



Exploring crystal structure, Hirshfeld surface and quantum mechanical attributes of symmetric thiophene Schiff base

Seher Meral¹ · Ayşen Alaman Agar² · Emine Berrin Cinar³ · Necmi Dege³ · Sibel Demir Kanmazalp⁴ · V. G. Vidya⁵ · V. G. Viju Kumar⁵

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Abstract

A novel compound (1E,1'E)-N,N'-(ethane-1,2-diyl)bis(1-(5-nitrothiophen-2-yl)methanimine) [EDNM] was synthesized from thiophene derivative in view to get multidentate ligand with potential biological activity. EDNM is characterized by FT-IR, ¹H and ¹³C NMR and UV–Vis spectroscopic techniques and confirmed by SCXRD. EDNM crystallizes in the monoclinic system with P2₁/c space group with Z value 4 and unit cell parameters *a* = 5.6540(3) Å, *b* = 17.9249(8) Å and *c* = 7.5077(5) Å. DFT was employed for theoretical evaluations using B3LYP with the basis set 6–311 + +G (d,p). Geometry optimization, vibrational analysis, NMR, electronic absorption, MEP, FMO, Mulliken charges and NBO analysis were performed, thereby establishing the nature of reactive sites, band energy gap and atomic charges of EDNM. Theoretical values matched well with the experimental findings. NBO analysis revealed the donor acceptor interactions in molecule. Analysis of global reactivity descriptors along with Fukui indices outlines the elaborate scheme of reactive sites of the molecule, and Hirshfeld surface investigation revealed the intermolecular interactions in crystal packing.

Keywords Thiophene · Schiff base · DFT · Fukui function · NBO · Molecular electrostatic potential · Hirshfeld surface

Introduction

Physicochemically, thiophene and its chemical modifications represent a prominent class of heterocyclic compounds that are capable of a wide range of biological functions. Transforming thiophene derivatives into multidentate Schiff bases to coordinate with a variety of metal ions makes them a popular choice in organometallic chemistry [1, 2]. Recently, well-designed synthetic routes for new bridged

Schiff bases in which imine groups are combined with alkyl or aryl groups have been reported [3]. Schiff base derived from pyridine carbaldehyde have been synthesized for their potential medical applications [4]. To impart synergic effect, biological activity sulphur is coupled with nitrogen atoms to exhibit better biological and chemical properties. It is also of great interest to study thiophene derivatives since thio-groups can form bonds between imines and result in stable metal complexes [5]. The use of non-platinum metal-chemotherapeutic drugs in treating cancer has been shown to have reduced cytotoxicity in a wider range of subsets [5]. There is a substantial amount of research on compounds with anticancer properties due to their ability to scavenge free radicals [6–8]. Chelating properties of Schiff bases contribute significantly to their antioxidant activity, and this could be used to develop anticancer compounds [9]. Due to their strong DNA-binding ability, transition metal complexes bearing S, O and N donor-chelating ligands make good anticancer agents. Schiff base transition metal complexes have been extensively studied owing to their ability to coordinate with metal ion centres via one or more sites. This leads to the amalgamation of numerous complexes with distinct metal centres, stereochemistry and applications.

✉ V. G. Viju Kumar
viju@universitycollege.ac.in

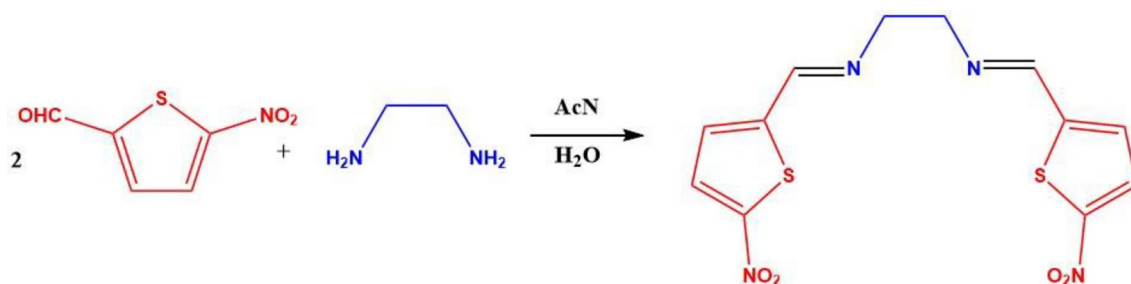
¹ Boyabat Vocational School, Sinop University, 57200 Sinop, Turkey

² Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

³ Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

⁴ Naci Topçuoğlu Vocational School, Biomedical Device Technology Program, Gaziantep University, Gaziantep, Turkey

⁵ Department of Chemistry, University College, Thiruvananthapuram, Kerala 695034, India



Scheme 1 Synthesis of EDNM

In chemical processes, azomethine groups provide molecules with different useful symmetry, and these properties give Schiff bases a lot of opportunities. Symmetrical and unsymmetrical Schiff bases have been obtained usually with aliphatic or aromatic diamines and behave as chelating agents. Another remarkable feature of Schiff bases is their use in energy applications, sensor devices and electrochemical surfaces by tuning π -electronic conjugation and spectroscopic behaviours which in turn depends on type of intermolecular interactions, steric factors in packing and energy profiles [6, 7]. The weak $N=C\cdots O$ interactions have substantial role in crystal architecture, and the motif can influence the assemblies during metal complex formation.

Hetero-aromatic compounds have gained recent attention for their biosimilarity. In particular, thermochemical stability and electro-optic responsivity draw attention on thiophene and thiophene derivatives [8]. Despite the fact that sulphur atoms containing Schiff bases have biological properties, they have been used in hard acidic media to inhibit surface corrosion [10]. In light of these studies, we synthesized a new thiophene-based tetradentate symmetrical Schiff base candidate for metal chelate and SCXRD reveals the unique structural features. DFT/B3LYP method with 6–311++G(d,p) basis set also lends insight into electronic structure and thermochemical parameters via *Gaussian 16* packet program using optimized geometrical parameters [11]. In this study, we analysed the title compound to obtain bond lengths, bond angles, dihedral angles, Mulliken charges, molecular electrostatic potential surfaces, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as well as NBO parameters. The result of analysing global reactivity descriptors and Fukui indices reveals the interesting pattern of reactive sites in the molecule [12]. The visualization of molecular assemblies with a variety of relatively weak interactions requires appropriate tools so that both quantitative and qualitative data can be collected. By employing Hirshfeld surface analysis and 2D-fingerprint plots, we can gain a better understanding of the interactions inside the crystal lattice [13]. A three-dimensional visual representation of molecular crystals

involves partitioning space into non-overlapping molecular surfaces. It is possible to encode a variety of information on the Hirshfeld surface, such as shape index (S), curvedness (C) and normalized contact distance (d_{norm}). In order to construct energy frameworks, single-point wave functions with B3LYP/6-31G(d,p) levels of theory are used to compute interaction energies inside a cluster of molecules [14]. Therefore, many different perspectives can be achieved when analysing the data.

Materials and methods

Synthesis of (1E,1'E)-N,N'-(ethane-1,2-diyl)bis(1-(5-nitrothiophen-2-yl)methanimine) [EDNM]

The symmetric Schiff base containing nitrothiophene moiety was obtained in 2:1 stoichiometric ratio of 5-nitrothiophene-2-carbaldehyde and 1,2-ethylenediamine solutions in acetonitrile. For this purpose, 0.0012 mmol (0.1886 mg) 5-nitrothiophene-2-carbaldehyde and 0.0006 mmol (0.0360 mg) 1,2-ethylenediamine were dissolved separately in 30 mL of acetonitrile and mixed slowly. During the 8-h reflux period, the mixture was constantly stirred approximately at 353 K. The obtained brown solid was washed with ether and cold ethanol, respectively. The resulted solid was dissolved in acetone and allowed to crystallize at room temperature. The Schiff base is obtained in 69% yield as brown crystalline solid.

The title compound obtained in brown solid form was washed with cold ethanol and permitted to crystallize at room temperature in acetone. The brown crystals of Schiff base is obtained in 69% yield. The obtained crystal was analysed by X-ray, UV–Vis and ^{13}C - ^1H NMR spectroscopies. The synthesis of the ligand is illustrated in Scheme 1.

Spectroscopic analysis

With the PerkinElmer Lambda 25 UV–visible spectrophotometer, the electronic spectrum was measured from 200

to 800 nm. PerkinElmer Spectrum 65 IR spectrophotometer recorded the FT-IR spectrum of EDNM from 400 to 4000 cm^{-1} and the ^1H and ^{13}C NMR on a Joel GS 400 MHz FT-NMR instrument. X-ray diffraction was recorded on a STOE IPDS 2 single-crystal X-ray diffractometer using MoK_α radiation ($k = 0.71073 \text{ \AA}$) by applying the ω -scan method. We solved the crystal structures using the direct method and refined them using the full-matrix least-squares method on F^2 using SHELXS and SHELXL-2014 programs in WinGX program suit, respectively [15, 16]. Using the PLATON program, geometrical calculations were performed [17]. We used MERCURY 3.10.1 to generate the molecular and packing diagrams [18]. The bond lengths of hydrogen atoms were fixed when locating them geometrically and calculated at these environments: 0.93 $\text{\AA}$ H-bond lengths in the phenyl ring and methylene ($-\text{CH}_2$) bond lengths at 0.97 $\text{\AA}$.

