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The prototropic tautomerism and substituent effect through strong electron-withdrawing group in (E)-5-(diethylamino)-2-[(3-nitrophenylimino)methyl]phenol



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HIGHLIGHTS

- Prototropic tautomerism is experimentally and theoretically investigated.
- The effect of substituent is emphasized on proton transfer process.
- The supramolecular structure of title compound is investigated.

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ABSTRACT

The prototropic tautomerism in *o*-Hydroxy Schiff bases results in two forms called phenol-imine and keto-amine. The preference of a particular form by the compound changes in the solid and solvent media. The choice can also be regulated by a substituent with a different electron-donating or withdrawing group. In the present study, the above-mentioned factors are considered in the investigation of (*E*)-5-(diethylamino)-2-[(3-nitrophenylimino)methyl]phenol compound (an *o*-Hydroxy Schiff basis) by experimental (XRD, FT-IR and UV-vis) and computational (DFT and TD-DFT) methods. The results show that the title compound adopts only phenol-imine form in the solid and solvent media. This was attributed to the substituent effect through strong electron-withdrawing nitro group.

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Introduction

A Schiff base consists of a functional group that contains a carbon–nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group [1]. Schiff bases can be formulated as $R_1R_2C=NR_3$ where R_1 , R_2 and R_3 represent aromatic or aliphatic groups. Their preparation is through a condensation reaction of primary amines with carbonyl compounds [1–5]. Schiff bases have wide range of applications spanning the industrial [6–10], pharmaceutical [11–13], biological [14–20] and chemical fields [21–26]. For instance, they are industrially used as dyes and pigments in textile [27] in addition to their application in pharmacology for the synthesis of antibiotics, antiallergic and antitumor substances

[28–30]. Schiff bases may have thermochromic and photochromic properties [31,32]. Their photochromic species can be used as optical switches and optical memories, variable electrical current, ion transport through membranes [33]. It was reported that the photochromism and thermochromism in Schiff bases were closely related to the prototropic tautomerism [32,34], molecular geometry (being planar or non-planar) [35], the crystal packing of the compound [35]. In addition, Schiff bases may exhibit interesting chemical properties, depending on the substituents with different electron-donating or electron-withdrawing groups [36]. Therefore, the investigation of Schiff bases by considering above-mentioned factors will contribute to general understanding of fundamental properties in these species. (E)-5-(diethylamino)-2-[(3-nitrophenylimino)methyl]phenol is a Schiff base with NO₂ and diethylamino groups as substituents. In the current study, the title compound was studied with experimental (XRD, FT-IR and

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UV-vis) and computational (DFT and TD-DFT) methods by focusing on the prototropic tautomerism, proton transfer process and substituent effect.

Experimental and computational methods

Synthesis

The title compound was prepared by refluxing a mixture of a solution containing 5-(diethylamino)-2-hydroxybenzaldehyde (0.5 g, 2.59 mmol) and a solution containing 3-nitroaniline (0.36 g, 2.59 mmol) in 20 mL ethanol. The reaction mixture has been stirred for 1 h under reflux. The crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation from acetone (yield 58%; m.p. 406–408 K).

Instrumentation

The melting point was determined by using StuartMP30 apparatus. FT-IR spectrum of the title compound was recorded on a Bruker Vertex 80 V spectrometer using KBr pellet. UV–vis absorption spectra were recorded on a Thermo scientific BioGenesis UV–vis spectrometer using a 1 cm path length of the cell. NMR spectra were recorded on 300 MHz Bruker spectrometer.

X-ray crystallography

XRD data were collected at 130 K with an Xcalibur diffractometer using Mo K_{α} radiation. The crystal structure was solved by direct methods using SHELXS-97 [37]. All non-hydrogen atoms were refined anisotropically by full matrix least-squares methods [37]. The H atoms were located in a difference Fourier map. Their coordinates and $U_{\rm iso}({\rm H})$ values were refined freely [O–H = 0.92(2) Å and C–H = 0.96(2)–1.01(2) Å]. WinGX [38], ORTEP-3 for Windows [39] and MERCURY [40] softwares were used for molecular drawings and other materials. Relevant crystal data, experimental conditions and final refinement parameters can be obtained from Cambridge Structural Database (CCDC: 809224).

