Int. J. Chem. Sci.: 14(4), 2016, 2029-2050
ISSN 0972-768X
www.sadgurupublications.com

NATURAL BOND ORBITAL (NBO) POPULATION ANALYSIS OF AN ENERGETIC MOLECULE 1-PHENYL-2-NITROGUANIDINE

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ABSTRACT

The DFT study was carried out using Gaussian 03 software package to appraise the molecular structure of high energy compound 1-phenyl-2-nitroguanidine at B3LYP/6-311++G(d,p) level. Natural Bond Orbital (NBO) analysis of the molecule was carried out in order to understand the electronic structure and hybridization of the atoms at same level of theory. The hyper conjugative interactions and charge delocalization acquired from NBO analysis was used to investigate the stability of compound. The π electron delocalization parameter (Q) as a geometrical indicator of a local aromaticity and the geometry based Harmonic Oscillator Measure Aromaticity (HOMA) have also been calculated at the same level of theory. The electron density based Fukui function was used to envisage the reactive site. On the basis of the principle of statistical thermodynamics, the standard molar heat capacity ($C_{\mathrm{p,m}}^{\theta}$), standard molar entropy (S_{m}^{θ}) and standard molar enthalpy (H_{m}^{θ}) from 200 to 800 K were derived from the scaled frequencies. The dipole moment (μ), polarizability (α) and hyperpolarizability (β) of the molecule have also been reported.

Keywords: Natural bond orbital, HOMA, Thermodynamic functions, Fukui function, Dipole moment (μ), Polarizability (α), Hyperpolarizability (β).

INTRODUCTION

High energy density compounds (HEDCs), have been receiving extensive recognition because of their assorted range of uses both in military and civilian applications[1-4] in the last few decades. An outsized number of nitramine based HEDCs have been synthesized and characterized and used as energetic materials in gunpowder, solid

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propellants in rocket, and explosive compounds. The process of synthesizing energetic materials like nitramines and qualifying them for military use has always not been a quick and easy task. Besides, the nitramines, nitro aromatics and nitro esters are also being used to design energetic compounds. Some of the recent research reports on high energetic compounds sketch that, nitramine compounds have been engaged to play an essential role in aeronautics, weapon industry and other domains in science and technology as it contains one or more covalently bonded N-NO_2 groups at different valency states.[5-7] The most remarkable characteristic feature of nitramines is the configuration of the bonds formed by the amine nitrogen atom in the molecule. Some of the reported nitramine compounds are RDX[8], CL-20[9], HMX[10], etc., which are the well-known explosives of the present.

Theivarasu and Murugesan[11] have already reported the topological, intra molecular hydrogen bonding and electrostatic potential (ESP) of the 1-phenyl-2-nitroguanidine molecule in an earlier study.[11] The prime aim of the present study is to analyse the nature of bonding in 1-phenyl-2-nitroguanidine (Fig. 1), by using high-level theoretical methodologies and the study of its molecular electronic structure by Natural Bond Orbital (NBO) analysis, which is done in par with our previous work.

Further, the thermodynamic functions, the standard molar heat capacity ( ), standard molar entropy ( ) and standard molar enthalpy ( ) elucidated on the basis of the principle of statistical thermodynamics[12] from 200 to 800 K were derived from the scaled frequencies. Other molecular properties namely π electron delocalization parameter (Q), Harmonic Oscillator Measure Aromaticity (HOMA), Fukui function, dipole moment (μ), polarizability (α), and hyper polarizability (β) have also been calculated at the same level of theory. The present investigation may be helpful in perception of further studies on 1-phenyl-2-nitroguanidine in different field of research as high energy material.

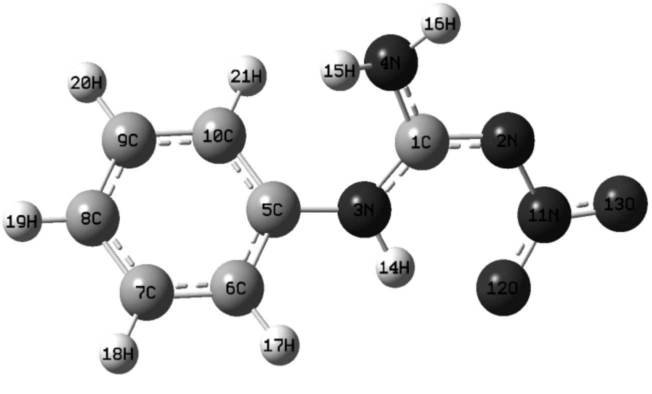

Fig. 1: Optimized structure of 1-phenyl-2-nitroguanidine at DFT/6-311++G(d,p) level

Calculation method

The DFT computation of 1-phenyl-2-nitroguanidine has been carried out with the Gaussian 03 package at the Becke 3-Lee-Yang-Parr (B3LYP)[13-16] level with standard 6-311++G(d,p) basis set. The geometric parameters were optimizable and no restrictions were thrusted upon the molecular structure at the time of optimization process. Subsequently, vibration analyses were performed for the optimized structures to confirm its identity as an energy minimum. The optimized structure was characterized to be true local energy minima on potential energy surfaces without imaginary frequencies.

NBO program[17] under Gaussian 03 software package was used to perform the Mulliken population analysis by the natural bond orbital method[18] at HF and B3LYP methods with 6-311++G(d,p) basis set. With the help of second-order perturbation theory all the donor and acceptor occupancies with their interaction energies received during the process were reported.

RESULTS AND DISCUSSION

Mulliken atomic charges

Calculation of atomic charges plays a quintessence role in the application of quantum chemical calculation in molecular system. It is observed that number of the molecular properties like electronic structure, dipole moment, molecular polarizability, and many other properties of the molecule are influenced by atomic charges[19].

Mulliken charges determine the electron population of each atom discussed in the basic functions. The Mulliken charges calculated at different levels and at same basic set are listed in Table 1. The distribution of electronic charges of the 1-phenyl-2-nitroguanidine molecule by the two different methods is illustrated by the plots shown in Fig. 2. Both the methods display similar charge distribution for the 1-phenyl-2-nitroguanidine molecule. The formation of donor and acceptor pairs involving the charge transfer in the molecules can be suggested from the charge distribution over the atoms.

