

Contents lists available at SciVerse ScienceDirect

### Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

# Molecular structure, heteronuclear resonance assisted hydrogen bond analysis, chemical reactivity and first hyperpolarizability of a novel ethyl-4-{[(2,4-dinitrophenyl)-hydrazono]-ethyl}-3,5-dimethyl-1*H*-pyrrole-2-carboxylate: A combined DFT and AIM approach

#### R.N. Singh\*, Amit Kumar, R.K. Tiwari, Poonam Rawat, Vikas Baboo, Divya Verma

Department of Chemistry, University of Lucknow, University Road, Lucknow 226007, India

#### ARTICLE INFO

Article history: Received 2 December 2011 Received in revised form 4 February 2012 Accepted 22 February 2012

Keywords: DFT Hydrogen bonded dimer AIM Ellipticity Reactivity descriptor NLO

#### ABSTRACT

А new ethyl-4-{[(2,4-dinitrophenyl)-hydrazono]-ethyl}-3,5-dimethyl-1H-pyrrole-2-carboxylate (EDPHEDPC) has been synthesized and characterized by FT-IR, <sup>1</sup>H NMR, UV-vis, DART-Mass spectroscopy and elemental analysis. Quantum chemical calculations have been performed by DFT level of theory using B3LYP functional and 6-31G(d,p) as basis set. The <sup>1</sup>H NMR chemical shifts are calculated using gauge including atomic orbitals (GIAO) approach in DMSO as solvent. The time dependent density functional theory (TD-DFT) is used to find the various electronic transitions and their nature within molecule. A combined theoretical and experimental wavenumber analysis confirms the existence of dimer. Topological parameters such as electron density ( $\rho_{BCP}$ ), Laplacian of electron density ( $\nabla^2 \rho_{BCP}$ ), kinetic electron energy density ( $G_{BCP}$ ), potential electron density ( $V_{BCP}$ ) and the total electron energy density  $(H_{BCP})$  at bond critical points (BCP) have been analyzed by Bader's 'Atoms in molecules' AIM theory in detail. The intermolecular hydrogen bond energy of dimer is calculated as -12.51 kcal/mol using AIM calculations. AIM ellipticity analysis is carried out to confirm the presence of resonance assisted intra and intermolecular hydrogen bonds in dimer. The calculated thermodynamic parameters show that reaction is exothermic and non-spontaneous at room temperature. The local reactivity descriptors such as Fukui functions  $(f_k^+, f_k^-)$ , local softnesses  $(s_k^-, s_k^+)$  and electrophilicity indices  $(\omega_k^+, \omega_k^-)$  analyses are performed to determine the reactive sites within molecule. Nonlinear optical (NLO) behavior of title compound is investigated by the computed value of first hyperpolarizability  $(\beta_0).$ 

© 2012 Elsevier B.V. All rights reserved.

#### 1. Introduction

Hydrazones are an important class of compounds due to their various properties and applications. They are versatile starting materials for the synthesis of a variety of N, O or S containing heterocyclic compounds such as oxadiazolines, thiazolidinones, triazolines, and various types of other organic compounds [1–7]. Due to the presence of N-N=C functional frame, [2+2] cycloadditions and 1,3 dipolar cycloadditions with hydrazones have been turned into a valuable tool for the synthesis of azetidinones and pyrazoles respectively [8,9]. Hydrazones having an azomethine proton  $-C\underline{H}=N-NH-$  constitute an important class of compounds for new drug development [10–14]. They are mainly used as

E-mail address: rnsvk.chemistry@gmail.com (R.N. Singh).

antimicrobial, antitubercular [15-19] and antidiabetic agents [20]. They have also been used as potentially DNA damaging and mutagenic agents [21,22]. They have strong coordinating ability towards different metal ions [23,24]. In addition, aroyl hydrazones and their mode of chelation with transition metal ions present in the living system have been of significant interest [25,26]. The anion receptor 2,4-dinitrophenylhydrazone of pyrrole- $\alpha$ -carboxaldehyde has been used for the development of potential chemosensors [27]. The chemical stability of hydrazones and their high melting points have recently made them attractive as prospective new materials for opto-electronic applications [28]. The nitro phenyl hydrazones exhibit a series of good organic nonlinear optical (NLO) properties [29-31]. In particular, the interest to this compound is being due to the above applications and fact that the pyrrole fragment is a constituent of many biological systems. In order to obtain information for significant application about pyrrole containing 2,4-dinitrophenylhydrazones, the title compound is synthesized

<sup>\*</sup> Corresponding author. Mobile: +91 9451308205.

<sup>1386-1425/\$ -</sup> see front matter © 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2012.02.086



Fig. 1. The optimized geometries of the reactants and products involved in chemical reaction calculated at B3LYP/6-31G(d,p) level.

and characterized. In the present paper we report the dimer structure of EFDMPCT using quantum chemical calculations and experimental FT-IR spectrum. Further, other results – optimized geometry, detailed spectroscopic analysis and chemical reactivity of the title compound – are also being reported.

#### 2. Experimental

All the chemicals used were of analytical grade. The solvent methanol was dried and distilled before use according to the standard procedure [32]. Ethyl-4-acetyl-3,5-dimetyl-1*H*-pyrrole-2-carboxylate was prepared by an earlier reported method [33]. 2,4-Dinitrophenylhydrazine was purchased from S.D. Fine. The <sup>1</sup>H NMR spectrum of EDPHEDPC was recorded in DMSO-d<sub>6</sub> on Bruker DRX-300 spectrometer using TMS as an internal reference. The UV-vis absorption spectrum of EDPHEDPC ( $1 \times 10^{-5}$  M in DMSO) was recorded on ELICO SL-164 spectrophotometer. The FT-IR-spectrum was recorded in KBr medium on a Bruker-spectrometer. The DART-Mass spectrum was recorded on JEOL-Acc TDF JMS-T100LC, Accu TOF mass spectrometer.

#### 2.1. Synthesis of ethyl-4-{[(2,4-dinitrophenyl)-hydrazono]ethyl}-3,5-dimethyl-1H-pyrrole-2-carboxylate (EDPHEDPC)

A ice cold mixture of ethyl-4-acetyl-3,5-dimetyl-1*H*-pyrrole-2carboxylate (0.100 g, 0.5122 mmol), 2,4-dinitrophenyl hydrazine (0.1014 g, 0.5122 mmol) and two drop of HCl as catalyst in 30 ml methanol was stirred for 12 h. After 12 h, the reaction mixture was stirred again for 60 h at room temperature. A red color precipitate was obtained. The precipitate was filtered off, washed with methanol and dried in air. The yield is 60.74% and the compound decomposes above 218 °C without melting.

#### 3. Computational details

All the calculations of the synthesized compound were carried out with Gaussian 03 program package [34] to predict the molecular structure, <sup>1</sup>H NMR chemical shifts, vibrational wavenumbers and energies of the optimized structures using density functional theory (DFT), B3LYP functional and 6-31G(d,p) basis set. B3LYP invokes Becke's three parameter (local, non local, Hartree-Fock) hybrid exchange functional (B3) [35] with Lee-Yang-Parr correlation functional (LYP) [36]. The basis set 6-31G(d,p) with 'd' polarization functions on heavy atoms and 'p' polarization functions on hydrogen atoms are used for better description of polar bonds of nitro group [37,38]. It should be emphasized that 'p' polarization functions on hydrogen atoms are used for reproducing the out of plane vibrations involving hydrogen atoms. Convergence criterion in which both the maximum force and displacement smaller than the cut-off values of 0.000450 and 0.001800 and r.m.s. force and displacement less than the cut-off values of 0.000300

and 0.001200 were used in the calculations. The time dependent density functional theory (TD-DFT) was carried out to find the electronic transitions. The optimized geometrical parameters were used in the vibrational frequency calculation to characterize all stationary points as minima and all the harmonic vibrational wavenumbers were found to be positive. All molecular structures were visualized using software Chemcraft [39] and Gauss-View [40]. Potential energy distribution along internal coordinates was calculated by Gar2ped software [41]. Internal coordinate system recommended by Pulay et al. was used for the assignment of vibrational modes [42].

#### 4. Results and discussion

#### 4.1. Thermodynamic properties

The optimized geometries of all the reactants and products involved in chemical reaction is shown graphically in Fig. 1, calculated at B3LYP/6-31G(d,p) level. For sake of simplicity reactants ethyl-4-acetyl-3,5-dimetyl-1H-pyrrole-2-carboxylate, 2,4dinitrophenylhydrazine and product EDPHEDPC and water are abbreviated as A. B. C and D respectively. The vibrational frequency calculations for all reactants and products were performed to determine the thermodynamic quantities at room temperature and their values are listed in (Supplementary Table) TS1. For overall reaction the enthalpy change of reaction ( $\Delta H_{\text{Reaction}}$ ), Gibbs free energy change of reaction  $(\Delta \textit{G}_{\text{Reaction}})$  and entropy change of reaction  $(\Delta S_{\text{Reaction}})$  are found to be -1.2525 kcal/mol, 3.0291 kcal/mol and -6.839 cal/mol-K respectively. The reaction has negative values for  $\Delta H_{\text{Reaction}}$  and  $\Delta S_{\text{Reaction}}$  but positive value for  $\Delta G_{\text{Reaction}}$  indicating that the reaction is exothermic and non-spontaneous at room temperature.

