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## Study of the molecular properties and natural bond orbital analysis of some acyloxy nitroso compounds by density functional theory method

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### ABSTRACT

Acyloxy nitroso compounds as new HNO donors can hydrolyze to nitroxyl, a nitrogen monoxide with distinct chemistry and biology. Many acyloxynitroso compounds, illustrate a bright brilliant blue color because of their  $n \rightarrow \pi^*$  electronic transition. In the present work, we are attempting to study the bonding natures of acyloxynitroso compounds by using density functional theory at the B3LYP level. Calculations of quantum chemical were performed with 6-31G (d, p) basis set implemented in Gaussian09 program. Obtained geometries from calculations of density functional theory were used to carry out Natural bond orbital analysis. In this analysis, stabilization energy related to the delocalization trend of electrons from donor to acceptor orbitals, was calculated. If the stabilization energy  $E^{(2)}$  between a donor bonding orbital and an acceptor orbital is big, then there is a powerful interaction between them. The great stabilizing efficacy is due to the strong orbital interactions between the lone pair orbitals of O (8) and  $\pi$  antibonding  $C_9-O_{11}$ . The redistribution of electron density in various bonding and antibonding orbitals and  $E^{(2)}$  energies have been calculated by natural bond orbital analysis using DFT method to give clear evidence of stabilization originating from the hyperconjugation of different intramolecular interactions.

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### KEYWORDS

Acyloxy nitroso;  
Density functional theory (DFT);  
Natural bond orbital (NBO);  
Stabilization energy.

### INTRODUCTION

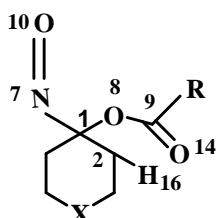
HNO is a serious biological agent and is *appropriate* for treatment of heart failure<sup>[1,2]</sup>. Also Nitroxyl (HNO) can react with heme of proteins that these reactions probably interfere biological actions of hemoglobin<sup>[3]</sup>. Nitroxyl must be generated from donors due to its fast dimerization to nitrous oxide<sup>[4]</sup>. Acyloxy nitroso

compounds as new type of HNO donors that has been introduced by Sha et al. which release HNO<sup>[5]</sup>. The privilege of these HNO donors is controlling of the HNO release rate. Acyloxy nitroso compounds hydrolyze to nitroxyl (HNO), a nitrogen monoxide with suitable chemical and biological properties<sup>[6]</sup>. Another *specifications* of these group of nitroso compounds is their blue color that is achieved due to  $n \rightarrow \pi^*$  electronic

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transition of the N–O bond<sup>[7,8]</sup>. this property of Acyloxy nitroso compounds mention that the comparatively low energy LUMO is affiliated with this bond and is sensitive to nucleophilic attack<sup>[9]</sup>.

Anandan et al. investigated molecular structure and conformational stability of 5-nitrososofuran and 5-nitrososofuran molecules using ab initio and density functional theory methods<sup>[10]</sup>. Theoretical study of many S-Nitroso-thiophenols has been carried out using B3PW91 and B3LYP levels by Xiao-Hong et al<sup>[11]</sup>. Natural bond orbital (NBO) analysis of several N-nitroso-N, N-dimethylphenylurea biological compounds have been investigated with DFT in MeCN solution by Zhou Zhang and et al<sup>[12]</sup>. Jacquemin with TD-DFT calculations on various nitroso dyes indicated transitions  $n$  to  $\pi^*$ <sup>[13]</sup>. Theoretical studies on N-nitrosocarbamates, a class of ambient nucleophiles have been performed by Vladimir Benin<sup>[14]</sup>. Since so far any theoretical data and analysis of the nature of the bonding on the structure of acyloxynitroso compounds has been published. In this work, we are trying to study the bonding natures and transitions of some acyloxy nitroso compounds based on natural bond orbital (NBO) analysis by using density functional theory at the B3LYP level of theory in both gas and water phases.