From Table 1, it is exact to state that in the molecule 1-phenyl-2-nitroguanidine, C_1 and C_5 atoms exhibit positive charges while C_6, C_7, C_8, C_9 and C_{10} atoms exhibit negative charges. It can be seen that the C_1 and C_5 are electron deficient and similar charge distribution is obtained at these positions by both the methods. Further, N_4 nitrogen atom is more negative than the other nitrogen atoms because of electron release by the amino group. However, NO_2 group withdraws electron and hence, the electron population at N_{11} nitrogen is less and exhibit positive charge.

Table 1: Mulliken atomic charges at different atoms of 1-phenyl-2-nitroguanidine molecule computed by HF/B3LYP/methods with 6-311++G(d,p) basic sets

Atoms	HF	B3LYP	Atoms	HF	B3LYP
C_1	0.341	0.021	O_{12}	-0.195	-0.091
N_2	-0.120	-0.006	O_{13}	-0.068	-0.023
N_3	-0.371	-0.130	H_{14}	0.405	0.358
N_4	-0.526	-0.363	H_{15}	0.288	0.265
C_5	0.194	0.236	H_{16}	0.323	0.309
C_6	-0.181	-0.132	H_{17}	0.148	0.176
C_7	-0.119	-0.158	H_{18}	0.149	0.190
C_8	-0.284	-0.360	H_{19}	0.147	0.159
C_9	-0.178	-0.187	H_{20}	0.149	0.192
C_{10}	-0.083	-0.030	H_{21}	0.162	0.197
N_{11}	0.179	0.330			

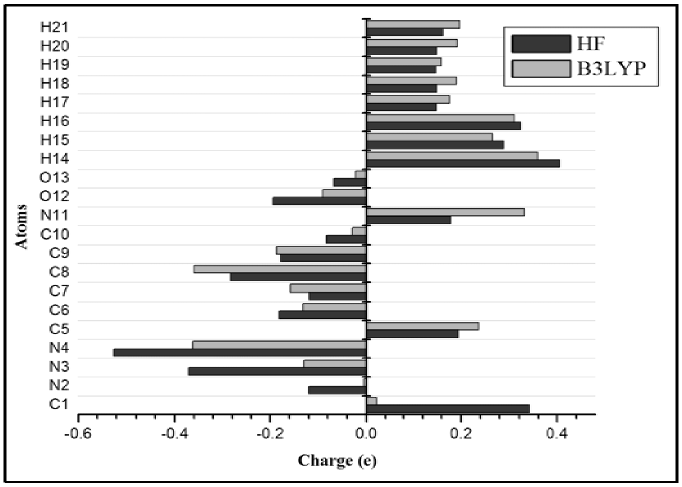

Fig. 2: Atomic charge distribution of 1-phenyl-2-nitroguanidine by HF/B3LYP methods with 6-311++G(d,p) basic sets

Hydrogen atoms in the 1-phenyl-2-nitroguanidine molecule show positive charge by both the methods. It is intriguing to observe that the values of ring hydrogen atoms are less than H_{15}, H_{16} and H_{14}, which are more electron deficient. Further, the oxygen of NO_2 group is negatively charged and the electron population is convincingly high at O_{12} and O_{13}. These observations establish the formation of intramolecular hydrogen bond in this molecule[11].

Frontier molecular orbital (FMOs)

Useful information on electronic structures of the molecule can be obtained from the molecular orbital analysis. The lowest unoccupied molecular orbital (LUMOs) and the highest occupied molecular orbital (HOMOs) are called Frontier molecular orbitals (FMOs).

FMOs have always been playing sound role in the quantum chemistry calculations. The energy gap ($\Delta E_{LUMO-HOMO}$) of a compound decides the kinetic stability, chemical reactivity and optical polarizability of the molecule.[20,21] It is predictable that larger is the energy gap of a compound, lower is the reactivity in the chemical and photochemical process with electron transfer.[22,23] The HOMO represents the ability to donate an electron and LUMO represents the ability to accept an electron.

The HOMO and LUMO energy were calculated at B3LYP/6-311++G(d,p) level of theory. The values are encapsulated as follows: HOMO (-0.2628 a.u) and LUMO (-0.0801 a.u), respectively. In addition, 3D plots of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) computed for the 1-phenyl-2-nitroguanidine compound is shown in Fig. 3.

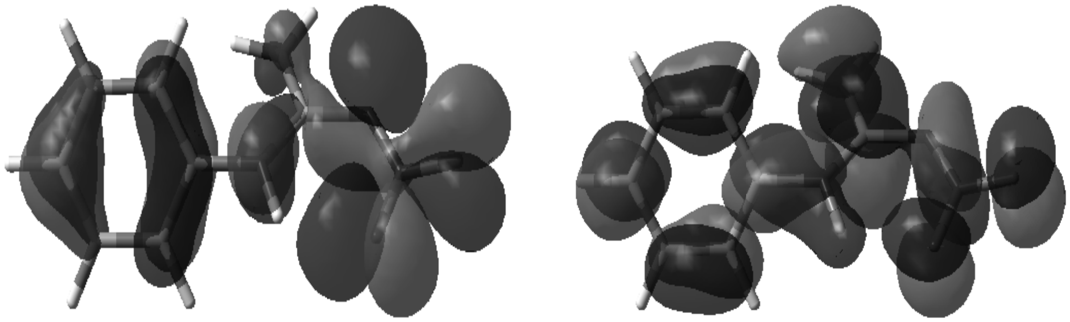
HOMO LUMO

Fig. 3: Molecular orbitals for the HOMO and LUMO of 1-phenyl-2-nitroguanidine

In the Fig. 3, the red section is positive and the negative one is green. It also shows that the HOMO and LUMO is approximately localized on the entire molecule. The energy gap between HOMO and LUMO is 0.1826 a.u. It is vibrantly evident that either C-N or N-N orbital participate in both the HOMO and the LUMO levels, indicating that the removal of an electron from the HOMO level, or inclusion of an electron to the LUMO level could deteriorate the molecular skeleton framework.

Natural population analysis

The natural population analysis performed on the electronic structure of the 1-phenyl-2-nitroguanidine molecule precisely portrays the distribution of electrons in various sub shells of their atomic orbitals. The accrual of charges on the individual atom and the accumulation of electron in the core, valence and Rydberg sub-shells are presented in Table 2.

