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Quantum Chemical Study for Structure, Electronic and NLO Properties of 2-Amino-4-nitrotoluene and 2-Amino-5-nitrotoluene

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Molecular structure, molecular orbital energies; and global reactivity parameters of 2-amino-4-nitrotoluene (2A4NT) and 2-amino-5-nitrotoluene (2A5NT) were studied using DFT/B3LYP/6-311++G(d,p) level of theory. The energy difference between HOMO and LUMO was found to be 3.35 eV and 3.41 eV, respectively. Computed electrophilicity index values (ω = 12.63 and 14.61) demonstrate that the molecules are strong electrophile. The reactive sites and charge distribution of the compounds were analyzed by MEP surface. The non-linear optical activity of title compounds was studied by calculating the values of total dipole moment and mean first order hyperpolarizability. The natural charges of the molecules were obtained from NBO analysis; and the entire atomic charges were acquired by means of Mulliken study. The NMR (^{13}C & ^{1}H) theoretical chemical shifts were predicted by using GIAO approach in DMSO-d_6 solvent. The values of energy, oscillator strength and absorption wavelength were computed from the UV-Vis spectra using TD-DFT method.

Keywords: 2-Amino-4-nitrotoluene, 2-Amino-5-nitrotoluene, Mulliken charges, Thermodynamic parameters.

INTRODUCTION

Toluene is commonly used as a mixture with other solvents in aerospace and automobile industries. It also finds its application in the preparation of paints, paint thinners, rubber, in preparation of some important aromatic hydrocarbons and in leather tanning process. Toluene is more reactive towards electrophilic substitution reaction [1,2]. Nitrotoluenes have a role as an environmental contaminant and a carcinogenic agent. 4-Nitrotoluene is used as an intermediate for the preparation of *p*-toluidine, *p*-nitrobenzoic acid and other similar compounds, which in turn act as raw material for plastic foams, dye stuffs, paints, medicine and agricultural chemical products [3,4]. Some of the substituted amino nitrotoluenes act as a useful tool for wastewater treatment because it can be used to measure nitrogen atoms in wastewater. They are also used as an analytical method to measure the concentration of amines, nitro compounds and other diazonium salts. 2-Amino-4-nitrotoluene is an key component of insoluble azo dyes, mainly used for cotton fabric dyeing and printing. About four decades ago, 2-amino-5-nitrotoluene (2A5NT) was identified as an excellent organic compound for generation of high frequencies of the order of terahertz. But, it requires a large single crystal of 2A5NT, which was then found to be difficult to synthesize. Wayne *et al.* [5] reported a stable method for growing large single crystals of 2A5NT that can be successfully used for generation of terahertz frequencies using the optical rectification of infrared light [6].

Different spectroscopic studies of benzene substituents such as methyl and halogen compounds were reported by several researchers [7-18]. Green *et al*. [7] and Dwivedi & Sharma [17] reported the vibrational spectra of few TXY type toluene halogens. Vibrational assignments and DFT analysis of 4-nitrotoluene have also been reported in the literature [18]. Structure as well as molecular vibrational analysis of 2-chloro-4-nitrotoluene and 4-chloro-2-nitrotoluene was undertaken by Kumar *et al.* [19]. The complete vibrational assignments using normal coordinate analysis of 2-amino-4-nitrotoluene (2A4NT) and 2-amino-5-nitrotoluene (2A5NT) was reported in earlier work [20]. However, the detailed quantum chemical study on structural parameters, FMO's, NLO behaviour, Mulliken charge analysis, MEP and thermodynamic parameters of these compounds are yet to be reported using DFT computations.

Hence, the optimized geometrical parameters, HOMO-LUMO energies, chemical reactivity descriptors, molecular electrostatic potential (MESP) surface, natural population (NPA) analysis and thermodynamic parameters have been discussed by using DFT study in this study.

