Synthesis, spectral and computational studies of some 2-(2-(3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole derivatives

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ABSTRACT. A series of some 2-(2-(3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole derivatives **11-14** have been synthesized using acetic acid as the catalyst. All the synthesized compounds were characterized by FT-IR, ¹H ¹³C NMR and HSQC spectral analysis. The molecular modelling was carried out for compound **11** by Gaussian 03W package and its HOMO–LUMO, Mulliken atomic charges, Molecular electrostatic potential (MEP), Hyperpolarizability, Thermodynamic properties and Natural bond orbital (NBO) analysis were discussed.

1. INTRODUCTION

Hydrazones are a versatile class of ligands having great physiological and biological activities and have been used as insecticides, anticoagulants, antitumour agents, antioxidants and plant growth regulators [1,2]. Their metal complexes have found applications in various chemical processes like non-linear optics, sensors, medicine etc [3]. Recently, second order NLO effects of organic molecules have been extensively investigated for their advantages over inorganic crystals. The organic NLO materials play an important role in second harmonic generation, frequency mixing and electro-optic modulation [4]. Most π -conjugated systems play a major role in determining second-order NLO response [5]. Searching organic materials with non-linear optical (NLO) properties is usually concentrated on molecules with donor–acceptor π -conjugation (D- π -A) and deals with the substituent effects on the degree of π -conjugation, steric hindrance and the hyperpolarisability of the substances [6]. Many piperidine derivatives are found to possess pharmacological activity and form an essential part of the molecular structures of important drugs [7, 8]. Recently attention has been focused on the application of the piperidone derivatives as prospective biophotonic materials [9, 10]. Since the pharmacological properties and the reactivity depend on their stereochemistry, efforts were made for the development of new synthetic techniques leading to stereoselective piperidines and their characterization [11, 12]. Thiazoles are the important group of heterocyclic compounds due to their drug utility [13]. In continuation of our earlier work some 2-(2-(3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazoles (**11–14**) were synthesized in the present study and their conformational behaviour was analyzed using ¹H and ¹³C NMR spectroscopy. The preferred conformations were further confirmed by means of conformational analysis performed by DFT calculations. From the DFT calculation hyperpolarizability calculation, NBO and HOMO–LUMO band gap have also been studied.

2. EXPERIMENTAL

2.1. General characterization techniques

TLC was carried out to monitor the course of the reaction and the purity of the product. Melting points were recorded in open capillaries and were uncorrected. IR spectra were recorded on AVATAR 330 FT-IR spectrometer with KBr pellets. ^1H NMR spectra were recorded at 400 MHz on BRUKER AMX spectrophotometer using CDCl_3 and TMS as internal standard. ^{13}C NMR spectra were recorded at 100 MHz on BRUKER AMX 400 MHz spectrometer using CDCl_3 and the ^1H - ^{13}C COSY correlation spectra were recorded on BRUKER AMX 400 MHz NMR spectrometer using standard parameters. All the chromatographic purifications were performed with silica gel (100-200 mesh) whereas all TLC (Silica gel) was performed on silica gel coated (Merk Kiesel 60 GF-254, 0.2 mm thickness) sheets. All reagents and solvents are commercially obtained (Alfa aesar, Himedia) and used directly without any further purification.

General procedure for synthesis of 2,4-Diaryl-3-azabicyclo [3.3.1]nonan-9-ones (1-4)

2r,4c-Diaryl-3-azabicyclo[3.3.1]-nonan-9-ones (**1-4**) were prepared by the condensation of appropriate ketones, aldehydes and ammoniumacetate in 1:2:1 ratio, using literature procedure [14]. The 2r,4c-diaryl-3-azabicyclo[3.3.1]-nonan-9-ones (**1-4**) afforded 3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one (**5-8**) upon refluxing with iodomethane in the presence of anhydrous potassium carbonate in acetone [15].

