

Scalar and Spin–Orbit Relativistic Corrections to the NICS and the Induced Magnetic Field: The case of the E_{12}^{2-} Spherenes (E = Ge, Sn, Pb)

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Abstract: Can relativistic effects modify the NICS and the B^{ind} values? In this manuscript we evaluate the relativistic corrections incorporated via the zeroth-order regular approximation to the calculations of nucleus-independent chemical shifts and the induced magnetic field (B^{ind}) in the E_{12}^{2-} spherenes (E = Ge, Sn, Pb). We found that both electron delocalization descriptors are strongly affected by the relativistic corrections. For instance, for plumbaspherene, the difference in values from the nonrelativistic to the relativity-included calculation is almost 40 ppm! Our results show that the changes observed in the NICS and B^{ind} values in the title cages are a consequence of the treatment of the relativistic effects. If these effects are included as scalar or spin–orbit calculations, then we can establish the next trend: Ge_{12}^{2-} is a nonaromatic species, Sn_{12}^{2-} is a low aromatic species, and Pb_{12}^{2-} is strongly aromatic, according to calculated NICS and B^{ind} values. Thus, any prediction of electron delocalization in molecules containing heavy elements without considering an adequate treatment for relativistic effects may lead to an erroneous chemical interpretation.

The discovery of fullerene has motivated the quest for other stable spherical clusters. A spherical molecule, what could be more perfect? No other analogous gas-phase clusters were found or yielded to bulk syntheses until 2007.¹ In that year, Cui et al. found that both stannaspherene and plumbaspherene are stable clusters with a delocalized spherical π -bonding, similar to buckminsterfullerene C_{60} .^{2,3} Stannaspherene and plumbaspherene are clusters formed by 12 Sn and Pb atoms, respectively, distributed in a perfect icosahedron. Both cages have diameters comparable to that of C_{60} and can be considered as inorganic analogues of the buckyball. The large internal space in such beautiful systems

can trap some transition-metal atom to form new endohedral cage clusters, $M@E_{12}$, analogous to endohedral fullerenes.^{4–12} Recently, Sun et al. reported that during the attempt to synthesize endohedral stannaspherenes, they crystallized a new $Pd_2@Sn_{18}^{4-}$ cluster,¹⁰ which can be viewed as the fusion of two $Pd@Sn_{12}^{2-}$ clusters, suggesting that a large number of endohedrally doped species can be synthesized in the bulk using the title systems.

Particularly for Pb_{12}^{2-} , it is considered that the large stability of the endohedral $M@Pb_{12}$ clusters is a delicate balance between the cavity size and aromaticity.¹³ In this context, Chen et al. calculated the nucleus-independent chemical shift (NICS) value at the Sn_{12}^{2-} cage center (2.5 ppm at the GIAO-B3LYP/LanL2DZdp//B3LYP/LanL2DZdp level), indicating a nonaromatic character of stannospherene.⁵ According to this result, it is not possible to associate large stability to aromaticity in this species. Recently, Tian and

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co-workers evaluated the NICS at the same position and obtained a value of -5.0 ppm (calculated at the B3LYP/aug-cc-pVDZ-PP level).¹⁴ They suggested that a large basis set, including d-orbitals, is needed to analyze aromaticity in the aforementioned compound, thus the presence of a d-orbital is essential to calculate correctly the NICS in Sn_{12}^{2-} . However, they did not discuss the role of the relativistic effects, which can also drastically affect the shielding tensor,^{15–22} and the descriptors derived from it, such as the NICS.^{23–26}

In this manuscript we evaluate the relativistic corrections incorporated via the zeroth-order regular approximation (ZORA) to the calculations of NICS^{27,28} and the induced magnetic field (\mathbf{B}^{ind}).^{29,30} We found that in the case of Sn_{12}^{2-} both electron delocalization descriptors are strongly affected by the relativistic corrections. We also include the Ge_{12}^{2-} and Pb_{12}^{2-} clusters in this study in order to compare the magnitude of these changes.

