



Exotic noble gas carbene-like ions



Andrea Echeverri, Norberto Moreno, Albeiro Restrepo, C.Z. Hadad*

Grupo de Química-Física Teórica, Instituto de Química, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

ARTICLE INFO

Article history:

Received 14 June 2014

In final form 23 September 2014

Available online 2 October 2014

ABSTRACT

Using a combination of theoretical techniques, this work studies the Kr_2C^{2+} species, which has electronic, structural, and some typical chemical characteristics of carbenes, and whose ground state is singlet. Similarly to the case of traditional carbenes, Kr_2C^{2+} is metastable and appears to be a candidate for a reactive intermediate.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Carbenes are among the most relevant entities in Chemistry, with frontier research about these substances being very active [1–3]. Carbenes are traditionally described as neutral molecular species where the central carbon atom has 6 electrons in its valence shell: two bonding electron pairs plus two paired (singlet state) or unpaired (triplet state) electrons. Thus, usually, they are metastable and very useful as reactive intermediates in many chemical reactions [1]. On the other side, starting with the synthesis in 1962 of the first noble gas (Ng) compound [4], researchers have found, both, theoretically and experimentally, hundreds of new species of those “inert” elements [5]. Very relevant to this Letter are the valuable descriptions of the molecular ions NgCH^+ (Ng = He, Ne, Ar, Kr, and Xe) [6,7], and Ng_2C^{2+} (Ng = He, Ne and Ar) [8], which were studied because of their significance as new noble gas containing compounds. Even though this class of species are charged, one very interesting question that arises naturally because of the exotic mixture of noble gas atoms in an ionic species sporting an electron-deficient central carbon atom is: are these types of compounds similar to carbenes? To explore this issue, we chose the unreported Kr_2C^{2+} species, where Kr is a better electron-donor than He, Ne, and Ar. We present here a prospective study on the stability of Kr_2C^{2+} focusing in analyzing its possible carbene-like nature. Our results show that this class of reactive gaseous species is a “kind of carbene” that could open future new chemical perspectives.

2. Computational details

Optimization, vibrational frequencies (analytical harmonic second order derivative calculations), energy, scan, intrinsic reaction

coordinate (IRC), and natural bond orbital (NBO, Version 3.1. [9]) calculations were carried out using the GAUSSIAN 09 package [10]. The preliminary search of the configurational space of the possible species involved in the Kr_2C^{2+} PES were carried out at the MP2/6-311+G(d) level of theory, which is adequate for describing the geometries of carbenes [11]. Energies of the located geometries were calculated at the CCSD(T)/Aug-cc-pVTZ//MP2/6-311+G(d) level. Additional optimizations for singlet and triplet Kr_2C^{2+} structures were carried out at the highly correlated CCSD/Aug-cc-pVTZ level, and their final energies are reported at the CCSD(T)/Aug-cc-pVTZ level. This allowed us to compare the results between MP2, CCSD and CCSD(T) methods for geometries and energies, and to validate the use of MP2 for geometries, and the use of the more correlated methods only for the energies for several structures reported in this paper. This choice of methodology has proven very effective for accurate calculations in previous studies of carbenes [11].

Energies of C^{2+} , C^+ , C^0 , Kr^+ , and Kr^0 species were calculated at the CCSD(T)/Aug-cc-pVTZ level; the zero point energy (ZPE) corrected energies for the Kr_2C^{2+} fragmentation possibilities are reported at the CCSD(T)/Aug-cc-pVTZ//CCSD/Aug-cc-pVTZ level.

The Kr_2C^{2+} kinetic stability studies, involving relaxed scans, intrinsic reaction coordinate (IRC-type) calculations, were carried out at the MP2/Aug-cc-pVTZ level of theory. The energy barrier for the fragmentation of Kr_2C^{2+} was calculated at the CCSD/Aug-cc-pVTZ//MP2/Aug-cc-pVTZ level.