Computational studies

Using *Gaussian 16* package, DFT calculations were performed with B3LYP/6–311 + + G(d,p) level theory and visualized the outcome with *GaussView 6.1* program. TD-DFT approach outlines the electronic properties, and GIAO method generated the ^1H and ^{13}C isotropic shielding data. Using *Crystal Explorer 21*, interactions in molecular crystal structures are visualized and quantified through Hirshfeld surfaces and their respective 2D-fingerprints. Additionally, the energy frameworks were constructed using *Tonto* based on B3LYP/6-311G (d,p) level of theory.

Results and discussion

Commentary on crystal structure

The solid-state structure of EDNM is presented in Fig. 1 which indicates the atomic numbering scheme. A summary of crystallographic data and selected bond lengths and angles is given in Tables 1 and 2. Hydrogen bond geometry is given in Table 3. The crystallographic studies reveal that

Table 1 Crystallographic data and refinement parameters

Crystal data	
CCDC number	870808
Chemical formula	$\text{C}_6\text{H}_5\text{N}_2\text{O}_2\text{S}$
MW	169.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c ($\text{\AA}$)	5.6540(3), 17.9249(8), 7.5077(5)
β ($^\circ$)	102.216 (5)
V ($\text{\AA}^3$)	743.66 (7)
Z	4
Radiation type	Mo K_α
μ (mm^{-1})	0.38
Crystal size (mm)	$0.59 \times 0.39 \times 0.05$
Data collection	
Diffractometer	STOE IPDS 2 diffractometer
Absorption correction	Integration
Tmin, Tmax	0.806, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7143, 1458, 1170
R_{int}	0.026
$(\sin \theta/\lambda)_{\text{max}}$ ($\text{\AA}^{-1}$)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.139, 1.05
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ $\Delta\rho_{\text{min}}$ ($e \text{ \AA}^{-3}$)	0.54, -0.27

the EDNM crystallizes in the monoclinic system with $P2_1/c$ space group. As part of the inversion centre, the molecule occupies a specific position 8i (mm2) at the middle of the C6–C6i bond [symmetry code: (i) $-x + 1, -y, -z + 1$]. The sulphur atom (S1) which is a part of the thiophene ring represents slightly smaller C1–S1 and S1–C4 bond lengths (1.708 (3) and 1.710 (3)), and they are similar to those of the related molecules. The EDNM molecule exhibits *E*-conformation concerning the azomethine ($\text{C}=\text{N}$) bond. The N1–C1 and N2=C5 distances in the compound of 1.431(4) and 1.264(4) $\text{\AA}$, respectively, are typical of a single- and

Fig. 1 Solid-state structures and the atom-numbering scheme of EDNM, showing also the 40% probability displacement ellipsoids for non-H atoms

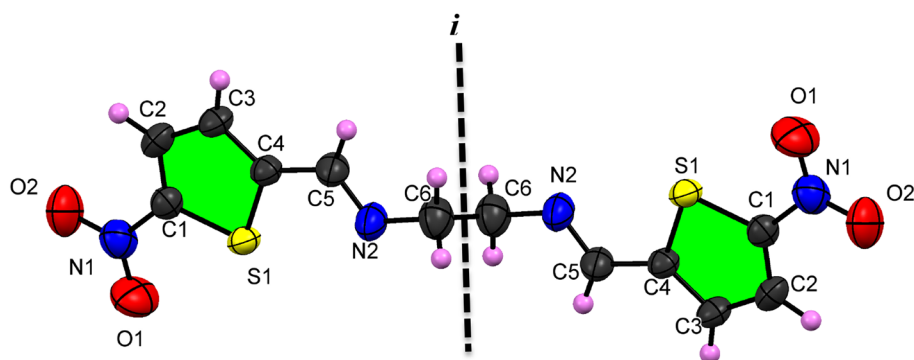


Table 2 Selected bond lengths (Å) and angles (°)

<i>Bond lengths (Å)</i>			
O1—N1	1.218 (4)	N1—O2	1.216 (4)
N1—C1	1.431 (4)	C5—N2	1.264 (4)
S1—C1	1.708 (3)	N2—C6	1.479 (4)
S1—C4	1.710 (3)		
<i>Bond angles (°)</i>			
O2—N1—O1	124.3 (3)	O2—N1—C1	118.4 (3)
C1—S1—C4	89.43 (13)	N2—C5—C4	121.0 (3)
O1—N1—C1	117.3 (3)	C5—N2—C6	118.1 (3)
N1—C1—S1	118.6 (2)		
<i>Torsion angles (°)</i>			
O1—N1—C1—S1	−2.7 (4)	O2—N1—C1—C2	−4.0 (5)
N2—C5—C4—S1	5.6 (4)	O2—N1—C1—S1	176.7 (3)

Table 3 Hydrogen bond geometries (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C5—H5...O2 ⁱ	0.93	2.63	3.469(4)	150
C3—H3...S1 ⁱⁱ	0.93	3.02	3.653(3)	127

Symmetry codes: (i) $[-x+2, y-1/2, -z+3/2]$; (ii) $[x+1, -y+1/2, z+1/2]$

double-bond character [19]. In EDNM, the five-membered thiophene ring defines a plane (P) [20]. The P is nearly coplanar to plane that consists of N1, O1 and N2 atoms,

with the dihedral angle between them being 3.47(1)°. The intermolecular interactions are caused by the presence of hydrogen on the Schiff base or S1 in the thiophene ring and also the oxygen atom in the nitro group. Atoms C5 and C3 in EDNM molecule at (*x*, *y*, *z*) act as hydrogen bond donor, via H5 and H3, to atom O2 at ($-x+2, y-1/2, -z+3/2$) and atom S1 at ($x+1, -y+1/2, z+1/2$), respectively [21, 22]. These interactions of the EDNM compound show a chain $R_4^4(18)$ motif as shown in Fig. 2. The almost face-to-face $\pi\cdots\pi$ stacked centroids of thiophene rings of the molecular pairs are $C1g\cdots C1g=3.7618$ Å at $[x, 1/2-y, 1/2+z]$.

Geometrical optimization

A geometrical optimization of the title compound was described using *Gaussian 16* theoretically in Fig. 3, which was in agreement with XRD data. The $C_6-N_2-C_5$ angle between thiophene and ethyl amine group is found to be 118.1° which is in agreement with theoretical value of 122.2°. The $N_2-C_5-H_5$ angle of 119.5° was agreeing with 122.7°, and the deviation from normal 120° can be due to the presence of double-bonded nitrogen and lone pair on nitrogen atom. The $N_2-C_6-C_6$ angle of 108.8° agrees to 110° and deviates from the normal tetrahedral angle. The $N_2-C_5-H_4$ angle of 121° corresponds to theoretical value of 122.2°. The bond length of C_5-N_2 is 1.264 Å agreeing to theoretical value of 1.271 Å, newly formed bond. The experimental C_5-N_2 bond length of 1.479 Å agrees to 1.449 Å value theoretically, characteristic of carbon nitrogen single

Fig. 2 A partial packing diagram of EDNM; intermolecular hydrogen bonding interactions have been indicated as broken lines

