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Crystal structure, spectroscopic characterization and density functional studies of (*E*)-1-((3-methoxyphenylimino)methyl)naphthalen-2-ol



SPECTROCHIMICA ACTA

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- The compound was characterized by IR, UV-vis spectroscopies and X-ray crystallography.
- Molecular geometry was theoretically determined by DFT method.
- The compound shows the phenolimine tautomeric form.
- Polarizability and first hyperpolarizability of the compound were calculated.

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ABSTRACT

The Schiff base compound (*E*)-1-((3-methoxyphenylimino)methyl)naphthalen-2-ol was synthesized from the reaction of 2-hydroxy-1-naphthaldehyde with 3-methoxyaniline. The structural properties of the compound has been characterized by using FT-IR, UV-vis and X-ray single-crystal methods. According to X-ray diffraction result, the title compound exists in the phenol-imine tautomeric form. The molecular geometry, vibrational frequencies of the compound in the ground state have been calculated using the density functional theory (DFT/B3LYP) method with the 6-311++G(d,p) basis set, and compared with the experimental data. The obtained results show that the optimized molecular geometry is well reproduce the crystal structure. The theoretical vibrational frequencies are in good agreement with the experimental values. The calculations of electronic absorption spectra of tautomeric forms of the compound were performed by using TD-DFT calculations both in the gas phase and ethanol solvent. To investigate the tautomeric stability, optimization calculations at the B3LYP/6-311++G(d,p) level were performed for the phenol-imine and keto-amine forms of the compound. According to calculated results, the OH form is more stable than NH form. In addition, molecular electrostatic potential (MEP), frontier molecular orbital analysis (HOMO-LUMO), thermodynamic and, non-linear optical (NLO) properties of the compound were investigated using same theoretical calculations.

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Introduction

Schiff bases have been widely used as starting materials in the synthesis of important drugs such as antibiotics, antiallergics, antitumors and antifungals due to their biological activities [1,2]. Compounds derived from 2-hydroxy-1-naphthaldehyde Schiff bases have attracted the interest of researchers because they show thermochromic and photochromic properties in the solid state [3].

These properties arise via H-atom transfer from the hydroxy O atom to the imine N atom [4,5]. It has been proposed that thermochromic molecules are planar, while photochromic molecules are non-planar [6]. Especially, photochromic compounds are used for the control and measurement of radiation intensity, optical computers and display systems [7]. In general, Schiff bases exhibit two possible tautomeric forms; the phenol-imine (OH) and keto-amine (NH) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds which are O—H...N in phenol-imine [8,9] and N—H...O in keto-amine [10,11] forms are observed in Schiff bases (Fig. 1). In addition, Schiff bases may have

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interesting chemical properties, depending on the substituents with different electron-donating or electron-withdrawing groups [12]. Therefore, non-linear properties of the Schiff bases use in the design of various molecular electronic devices such as optical switches and optical data storage devices [13,14].

In recently years, theoretical calculation methods are used to describe the molecular structures and spectroscopic properties as well as experimental studies. Density functional theory (DFT) which is one of these methods have been widely used in literature because of its great accuracy in reproducing the experimental values in molecule geometry, vibrational frequencies, atomic charges, dipole moment, electronic properties, etc. [15–18].

In this paper, we have been reported the synthesis, characterization and crystal structure of (E)-1-((3-methoxyphenylimino)methyl)naphthalen-2-ol, as well as theoretical studies on it using the DFT/B3LYP/6-311++G(d,p) method. The aim of this study is to investigate molecular structure, tautomeric forms, vibrational frequencies and electronic absorption spectrum of the title compound, both experimentally and theoretically. The properties of the structural geometry, molecular electrostatic potential (MEP), frontier molecular orbitals (FMOs), thermodynamic and non-linear optical (NLO) properties for the compound at the B3LYP/6-311++G(d,p) level were studied.

Experimental and computational method

Svnthesis

The compound (E)-1-((3-methoxyphenylimino)methyl)naphthalen-2-ol was prepared by reflux a mixture of a solution containing 2-hydroxy-1-naphthaldehyde (17.2 mg; 0.1 mmol) in 20 ml ethanol and a solution containing 3-methoxyaniline (12.3 mg, 0,1 mmol) in ethanol (20 ml). The reaction mixture was stirred during 3 h under reflux. The crystals of (E)-1-((3-methoxyphenylimino)methyl)naphthalen-2-ol for X-ray analysis were obtained from ethanol solution by slow evaporation (yield 74%; m.p 368-370 K).

Instrumentation

The FT-IR spectrum of the title compound was recorded in the 4000–400 cm⁻¹ region with a Shimadzu FTIR-8900 spectrophotometer using KBr pellet. Electronic absorption spectrum was measured on a Unicam UV-vis spectrophotometer in EtOH solvent. The FT-IR spectrum of the title compound was recorded at room temperature with scanning speed of 10 cm min⁻¹ and the spectral resolution of 4.0 cm⁻¹. The ultraviolet absorption spectrum of the title compound was examined in the range 200-600 nm using a Unicam UV-vis spectrophotometer equipped with a 10 mm quartz cell. The UV pattern is taken from a 1.57×10^{-5} M solution of the title compound, dissolved in ethanol at 20 °C.

