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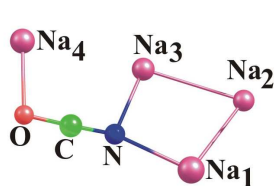
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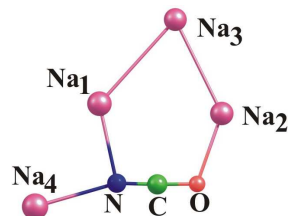
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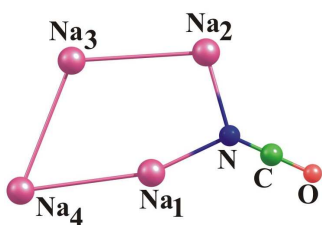
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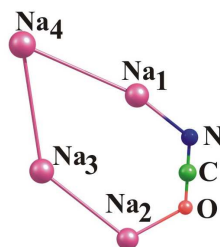
1, glob. min.



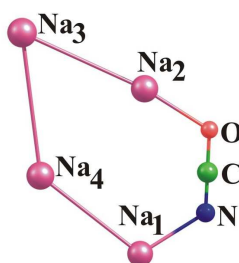
2, +0.6 kcal/mol



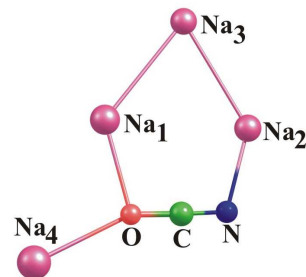
3, +2.0 kcal/mol



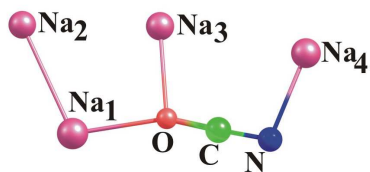
4, +2.7 kcal/mol



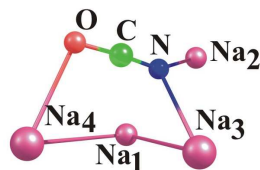
5, +2.9 kcal/mol



6, +3.5 kcal/mol

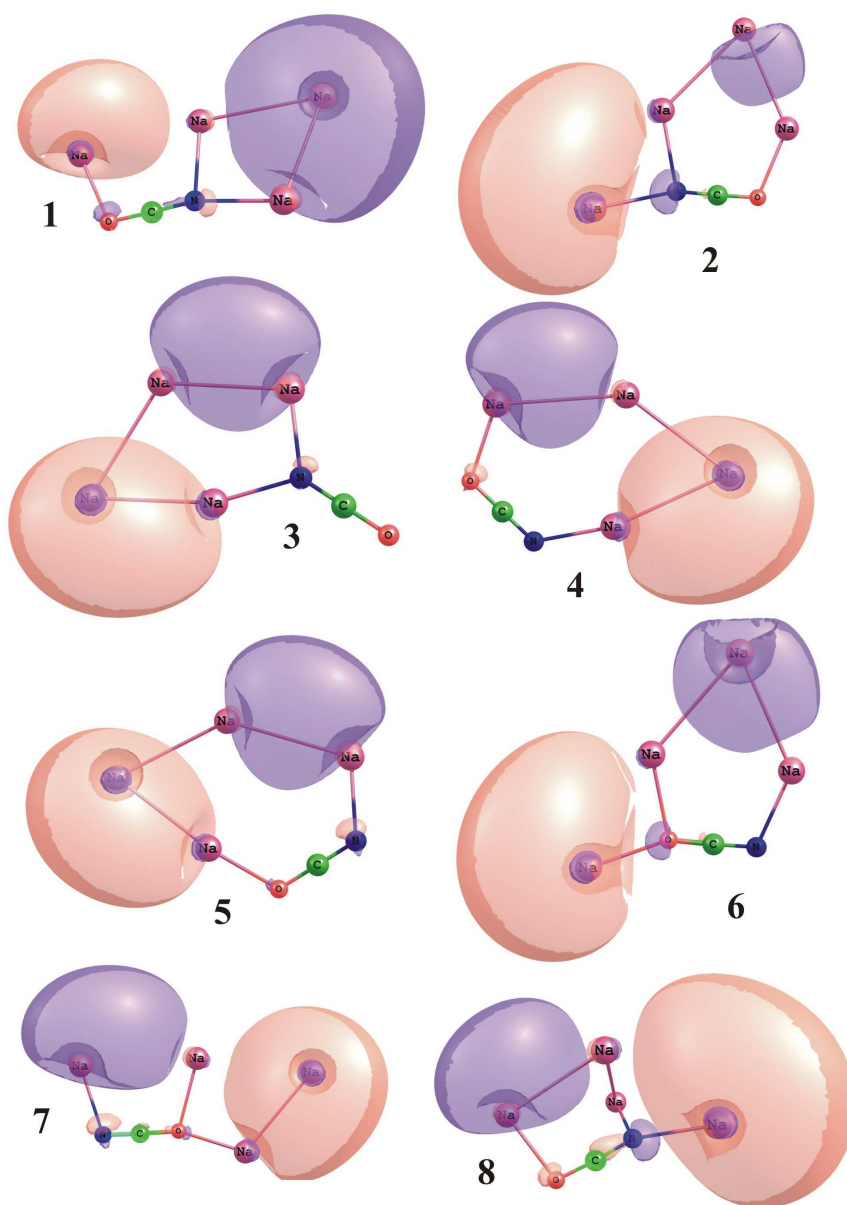


7, +3.9 kcal/mol

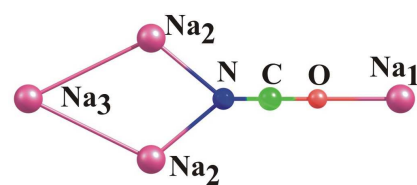


8, +8.8 kcal/mol

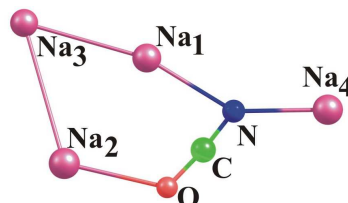
The MP2/6-311+G(d) equilibrium structures of the Na₄OCN isomers
144x234mm (300 x 300 DPI)