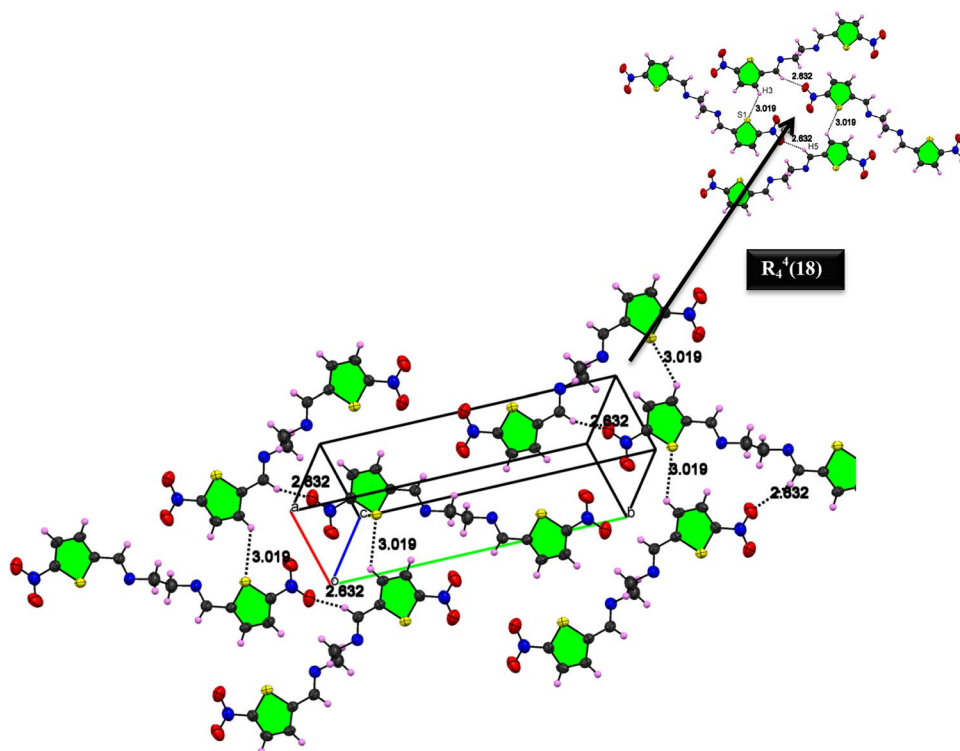
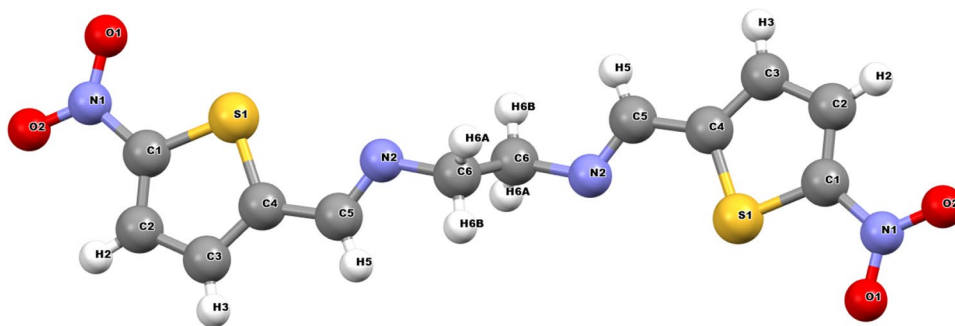


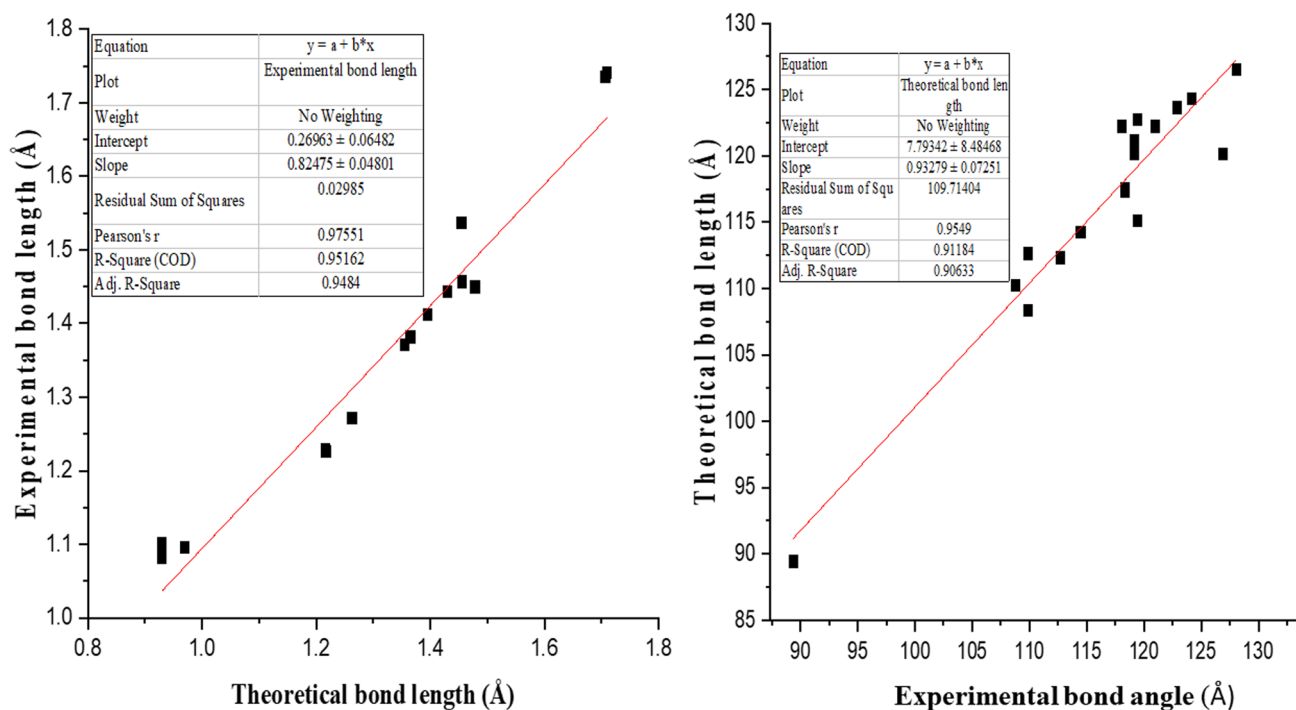
Fig. 3 Optimized geometrical structure of EDNM

bond. The C_5-N_2 bond distance of 1.264 Å is agreeing to 1.271 Å, which comes exactly in the range of $C=N$ bond. The C_6-H_6 bond length of 1.45 Å agrees theoretically to 1.536 Å, and C_4-C_5 bond length of 1.456 Å agrees exactly with theoretical value. Bond length and bond angle values clearly indicate that the double bond is not getting delocalized into C_6-C_6 single bond between the two nitrogen atoms. The $N_2-C_6-C_6-N_2$ dihedral angle is 180° with both nitrogen atom pointing away towards thiophene. It can be concluded that molecule has a centre of symmetry. The bond distance and angles in theoretical calculations are found slightly higher than what has been observed experimentally. These correlation diagrams compare theoretical and experimental bond angles and bond lengths of the compound here in Fig. 4. It is most likely that these inconsistencies arise from the fact that the DFT calculations are conducted on a

gas-phase molecule, although the experimental observations are obtained in the solid state.

^{13}C - ^1H NMR spectra

The EDNM was analysed by ^{13}C and ^1H NMR spectra. The ^{13}C NMR spectra of EDNM were taken in $CDCl_3$ solvent, and the solvent peak was observed at 77 ppm as triplet due to the carbon atom of the solvent. The EDNM has six different carbon atoms in ^{13}C NMR spectrum. The imine carbon was detected at 154.98 ppm. The imine peak has been designated at 155–60 ppm, according to literature [23]. The C-attached NO_2 moiety in the thiophene ring has been detected at about 153 ppm [24]. One of the thiophene carbons near the sulphur atom shows a singlet at 148.07 ppm, and others are at the lower frequency of 128.941 and 128.37 ppm [25]. The

**Fig. 4** Linear correlation diagrams for theoretical (DFT) and experimental (SCXRD) bond lengths and angles

EDNM contains two thiophene rings attached to each other with N, N'-(ethane-1,2-diyl)dimethanimine moiety where two carbon atoms were recorded at 60.49 ppm [26].

DFT calculations using GIAO method show the imine carbon atom singlet at 162.65 ppm. The carbon atom between sulphur and imine carbon appears at 163.91 ppm, and other thiophene carbon between nitro group and sulphur atom appears at 165.03 ppm. The carbon attached to carbon carrying nitro group shows peak at 137.09 ppm, and other carbon in thiophene ring shows peak at 136.62 ppm. The carbon atom stationed between imine nitrogen atoms shows peak at 67.59 ppm.

The ^1H -NMR spectra were recorded in CDCl_3 . In the low-frequency region, solvent peak at 1.25 ppm was encountered. The thiophene moiety is attached to each other with an aliphatic chain, and protons near the imine group were determined at 3.93 ppm [27]. The singlet peak at the highest frequency was for the imine proton at 8.99 ppm [28]. At the region of about 7.19–7.84 ppm, the aromatic thiophene protons were observed such as multiple peaks. The formation of the symmetrical Schiff base can also be expressed as the absence of a peak belonging to the free NH_2 group in the ^1H NMR spectra.

The theoretical ^1H NMR shows a singlet at 8.916 ppm for imine group proton, and the aliphatic proton near imine groups shows peak at 3.5 ppm and 4.6 ppm with a resultant peak at 4.085 ppm. The two aromatic protons appear at 8.757 and 8.243 ppm. The experimental values mostly agree with theoretical findings.

