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REGULAR ARTICLE

# A DFT and Natural Resonance Theory investigation of the electronic structure of mesoionic compounds

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**Abstract** Mesoionic compounds are a class of heterocyclic molecules which have an unusual electronic structure. Although there are reports about their synthetic, optical and biological applications, some of their properties are not fully understood. In this work, an electronic structure investigation of three different mesoionic rings was made by means of DFT, Natural Bond Orbitals and Natural Resonance Theory calculations; we varied the substituents at three positions, totalizing 54 structures. Our results showed that C2–X bond is the longest endocyclic bond and the most susceptible to undergo cleavage. In addition, 1,3-oxazol-5-one (**NOO**) rings are more likely to open than 1,3-diazole-4-thione (**NNCS**) and 1,3-thiazole-5-thione (**NSS**) ones. Natural resonance analysis provided us a better understanding of the important canonical forms for those compounds which could be a good starting point for higher-level multi-reference calculations. We also found out that substituent groups may affect the electronic structure of those compounds as much as the ring structure itself.

**Keywords** Mesoionic compounds · DFT · Frontier orbitals · NBO analysis · Natural Resonance Theory

## 1 Introduction

Mesoionic compounds are heterocyclic molecules which have been studied since late nineteenth century [1, 2]. Their unusual structures have challenged and motivated researchers who tried to describe it. Although they have been extensively studied by experimentalists [3–6], there are still few theoretical studies about them [7–9].

The first mesoionic definition was proposed by Baker and Ollis [10]. They stated that mesoionic compounds were five- or six-membered heterocycles which had a positive charge in the atoms of the ring and a negative one in an exocyclic group. They also could not be represented by a single covalent or polar structure. The only adequately way to represent them was as a hybrid of many resonance structures.

Almost 20 years later, Ollis and Ramsden [2] stated that the term mesoionic should be restricted to five-membered rings. They also classified the mesoionic compounds in two different types according to each atomic contribution to the $\pi$-electron system. Those types (named A and B) are shown in Fig. 1 (where a, b, c, d, e and f can be either a carbon or a heteroatom).

Another definition was proposed by Oliveira et al. [11] who stated that mesoionic compounds were five-membered heterocyclic betaines with a side chain whose $\alpha$-atom was also in the ring plane. They argued that the electrons were delocalized over two regions: (1) one which had a negative $\pi$-charge and was associated with HOMO (2) and other which had a positive $\pi$-charge and was associated with LUMO. Figure 2 illustrates the structure of those compounds according to that definition.

The aromaticity of mesoionic compounds is a controversial issue. Previous definitions stated that these compounds had some aromatic characters [2, 10]; however,

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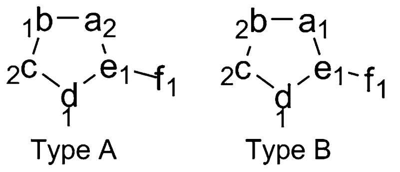


**Fig. 1** Type A and Type B mesoionic structures. The numbers indicate each atomic contribution to π-electron system

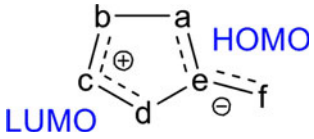


**Fig. 2** Schematic representation of mesoionic compounds according to Oliveira et al. [11] definition

Simas et al. [12] have carried out an extensive research about that subject and collected plenty of evidence to the contrary. The authors pointed out several theoretical and experimental studies which provided evidences on the large charge separation existing on mesoionic compounds. In addition, as opposed to classical aromatic compounds, a same mesoionic compound could act as an electrophile or a nucleophile in different reactions [13]. Finally, Simas et al. [12] concluded that mesoionic compounds could not be classified as aromatic substances.

A NMR study by Jaźwiński and Staszewska-Krajewska [14] suggested that some mesoionic compounds are aromatic, while the ones which have two heteroatoms in the ring are not. The $^1J_{CC}$ coupling and aromatic indices also indicated that 1,3-diazoles, 1,3-oxazoles and 1,3-thiazoles mesoionic systems are unsaturated compounds instead of aromatic ones [14]. A further NMR and X-ray investigation also pointed out that such mesoionic systems are very sensitive to changes in substituent groups [15].

Sydnones were the first mesoionics largely studied by scientific community [16, 17]. These compounds are obtained by reaction of N-nitroso-N-aryl-glycines with acetic anhydride producing sydnone mesoionic compound on good yields [18]. Sydnones have been used as starting material to prepare many other mesoionic rings, for example, by 1,3-dipolar cycloaddition reactions [19]. Besides that, many other heterocyclic compounds are produced from mesoionic ones using this same kind of reaction [4, 5, 20–22].