Compound	R	X
1	CH <sub>3</sub>	CH <sub>2</sub>
2	C(CH <sub>3</sub> ) <sub>3</sub>	CH <sub>2</sub>
3	CF <sub>3</sub>	CH <sub>2</sub>
4	CH <sub>3</sub>	O
5	C(CH <sub>3</sub> ) <sub>3</sub>	O

Figure 1 : Structures of acyloxynitroso compounds

### COMPUTATIONAL METHODS

All geometry optimizations were fully carried out without any symmetry restrictions, in both gas and water phases, using the B3LYP theoretical method<sup>[15-17]</sup>. The quantum chemical calculations were performed with

the 6-31G basis set fulfilled in the Gaussian09 program<sup>[18]</sup>. The resulting geometries were then confronted as minima by frequency calculations. Also, the computation of the second order perturbation of interaction energy at the optimised geometries for several of acyloxy nitroso compounds was carried out using the NBO analysis.

Natural bond orbital (NBO) analysis emanated as a technique for studying hybridisation, covalent and non-covalent effects in polyatomic wave functions<sup>[19]</sup>. NBO analysis is based on a method for optimally transforming a given wave function into a localised form, corresponding to the one-centre (lone pairs) and two-centre (bonds) elements of the chemist's Lewis structure illustration. In NBO analysis, the input atomic orbital basis set is converted with natural atomic orbitals and hybrids to natural bond orbitals. NBO analysis emphasises on intermolecular orbital interactions especially charge transfer in complexes. This is performed by checking all feasible interactions between empty acceptor and filled donor NBOs and estimation their energetic significance by second-order perturbation approach. Lone pair electron and antibonding interaction can be quantitatively depicted in terms of the NBO method that is interpreted via the second order perturbation interaction energy ( $E^{(2)}$ )<sup>[20-23]</sup>.  $E^{(2)}$  shows the approximation of the off-diagonal NBO Fock matrix elements. For each acceptor NBO ( $j$ ) and donor NBO ( $i$ ), the stabilisation energy intercommunicated with electron delocalisation between the acceptor and the donor is defined as:

$$E^{(2)} = -q_i \frac{(F_{ij})^2}{\epsilon_i - \epsilon_j} \quad (1)$$

Where  $\epsilon_i$  and  $\epsilon_j$  are diametric elements (orbital energies),  $q_i$  is the donor orbital occupation and  $F_{ij}$  is the off-diametric NBO Fock matrix element<sup>[24,25]</sup>.

### RESULTS AND DISCUSSION

The optimized structures and conformational stability obtained by the DFT method for acyloxy nitroso compounds have been studied. The substitution of R group and replacement of carbon with oxygen little affects the bond length and angles of acyloxy nitroso compounds. TABLE 1 indicates the calculated quantum chemical parameters which are relevant to the molecular electronic structure of the molecules, including

**TABLE 1 : Calculated ionization energy, I, electroaffinity energy, A, gap energy,  $\Delta E$ , hardness,  $\eta$  (in Hartree), dipole moment,  $\mu$  (in Debye) for the gas phase at B3LYP/6-31G (d) level of theory**

No.	1	2	3	4	5
HOMO	-0.1804	-0.2984	-0.3118	-0.1849	-0.2728
LUMO	0.1372	0.1106	0.1121	0.1298	0.1240
Dipole Moment	2.5884	2.8560	2.3153	2.3940	2.3536
Ionization Energy	0.1804	0.2984	0.3118	0.1849	0.2728
Electron Affinity Energy	-0.1372	-0.1106	-0.1121	-0.1298	-0.1240
Softness	6.2966	4.8890	4.7175	6.3532	5.0395
Hardness	0.1588	0.2045	0.2119	0.1574	0.1984
Gap energy	-0.3176	-0.4090	-0.4239	-0.3148	-0.3968

**TABLE 2 : Second-order interaction energies ( $E^{(2)}$ , kcal/mol) and partial electron transfer (Q) between donor and acceptor orbitals in acyloxy nitroso compounds, at B3LYP/6-31G (d) level of theory (gas phase)**

