φ-Aromaticity in prismatic \{Bi_6\}-based clusters: facts and artifacts

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Aromaticity is one of the most important concepts in chemistry that addresses the interplay between molecular topology, chemical bonding, and stability.\(^1\) 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 that are associated with considerable aromatic stabilization.\(^2\) Very recently in this journal Peerless \textit{et al.} isolated the heterometallic cluster \([\{\text{CpRu}\}_3\text{Bi}_6\}^- (\text{I}^-)\) containing at its heart the Bi\(_6^{2-}\) cage of elongated (trigonal) prism topology.\(^3\) To explain the unusual stability, high symmetry, and magnetic-response properties of the cluster the authors introduced the so-called \(\varphi\)-aromaticity. Unfortunately, in this case introducing a new type of aromaticity is completely unjustified.

First, clusters containing elongated prisms iso(valence)electronic with Bi\(_6^{2-}\) are known.\(^4\)-\(^9\) For instance, the Te\(_6^{4+}\) prism was isolated in the solid state for the first time by Burns \textit{et al.} in 1979,\(^5\) and later by Collins \textit{et al.}\(^7\) and Beck \textit{et al.}\(^8\) Ziegler and collaborators investigated the electronic structure of Te\(_6^{4+}\) and found a weak six-center four-electron (6c–4e) transannular \(\pi^*–\pi^*\) bonding between two \{Te\(_3\)\} units, but no signs of aromaticity.\(^9\) It should be noted that elongated prisms Te\(_6^{4+}\) and Bi\(_6^{2-}\) are derived by reduction of much more regular Te\(_6^{6+}\) and 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 C\(_6\)H\(_6\) prismane.\(^10\) Particularly important for understanding stability of the prisms are the three transannular \(\sigma\)-bonds and the corresponding molecular orbitals (MO) presented in Figure
In regular prisms none of the transannular antibonding MOs is occupied including the $\varphi$-type lowest unoccupied molecular orbital (LUMO) $a_2^\prime$, which in turn becomes the highest occupied MO (HOMO) upon reduction.9 Peerless et al.3 have overlooked the fact that the transannular antibonding $\varphi$-type orbital $a_2^\prime$ (HOMO) in Bi$_6^{2-}$ interferes with the corresponding transannular bonding orbital $a_1^\prime$ (HOMO-9) giving rise to a pair of resonating 6p$_{2-6p_2}$ lone-pairs; the remaining occupied orbitals $e'$ represent the delocalized 6c–4e $\pi^*-\pi^*$ transannular bonding.9 The 6p$_{2-6p_2}$ strong repulsion counteracts the weak 6c–4e bonding and consequently Bi$_6^{2-}$ easily dissociates into two Bi$_3^+$ rings ($\Delta G^0 = -124.5$ kJ mol$^{-1}$), while the dissociation of the elemental Bi$_6$ into 2Bi$_3^+$ is
thermodynamically unfavorable ($\Delta G^\circ = +206.1$ kJ mol$^{-1}$). Thus, it is clear that adding two electrons to the $\phi$-type MO introduces destabilization of the cluster rather than aromatic stabilization.

Second, Peerless et al.$^3$ speculate that the isolated cluster $1^-$ is aromatic while the heterometallic cluster $[(\text{cod} \text{Ir})_3\text{Bi}_6]^- (2^-)$ is not due to its lower symmetry.$^3$ In particular, the authors consider that the more regular $\{\text{Bi}_6\}$ prism in $1^-$ is better described as the $\text{Bi}_6^{2-}$ (allegedly featuring $\phi$-aromaticity) whereas that of more structurally distorted $2^-$ by the non-aromatic $\text{Bi}_6^{4-}$. However, the authors should be aware that symmetry cannot be used as an aromaticity criterion per se,$^2$ and distorted aromatic systems are known to preserve to some extent their bonding patterns and aromatic character.$^{11}$ In fact, the average Wiberg bond index (WBI)$^{12}$ 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 $1^-$ and $2^-$ 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 $1^-$ more symmetric is higher hapticity of the $\eta^5$-Cp ligands (vs the $\eta^4$-cod in $2^-$) 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 ($\text{Bi}_6$) to 1.10 ($\text{Bi}_6^{2-}$) is too small to be interpreted as the sign of multibond or local aromaticity in the elongated prism $\text{Bi}_6^{2-}$. To put it into a context, the $\Delta$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 archetypical carbon-carbon multibond in the $\pi$-aromatic cyclopropenyl cation.
Finally, the authors seem very confident in the numbers they provide to confirm the ‘magnetic aromaticity’ in the model prism Bi$_6^{2-}$ and the isolated clusters. Negative values of the nucleus independent chemical shift (NICS)$^{13}$ 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 are often difficult to interpret if we do not distinguish between the chemically meaningful aromatic currents and the artifactual interferences of the local currents induced around lone-pairs and/or localized bonds (cf., the case of the P$_4$ and Si$_4^{1+}$ tetrahedrons).$^2$ Unfortunately, in the case of the elongated prism Bi$_6^{2-}$ we face this problem (Figure 1c). Orbital decomposition of the magnetic shielding in the centroid of the Bi$_6^{2-}$ prism and the isolated clusters leaves no doubt that strong negative values of NICS reported by Peerless et al. come mostly from the local induced currents generated by the six 6s$^2$ lone pairs surrounding the prism that cannot be associated with electron delocalization and aromaticity. 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).$^{14}$ For this reason, the net current associated with the transannular bonding HOMO-9 in Bi$_6^{2-}$ is too weak to interfere and cancel the strong current associated with the transannular antibonding $\phi$-type HOMO (Figure 1d). Consequently, the non-bonding pair of orbitals $a_1'$ and $a_2'$ is magnetically decoupled leading to the artifactual diatropic net current that carries no chemically meaningful information about electron delocalization and aromaticity.
To summarize, introducing the φ-aromaticity concept is not justified as the electronic structure and bonding in the elongated prisms like Bi$_6^{2-}$ have been known for about 30 years.$^9$ Moreover, none of the model Bi$_6^{q}$ prisms ($q = 0, 2, 4$) and the clusters isolated by Peerless et al.$^3$ can be regarded as aromatic. This is mainly because the prism topology actually prevents aromaticity to exists in the three-dimensional {Bi$_6$}-based clusters, a direct manifestation of which is lack of the triply degenerated MO energy levels.$^2$ The φ-aromaticity concept should rather be used in the context of planar clusters with laterally overlapping orbitals of the $n\pi_3$ type, which do not impair the subsystem of σ-bonds. The transannular antibonding φ-HOMO in 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 used to perform the present work are presented in the Supplementary Information.

**References**


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Ethics declarations

Competing interests

The authors declare no competing interests.

Supplementary information

This file contains Computational Methods and References.