Synthesis of 2-hydrazinobenzothiazole 10

2-Hydrazinobenzothiazole was prepared [16] by refluxing an equimolar solution of 2-mercaptobenzothiazole (0.2 mmol) and hydrazine hydrate (0.2 mmol) in methanol (150 mL) on a steam bath for 10 h. It was cooled, filtered and washed with ice water. The product was dried and recrystallised from ethanol to yield the pure compound **10** yield;61%.m.p;202°C

Synthesis of 2-(2-(3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole 11-14

To a boiling solution of 3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one (0.1mmol) in methanol, 2-hydrazinobenzothiazole (0.1 mmol) was added with constant stirring and the reaction mixture was refluxed for 2–3 h on a water bath. After cooling, the product was filtered and then washed with water. The products (**11–14**) were purified by column chromatography. All the synthesized compounds were obtained in good yield and their analytical data are given in Table 1 and their synthetic methodology is given in Scheme 1

Table 1: Physical data of compounds **11-14**

Compound	R ₁	R ₂	Yield %	Melting point (° C)
11	H	H	74	201-203
12	OMe	OMe	76	194-198
13	F	F	80	195-198
14	Br	Br	78	210-212

Scheme 1 2-(2-(3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole (**11**)

White solid; yield 74 %; mp 201-203 °C; IR (KBr, λ_{max} cm⁻¹) 3212-3377 (N-H st), 2778-2985 (C-H st), 1649 (C=N st); ¹H NMR (400 MHz, CDCl₃) δ 2.67 (s, 1H, H-1e), 4.54 (s, 1H, H-2a), 4.29 (s, 1H, H-4a), 2.98 (m, 1H, H-5e), 2.83 (s, 1H, 7a), 1.61 (m, 2H, H-6e, H-8e), 1.46 (m, 3H, H-7e, H-8a, H-6a), 7.66 (s, 1H, =N-NH), 1.79 (d, 3H, CH₃), 7.09-7.61 (m, 10H aromatic protons); ¹³C (100 MHz, CDCl₃) δ 46.08 (C-1), 65.13 (C-2), 63.71 (C-4), 39.44 (C-5), 27.18 (C-6), 21.38 (C-7), 28.45 (C-8), 153.45 (C-9), 30.59 (CH₃), 142.41 (C-2'), 141.95 (C-4'), 121.35-130.71 (Aromatic carbons).

2-(2-(2,4-bis(4-methoxyphenyl)-3-methyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole (**12**)

White solid; yield 76 %; mp 194-198 °C; IR (KBr, λ_{max} cm⁻¹) 3212-3377 (N-H st), 2778-2985 (C-H st), 1649 (C=N st); ¹H NMR (400 MHz, CDCl₃) δ 2.57 (s, 1H, H-1e), 3.67 (s, 1H, H-2a), 3.52 (s, 1H, H-4a), 2.91 (m, 2H, H-5e and H-7a), 1.25 (m, 2H, H-6e, H-8e), 0.99 (m, 3H, H-7e, H-8a, H-6a), 7.76 (s, 1H, =N-NH), 1.92 (s, 3H, CH₃), 6.92-7.70 (m, 8H aromatic protons); ¹³C (100 MHz, CDCl₃) δ 43.65 (C-1), 74.20 (C-2), 72.38 (C-4), 40.39 (C-5), 22.68 (C-6), 21.23 (C-7), 27.61 (C-8), 158.71 (C-9), 28.96 (CH₃), 133.80 (C-2'), 132.27 (C-4'), 113.62-130.36 (Aromatic carbons).