Total energy of the dimer is calculated as -2768.42575645 a.u. at B3LYP/6-31G(d,p) level. The binding energy of dimer is computed as the difference between the calculated total energy of the dimer and the energies of the two isolated monomers and found to be -14.52 kcal/mol. The calculated hydrogen binding energy of dimer formation has been corrected for the basis set superposition error (BSSE) via the standard counterpoise method [43] and found to be -10.35 kcal/mol.

The calculated changes in thermodynamic quantities during the dimer formation in gaseous phase have the values  $\Delta H$ (-12.95 kcal/mol),  $\Delta G$  (-1.63 kcal/mol) and  $\Delta S$  (-37.98 cal/mol-K) indicating that the dimer formation is exothermic and spontaneous. The calculated equilibrium constant using the formula  $\Delta G = -RT \ln K$  between monomer and dimer is quite high (K = 15.71) indicating that dimer formation is highly preferred and as a result even anti conformer gets converted to syn and finally forms the dimer. The thermodynamics quantities (enthalpy, Gibbs free energy, entropy), their change and equilibrium constant of conversion from monomer to dimer are given in (*Supplementary Table*) TS2.



Fig. 2. The optimized geometries of ground state syn and anti conformers using B3LYP/6-31G(d,p).

#### 4.2. Molecular geometry

The calculated ground state syn and anti conformers of the product ethyl-4-{[(2,4-dinitrophenyl)-hydrazono]-ethyl}-3,5dimethyl-1H-pyrrole-2-carboxylate are shown in Fig. 2. They have energy -1384.20131188 and -1384.20075305 a.u. respectively at room temperature with energy difference 0.35067 kcal/mol and supposed to exist in ratio 65.4:34.6 respectively in the gas phase as per Boltzmann distribution. But the syn conformer has geometrical suitability for intermolecular hydrogen bonding by having pyrrolic NH and ester CO on same side and their role lie in molecular association resulting into dimer. The geometrical parameter of the syn conformer is given in Table 1 and the bond length and bond angle of intermolecular hydrogen bonds formed in the dimer product are given in Table 2. The geometrical parameter of the anti conformer are given in (Supplementary Table) TS3 for the information. The optimized geometry of dimer is shown in Fig. 3, with atomic numbering.

The asymmetry of the N1–C2 and N1–C5 bonds can be explained by electron withdrawing character of the ethoxycarbonyl group and conjugation of the N1–C5 with C4–C3–C2 skeleton. It leads to the elongation of N1–C2 bond. These effects are not only in quantum calculation but also reflect in crystal structure of the ethyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate [44], Table 1

The selected optimized geometrical parameters of monomer (syn conformer) using B3LYP/6-31G(d,p).

Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
R(1.2)	1.3821	A(2.1.28)	121.5071	D(1.2.9.13)	-179.423
R(1.5)	1.3523	A(1.2.9)	116.0081	D(2,3,8,33)	-96.5741
R(1.28)	1.0107	A(2,3,8)	125.9323	D(3.4.7.10)	146.4457
R(2,3)	1.3915	A(3.4.7)	127.67	D(1.5.6.31)	148.6313
R(2,9)	1.4596	A(1,5,6)	121.3019	D(4,7,10,11)	176.782
R(3,4)	1.4359	A(4,7,10)	116.9025	D(4,7,44,46)	118.8856
R(3,8)	1.5027	A(4,7,44)	120.2683	D(2,9,13,14)	-179.871
R(4,5)	1.4071	A(10,7,44)	122.7695	D(7,10,11,19)	178.6891
R(4,7)	1.4656	A(3,8,32)	110.4775	D(10,11,19,20)	179.7639
R(7,10)	1.3001	A(2,9,12)	122.4425	D(9,13,14,15)	-179.9919
R(9,12)	1.2233	A(2,9,13)	113.9611	D(13,14,15,38)	179.7226
R(9,13)	1.3506	A(12,9,13)	123.5955	D(21,16,17,41)	-179.7182
R(10,11)	1.3677	A(7,10,11)	116.7331	D(17,16,21,43)	179.9061
R(11,19)	1.3568	A(10,11,19)	120.7725	D(17,16,25,26)	-179.7765
R(11,35)	1.0182	A(10,11,35)	123.5018	D(16,17,18,42)	-179.6326
R(13,14)	1.448	A(19,11,35)	115.7108	D(17,18,19,11)	179.6913
R(14,15)	1.516	A(9,13,14)	115.5283	D(11,19,20,21)	-179.6561
R(16,17)	1.4063	A(13,14,15)	107.5019	D(19,20,21,43)	179.8898
R(16,21)	1.3807	A(20,22,23)	118.6365	D(19,20,22,24)	-179.1823
R(17,18)	1.3746	A(20,22,24)	118.8022		
R(18,19)	1.4227	A(23,22,24)	122.5613		
R(19,20)	1.432	A(16,25,26)	117.9542		
R(20,21)	1.3961	A(16,25,27)	117.3846		
R(22,23)	1.2495	A(26,25,27)	124.6612		
R(22,24)	1.2282	A(7,44,45)	111.6514		
R(25,26)	1.2320				
R(25,27)	1.2336				

#### Table 2

The intermolecular hydrogen bonded geometrical parameters in dimer [bond length (Å) and bond angle  $(\circ)$ ].

X—H···O	Х—Н	H···O	X···O	X—H…0
N1-H28086	1.02080	1.89853	2.87794	159.73307
N76-H82012	1.02081	1.89801	2.87758	159.77263
C77-H83012	1.09253	2.60645	3.46857	135.23734
C6-086H29	1.09252	2.60378	3.46938	135.57715

methyl 4-p-tolyl-1*H*-pyrrole-2-carboxylate [45]. The N=O bonds in ortho-nitro group are more unsymmetrical due to the formation of intramolecular hydrogen bond (N11–H35…O23…N22). This is not only observed in our geometry but also reported in crystal structure of hydrazones [46].



**Fig. 3.** The optimized geometry of dimer for lower energy ground state *syn*-conformer using B3LYP/6-31G(d,p).

#### Table 3

Experimental and theoretical <sup>1</sup>H NMR chemical shifts using B3LYP/6-31G(d,p) in DMSO-d<sub>6</sub> as the solvent ( $25 \,^{\circ}$ C).

Atom no.	$\delta_{ m exp}$	$\delta_{ m calcd}$
H28	10.2	7.85377
H29		1.35077
H30	2.42	1.88487
H31		1.96757
H32		2.49717
H33	2.48	1.61427
H34		1.33487
H35	11.73	11.2851
H36	4.23	3.70727
H37		3.72217
H38		0.54707
H39	1.29	0.90417
H40		0.87727
H41	8.3	7.76177
H42	7.8	7.38567
H43	8.56	8.78657
H45		1.84307
H46	3.77	1.56107
H47		1.52147

In dimer, two hydrogen bonds are formed by heteronuclear intermolecular hydrogen bonding  $(N-H \cdots O=C)$  between pyrrolic (N-H) and carbonyl (C=O) of ester. In intermolecular hydrogen bonds, the N-H bond acts as proton donor and C=O bond as proton acceptor. According to the Etter terminology [47], the cyclic ester dimer form the ten-membered pseudo ring denoted as  $R_2^2(10)$  or more extended sixteen-membered pseudo ring  $R_2^2(16)$  including pyrrole ring. The superscript designates the number of acceptor centers whereas the subscript designates the number of donors in the motif. In dimer both proton donor (N-H bond) and proton acceptor (C=O bond) are elongated by 0.0101 Å and 0.0091 Å respectively.

#### 4.3. <sup>1</sup>H NMR spectroscopy

The geometry of the title compound, together with that of tetramethylsilane (TMS) is fully optimized. <sup>1</sup>H NMR chemical shifts are calculated with GIAO approach using B3LYP method and 6-31G(d,p) basis set [48]. Chemical shift of any X proton (CS<sub>X</sub>) is equal to the difference between isotropic magnetic shielding IMS of (TMS) and proton (X). It is defined by an equation written as  $[CS_X = IMS_{TMS} - IMS_X]$ . The experimental and calculated values of <sup>1</sup>H NMR chemical shifts of the title compound are given in Table 3. The value of correlation coefficient ( $R^2 = 0.9545$ ) between experimental and calculated chemical shifts show that there is a good agreement between them. The chemical shift of proton H35 appeared at 11.73 ppm due to deshielding which is consequence of the intramolecular hydrogen bond N11–H35…O23…N22.

#### 4.4. UV-vis spectroscopy

The nature of the transitions observed in the UV–vis spectrum of EFDMPCT has been studied by the time dependent density functional theory (TD-DFT). The observed and calculated electronic transitions of high oscillatory strength are listed in Table 4. Experimental UV–vis spectrum of the title compound is shown in Fig. 4.



Fig. 4. Experimental UV-vis spectrum of EDPHEDPC.

Frontier molecular orbitals (FMOs), HOMO and LUMO plot are given in *Supplementary Fig. 1*. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very popular quantum chemical parameters. The FMOs are important in determining molecular reactivity and the ability of a molecule to absorb light. The vicinal orbitals of HOMO and LUMO play the same role of electron donor and electron acceptor respectively. The energies of HOMO and LUMO and their neighboring orbitals are all negative, which indicate the title molecule is stable [49]. The HOMO–LUMO energy gap is an important stability index. The HOMO–LUMO energy gap of title molecule reflects the chemical stability of the molecule.