Computational Details

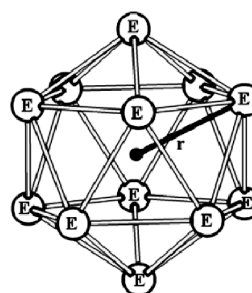
The geometries of these molecules have been optimized using the exchange functional of Becke with the correlation functional of Perdew (this combination is the so-called BP86 density functional).^{31,32} Uncontracted Slater-type orbitals (STOs) were employed as the basis functions for the self-consistent field (SCF) calculations. The basis sets have triple- ζ quality augmented by two sets of polarization functions (TZ2P), that is, d and f functions for the all atoms. In addition, we performed harmonic frequency calculations in order to check for the correct assessment of the minima points studied. The shielding tensors were calculated at the BP86, PW91,³³ and SAOP^{34,35} levels in conjunction with a TZ2P basis set. Both the scalar and the spin-orbit (SO) relativistic effects on the geometry and the shielding tensor calculations were incorporated via the ZORA.^{36–40} Shielding tensors were calculated with the gauge-independent atomic orbital (GIAO) method. All calculations were carried out with the ADF2009 package.^{41,42}

Results and Discussion

Table 1 summarizes the geometrical results obtained for the $I_h - \text{E}_{12}^{2-}$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) clusters at the BP86/TZ2P level. The largest deviation from the BP86/TZ2P level is obtained using the SO-ZORA correction for Pb_{12}^{2-} (0.08 Å). Note that while the relativistic effects induce a slightly diminution of the icosahedron inner space for the Ge_{12}^{2-} and Sn_{12}^{2-} clusters, they expand the Pb_{12}^{2-} cage. Differences between the ZORA and SO-ZORA approaches are not very significant in terms of geometrical parameters. In order to avoid any possible error source and confusion, we took the geometries optimized at the SO-ZORA-BP86/TZ2P level to calculate the shielding tensors using the different theoretical approximations.

Let us first concentrate on stannaspherene. The shielding tensor is well-defined at any position of the space. Obviously, NICS and \mathbf{B}^{ind} can also be calculated at any point of the space.^{43,44} The first one is a scalar molecular field, and the second is a vector molecular field.⁴⁵ Figures 1A and B depict the NICS and the z -component of the \mathbf{B}^{ind} (B_z^{ind}) profiles of

Table 1. Relevant Geometrical Parameters of $I_h - \text{E}_{12}^{2-}$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$)^a



	Ge		Sn		Pb	
	E–E	<i>r</i>	E–E	<i>r</i>	E–E	<i>r</i>
BP86/TZ2P	2.745	2.611	3.132	2.979	3.169	3.014
ZORA-BP86/TZ2P	2.736	2.602	3.130	2.976	3.250	3.090
SO-ZORA-BP86/TZ2P	2.735	2.601	3.129	2.975	3.251	3.091

^a *r* is the distance between the cage center and one E atom. Both distances are given in Å.

Sn_{12}^{2-} , respectively. Given the spherical symmetry of this compound, the NICS and B_z^{ind} values calculated at the cage center, NICS(0) and $B_z^{\text{ind}}(0)$, using the BP86/TZ2P level are both 8.1 ppm. One can assume that the system is antiaromatic (using these magnetic descriptors), the conclusion previously reached by Chen et al.⁵ However, the relativistic effects modify strongly both electron delocalization descriptors. Using ZORA and SO-ZORA approaches, the NICS(0) and $B_z^{\text{ind}}(0)$ values are negative (-4 ppm), i.e., there is a drastic change of approximately 12 ppm. Of course, the chemical interpretation also changes; now the system can be considered slightly aromatic as was pointed out by Tian and co-workers.¹⁴ The same trend is obtained at the PW91 or SAOP levels. Obviously, there are some changes in the values, but it is possible to appreciate drastic changes in magnitude induced by the inclusion of relativistic effects (see Table 1). Interestingly, the profiles show a minimum at approximately 2.5 and 3 Å for NICS and B_z^{ind} , respectively, from the cage center, which coincides with the three-membered ring center, indicating a σ -delocalization increase at each icosahedron face, as is observed in other all-metal clusters (see also Table 1 in Supporting Information).^{46–51}

Next, we will compare the stannaspherene NICS profiles with those obtained for Ge_{12}^{2-} and Pb_{12}^{2-} . In the first case (Figure 2), the relativistic effects change by less than 6 ppm in the NICS and B_z^{ind} values; it is not unexpected that Ge, the lightest element among the series, is also the least affected by the inclusion of relativistic effects. However, for the case of plumbaspherene (see Figure 3), the addition of relativistic effects to NICS/ B_z^{ind} profiles may modify the conclusion about aromaticity of this cluster. In Figure 3 one can see that the difference from the nonrelativistic to the relativity-included calculation is almost 40 ppm! Just by examining the nonrelativistic results one would argue that Pb_{12}^{2-} is a nonaromatic molecule, however, when taking into account the relativistic effects, the large negative NICS/ B_z^{ind} values indicate a high degree of aromaticity. Moreover, by inspecting the B_z^{ind} profiles one can observe that plumbaspherene

