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MANIFESTATION OF POLAR EFFECTS IN BIFUNCTIONAL CARBORANYL MOIETIES

Bakalářská práce

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ABSTRACT

An introduction to the carborane chemistry and its utilisation was outlined, key references for up to date insight were provided. Two new bifunctional *meta*–carborane derivatives were prepared and characterised by ^{13}C, ^{11}B, and ^{1}H NMR spectroscopy, ESI-MS, IR spectroscopy, acid-base titration, melting point determination and computational analysis. Electron-accepting and donating directions in the synthesised carborane isomers were manifested by comparison with the parent compounds. The mutual influence of the functional groups attached to the *meta*–carborane cluster was discussed with regard to the collected experimental data. And a short contemplation of the utilisation of the observed effects for SAMs tailoring was carried out.

KEY WORDS

Dicarba–*closo*–dodecaborane, *meta*–Carborane, Carborane Thiol, Carborane Carboxylic Acid, Self Assembled Monolayers

CONTENT

HISTORY OF BORANE CHEMISTRY

Borane chemistry was established with the work of Stock and Massenez in 1912.[1] They developed new vacuum techniques for treating volatile and reactive substances and described the preparation of a series of boron compounds, including B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$. Some of their basic properties are stated in **Table 1**. The original synthesis unfortunately provided very low yields, making the development of borane chemistry difficult.

Table 1. Basic characteristics and properties of selected boranes; melting point (m.p.) and boiling point (b.p.) temperature (data taken from: Muetterties *Boron Hydride Chemistry*[2]).

	m.p. (°C)	b.p. (°C)	notes
B_2H_6	–165.5	–92.5	violently inflames at room temperature
B_5H_9	–46.8	58.4	
B_4H_{10}	–120	16	spontaneously decomposes at room temperature
B_5H_{11}	–123.3	65	
B_6H_{10}	–65.1	108	
$B_{10}H_{14}$	99.5	231	stable, crystalline

The question of the structure of boranes was tackled with diborane, being solved through electron diffraction analysis, which gave misleading conclusions of an ethane like structure at first,[3] but inclined towards a hydrogen bridged molecule as depicted in **Figure 1**, when investigated again in 1951.[4]

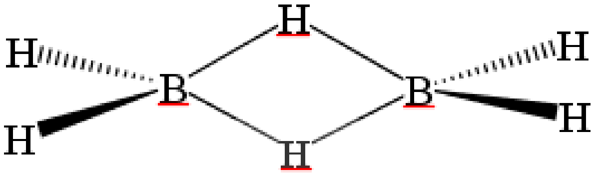

Figure 1. The structure of diborane.

Various bonding pattern theories emerged, of which some are mentioned below. A two-centre one-electron bond, giving numerous resonance structures, thus making the outlets clouded and far too complex.[5]

Boron-boron double bond with two protons placed in the half-planes of a π– electron cloud,[6] resulting in the bridging protons being acidic, which contradicts with experiments, as the bridging protons of diborane and similar molecules are hydridic.[7] And a three-centre two-electron (3c2e) bond between the two boron atoms and one hydrogen atom, a theory suggested by Longuet-Higgins in 1949.[8] He presented the bond as being formed by one sp^3 hybrid orbital from each boron atom and 1s orbital from a hydrogen atom. The last concept was used by Eberhardt, Crawford and Lipscomb, for drafting a systematic description of bonding in higher boranes by 3c2e bonds, formed by AOs of either three boron atoms or two boron and one hydrogen atom.[9] With improvements, these principles are used for the basic description of borane clusters to date and are briefly discussed in the next section.

The high symmetry in boranes was emphasized by the utilisation of delocalised bonding, as their thermal and hydrolytic stability, alongside with the unusually high value of magnetic susceptibility, pointed towards their aromatic character.[10] The earliest linear combination of atomic orbitals (LCAO) analysis of borane structures, performed by Longuet-Higgins and Roberts in the mid 1950's, predicted icosahedral $[B_{12}H_{12}^{2-}]$.[11] The dodecaborane dianion was synthesised in the following years, alongside other predicted *closo*–boranes, $[B_nH_n]^{2-}]$.[12,13] The descriptive methods were improved and simplified by Wade and Mingo in 1971, those are presented in the next section.[14]

An investigation on the use of boranes as potential high energy fuels for aircraft engines led to improvements in their synthesis and a large-scale production in the 1950's.[15] This idea, surprisingly far later, proved to be blind, as combustion of boranes with oxygen gives boron trioxide, a glass like solid with the melting and boiling points of 450 °C and 1860 °C, respectively. This glass product made the driving system malfunction. Although the original purpose of the research was not fulfilled, it resulted in a fast development of the solely man-made chemistry of boranes and their derivatives, as well as concepts of their structure and bonding.[16] The availability of $B_{10}H_{14}$ as a starting precursor made possible the discovery of many other polyhedral boranes, carboranes and metalloboranes.[17,18]

STRUCTURAL AND BONDING PATTERNS

The molecular structures of boron cluster hydrides are derived from deltahedral shapes (**Fig. 3**). This has been recognised as the key aspect in the categorisation of boranes and their structural analogues. The classes are based on the openness of respective molecular frameworks and are further explained in binary boranes.

closo–Boranes are usually denoted with the formula [$B_nH_n^{2-}$], with boron atoms forming highly symmetrical closed polyhedral skeletons with *n* vertices. Their 3D-aromatic or *pseudo*–aromatic character is a topic discussed ever since the prediction of the *closo*–dodecaborane dianion and is often addressed by the means of computational chemistry.[19]

Other borane types are summarised in **Table 2**. Their reactivity escalates from *closo*– to *hypho*–boranes, as in each group the boron atoms fill only *n* vertices of the associated deltahedron, making the borane structure more open.

Table 2. Borane types, based on their composition and the number of vertices.

Type	Composition	Manifested structural pattern
closo–Boranes	B_nH_n	*n*–vertex deltahedron
nido–Boranes	B_nH_{n+4}	(*n+1*)–vertex deltahedron
arachno–Boranes	B_nH_{n+6}	(*n+2*)–vertex deltahedron
hypho–Boranes	B_nH_{n+8}	(*n+3*)–vertex deltahedron
conjucto–Boranes	combination of boranes stated above	

The bonding is interpreted *via* localised and delocalised bonds. Molecules of low symmetry are described with localised 3c2e bonds accompanied with the classical two-centre two-electron (2c2e) bonds. On the other hand, high symmetry of closed deltahedral boranes enables the use of molecular orbitals (MOs) extended over the whole boron skeleton. The theoretical methods are nowadays hidden in elaborate computational packages, but the main ideas were fashioned into simple counting rules for textbook characterisations and prediction of new structures.