From Table 2, it has been found that most electronegative charge of -0.84217e and -0.63621e is accumulated on N_4 and N_3 atoms and most electropositive charge of 0.64445e and 0.13002e is collected on C_1 and C_5 atom. According to electrostatic point of view of the molecule, most electronegative atoms have the inclination to donate an electron. Whereas, most electropositive atoms have the tendency to accept an electron. Hence, the natural population analysis shows that electrons in the 1-phenyl-2-nitroguanidine molecule are distributed on the sub-shell as follows:

Core : 25.99101 (99.9654% of 26)
Valence : 67.74669 (99.6275% of 68)
Rydberg : 0.26230 (0.2790% of 94)

Table 2: Accumulation of natural charges, population of electrons in core, valance, Rydberg orbitals of 1-phenyl-2-nitroguanidine

Atom No.	Natural charge (e)	Natural population (e)			
		Core	Valence	Rydberg	Total (e)
C_1	0.64445	1.99929	3.32815	0.02812	5.35555
N_2	-0.45075	1.99931	5.43007	0.02137	7.45075
N_3	-0.63621	1.99927	5.62474	0.01219	7.63621
N_4	-0.84217	1.99946	5.83015	0.01257	7.84217
C_5	0.13002	1.99894	3.85263	0.01841	5.86998
C_6	-0.24488	1.99903	4.23232	0.01353	6.24488
C_7	-0.22227	1.99912	4.20880	0.01435	6.22227
C_8	-0.24073	1.99911	4.22761	0.01402	6.24073

Cont…

Atom No.	Natural charge (e)	Natural population (e)			
		Core	Valence	Rydberg	Total (e)
C_9	-0.22355	1.99912	4.20990	0.01453	6.22355
C_{10}	-0.27250	1.99904	4.25984	0.01362	6.27250
N_{11}	0.61972	1.99969	4.33072	0.04987	6.38028
O_{12}	-0.49033	1.99982	6.47550	0.01501	8.49033
O_{13}	-0.36332	1.99981	6.34568	0.01783	8.36332
H_{14}	0.47405	0.00000	0.52112	0.00483	0.52595
H_{15}	0.42724	0.00000	0.57045	0.00230	0.57276
H_{16}	0.44139	0.00000	0.55596	0.00265	0.55861
H_{17}	0.25099	0.00000	0.74758	0.00143	0.74901
H_{18}	0.24822	0.00000	0.75045	0.00133	0.75178
H_{19}	0.24638	0.00000	0.75230	0.00132	0.75362
H_{20}	0.24736	0.00000	0.75129	0.00134	0.75264
H_{21}	0.25686	0.00000	0.74144	0.00171	0.74314

Natural bond orbital analysis

Natural bond orbital studies, provides a resourceful method for analyzing intra- and intermolecular bonding and interaction among bonds in the molecule. The NBO analysis is an appropriate source for analysing charge transfer or conjugative interaction in molecular system.

In Weinhold's NBO calculation, hyperconjugation has a stabilizing effect that arises from delocalization of electron density from filled (bonding or lone pair) Lewis type NBO to another neighboring electron deficient orbital (non-Lewis type NBO, such as antibonding or Rydberg) when these orbitals are aptly oriented. For each donor NBO (*i*) and acceptor NBO (*j*), stabilization energy can be described by means of second-order perturbation interaction energy E(2) and estimated by the following equation:

$$E(2) = \Delta E_{i,j} = q_i \frac{F\,(i,j)^2}{\varepsilon_j - \varepsilon_i} \qquad \ldots(1)$$

where q_i is the donor orbital occupancy ε_i and ε_j are diagonal elements (orbital energies) and $F_{(i,j)}$ is the off-diagonal NBO Fock matrix elements.[24]

In previous works[21,25], electron donor orbital, electron acceptor orbital and interacting stabilization energy resulting from the second-order micro-disturbance theory are reported. The larger is the *E(2)* value, the more intensive is the interaction between the ‘‘filled’’ (donor) Lewis-type NBOs and ‘‘empty’’ (acceptor) non-Lewis NBOs. To estimate the nature of bonds, we have performed detailed NBO analysis at B3LYP/6-311++G(d,p) basis set and the results obtained are tabulated as Table 3 and Table 4. The occupancies of most interacting NBO's along with their percentage of hybrid atomic orbital contributions were compiled in Table 3.

Table 3: Natural atomic orbital occupancies of most interacting NBOs of 1-phenyl-2-nitroguanidine along with their percentage of hybrid atomic orbitals

Parameters[a]	Occupancies (e)	Hybrids	AO[b] (%)
σ N_4- C_1	1.98825	$sp^{1.71}$	s(36.80%)p(63.09%)d(0.11%)
σ C_1- N_2	1.98239	$sp^{1.87}$	s(34.79%)p(65.13%)d(0.08%)
σ C_1- N_3	1.98600	$sp^{1.93}$	s(34.06%)p(65.84%)d(0.10%)
σ N_3- C_5	1.98369	$sp^{1.73}$	s(36.59%)p(63.35%)d(0.06%)
σ N_2- N_{11}	1.98917	$sp^{3.33}$	s(23.04%)p(76.73%)d(0.23%)
σ N_{11}- O_{12}	1.99640	$sp^{2.07}$	s(32.56%)p(67.33%)d(0.11%)
σ N_{11}- O_{13}	1.99531	$sp^{2.00}$	s(33.32%)p(66.58%)d(0.10%)
LP N_2	1.91253	$sp^{1.47}$	s(40.50%)p(59.38%)d(0.12%)
LP O_{12}	1.96889	$sp^{0.37}$	s(72.91%)p(27.06%)d(0.02%)
LP O_{13}	1.98211	$sp^{0.33}$	s(75.01%)p(24.97%)d(0.02%)
σ*N_4- C_1	0.02711	$sp^{1.71}$	s(36.80%)p(63.09%)d(0.11%)
σ*C_1- N_2	0.02258	$sp^{1.87}$	s(34.79%)p(65.13%)d(0.08%)
σ*C_1- N_3	0.04712	$sp^{1.93}$	s(34.06%)p(65.84%)d(0.10%)
σ*N_2- N_{11}	0.09858	$sp^{3.33}$	s(23.04%)p(76.73%)d(0.23%)
σ*N_3- C_5	0.03142	$sp^{1.73}$	s(36.59%)p(63.35%)d(0.06%)
σ*N_{11}-O_{12}	0.07969	$sp^{2.07}$	s(32.56%)p(67.33%)d(0.11%)
σ*N_{11}-O_{13}	0.05100	$sp^{2.00}$	s(33.32%)p(66.58%)d(0.10%)

[a]For numbering of atoms refer Fig. 1. [b]Percentage of s-type and p-type subshells of an atomic orbitals are given in their respective brackets

From the Table 3, the percentage of hybrid atomic orbitals of oxygen lone pair atoms O_{12}, O_{13} show that they are partially contributed to both s-type and p-type sub shells. In contrast, all the antibonding orbitals are mainly contributed to p-type sub-shell. However in case of lone pair atom, N_2 predominantly contributed to p-sub shell. The percentage of hybrid atomic orbitals of the 1-phenyl-2-nitroguanidine molecule shows that they are partially contributed to both s-type and p-type sub-shells and the antibonding orbitals are mainly contributed to p-type sub-shell.