X-ray crystallography

A suitable yellow prism-shaped crystal sample of size $0.71 \times 0.35 \times 0.15$ mm was chosen for the X-ray study and then carefully mounted on the goniometer. Data collection was performed on a STOE IPDS II diffractometer by the w scan technique using graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 296 K. The systematic absences and intensity symmetries indicate that crystal have to the monoclinic C2/c space group. A total of 11843 reflection (2770 unique) with $[1.4^{\circ} < \theta < 26^{\circ}]$ were collected in the *w* scan mode and cell parameters were determined using X-AREA software [19]. Absorption correction hv $(\mu = 0.09 \text{ mm}^{-1})$ was obtained by the integration method via X-RED32 software [19]. The crystal structure was solved by direct methods using SHELXS-97 [20]. The maximum peaks and deepest hole observed in the final $\Delta \rho$ map were 0.16 and $-0.11 \text{ e}\text{\AA}^3$, respectively. The scattering factors were taken from SHELXL-97 [20]. The molecular graphics were done using Ortep-3 for Windows [21]. The data collection conditions and parameters of refinement process are listed in Table 1.

Computational procedures

All theoretical computations were done by using Gaussian 03 W program package [22]. For calculation of molecule geometry was used the obtained atomic coordinates from X-ray geometry. Geometry optimization of the title molecule was performed by using DFT method with Becke's three parameters hybrid exchange-correlation functional (B3LYP) [23] at 6-311++G(d,p) basis set [24]. The harmonic vibrational frequencies were calculated at the same level of theory for the optimized structure. The assignments of vibrational bands have been made by using GaussView molecular visualization program [25]. Additionally, the calculated vibrational frequencies were clarified by means of the potential energy distribution (PED) analysis and assignments of all the fundamental vibrational modes using VEDA 4 program [26].

The electronic absorption spectra of phenol-imine (OH) and ketoamine (NH) forms were calculated using the time-dependent density functional theory (TD-DFT) method [27–30]. The tautomeric stability, total energy, HOMO and LUMO energies for the OH and NH forms of the compound were calculated at the 6-311++G(d,p)level in the gas phase. Besides, the energetic and dipole moments behavior in solvent media of the compound were carried out by using Polarizable Continuum Model (PCM) [31–34]. To investigate the reactive sites of the compound, the molecular electrostatic potential was evaluated using the B3LYP/6-311++G(d,p) method. The linear polarizability and first hyperpolarizability properties of the compound were obtained from molecular polarizabilities based on theoretical calculations. In addition, thermodynamic properties of title compound were obtained by applying same level of theory.



Phenol-imine (OH) form

Fig. 1. Tautomeric forms of the title compound.

Table	- 1
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Crystal	data	and	refinement	for	the	title	compound.
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C ₁₈ H ₁₅ NO ₂
Prism/Yellow
301.37
Monoclinic
C2/c
a = 29.5054(17) Å
b = 5.0327(2) Å
<i>c</i> = 19.4952(11) Å
$\beta = 103.749(4)^{\circ}$
2811.9(3) Å ³
8
1.310
0.09
1168
$0.71\times0.35\times0.15$
STOE IPDS II/w-scan
Integration
0.960
0.989
11,843, 2770, 1818
$I > 2\sigma(I)$
0.040
26.0
F^2
0.048, 0.121, 1.04
2770
191
$w = 1/[\sigma^2(F_0^2)) + (0.0573P)^2 + 0.2501P]$
$P = (F_0^2 + 2F_c^2)/3$
0.16, -0.11



Results and discussion

Description of the crystal structure

The title compound crystallizes in the monoclinic space group C2/c with Z = 8 in the unit cell. The asymmetric unit in the crystal structure contains only one molecule. It is known that tautomeric forms of Schiff base compounds have to two types of intramolecular hydrogen bonds which belong to O-H…N in phenol-imine form and N—H…O in keto-amine one. Single-crystal X-ray study shows that the title compound adopts the phenol-imine tautomeric form. The C11–N1 and C2–O1 bond lengths have a significant influence in determining the tautomeric form. The C11-N1 bond distance [1.288 (2)Å] is consistent with the C=N double bond and the C2–O1 bond [1.323 (2) Å] is consistent with the C–O single bonding. These bond distances are comparable with those of compounds previously reported as phenol-imine [35,36]. The dihedral angle between the C1-C10 and C12-C17 rings is 27.21 (5)°. Therefore, the molecular structure of the compound is nonplanar and the compound may exhibit photochromic property. The molecular structure is stabilized by an intramolecular O1-H1...N1 hydrogen bond (Fig. 2a). Intramolecular N1...O1 [2.534 (2) Å] hydrogen bond length is meaningfully shorter than the sum of the Van der Waals radius of the N and O atoms [3.07 Å] [37]. The details of the hydrogen bonds are summarized in Table 2.

Optimized structure

Geometric optimization of investigated compound was performed by using DFT/B3LYP method with 6-311++G(d,p) basis set (Fig. 2b). The some bond lengths, bond angles and torsion angles of the optimized structure are listed in Table 3 and compared with the experimental data of the compound. As can be seen from Table

Fig. 2. (a) Ortep-3 diagram of the title compound. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular hydrogen bond is shown as a dashed line. (b) The theoretical geometric structure of the title compound (at B3LYP/6-311++G(d,p) level).