LCAO method describes the 3c2e bond as a combination of 1s hydrogen atom orbital (AO) and 2s, 2p boron AOs with the required hybridisation. Two kinds of 3c2e bond are used for boranes, the BBB and BHB bond, with their schematic orbital contributions presented in **Figure 2**. The LCAO method gives three MOs, one being bonding and the other two either nonbonding or antibonding.[20]

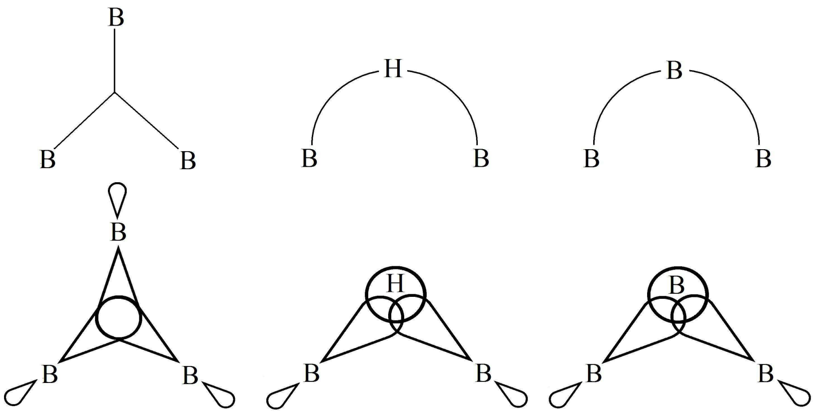

Figure 2. Schematic depiction of the three-centre two-electron bonds with respective AO contributions.

Carbon atoms are capable of participating in multi-centre bonding as well, with examples found in carboranes, metal complexes featuring agostic interactions and non-classical carbocations such as $C_6Me_6^{2+}$.[21] Their structure is however usually described with delocalised MOs.

The use of 3c2e bonding in the characterisation of boranes was elaborated by Lipscomb in the *equations of balance*, which are as follows.[22] Each boron atom in the molecule shares four AOs and three electrons, with the one electron deficiency being compensated with one 3c2e bond, there must be an equal number of 3c2e bonds and boron atoms, with the other orbitals and electrons used for classical bonding. Moreover, the relationship between the number of all boron (p) and hydrogen ($p+q$) atoms, boron atoms with two terminal hydrogen atoms BH_2(x), classical BB bonds (y) and 3c2e BHB (s) and BBB (t) bonds in the molecule is:

$$s + t = p$$

$$s + x = q$$

$$p = t + y + q/2$$

Those relations were further extended to accommodate novel molecule types.[23]

The rules issuing from the use of delocalised MOs were summarised and simplified by Wade.[24] The principle dealing with simple clusters presumes, that the molecule is constructed from basic building blocks such as B–H or C–H fragments. Each fragment is composed of a localised MO and contributes its spare electrons and AOs to the formation of the skeletal framework, *i.e.* two electrons and three AOs in the case of the B–H fragment and three electrons and three AOs in the case of the C–H fragment. The geometry is then determined by the total number of electrons accessible to

