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PAPER

CBe₅E⁻ (E = Al, Ga, In, Tl): planar pentacoordinate carbon in heptaatomic clusters†

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A series of clusters with the general formula CBe₅E⁻ (E = Al, Ga, In, Tl) are theoretically shown to have a planar pentacoordinate carbon atom. The structures show a simple and rigid topological framework—a planar EBe₄ ring surrounding a C center, with one of the ring Be–Be bonds capped in-plane by a fifth Be atom. The system is stabilized by a network of multicenter σ bonds in which the central C atom is the acceptor, and π systems as well by which the C atom donates charge to the Be and E atoms that encircle it.

Molecules with planar pentacoordinate carbon (ppC) centers are oddities in chemistry. There is increasing theoretical evidence, however, that when metals surround carbon atoms it is possible for unusual coordinations to emerge and persist. Molecular systems with ppC atoms have been achieved computationally, for example, in hyparenes,[1] hydrocopper complexes,[2] boron–carbon clusters,[3] and in mixed metal–carbon clusters.[4–6] Unfortunately, most of those structures are just local minima on their corresponding potential energy surfaces (PES) such that they are impractical as targets for experimental detection, especially at the conditions under which such clusters are typically generated and studied.

In 2008, Pei *et al.* reported the first global minimum structure containing a ppC: CAl₅⁺.[7] We recently found *in silico* that the most stable structures of the CAl₄Be, CAl₃Be₂⁻ and CAl₂Be₃²⁻ clusters also possess ppC centers.[8] Those predictions prompted us to examine a wider range of small rings that combine beryllium with group 13 elements since such combinations of elements seem to provide excellent

(spatial and electronic) conditions for the stability of ppC centers in compounds.

We report herein a series of systems with the general formula CBe₅E⁻ (E = Al, Ga, In, Tl) that are minima (global minima for E = Al, and Ga) when the C atom is in a planar pentacoordinate environment, and which show substantial promise as experimentally attainable species. We found that for both spatial and electronic reasons the preference for a planar pentacoordinate carbon in the minimum energy isomer is quite sensitive to the identity of E. The prospects for the experimental identification of the lowest energy pentacoordinate systems are also discussed.

Computational methods

Our computational procedure utilizes the *ab initio* Gradient Embedded Genetic Algorithm (GEGA)[9,10] to generate starting structures (at the B3LYP[11,12]/LANL2DZ[13] level), which are screened using density-functional theory (at the B3LYP/def2-TZVPP[14]) to establish a hierarchical ordering of the isomers based on the computed energies. Starting with the most competitive minimum energy structures from the previous steps, an evaluation of the relative energies at a high level *ab initio* method (CCSD(T)[15]/def2-TZVPP//B3LYP/def2-TZVPP) is used to identify the lowest energy isomer. All these computations were done using the Gaussian 09 suite of programs.[16]

To further confirm the thermal stability of the predicted ppC structures at room temperature, Born–Oppenheimer molecular dynamics (BOMD) calculations were performed using the deMon2k[17] program, employing the generalized gradient approximation (GGA) PW91[18] functional and the double zeta plus valence polarization (DZVP-GGA)[19,20] all-electron basis sets. The temperature in the canonical BOMD simulations was controlled by a Nosé chain thermostat.[21,22] For CBe₅Al⁻ and

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† Electronic supplementary information (ESI) available: Molecular dynamics movie of the CBe₅Al⁻ cluster. See DOI: 10.1039/c2cp40839b

CBe_5Ga^-, four trajectories were recorded at 300 K. The systems were sampled for 30 ps with 1 fs step size.

The induced magnetic field ($\boldsymbol{B}^{ind}$) computations[23,24] were performed the using PW91 functional in conjunction with the DZVP basis sets for CBe_5Al^- and CBe_5Ga^-. The shielding tensors were computed using the IGLO[25] method. The deMon2k program[17] was used to compute the molecular orbitals, and the deMon-NMR package[26] for the shielding tensors. Induced magnetic fields are given in ppm of the external field applied perpendicular to the molecular plane. Assuming an external magnetic field of $|\boldsymbol{B}^{ext}| = 1.0$ T, the unit of $\boldsymbol{B}^{ind}$ is 1.0 μT, which is equivalent to 1.0 ppm of the shielding tensor. In order to compute the induced magnetic fields the molecules were oriented so that the carbon atom is located at the origin of the coordinate system. The external field is applied perpendicular to the molecular plane.

