

# On the Aromaticity and $^{13}\text{C}$ -NMR Pattern of Pentagonal-Pyramidal Hexamethylbenzene Dication $[\text{C}_6(\text{CH}_3)_6]^{2+}$ : A $\{\text{C}_5(\text{CH}_3)_5\}^- - \{\text{CCH}_3\}^{3+}$ Aggregate

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## Abstract

The experimentally characterized hexamethylbenzene dication  $\text{C}_6(\text{CH}_3)_6^{2+}$  shows a pentagonal-pyramidal structure involving a carbon-capped five-membered ring. The structural characterization of this hypercoordination (or hypervalency) gives rise if the aromatic behavior re-mains in the resulting pentagon ring. Here, we investigated the induced magnetic field of  $\text{C}_6(\text{CH}_3)_6^{2+}$  to gain a deeper understanding of the resulting non-classical structural situation in a representative pentagonal-pyramidal structure. Our results support the view of a  $\text{C}_5(\text{CH}_3)_5^- / \text{CCH}_3^{3+}$  structure, depicting a  $\pi$ -aromatic pentamethylcyclopentadienyl anion with a  $6\pi$ -electron kernel, with a capped carbon which does not decrease the characteristic shielding cone property of the aromatic ring. Hence, carbon-capped rings are suggested to retain the aromatic behavior from the former aromatic ring. We expect that the analysis of both the overall magnetic response and NMR chemical shifts may be informative to unravel the characteristic patterns in the formation of hypervalent carbon atoms involving non-classical chemical environments. © 2021 by the authors. Licensee MDPI, Basel, Switzerland.

## Author keywords

aromaticity; carbon; DFT; hypercoordination; shielding