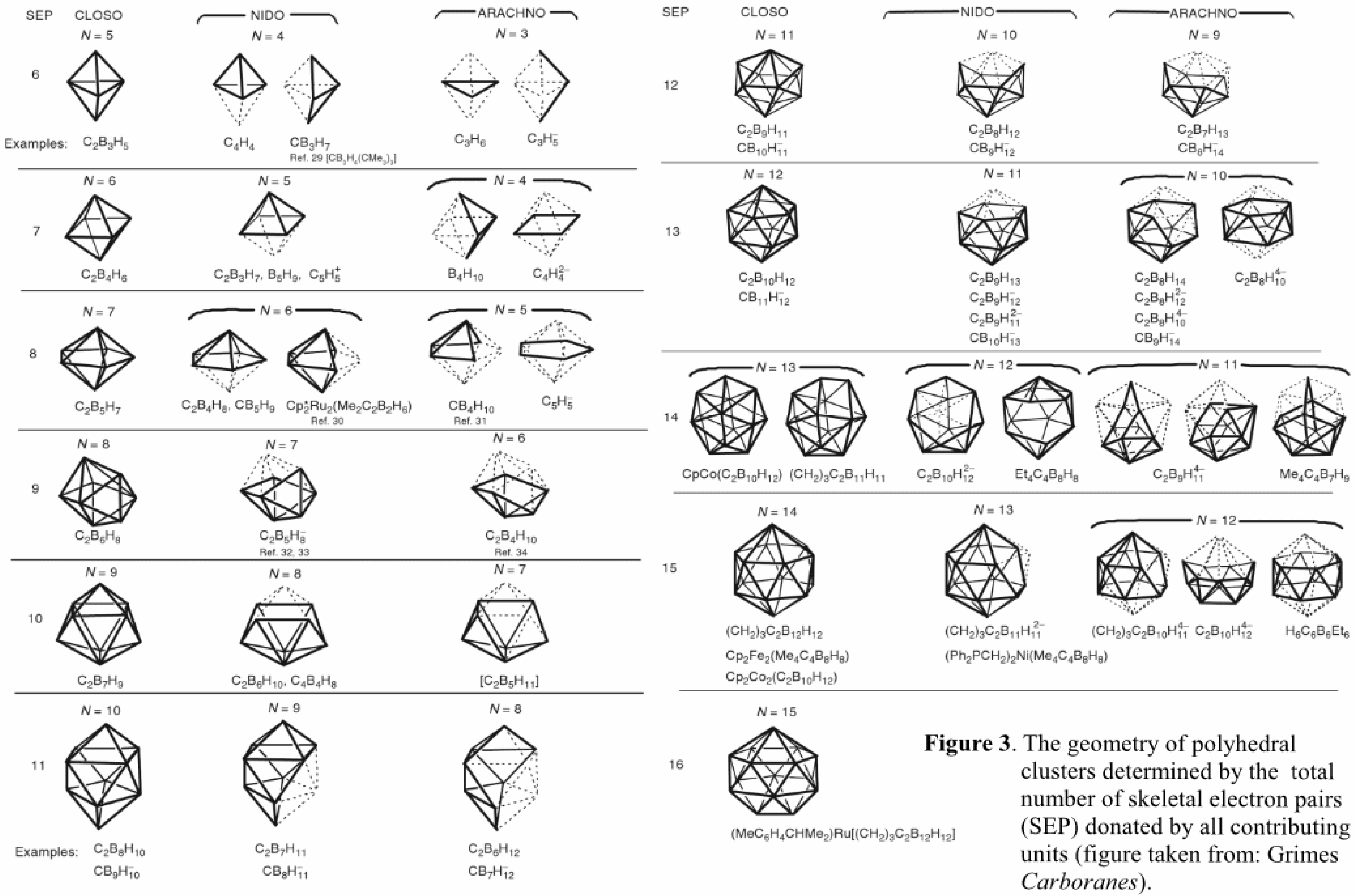

Figure 3. The geometry of polyhedral clusters determined by the total number of skeletal electron pairs (SEP) donated by all contributing units (figure taken from: Grimes *Carboranes*).

the skeletal bonding (**Fig. 3**). The Wade's principles are further modified for application to more complex clusters containing heteroatoms, capping vertexes, multi cluster systems *etc*.[25]

DICARBA-*closo*–DODECABORANE

Three structural isomers of the *12*–vertex dicarba-*closo*–dodecaborane (herein further referred to as carborane or CB) are known, *ortho*–carborane $1,2–C_2B_{10}H_{12}$, *meta*–carborane $1,7–C_2B_{10}H_{12}$ and *para*–carborane $1,12–C_2B_{10}H_{12}$, differing in the positions of carbon atoms (**Fig. 4**).

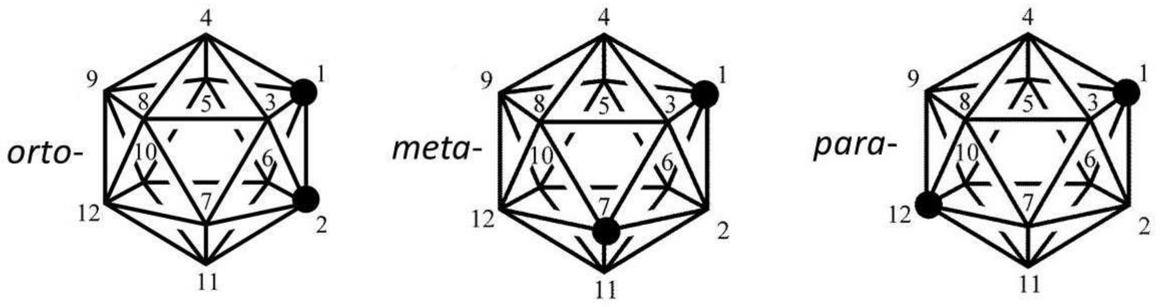

Figure 4. The structural isomers of the *closo*–carboranes (*ortho*–, *meta*– and *para*–), pictured with the numbering system of distinct positions. The lines connecting the vertices do not represent chemical bonding and are present to highlight the icosahedral structure. Hydrogen atoms at vertices of the icosahedra are omitted for clarity, the larger black dots indicate the positions of the carbon atoms.

Structure

The structure of carboranes is derived from the dodecaborane dianion $[B_{12}H_{12}^{2-}]$ structure, a regular icosahedron with the edge length of approximately 1.8 Å. The formal substitution of two boron vertices by carbon atoms leads to a subtle distortion of the icosahedron, the carbon vertices are slightly embedded inwards.

The effect of carboxyl (–COOH) and thiol (–SH) substituents on the carborane skeleton is apparent in **Table 3**, where selected interatomic distances, r(C1–C2) and r(B9–B12) are shown for *ortho*-carborane and its 1,2– and 9,12–disubstituted derivatives. It is evident, that both functional groups increase the respective interatomic distances. The effect of the –SH group attached to the carbon atoms is strikingly larger, as the other two shown derivatives exhibit only a slight difference. However, the distances provided in **Table 3** for 1,2–$(SH)_2$–*o*–carborane are computational, unlike the rest of the data.

Table 3 – Interatomic distances of selected vertices in *ortho*-carborane derivatives determined by crystallography and computational analysis.

	r(C1–C2) / Å	*r*(B9–B12) / Å
$[B_{12}H_{12}^{2-}]$	-	1.775(27)[a, b]
o–CB	1.630(6)[a, b]	1.775(16)[a, b]
1,2–$(COOH)_2$–*o*–CB	1.654(6)[a]	1.782(5)[a]
1,2–$(SH)_2$–*o*–CB	1.803[c]	1.771[c]
9,12–$(SH)_2$–*o*–CB	1.640(3)[a]	1.797(3)[a]

a) Data from an X-ray structural analysis.[26,27,28,29]

b) Average value for the molecules in the crystallographic unit cell.

c) Computational data.[30]

Symmetry

The symmetry analysis of carboranes renders information about the equivalence of some vertex positions. This is important for the evaluation of nuclear magnetic resonance (NMR) spectra. **Table 4** shows equivalent positions for the parent *meta*–carborane and its derivatives substituted at positions C1 and B9. The derivative of *meta*–carborane with a substituent introduced in the position C1 has the same symmetry as *meta*–carborane substituted by two different functional groups in both carbon positions, *i.e.* the symmetry of 1–X–*m*–$C_2B_{10}H_{11}$ is equal to the symmetry of 1–X–7–Y–*m*–$C_2B_{10}H_{10}$. Bifunctional derivatives of *meta*–carborane were prepared as part of this study and their symmetry was utilised in their characterization.

Table 4. List of equivalent positions in derivatives of *meta*–carborane. The derivatives in the table are positioned to depict the reducing symmetry.

1–X–*m*–CB	*m*–CB	9–X–*m*–CB	1–X–9–Y–*m*–CB
1	1,7	1	1
7		7	7
2,3	2,3	2	2
		3	3
4,6	4,6,8,11	4,8	4
			8
8,11		6,11	6
			11
9,10	9,10	9	9
		10	10
5	5,12	5,12	5
12			12

Charge Distribution

The charge distribution over boron vertices shows a relation with the distance between particular boron vertex and carbon atoms. The more distant the boron atom is in the cluster from the carbon atoms, the higher is its electron density,[31] resulting in mesurable dipole moments of approximately 4.53 D for *ortho*– and 2.85 D for *meta*–carborane.[32] A feature arising from this non-uniform electron distribution is the electron accepting and donating properties of the C– and B–substituted carboranyl moieties. Among the B–substituted carboranyl moieties, the electron donating character of the carborane cage increases in the following order:

3–*o* ≤ 2–*m* < 4–*o* ≤ 4–*m* ≤ 2–*p* < 5–*m* < 8–*o* ≤ 9–*m* < 9–*o*

The same order is proved in electrophylic reactions and acidity of carboxylated and thiolated derivatives.[33,34]

NMR Spectroscopy Evaluation

Numerous studies have been reported to assign NMR peaks to the respective boron, carbon and hydrogen atoms in carborane isomers bearing different substituents. General trends and unexpected deviations were observed.

