Aromaticity

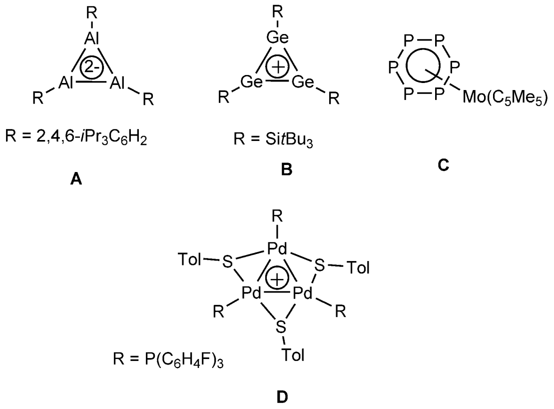
International Edition: DOI: 10.1002/anie.201510689
German Edition: DOI: 10.1002/ange.201510689

A Cyclotriborane Dianion and the Triboron Cation: "Light Ends" of the Hückel Rule

*Bernd Wrackmeyer**

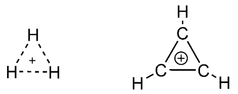
aminoboron halides · aromaticity · boron · dehalogenation · Hückel rule

Playing with rules, or sometimes against rules, is part of human nature, and is often inspiring in social life as well as in research. The development of modern inorganic chemistry, where the role of organic groups is reduced mainly to providing kinetic stabilization, has opened an almost unlimited playground full of challenging tasks. When looking for common properties of species **A**–**D** (Scheme 1), one might be puzzled at first glance. However, when the π electrons are counted, either two or six of them are found, which is reminiscent of the $(4n+2)$ Hückel rule (with $n=0, 1$),[1] and confirms the π aromaticity of these non-carbon cycles, which require kinetically stabilizing substituents or complexation.



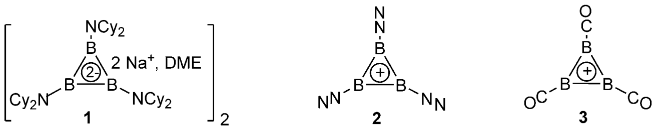
Scheme 1. Selected examples of non-carbon Hückel π-aromatic systems: **A**,[2] **B**,[3] **C**,[4] and **D**.[5]

The concept of aromaticity has gone through major changes ever since it was first described in the 19th century. Nowadays, a distinction should be made at least between σ and π aromaticity (Scheme 2); the triangular $[\mathrm{H_3}]^+$ cation, with its three-center two-electron (3c2e) bond, is prototypical for σ aromaticity,[6] whereas the cyclopropenium cation, $[\mathrm{C_3H_3}]^+$, with its two π electrons, fulfills the Hückel rule ($n=0$) and is thus π-aromatic.[7]



Scheme 2. σ Aromaticity (left) and π aromaticity (right).

Cyclic delocalization of π electrons is evident in countless heterocycles and typical of classical Hückel π-aromatic and π-antiaromatic structures. Isolobal replacement[8] of carbon by boron (e.g., replacing a CH fragment by $\mathrm{BH^-}$) is known to lead to π aromaticity, for example, in borole dianions, $[\mathrm{R{-}BC_4H_4}]^{2-}$,[9] or borabenzene anions, $[\mathrm{R{-}BC_5H_5}]^-$.[10] Because of its electron deficiency, boron can be used for the construction of three-dimensional scaffolds in which the bonding can be described in terms of σ aromaticity. Nonclassical bonding situations that are best explained in terms of (σ + π) double aromaticity have been described for $\mathrm{B_3}$, $\mathrm{CB_2}$, and $\mathrm{B_4}$ frameworks.[11,12] However, a simple Hückel π system built solely from boron atoms was realized only recently, when Braunschweig et al.[13] succeeded in the synthesis and characterization of the aromatic triboracyclopropenyl dianion $[(\mathrm{R_2N{-}B})_3]^{2-}$ (**1**; R = cyclohexyl, Cy) as the disodium salt (Scheme 3). An orange crystalline dimer was formed in the presence of 1,2-dimethoxyethane (DME), and slowly decomposed upon storage at low temperatures as well as in THF. The dimeric nature of **1** is preserved in solution, according to the measured and calculated ^{11}B chemical shifts ($\delta\,^{11}$B). An extensive theoretical analysis of **1** reproduced the fairly short B–B (161.7(6), 162.3(6), and 162.8(6) pm) and remarkably elongated B–N distances (mean value 152.9 pm, compared to ca. 140 pm in aminoboranes), and strongly supports its



Scheme 3. Hückel 2π aromatic systems: **1**: The Na$^+$ cations are in contact with the boron atoms (B–Na 256.1(5), 260.5(5), 298.1(5), 267.5(14), 269.0(15), 256.6(14) pm), and two of these Na$^+$ ions are additionally coordinated by DME; B–B (mean value) 162.3 pm. Values calculated for **2**: B–B 155.7, B–N 147.6, N–N 110.9 pm. Values calculated for **3**: B–B 156.5, B–C 150.0, C–O 113.1 pm.