Further, the maximum occupancy values for most interacting NBOs of 1-phenyl-2-nitroguanidine suggest that the p-character of the hybrid orbitals mainly controls the most interacting NBOs.

Table 4: Second-order perturbation analysis of the interaction between donor and acceptor orbitals of 1-phenyl-2-nitroguanidine calculated at B3LYP/6-311++G(d,p)

Donor Lewis NBO (i)	Acceptor non-Lewis NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u	F(i,j) a.u.	Donor Lewis NBO (i)	Acceptor non-Lewis NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u	F(i,j) a.u.
$\sigma C_1- N_2$	$\sigma^* N_4- C_1$	0.50	1.31	0.023	$\pi C_1- N_2$	$\sigma^* N_4- H_{15}$	0.55	0.77	0.018
	$\sigma^* N_4- H_{15}$	1.88	1.31	0.044		$\pi^* C_1- N_2$	6.14	0.30	0.038
	$\sigma^* C_1- N_3$	1.94	1.34	0.045		$\pi^* N_{11}- O_{13}$	41.03	0.21	0.084
	$\sigma^* N_3- C_5$	2.80	1.26	0.053	$\sigma N_2- N_{11}$	$\sigma^* N_4- C_1$	3.07	1.33	0.057
	$\sigma^* N_{11}- O_{13}$	2.87	1.31	0.055	$n_1 N_2$	$\sigma^* N_4- C_1$	2.67	0.83	0.042
$\sigma C_1- N_3$	$\sigma^* N_4- C_1$	0.83	1.31	0.029		$\sigma^* N_4- H_{16}$	1.00	0.85	0.026
	$\sigma^* N_4- H_{16}$	1.75	1.33	0.043		$\sigma^* C_1- N_3$	14.68	0.86	0.10
	$\sigma^* C_1- N_2$	0.96	1.37	0.032		$\sigma^* N_{11}- O_{12}$	11.03	0.76	0.082
	$\sigma^* N_3- C_5$	1.85	1.27	0.043		$\sigma^* N_{11}- O_{13}$	1.51	0.84	0.032
	$\sigma^* N_3- H_{14}$	1.23	1.32	0.036	$\sigma N_3- H_{14}$	$\sigma^* N_4- C_1$	6.64	1.1	0.076
	$\sigma^* C_5- C_6$	1.05	1.42	0.034		$\sigma^* C_1- N_3$	0.95	1.13	0.029
$\sigma N_3- C_5$	$\sigma^* C_1- N_2$	3.44	1.31	0.06		$\sigma^* N_3- C_5$	0.67	1.05	0.024
	$\sigma^* C_1- N_3$	2.00	1.28	0.045		$\pi^* C_5- C_6$	1.70	0.67	0.03
	$\sigma^* N_3- H_{14}$	0.96	1.25	0.031		$\sigma^* C_5- C_{10}$	2.52	1.20	0.049

Cont…

Donor Lewis NBO (i)	**Acceptor non-Lewis NBO (j)**	**E(2) kcal/ mol**	**E(j)- E(i) a.u**	**F(i,j) a.u.**	**Donor Lewis NBO (i)**	**Acceptor non-Lewis NBO (j)**	**E(2) kcal/ mol**	**E(j)- E(i) a.u**	**F(i,j) a.u.**
	σ*C$_5$- C$_6$	1.29	1.35	0.037	n$_1$N$_3$	π*C$_1$- N$_2$	80.72	0.25	0.126
	σ*C$_5$- C$_{10}$	1.45	1.35	0.039		σ*C$_5$- C$_6$	3.28	0.81	0.046
	σ*C$_6$- C$_7$	1.43	1.37	0.04		π*C$_5$- C$_6$	19.36	0.28	0.065
	σ*C$_9$- C$_{10}$	1.35	1.37	0.038		σ*C$_5$- C$_{10}$	3.74	0.81	0.049
n$_1$ N$_4$	σ*N$_4$- H$_{15}$	0.66	0.76	0.02	σN$_4$- C$_1$	σ*N$_4$- H$_{16}$	0.51	1.32	0.023
	σ*C$_1$- N$_2$	0.51	0.81	0.018		σ*N$_4$- H$_{15}$	0.55	1.31	0.024
	π*C$_1$- N$_2$	52.38	0.28	0.109		σ*C$_1$- N$_2$	1.17	1.36	0.036
σN$_4$- H$_{15}$	σ*C$_1$- N$_2$	3.59	1.18	0.058		σ*C$_1$- N$_3$	0.60	1.33	0.025
	π*C$_1$- N$_2$	1.39	0.66	0.027		σ*N$_2$- N$_{11}$	3.62	1.17	0.058
σC$_5$-C$_6$	σ*C$_1$-N$_3$	2.52	1.19	0.049		σ*N$_3$- H$_{14}$	1.91	1.3	0.045
	σ*N$_3$-C$_5$	0.86	1.11	0.028	σN$_4$- H$_{16}$	σ*C$_1$- N$_2$	0.55	1.17	0.023
	σ*C$_5$-C$_{10}$	3.83	1.26	0.062		σ*C$_1$- N$_3$	5.94	1.15	0.074
	σ*C$_6$-C$_7$	2.42	1.28	0.05	πC$_5$-C$_6$	σ*C$_1$-N$_3$	1.92	0.74	0.034
	σ*C$_6$-H$_{17}$	1.26	1.18	0.034		σ*N$_3$-H$_{14}$	0.91	0.72	0.023
	σ*C$_7$-H$_{18}$	2.11	1.19	0.045		π*C$_7$-C$_8$	20.99	0.29	0.069
	σ*C$_{10}$-H$_{21}$	2.12	1.18	0.045		π*C$_9$-C$_{10}$	19.44	0.29	0.067
σC$_6$-C$_7$	σ*N$_3$-C$_5$	3.91	1.11	0.059	σC$_5$-C$_{10}$	σ*N$_3$-C$_5$	0.85	1.12	0.027
	σ*C$_5$-C$_6$	2.7	1.25	0.052		σ*N$_3$-H$_{14}$	1.54	1.16	0.038
	σ*C$_6$-H$_{17}$	1.49	1.17	0.037		σ*C$_5$-C$_6$	3.85	1.26	0.062
	σ*C$_7$-C$_8$	2.47	1.27	0.05		σ*C$_6$-H$_{17}$	1.97	1.18	0.043
	σ*C$_7$-H$_{18}$	1.23	1.18	0.034		σ*C$_9$-C$_{10}$	2.54	1.28	0.051
	σ*C$_8$-H$_{19}$	2.26	1.18	0.046		σ*C$_9$-H$_{20}$	2.05	1.19	0.044
σC$_7$-C$_8$	σ*C$_6$-C$_7$	2.43	1.27	0.05		σ*C$_{10}$-H$_{21}$	1.33	1.19	0.035
	σ*C$_6$-H$_{17}$	2.39	1.17	0.047	σC$_6$-H$_{17}$	σ*N$_3$-C$_5$	0.58	0.93	0.021
	σ*C$_7$-H$_{18}$	1.31	1.18	0.035		σ*C$_5$-C$_6$	0.64	1.08	0.023
	σ*C$_8$-C$_9$	2.35	1.27	0.049		σ*C$_5$-C$_{10}$	4.26	1.08	0.06
	σ*C$_8$-H$_{19}$	1.29	1.18	0.035		σ*C$_6$-C$_7$	0.82	1.1	0.027