2-(2-(2,4-bis(4-fluorophenyl)-3-methyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole (13)

White solid; yield 80 %; mp 195-198 °C; IR (KBr, λ_{max} cm⁻¹) 3212-3377 (N-H st), 2778-2985 (C-H st), 1649 (C=N st); ¹H NMR (400 MHz, CDCl₃) δ 2.62 (s, 1H, H-1e), 4.43 (s, 1H, H-2a), 4.29 (s, 1H, H-4a), 2.97 (m, 1H, H-5e) 2.76, (s, 1H, H-7a), 1.21 (m, 2H, H-6e, H-8e), 0.88 (m, 3H, H-7e, H-8a, H-6a), 7.65 (s, 1H, =N-NH), 1.79 (s, 3H, CH₃), 7.07-7.56 (m, 8H aromatic protons); ¹³C (100 MHz, CDCl₃) δ 58.05 (C-1), 71.85 (C-2), 70.5 (C-4), 39.5 (C-5), 28.79 (C-6), 24.28 (C-7), 29.57 (C-8), 160.85 (C-9), 30.98 (CH₃), 165.0 (C-2'), 163.4 (C-4''), 115.27-152.15 (Aromatic carbons).

2-(2-(2,4-bis(4-chlorophenyl)-3-methyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole (14)

White solid; yield 78 %; mp 210-212 °C; IR (KBr, λ_{max} cm⁻¹) 3212-3377 (N-H st), 2778-2985 (C-H st), 1649 (C=N st); ¹H NMR (400 MHz, CDCl₃) δ 2.63 (s, 1H, H-1e), 4.40 (s, 1H, H-2a), 4.23 (s, 1H, H-4a), 2.96 (m, 1H, H-5e) 2.71 (s, 1H, H-7a), 1.48 (m, 2H, H-6e, H-8e), 0.85 (m, 3H, H-7e, H-8a, H-6a), 7.66 (s, 1H, =N-NH), 1.76 (s, 3H, CH₃), 7.10-7.54 (m, 8H aromatic protons); ¹³C (100 MHz, CDCl₃) δ 46.3 (C-1), 64.9 (C-2), 63.2 (C-4), 38.9 (C-5), 27.2 (C-6), 21.5 (C-7), 28.5 (C-8), 159.5 (C-9), 31.2 (CH₃), 137.5 (C-2'), 137.0 (C-4''), 115.3-128.7 (Aromatic carbons).

3. RESULTS AND DISCUSSION

Spectral analysis

For the representative compound **12**, the IR, ¹H and ¹³C signals were unambiguously assigned based on the observed correlations in the HSQC spectra. For all the other compounds the ¹H and ¹³C signals were assigned by comparison with **12** and their ¹H and ¹³C NMR chemical shift values. The signals for the aromatic protons and carbons in **11-14** were assigned based on known substituent effects [17, 18]. In the IR spectrum of compound **12**, the stretching frequency at 1595 cm⁻¹ is due to C=N and the absorption band observed 3369 cm⁻¹ is due to NH proton of hydrazine moiety. The aromatic C-H stretching frequencies are observed at 3061 cm⁻¹.

High resolution ¹H NMR, ¹³C NMR spectrum has been recorded for compound **12** in CDCl₃ and their signals are analysed as follows. In the ¹H NMR spectrum of compound **12**, characteristic hydrazine NH proton (=N-NH-) is expected to appear in the most downfield region. A broad signal resonating at 7.76 ppm was assigned to NH proton of the hydrazone part. Methylene protons (both H6e and H8e) of C-6 and C-8 carbon proton resonated as multiplets at 1.25 ppm. Benzylic protons H-2a and H-4a were observed at 3.67 and 3.52 ppm each corresponding one proton integral values. In addition, signals appearing at 2.57 and 2.91 ppm were designated correspondingly for H-1e and H-5e bridgehead protons.

Among the cyclohexane ring proton (H-6, H-7 and H-8) signals, H-7a proton resonated in the deshielded region than its corresponding equatorial and other methylene (C-6 and C-8) protons. This is due to the deshielding effect exerted by the nitrogen lone pair and it creates vander waals interaction. Due to this, C-H(7a) bond becomes polarized and as a consequence, carbon and the attached proton acquire negative and positive charges, respectively. As a result, the H-7a proton signal is highly deshielded. A multiplet observed at 2.91 ppm is unambiguously assigned to H-7a proton which is merged with H-5e proton. Similarly another multiplet observed at 0.99 ppm is assigned to H-7e proton. In piperidine ring, the nitrogen connected the methyl protons signal is appeared as a singlet observed at 1.92 ppm with the three protons integral. The aryl protons are appeared in the region of 6.92-7.70 ppm.