To generate candidate structures for the $\text{Kr}_2\text{C}^{2+}-\text{N}_2$ interactions, we used our ASCEC program in its molecular cluster capabilities [12–14]. ASCEC contains a modified Metropolis acceptance test in an adapted version of the Simulated Annealing optimization procedure. To construct the initial geometries, aiming at total independence of the initial guess, the two interacting molecules were placed at the same position, allowing them to evolve under the annealing conditions. We placed the molecules at the centers of cubes of 7, 8 Å sides ($343, 512 \text{ \AA}^3$ volumes), and calculated the

* Corresponding author.

E-mail address: cacier.hadad@udea.edu.co (C.Z. Hadad).

energies of Markovian chains of randomly generated configurations. We produced two independent ASCEC runs in each case to ensure a good scan of the PES. Detailed descriptions of the workings of the ASCEC algorithm can be found in Refs. [12,13]. The optimization of the candidate $\text{Kr}_2\text{C}^{2+}\text{-N}_2$ structures were carried out at the MP2/Aug-cc-pVTZ level. Frequency calculations were used to characterize all stationary points as true minima (no negative eigenvalues of the Hessian matrix). The interaction energy between the Kr_2C^{2+} and N_2 moieties leading to the formation of the $\text{Kr}_2\text{C}^{2+}\text{-N}_2$ species was calculated at the CCSD(T)/Aug-cc-pVTZ//MP2/Aug-cc-pVTZ level.

Topological analyses of the electron densities within the framework of the Bader's Quantum theory of Atoms in Molecules, QTAIM [15], were calculated using the AIMALL (Version 13.05.06) program [16].

3. Results and discussion

3.1. Kr_2C^{2+} configurational space

Let us start with a preliminary characterization of the singlet (S), and triplet (T), Kr_2C^{2+} configurational space. Figure 1 shows the located structures.

The global minimum corresponds to the angular singlet (A-S) structure, followed in energy order by the angular triplet (A-T). We also found another local minimum, a linear Kr-Kr-C singlet structure (L-S), but with even higher energy. Intrinsic reaction coordinate calculations suggest that L-S^\ddagger and L-T^\ddagger are the transition states for the A-S and A-T angular inversion respectively, with corresponding ZPE corrected barrier energies of 32.57 and 38.93 kcal mol⁻¹ at the MP2/6-311+G(d) level and of 28.43 and 35.00 kcal mol⁻¹ at the CCSD(T)/Aug-cc-pVTZ//MP2/6-311+G(d) level. Likewise, the A-S^\ddagger structure proved to be the

transition state for the interconversion between the A-S and L-S structures, with A-S to L-S ZPE corrected energy barrier of 52.91 kcal mol⁻¹ at MP2/6-311+G(d) level and of 47.26 at CCSD(T)/Aug-cc-pVTZ//MP2/6-311+G(d) level, and with L-S to A-S ZPE corrected energy barrier of 6.59 kcal mol⁻¹ at MP2/6-311+G(d) level and of 3.72 at CCSD(T)/Aug-cc-pVTZ//MP2/6-311+G(d) level. In this particular case, the equilibrium should be strongly shifted toward the formation of A-S from L-S.

A-T and L-S have, respectively, energies of about 30kT and 78kT (*kT*, the thermal energy at 298 K) higher than A-S at the MP2/6-311+G(d) level and of 43kT and 73kT at the CCSD(T)/Aug-cc-pVTZ//MP2/6-311+G(d) level. Therefore, if A-S, A-T and L-S were stable at room temperature, a Kr_2C^{2+} gaseous sample would consist almost exclusively of the A-S species. A further reoptimization at the CCSD/Aug-cc-pVTZ level of theory for the A-S and A-T structures, gave the structural and vibrational data shown in parenthesis in Figure 1. The energy difference, ΔE_0 , between A-T and A-S structures, obtained at the CCSD(T)/Aug-cc-pVTZ//CCSD/aug-cc-pVTZ level of theory is 25.24 kcal mol⁻¹. Those data indicate only marginal changes in geometries, but some energetic variations, validating the MP2 treatment of geometries further in this paper, and the calculation of energies at higher correlated levels. From now on we will refer to singlet and triplet angular species as S and T structures, respectively.

3.2. Thermochemical analysis

Judging by the high values of the S and T lowest frequencies, and by the fact that the set of structures in Figure 1 interconvert to each other without molecular fragmentation, we can anticipate that S and T, when isolated, should be kinetically stable. But before we do a kinetic analysis, let us check, in Table 1, the S and T energetics with respect to their fragmentation possibilities.

