ELSEVIER

Journal of Molecular Structure 570 (2001) 91–95

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

Conformational and structural analysis of *N*-*N*′-bis (4-methoxybenzylidene)ethylenediamine

C. Ünaleroğlu[a,*], B. Temelli[a], T. Hökelek[b]

[a]*Department of Chemistry, Hacettepe University, 06532 Beytepe-Ankara, Turkey*
[b]*Department of Physics, Hacettepe University, 06532 Beytepe-Ankara, Turkey*

Received 17 August 2000; accepted 3 January 2001

Abstract

The Schiff base compound, *N*-*N*′-bis(4-methoxybenzylidene)ethylenediamine ($C_{18}H_{20}N_2O_2$) has been synthesized and its crystal structure has been investigated by X-ray analysis and PM3 method. The compound crystallizes in monoclinic space group $P2_1/n$ with $a = 10.190(1)$, $b = 7.954(1)$, $c = 10.636(1)$ Å, $\beta = 111.68(1)°$, $V = 801.1(1)$ Å^3, $Z = 2$ and $D_{cal} = 1.229$ Mg m^{-3}. The title structure was solved by direct methods and refined to $R = 0.056$ for 2414 reflections [$I > 3.0\sigma(I)$] by full-matrix anisotropic least-squares methods. The energy profile of the compound was calculated by PM3 method as a function of θ[N1′–C9′–C9–N1]. The most stable molecular structure of the title compound is the *anti* conformation, which is different in energy by 5.0 and 1.0 kcal mol^{-1} from the eclipsed conformation I and *gauche* conformations, (III and V), respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Structural analysis; Schiff base; Chelating ligands

1. Introduction

Schiff bases and their biologically active complexes have been studied during the last decade. Schiff bases have often been used as chelating ligands in the field of coordination chemistry [1] for obtaining thermotropic liquid crystalline polymers [2,3] and their metal complexes have been used as radiopharmaceuticals for cancer targeting [4], as dioxygen carriers [5] and as model systems for biological macromolecules [6,7]. The Schiff base complexes have also been used in catalytic reactions [8,9]. Although a series of Schiff base complexes have been investigated crystallographically, there are only a very limited number of reports about the free Schiff bases in the literature [10–15]. The phenyl derivative Schiff bases are used as corrosion inhibitors for aluminum in hydrochloric solution [16]. Knowing the structures of free Schiff bases in solution and in solid state is important in view of the comparison with the conformational analysis results. For these reasons, the synthesis, structural and conformational studies of the title compound were undertaken.

2. Experimental

2.1. Reagents and techniques

Anisalaldehyde(BDH), ethylenediamine(Aldrich), methanol and ethanol(Carlo Erba)were used in this study. Infrared spectrum was recorded using a

* Corresponding author. Tel.: +903-122992163; fax: +903-122992163.
E-mail address: canan@eti.cc.hun.edu.tr (C. Ünaleroğlu).

PII: S0022-2860(01)00469-0

Table 1
Experimental data and structure-refinement parameters

Compound	$C_{18}H_{20}N_2O_2$
Color/shape	Colorless/plate
Formula weight	296.37
Space group	$P2_1/n$
Temperature(K)	298
Cell constants	$a = 10.190(1)$, $b_2 = 7.954(1)$, $c = 10.636(1)$ Å, $\beta = 111.68(1)°$
Cell volume (Å^3)	801.1(1)
Formula units/unit cell	2
D_{calc}(Mg m^{-3})	1.229
μ_{calc}(mm^{-1})	0.65
Diffractometer/scan	Enraf–Nonius CAD-4/$\omega-2\theta$
Radiation used, graphite monochromator	Cu K_α($\lambda = 1.54184$ Å)
Maximum crystal dimension(mm)	$0.20 \times 0.20 \times 0.30$
Standard reflection	3
Decay of standard	$< 1\%$
Reflections measured	3446
θ (max) (°)	74.35
Range of h, k, l	$-9 \le h \le 9$, $-11 \le k \le 12$, $0 \le l \le 13$
Number of reflections	2414 with $I > 3.0\sigma(I)$
Corrections applied	Lorentz-polarization
Computer programs	SHELXS86 [17] MoIEN [18], ORTEP [19]
Source of atomic scattering factors	Int. Table for X-ray Cryst. Vol. IV, 1976 [20]
Structure solution	Direct methods
Treatment of hydrogen atoms	Hydrogen atoms were obtained from difference map and refined isotropically
No. of parameters var.	140
Weight	$w = 1/[\sigma F^2 + (0.02F)^2]$
GOF	1.25
R	0.056
R_w	0.072
$(\Delta/\sigma)_{max}$ (e Å^{-3})	0.57
$(\Delta/\sigma)_{min}$ (e Å^{-3})	−0.25