In ¹³C NMR spectrum of compound **12**, the benzylic (C-2/C-4) carbon signals appeared at 74.20 and 72.38 ppm and bridgehead (C-1/C-5) carbon signals appeared at 43.65 and 40.39 respectively. Moreover, the signals which are appeared in the aliphatic region at 27.61 and 21.23 ppm are assigned to C-8/C-6 and C-7 carbon, respectively. A collection of signals observed in the region of 113.62-133.80 ppm are assigned to aryl carbons and a signal observed at 158.71 ppm is assigned to C=N imine carbon.

4. COMPUTATIONAL STUDY

Quantum mechanical calculations were used to carry out for compound **11** and the optimized geometry, NLO, NBO, HOMO–LUMO and thermodynamic parameter are obtained with Gaussian-03 program using the Becke3-Lee-Yang-Parr (B3LYP) functions supplemented with the standard 6-31G(d,p) basis set [19,20]. Optimized structure is shown in Fig. 1

Fig. 1. Optimized molecular structure of compound **11**

The density functional theory has been used to calculate the mean polarizability $\langle\alpha\rangle$ and the total first static hyperpolarizability β and are given in terms of x, y, z components as follows.

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

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

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

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

The β components of Gaussian output are reported in atomic units and therefore the calculated values are converted into e.s.u. units (1 a.u. = 8.3693×10^{-33} e.s.u).

HOMO-LUMO Analysis

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important, their energies and HOMO–LUMO energy gap are calculated by B3LYP level with 6-311G (d, p) basis set. The HOMO–LUMO pictures of compound **11** were shown in Fig. 2. The calculated frontier molecular orbital energies [HOMO, LUMO] and their energy gap (DE) of compound **11** were -5.22840 eV -1.55913 eV and 3.66927 eV respectively. The HOMO orbital is mostly located on phenylthiazole ring and C=N atoms of the piperidine ring. Whereas LUMO is located at phenyl and piperidine ring. The energies of both HOMO and LUMO orbitals are influenced by the presence of benzothiazole ring. The energy of HOMO was directly related to the ionization potential and LUMO was directly related to the electron affinity. The energies of HOMO, LUMO and their low energy gap [3.66927 eV] reflect the chemical activity of the molecule and potential application of compound **11** as NLO material.

Homo= -5.22840 eV

Lumo= -1.55913 eV

Energy Gap= 3.66927 eV

Fig.2. HOMO–LUMO orbital picture of compound **11**

Mulliken atomic charge

Distributions of positive or negative charges are vital to increasing or decreasing of bond length between the atoms. The survey of literature reveals that effective atomic charge calculations are given an important role in the application of chemical calculation to molecular system because of its related properties like atomic charges, dipolemoment, molecular polarizability, electronic structure, acidity-basicity behaviour and more lot of properties of molecular system [21]. The charge distribution on the molecule has an important influence on the vibrational spectra. The calculated Mulliken charge distributions of compound **11** are shown in Fig 4.

Fig. 4. Mulliken charge distributions of compound **11**

The corresponding Mulliken's charge distributions revealed that the substitution of the aromatic ring by an N and S atom leads to a redistribution of electron density of the thiazole ring to entire molecule. Moreover, for S-48 (0.38554) atom in the thiazole molecule, accommodate higher positive charge than the other hydrogen atoms. The Mulliken atomic charge of compound **11** shows that the H-41 atom has more positive atomic charge [0.36714e] than the other hydrogen atoms. This is due to the presence of electronegative C=N *syn* effect. Mulliken population analysis revealed that N-6 and N-49 atoms have maximum negative charge (-0.59752 and -0.56271) than the rest of the atoms.

