

# Does $\phi$ -Aromaticity exist in prismatic $\{\text{Bi}_6\}$ -based clusters?

Dariusz W. Szczepanik<sup>1\*</sup> and Miquel Solà<sup>2\*</sup>

1. *K. Guminski Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Gronostajowa, 2, 30-387 Kraków, Poland.*
2. *Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany, 69, 17003 Girona, Catalonia, Spain.*

Corresponding author's emails:

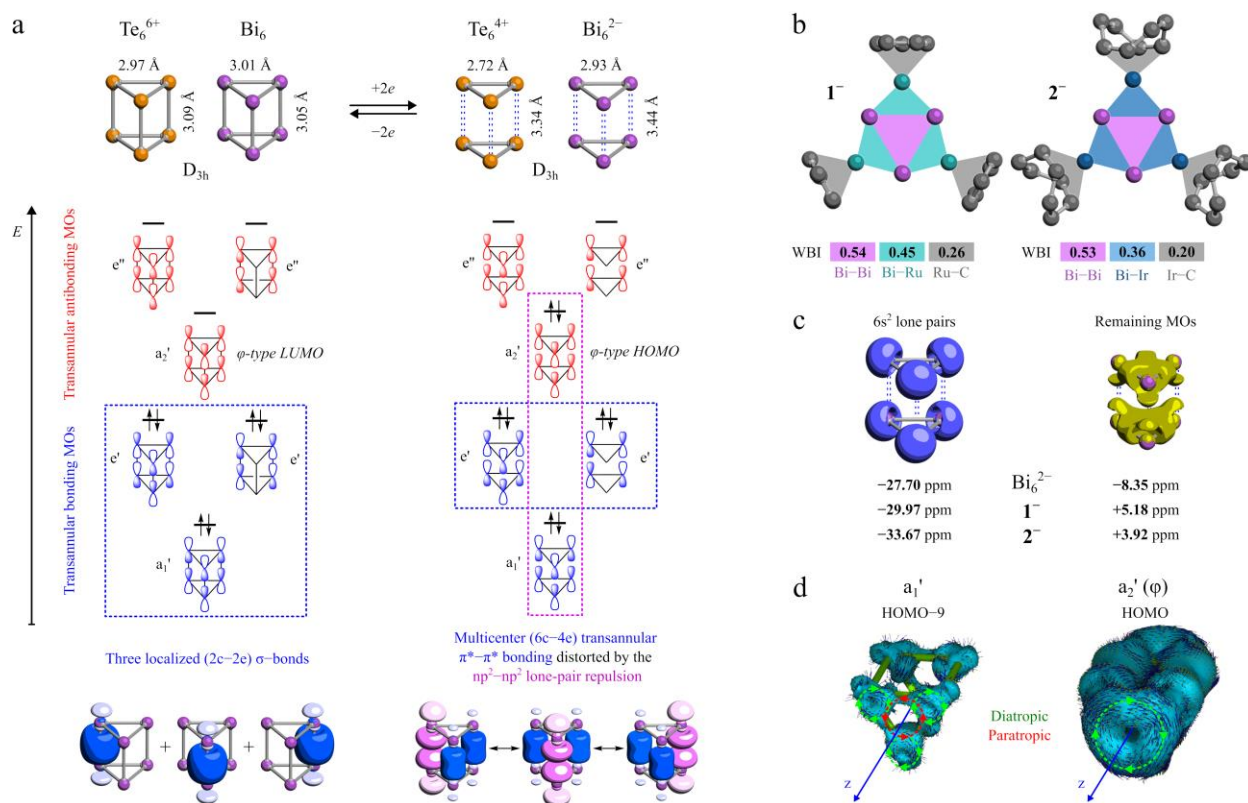
[dariusz.szczepanik@uj.edu.pl](mailto:dariusz.szczepanik@uj.edu.pl)

[miquel.sola@udg.edu](mailto:miquel.sola@udg.edu)

ARISING FROM B. Peerless et al. *Nature Chemistry* **15**, 347-356 (2023).

Aromaticity is one of the most important concepts in chemistry that addresses the interplay between molecular topology, chemical bonding, and stability.<sup>1</sup> The concept is not restricted to the carbon-based molecular rings, and for various chemical elements there might be a wealth of topologically differentiated two- and three-dimensional structures associated with considerable aromatic stabilization.<sup>2</sup> Very recently in this journal Peerless *et al.* isolated and investigated the heterometallic cluster  $[\{\text{CpRu}\}_3\text{Bi}_6]^-$  (**1**) containing at its heart the  $\text{Bi}_6^{2-}$  cage of the elongated trigonal prism topology.<sup>3</sup> 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  $\phi$ -aromaticity. Here, we show that introducing a new type of aromaticity in this case seems unjustified and somewhat misleading.