Cont…

Donor Lewis NBO (i)	Acceptor non-Lewis NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u	F(i,j) a.u.	Donor Lewis NBO (i)	Acceptor non-Lewis NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u	F(i,j) a.u.
	$\sigma^*C_9-H_{20}$	2.37	1.17	0.047		$\sigma^*C_7-C_8$	3.5	1.1	0.055
πC_7-C_8	$\pi^*C_5-C_6$	22.05	0.27	0.068	σC_8-C_9	$\sigma^*C_7-C_8$	2.34	1.27	0.049
	$\pi^*C_9-C_{10}$	22.36	0.27	0.07		$\sigma^*C_7-H_{18}$	2.34	1.18	0.047
σC_7-H_{18}	$\sigma^*C_5-C_6$	3.85	1.08	0.057		$\sigma^*C_8-H_{19}$	1.31	1.18	0.035
	$\sigma^*C_6-C_7$	0.68	1.1	0.024		$\sigma^*C_9-C_{10}$	2.46	1.27	0.05
	$\sigma^*C_7-C_8$	0.65	1.1	0.024		$\sigma^*C_9-H_{20}$	1.32	1.18	0.035
	$\sigma^*C_8-C_9$	3.51	1.1	0.055		$\sigma^*C_{10}-H_{21}$	2.32	1.17	0.047
σC_8-H_{19}	$\sigma^*C_6-C_7$	3.57	1.1	0.056	σC_9-C_{10}	$\sigma^*N_3-C_5$	4.36	1.11	0.062
	$\sigma^*C_7-C_8$	0.67	1.1	0.024		$\sigma^*C_5-C_{10}$	2.88	1.25	0.054
	$\sigma^*C_8-C_9$	0.69	1.1	0.024		$\sigma^*C_8-C_9$	2.52	1.27	0.051
	$\sigma^*C_9-C_{10}$	3.63	1.1	0.056		$\sigma^*C_8-H_{19}$	2.24	1.18	0.046
πC_9-C_{10}	$\pi^*C_5-C_6$	22.14	0.27	0.07		$\sigma^*C_9-H_{20}$	1.21	1.18	0.034
	$\pi^*C_7-C_8$	18.88	0.28	0.065		$\sigma^*C_{10}-H_{21}$	1.55	1.18	0.038
σC_9-H_{20}	$\sigma^*C_5-C_{10}$	3.91	1.07	0.058	$\sigma C_{10}-H_{21}$	$\sigma^*C_5-C_6$	4.15	1.08	0.06
	$\sigma^*C_7-C_8$	3.52	1.1	0.055		$\sigma^*C_5-C_{10}$	0.7	1.08	0.025
	$\sigma^*C_8-C_9$	0.66	1.1	0.024		$\sigma^*C_8-C_9$	3.5	1.1	0.055
	$\sigma^*C_9-C_{10}$	0.68	1.1	0.024		$\sigma^*C_9-C_{10}$	0.88	1.1	0.028
$\sigma N_{11}-O_{13}$	$\sigma^*C_1-N_2$	1.73	1.57	0.047	n_1O_{12}	$\sigma^*N_2-N_{11}$	6.11	1.07	0.072
$\pi N_{11}-O_{13}$	$\pi^*C_1-N_2$	4.8	0.41	0.039		$\sigma^*N_3-H_{14}$	6.09	1.2	0.076
	$\pi^*N_{11}-O_{13}$	13.09	0.32	0.058		$\sigma^*N_{11}-O_{13}$	0.68	1.21	0.026
n_2O_{12}	$\sigma^*N_2-N_{11}$	10.81	0.62	0.073	n_3O_{12}	$\pi^*C_1-N_2$	0.65	0.24	0.011
	$\sigma^*N_3-C_5$	0.59	0.7	0.018		$\pi^*N_{11}-O_{13}$	131.17	0.16	0.127
	$\sigma^*N_3-H_{14}$	18.11	0.75	0.104	n_2O_{13}	$\sigma^*C_1-N_2$	1.08	0.76	0.026
	$\sigma^*N_{11}-O_{13}$	18.73	0.76	0.106		$\sigma^*N_2-N_{11}$	17.18	0.57	0.088
n_1O_{13}	$\sigma^*N_2-N_{11}$	3.33	1.08	0.054		$\sigma^*N_{11}-O_{12}$	21.22	0.63	0.103
	$\sigma^*N_{11}-O_{12}$	2.7	1.15	0.05					

Table 4 presents the second order perturbation energies, which is otherwise called stabilization energies or interaction energies of all interacting NBOs of 1-phenyl-2-nitroguanidine. In the molecule under investigation, the hetero atom N_3 can interact with the aromatic ring. These intramolecular interactions can be established in the NBO analysis.

The resonance in the molecules is related with the most significant interaction n → σ* and n → π*. The energies of electron donating from the n_1N_3 atom of the donor groups to the antibonding acceptor σ^*C_5- C_6 (3.28 kcal/mol), σ^*C_5- C_{10} (3.74 kcal/mol) of the phenyl group shows less stabilization and further n_1N_3 to π^*C_5- C_6, π^*C_1- N_2 leads to strong stabilization energy of 19.36 kcal/mol and 80.72 kcal/mol.