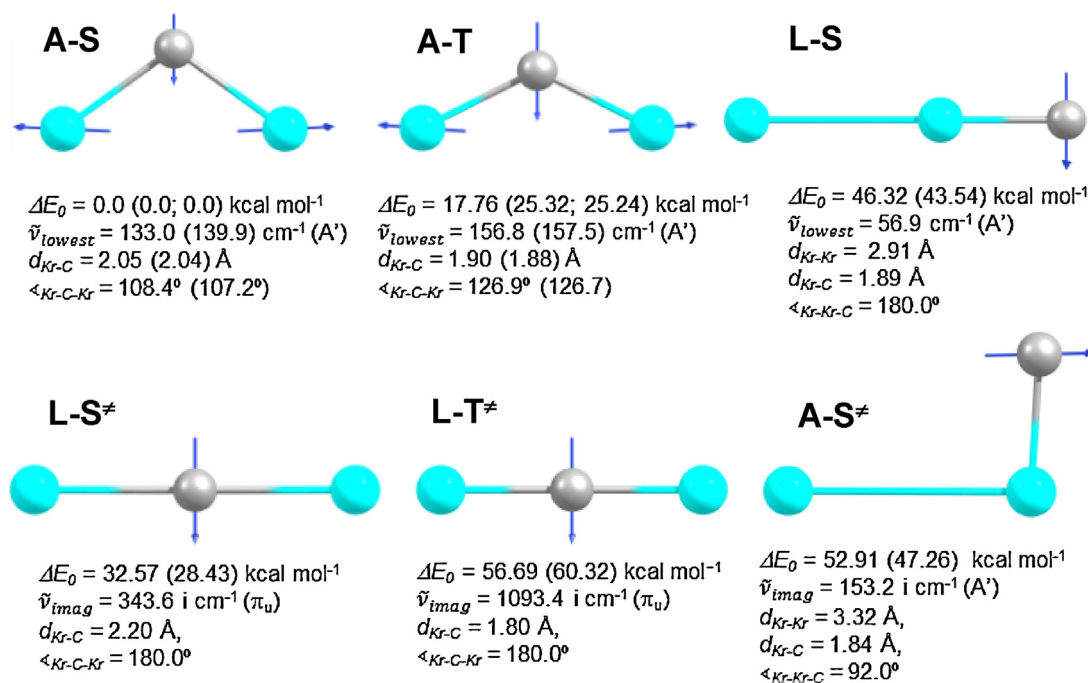


Figure 1. Located structures for the singlet (S), and triplet (T) states in the exploration of the MP2/6-311+G(d) configurational spaces of Kr_2C^{2+} . A and L are symbols for angular and linear geometries, respectively, and \ddagger for transition states. The corresponding lowest, $\tilde{\nu}_{lowest}$, or imaginary, $\tilde{\nu}_{imag}$, frequencies, with their associated displacement vectors, together with relative ZPE corrected energies, ΔE_0 , and molecular relevant distances and angles, are shown. The first data in parenthesis for ΔE_0 in A-S and the A-T cases, and the ΔE_0 data in parenthesis for the other structures are relative ZPE corrected energies at the CCSD(T)/Aug-cc-pVTZ level, calculated over the MP2/6-311+G(d) geometries. The second data in parenthesis for ΔE_0 values, and the data in parenthesis for the geometrical and vibrational properties in the A-S and the A-T cases, were obtained based on a further geometrical optimization at CCSD/Aug-cc-pVTZ level. The ΔE_0 values reported in those cases were obtained at CCSD(T)/Aug-cc-pVTZ//CCSD/aug-cc-pVTZ level of theory, and were corrected with the ZPEs generated at the CCSD/aug-cc-pVTZ level.