Literature points out a wide range of applications for mesoionic compounds such as biological activity, nonlinear optical (NLO) properties and heterocyclic intermediates. Reports of biological activity of mesoionic molecules against melanoma [23], Chagas' disease [24] and Leishmania [25, 26] have provided promising compounds for drug design research against those diseases. Theoretical [8, 27, 28] and experimental [29–31] studies have assessed NLO properties of mesoionic compounds such as first-, second- and third-order hyperpolarizabilities and two-photon absorption. These results have indicated they may be used to build nonlinear optical devices.

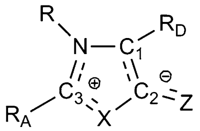
Although there are some theoretical studies about mesoionic compounds [8, 11, 27, 32], few of them evaluated electronic structure features of a large group of molecules using high-level calculations [7, 9, 33].

Fabian and Hess [9] have theoretically evaluated properties of some sulfur-containing mesoionic and nonmesoionic molecules and compared them to each other. Their results showed that some mesoionic compounds had long C–S bonds which could easily break and be converted into open-chain structures. Although calculated values for Nuclear Independent Chemical Shift (NICS) pointed out some degree of aromaticity for those compounds, charge separation into the mesoionic ring was in agreement with previously reported by Simas et al. [12].

So, in order to expand the scope of previous theoretical studies of mesoionic compounds, we have studied three different mesoionic rings: 1,3-diazole-4-thione (**NNCS**), 1,3-thiazole-5-thione (**NSS**) and 1,3-oxazol-5-one (**NOO**) by a combination of DFT, Natural Bond Orbitals (NBO) and Natural Resonance Theory (NRT) approaches. For each mesoionic ring, different substituent groups were placed in pre-defined positions, resulting in a set of 54 structures. Figure 3 shows the base structure adopted in this work to generate all compounds.

The X and Z groups determine the type of mesoionic system: **NNCS**, **NSS** or **NOO**. $R_A$ and $R_D$ are electron-attractor and electron-donor groups (or H as reference), respectively; placing these substituents at those positions tend to improve the nonlinear optical properties of mesoionic compounds [27]. R was chosen to be either H or $CH_3$ group.

**Fig. 3** Mesoionic structures calculated in this article



X and Z: $NCH_3$ and S (**NNCS**), S and S (**NSS**) and O and O (**NOO**)
R: H and $CH_3$
$R_A$: H, F and $CF_3$
$R_D$: H, $CH_3$ and $NH_2$

## 2 Computational methods

Geometry optimizations were performed to predict ground state geometries of the 54 mesoionic compounds at gas phase. No symmetry considerations were imposed, and we have used restricted M06-2X/cc-pVTZ theoretical level [34]. Subsequently, frequency calculations for each molecule were carried out (considering both same DFT functional and basis set) in order to guarantee that the geometry was a true minimum. All calculations were carried out using Gaussian G09 program [35], and GaussView 5.0 [36] was used to visualize minimum geometry structures.[1]

To get a better understanding of the bonding aspects of the studied systems, Natural Bonding Orbitals (NBO) [37, 38] calculations were also performed using NBO 5.9 package installed into Gaussian. Bonding orbital contributions for the frontier orbitals were assessed, and Natural Resonance Theory (NRT) [39–41] analysis has also been performed.

## 3 Results and discussion

### 3.1 Optimized structures

The 54 structures were fully optimized to find their ground state geometries. Six of these molecules suffered a bond breaking (there were no natural bond orbitals associated with C2–X and their bond orders were almost null, see Table S3 at Supplementary Information). For these cyclic compounds, the side chain $\alpha$-atom and the five ring atoms were in the same plane. The optimized geometries of all structures can be visualized in Supplementary Information material (Fig. S1, S2, S3). We named each molecule by a combination of its general mesoionic group (**NNCS**, **NSS** or **NOO**) plus a letter which specifies the substituent groups present in its structure. For example, **NNCSf** and **NSSf** have the same R, $R_A$ and $R_D$ in their structures. The bond features for the different rings were analyzed using the mean distances and standard deviations of the bonds of each ring type (Table 1).

In Table 1, we notice that the mean values for C1–N, C1–C2 and C3–N (see Fig. 3) bond lengths do not vary much from one type of ring to another. On the other side, C2–X, C3–X and C2–Z bonds exhibit greater variation among the mesoionic systems because C–S bond lengths (**NSS** and **NNCS**) are larger than C–N (**NNCS**) and C–O (**NOO**) ones. Aside from differences, due to variation of the X atom, C2–X exhibited some interesting features:

**Table 1** Mean bond lengths (in Å) and standard deviations of bond lengths (in parentheses) for each type of ring

| Bond | NNCS | NSS | NOO |
|---|---|---|---|
| C1–N | 1.38 (0.016) | 1.37 (0.016) | 1.38 (0.006) |
| C1–C2 | 1.38 (0.007) | 1.39 (0.010) | 1.40 (0.005) |
| C3–N | 1.32 (0.008) | 1.32 (0.010) | 1.31 (0.002) |
| C2–X | 1.41 (0.014) | 1.79 (0.022) | 1.49 (0.018) |
| C3–X | 1.33 (0.011) | 1.69 (0.004) | 1.30 (0.005) |
| C2–Z | 1.69 (0.004) | 1.67 (0.006) | 1.20 (0.004) |

1. **NNCS** compounds have a mean distance of 1.41 Å, which is slightly shorter than a carbon–nitrogen single bond of pyrrolidine (1.47 Å, experimental data) [42];
2. **NOO** exhibits a carbon–oxygen bond length of about 1.49 Å, that is closer to C–O single bond on 2,3-dihydrofuran (1.45 Å) than on furan (1.37 Å) (Fig. 4);
3. **NSS** presents a typical carbon–sulfur single bond length of 1.79 Å, which is an intermediate bond length between the single bond of thiophene (1.73 Å) and 2,3-dihydrothiophene (1.84 Å) (Fig. 4); a very similar C–S bond length (1.80 Å) was reported in a X-ray study of thiatriazole compounds [43].

Our results showed that C2–X is the longest endocyclic bond for all three ring types. A similar result was also observed by Fabian and Hess [9] and Jaźiwińsk et al. [43]. They both noticed very long C–S bonds in some sulfur-containing mesoionic compounds. In the same way, mesoionic compounds studied by Wiench et al. [32] exhibited long C2–X (C–S) bond lengths ranging from 1.76 to 1.85 Å. In this work, C–S bonds at C2–Z and C3–X positions had shorter bond lengths (1.67–1.69 Å, see Table 1) than at C2–X positions (1.79 Å). Thus, this is an

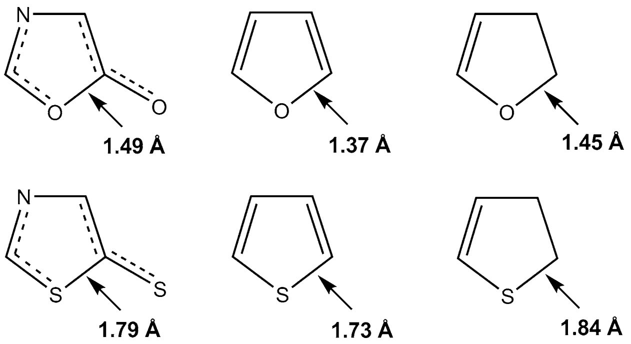


**Fig. 4** C2–X bond distances for **NSS** and **NOO** compounds (mean values) in the first column and related bond distances from analog heterocyclic systems obtained from CCD/6−31 + G(d) calculations [44]

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[1] The bond type for each bond of the optimized structures shown in Figs. 5, 6, 7 and 8 was arbitrarily chosen by GaussView criteria and does not correspond to the real nature (single, double, triple or resonant) of those bonds.

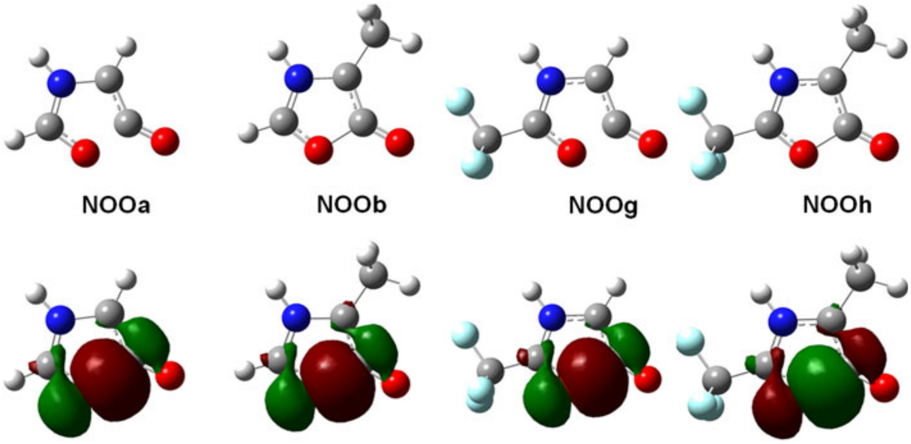

**Fig. 5** Some **NOO** compounds and their respective C2–X bonding orbitals

evidence that C2–X is the weakest bond of the mesoionic system and the most susceptible to ring opening.

**NOOa** and **NOOg** were the **NOO** systems which had the longest C2–X bonds. Nevertheless, they exhibited a NBO bonding orbital associated with that bond very similar to other **NOO** compounds (Fig. 5).