Vibrational spectroscopy

The formation of the symmetrical Schiff base is evident by the disappearance of the NH_2 peak at 3400 cm^{-1} and the $\text{C}=\text{O}$ peak at 1700 cm^{-1} with respect to the starting materials. The IR spectra reveal the C-H vibrations of the

thiophene ring at $3058\text{--}3100\text{ cm}^{-1}$ and close by, aliphatic vibrations in agreement with the literature [28]. These $\text{C}=\text{C}$ aromatic double-bond vibrations were noticed at 1537 cm^{-1} and 1465 cm^{-1} in the synthesized Schiff base. The primary attention falls on the imine bond, and this strong band was detected at a lower wavelength of 1624 cm^{-1} than the carbonyl bond [29]. The N–O group has two sharp peaks for asymmetric and symmetric N–O stretching vibration at about 1503 and 1332 cm^{-1} . The C–S vibration was detected at 813 cm^{-1} [30].

FT-IR of EDNM was theoretically analysed using B3LYP/6–311 + G(d,p) level of DFT. The C–H vibrations of thiophene ring is found at 3056 cm^{-1} along with C–H vibration at 3098 cm^{-1} . Aromatic double-bond vibrations were obtained at 1529 cm^{-1} and at 1467 cm^{-1} . The strong and characteristic imine vibration is observed at 1646 cm^{-1} . The N–O group sharp peaks for asymmetric and symmetric vibrations are found at 1505 and 1325 cm^{-1} . Values obtained experimentally are shown in Fig. 5. Theoretical FT-IR data with multiplier of 0.9680 are in accord with instrumental data.

Electronic absorption spectroscopy

The EDNM has an imine bond and thereby shows $n\text{--}\pi^*$ and $\pi\text{--}\pi^*$ transitions. Different polar solvents exhibit lower or higher electronic transition frequencies due to more stable n and π^* orbitals [31, 32]. Methanol, ethanol and acetonitrile were used as solvents in this study. Two broad peaks can be seen in the electronic spectrum where the first broad peak shifts from a lower frequency to a higher frequency with increased solvent polarity. In this respect, the peak at 230 nm is designated as $\pi\text{--}\pi^*$ transition and the other peak at 320 nm is $n\text{--}\pi^*$ transition of imine bond. The spectrum is given in Fig. 6. TD-DFT calculations provide a broadband at 345.81 nm.

Fig. 5 FT-IR spectra of EDNM

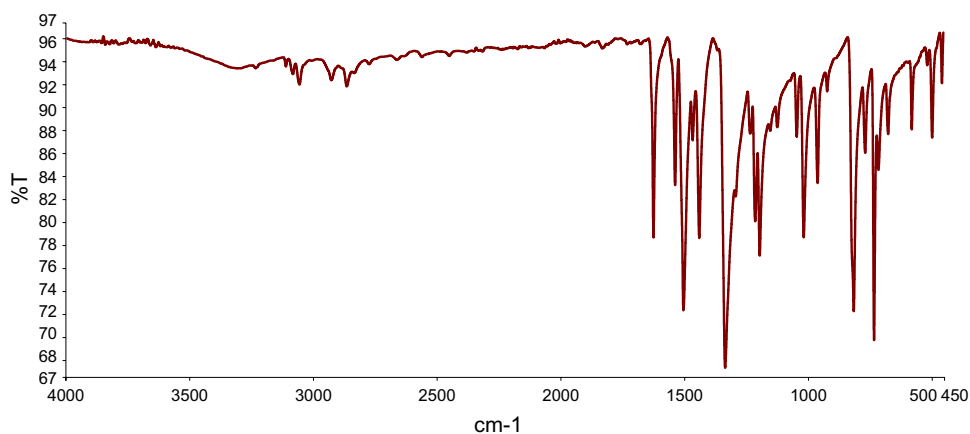
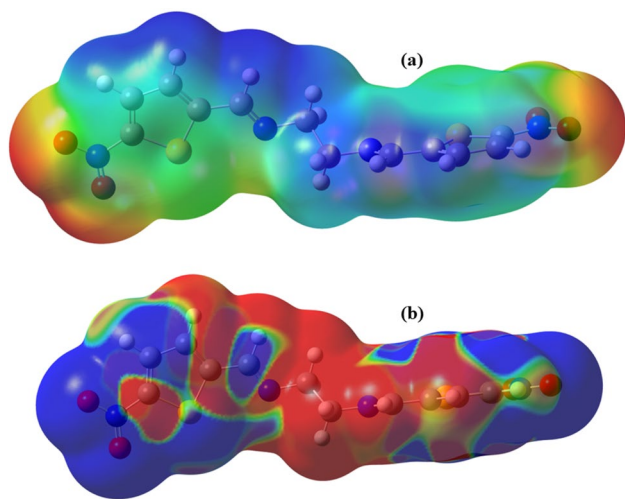
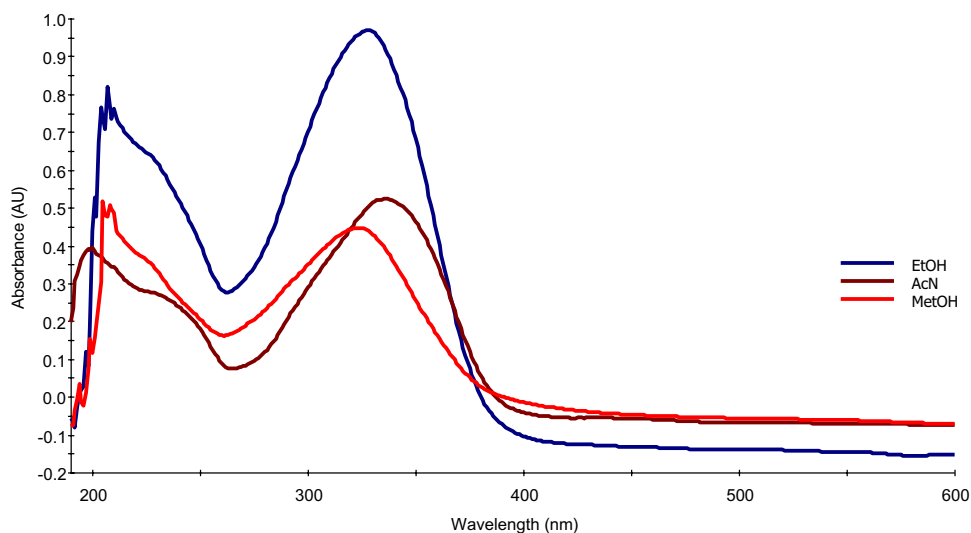


Fig. 6 UV–Vis spectrum of EDNM**Fig. 7** **a** ESP on to the total electron density surface (Isovalue = 0.0004) **b** MEP plot depicting difference of SCF and CI mapped on to ground state

Molecular electrostatic potential (MEP)

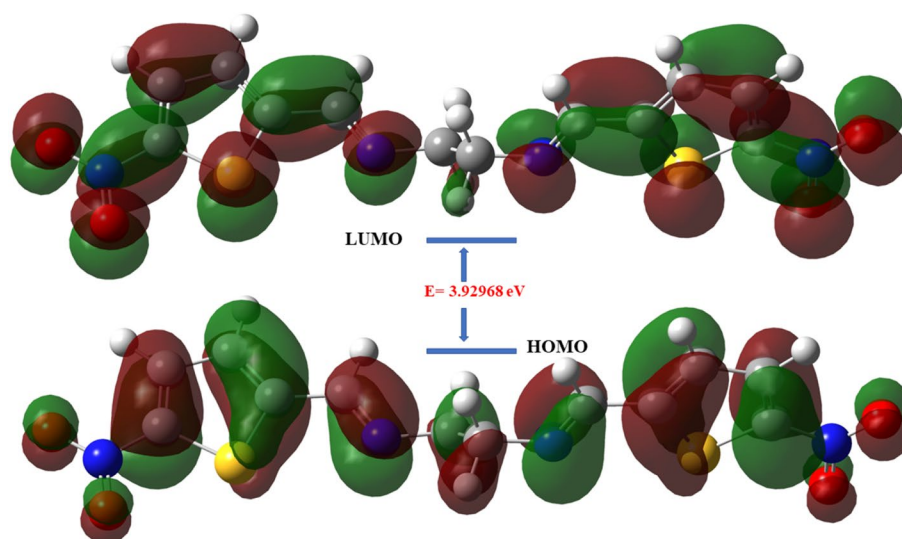
MEP type of descriptor is useful not only for visualizing the beneficial areas for electrophilic or nucleophilic attack but also H-bonding in molecular systems. Map allows the visualization of molecules with variable charges. Identifying molecular interactions can be done using charge distributions. MEP's significance lies in the simultaneous display of size, shape and electrostatic potential of the molecules as well as their positive, negative and neutral states based on the grading of colours [14, 33, 34]. As seen in MEP,

the negative potential of EDNM is seen around the nitrogen atom of C=N and the sandwiched ethylene molecule between two nitrogen atoms and is in red colour as shown in Fig. 7a. The aforesaid position is where the nucleophile is most likely to attack. The rest of the portions are of positive potential and are shown in blue colour, where the electrophilic attack is preferred. The subtraction of first excited-state electron density from the total CI density as a result of TD-DFT computation and ground-state electron density considering SCF density is mapped onto the total SCF density is shown in Fig. 7b. The blue field depicts positive electron density, and the red terrain depicts opposite of it. When electronic transition is made from ground to excited state, electron density shifts from azomethine central region to thiophene ring residues at both ends.