Computational procedure

All computations were performed by Gaussian 03W software [41]. GaussView program was used for molecular visualization of calculated structures [42]. The gas phase geometry optimizations for two tautomeric structures of the title compound were carried out at DFT level by using the hybrid functional B3LYP (Becke's three-parameter hybrid functional with LYP correlation functional) [43] with 6-311G(d,p) basis set [44]. The initial structures for the geometry optimizations were taken from X-ray measurement. The vibrational frequencies and the non-linear optical properties of enol form were also calculated at B3LYP level. Electronic excitations of the title compound were calculated by using TD-DFT [45–48] for gas phase. The calculation was started from optimized geometry of the title compound in gas phase, maintaining the same level of theory as in optimization process.

Results and discussion

Molecular structure from experimental and computational standpoints

The title compound contains NO₂ and diethylamino groups as substituents. It adopts eclipsed conformation referring to its ethyl groups. The related torsion angles $[C4-N2-C14-C15 = -74.7(2)^{\circ}]$ and $C4-N2-C16-C17 = 84.0(2)^{\circ}]$ have comparable values with those observed in the compounds with methyl [49], iodine [50] and bromine [51] substituents. *o*-Hydroxy Schiff bases show prototropic tautomerism via intramolecular proton transfer between the phenolic oxygen and imino nitrogen atoms. The process of proton transfer ends up with two tautomeric forms known as enol and keto structures. These are illustrated for the title compound in Fig. 1. Previous studies showed that *o*-Hydroxy Schiff bases can exist in one or both of these forms in the solid state [52–54]. XRD study reveals the preference of enol structure by the title compound in the solid state (Fig. 2). The enol form of the title compound can also be inferred from the harmonic oscillator model of



Enol Form

Keto Form





Fig. 2. Crystallographically obtained molecular structure of the title compound.

 Table 1

 Hydrogen bond interactions (Å, °) in the title compound.

D—H…A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdot}{\cdot}{\cdot}A)$	<d—h···a< td=""></d—h···a<>
$\begin{array}{c} C15-H15B\cdots O3^{i}\\ C17-H17B\cdots O2^{ii}\\ C5-H5\cdots O2^{iii}\\ C10-H10\cdots O1^{iv}\\ O1-H1\cdots N1 \end{array}$	1.02(2) 1.02(2) 1.00(2) 0.97(2) 0.92(2)	2.67(2) 2.55(2) 2.69(2) 2.59(2) 1.74(2)	3.533(2) 3.560(2) 3.547(2) 3.263(2) 2.594(2)	142.3(14) 169.2(13) 143.3(14) 126.5(12) 152.0(18)

Symmetry codes: (i) -1/2 + x, 1/2 - y, -1/2 + z, (ii) 2 - x, y, 3/2 - z, (iii) 3/2 - x, -1/2 + y, 3/2 - z, (iv) 2 - x, -1 + y, 3/2 - z.

aromaticity (HOMA) index by using the following equation for the rings [55,56]:

$$HOMA = 1 - \left[\frac{\alpha}{n} \sum_{i=1}^{n} (R_i - R_{opt})^2\right]$$
(1)

where *n* is the number of bonds in the ring, α is a constant equal to 257.7 and R_{opt} is equal to 1.388 Å for CC bonds. For purely aromatic compounds, HOMA index is equal to 1 while it is equal to 0 for non-aromatic compounds. The HOMA indices in the range of 0.900–0.990 and 0.500–0.800 correspond to aromatic and the non-aromatic rings, respectively [57,58]. In the current study, the calculated HOMA indices for C1/C6 and C8/C13 rings are 0.898 and 0.990, respectively. These results show that C8/C13 and C1/C6 rings in the title compound have purely aromatic character. The computational study was performed at DFT/B3LYP level for further analysis on the molecular structure of title compound. The discrepancies between XRD and DFT structures were analyzed quantitatively by R.M.S. overlay. The R.M.S. fit based on atomic positions is 0.203 Å, indicating the agreement between the two structures (Table S1). The experimental values for C2–O1 (1.360(2) Å) and C7–N1

(1.298(2) Å) distances indicate the single and double bond character of these bonds, respectively. Their counterparts in the optimized structure are 1.339 Å and 1.296 Å.

