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Studies on Optical Activity, X-ray and Electronic Characteristics of 4-(4-Chlorophenylazo)-2-(*p*-tolylimino-methyl)phenol

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The bidentate monoazo Schiff base compound 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base compound was prepared and characterized by several spectroscopic methods. In the present study 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base compound has been investigated by X-ray analysis and AM1 semi-empirical quantum mechanical method. The crystal is in the monoclinic space group pc with a = 19.450(4) Å, b = 6.941 (10) Å, c = 6.116 (13) Å, $d_{calc.}$ = 1.415 g/m^3, V = 821/2 (3) Å^3, α = 90°, β = 95.927°, γ = 90° and R = 0.0650 for 2408 independent reflections. The title compound has an intermolecular hydrogen bonding, N···H—O 2.550 Å between H (1) and N (3) atoms. The geometry data of the title compound were investigated by AM1 semi-empirical quantum calculation. The optimized geometry of the molecular structure corresponding to the planar conformation and the computed structural data of the isolated molecule are compared with the experimental data. The AM1 optimization geometries of the Schiff base are in agreement with the crystallographic data. In the next part of this study the first hyperpolarizability (β_μ) for 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base compound was calculated by using AM1 semi-empirical method. The calculated hyperpolarizability (β_μ) for this compound is 31.4 times that of urea so this Schiff base compound has a good nonlinear optical property.

Key Words: 4-(4-Chlorophenylazo)-2-(*p*-tolylimino-methyl)phenol, X-ray study, AM1, Electronic property, Nonlinear optical property, Hyperpolarizability.

INTRODUCTION

Schiff bases have been used as ligands in metal coordination chemistry. The Schiff bases derived from salicylaldehyde (salens) polydentate ligands are known to form stable complexes with transition metal ions[1]. The resulting salen complexes have attracted increasing attention, mainly due to their peculiar properties[2] and their reactivity mainly in the area of binding small molecules[3, 4]. Schiff bases are reagents, which play a significant role in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigation of the drugs used in pharmacology, biochemistry and physiology[5]. In addition, they have potential applications are as metallomesogens and in the development of photonic devices[6]. N-Substituted salen type show photochromism and thermochromism in the solid state. Intramolecular proton transfer from the hydroxyl group to the imine group was happen and produces thermochromism[7].

On the other hand, Schiff bases are important analytical reagents, because they enable simple and inexpensive determination of various organic and inorganic substances. Also there are two principal ways of the analytical application of these compounds: first, the determination of organic compounds bearing an amino or an active carbonyl group by the formation of coloured (chromophore-containing), fluorescent or insoluble Schiff bases, and second, the determination of various metal ions, as well as amino and carbonyl compounds, by using complex formation reactions[8-10].

The theoretical calculations have been used for investigation of the electronic properties and the structure of compounds and a comparison of the theoretical data with experimental data is a common procedure for many researches. Recently we reported some theoretical work about the investigation of the structure and nonlinear optical properties of some azo Schiff base compounds[11-13].

In recent years much attention has been paid to the synthesis and development of second-order nonlinear optical (NLO) molecule-based materials. This study focuses on preparation of a single crystal and second-order NLO property for this compound within the proven INDO/SCI-SOS (ZINDO) formalism[14], to describe the electronic structure and nonlinear optical property (NLO) relationships of this monoazo Schiff base compound.

The structure of 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base compound is shown in Fig. 1.

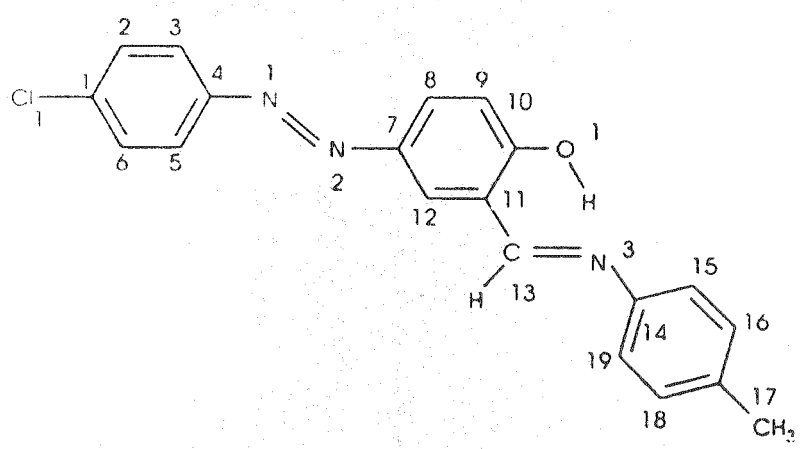

Fig. 1. Structure of 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base

EXPERIMENTAL

Solvents were dried and purified before use according to published procedure[15]. The other materials were used without further purification.