Frontier molecular orbital (FMO) analysis

Along with indexing stability, chemical reactivity and forecasting the reactive locale, FMO orbitals and band gaps can also reveal many reactions, UV–Vis, biological activity, electrical shifting ability, chemical hardness/softness and optical properties. Ionization potential determines the LUMO energy, while electron affinity determines the HOMO energy. A simple indicator of kinetic level of molecules has been found to be the HOMO–LUMO energy separation. It is seen that in HOMO (87) the electron density is localized almost on whole molecule, mainly on oxygen atom of nitro and nitrogen of C=N group (Fig. 8). In LUMO (88), electron density is on either side ethylene moiety uniformly distributed, especially upon nitrogen atom and sulphur atom. The EDNM has large band gap energy of 3.9297 eV.

Fig. 8 HOMO and LUMO of EDNM



Band gaps with large values indicate kinetic stability and low chemical reactivity [11]. It has recently been demonstrated that intramolecular charge transfer can be evidenced by using band gaps.

Mulliken charges

Mulliken atomic charge calculation applies quantum chemical calculation to molecular systems reflecting the vibrational sphere of molecule and assessing the electronic structure as a function of atomic displacement; it attributes accordingly explicit to the chemical bonds within the molecule. It is the atomic contribution of molecular systems that determine the parameters such as polarizability, reactivity and dipole moment.

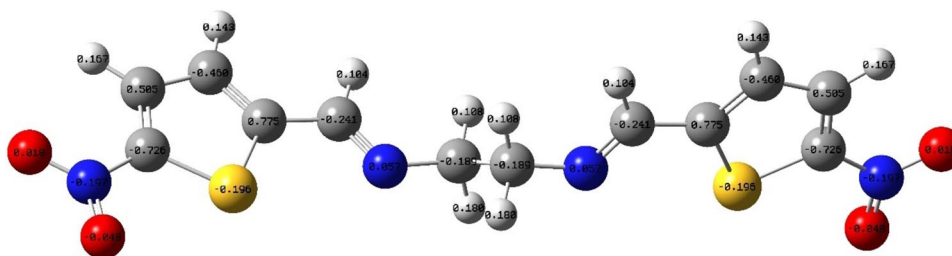
The two nitrogen atoms of nitro group on either side of the title compound have maximum negative charge of -0.197 attached between two oxygen and carbon atom (Fig. 9). The other nitrogen atoms of both $C=N$ group experience a positive charge of 0.057 . The two sulphur atoms present on either side of thiophene ring have a negative charge of -0.196 . The one among two oxygen atoms of both nitro group has least negative charge of -0.048 pointing away from the molecule downwards, in the direction towards sulphur atom. The other two oxygen atoms of nitro group

experience a positive charge of 0.018 . Among the twelve carbon atoms, carbon atom sandwiched between the sulphur and nitrogen experiences negative charge of -0.726 . The carbon alternative to the aforesaid negative carbon on either thiophene ring experiences a negative charge of -0.460 . The carbon atom of $C=N$ group experiences least negative charge of -0.241 , and ethylene carbon atoms have a positive charge of 0.189 . Both C2 carbon atoms and C4 carbon atoms on thiophene ring experience positive charge of 0.505 and 0.775 , respectively. All ten hydrogen atoms are of positive in nature. The hydrogen atoms on either ring of thiophene in C2 and C3 positions have positive charge of 0.167 and 0.143 , respectively. The two hydrogen atoms attached to two $C=N$ group show a positive charge of 0.104 . The hydrogen atoms of ethylene group have 0.108 and 0.180 positive charges. The chances of electrophilic attack on $C=N$ group are very less due to positive charge on nitrogen atom.

Natural bond orbital (NBO) analysis

Generally, NBO analysis is performed for understanding hybridization, nature of bonding and second-order interactions enclosed by two subsystems, filled and vacant orbitals in a more detailed way. There exists a direct correlation between natural bond orbitals and intermolecular

Fig. 9 Mulliken charges of EDNM



delocalization. The majority feasible natural Lewis structure can be obtained because optimum electron density percentages are included in orbital details.

Among the 472 NAOs, NAO 81 is having highest energy for fifth C orbital of the natural minimum basis set among all orbitals of carbon. NAO 81 is the core electron present in s orbital on carbon with 1.99886 occupancy of electrons. NAO 1 has highest energy for first sulphur orbital of core electron present in s orbital on sulphur with occupancy of 2 electrons. NAO 359 has highest energy for nitrogen in s orbital with electron occupancy 1.99926. The natural minimal basis set exhibits high percentage of 99.6522% contribution to molecular charge distribution. It is indicative that natural minimal basis set contributes majority in outlining the molecular properties. The natural Rydberg basis set contributes only 0.3478%.

The natural populations are abridged as an impressive electron configuration for particular of the 32 atoms in non-integer molecular environment. From natural electronic configuration, the S(1) atom can be described as $1s^2 2s^2 2p^6 3s^2 3p^4 4s^0 4p^0$ in promoted configuration. Out of the total 174 orbitals, Lewis orbitals contribute 169.57087 (97.455% of 174), valence non-Lewis orbitals impart to 4.01435 (2.307% of 174) and Rydberg non-Lewis confers 0.41478 (0.238% of 174). Here it illustrates the percentage of total electron density. The first NBO output is two centred bonds with 1.96973 electrons between sulphur (atom 1) and carbon (atom 2), constituting the σ_{SC} bond. $\sigma_{SC} = 0.6933(sp^{4.2})S + 0.7207(sp^{3.10})C$. For σ_{SC} formed from a $sp^{4.2}$ hybrid with 80.29% *p*-character on sulphur interacting with a $sp^{3.10}$ hybrid with 75.45% *p*-character on carbon. This roughly indicates the concept of sp^3 hybrids for both interacting atoms.

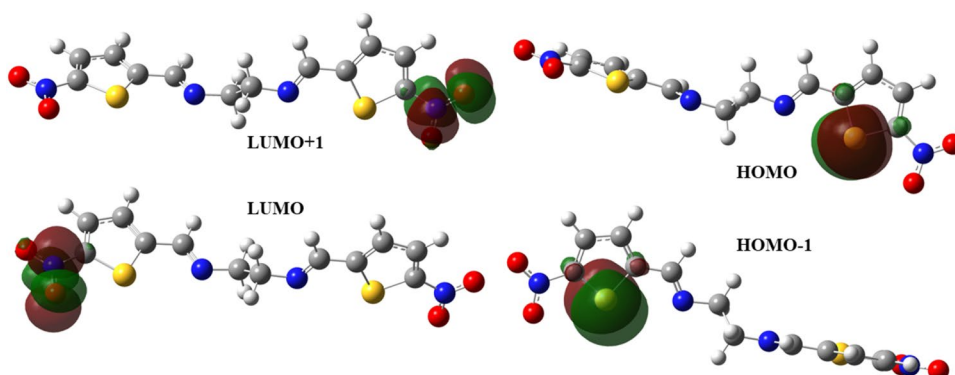
Natural hybrid orbital (NHO) directional analysis gives a clear picture of angular properties of NHOS of all combining atoms. This is calculated with respect to deviation from line of centres in terms of polar coordinates for individual orbitals of combining atoms. In case of S(1)-C(2) σ_{SC} bond, the sulphur NHO of σ_{SC} bond is bent away from line of S-C centre by 8.6 degree and the carbon NHO by 5.6

degree. NHO directionality and bond bending deviations can be seen only for sigma and pi bonds and not for lone pairs. This information can be useful for anticipating direction of geometry changes during geometrical optimization [14].

In order to estimate donor–acceptor interactions in NBO basis, the second-order perturbative analysis is carried out. The strongest stabilization energy of 165.70 kcal/mol is the σ_{ON}^* interaction between lone pair interaction of oxygen (NBO 87) as donor and antibonding $N_{20}-O_{21}$ (NBO 471) as acceptor. This appears to be HOMO where the electron density is concentrated mainly on the sulphur atom (Fig. 10). The next higher energy of 163.70 kcal/mol is the σ_{ON}^* interaction between lone pair interaction of oxygen (NBO 80) donor and antibonding $N_{17}-O_{19}$ (NBO 469) as acceptor, designated as HOMO-1, where the electron density shifts to the sulphur atom on the other end of molecule. So, from HOMO to HOMO-1 the electron shifting takes place from one end to the other end of molecule but concentrated on sulphur atom. Stabilization energy of 85.90 kcal/mol is the π_{CN}^* interaction. This interaction is between antibonding interaction of $C_{12}-C_{13}$ (NBO 458) and antibonding interaction of $N_{10}-C_{11}$ (NBO 454) and also from C_2-C_3 (NBO 435) and antibonding interaction of $N_{10}-C_{11}$ (NBO 444). The above filled non-Lewis NBOs act as donor as well as acceptor and thereby loss of occupancy from localized NBOs occurs. For HOMO-2 and for HOMO-3, the electron density is intense on the oxygen atom of nitro group on the one end and in other on the other end of molecule. In LUMO, the electron density is concentrated on the nitrogen atom and oxygen atom of NO_2 group on the one end and in LUMO + 1, on the other end of molecule. In LUMO + 2, the electron density is concentrated on C=C of thiophene ring between the nitro group and sulphur atom and in LUMO + 3, to the other end of molecule.

