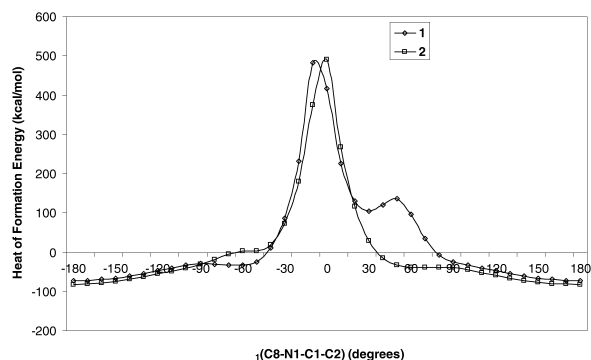
Fig. 5. AM1 calculated conformation energies of the θ_1 (C8-N1-C7-C6) torsion angle for **1** and **2**.
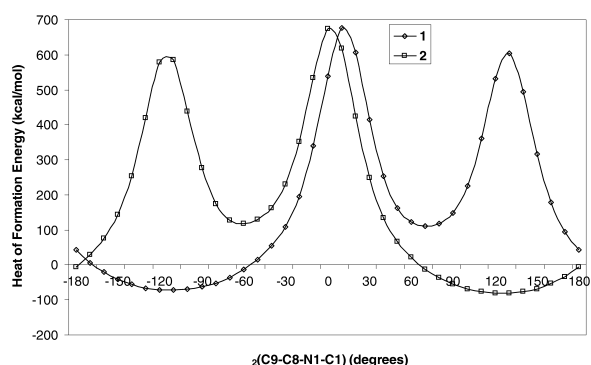

Fig. 6. AM1 calculated conformation energy of the θ_2 (C9-C8-N1-C7) torsion angle for **1** and **2**.

0.216 Å and H(C9)...C8) = 0.441. The planarity of **1** and **2** are controlled by the θ_1(C8-N1-C1-C2) and θ_2(C9-C8-N1-C1) torsion angles. The non-planar con-

formations and heat of formation energies of **1** and **2** according to the θ_1(C8-N1-C1-C2) and θ_2(C9-C8-N1-C1) torsion angles are the most stable conformations (see Fig. 5 and 6). Burgi and Dunitz carried out an extensive theoretical and experimental study on the non-planar conformation of the N-benzylideneaniline and related compounds [23]. Their explantion 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 increasing non-planarity, and **(b)** the π-electron system, itself divisible into two components, including, on the one hand, delocalization between the –HC1=N1- double bond and the aniline phenyl ring, (which is maximized for a planar conformation) and, on the other hand, delocalization of the nitrogene 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, the AM1 optimized geometries of the crystal structures of **1** and **2** corresponding to non-planar conformation is the most stable conformation in all considered calculations. The results strongly indicate that the most stable conformation is primarily determined by non-bonded hydrogen-hydrogen repulsions. The interactions between the N- lone pair atom and the π electrons of the rotated methoxybenzylidene ring, however, might also contribute to the conformational energies of **1** and **2**.

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