COMPUTATIONAL METHODS

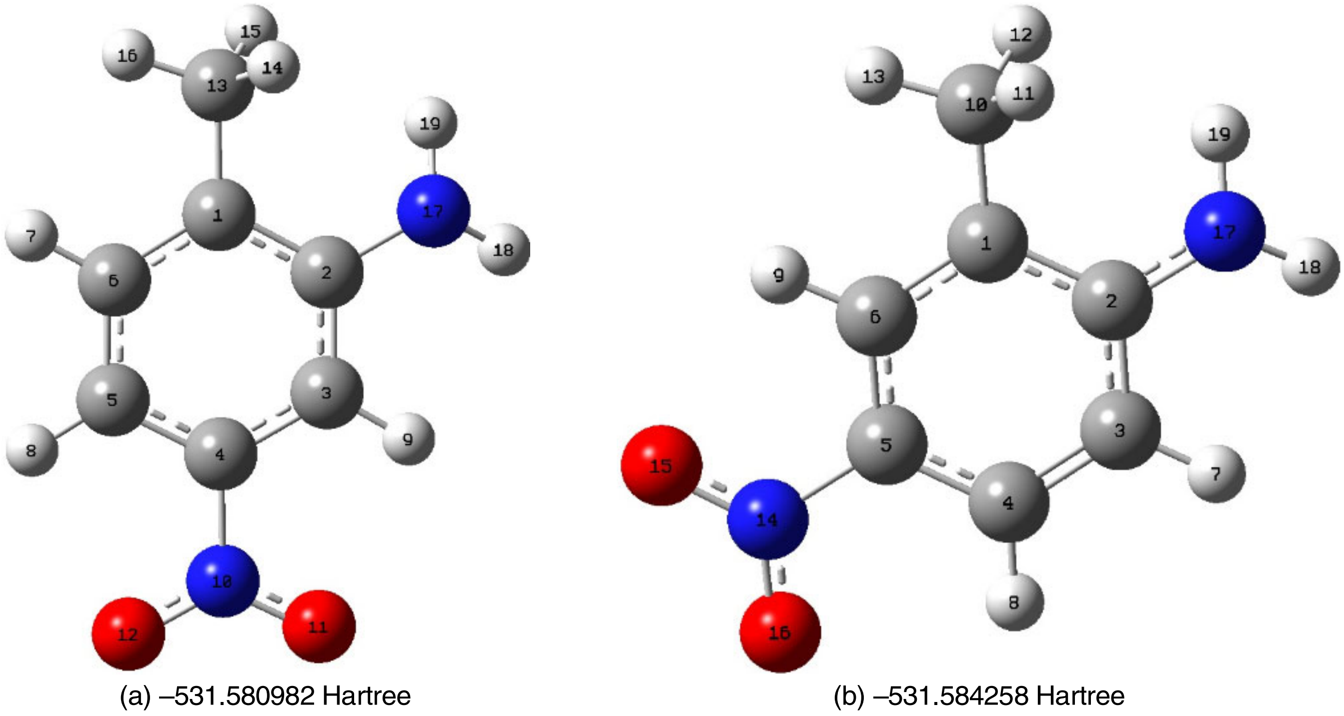
All the required calculations of 2-amino-4-nitrotoluene (2A4NT) and 2-amino-5-toluene (2A5NT) were made by DFT method employing B3LYP [21,22] level of computations using 6-311++G(d,p) higher basis set implemented in Gaussian 09W programme [23]. The most stable structures conforming to the lowest possible energy surface have been acquired by solving self-consistent field (SCF) equation iteratively. Frontier molecular orbitals (FMO's) as well as MEP surface of the molecules have been obtained by using Gauss View 5.0 program. The NLO behaviour was studied by computing polarizability, hyperpolarizability and dipole moment values. The natural population and Mulliken charge analysis of the title molecules also evaluated. The NMR (^{1}H &^{13}C) chemical shifts were performed using DFT method by employing GIAO (gauge-independent atomic orbital) approach.

RESULTS AND DISCUSSION

Optimized molecular geometry: All the pre-requisite quantum chemical computations were done in the gas phase. The optimized structures along with atoms labeling are illustrated in Fig. 1a-b. The selected molecules are found to be C1 point group symmetry with 19 atoms constituting each structure. The title molecules comprise amino group, nitro as well as methyl groups linked with benzene ring. The minimum energy of 2A4NT and 2A5NT are -531.580982 Hartree and -531.584257 Hartree, respectively. The zero-point vibrational energy of 2A4NT and 2A5NT are 91.999 Kcal/mol and 92.031 Kcal/mol. The most stable theoretical bond length, bond angle and torsional angle of 2-amino-4-nitrotoluene and 2-amino-5-nitrotoluene were investigated using aforesaid DFT higher basis set are shown in Tables 1 and 2.

In current studies, the average bond distance (C-C) of 2A4NT and 2A5NT in benzene ring are 1.396 Å and 1.397 Å. The bond distances of carbon with methyl carbons (C1-C13/C10) in 2A4NT and 2A5NT are 1.505 Å and 1.507 Å, respectively. The average bond angle of nitro group (N-O) in 2A4NT and 2A5NT are 1.225 Å and 1.229 Å; and the average bond angle (C-C-C) of 2A4NT and 2A5NT in benzene ring are found to be 119.99 Å and 120.09 Å, respectively. The average bond angle (O-N-C) is 117.80 Å and 117.97Å; while average bond angle (H-N-C) is 116.53 Å and 118.27 Å, whereas, the average dihedral angle in benzene ring is 0.003 Å and 0.0007 Å in 2A4NT and 2A5NT, respectively.

HOMO-LUMO analysis and chemical reactivity parameters: HOMO is the electron contributing ability, while LUMO is the electron accepting ability. The HOMO and LUMO energy gap is accountable for the stability and chemical reactivity of the compound [24]. The HOMO, LUMO energies and its band gap of title compounds are computed by DFT computations with three functional (B3LYP) using same basis set. The HOMO and LUMO plots of 2A4NT and 2A5NT are depicted in Fig. 2a-b. The energy difference between HOMO-LUMO in gas phase of 2A4NT and 2A5NT is estimated at 3.3516 eV and 3.4177 eV. This lower energy gap of title molecules shows the chemically more active [25].