---

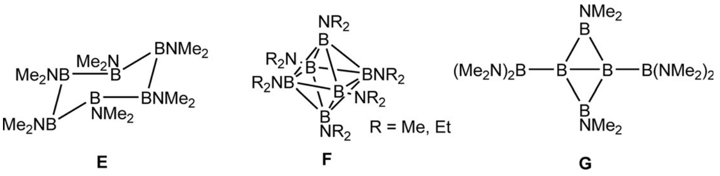
[*] Prof. Dr. B. Wrackmeyer
Anorganische Chemie II, Universität Bayreuth
95440 Bayreuth (Germany)
E-mail: b.wrack@uni-bayreuth.de

π-aromatic character. This property was corroborated by the nucleus-independent chemical shift (NICS) value, a criterion for aromaticity,[14] which was found to be similar to that of benzene, and the aromatic stabilization energy (ASE),[14] which is similar to that of the cyclopropenium cation. Therefore, the dianion in **1** can be regarded as the "light end" of Hückel 2π aromatic compounds, despite the enormous ring strain. Very recently, Frenking et al. presented spectroscopic evidence and convincing calculations[15] for the $[B_3]^+$ cations **2** and **3** (Scheme 3), which were generated in the presence of N_2 or CO in the gas phase by pulsed laser techniques. The boron atoms are linked to each other by 6e, and the remaining 2e are considered as being delocalized in a 2π-aromatic system. The ligands N_2 and CO serve as σ donors.

As the dehalogenation of $Cy_2N{-}BCl_2$, which can be conveniently monitored by ^{11}B NMR spectroscopy, with an excess of sodium sand in DME provides a straightforward route to **1**,[13] related processes should be briefly summarized. After pioneering studies on the reduction of aminoboron halides,[16,17] the first cyclic derivative, orange-red $(Me_2N{-}B)_6$ (**E**), was reported by Nöth and Pommerening only in 1980. Compound **E** was shown to be a six-membered ring of boron atoms in chair conformation (Scheme 4).[18] An isomer with an octahedral *hypercloso* structure was partly described for $(Et_2N{-}B)_6$ (**F**) by Baudler et al. They also claimed to have obtained a mixture containing the cyclotriborane $(Et_2N{-}B)_3$,[19] which, however, could not be confirmed by Berndt and co-workers.[20] On the other hand, the *hypercloso* octahedral structures of deep-black $(R_2N{-}B)_6$ (**F**; R = Me, Et) and their dianions, $\mathbf{F}^{2-}$, were fully described. Another constitutional isomer of $(Me_2N{-}B)_6$, **G**, was also detected (see also Siebert et al.[21]). In principle, cyclotriboranes can be considered as precursors of **E**, **F**, and **G**. Experiments and calculations indicate that **E** is thermodynamically more stable than **F** (R = Me).[20]

On several occasions, aminodiborane(4) halides served as starting materials for the reduction,[17c,20,21] and this approach also proved successful for the synthesis of $(R_2N{-}B)_4$ (R_2N = $i$$Pr_2N$ or 2,2′,6,6′-tetramethylpiperidino) with a folded B_4 ring (blue) or a tetraboratetrahedrane (yellow), respectively.[22]

Unambiguous mechanistic evidence for the processes that take place during the dehalogenation of aminoboron halides is still not available, neither for **1** nor for other systems. Following the work of Meller et al., it seems justified to assume an elusive carbenoid-analogous species, "$R_2N{-}B$", as a subvalent reactive intermediate,[23] and numerous examples of addition and insertion reactions of "$R_2N{-}B$" can be found in the literature. Interestingly, the reaction conditions employed by Meller et al. to generate "$R_2N{-}B$" were not very different from those used for the synthesis of **1** by Braunschweig and co-workers[13] (frequently even the same solvent, DME, was used). If $R_2N{-}B$ could be combined with two B−CO fragments or with $(NHC^s)B{\equiv}B(NHC^s)$[24] (NHC^s = saturated N-heterocyclic carbene), neutral Hückel 2π-aromatic systems would be formed.



Scheme 4. Structurally characterized isomers of $(R_2N{-}B)_6$: **E**,[18] **F**,[20] and **G**.[21]

Apparently, a favorable combination of reaction conditions, including suitable substituents at the nitrogen atoms and Na^+ as the counterion, enabled the synthesis of the first aromatic triboracyclopropenyl dianion as part of compound **1**, representing a milestone in the history of Hückel π-aromatic compounds. The importance of this finding has also to be appreciated with regard to the chemical properties of **1**, in particular considering its unusually high negative potential ($E = -2.42$ V relative to the ferrocene/ferrocenium couple). The search for other derivatives of **1** for further insight into its exciting chemistry has just started.

