Front. Chem. China 2011, 6(2): 69–75
DOI 10.1007/s11458-011-0231-z

RESEARCH ARTICLE

Theoretical investigation of some O-nitrosyl carboxylate biologic molecules — A natural bond orbital study

Ruizhou ZHANG[1], Zhenguo LI[2], Xiaohong LI (✉)[1] and Xianzhou ZHANG[3]

Theoretical study of several O-nitrosyl carboxylate compounds have been performed using quantum computational ab initio RHF and density functional B3LYP and B3PW91 methods with 6-31G basis set. Geometries obtained from DFT calculations were used to perform the natural bond orbital (NBO) analysis. It is noted that weakness in the O_3-N_2 bond is due to $n_{O_1} \rightarrow \sigma^*_{O_3\text{-}N_2}$ delocalization and is responsible for the longer O_3-N_2 bond lengths in O-nitrosyl carboxylate compounds. It is also noted that decreased occupancy of the localized $\sigma_{O_3\text{-}N_2}$ orbital in the idealized Lewis structure, or increased occupancy of $\sigma^*_{O_3\text{-}N_2}$ of the non-Lewis orbital, and their subsequent impact on molecular stability and geometry (bond lengths) are related with the resulting *p* character of the corresponding sulfur natural hybrid orbital (NHO) of $\sigma_{O_3\text{-}N_2}$ bond orbital. In addition, the charge transfer energy decreases with the increase of the Hammett constants of subsitutent groups.**

Keywords natural bond orbital (NBO), O-nitrosyl carboxylate compounds, second order delocalization energies, natural hybrid

1 Introduction

Nitric oxide (NO) is one of the smallest known biologically active messenger molecules and plays key roles in regulating many important physiologic functions in living bodies [1–4]. To understand the physiologic activities of NO as a biologic second messenger, it is obviously essential to have some knowledge of the chemical fundamentals that govern those functions at the molecular level. Since NO is such a small diatomic molecule and is expected not to be too strongly affected by steric or molecule shape-dependent recognition factors that large molecules often encounter, the binding force of NO with a particular active site can therefore be represented by the bond energy of the Y-NO type, where Y represents the atom in a carrier to which NO is directly attached. In other words, the Y-NO bond energy should play a key role in directing NO to migrate. However, due to a lack of the means for effectively separating the interference of the secondary bond rupture in gas-phase measurement, no bond information for relatively large organic molecules has been provided in literature. This has spurred us to initiate research on the Y-NO bond energies of molecules in solution. (Note that most NO-related chemical and biologic reactions occur in the condensed phase).

As a unique class of such NO-carrying vehicles, O-nitrosyl carboxylate compounds are generally believed to take a most active part in many biologic functions of nitric oxide, especially in the processes of NO-storage, transport, and delivery [5]. Casado et al. [6] showed that nitrosation of the amino group in amino acids proceeded via the initial formation of nitrosyl carboxylate (-COONO), followed by an intramolecular NO migration from oxygen to nitrogen. The use of nitrite compounds as NO donors in many chemical and biologic reaction systems has also long been recognized [7,8]. It is therefore believed that the quantitative measures of the O-NO bond information in the present study may serve as a guide for selecting efficient NO donor compounds and for a more insightful understanding of relevant NO-involving reactions.

Recently we have reported the best method to compute the bond dissociation energies of the O-NO bond in O-nitrosyl carboxylate compounds [9]. However, our library survey showed that there are no published experimental or theoretical data on the structure of some O-nitrosyl carboxylate compounds. In addition, to the best of our knowledge, we have not seen the analysis of bond natures of some O-nitrosyl carboxylate compounds.

In the present work, we attempted to study the thermodynamic stabilities and bonding natures of some O-nitrosyl carboxylate compounds using RHF and density functional theory at the B3LYP and B3PW91 level of theory throughout with the 6-31G** basis set implemented in the Gaussian03 program suite [10]. Geometries obtained from DFT calculations were then used to perform the natural bond orbital (NBO) analysis briefly describing the basic idea of the natural atomic orbitals (NAO) and NBOs analysis as the use of one electron density matrix to define the shape of the atomic

Received January 21, 2011; accepted February 11, 2011
1. College of Physics and Engineering, Henan University of Science and Technology, Luoyang 471003, China
2. School of Mathematics and Statistics, Henan University of Science and Technology, Luoyang 471003, China
3. College of Physics and Information Engineering, Henan Normal University, Xinxiang 453007, China
E-mail: lorna639@126.com

orbitals in the molecular environment, and were used to drive molecular bonds from electron density between atoms. Finally, the relative stabilities and the nature of the central bonds in some O-nitrosyl carboxylate compounds were systematically and quantitatively investigated by the NBO analysis method.