Table 1
Fragmentation possibilities and their ZPE corrected energies, ΔF_0 , for the $\text{Kr}_2\text{C}^{2+}({}^1\text{A}_1)$ and $\text{Kr}_2\text{C}^{2+}({}^3\text{B}_1)$ species.^a

Reaction	ΔF_0 (MP2)	ΔF_0 (CCSD(T))
$\text{Kr}_2\text{C}^{2+}({}^1\text{A}_1) \rightarrow \text{KrC}^{2+}({}^1\Sigma^+) + \text{Kr}^0({}^1\text{S})$	+59.21	+63.50
$\rightarrow 2\text{Kr}^0({}^1\text{S}) + \text{C}^{2+}({}^1\text{S})$	+218.82	+231.82
$\rightarrow \text{KrC}^+({}^2\Pi) + \text{Kr}^+({}^2\text{P})$	-46.54	-37.79
$\rightarrow \text{Kr}_2^+({}^2\Pi) + \text{C}^+({}^2\text{P})$	-45.06	-33.63
$\rightarrow \text{Kr}^+({}^2\text{P}) + \text{Kr}^0({}^1\text{S}) + \text{C}^+({}^2\text{P})$	-19.51	-3.98
$\text{Kr}_2\text{C}^{2+}({}^3\text{B}_1) \rightarrow \text{KrC}^{2+}({}^3\Pi) + \text{Kr}^0({}^1\text{S})$	+95.94	+102.03
$\rightarrow 2\text{Kr}^0({}^1\text{S}) + \text{C}^{2+}({}^3\text{P})$	+332.43	+357.16
$\rightarrow \text{KrC}^+({}^2\Pi) + \text{Kr}^+({}^2\text{P})$	-64.30	-63.03
$\rightarrow \text{Kr}_2^+({}^2\Pi) + \text{C}^+({}^2\text{P})$	-62.82	-58.87
$\rightarrow \text{Kr}^+({}^2\text{P}) + \text{Kr}^0({}^1\text{S}) + \text{C}^+({}^2\text{P})$	-37.27	-29.22

^a All values in kcal mol⁻¹. The MP2/6-311+G(d) energies corrected by the ZPE on the optimized geometries obtained at the same level. The CCSD(T)/Aug-cc-pVTZ energies on the CCSD/Aug-cc-pVTZ optimized geometries were corrected for the CCSD ZPEs. Positive ΔF_0 values describe endothermic reactions while negative ΔF_0 define exothermic ones.

Taking into account that the first and second ionization energies of carbon are 259.67 and 562.30 kcal mol⁻¹, respectively [17], and that CCSD(T)/Aug-cc-pVTZ energy calculations for the $\text{KrC}^+({}^2\Pi) \rightarrow \text{KrC}^{2+}({}^1\Sigma^+) + \text{e}^-$ and $\text{KrC}^+({}^2\Pi) \rightarrow \text{KrC}^{2+}({}^3\Pi) + \text{e}^-$ processes give 424.26 and 487.20 kcal mol⁻¹, respectively, we conclude that the generation of doubly charged KrC^{2+} and C^{2+} species are endothermic fragmentation paths. We have included them because, according to Frenking et al. [8], the fragmentation leading to donor-acceptor, $\text{Ng}^0\text{-NgC}^{2+}$ (or C^{2+}) products, must be the allowed paths, and also to show that their inverse reactions are possible pathways for the synthesis of the S and T species. Therefore, in this purely thermodynamic sense, the best way to synthesize Kr_2C^{2+} would be to start from doubly ionized carbon (acceptor) and neutral krypton (donor). The first ionization energy of krypton is 322.84 kcal mol⁻¹ [17], which is larger than that of carbon, therefore, the formation of the C^0 species from Kr_2C^{2+} is unlikely, thus, the consideration of the paths leading to Kr^{2+} or Kr_2^{2+} fragmentation products is unnecessary.

As can be seen in Table 1, the dissociation pathways leading to monocations are exothermic. Regardless of what products are allowed, the question of the kinetic viability of Kr_2C^{2+} bond breaking and the calculation of the energy barriers that separate Kr_2C^{2+} from its fragmentation products need to be addressed in order to evaluate the stability of this species and its possible existence as a metastable carbene-like reactive intermediate.