SHIMADZU FTIR-8101 spectrophotometer as KBr discs, in the range of 400–4000 cm^{-1} UV-visible spectrum was measured using a UNICAM UV/VIS spectrophotometer in CH_3OH solvent, in the range of 190–600 nm. Melting point was measured on a Gallenkamp apparatus using a capillary tube.

2.2. Synthesis of N-N′-bis (4-methoxybenzylidene)ethylenediamine

Anisalaldehyde (3.62 ml, 33.6 mmol) was dissolved in ethanol (20 ml). Then ethylenediamine (1.00 ml,14.66 mmol) was added and the solution was heated at 60°C. After 1 h, the reaction was completed. The product was filtered and crystallized in methanol, 3.9 g (89.78%) yield, m.p. 110.8°C. IR (KBr, cm^{-1}); 2840–2900 ($\surd_{C-H}$ aliphatic); 3080($\surd_{C-H}$ aromatic); 1641 ($\surd$(C=N); 1109 ($\surd$C–O). $\surd_{max}$ ($CHCl_3$, nm), 304.

2.3. Crystallography

The experimental data, methods and the procedures used to elucidate the structure and other related parameters are given in Table 1. The structure was solved by direct methods, SHELXS86 [17]. The positions of H atoms were clarified from difference synthesis and refined isotropically. The structure was refined by MOIEN [18] and the molecular structure (Fig. 1) was drawn by ORTEP [19].

2.4. Method of calculation

Theoretical calculations were carried out at the restricted Hartree–Fock level (RHF) using PM3 [21] semi-empirical SCF-MO methods in the MOPAC 7.0 [22], implemented in the Intel Pentium II computer. All calculations were carried out with the complete geometry optimization at precise level, and the

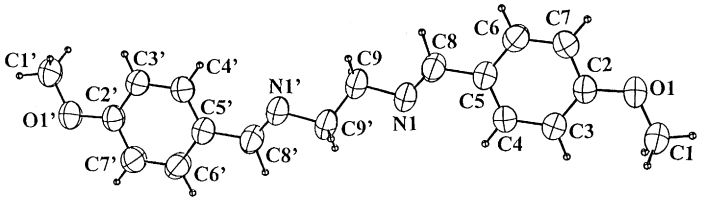

Fig. 1. An ORTEP [19] drawing of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 2
Atomic coordinates and equivalent displacement parameters with e..s.d.'s in parentheses. (anistropically refined atoms are given in the form of isotropic equivalent displacement parameters defined as: (4/3)[$a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$]

Atom	x	y	Z	B(Å^2)
O1	0.9448(1)	−0.0180(2)	1.3253(1)	5.26(3)
N1	0.5784(2)	0.0187(2)	0.6873(1)	5.53(4)
C1	1.0766(2)	0.0667(3)	1.3620(2)	5.87(5)
C2	0.8599(2)	−0.0229(2)	1.1914(2)	4.23(3)
C3	0.8857(2)	0.0648(2)	1.0911(2)	4.65(4)
C4	0.7922(2)	0.0509(2)	0.9584(2)	4.67(4)
C5	0.6738(2)	−0.0496(2)	0.9241(2)	4.45(4)
C6	0.6505(2)	−0.1382(2)	1.0268(2)	5.43(4)
C7	0.7414(2)	−0.1237(2)	1.1591(2)	5.30(4)
C8	0.5731(2)	−0.0675(2)	0.7836(2)	5.00(4)
C9	0.4700(2)	−0.0128(3)	0.5532(2)	5.64(5)
H11	1.124(2)	0.067(2)	1.460(2)	5.7(4)[a]
H12	1.066(2)	0.165(3)	1.332(2)	8.5(6)[a]
H13	1.142(2)	0.033(2)	1.315(2)	7.5(5)[a]
H31	0.967(2)	0.130(2)	1.112(1)	4.9(4)[a]
H41	0.810(1)	0.109(2)	0.891(1)	4.7(4)[a]
H61	0.570(2)	−0.208(2)	1.001(2)	5.9(4)[a]
H71	0.725(2)	−0.176(2)	1.228(2)	6.8(5)[a]
H81	0.498(2)	−0.177(3)	0.769(2)	8.2(5)[a]
H91	0.437(2)	−0.139(3)	0.548(2)	8.5(6)[a]
H92	0.385(2)	0.071(3)	0.537(2)	9.1(6)[a]

conformers located at minima were characterized by the calculations of vibrational frequencies.