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 1962–1964
Angew. Chem. **2016**, *128*, 1998–2000

---

[1] E. Hückel, *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*, Verlag Chemie, Berlin, **1940**.
[2] R. J. Wright, M. Brynda, P. P. Power, *Angew. Chem. Int. Ed.* **2006**, *45*, 5953; *Angew. Chem.* **2006**, *118*, 6099.
[3] V. Y. Lee, A. Sekiguchi, *Angew. Chem. Int. Ed.* **2007**, *46*, 6596; *Angew. Chem.* **2007**, *119*, 6716.
[4] L. Nyulászi, *Chem. Rev.* **2001**, *101*, 1229.
[5] S. Blanchard, L. Fensterbank, G. Gontard, E. Lacote, G. Maestri, M. Malacria, *Angew. Chem. Int. Ed.* **2014**, *53*, 1987; *Angew. Chem.* **2014**, *126*, 2018.
[6] a) J. O. Hirschfelder, *J. Chem. Phys.* **1938**, *6*, 795; b) D. Cremer, *Tetrahedron* **1988**, *44*, 7427.
[7] a) R. Breslow, *Acc. Chem. Res.* **1973**, *6*, 393; b) H. Hopf, *Classics in Hydrocarbon Synthesis. Targets, Concepts, Perspectives*, Wiley-VCH, Weinheim, **2000**; c) T. M. Krygowski, H. Szatylowicz, O. A. Stasyuk, J. Dominikowska, M. Palusiak, *Chem. Rev.* **2014**, *114*, 6383.
[8] a) R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711; *Angew. Chem.* **1982**, *94*, 725; b) I. Fernandez, G. Frenking, G. Merino, *Chem. Soc. Rev.* **2015**, *44*, 6452.
[9] G. E. Herberich, M. Hostalek, R. Laven, R. Boese, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 317; *Angew. Chem.* **1990**, *102*, 330.
[10] a) G. E. Herberich, *Special Publication—Royal Society of Chemistry*, **1997**, *201* (Advances in Boron Chemistry), 211–223; b) A. J. Ashe, S. Al-Ahmad, X. Fang, *J. Organomet. Chem.* **1999**, *581*, 92.
[11] a) W. Mesbah, C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem. Int. Ed.* **2003**, *42*, 1717; *Angew. Chem.* **2003**, *115*, 1758; b) W. C. McKee, J. I. Wu, M. Hofmann, A. Berndt, P. v. R. Schleyer, *Org. Lett.* **2012**, *14*, 5712.
[12] M. Hofmann, A. Berndt, *Heteroat. Chem.* **2006**, *17*, 224.
[13] T. Kupfer, H. Braunschweig, K. Radacki, *Angew. Chem. Int. Ed.* **2015**, *54*, 15084; *Angew. Chem.* **2015**, *127*, 15299.
[14] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 2842.
[15] J. Jin, G. Wang, M. Zhou, D. M. Andrada, M. Hermann, G. Frenking, *Angew. Chem. Int. Ed.* **2016**, *55*, 2078; *Angew. Chem.* **2016**, *128*, 2118.
[16] R. J. Brotherton, A. L. McCloskey, L. L. Petterson, H. Steinberg, *J. Am. Chem. Soc.* **1960**, *82*, 6242.
[17] a) H. Nöth, W. Meister, *Chem. Ber.* **1961**, *94*, 509; b) K. H. Hermannsdörfer, E. Matejikova, H. Nöth, *Chem. Ber.* **1970**, *103*, 516; c) G. Linti, D. Loderer, H. Nöth, K. Polborn, W. Rattay, *Chem. Ber.* **1994**, *127*, 1909.

[18] H. Nöth, H. Pommerening, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 482; *Angew. Chem.* **1980**, *92*, 481.
[19] M. Baudler, K. Rockstein, W. Oehlert, *Chem. Ber.* **1991**, *124*, 1149.
[20] W. Mesbah, M. Soleimani, E. Kianfar, G. Geiseler, W. Massa, M. Hofmann, A. Berndt, *Eur. J. Inorg. Chem.* **2009**, 5577.
[21] A. Maier, M. Hofmann, H. Pritzkow, W. Siebert, *Angew. Chem. Int. Ed.* **2002**, *41*, 1529; *Angew. Chem.* **2002**, *114*, 1600.
[22] C.-J. Maier, H. Pritzkow, W. Siebert, *Angew. Chem. Int. Ed.* **1999**, *38*, 1666; *Angew. Chem.* **1999**, *111*, 1772.
[23] A. Meller, *Pure Appl. Chem.* **1991**, *63*, 395.
[24] J. Böhnke, H. Braunschweig, W. C. Ewing, C. Hörl, T. Kramer, I. Krummenacher, J. Mies, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 9082; *Angew. Chem.* **2014**, *126*, 9228.

Received: November 18, 2015