3, most of molecular geometric parameters are slightly different from the experimental ones. The biggest differences between experimental and calculated bond lengths and angles as 0.026 Å in C3–C4 bond and are 2.10° in C11–N1–C12 angle, respectively. According to crystallographic studies, the dihedral angle between the naphthalene and phenyl rings is 27.21 (5)°, while this angle has been calculated at 37.42° for optimized structure. In order to compare the theoretical results with the experimental values, root mean square error (RMSE) is used. The calculated RMSE for bond lengths and bond angles are 0.013 Å and 0.574°, respectively. The linear correlations coeffections between experimental and calculated bond lengths and bond angles are 0.9359 and 0.9438, respectively (Figs. S1 and S2 in the Supplementary materials). It is well known that the experimental results in the solid state are related to molecular packing, but the theoretical results are related to the gas phase of the isolated molecules. Besides, this crystallographic study shows that molecular structure has one intramolecular hydrogen bond, and no intermolecular classical hydrogen bond. However, these differences have been more appeared at bonds affected from tautomerism. The X-ray structure of the compound is compared with its DFT optimized counterpart (see Fig. S3 in Supplementary materials). The RMSE fit of the atomic position of the compound to those of its DFT optimized counterpart is

Table 2 Hvdrogen-bond geometry (Å. °)

D—H…A	D—H	H…A	D…A	D—H…A		
01-H1N1	0.82	1.80	2.534 (2)	148		

Table 3

Selected molecular structure parameters.

Parameters	Experimental ^a	DFT/6-311++G(d,p)
Bond lengths (Å)		
C1–C11	1.425 (2)	1.446
C1-C2	1.407 (3)	1.409
C1-C10	1.440 (2)	1.445
C3—C4	1.339 (3)	1.365
C2-01	1.323 (2)	1.334
C2—C3	1.410 (3)	1.417
C5–C6	1.404 (3)	1.415
C5–C10	1.415 (2)	1.430
C9–C10	1.415 (2)	1.419
C11-N1	1.288 (2)	1.293
C12–C13	1.385 (3)	1.404
C12-N1	1.416 (2)	1.408
C13–C14	1.377 (3)	1.386
C16–C17	1.386 (3)	1.398
C16-02	1.371 (2)	1.365
C18-02	1.419 (2)	1.421
Max. dif.		0.026
RMSE		0.013
Bond angles (°)		
C2-C1-C11	118.95 (17)	119.39
C11-C1-C10	122.04 (16)	121.51
C2-C1-C10	118.99 (16)	119.08
01–C2–C1	122.53 (17)	122.55
C11-N1-C12	123.16 (15)	121.06
C16-02-C18	117.85 (17)	118.61
C12-C17-C16	120.15 (17)	120.32
02-C16-C17	114.76 (17)	115.32
C13-C12-N1	117.45 (17)	118.02
C17-C12-N1	123.18 (16)	122.32
N1-C11-C1	122.62 (17)	122.50
C9-C10-C1	123.83 (17)	123.66
Max. diff.		2.10
RMSE		0.574
Torsion angles (°)		
C1-C11-N1-C12	-178.87 (5)	-176.30
C2-C1-C11-N1	0.8 (3)	2.25
C10-C1-C11-N1	-177.59 (16)	-178.32
02-C16-C17-C12	-177.96 (16)	-179.58
C11-N1-C12-C17	26.0 (3)	38.64

^a The values in paranthesis are standard uncertainty (s.u).

0.0207 Å. According to these results, it is seen that the B3LYP calculation well reproduce the geometry of the compound.

Vibrational analysis

FT-IR spectrum of the investigated compound was measured in the 4000–400 cm⁻¹ region using KBr pellet on a Shimadzu FT-IR 8900 spectrophotometer (Fig. 3a). FT-IR spectra of compounds derived from 2-hydroxy-1-naphthaldehyde Schiff bases have some characteristic stretching bands (OH, CH, CN, CO). The vibrational frequencies of the compound were calculated by using B3LYP/6-311++G(d,p) method (Fig. 3b). Determinations of the calculated vibrational bands have been made by using GaussView molecular visualization program. Furthermore, theoretical vibrational frequencies of the title compound were interpreted by means of PEDs using VEDA 4 program [26]. The assignments of the observed vibration bands have been performed and compared with the calculated frequencies. The experimental and calculated vibrational frequencies, and their assignments are given in Table 4.

Because of the states such as negligence of anharmonicity, incomplete inclusion of electron correlation effects and basis set deficiencies, the calculated harmonic vibrational frequencies become bigger than the observed ones [38,39]. For this reason, the calculated wavenumbers are usually scaled by scaling factor to compare with observed wavenumbers and at the present work, the scaling factors are taken as 0.983 for frequencies less than



Fig. 3. (a) Experimental and (b) theoretical FT-IR spectra of the title compound.

 1700 cm^{-1} and 0.958 for frequencies higher than 1700 cm^{-1} for B3LYP/6-311++G(d,p) level [39].

