Study on the Second Order Optical Properties of *N*-(2,4-Dichloro)-salicylaldimine

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N-(2,4-Dichloro)-salicylaldimine was synthesized, characterized by elemental analysis, FT-IR, and UV-visible spectroscopy, and its crystal structure was determined. The title compound is almost planar and contains short intramolecular O-H…N hydrogen bonds [O1-N1 2.601(1) Å]. It remains transparent in the visible region and has solvatochromic behavior in the UV region in the range 198 – 349 nm, implying non-zero microscopic first hyperpolarizability. The *ab-initio* quantum mechanical calculations (finite field second-order Møller Plesset perturbation theory) of the studied compound have been carried out to compute the electric dipole moment ($\boldsymbol{\mu}$) and the first hyperpolarizability ($\boldsymbol{\beta}$) values. The *ab-initio* results also show that this ligand might have microscopic nonlinear optical behavior with non-zero values.

Key words: Nonlinear Optics; First Hyperpolarizability; UV-visible Spectroscopy; Crystal Structure; *Ab-initio* Calculation.

1. Introduction

Over the past decade, due to its applications in optical communication and processing, quadratic nonlinear optical (NLO) behavior has attracted interest of a large number of researchers in the search of materials with large microscopic and macroscopic quadratic NLO response [1, 2]. Progress has been made in finding new organic molecules with large second-order polarizability, $\boldsymbol{\beta}$. Among the materials producing NLO effects, organic materials are of considerable importance owing to their synthetic flexibility large hyperpolarizabilities, ultra-fast response times, and high laser damage thresholds, compared to inorganic materials. Schiff base compounds have been investigated during the last years because of their potential applicability in optical communications, and many of them have NLO behavior [3]. The aim of our present paper was to characterize newly synthesized Schiff base ligands having donor hydroxy and acceptor chloro substituents (Fig. 1) with several spectroscopic and crystallographic techniques, and to compute the electric dipole moment $\boldsymbol{\mu}$ and first hyperpolarizability $\boldsymbol{\beta}$ of this compound by *ab-initio* finite field second-order Møller Plesset perturbation (FF MP2) method. Our interest is not only to predict $\boldsymbol{\mu}$ and $\boldsymbol{\beta}$ values of *N*-(2,4-dichloro)-salicylaldimine, but also to relate the microscopic NLO mechanism with the structural and linear optical (UV-visible) properties.

2. Experimental

2.1. Reagent and Techniques

2-Hydroxy-1-salicylaldehyde, 2,4-dichloroaniline, ethanol and $CDCl_3$ were purchased from Merck (Germany), methanol and acetonitrile from Aldrich Chemical Co. The elemental analysis was performed on a LECO CHNS-932 C-, H-, N-analyser. Infrared absorption spectra were obtained from a Mattson 1000 FT-IR spectrometer in KBr pellets and reported in cm^{-1}. UV-visible spectra were measured using a Perkin Elmer Lambda 2 series spectrophotometer.

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Table 1. Crystal and experimental data.

Compound	$C_{13}H_9Cl_2NO$
Colour/shape	Yellow/prismatic
Formula weight	266.11
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 4.729(1)$ Å $b = 12.855(1)$ Å, $\beta = 92.13(2)°$ $c = 19.358(2)$ Å
Volume	1176.0(3) Å^3
Z	4
Density (calculated)	1.503 g cm^{-3}
Absorption coefficient	0.532 mm^{-1}
$F(0\,0\,0)$	544
Crystal size	$0.08 \times 0.16 \times 0.80$ mm^3
θ range for data collection	3.17° to 30.16°
Index ranges	$-6 \le h \le 6$; $-0 \le k \le 17$; $0 \le l \le 26$
Independent reflections	3139
Reflections observed $[I > 2\sigma(I)]$	3132
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3132 / 0 / 158
Goodness-of-fit on F^2	1.171
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0642$; $wR = 0.1367$
(Δ/σ)max	0.001
Largest diff. peak and hole	0.536 and -0.484 e×Å^{-3}

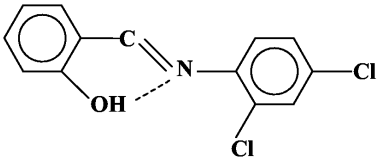

Fig. 1. Chemical structure of *N*-(2,4-dichloro)-salicylaldimine.