HOMO energy  $= -5.8864 \, \text{eV}$ 

LUMO energy  $= -2.764 \, \text{eV}$ 

#### HOMO-LUMO energy gap = 3.1228 eV

TD-DFT calculations using B3LYP/6-31G(d,p), predict three intense electronic transitions at  $\lambda_{max} = 298.79$  nm, f = 0.2718;  $\lambda_{max} = 267.21$  nm, f = 0.1775 and  $\lambda_{max} = 243.48$  nm, f = 0.4128 are in agreement with the experimental electronic transitions at  $\lambda_{max} = 288$ , 242 and 227 nm respectively. The calculated values for wavelength of maximum absorption ( $\lambda_{max}$ ) are also in agreement with the reported  $\lambda_{max}$  in literature [50]. According to the TD-DFT calculations, the experimental band at 288, 242 and 227 nm originates mainly due to the H–2  $\rightarrow$  L+1, H–5  $\rightarrow$  L and H–1  $\rightarrow$  L+3 transitions respectively. On the basis of calculated molecular orbital coefficient analysis, these electronic excitations show  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions.

#### 4.5. Vibrational assignments

The experimental and calculated vibrational wavenumbers of dimer at B3LYP/6-31G(d,p) level and their assignments using PED are given in Table 5 . The calculated (monomer, dimer) and the experimental FT-IR spectra of EDPHEDPC in the region  $4000-400 \text{ cm}^{-1}$  are shown graphically in *Supplementary Fig. 2*. The total number of atoms in monomer and dimer are 49 and 98

Table 4

Comparison between experimental and calculated electronic transitions: energy, oscillatory strength,  $\lambda_{max}$  (nm) using TD-DFT/B3LYP/6-31G(d,p) in DMSO at 25 °C.

S. no.	Orbital transitions	Energy (eV)	Oscillatory strength, f	Calculated $\lambda_{max}$	Observed $\lambda_{max}$	% contribution	Assignment
1	$H{-}1 \rightarrow L{+}1$	3.3993	0.1878	364.74		48.94	
2	$H-2 \rightarrow L+1$	4.1496	0.2718	298.79	288	31.65	$\pi\!\rightarrow\!\pi^*$
3	$H{-}5 \rightarrow L$	4.6399	0.1775	267.21	242	35.57	$n \! \rightarrow \! \pi^{*}$
4	$H{-}1 \rightarrow L{+}3$	5.0921	0.4128	243.48	227	40.52	$\pi\!\rightarrow\!\pi^*$

R.N. Singh et al.	/ Spectrochimica	Acta Part A 92	(2012)	) 295–304
-------------------	------------------	----------------	--------	-----------

#### Table 5

Experimental and calculated (selected) vibrational wavenumbers (cm<sup>-1</sup>) of dimer using B3LYP/6-31G(d,p) with assignments [IR<sub>int</sub> (Kmmol<sup>-1</sup>)].

Mode no.	Wavenumb	ers	IR <sub>int</sub>	Experimental wavenumbers	Assignment (PED)≥5%
	Unscaled	Scaled			
276	3480	3343	67.49	3426	v(N61—H65)(99)
275	3480	3343	66.71		ν(N11—H35)(99)
274	3467	3331	2872.82	3269	$\nu(N1-H28)(50)-\nu(N76-H82)(48)$
273	3461	3325	11.88		$\nu(N76-H82)(51)-\nu(N1-H28)(49)$
271	3269	3140	42.26		v(C53—H57)(83)-v(C21—H43)(16)
260	3141	3017	55.66	2983	ν(C89–H93)(28)–ν(C89–H94)(23), ν(C15–H39)(19)–ν(C15–H40)(16)
264	3160	3036	11.06		v(C8—H32)(79)-v(C8—H34)(19)
258	3133	3010	45.15		$\nu$ (C89–H92)(38)– $\nu$ (C15–H38)(24)– $\nu$ (C89–H94)(12)– $\nu$ (C89–H93)(8),
250	2445	2002	45.05		$\nu(C15-H40)(8), \nu(C15-H39)(5)$
256	3115	2992	17.05		V(C/-U44)(20) - V(C0-H31)(18), V(C77-U84)(17) = V(C77-U85)(15) = V(C77-U82)(12) = V(C6-U30)(12)
254	2111	2020	10.14	2021	V(C7 - H84)(17) - V(C7 - H85)(15) - V(C7 - H83)(13) - V(C6 - H29)(12)
234	2111	2989	19.14	2921	$V(C^{3}-Rol)(01) - V(C^{3}-Rol)(19), V(C^{3}-Rol)(12), V(C^{3}-Rol)(12)$
255	3106	2989	12.14		$\nu(C8 - H01)(40) - \nu(C8 - H00)(33) + \nu(C14 - H37)(6)$
232	5100	2304	12,22		$\nu(C80 - H94)(6) - \nu(C89 - H93)(5) - \nu(C14 - H36)(5)$
248	3063	2942	55 62		$\nu(C13 - H36)(29) \nu(C13 - H37)(24) - \nu(C88 - H90)(24) - \nu(C88 - H91)(20)$
245	3058	2938	31		$\nu(C15-H38)(19)$ $\nu(C15-H40)(18)$
210	5050	2000	31		$\nu(C15 - H39)(17) - \nu(C89 - H92)(16) - \nu(C89 - H94)(15) - \nu(C89 - H93)(4)$
244	3053	2933	10.25		$\nu$ (C7–C44)(57), $\nu$ (C6–H29)(21), $\nu$ (C6–H31)(18)
243	3053	2933	15.96	2853	v(C77—H84)(48), v(C77—H83)(23), v(C77—H85)(15)
241	3040	2920	43.23		ν(C8-H33)(43)-ν(C75-H80)(37), ν(C8-H34)(7)-ν(C75-H81)(6)
238	1724	1656	1932.14	1664	ν(C9-012)(26)-ν(C78-086)(25), δ(C9C14013)(13)-δ(012C9013)(11)
236	1671	1605	363.74		ν(C17-C18)(10), ν(C52-C54)(10), ν(C20-C21)(6),
					$\nu(C53-C56)(6) - \nu(C16-C21)(6) - \nu(C50-C53)(6)$
235	1670	1604	804.68	1619	ν(C52C54)(9)-ν(C17C18)(9),
					ν(C53-C56)(6)-ν(C20-C21)(6)-ν(C50-C53)(6), ν(C16-C21)(6)
233	1653	1588	1148.71	1565	ν(N25—O27)(11)-ν(N49—O51)(10)-ν(N25—O26)(10), ν(O48—N49)(10)
231	1643	1578	18.46		$\nu(N64-C66)(26)-\nu(C7-N10)(26)$
230	1624	1560	16.48		ν(N60—O63)(13), ν(N22—O24)(12), (δ-N64H65N61)(10),
					$(\delta - N10H35N11)(10) - \nu(N60 - O62)(7) - \nu(N22 - O23)(7)$
229	1624	1560	18.41		$\nu(N22-O24)(13) - \nu(N60-O63)(12),$
220	1007	1544	26.10		$(0-N10H35N11)(10)-(0-N64H65N61)(10)-\nu(N22-023)(7), \nu(N60-062)(7)$
228	1607	1544	36.19	1511	R(0-C2H28N1)(29), (T-U86H28)(15)-R(0-C70H82N76)(7)
227	1507	1557	16 59	1511	$R(0-C2\pi 26N1)(24), (1-060\pi 26)(15), R(0-C70\pi 62N70)(0)$
220	1597	1554	10.56		$\nu(1149-051)(7), \nu(1125-027)(7) - \nu(C50-C55)(7) - \nu(C10-C21)(7),$ $\nu(N60-062)(6), \nu(048-N40)(6)$
					$\nu(100 - 003)(0) - \nu(046 - 1043)(0),$ $\nu(N22 - 024)(6) - \nu(N25 - 026)(6) - \nu(N60 - 062)(5) - \nu(N22 - 023)(5)$
225	1596	1533	31 92		$\nu(N25 - 027)(6) - \nu(N49 - 051)(6) - \nu(C16 - C21)(6) - \nu(C50 - C53)(6)$
225	1550	1555	51.52		$\nu(N22-024)(5) - \nu(N60-063)(5) - \nu(N25-026)(5), \nu(048-N49)(5)$
224	1565	1503	55.8		$\nu(N11-C19)(9), \nu(C58-N61)(9), \nu(C16-C17)(8), \nu(C50-C52)(8)$
223	1564	1502	761.66	1449	$\nu(C58-N61)(10)-\nu(N11-C19)(10), \nu(C50-C52)(9)-\nu(C16-C17)(9)$
222	1557	1495	256.39		$(\delta_{as}-Me2')(21), (\tau-H82012)(15), (\tau-H84C14)(7)-(\rho-Me2')(7)-(\tau-C70C77)(6)$
220	1535	1474	16.28		$(\delta_{as}-Me2')(39), (\tau-H82012)(16)-(\tau-C70C77)(8)-(\rho-Me2')(5),$
					(δ <sub>sc</sub> -C88H90H91)(5)
219	1535	1474	20.1		(τ-H84C14)(34), (δ <sub>sc</sub> -H36H37C14)(14), (δ <sub>as</sub> -Me1)(7), (τ-C15C14)(6),
					(ω-H36H37C14)(5)
218	1529	1469	11.56		(δ <sub>as</sub> -Me2')(25), (τ-H82012)(9)-(τ-H84C14)(6)-(δ <sub>sc</sub> -H36H37C14)(6)-(δ <sub>as</sub> -
					Me')(6)–(τ-C70C77)(5)–(τ-C15C14)(5)
217	1529	1469	54.61		$(\delta_{as}-Me2')(19), (\tau-H84C14)(16), (\tau H82012)(8), (\tau-O86H28)(6),$
24.6	4540	1 450	10.00		$(\delta_{sc} - H36H37C14)(6), (\tau - C15C14)(5)$
216	1519	1459	48.39		$(\delta_{as}-Me2')(28), (\tau-H82012)(13)-(\tau-C/0C/7)(10),$
215	1510	1459	55 22		$(O_{as} - IVIES)(7) - (O_{as} - IVIES)(5) - (O_{as} - IVIEI)(5)$ (8 Mo2/)(26) (7 H92012)(14) (7 C70C77)(12) (8 Mo2/)(6)
215	1510	1438	11 /1		$(\delta_{as}^{-1})(25), (1-1102012), (14)-(1-070077), (12)-(0_{as}^{-1})(25), (0)$ $(\delta_{as}^{-1})(25)-(\sigma_{as}^{-1})(25), (15)-(15), (14)-(14)-(14), (15), (12)-(15), (12)-(15), (12), ($
212	1505	1445	11.41		$(\delta_{as} - Me1)(6)_{-(\pi-C5C6)(5)}$
211	1509	1449	25.88		$(\delta_{xc}-Me^{2})(34)(\tau-H82012)(13)-(\tau-C70C77)(13)(\tau-O86H28)(7)-(\delta_{xc}-Me^{2})(6)$
211	1000	1110	20100		$(\tau - C89C88)(5)$
210	1504	1445	10.24		$(\delta_{as}-Me2)(12), (\delta_{as}-Me1')(11)-(\delta_{as}-Me3)(8), (\tau-086H28)(7)-(\delta_{as}-Me3')(6)$
209	1504	1445	25.96		$(\delta_{as}-Me1')(13)-(\delta_{as}-Me2)(11)-(\delta_{as}-Me3')(8), (\delta_{as}-Me3)(7)$
207	1500	1441	11.59		$(\delta_{as}-Me')(54), (\tau-H30C89)(16)-(\tau-O86H28)(13)-(\tau-C15C14)(5)$
206	1495	1436	74.58		(δ <sub>as</sub> -Me2')(45)–(δ <sub>as</sub> -Me1)(7), (τ-H82012)(6)
205	1494	1435	19.21		$(\tau$ -C70C77)(17)- $(\tau$ -O86H28)(9), $(\delta_{as}$ -Me2')(8)- $(\delta_{as}$ -Me2')(6)- $(\delta_{s}$ -Me2')(6),
					(ρ-Me2')(5)–(τ-H84C14)(5)–(ρ-Me2')(5)
203	1493	1434	96.81		$(\delta_{as}-Me2')(64)$ , ( $\tau$ -H82012)(17)-( $\tau$ -C70C77)(10)
201	1485	1426	14.6		$(\delta_{as}-Me2')(54), (\tau-H82012)(17)-(\tau-C70C77)(12)$
199	1477	1419	454.57	1382	$(\tau - C/0C77)(12) - (\tau - 0.86H28)(9)$
198	1472	1414	22.29		(τ-H84C14)(22)-(τ-C70C77)(16), (τ-H30C89)(9), (τ-O86H28)(7)-(τ-C5C6)(5)
197	1472	1414	214.34		$(\tau - U8bH28)(21) - (\tau - C/UC77)(14) - (\tau - H30C89)(8) - (\tau - H82012)(7),$
105	1407	1400	70 70		$(\tau - H\delta 4U(4)(5) - (\omega - H\beta 6H\beta / U(4)(5))$
195	1467	1409	/0.76		$(o_{as}-ivie2')(19)-(\tau-U/UU//)(10)-v(C53-C56)(9), v(C52-C54)(8),$
193	1437	1380	17 42		ν(ζου ζοιμι)-ν(ζιι σιομο), (1-ποσυισμο) (π-Η84(14)(26) (ω-Η36Η37(14)(12)-(π-Η820(12)(12)-(δ -Με2)(12)-(δ -
		1000	. / . 12		$Me_{1}(8) = (\tau - H30C89)(8).$
					$(\delta_s - Me1)(5)$