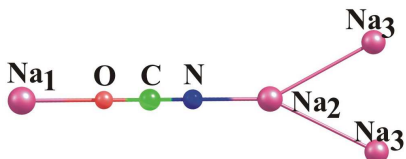
Singly occupied molecular orbitals (SOMO) of the Na_4OCN isomers
165x232mm (300 x 300 DPI)



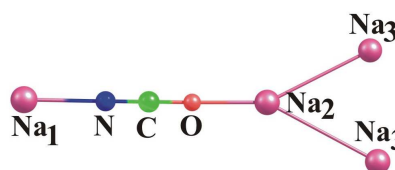
1⁺, +1.4 kcal/mol



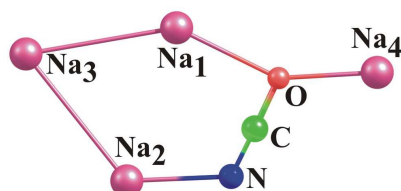
2⁺, +0.8 kcal/mol



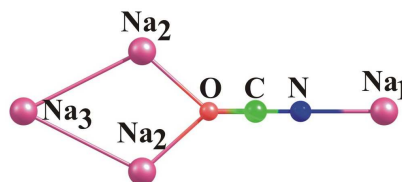
4⁺, +3.8 kcal/mol



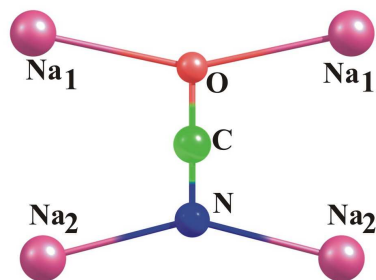
5⁺, +1.8 kcal/mol



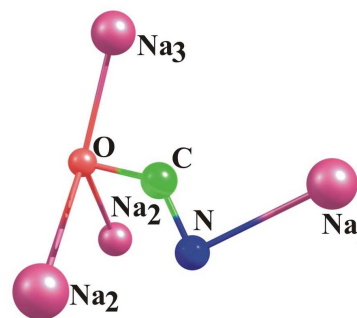
6⁺, +8.0 kcal/mol



7⁺, glob. min.



9⁺, +7.7 kcal/mol



10⁺, +13.1 kcal/mol

The MP2/6-311+G(d) equilibrium structures of the Na_4OCN^+ cationic isomers
184x250mm (300 x 300 DPI)

Low Ionization Potentials of Na₄OCN Superalkali Molecules

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Abstract

The structure and properties of hypermetalated Na₄OCN molecules and their corresponding Na₄OCN⁺ daughter cations were investigated using ab initio methods at the CCSD(T)/6-311+G(3df)//MP2/6-311+G(d) level of theory. Eight neutral Na₄OCN geometrically stable isomers were found to possess similar electronic energies. The vertical ionization potentials (IP) of the Na₄OCN isomeric systems (determined at the OVGf/6-311+G(3df) level) were calculated to span the 4.117-4.640 eV range which allowed to classify the Na₄OCN species as superalkali molecules (the predicted ionization potentials are smaller than the IP of the Na atom, 5.14 eV). The global minimum on the Na₄OCN ground-state neutral potential energy surface was found to correspond to the kite-shaped structure whose vertical IP was estimated to be 4.478 eV.

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1. Introduction

The term “superalkalies” was introduced in 1982 by Gutsev and Boldyrev [1] to describe molecular systems whose first ionization potential (IP) is smaller than that of the alkali metals (IP (in eV): Li, 5.39; Na, 5.14; K, 4.34; Rb, 4.17; Cs, 3.89) [2]. For example, the Li_3O molecule was reported to possess the superalkali nature with the IP of 3.54 ± 0.3 eV [3-5] which is lower than the ionization potential of Cs atom (3.89 eV). The superalkalies belong to a group of hypervalent or hypermetalated molecules. This term describes ML_{k+n} species (where L is an alkali metal atom, k is the maximum formal valence of the central atom M, and $n \geq 1$) [1,6-9] containing two or more metal atoms in stoichiometries that exceed normal valence expectations. The strong bonding interactions among the alkali metal “ligands” (L) which help to offset the octet-rule-violating structure and antibonding L-M interactions are believed to be the major contributions to both the structure and stability of these species [1,6-16]. Since the first evidence of the Li_3O molecule in 1978 [11], a number of lithium and other alkali metal containing compounds with unusual stoichiometries (e.g., Li_4O , Li_5O , Li_2Cl , Li_2F , Li_6C , Na_3O , Na_4O) have been studied theoretically and experimentally [1,3,22]. The most prominent examples of superalkalies are small (i.e., triatomic) alkali metal clusters and hyperalkali molecules ML_{k+n} with $n=1$ which are characterized by the lowest IPs (i.e., Li_3 4.11 eV vs. Li_4 4.74 eV [23] or Na_3O 3.13 eV vs. Na_4O 3.60 eV [22]).

Superalkalies are of a great importance in chemistry since they can be used as components of new nontraditional salts in which the anions are molecular systems exhibiting low electron affinity. The first salts of this type, i.e., $\text{Li}_3\text{O}^+\text{NO}^-$ and $\text{Li}_3\text{O}^+\text{NO}_2^-$, were synthesized in the 70's by Jensen and the presence of the Li_3O^+ cation has been confirmed by the X-ray diffraction [24-26].

In this contribution we present our theoretical investigation of the electronic and geometric structure of the Na_4OCN system exhibiting “superalkali nature”. In particular, we focused our studies on the various structures of Na_4OCN and its corresponding cation Na_4OCN^+ . Our goal was to investigate if such species are geometrically and thermodynamically stable and whether they possess small IP values. We believe that the vertical ionization potentials we provide in this work might be found useful for experimental chemists, especially those designing new materials in which strong reducers are involved.