Structural preferences

The most stable CBe_5E^- (E = Al, Ga, In, Tl) structures within 10 kcal mol^{-1} above the respective global minima are shown in Fig. 1. For E = Al and Ga, the planar pentacoordinate isomer **A** is the lowest energy structure, and it is the second lowest energy minimum on the PES for the In and Tl cases. The preferred structure, in the case of the In and Tl systems, **B** is an extraordinary three-dimensional cluster with a square pyramidal CBe_4 fragment, but that is more stable by only 1.2 and 1.8 kcal mol^{-1} relative to structure **A** in Fig. 1 with the ppC center.

	A	**B**	**C**	**D**	**E**
Al	**0.0**	2.7	2.8	3.5	4.0
Ga	**0.0**	1.4	1.9	8.7	4.1
In	1.2	**0.0**	3.1	10.4	1.2
Tl	1.8	**0.0**	4.8	13.6	2.4

	F	**G**	**H**	**I**	**J**
Al	4.2	4.3	4.5	4.7	5.2
Ga	4.8	5.2	4.5	6.5	6.9
In	4.1	2.2	6.7	8.9	8.1
Tl	5.6	2.8 (1)^b	8.9 (1)^b	10.1	9.9

	K	**L**	**M**	**N**
Al	7.0	9.4	10.4	12.8
Ga	8.0	31.0	9.1	10.7
In	3.3	33.1	7.2	12.4
Tl	3.4	--- ^{a}	8.2	14.1

^{a}This structure does not converge. ^{b}In parentheses is the number of imaginary frequencies.

Fig. 1 ΔE(kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVPP// B3LYP/def2-TZVPP level for the most stable isomers of CBe_5E^- (E = Al, Ga, In, Tl).
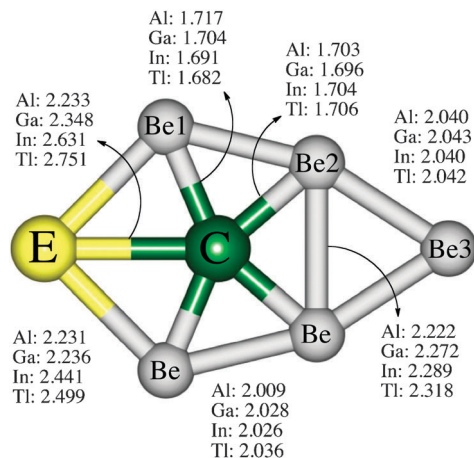
Fig. 2 Key geometrical parameters of the CBe_5E^- (E = Al, Ga, In, Tl) clusters. The bond lengths are given in Å units and have been computed at the B3LYP/def2-TZVPP level of theory.

Several other low energy isomers have been present for the Ga, In, and Tl systems that are also identified on the PES of the Al system. It is quite remarkable, therefore, that the systems with planar pentacoordinate centers are found to be so competitive even for the In and Tl clusters that have a noticeably different ordering of the relative energies of the stable (local minima) conformations.

The structural parameters for isomer **A** are summarized in Fig. 2. For the rest of this discussion, we will focus on that geometry. The interatomic separation between the central C and the Be atoms in the ring (Fig. 2) ranges from 1.682 to 1.717 Å, depending on the identity of E. Recently, Wang *et al.* reported that planar tetracoordinate carbon arrangements can be achieved by employing multiple substituents on a framework of beryllium atoms,[27] despite its rather weak π-acceptor ability. In those cases, the reported C–Be bond lengths were somewhat shorter, ranging from 1.61 to 1.66.

For the CBe_5Al^- structure, the C–Al bond length is 2.233 Å. This separation is slightly longer than both the typical C–Al bond distance (of ~ 2.00 Å) and the computed distance in the CAl_5^+ structure (2.12 Å at the CCSD(T)/aug-cc-pVTZ level of theory).[7] The longer C–E distances are unsurprising since the Be atoms limit, in fact, how closely the E atom can approach the C atom in the ring center.

