

A Theoretical Investigation of Zn-Zn and Be-Be One Electron Bond

Kangkan Sarma¹, Amlan Kalita¹, and Ankur Guha¹

¹Cotton University

March 2, 2022

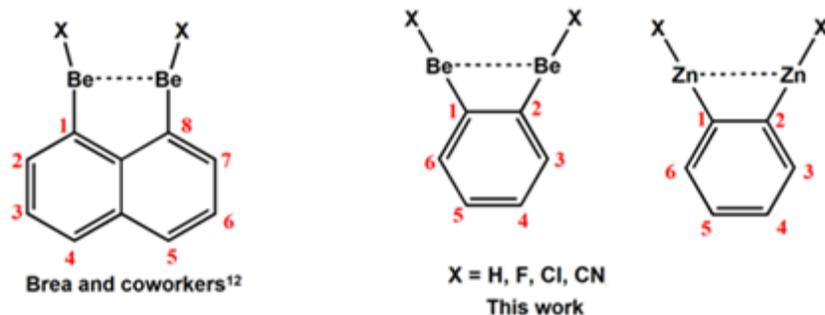
Abstract

Attachment of one electron to 1,2-diBeX-benzene and 1,2-diZnX-benzene derivatives leads to the formation of stronger Be-Be and Zn-Zn interaction. This is reflected in the dramatic shortening of the Be-Be and Zn-Zn distance. The formation of these 2-center-1-electron bonds have also been confirmed by topological survey of electron density using quantum theory of atoms in molecules and electron localization function. The formation of these bonds is expected to render stability to these radical anions. These radical anions are stable towards electron detachment and computed bond dissociation energy values are also significant.

Introduction

Homonuclear metal-metal bonds has always attracted chemists due to their enormous applications.¹ One such landmark advancement in this area was triggered by the discovery of first Zn(I) – Zn(I) σ bonded complex $[(\eta^5\text{-Cp}^*)_2\text{-Zn}_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) by Carmona and coworkers.² This seminal discovery has paved the way for isolation of various Zn(I) – Zn(I) bonded complexes involving various ligands.³ Recent years has also witnessed examples of multiply bonded Zn-Zn complexes.^{4,5}

Bare Zn₂ dimer, characterized by UV spectroscopy, appears to be a van der Waals complex with a Zn-Zn distance of 4.19 Å.⁶ In principle, the nature of bond in Zn₂ and Be₂ is almost similar as Be₂ has also been characterized in gas phase and described as van der Waals complex with Be-Be distance of 2.45 Å.⁷⁻⁹ The close analogy between the Zn₂ and Be₂ dimer is their similarity in valence electronic configuration (Be = 2s²2p⁰; Zn = 3d¹⁰4s²4p⁰) and exhibit typical Morse-van der Waals type potential.^{10,11} Thus, it appears that Zn will prefer similar chemistry as that of Be to a large extent. Brea and coworkers investigated an interesting phenomenon of single electron intramolecular Be-Be bond in 1,8-diBeX-naphthalene radical anion derivatives (Scheme 1).¹² Their calculations reveal that the extra electron forms the Be-Be bond with dramatic shortening of the Be-Be bond with respect to the neutral molecule. Both –BeX and –ZnX are acidic in nature and there is similarity in valence electron configuration of Be and Zn, we therefore, expect that Zn will exhibit similar intramolecular one electron bond formation. It should be noted that the distance between the H atoms of naphthalene attached to C1 and C8 atoms is almost similar (2.47 Å) to the distance between the H atoms attached to C1 and C2 atoms of benzene (Scheme 1). The choice of C1 and C8 disubstituted BeX in the work of Brea and coworkers¹² is obvious as these two positions are chemically most reactive.¹³ However, all positions in benzene are chemically equivalent. Thus, one can envision that similar intramolecular one electron Be-Be and Zn-Zn bonds formation will be possible in substituted benzene derivatives. We therefore, have undertaken a detailed theoretical study on the possible existence of intramolecular one-electron Be-Be and Zn-Zn bonds in 1,2-diBeX-benzene and 1,2-diZnX-benzene radical anion derivatives (Scheme 1). The probable questions that are likely to be answered in the contribution are – How strong can this one electron bond be? What will be the effect of X group? Are these radical anions experimentally realizable?