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2. Methods

We present the equilibrium geometrical structures of the Na_4OCN and Na_4OCN^+ species for which we also calculated harmonic vibrational frequencies (available upon request). For this purpose we applied the second-order Møller–Plesset (MP2) perturbational method with the 6-311+G(d) basis set [27, 28]. The coupled-cluster method with single, double and non-iterative triple excitations (CCSD(T)) [29] was used to calculate the final energies of the species at their geometries obtained with the MP2 method. In order to provide reliable vertical ionization potentials (VIP) of superalkali species studied we performed direct calculations of the electron binding energies at the neutral (Na_4OCN) and cationic (Na_4OCN^+) equilibrium geometries which resulted in estimating the VIP_n and VIP_c , respectively. However, we limit our discussion to the ionization potentials obtained for the neutral equilibrium geometries (i.e., VIP_n) as they seem more important for experimentalists, whereas the VIP_c values are only provided for comparison. A *direct* scheme applied to calculate the ionization potentials was the outer valence Green function (OVGF) method (*B* approximation) [30-38]. Since the OVGF approximation remains valid only for outer valence ionizations for which the pole strengths (PSs) are greater than 0.80-0.85 [39] we verified that the smallest PS found for the states studied in this work is 0.80. As far as the basis sets are concerned, we applied the 6-311+G(3df) basis [27, 28] for calculating the VIP values and the final CCSD(T) energies of the species. The partial atomic charges were fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme [40].

All calculations were performed with the Gaussian03 program [41] while the plots showing the molecular structures were generated with the ChemCraft program [42].

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3. Results

As it was explained in the preceding sections, the most favorable stoichiometry for the superalkali species matches the ML_{k+1} formula (where L is an alkali metal atom and k stands for the maximum formal valence of the central atom M). Due to the anticipated potential energy surface (PES) complexity, the superalkali molecules with more complex center M (i.e., built of more than one atom, such as OH [43, 44] or CN [45, 46]) are of particular interest since the existence of several minima of comparable stability might be expected. The electrostatic attraction between the cationic metallic network $L^{(k+1)+}$ and anionic M^- (regardless of the complexity of center M) contributes to the stability of the system. Therefore, we decided to verify these assumptions for hypermated molecules composed of *ambidentate* centers M, such as OCN. The cyanate group (OCN), which we chose as a representative polyatomic center M, is an important halogenoid characterized by relatively large electron affinity ($EA(OCN)=3.609\pm 0.05$ eV [47]) comparable to that of the chlorine atom ($EA(Cl)=3.61$ eV [48]). The term halogenoid (or pseudohalogen) was introduced in 1925 [49] for strongly bound, linear or planar univalent radicals X^\cdot (such as CN, OCN, N_3 , SCN) which form X^- anions and HX acids.

As we described recently, the Na_2OCN system, matching the ML_{k+n} formula for $n=1$, is capable of forming stable molecules of superalkali nature [50]. Moreover, we noticed that the OCN group in addition to its *ambidentate* nature (exhibited by the ability of forming stable Na_2OCN and Na_2NCO isomeric structures) is also able to act as a 'bridge' between two alkali metal atoms. In particular, the lowest energy Na_2OCN isomer is of C_{2v} symmetry with both sodium atoms connected to the isocyanate (-NCO), however, C_s -symmetry structure (with the OCN in the bridging position between two alkali metal atoms) is only 0.4 kcal/mol higher in energy whereas the structure with both Na atoms linked to the cyanate fragment (-OCN) is 10.9 kcal/mol higher in energy. The vertical ionization potentials (VIP_n) for the Na_2OCN isomers were found to span the 4.747-5.072 eV range [50].

The *ambidentate* nature of the OCN moiety and its capability of binding two alkali metal atoms to either O-end or N-end (as confirmed by the existence of both Na_2OCN and Na_2NCO systems) [50] have motivated us to verify whether the Na_4OCN (which matches more general ML_{k+n} formula with $n=3$) is capable of forming stable molecules exhibiting superalkali nature.

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3.1. Neutral Species

We begin our discussion with providing the results obtained for the neutral Na_4OCN species. An extensive exploration of the ground-state neutral potential energy surface led to 8 stable isomers whose equilibrium structures are depicted in Figure 1 whereas the corresponding geometrical parameters are gathered in Table 1.

The structure corresponding to the global minimum of Na_4OCN (termed **1** in Figure 1) contains a four-member ring involving three sodium atoms and one nitrogen atom. The remaining Na atom is linked to the O-end of the OCN fragment and the resulting symmetry is C_s due to the planarity of the molecule. As a consequence, the structure **1** resembles the most stable structure previously found for Na_3OCN molecule [51], however, with one additional Na atom linked to the oxygen (Na_4 , see Figure 1). The OCN fragment is almost linear (the OCN valence angle reads 177.8°) while the Na-Na and Na-N bond lengths were found to span the 3.40-3.67 Å and 2.31-2.44 Å range, respectively (see Table 1). The C_s -symmetry structure **1** is thermodynamically stable with respect to various channels of isomerization and fragmentation. In particular, if one considers the fragmentation path leading to the sodium atom and Na_3OCN neutral molecule, the system **1** is thermodynamically stable by 12.1 kcal/mol (at the CCSD(T)/6-311+G(3df)//MP2/6-311+G(d) level). The VIP_n value (i.e., the vertical ionization potential calculated for the equilibrium geometry of the neutral system) calculated for isomer **1** of Na_4OCN with the OVGf method reads 4.478 eV which is lower than the ionization potential of the sodium atom (5.14 eV).

The second low energy structure of Na_4OCN (local minimum **2**) was found to be higher in energy than the isomer **1** by only 0.6 kcal/mol which may suggest the presence of similar amounts of these isomers at room temperature. The structure **2** is planar (C_s -symmetry) with the OCN moiety and three sodium atoms engaged in the six-member ring mimicking a pentagon (see Figure 1). The remaining sodium atom (Na_4) is bound to the N-end of the OCN group and the corresponding bond length was found to be relatively large (3.35 Å) in comparison to the Na_1 -N distance (2.40 Å). As it was observed for the global minimum **1**, the OCN fragment is quasi-linear ($\angle(\text{OCN})=177.9^\circ$) and the Na-Na bond lengths are in the 3.36-3.64 Å range (see Table 1). The vertical ionization potential calculated for the structure **2** (4.112 eV) was found to be even lower (by 0.366 eV) than the VIP_n of the isomer **1**.

