

Comments on the Matters Arising article “Does ϕ -Aromaticity exist in prismatic $\{\text{Bi}_6\}$ -based clusters?” by Dariusz W. Szczepanik and Miquel Solà

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Abstract

We read the Matters Arising article by Dariusz W. Szczepanik and Miquel Solà with interest, and recognized several misinterpretations (based on oversimplifications) of our work and also errors that results from inappropriate/insufficient methods applied in their follow-up studies. This led to erroneous statements, which the authors additionally mixed with statements on aromaticity, which does not fully comply with definitions that have been well-established, e.g., for benzene. In this comment, we outline the misinterpretations, errors, and questionable statements, thereby referring to our work and further literature to underline the facts.

Comments

In their article,^[1] the authors tend to cite our statements^[2] in an oversimplified and therefore misleading way and moreover draw conclusions that disagree with computations using appropriate quantum chemical methods.

i) The sentence^[1] “Very recently in this journal Peerless et al. isolated the heterometallic cluster $\{[\text{CpRu}]_3\text{Bi}_6\}^-$ (1^-) containing at its heart the Bi_6^{2-} cage of elongated (trigonal) prism topology” ignores that we discuss the charge of the underlying $\{\text{Bi}_6\}$ unit at length as it is very difficult to actually define a charge in this highly intermetallic cluster; hence, we carefully compare the experimental cluster with different (hypothetical!) Bi_6^{q-} anions based on the structure/symmetry of the $\{\text{Bi}_6\}$ unit composition and shape of the molecular orbitals (MOs) in both species. As a result we see the best match with Bi_6^{2-} , which is a distinct difference in the narrative.

ii) In their next sentence, they write “To explain its exceptionally high abundance and selective formation tendency (as compared to other Zintl clusters) as well as the unusual magnetic-response properties, the authors introduced the so-called ϕ -aromaticity”. Note that we did NOT make a statement on the ‘high abundance and the selective formation’ of the compounds as a consequence of aromaticity (although its exceptionally pure formation indeed is worthwhile!). In the conclusion we accurately state that^[2] “We [...] conclude that the different metal complex fragments serve to stabilize different bonding types. This is in line with the nature of the two ligand types in terms of electron-donating or electron-withdrawing properties, as corroborated by natural bond orbital analyses.

iii) In the second paragraph, the authors comment on the bonding situation in different trigonal prisms – which is critical given that even (valence)isoelectronic prisms made of (CH) units versus Te versus Bi atoms differ significantly (like C differs from Pb), as we outline in our article for the case of prismane (and its dianion). More importantly however, they elaborate on (hypothetical) Bi_6^{2-} , implying that we discussed it as being more stable than Bi_6 owing to the ϕ -aromatic contribution – again, which we did not. On the contrary, we explicitly refer to the decreased Wiberg bond indices^[3] (WBIs) and the elongated bonds between the two triangles upon adding charges to the Bi_6 prism. In detail, we noted that the WBI of the three transannular bonds decreases, whereas the WBI of the six annular bonds increases (easily rationalized by the nodal structure of the ϕ -type orbital). So, we already said everything that needs to be said on that topic.

iv) Most importantly, the computational framework seems to be questionable in part. First, the authors used a different basis set (def2-TZVP^[4] vs. dhf-TZVP^[5]) and the $\omega\text{B97X-D}$ functional^[6] for their calculations. Note that the

dhf-TZVP basis sets were designed to improve upon the def2-TZVP basis, especially for transition-metal systems.^[4,5] This (and the lack of a model to simulate the counterions, see below) explains why some of our optimized structures are transition states within the computational framework of Szczepanik and Solà. In our original work, we used the TPSS/dhf-TZVP^[5,7] approach with the conductor-like screening model^[8,9] (COSMO) for the geometries. Of course, different computational settings may affect the potential energy surface and a (local) minima obtained with one approach does not necessarily have to be a minima with another approach. Second, the authors did not consider models to compensate the negative charge, i.e., simulate the counter ions. However, this is of great relevance for anions, as positive energies for the highest occupied molecular orbital (HOMO) are usually obtained without such models, and therefore urgently needed to make any statements about energetics of negatively charged molecules. Without COSMO or similar models, the dissociation energy of negatively charged prisms will be positive as it increases the spatial distance of the negative charges and will reduce the respective Coulomb repulsion. Therefore, we have re-performed the calculations for the separation of Bi_6^{2-} into two Bi_3^- fragments with the well-established conductor-like screening model. This shows the inverse: Bi_6^{2-} is more stable than two Bi_3^- . The dissociation enthalpies are: +260 kJ/mol for Bi_6 and +196 kJ/mol for Bi_6^{2-} at the TPSS/dhf-TZVP/COSMO level of theory. Note that prism structures are local minima and the Bi_3 structures were optimized herein and confirmed to be minima. Quadrature weight derivatives were included for the density functional theory (DFT) part. We have re-performed the calculations including optimizations with $\omega\text{B97X-D}$ and the dissociation enthalpies are +272 kJ/mol and +172 kJ/mol, respectively. Overall, the dissociation is thermochemically unfavorable for both Bi_6 and Bi_6^{2-} , and a model to treat the counterions is desperately needed (a fact well-known from basic quantum chemistry). Again, the results are easily rationalized by the nodal structure of the ϕ -type orbital, which strengthens the bonds within the Bi_3 rings but weakens the bonds between the two rings. Furthermore, we carried out scalar-relativistic and relativistic spin-orbit calculations of the complete fragmentation pathways. Both effective-core potentials and all-electron relativistic Hamiltonians were applied. None of these calculations shows signs of destabilization (see separate file entitled Fragmentation.pdf).

