

Carborane: Dedicated to the Work of Professor Alan Welch

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In the 1950s, borohydrides arose as promising components of new rocket and aviation fuels. This led to the discovery of a new class of compounds—polyhedral boron hydrides and the creation of a new chapter in the chemistry of organoelement compounds, which are intrinsically attractive structures. It was one of the most important discoveries of the 20th century in the field of chemistry.

Polyhedral boron hydrides lie at the intersection of organic and inorganic chemistry. The main theoretical interest in the chemistry of these compounds is due to their unusual type of chemical bond and their three-dimensional aromaticity. The aromatic nature of polyhedral boron hydrides determines many properties that distinguish them from most boron hydrides and organoboron compounds: high thermal stability, kinetic stability of the borane cluster, a pronounced tendency towards substitution reactions and isomerisations.

The replacement of one or more boron atoms in a polyhedral cluster by atoms of other elements enables further diversification. The formation of carboranes, i.e., the inclusion of one or two carbon atoms in a boron cluster, leads to some radical changes. On one hand, it is the acidic character of the CH protons that makes it possible to replace the hydrogen atom(s) with various functional groups using standard organic synthesis methods. On the other hand, it becomes possible to remove one or more boron vertices, which significantly expands the range of structural types of carboranes. Thus, in addition to closed (*closo*-carboranes) structures, open (*arachno*- and *nido*-carboranes) ones become accessible. Moreover, open structures, such as the 7,8-dicarba-*nido*-undecaborate anion (*nido*-carborane) and its derivatives, are very promising ligands for the synthesis of metal complexes. The deprotonated form of *nido*-carborane (dicarbollide dianion $[7,8-C_2B_9H_{11}]^{2-}$) is a three-dimensional cluster with an open pentagonal face capable of forming strong π -bonds with transition metal cations, which makes it a unique ligand with unusual steric, electronic and chemical properties that are sometimes inaccessible for organic ligands.

For more than half a century, scientists from all over the world have been studying the properties of carboranes, as well as the possibility of obtaining new substances and materials with desired properties. The study of these compounds significantly expanded the modern understanding of molecular structures and the nature of chemical bonds, such as Wade–Mingos rules and the three-dimensional aromaticity concept, which is currently used to describe the structure of not only polyhedral boron hydrides but also transition metal clusters, fullerenes and their derivatives, etc.

One of the scientists who made a significant contribution to the development of the chemistry of carboranes is the British chemist Alan Welch.

Alan Welch undertook his PhD with Mike Hursthouse (who established the National Crystallography Service in the UK), then a postdoctoral degree in heteroboranes with FGA Stone in Bristol, and another postdoctoral degree with H-B Bürgi at ETH Zürich. From a lectureship at Edinburgh University, he joined Heriot Watt University in 1994 and



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established the crystallography facility at Heriot Watt, as well as leading his internationally recognized research group in heteroborane chemistry.

Later, Alan Welch worked on the synthesis of new heteroborane compounds, in particular, metallocarboranes. His group investigated their spectroscopic and structural characterization and studied their isomerisations and reactivity. The chemistry of supraicosahedral heteroboranes, bis(carboranes), nitrosocarboranes, and non-Wadlan metallocarboranes was significantly expanded by Prof. Alan Welch's group.

These eight papers form a Special Issue of *Crystals* to commemorate the excellent contribution made to carborane chemistry by Prof. Alan Welch, who retired from Heriot Watt University, Edinburgh, this year.

The papers illustrate the very comprehensive world of heteroborane chemistry, from liquid crystals to BNCT agents, di-halogen bonding to quantum chemical calculations of tetrel complexes of the carbonium ylide $\text{CB}_{11}\text{H}_{11}$, nickelacarboranes as potential acid-base sensors to revealing how the selective formations of metallocarborane diastereomers can arise and metallocarboranes as radical cation salts with dielectric or semiconductor properties.

A computational study by Drahomír Hnyk and co-workers used DFT to successfully describe the reactions of experimentally known *closo*- $\text{C}_2\text{B}_8\text{H}_{10}$ with bases such as hydroxides and amines. The formation of $[\text{arachno-4,5-C}_2\text{B}_6\text{H}_{11}]^-$ was established computationally when this was not demonstrable experimentally [1].

Laskova and co-workers developed BNCT (boron neutron capture therapy) agents that incorporate amino acids that are potentially taken up by malignant brain tumour cells. The recent synthesis and biological evaluation of *m*-carboranyl-cysteine as an agent for boron neutron capture therapy inspired the group to synthesize the analogue based on readily available 1-mercapto-*o*-carborane. The synthesis was optimised by using the “free of base” method [2].

Mandal was one of Alan Welch's PhD students, and his work is on bis(nickelation) of bis(*o*-carborane), which forms diastereoisomeric mixtures on metalation of the second carborane cage and additionally undergoes isomerisation. It was found that stereospecificity was influenced by intramolecular dihydrogen bonding, whereas a specific isomerisation outcome was related to the stereo-electronic nature of bis(phosphine) ligands [3].