2.2. Preparation of N-(2,4-Dichloro)-salicylaldimine

The title compound was prepared by condensation of 2-hydroxy-1-salicylaldehyde (0.01 mol) and 2,4-dichloroaniline (0.01 mol) in 150 ml of ethanol. The reaction mixture was stirred for 6 h, and then placed in a freezer for 24 h. The yellow precipitate was collected by filtration and then washed with cold ethanol: M.p. 89.5 °C; yield: 2.11 g (89%). Found: C 67.89, H 4.71, N 5.77. $C_{13}H_{10}NOCl$; C 67.81, H 4.65, N 5.70. The chemical structure of *N*-(2,4-dichloro)-salicylaldimine is given in Figure 1.

2.3. X-Ray Structure Determination

The data collection was performed on an Enraf-Nonius diffractometer employing graphite-monochromatized Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Details of the X-ray data, structure solution and structure refinement are given in Table 1. Data reduction and corrections for absorption and crystal decomposition (1.2%) were carried out using the MoIEN Single Crystal Structure Analysis Software [4]. The structure was solved by SHELXS-97 and refined with SHELXL-97 [5]. The positions of H atoms bonded to C atoms were calculated (C-H distance 0.93 Å) and included in the structure factor calculation using a riding model. The hydroxy H atom H1 was found from a difference Fourier map calculated for the refinement process as a small positive electron density. Some selected bond distances and angles are listed in Table 2, and an ORTEP view of the molecular structure is given in Figure 2. Crystallographic data for the structure reported in the paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC253267. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 2. Selected bond lenghts (Å) and angles (°).

C1-N1	1.424(1)	C2-C3	1.385(1)
C4-Cl2	1.741(1)	C5-C6	1.381(1)
C6-Cl1	1.733(1)	C7-N1	1.275(1)
C12-C13	1.382(1)	C13-O1	1.332(1)
C2-C1-N1	125.3(1)	C6-C1-N1	116.8(1)
C3-C4-Cl2	119.4(1)	C5-C4-Cl2	119.0(1)
C5-C6-Cl1	118.5(1)	C1-C6-Cl1	120.1(1)
N1-C7-C8	121.6(1)	O1-C13-C12	119.2(1)
O1-C13-C8	121.8(1)	C7-N1-C1	121.5(1)

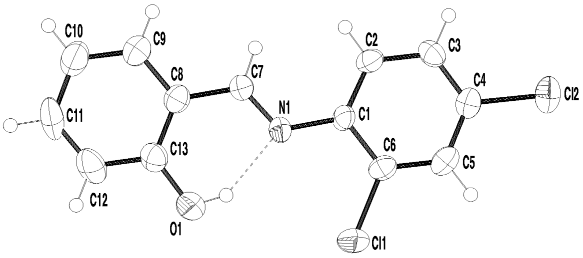

Fig. 2. The molecular structure of *N*-(2,4-dichloro)-salicylaldimine. The displacement ellipsoids are plotted at the 50% probability level.

3. Theoretical Calculations

As the first step of our *ab-initio* calculation of the investigated compound, the geometry taken from the starting structures based on its crystallographic data in Table 2 was optimized in the HF (closed-shell restricted Hartree-Fock) level. Then the electric dipole