2 Computational methods

All geometry optimizations were fully carried out without any symmetry limitation using RHF, B3LYP, B3PW91 methods [11–15]. All calculations were performed with 6-31G** basis set implemented in G03 program. The resulting geometries were then verified as minima by frequency calculations.

NBO analysis was then performed by the NBO 3.1 program [16] included in GAUSSIAN 03 package of programs at RHF, B3LYP and B3PW91 level of theory. In this context, a study of hyperconjugative interactions has been completed. Hyperconjugation may be given as a stabilizing effect that arises from an overlap between an occupied orbital with another neighboring electron deficient orbital when these orbitals are properly oriented. This noncovalent bonding-antibonding interaction can be quantitatively described in terms of the NBO approach that is expressed by means of the second-order perturbation interaction energy $(E^{(2)})$ [17–20]. This energy represents the estimate of the off-diagonal NBO Fock matrix elements. It can be deduced from the second-order perturbation approach [21]

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

where q_i is the ith donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies), and $F(i,j)$ is the off-diagonal NBO Fock matrix element.

3 Results and discussion

3.1 Geometry optimization

The selected O-nitrosyl carboxylate compounds are listed in Fig. 1. All of the optimized structural characteristics calculated for the selected compounds in the ground state at the RHF, B3LYP and B3PW91 levels of theory are reported in Table 1. 6-31G** basis set is used.

As can be seen from Table 1, the two DFT methods used in this study have resulted in very similar values for the related bond lengths and angles. However, their results are slightly different from those obtained by RHF method. The bond lengths calculated by RHF method are the shortest among the three computational methods, while the bond angles calculated are the largest among the selected methods except the O_3-C_4-O_5 bond angle. For the selected compounds, the longest bond length is calculated by B3LYP method. From Table 1, it is also noted that CH_3COO-NO has the longest N_2-O_3 bond length, while 4-H-PH-COO-NO has the shortest N_2-O_3 bond length.

An interesting point observed in the selected molecules was the change of the bond length and angle with the Hammett constants of substituent group on HCOONO. The Hammett constants [22] of CH_3, C_2H_5, $(CH_3)_2CH$ and phenyl groups are -0.17, -0.15, -0.11 and -0.01, respectively. It is noted that the N_2-O_3 bond length and the O_3-C_4-O_5 bond angle decrease with the augment of Hammett constants, while the C_4-O_5 bond length increases with the increase of Hammett

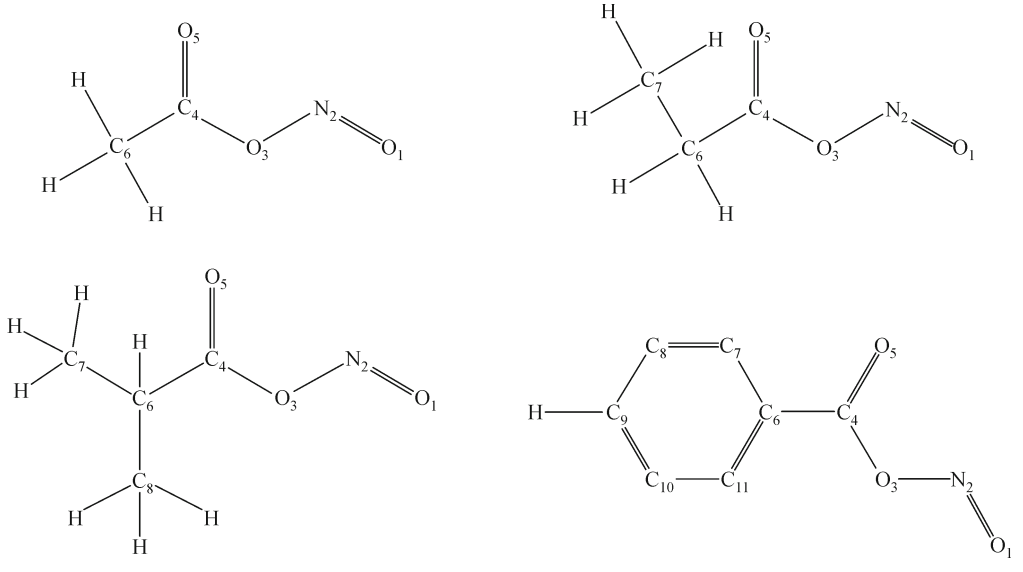

Figure 1 The selected O-nitrosyl carboxylate compounds

constants. The listed dihedral angles are either 0° or 180° at RHF/6-31G**, B3LYP/6-31G** and B3PW91/6-31G** level except the O_5-C_4-C_6-C_7 dihedral angle of $(CH_3)_2CHCOO$-NO, which indicates that the atoms are in a plane.