3.3. Kinetic analysis

Relaxed scan calculations at the MP2/Aug-cc-pVTZ level for the elongation and breaking of one or the two (synchronous elongation) KrC bonds give PE profiles with energy barriers of 62.11 (one bond) and 98.48 (two bonds) kcal mol⁻¹, for the S structure, and of 30.43 (one bond) and 68.72 (two bonds) kcal mol⁻¹, for the T structure. Based on these calculations, we found a transition state and ran the corresponding IRC for the molecular dissociation of S, the ground state singlet structure. The energy barrier is high, 62.13 kcal mol⁻¹ (64.74 kcal mol⁻¹ at the CCSD/Aug-cc-pVTZ//MP2/Aug-cc-pVTZ level). No calculation of relaxed scan or IRC type resulted in the dissociation to Kr_2^+ and C^+ products, which indicates that these pathways would be disfavored.

The important point about all these calculations, relaxed scans and IRCs, is that the energy barriers to fragmentation are high, especially in the case of the ground state singlet species, which is separated from its fragmentation products at least by an energy barrier of 64.74 kcal mol⁻¹, i.e. approximately 109.2 times kT (at 298 K). Therefore, Kr_2C^{2+} compounds, if isolated, should be kinetically stable. Hence, they have the usual characteristics of the

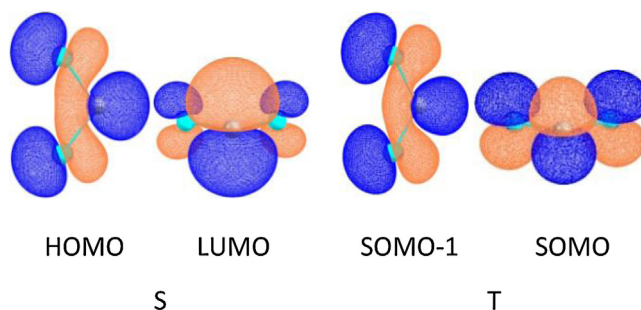


Figure 2. Frontier orbitals for the Kr_2C^{2+} singlet (S) state, and SOMO (α) and SOMO-1 (α) orbitals for the Kr_2C^{2+} triplet (T) state. All figures using the same isosurface value.

carbenes of being metastables and could, at least in the gas phase, be intermediates for chemical reactions. This last point could be tested, in part, by means of typical reactions. We now address the following question: are S and T carbene-like species?

3.4. The carbene-like characteristics of Kr_2C^{2+}

3.4.1. Electronic structure and bonding

We analyzed the Kr_2C^{2+} frontier delocalized molecular orbitals, MOs, and, in the case of the S structure, the relevant localized natural bonding orbitals, NBOs [18]. Figure 2 shows the HOMO and LUMO orbitals for S, and the SOMO (single occupied molecular orbital) and SOMO-1 orbitals for T. We found that the HOMO of the singlet structure mainly consists of a combination of s and p-like orbitals of carbon with p-like orbitals of krypton. Those p-like orbitals are all in the molecular plane and directed parallel to the line that bisects the KrCkr angle. Unambiguously, this MO has the characteristics of the typical HOMO σ -like orbital responsible for the nucleophilic properties of a singlet carbene. The LUMO of the singlet structure basically consists of the antibonding combination of p-like orbitals of C and Kr, which are perpendicular to the molecular plane, with the largest contribution coming from the p-orbital of C. Again, this MO is similar to the typical LUMO p-like orbital, responsible for the electrophilic properties of a singlet carbene. Likewise, the SOMO-1 and SOMO orbitals of the triplet state, each occupied by one α electron, are similar in shape to the HOMO and LUMO orbitals of the singlet state, respectively. Those findings, together with the known fact that the angle in triplet carbenes is larger than in singlets [11], as is the case in this Letter (Figure 1), strongly suggest that Kr_2C^{2+} , should be characterized as a carbene-like species.

Since the ground state is singlet, we continue our report with the S species. NBO [18] analysis predicts that C and Kr atoms are bonded, but that there is not a bond between Kr atoms: each localized C–Kr bond orbital (2 electrons, single bond) basically arises from the interactions between the C and Kr valence p orbitals, located in the molecular plane, with a small contribution from the Kr 4s orbital. The contribution from Kr valence atomic orbitals to this localized molecular orbital is around 70%. The bond would be covalent and polarized, with the electronic density directed toward Kr. As discussed in the next subsection, QTAIM [15] analysis supports that the Kr–C bond has covalent character.