This energy value shows the resonance interaction between the hetero atom and the aromatic ring. The second order perturbation energies corresponding to the hyper conjugative interaction of phenyl ring such as; $\pi C_5\text{-}C_6 \rightarrow \pi^*C_7\text{-}C_8$ (20.99 kcal/mol), $\pi C_5\text{-}C_6 \rightarrow \pi^*C_9\text{-}C_{10}$ (19.44 kcal/mol), $\pi C_7\text{-}C_8 \rightarrow \pi^*C_5\text{-}C_6$ (22.05 kcal/mol), $\pi C_7\text{-}C_8 \rightarrow \pi^*C_9\text{-}C_{10}$ (22.36 kcal/mol), $\pi C_9\text{-}C_{10} \rightarrow \pi^*C_5\text{-}C_6$ (22.14 kcal/mol) and $\pi C_9\text{-}C_{10} \rightarrow \pi^*C_7\text{-}C_8$ (18.88 kcal/mol) are considerably very large. The aforesaid hyper conjugative interactions are most responsible for the stability of the aromatic ring.

The other important interaction in this molecule is the interaction n → σ* energies, which is related to the resonance in nitroguanyl group of the molecule are electron donation from $n_1N_2 \rightarrow \sigma^*C_1$- N_3 (14.68 kcal/mol) and σ^*N_{11}- O_{12} (11.03 kcal/mol), n_1 $N_4 \rightarrow \pi^*C_1$- N_2 (52.38 kcal/mol), $n_2O_{12} \rightarrow \sigma^*N_{11}\text{-}O_{13}$ (18.73 kcal/mol), $n_2O_{13} \rightarrow \sigma^*N_2$- N_{11} (17.18 kcal/mol) and σ^*N_{11} – O_{12}(21.22 kcal/mol). These observations indicate that there is conjugative interaction within the atom in nitroguanyl group. A few non-bonding interaction of 0.65 kcal/mol and 131.17 kcal/mol are obtained for $n_3O_{12} \rightarrow \pi^*C_1$- N_2, $n_3O_{12} \rightarrow \pi^*N_{11}$- O_{13}. Also such non-bonding interactions increase the stability of a molecule as well.

One of the important hyperconjugative interactions is $n_2O_{12} \rightarrow \sigma^*N_3$- H_{14} (18.11 kcal/mol), which is responsible for intramolecular hydrogen bonding between N_3- H_{14} and O_{12} atoms. To investigate the hydrogen bonding in the molecules, the bridged hydrogen atom, which is directly involved in the intramolecular hydrogen bonding was analysed. From Table 2, the natural atomic charge value of H_{14} atom is found to be more positive than all other hydrogen atoms in the molecule suggesting the presence of intramolecular hydrogen bonding, which was reported earlier[11].

Thermodynamic properties

The principle of statistic thermodynamics is based on the scaled frequencies and thermodynamic properties such as standard molar heat capacity ($C^{\theta}_{\mathrm{p,m}}$), standard molar entropy (S^{θ}_{m}) and standard molar enthalpy (H^{θ}_{m}) ranging from 200 to 800 K are calculated using a self-compiled program to calculate their properties. The values are summed up in Table 5. It is seen that $C^{\theta}_{\mathrm{p,m}}$, S^{θ}_{m} and H^{θ}_{m} increase apparently with the rising temperature. This is because the main contributions to the thermodynamic functions are from the translation and rotation of molecules, which is comparatively higher than the contribution of vibration, when temperature is low. However, at higher temperature, the vibrations are intensified and therefore, make more contributions to the thermodynamic properties that lead to the increase in the thermodynamic functions.

The temperature-dependent relations for $C^{\theta}_{\mathrm{p,m}}$, S^{θ}_{m} and H^{θ}_{m} in the range of 200-800 K are shown in Fig. 4. It is noticeable that, as the temperature increases, the gradients of $C^{\theta}_{\mathrm{p,m}}$, and S^{θ}_{m} decrease, while that of H^{θ}_{m} increases constantly. The correlation equation between the thermodynamic functions and different temperature were also calculated. As illustrated in Fig. 4, standard molar enthalpy (H^{θ}_{m}), standard molar entropy (S^{θ}_{m}) and standard molar heat capacity ($C^{\theta}_{\mathrm{p,m}}$) correlate well with temperature and the linear correlation coefficients are 0.99404, 0.99812 and 0.96235, respectively. The data present functional information on the thermodynamic properties of the 1-phenyl-2-Nitroguanidine.

Table 5: Thermodynamic properties of the 1-phenyl-2-nitroguanidine compounds at different temperatures[a]

Temperature	H^{θ}_{m}	$C^{\theta}_{\mathrm{p,m}}$	S^{θ}_{m}
200	-640.758970	95.34	353.53
295	-640.753938	137.87	400.74
300	-640.753826	138.64	401.58
400	-640.746822	175.00	447.50
500	-640.738250	201.01	492.04
600	-640.728638	217.58	533.19
700	-640.718156	228.19	569.62
800	-640.707118	234.78	602.42

[a]Units: T : K ; $C^{\theta}_{\mathrm{p,m}}$: J.mol^{-1}; S^{θ}_{m}: J.mol^{-1}; H^{θ}_{m}: a.u