The compound adopts *E* configuration with respect to the C=N double bond. The strong intramolecular interaction involving phenolic atom (O1) and nitrogen atom (N1) constitutes an S(6) ring [59,60]. This H-bond is characterized by O1...N1 distance of 2.594 Å (Table 2), being shorter than the sum of the van der Waals' radii for N and O [61]. It is known that there is a strong correlation between the strength of the H-bond and the delocalization of the system of conjugated double bonds, and the effect is qualitatively interpreted by resonance-assisted hydrogen bond (RAHB) model [62]. The observed O····N distance (2.594 Å) for the title compound are significantly shorter than 2.656 Å which was reported for O—H···N in the class of RAHB [63]. The possibility for the title compound to exhibit thermochromic or photochromic properties is related respectively to its planar or non-planar geometry which can be determined by the dihedral angle between C1/C6 and C9/C14 rings [32]. The experimental value for the dihedral angle is 28.1° while the computed one is 38.5°. Both results indicate possible appearance of photochromic properties.

 Table 2

 The energies and dipole moments of enol and keto forms.

	Enol form	Keto form
E _{tot} (a.u.)	-1049.35887155	-1049.35078159
μ (D)	9.1473	8.6188
E_{LUMO} (eV)	-2.435	-2.731
E_{HOMO} (eV)	-5.628	-5.583
ΔE (eV)	3.193	2.852
$\Delta L(CV)$	5,155	2.052



Fig. 3. The gradual demonstration of the formation of 2D sheet structures in (010) and parallel planes.



Fig. 4. Relative energy profile during the proton transfer process.



Fig. 5. The changes in C2–O1, C1–C7 and C7–N1 bond lengths during the proton transfer process.

The 3D supramolecular structure of the title compound is selfassembled through C-H-O interactions (Table 1) between C-H (aliphatic and aromatic), phenol and NO₂ groups with the followmolecular arrangement: The (i) intermolecular C15-H15B...O3ⁱ (i: -1/2 + x, 1/2 - y, -1/2 + z) H-bonds connect adjacent molecules to form an undulating C(15) chain along [101] (Fig. 3a). (ii) The chains formed in this way are further connected by C17–H17B···O2ⁱⁱ (ii: 2 - x, y, 3/2 - z) interactions (Fig. 3b), resulting in a tape structure with $R_4^4(20)$ [59,60] synthons located at (1/4 + n, 1/4, n; n = 0 or half-integer) positions. (iii) Further analysis shows that the tape structures are mutually linked by C5–H5···O2ⁱⁱⁱ (iii: 3/2 - x, -1/2 + y, 3/2 - z) interactions to form 2D sheet structures in (010) and parallel planes (Fig. 3c). From topologic point of view, each discrete molecule in the 2D sheet can be considered as a node. In this sense, each node is connected to four nodes. As a result, a 2D topologic structure (a square grid) is formed, which is defined as (4,4)-net in Wells nomenclature or $(4^{4}6^{2})$ in Schläfli notation [64]. (iv) The increase in the dimensionality of the network is provided by another interaction of C—H··O type. More specifically, the 2D sheets in Fig. 3c are inter-connected by C10—H10···O1^{iv} (iv: 2 - x, -1 + y, 3/2 - z) interactions to construct 3D structure of the network.

The intramolecular proton transfer process in gas phase

The total energies, dipole moments and the highest occupied molecular orbital (HOMO) and the lowest-lying unoccupied molecular orbital (LUMO) energies of enol and keto structures are given in Table 2. Comparing the total energies of the two tautomers, the enol form is more stable than the keto form by 5.08 kcal/mol. This is an expected result since the enol form has two aromatic rings and o-Hydroxy Schiff bases generally prefer the enol structure. The intramolecular proton transfer was investigated in the gas phase for the title compound by performing a PES scan process at the B3LYP/6-311G(d,p) level in order to determine its effects on the molecular geometry. The process was started from optimized enol geometry by selecting O1-H1 bond as redundant internal coordinate. The graph of the relative energy versus the O1-H1 bond distances is given in Fig. 4. The energy values were calculated relative to the energy of stable enol form. Fig. 4 shows two minima representing the stable forms. In the figure, the keto form corresponds to a local minimum while the global minimum represents the stable enol form. The potential energy needed for the transition from enol form to keto form was calculated as 6.53 kcal/mol.