The O—H group has three vibrations as stretching, in-plane and out-of-plane bending vibrations. Free O-H stretching band observes at interval 3700–3550 cm⁻¹ region [40]. If there is inter and intramolecular hydrogen bonding, this stretching band is shifted to lower wavenumber, and so O-H stretching band is observed at interval 3200–2800 cm⁻¹ [41]. According to this result. the observed phenyl and methyl C-H stretching bands in this interval are covered to O-H stretching band. In addition, the O-H stretching band has been calculated at 2892 cm⁻¹ for optimized structure. The free O-H in-plane and out-of-plane bending vibrations of containing phenol ring compounds arise in the region $1330-1420 \text{ cm}^{-1}$ and $650-770 \text{ cm}^{-1}$, respectively [42]. The O–H in plane and out of plane bending vibrations have been shifted to high frequency region because of intramolecular O-H...N hydrogen bonding interaction. Therefore, O-H in plane bending vibration has been observed at 1576 cm⁻¹ as combination with other bands, while the O-H out of plane bending vibration has been observed at 906 cm⁻¹. The calculated values of O-H in-plane bending and outof-plane are at 1578 cm⁻¹ and 909 cm⁻¹, respectively.

The aromatic C—H stretching, C—H in-plane bending and C—H out-of-plane bending vibrations appear in $3000-3100 \text{ cm}^{-1}$, $1100-1500 \text{ cm}^{-1}$ and $800-1000 \text{ cm}^{-1}$ frequency ranges, respectively [42]. The absorption band at 3059 cm⁻¹ corresponds to the aromatic C-H stretching vibrations of the compound and the aliphatic C–H stretching vibration was observed at 3007 cm⁻¹. These bands were calculated at 3036 and 3002 cm^{-1} with B3LYP, respectively. C-H in-plane bending vibrations are observed at 1328, 1185 and 1147 cm⁻¹ for the compound. Similarly, the C–H out-of-plane bending vibrations are arised at 927, 851, 831 and 772 cm⁻¹. In our calculations the C–H in-plane bending vibrations are found as 1331, 1184 and 1149 cm⁻¹, while the C-H out-ofplane bending vibrations are computed as 941, 852, 823 and 770 cm⁻¹ for the compound. The asymmetric and symmetric vibrations for the CH₃ group of the title compound were observed at 2962 cm⁻¹ and 2835 cm⁻¹, respectively. The observed band at Table 4

Comparison of the experimental and calculated vibrational frequencies (cm⁻¹).

Assignments (% PED ^a)	Experimental IR (cm^{-1})	Calculated (cm ⁻¹) B3LYP/6-311++G(d.p)
··· (CH) (00)	2050	2026
$O_{\text{aromatic}}(CH)(55)$	2007	2002
$U_{\text{aliphatic}}(CH)(100)$	2042	2026
$U_{as}(CH_3)$ (99)	2942	2950
$\mathcal{U}(\mathbf{OH})$ (96)	2800-3200	2892
$U_{s}(CH_{3})$ (91)	2835	2879
v(NC)(17) + v(CC)(16)	1623	1634
$\upsilon(CC)(23) + \upsilon(NC)(17) + \beta(HOC)(13)$	1576	1578
$\delta(CH_3)$ (82)	1486	1479
$\beta(CH_3)(21) + \beta(HCC)(17) + \upsilon(CC)(11)$	1432	1440
$\beta_{\text{aliphatic}}(\text{HCN})(31) + \upsilon(\text{NC})(11)$	1394	1403
$\upsilon(CC)$ (11) + $\beta_{aliphatic}(HCN)$ (11)	1328	1331
$v(CC)$ (39) + $\beta(HCC)$ (23)	1313	1327
$v(COH) (20) + \beta(HCC) (27)$	1285	1295
$v_{as}(COC) (16) + v(NC) (13) + \beta(CCC) (12) + \beta(HCC) (11)$	1255	1258
$\rho(CH_3)(20) + \beta(HCC)(17)$	1185	1184
$\beta(HCC) (34) + \upsilon(NC) (12)$	1147	1149
$v_{s}(COC) (50) + \beta(HCC) (17)$	1080	1056
$\gamma_{\text{aliphatic}}(\text{HCCC})$ (43)	962	976
$\gamma(\text{HCCC})$ (84)	927	941
γ(HOCC) (93)	906	909
$\gamma(\text{HCCC})$ (69)	851	852
$\gamma(\text{HCCC})$ (38)	831	823
$\gamma(\text{HCCC})$ (62)	772	770
$\beta_{\text{number}}(\text{CCC})(15) + \beta_{\text{nbarry}}(\text{CCC})(12)$	718	716
$\beta_{n,n,n,t}(CCC)(21)$	647	655
$\beta_{\text{naple}}(CC)(31)$	584	584
$\gamma_{\text{number}}(CCCC)$ (65)	536	536
$\gamma_{\text{phenyl}}(\text{CCCC})$ (39) + γ HCCC (14)	470	462

Vibrational modes: υ, stretching; s, symmetric; as, asymmetric; δ, scissoring; β, in-plane bending; γ, out of plane bending; ρ, rocking.

^a Potential energy distribution (PED), less than 10% are not shown.

1432 cm⁻¹ can be assigned to the scissoring mode of CH₃ group. The absorption bands at 1600–1400 cm⁻¹ are due to C=C stretching vibrations of the aromatic compounds [42]. The C=C stretching vibrations of aromatic rings for the compound were observed at interval 1584–1571 cm⁻¹. On the other hand, the absorption bands at 647 and 584 cm⁻¹ can be attributed to the CCC in-plane bending vibrational modes of phenyl and naphthalene rings. Similarly, the observed absorption bands at 536 and 470 cm⁻¹ can be assigned to the CCCC out-of-plane bending vibrational mode of phenyl ring and naphthalene rings.