1
2 The next Na_4OCN low energy isomer (**3**) is planar (C_s -symmetry) and contains four
3 sodium atoms forming a quasi-rhombic frame connected to the N-end of the OCN moiety via two
4 Na-N bonds, see Figure 1. The OCN fragment is almost perfectly linear in **3** ($\angle(\text{OCN})=179.7^\circ$)
5 whereas the Na-Na bond lengths are in the 3.49-3.69 Å range (see Table 1). The energy of
6 shovel-shaped structure **3** is only 2.0 kcal/mol higher than the energy of the global minimum (**1**).
7 The vertical ionization potential calculated for the isomer **3** (4.550 eV) is only slightly higher (by
8 0.072 eV) than that predicted for the global minimum structure **1**.
9

10 The fourth (**4**) and fifth (**5**) geometrically stable structures of Na_4OCN were found to be
11 higher in energy by 2.7-2.9 kcal/mol than the global minimum **1**. These isomers possess very
12 similar electronic energies (the energy difference is only 0.2 kcal/mol) and differ by the OCN
13 fragment orientation with respect to the Na-Na-Na-Na framework, see Figure 1. Both **4** and **5**
14 structures are planar (C_s -symmetry) and cyclic, with the quasi linear OCN moiety (the deviations
15 from linearity do not exceed 0.3°), see Table 1. The VIP_n values predicted for the isomers **4** and
16 **5** are similar to the VIP_n of isomer **1** and equal to 4.640 and 4.584 eV, respectively.
17

18 The sixth geometrically stable structure of Na_4OCN (labeled **6** in Figure 1 and Table 1)
19 was found to be higher in energy by 3.5 kcal/mol than the most stable isomer **1**. This structure
20 can be viewed as the analogous to **2** (see Figure 1) with its similar pentagon-like frame involving
21 three Na atoms and the OCN group, however, the remaining sodium atom (Na_4) is linked to the
22 oxygen instead of nitrogen atom. Similarly to the previously described structure **2**, the OCN
23 fragment is quasi-linear in structure **6** ($\angle(\text{OCN})=178.1^\circ$) and the Na-Na bond lengths are in the
24 3.44-3.56 Å range (see Table 1). The vertical ionization potential calculated for **6** (4.273 eV) is
25 higher by 0.15 eV than that predicted for the analogous structure **2** and smaller by 0.21 eV than
26 the VIP_n estimated for the global minimum structure **1**.
27

28 Another geometrically stable isomer of Na_4OCN , labeled **7** in Figure 1, was found to be
29 higher in energy by 3.9 kcal/mol than the global minimum **1**. The OCN fragment is almost linear
30 in **7** ($\angle(\text{OCN})=177.9^\circ$) and it connects to the sodium atoms through its both termini. In particular,
31 the nitrogen atom is linked to one Na atom (Na_4) whereas the oxygen atom forms two bonds
32 (O-Na_1 and O-Na_3), see Figure 1. The remaining sodium atom (Na_2) is bound to the Na_1 atom and
33 the resulting system is planar (C_s -symmetry). The calculated VIP_n value for the structure **7** is
34 4.350 eV. Even though the isomer **7** is less stable and possesses slightly larger VIP_n than the
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2 isomer **1**, we consider it particularly important as its ionization leads to the most stable positively
3 charged species Na_4OCN^+ (see the discussion provided in the following section).
4

5 The least stable isomer we obtained for the Na_4OCN neutral molecule (labeled **8** in
6 Figure 1 and Table 1) is 8.8 kcal/mol higher in energy than **1** and contains bent $\text{Na}_3\text{-Na}_1\text{-Na}_4$
7 fragment connected to the both ends of the OCN moiety. The fourth remaining sodium atom
8 (Na_2) is bound to the N atom, see Figure 1. Interestingly, the isomer **8** is characterized by the
9 lowest vertical ionization potential (4.117 eV) among all geometrically stable Na_4OCN isomers
10 described in this contribution.
11

12 As discussed in this section, the VIP_n values obtained for all eight isomers of Na_4OCN are
13 relatively low and span the 4.117-4.640 eV range. In particular, the reported VIP_n s are not only
14 lower than the ionization potential of the sodium atom (5.14 eV) but also lower than the VIP_n
15 values recently found for the Na_2OCN molecules (4.747-5.072 eV) [50]. Hence, we conclude that
16 the Na_4OCN isomers should be classified as superalkalies [10] as they are expected to act as
17 electron donors.
18

19 The singly occupied molecular orbitals (SOMO) of all **1-8** isomers are depicted in Figure
20 2. The large number of sodium atoms in Na_4OCN supports its classification as a hypermetalated
21 molecule, however, the presented SOMO orbitals seem different from those usually described for
22 'typical' hypermetalated species. In particular, an unpaired electron in the hypermetalated ML_{k+n}
23 system is accommodated in an orbital which is antibonding with respect to the central atom (M)
24 and the surrounding metal atoms (L_{k+n}) whereas the bonding interaction among all metal atoms L
25 is observed (the latter interaction allows to form a metal network) [45]. Because of this, the
26 hypermetalated molecules are usually described as salts composed of the metallic cation $[\text{L}_{k+n}]^+$
27 and the $[\text{M}]^-$ anion. For most of the Na_4OCN isomers, however, the unpaired valence electron
28 density is split into two pairs of alkali metal atoms and hence the Na_4OCN species cannot be
29 described as a complex of OCN^- and Na_4^+ radical cation (i.e., similar to other hypermetalated
30 molecules). This seems to imply that the Na_4OCN might be considered as consisting of metallic
31 Na_2^+ and anionic Na_2OCN^- subunits. Moreover, the localization of the metallic Na_2^+ subunit
32 (with respect to the OCN fragment) turns out to be important for the ionization process, as
33 described in the following section.
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3.2. Cationic Species

Since the isomers of the Na_4OCN molecule exhibit very low ionization potentials (4.117-4.640 eV) it is important to discuss the structure and properties of the corresponding daughter cationic species (generated by the unpaired electron removal). Hence, we performed the geometry optimizations of the cationic species using the neutral **1-8** structures as the initial geometries. Such an approach seems justified because it reproduces the actual geometry relaxation of the system after an electron removal (the electron loss is much faster than the structure relaxation and thus the initial cation structure is expected to be that of its corresponding neutral parent). In addition, we independently searched for other geometrically stable cationic structures (i.e., the cationic structures that are qualitatively different than any of the neutral isomer). The geometrically stable structures that we found for Na_4OCN^+ cations are depicted in Figure 3 whereas the corresponding geometrical parameters are collected in Table 2.