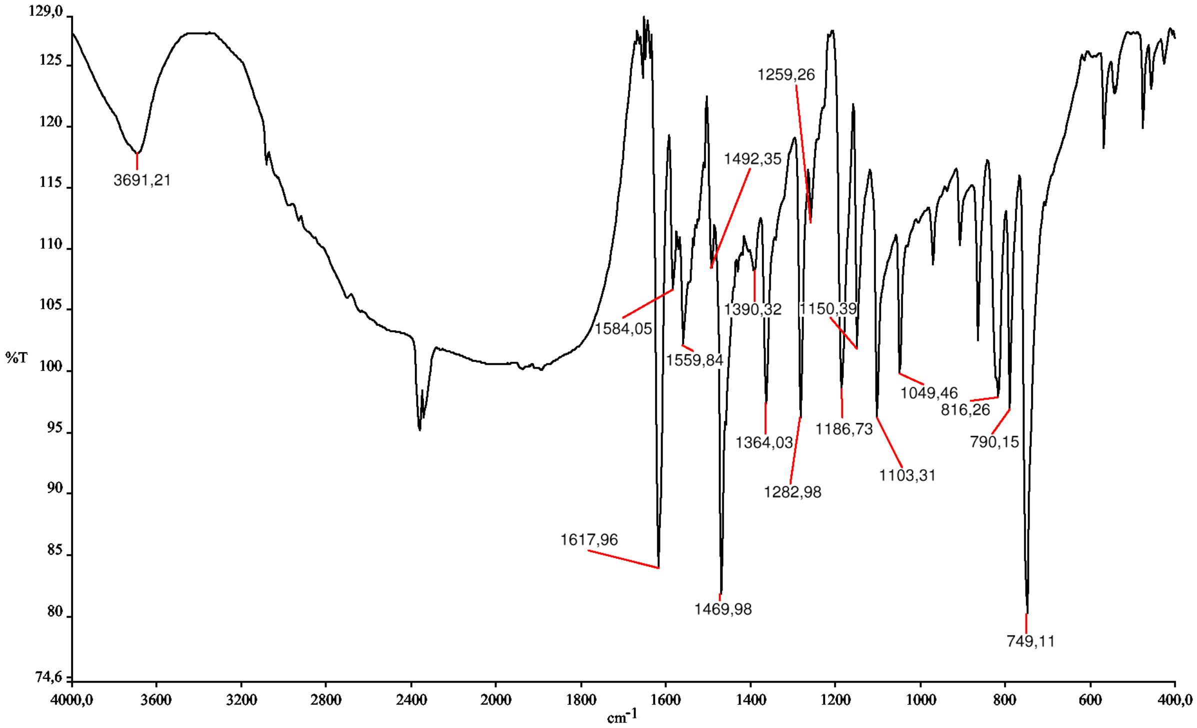

Fig. 3. FT-IR spectrum of *N*-(2,4-dichloro)-salicylaldimine.

moment and $\boldsymbol{\beta}$ tensor components were calculated by using the FF MP2 method at the 3-21+G** polarized and diffused basis set level, which has been found to be more than adequate for obtaining reliable trends in the first hyperpolarizability values. All $\boldsymbol{\mu}$ and $\boldsymbol{\beta}$ calculations were performed using GAUSSIAN98W [6], on an Intel Pentium IV 1.7 GHz processor with 512 MB RAM and Microsoft windows as the operating system.

We report β_{tot} (total first hyperpolarizability) for the synthesized molecule. The components of the first hyperpolarizability can be calculated using the equation

$$\beta_i = \beta_{iii} + 1/3 \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}). \quad (1)$$

Using the *x*, *y* and *z* components, the magnitude of the first hyperpolarizability tensor can be calculated by:

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}. \quad (2)$$

The complete equation for calculating the magnitude of the first hyperpolarizability from the GAUSSIAN98W output is

$$\beta_{\text{tot}} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2\right]^{1/2}. \quad (3)$$

To calculate all the electric dipole moments and first hyperpolarizabilities $(x,y,z) = (0,0,0)$ was chosen for the center of mass of the compound.