The title compound exhibits a strong band at 1623 cm⁻¹ which is assigned to C=N stretching vibration. The C-OH stretching vibration is determined at 1285 cm⁻¹ and this band supports phenol-imine form of the compound. The C=N, C-OH stretching bands have been calculated at 1634 cm⁻¹ and 1295 cm⁻¹ for optimized structure, respectively. Besides, C-O-C asymmetric and symmetric stretching band were experimentally observed at 1255 cm⁻¹ and 1080 cm⁻¹, and these bands were calculated at 1258 cm⁻¹ and 1056 cm⁻¹, respectively. These results are in agreement with the literature [42].

The correlation graphics between the calculated and experimental IR vibrational frequnecies of the compound is presented in Fig. 4 and correlation coefficient is obtained as 0.9995. As we can see from the correlation graph in Fig. 4, the experimental values are in a good agreement with the calculation ones. Characteristic bands of the compound strongly confirm that the compound has the phenol-imine form in the solid state.

UV-vis spectroscopy and HOMO-LUMO analysis

The UV–vis electronic absorption spectrum of the compound in ethanol was recorded within 200–600 nm range at the room temperature. The absorption wavelengths were observed at 230 and 315 nm in ethanol. These wavelengths may be due to $\pi \rightarrow \pi^*$



Fig. 4. Correlaction graph of calculated and experimental frequencies of the title compound.

transitions of the naphthalene and benzene rings. However, another absorption wavelength at 439 nm was observed in the spectrum of the title compound. The 2-hydroxy Schiff bases may be show electronic absorption band in the range greater than 400 nm in polar and nonpolar solvents. This new band generally occurs compounds which belong to the keto-amine form [43– 46]. Electronic absorption spectrum of the compound in ethanol shows that molecular structure shifted from phenol-imine form to keto form. This proton charge transfer is influenced by H-donor-acceptor property of solvent rather than solvent polarity. Ethanol, which has a hydrogen atom bound to an oxygen, is a protic solvent. This property of ethanol causes two stable states which are one phenol and the other keto forms in solvent of molecule. [47]. These results are similar to those found in related compounds. [47–49].

Electronic absorption spectra of OH and NH forms of the title compound were calculated by using TD-DFT method based on the B3LYP/6-311++G(d,p) level optimized structure in gas phase. The TD-DFT theoretical absorption wavelengths of OH form have

vent are found at 242, 351 and 421 nm. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are called as frontier molecular orbitals (FMOs). The FMOs are very important in determining molecular properties such as electric, optic, UV-vis spectra, and chemical reactions [50]. According to TD-DFT calculations, the theoretical wavelengths of the title compound have been arised at 378 nm (HOMO \rightarrow LUMO), 318 nm (HOMO-2 \rightarrow LUMO) and 225 nm (HOMO-1 \rightarrow LUMO+2). Fig. 5 shows the distributions and energy levels of the FMOs computed at the B3LYP/6-311++G(d,p) level for the title compound. The energy difference between the HOMO and LUMO is 3.727 eV, for the title compound. As seen from Fig. 5, the HOMO-2, HOMO-1, HOMO and, LUMO electrons are almost delocalized on the whole structure while the LUMO+2, electrons are only delocalized on the naphthalene ring.

are calculated at 233, 309 and 410 nm, while ones in ethanol sol-

Molecular orbital coefficients analyses based on optimized geometry indicate that, for the title compound, the frontier molecular orbitals are mainly composed of *p*-atomic orbitals, so the electronic transitions are mainly derived from the contribution of bands $\pi \rightarrow \pi^*$.

Total energies in solvent media

The NH and OH tautomers of the title compound is given in Fig. 1. To investigate the tautomeric stability, optimization calculations at B3LYP/6-311++G(d,p) level were performed for the NH and OH forms of the title compound. Total energy, HOMO and LUMO energies, dipole moment and chemical hardness (η) were also calculated with the same level of theory and the results were given in Table 5. The chemical hardness is guite useful to explain the chemical stability. The molecules having a large HOMO-LUMO energy gap will be more stable and less reactive than soft molecules having small HOMO-LUMO energy gap [51]. From Table 5, the total energy of the OH form is lower than the NH form, while chemical hardness of the OH form is greater than the NH one, which indicates that the OH form of the title compound is more stable than its NH form in the gas phase. In additional, in order to evaluate the solvent effect to the herein above mentioned properties of the title compound, we carried out calculations in three kinds of solvent (water, ethanol, and chloroform) with the B3LYP/6-311++G(d,p) level using the PCM model and the results are given in Table 5. From Table 5, we can conclude that the total molecular



Fig. 5. Molecular orbital surfaces and energy levels given in parantheses for the HOMO-2, HOMO-1, HOMO, LUMO and LUMO+2 of the title compound computed at B3LYP/ 6-311++G(d,p) level.

Table 5

Calculated energies	dipole moments,	frontier orbital	energies and	chemical hardness.