The vibrational analysis of isomer **A** at the B3LYP level shows that the lowest energy modes of the clusters are 99 (Al), 89 (Ga), 77 (In), and 72 cm^{-1} (Tl), and all of them involve the displacement of the C–E or Be_3 fragments out of the plane of the molecule. Born–Oppenheimer molecular dynamics (BOMD) simulations at the PW91/DZVP-GGA level support the thermal stability of the title species. The simulations were started from the equilibrium geometry, with random velocities assigned to the atoms. From the analysis of the structural evolution along the recorded trajectories, both simulations show that the ppC structure remains intact during the 30 ps run (see the movie included in the ESI†).

Why the ppC geometry?

The central C atom in structure **A** is involved in a system of multicenter bonds to the five atoms, one E and four Be, surrounding it. The extra Be atom that is on the perimeter

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of the five membered ring has no significant direct interaction with the C atom, even though some electron density from that atom is delocalized into the five membered EBe_4 ring.

The preference for this $(EBe_4 + Be)$ structure over the alternative hexacoordinate EBe_5 ring or, for that matter, the $(Be_5 + E)$ structure with E outside, is interesting. There is no obvious reason for the former structure to be preferred over the latter two alternatives. Yet, neither the hexacoordinate nor the $(Be_5 + E)$ structure is even a local minimum for any of the CBe_5E^- structures considered. Isomer **N** in Fig. 1 is non-planar hexacoordinate, and **E** has a five membered ring with atom E outside the ring. But in both of those cases it is a Be atom that is at the ring center, not the C atom.

A possible explanation for the stability of **A** over the structural analogues of **N** and **E** with C in the center is the greater polarity and stability of the E–C bond over the bridging E–Be bonds that would otherwise be formed (compare the local bonding environments of the E atom in **A** vs. **E**). A six membered Be_5E ring is unfavorable too, it seems, since the resulting ring turns out to be large and spatially incompatible with the small carbon atom.

Indeed, as we mentioned above, the C–E and C–Be bond lengths in all of the CBe_5E^- structures are already somewhat longer than the corresponding covalent single bond distances, and the individual C–E and C–Be Wiberg bond indices (WBIs)[28] are rather small, too. They range from 0.30 in CBe_5Tl^- to 0.42 in CBe_5Ga^-, and the C–Be indices ($WBI_{C–Be1} \approx 0.52$, $WBI_{C–Be2} \approx 0.63$) are quite independent of the identity of E. The interactions between the central C and the Be atom outside the five-membered ring are quite weak, and this is reflected in the rather small bond index (≈ 0.12). Taken together, these contributions give a total bond index for the central carbon atom of approximately 2.8. So, even though no single C–Be or C–E bond comes close to the nominal bond order of 1.0 for a free single bond, the fractional contributions from the individual C–E and C–Be interactions in structure **A** reinforce each other and stabilize the hypercoordinate structure.

The net charge transfer from the peripheral atoms to the central C atom in molecules is achieved primarily through the σ bonding framework. The natural population analysis (NPA)[29] charges on the C atoms are -2.18 (Al), -2.16 (Ga), -2.19 (In), and -2.20 (Tl). These charges are smaller, however, than those calculated for in CAl_5^+ ($-2.9 |e|$),[7] CAl_4Be ($-2.87|e|$), and $CAl_3Be_2^-$ ($-2.96|e|$),[8a] and this is likely because Be is less electropositive than Al. Nonetheless, carbon is a σ acceptor in our title molecules, and this is partially off-set by some donation from its $2p_z$ orbital to the π system of the surrounding ring. The valence orbital populations at C are ($2s^{1.44} 2p_x^{1.68} 2p_y^{1.64} 2p_z^{1.40}$) for CBe_5Al^-, and ($2s^{1.44} 2p_x^{1.69} 2p_y^{1.62} 2p_z^{1.39}$), ($2s^{1.45} 2p_x^{1.69} 2p_y^{1.62} 2p_z^{1.40}$), and ($2s^{1.46} 2p_x^{1.69} 2p_y^{1.62} 2p_z^{1.40}$) for E = Ga, In, and Tl, respectively. The higher $2p_x$ and $2p_y$ occupancies compared to the situation for the $2p_z$ orbitals are the result of this π back-donation, which helps to stabilize the planar structure. Interestingly, the $1.4 |e|$ occupancies of the $2p_z$ orbital of the ppCs in this work are $0.2 |e|$ smaller than they are in the CAl_4Be, and $CAl_3Be_2^-$ ppC cluster.[8a] So, even though the σ-bonding is apparently weaker in the title compounds compared to the latter systems, the π interactions are a bit more substantial.