From natural bond orbital summary, it is found that oxygen lone pair (NBO 80) is seen as lowest occupancy of 1.45154 electrons and highest energy -0.28900 au Lewis NBO and delocalized into antibonds 458, 435, 463, 436 vicinal σ_{CH}^* NBOs. The Lewis NBO 1–87 describes 97.4545% of total electron density, with

Fig. 10 Selected natural bond orbitals



remaining non-Lewis density found primarily in valence shell antibonds.

Reactivity descriptors

As one of the most powerful methods of studying chemical reactivity, DFT captures global reactivity descriptors like chemical potential ($\mu = -0.2121$ a.u), global hardness ($\eta = 0.6109$ au), global softness ($S = 16.3693$ au) and global electrophilicity index ($\omega = 0.3683$ a.u) from the HOMO and LUMO energies [34]. The band gap from quantum mechanical descriptors HOMO- LUMO is 3.3247 eV which points various chemical and spectroscopic properties. The resistance to electron density loss is measured in μ which is -5.7721 eV, indicating that the title molecule primarily acts as an electron acceptor. Electron withdrawing ability is also evident from the high value of electronegativity ($\chi = 5.772$ eV). When molecules acquire additional electron densities from their environment (ΔN), their electrophilicity index ($\omega = 10.0210$) measures the energy stabilization. The higher value of ω shows that the molecule behaves as a strong electrophile favouring high reactivity involving polar reactions. The maximum number of electrons that can be acquired by the electrophile in the present case $\Delta N_{\max}$ is 3.5. ω -index greater than 4.0 eV is often referred to as superelectrophiles.

A molecule's chemical hardness is its resistance to exchange electron density with its neighbouring environment, while its softness is the opposite of chemical hardness. With a high global softness ($S = 16.3693$ au) and low hardness ($\eta = 0.6109$ au) value, the molecule is more likely to exchange its electron density with the environment, indicating high polarizability.

Analysis of global reactivity descriptors along with Fukui indices outlines the interesting scheme of reactive sites of the molecule. To locate active sites of EDNM, we have considered the Fukui function [35]. The Fukui function is a regional equity obtained by condensing values to member atoms expressed by:

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_{v(\vec{r})} = \left(\frac{\partial \mu}{\partial v(\vec{r})} \right)_N$$

where ρ is the electronic density and N is the number of the electrons at a fixed potential $v(\vec{r})$ acting on an electron.

Condensed Fukui functions are calculated from single-point energy calculation with exemplary chemistry at B3LYP/6–311 G(d,p) incorporating NBO analysis depicting natural population analysis (Fig. 11).

The condensed affairs are resolved through a finite difference scheme to evaluate $f(\vec{r})$.

For nucleophilic attack, $f_k^+ = q_k(N+1) - q_k(N)$

For electrophilic attack, $f_k^- = q_k(N) - q_k(N-1)$

For radical attack, $f_k^0 = \left(\frac{1}{2} \right) [q_k(N+1) - q_k(N-1)]$ where $q_k(N-1)$, $q_k(N)$ and $q_k(N+1)$ are the number of electrons associated with the k th atom.

Frontier-controlled reactions occur at sites with high Fukui functions while charge controlled at lower Fukui function. Both C(6) atoms residing between the pair of $-N=C-$ bonds are found to be susceptible to nucleophilic attack (Fig. 3). Since carbon sites have a large charge density, they are ideal for nucleophilic attack, because nitrogen atoms disperse the charge by means of resonance effects to gain stability and induce carbocation formation. N(1) atoms of both nitro groups exhibit higher Fukui functions for electrophilic activity. The electrophilic activity follows the order $N(1) > C(6)$.

Hirshfeld surface (HS) analysis

For analysing intermolecular interactions and crystal packing, Hirshfeld surface (HS) analysis is an indispensable tool. In this case, the 0.5 isosurface unveil Hirshfeld surface, with the continuous scalar function generated from the following expression.

$$w_A(r) = \rho_{\text{promol}}(r) / \rho_{\text{procrystal}}(r) = \sum_{A \in \text{molecule}} \rho_A(r) / \sum_{C \in \text{crystal}} \rho_C(r)$$

The various parameters are weight function $w_A(r)$, atomic electron density $\rho_A(r)$, promolecule electron density $\rho_{\text{promol}}(r)$ and procrystal electron density $\rho_{\text{procrystal}}(r)$.

For better understanding of the lattice, surface properties are represented by a variety of colour schemes. An intermolecular interaction pattern for a reference HS can be quantitatively described by two-dimensional finger print plots. The molecule shows Hirshfeld surface volume as $364.2 \text{ \AA}^3$, globularity 0.695 and asphericity value 0.557. HS mapped over d_{norm} in three-dimensional perspective ranging from -0.013 to $+1.301 \text{ \AA}$ is shown (Fig. 12).

Using d_e and d_i , *Crystalexplorer 21* calculates the normalized contact distance d_{norm} for the closest nucleus externally and internally to the HS surface from the crystallographic data. The blue shading shows atoms in close contacts longer than vdW than the red shade, and the red shaded spots depict the reverse. When distances are nearly vdW, white colour predominates.

A very scientific and accurate way to identify close contacts is achieved by using the d_{norm} surface, which conveys

Fig. 11 Fukui reactivity indices (top) f_k^- for electrophilic (bottom) f_k^+ for nucleophilic