3. Results and discussion

3.1. Crystal structure analysis

Single crystal X-ray structure of the title compound was reported to further corroborate the structure assignments. The final coordinates and equivalent isotropic displacement parameters are given in Table 2. The molecular structure with the atom numbering scheme is shown in Fig. 1. The bond lengths and angles with torsion angles are given in Table 3. The asymmetric unit contains only one-half molecule. As a whole, the title molecule is in the staggered conformation [N1–C9–C9′–N1′ = −180.0(2)°]. The phenyl rings and the C=N imine bonds are slightly deviated from co-planarity as supported by the N1–C8–C5–C6[173.1(2)°] and N1–C8–C5–C4 [−7.6(3)°] torsion angles.

3.2. Computational study

In order to define the conformational flexibility of the title compound, semi-empirical calculations using

Table 3
The bond lengths (Å) and angles (°) with some selected torsion angles (°). Symmetry code (′): $-x+1, -y, -z+1$

O1–C1	1.422(2)	C2–C7	1.383(2)
O1–C2	1.367(2)	C3–C4	1.385(2)
N1–C8	1.250(2)	C4–C5	1.379(2)
N1–C9	1.467(2)	C5–C6	1.392(3)
C2–C3	1.379(3)	C5–C8	1.474(2)
C9–C9′	1.486(3)	C6–C7	1.374(2)
C1–O1–C2	118.0(1)	C3–C4–C5	121.4(2)
C8–N1–C9	117.3(2)	C4–C5–C6	118.2(1)
O1–C2–C3	124.3(1)	C4–C5–C8	122.5(2)
O1–C2–C7	115.7(2)	C6–C5–C8	119.3(2)
C3–C2–C7	119.9(1)	C5–C6–C7	121.0(2)
C2–C3–C4	119.5(2)	C2–C7–C6	120.0(2)
N1–C9–C9′	110.1(2)	N1–C8–C5	123.6(2)
C1–O1–C2–C3	−7.7(3)	C2–C3–C4–C5	−0.3(3)
C1–O1–C2–C7	172.4(2)	C3–C4–C5–C6	−0.3(3)
C9–N1–C8–C5	−179.6(2)	C3–C4–C5–C8	−179.6(2)
O1–C2–C3–C4	−179.9(2)	C4–C5–C6–C7	1.2(3)
C7–C2–C3–C4	0.0(3)	C8–C5–C6–C7	−179.5(2)
O1–C2–C7–C6	−179.3(2)	C4–C5–C8–N1	−7.6(3)
C3–C2–C7–C6	0.8(3)	C6–C5–C8–N1	173.1(2)
C8–N1–C9–C9′	−146.5(2)	C5–C6–C7–C2	−1.5(3)