3.2 Character of NHO on the selected compounds

A natural atomic orbitals (NAO) is defined as a valence-shell atomic orbital derived from the diagonalization of the localized block of the full density matrix of a given molecule, associated with basis functions $\chi_i(A)$ on that atom, and fulfilling the simultaneous requirement of ortho-normality and maximum occupancy. Although in an isolated atom, NAOs coincide simply with natural orbitals, in polyatomic molecule (in contrast to natural orbitals that become delocalized over all nuclear centers); the NAOs mostly retain one-center character. Consequently, NAOs are considered optimal for describing the molecular electron density around one-center in polyatomic molecules. Also, a NHO result from a symmetrically orthogonalized directed hybrid orbital derived through unitary transformation of NAO centered on a particular atom. Finally, according to the simple bond orbital picture, a natural bond orbital (NBO) is defined as an orbital formed from NHOs. Therefore, for a localized r-bond between atoms A and B, the NBO is defined as:

$$\sigma_{AB} = c_A h_A + c_B h_B \quad (2)$$

where h_A and h_B are the natural hybrids centered on atoms A and B, respectively. The NBOs closely correspond to the picture of localized bonds and lone pairs as basic units of molecular structure, and therefore it will be possible to interpret conveniently ab initio wave functions in terms of the classical Lewis structure concepts by transforming these functions to the NBO forms [23].

In Table 2, we present the resulting natural atomic hybrids h_A on some atoms with the polarization coefficient c_A for each hybrid (in parentheses) in the corresponding NBO. The inspection of the results reported in Table 2 reveals that:

- The p characters of oxygen NHO$\sigma_{N_2\text{-}O_3}$ and nitrogen NHO$\sigma_{N_2\text{-}O_3}$ bond orbitals decrease with increasing Hammett constants of substituent group on HCOONO.
- The p characters of oxygen NHO$\sigma_{O_1\text{-}N_2}$ and nitrogen NHO$\sigma_{O_1\text{-}N_2}$ bond orbitals don not change with increasing Hammett constants of substituent group on HCOONO.
- The decreasing p characters on oxygen NHO$\sigma_{N_2\text{-}O_3}$ and nitrogen NHO$\sigma_{N_2\text{-}O_3}$ bond orbitals result in a shortening of the O_3-N_2 bond.
- Small and nearly equal values of the calculated d contribution of O_3 atom show that 3d orbitals have little importance in bonding of the aliphatic O-nitrosyl carboxylate compounds.

The NBO [23] analysis shows that there is a strong hyperconjugative interaction $n_{O_1} \rightarrow \sigma^*_{O_3\text{-}N_2}$ in the compounds studied (Table 3). For example, the second order energy $(E^{(2)})$ for CH_3COO-NO is 63.26 kcal/mol at B3LYP level. This interaction weakens the O_3-N_2 bond and elongates the O_3-N_2 bond length in the selected O-nitrosyl carboxylate compounds. In addition, it is found that these compounds are characterized by strong $n_{O_3} \rightarrow \sigma^*_{N_2=O_1}$ delocalization, which induces partial π character. From Table 3, it is noted that $E^{(2)}$ decreases with increasing Hammett constant of substituent group, which results in shortening of the O_3-N_2 bond. The second order delocalization energies for CH_3COONO, CH_3CH_2COONO, $(CH_3)_2CHCOONO$, 4-H-PHCOONO at B3LYP level are 63.26, 63.00, 62.72, 62.07 kcal/mol, respectively. And the O_3-N_2 bond lengths are 1.5258, 1.5247, 1.5234, 1.5229Å, respectively. The above analysis indicates that the weakness in the O_3-N_2 bond is due to $n_{O_1} \rightarrow \sigma^*_{O_3\text{-}N_2}$ delocalization and is responsible for the longer O_3-N_2 bond lengths, thereby contributing to the nitro oxide releasing ability in the selected O-nitrosyl carboxylate compounds, though the O_3-N_2 bond has partial double bond and character.