Scheme 1 . Schematic representations of the molecules considered in the study by Brea and coworkers¹² and in this work.

Computational Details

All the structures were fully optimized without any symmetry constraints at M06-2X/def2-TZVP level of theory.¹⁴ Harmonic vibrational frequency calculations were performed at the same level of theory to understand the nature of the stationary states. All structures were found to be at their local minima with all real values of the Hessian matrix. Unrestricted formalism was adopted for the open shell systems and otherwise mentioned; we observed negligible spin contamination ($< 1\%$) in all open shell calculations. To verify the mono-determinant character of the wavefunction, T_1 diagnostic values were evaluated using CCSD(T)/def2-TZVP single point calculations on the M06-2X optimized geometries. Electronic structures of the systems were studied using natural bond orbital (NBO) analyses¹⁵ and adaptive natural density partitioning (AdNDP) scheme.¹⁶ All these calculations were performed using GAUSSIAN16 suite of program.¹⁷

Further, the topological properties of electron density were analyzed within the framework of quantum theory of atoms in molecules (QTAIM)¹⁸ and electron localization function (ELF).¹⁹ All these calculations were performed using Multiwfn program code.²⁰

Results and Discussion

Figure 1 shows the optimized geometries of the radical anions. The T_1 diagnostic values of the CCSD(T)/def2-TZVP//M06-2X/def2-TZVP calculations are all lower than 0.02 suggesting single determinant character of the wave functions. For the Be containing compounds, high lying isomers are also located in the potential energy surface which feature no Be-Be interaction. These no Be-Be bond isomers are very high in energy and represents bond stretch isomers which were theoretically explained in 1972 by Hoffmann and co-workers for the polytopal rearrangement of $(\text{CH})_5^+$, $(\text{CH})_5$ and $(\text{CH})_4\text{CO}$.²¹ However, for Zn containing compounds, such high lying isomers (or bond stretch isomers) were not located on the potential energy surface. It is to be noted that all these molecules shown in Figure 1 are local minima in the potential energy surface with real values of Hessian matrix. The Be-Be distance in these compounds ranges from 2.586 to 2.450 Å with the shortest been found with $-\text{CN}$ as the substituent attached to Be atoms. The computed Wiberg bond indices (WBIs) are in the range of 0.146 to 0.195. Similarly, for Zn containing compounds, the Zn-Zn bond distance ranges from 2.909 to 3.023 Å. The computed WBIs are in the range of 0.258 to 0.268. Thus, these radical anions feature a strong Be-Be and Zn-Zn bonds.