The ionization of the most stable isomer **1** leads to the C_{2v} -symmetry structure **1**⁺ in which three sodium atoms form a four-member ring with the N-end of the OCN moiety while the fourth Na atom is bound to the O-end of the OCN group (see Figure 3). As a result, the **1**⁺ cation contains the linear Na-O-C-N fragment, unlike the neutral parent **1** in which the corresponding Na-O-C-N moiety is significantly bent (see Figure 1). Despite this large difference in the Na-O-C valence angle (from 109° in **1** to 180° in **1**⁺), the **1**→**1**⁺ ionization process causes only small changes in the Na-N, N-C and C-O bond distances (the differences do not exceed 0.12 Å). The charge population analysis indicates that the excess positive charge is not equally distributed among the metal atoms as the terminal sodium atom (Na_1) linked to O-end of the OCN group bears the +1.02 a.u. partial charge whereas the charges found for the three remaining sodium atoms are in the 0.10-0.27 a.u. range. Surprisingly, the significant positive partial charge of 1.3 a.u. is predicted for the carbon atom in the **1**⁺ cation. The localization of such a significant positive partial charge on the Na_1 atom is likely responsible for the shortage of the Na-O bond (by 0.21 Å) upon an ionization (i.e., with respect to the Na-O bond predicted for the neutral isomer **1**) whereas the bonds formed by the carbon atom (i.e., C-O and C-N) are only slightly affected (the differences in the bond lengths do not exceed 0.007 Å).

Detachment of an electron from isomers **2**, **3**, and **8** leads to the same C_s -symmetry structure of the cation which we decided to term **2**⁺ (rather than **3**⁺ or **8**⁺) due to its structural

1
2 similarity to the neutral isomer **2**. Hence, the cationic isomers that would have been labeled 3^+
3 and 8^+ are absent (the ionization of any of **2**, **3**, or **8** leads to the same cation (2^+). The 2^+ cation
4 contains a quasi-pentagon frame (built of three sodium atoms and nearly linear OCN fragment)
5 with the remaining Na atom linked to the nitrogen, see Figure 3. In fact, the geometries of the
6 neutral parent **2** and its 2^+ cationic daughter differ only slightly. Namely, the Na₄-N, Na₁-Na₃, and
7 Na₁-Na₂ bonds shorten by 0.10-0.23 Å whereas the Na₂-O, Na₁-N, and Na₂-Na₃ bonds elongate
8 by 0.05-0.18 Å (see Figures 1 and 3 for atom numbering and Tables 1 and 2 for detailed values of
9 geometrical parameters). The most significant geometry change upon the $2 \rightarrow 2^+$ ionization was
10 found in the case of the Na₁-N-Na₄ valence angle which increases from 91° (in **2**) to 139° (in 2^+).
11 As a result, the two sodium atoms become more distant with respect to each other (the Na₁-Na₄
12 separation in the cation reads 4.451 Å), see Figure 3. As far as the charge population analysis is
13 concerned, the ionization of either **2**, **3** or **8** causes all sodium atoms to bear larger positive partial
14 charges (up to $q(\text{Na}_4)=+0.9$ a.u. in 2^+) while the OCN fragment becomes more negative (from ca.
15 -0.1, -0.3 and +0.3 a.u. for **2**, **3** and **8**, respectively, to -0.5 a.u. for 2^+ ; see Tables 1 and 2).
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23 The ionization of the **4** and **5** neutral isomers (exhibiting similar electronic energies) leads
24 to two different isomeric C_{2v} -symmetry structures (labeled 4^+ and 5^+ , respectively) in which the
25 linear OCN fragment is in the bridging position between one sodium atom (bound to either
26 oxygen in 4^+ or nitrogen in 5^+) and the top of the isosceles sodium triangle, see Figure 3. In fact,
27 the only structural difference between 4^+ and 5^+ cations is related to the orientation of the OCN
28 moiety with respect to the Na-triangle. As a result, both systems become less compact than their
29 corresponding **4** and **5** neutral parents as the seven-member rings open upon the ionization. In
30 addition, the resulting 5^+ cation is lower in energy than the 4^+ isomer (on the contrary to the
31 neutral parent **4** and **5** species, see the discussion provided in the preceding section) by about 2
32 kcal/mol. The Na-N and Na-O bonds in 4^+ and 5^+ are shorter (by 0.05 and 0.14 Å for 4^+ and by
33 0.07 and 0.06 Å for 5^+ , respectively) whereas the bond lengths in the OCN moiety remain almost
34 unchanged upon the ionization (the differences are smaller than 0.008 Å; see Figures 1 and 3, and
35 Tables 1 and 2). The charge population analysis indicates that the excess positive charges in 4^+
36 and 5^+ are localized mostly on the terminal sodium atoms Na₁ (carrying the partial charges of ca.
37 +0.9 a.u.; see Table 2) forming bonds with the negatively charged oxygen (in 4^+) or nitrogen (in
38 5^+) atoms. Therefore, we conclude that the corresponding **4** and **5** isomers might be viewed as
39 $(\text{Na}_2^+)(^-\text{OCNNa}_2)$ and $(\text{Na}_2^+)(^-\text{NCONa}_2)$ systems, respectively.
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2 The ionization of the isomer **6** leads to the isomer 6^+ cation whose structure is very
3 similar to that of its corresponding neutral parent. In particular, the $6 \rightarrow 6^+$ process causes the
4 shortening of the Na₄-O, Na₁-Na₃, and Na₁-Na₂ bonds by 0.09-0.23 Å, and the elongation of the
5 Na₂-N, Na₁-O and Na₂-Na₃ bonds by 0.03-0.19 Å (see Figures 1 and 3). These changes in the
6 bond lengths are accompanied with the considerable increase of the valence Na₁-O-Na₄ angle
7 (from 98° to 150°) when the 6^+ cation is formed. The performed charge population analysis
8 indicates that the excess positive charge in 6^+ is not equally distributed among all sodium atoms,
9 in fact, the terminal Na atom (Na₄) bears the largest partial positive charge of ca. +0.9 a.u.
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11 The ionization of the neutral structure **7** causes significant geometry reorganization and
12 leads to the C_{2v}-symmetry structure 7^+ which is analogous to 1^+ , however, the 7^+ and 1^+ differ in
13 the relative OCN group orientation, see Figures 1 and 3. Importantly, the kite-shaped 7^+ cation of
14 C_{2v} symmetry is the global minimum on the ground state cationic Na₄OCN⁺ potential energy
15 surface. In order to verify the Na₄OCN⁺ (represented by the structure 7^+) susceptibility to
16 fragmentation we considered the Na₄OCN⁺ → Na₃OCN + Na⁺ and Na₄OCN⁺ → Na₂OCN⁺ + Na₂
17 processes and found them energetically unfavorable (by 43.0 and 21.7 kcal/mol, respectively)
18 which indicates that the Na₄OCN⁺ is stable towards such decompositions. The $7 \rightarrow 7^+$ ionization
19 process causes only small changes (i.e., not exceeding 0.12 Å) in the Na-O, N-C and C-O bonds
20 whereas the Na-N-C valence angle is strongly affected and increases from 106° in **7** to 180° in 7^+ ,
21 see Tables 1 and 2). Similarly to the 1^+ cation, the charge population analysis indicates that the
22 excess positive charge in 7^+ is distributed mostly between the carbon atom and the terminal
23 sodium atom (Na₁).
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25 Further exploration of the Na₄OCN⁺ cationic potential energy surface led to two
26 additional minimum energy structures labeled 9^+ and 10^+ , see Figure 3. Since the attachment of
27 an electron to these both cationic species results in thermodynamically unstable neutral structures
28 with respect to decomposition (Na atom loss, by ca. 14-17 kcal/mol), we conclude that the 9^+ and
29 10^+ cations do not possess their corresponding neutral parents. The C_{2v}-symmetry isomer 9^+ is
30 higher in energy by 7.7 kcal/mol than the lowest energy cationic structure 7^+ . The 9^+ structure is
31 characterized by rather large Na-O and Na-N distances (2.60 and 2.46 Å, respectively) with
32 respect to other sodium-oxygen and sodium-nitrogen distances found for most Na₄OCN⁺ isomers
33 studied in this work. The charge population analysis indicates that the excess positive charge in
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2 9^+ is delocalized over all atoms excluding the carbon atom which carries the partial charge of ca.
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4 -0.7 a.u.; see Table 2.