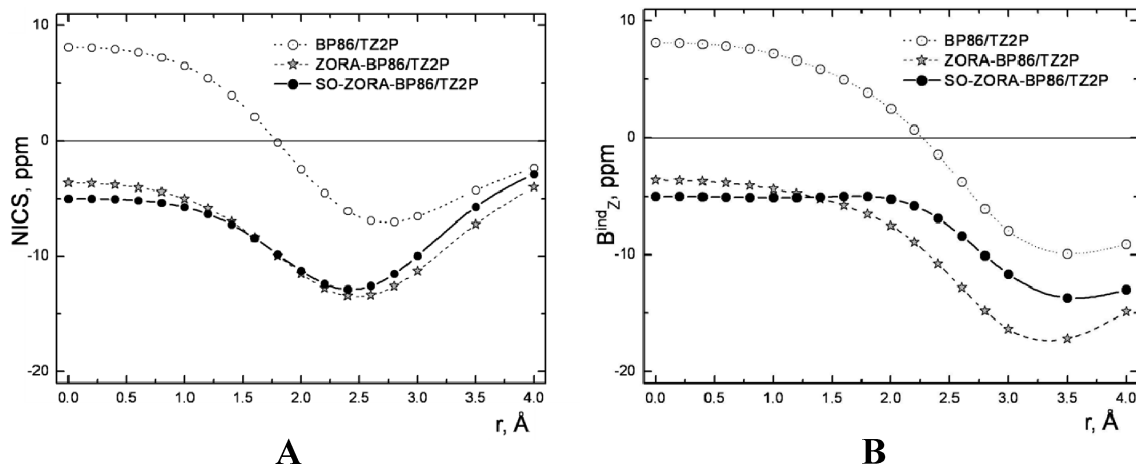


Figure 1. (A) NICS profile and (B) B_z^{ind} profile for Sn_{12}^{2-} .

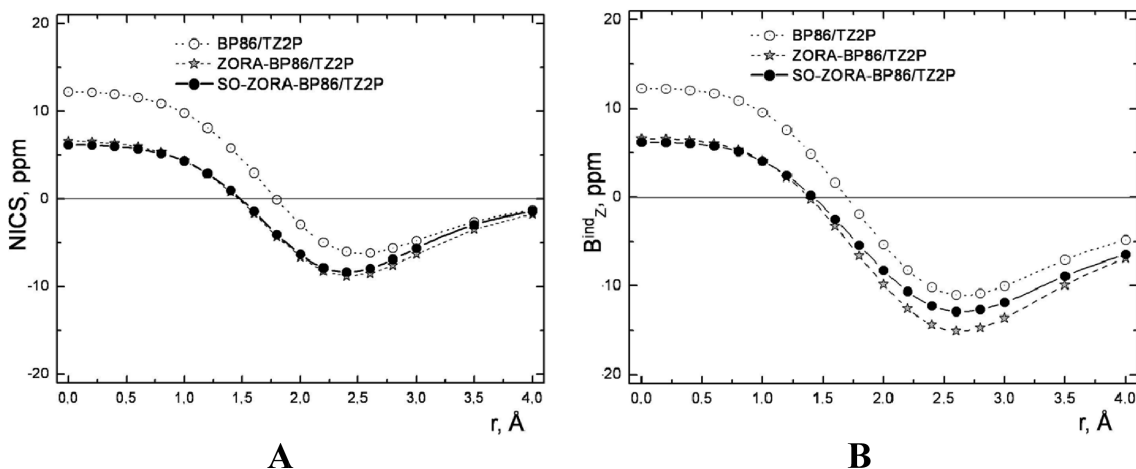


Figure 2. (A) NICS profile and (B) B_z^{ind} profile for Ge_{12}^{2-} .