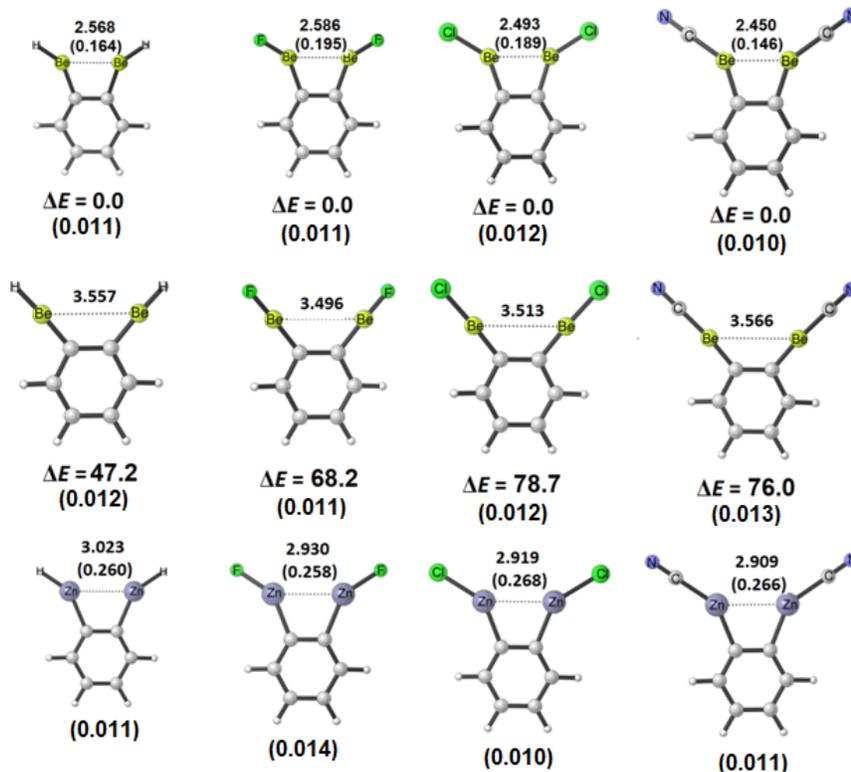


Figure 1 . Optimized geometries of the radical anions featuring 2 centre 1 electron bonds. Bond lengths are in Å and Wiberg bond indices (WBI) are given within parenthesis. Relative energies are in kJ/mol. T_1 diagnostic values of the CCSD(T)/def2-TZVP calculations are given within parenthesis.

The electronic structure of these radical anions were analyzed with adaptive natural density partitioning (AdNDP) scheme.¹⁶ AdNDP is a powerful tool which helps in understanding the distribution of electron pairs involving single, double and multiple centres. It provides unique identification of n-centre-n-electron bonds where the highest value of n is the total number of atoms in the molecule. Figure 2 shows the Be-Be and Zn-Zn bonds recovered using AdNDP scheme. AdNDP analyses identifies the presence of 2 centre 1-electron Be-Be and Zn-Zn bonds in all these molecules with occupation number close to 1.0 |e|. Analyses of the spin density also reveals that the location of the spin density is between two Be and Zn atoms in their lowest energy structures indicating the formation of one electron bond between them. In contrast, the spin density is mostly localized in the C-Be bonds in the bond stretch isomers of 1,2-diBeX anion radicals (Figure 3).

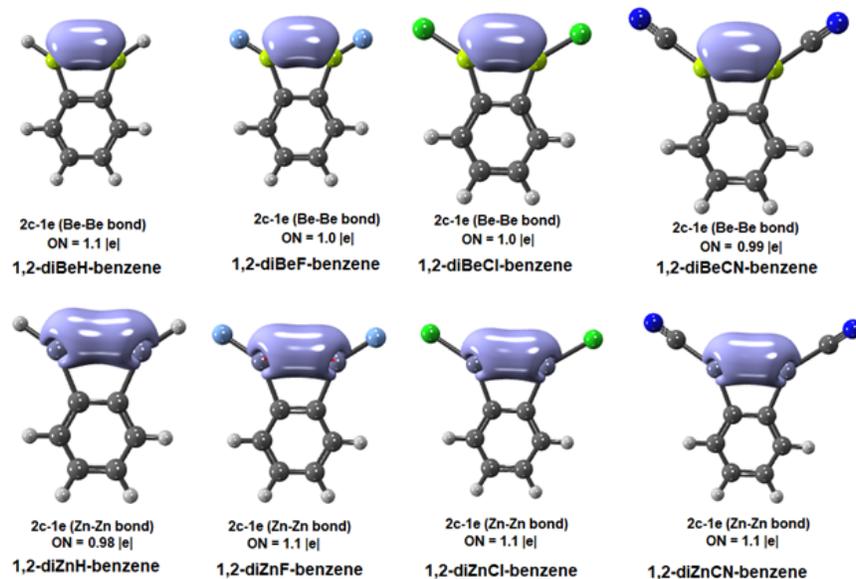


Figure 2 . Be-Be and Zn-Zn bonds recovered using AdNDP analyses.