v) Apart from this wrong conclusion, we do not consider the authors' discussion of stability, as presented in the Matters Arising article, helpful. Note that the 'stabilization by aromaticity', hence the 'resonance energy' defined on the example of benzene, does not refer to the stability against fragmentation, but refers to the stabilization of the fully delocalized ('conjugated') system as compared to the localized analogue – like benzene versus cyclohexatriene. In the present case, this compares well with the change from an unsymmetric (localized) $\{\text{Bi}_6\}$ cage to the symmetric one. Moreover, we refer to the fact that four of the six π -type MOs that are responsible for the π -aromaticity of benzene comprise nodal planes (thus, are 'antibonding' for parts of the six-membered ring), which does not affect the overall stabilization – note that 50% of the bonds in the benzene ring are being destabilized (= get longer) and 50% are being stabilized (= get shorter) as compared to cyclohexatriene. A similar thing happens to the unsymmetric prism: three bonds get longer, while six bonds get shorter upon symmetrization. In summary, the presence of nodal planes in an MO does not mean that the whole molecule is destabilized by its occupation (in line with the energetic considerations above).

vi) In the third paragraph, one reads "Peerless *et al.* [...] speculate that the isolated cluster $\mathbf{1}^-$ is aromatic while the heterometallic cluster $\{[(\text{cod})\text{Ir}]_3\text{Bi}_6\}^-$ ($\mathbf{2}^-$) is not due to its lower symmetry". First, this reduction to symmetry arguments is another gross oversimplification of our study, as we thoroughly discussed the charge and electrons accumulated at the Bi_6 core. Here, the Ir-based cluster accumulates more electrons on the Bi_6 prism than the Ru-based cluster. So, our assessment of the Ru-based cluster to be closer to Bi_6^{2-} and the Ir-based one being closer to Bi_6^{4-} was based on both geometrical structures and quantum chemical wavefunction analysis. Second, we like to point out that we classified both the Ru-based and the Ir-based clusters as aromatic (in contradiction to what is written in the quoted sentence) and featuring many similarities:^[2] "According to the computational studies and the experimentally determined structures, the heteroatomic clusters $\mathbf{1}^-$ and $\mathbf{2}^-$, and the similar $\{[(\text{CO})_3\text{Mo}]_3\text{Bi}_6\}^{4-}$, are clearly aromatic based on the magnetic criterion and sustain exceptionally strong diatropic ring currents according to the calculations. However, only the regular cluster $\mathbf{1}^-$ shows substantial signs of ϕ -aromaticity according to the symmetry criterion. Compared to the current density plot of $(\text{Bi}_6)^{2-}$, the clusters $\mathbf{1}^-$ and $\mathbf{2}^-$ show a reduced degree of σ -aromaticity. Particularly for $\mathbf{1}^-$, this can be rationalized by the nodal structure of the HOMO-2 (MO 144a in Fig. 4). This MO corresponds to the lowest unoccupied MO of $(\text{Bi}_6)^{2-}$ (MO 71a in Fig. 4)." So, the citation of our work is just incorrect.

vii) Regarding the orbital decomposition of the current *via* nucleus-independent chemical shift^[10] (NICS), and the contribution of the lone pairs (final point), we note that the orbital decomposition of an NMR shielding tensor is not uniquely defined and different approaches exist.^[11-14] The orbital decomposition has to be done for the unperturbed density matrix and the perturbed density matrix of the coupled-perturbed Kohn-Sham formalism. The latter involves the orbital rotation matrix of the response equations and consequently mixes orbitals, thus limiting the

applicability of orbital decomposition approaches. Also, NICS is an indirect measure of the ring current,^[15] and we have calculated both the ring current directly and also NICS values at various points in space, including the prism center and all Bi_3 and Bi_4 faces, with a few well-established DFT methods. In doing so, we showed that the main contribution to the ring current stems from σ -type contributions,^[2] yet the ϕ -type orbital is a distinct and unique feature of both Bi_6^{2-} and the experimentally observed cluster 1^- . To complement the data in our original work, we list the NICS(y) values for Bi_6 and Bi_6^{2-} , with y denoting the distance above the upper triangle in Bohr. For Bi_6 , we obtain -11.7 ppm ($y = 1$), -8.0 ppm ($y = 2$), and -6.7 ppm ($y = 3$) with TPSS/dhf-TZVP/COSMO. For Bi_6^{2-} , the respective NICS read -48.6 ppm ($y = 1$), -32.0 ppm ($y = 2$), and -16.6 ($y = 3$) ppm. The ϕ -type frontier orbitals of the $\{\text{Bi}_6\}$ prisms further allow for a straightforward rationalization of the ring current strengths and the ring current shapes of Bi_6 , Bi_6^{2-} , and Bi_6^{4-} , see Supplementary Figures 10 and 22 of our original work.^[2]

viii) We would like to emphasize that the group of Sun^[16] also classified the related Mo compound as ‘overall spherically aromatic’. The list of references as provided by the authors indicates that they refer to a specific group of authors, while they obviously disregard the seminal work of other experts in the field (e.g., Sundholm et al.). This is in contrast to our article in which we referred to many different colleagues upon corresponding literature studies.