Molecular electrostatic potential

A multipole expansion is a computationally convenient single center formation that allows one to quantitatively compute the degree to which a positive or negative charge is attracted to or repelled by the molecule that is being represented by the multipole expansion [22]. In the contour map, the regions with red colors are regarded as the most electronegative (electrophilic) regions and the regions with blue colours are the most positive (nucleophilic) regions. The MEP surface is plotted over the optimized electronic structure of compound **11** at the B3LYP/6-311G(d, p) level. Fig. 3 shows the mapped surface of compound **11** and the red colour corresponds to maximum negative charge density and deep blue colour to positive charge.

Fig. 3. MEP map of compound **11**

This description indicates that the negative charge density is large on the C-N bond present in the thiazole ring. In the title molecule, the C=N, NH and C=N (thiazole ring) groups connected to the ring system have the most nucleophilic (positive) regions.

Thermodynamic properties

Several calculated thermodynamic parameters are presented in Table 2. Scale factors have been recommended [23] for an accurate prediction in determining the zero-point vibrational energies (ZPVE), and the entropy S_{vib} (T). The variations in the ZPVEs seem to be insignificant

Table 2: Thermodynamic properties of compound **11**

Parameters	B3LYP/6-31G(d,p)
Total Energies	-1698.13463277
Zero-point Energy	289.75326 (Kcal/Mol)
Rotational constants GHZ):	0.18331, 0.06488, 0.05303
Entropy Total	183.381
Translational	44.189
Rotational	37.475
Vibrational	101.716

Hyperpolarizability

The first hyperpolarizabilities (β_0 , α and μ) of compound **11** is calculated using B3LYP/6-31G(d,p) level of theory, based on the finite- field approach. Many organic molecules, containing conjugated π electrons are characterized by large values of molecular first hyper polarizabilities [24–27]. The intra-molecular charge transfer from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR activity strong at the same time. The present study reveals that the π - π interaction can make larger intra-molecular interaction and hence the polarizability of the molecule increases. It is evident from Table 3.

Table 3: The molecular electric dipole moments μ (Debye), Polarizability (α_0) and hyperpolarizability (β_0) values of compound **11**

Parameters	B3LYP/6-31G(d,p)
Dipole moment (μ)	Debye
μ_x	-1.9785286
μ_y	0.9772086
μ_z	0.1498680
M	2.21178 Debye
Polarizability (α_0)	$\times 10^{-30}$ esu
α_{xx}	526.2469097
α_{xy}	-29.0799703
α_{yy}	397.4761297
α_{xz}	31.8783087
α_{yz}	37.1928834
α_{zz}	201.1100598
α_0	0.99075×10^{-30} esu

<i>Hyperpolarizability (β_0)</i>	<i>$\times 10^{-30} \text{esu}$</i>
β_{xxx}	387.0239440
β_{xyy}	-595.3752297
β_{xyy}	139.1201007
β_{yyy}	476.2105644
β_{xxz}	-324.3052491
β_{xyz}	97.4820939
β_{yyz}	7.1176831
β_{xzz}	-74.0225143
β_{yzz}	14.0294957
β_{zzz}	-43.3777732
β_0	$5.07792 \times 10^{-30} \text{esu}$

Standard value for urea ($\mu=1.3732$ Debye, $\beta_0=0.3728 \times 10^{-30} \text{esu}$): **esu**-electrostatic unit.

The molecular dipole moment (μ), molecular polarizability(α) and hyperpolarizability (β_0) are calculated as 2.21178 (D), $0.99075 \times 10^{-30} \text{esu}$ and $5.07792 \times 10^{-30} \text{esu}$ respectively. The β_0 value of the title compound is ~13.62 times greater than that of urea.

Natural bond orbital (NBO) analysis

The NBO analysis explained the charge transfer (CT) or hyperconjugative interaction in the molecular system. The larger E2 value, the more intensive is the interaction between electron donor and electron acceptors. NBO analysis will provide information about the transfer of electrons from one end of the molecule to the other end and how best the molecule can act as NLO material. The second order perturbation theory of B3LYP/6-31G(d,p) level in the NBO analysis shows strong intramolecular hyperconjugative interactions, which were presented in Table 4.