Synthesis: The 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl)phenol Schiff base was prepared by Schiff method[16]. Single crystals for this Schiff base compound were obtained from ethanolic solution at room temperature and separated by hand. Single crystal X-ray diffraction data for this mono-azo Schiff

base compound was collected[17] on a Bruker SMART CCD diffractometer at 120 K. Then the data were reduced and the structure was solved by direct methods, using the program SHELXTL version 5.1 and refined by the full-matrix least squares[18] on F^2. Monochromatized Mo K_α radiation was 0.71073 Å. Details of the X-ray experimental and crystal data are summarized in Table-1 and perspective drawing of the molecule is shown[19] in Fig. 2.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR THE INVESTIGATION OF 4-(4-CHLOROPHENYL-AZO)-2-(*p*-TOLYLIMINO-METHYL) PHENOL SCHIFF BASE COMPOUND

Empirical formula	$C_{20}H_{16}ClN_3O$	
Formula weight	349.81 g mol^{-1}	
Temperature	120(2) K	
Wavelength	0.71073	
Crystal system	Monoclinic	
Space group	P c	
Unit cell dimensions	a = 19.450 (4) Å	a = 90°
	b = 6.9414 (10) Å	b = 95.978 (3)°
	c = 6.1160 (13) Å	g = 90°
Volume and Z	821.2 (3)) $Å^3$ and 2	
Density (calculated)	1.415 mg m^{-3}	
Absorption coefficient	0.246 mm^{-1}	
F(000)	364	
Crystal size θ range for data collection	0.3 × 0.1 × 0.1 mm^3	
Index ranges	$-16 \le h \le 24, -8 \le k \le 6, -7 \le l \le 6$	
Reflections collected	4920	
Independent reflections	2408 [R (int.) = 0.0650]	
Completeness to θ = 26.98	96.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.694287 and 0.305535	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2408/2/227	
Goodness-of-fit on F^2	1.055	
Final R indices for 1552 refl. with I > 2 sigma (I)	R1 = 0.0629, wR2 = 0.1112	
R indices (all data)	RL = 0.0949, wR2 = 0.1188	
Absolute structure parameter	0.68 (14)	
Largest diff. peak and hole	0.437 and –0.307 e $Å^{-3}$	

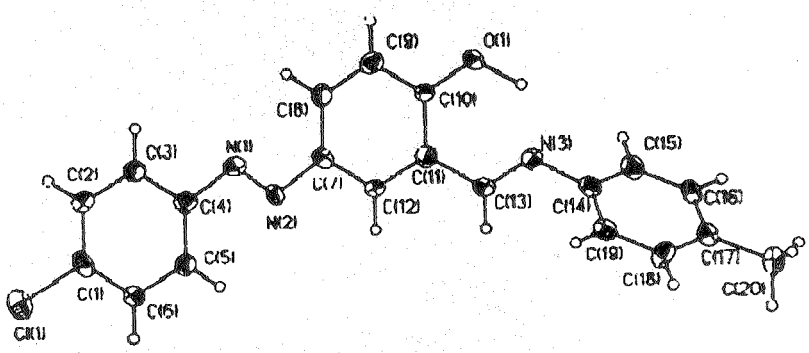

Fig. 2. View of 4-(4-chlorophenylazo)-2-(*p*- tolylimino-methyl)phenol Schiff base compound (numbering of atoms corresponds to Table-2)

The unit-cell package for this Schiff base is displayed in Fig. 3; atomic coordinates for this Schiff base are shown in Table-2.

TABLE-2
ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($A^2 \times 10^3$) FOR 4-(4-CHLOROPHENYLAZO)-2-(*p*-TOLYLIMINO-METHYL) PHENOL SCHIFF BASE COMPOUND