(a) –531.580982 Hartree

(b) –531.584258 Hartree

Fig. 1. Optimized geometric structures of (a) 2A4NT and (b) 2A5NT along with labelling of atoms

TABLE-1
OPTIMIZED STRUCTURAL PARAMETERS OF 2-AMINO-4-NITROTOLUENE COMPUTED AT DFT/6-311++G(d, p) BASIS SET

Bond length (Å)	DFT value	Bond angle (°)	DFT value	Dihedral angle (°)	DFT value
C1-C2	1.415	C1-C2-C3	119.52	C1-C2-C3-C4	0.05
C2-C3	1.398	C2-C3-C4	119.47	C2-C3-C4-C5	0.16
C3-C4	1.388	C3-C4-C5	122.42	C3-C4-C5-C6	-0.16
C4-C5	1.389	C4-C5-C6	117.51	C4-C5-C6-C1	-0.07
C5-C6	1.391	C5-C6-C1	122.28	C5-C6-C1-C2	0.28
C6-C1	1.396	C6-C1-C2	118.81	C6-C1-C2-C3	-0.27
C6-H7	1.084	H7-C6-C5	119.05	N10-C4-C3-C2	179.91
C5-H8	1.080	H8-C5-C6	120.35	O11-N10-C4-C3	-0.15
C3-H9	1.082	H9-C3-C2	121.15	O12-N10-C4-C3	179.89
C4-N10	1.478	N10-C4-C3	118.45	C13-C1-C6-C5	-179.31
N10-O11	1.226	O11-N10-C4	117.85	C13-C1-C2-C3	179.33
N10-O12	1.225	O12-N10-C4	117.76	H14-C13-C1-C2	121.93
C1-C13	1.505	C13-C1-C6	121.06	H15-C13-C1-C6	-118.25
C13-C14	1.095	H14-C13-C1	111.28	H16-C13-C1-C6	1.56
C13-H15	1.097	H15-C13-C1	111.74	H16-C13-C1-C2	-178.03
C13-H16	1.091	H16-C13-C1	111.09	N17-C2-C3-C4	177.12
C2-N17	1.393	N17-C2-C1	120.40	N17-C2-C1-C6	-177.32
N17-H18	1.008	H18-N17-C2	116.07	H18-N17-C2-C3	18.33
N17-H19	1.008	H19-N17-C2	116.99	H19-N17-C2-C3	-178.03

TABLE-2
OPTIMIZED STRUCTURAL PARAMETERS OF 2-AMINO-5-NITROTOLUENE COMPUTED AT DFT/6-311++G(d, p) BASIS SET

Bond length (Å)	DFT value	Bond angle (°)	DFT value	Dihedral angle (°)	DFT value
C1-C2	1.418	C1-C2-C3	119.69	C1-C2-C3-C4	0.17
C2-C3	1.407	C2-C3-C4	121.60	C2-C3-C4-C5	0.03
C3-C4	1.383	C3-C4-C5	118.89	C3-C4-C5-C6	-0.13
C4-C5	1.393	C4-C5-C6	121.01	C4-C5-C6-C1	0.03
C5-C6	1.394	C5-C6-C1	120.78	C5-C6-C1-C2	0.17
C6-C1	1.387	C6-C1-C2	118.61	C6-C1-C2-C3	-0.27
C3-H7	1.085	H7-C3-C2	119.31	H7-C3-C2-C1	-179.70
C4-H8	1.081	H8-C4-C3	121.39	H8-C4-C3-C2	179.89
C6-H9	1.082	H9-C6-C5	118.80	H9-C6-C5-C4	-179.89
C1-C10	1.507	C10-C1-C6	121.02	C10-C1-C6-C5	-179.54
C10-H11	1.096	H11-C10-C1	111.52	H11-C10-C1-C6	120.78
C10-H12	1.097	H12-C10-C1	111.84	H12-C10-C1-C6	-118.88
C10-C13	1.090	H13-C10-C1	110.85	H13-C10-C1-C2	-178.97
C5-N14	1.461	N14-C5-C4	119.55	N14-C5-C4-C3	179.83
N14-O15	1.229	O15-N14-C5	118.02	O15-N14-C5-C4	-179.88
N14-O16	1.229	O16-N14-C5	117.93	O16-N14-C5-C4	0.11
C2-C17	1.379	N17-C2-C1	120.27	N17-C2-C3-C4	177.83
C17-H18	1.008	H18-N17-C2	117.85	H18-N17-C2-C3	16.09
C17-H19	1.007	H19-N17-C2	118.70	H19-N17-C2-C3	161.81

HOMO is directly connected to electronegativity and LUMO is linked to electron affinity. The reactivity descriptors including chemical hardness (η), softness (S), electronic chemical potential (μ) and electrophilicity index (ω) are discussed and reported by earlier researchers [26,27] are listed in Table-3. A high ω value shows the good electrophilicity, whereas a low ω value signifies a poor electrophile [28]. Softness and hardness are related to the polarizability of the molecule. The large energy gap represents the soft molecules and are highly polarizable, whereas small energy gap measures the soft molecule and less polarisable. The energy difference among HOMO and LUMO creates the charge transfer interaction occurring in the compound, which makes the compound possess to be NLO active [29].