The first striking feature in the ^{11}B spectra is the apparent inverse relation between chemical shielding and charge distribution over the carborane skeleton. While the charge distribution in principle rises with the distance from the carbon atoms, the boron nuclei in *meta*–carborane experience shielding in the order B(5,12), B(9,10), B(4,6,8,11), B(2,3), from low field to high field respectively.[35]

Another important feature for the evaluation of ^{11}B spectra is the vicinal and antipodal effect. In halogen B–substituted carboranes an upfield shift has been observed for the antipodal nuclei and a downfield shift for the vicinal. An interesting back-donation was observed for the iodine-bonded boron atom, resulting in a strong upfield shift of the jointed boron nucleus.[36]

The ^{1}H spectra feature the same basic trend, the boron bonded protons experience stronger shielding with the closing distance to the skeletal carbon atoms.[37] Deshielding of the protons is observed in halogen-substituted carboranes, the effect lowers with rising distance from the halogen substituent.[38]

The ^{13}C signals of the skeletal carbon atoms follow the vicinal and antipodal effects outlined for ^{11}B.

The assignment of peaks in NMR spectra is interesting mainly for the better understanding of the communication between the carborane cage and different functional groups. It was set out as an objective to assign ^{11}B peaks in *mono*– and *poly*– substituted *meta*–carborane derivatives. This task however proved too complex, as chemical shifts have been studied mainly for B–halogenated and B–methylated carboranes. Further complicating is the non–trivial relation between the chemical shifts observed in *poly*–substituted carboranes and the chemical shifts examined for the same substituents in *mono*– substituted carboranes.

A correlation between the acidity and ^{1}H chemical shift of the –SH moiety attached to the carborane cluster (**Tab. 5**) was intended to be used as an indirect probe of the acidic character of the sulphur bonded proton in carboxylated mercaptocarboranes.

Table 5. The acid dissociation constants and respective ^{1}H NMR chemical shifts of thiolated carboranes. The dissociation constants were determined under identical conditions in 50% ethanol, the ^{1}H NMR spectra were measured in $CDCl_3$.[39]

	^{1}H NMR (SH)	pK_A
1–SH–*o*–CB	3.95	3.30
8–SH–*o*–CB	0.46	9.32
9–SH–*o*–CB	0.45	10.08
1–SH–*m*–CB	3.36	5.30
4–SH–*m*–CB	0.72	7.38
9–SH–*m*–CB	0.43	9.45
1–SH–*p*–CB	3.16	5.85
2–SH–*p*–CB	0.79	7.75

Synthesis

Dicarba–*closo*–dodecaborane

The *ortho*–carborane is mainly prepared by the reaction of dodecaborane(14) with a Lewis base, giving a *nido*–$L_2B_{10}H_{12}$ intermediate, which readily reacts with acetylenes (**Fig. 5**).[40]

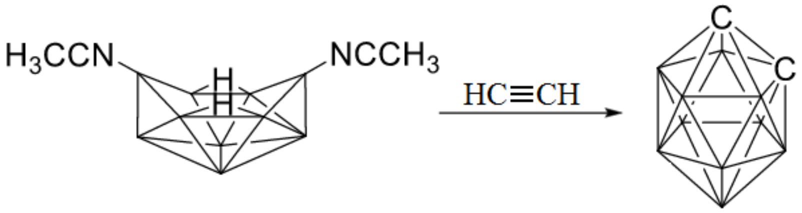

Figure 5. Acetylene insertion into $L_2B_{10}H_{12}$ (L = CH_3CN) to give *ortho*–carborane (figure taken from: Berkeley's *dissertation*).[41]

Another procedure exploits the exchange of cations between sodium borohydride and tetraalkylamonium salt, forming R_4NBH_4, R = alkyl, which is then pyrolyzed to give a mixture comprising a high fraction of *closo*–$B_{10}H_{10}^{2-}$. The *closo*–decaborane dianion cage opens in the presence of a Lewis base and a proton donor, forming the *nido*–$L_2B_{10}H_{12}$ intermediate, used in the reaction discussed above.[42]

The *meta*– and *para*–carboranes are prepared through thermal isomerization of *ortho*–carborane. The conversion to *meta*–carborane occurs above 425 °C, giving almost quantitative yields *via* vapour phase isomerization at 600 °C in less than a minute.[43] The *para*–carborane needs temperatures above 600 °C for the isomerization to occur, leading to degradation of the carborane skeleton, forming undefined polymer-like matter. Therefore the procedure results in a low yields for *para*–carborane.[44]

Introduction of –SH Group to B–Vertices

The classical route to B–thiolated carboranes is based on the reaction of the respective carborane isomer with an excess of sulphur over aluminium trichloride ($AlCl_3$), followed by hydrolysis. This reaction has been demonstrated for example on *meta*–carborane, and gave 9,10–$(SH)_2$–*m*–carborane in a high yield.[45] This reaction is however limited to the vertices with a relatively high electron density and restricts any regioselective demands.