4. Results and Discussion

4.1. FT-IR Study

The observed vibrational bands in the range 749–3691 cm^{-1} are illustrated in Figure 3. Vibration bands with the wave numbers of 1617 ($\nu_{\text{C=N}}$), 1599, 1584 ($\nu_{\text{C=C}}$), 1492, 1469, 1390, 1364, 1282, 1259, 1186, 1150, 1103, 1049, 816 and 790 cm^{-1} have been observed. The absorption band assignable to the streching of the C=N bond was observed at 1617 cm^{-1}, and this value agrees with that reported for the IR spectrum of a substituted aromatic Schiff base, which possesses the formulation $C_6OH_5CH{=}NC_6H_3Cl_2$. The observation of phenolic $\nu_{\text{C-O}}$ at 1364 cm^{-1} is an evidence for the existence of the enol form (N...H-O) intramolecular hydrogen bonding only in the solid state [7].

4.2. UV-visible Spectroscopy

Electronic absorption spectral studies of compounds in solution, designed to possess NLO properties, are

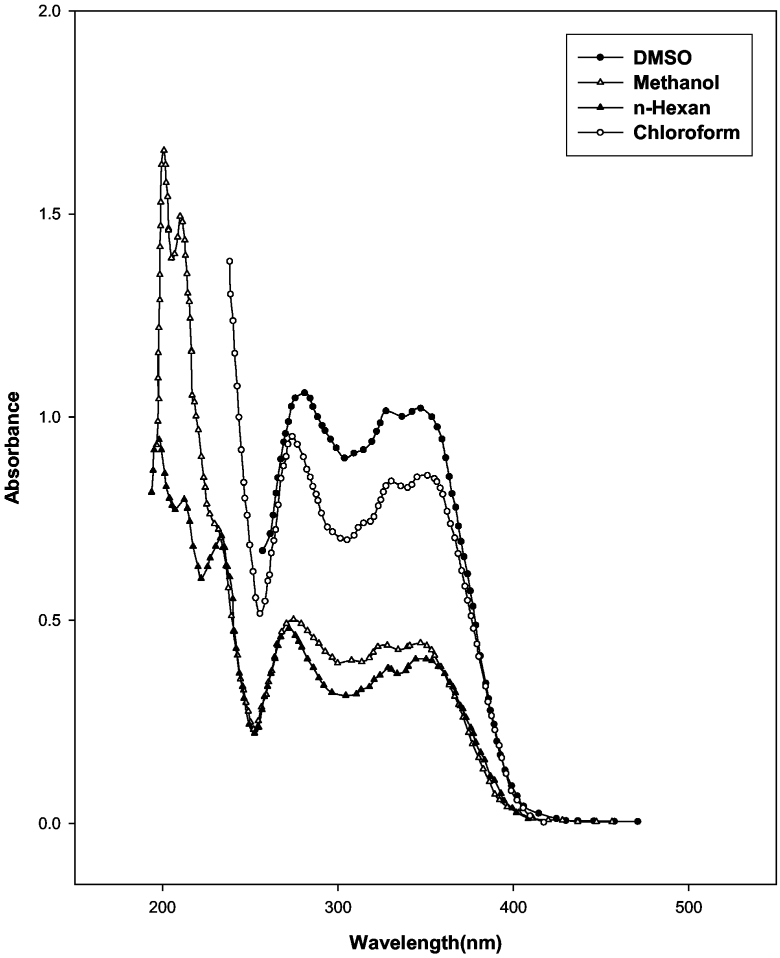

Fig. 4. UV-visible absorption spectra of *N*-(2,4-dichloro)-salicylaldimine in DMSO, methanol, *n*-hexan and chloroform.

Table 3. The maximum absorption wavelengths λ [nm] (and molar extinction coefficients ε [M^{-1} cm^{-1}]) obtained from the UV-visible spectral analysis of *N*-(2,4-dichloro)-salicylaldimine in solvents of different polarity.