In the NBO analysis [23], the direction of a hybrid is specified in terms of the polar and azimuthal angles of the vector describing its p-component. The hybrid direction is then compared with the direction of the line of centers between the two nuclei to determine the bending of the bond, expressed as the deviation angle (Dev, in degrees) between these two directions. In our present study, for $n_{O_1} \rightarrow \sigma^*_{O_3\text{-}N_2}$ of CH_3COONO, N_2 NHO of O_3-N_2 bond is bent away from the line of O_3-N_2 centers by 5.0 (which is the biggest deviation angle in the molecule), whereas O_3 NHO is bent away from the line of O_3-N_2 centers by 2.2. The information is often useful in anticipating the direction of geometry changes resulting from geometry optimization. For CH_3CH_2COONO, $(CH_3)_2CHCOONO$, and 4-H-PHCOONO, N_2 NHO and O_3 NHO of O_3-N_2 bond are bent away from the line of O_3-N_2 centers by 5.0 and 2.3, 4.9 and 2.2, 4.9 and 2.1, respectively.

3.3 Donor-acceptor (bond-antibond) interactions

In the NBO analysis [23], in order to compute the span of the valence space, each valence bonding NBO (σ_{AB}), must in turn, be paired with a corresponding valence antibonding NBO (σ^*_{AB}):

$$\sigma^*_{AB} = c_A h_A - c_B h_B \quad (3)$$

Namely, the Lewis σ-type (donor) NBOs are complemented by the non-Lewis σ^*-type (acceptor) NBOs that are formally empty in an idealized Lewis structure picture. Readily, the general transformation to NBOs leads to orbitals that are

Table 1 The related bond lengths/Å and bond angles/(°) calculated for the selected O-nitrosyl carboxylate compounds using RHF, B3LYP and B3PW91 levels of theory with 6-31G** basis set

Parameter	CH_3COO-NO			CH_3CH_2COO-NO			4-H-PH-COO-NO			$(CH_3)_2CHCOO$-NO		
	RHF	B3LYP	B3PW91	RHF	B3LYP	B3PW91	RHF	B3LYP	B3PW91	RHF	B3LYP	B3PW91
E(Hartree)	−356.3626	−358.2984	−358.1591	−395.3712	−397.5874	−397.4342	−546.8200	−549.9900	−549.7700	−434.3800	−436.8700	−436.7068
N_2-O_1	1.1451	1.1611	1.1606	1.1455	1.1614	1.1609	1.1453	1.1612	1.1607	1.1456	1.1616	1.1612
N_2-O_3	1.3875	1.5258	1.5018	1.3863	1.5247	1.5003	1.3866	1.5229	1.4992	1.3857	1.5234	1.4988
O_3-C_4	1.3640	1.3834	1.3810	1.3642	1.3833	1.3808	1.3618	1.3837	1.3797	1.3655	1.3853	1.3824
C_4-O_5	1.1768	1.2028	1.2007	1.1774	1.2036	1.2014	1.1808	1.2080	1.2058	1.1781	1.2039	1.2017
O_1-N_2-O_3	109.4	108.3	108.4	109.5	108.3	108.5	109.3	108.3	108.4	109.5	108.3	108.5
N_2-O_3-C_4	115.1	113.0	113.0	115.1	113.1	113.1	115.0	112.9	112.9	115.3	113.3	113.3
O_3-C_4-O_5	123.6	124.5	124.4	123.5	124.4	124.4	123.1	123.7	123.8	123.1	124.0	124.0
O_1-N_2-O_3-C_4	−180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	−180.0	180.0	180.0
N_2-O_3-C_4-O_5	−0.0	−0.0	−0.0	−0.0	−0.0	−0.0	0.0	0.0	0.0	0.0	−0.0	−0.0
O_5-C_4-C_6-C_7	–	–	–	−0.0	−0.0	0.0	0.0	0.0	0.0	117.5	117.5	117.6

Table 2 Calculated natural hybrid orbitals (NHOs) and the polarization coefficient for each hybrid in the corresponding NBO (in parentheses) for the selected O-nitrosyl carboxylate compounds using the selected methods