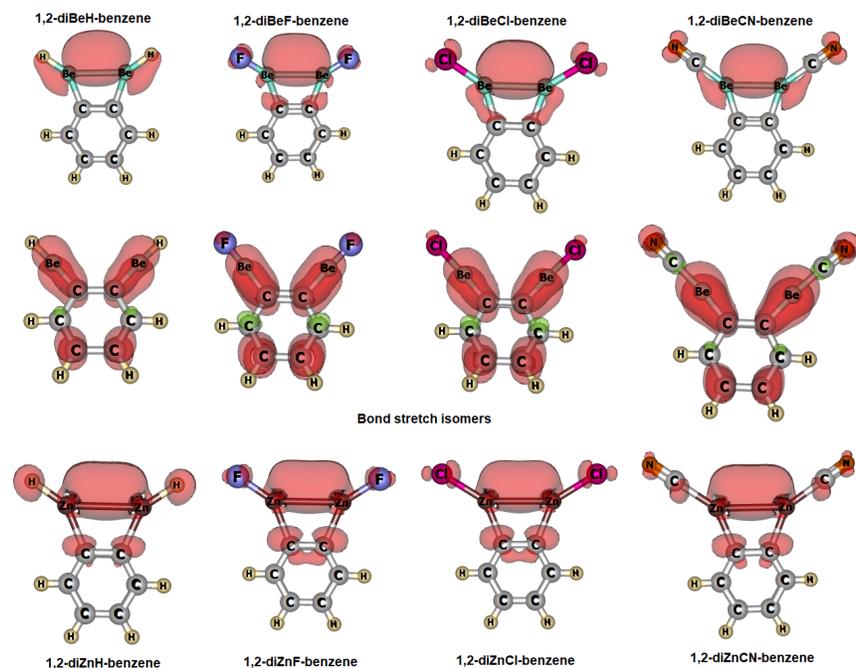


Figure 3 . Spin density plots of 1,2-diBeX and 1,2-diZnX radical anions. Bond stretch isomers of 1,2-diBeX radical anions are shown in the middle column. Contour value used in 0.03.

We then turned our attention to investigate the electronic structure of the studied systems. For this, we performed quantum theory of atoms in molecules (QTAIM),¹⁸ electron localization function (ELF)¹⁹ and natural bonding orbital (NBO) analyses.¹⁵ Table 1 contains the numerical values.

Table 1 . Electron density at the Be-Be and Zn-Zn bond critical points (ρ), laplacian of electron density ($[\nabla^2]\rho$), local electronic energy density, ELF population of the Be-Be and Zn-Zn bonds $V(M,M)$, NBO populations of Be-Be and Zn-Zn bonds and hybridization of the Be-Be and Zn-Zn bond. All values are in a.u.

Compounds	X	ρ	$[\nabla^2]$	$H(\mathbf{r})$	$V(M,M)$	Electron Population	Hybridization
	H	0.024	-0.007	-0.006	0.832	0.907	s(71.1%)p(28.7)
	F	0.022	-0.011	-0.005	0.901	0.921	s(75.3%)p(24.3)
	Cl	0.026	-0.013	-0.007	0.903	0.927	s(74.6%)p(25.0)
	CN	0.027	-0.013	-0.007	0.892	0.839	s(75.3%)p(24.2)
	H	0.02	0.009	-0.004	0.691	0.937	s(63.8%)p(36.2)
	F	0.02	0.001	-0.005	0.723	0.981	s(62.1%)p(37.0)
	Cl	0.02	0.011	-0.005	0.717	0.979	s(60.8%)p(38.6)
	CN	0.02	0.010	-0.005	0.762	0.962	s(52.4%)p(47.1)