Overall, our statements were distorted and the lack of charge compensation results in incorrect thermochemical properties. Therefore, the counterstatements can unfortunately not be considered as a state-of-the-art evaluation of the subject matter.

Computational Methods

For the new calculations, we used the methods of our original work.^[2] In detail, all calculations were performed with the TURBOMOLE^[17-20] program suite. Small-core Dirac–Fock effective core-potentials^[21] were combined with the dhf-TZVP basis sets.^[5] The resolution of the identity approximation^[22] (RI-J) was applied with tailored auxiliary basis sets.^[5] Large grids (gridsize 3a) are employed for the numerical integration of the exchange-correlation terms,^[23-25] weight derivatives were included for gradients and the Hessian. Harmonic vibrations were calculated analytically.^[26-28] Thresholds of 10^{-8} E_h for the total energy and 10^{-7} for the root mean square of the density matrix norm were applied in the self-consistent field (SCF) procedure. For the structure optimizations with $\omega\text{B97X-D}$ carried out herein, thresholds of 10^{-6} E_h for the total energy and 10^{-3} E_h/bohr for the maximum gradient were chosen. Structures were confirmed to be (local) minima with the analytical Hessian.^[26-28] Newly optimized structures for the Bi_3 triangles with TPSS and for the dissociation study with $\omega\text{B97X-D}$ are given below in Ångström with SCF energies in Hartree. The number of unpaired electrons was confirmed with the fractional occupation numbers (FON) approach, also called Fermi smearing, and reducing the temperature from 300 K to 50 K throughout the SCF procedure.^[29]

Fragmentation studies were carried out with the aforementioned methodology and also self-consistent two-component calculations for spin–orbit coupling.^[30,31] As the self-consistent treatment necessitates additional basis functions,^[32] the dhf-TZVP-2c orbital and auxiliary basis sets were applied together with the respective Dirac–Fock ECPs.^[5,21] COSMO was again applied throughout to model the counter ions. We stress that spin–orbit coupling, i.e. the splitting of the p states into two $p_{1/2}$ and four $p_{3/2}$ affects the electronic configuration. For instance, Bi^+ converges to a Kramers-restricted solution. Results were corroborated with relativistic all-electron exact two-component (X2C) theory utilizing the diagonal local approximation to the unitary decoupling transformation (DLU).^[33,34] These calculations use the x2c-TZVPall/x2c-TZVPall-2c basis sets^[35] with a finite nucleus model and the modified screened nuclear spin–orbit (mSNSO) approach to account for the two-electron picture-change effects.^[36] For TPSS, we also considered the contribution of the paramagnetic current density in the SCF procedure (cTPSS).^[37]

Optimized Structures

Bi₃ radical triangle, TPSS

SCF = -643.817556

Bi -1.7007990 -0.0037705 1.5349623

Bi 0.9762503 -1.4261813 1.5352622

Bi 0.7831215 1.4315750 1.5339215

Bi₃ anion triangle, two unpaired electrons, TPSS

SCF = -643.944681

Bi -1.7045028 -0.0585588 1.6989779

Bi 0.9027933 -1.4452386 1.6995200

Bi 0.8018259 1.5038588 1.6995422

Bi₃ radical triangle, ω B97X-D

SCF = -644.189075

Bi -1.7054937 0.0530840 1.5198768

Bi 0.9056212 -1.4284205 1.5197967

Bi 0.7955815 1.4100312 1.5181196

Bi₆ prism, ω B97X-D

SCF = -1288.483635

Bi -1.7402580 -0.0029779 1.5171750

Bi 0.8687493 -1.4841881 1.5184908

Bi 0.8482757 1.5131508 1.5174142

Bi -1.7463259 -0.0063986 -1.5183036

Bi 0.8658290 -1.4826548 -1.5167019

Bi 0.8408376 1.5143330 -1.5178704

Bi₃ anion triangle, two unpaired electrons, ω B97X-D

SCF = -644.3201048

Bi -1.7200371 0.0120485 1.6965535

Bi 0.8224215 -1.4434185 1.6993008

Bi 0.8129142 1.4839875 1.6993272

Bi₆²⁻ prism, ω B97X-D

SCF = -1288.707616

Bi -1.7040935 -0.0005506 1.6803781

Bi 0.8276748 -1.4581907 1.6936514

Bi 0.8247580 1.4615978 1.6955992

Bi -1.6885405 0.0067600 -1.6920085

Bi 0.8434996 -1.4506470 -1.6816348

Bi 0.8416629 1.4685564 -1.6765712

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