	Bond	O_1-N_2		N_2-O_3		O_3-C_4	
	Hybrids	O_1	N_2	N_2	O_3	O_3	C_4
CH_3COO-NO	RHF	$sp^{1.97}d^{0.02}$(0.7566)	$sp^{2.29}d^{0.02}$(0.6538)	$sp^{5.63}d^{0.04}$(0.6061)	$sp^{3.61}d^{0.00}$(0.7954)	$sp^{1.84}d^{0.00}$(0.8424)	$sp^{2.79}d^{0.02}$(0.5389)
	B3LYP	$sp^{2.15}d^{0.02}$(0.7597)	$sp^{2.64}d^{0.01}$(0.6503)	$sp^{10.82}d^{0.03}$(0.6029)	$sp^{6.13}d^{0.01}$(0.7978)	$sp^{2.06}d^{0.00}$(0.8326)	$sp^{2.77}d^{0.01}$ (0.5539)
	B3PW91	$sp^{2.16}d^{0.02}$ (0.7587)	$sp^{2.64}d^{0.01}$ (0.6514)	$sp^{9.88}d^{0.03}$ (0.6037)	$sp^{5.68}d^{0.01}$ (0.7972)	$sp^{2.06}d^{0.00}$(0.8327)	$sp^{2.79}d^{0.01}$ (0.5537)
CH_3CH_2COO-NO	RHF	$sp^{1.98}d^{0.02}$(0.7566)	$sp^{2.29}d^{0.02}$(0.6539)	$sp^{5.60}d^{0.04}$(0.6064)	$sp^{3.60}d^{0.00}$(0.7951)	$sp^{1.82}d^{0.00}$(0.8422)	$sp^{2.78}d^{0.02}$(0.5392)
	B3LYP	$sp^{2.15}d^{0.02}$(0.7596)	$sp^{2.64}d^{0.01}$(0.6504)	$sp^{10.77}d^{0.03}$(0.6030)	$sp^{6.10}d^{0.01}$(0.7977)	$sp^{2.04}d^{0.00}$(0.8324)	$sp^{2.76}d^{0.01}$ (0.5542)
	B3PW91	$sp^{2.16}d^{0.02}$ (0.7586)	$sp^{2.64}d^{0.01}$ (0.6516)	$sp^{9.82}d^{0.03}$ (0.6038)	$sp^{5.64}d^{0.01}$ (0.7971)	$sp^{2.03}d^{0.00}$(0.8325)	$sp^{2.77}d^{0.01}$ (0.5540)
4-H-PH-COO-NO	RHF	$sp^{1.98}d^{0.02}$(0.7566)	$sp^{2.29}d^{0.02}$(0.6538)	$sp^{5.54}d^{0.04}$(0.6046)	$sp^{3.58}d^{0.00}$(0.7966)	$sp^{1.80}d^{0.00}$(0.8408)	$sp^{2.79}d^{0.02}$(0.5413)
	B3LYP	$sp^{2.15}d^{0.02}$(0.7596)	$sp^{2.64}d^{0.01}$(0.6504)	$sp^{10.66}d^{0.03}$(0.6009)	$sp^{6.00}d^{0.01}$(0.7993)	$sp^{2.04}d^{0.00}$(0.8312)	$sp^{2.79}d^{0.01}$ (0.5559)
	B3PW91	$sp^{2.16}d^{0.02}$ (0.7586)	$sp^{2.64}d^{0.01}$ (0.6516)	$sp^{9.68}d^{0.03}$ (0.6017)	$sp^{5.56}d^{0.01}$ (0.7988)	$sp^{2.02}d^{0.00}$(0.8313)	$sp^{2.79}d^{0.01}$ (0.5558)
$(CH_3)_2CHCOO$-NO	RHF	$sp^{1.98}d^{0.02}$(0.7566)	$sp^{2.29}d^{0.02}$(0.6539)	$sp^{5.58}d^{0.04}$(0.6061)	$sp^{3.59}d^{0.00}$(0.7954)	$sp^{1.80}d^{0.00}$(0.8438)	$sp^{2.88}d^{0.02}$(0.5367)
	B3LYP	$sp^{2.15}d^{0.02}$(0.7596)	$sp^{2.64}d^{0.01}$(0.6503)	$sp^{10.70}d^{0.03}$(0.6026)	$sp^{6.06}d^{0.01}$(0.7981)	$sp^{2.02}d^{0.00}$(0.8340)	$sp^{2.86}d^{0.01}$ (0.5517)
	B3PW91	$sp^{2.16}d^{0.02}$ (0.7586)	$sp^{2.64}d^{0.01}$ (0.6516)	$sp^{9.74}d^{0.03}$ (0.6035)	$sp^{5.60}d^{0.01}$ (0.7974)	$sp^{2.01}d^{0.00}$(0.8342)	$sp^{2.87}d^{0.01}$ (0.5515)

Table 3 Second order delocalization energies $E^{(2)}$/(kcal·mol^{-1}) in the selected compounds at various levels