Liquid crystals incorporating carboranes were explored by Núñez and co-workers. They varied substituents on *o*-carborane to tune liquid crystal properties employing the mesogen cholesteryl benzoate. They found that the methyl substituent produced a blue phase, whilst the phenyl substituent species was not mesogenic [4].

Stogniy, Sivaev and co-workers synthesized half-sandwich nickel(II) complexes with amidine ligands where breakage of the Ni–N bond on acidification results in a colour change, which gives these complexes potential as acid-base indicators [5].

High-level quantum-chemical computations (G4MP2) were employed by Oliva-Enrich and co-workers to examine tetrel bonding (interaction between any electron donating system and a group of 14 elements acting as a Lewis acid) to predict the formation of tetrel complexes between the icosahedral carbonium ylide $\text{CB}_{11}\text{H}_{11}$ and a set of simple molecules and anions. The electronic structure of the complexes was analysed with AIM and ELF methods, showing the C---X sharing and closed-shell interactions in the complexes [6].

Intermolecular halogen bonding, in this case, the diiodo bond, was investigated by Sivaev and co-workers. They obtained 1,12-diiodo-*ortho*-carborane, and its crystal structure was determined by X-ray diffraction, which revealed the existence of the I---I halogen bond in its crystal structure. Such dihalogen bonding is not found in 1,12-dibromo-*ortho*-carborane. Quantum chemical calculations determined the noncovalent interaction preferences in 1,12-diiodo- and 1,12-dibromo-*ortho*-carboranes, which were in agreement with experimental findings [7].

Radical-cation salts based on tetramethyltetrafulvalene (TMTTF) and tetramethyl-tetraselenefulvalene (TMsTSF) with metallocarborane anions were also explored by Sivaev and co-workers. The iron bis(1,2-dicarbollide) and chromium bis(1,2-dicarbollide) salts were synthesized by electrocrystallisation, and their characterisation revealed that the re-

sulting TMTTF radical-cation salts are dielectrics, whilst the TMTSF species is a narrow-gap semiconductor [8].

Thus, this Special Issue combines the latest achievements in the field of theoretical and experimental chemistry of carboranes. We thank all the authors who took part in this issue and look forward to further fruitful and impressive developments in the chemistry of carboranes.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Holub, J.; Fanfrlík, J.; McKee, M.L.; Hnyk, D. Reactions of Experimentally Known *Closo*-C₂B₈H₁₀ with Bases: A Computational Study. *Crystals* **2020**, *10*, 896. [[CrossRef](#)]
2. Laskova, J.; Kosenko, I.; Ananyev, I.; Stogniy, M.; Sivaev, I.; Bregadze, V. “Free of Base” Sulfa-Michael Addition for Novel *o*-Carboranyl-DL-Cysteine Synthesis. *Crystals* **2020**, *10*, 1133. [[CrossRef](#)]
3. Mandal, D.; Rosair, G.M. Exploration of Bis(nickelation) of 1,1'-Bis(*o*-carborane). *Crystals* **2021**, *11*, 16. [[CrossRef](#)]
4. Ferrer-Ugalde, A.; González-Campo, A.; Planas, J.G.; Viñas, C.; Teixidor, F.; Sáez, I.M.; Núñez, R. Tuning the Liquid Crystallinity of Cholesteryl-*o*-Carborane Dyads: Synthesis, Structure, Photoluminescence, and Mesomorphic Properties. *Crystals* **2021**, *11*, 133. [[CrossRef](#)]
5. Stogniy, M.Y.; Erokhina, S.A.; Suponitsky, K.Y.; Sivaev, I.B.; Bregadze, V.I. Coordination Ability of 10-EtC(NHPr)=HN-7,8-C₂B₉H₁₁ in the Reactions with Nickel(II) Phosphine Complexes. *Crystals* **2021**, *11*, 306. [[CrossRef](#)]
6. Ferrer, M.; Alkorta, I.; Elguero, J.; Oliva-Enrich, J.M. Carboranes as Lewis Acids: Tetrel Bonding in CB₁₁H₁₁ Carbonium Ylide. *Crystals* **2021**, *11*, 391. [[CrossRef](#)]
7. Suponitsky, K.Y.; Anisimov, A.A.; Anufriev, S.A.; Sivaev, I.B.; Bregadze, V.I. 1,12-Diiodo-*Ortho*-Carborane: A Classic Textbook Example of the Dihalogen Bond. *Crystals* **2021**, *11*, 396. [[CrossRef](#)]
8. Chudak, D.M.; Kazheva, O.N.; Kosenko, I.D.; Shilov, G.V.; Sivaev, I.B.; Abashev, G.G.; Shklyayeva, E.V.; Buravov, L.I.; Pevtsov, D.N.; Starodub, T.N.; et al. New Radical-Cation Salts Based on the TMTTF and TMTSF Donors with Iron and Chromium Bis(Dicarbollide) Complexes: Synthesis, Structure, Properties. *Crystals* **2021**, *11*, 1118. [[CrossRef](#)]