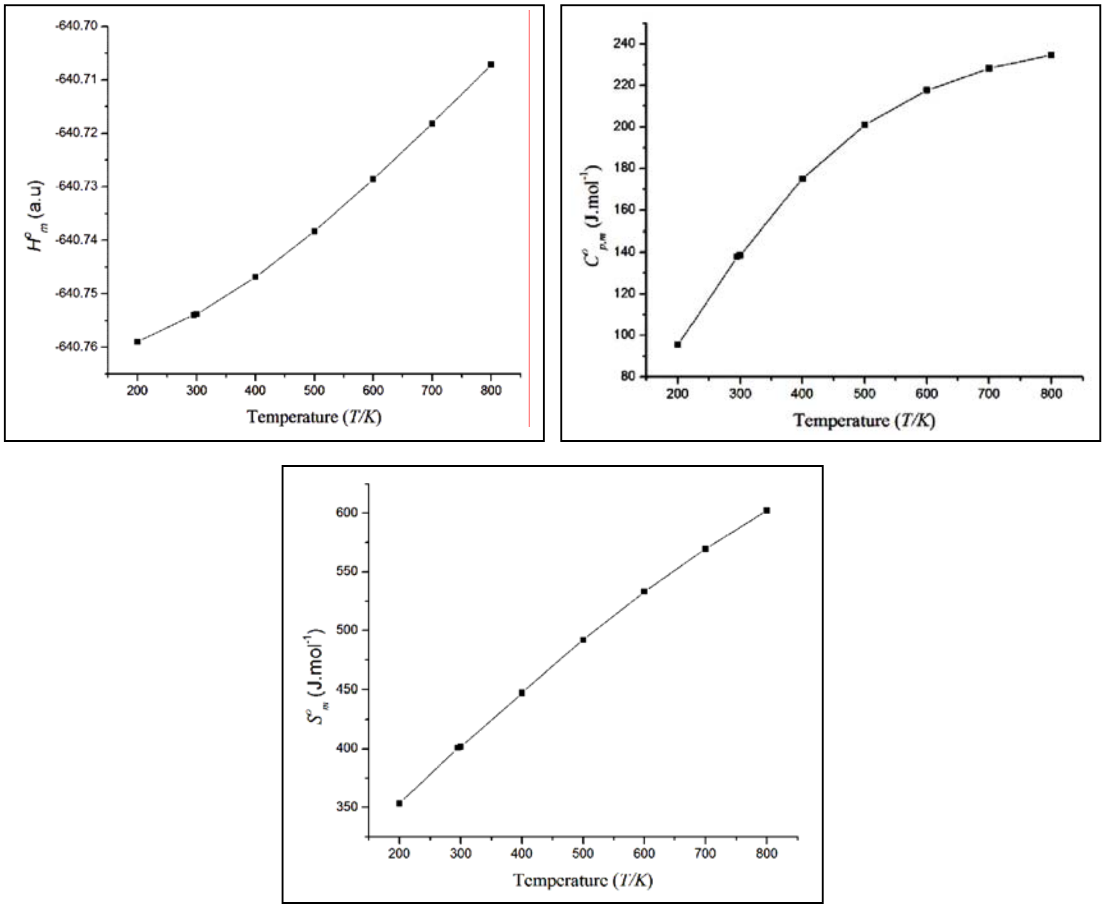

Fig. 4: Relationships between the thermodynamic functions ($C^{\theta}_{p,m}$, S^{θ}_{m}, H^{θ}_{m}) and temperature (T/K) for 1-phenyl-2-nitroguanidine at B3LYP/6-311++G (d,p) basic set

Fukui function

The hard/soft acid-base principle has been termed as an excellent predictor of chemical reactivity since ages.[26-29] Fukui function is a renowned concept in theoretical density functional theory; it has been extensively used in the prediction of reactive site. The Fukui functions can be defined in terms of the ionization potential 'I' and the electron affinity 'A' which lead to:

Nucleophilic attack: $f^{+}(r) = \rho_{N+1}(r) - \rho_{N}(r)'$ …(2)

Electrophilic attack: $f^{-}(r) = \rho_{N}(r) - \rho_{N-1}(r)'$ …(3)

where, ρ_{N-1}, ρ_N and ρ_{N+1} are the electron density of cationic, neutral and anionic species, respectively. Under the Mulliken population analysis approach, the condensed Fukui functions[30] at the atom k are,[31,32]

Nucleophilic attack: $f_k^+ = q_{N+1}^k - q_N^k$ …(4)

Electrophilic attack: $f_k^- = q_N^k - q_{N-1}^k$ …(5)

Radical attack: $f_k^o = q_{N+1}^k - (q_{N-1}^k)/2$ …(6)

Where q_{N-1}^k, q_N^k and q_{N+1}^k are the charge at atom k of the cationic, neutral and anionic species, respectively.

In the present study, single-point energy calculations were obtained for the molecular geometry optimized at B3LYP/6–311G++(d,p) level, the same level of theory have also been used for the anion and cation of the conformers using the ground state with doublet multiplicity. The atomic charge of the individual atoms calculated by Mulliken population analysis (MPA) is listed in Table 6 and is used for the Fukui functions calculation.

Table 6: The calculated Mulliken charges and Fukui indices for 1-phenyl-2-nitroguanidine molecule at B3LYP/6-311++G(d,p)

Atoms	N	N+1	N-1	f^-	f^+	f^o
C_1	0.021	0.005	-0.042	0.063	-0.016	0.024
N_2	0.006	0.138	-0.022	0.028	0.132	0.080
N_3	-0.130	-0.046	-0.138	0.008	0.084	0.046
N_4	-0.363	-0.336	-0.413	0.050	0.027	0.039
C_5	-0.072	-0.075	-0.065	-0.007	-0.003	-0.005
C_6	-0.132	-0.084	-0.194	0.062	0.048	0.055
C_7	-0.158	-0.137	-0.164	0.006	0.021	0.014
C_8	-0.360	-0.308	-0.404	0.044	0.052	0.048
C_9	-0.187	-0.154	-0.202	0.015	0.033	0.024
C_{10}	-0.030	0.010	-0.079	0.049	0.040	0.045
N_{11}	-0.330	-0.321	-0.400	0.070	0.009	0.040

Cont…

Atoms	N	N+1	N-1	f^-	f^+	f°
O_{12}	-0.091	-0.012	-0.219	0.128	0.079	0.104
O_{13}	-0.023	0.114	-0.199	0.176	0.137	0.157
H_{14}	0.358	0.380	0.336	0.022	0.022	0.022
H_{15}	0.265	0.277	0.242	0.023	0.012	0.018
H_{16}	0.309	0.343	0.271	0.038	0.034	0.036
H_{17}	0.176	0.226	0.142	0.034	0.050	0.042
H_{18}	0.190	0.253	0.137	0.053	0.063	0.058
H_{19}	0.159	0.230	0.103	0.056	0.071	0.064
H_{20}	0.192	0.255	0.139	0.053	0.063	0.058
H_{21}	0.197	0.242	0.171	0.026	0.045	0.036

Table 6 illustrates the values of the f_k^+, f_k^- and f_k^o obtained for the 1-phenyl-2-nitroguanidine molecule, as evaluated through NBO natural charges calculated at B3LYP/6-311++G(d,p) level of theory. Analysis of the f_k^+ value for the above mentioned atoms disclosed that the N_2, N_3, O_{12} and O_{13} atoms have a higher f_k^+ value, and have become the nucleophilic attack sites for 1-phenyl-2-nitroguanidine molecule. The O_{13} and N_2 atoms were the most appropriate site for nucleophilic attack. Table 6 substantiates that at the DFT level the most susceptible site of an electrophilic attack and a free radical attack is located on O_{12} and O_{13}.