Very interesting is the prediction of a lone electron pair located on a carbon atomic hybrid orbital, with 92.0% of 2s character and with 7.9% of contribution from the p orbital bisecting the KrCkr angle. This is similar to the typical singlet carbene nucleophilic lone pair, in this localized electronic scheme. Likewise, NBO calculations predict an almost empty (0.14 electrons) carbon p orbital, perpendicular to the molecular plane (similar to the typical electrophilic orbital of singlet carbenes).

Table 2
Selected QTAIM data at bond critical points for structures showed in Figure 4.^a

Specie	Atom pair	$\rho_c \times 10^2$	$\nabla^2 \rho_c \times 10^2$	$ V_c /G_c$	$H_c \times 10^2$
Kr_2C^{2+}	C1–Kr2	13.09	−7.15	2.39	−6.35
	C1–Kr3	13.09	−7.15	2.39	−6.35
$[\text{Kr}_2\text{CN}_2]^{2+}$	C1–Kr2	10.79	+1.10	1.94	−4.26
	C1–Kr3	10.79	+1.10	1.94	−4.26
	C1–N4	20.61	−50.23	3.27	−22.46
	N5–N4	62.83	−251.78	3.06	−122.10

^a ρ_c : electron density, $\nabla^2 \rho_c$: Laplacian, $|V_c|/G_c$: ratio between the absolute value of the potential energy density and the kinetic energy density, and H_c : total energy density. All values in a.u.

Very interesting also is a result of Second Order Perturbation Theory Analysis of the Fock Matrix within NBO [18]: this predicts a stabilizing interaction between the above mentioned antibonding localized empty p orbital and 2 occupied p-like lone-pair orbitals of the same symmetry, but located on each Kr atom, respectively. The stabilizing interaction energy is 26.03 kcal mol^{−1} for each Kr–C pair! This fact explains the great stability of the singlet state, as it is the case in stable traditional singlet carbenes.

3.4.2. Singlet carbene-like electrophilic power

In order to probe the “p-acceptor-like character of Kr_2C^{2+} leading to the formation of the corresponding adducts with electron-donor molecules, we performed stochastic walks on the configurational space for the interaction of Kr_2C^{2+} with N_2 , the major molecular component of air, as exemplifying case. Even though N_2 is very inert, it has lone electron pairs and electronic charge in the π orbitals, which can interact with our carbene-like species because Kr_2C^{2+} is very reactive, due to its large charge. After the ASCC-optimization process [12,13] described in Section 2, we found one $\text{Kr}_2\text{C}^{2+}-\text{N}_2$ stable structure, corresponding to a minimum in the MP2/6-311+G(d) PES. Additional refinement with optimization at the MP2/Aug-cc-pVTZ level, produced the global minimum depicted in Figure 3, which highlights that $\text{Kr}_2\text{C}^{2+}-\text{N}_2$ is, in part, stabilized by nitrogen electronic donation to the empty p-like orbital of the singlet carbene-like Kr_2C^{2+} species.

Judging by the value of the interaction distance, 1.536 Å for (nitrogen)–(carbene-like carbon), the (nitrogen)–(carbene-like p empty orbital) seems to be a chemical bond with a high degree of covalency. QTAIM strongly supports this hypothesis (see below). In addition, the MP2/Aug-cc-pVTZ stabilization energy with respect to separated Kr_2C^{2+} and N_2 species, is 41.35 kcal mol^{−1} at the MP2/Aug-cc-pVTZ level, and 33.09 kcal mol^{−1} at the CCSD(T)/Aug-cc-pVTZ//MP2/Aug-cc-pVTZ level. These are large interaction energies, supporting this view of a strong (covalent) interaction.

On the other hand, due to the Kr_2C^{2+} large charge, we expect that the nucleophilic power of Kr_2C^{2+} is diminished. We are currently studying this property, in a wider scope investigation whose subject is the similarities (if any) in Kr_2C^{2+} reactivity when compared to singlet carbenes in the presence of some typical reagents of carbene chemistry.