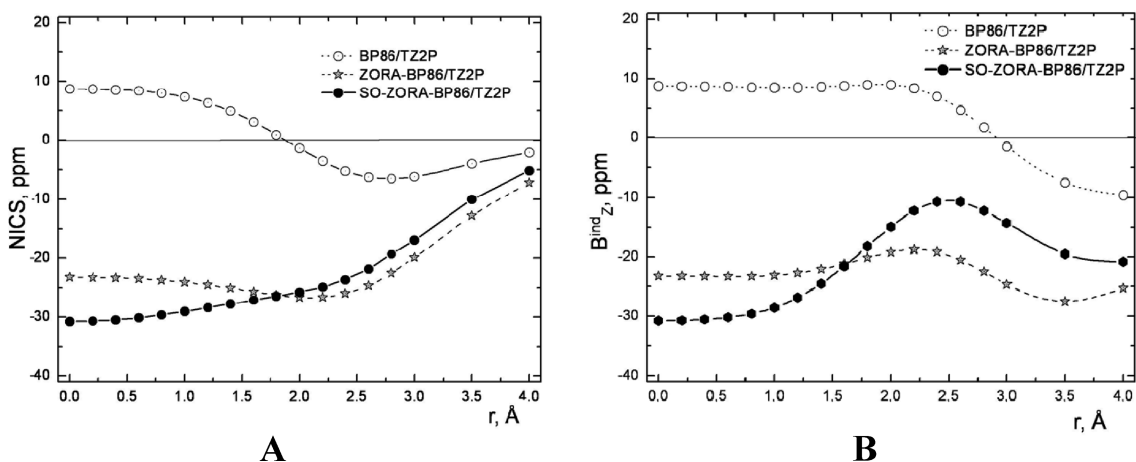


Figure 3. (A) NICS profile and (B) B_z^{ind} profile for Pb_{12}^{2-} .

possesses a maximum (between 2 and 2.5 Å) close to the center of the three-membered ring Pb–Pb–Pb (located at 3.0 Å), while its homologues show a minimum close to this region.

In several papers it is discussed whether NICS or NICS_{zz} (which is identical to B_z^{ind}) are enough to determine the aromatic character of a molecule.^{52–58} Nevertheless, these indices have become a popular probe of aromaticity in a variety of molecules. In view of the fact that the NICS and

B_z^{ind} indices are extensively used by computational and theoretically oriented experimental chemists, there is an important warning: the relativistic effects can drastically change the NICS and the B_z^{ind} values and, thus, the chemical interpretation. We have obtained profiles using PW91 and SAOP functionals, and the picture obtained is qualitatively the same, reaffirming the enhanced influence of relativistic effects in the calculations of NICS and B_z^{ind} values, no matter which functional is used (See the Supporting Information).

Table 2. The z-Component of the Induced Magnetic Field (B^{ind}_z) in ppm Calculated at the Cage Center^a

	Ge	Sn	Pb
BP86/TZ2P	12.5	8.1	8.7
ZORA-BP86/TZ2P	6.8	−3.6	−23.2
SO-ZORA-BP86/TZ2P	6.4	−5.0	−30.8
PW91/TZ2P	12.7	8.9	9.3
ZORA-PW91/TZ2P	7.0	−3.2	−23.4
SO-ZORA-PW91/TZ2P	6.6	−4.5	−30.8
SAOP/TZ2P	7.8	4.8	5.0
ZORA-SAOP/TZ2P	2.5	−6.0	−22.8
SO-ZORA-SAOP/TZ2P	2.2	−7.2	−30.9

^a Given the spherical symmetry of the title compounds, the B^{ind}_z and the NICS values calculated at the cage center are the same.

Thus, we can safely conclude that the results found are not an artifact of BP86 functional.

With this scenario one could anticipate that relativistic effects are important in any molecule containing a heavy element. Indeed, our results show that the changes observed in the NICS and B^{ind} values in the title cages are a consequence of the treatment of the relativistic effects. If these effects are included as scalar or spin–orbit calculations, then we can establish the following trend: Ge_{12}^{2-} is a nonaromatic species, Sn_{12}^{2-} is a low aromatic species, and Pb_{12}^{2-} is strongly aromatic. So, any prediction of electron delocalization for these clusters without considering relativistic effects is likely to be erroneous.