Table 5 (Continued)

Mode no.	Wavenum	/avenumbers IR <sub>int</sub>		WavenumbersIRExperimental wavenumbersAssignment (PED) $\geq$ 5%		Assignment (PED) $\geq$ 5%
	Unscaled	Scaled				
190	1427	1371	66.51		$(\tau-H82012)(26), (\delta_s-Me2')(24)-(\tau-O86H28)(18)-(\delta_s-Me1)(12)-(\tau-H84C14)(7)$	
188	1417	1361	12.89		$(\delta_{s}-Me3)(76), \nu(C7-C44)(5)$	
187	1417	1361	19.71		$(\delta_{s}-Me3')(78), \nu(C66-C68)(5)$	
186	1403	1348	33.99		$(\delta_{as}-Me2')(17)-(\tau-C70C77)(16)-(\omega-H36H37C14)(6),$	
182	1389	1334	142 55		(1-C3C0)(3)-(1-B30C09)(3) $(\omega-H36H37C14)(16)(\pi-C70C77)(10)-(8 -Me2')(10)(\pi-H84C14)(5)$	
181	1388	1333	436.63		$(\omega - H36H37C14)(16), (\tau - H84C14)(15) - (\tau - C70C77)(11), (\delta_{22} - Me2')(9)$	
180	1382	1327	475.45		(ω-H36H37C14)(10), (τ-C70C77)(9)–( $\delta_{as}$ -Me2')(7)	
179	1382	1327	1037.86	1285	(ω-H36H37C14)(9), (τ-H84C14)(8)–(τ-C70C77)(8),	
					(δ <sub>as</sub> -Me2')(6)-ν(N49-051)(5), ν(N25-027)(5)	
178	1357	1303	174.03		$\nu(C56-C58)(10),$	
					$\nu(C50-C53)(7)-\nu(N60-O63)(6)-\nu(N60-O62)(6)-\nu(C54-C58)(6),$	
177	1257	1202	201 7		v(C19 - C20)(6)	
177	1557	1505	251.7		$\nu(C16-C21)(7)-\nu(N22-024)(6)-\nu(N22-023)(6)-\nu(C18-C19)(6)-\nu(C56-C58)(6)$	
176	1326	1274	14.34		$(\omega-H36H37C14)(17).$	
					$(\tau - H84C14)(15) - R(\delta - C2H28N1)(9) - (\tau - O86H28)(9) - (\tau - C70C77)(8)$	
175	1324	1272	933.29	1230	(ω-H36H37C14)(18)-R(δ-C2H28N1)(11), (τ-H84C14)(9),	
					(τ-C70C77)(8)–(τ-O86H28)(8), δ(O12C9O13)(5)	
174	1311	1259	84.59		$\nu$ (N22-O23)(6), $\nu$ (N60-O62)(5), ( $\tau$ -O86H28)(5),	
					$R(\delta-C2H28N1)(4)-\nu(C20-N22)(3)$	
173	1310	1258	346.19		$(\tau - H84C14)(6) - (\tau - H82012)(6) - R(\delta - C2H28N1)(5),$	
160	1700	1027	121 71		V(1000-002)(5) - V(1022-023)(5)	
168	1233	1199	18 21		$R_1(\delta_{-C19H42C18}(8) - R_1(\delta_{-C52H59C54}(8) R_1(\delta_{-C16H43C21}(6))$	
100	12 10	1155	10.21		R1(δ-C50H57C53)(6)	
167	1248	1199	75.67		R1(δ-C52H59C54)(9), R1(δ-C19H42C18)(9)-R1(δ-C50H57C53)(7),	
					R1(δ-C16H43C21)(7)	
166	1242	1193	14.36		δ(012C9013)(13), R(δ-C2H28N1)(9), (ω-H36H37C14)(9), ν(N1-C2)(7),	
					(τ-086H28)(7), (τ-H84C14)(7), ν(C74—N76)(7)-ν(C9—013)(5)	
165	1240	1191	582.47	1191	(τ-086H28)(15), R(δ-C2H28N1)(12), δ(012C9013)(11), (ω-H36H37C14)(7),	
160	1162	1117	12 20		$\nu(N1-C2)(7)-\nu(C/4-N76)(7)-\nu(C9-013)(5), \nu(C/8-087)(5)$	
102	1105	1117	15.29		$(0-K1)(3) - (0-K1)(7), \nu(C10-N23)(7), \nu(N49-C30)(0), \nu(C20-N22)(0),$ $\nu(C56-N60)(5), \nu(N10-N11)(5)$	
161	1163	1117	103 78		$(\delta - R^{1})(8)$ $(\delta - R^{1})(7) - \nu(N49 - C50)(7)$	
101	1105	1117	105.70		$\nu(C16-N25)(6)-\nu(C56-N60)(6)-\nu(N61-N64)(5), \nu(C20-N22)(5),$	
					$\nu(N10-N11)(5)$	
160	1157	1111	17.37		R1(δ-C18H41C17)(15)-R1(δ-C50H55C52)(13)-R1(δ-C19H42C18)(9),	
					$R1(\delta-C52H59C54)(7)-\nu(N10-N11)(6)-\nu(N61-N64)(5)$	
159	1156	1110	309.86		R1(δ-C50H55C52)(16),	
					$R1(\delta-C18H41C17)(13)-R1(\delta-C52H59C54)(9)-R1(\delta-C19H42C18)(7),$	
159	1146	1101	227 0	1101	V(1001-004)(5) ( $\pi O(26U28)(17)$ ( $\pi O(100)(\pi O(15O14)(0))$ ( $\delta U(26U27O14)(8)$	
138	1140	1101	557.0	1101	$\delta((-9C14O13)(7) - (p-Me)(5) (\tau - C13C14)(5), (0_{sc} - M3O137C14)(8), \delta((-9C14O13)(7) - (p-Me)(5) (\tau - C89C88)(5)$	
157	1146	1101	50.88		$(\tau - 0.86H28)(19)$ ( $\rho - Me')(11)$ ( $\tau - C15C14)(8)$ ( $\delta_{ee} - H36H37C14)(8)$	
					$\delta$ (C9C14O13)(7)-( $\tau$ -C89C88)(6), ( $\rho$ -Me)(5)	
156	1138	1093	267.92		(τ-086H28)(21)-(ρ-Me')(14), (τ-C15C14)(11), (τ-C89C88)(8), δ(C9C14O13)(7),	
					(ρ-Me)(7), (δ <sub>sc</sub> -H36H37C14)(6)	
155	1137	1092	65.13		(τ-086H28)(20), (ρ-Me')(15), (τ-C15C14)(11)–(τ-C89C88)(8), δ(C9C14O13)(7),	
					(ρ-Me)(7), (δ <sub>sc</sub> -H36H37C14)(6)	
154	1127	1082	27.35		$(\tau - 0.86H28)(8), \nu(N10-N11)(7), \nu(N61-N64)(7), (\rho-Me')(6), (\tau - C15C14)(5),$	
152	1000	1047	10.3		(T-H82UI2)(5) (#_H82012)(13) (p_Me3)(12)_(p_Me3)(8)_(p_Me2)(8) (#_C70C77)(5)	
150	1080	1047	32.14		$R_1(\delta_{-C16H43C21})(13)$ $\nu(C20-N22)(10)$ ( $\delta_{-R1})(9)$ $\nu(C16-C17)(6)$	
150	1000	1057	52.14		$\nu(C16-C21)(5)$	