Alternative synthesis use the reaction of *mono*– or *poly*– iodinated carborane with triisopropylsilanethiolate ($Si(i–Pr)_3S^-$), catalysed by tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), the needed $Si(i–Pr)_3S^-$ anion is generated from proton transfer between triisopropylsilanethiol ($Si(i–Pr)_3SH$), and a base. The product of this cross–coupling reaction is then hydrolysed with aqueous acid, the reaction gives *meta*–carborane thiolated at the former iodine positions.[46]

The next synthesis is interesting for the generation of *ortho*–carborane iodinated at the B(3) position, The 3–I–*o*–carborane might be then utilised in the catalysed thiolation as stated above. The reaction of *ortho*-carborane with alkoxides cleaves one boron vertex, giving *nido*–$C_2B_9H_{11}^{2-}$, the *nido*-anion reacts with RBX_2, where X = alkyl, aryl, halogen and X = halogen, giving R–3–*o*–carborane.[47,48] The procedure can be applied to *meta*–carborane as well.[49]

Substitution at Carbon Vertices

The C–H carborane vertices are relatively acidic and readily react with strong bases, such as organolithium reagents. The lithiation of carboranes with *n*-butyllithium thus takes place only at the carbon vertices and leads potentially to *mono*– or *di*– lithiated carboranes. Those may undergo different subsequent reactions. Reaction with elemental sulphur leads to lithium thiolates as an intermediate species, exposure to CO_2 leads to lithium carboxylates. Acidic hydrolysis then gives carborane thiols or carborane carboxylic acids in good yields.[50,51] Other reactions common to organometallic compounds may be carried out too. However, the possibilities narrow for thiolated carboranes. Protective method has been elaborated to conceal the undesired reactivity of thiolate anions. Reaction of carborane thiols with a strong base and methoxy methyl-bromide renders (methoxy-methylthio)–carborane, which may undergo any subsequent reaction typical for the organometallic compounds. The protecting group may be cleaved in a reaction with $HgCl_2$.[52]

Organic Analogues

For the comparison of the effects, which –COOH and –SH moieties bestow upon each other, organic aromatic analogues are described through acid dissociation constants and ^{1}H NMR chemical shifts of the sulphur bonded proton (**Tab. 6**).

Table 6 – Acid dissociation constants and ^{1}H NMR chemical shifts (–SH group) of *mono*- and *di*-substituted benzene derivatives. Respective titrations were carried out under identical conditions, NMR experiments were carried out in $CDCl_3$.

	^{1}H NMR (SH)	pK_A(SH)	pK_A(COOH)
benzoic acid	–	–	9.41[a]
thiophenol	3.40[c]	6.62[b]	–
thiosalicylic acid	4.67[d]	8.2[b]	–
m–mercapto benzoic a.	3.58[d]	6.15[b]	8.9[a]
p–mercapto benzoic a.	3.65[d]	5.9[b]	9.29[a]

a) Potentiometric titration in methanol.[53]
b) Spectrophotometric titration in H_2O.[54]
c) Data taken from: CAS online database.[55]
d) Data taken from: Jiang *et al. A General and Efficient Approach to Aryl Thiols*.[56]

The trend in acidity of the –COOH groups in mercaptobenzoic acids can be outlined with Kekules structures (**Fig. 6**). The increased electron density in positions *ortho*– and *para*– arising from the mesomeric effect of the –SH moiety on the benzene ring forecasts *ortho*– and *para*–mercaptobenzoic acid to be of lower acidity then *meta*–mercaptobenzoic acid, where it is only an inductive effect that plays a significant role. For this reason it would be further interesting to observe, whether a similar trend would arise in C–substituted *ortho*– and *para*–carborane isomers.

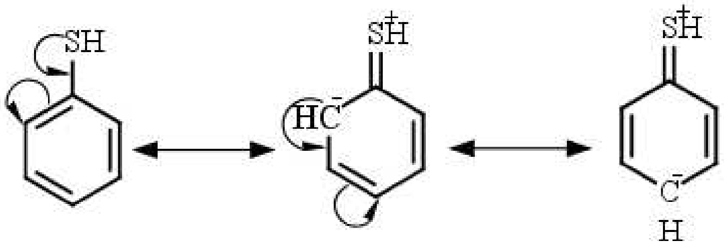

Figure 6 – Mesomeric structures of thiophenol.

UTILISATION OF BORANE AND CARBORANE CLUSERS

Unusual properties of borane and carborane clusters offer a wide range of applications, however their price limits them for a low scale use or cases without alternatives. Of interest is the behaviour of thiolated *closo*–carboranes in the form of self-assembled monolayers (SAM)s on metal surfaces, other utilised properties are listed briefly. A review covering the applications of carboranes was recently published by Grimes.[57] Recent works on application of c*loso*–carboranes in health care are presented in a review by Valliant et al.[58]

SAMs

The ability of molecules to form *mono*–molecular layers by adhesion on surfaces is investigated for various systems, comprised for example of organic thiols and noble metals, where the thiol or thiolate groups anchor the organic units to the surface. Diverse surfaces and suitable anchoring groups are discussed in a review by Gooding.[59] SAMs of thiolates on metal surfaces are reviewed by Love.[60]

Constitution of the SAM building units enables to tailor physicochemical properties of surfaces, *i.e.* granting partial control over the metals work function, their resistance to corrosion, wetting and adhesion, surface reactivity *etc*. Cage molecules offer symmetrical, spatially demanding units, these impose an ordered surface orientation, thus more transparent control over the system. The benefits arising from the use of cage molecules are reviewed by Hohman.[61]

The work function of metals can be altered by the adsorption of molecules with oriented dipoles. The adsorbed molecules, with negative poles oriented from the surface, increase the work function and *vice versa*, the magnitude of the effect dependent on the adsorbate.[62] The thiolated *closo*–carborane cage offers a wide range of molecular dipoles, *i.e. ortho*–, *meta*– and *para*–isomers thiolated at different positions, to be used in the work function alternation.[63] Additional attachment of substituents to the carborane cluster alters its charge distribution and dipole moment, thus fine tuning of the work function may be achieved.[64]

The enhanced resistance of the substrate metal to corrosion is investigated in a system of dithiolated *ortho*–carborane SAMs on silver surfaces under a sulphane atmosphere, where the carborane monolayers proved to have better protective ability than SAMs composed of thiolated alkyl and aryl compounds.[65]

More distinctive applications of carborane SAMs are still to be explored, unlike SAMs in general, they resemble a virgin field of surface science. Their high thermal and chemical stability, symmetrical architecture, steric demands and relatively high dipole moments provide interesting foundational units. The carborane clusters may be further functionalized to offer selective reactive centres. It is in the scope of this study to compare polar effects of *poly*–substituted carborane derivatives. Provided, that the electron–donating and accepting qualities of respective skeletal positions remain alike after additional substitution, properties of the functional groups may be adjusted by their skeletal positioning, as explored in the charge distribution section. Leading for example to adjustable stability constants of complexes.