No.	Donor	Acceptor	$E^{(2)}$ (kcal/mol)	$E(j)-E(i)$ (a.u)	$F(i,j)$ (a.u)	Q(me)
1	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	3.97	0.82	0.052	0.1920
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	3.69	0.84	0.050	0.1977
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	44.96	0.34	0.11	0.2014
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	30.97	0.61	0.124	0.1959
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	17.02	0.64	0.095	0.1925
2	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	4.92	0.76	0.055	0.1971
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	3.92	0.69	0.047	0.1952
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	19.38	0.62	0.098	0.1995
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	42.37	0.35	0.109	0.1990
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	32.05	0.35	0.094	0.2024
3	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	3.93	0.82	0.051	0.1976
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	3.53	0.81	0.049	0.1899
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	17.25	0.28	0.062	0.2004
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	44.08	0.36	0.113	0.1982
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	29.39	0.37	0.093	0.2005
4	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	4.05	0.82	0.052	0.1958
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	3.92	0.80	0.050	0.2000
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	15.30	0.61	0.086	0.2012
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	44.68	0.34	0.110	0.2002
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	31.05	0.61	0.124	0.1964
5	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	3.92	0.80	0.050	0.2001
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	3.72	0.71	0.046	0.1990
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	15.36	0.61	0.087	0.1974
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	44.25	0.34	0.110	0.1983
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	30.45	0.62	0.121	0.2056

ionisation potential (I), electron affinity (A), dipole moment ( $\mu$ ), gap energy and hardness ( $\eta$ ). I and A values were computed by means of Koopmans' theorem<sup>[26]</sup>. This theorem appoints a relationship between LUMO and HOMO with the electron affinity and the ionisation potential, respectively. Although there is not a nominal

argument of Koopmans theorem by DFT method, its validity is usually admitted. The received amounts of I and A were used for the calculation of the electronegativity  $\chi$  and global hardness  $\eta$  in each of the molecules. According to the TABLE 1 the highest values of  $I = -E_{\text{HOMO}}$  show the trend of  $3 > 2 > 5 > 4 > 1$ . The calcula-

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**TABLE 3 : Second-order interaction energies ( $E^{(2)}$ , kcal/mol) and partial electron transfer ( $Q$ ) between donor and acceptor orbitals in acyloxy nitroso compounds, at B3LYP/6-31G (d) level of theory (water phase)**

No.	Donor	Acceptor	$E^{(2)}$ (kcal/mol)	$E(j)-E(i)$ (a.u)	$F(i,j)$ (a.u)	$Q$ (me)
1	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	3.75	0.84	0.05	0.2009
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	4.10	0.81	0.052	0.1959
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	45.38	0.34	0.111	0.1997
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	30.70	0.62	0.124	0.1974
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	16.51	0.65	0.094	0.1937
2	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	4.13	0.54	0.042	0.2016
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	4.23	0.77	0.051	0.1997
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	17.33	0.59	0.091	0.1969
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	43.88	0.34	0.106	0.2117
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	35.52	0.62	0.133	0.1985
3	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	3.77	0.55	0.041	0.1967
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	3.81	0.75	0.048	0.1978
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	50.44	0.33	0.116	0.1972
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	32.75	0.65	0.132	0.1948
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	25.35	0.57	0.108	0.1976
4	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	3.95	0.85	0.052	0.1980
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	4.16	0.81	0.053	0.19132
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	45.66	0.34	0.11	0.2046
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	30.79	0.62	0.124	0.1980
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	16.46	0.65	0.094	0.1931
5	$\sigma(C_2-H_{16})$	$\sigma^*(C_1-N_7)$	3.96	0.55	0.042	0.1969
	$\sigma(C_2-C_5)$	$\sigma^*(C_1-O_8)$	3.87	0.81	0.05	0.1999
	LP (2)O <sub>8</sub>	$\pi^*(C_9-O_{14})$	17.47	0.59	0.092	0.1942
	LP (2)O <sub>14</sub>	$\sigma^*(O_8-C_9)$	44.09	0.34	0.109	0.2012
	LP (2)O <sub>14</sub>	$\sigma^*(C_9-C_{10})$	35.62	0.61	0.133	0.1959

tions show that molecule 3 had the highest HOMO levels. Higher values of  $E_{\text{HOMO}}$  are likely to indicate potential of the molecule to forgive electrons to the appropriate acceptor molecule of low unoccupied molecular orbital energy. R=C(CH<sub>3</sub>)<sub>3</sub> substitution increased the dipole moment of molecule 1 and R=CF<sub>3</sub> decreased it. So, these groups can advance the polarity and solubility of the acyloxy nitroso compound in the biochemistry surroundings. Consideration of the gap energies of nitroso compounds display that the CF<sub>3</sub> and C(CH<sub>3</sub>)<sub>3</sub> groups caused the greatest decrease in the gap energy.