149	1080	1037	39.4		$R1(\delta-C50H57C53)(12)-(\tau-H82012)(11), \nu(C56-N60)(9)-(\delta-R1')(8),$	
					$(\rho-Me2')(7), \nu(C50-C52)(6)$	
147	1064	1022	12.74		(ρ-Me2')(22), (τ-H82012)(20)-(τ-C70C77)(12), (τ-H84C14)(9), (τ-O86H28)(8)	
144	1057	1015	13.32		(τ-H82012)(39)–(ρ-Me2')(17), (ρ-Me2')(5)	
141	1048	1006	77.65	1023	$\nu$ (C88–C89)(10)– $\nu$ (C14–C15)(10),	
124	080	050	110	004	$\nu(013-C14)(10)-\nu(087-C88)(9)-(\tau-H84C14)(8), (\rho-Me2)(7), (\rho-Me2)(6)$	
134	989	950	1002	884	$\nu(C_{1} - C_{44})(16) - \nu(C_{5} - C_{6})(13), (\rho - NIe3)(11) - (\rho - NIe3)(8)$	
133	989 967	920	18.83		$\nu(\cos(-\cos)(10), \nu(-)(-(44)(12), (\rho-Me3)(10), (\rho-Me3)(8))$ $R1(\omega-C21H43)(77), (R1-puckering)(10)$	
132	907 944	929	9.44 10.07		$\pi_1(w - c_{211145})/(7), (\pi_1 - \mu(c_{11118})/(10))$ $\eta(c_{16} - N_{25})/(8) \eta(N_{49} - c_{50})/(7) - \eta(c_{26} - N_{60})/(6) (8 - \rho_{15})/(5)$	
150	5-1-1	500	10.07		$(\delta - R1)(5)$	
129	944	906	30.41		$\nu(N49-C50)(8)-\nu(C16-N25)(7)-\nu(C56-N60)(7), \nu(C20-N22)(6),$	
-					(δ-R1')(5)–(δ-R1')(5)	
127	905	869	18.28		(τ-086H28)(18)-(ρ-Me')(12), (ω-H36H37C14)(8), (τ-C15C14)(6), (ρ-Me)(6),	
					(τ-H84C14)(6), ν(O13-C14)(5), (τ-C89C88)(5), (τ-H82O12)(5)	
122	862	828	14.75		$R1(\omega-C54H59)(46), R1(\omega-C52H55)(22)-R1(\omega-C58N61)(8)-(\tau-R1')(6)$	
121	862	828	13.38		R1(ω-C18H42)(46), R1(ω-C17H41)(22), R1(ω-C19N11)(8), (τ-R1)(6)	

Table 5 (Continued)

Mode no.	Wavenumbers		IR <sub>int</sub>	Experimental wavenumbers	Assignment (PED) $\geq$ 5%
	Unscaled	Scaled			
119	841	808	50.85	829	(δ-027026N25)(19)-(δ-051048N49)(18), (δ-023024N22)(15)-(δ-062063N60)(14)-(δ-R1)(6)-(δ-R1')(6)
118	829	796	114.24	776	(ω-N1H28)(51)-(τ-O86H28)(47)
110	758	728	15.44		(τ-O86H28)(16)-(ω-N1H28)(14)
106	746	716	24.1	662	R1(ω-C50N49)(16), R1(ω-C16N25)(14),
					(R1'-puckering)(11)–(R1-puckering)(9)–R1(ω-C56N60)(5)
105	746	716	21.57		(ω-C9C2)(20), R1(ω-C16N25)(9), (ω-C2C9)(9)-R1(ω-C50N49)(8),
					(ω-N1H28)(7), (ω-C74C78)(7)-(R1-puckering)(6)-(R1'-puckering)(5)
103	719	690	10.77		$(\omega - N1H28)(15), (\tau - C70C77)(13), (\tau - R)(13) - (\tau - R')(10), (\omega - C5C6)(9),$
					$(\tau - R)(8) - (\omega - C70C77)(6), (\tau - H82012)(6)$
98	664	637	35.98		(τ-R)(21), (ω-N1H28)(12)-(δ-R1)(7), (ω-C2C9)(6)-(τ-C9C2)(6)-(δ-R1)(5)
95	647	621	63.41	627	(ω-N61H65)(14), (τ-H82012)(13), (ω-N11H35)(11)-(τ-R)(8)-(ω-N1H28)(6),
					(τ-C70C77)(6)
94	641	615	49.36		(ω-C2C9)(28), (τ-R)(15)-(τ-C9C2)(13)-(ω-C74C78)(8),
					(ω-N1H28)(7)–(ω-C9C2)(6)
90	632	607	15.27		(τ-R)(19), (ω-C2C9)(17)–(τ-C9C2)(12),
					(ω-N1H28)(10)-(ω-C74C78)(7)-(ω-C9C2)(7)
84	536	514	15.89		(ρ-C16N25)(22)-(δ-O51C50N49)(22)
79	478	459	35.27	476	(τ-H82012)(14), R(δ-C67C77C70)(10), (τ-C70C77)(7), (ω-N1H28)(7),
					δ(012C9013)(5)
73	421	404	13.82		$(\tau\text{-H82012})(17) - (\delta_{sc}\text{-H36H37C14})(14), (\tau\text{-O86H28})(12) - (\omega\text{-C2C9})(10)$

 $\nu$ , stretching;  $\delta_{sc}$ , scissoring;  $\rho$ , rocking;  $\omega$ , wagging; t, twisting;  $\delta$  and  $\delta'$ , deformation;  $\delta'_{as}$ , asymmetric deformation;  $\tau$ , torsion. R, pyrrole ring; R1, benzene ring.

respectively, which gives 141 and 288, (3n - 6) vibrational modes for monomer and dimer respectively. The calculated vibrational wavenumbers are higher than their experimental values for the majority of the normal modes. The vibrational frequency usually is overestimated in DFT due to two factors: (1) the overall neglect of anharmonicity and (2) an incomplete description of electron correlation due to the use of an incomplete basis set. Therefore, calculated wavenumbers at B3LYP/6-31G(d,p) level are scaled down using single scaling factor 0.9608 [51], to discard the anharmonicity present in real system. The observed wavenumbers are in good agreement with the calculated wavenumbers of dimer than monomer. Therefore, observed wavenumbers are assigned using dimer PED. The monomers as well as the dimer possess C1 symmetry; therefore the vibrational modes will be active for both IR and Raman. The Raman spectrum of the compound was calculated and found equal in frequencies and intensities.