It is evident from Table 1 that accumulation of significant electron density between the Be-Be and Zn-Zn bond critical points. The negative values of laplacian of electron density, $[\nabla^2]\rho$ and total electronic energy density, $H(\mathbf{r})$ suggests significant covalency in the Be-Be bonds. However, the positive value of laplacian of electron density, $[\nabla^2]\rho$ and negative value of total electronic energy density, $H(\mathbf{r})$ for Zn-Zn bond suggests polar covalent character. The calculated values of ELF populations, $V(M,M)$ are significantly higher for Be-Be bonds but somewhat smaller for Zn-Zn bonds. The electron population of the Be-Be bond and Zn-Zn bonds obtained through NBO analyses¹⁵ are very close to the value of 1.0 suggesting 2-centre-1-electron interaction. The hybridization of the Be-Be and Zn-Zn bonds have significant ns (2s for Be and 4s for Zn) character supporting covalent nature of these bonds. The contribution of s character decreases slightly for Zn-Zn bonds which has also reflected in the ELF basin populations, $V(Zn,Zn)$ (Table 1). The $V(Zn,Zn)$ values of Zn-Zn bonds are close to 0.7 while they are close to 0.9 for Be-Be bonds. Figure 4 shows the molecular graphs and 3D ELF plots of the compounds.

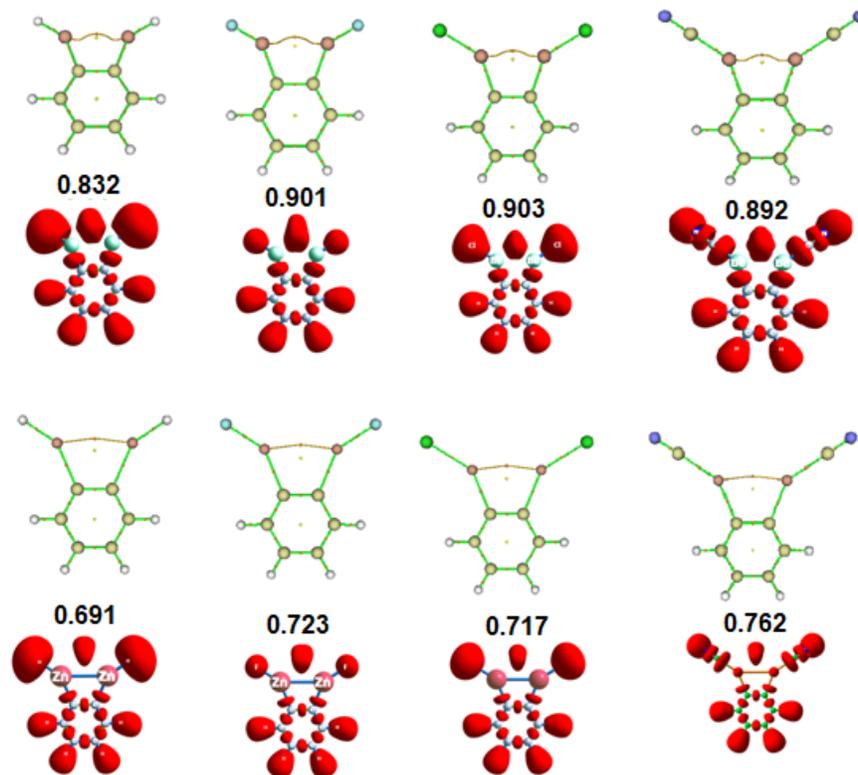
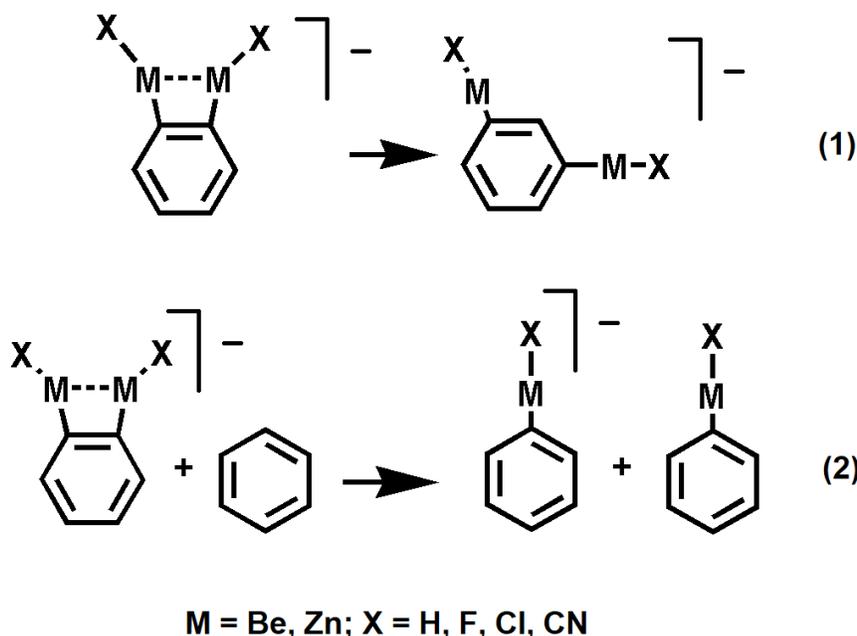