The valence molecular orbitals for the lightest member of the family, CBe_5Al^-, are depicted in Fig. 3. As expected for
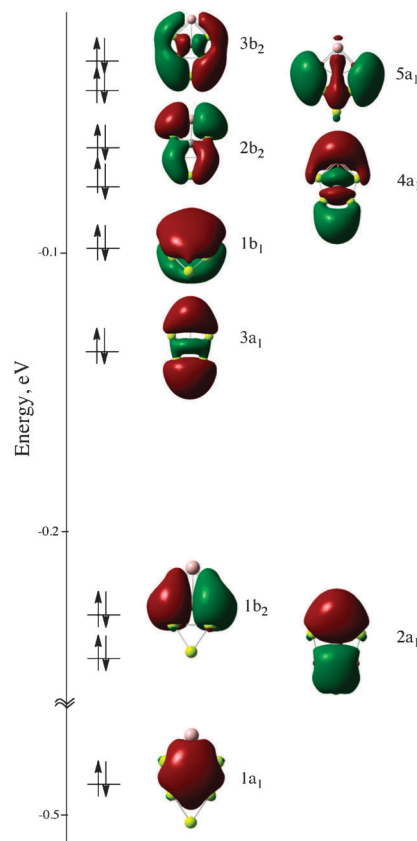

Fig. 3 Occupied valence molecular orbitals of **A**.

planar hypercoordinate carbon systems[30–33] a significant contribution of the perpendicular $2p_z$ orbital of the central C atom to the π-system in the molecule is observed. This is a primary feature of the $1b_1$ orbital (Fig. 3) that involves the p_z orbital on each atom of the five-membered ring. This MO is not solely responsible for the stability of the ppC system, however; as we confirm presently, the filling of this MO does not guarantee a preference for the planar structure. Given that the minimum energy structures with ppCs possess formally two delocalized π electrons, they satisfy the $(4n + 2)$ Hückel rule. The HOMO–LUMO gap in the systems at the B3LYP level (5.74, 5.82, 5.66, 5.65 eV for Al, Ga, In, Tl, respectively) supports their stability. By all of these measures, the gallium compound seems to be especially stable: it has the shortest C–Be distances, the largest total WBI (2.81), and the largest HOMO–LUMO gap.

Electron counts

Our experience with systems that contain planar tetra- and pentacoordinate C centers suggests that certain electron counts are crucial to the stability of molecules with C centers in non-classical coordination environments. Indeed, Schleyer made this point elegantly in his discussion of the CAl_5^+ system.[7] With its eighteen electrons, CBe_5Al^- has the same number of electrons as do the other small metal clusters, CAl_4Be and $CAl_3Be_2^-$,[8a] and the CAl_5^+ cation that all have a planar pentacoordinate global minimum. The key difference here, however, is that the CBe_5E^- compounds are seven atom
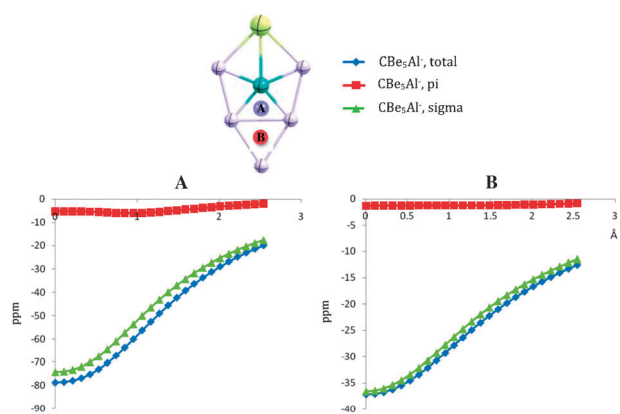
rather than six atom systems with a somewhat more complicated geometry. So, there is no reason to expect the planar penta-coordinate (CBe_5E^-) species considered in this work to be stabilized by the same 18 electron count. However, the basic fragment, CBe_4E ring hexatomic (which is common to the CAl_5^+, CAl_4Be and $CAl_3Be_2^-$ systems), is present in CBe_5E^-, and as the NPA data confirm (*vide supra*) the central C atom in the latter compound is stabilized by a net charge transfer from the peripheral Be and E atoms, which is also the case in the hexatomic systems studied previously. Moreover, the NPA charges suggests that the Be atom outside the ring is positive (see Fig. S1, ESI†). In principle, if we assume that the beryllium atom outside the five-membered ring acts as a dication, the total charge of CBe_4E is -3 and thus the CBe_4E fragment has 18 electrons. In other words, CBe_5E^- could be described as the interaction of CBe_4E^{3-} and Be^{2+}. So, the same basic electronic driving force and of course the same number of electrons appear to be required to stabilize these heptatomic clusters.