5 The least stable isomer 10^+ is 13.1 kcal/mol higher in energy than 7^+ . Its relatively
6 compact structure is likely caused by the significantly bent configuration of the OCN fragment.
7 This, in turn, leads to the strong electrostatic repulsion among the positively charged Na atoms
8 (see Figure 3 and Table 2). Since the bent structure of the OCN group seems unusual [52] in
9 compounds containing alkali metal atoms, we propose to view the 10^+ as the complex of Na_3O^+
10 and NaCN. This is supported by the fact that the 10^+ possesses the longest O-C bond distance
11 (1.365 Å) among all studied Na_4OCN molecules and Na_4OCN^+ cations (see Tables 1 and 2).
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16 17 **4. Summary**

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20 On the basis of our *ab initio* CCSD(T)/6-311+G(3df) and OVGF/6-311+G(3df)
21 calculations for the Na_4OCN and Na_4OCN^+ species (whose structures were determined at the
22 MP2/6-311+G(d) level) we concluded the following:
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- 24 (1) The neutral Na_4OCN molecules are geometrically and thermodynamically stable species
25 represented by at least eight isomeric structures.
- 26 (2) The co-existence of seven different Na_4OCN isomers is anticipated at room temperature
27 due to their similar electronic energies (within 4 kcal/mol).
- 28 (3) The vertical ionization potentials (VIP_n) of Na_4OCN systems are in the range of 4.117-
29 4.640 eV (lower than the IP of Na (5.14 eV)) which justifies their classification as
30 superalkalies.
- 31 (4) The VIP_n predicted for the Na_4OCN systems (4.117-4.640 eV) are substantially lower
32 than those estimated earlier for the Na_2OCN species (4.747-5.072 eV).
- 33 (5) The ionization of the Na_4OCN species may lead to at least 7-8 various isomeric Na_4OCN^+
34 structures characterized by the similar electronic energies.
- 35 (6) The lowest-energy isomer of Na_4OCN possesses a kite-shaped C_s -symmetry structure, the
36 vertical ionization potential of which is 4.478 eV.
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Table 1. The MP2 geometrical parameters (bond lengths in Å, angles in degrees) and partial atomic charges (in a.u.) fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme for the Na₄OCN isomers. See Figure 1 for atom numbering. Vertical ionization potentials (VIP_n) in eV.