3.5. QTAIM analysis

Figure 4 shows molecular graphs of the species we are interested in, Table 2 list some relevant QTAIM data.

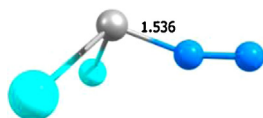


Figure 3. MP2/Aug-cc-pVTZ optimized structure for the interaction of Kr_2C^{2+} with the N_2 molecule. Distance in Å.

In a molecular graph for an equilibrium structure, the lines of the greatest electronic density between interacting atoms are the bond paths, BPs. They indicate some kind of interaction. The bond critical point, BCP, is the minimum of electron density in a BP. They are indicated as medium size circles at some position within each BP.

QTAIM properties calculated at BCPs allow characterization of the interactions. In the isolated Kr_2C^{2+} ion, electron densities at BCPs, ρ_c , are relatively large, and their Laplacians, $\nabla^2 \rho_c$, are smaller than zero. Negative Laplacians at BCPs are indicative of covalent bonding [15]. Likewise, when the $|V_c|/G_c$ ratio is greater than or equal to 2, the interaction is characterized as covalent bonding [15,19]. Our results show that both criteria are satisfied, suggesting that Kr–C interactions in Kr_2C^{2+} can be classified as covalent bonds.

When Kr_2C^{2+} interacts with N_2 , the covalent character of the C–Kr bonds decrease. In fact, according to Table 2, $\nabla^2 \rho_c > 0$ or close to zero, which indicates closed shell interaction [15,19]. However, C1–Kr2 and C1–Kr3 $|V_c|/G_c$ values are close or equal to 2 and, as stated in other cases [19], when the total energy density $H_c = G_c + V_c$ at the BCP, for closed shell interactions, is smaller than zero with $1 \leq |V_c|/G_c \leq 2$, the bonding, although not entirely covalent, has

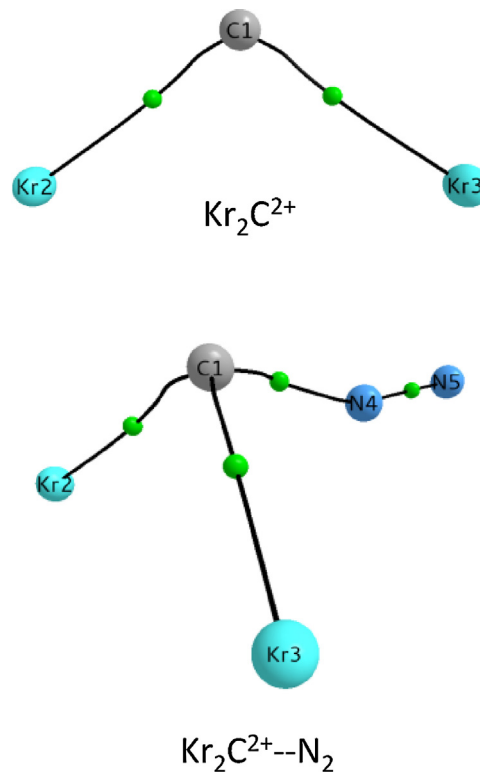


Figure 4. Molecular graphs of singlet Kr_2C^{2+} , $\text{Kr}_2\text{C}^{2+}-\text{N}_2$ species. Bond critical points, BCPs, are shown as medium size green spheres in the bond paths. (For interpretation of reference to colors in this figure legend, the reader is referred to the web version of this article.)

a covalent character. We conclude that the intramolecular C–Kr bonding decreases its covalent character, and probably its strength, in the presence of electron-donor molecules.

The C1–N4 stabilizing interaction corresponds to a covalent bond, as can be appreciated by its (very) negative $\nabla^2\rho_c$, and by the $|V_c|/G_c$, and H_c values.