Compounds	RHF/6-31G**	B3LYP/6-31G**	B3PW91/6-31G**
CH_3COO-NO			
$n_{O_1} \rightarrow \sigma^*_{O_3-N_2}$	57.46	63.26	60.89
$n_{O_3} \rightarrow \sigma^*_{N_2=O_1}$	35.11	20.78	22.52
CH_3CH_2COO-NO			
$n_{O_1} \rightarrow \sigma^*_{O_3-N_2}$	57.13	63.00	60.59
$n_{O_3} \rightarrow \sigma^*_{N_2=O_1}$	35.46	20.95	22.74
4-H-PHCOONO			
$n_{O_1} \rightarrow \sigma^*_{O_3-N_2}$	57.46	62.07	60.74
$n_{O_3} \rightarrow \sigma^*_{N_2=O_1}$	35.28	21.09	22.78
$(CH_3)_2CHCOO$-NO			
$n_{O_1} \rightarrow \sigma^*_{O_3-N_2}$	56.99	62.72	60.22
$n_{O_3} \rightarrow \sigma^*_{N_2=O_1}$	35.58	21.04	22.87

unoccupied in the formal Lewis structure. As a result, the filled NBOs of the natural Lewis structure are well adapted to describing covalency effects in molecules. Since the non-covalent delocalization effects are associated with $\sigma \rightarrow \sigma^*$ interactions between filled (donor) and unfilled (acceptor) orbitals, it is natural to describe them as being of donor-acceptor, charge transfer, or generalized "Lewis base-Lewis acid" type. The antibonds represent unused valence-shell capacity and spanning portions of the atomic valence space that are formally unsaturated by covalent bond formation. Weak occupancies of the valence antibonds signal irreducible departures from an idealized localized Lewis picture, i.e., true "delocalization effects".

As a result, in the NBO analysis, the donor–acceptor (bond–antibond) interactions are taken into consideration by examining possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs and then estimating their energies by second-order perturbation theory. These interactions (or energetic stabilizations) are referred to as "delocalization" corrections to the zeroth - order natural Lewis structure. Here, the interaction energies that exceed 0.5 kcal/mol are considered.

The most important interaction between "filled" (donor) Lewis-type NBOs and "empty" (acceptor) non-Lewis NBOs is reported in Table 4. The results of NBO analysis collected in Table 4 show that the lp(O_3) participate as donors and the BD*(O_1-N_2) antibond as acceptors [lp(O_3)→ BD*(O_1-N_2)], with charge transfer energy values as: 20.78, 20.95, 21.04, 21.09 kcal/mol for CH_3COONO, CH_3CH_2COONO, $(CH_3)_2CHCOONO$, 4-H-PHCOONO at B3LYP level, respectively. This shows that the charge transfer energy increases with the increase of the Hammet constants of subsitutent groups. This interaction is the most important interaction in the O-nitrosyl carboxylate compounds. The amount of destabilization energy calculated within the NBO approach does not greatly differ in the compounds examined, thus it can be inferred that the strength of the O-NO bond changes only slightly in the different compounds, which is consistent with our calculated results [24] and the experimental results [25].

Table 5 shows calculated natural orbital occupancy (number of electron, or "natural population" of the orbitals). It is noted that for $\sigma_{O_3\text{-}N_2}$ bond orbital, the maximum occupancy is obtained for CH_3CH_2COO-NO (1.98633); for $\sigma^*_{O_3\text{-}N_2}$ bond orbital, the maximum occupancy is obtained for CH_3COO-NO (0.22033). As we described above, small occupancies of the antibond orbitals correspond, in Hartree-Fock theory, to irreducible departure from the idealized Lewis picture and thus to small non-covalent corrections to the picture of localized covalent bonds.

Decreased occupancy of the localized $\sigma_{O_3\text{-}N_2}$ orbital in the idealized Lewis structure, or increased occupancy of $\sigma^*_{O_3\text{-}N_2}$ of the non-Lewis orbital, and their subsequent impact on molecular stability and geometry (bond lengths) are also related with the resulting *p* character of the corresponding oxygen NHO of $\sigma_{O_3\text{-}N_2}$ bond orbital.

In Table 2, for CH_3COONO, CH_3CH_2COONO, $(CH_3)_2CHCOONO$, 4-H-PHCOONO at B3LYP level, the *p* characters of oxygen $\sigma_{O_3\text{-}N_2}$ in selected compounds are 6.13, 6.10, 6.06, 6.00, respectively. Similarly, the O-NO bond length is 1.5258, 1.5247, 1.5234, 1.5229 Å, respectively. Therefore, the results suggest that the O_3-N_2 bond lengths of these compounds are in essence controlled by the *p* character of these hybrid orbitals and also by the nature of the O_3-N_2 bond.