TABLE-3
CALCULATED HOMO-LUMO ENERGIES AND GLOBAL REACTIVITY DESCRIPTOR PARAMETER VALUES OF 2-AMINO-4-NITROTOLUENE AND 2-AMINO-5-NITROTOLUENE

Parameter	2A4NT	2A5NT
HOMO energy	-8.914158	-8.774569
LUMO energy	-5.562539	-5.356821
Energy gap E_g ($E_{HOMO} - E_{LUMO}$)	3.351621	3.417748
Ionization energy (I)	8.914158	8.774569
Electron affinity (A)	5.562539	5.356821
Global hardness (η)	1.675811	1.708874
Chemical softness (S)	0.298363	0.292590
Chemical potential (μ)	7.238348	7.065695
Electrophilicity index (ω)	15.632341	14.607294

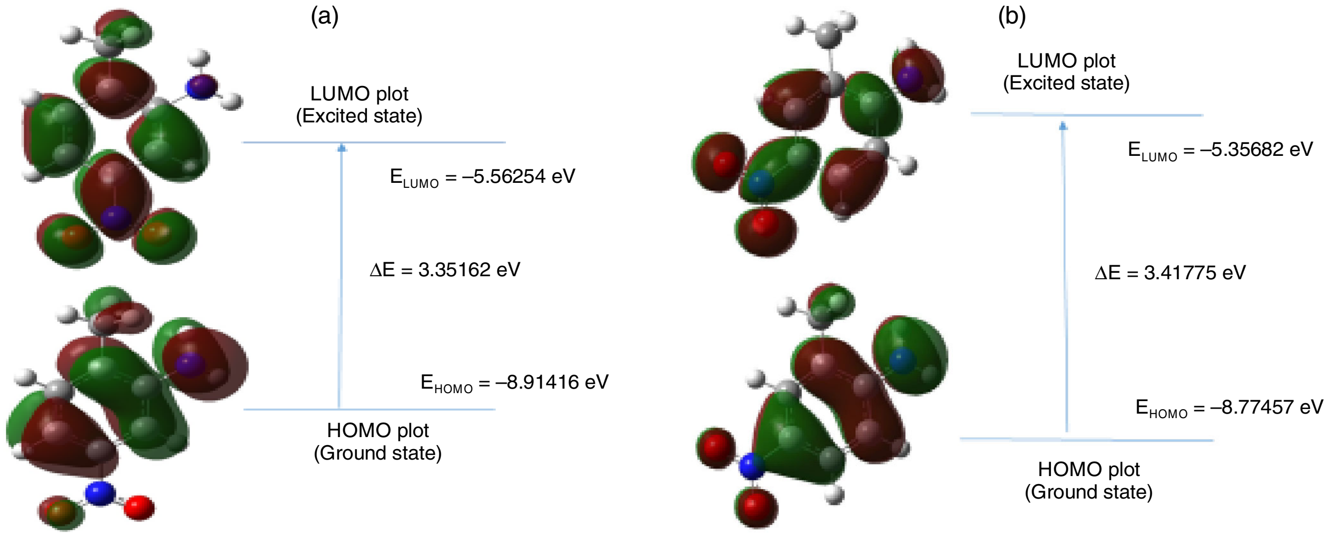


Fig. 2. Frontier molecular orbitals of (a) 2A4NT and (b) 2A5NT

Molecular electrostatic potential (MEP) surface: The molecular electrostatic potential (MEP) surfaces of headline compounds have been investigated from the most stable optimized structures by DFT/B3LYP level of theory using standard basis set 6-311++G(d,p) and 3D plots of MEPs are illustrated in Fig. 3. MEPs are used to find the relative polarities of the molecules, hydrogen bonding exchanges and analysis of biological recognition [30]. In present study, the reactive sites at the molecule surfaces are demonstrated by different colours like blue, red and green as plotted in Fig. 3a-b. The red colour portion in the molecules signifies the areas of negative potential whereas blue colour denotes the zones of positive potential. The green colour portion represents the neutral potential. The negative portions are associated to electrophilic attack, whereas the positive regions are associated to nucleophilic attack. The decrease in electrostatic potential follows as blue > green > yellow > orange > red [31]. The investigated MEP surface map of the molecules shows the positive potentials over the hydrogen fragments, whereas the negative potentials over the oxygen atoms.