Electron delocalization

To improve our understanding of the electron delocalization in the CBe_5E^- anion we carried out a computational analysis of the ring current and possible aromaticity in the species. For this purpose, we considered two points in the structures, which are identified as 'A' and 'B' in Fig. 4. The graphs in that figure show the profiles along the z-axis for the σ- and π-contributions of the z-component of the induced magnetic field (B_z^{ind}) (the $NICS_{zz}$ index plotted as a scalar field).[34] The B_z^{ind} value at the center of any three membered ring ($B_z^{ind}(0)$) within the carbon centered five membered ring in CBe_5Al^- and CBe_5Ga^- is higher than -80 ppm (see Fig. 4), approximately five times the value in benzene (-15.9 ppm). Clearly, the σ-system is very diatropic (and similar to that reported for Al_4^{2-} and CAl_4^{2-}).[35,36] Additionally, the contribution of the π-system is also diatropic, even though the effect is far smaller than it is for the σ-system. So, by this magnetic index, the ppC systems considered in this work could be classified as double aromatic although the σ contribution clearly dominates.

Moreover, our calculations reveal that the three-membered Be ring is also σ-aromatic, with a sizeable value of B_z^{ind} at the center of the ring of -35 ppm, as shown in Fig. 4. A straight-forward electron counting yields two valence electrons for this three-membered ring, which (in accordance with the molecular orbital description of aromaticity in all-metal rings)[37] occupy the delocalized σ-type valence molecular orbital $3a_1$ of Fig. 3. This accounts for the σ-aromatic and the negligible π-aromaticity of this ring as revealed by the calculated induced magnetic field on a line perpendicular to the ring and passing through the center of the ring.[38]

Summary and conclusion

In summary, we propose two planar pentacoordinate carbon species, which are global minima for their stoichiometries and are likely to exist in gas phase. The structures show a simple and rigid topological framework—a planar EBe_4 ring surrounding a C center, with one of the ring Be–Be bonds capped in-plane by a fifth Be atom. The system is stabilized by a network of multicenter σ bonds in which the central C atom is the acceptor, and π systems as well by which the C atom donates charge to the Be and E atoms that encircle it. We find that the planar structures are double (σ and π) aromatic. The presence of a global minimum energy ppC-containing cluster raises hope that this species can be prepared experimentally even at moderate to high temperatures. The limitations of working experimentally with Be do not escape us, but the systems we have considered provide a model for developing stable planar pentacoordinate systems and demonstrate that even for heptaatomic main group clusters a planar C center is feasible. The 18 electron preference proposed by Schleyer and Boldyrev[39] for the five-membered systems extends to these slightly larger clusters as well, but they are stabilized by isolating one of the Be atoms from the ring structure, and engaging its electron density in the more dominant five membered ring system to which it is attached.

Notes and references

1 Z. X. Wang and P. v. R. Schleyer, *Science*, 2001, **292**, 2465.
2 S. D. Li, C. Q. Miao and G. M. Ren, *Eur. J. Inorg. Chem.*, 2004, 2232.
3 J. X. Liang, W. H. Jia, C. J. Zhang and Z. X. Cao, *Acta Phys.-Chim. Sin.*, 2009, **25**, 1847.
4 Q. Luo, *Sci. China, Ser. B: Chem.*, 2008, **51**, 1030.
5 W. Yamaguchi, *Int. J. Quantum Chem.*, 2010, **110**, 1086.
6 A. D. Zdetsis, *J. Chem. Phys.*, 2011, **134**.
7 Y. Pei, W. An, K. Ito, P. v. R. Schleyer and X. C. Zeng, *J. Am. Chem. Soc.*, 2008, **130**, 10394.
8 (*a*) J. O. C. Jimenez-Halla, Y. B. Wu, Z. X. Wang, R. Islas, T. Heine and G. Merino, *Chem. Commun.*, 2010, **46**, 8776; (*b*) Y.-B. Wu, Y. Duan, H.-G. Lu and S.-D. Li, *J. Phys. Chem. A*, 2012, **116**, 3290.