Of all fifty-four molecules, six **NOO** compounds resulted in acyclic structures (with no C2–X bond) after geometry optimization (Fig. 6); only the **NOO** compounds which had $R_A = F$ experienced that effect. This result leads us to believe that fluorine atom affects C2–X bond destabilizing the mesoionic ring structure. Interestingly, when the F group is replaced by $CF_3$, there was no ring cleavage after geometry optimization. In fact, the group electronegativity of $CF_3$ (2.985) [45] is much lower than electronegativity of F (4.000). Thus, C3 charge suffers a remarkable increase when $CF_3$ is replaced by F: (1) at NNCS compounds, it changes from +0.223 to +0.771; (2) at NSS compounds, it changes from −0.136 to +0.443; (3) at NOO compounds, it changes from +0.404 to +0.981.

On the other hand, the NSS structures did not undergo ring opening even in the presence of the strong field effect of the fluorine atom, which indicates that cyclic geometries are preferably over acyclic ones for these systems (Fig. 6). C2–X bonds of NSS systems are less suitable to bond breaking due to its bond order of about 1.05, while NOO

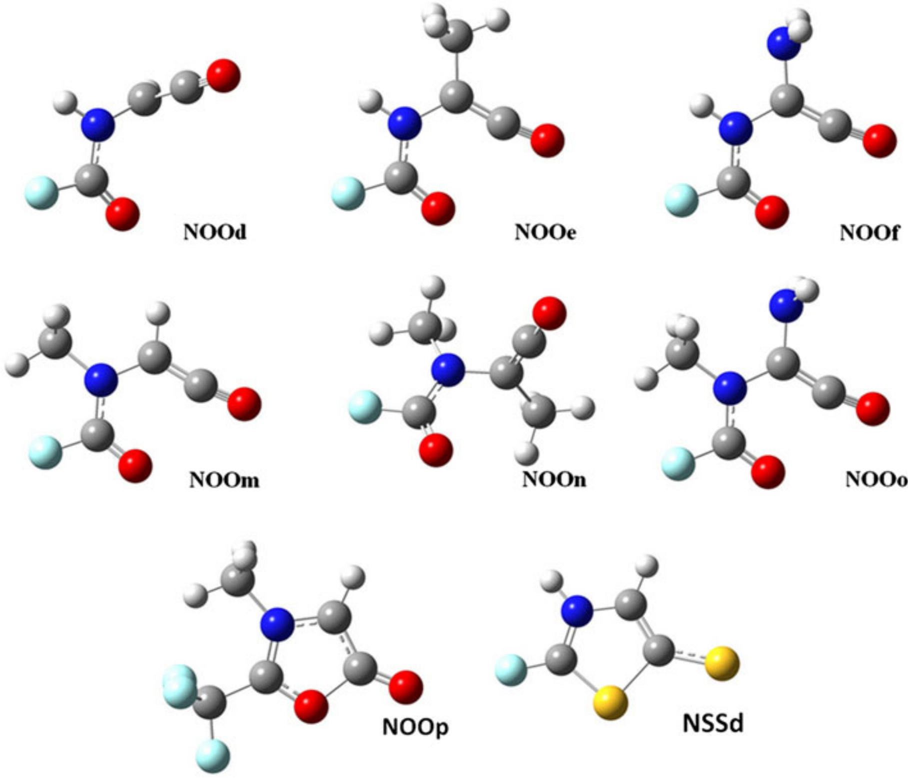

**Fig. 6** Optimized geometries for the acyclic **NOO** compounds (**d**, **e**, **f**, **m**, **n** and **o**), a $CF_3$-containing **NOO** (**NOOp**) and a F-containing **NSS** compound (**NSSd**)

**Table 2** C2–X interatomic distances for F-containing **NOO** compounds

| Optimized structure | Interatomic distance (Å) |
|---|---|
| **NOOd** | 3.53 |
| **NOOe** | 2.64 |
| **NOOf** | 2.63 |
| **NOOm** | 2.53 |
| **NOOn** | 3.49 |
| **NOOo** | 2.44 |

compounds exhibited a bond order of about 0.92[2] (bond orders calculated by NRT, see table S3 at Supplementary Material).

**NOOe**, **NOOf**, **NOOm** and **NOOo** have remained as planar structures, while **NOOd** and **NOOn** have undergone not just a bond breaking but also a twist in the N–C1–C2–Z dihedral angle which led them to nonplanar geometries. Those **NOO** acyclic compounds exhibited C2–X distances greater than 2.4 Å, which is much longer than expected for a C–O single bond. **NOOd** and **NOOn** had even larger distances (around 3.5 Å) due to their nonplanar geometry (Table 2).