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Supporting Information Available: The NICS and the B^{ind} values calculated at the face center and the NICS and Bindz profiles calculated at the PW91 and SAOP levels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Cui, L. F.; Wang, L. S. *Int. Rev. Phys. Chem.* **2008**, *27*, 139.
- (2) Cui, L. F.; Huang, X.; Wang, L. M.; Li, J.; Wang, L. S. *J. Phys. Chem. A* **2006**, *110*, 10169.
- (3) Cui, L. F.; Huang, X.; Wang, L. M.; Zubarev, D. Y.; Boldyrev, A. I.; Li, J.; Wang, L. S. *J. Am. Chem. Soc.* **2006**, *128*, 8390.
- (4) Chen, X.; Deng, K. M.; Liu, Y. Z.; Tang, C. M.; Yuan, Y. B.; Hu, F. L.; Wu, H. P.; Huang, D. C.; Tan, W. S.; Wang, X. *Chem. Phys. Lett.* **2008**, *462*, 275.
- (5) Chen, Z. F.; Neukermans, S.; Wang, X.; Janssens, E.; Zhou, Z.; Silverans, R. E.; King, R. B.; Schleyer, P. v. R.; Lievens, P. *J. Am. Chem. Soc.* **2006**, *128*, 12829.
- (6) Cui, L. F.; Huang, X.; Wang, L. M.; Li, J.; Wang, L. S. *Angew. Chem.-Int. Ed.* **2007**, *46*, 742.
- (7) Dognon, J. P.; Clavaguera, C.; Pyykkö, P. *Angew. Chem.-Int. Ed.* **2007**, *46*, 1427.
- (8) Kocak, F. S.; Zavalij, P.; Lam, Y. F.; Eichhorn, B. W. *Inorg. Chem.* **2008**, *47*, 3515.
- (9) Matxain, J. M.; Piris, M.; Formoso, E.; Mercero, J. M.; Lopez, X.; Ugalde, J. M. *ChemPhysChem* **2007**, *8*, 2096.
- (10) Sun, Z. M.; Xiao, H.; Li, J.; Wang, L. S. *J. Am. Chem. Soc.* **2007**, *129*, 9560.
- (11) Wang, J. Q.; Stegmaier, S.; Wahl, B.; Fassler, T. F. *Chem.-Eur. J.* **2010**, *16*, 1793.
- (12) Zdetsis, A. D. *J. Chem. Phys.* **2009**, *131*.
- (13) Neukermans, S.; Janssens, E.; Chen, Z. F.; Silverans, R. E.; Schleyer, P. v. R.; Lievens, P. *Phys. Rev. Lett.* **2004**, *92*.
- (14) Chen, D. L.; Tian, W. Q.; Feng, J. K.; Sun, C. C. *J. Phys. Chem. A* **2007**, *111*, 8277.
- (15) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1996**, *261*, 335.
- (16) Schreckenbach, G.; Ziegler, T. *Int. J. Quantum Chem.* **1997**, *61*, 899.
- (17) Kaupp, M.; Malkina, O. L.; Malkin, V. G.; Pyykkö, P. *Chem.-Eur. J.* **1998**, *4*, 118.
- (18) Wolff, S. K.; Ziegler, T. *J. Chem. Phys.* **1998**, *109*, 895.
- (19) Buhl, M.; Kaupp, M.; Malkina, O. L.; Malkin, V. G. *J. Comput. Chem.* **1999**, *20*, 91.
- (20) Visscher, L.; Enevoldsen, T.; Saue, T.; Jensen, H. J. A.; Oddershede, J. *J. Comput. Chem.* **1999**, *20*, 1262.
- (21) Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 7689.
- (22) Vankova, N.; Heine, T.; Kortz, U. *Eur. J. Inorg. Chem.* **2009**, 5102.
- (23) Corminboeuf, C. *Chem. Phys. Lett.* **2006**, *418*, 437.
- (24) Alvarado-Soto, L.; Ramirez-Tagle, R.; Arratia-Perez, R. *Chem. Phys. Lett.* **2008**, *467*, 94.
- (25) Tsipis, A. C.; Kefalidis, C. E.; Tsipis, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 9144.
- (26) Munoz-Castro, A.; Arratia-Perez, R. *J. Phys. Chem. A* **2010**, *114*, 5217.
- (27) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
- (28) Chen, Z. F.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.
- (29) Merino, G.; Heine, T.; Seifert, G. *Chem.-Eur. J.* **2004**, *10*, 4367.
- (30) Heine, T.; Islas, R.; Merino, G. *J. Comput. Chem.* **2007**, *28*, 302.
- (31) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098.
- (32) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822.
- (33) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Sing, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 6671.
- (34) Gritsenko, O. V.; Schipper, P. R. T.; Baerends, E. J. *Chem. Phys. Lett.* **1999**, *302*, 199.