NLO effect: The static dipole moment (μ_t) and first-order hyperpolarizability (β_t) values of any materials are decided by NLO effects. When electromagnetic radiation passes through the nonlinear behaviour of the compound and interact with it, as a result, a change in amplitude, frequency, phase or other characteristics of incident radiation, produces new fields [32,33]. Polarizability, dipole moment and first-order hyperpolarizability calculated at DFT method for 2A4NT and 2A5NT and to investigate their NLO behaviour. These parameters are obtained from Gaussian 09 out file. The total polarizability, mean dipole moment and mean hyperpolarizability were evaluated using following equations:

Total dipole moment $(\mu_t) = (\mu^2x + \mu^2y + \mu^2z)^{1/2}$

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

The total polarizability $(\alpha_t) = [\alpha xx + \alpha yy + \alpha zz]/3$

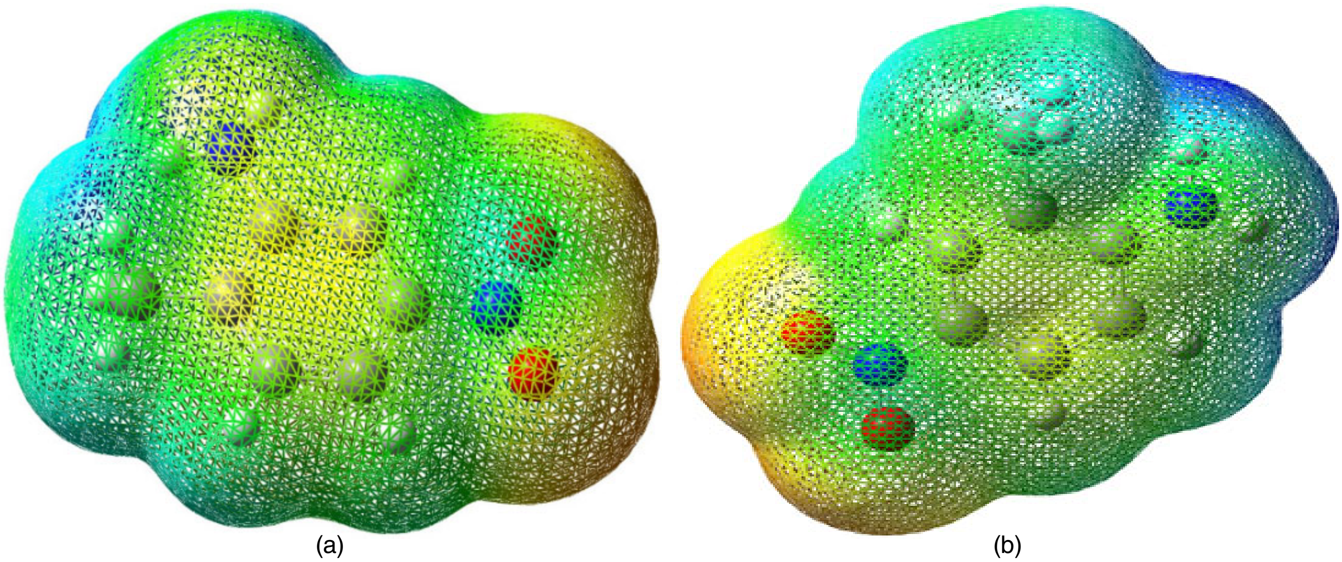


Fig. 3. Molecular electrostatic surface potential of (a) 2A4NT and (b) 2A5NT

TABLE-4
VALUES OF TOTAL DIPOLE MOMENT μ_t (Debye); POLARIZABILITY σ_t (1.4818×10^{-24} cm^3) AND FIRST ORDER HYPERPOLARIZABILITY β_t (10^{-30} cm^5/e.s.u) OF 2-AMINO-4-NITROTOLUENE (2A4NT) AND 2-AMINO-5-NITROTOLUENE (2A5NT) BY DFT/B3LYP/6-311++G(d,p)

Parameter	2A4NT	2A5NT	Parameter	2A4NT	2A5NT
αxx	152.08381	166.941075	βxxx	-887.3760313	1775.4965672
αxy	2.5296445	2.5280533	βxxy	110.644948	345.9420562
αyy	121.11728	117.3746955	βxyy	-63.4912819	-86.1196589
αxz	0.0325991	0.2318336	βyyy	-190.9754627	-78.8896097
αyz	-0.217390	0.1308711	βxxz	9.1775442	19.2737703
αzz	60.66342	60.3517268	βyyz	2.1493197	2.171692
αt	111.28817	114.889165	βxzz	9.238038	5.3285705
μx	6.3700	-7.5612	βyzz	76.4845071	-93.104826
μy	0.3042	-0.9394	βzzz	-2.0588005	-19.3462412
μz	0.8373	0.6644	βyyz	11.5188043	9.2223766
μt	6.4320	7.6476	βt	8.282	14.772

In this study, the total dipole moment and first order hyperpolarizability of 2A4NT and 2A5NT were found to be 6.432 Debye and 7.648 Debye; and 8.282 and 14.772, respectively. All the component values are presented in Table-4. The computed values of μ_t and β_t are compared with prototypical value of urea (μ_t = 1.3732 Debye and $\beta_t = 0.3728 \times 10^{-30}$). Urea is the good NLO material and considered as a threshold for evaluation. The selected molecules are having higher μ_t and β_t values than the urea. Hence, the selected molecules have a respectable NLO behaviour and these compounds may be used in medical chemistry [34].