## 3.2 Frontier orbitals

Frontier Kohn–Sham (KS) orbitals were obtained, and we found out that they are not localized orbitals as suggested by most recent mesoionic definition [11]. Similar delocalized frontier orbitals were obtained by Fabian and Hess [9] for 1,3-ditholylium-4-olate compound. Highest Occupied Kohn–Sham Orbital (HOKO) and Lowest Unoccupied Kohn–Sham Orbital (LUKO) for **NNCSa**, **NSSa** and **NOOa** structures are shown in Fig. 7.

Although there is much discussion about the meaning of Kohn–Sham orbitals, some authors claim that KS frontier orbitals can be analyzed qualitatively in a similar way as canonical molecular orbitals [46]. As a way to reinforce the previous frontier orbitals analysis, the same three compounds shown in Fig. 7 were optimized using RHF/6−311 + G(d,p) level of theory and their frontier orbitals were also determined through this calculation. The corresponding frontier orbitals from Hartree–Fock (HF) calculation are shown in Fig. 8.

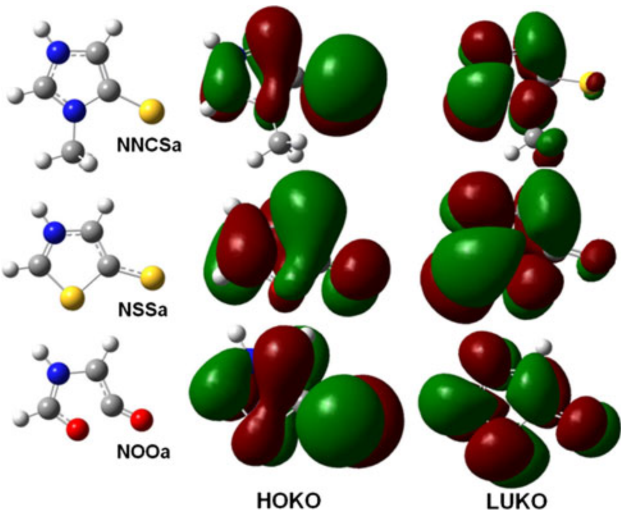

**Fig. 7** Kohn–Sham Frontier Orbitals, HOKO and LUKO, of **NNCSa**, **NSSa** and **NOOa** structures

Figures 7 and 8 show that HOMO and HOKO orbitals are much alike. They both had 3 pairs of lobes: (1) covering N and C3 atoms, (2) delocalized over C1, C2 and X atoms and (3) around the Z atom. Although both KS and HF had some agreement about HOMO/HOKO orbitals, the virtual frontier orbitals were very different from each other. LUKO orbitals were delocalized over the whole molecule, while LUMO orbitals presented themselves in a localized way, in agreement with Oliveira et al. [11] mesoionic definition.

Although we have investigated some features of the LUKO and LUMO orbitals for **NNCSa**, **NSSa** and **NOOa** compounds, a rigorous analysis cannot be made about them because both HF and KS methods do not optimize virtual orbitals. To go further, we decided to perform a quantitatively analysis of frontier orbitals using a NBO approach.

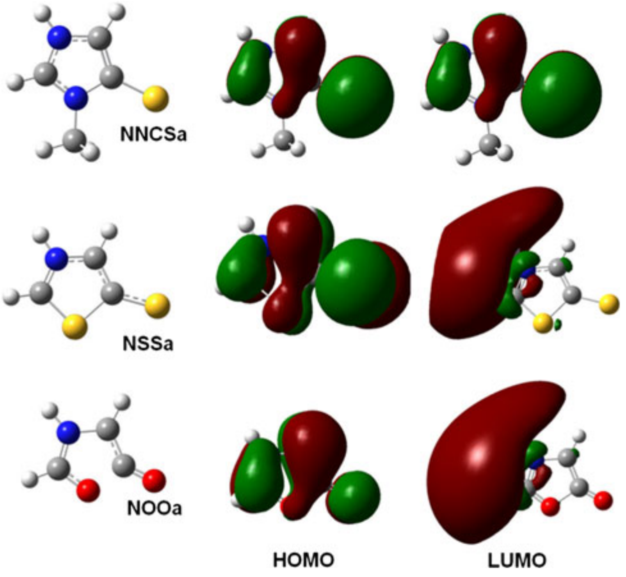

**Fig. 8** Hartree–Fock Frontier Orbitals, HOMO and LUMO, of **NNCSa**, **NSSa** and **NOOa** compounds

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[2] The NOO compounds which underwent ring cleavage were not considered in the calculation of this bond order.

NBO contributions to frontier orbitals were determined through a canonical molecular orbitals (CMO) analysis [47].