4. Conclusions and perspectives

Taking into consideration the following points:

- Preliminary configurational space exploration of the Kr_2C^{2+} species indicates that singlet and triplet angular Kr–C–Kr geometries are the most energetically stable structures, and that any other Kr_2C^{2+} molecular geometries convert into to them.
- CCSD(T)/Aug-cc-pVTZ//CCSD/Aug-cc-pVTZ calculations indicate that the singlet angular Kr_2C^{2+} species is 25 kcal mol⁻¹ more stable than the triplet one and that the value of its lowest vibrational frequency is greater than 100 cm⁻¹.
- Kinetic analysis shows that energy barriers for all Kr_2C^{2+} rupture possibilities are quite high, especially for the ground state singlet Kr_2C^{2+} .
- Delocalized (HF) and localized (NBO) orbital molecular analysis, and the QTAIM methodology, indicate that Kr_2C^{2+} has the typical electronic characteristics of covalent bonded carbene-like species.
- NBO analysis explains that singlet Kr_2C^{2+} is more stable than the triplet state, because there are strong interactions between the lone electron pairs of Kr atoms and the empty p-like orbital of the carbene carbon.
- Singlet Kr_2C^{2+} species has the typical carbene-like chemical characteristics of being electrophilic, through its empty p-like orbital, and that this tendency is strong. It forms donor–acceptor adducts with very unreactive species, such as N_2 (electron donor).
- Almost all traditional carbene species known are metastable reactive intermediates.

We conclude that Kr_2C^{2+} , whose ground state is singlet, is a kind of noble gas carbene ion, which, in gaseous state, is metastable

(trapped by relatively high energy barriers) and could be a reactive intermediate in carbene-like chemical reactions. We are currently probing this last point by means of singlet carbene-like typical chemical reactions. The results will be published elsewhere.

Acknowledgments

We are thankful to Universidad de Antioquia for financial support through Estrategia de Sostenibilidad 2013–2014 and CODI project No. 644.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at [doi:10.1016/j.cplett.2014.09.059](https://doi.org/10.1016/j.cplett.2014.09.059).

References

- [1] G. Bertrand, S.A. FontisMedia (Eds.), *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagent*, Marcel Dekker, Inc., Lausanne, Switzerland, 2005.
- [2] R. Moss, *Chem. Rev.* 113 (2013) 6903.
- [3] J. Wang, J. Kubicki, T.L. Gustafson, M.S. Platz, *J. Am. Chem. Soc.* 130 (2008) 2304.
- [4] N. Bartlett, *Proc. Chem. Soc.* (6) (1962) 218.
- [5] W. Grochala, *Chem. Soc. Rev.* 36 (2007) 1632.
- [6] J.M. Hughes, E.I. von Nagy-Felsobuki, *Chem. Phys. Lett.* 272 (1997) 313.
- [7] A. Papakondylis, I.S.K. Kerkines, A. Mavridis, *J. Phys. Chem. A* 108 (2004) 11127.
- [8] G. Frenking, W. Koch, F. Reichel, D. Cremer, *J. Am. Chem. Soc.* 112 (1990) 4240.
- [9] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1.
- [10] M.J. Frisch, et al., *Gaussian 09, Revision A. 01*, Gaussian, Inc., Wallingford CT, 2009.
- [11] C. Gonzalez, A. Restrepo, M. Marquez, K. Wiberg, *J. Am. Chem. Soc.* 118 (1996) 5408.
- [12] J.F. Pérez, C.Z. Hadad, A. Restrepo, *Int. J. Quantum Chem.* 108 (2008) 1653.
- [13] J.F. Pérez, E. Florez, C.Z. Hadad, P. Fuentealba, A. Restrepo, *J. Phys. Chem. A* 112 (2008) 5749.
- [14] J. Pérez, A. Restrepo, ASCEC V–02: *Annealing Simulado con Energía Cuántica. Property, Development and Implementation*, Grupo de Química–Física Teórica, Instituto de Química, Universidad de Antioquia, Medellín, Colombia, 2008.
- [15] R. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, USA, 1994.
- [16] A. Todd, T.K. Keith, AIMAll (Version 13.05.06), Gristmill Software, Overland Park KS, USA, 2013 (www.aim.tkgristmill.com).
- [17] J.E. Sansonettia, W.C. Martin, *J. Phys. Chem. Ref. Data* 34 (2005) 1559.
- [18] E.D. Glendening, C.R. Landis, F. Weinhold, *WIREs Comput. Mol. Sci.* 2 (2012) 1.
- [19] S. Grabowski, *J. Chem. Rev.* 111 (2011) 2597.