DMSO	Methanol	*n*-Hexan	Chloroform
347.9 (1795)	344.3 (3256)	344.0 (2464)	349.9 (6336)
329.1 (1784)	326.6 (3182)	325.3 (2378)	330.0 (6211)
311.6 (1585)	310.0 (2960)	308.3 (1971)	313.3 (5397)
279.1 (1860)	275.3 (3693)	271.5 (2982)	274.0 (6987)
	211.3 (11028)	234.3 (4374)	
	201.5 (12390)	211.6 (4929)	
		198.3 (5822)	

important for two reasons. Firstly, it is necessary to know the transparency region. Secondly, the solvatochromic behavior of the sample is generally considered as indicative of high molecular first hyperpolarizability [8]. The NLO properties and UV-visible studies of push-pull ferrocene complexes containing heteroaromatic rings in the conjugation chain were investigated by Justin Thomas et al. [8]. High bathochromic shift, generally considered as indicative of high $\boldsymbol{\beta}$ values, and hence potential NLO properties have been observed in dichloromethane. Di Bella et al. [9] have reported that the bis(salicylaldiminato) nickel(II) compound exhibits interesting linear optical spectroscopic features which will be seen to be related to the second-order NLO response. The optical absorption spectrum (> 280 nm) of archetypical Ni (salen) consists of two overlapping principal features assigned to two different types of transitions. There is a broad band in the region between 300 and 360 nm involving mainly $\pi \rightarrow \pi^*$ transitions, and a relatively intense structure in the 400 – 480 nm region. The band at around 400 nm exhibits a solvatochromic shift, characteristic of a large dipole moment, and frequently suggestive of a large hyperpolarizability. Moreover, a negative solvatochromism, i. e. a hypsochromic shift is observed,

Table 4. Calculated $\boldsymbol{\beta}$ components and β_{tot} value of *N*-(2,4-dichloro)-salicylaldimine.

β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	$\beta_{\mathrm{tot}} \times 10^{-30}$ esu
37450.593	291.868	−10480.001	−6092.266	1367.234	5200.327	8960.659	−2366.407	−9249.259	11308.246	36055.243

thus indicating a reduction of the dipole moment upon electronic excitation.

To determine the transmission range and hence to know the suitability of the title compound for microscopic nonlinear optical applications, the UV-visible spectra have been recorded by using the spectrometer in the range of 190 – 1100 nm. The optical absorption spectra for the investigated compound in dimethylsulfoxide (DMSO), methanol, chloroform polar solvents, and in an *n*-hexane nonpolar solvent are illustrated in Figure 4. Table 3 shows the maximum absorption wavelengths (λ) and molar extinction coefficients (ε) obtained from the UV-visible spectral analysis of *N*-(2,4-dichloro)-salicylaldimine in all the solvents which are able to dissolve the synthesized molecule. All the absorption bands of the studied compound lie in the UV region. Hence the recorded spectrum shows good transparency in the visible region, which might enable the achievement of microscopic NLO response with non-zero values [2]. All absorption bands are to be assigned to $\pi \rightarrow \pi^*$ transitions (Table 3). The $\boldsymbol{\beta}$ values computed here might be correlated with the UV-visible spectroscopic data in order to understand the molecular structure-NLO property relationship in view of a future optimization of the microscopic NLO properties of the investigated ligand. Therefore the validity of the FF MP2 approximation used in all computations might also be illustrated by analyzing the relationship between calculated values of $\boldsymbol{\beta}$ and measured values of λ. The synthesized compound exhibits solvatochromism, i. e. its maximal absorption peaks show bathochromic behavior with band shift < 400 nm, generally considered as indicative of non-zero molecular first hyperpolarizabilities. The red shifts in absorption are also accompanied by non-zero upward shifts in all $\boldsymbol{\beta}$ components (see Tables 3, 4).

4.3. Description of the Crystal Structure

In 2-hydroxy Schiff base ligands, short hydrogen bonds are observed between the 2-hydroxy group and the imine nitrogen atom. Sometimes the hydrogen atom from the phenol group is completely transferred to the imine nitrogen. The hydrogen bond type (either O-H…N or O…H-N) depends neither on the stereochemistry of the molecule nor on the sort of substituent to the imine N atom, but on the kind of aldehyde used. *N*-(2,4-dichloro)-salicylaldimine contains short intramolecular O-H…N hydrogen bonds [O1-H1 0.77(1) Å, H1-N1 2.20(1) Å O1-N1 2.601(1) Å], which means that the compound is in the enol form as in *N*-(2-fluoro-3-methoxy)-salicylaldimine [O1-H1 0.87(3) Å, H1-N1 1.78(3) Å, O1-N1 2.575(2) Å]. The C=N imine bonds and C-N-C bond angles can be compared with the 1.275(1) Å and 121.5(1)° values in *N*-(2-fluoro-3-methoxy)-salicylaldimine [10].