First, clusters containing elongated trigonal prisms iso(valence)electronic with  $\text{Bi}_6^{2-}$  are known.<sup>4-9</sup> For instance, the elongated prism  $\text{Te}_6^{4+}$  was isolated in the solid state for the first time by Burns *et al.* in 1979,<sup>5</sup> and later by Collins *et al.*<sup>7</sup> and Beck *et al.*<sup>8</sup> Ziegler and collaborators investigated the electronic structure of  $\text{Te}_6^{4+}$  and found a weak six-center four-electron (6c-4e) transannular  $\pi^*$ - $\pi^*$  bonding between two  $\{\text{Te}_3\}$  units, but no signs of aromaticity.<sup>9</sup> It should be noted that elongated prisms  $\text{Te}_6^{4+}$  and  $\text{Bi}_6^{2-}$  are derived by reduction of much more regular  $\text{Te}_6^{6+}$  and  $\text{Bi}_6$  containing in their valence shells 30 electrons distributed over six unhybridized *s*-type lone pairs and nine perfectly localized two-center two-electron (2c-2e)  $\sigma$ -bonds; same  $\sigma$ -bonding scheme present in non-aromatic  $\text{C}_6\text{H}_6$  prismane.<sup>10</sup> Particularly important for understanding stability of the prisms are



**Figure 1.** a) Geometry, molecular orbitals, and the corresponding localized orbitals for the {Te<sub>6</sub>}- and {Bi<sub>6</sub>}-based regular and elongated prisms; b) Averaged Wiberg bond indices (WBI)<sup>12</sup> for different chemical bonds in 1<sup>-</sup> and 2<sup>-</sup>; c) Contributions from the 6s<sup>2</sup> lone-pairs and all remaining MOs to the NICS<sup>13</sup> values in Bi<sub>6</sub><sup>2-</sup>, 1<sup>-</sup>, and 2<sup>-</sup>; d) Contributions to the net current density from orbitals a<sub>1</sub><sup>'</sup> and a<sub>2</sub><sup>'</sup> in the Bi<sub>6</sub><sup>2-</sup> prism visualized by the anisotropy of the induced current density (AICD).<sup>15</sup> Calculations done at the ωB97X-D/x2c-TZVPall-2c//ωB97X-D/def2-TZVP level of theory (see ESI for more details).

the three transannular σ-bonds and the corresponding molecular orbitals (MO) presented in **Figure 1a**. In regular prisms none of the transannular antibonding MOs is occupied including the φ-type lowest unoccupied molecular orbital (LUMO) a<sub>2</sub><sup>'</sup>, which in turn becomes the highest occupied MO (HOMO) upon reduction.<sup>9</sup> Peerless *et al.*<sup>3</sup> have overlooked the fact that the transannular antibonding φ-type orbital a<sub>2</sub><sup>'</sup> (HOMO) in Bi<sub>6</sub><sup>2-</sup> interferes with the corresponding transannular bonding orbital a<sub>1</sub><sup>'</sup> (HOMO-9) giving rise to a pair of the resonating 6p<sup>2</sup> lone-pairs; the remaining occupied degenerated MOs e' represent the delocalized 6c-4e π\*-π\* transannular bonding.<sup>9</sup> The

$6p^2-6p^2$  strong repulsion counteracts the weak  $6c-4e$  transannular bonding and consequently  $\text{Bi}_6^{2-}$  dissociation into two  $\text{Bi}_3^-$  rings is thermodynamically favorable ( $\Delta G^\circ = -124.5 \text{ kJ mol}^{-1}$ ), while the dissociation of the elemental  $\text{Bi}_6$  into  $2\text{Bi}_3\cdot$  is unfavorable ( $\Delta G^\circ = +206.1 \text{ kJ mol}^{-1}$ ). Thus, it is clear that adding two electrons to the  $\phi$ -type MO introduces destabilization of the  $\text{Bi}_6$  cluster rather than aromatic stabilization.