Mulliken and natural charge analysis: The atomic charges (Mulliken and Natural) of 2-amino-4-nitrotoluene and 2-amino-5-nitrotoluene were investigated by DFT/B3LYP/6-311++G(d,p) methods. The calculation of these charges shows an imperative role in the application of quantum mechanical computations for the molecular system [35]. The distribution of charges in the compounds affects the polarizability, dipole moment and electronic structure. The computed natural charges are acquired from NBO study and all the atomic distribution of charges were calculated using Mulliken population analysis. The computed Mulliken and natural charges of various atoms are illustrated in Table-5 and the graphical plot in Fig. 4. In Mulliken charge study, the maximum positive charges found for atoms (C1, H18 and H19) were 0.7644, 0.2637 and 0.2641in 2A4NT, while 1.6963, 0.2587 and 0.2587 in 2A5NT. The maximum negative charges were obtained for the atoms (C2, C13 and C6) are -0.8477, -0.3504 and -0.3408 in 2A4NT, while -1.5709 (C1), -0.6525 (C5), -0.4205 (N10) in 2A5NT. The maximum positive charge of title molecule were found at H19 and N17, under natural population analysis.

TABLE-5
MULLIKEN CHARGES AND NPA ANALYSIS OF 2-AMINO-4-NITROTOLUENE AND 2-AMINO-5-NITROTOLUENE

Atom	Mulliken charges		Natural population analysis	
	2A4NT	2A5NT	2A4NT	2A5NT
C1	0.764401	1.69638	-0.047336	-0.154874
C2	-0.847703	-1.570925	0.003774	0.057838
C3	-0.182636	-0.1417581	0.023632	0.098309
C4	-0.269999	0.377758	-0.002700	-0.021875
C5	0.043633	-0.652478	-0.000844	0.000663
C6	-0.340827	-0.159224	-0.008854	0.021957
H7	0.180106	0.165855	0.000219	0.002134
H8	0.244669	0.244053	0.000078	-0.000557
H9	0.227234	0.219817	0.001686	0.000775
N10/C10	-0.185500	-0.420543	0.000128	-0.023050
O11/H11	-0.006570	0.175815	-0.000368	-0.005292
O12/H12	-0.011933	0.156385	-0.000091	0.002261
C13	-0.350367	0.167772	-0.008967	0.002043
H14/N14	0.203029	-0.188265	0.001166	0.000357
H15/O15	0.168336	-0.018040	-0.000036	-0.000070
H16/O16	0.142293	-0.025300	0.000256	0.000031
N17	-0.306007	-0.260615	0.389244	0.362033
H18	0.263687	0.250532	-0.055243	-0.038249
H19	0.264153	0.258745	0.440103	0.436823

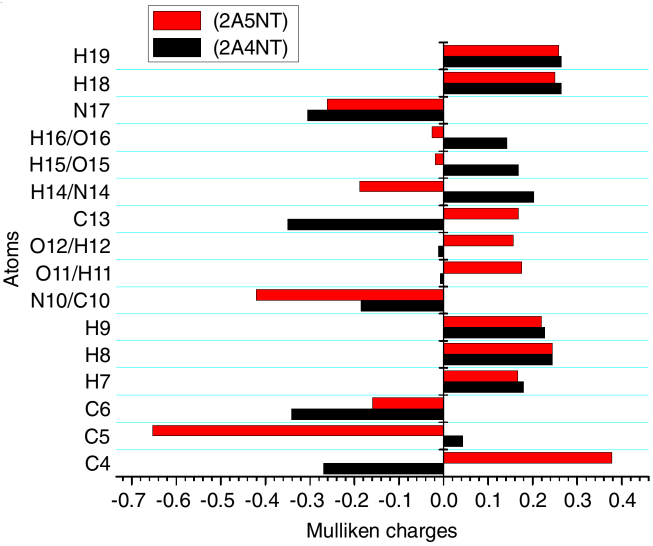


Fig. 4. Mulliken charge analysis of 2A4NT and 2A5NT

NMR spectral analysis: The DFT/B3LYP method with 6-311++G(d,p) basis set through gauge independent atomic orbital (GIAO) method were used to estimate the NMR spectral values of the studied molecules. The GIAO [36,37] scheme is greatest method for computing the isotropic nuclear magnetic shielding tensors. The calculated chemical shifts of 2A4NT and 2A5NT calculated in DMSO-d_6 solvent are listed in Table-6. The carbon NMR spectral values of aromatic compounds are generally > 100 ppm [38,39]. The NMR (^{1}H) spectral values of 2A4NT and 2A5NT molecules was obtained in the range