Table 4 The second order perturbation energies $E^{(2)}$/(kcal·mol^{-1}) corresponding to the most important charge transfer interactions (donor→ acceptor) in the compounds studied using B3LYP/6-31G** method

Don.NBO	Acc.NBO	$E^{(2)}$/(kcal·mol^{-1})			
		CH_3COO-NO	CH_3CH_2COO-NO	4-H-PHCOONO	$(CH_3)_2CHCOO$-NO
lpO_3[a)]	BD*(O_1-N_2)	20.78	20.95	21.09	21.04
lpN_2	BD*(C_4-O_3)	0.76	0.79	0.81	0.80
lpO_5	BD*(C_4-C_6)	18.74	19.07	17.93	17.96

a) lp stands for lone-pair.

Table 5 The important calculated valence non-Lewis and Rydberg non-Lewis, $\sigma_{O_3\text{-}N_2}$ and $\sigma^*_{O_3\text{-}N_2}$ bond orbital occupancies at B3LYP/6-31G**

	CH_3COO-NO	CH_3CH_2COO-NO	4-H-PHCOONO	$(CH_3)_2CHCOO$-NO
$\sigma_{O_3\text{-}N_2}$	1.98628	1.98633	1.98604	1.98622
$\sigma_{N_2=O_1}$	1.99638	1.99635	1.99627	1.99633
$\sigma_{O_3\text{-}C_4}$	1.99341	1.99309	1.99263	1.99284
Olp1	1.97922	1.97852	1.97790	1.97798
Olp2	1.74052	1.74052	1.74014	1.74002
$\sigma^*_{O_3\text{-}C_4}$	0.12192	0.11921	0.11641	0.12299
$\sigma^*_{N_2=O_1}$	0.00507	0.00507	0.00513	0.00513
$\sigma^*_{O_3\text{-}N_2}$	0.22033	0.21994	0.21838	0.21914
Valence non-Lewis	0.73663	0.77856	1.92601	0.80779
Rydberg non-Lewis	0.08110	0.09278	0.13912	0.10519

Table 6 Atomic charge distribution described in terms of natural population analysis (NPA) for the selected compounds studied using B3LYP/6-31G** method

	CH_3COO-NO	CH_3CH_2COO-NO	4-H-PHCOONO	$(CH_3)_2CHCOO$-NO
O_1	−0.150339	−0.152112	−0.156629	−0.153040
N_2	0.337157	0.337205	0.346366	0.337051
O_3	−0.419251	−0.432554	−0.455184	−0.429598
C_4	0.599167	0.625252	0.620901	0.624432
O_5	−0.427506	−0.437109	−0.455826	−0.441528
C_6	−0.386638	−0.270747	0.009159	−0.132963

3.4 Natural population analysis

The natural population analysis (NPA) was evaluated in terms of natural atomic orbital occupancies [26,27]. Table 6 reveals the molecular charge distribution on the skeletal atoms for selected O-nitrosyl carboxylate compounds. Generally, it is noted that the strong negative partial charges on the skeletal atoms (especially O_1, O_3, O_5) for the selected compounds decrease with increasing Hammett constant of substituent groups, while the positive partial charges on the skeletal atoms (especially N_2, C_4) for the selected compounds increase with the increasing Hammett constant of substituent groups. These partial charge distributions on the skeletal atoms show that the electrostatic repulsion or attraction between atoms can contribute significantly to the intra- and intermolecular interaction.

4 Conclusions

In the present study, natural bond orbital population analysis of several O-nitrosyl carboxylate compounds have been performed using quantum computational ab initio RHF and density functional B3LYP and B3PW91 methods with 6-31G** basis set. According to our results, following conclusions can be obtained for the selected O-nitrosyl carboxylate compounds studied:

1) The N_2-O_3 bond length and the O_3-C_4-O_5 bond angle decrease with the augment of Hammett constants, while the C_4-O_5 bond length increase with the increase of Hammett constants.

2) The *p* characters of oxygen $NHO\sigma_{N_2\text{-}O_3}$ and nitrogen $NHO\sigma_{N_2\text{-}O_3}$ bond orbitals decrease with increasing Hammett constants of substituent group on HCOONO, which results in shortening of the O_3-N_2 bond.