- (35) Schipper, P. R. T.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Chem. Phys.* **2000**, *112*, 1344.
- (36) Chang, C.; Pelissier, M.; Durand, P. *Phys. Scr.* **1986**, *34*, 394.
- (37) Lindroth, E.; Heully, J. L.; Lindgren, I.; Martensson-Pendrill, A. M. *J. Phys. B: At., Mol. Opt. Phys.* **1987**, *20*, 1679.
- (38) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.
- (39) van Lenthe, E.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1996**, *105*, 6505.
- (40) van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. *Int. J. Quantum Chem.* **1996**, *57*, 281.
- (41) Baerends, E. J.; Autschbach, J.; Berger, J. A.; Bérces, A.; Bickelhaupt, F. M.; Bo, C.; Boeij, P. L. D.; Boerrigter, P. M.; Cavallo, L.; Chong, D. P.; Deng, L.; Dickson, R. M.; Ellis, D. E.; Faassen, M. v.; Fan, L.; Fischer, T. H.; Guerra, C. F.; Gisbergen, S. J. A. v.; Götz, A. W.; Groeneveld, J. A.; Gritsenko, O. V.; Grüning, M.; Harris, F. E.; Hoek, P. v. d.; Jacob, C. R.; Jacobsen, H.; Jensen, L.; Kadantsev, E. S.; Kessel, G. v.; Klooster, R.; Kootstra, F.; Krykunov, M. V.; Lenthe, E. v.; Louwen, J. N.; McCormack, D. A.; Michalak, A.; Neugebauer, J.; Nicu, V. P.; Osinga, V. P.; Patchkovskii, S.; Philipsen, P. H. T.; Post, D.; Pye, C. C.; Ravenek, W.; Rodriguez, J. I.; Romaniello, P.; Ros, P.; Schipper, P. R. T.; Schreckenbach, G.; Snijders, J. G.; Solà, M.; Swart, M.; Swerhone, D.; Velde, G. t.; Vernooijs, P.; Versluis, L. V. L.; Visser, O.; Wang, F.; Wesolowski, T. A.; Wezenbeek, E. M. v.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Yakovlev, A. L.; Ziegler, T. *ADF 2008.01*, SCM, Theoretical Chemistry; Scientific Computing and Modelling NV, Vrije Universiteit: Amsterdam, The Netherlands, 2008.
- (42) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.
- (43) Jimenez-Halla, J. O. C.; Matito, E.; Robles, J.; Sola, M. *J. Organomet. Chem.* **2006**, *691*, 4359.
- (44) Tiznado, W.; Perez-Peralta, N.; Islas, R.; Toro-Labbe, A.; Ugalde, J. M.; Merino, G. *J. Am. Chem. Soc.* **2009**, *131*, 9426.
- (45) Merino, G.; Vela, A.; Heine, T. *Chem. Rev.* **2005**, *105*, 3812.
- (46) Boldyrev, A. I.; Wang, L. S. *Chem. Rev.* **2005**, *105*, 3716.
- (47) Chen, Z. F.; Corminboeuf, C.; Heine, T.; Bohmann, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 13930.
- (48) Kuznetsov, A. E.; Birch, K. A.; Boldyrev, A. I.; Li, X.; Zhai, H. J.; Wang, L. S. *Science* **2003**, *300*, 622.
- (49) Li, X.; Kuznetsov, A. E.; Zhang, H. F.; Boldyrev, A. I.; Wang, L. S. *Science* **2001**, *291*, 859.
- (50) Islas, R.; Heine, T.; Ito, K.; Schleyer, P. v. R.; Merino, G. *J. Am. Chem. Soc.* **2007**, *129*, 14767.
- (51) Islas, R.; Heine, T.; Merino, G. *J. Chem. Theory Comput.* **2007**, *3*, 775.
- (52) Lazzeretti, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 217.
- (53) Viglione, R. G.; Zanasi, R.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 2265.
- (54) Faglioni, F.; Ligabue, A.; Pelloni, S.; Soncini, A.; Viglione, R. G.; Ferraro, M. B.; Zanasi, R.; Lazzeretti, P. *Org. Lett.* **2005**, *7*, 3457.
- (55) Osuna, S.; Poater, J.; Bofill, J. M.; Alemany, P.; Sola, M. *Chem. Phys. Lett.* **2006**, *428*, 191.
- (56) Feixas, F.; Jimenez-Halla, J. O. C.; Matito, E.; Poater, J.; Sola, M. *Pol. J. Chem.* **2007**, *81*, 783.
- (57) Feixas, F.; Matito, E.; Poater, J.; Sola, M. *J. Phys. Chem. A* **2007**, *111*, 4513.
- (58) Islas, R.; Martinez-Guajardo, G.; Jimenez-Halla, J. O. C.; Sola, M.; Merino, G. *J. Chem. Theory Comput.* **2010**, *6*, 1131.