Second, Peerless *et al.*<sup>3</sup> 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.<sup>3</sup> In particular, the authors consider that the more regular  $\{\text{Bi}_6\}$  prism in  $\mathbf{1}^-$  is better described as the  $\text{Bi}_6^{2-}$  (allegedly featuring  $\phi$ -aromaticity) whereas that of more structurally distorted  $\mathbf{2}^-$  by the non-aromatic  $\text{Bi}_6^{4-}$ . The authors should be aware, however, that symmetry cannot be used as an aromaticity criterion *per se*,<sup>2</sup> and distorted aromatic systems are known to preserve their bonding patterns and aromatic character.<sup>11</sup> In fact, the average Wiberg bond index (WBI)<sup>12</sup> clearly shows that the covalent bonding Bi–Bi inside the prisms is almost the same in both clusters (**Figure 1b**). More specifically, the average WBI values for the annular (transannular) Bi–Bi bonds in  $\mathbf{1}^-$  and  $\mathbf{2}^-$  read 0.65 (0.32) and 0.61 (0.36), respectively, and therefore they do not differ significantly enough to justify differentiation of the clusters in terms of aromaticity. What really makes the cluster  $\mathbf{1}^-$  more symmetric is higher hapticity of the  $\eta^5$ -Cp ligands (*vs* the  $\eta^4$ -cod in  $\mathbf{2}^-$ ) implying more *d*-orbitals involved in bonding, and, consequently, noticeably larger average WBI values for the bismuth-metal bonds (**Figure 1b**). It should also be noticed that the reported by the authors increase of WBI for the annular Bi–Bi bonds upon reduction from 0.99 ( $\text{Bi}_6$  with no  $\pi$ -electrons) to 1.10 ( $\text{Bi}_6^{2-}$ ) is too small to be interpreted as a sign of local  $\pi$ -aromaticity in the  $\{\text{Bi}_3\}$  subunits. To put it into a context, the  $\Delta\text{WBI}$  of 0.11 equals to the weak interaction between the formally non-bonded *para*-related carbon atoms

in benzene, and is nowhere near the  $\pi$ -component of 0.44 for the  $\pi$ -aromatic cyclopropenyl cation. Additional arguments against local aromaticity in  $\text{Bi}_6^{2-}$  can be found in Supporting Information.

Finally, the authors seem confident in the numbers provided to confirm the ‘magnetic aromaticity’ in the elongated prism  $\text{Bi}_6^{2-}$  and the isolated clusters. Negative values of the nucleus independent chemical shift (NICS)<sup>13</sup> are indeed reliable indicators of aromaticity in the planar organic rings with  $\pi$ -conjugated bonds. However, for topologically diversified systems the magnetic-response criteria of aromaticity like NICS are often difficult to interpret if we do not distinguish between the chemically meaningful aromatic currents and the artifactual interferences of the local currents (cf., the case of the  $\text{P}_4$  and  $\text{Si}_4^{4-}$  tetrahedrons).<sup>2</sup> Unfortunately, in the case of the elongated prism  $\text{Bi}_6^{2-}$ , we face this problem (**Figure 1c**). Molecular orbital decomposition of the magnetic shielding in the centroid of the  $\text{Bi}_6^{2-}$  prism and the isolated clusters reveals that negative values of NICS reported by Peerless *et al.*<sup>3</sup> come mostly from the local induced currents generated by six  $6s$ -type lone pairs surrounding the prism, and hence they can by no means be associated with aromaticity (see Supporting Information for more details). Moreover, the authors should bear in mind that in the external magnetic field electrons occupying the outermost energy levels (HOMO, HOMO-1, etc.) always ‘circulate’ more intensively over the ring/cage than the electrons occupying inner MOs (cf. the Fowler-Steiner theory).<sup>14</sup> For this reason, the induced current associated with the transannular bonding HOMO-9 in  $\text{Bi}_6^{2-}$  is too weak to interfere and cancel the strong net current associated with the transannular antibonding  $\varphi$ -type HOMO (**Figure 1d**). Consequently, the effective non-bonding character of the pair of orbitals  $a_1'$  and  $a_2'$  is magnetically decoupled leading to the artifactual diatropic net currents in the  $\{\text{Bi}_3\}$  units that mimic the aromatic ring currents, but

in fact they carry no chemically meaningful information about the resonance electronic structure and aromatic stabilization.

To summarize, the electronic structure and bonding in the elongated trigonal prisms like  $\text{Bi}_6^{2-}$  have been known for about 30 years,<sup>9</sup> and therefore introducing the ‘new’ concept of  $\varphi$ -aromaticity to characterize this family of inorganic cages seems unjustified. Moreover, none of the model  $\text{Bi}_6^{-q}$  prisms ( $q = 0, 2, 4$ ) and the clusters isolated by Peerless *et al.*<sup>3</sup> can be truly regarded as aromatic. This is mainly because the trigonal prism topology actually prevents aromatic stabilization to exist in the three-dimensional  $\{\text{Bi}_6\}$ -based clusters, a direct manifestation of which is lack of the triply degenerated MO energy levels.<sup>2</sup> The term ‘ $\varphi$ -aromaticity’ should rather be used in the context of planar systems with laterally overlapping orbitals of the  $nf_{z3}$  type, which enable  $\varphi$ -type conjugation and at the same time do not impair the subsystem of  $\sigma$ -bonds. The transannular antibonding  $\varphi$ -type HOMO in  $\text{Bi}_6^{2-}$  does not fulfill this requirement bringing destabilization and distortion rather than aromatic stabilization (neither global nor local).

## Data Availability

All data generated or analyzed during this study are included in this published Article. Details of the computational methods and methodology used to perform the present work are presented in the Supplementary Information.