3) There is a strong hyperconjugative interaction $n_{O_1} \rightarrow \sigma^*_{O_3\text{-}N_2}$ in the compounds studied and the weakness in the O_3-N_2 bond is due to $n_{O_1} \rightarrow \sigma^*_{O_3\text{-}N_2}$ delocalization and is responsible for the longer O_3-N_2 bond lengths, thereby contributing to the nitro oxide releasing ability in selected compounds, though the O_3-N_2 bond has partial double bond and character.

4) The charge transfer energy $E^{(2)}$ decreases with increasing Hammett constant of substituent group, which results in shortening of the O_3-N_2 bond.

5) The electrostatic repulsion or attraction between atoms can contribute significantly to the intra- and intermolecular interaction.

Acknowledgements We gratefully thank the National Natural Science Foundation of China (Grant No. 10774039) and the grant

from Development Program in Science and Technology of Henan Province (Grant No. 102300410114), Foundation for University Key Teacher by the Ministry of Education of Henan Province, and Henan University of Science and Technology for Young Scholars (Grant No. 2009QN0032) for their support of this work.

References

1. Fukuto, J. M.; Ignarro, L. J., *Acc. Chem. Res*. **1997**, *30*, 149–152
2. Butler, A. R.; Williams, D. L. H., *Chem. Soc. Rev*. **1993**, *22*, 233
3. Gnewuch, C. T.; Sosnovsky, G., *Chem. Rev*. **1997**, *97*, 829–1014
4. Ignarro, L. J., *Annu. Rev. Pharmacol. Toxicol*. **1990**, *30*, 535–560
5. Gil, R.; Casado, J.; Izquierdo, C., *Int. J. Chem. Kinet*. **1994**, *26*, 1167–1178
6. Casado, J.; Castro, A.; Leis, J. R.; Mosquera, M.; Peria, M.; Chem, E. J.Soc., *Soc*. *Perkin Trans*. **1985**, *2*, 1859
7. Iglesias, E., *J. Am. Chem. Soc*. **1998**, *120*, 13057–13069
8. Ryzhov, V.; Klippenstein, S. J.; Dunbar, R. C.; *J. Am. Chem.Soc*. **1996**, *118*, 5462–5468
9. Li, X. H.; Zhang, R. Z.; Yang, X. D., *J. Mol. Struct. THEOCHEM* **2007**, *817*, 43–46
10. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., GAUSSIAN 03, Revision B.02, Gaussian, Inc., Pittsburgh, PA, 2003
11. Becke, A. D., *J. Chem. Phys*. **1993**, *98*, 5648
12. Lee, C.; Yang, W.; Parr, R. G., *Phys. Rev. B* **1988**, *37*, 785–789
13. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H., *Chem. Phys. Lett*. **1989**, *157*, 200–206
14. Perdew, J. P.; Wang, Y., *Phys. Rev. B* **1992**, *45*, 13244–13249
15. Perdew, J. P., *Phys. Rev. B* **1986**, *33*, 8822–8824
16. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F., NBO Version 3.1
17. Reed, A. E.; Weinhold, F., *J. Chem. Phys*. **1985**, *83*, 1736
18. Reed, A. E.; Weinstock, R. B.; Weinhold, F., *J. Chem. Phys*. **1985**, *83*, 735
19. Reed, A. E.; Weinhold, F., *J. Chem. Phys*. **1983**, *78*, 4066
20. Foster, J. P.; Weinhold, F., *J. Am. Chem. Soc*. **1980**, *102*, 7211–7218
21. Chocholoušová, J.; Vladimir Špirko, V.; Hobza, P., *Phys. Chem. Chem. Phys*. **2004**, *6*, 37
22. Cao, C. Z., *Substituent Effects in Organic Chemistry*. Beijing: Science Press, 2003
23. Reed, A. E.; Curtiss, L. A.; Weinhold, F., *Chem. Rev*. **1988**, *88*, 899–926
24. Li, X. H.; Zhang, R. Z.; Cheng, X. L.; Yang, X. Y., *J. Mol. Struct. THEOCHEM* **2007**, *821*, 47–52
25. Luo, Y. R., *Handbook of Bond Dissociation Energies in Organic Compounds*, CRC Press, Boca Raton, 2003
26. Häser, M.; Ahlrichs, R., *J. Comput. Chem*. **1989**, *10*, 104
27. Ahlriches, R.; Barr, M.; Haser, M.; Horn, H.; Komel, C., *Chem. Phys. Lett*. **1989**, *162*, 65