ELECTRONIC STRUCTURE, BONDING AND REACTIVITY OF EMERGING BORON-BASED SYSTEMS: INSIGHTS FROM THEORY

Felipe Fantuzzi

School of Chemistry and Forensic Science, University of Kent, Canterbury, UK

Boron-based molecules featuring new structural motifs and bonding schemes have emerged and are promising in applications such as the activation of small molecules, homogeneous and heterogeneous catalysis, hydrogen production and storage, and materials for organic light-emitting diodes. To adequately describe these novel systems, high-level multireference approaches are usually required beyond standard density functional theory. In this work, we highlight recent developments in boron chemistry through the lens of computational chemistry and electronic structure theory. Particularly, we present studies on carbene-stabilised borylenes [1,2], diborylalkenes [3], boron-doped polycyclic aromatic backbones [4-6], molecules featuring boron–boron multiple bonds [7,8], highly strained diborete biradicaloids [9], and analogous isoelectronic systems [10]. The results demonstrate that the reactivity, ground-state multiplicity, and bonding situation of these boron-based molecules are controlled by the electronic structure, which can be fine-tuned by e.g., systematic modifications on the carbene backbone structure and substituents. These boron-based systems hold great potential for the generation of a new class of transition metal-free catalysts and materials in various fields, including pharmaceutical, agricultural, renewable energy, and optoelectronic industries.

[1] F. Fantuzzi, Y. Jiao, R. D. Dewhurst, F. Weinhold, H. Braunschweig, B. Engels. *Chem. Sci.* **2022**, *13*, 5118–5129.

[2] F. Fantuzzi, R. Moral, R. D. Dewhurst, H. Braunschweig, A. K. Phukan. *Chem. Eur. J.* **2022**, *28*, e202104123.

[3] P. Schmid, F. Fantuzzi, J. Klopf, N. B. Schröder, R. D. Dewhurst, H. Braunschweig, V. Engel, B. Engels. *Chem. Eur. J.* **2021**, *27*, 5160–5170.

[4] C. Saalfrank, F. Fantuzzi, T. Kupfer, B. Ritschel, K. Hammond, I. Krummenacher, R. Bertermann, R. Wirthensohn, M. Finze, P. Schmid, V. Engel, B. Engels, H. Braunschweig. *Angew. Chem. Int. Ed.* **2020**, *59*, 19338–19343.

[5] S. E. Prey, C. Herok, F. Fantuzzi, M. Bolte, H.-W. Lerner, B. Engels, M. Wagner. *Chem. Sci.* **2023**, *14*, 849–860.

[6] S. E. Prey, J. Gilmer, S. V. Teichmann, L. Čaić, M. Wenisch, M. Bolte, A. Virovets, H.-W. Lerner, F. Fantuzzi, M. Wagner. *Chem. Sci.* **2023**, Advance Article (DOI: 10.1039/D3SC00555K).

[7] T. Brückner, F. Fantuzzi, T. E. Stennett, I. Krummenacher, R. D. Dewhurst, B. Engels, H. Braunschweig. *Angew. Chem. Int. Ed.* **2021**, *60*, 13661–13665.

[8] T. Brückner, B. Ritschel, J. O. C. Jiménez-Halla, F. Fantuzzi, D. Duwe, R. D. Dewhurst, H. Braunschweig. *Angew. Chem. Int. Ed.* **2023**, *62*, e202213284.

[9] A. Gärtner, L. Meier, M. Arrowsmith, M. Dietz, I. Krummenacher, R. Bertermann, F. Fantuzzi, H. Braunschweig. *J. Am. Chem. Soc.* **2022**, *144*, 21363–21370.

[10] J. Gilmer, T. Trageser, L. Čaić, A. Virovets, M. Bolte, H.-W. Lerner, F. Fantuzzi, M. Wagner. *Chem. Sci.* **2023**, Advance Article (DOI: 10.1039/D3SC01395B).