Using that analysis, we found out that, in general, frontier orbitals had contributions from some different NBOs but a few of them contributed much more than others. Most compounds exhibited a similar behavior for HOKO: LP(Z) (lone pair orbital from Z atom) and BD (C1–C2) (bonding orbital associated with C1–C2 bond) together participated with about 70 % for LOKO. LP(Z) contributions were larger than BD(C1–C2) ones for **NNCS** and **NSS** compounds but the opposite occurred for **NOO**. We present these contributions in Table 3. A few exceptions from the mentioned behavior occurred in the following compounds: **NNCSh**, **NOOi** and the acyclic **NOO** structures, they had noticeable participation of other NBO orbitals such as BD(C2–Z) (**NNCSh**), BD*(C1–C2) (**NOOi**) and a larger contribution of BD(C1–C2) (acyclic **NOO**). Their CMO analysis is detailed in Supplementary Information (Table S1).

Natural Bond Orbitals contributions to LUKO are shown in Table 4. CMO analysis for LUKO exhibited that **NNCS** compounds had a different pattern from **NSS** and **NOO** ones. **NNCS** had a major contribution from BD*(C3–X) (antibonding orbital associated with C3–X bond) and LP(N) (lone pair orbital from N atom), while **NSS** and **NOO** showed larger contributions from BD*(N–C3) (antibonding orbital associated with N–C3 bond) and LP(X) (lone pair orbital from X atom). Some molecules did not follow the same pattern, such as $CF_3$-containing **NNCS** compounds (which had great contribution of BD*(N–C3) orbital) and the acyclic **NOO** structures (which had large participation of BD*(C2–Z)). Their contributions are also detailed in Supplementary Information (Table S2).

**Table 3** NBO minimum and maximum squared contributions to **NNCS**, **NSS** and **NOO** HOKO orbitals

| | LP(Z) | BD(C1–C2) | BD*(C3–X) | BD(N–C3) |
|---|---|---|---|---|
| **NNCS** | 0.63–0.68 | 0.10–0.15 | 0.07–0.11 | – |
| **NSS** | 0.56–0.64 | 0.09–0.14 | – | – |
| **NOO** | 0.17–0.26 | 0.39–0.47 | – | 0.11–0.13 |

**Table 4** NBO minimum and maximum squared contributions to **NNCS**, **NSS** and **NOO** LUKO orbitals

| | BD* (C3–X) | LP(N) | BD* (N–C3) | LP(X) | BD (C1–C2) |
|---|---|---|---|---|---|
| **NNCS** | 0.54–0.63 | 0.15–0.18 | – | – | 0.06–0.11 |
| **NSS** | – | – | 0.43–0.58 | 0.17–0.19 | 0.05–0.14 |
| **NOO** | – | – | 0.54–0.69 | 0.10–0.12 | 0.10–0.13 |

In Table 3, it is clear that NBOs associated with C1, C2 and Z atoms contributed with most of HOKO, we noticed that these same atoms are related to the negatively charged region (and HOMO) mentioned by Oliveira et al. [11]. In a similar way, N, C3 and X (which had a large contribution to LUKO) are associated with positively charged region (and LUMO) presented by mesoionic definition. Thus, CMO analysis points out some degree of localization for the frontier orbitals of mesoionic compounds, which agrees with Oliveira et al. [11] definition.

## 3.3 Resonance Theory Analysis

The NRT calculation was carried out with NBO 5.9 program (using default settings) in order to obtain the weightings (%) of each canonical form.

Most compounds showed a large number of resonance structures ranging from 90 to 400 structures. That behavior is expected for mesoionic compounds as indicated by most mesoionic definitions. Figure 9 shows general representation of canonical forms to **NOO**, **NSS** and **NNCS** sets of compounds which contributed with 3.0 % or more to at least one of the studied molecules.

Although large number of canonical forms have contributed to **NNCS** and **NSS** resonance hybrids, a few of them (**1**, **2**, **3** and **8**) have together a contribution of about 30–50 % for most compounds. Those four general structures agree well with Oliveira et al. [11] mesoionic definition as they assigned C1–N and C2–X as single bonds. It can be noticed that π bonds are delocalized on [N=C3–X ↔ N–C3=X] and [C1=C2–Z ↔ C1–C2=Z]. Nevertheless, canonical forms **4–7** (which have some significant weightings) exhibited a double bond to either C1–N or C2–X bonds.

Some compounds (especially **NNCS** ones which had $R_A = CF_3$) had unusual canonical bicyclic structures (**9**, **10**, **11** and **27**) with important weightings. There were also some **NSS** compounds which had small contributions from bicyclic structures such as **9**, **11** and **12**.

The most surprising behavior of the **NSS** compounds occurred with the rings which have $R_A = CF_3$: **NSSg**, **NSSh**, **NSSi**, **NSSp**, **NSSq** and **NSSr** (to consult all compound structures, see Supplementary Information). Those compounds had weightings of 100 % for a single resonance structure (**2**). That is a highly unexpected result for the NRT calculation of those compounds because other very similar molecules are highly delocalized. We believe that this is a limitation in NRT algorithm implemented in NBO 5.9 program to find other resonance structures for those compounds. A different calculation setting for these compounds is discussed later in this paper.