N-(2,4-dichloro)-salicylaldimine is almost planar. Schiff base moieties A [C7-C13, O1; planar with a maximum deviation of 0.009(1) Å for the C9 atom] and B [N1, C1-C6, Cl1, Cl2; planar with a maximum deviation of $-0.038(1)$ Å for the Cl1 atom] are inclined by an angle of 5.1(4)°, reflecting mainly the twist about C7-N1 [C8-C7-N1-C1 = $-176.6(1)^\circ$].

Clearly, the enol tautomer accurs more often than the keto form. This is evident from the observed C13-O1 bond distances of 1.332(1) Å, which are consistent with a single bond, and the N1=C7 bond distances of 1.275(1) Å, which are indicative of a double bond. The structure of the synthesized compound is the same in the solid state and in solution. In conclusion, FT-IR and X-ray results show that *N*-(2,4-dichloro)-salicylaldimine exists in the enol form.

4.4. Computational Results and Discussion

One aim of research in NLO behavior might be to synthesize materials with useful NLO properties for specific applications. The value of $\boldsymbol{\beta}$ of the constituent molecules is essential for a structure-based understanding of molecules. Molecules containing conjugated π-electron systems with charge asymmetry exhibit large values of $\boldsymbol{\beta}$. The largest values occur when the molecule contains substituents that induce asymmetry in the charge distribution of the molecule [3]. Organic molecules with remarkable nonlinear activity mostly contain a π-electron conjugated moiety with an electron donor group and an acceptor group at the ends of a conjugated structure. The donor and acceptor groups provide the infrastructure to introduce the charge asymmetry required for second-order nonlinearity. Therefore, for designing new organic materials such as NLO Schiff base ligands one has to investigate the effect of donor/acceptor substituents on the second-order nonlinearity of these compounds. The computational approach allows to determine molecular NLO properties in an inexpensive way. The microscopic nonlinear response in organic molecules, especially *ab-initio* MP2 calculations, allow a relatively accurate prediction of the NLO activity [11, 12]. The Schiff base system studied here has donor a hydroxy (-OH) group at *ortho* positions and two acceptor chloro (-Cl) substituents at *ortho* and *para* positions. We have calculated the electric dipole moment $\boldsymbol{\mu}$ and the first hyperpolarizabilities $\boldsymbol{\beta}$ of the investigated ligand. In the Schiff bases, the valence orbitals of the nitrogen atom are the hybridized sp^2, with the orbitals of the nonbonding pair of electrons being coplanar with the bonding orbital [13]. This lone-pair orbital has a comparatively large electron density, is markedly polar, and thus aids in the formation of a strong intramolecular hydrogen bond between the *ortho* hydroxyl group and nitrogen, resulting in a 6-membered ring as shown in Figure 1. The configuration of the orbitals and their electron density play an important role in strengthening the hydrogen bond. Also, the changes in the strength of the intramolecular hydrogen bonds are due to the transmission of inductive and resonance effects from the substituent group to the nitrogen orbital through a number of intermediate atoms. In the case of chloro substitution at the *ortho* position, there is an orbital-orbital repulsive interaction between the OH bonding orbital and the Cl atom, which may be a major contributor to the small energy of the intramolecular hydrogen bonds formed by it. The nitrogen orbital is ellipsoidal with a small cross-sectional area, while the non-bonding orbitals of the halogen combine to produce a nearly spherical orbital. This electron-rich *ortho* (-Cl) substituent enhances the donor character of the amino N atom. The substituent is close to the N atom, together with the electron-donating OH on the salicylaldehyde group, and joins the donor-acceptor groups, assuming that strong electronic coupling occurs through the bridge of all separations. With *ortho* chloro substitution, the resonance effect predominates as compared to the inductive effect. In the case of multiple substituents, the total polar effects may be additive. In the case of disubstitution in one moiety of the Schiff base ligand in which both groups are either electron donating or electron attracting, the polar effects may be additive [13]. In this study, because both disubstituted atoms are the same acceptor (-Cl), it could be thought that the *ortho* Cl substituent together with the *para* Cl substituent might yield microscopic NLO behavior with a non-zero value. With great possibility the intramolecular hydrogen bond between O1 and N1 atoms of the synthesized compound here affects the non-zero β_{tot} value given in Table 4. Many organic compounds crystallize in a centrosymmetric fashion, in which case the crystals do not exhibit macroscopic second-order nonlinearity. The centrosymmetric nature of the crystal structure of the investigated compound suggests no macroscopic NLO behavior in the bulk phase. However, this compound is a polar molecule having non-zero dipole moment components (Table 5), and such compounds may have large microscopic first hyperpolarizabilities, and hence may have microscopic NLO behavior [14].