Fig. 4 Profile of the induced magnetic field, B_z^{ind}. The external field is $|B^{ext}| = 1.0$ T and the units of the B_z^{ind} are ppm or μT.

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Phys. Chem. Chem. Phys., 2012, **14**, 14764–14768 | 14767

9 A. N. Alexandrova, A. I. Boldyrev, Y.-J. Fu, X. Yang, X.-B. Wang and L.-S. Wang, *J. Chem. Phys.*, 2004, **121**, 5709.

10 A. N. Alexandrova and A. I. Boldyrev, *J. Chem. Theory Comput.*, 2005, **1**, 566.

11 C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

12 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

13 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.

14 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

15 J. A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys.*, 1987, **87**, 5968.

16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, Gaussian, Inc., Wallingford, CT, 2009.

17 A. M. Köster, P. Calaminici, M. E. Casida, V. D. Dominguez, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J. M. del Campo, J. U. Reveles, A. Vela, B. Zuniga-Gutierrez and D. R. Salahub, *The deMon developers*, Cinvestav, Mexico City, 2006.

18 J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter*, 1992, **45**, 13244.

19 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.

20 P. Calaminici, F. Janetzko, A. M. Koster, R. Mejia-Olvera and B. Zuniga-Gutierrez, *J. Chem. Phys.*, 2007, **126**, 044108.

21 S. Nosé, *J. Chem. Phys.*, 1984, **81**, 511.

22 S. Nosé, *Mol. Phys.*, 1984, **52**, 255.

23 G. Merino, T. Heine and G. Seifert, *Chem.–Eur. J.*, 2004, **10**, 4367.

24 R. Islas, T. Heine and G. Merino, *Acc. Chem. Res*, 2012, **45**, 215.

25 W. Kutzelnigg, U. Fleischer and M. Schindler, *The IGLO-Method: Ab Initio Calculation and Interpretation of NMR Chemical Shifts and Magnetic Susceptibilities*, Springer-Verlag, Heidelberg, 1990.

26 V. G. Malkin, O. L. Malkina and D. R. Salahub, *Chem. Phys. Lett.*, 1993, **204**, 80.

27 Z.-X. Wang, C.-G. Zhang, Z. Chen and P. v. R. Schleyer, *Inorg. Chem.*, 2008, **47**, 1332.

28 K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

29 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.

30 R. Hoffmann, R. W. Alder and C. F. Wilcox Jr., *J. Am. Chem. Soc.*, 1970, **92**, 4992.

31 J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger and J. A. Pople, *J. Am. Chem. Soc.*, 1976, **98**, 5419.

32 R. Keese, *Chem. Rev. (Washington, D. C.)*, 2006, **106**, 4787.

33 G. Merino, M. A. Méndez-Rojas, A. Vela and T. Heine, *J. Comput. Chem.*, 2007, **28**, 362.

34 T. Heine, R. Islas and G. Merino, *J. Comput. Chem.*, 2007, **28**, 302.

35 R. Islas, T. Heine and G. Merino, *J. Chem. Theory Comput.*, 2007, **3**, 775.

36 A. C. Castro, M. Audiffred, J. M. Mercero, J. M. Ugalde, M. A. Mendez-Rojas and G. Merino, *Chem. Phys. Lett.*, 2012, **519–520**, 29.

37 S. Giri, D. R. Roy, S. Duley, A. Chakraborty, R. Parthasarathi, M. Elango, R. Vijayaraj, V. Subramanian, R. Islas, G. Merino and P. K. Chattaraj, *J. Comput. Chem.*, 2010, **31**, 1815.

38 J. M. Mercero, I. Infante and J. M. Ugalde, in *Aromaticity and Metal Clusters*, ed. P. K. Charraraj, CRC Press, Boca Raton, 2011.

39 P. v. R. Schleyer and A. I. Boldyrev, *Chem. Commun.*, 1991, 1536.

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