The most important interaction energies correspond to the transfer of electrons from C46 - C47 to antibonding orbital of C51 - C53 and C46 - C47 to antibonding orbital of C50 - C52 were found to be 1188.93 and 853.75 kJ mol⁻¹ respectively for the compound **11**. These values reveal that the delocalisation towards thiazole ring is the primary process rather than the delocalisation towards the side chain C=N and C-S moiety.

Table 4: NBO properties of compound **11**

Donor (I)	Type	ED/ e	Acceptor (J)	Type	ED/ e	E2	E(j)-E(i)	F(i, j)
C11 - C12	π	1.62329	C1 - C2	π^*	0.29958	57.66	13.78	0.27
			C13 - C16		0.31551	80.96	19.35	0.28
			C14 - C18		0.33119	84.06	20.09	0.28
C13 - C16	π	1.67796	C11 - C12	π^*	0.38045	79.24	18.94	0.28
			C14 - C18		0.33119	82.01	19.6	0.28
C14 - C18	π	1.65087	C11 - C12	π^*	0.38045	86.99	20.79	0.28
			C13 - C16		0.31551	83.43	19.94	0.28
C22 - C23	π	1.62309	C4 - C5	π^*	0.26578	51.84	12.39	0.28
			C24 - C27		0.31803	81.71	19.53	0.27
			C25 - C29		0.33202	84.47	20.19	0.27
C24 - C27	π	1.67956	C22 - C23	π^*	0.37739	79.08	18.9	0.28
			C25 - C29		0.33202	81.59	19.5	0.28
C25 - C29	π	1.65279	C22 - C23	π^*	0.37739	86.48	20.67	0.28

			C24 - C27		0.31803	83.93	20.06	0.28
C45 - N49	π	1.88824	C46 - C47	π^*	0.46606	68.07	16.27	0.34
			C50 - C52		0.33181	72.09	17.23	0.29
			C51 - C53		0.35311	88.49	21.15	0.29
C50 - C52	π	1.69562	C46 - C47	π^*	0.46606	88.87	21.24	0.27
			C51 - C53		0.35311	79.91	19.1	0.28
C51 - C53	π	1.68846	C46 - C47	π^*	0.46606	77.78	18.59	0.27
			C50 - C52		0.33181	82.05	19.61	0.28
LP (1) N6	n	1.66112	C1 - C2	π^*	0.29958	97.91	23.4	0.28
C53 - H56	σ	1.98212	C4 - C5	π^*	0.26578	84.56	20.21	0.29
LP N42	n	1.91901	C2 - C3	σ^*	0.04653	53.85	12.87	0.83
LP N43	n	1.68097	C3 - N42	π^*	0.15499	99.45	23.77	0.3
			C45 - N49		0.3796	224.51	53.66	0.28
LP S48	n	1.76868	C45 - N49	π^*	0.3796	85.48	20.43	0.25
LP N 49	n	1.87066	C45 - S48	σ^*	0.10173	84.18	20.12	0.47
C45 - N49	$\pi -$	0.3796	C46 - C47	π^*	0.46606	404.93	96.78	0.02
C46 - C47	π	0.46606	C50 - C52	π^*	0.33181	853.75	204.05	0.02
			C51 - C53		0.35311	1188.93	284.16	0.01

5. CONCLUSION

A series of the heterobicyclic 2-(2-(3-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinyl)benzo[d]thiazole derivatives **11–14** were synthesized and characterized by FT-IR, ^1H ^{13}C NMR and HSQC spectral techniques. The energies of frontier molecular orbitals HOMO LUMO, MEP, charge distribution and NBO of compound **11** have been calculated by using B3LYP method with 6-311G (d, p) basis set. DFT studies revealed the first molecular hyperpolarizability of compound **11** is ~ 13.62 times greater than urea. Hence these title molecules possess considerable NLO property.

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