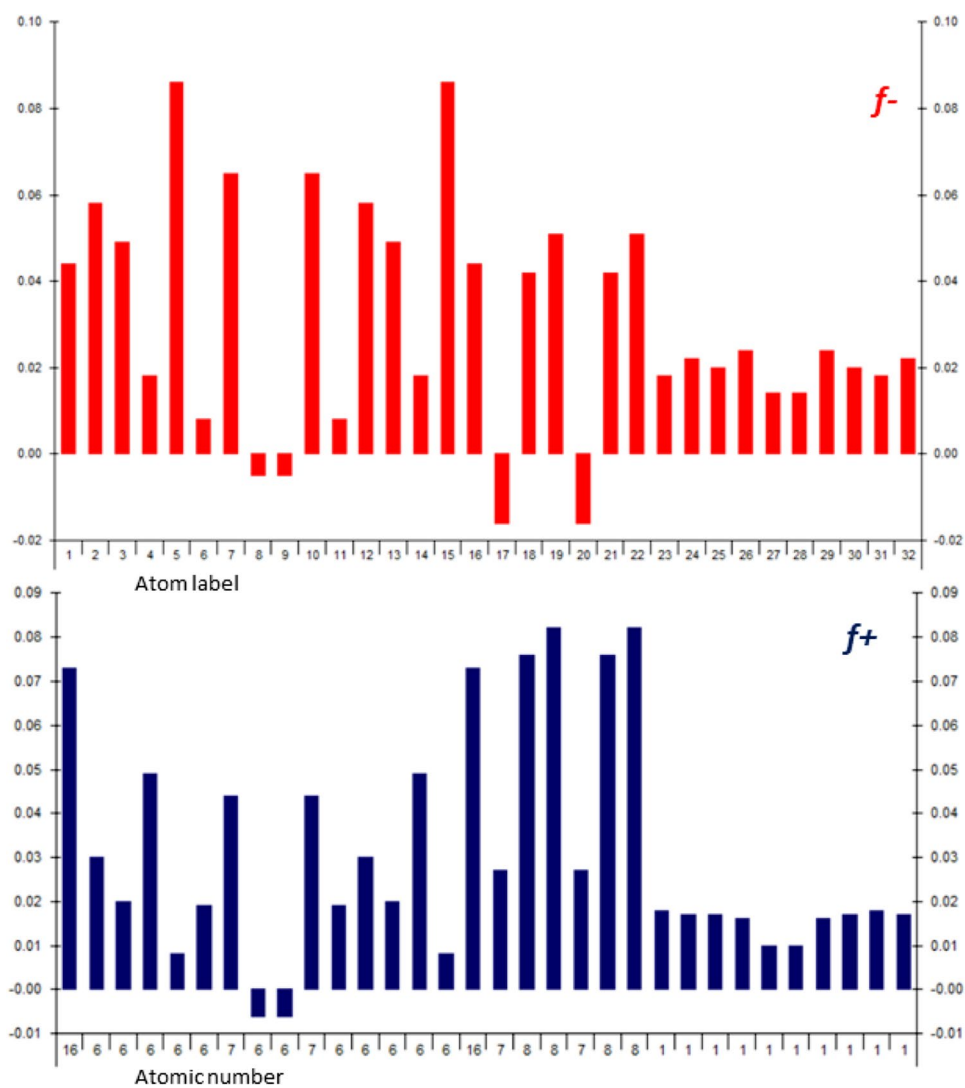


Fig. 12 HS mapped over d_{norm}

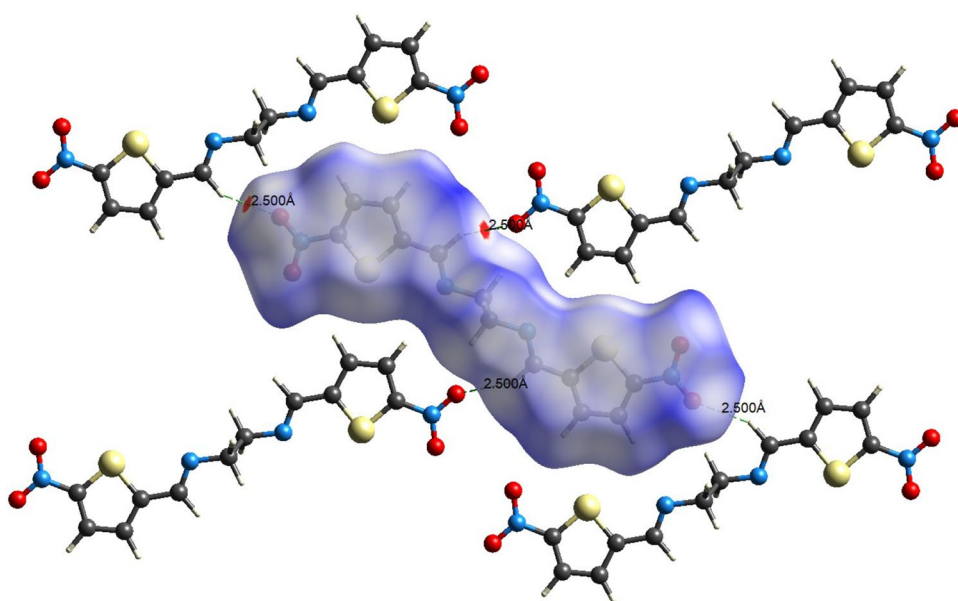
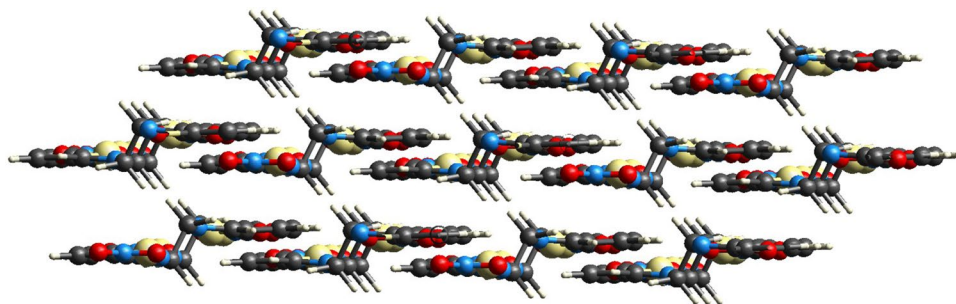


Fig. 13 Crystal packing viewed through b-axis



the presence of prominent molecular interactions using bright red spots.

The S-shaped centrosymmetric molecules in transoid conformation arranges into wave-like layers and further

packs into 3D lattice. The HS surface shows remarkable features along the XY plane where four molecules surround a reference molecule [36]. Every molecule interacts with four other molecules through four prominent close contact

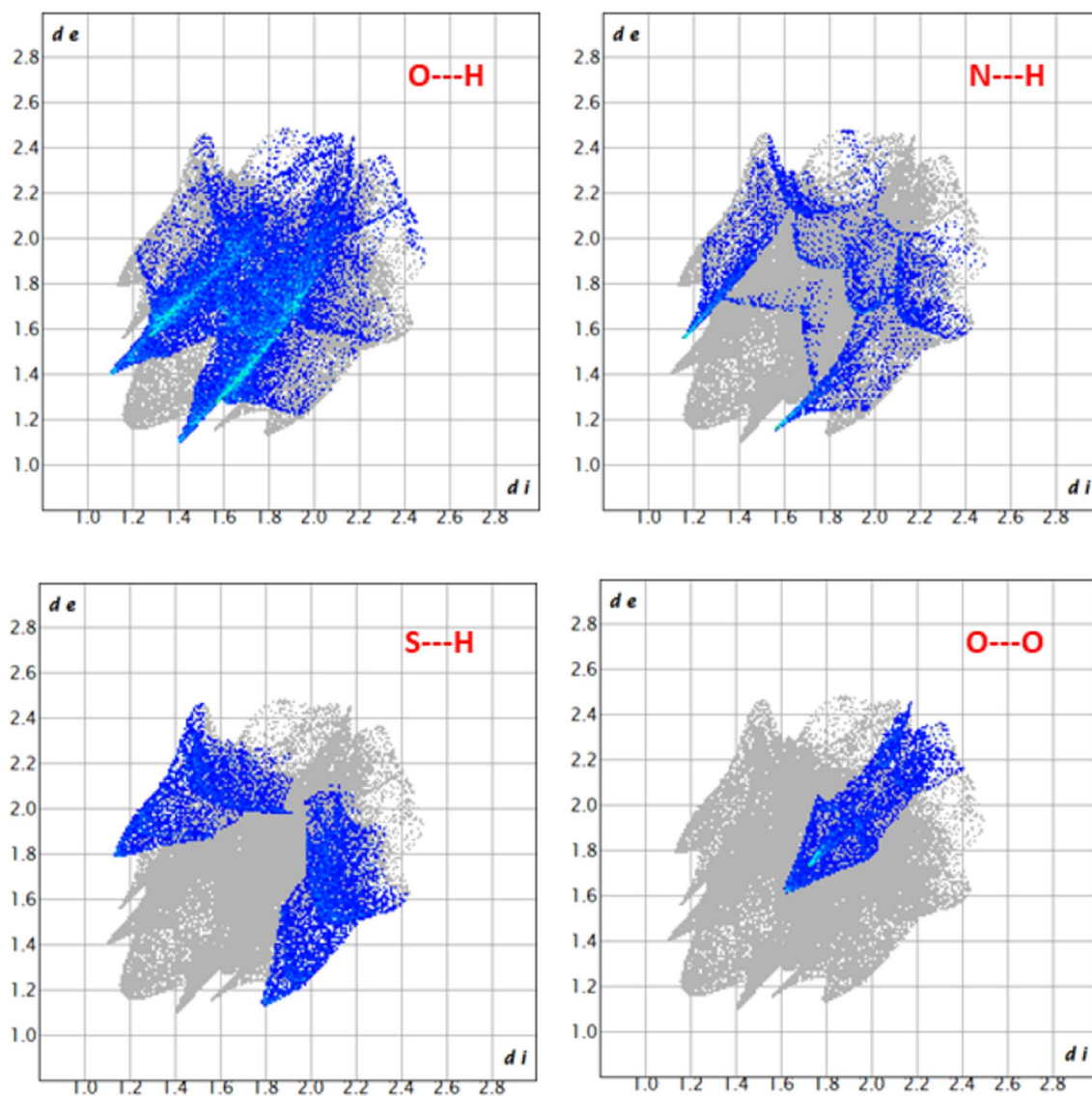


Fig. 14 Two-dimensional fingerprint plots

with a distance of 2.50 Å which is evident from the four bright red spots on HD surface. From inside an HS surface, the two $\text{N}=\text{C}-\text{H}\dots\text{O}$ interactions directed on the opposite sides bring closer two molecules to the reference HS surface. Also $-\text{N}=\text{O}\dots\text{H}$ interactions extended by the pair of nitro groups hold another pair of molecules fixed around the reference molecule. The symmetric arrangement of individual molecules in the lattice is presented (Fig. 13).

The maximum closest internuclear distance in which two respective layers approach is 2.355 Å which is characterized by $\text{N}=\text{C}-\text{H}\dots\text{H}$ (sp^3) interaction. The dihedral angle $=\text{N}-\text{C}-\text{C}=\text{N}$ is 180° and the pair of CH_2 groups orient in staggered manner and the thiophene rings keep in antiparallel orientation.

The immediate surroundings of a molecule influence the 2D fingerprint plots, the filtering is effected by element type, and surface area is presented as the percentage of total HS area indicating close contacts between atoms inside and outside the surface.