	Gas phase (NH) $(\varepsilon = 1)$	Gas phase (OH) $(\varepsilon = 1)$	Chloroform (OH) $(\varepsilon = 4.9)$	Ethanol (OH) $(\varepsilon = 24.55)$	Water (OH) (ε = 78.39)
E _{total} (hartree)	-900.38608	-900.38649	-900.39747	-900.40203	-900.40378
E_{HOMO} (eV)	-5.649	-5.876	-5.912	-5.941	-5.937
$E_{\rm LUMO}~(\rm eV)$	-2.334	-2.149	-2.176	-2.201	-2.192
η (eV)	1.675	1.863	1.868	1.870	1.872
μ (D)	4.024	2.629	3.155	3.394	3.505

energies obtained by PCM method decrease with the increasing polarity of the solvent, while the hardness will increase with the increase of the polarity of the solvent. Solvent effects improve the charge delocalized in the molecules, therefore, inducing the dipole moments to be raised. Ground-state dipole moment is an important factor in measuring solvent effect a large ground-state dipole moment gives rise to strong solvent polarity effects [16,52,53].

According to these results, the stability of the title compound increases in going from the gas phase to the solution phase.

Molecular electrostatic potential

The molecular electrostatic potential V(r) that is created in the space around a molecule by its nuclei and electrons are well established as a guide to molecular reactive behavior. It is defined by Eq. (1):

$$V(r) = \sum_{A} \frac{Z_{A}}{R_{A} - r} - \int \frac{\rho(r')}{r' - r} dr'$$
(1)

where Z_A is the charge of nucleus A, located at R_A , $\rho(r')$ is the electronic density function of the molecule, and r' is the dummy integration variable [54,55]. The MEP have been used for explaining and predicting relative reactivities sites for electrophilic and nucleophilic attack, investigation of hydrogen bonding interactions, molecular cluster and crystal behavior and the correlation and prediction of a wide range of macroscopic properties [56–58]. The molecular electrostatic potential at the B3LYP/6-311++G(d,p) optimized geometry was calculated. MEP is shown in Fig. 6. The negative (red¹ and yellow) and the positive (blue) regions in the MEP were related to electrophilic reactivity and nucleophilic reactivity, respectively.

As can be seen in Fig. 6, negative electrostatic potential regions are mainly localized over the O1 atom and O2 atoms. The negative V(r) values are -0.041 a.u. for O1 atom which is the most negative region, -0.021 a.u. for O2 atom. In additional, the most positive regions were observed around the hydrogen atoms of CH₃ group. These regions are the most suitable sites for nucleophilic attack. These sites give the information about intermolecular interaction regions of molecule.

Non-linear optical effects

Non-linear optical materials (NLO) have been attractive in recent years with respect to their future potential applications in the communications and photonic industries [59,60]. Organic molecules that exhibit extended π conjugation, in particular, show enhanced second order NLO properties [61]. The total static dipole moment (μ), the linear polarizability (α) and the first hyperpolarizability (β) using the *x*, *y*, *z* components are defined as [62,63]:



Fig. 6. Molecular electrostatic potential map calculated at B3LYP/6-311++G(d,p) level.

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$
(2)

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{3}$$

$$\beta = \sqrt{\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz}\right)^2 + \left(\beta_{zzz} + \beta_{xxz} + \beta_{yyz}\right)^2} \tag{4}$$

It is well known that the higher values of molecular polarizability and hyperpolarizability are important for more active NLO properties. The polarizabilities and hyperpolarizability are reported in terms of atomic units (a.u) and the calculated values have been converted by using $1 \text{ a.u}^3 = (0.529)^3 \text{ Å}^3$ for α and $1 \text{ a.u} = 8.641 \times 10^{-33} \text{ cm}^5/\text{esu}$ for β [59]. To understand the NLO properties of the title compound, the linear polarizability (α) and the first hyperpolarizability (β) were calculated at the B3LYP/6-311++G(d,p) level using Gaussian 03 W program package. The calculated polarizability (α) and first hyperpolarizability (β) for the compound are 38.547 Å³ and 4.711 × 10⁻³⁰ cm⁵/esu, respectively.

Urea is one of the essential molecules used for determination of the NLO properties of molecular systems. Therefore, it is used as reference molecule in NLO studies. The calculated α and β values with B3LYP/6-311++G(d,p) method of urea are 3.8312 Å³ and 0.372 × 10⁻³⁰ cm⁵/esu [62]. The polarizability and first hyperpolarizability for title molecule is approximately 10.1 and 12.6 times than those of urea These results indicate that title compound is a good candidate of non-linear optical material.

Thermodynamic properties

In order to determine thermodynamical properties of the title compound, the standard thermodynamic functions, heat capacity

 $^{^{1}\,}$ For interpretation of color in Fig. 6, the reader is referred to the web version of this article.

 Table 6

 Thermodynamic properties of the title compound at different temperatures.

T (K)	H_m^0 (kcal/mol)	$C_{p,m}^0$ (cal/mol K)	S_m^0 (cal/mol K)
200	5.151	46.576	111.853
250	8.257	57.966	123.907
298.15	11.243	67.918	134.346
300	11.540	69.505	135.858
350	15.395	80.709	147.728
400	19.791	91.219	159.466
450	24.693	100.845	171.011
500	30.052	109.538	182.300

 $(C_{p,m}^{0})$, entropy (S_{m}^{0}) , and enthalpy (H_{m}^{0}) based on the vibrational analysis at B3LYP/6-311++G(d,p) level and statistical thermodynamics for the compound were obtained and listed in Table 6. The table shows that the standard heat capacities, entropies, and enthalpies increase at temperatures from 200.00 to 500.00 K, because the intensities of the molecular vibration increase with increasing temperature. The correlation equations between these thermodynamic properties and temperature *T* are as follows:

$$\begin{split} & C^0_{p,m} = -6.39744 + 0.28305T - 1.00776T^2 \times 10^{-4} \quad (R^2 = 0.99936) \\ & S^0_m = 62.89786 + 0.24762T - 0.16953T^2 \times 10^{-4} \quad (R^2 = 0.99975) \\ & H^0_m = -1.44269 + 0.01342T + 0.99153T^2 \times 10^{-4} \quad (R^2 = 0.99991) \end{split}$$

All the thermodynamic data supply helpful information for the further study on the compound. They can be used to calculate the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermo chemical field [62,64].