Figure 4. Molecular graphs of the compounds (first row for Be compounds and third row for Zn compounds) and 3D ELF plots of the compounds (second row for Be compounds and fourth row for Zn compounds). Population of the M-M disynaptic, $V(M,M)$ ($M = \text{Be}, \text{Zn}$) basins are also given in $|e|$.

We then turned our attention to investigate the strength of M-M ($M = \text{Be}, \text{Zn}$) bonds. For, this we have used two isodemic equations (Scheme 2). Moreover, stability of the radical anions towards electron detachment is very important. To check the stability of the radical anions towards electron detachment, we have also calculated the adiabatic detachment energies (ADEs). All these are collected in Table 2. It is evident from Table 2 that the M-M BDEs based on both the isodesmic equations are significant suggesting strong 2-centre-1-bonds. It should also be noted that in Figure 1 the other minimum energy structures of Be compounds are higher in energy where there was no Be-Be interaction. Thus, the energy difference between the two isomers may also be taken as a direct measure of BDE of the Be-Be bonds. The BDE values obtained with this direct approach are very similar to those obtained using isodesmic equations. However, such direct measure of BDE for the Zn compounds cannot be made as we could not locate any high lying isomers for Zn compounds. In every case, the calculated BDEs are highest for $X = \text{CN}$. A positive value (or less negative value) of ADE suggests that the anion is less stable towards electron detachment. The calculated value of ADE for benzene is -19 kJ/mol whereas for all these radical anions studied here have significantly negative values of ADE (more negative than benzene) suggesting the stability of these anion radical towards electron detachment. The formation of M-M one electron bond is responsible to provide stability to these anion radicals.



Scheme 2 . Isodesmic equations to evaluate M-M (M = Be, Zn) bond dissociation energies.

Table 2 . M-M (M = Be, Zn) bond dissociation energies (kJ/mol) based on equation 1 and 2 (Scheme 2) and adiabatic detachment energies (ADE in kJ/mol).