Natural bonding orbitals (NBO) calculations were performed using the Gaussian 09 package with DFT method at B3LYP level until understand various second-order interactions between the occupied orbitals and the unoccupied orbitals of system, which is a criterion of hyperconjugation or intermolecular

delocalisation. NBO analysis supplies the most accurate possible natural Lewis structure, because all orbital information is numeral chosen to include the highest feasible percent of the electron density. An important characteristic of the NBO method is that it gives us information about interactions in both virtual orbital and filled spaces that could appointed the analysis of inter and intra-molecular interactions. The interactions cause in absence of occupation from the localised NBO of the idealised Lewis structure into an nonoccupied non-Lewis orbital. In the NBO analysis, the general alteration to NBOs leads to orbitals that are unoccupied in the nominal Lewis structure. As a result, the filled NBOs of the natural Lewis structure are well adapted to describe covalence effects in these compounds. Since the non-covalent delocalization factors are intercommunicated with interactions between filled and unfilled orbitals. It is normal to explain them as being of donor to

acceptor charge transfer, or generalized Lewis acid-Lewis base type. Antibonding display unused valence shell capacity and palming fractions of the atomic valence space that are formally unsaturated by covalent bond formation.

Weak occupancies of the valence antibonding signal irreducible departures from an idealized localized Lewis picture, namely delocalization effects. Thereupon, in the NBO analysis, the donor-acceptor (bonding-antibonding) interactions are taken into consideration by examining all possible interactions between donors Lewis-type NBOs. The stabilisation energy,  $E^{(2)}$ , supplies a quantitative standard of the stability of the interaction between an electron donor and the receptor. *With higher the values of  $E^{(2)}$* , stronger interactions are between the electron donor orbital  $i$  and receptor orbital  $j$ , that is to say,  $i$  has a more tendency to enable an electron to  $j$  and the grade of electron delocalisation is greater. NBO analysis relies on the role of interarmolecular interactions in the acyloxy nitroso compounds. According to the values of stabilisation energy in TABLE 2, in most compounds, the antibonding orbitals of the acceptor can interact with the lone pair of O (8) and O (14) of the acyloxy nitroso compounds as the donor orbital. The data display that the calculated stabilisation energy,  $E^{(2)}$ , for the acyloxy nitroso compounds is normally due to the interaction of the antibonding orbitals with the lone pair electrons of O (8) and O (14). The greatest  $E^{(2)}$  values appear in the  $LP(2)O_8 \rightarrow \pi^*(C_9-O_{14})$  interaction. This designates that the modality of this interaction is the O (8) atom of offering its lone pair electrons to  $\pi^*(C_9-O_{14})$ .

As predicted for nitroso compounds, the electronic excitation responsible for the color presents a typical  $n \rightarrow \pi^*$  character associated to a small oscillator force. Many acyloxy nitroso compounds, normally demonstrate a brilliant bright blue color due to their  $n \rightarrow \pi^*$  electronic transition. This interaction is the most important interaction in the acyloxy nitroso compounds. The polarized continuum model (PCM) developed by Tomasi and coworkers<sup>[27]</sup> was employed. In this PCM model, the atomic radii of the spheres used to build the molecular cavity were adjusted by introducing chemical consideration such as hybridization, formal charge, and the first neighbor inductive effect. The effect of the escaped electronic charge outside the cavity was corrected for with an additional set of charges on the cav-

ity surface, distributed according to the solute electronic density in each point of the surface. In water gas,  $LP(2)O_8 \rightarrow \pi^*(C_9-O_{14})$  and  $LP(2)O_{14} \rightarrow \sigma^*(O_8-C_9)$  interactions have the greatest of  $E^{(2)}$  values which the first transition in many acyloxy nitroso compounds, typically demonstrate a brilliant bright blue color due to their  $n \rightarrow \pi^*$  electronic transition.

## CONCLUSIONS

Acyloxy nitroso compounds release HNO through hydrolysis and nitroxyl (HNO) has emerged as a unique nitrogen monoxide demonstrating different chemistry and biology. The optimized structural, energetical parameters determined by the DFT method for acyloxy nitroso compounds. Also NBO analysis was performed that strong interaction  $LP(2)O_8 \rightarrow \pi^*(C_9-O_{14})$  typically demonstrate a brilliant bright blue color due to their  $n \rightarrow \pi^*$  electronic transition.

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