Table 5. The *ab-initio* calculated electric dipole moment $\boldsymbol{\mu}$ (Debye) and dipole moment components for *N*-(2,4-dichloro)-salicylaldimine.

μ_x	μ_y	μ_z	$\boldsymbol{\mu}$
6.4128	10.1331	0.0463	11.9919

The higher dipole moments are associated, in general, with even larger projections of β_{tot} quantities. The dipoles may oppose or enhance one another, or at least bring the dipoles the required or out of the required net alignment necessary for NLO properties such as β_{tot} values. Several research groups have tried to identify molecules with potentially optimal nonlinearities through the two-level model. For example, Risser et al. [15] used a four-site Hückel model to examine how each of the two-level parameters varies with the electron donating and electron accepting abilities of appended substituents. The $\boldsymbol{\beta}$ responses derived from this model were not optimized with maximal electronic asymmetry to a given bridge structure. The maximum was due to the behavior of non-zero $\boldsymbol{\mu}$ values. One of the conclusions obtained from this work is that non-zero $\boldsymbol{\mu}$ values might permit to find non-zero $\boldsymbol{\beta}$ values. In this study, the first hyperpolarizabilities are computed by the numerical second-derivatives of the electric dipole moments according to the applied field strength in FF approach. There are rather strong relationships among the calculated $\boldsymbol{\mu}$ and β_{tot} values of the compound. Therefore, these $\boldsymbol{\mu}$ values of the compound in Table 5 may be responsible for enhancing and decreasing the β_{tot} values given in Table 4. It is important to stress that, in these β_{tot} investigations, we did not take into account the effect of the field on the nuclear positions, i. e. we evaluated only the electronic component of β_{tot}. The vibrational contributions which, for conjugated systems, can be important according to the NLO process are left for further investigations.

5. Conclusions

N-(2,4-dichloro)-solicylaldimine is almost planar. The crystals of the synthesized compound have been subjected to FT-IR technique to confirm the presence of the functional groups. It is seen that both spectroscopic studies confirm the functional groups present in this molecule. From UV-visible spectroscopy it is clear that the investigated compound is transparent in the entire visible region and the absorption takes place in the UV range between 198 and 349 nm. Owing to the good transparency in the visible region, it could be said that this ligand might have microscopic NLO behavior with non-zero values. Moreover, it is observed that the maximal absorption peaks of *N*-(2,4-dichloro)-salicylaldimine exhibit solvatochromism, generally indicating the presence of microscopic first hyperpolarizabilities with non-zero values. The electric dipole moments and the first hyperpolarizabilities of the investigated compound have been calculated by the FF MP2 method with a 3-21+G** basis set. The *ab-initio* calculated non-zero μ value of this ligand shows that the synthesized compound might have microscopic first hyperpolarizabilities obtained by the numerical second-derivative of the electric dipole moment according to the applied field strength.

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