Compounds	X	BDE	BDE	ADE
		Eq 1	Eq 2	
	H	47.4	67.1	-44.1
	F	66.3	72.0	-52.8
	Cl	78.6	81.7	-92.1
	CN	80.5	111.9	-176.8
	H	56.9	60.1	-56.9
	F	52.4	73.7	-127.2
	Cl	52.7	72.1	-142.7
	CN	62.7	87.7	-177.3

Conclusion

Quantum chemical calculations predict that attachment of one electron to 1,2-diBeX-benzene and 1,2-diZnX-benzene derivatives leads to the formation of a strong 2-center-1-electron bond encompassing the two metal centres. Topological features of electron density within the realm of quantum theory of atoms in molecules and electron localization function also supports the formation of these bonds. One important aspect of these radical anions is their stability towards electron detachment. The calculated adiabatic detachment energies of these radical anions are significantly negative suggesting their stability. Moreover, the calculated bond dissociation energy values are also significant.

Conflicts of interest

Authors declare no conflict of interest.

Funding Information

No funding was received for this work.

Supporting Information

Cartesian coordinates of all the molecules considered in this study along with their total energies in a. u.

References

1. (a) F. A. Cotton, C. A. Murillo, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 3rd ed.; Springer: Berlin, Germany, 2005. (b) Liddle, S. T. *Molecular Metal-Metal Bonds. Compounds, Synthesis Properties*; Wiley-VCH: Weinheim, Germany, **2015**.
2. I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, 305, 1136-1138.
3. (a) A. Grirrane, I. Resa, A. Rodríguez, E. Carmona, *Coord. Chem. Rev.* **2008**, 252, 1532-1539. (b) E. Carmona, A. Galindo, *Angew. Chem., Int. Ed.* **2008**, 47, 6526-6536. (c) T. Li, S. Schulz, P.W. Roesky, *Chem. Soc. Rev.* **2012**, 41, 3759-3771. (d) T. D. Lohrey, L. Maron, R. G. Bergman, J. Arnold, *J. Am. Chem. Soc.* **2019**, 141, 800-804.
4. J. Echeverria, A. Falceto, S. Alvarez, *Angew. Chem. Int. Ed.* **2017**, 129, 10285-10289.
5. X Liu, M. Zhang, S. Wu, R. Zhong, Y. Liu, A. M. Arif, Y. Geng, Z. Su, *ChemPhysChem*, **2020**, 21, 459-463.
6. M. A. Czajkowski, J. Koperski, *Spectrochim. Acta A* **1999**, 55, 2221-2229.
7. J. M. Merritt, V. E. Bondybey, M. C. Heaven, *Science* **2009**, 324, 1548-1551.
8. V. E. Bondybey, J. H. English, *J. Chem. Phys.*, **1984**, 80, 568.
9. V. E. Bondybey, *Chem. Phys. Lett.*, **1984**, 109, 436.
10. K. Patkowski, R. Podeszwa, K. Szalewicz, *J. Phys. Chem. A* **2007**, 111, 12822.
11. L. Bucinsky, S. Biskupic, M. Ilcin, V. Lukes, V. Laurinc, *J. Comput. Chem.* **2008**, 30, 65.
12. O. Brea, O. Mo, M. Yañez, I. Alkorta and J. Elguero, *Chem. Commun.* **2016**, 52, 9656-9659.
13. J. D. Roberts, M. C. Caserio, *Basic principles of organic chemistry*. **1977**, WA Benjamin, Inc.
14. Y. Zhao, D. G. Truhlar. *Theor. Chem. Acc.*, **2008**, 120, 215.
15. A. E. Reed, F. Weinhold, L. A. Curtiss, *Chem. Rev.* **1998**, 88, 899-926.
16. D. Y. Zubarev, A. I.; Boldyrev, *Phys. Chem. Chem. Phys.* **2008**, 10, 5207-5217.
17. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
18. R. W. F. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford Univ. Press, Oxford, **1990**.
19. (a) B. Silvi, A. Savin, *Nature*, **1994**, 371, 683-686; (b) A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, 92, 5397-5403.
20. T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, 33, 580.

21. W. D. Stohere, R. Hoffmann, *J. Am. Chem. Soc.* **1972** , 94, 1661-1668.