Electron delocalization and HOMA

The π–electron delocalization has always influenced the physical and chemical properties of simple and complex molecules. The π–electron delocalization appears together with other similar phenomenon like aromaticity,[33] Gilli et al.[34] introduced the Q parameter for the π-electron delocalization, and the parameter Q can be calculated from the following equation.[35]

$$Q = (d_4 - d_1) + (d_2 - d_3) \qquad \ldots(7)$$

where d_1, d_2, d_3 and d_4 are bond lengths. The values of Q-parameters for the studied systems are given in Table 7. It is seen from table, the value of Q-parameter is low indicating strong delocalization in the nitrogunayl group.

Table 7: Experimental and calculated bond lengths (Å) of selected bonds of 1-phenyl-2-nitro guanidine molecule

Level	N_{11}-O_{12}	N_{11}-N_2	N_2- C_1	C_1-N_3	Q
Exp.	1.250	1.336	1.360	1.323	0.049
HF/6-311G	1.262	1.344	1.367	1.339	0.054
B3LYP	1.256	1.337	1.368	1.338	0.051

Harmonic Oscillator Measure Aromaticity (HOMA) is another geometrical parameter for describing the π-electron delocalization. The generalized HOMA can be written as[36,37].

$$HOMA = 1 - \frac{1}{n}\sum_{i=1}^{n} \alpha_i \left(R_{opt,i} - R_i\right)^2 \qquad \ldots(8)$$

where α_i is the normalization constant, n is the total number of bonds in the molecule, R_{opt} is the optimum bond length that is presumed to be realized when full delocalization of π electrons occur, and R_i is the running bond lengths. The optimal bond length values are, C–N, N-N and N-O bonds: $R_{\text{opt},i\ \text{C-N}} = 1.3340$ Å, $R_{\text{opt},i\text{N-N}} = 1.3090$ Å and $R_{\text{opt},i\text{N-O}} = 1.2480$ Å, and the normalization constant are, $\alpha_{\text{C-N}} = 93.52$, $\alpha_{\text{N-N}} = 130.33$ and $\alpha_{\text{N-O}} = 57.21$, respectively.[33]

Our earlier studies[11] show that, the 1-phenyl-2-nitroguanidine compound exhibit nonplanar structure, but contains almost two planar fragments: nitrogunayl and phenyl groups. The HOMA value for the phenyl group is 0.988 and the nitrogunayl group is 0.9575.

The HOMA index for the phenyl group is almost equal to unity, where all bonds are identical to optimal R_{opt} value and the ring is fully aromatic. For completely nonaromatic ring system, HOMA = 0 and for ring system with anti-aromatic character HOMA value is significantly negative. The higher the HOMA value, the more ‘aromatic’ is the ring and, hence, the more delocalized p electrons of the system.

First order hyperpolarizability calculations

Polarizabilities and hyperpolarizabilities of the molecule are characterized by the responses of the molecule in an applied electric field. The strength of molecular interaction, the intensities of Raman scattering, reactivity of the molecule, and many other optical properties of the molecule[38,39] are determined by their polarizabilities and hyperpolarizabilities.

Based on Finite-Field method, the polarizabilities and hyperpolarizabilities of the molecule was calculated at B3LYP/6 – 311G++(d,p) level of theory, to derive the relationships among photocurrent generation, molecular structure and NLO, The first order hyperpolarizability of the 1-phenyl-2-nitroguanidine molecule is reported in Table 8 along with other related properties.

From Table 8, the dipole moment value calculated for the molecule was found to be 7.69903 Debye at B3LYP/6 – 311G++(d,p) level of theory. The isotropic polarizabilities and polarizabilities anisotropy invariants were also calculated for the molecule at the same level of theory. The calculated anisotropy of the polarizability of 1-phenyl-2-nitroguanidine is 113.220 a.u.

Table 8: The calculated electric dipole moments (Debye), polarizability (a.u), B components and β_{tot} value (a.u) of 1-phenyl-2-nitroguanidine molecule at B3LYP/6–311G++(d,p)

Parameters	DFT/ 6-311++G(d,p)	Parameters	DFT/6-311++G(d,p)
μ_x	1.87398	β_{xxx}	-48.26201
μ_y	-7.14232	β_{yxx}	-12.62441
μ_z	2.17956	β_{xyy}	186.13369
μ	7.69903	β_{yyy}	-188.14824
α_{xx}	127.107	β_{zzz}	6.14685
α_{xy}	-34.559	β_{xzz}	-4.68149
α_{yy}	160.127	β_{yzz}	6.75436
α_{xz}	8.184	β_{zxx}	72.78391
α_{yz}	-3.084	β_{zyy}	-18.97236
α_{zz}	52.427	β_{xyz}	-65.24566
α_0	113.220	β_{tot}	137.62937

The magnitude of the molecular hyperpolarizability β is one of key factors in a NLO system. The first order hyperpolarizability value (β_0) calculated at B3LYP/6–311G++(d,p) level for the molecule is 137.62937 a.u. Total dipole moment of 1-phenyl-2-nitroguanidine molecule is slightly greater than the 2-nitroguanidine molecule. This result suggests that the molecule 1-phenyl- 2-nitroguanidine is nonlinear.

CONCLUSION

The present study discusses the delocalization patterns of charge and electron densities of atoms of 1-phenyl-2-nitroguanidine that have been explained by performing molecular orbital simulations at density functional B3LYP method with standard 6–311G++(d,p) basis set. The charge transfer occurs within the molecule is substantiated by the Mulliken atomic charges analysis. The natural population analysis on the 1-phenyl-2-nitroguanidine compound completely illustrates the accumulation of electrons in core, valence and Rydberg sub-shell of their atomic orbitals. The natural hybrid atomic orbitals performed in this study enable us to know about sub-shell type, the contribution of specified atomic electrons to s-type and p-type sub-shells and their hybridization details.

The NBO analysis has provided the details of the type of hybridization and the nature of bonding in 1-phenyl-2-nitroguanidine. The second order perturbation results received in this study showed the most significant hyperconjugative interactions responsible for the stability of a molecule. It also showed that a non-bonding interaction takes place from the lone pair oxygen atom O_{12} to antibonding π^*C_1- N_2 and π^*N_{11}- O_{13} increases the stability of the molecule. From the first order hyperpolarizability values, it is predicted that the molecule might have a reasonably good NLO behavior.

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Revised : 13.07.2016 *Accepted : 15.07.2016*