Other applications

Polymers with embedded *closo*-carborane clusters among the monomeric units exhibit enhanced thermal and chemical stability, for example in polycarboranesiloxanes.[66] Carboranes have also been applied to metal-organic frameworks (MOFs), coordination polymers with high porosity suited for ionic exchange, gas storage and separation and catalysis.[67]

Sandwich type complexes of open carborane frameworks joined with platinum metals exhibit catalytic properties in the hydrogen transfer reactions, behaving as homogeneous catalysts for hydrogenation, hydrosilylation and isomerization of unsaturated organic compounds.[68]

The borane and carborane anions, whose ionic nature arises from the skeleton, not an attached moiety, form salts soluble in organic solvents. Their solubility might be utilised in inter-phase transfers of cations, solvent extraction of metals through the formation of complexes, *etc*.[69]

Molecular properties of c*loso*–carboranes enables their use as biologically active compounds. Their hydrophobic character helps the interaction between pharmaceuticals and their receptors and slows down the metabolic segregation of drugs.[70] Biologically active boron compounds are synthesised for the use in boron neutron capture therapy (BNCT) and have been labelled with radioactive elements to monitor its distribution in the organism. Radio-labelled carborane compounds found wider applications in tumor imaging techniques, since their artificial structure resists enzymatic reactions, thus cleavage of the radioactive marker.[71]

SCOPE OF THE STUDY

This study engages the communication between moieties and carborane skeleton. It aims to analyse whether the electron–donating and accepting properties of respective skeletal positions differ after an additional substitution of the *meta*–carborane cluster. The possible influence of substituents on the polar effect is investigated by means of acidity and ^{1}H NMR chemical shifting of –COOH and –SH moieties attached to a *meta*–carborane cluster. Attention is also paid to the changes in the interatomic distances within the carborane skeleton, as they could very well reflect the differences in the distribution of electron density over the framework, thus influencing qualities of attached moieties.

RESULTS AND DISCUSSION

Two new bifunctional derivatives of *meta*–carborane were prepared, 1–COOH–7–SH–*m*–carborane and 1–COOH–9–SH–*m*–carborane.
A straightforward synthesis, without the need of protecting the –SH group was developed (**Fig. 7)**. The compounds were confirmed with ^{11}B and ^{1}H NMR spectra, as the number of peaks, their splitting to doublets and their integrals matched the prediction. However, the computed values for NMR chemical shifts gave only a close approximation (**Supp. Inf.**).

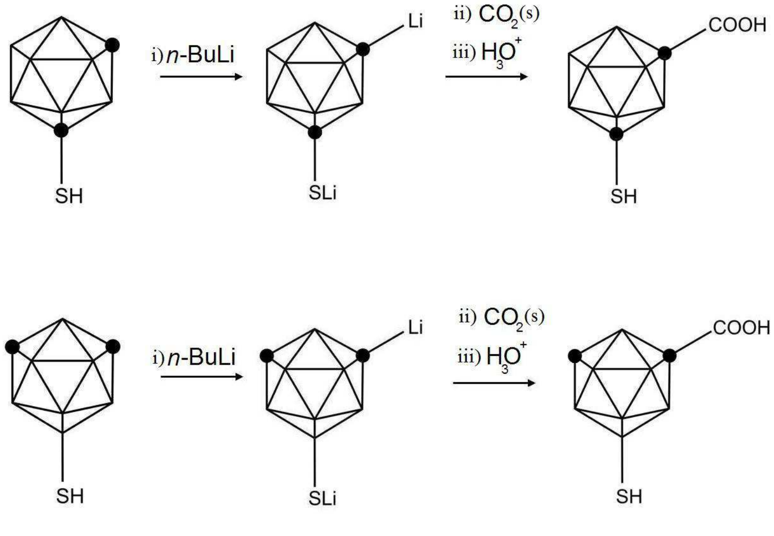

Figure 7 – Reaction scheme for the carboxylation of carborane thiols.

The synthesised compounds were characterised by ^{13}C, ^{11}B, and ^{1}H NMR spectroscopy, electron spray ionization-mass spectrometry (ESI-MS), infra red spectroscopy (IR), acid dissociation constant (pK_A) and melting point (m.p.) determinations and computational analysis. The acquired data are presented in the **Supplementary Information** section. Additional ^{1}H NMR analysis were carried out for the parent compounds, *i.e.* 1–COOH–*m*–CB, 1–SH–*m*–CB and 9–SH–*m*–CB, pK_A was determined for 1–COOH–*m*–CB (**Tab. 8**).

The method adopted in this work for the assignment of NMR signals, was observation of collapses in doublet signals in ^{1}H and ^{11}B NMR spectra after application of decoupling frequencies for ^{11}B and ^{1}H, respectively, leaving singlet signals unchanged. However, this method gave information only for the assignment of the singlet signals, such as the ^{1}H signal arising from the –*S*H and –COOH moieties. Chemical shifts were further analysed by comparison with *meta*–carborane, subsequent spectral changes with additional substituents and confrontation with the NMR spectra acquired by quantum computational methods.

The thiol based proton chemical shifts in ^{1}H NMR spectra were used to compare the electron donating and withdrawing effects of different C– and B– substituted carboranyl groups by the means outlined in the NMR Spectroscopy Evaluation section for the acidity of the thiol moiety. However it is only possible to show whether the effect, which the carborane skelet imparts after its additional substitution, is amplified or reduced, but not to which extent. This unfortunately offers only a diminishable insight in to the communication of moieties over the carborane cluster.

The ^{1}H chemical shifts and pK_A values of the –SH and –COOH groups attached to *meta*–carborane derivatives are listed in **Table 8**. The first pK_A of compounds bearing –SH as well as –COOH group is denoted as arising from the –COOH moiety and the second from the –SH group, as abnormal behavior was not expected.[72]

Both of the prepared isomers embody the same trend in electron donation at B(9) vertex and electron accepting at C vertices like the parent compounds. As may be directly concluded from the measured pK_A. The carbon positions stabilize the formation of anions, thus the –SH and –COOH moieties render relatively acidic protons. The B(9) vertices on the other hand grant thiol groups with acid dissociation constants greater by several orders. The trend can be concluded from the ^{1}H NMR spectra as well. The chemical shifts of the same moieties in respective compounds differing only slightly.

Table 8 – Acid dissociation constants and ^{1}H NMR chemical shifts of the –SH and –COOH groups in *mono*- and *di*-substituted *meta*–carborane derivatives. The pK_A were determined by potentiometric titration in 50% ethanol. The NMR experiments were carried out in $CDCl_3$. Identical conditions were kept for all measurements.