#### 4.5.1. N–H vibrations

In the experimental FT-IR spectrum of EDPHEDPC, the N–H stretch of pyrrole ( $\nu_{\rm NH}$ ) is observed at 3269 cm<sup>-1</sup>, whereas it is calculated as 3331 cm<sup>-1</sup> in dimer and 3500 cm<sup>-1</sup> in monomer. The observed wavenumber at 3269 cm<sup>-1</sup> is in good agreement with the calculated wavenumber of dimer. The observed value of  $\nu_{\rm NH}$  also correlates with the earlier reported strong absorption at 3358 cm<sup>-1</sup> for hydrogen bonded pyrrole-2-carboxylic acid recorded in KBr pellet, but it deviates to the reported free  $\nu_{\rm NH}$  band at higher wavenumber 3465 cm<sup>-1</sup>, recorded in CCl<sub>4</sub> solution [52]. Therefore, solid state spectrum of EDPHEDPC attributes to the vibration of hydrogen-bonded N–H group. The observed N–H wagging mode of pyrrole at 797 cm<sup>-1</sup> corresponds to the calculated wavenumber at 808 cm<sup>-1</sup>. The observed N–H deformation of pyrrole at 1537 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1536 cm<sup>-1</sup>. The hydrazide N–H stretching vibration is observed at 3426 cm<sup>-1</sup>, whereas it is calculated as 3340 cm<sup>-1</sup>.

#### 4.5.2. C-H vibrations

Four methyl groups are present in the molecule. They are abbreviated as Me, Me1, Me2 and Me3. Me1 and Me2 are directly attached to the C5 and C3 carbon of pyrrole ring . Me and Me3 are attached to the  $CH_2$  of ester and C7 carbon respectively. The observed stretching vibration of Me, Me1 and Me2 at 2983, 2853 and 2921 cm<sup>-1</sup> are in agreement with the

calculated wavenumber at 3018, 2933 and 2989 cm<sup>-1</sup> respectively. A combination band of Me-rocking and CH<sub>2</sub>-scissoring observed at 1101 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1110 cm<sup>-1</sup>. The observed rocking mode of Me and Me2 at 1023 cm<sup>-1</sup> corresponds to the calculated wavenumber at 1007 cm<sup>-1</sup>. The CH<sub>2</sub> wagging mode is observed at 1285 cm<sup>-1</sup>, whereas it is calculated as 1328 cm<sup>-1</sup>.

#### 4.5.3. C–O vibrations

The stretching mode of carbonyl group ( $\nu_{C=0}$ ) is observed at 1664 cm<sup>-1</sup>, whereas it is calculated as 1655 cm<sup>-1</sup> in dimer and 1692 cm<sup>-1</sup> in monomer. The observed  $\nu_{C=0}$  absorption band at 1664 cm<sup>-1</sup> is in good agreement with the calculated wavenumber of dimer. The observed  $\nu_{C=0}$  also agrees well with the earlier reported wavenumber at 1665 cm<sup>-1</sup> for dimer of syn-pyrrole-2-carboxylic acid [52]. Therefore,  $\nu_{C=0}$  stretching mode in EDPHEDPC confirms the involvement of C=O group in intermolecular hydrogen bonding. The observed C9–013 stretching mode at 1191 cm<sup>-1</sup> is observed at same wavenumber at 1191 cm<sup>-1</sup> with 5% contribution in dimer PED. The O12C9O13 deformation is observed at 1230 cm<sup>-1</sup>, whereas it is calculated as 1272 cm<sup>-1</sup>.

#### 4.5.4. N=O vibrations

The molecule under investigation possesses two nitro groups. The nitro groups show two type of stretching vibrations as asymmetric and symmetric. Asymmetric stretching vibrations are always observed at higher wavenumber than symmetric stretching vibrations. The observed asymmetric stretching vibrations of N=O ( $\nu_{N=0}$ ) at 1565 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1588 cm<sup>-1</sup>. Symmetric stretching vibration of  $\nu_{N=0}$  is observed at 1285 cm<sup>-1</sup>, whereas it is calculated as 1328 cm<sup>-1</sup>. The observed NO<sub>2</sub> deformation at 829 cm<sup>-1</sup> corresponds to the calculated wavenumber at 797 cm<sup>-1</sup>. The observed wavenumbers are in agreement with the earlier reported wavenumbers for asymmetric and symmetric vibration of nitro group at 1600 cm<sup>-1</sup> and 1319 cm<sup>-1</sup> respectively [53].

#### 4.5.5. C–N and C–C vibrations

The C19–N11 stretching vibration is observed at  $1449 \text{ cm}^{-1}$ , whereas it is calculated as  $1503 \text{ cm}^{-1}$ . The observed C16–N25 wagging mode at  $662 \text{ cm}^{-1}$  corresponds to the calculated wavenumber at 718 cm<sup>-1</sup>. The C=N stretching vibration is assigned at  $1579 \text{ cm}^{-1}$ 

in dimer PED. The observed C–C stretches in benzene ring at 1619,  $1449 \,\mathrm{cm}^{-1}$  correspond to the calculated wavenumber at 1605,  $1503 \,\mathrm{cm}^{-1}$  respectively. The observed pyrrole ring deformation at  $1230 \,\mathrm{cm}^{-1}$  corresponds to the calculated wavenumber at  $1273 \,\mathrm{cm}^{-1}$ . Puckering mode of benzene ring is observed at  $662 \,\mathrm{cm}^{-1}$ , whereas it is calculated as  $718 \,\mathrm{cm}^{-1}$  with 11% contribution in dimer PED.

#### 4.6. AIM calculations

# 4.6.1. $\pi$ -Delocalization effect in resonance assisted intra and intermolecular hydrogen bonds (RAHB) and topological parameters

Geometrical as well as topological parameters are useful tool to characterize the strength of hydrogen bond. The geometrical criteria for the existence of hydrogen bond are as follows: (i) The distance between proton (H) and acceptor (A) is less than the sum of their van der Waal's radii of these atoms. (ii) The 'donor (D)–proton (H)…acceptor (A)' angle is greater than 90°. (iii) The elongation of 'donor (D)–proton(H)' bond length is observed.

As the above criteria are frequently considered as insufficient, the existence of hydrogen bond could be supported further by Koch and Popelier criteria [54] based on 'Atoms in molecules' theory: (i) The existence of bond critical point for the 'proton (H)...acceptor (A)' contact as a confirmation of the existence of hydrogen bonding interaction. (ii) The value of electron density ( $\rho_{H\dots A}$ ) should be within the range of 0.002-0.040 a.u. (iii) The corresponding Laplacian  $\nabla^2 \rho_{BCP}$  should be within the range of 0.024–0.139 a.u. According to Rozas et al. [55], the interactions may be classified as follows: (i) Strong H-bonds are characterized by  $\nabla^2 \rho_{BCP} < 0$  and  $H_{\rm BCP}$  < 0 and their covalent character is established. (ii) Medium H-bonds are characterized by  $\nabla^2 \rho_{BCP} > 0$  and  $H_{BCP} < 0$  and their partially covalent character is established. (iii) Weak H-bonds are characterized by  $\nabla^2 \rho_{BCP} > 0$  and  $H_{BCP} > 0$  and they are mainly electrostatic. The weak interactions are characterized by  $\nabla^2 \rho_{BCP} > 0$  and  $H_{BCP} > 0$  and the distance between interacting atoms is greater than the sum of van der Waal's radii of these atoms.

Molecular graph of the dimer using AIM program at B3LYP/6-31G(d,p) level is given in Supplementary Fig. 3. Geometrical as well as topological parameters for bonds of interacting atoms in dimer are given in (Supplementary Table) TS4. On the basis of these parameters, O23···H35, O62···H65 are medium hydrogen bonds, 012...H82, 086...H28 are weak hydrogen bonds and N10...H42, N64...H59, O13...H32, O87...H79, C8...H45, C75...H71, C6...N10, C77...N64, O12...H83, O86...H29 are weak interactions. The various type of interactions visualized in molecular graph are classified on the basis of geometrical, topological and energetic parameters. In this article, the Bader's theory application is used to estimate hydrogen bond energy (E). Espinosa proposed proportionality between hydrogen bond energy (E) and potential energy density ( $V_{BCP}$ ) at H···O contact:  $E = (1/2)(V_{BCP})$  [56]. According to AIM calculations, the binding energy of dimer is sum of the energies of all intermolecular interactions and this is calculated as -15.4539 kcal/mol. The intermolecular hydrogen bond energy of dimer is sum of the energies of both heteronuclear intermolecular hydrogen bonds (N-H···O) and this is calculated as -12.5074 kcal/mol.