Conclusion

In this study, (E)-1-((3-methoxyphenylimino)methyl)naphthalen-2-ol has been characterized by using IR, UV-vis, and X-ray single-crystal diffraction. The X-ray and FT-IR values show that the title compound exists in the phenol-imine form, which is stabilized by the intramolecular O-H...N hydrogen bond. Besides, the molecular structure of the compound is non-planar and the compound exhibits photochromic property. The obtained optimized geometric parameters and vibrational frequency values are in a very good agreement with the experimental data. According to UV-vis spectrum of the compound in ethanol, absorption band of the molecule was observed above the 400 nm due to hydrogen bond property of solvent. Calculated results reveal that phenolimine form of the title compound is more stable than its ketoamine form. The total energy of the title compound decreases with increasing polarity of the solvent. The calculated NLO properties of the title compound are much greater than ones of urea. This study demonstrates that the title compound can be used as a good nonlinear optical material. The correlations between the thermodynamic properties and temperature were also obtained.

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Appendix A. Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 946523. Copies of the data can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: +44 1223 336 033; e-mail: data_request@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.saa.2013.10.111.

References

- [1] R.H. Lozier, R.A. Bogomolni, W. Stoeckenius, Biophys. J. 15 (1975) 955-962.
- [2] E.M. Hodnett, W.J. Dunn, J. Med. Chem. 13 (1970) 768–770.
- [3] M.D. Cohen, G.M.J. Schmidt, S. Flavian, J. Chem. Soc. (1964) 2041-2051.
- [4] E. Hadjoudis, M. Vitterakis, I.M. Mavridis, Tetrahedron 43 (1987) 1345–1360.
 [5] X.X. Xu, X.Z. You, Z.F. Sun, X. Wang, H.X. Liu, Acta Crystallogr. C 50 (1994)
- [6] L. Moustakali-Mavridis, E. Hadjoudis, A. Mavridis, Acta Crystallogr. B34 (1978)
 [6] I. Moustakali-Mavridis, E. Hadjoudis, A. Mavridis, Acta Crystallogr. B34 (1978)
- 3709–3715.
 [7] H. Dürr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems,
- [7] H. Duri, in Bouas-Latteri (Eds.), Photochronism. Molecules and Systems, Elsevier, Amsterdam, 1990.
 [8] Y.B. Alpaslan, N. Süleymanoğlu, E. Öztekin, F. Ersahin, E. Ağar, S. Isık, J. Chem.
- Crystallogr. 40 (2010) 950–956.
 C. Albayrak, B. Koşar, S. Demir, M. Odabaşoğlu, O. Büyükgüngör, J. Mol. Struct.
- 963 (2010) 211–218.
- [10] H. Ünver, M. Kabak, D.M. Zengin, T.N. Durlu, J. Chem. Crystallogr. 31 (2001) 203-209.
- [11] A. Özek, S. Yüce, Ç. Albayrak, M. Odabaşoğlu, O. Büyükgüngör, Acta Crystallogr. E60 (2004) 0828–0829.
- [12] A. Blagus, D. Cinčić, T. Friščić, B. Kaitner, V. Stilinović, Maced, J. Chem. Eng. 29 (2010) 117–138.
- [13] A.P. Alivisatos, P.F. Barbara, A.W. Castleman, J. Chang, D.A. Dixon, M.L. Klein, G.L. McLendon, J.S. Miller, M.A. Ratner, P.J. Rossky, S.I. Stupp, M.E. Thompson, Adv. Mater. 10 (1998) 1297–1336.
- [14] L. Dalton, Adv. Polym. Sci. 158 (2002) 1–86.
- [15] P.M.W. Gill, B.G. Johnson, J.A. Pople, M.J. Frisch, Chem. Phys. Lett. 197 (1992) 499–505.
- [16] H. Tanak, A. Ağar, M. Yavuz, J. Mol. Mod. 16 (2010) 577-587.
- [17] H. Gökçe, S. Bahçeli, Spectrochim. Acta Part A 78 (2011) 803-808.
- [18] B. Koşar, Ç. Albayrak, C.C. Ersanlı, M. Odabaşoğlu, O. Büyükgüngör, Spectrochim. Acta Part A 93 (2012) 1–9.
- [19] Stoe & Cie, X-AREA (Version 1.18) and X-RED32 (Version 1.04), Darmstadt, Germany, 2002.
- [20] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112–122.
- [21] L.J. Farrugia, ORTEPIII for Windows J. Appl. Crystallogr. 30 (1997) 565.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision E.01, Gaussian Inc., Wallingford, CT, 2004.
- [23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
- [24] C. Peng, P.Y. Ayala, H.B. Schlegel, M.J. Frisch, J. Comput. Chem. 17 (1996) 49-
- [25] R. Dennington II, T. Keith, J. Millam, GaussView, Version 4.1.2, Semichem Inc., Shawnee Mission, KS, 2007.
- [26] M.H. Jamróz, Vibrational Energy Distribution Analysis VEDA 4, Warsaw, 2004.
- [27] E. Runge, E.K.U. Gross, Phys. Rev. Lett. 52 (1984) 997-1000.
- [28] R.E. Stratmann, G.E. Scuseria, M.J. Frisch, J. Chem. Phys. 109 (1998) 8218-8224.
- [29] R. Bauernschmitt, R. Ahlrichs, Chem. Phys. Lett. 256 (1996) 454–464.
- [30] M.E. Casida, C. Jamorski, K.C. Casida, D.R. Salahub, J. Chem. Phys. 108 (1998) 4439–4449.
- [31] S. Miertus, E. Scrocco, J. Tomasi, Chem. Phys. 55 (1981) 117-129.
- [32] V. Barone, M. Cossi, J. Phys. Chem. A102 (1998) 1995-2001.
- [33] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 24 (2003) 669-681.
- [34] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 105 (2005) 2999–3093.
- [35] H. Ünver, M. Yıldız, A. Kiraz, N. Ocak-İskeleli, A. Erdönmez, B. Dülger, T.N. Durlu, J. Chem. Crystallogr. 36 (2006) 229–237.
- [36] H. Tanak, J. Phys. Chem. A115 (2011) 13865-13876.
- [37] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.
- [38] A.E. Özel, S. Çelik, S. Akyüz, S. Keçel, Vib. Spectrosc. 53 (2010) 151.
- [39] H. Gökçe, S. Bahçeli, Spectrochim. Acta Part A 116 (2013) 242–250.
- [40] A. Teimouri, A.N. Chermahini, K. Taban, H.A. Dabbagh, Spectrochim. Acta Part A 72 (2009) 369–377.
- [41] H.A. Dabbagh, A. Teimouri, A.N. Chermahini, M. Shahraki, Spectrochim. Acta Part A 69 (2008) 449–459.