## References

1. Solà, M., Boldyrev, A. I., Cyrański, M. K., Krygowski, T. M. & Merino, G. *Aromaticity and Antiaromaticity: Concepts and Applications*. (John Wiley & Sons, Chichester, 2023).

2. Bakouri, O.E., Szczepanik, D.W., Jorner, K., Ayub, R., Norrby, P.O., Bultinck, P., Solà, M. & Ottosson, H. Three-dimensional fully  $\pi$ -conjugated macrocycles: When classically 3D-aromatic and when 2D-aromatic-in-3D? *J. Am. Chem. Soc.* **144**, 8560–8575 (2022).
3. Peerless, B., Schmidt, A., Franzke, Y.J. & Dehnen, S.  $\varphi$ -Aromaticity in prismatic  $\{\text{Bi}_6\}$ -based clusters. *Nat. Chem.* **15**, 347-356 (2023).
4. Devillanova, F.A. & du Mont, W.-W., *Handbook of Chalcogen Chemistry. New Perspectives in Sulfur, Selenium and Tellurium, 2nd Edition, Volume 1* Ch. 7 (RSC Publishing, Cambridge, 2013).
5. Burns, R.C., Gillespie, R.J., Luk, W.-C. & Slim, D.R., Preparation, spectroscopic properties, and crystal structures of  $\text{Te}_6(\text{AsF}_6)_4 \cdot 2\text{AsF}_3$  and  $\text{Te}_6(\text{AsF}_6)_4 \cdot 2\text{SO}_2$ : a new trigonal-prismatic cluster cation, hexatellurium(4+). *Inorg. Chem.* **18**, 3086–3094 (1979).
6. Burns, R.C. & Gillespie, R.J. Vibrational spectra and analysis of  $\text{Te}_6^{4+}$ , a trigonal-prismatic cluster cation. *Spectrochim. Acta A Mol. Spectrosc.* **39**, 439–447 (1983).
7. Collins, M.J., Gillespie, R.J. & Sawyer, J.F., Hexatellurium octaselenium hexakis(hexafluoroarsenate) sulfur dioxide, *Acta Cryst. C* **44**, 405–409 (1988).
8. Beck, J. & Steden, F. Redetermination of  $\text{Te}_6[\text{AsF}_6]_4 \cdot 2\text{SO}_2$  at 125 K. *Acta Cryst. E* **59**, i158–i160 (2003).
9. Lyne, P.D., Mingos, D.M.P. & Ziegler, T., A Theoretical Study of  $\text{Te}_6^{4+}$  and  $\text{Te}_4\text{S}_4^{2+}$ . *J. Chem. Soc. Dalton Trans.*, 2743–2747 (1992).
10. Katz, T.J. & Acton, N. Synthesis of prismane. *J. Am. Chem. Soc.* **95**, 2738–2739 (1973).
11. Feixas, F., Matito, E., Poater, J. & Solà, M. Aromaticity of distorted benzene rings: exploring the validity of different indicators of aromaticity. *J. Phys. Chem. A* **111**, 4513–4521 (2007).

12. Wiberg, K. B. Application of the Pople-Santry-Segal CNDO method to the cyclopropylcarbanyl and cyclobutyl cation and to bicyclobutane. *Tetrahedron* **24**, 1083–1096 (1968).
13. Schleyer, P. v. R., Maerker, C., Dransfeld, A., Jiao, H. & Hommes, N. Nucleus-independent chemical shifts. *J. Am. Chem. Soc.* **118**, 6317–6318 (1996).
14. Steiner, E. & Fowler, P.W. Patterns of Ring Currents in Conjugated Molecules: A Few-Electron Model Based on Orbital Contributions. *J. Phys. Chem. A* **105**, 9553–9562 (2011).
15. Geuenich, D. & Herges, R. Delocalization of Electrons in Molecules. *J. Phys. Chem. A* **105**, 3214–3220 (2001).

## **Acknowledgments**

The research was supported with funds from the National Science Centre, Poland (project 2021/42/E/ST4/00332), the Spanish Ministerio de Ciencia e Innovación (project PID2020-13711GB-I00), and the Generalitat de Catalunya (project 2021SGR623). For the purpose of open access, the authors have applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

## **Author information**

Authors and Affiliations

**K. Guminski Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University**

Dariusz Wojciech Szczepanik, ORCID: 0000-0002-2013-0617



**Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona**

Miquel Solà, ORCID: 0000-0002-1917-7450

### Contributions

Both authors have contributed equally to the work.

### Corresponding author

Correspondence to Dariusz Wojciech Szczepanik and Miquel Solà.

### **Ethics declarations**

#### Competing interests

The authors declare no competing interests.

### **Supplementary information**

This file contains computational and methodological details, input files with the optimized XYZ coordinates, and additional references.