The ellipticity ( $\varepsilon$ ) at BCP is a sensitive index to monitor the  $\pi$ character of bond. The  $\varepsilon$  is related to  $\lambda_1$  and  $\lambda_2$ , which correspond to the eigen values of Hessian and defined as by a relationship:  $\varepsilon = (\lambda_1/\lambda_2) - 1$ . In order to investigate the effect of  $\pi$ -electron delocalization in bonds associated with N and O atoms of N–H···O heteronuclear inter and intramolecular hydrogen bonds, the analysis of the bond ellipticity is performed. In dimer, inter and intramolecular hydrogen bonds are associated with the sixteenmembered and six-membered pseudo ring respectively. These rings are abbreviated as Ring1 and Ring2 respectively. The  $\varepsilon$  values for bonds involved in Ring1 and Ring2 are given in (*Supplementary Table*) TS5. In Ring1, the values of  $\varepsilon$  for bonds O12–C9, C9–C2, C2–C3, C3–C4, C4–C5, C5–N1 associated with the N1–H28 $\cdots$ O86 and for bonds O86–C78, C78–C74, C74–C69, C69–C67, C67–C70, C70–N76 associated with the N76–H82 $\cdots$ O12 are in the range of 0.1006–0.2857. In Ring2, the values of  $\varepsilon$  for bonds O23–N22, N22–C20, C20–C19, C19–N11 associated with the N11–H35 $\cdots$ O23 are in the range of 0.1130-0.2299. These values of  $\varepsilon$  correspond to the aromatic bonds reported in literature [57]. The  $\varepsilon$  values confirm the presence of resonance assisted intermolecular and intramolecular hydrogen bonds in Ring1 and Ring2 of dimer.

#### 4.7. Chemical reactivity

#### 4.7.1. Global reactivity descriptors

On the basis of Koopman's theorem [58], global reactivity descriptors electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), global hardness ( $\eta$ ), global softness (S) and global electrophilicity index ( $\omega$ ) are calculated using the energies of frontier molecular orbitals  $\varepsilon_{\text{HOMO}}$ ,  $\varepsilon_{\text{LUMO}}$  and given by Eqs. (1)–(5) [59–62]

$$\chi = -(1/2)(\varepsilon_{\text{LUMO}} + \varepsilon_{\text{HOMO}}) \tag{1}$$

$$\mu = -\chi = (1/2)(\varepsilon_{\text{LUMO}} + \varepsilon_{\text{HOMO}})$$
<sup>(2)</sup>

$$\eta = (1/2)(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}) \tag{3}$$

$$S = (1/2)\eta \tag{4}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{5}$$

According to Parr et al., electrophilicity index  $(\omega)$  is a global reactivity index similar to the chemical hardness and chemical potential. This is positive and definite quantity. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ( $\Delta N$ ) from the environment. The direction of the charge transfer is completely determined by the electronic chemical potential of the molecule because an electrophile is a chemical species capable of accepting electrons from the environments. Therefore its energy must decrease upon accepting electronic charge and its electronic chemical potential must be negative. The energies of frontier molecular orbitals ( $\varepsilon_{\text{HOMO}}$ ,  $\varepsilon_{\text{LUMO}}$ ), energy band gap ( $\varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}}$ ), electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), global hardness ( $\eta$ ), global softness (S) and global electrophilicity index  $(\omega)$  for reactants A, B and product C are listed in (Supplementary Table) TS6. The calculated high value of electrophilicity index  $(\omega)$  for EDPHEDPC shows that the title molecule behaves as a strong electrophile than reactants A and B.

#### 4.7.2. Local reactivity descriptors

Fukui functions  $(f_k^+, f_k^-, f_k^0)$ , local softnesses  $(s_k^+, s_k^-, s_k^0)$  and local electrophilicity indices  $(\omega_k^+, \omega_k^-, \omega_k^0)$  have been described earlier in literature [62,63]. Using Hirshfeld population analyses of neutral, cation and anion state of molecule, Fukui functions are calculated at same calculation method B3LYP/6-31G(d,p) using Eqs. (6)–(8)

 $f_k^+ = [q(N+1) - q(N)], \text{ for nucleophilic attack}$  (6)

$$f_k^{-} = [q(N) - q(N-1)], \text{ for electrophilic attack}$$
(7)

$$f_k^0 = (1/2)[q(N+1) + q(N-1)],$$
 for radical attack (8)

where N, N - 1, N + 1 are total electrons present in neutral, cation and anion state of molecule respectively.

Local softnesses and electrophilicity indices are calculated using the following equations ((9) and (10)).

$$s_{k}^{+} = Sf_{k}^{+}, \quad s_{k}^{-} = Sf_{k}^{-}, \quad s_{k}^{0} = Sf_{k}^{0}$$
(9)

$$\omega_{k}^{+} = \omega f_{k}^{+}, \quad \omega_{k}^{-} = \omega f_{k}^{-}, \quad \omega_{k}^{0} = \omega f_{k}^{0}$$
(10)

where +, -, 0 signs show nucleophilic, electrophilic and radical attack respectively.

Electrophilic reactivity descriptors  $(f_k^+, s_k^+, \omega_k^+)$  and nucleophilic reactivity descriptors  $(f_k^-, s_k^-, \omega_k^-)$  for selected atomic sites of EDPHEDPC are listed in (*Supplementary Table*) TS7, using Hirshfeld population analyses. The maximum values of all the three local electrophilic reactivity descriptors  $(f_k^+, s_k^+, \omega_k^+)$  at C(7) indicate that this site is more prone to nucleophilic attack. The calculated local reactivity descriptors of synthesized molecule EDPHEDPC favor the formation of new heterocyclic compounds such as azetidinones, oxadiazolines and thiazolidinones by attack of nucleophilic part of the dipolar reagent on the C(7) site and electrophilic part of dipolar reagent on the N(10) site of C7=N10 bond.

## 4.8. Dipole moment ( $\mu_0$ ), mean polarizability ( $\alpha_0$ ), anisotropy of polarizability ( $\Delta \alpha$ ) and first hyperpolarizability ( $\beta_0$ )

First hyperpolarizability is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The 27 components of the 3D-matrix can be reduced to 10 components due to the Kleinmann symmetry [62]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the  $3 \times 3 \times 3$  matrix is a tetrahedral. The components of  $\beta_0$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous this expansion becomes:

$$E = E^{0} - \mu_{i}F_{i} - (1/2)\alpha_{ij}F_{i}F_{j} - (1/6)\beta_{ijk}F_{i}F_{j}F_{k} - \cdots$$

where  $E^0$  is the energy of the unperturbed molecules,  $F_i$  is the field at the origin and  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$  are the components of dipole moment, polarizability, and first hyperpolarizability respectively. The total dipole moment ( $\mu_0$ ), the mean polarizability ( $|\alpha_0|$ ), the anisotropy of the polarizability ( $\Delta \alpha$ ) and the total first hyperpolarizability ( $\beta_0$ ) using *x*, *y*, *z* components are defined as [64]:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \tag{11}$$

$$|\alpha_0| = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$
(12)

$$\Delta \alpha = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2}$$
(13)

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \tag{14}$$

where

- $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$
- $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Since the *x*, *y*, *z* components of  $|\alpha_0|$ ,  $\Delta \alpha$  and  $\beta_0$  of Gaussian 03 output are reported in a atomic mass unit (a.u.), the calculated values have been converted into electrostatic unit (esu) (for  $\alpha_0$ : 1 a.u. = 0.1482 × 10<sup>-24</sup> esu; for  $\beta_0$ : 1 a.u. = 0.0086393 × 10<sup>-30</sup> esu). The total dipole moment ( $\mu_0$ ), mean polarizability ( $\alpha_0$ ), anisotropy of the polarizability ( $|\alpha_0|$ ) and the total first hyperpolarizability ( $\beta_0$ ) of A, B and C are listed in (*Supplementary Table*) TS8. The  $\beta_0$  values for A, B and C are calculated as 0.8326 × 10<sup>-30</sup>, 1.4131 × 10<sup>-30</sup>, 6.1032 × 10<sup>-30</sup> esu respectively. For title compound C,  $\beta_0$  is seven times that of A and four times that of B. The  $\beta_0$  values for hydrazone complexes are also reported in the literature in the range of 2.6–10.1 × 10<sup>-30</sup> esu [65]. Therefore, the calculated results will

show that the titled molecule might have medium non-linear optical (NLO) response.

#### 5. Conclusions

The title compound EDPHEDPC is synthesized and characterized by various spectroscopic and elemental analysis. The calculated <sup>1</sup>H NMR chemical shifts are in good agreement with the observed chemical shifts. The <sup>1</sup>H NMR signal of N11–H35 at high value of chemical shifts 11.73 ppm confirms the presence of intramolecular hydrogen bond N11-H35...O23. The observed electronic absorption spectra have some blue shifts compared with the theoretical data and molecular orbital coefficient analysis suggests that electronic transitions are assigned to  $\pi \rightarrow \pi^*$ . In the present study, experimental and calculated vibrational wavenumber analysis confirms the existence of dimer by involvement of heteronuclear association through pyrrolic (N–H) and carbonyl (C=O) oxygen of ester. The calculated binding energies of dimer using both DFT and AIM theories are -14.32 and -15.41 kcal/mol respectively. AIM theory is more appropriate than DFT theory since this is also applicable to calculate the intermolecular hydrogen bond energy of dimer. The intermolecular hydrogen bond energy of dimer is calculated to be -12.29 kcal/mol. The results of AIM ellipticity confirm the existence of resonance assisted intra and intermolecular hydrogen bonds in dimer. In addition, theoretical results from reactivity descriptors show that C(7) is more reactive site for nucleophilic attack. Therefore, title molecule may be used as precursor for the syntheses of new heterocyclic compounds such as azetidinones, oxadiazolines and thiazolidinones. The computed value of first hyperpolarizability ( $\beta_0$ ) shows that EDPHEDPC is an attractive molecule in future for nonlinear optical (NLO) applications.