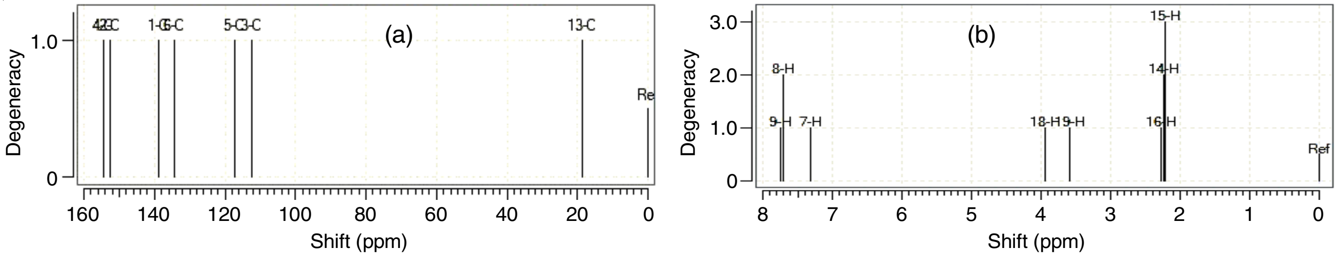


Fig. 5. NMR chemical shifts (a) ^{13}C (b) ^{1}H of 2A4NT at DFT/B3LYP/6-311++G(d,p) method

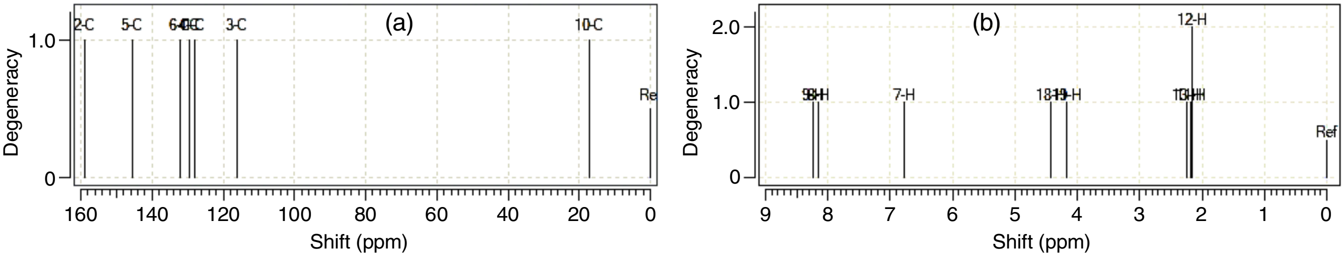


Fig. 6. NMR chemical shifts (a) ^{13}C (b) ^{1}H of 2A5NT at DFT/B3LYP/6-311++G(d,p) method

TABLE-6
THEORETICAL NMR (^{1}H & ^{13}C) CHEMICAL SHIFT VALUES FOR 2A4NT AND 2A5NT USING B3LYP/6-311++G(d,p) BASIS SET

Atoms	2A4NT	Atom	2A5NT
4C	154.267	2C	158.88
2C	152.57	5C	145.397
1C	138.951	6C	132.258
6C	134.492	1C	129.384
5C	117.039	4C	127.992
3C	112.205	3C	115.954
13C	18.552	10C	17.302
9H	7.742	9H	8.236
8H	7.715	8H	8.144
7H	7.319	7H	6.770
18H	3.946	18H	4.429
19H	3.597	19H	4.175
16H	2.273	13H	2.238
14H	2.218	11H	2.18
15H	2.245	12H	2.16

from δ 2.22-7.74 ppm and δ 2.16-8.23 ppm. This difference in NMR signal values is owed due to the electronic environment of the ^{1}H (protons). The ^{13}C NMR spectra for 2A4NT and 2A5NT molecules were observed from δ 154.267-18.55 ppm and δ 158.88-17.302 ppm. The theoretical NMR (^{1}H & ^{13}C) spectra of headline molecules are illustrated in Figs. 5 and 6.

UV-visible analysis: The UV-Visible studies of the title compounds were investigated from the fully optimized structures by using TD-DFT method using B3LYP/6-311++G(d,p) level in DMSO-d_6 solvent. The maximum electronic transitions along with corresponding wavelengths, band gap energies, excitation energies and oscillator strengths are computed and are presented in Table-7. In this study, the maximum electronic transitions were found at 362.2 and 363.98 for title compounds. The theoretically calculated electron absorption spectra of chosen compounds are illustrated in Figs. 7 and 8.