- [42] R.M. Silverstein, F.X. Webster, D.J. Kiemle, Spectrometric Identification of Organic Compounds, seventh ed., John Wiley & Sons, New York, 2005.
- [43] M. Yıldız, Z. Kılıç, T. Hökelek, J. Mol. Struct. 441 (1998) 1–10.
- [44] H. Nazır, M. Yıldız, H. Yılmaz, M.N. Tahir, D. Ülkü, J. Mol. Struct. 524 (2000) 241–250.
- [45] H. Ünver, M. Yıldız, D.M. Zengin, S. Özbey, E. Kendi, J. Chem. Crystallogr. 31 (2001) 211–216.
- [46] S.R. Salman, F.S. Kamounah, Spectrosc. Lett. 35 (2002) 327–335.
- [47] Ç. Albayrak, G. Kastaş, M. Odabaşoğlu, R. Frank, Spectrochim. Acta Part A 81 (2011) 72–78.
- [48] H. Tanak, A. Ağar, M. Yavuz, Int. J. Quantum Chem. 111 (2011) 2123–2136.
- [49] S.H. Alarcon, D. Pagani, J. Bacigalupo, A.C. Olivieri, J. Mol. Struct. 475 (1999) 233–240.
- [50] I. Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, London, 1976.
- [51] N. Özbek, G. Kavak, Y. Özcan, S. Ide, N. Karacan, J. Mol. Struct. 919 (2009) 154–159.
- [52] A. Masternak, G. Wenska, J. Milecki, B. Skalski, S. Franzen, J. Phys. Chem. 109 (2005) 759–766.

- [53] Y. Le, J.F. Chen, M. Pu, Int. J. Pharm. 358 (2008) 214–218.
- [54] P. Politzer, P.R. Laurence, K. Jayasuriya, Environ. Health Perspect. 61 (1985) 191–202.
- [55] P. Politzer, P. Lane, Struct. Chem. 1 (1990) 159–164.
- [56] J.S. Murray, K. Sen, Molecular Electrostatic Potentials Concepts and Applications, Elsevier Science B.V, Amsterdam, The Netherlands, 1996.
- [57] A. Pirnau, V. Chiş, O. Oniga, N. Leopold, L. Szabo, M. Baias, O. Cozar, Vib. Spectrosc. 48 (2008) 289–296.
- [58] H. Gökce, S. Bahceli, O. Akyıldırım, H. Yüksel, O.G. Kol, Lett. Org. Chem. 10 (2013) 395–441.
- [59] D.R. Kanis, M.A. Ratner, T.J. Marks, Chem. Rev. 94 (1994) 195-242.
- [60] P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.
- [61] S.K. Thanthiriwatte, K.M. Nalin de Silva, J. Mol. Struct.: Theochem. 617 (2002) 169–175.
- [62] R. Zhang, B. Du, G. Sun, Y. Sun, Spectrochim. Acta A 75 (2010) 1115-1124.
- [63] H. Tanak, Comput. Theor. Chem. 967 (2011) 93-101.
- [64] T. Rajamani, S. Muthu, M. Karabacak, Spectrochim. Acta Part A 108 (2013) 186–196.