#### Acknowledgments

The authors are thankful to the Directors of IIT Kanpur and CDRI Lucknow for providing spectral measurements of EDPHEDPC and the CSIR New Delhi for financial supports.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2012.02.086.

#### References

- [1] Y. Nakayama, Y. Sanemitsu, J. Org. Chem. 49 (1984) 1703-1707.
- [2] H.N. Dogan, A. Duran, S. Rollas, G. Sener, Y. Armutak, M.K. Uysal, Med. Sci. Res. 26 (1998) 755–758.
- [3] S.G. Küçükgüzel, A. Kocatepe, E. De Clercq, F. Sahin, M. Güllüce, Eur. J. Med. Chem. 41 (2006) 353–359.
- [4] S.G. Küçükgüzel, E.E. Oruç, S. Rollas, F. Sahin, A. Ozbek, Eur. J. Med. Chem. 37 (2002) 197–206.
- [5] V.N. Korotchenko, A.V. Shastin, V.G. Nenaidenko, E.S. Balenkova, Russ. J. Org. Chem. 39 (2003) 527–531.
- [6] L.E. Kaïm, L. Gautier, L. Grimaud, L.M. Harwood, V. Michaut, Green Chem. 54 (2003) 447–479.
- [7] A. Kotali, I.S. Lafazanis, ARKIVOC vi (2003) 91-94.
- [8] X. Deng, N.S. Mani, Org. Lett. 10 (2008) 1307-1310.
- [9] X. Deng, N.S. Mani, J. Org. Chem. 73 (2008) 2412–2415.
- [10] N.P. Belskaya, W.W. Dehaen, V.A. Bakulev, ARKIVOC i (2010) 275-332.
- [11] S. Rollas, Molecules 12 (2007) 1910-1939.
- [12] S.D. Toliwal, J. Kalpesh, G. Akshay, B. Anjum, J. Appl. Chem. Res. 10(2009)64–72.
- [13] P. Kumar, D. Sharma, Acta Pharm. Sci. 52 (2010) 169–180.
- [14] J.R. Dimmock, S.C. Vashishtha, J.P. Stables, Eur. J. Med. Chem. 35 (2000) 241-249.
- [15] A. Rauf, M.R. Banday, R.H. Mattoo, Acta Chim. Slov. 55 (2008) 448-452.
- [16] S. Rollas, N. Gülerman, H. Erdeniz, Farmaco 57 (2002) 171–174.
- [17] V.O. Kozminykh, A.O. Belyaev, E.N. Koz'minykh, E.V. Bukanova, T.F. Odegova, Pharm. Chem. J. 38 (2004) 368–372.
- [18] L.W. Zheng, L.L. Wu, B.X. Zhao, W.L. Dong, J.Y. Miao, Bioorg. Med. Chem. 17 (2009) 1957–1962.
- [19] D. Sriram, P. Yogeeswari, R.V. Devakaram, Bioorg. Med. Chem. 14 (2006) 3113-3118.

- [20] T.L. Smalley Jr., A.J. Peat, J.A. Boucheron, S. Dickerson, D. Garrido, F. Preugschat, S.L. Schweiker, S.A. Thomson, T.Y. Wang, Bioorg. Med. Chem. 16 (2006) 2091–2094.
- [21] L.F. Xu, S. Shan, W.L. Wang, S.H. Wang, Acta Crystallogr. E64 (2008) 01229.
- [22] N. Okabe, T. Nakamura, H. Fakuda, Acta Crystallogr. C49 (1993) 1678-1680.
- [23] N. Raman, S. Ravichandran, C. Thangaraja, J. Chem. Sci. 116 (2004) 215–219.
- [24] J.P. Jasinski, C.J. Guild, C.S.C. Kumar, H.S. Yathirajan, A.N. Mayekar, Bull. Korean Chem. Soc. 31 (2010) 881-886.
- [25] L. Lalib, L.A. Mohamed, M.F. Iskander, Transition Met. Chem. 25 (2002) 700-705.
- [26] M.A. Affan, I.P.P. Foo, B.A. Fasihuddin, E.U.H. Sim, M.A. Hapipah, Malay. J. Anal. Sci. 13 (2009) 73-85.
- [27] M. Yu, H. Lin, H. Lin, Ind. J. Chem. Sec. A 46 (2007) 1437–1439.
- [28] B. Szczesna, U. Lipkowska, Supramol. Chem. 13 (2001) 247-251.
- [29] S. Vijayakumar, A. Adithya, K.N. Sharafudeen, Balakrishna, K. Chandrasekharan, J. Mod. Optics 57 (2010) 670–676.
- [30] S. Vijayakumar, A. Adhikari, B. Kalluraya, K.N. Sharafudeen, K. Chandrasekharan, J. Appl. Polym. Sci. 119 (2011) 595-601.
- [31] O. Kwon, M. Jazbinsek, H. Yun, J. Seo, E. Kim, Y. Lee, P. Gunter, Cryst. Growth Des. 8 (2008) 4021–4025.
- [32] A.I. Vogel, Practical Organic Chemistry, Pretence Hall Publication, New York, 1956, 344 pp.
- [33] E.J.H. Chu, T.C. Chu, J. Org. Chem. 19 (1954) 266-269.
- [34] M.J. Frisch, et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- [35] A.D. Becke, J. Chem. Phys. 98 (1993) 5648-5652.
- [36] C.T. Lee, W.T. Yang, R.G.B. Parr, Phys. Rev. 37 (1988) 785-790.
- [37] D.A. Petersson, M.A. Allaham, J. Chem. Phys. 94 (1991) 6081-6090.
- [38] G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Allaham, W.A.J. Mantzaris, J. Chem. Phys. 89 (1988) 2193-2218.
- [39] G.A. Zhurko, D.A. Zhurko, Chemcraft: lite version build 08 (freeware), 2005.
- [40] Computer Program Gauss View 3.09, Ver. 2, Gaussian, Inc., Pittsburgh, PA.
- [41] J.M.L. Martin, V. Alsenoy, C.V. Alsenoy, Gar2ped, University of Antwerp, 1995.
- [42] P. Pulay, G. Fogarasi, F. Pang, J.E. Boggs, J. Am. Chem. Soc. 101 (1979) 2550-2560.
- [43] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553-556.

- [44] C.T. Arrannja, M.R. Siva, A.M. Beja, A.F.P.V. Ferreira, A.J.F.N. Sobral, Acta Crystallogr. E64 (2008) 01989.
- [45] M.G. Gardiner, R.C. Jones, S. Ng, J.A. Smith, Acta Crystallogr. E63 (2007) 0470.
- [46] S. Shan, Y.-L. Tian, S.-H. Wang, W.-L. Wang, Y.-L. Xu, Acta Crystallogr. E64 (2008) 01153.
- [47] M.C. Etter, Acc. Chem. Res. 23 (1990) 120-126.
- [48] K. Wolinski, J.F. Hinton, J.F. Pulay, J. Am. Chem. Soc. 112 (1990) 8251-8260.
- [49] S.W. Xia, X. Xu, Y.L. Sun, Y.L. Fan, Y.H. Fan, C.F. Bi, D.M. Zhang, L.R. Yang, Chin. J. Struct. Chem. 25 (2006) 849–853.
- [50] D. Jackuemin, E.A. Perpète, J. Mol. Struct. Theochem. 804 (2007) 31-34.
- [51] N. Sundaraganesan, E. Kavitha, S. Sebastian, J.P. Cornard, M. Martel, Spectrochim. Acta Part A 74 (2009) 788-797.
- [52] A.T. Dubis, S.J. Grabowski, D.B. Romanowska, T. Misiaszek, J. Leszczynski, J. Phys. Chem. A 106 (2002) 10613–10621.
- [53] N. Sundaraganesan, S. Ayyappan, H. Umamaheswari, B.D. Joshua, Spectrochim. Acta Part A 17 (2007) 17–27.
- [54] U. Koch, P. Popelier, J. Phys. Chem. A 99 (1995) 9747–9754.
- [55] I. Rozas, I. Alkorta, J. Elguero, J. Am. Chem. Soc. 122 (2000) 11154-11161.
- [56] E. Espinosa, E. Molins, C. Lecomte, Chem. Phys. Lett. 285 (1998) 170-173.
- [57] I.F. Matta, R.J. Boyd, An Introduction to the Quantum Theory of Atoms in Molecules, Wiley-VCH Verlag GmbH, 2007.
- [58] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, New York, 1989.
- [59] R.G. Parr, R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 7512-7516.
- [60] P. Geerlings, F. De Proft, W. Langenaeker, Chem. Rev. 103 (2003) 1793-1873.
- [61] R.G. Parr, L. Szentpály, S. Liu, J. Am. Chem. Soc. 121 (1999) 1922–1924.
- [62] P.K. Chattaraj, S. Giri, J. Phys. Chem. A 111 (2007) 11116-11121.
- [63] D.A. Kleinmann, Phys. Rev. 126 (1962) 1977–1979.
- [64] H. Alyar, Z. Kantarci, M. Bahat, E. Kasap, J. Mol. Struct. 834-836 (2007) 516-520.
- [65] Y.P. Tian, W.T. Yu, C.Y. Zhao, M.H. Jiang, Z.H. Cai, H.K. Fun, Polyhedron 21 (2002) 1217–1222.