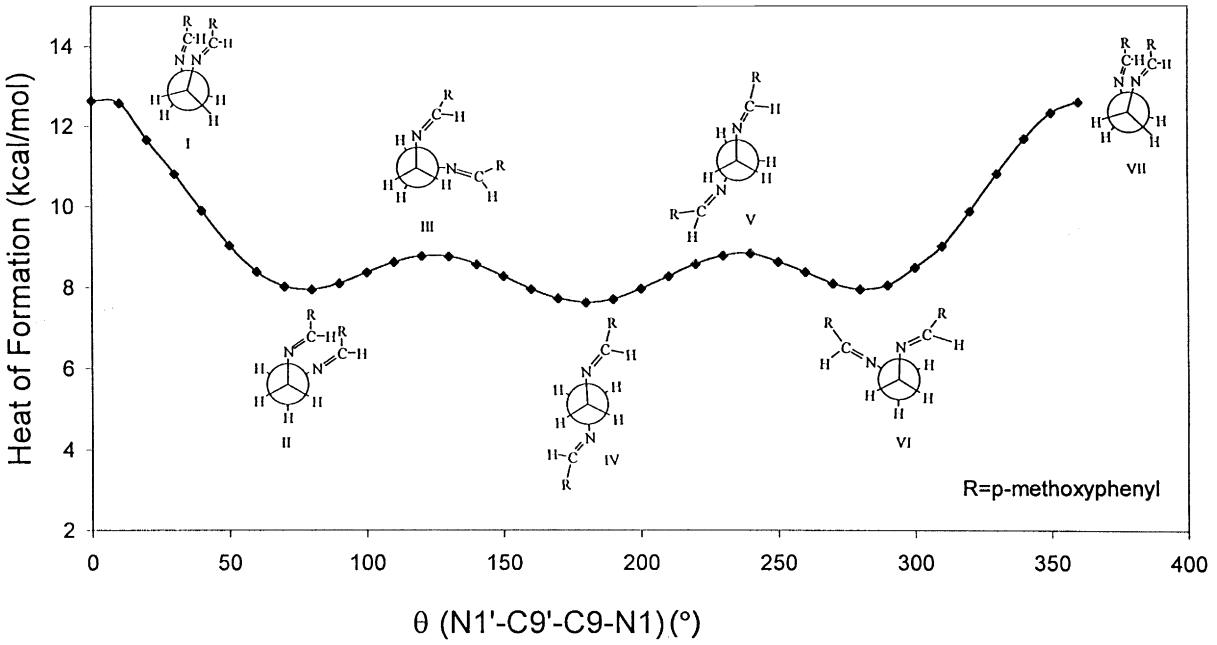

Fig. 2. PM3 calculated conformation energy profile of the θ[N1′–C9′–C9–N1] torsion Angle (°).

PM3 molecular method were carried out. The energy profile, which was obtained from PM3 method (Fig. 2) as a function of θ[N1′–C9′–C9–N1] shows three minima at 60, 180 and 300° and three maxima at 0, 120 and 240°. The maxima positions correspond to the eclipsed conformations. The eclipsed conformation I is approximately 3.85 kcal mol^{-1} unstable than the eclipsed conformations III and V. In addition to the torsional strain in conformation I, the van der Waals interactions between the lone pair electrons of nitrogen atoms and also between the electrons of the –N=C– double bonds, cause strong repulsions than the other conformations. Minima points in the diagram correspond to the energetically favored *gauche* conformations for II and VI and *anti* conformation for IV. The difference in energy between eclipsed conformation I and the *anti* conformation IV is 5.0 kcal mol^{-1}. The *gauche* conformations have approximately 1.0 kcal mol^{-1} more energy than the *anti* conformation. Conformational calculation using PM3 method reveals that the most energetically stable structure is the *anti* conformation. This conformation is controlled by the [N1′–C9′–C9–N1] torsion angle which is found as 180° by calculation and also by X-ray analysis. Calculated torsion angles for θ[N1–C8–C5–C6] and θ[N1–C8–C5–C4] are 179.9° and −0.1°, respectively. These torsion angles indicate that the non-hydrogen phenyl and the conjugated imine group atoms lie in a plane. This planarity is slightly deviated in the crystal structure with torsion angles of 173.1(2)° [θ (N1–C8–C5–C6)] and −7.6(3)° [θ (N1–C8–C5–C4)]. As can be seen from Tables 4–6, the calculated and experimental values are in good agreement with the exceptions of

Table 4
Comparison of the bond lengths (Å)

	X-ray analysis	PM3
O1–C1	1.422(2)	1.406
O1–C2	1.367(2)	1.379
N1–C8	1.250(2)	1.292
N1–C9	1.467(2)	1.463
C2–C3	1.379(3)	1.403
C2–C7	1.383(2)	1.399
C3–C4	1.385(2)	1.386
C4–C5	1.379(2)	1.399
C5–C6	1.392(3)	1.397
C5–C8	1.474(2)	1.466
C6–C7	1.374(2)	1.398

Table 5
Comparison of the bond angles (°)

	X-ray analysis	PM3
C1–O1–C2	118.0(1)	117.5
C8–N1–C9	117.3(2)	121.7
O1–C2–C3	124.3(1)	125.4
O1–C2–C7	115.7(2)	114.1
C3–C2–C7	119.9(1)	120.5
C2–C3–C4	119.5(2)	119.5
C3–C4–C5	121.4(2)	120.5
C4–C5–C6	118.2(1)	119.4
C4–C5–C8	122.5(2)	122.4
C6–C5–C8	119.3(2)	118.3
C5–C6–C7	121.0(2)	120.9
C2–C7–C6	120.0(2)	119.2
N1–C8–C5	123.6(2)	121.7