Species (symmetry) VIP _n	Geometry	Partial atomic charges
1 (C _s) 4.478	r(Na ₁ N)=2.309; r(Na ₃ N)=2.435; r(Na ₁ Na ₂)=3.396; r(Na ₂ Na ₃)=3.673; r(Na ₄ O)=2.343; r(OC)=1.219; r(CN)=1.205; ∠(NNa ₁ Na ₂)=114.55; ∠(OCN)=177.80 ∠(Na ₁ Na ₂ Na ₃)=55.27; ∠(Na ₃ NC)=107.05; ∠(Na ₄ OC)=109.20; ∠(Na ₁ Na ₂ Na ₃)=55.27	$q^{Na(1)}=0.170$; $q^{Na(2)}=-0.057$; $q^{Na(3)}=-0.009$; $q^{Na(4)}=0.124$; $q^O=-0.117$; $q^C=-0.101$; $q^N=-0.010$
2 (C _s) 4.119	r(Na ₁ N)=2.399; r(Na ₂ O)=2.304; r(Na ₁ Na ₃)=3.638; r(Na ₂ Na ₃)=3.363; r(Na ₄ N)=3.347; r(OC)=1.220; r(CN)=1.204; ∠(Na ₁ NNa ₄)=91.26; ∠(Na ₁ NC)=106.06; ∠(Na ₁ Na ₃ Na ₂)=66.30; ∠(ONa ₂ Na ₃)=132.55; ∠(Na ₂ OC)=111.08; ∠(OCN)=177.86	$q^{Na(1)}=-0.016$; $q^{Na(2)}=0.246$; $q^{Na(3)}=-0.010$; $q^{Na(4)}=-0.103$; $q^O=-0.179$; $q^C=-0.221$; $q^N=0.283$
3 (C _s) 4.550	r(Na ₁ N)=2.295; r(Na ₂ N)=2.289; r(Na ₂ Na ₃)=3.565; r(Na ₁ Na ₄)=3.492; r(Na ₃ Na ₄)=3.694; r(OC)=1.197; r(CN)=1.218; ∠(Na ₁ NNa ₂)=99.63; ∠(Na ₂ NC)=130.29; ∠(Na ₁ Na ₄ Na ₃)=60.80; ∠(Na ₂ Na ₃ Na ₄)=115.01; ∠(NNa ₂ Na ₃)=102.27; ∠(OCN)=179.67	$q^{Na(1)}=0.065$; $q^{Na(2)}=0.213$; $q^{Na(3)}=-0.031$; $q^{Na(4)}=0.082$; $q^O=-0.632$; $q^C=0.666$; $q^N=-0.363$
4 (C _s) 4.640	r(Na ₁ N)=2.256; r(Na ₁ Na ₄)=3.532; r(Na ₃ Na ₄)=3.597; r(Na ₃ Na ₂)=3.637; r(Na ₂ O)=2.240; r(OC)=1.230; r(CN)=1.199; ∠(Na ₂ OC)=115.53; ∠(Na ₁ NC)=126.03; ∠(Na ₁ Na ₄ Na ₃)=61.84; ∠(Na ₂ Na ₃ Na ₄)=138.72; ∠(OCN)=179.76	$q^{Na(1)}=0.241$; $q^{Na(2)}=0.304$; $q^{Na(3)}=-0.066$; $q^{Na(4)}=0.055$; $q^O=-0.322$; $q^C=0.278$; $q^N=-0.490$
5 (C _s) 4.584	r(Na ₁ N)=2.255; r(Na ₁ Na ₄)=3.646; r(Na ₃ Na ₄)=3.667; r(Na ₃ Na ₂)=3.476; r(Na ₂ O)=2.237; r(OC)=1.230; r(CN)=1.200; ∠(Na ₂ OC)=119.92; ∠(Na ₁ NC)=119.84; ∠(Na ₁ Na ₄ Na ₃)=136.44; ∠(Na ₂ Na ₃ Na ₄)=61.21; ∠(OCN)=179.94	$q^{Na(1)}=0.334$; $q^{Na(2)}=0.196$; $q^{Na(3)}=0.073$; $q^{Na(4)}=-0.068$; $q^O=-0.333$; $q^C=0.335$; $q^N=-0.536$
6 (C _s) 4.273	r(Na ₁ O)=2.365; r(Na ₄ O)=2.302; r(Na ₁ Na ₃)=3.563; r(Na ₂ Na ₃)=3.442; r(Na ₂ N)=2.305; r(OC)=1.241; r(CN)=1.196; ∠(Na ₁ ONa ₄)=98.43; ∠(NNa ₂ Na ₃)=131.08; ∠(ONa ₁ Na ₃)=128.04; ∠(Na ₁ OC)=106.88; ∠(OCN)=178.13; ∠(Na ₁ Na ₃ Na ₂)=66.22; ∠(Na ₂ NC)=109.64;	$q^{Na(1)}=-0.025$; $q^{Na(2)}=0.315$; $q^{Na(3)}=-0.028$; $q^{Na(4)}=-0.104$; $q^O=0.356$; $q^C=-0.106$; $q^N=-0.408$

<p>7 (C_s) 4.350</p>	<p>r(Na₁O)=2.253; r(Na₃O)=2.412; r(Na₁Na₂)=3.338; r(Na₄N)=2.334; r(OC)=1.242; r(CN)=1.196; ∠(Na₁ONa₃)=93.07; ∠(Na₃OC)=108.20; ∠(Na₄NC)=106,35; ∠(OCN)=177.87; ∠(ONa₁Na₂)=112.48</p>	<p>$q^{Na(1)}=0.108$; $q^{Na(2)}=-0.015$; $q^{Na(3)}=-0.106$; $q^{Na(4)}=0.203$; $q^O=0.290$; $q^C=-0.214$; $q^N=-0.265$</p>
<p>8 (C_i) 4.117</p>	<p>r(Na₂N)=2.628; r(Na₃N)=3.378; r(Na₁Na₄)=3.731; r(Na₄O)=2.449; r(Na₁Na₃)=3.309; r(OC)=1.213; r(CN)=1.214; ∠(Na₂NNa₃)=115.72; ∠(Na₁Na₃N)=51.43; ∠(Na₃Na₁Na₄)=65.05; ∠(Na₁Na₄O)=75.37; ∠(Na₂NC)=99.74; ∠(Na₄OC)=104.29; ∠(OCN)=175.49; ∠(Na₃Na₁Na₄O)=74.62; ∠(Na₄OCN)=-10.61; ∠(Na₁Na₃NC)=98.66; ∠(Na₂NCNa₃)=-175.85;</p>	<p>$q^{Na(1)}=-0.099$; $q^{Na(2)}=-0.106$; $q^{Na(3)}=-0.173$; $q^{Na(4)}=0.113$; $q^O=-0.022$; $q^C=-0.569$; $q^N=0.856$</p>

Table 2. The MP2 geometrical parameters (bond lengths in Å, angles in degrees) and partial atomic charges (in a.u.) fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme for the Na_4OCN^+ cationic species. See Figure 3 for atom numbering. Vertical ionization potentials (VIP_c) in eV.