The molecular geometry and its relevance to the intramolecular proton transfer can also be examined by considering the changes in HOMA index of C1/C6 ring and indicative bond lengths for each step in the scan process. The changes in C2–O1, C1–C7 and C7–N1 bond lengths during the transfer process are shown in Fig. 5. The bond lengths of stable enol form, C2–O1 (1.339), C1–C7 (1.432) and N1–C7 (1.296) were found as 1.264, 1.384

and 1.340 Å at the fifteenth step of scan where the stable keto tautomer was observed. It is seen that the intramolecular proton transfer affects the double and single characters of these indicative bonds. The HOMA index of C1/C6 ring was calculated at each step of the scan process. The change of HOMA index in terms of scan coordinate is shown in Fig. 6. As expected, the aromaticity level of C1/C6 ring decreases with the scan coordinate from 0.9 to 1.6 Å.

UV-vis absorption spectra

Experimental UV-vis spectra of the title compound in three organic solvents of different polarities (Benzene, DMSO and EtOH) are shown in Fig. 7. An absorption band near 360 nm in three solvents is observed. The absorption band for the ketoamine form occurs above 400 nm with respect to previous experimental and computational results [65,66]. The experimental spectra of the title compound show no absorption peak in this region. Considering the absence of a peak above 400 nm, it can be said that the title compound adopts only phenol-imine form in solution. Previous experimental studies indicate that some compounds including N,N-diethyl amino group exist in both phenol-imine and keto-amine forms in EtOH [49-51]. However, the title compound exists in only phenol-imine form in EtOH. This result can be attributed to the powerful electronwithdrawing nature of the nitro group (-NO₂). The strong electron-withdrawing nitro group with inductive effect withdraws electron density from π system of ring it is bonded to and decreases the electron density on nitrogen atom of imino group. Therefore, such an effect makes the formation of keto-amine form difficult even in solution.

HOMO and LUMO orbitals play an important role in reaction between molecules and in electronic spectrum of a molecule [67]. The frontier molecular orbitals of title compound were given in Fig. 8. The first 10 spin-allowed singlet-singlet excitations for the title compound were calculated by TD-DFT approach. TD-DFT calculations started from optimized geometry were performed for gas phase to calculate excitation energies. The percentage contributions of molecular orbitals to the formation of bands were ob-



Fig. 7. UV-vis spectra of the title compound in DMSO, EtOH and benzene.

tained by using SWizard Program [68]. The results show that the two important excitation energy values with oscillator strength (*f*) larger than 0.16 are located at 349.2 nm [HOMO \rightarrow LUMO+1 (48%), HOMO-1 \rightarrow LUMO (16%)] and 350.7 nm [HOMO-1 \rightarrow LU-MO (82%), HOMO \rightarrow LUMO+1 (13%)]. Considering TD-DFT calculations, it can be said that the excitation energy value near 360 nm arises from HOMO \rightarrow LUMO+1 and HOMO-1 \rightarrow LUMO transitions of the title compound.

FT-IR spectroscopy

The experimental and calculated FT-IR spectra of the title compound are given in Fig. 9. The calculations were performed at



Fig. 6. The changes in HOMA index of C1/C6 ring during the proton transfer process.



Fig. 8. The frontier molecular orbitals of title compound in gas phase.

B3LYP/6-311G(d,p) theory level and resulting frequencies were scaled by 0.9682 [69] in order to correlate experimental and computational results. In addition, the calculated frequencies were investigated with VEDA 4 program by considering PEDs [70]. The experimental and the calculated frequencies were given in Table S2 comparatively.