	^{1}H NMR		pK_A	
	–SH	–COOH	–SH	–COOH
1–COOH–*m*–CB	–	9.89	–	3.76
1–SH–*m*–CB	3.39	–	4.9[a]	–
1–COOH–7–SH–*m*–CB	3.46	10.41	4.25	3.01
1,7–$(SH)_2$–*m*–CB	–	–	4.42 and 5.71[ab]	–
9–SH–*m*–CB	0.47	–	9.45[c]	–
1–COOH–9–SH–*m*–CB	0.52	9.84	9.23	3.23

[a] Data taken from a yet to be published article from our laboratory.[73]

[b] The p$K_{A,1}$ and p$K_{A,2}$ are shown in the same column, as they both arise from the –SH moiety.

[c] Titration carried out in a different laboratory.[74]

As can be seen, connecting the –COOH group to the carbon vertex results in a slight downfield shift of these peaks. This observation extends to thiophenol and its carboxylated derivatives as well (**Tab. 6**). However, the differences in chemical shifts are minor, so they could also arise from the intermolecular interactions. Thus the little difference inclines towards a very weak influence of the –COOH moiety on the electron surroundings of the –SH proton.

A slightly larger difference in the chemical shifts is observed for the –COOH proton in 1–COOH–*m*–CB and its derivative thiolated at the second carbon vertex. Moreover the difference in the pK_A(COOH) of *meta*–carborane carboxylic acid and its different thiol–derivatives is to be taken as a measure of the communication between the –SH group and the carborane skelet, the differing electron density then influencing the stability of the carboxylate anion. The differences are comparable for benzoic acid and its *meta*–thiolated derivative (**Tab. 6**). Further, it is possible to observe that those effects are greater for the –SH group attached to the carbon vertex than to the B(9) vertex. The difference in the chemical shifts after the connection of the –SH moiety to B(9) vertex has an adverse effect, but of a very low magnitude. This observations might lead to the conclusion that the communication of the carborane cluster with adjunct moieties is superior at the carbon vertices.

The pK_A values appointed to the –SH groups in *meta*–carborane thiol, *meta*–carborane dithiol and mercapto–*m*–carborane carboxylic acid show a difference which is further demonstrated in **Table 9**, the moieties affecting the dissociative –SH groups are underlined there.

Table 9 – Acid dissociation constants of substituted *meta*–carborane thiols with highlighted second substituents.

		Substituent affecting pK_A(SH)	pK_A(SH)
1–SH–*m*–CB		–	4.9
1–COOH–7–SH–*m*–CB		$–\mathrm{COO}^-$	4.25
1,7–$(\mathrm{SH})_2$–*m*–CB	p$K_\mathrm{A,1}$	–SH	4.42
	p$K_\mathrm{A,2}$	$–\mathrm{S}^-$	5.71

It is evident from the presented data, that the negative charge of the carboxylate anion does not pervade through the carborane skelet, since the presence of the carboxylate anion increases the acidity of the –SH group, thus stabilising the forming thiolate anion in a similar way as the second –SH substituent. On the other hand, the thiolate anion decreases acidity of the –SH group, these observations imply on a different type of bonding with the carborane skelet.

Comparison of these observations with acid dissociation constants measured for *para*–carborane thiol derivatives (**Tab. 10**) hint, that the trends in communication between the carborane framework and attached moieties should be explored separately for *ortho–, meta–, and para*–carborane.

Table 10 – Acid dissociation constants of carboxylated *para*–carboranethiol and the parent compound, determined by potentiometric titration in 50% ethanol under identical conditions (data taken from a yet to be published article from our laboratory).[75]

	pK_A(COOH)	Substituent affecting pK_A (SH)	pK_A(SH)
1–SH–*p*–CB	–	–	3.4
1–COOH–12–SH–*p*–CB	3.6	$–COO^-$	6.4

Structures of the synthesised compounds were not yet established by X-ray structural analysis, computed structures were used for the exploration of changes in the carborane skelet after its substitution instead. Interatomic distances of antipodal vertices were chosen to demonstrate these changes and are listed in **Table 11**. The differences are however very subtle, with only the difference between 1,7–$(COOH)_2$–*m*–carborane and 1–COOH–7–SH–*m*–carborane for *r*(B2-B9) reaching a little over 1 % (0.033 Å). Thus it is inconvenient to draw conclusions, other than that the substituents have minimal influence on the carborane framework, without additional data on the molecular structure.

However, it is interesting to point out the differences between disubstituted *ortho*–carboranes (**Tab. 3**), where the prolongation of interatomic distances between neighbouring vertices is most apparent in the *ortho*–carborane dithiol with the –SH groups attached at the carbon vertices. This could be interpreted as an answer to spatial demands of the –SH moiety, as the *r*(C1–C2) distance in *ortho*–carborane is shorter than the *r*(B9–B12) distance and they almost even out in the respective dithiolated derivatives. Or another aspect for consideration might be the position dependent communication between the carborane skeleton and attached moieties, as investigated for the chemical shifts and acid dissociation constants of disubstituted *m*-carborane derivatives. For this reason it would be interesting to acquire some X-ray diffraction data of interatomic distances for *ortho*–, *meta*– and *para*–carborane derivatives disubstituted at carbon and boron vertices.

Table 11 – Interatomic distances of selected antipodal vertices in *meta*–carborane and its derivatives determined by crystallography and computational analyses.

	r(C1–B12) /Å	*r*(C7–B5) /Å	*r*(B2–B9) /Å
m–CB	3.208(13)[a]		3.374(15)[a]
1,7–$(COOH)_2$–*m*–CB	3.223(6)		3.400(5)
1–COOH–7–SH–*m*–CB	3.208[b]	3.233[b]	3.362[b]
9–SH–*m*–CB	3.277(127)[a,c]		3.396(4)[a,c]
1–COOH–9–SH–*m*–CB	3.212[b]	3.205[b]	3.381[b]

a) Average value for the molecules in the crystallographic unit cell from X-ray structural analysis.[76,77]

b) Computational data.

c) Yet to be published data, determined by crystallography.[78]