Table 6
Comparison of the torsion angles (°)

	X-ray analysis	PM3
C1–O1–C2–C3	−7.7(3)	0.1
C1–O1–C2–C7	172.4(2)	−0.1
C9–N1–C8–C5	−179.6(2)	−178.9
O1–C2–C3–C4	−179.9(2)	−179.9
C7–C2–C3–C4	0.0(3)	0.0
O1–C2–C7–C6	−179.3(2)	−179.9
C3–C2–C7–C6	0.8(3)	0.0
C2–C3–C4–C5	−0.3(3)	0.0
C3–C4–C5–C6	−0.3(3)	0.0
C3–C4–C5–C8	−179.6(2)	−179.9
C4–C5–C6–C7	1.2(3)	0.0
C8–C5–C6–C7	−179.5(2)	−179.9
C4–C5–C8–N1	−7.6(3)	−0.1
C6–C5–C8–N1	173.1(2)	179.9
C5–C6–C7–C2	−1.5(2)	0.0
N1′–C9′–C9–N1	−180.0(2)	−180.0
C9′–C9–N1–C8	−146.5(2)	−141.3

C8–N1–C9 bond and C9′–C9–N1–C8 torsion angles.

In conclusion, the most stable molecular structure for the compound is in the *anti* conformation as confirmed by X-ray structure analysis and computation. The phenyl rings and conjugated imine groups are slightly deviated from planarity by X-ray analysis and exactly planar by PM3 method.

References

[1] A.D. Garnovski, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1.
[2] C.H. Li, T.C. Chang, J. Polym. Sci. Polym. Chem. 28 (1990) 3625.
[3] C.H. Li, T.C. Chang, Eur. Polym. J. 27 (1991) 35.
[4] P.J. Blower, Transition Met. Chem. 23 (1998) 109.
[5] W.K. Lin, N. Alcock, D.H. Busch, J. Am. Chem. Soc. 113 (1991) 7603.
[6] O.P. Anderson, A.L. Cour, M. Findeisen, L. Hennig, O. Simonsen, L. Taylor, H. Toftlund, J. Chem. Soc. Dalton Trans. (1997) 111.
[7] S. Uhlenbrock, R. Wegner, B. Krebs, J. Chem. Soc. Dalton Trans. (1996) 3731.
[8] D.E. Hamilton, R.S. Drago, A. Zombeck, J. Am. Chem. Soc. 109 (1987) 374.
[9] P.R. Woodman, C.J. Sanders, N.W. Alcock, P.B. Hitchcock, P. Scott, New , J. Chem. 23 (1999) 815.
[10] M. Yıldız, Z. Kılıç, T. Hökelek, J. Mol. Struc. 441 (1998) 1.
[11] T. Hökelek, N. Gündüz, Z. Hayvalı, Z. Kılıç, Acta Crystallogr. C 51 (1995) 880.
[12] T. Hökelek, Z. Kılıç, M. Işiklan, M. Toy, J. Mol. Struct. 523 (2000) 61.
[13] T. Hökelek, N. Gündüz, Z. Hayvalı, Z. Kılıç, J. Chem. Cryst. 25 (1995) 831.
[14] F. Ercan, S.G. Öztas, N. Ancin, T. Hökelek, M. Tüzün, D. Ülkü, J. Chem Cryst. 26 (1996) 243.
[15] M. Gavranic, B. Kaitner, E. Mestrovic, J. Chem. Cryst. 26 (1996) 23.
[16] G.K. Gomma, M.H. Wahdan, Mater. Chem. Phys. 39 (1995) 209.
[17] G.M. Sheldrick, Acta Cryst. A 46 (1990) 467.
[18] C.K. Fair, MoIEN, An Interactive Intelligent System for Crystal Structure Analysis, Enraf-Nonius, Delft, The Netherlands, 1990.
[19] C.K. Johnson, Ortep II, Report ORNL-5138.Oak Ridge National Laboratory. TN, 1976.
[20] The International Tables for X-ray Crystallography, Vol. IV from 1974 are published by the Kynoch Press, Birmingham, England and now distributed by the Kluwer Academic Publishers, Dordrecht, The Netherlands.
[21] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209.
[22] J.J.P. Stewart, MOPAC 7.0 QCPE, University of Indiana, Bloomington, IN, USA.