**NOO** compounds which remained in cyclic forms after geometry optimization also had important contribution from

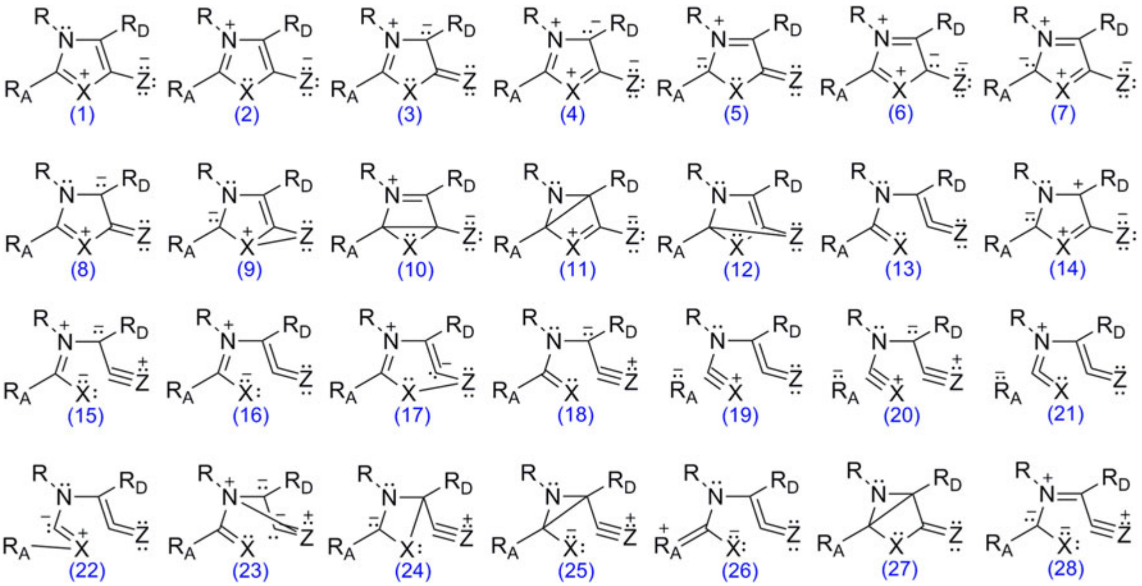

**Fig. 9** General representation of canonical structures to **NOO**, **NSS** and **NNCS** sets of molecules which contributed with 3.0 % or more to at least one of the studied compounds

**1**, **2** and **3** structures although their weightings were slightly smaller than those of **NNCS** and **NSS** ones. In addition, there were small but significant contributions from canonical forms in which there was no C2–X bond (**13**, **15**–**17**), which is a further evidence of the weak character of those bonds. Some bicyclic structures also had slight but noticeable weightings for those **NOO** compounds.

The **3**, **5** and **8** general canonical structures were the most important resonance structures to exhibit a double bond between C2 and Z atoms for all rings. The sum of the weightings of those general canonical structures for each type of ring varied as it follows: (1) **NNCS**: 10–21 %; (2) **NSS**: 18–30 %; (3) **NOO**: 30–35 %. Also, **NOO** rings had contributions from **15** to **16** general canonical structures which showed either a double or a triple bond between C2 and Z atoms.

We believe that C2–Z bond has a lower π character in **NNCS** and **NSS** compounds due to presence of sulfur exocyclic atom. Because of the large energy difference between carbon 2p atomic orbital and sulfur 3p atomic orbital, the resonance interaction is not so effective. On the other hand, **NOO** are not as affected due to the similar energy between carbon 2p atomic orbital and oxygen 2p atomic orbital. The strong double-bond character of exocyclic C–O bond was also reported for a mesoionic thiatriazole compound [43].

**NOO** compounds which presented a bond breaking during geometry optimization were also analyzed by NRT. None of their canonical structures showed existence of C2–X bond, which clearly differentiates them from the other **NOO** compounds studied in this work. In addition, some unusual three- and four-membered cyclic resonance structures (**23**–**25**) showed small weightings for those molecules.

A second NRT calculation was carried out for the six **NSS** (**NSSg**, **NSSh**, **NSSi**, **NSSp**, **NSSq** and **NSSr**) molecules which exhibited only one canonical structure (in the previous calculation). In that second calculation, we adopted a different strategy than used by default NRT options. We explicitly defined some reference canonical structures in the input file; the algorithm searches for other canonical structures using the references as a starting point. This was possible by using NRTSTR keyword. The **1**, **2** and **3** structures were chosen as reference canonical structures because they had the largest weightings in most of other **NSS** molecules.