The O–H interactions are affected through the close contact by nitro group and $-\text{N}=\text{C}-\text{H}$ interaction and constitute reciprocal contact, 34.4% of HS surface and evident as a pair of sharp, symmetric spikes with equal length (Fig. 14). Sulphur shows prominent contact with H atoms only which is 12.6% reciprocally. N–N (1.8%) and S–S (1.4%) interactions are very feeble. H–H interactions constitute the central broad spike which is the prominent spear head in all fingerprint plots. S–H close contacts appear as two wings and contribute 12.6% to total HS surface. N–H contacts arise from CH of thiophene ring and $-\text{C}=\text{N}$ interaction at a distance of 2.714 Å (9.2%). Central arrowhead-shaped O–O close contacts are attributed to the nitro groups. The plots do not provide indications of N–S and O–S interactions.

Single-point wave function with B3LYP/6-31G(d,p) is employed to check out energy of interaction within a clump of molecules generated within a radius of 5.80 Å, in order to simulate energy frameworks in an inexorable manner (Fig. 15) [37]. To calculate the combination of intermolecular interaction energy (E_{tot}), the algorithm combines

Fig. 15 Cluster of molecules generated in 5.8 Å radius with reference molecule depicted in black colour

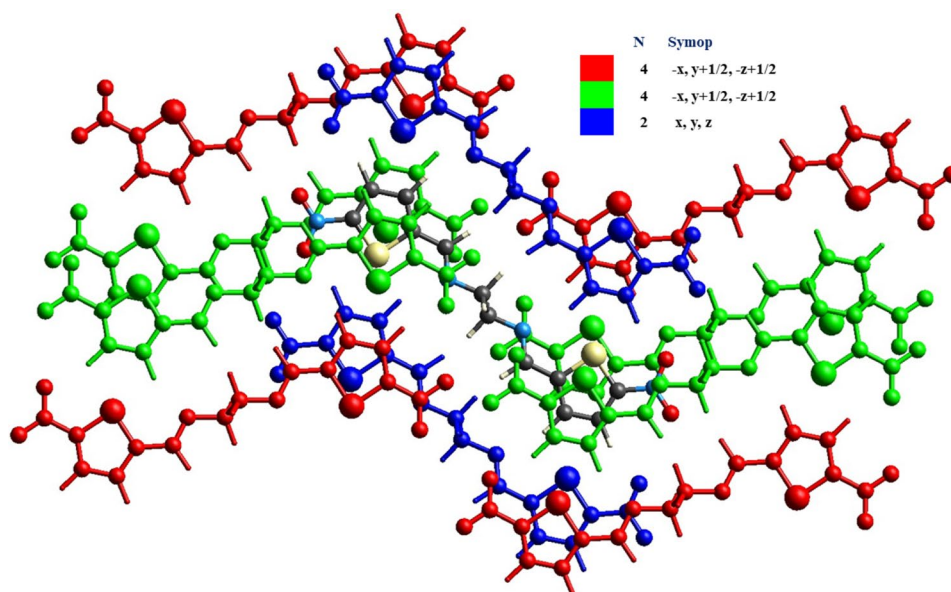


Fig. 16 Coulomb energy framework diagram at B3LYP/6-31G(d,p) theory

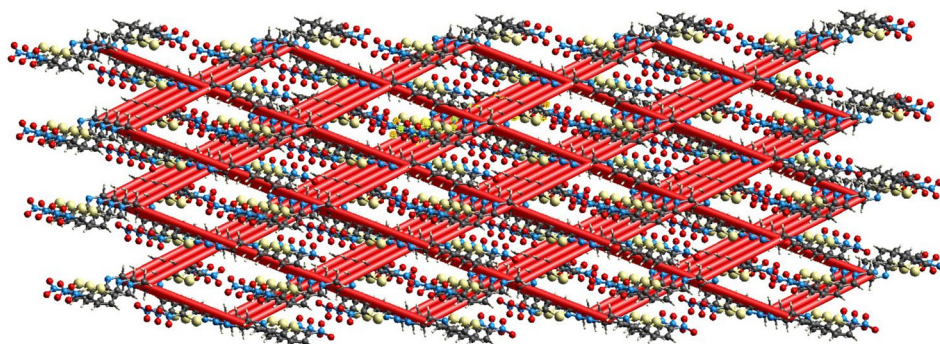
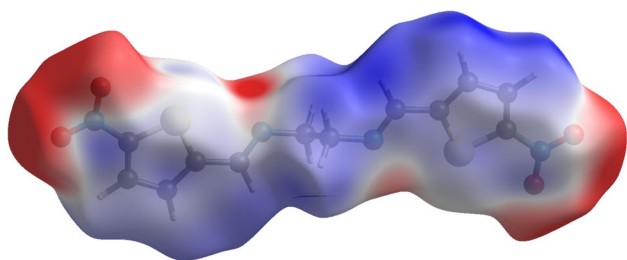
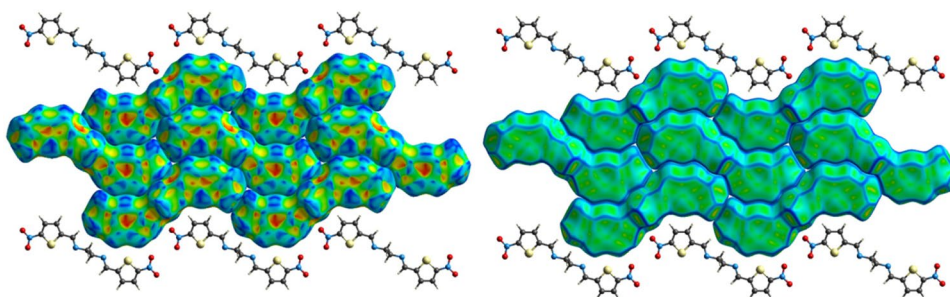


Table 4 Interaction energies within a cluster of 5.8 Å^o radius

N	R (Å)	E _{ele}	E _{pol}	E _{dis}	E _{rep}	E _{tot}
(kJ mol ⁻¹)						
4	10.84	− 23.6	− 4.0	− 19.9	21.6	− 32.0
4	9.72	− 13.3	− 2.3	− 39.7	26.0	− 34.3
2	5.65	6.7	− 3.2	− 30.6	17.6	− 11.1

Fig. 17 EDNM mapped with shape index (left) and curvedness (right)**Fig. 18** Molecular ESP mapped on the HS of EDNM

the electrostatic (E_{ele}), polarization (E_{pol}), dispersion (E_{disp}) and exchange repulsion (E_{rep}) energies in conjunction with appropriate scaling factors of 1.057, 0.740, 0.871 and 0.618, respectively. As different thicknesses of cylinders are shown, the appropriate strengths in interaction energies are displayed (Fig. 16). An overview of the Coulomb energy profile is presented, and for clarity's sake, weaker contacts below the threshold value of 5 kcal/mol were not included. Creating coulomb energy frameworks is similar to fabricating total energy (Table 4). N gives the number of molecules with molecular centroid-to-centroid length 'R'. Energy values are presented in kJ mol⁻¹ and R in Å^o unit. Shape index and curvedness reveal the packing strategy involving the complementarity and probabilities of interacting molecules in vicinity (Fig. 17).

Molecular electrostatic potentials are charted over HS in the range − 0.0402 au (electronegative, red) to 0.0546 au (electropositive, blue) using B3LYP/6-311G(d,p) employing *Tonto* (Fig. 18). The graphic shows that

negative potentials stay over imine nitrogen atoms and nitro groups in thiophene rings. Positive potentials with bright blue region span over hydrogen atoms of thiophene rings and -CH- of imine bonds [38].

Conclusion

The title compound (1E,1'E)-N,N'-(ethane-1,2-diyl)bis(1-(5-nitrothiophen-2-yl)methanimine) has been synthesized in good yield, and crystal structure was confirmed by SCXRD. The computational and experimental parameters for bond length, bond angle, FT-IR, ¹H, ¹³C NMR and UV–Vis are in good agreement. The MEP study reveals the most electronegative area at C=N bond. The FMO study shows that the energy gap of EDNM is 3.9297 eV, revealing the reactive property to be soft in nature. The NBO studies show highest delocalization energy E(2) 165.70 kcal/mol is associated with delocalization of donor NBO 87. LP (3) O22 to acceptor NBO 471. BD*(2) N20—O21. The structure of EDNM fully explored in terms of three-dimensional packing, intermolecular interactions and potential functional properties with respect to Hirshfeld surface. The centrosymmetric molecules in transoid conformation arranges into wave-like layers and further packs into 3D lattice. From inside a HS surface, the two N=C–H...O interactions helps in bringing closer two molecules to the reference HS surface. Also –N=O...H interactions extended by the pair of nitro groups hold another pair of molecules to a reference molecule. The

O–H interactions are affected through the close contact by nitro group and $-N=C-H$ interaction and constitute reciprocal contact of 34.4% of HS surface. Nitrogen atoms of both nitro groups exhibit higher Fukui functions for electrophilic activity. The optimized geometry clearly suggests that the simultaneous use of possible ligand sites for macrocyclic effect is considerably reduced.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s13738-023-02900-z>.

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