Species (symmetry) VIP _c	Geometry	Partial atomic charges
1⁺ (C _{2v}) 3.453	r(Na ₁ O)=2.133; r(Na ₂ N)=2.425; r(Na ₂ Na ₃)=3.522; r(OC)=1.223; r(CN)=1.198; ∠(Na ₂ NNa ₂)=79.91; ∠(Na ₂ Na ₃ Na ₂)=52.49; ∠(Na ₂ NC)=140.05; ∠(NNa ₂ Na ₃)=113.80;	$q^{\text{Na}(1)}=1.019$; $q^{\text{Na}(2)}=0.268$; $q^{\text{Na}(3)}=0.102$; $q^{\text{O}}=-1.102$; $q^{\text{C}}=1.340$; $q^{\text{N}}=-0.895$
2⁺ (C _s) 3.403	r(Na ₁ N)=2.498; r(Na ₂ O)=2.356; r(Na ₁ Na ₃)=3.472; r(Na ₂ Na ₃)=3.545; r(Na ₄ N)=2.246; r(OC)=1.211; r(CN)=1.210; ∠(Na ₁ NNa ₄)=139.49; ∠(Na ₁ NC)=93.55; ∠(Na ₁ Na ₃ Na ₂)=61.83; ∠(NNa ₁ Na ₃)=164.07; ∠(ONa ₂ Na ₃)=122.53; ∠(Na ₂ OC)=118.23; ∠(OCN)=177.37	$q^{\text{Na}(1)}=0.164$; $q^{\text{Na}(2)}=0.293$; $q^{\text{Na}(3)}=0.177$; $q^{\text{Na}(4)}=0.869$; $q^{\text{O}}=0.001$; $q^{\text{C}}=-0.265$; $q^{\text{N}}=-0.240$
4⁺ (C _{2v}) 2.973	r(Na ₁ O)=2.101; r(Na ₂ N)=2.251; r(Na ₂ Na ₃)=3.695; r(OC)=1.232; r(CN)=1.191; ∠(Na ₃ Na ₂ Na ₃)=53.65; ∠(Na ₃ Na ₂ N)=153.18	$q^{\text{Na}(1)}=0.924$; $q^{\text{Na}(2)}=0.033$; $q^{\text{Na}(3)}=0.269$; $q^{\text{O}}=-0.477$; $q^{\text{C}}=-0.037$; $q^{\text{N}}=0.019$
5⁺ (C _{2v}) 2.670	r(Na ₁ N)=2.182; r(Na ₂ O)=2.181; r(Na ₂ Na ₃)=3.662; r(OC)=1.222; r(CN)=1.195; ∠(Na ₃ Na ₂ Na ₃)=54.52; ∠(Na ₃ Na ₂ O)=152.74	$q^{\text{Na}(1)}=0.930$; $q^{\text{Na}(2)}=-0.036$; $q^{\text{Na}(3)}=0.293$; $q^{\text{O}}=0.191$; $q^{\text{C}}=0.098$; $q^{\text{N}}=-0.767$
6⁺ (C _s) 3.639	r(Na ₂ N)=2.336; r(Na ₁ O)=2.544; r(Na ₂ Na ₃)=3.628; r(Na ₄ O)=2.210; r(Na ₁ Na ₃)=3.421; r(CN)=1.192; r(OC)=1.252; ∠(Na ₁ ONa ₄)=150.42; ∠(Na ₄ OC)=118.42; ∠(ONa ₁ Na ₃)=143.88; ∠(NNa ₂ Na ₃)=126.05; ∠(Na ₂ NC)=118.78; ∠(Na ₁ Na ₃ Na ₂)=61.39; ∠(OCN)=178.74	$q^{\text{Na}(1)}=0.105$; $q^{\text{Na}(2)}=0.356$; $q^{\text{Na}(3)}=0.173$; $q^{\text{Na}(4)}=0.879$; $q^{\text{O}}=-0.060$; $q^{\text{C}}=-0.254$; $q^{\text{N}}=-0.199$
7⁺ (C _{2v}) 3.110	r(Na ₁ N)=2.208; r(Na ₂ O)=2.375; r(Na ₂ Na ₃)=3.515; r(OC)=1.234; r(CN)=1.191; ∠(Na ₂ ONa ₂)=84.15; ∠(Na ₂ Na ₃ Na ₂)=53.84; ∠(Na ₂ OC)=137.93	$q^{\text{Na}(1)}=1.045$; $q^{\text{Na}(2)}=0.290$; $q^{\text{Na}(3)}=0.136$; $q^{\text{O}}=-0.896$; $q^{\text{C}}=1.630$; $q^{\text{N}}=-1.493$
9⁺ (C _{2v}) 3.902 ^a	r(Na ₁ O)=2.598; r(Na ₂ N)=2.461; r(Na ₁ Na ₂)=3.596; r(OC)=1.227; r(CN)=1.204; ∠(Na ₂ NNa ₂)=150.99; ∠(Na ₁ ONa ₁)=155.79;	$q^{\text{Na}(1)}=0.258$; $q^{\text{Na}(2)}=0.317$ $q^{\text{O}}=0.359$; $q^{\text{C}}=-0.736$; $q^{\text{N}}=0.227$
10⁺ (C _i) 2.892	r(Na ₁ N)=2.274; r(Na ₂ O)=2.375; r(Na ₃ O)=2.212; r(OC)=1.365; r(CN)=1.271; ∠(Na ₁ NC)=85.29; ∠(Na ₂ ONa ₂)=90.26; ∠(Na ₃ OC)=87.80; ∠(OCN)=127.67; ∠(Na ₃ ONa ₂ Na ₂)=156.28; ∠(Na ₂ ONa ₂ C)=-79.17	$q^{\text{Na}(1)}=0.839$; $q^{\text{Na}(2)}=0.826$ $q^{\text{Na}(3)}=0.757$; $q^{\text{O}}=-0.609$; $q^{\text{C}}=-0.879$; $q^{\text{N}}=-0.772$

^a CCSD(T)/6-311+G(3df) result (the PS value for the OVGf calculation was too small)

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Captions for figures**Figure 1.**

The MP2/6-311+G(d) equilibrium structures of the Na₄OCN isomers.

Figure 2.

Singly occupied molecular orbitals (SOMO) of the Na₄OCN isomers.

Figure 3.

The MP2/6-311+G(d) equilibrium structures of the Na₄OCN⁺ cationic isomers.

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