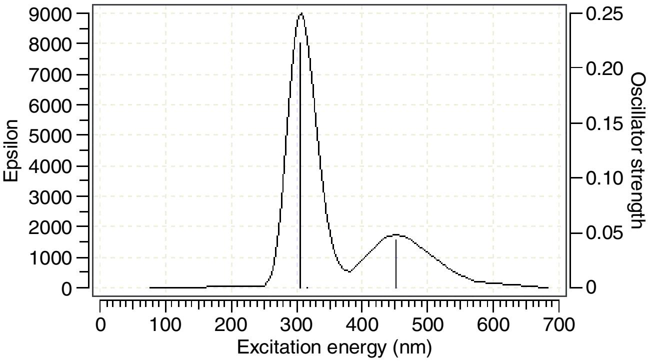


Fig. 7. UV-visible spectra of 2A4NT at DFT/B3LYP/6-311++G(d,p) method

Thermodynamic parameters: Several thermodynamic parameters such as zero-point vibrational energy (E_o), entropy (S), specific heat (C_v) at constant volume, self-consistent field (SCF) energy, vibrational energy (E_{vib}) and rotational constants (A, B and C) of the test molecules were investigated using

TABLE-7
THEORETICAL ELECTRONIC ABSORPTION SPECTRAL VALUES OF 2A4NT AND 2A5NT BY TD-DFT AND B3LYP/6-311++G(d,p) METHOD

2-Amino-4-nitrotoluene (2A4NT)				2-Amino-5-nitrotoluene (2A5NT)			
DMSO-d_6				DMSO-d_6			
Band gap E (ev)	Oscillator strength (f)	Wavelength (λ_{max}) (nm)	Energy (cm^{-1})	Band gap E (ev)	Oscillator strength (f)	Wavelength (λ_{max}) (nm)	Energy (cm^{-1})
2.751	0.0432	450.77	22184.3	–	–	–	–
3.919	0.0001	316.29	31616.6	3.965	0.4155	363.98	31982.6
4.047	0.2221	306.36	32641.3	3.406	0.0154	311.06	27474

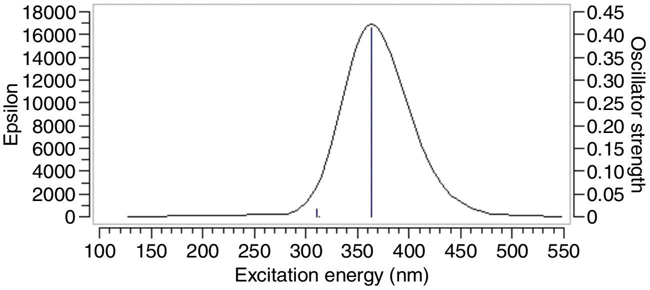


Fig. 8. UV-Visible spectra of 2A5NT at DFT/B3LYP/6-311++G(d,p) method

rigid harmonic oscillator terms [40] by DFT technique with same level of theory. These parameters show a pivotal role in various physical and chemical phenomena and are tabulated in Table-8. All the thermodynamic functions computations have been done in gas phase at 1 atmospheric pressure for 1 mole of perfect gas.

TABLE-8
THERMODYNAMIC PARAMETERS AND ROTATIONAL CONSTANTS OF 2-AMINO-4-NITROTOLUENE (2A4NT) AND 2-AMINO-5-NITROTOLUENE (2A5NT)

Parameters	2A4NT	2A5NT
SCF energy (Hartree)	-531.58098229	-531.58425765
RMS gradient norm (a.u)	0.00001934	0.00003005
Zero-point vibrational energy (E_n) (kcal mol^{-1})	91.99934	92.03082
Thermal energy (thermal) (E_{total})	98.221	98.260
Heat at constant volume (Cv) (calmol^{-1} K^{-1})	37.862	37.968
Entropy (S) (cal mol^{-1} K^{-1})	97.385	97.079
Vibrational energy (E_{vib}) (kcal mol^{-1})	96.444	96.482
Rotational constant (GHz)		
A	2.47164	2.43084
B	0.72410	0.72805
C	0.56221	0.56236

Conclusion

The current study reported the most stable optimized geometry of 2-amino-4-nitrotoluene and 2-amino-5-nitrotoluene molecules by DFT computations with B3LYP/6-311++G(d,p) level of theory. The optimized geometrical parameters, molecular orbital energies and its band gap energy of studied molecules were investigated. The optimized title compounds belong to C1 point group symmetry. The investigated band gap of HOMO-LUMO molecules shows the chemically more active and low kinetic stability. The calculated dipole moment of title compounds was obtained at 6.432 Debye and 7.648 Debye, which indicates it as polar. The calculated values of first order hyperpolarizability of 2A4NT and 2A5NT were higher than urea and are found to possess a good NLO behaviour. The chemical activity of the selected compounds was traced from the MEP maps. The Mulliken charges and thermodynamic parameters were investigated for title molecules. The NMR chemical shifts and UV-Visible spectral values were also analyzed.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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