The O-H stretching vibration was calculated to be at 3133 cm⁻¹. However, this mode was observed at 3000-1700 cm⁻¹ in the experimental spectrum since it is broadened by the strong intramolecular hydrogen bond between C=N and O-H groups. It was reported that the two bands around 1550-1500 and 1360–1290 cm⁻¹ correspond to asymmetrical and symmetrical stretching vibrations of aromatic nitro group, respectively [71]. These modes are observed at 1520 and 1353 cm⁻¹ experimentally and at 1548 and 1337 cm⁻¹ computationally. The asymmetrical and symmetrical stretching vibrations of methylene groups occur near 2926 and 2853 cm⁻¹ while those of methyl groups are near 2962 and 2872 cm⁻¹, respectively [71]. Corresponding vibrations of methylene and methyl groups in the title compound are observed at 2977, 2936 and 2890 cm⁻¹. B3LYP results for these vibrations are 2973, 2948, 2943, 2938, 2936 cm⁻¹. The bending vibrations of methyl and methylene groups in the title compound are at 1450, 1424 and 1382, 1301 cm^{-1} , respectively. The calculated values are 1458, 1453, 1449, 1444, 1440, 1369, 1364, 1302 cm⁻¹. The typical aromatic C-H bands of the title compound are at 3084 cm⁻¹, and calculated results span the range 3057-3129 cm⁻¹. The strong peak at 1629 cm⁻¹ in experimental spectrum has been attributed to C=N stretching vibration. This mode was calculated to be 1611 cm^{-1} . The absorption bands at $1600-1585 \text{ cm}^{-1}$ and $1500-1400 \text{ cm}^{-1}$ arise from skeletal vibrations, involving C–C stretching within the aromatic ring [71]. The C–C stretching modes of aromatic rings of the title compound were observed at 1594, 1575 cm⁻¹. Skeletal vibrations at 1500-1400 cm⁻¹ overlap stretching vibration of the nitro group.

NMR spectra

The ¹H NMR spectrum of the title compound was recorded in CDCl₃ (Fig. 10). The resonance of hydroxyl proton is at 13.19 ppm which is typical for intramolecular hydrogen bonding (O-H···N) proton. The resonance of imino proton is at 8.48 ppm.



Fig. 9. The comparison of experimental (a) and calculated (b) FT-IR spectra of the title compound.



Fig. 10. ¹H NMR spectrum of the title compound in CDCl₃.

In ¹H NMR spectrum of the title compound, the absorption peaks of aromatic ring protons are between 6 and 8 ppm (Fig. 10). The H3 proton is coupled to the H5 proton and shows doublet peaks at 6.20 ppm ($J_{3,5}$ = 2.4 Hz). The H5 proton coupled to H6 shows doublet and gives another doublet by coupling H3 as being 6.29 ppm ($J_{5,6}$ = 9 Hz, $J_{5,3}$ = 2.4 Hz). The H6 proton is coupled to the H5 proton and shows doublet at 7.20 ppm $(J_{6.5} = 9 \text{ Hz})$. The H10 proton is coupled to the H11 and H9 protons and give the triplet at 7.28 ppm ($J_{10,11} = J_{10,9} = 8.1$). The H11 proton coupled to H10 shows doublet and gives triplet by coupling H13 and H9 as being 8.03 ($J_{11,10}$ = 8.1 Hz, $J_{11,13}$ = $J_{11,9}$ = 2.4 Hz). The H9 proton coupled to H10 shows doublet and gives triplet by coupling H11 and H13 as being 7.51 ppm ($J_{9,10}$ = 8.1 Hz; $J_{9,11}$ = $J_{9,13}$ = 2.4 Hz). The H13 proton is coupled to the H11 and H9 protons and shows triplet at 8.07 ppm ($J_{13,11} = J_{13,9} = 2.4$ Hz). H14 protons couple to H15 protons, they give a quartet (3.42 ppm, $J_{14.15}$ = 7.2 Hz) and a triplet (1.22 ppm, $J_{15.14}$ = 7.2 Hz) (Fig. 10), respectively. These results are in accordance with the literature values [71]. The absorption of ring protons is in the range of 6-8 ppm which corresponds to aromatic character. This result reveals that the title compound adopts enol form in solution.