Atom	X	Y	Z	U(eq)
Cl(1)	14593(1)	7990(2)	10272(3)	45(1)
O(1)	9119(2)	6859(5)	−1005(5)	28(1)
N(1)	12033(2)	7103(6)	4251(8)	29(1)
N(2)	11504(2)	7920(6)	4772(7)	23(10)
N(3)	8428(2)	7816(6)	2147(7)	28(1)
C(1)	13838(3)	7734(8)	8518(10)	32(1)
C(2)	13861(3)	6947(7)	6457(9)	32(1)
C(3)	13250(3)	6734(7)	5099(10)	28(1)
C(4)	12625(3)	7325(8)	5791(10)	25(1)
C(5)	12610(3)	8094(7)	7899(10)	25(1)
C(6)	13220(3)	8276(7)	9281(9)	31(1)
C(7)	10914(2)	7709(8)	3181(9)	28(1)
C(8)	10941(3)	6994(7)	1049(9)	28(1)
C(9)	10339(2)	6736(7)	−330(9)	28(1)
C(10)	9699(3)	7162(6)	360(10)	22(1)
C(11)	9667(2)	7881(7)	2526(8)	25(1)
C(12)	10282(2)	8157(7)	2897(9)	24(1)
C(13)	8994(2)	8092(7)	3374(8)	27(1)
C(14)	7781(2)	7711(7)	3048(9)	27(1)
C(15)	7193(2)	8297(7)	1773(9)	29(1)
C(16)	6549(3)	8109(7)	2567(10)	25(1)
C(17)	6488(3)	7304(8)	4616(9)	27(1)
C(18)	7092(3)	6696(8)	5913(9)	30(2)
C(19)	7734(3)	6885(7)	5127(8)	30(1)
C(20)	5780(3)	7049(8)	5460(10)	31(2)

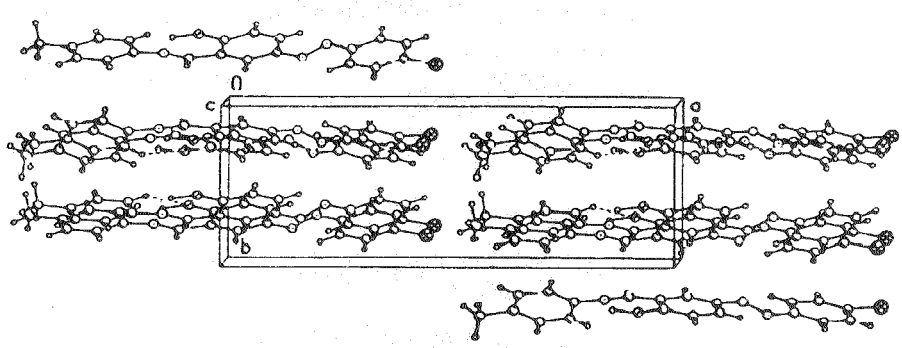

Fig. 3. Molecular package for 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base in crystal

Molecular Orbital Calculations

The electronic properties for 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base were calculated using AM1 semi-empirical self-consistent field-molecular orbital (SCF-MO) Hamiltonian by MOPAC 7.0 and ZINDO program packages[20].

Geometry optimization for this compound was done by using MOPAC 7.0 program package and running on a Pentium II pc and were calculated from the crystallographic coordinate atoms. All semi-empirical calculations were performed using Austin Model 1 (AM1) at high precision[21], and the geometry of the molecule was previously optimized (Fig. 4). This theoretical method has been widely used to predict coordination sites for the ligands, the net charges calculated for all atoms in the structure of 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base were shown[22] in Fig. 4.

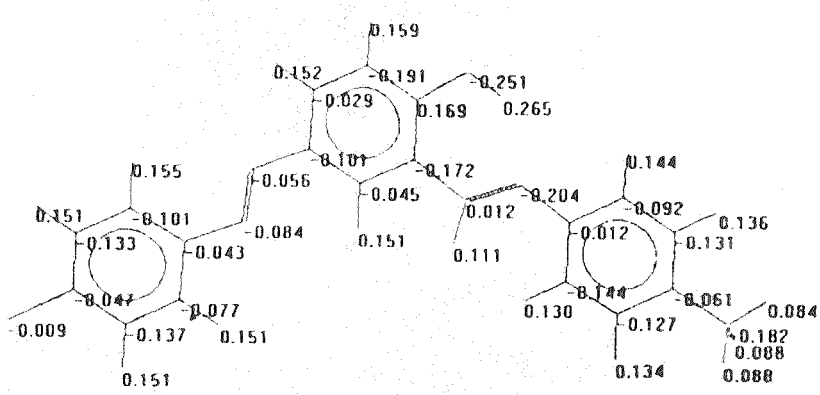

Fig. 4. Calculated net charges on all the atoms for 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base by using AM1 semi-empirical method

Some important bond lengths, bond angles and torsion angles for 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base with comparison of crystallographic data were shown in Table-3.