Surprisingly, **1** and **3** general canonical structures had very small contributions of about 3.0 % to the resonance hybrid. On the other hand, **2** was the general canonical form which contributed the most that also occurred with the other **NSS** molecules. The **5** and **6** forms presented meaningful weightings which reveal us a double-bond character in C1–N stronger than those of other **NSS** molecules. Finally, bicyclic forms such as **9**, **11** and **12** also exhibited some small contributions.

In order to better analyze the importance of the resonance structures, we classified them in groups according to their features. There were four groups defined as it follows:

(I) “well-behaved” cyclic structures which had C1–N and C2–X as single bonds and that agree well with mesoionic definition (**1**–**3** and **8**) [11];

(II) "well-behaved" cyclic structures which exhibited a double bond between C1 and N or between C2 and X atoms (**4**–**7** and **14**);
(III) "unusual" bicyclic structures which preserved C2–X bond (**9**–**12** and **27**);
(IV) all the structures which did not exhibit a C2–X bond (**13**–**26** and **28**).

A summary of the contributions of each group of canonical forms to each ring type is shown in Table 5.

Some comments about Table 5 are relevant. Each column represents a class of the studied compounds (**NNCS**, **NOO** and **NSS**), while the rows are associated with the groups of canonical forms (**I**–**IV**). The first three columns (**NNCS** and **NSS** compounds) display greater contributions from groups **I** and **II**, which agrees well with expected from mesoionic compounds. Meanwhile, groups **III** and **IV** had negligible weightings. These results point out the essentially cyclic character of those two classes of compounds.

Nevertheless, **NOO** compounds with $R_A = F$ (the last column) exhibited a great contribution from group **IV** and no significant participation from **I**–**III** that highlights the acyclic character of those compounds. In a different way, **NOO** compounds with $R_A = H$ or $CF_3$ (fourth column) had effective contribution from all groups of canonical structures (**I**–**IV**), which points out that they are cyclic compounds (due to greater participation of **I** and **II**) but with weaker C2–X bonds (because of relevant contribution of **IV**) than those of **NNCS** and **NSS** compounds.

**Table 5** General resonance structures weighting range: minimum, maximum and mean values (in parentheses) for each group of canonical forms

| | NNCS | NSS[a] | NSS[b] | NOO[c] | NOO[d] |
|---|---|---|---|---|---|
| **I** | 28.5–55.9 | 34.8–52.1 | 22.7–34.4 | 31.0–57.3 | *** |
| | (42.2) | (40.4) | (29.2) | (38.6) | (***) |
| **II** | ***–26.5 | 15.2–31.2 | 26.2–34.2 | 4.3–28.9 | *** |
| | (13.5) | (22.2) | (29.7) | (18.3) | (***) |
| **III** | ***–21.5 | ***–9.3 | 4.9–9.3 | ***–7.3 | *** |
| | (7.8) | (4.6) | (7.0) | (4.6) | (***) |
| **IV** | *** | ***–3.3 | *** | 3.1–25.2 | 60.8–83.3 |
| | (***) | (***) | (***) | (11.7) | (75.7) |

All data are expressed as percentage. Contributions smaller than 3.0 % are shown as ***

[a] **NSS** compounds which failed at the NRT calculations are not included

[b] NRT analysis of the **NSS** compounds which had $CF_3$ group using NRTSTR keyword

[c] Cyclic **NOO** compounds

[d] Acyclic **NOO** compounds ($R_A = F$)

## 4 Conclusions

Our results have shown that **NNCS** and **NSS** mesoionic rings are less susceptible to ring opening than **NOO** ones. The oxygen-containing rings showed a weak C2–X bond, and for some of these systems, geometry optimization led to acyclic structures with no C2–X bonding. This same bond seems to be a stability indicator for mesoionic systems as observed in other works [9]. In addition, the CMO analysis pointed out that a few NBOs (two or three) significantly contribute to the frontier orbitals. This observation supports the localized character of those orbitals in mesoionic compounds.

Natural Resonance Theory calculations confirmed the strong mesomeric character of the mesoionic compounds. Most compounds exhibited larger contributions from cyclic "well-behaved" canonical structures (groups **I** and **II**), but bicyclic and acyclic structures (groups **III** and **IV**) also played a minor role in some resonance hybrids. The structures of larger weightings (such as **1**, **2** and **3**) may prove to be good starting points for higher-level multireference calculations.

Initial NRT results for $CF_3$–containing **NSS** compounds proved to be unsatisfactory. However, when reference structures were manually inserted (using NRTSTR keyword), it was quite successful as it found many canonical forms for each compound. Nevertheless, the weightings of such canonical structures were very different from those of other **NSS** molecules which may be due to $CF_3$ influence or to a limitation of NBO program when default parameters are not used.

Finally, we found out that substituent groups play an important role to the electronic structure of such systems because a change in one of such groups resulted in meaningful changes in the molecular properties as noted by a previous work [15].

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