In the ¹³C NMR spectrum of the title compound recorded in CDCl₃ (Fig. 11), the imino carbon (C7) peak was observed at 162.401 ppm, and the phenolic carbon (C2) peak appeared at 163.744 ppm. The ¹³C NMR spectrum of the title compound shows peaks at 152.427 ppm (C8), 150.551 ppm (C4) and 149.071 ppm (C12). The C1, C3, C5 and C6 carbons of aromatic ring are at 108.730 ppm, 97.504 ppm, 104.245 ppm and 134.439 ppm, respectively. The C13, C11, C10 and C9 carbons are at 115.074 ppm, 119.803 ppm, 129.945 ppm and 127.871 ppm, respectively. The CH₂ (C14) and CH₃ (C15) peaks of ethyl group are seen at 44.702 ppm and 12.688 ppm, respectively (Fig. 11). The results agree well with the reported values [71].

Non-linear optical (NLO) properties

The non-linear optical properties have an important role for the design of materials, in modern communication technology, signal processing, optical switches and optical memory devices [72]. The non-linear optical properties of the organic molecules ensue from delocalized π electrons that move along molecule. The increase of the conjugation on molecule results in an increase in its non-linear optical properties. Addition of donor and acceptor groups also increases non-linear optical properties of a molecule. If the donor and acceptor groups are powerful, delocalization of π electron cloud on organic molecules increases and as a result of this the polarizability and first hyperpolarizability of organic molecules increase [73]. The title compound, a Schiff Base has the delocalized π electron system. In order to investigate the effect of π electron system and donor-acceptor group on its non-linear optical property was computationally studied by DFT (B3LYP) theorv level.

The average linear polarizability α , and the first hyperpolarizability β can be calculated by using the Eqs. (2), (3), respectively [72].

$$\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^{2} + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^{2} + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^{2}]^{1/2}$$
(3)

The polarizability and the first hyperpolarizability were calculated at the level of B3LYP/6-311G(d,p) and the calculated results are given in Table 3.

The calculated polarizability (α) and first hyperpolarizability (β) of title compound are 40.73 Å³ and 57.15 × 10⁻³⁰ cm⁵/esu that are greater than those of urea (α and β of urea of 3.8312 Å³ and



Fig. 11. ¹³C NMR spectrum of the title compound in CDCl₃.

Table 3 Calculated polarizability and first hyperpolarizability components (a.u.) for the title compound.

α _{xx}	484.2728381	β_{xxx}	6732.3617728
α _{xv}	12.7349048	β_{xxy}	954.6803769
α _{vv}	215.4352025	β_{xyy}	-73.9420964
α _{xz}	13.5826842	β _{ννν}	-70.4908562
α _{vz}	4.7702881	β_{xxz}	119.0814365
α _{zz}	125.6323023	β_{xyz}	236.0247558
		β_{yyz}	-23.5312242
		β_{xzz}	-107.8030919
		β_{yzz}	25.8574634
		β_{zzz}	-10.1765636

 0.37289×10^{-30} cm⁵/esu), respectively [74]. In addition, it is found that the first hyperpolarizability of title compound is greater than those of related Schiff bases [75,76]. The strong electron withdrawing -NO₂ group and electron-donating N,N-diethylamino group increase the movement of π electron cloud. This leads to an increase in conjugation and consequently an increase in non-linear optical properties. The results show that the title compound can be used as a good non-linear optical material.

Conclusions

The XRD study reveals that the title compound in the solid state (a) prefers phenol-imine structure, (b) can possibly show photochromic properties based on its non-planar geometry and (c) has a 3D supramolecular structure assembled by C–H…O interactions between C-H (aliphatic and aromatic), phenol and NO₂ groups. The experimental FT-IR study, harmonic oscillator model of aromaticity (HOMA) index and density functional theory (DFT) results (gas phase) also indicate the existence of phenol-imine tautomeric form. It is concluded on the basis of UV-vis studies that the title compound adopts only phenol-imine form in three organic solvents of different polarities (Benzene, DMSO and EtOH). The result was attributed to the substituent effect through strong electronwithdrawing nitro group. The UV-vis results are also correlated with those of time-dependent density functional theory (TD-DFT). The investigation of non-linear optical properties suggests that the title compound can be used as a non-linear material.

Appendix A. Supplementary material

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 809224. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Tables S1 and S2 are also provided. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.05.044.

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