TABLE-3
SELECTED BOND LENGTHS (Å), BOND ANGLES (°) AND TORSION ANGLES (°) FOR 4-(4-CHLOROPHENYLAZO)-2-(*p*-TOLYLIMINO-METHYL) PHENOL SCHIFF BASE CALCULATED BY AM1 SEMI-EMPIRICAL METHOD AND X-RAY DIFFRACTION RESULTS

Selected bonds	Bond length (Å) calcd. by AM1 method	Bond length (Å) by X-ray
Cl(1)-C(1)	1.696	1.735
C(4)-C(5)	1.412	1.398
C(4)-N(1)	1.435	1.419
N(1)-N(2)	1.231	1.246
N(2)-C(7)	1.433	1.432
C(10)-C(11)	1.410	1.423
C(10)-O(1)	1.362	1.348
O(1)-H(1)	0.973	1.199
C(11)-C(13)	1.467	1.464
C(13)-N(3)	1.291	1.281
N(3)-C(14)	1.406	1.427
C(17)-C(20)	1.480	1.530
Selected angles	**Bond angles (Å) calcd. by AM1 method**	**Bond angles (°) by X-ray**
O(1)-C(10)-C(9)	117.18	119.90
O(1)-C(10)-C(11)	125.75	121.32
C(10)-C(11)-C(13)	122.76	119.50
C(11)-C(13)-N(3)	123.00	121.50
C(13)-N(3)-C(14)	123.74	121.30
Selected torsion angles	**Torsion angles (°) calcd. by AM1 method**	**Torsion angles (°) by X-ray**
C(14)-N(3)-C(13)-C(11)	175.50	169.60
N(3)-C(13)-C(11)-C(10)	–4.97	–6.60
O(1)-C(10)-C(11)-C(12)	178.00	179.40
C(7)-N(2)-N(1)-C(4)	180.00	179.00

Nonlinear optical property calculation

Molecular orbital calculations were performed under semi-empirical levels. First, the geometric structure of the present Schiff base was optimized with AM1 method. Then, based on the optimized geometry, a semi-empirical ZINDO/SOS approach was used to generate the molecular orbital and the first hyperpolarizability (β_μ) was provided. 4-(4-Chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base reveals the large second order nonlinear optical response, because it has delocalized π-system. From Table-4, the value of hyperpolarizability (β_μ) for the present Schiff base is rather large compared with the value for urea. The

molecular hyperpolarizability value (β_μ) for this compound is 31.4 times that of urea (β_μ for urea 0.14×10^{-30} esu).

TABLE-4
NONLINEAR OPTICAL PROPERTIES OF
4-(4-CHLOROPHENYLAZO)-2-(*p*-TOLYLIMINO-METHYL) PHENOL SCHIFF BASE

μ (Deby)		$\beta_\mu \times 10^{-30}$ (esu)
μ_x	0.728	
μ_y	2.365	14.77
μ_z	–0.028	
μ_{total}	2.474	

RESULTS AND DISCUSSIONS

1. The optimized structure for 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base by MOPAC 7.0 program package shows that the most stable conformer has one hydrogen bonding between H(1) and N(3) with distance 2.0663 Å (X-ray data: 2.550 Å).

2. The negative net charges on O(1) and N(3) atoms in Fig. 4 shows that the coordination sites for 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base are O(1) and N(3) atoms (Fig. 1).

3. Comparison between the theoretical data (bond lengths, bond angles and torsion angles) shows a lot of agreement with the X-ray experimental results.

4. The 4-(4-chlorophenylazo)-2-(*p*-tolylimino-methyl) phenol Schiff base compound has a good NLO property (calculated $\beta_\mu = 14.77 \times 10^{-30}$ esu). The linear absorption spectrum of the present Schiff base in a solution of DMF exhibits one intense band near 358 nm. The AM1 electronic spectrum calculation by ZINDO program gives a strong electron transition near 30871 cm^{-1} with oscillator strength 0.323. The optical transition associated with this band is mainly the contribution on a $\pi \rightarrow \pi^*$ transition, this excitation mainly responsible for the NLO response. It should be noted that this Schiff base has a good hyperpolarizability (β_μ) for use in photonic devices.

5. The semi-empirical calculation shows that the molecular structure of the present Schiff base is planar. All the three torsion angles C(14)-N(3)-C(13)-C(11), O(1)-C(10)-C(11)-C(12) and C(7)-N(2)-N(1)-C(4) are 180°, and in all calculations it was found that the most stable structure is the optimized X-ray structure.

Conclusion

The AM1 optimization geometry of the structure of the present Schiff base indicates that the most stable conformation has a hydrogen bonding between oxygen atom in hydroxyl group with N-lone pair electrons from imine group. In the optimized structure O(1) and N(3) atoms have more negative charge density (Fig. 4) than the other atoms in the present Schiff base and these atoms are the coordination sites for this compound in binding to the transition metal ions.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication No. CCDC 239985[23]

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23. Further information may be obtained from Cambridge CB21EZ, UK, by quoting the depository number CCDC 239985. E-mail: deposit@CCDC.com.au.uk

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