CONCLUSIONS

Two new *meta*–carborane derivatives, *i.e.* 1–COOH–7–SH–*m*–carborane and 1–COOH–9–SH–*m*–carborane were prepared and characterised. The acid dissociation constants and ^{1}H NMR signals of the synthesised isomers manifest a distribution of the electron density, that is comparable with the electron density of the parent compounds. The mutual interaction in *meta*–carborane derivatives between the carboxyl, carboxylate, thiol and thiolate functional groups and the *meta*–carborane skeleton have been investigated by the use of ^{1}H NMR spectroscopy, acid dissociation constants and X-ray and computational structural analysis. The acquired data indicate that the –COOH and $-COO^-$ groups have a relatively small, if any effect on the thiol moiety, both groups surprisingly somewhat rising its acidity. The thiol group affects the –COOH moiety in an ordinary manner, slightly rising its acidity too. The extent of the influence of the thiol moiety is dependent upon its positioning on the carborane cluster, the effect is greater with both groups attached to carbon vertices. Thiolate anion lowers the acidity of a second connected –SH group in a dithiolated *meta*–carborane as expected. These effects are consistent with simple theoretical predictions by Lipscomb, in which two types of substituents are distinguished on the basis of their orbital interaction with the carborane cage.[79] It is important to note, that the carboxyl and thiol substituents evince a differing behaviour in disubstituted *para*–carborane. Thus the investigation of respective *closo*–*c*arborane isomers should be approached to some extent separately.

The generally consistent polar effect of the carborane cage may be utilised to design SAMs building units with properties altered with the positioning as outlined in the SAMs section. Moreover, the substituent dependent changes can be used for an additional small scale adjustments. Aryl analogues in comparison offer a less range of modification.

EXPERIMENTAL METHODS

Chemicals

The starting materials *meta*–carborane, 1–SH–*m*–carborane and 9–SH–*m*–carborane were purchased from Katchem s.r.o. Their characterisation was carried out through ^{11}B and ^{1}H NMR spectroscopy. *n*–Butyllithium 2.5 M in hexanes was bought from Aldrich (batch n. 230707). Diethyl ether p.a. grade was bought from Penta s.r.o. and for the main reaction was dried with Sodium and benzophenon, boiling under argon atmosphere until blue colour appeared. Hydrochloric acid 33%, p.a. was bought from Penta s.r.o. Magnesium sulphate anhydrous p.a. was bought from Penta s.r.o.

Synthesis

All the reactions were carried out in a similar procedure. The differing starting compounds, quantities of reactants and solvents, methods of purification and accompanying observations are stated for each synthesis separately. Their occurrence in the description of the parent procedure is denoted by bold numbers in parentheses.

meta–Carborane derivative **(1)** was dissolved in diethyl ether **(2)** under argon atmosphere in a three necked flask that was placed in a cooling bath of acetone with dry ice. Upon cooling to –78 °C *n*–butyllithium **(3)** was added dropwise through a septum by a syringe **(4)**. The mixture was allowed to stir for 1 hour, then opened and excess of crushed dry ice was added. The mixture was then withdrawn from the cooling bath and allowed to slowly warm up to the laboratory temperature under argon atmosphere. Within one hour the gas evolvement ceased and a white precipitate was found. Distilled water **(5)** was added **(6)** and the aqueous phase acidified with 30 ml of diluted HCl (by volume 1 part distilled water to 1 part of 33% HCl) **(7)**. The aqueous mixture was shaken out three times to 30 ml of diethyl ether **(8)**. The three diethyl ether phases were joined and dried over $MgSO_4$ for ~ 1 day. The mixture was filtrated and the solvent evaporated under reduced pressure on a rotary vacuum evaporator. **(9)**

Specification of reagents, their quantities and accompanying observations are specified below.

Preparation of 1–COOH–*m*–carborane

(1) *meta*–carborane (4. 0 g, 27.7 mmol)

(2) 80 ml of diethyl ether

(3) *n*–butyllithium (10.2 ml, 25.5 mmol)

(4) no suspension formed

(5) 50 ml of distilled water, ether phase is clear, aqueous phase is dim

(6) the phases were separated, the ether phase was then shaken out one more time with 50 ml of distilled water and the aqueous phases were joined

(7) white precipitate is formed instantly and a boundary is formed slowly between a clear, aqueous and white, oil like liquid

(8) the mixture clears out and only aqueous and ether phases are present

(9) The crude product was dissolved in a hot pentane–chloroform mixture and the saturated solution placed in a freezer (~ –20 °C). Crystals of the purified product emerged overnight.

Preparation of 1–COOH–9–SH–*m*–carborane

(1) 9–mercapto–*m*–carborane (3.0 g, 17.0 mmol)

(2) 200 ml of diethyl ether

(3) *n*–butyllithium (15.0 ml, 37.5 mmol)

(4) white precipitate formed few minutes after addition of *n*–butyllithium

(5) 300 ml of distilled water, two opaque phases emerge

(9) the mixture dried overnight with $MgSO_4$, was filtered, evaporated and than sublimed under 5,9 · 10–2 mBar, while heated in an oil bath to 80 °C. The white product crystallised just above the oil level, while a brown acetone–soluble residue was left in the flask.

Preparation of 1–COOH–7–SH–*m*–carborane

(1) 1–mercapto–*m*–carborane (1.0 g, 5.7 mmol)

(2) 80 ml of diethyl ether

(3) *n*–butyllithium (5.0 ml, 12.5 mmol)

(4) white precipitate formed in half hour after addition of n–butyllithium

(5) 50 ml of distilled water, ether phase is opaque, aqueous phase is clear

(6) the phases were separated, the ether phase was then shaken out one more time with 50 ml of distilled water, the ether phase is clear and the second aqueous phase is dim, the aqueous phases were joint

(9) The mixture was filtered and evaporated to orange oily liquid which grew crystals overnight in the fridge, it was than sublimed under 1,3 · 10–1 mBar while heated in an oil bath to 80 °C. The white product crystallised just above the oil level, while in the flask was left a brown acetone–soluble residue and another compound crystallised above in the apparatus. The yield was 66 %.

NMR Spectroscopy

The NMR spectra were measured on a Varian Mercury Plus 400 NMR spectrometer under standard conditions, using deuterated chloroform as solvent. The chemical shifts are referenced to $BF_3 \cdot OEt_2$ for ^{11}B and TMS for ^{1}H and ^{13}C, with the reference frequency calibrated from the locked frequency of the solvent according to VnmrJ values for the solvent shift.

Computational details

Quantum chemistry calculations were performed by the NWChem[80] package. The geometries were optimised by the means of the density functional theory with the hybrid exchange–correlation functional PBE0[81,82,83,84]. Jensen's triple–zeta polarisation consistent basis set pc-2[85] was used. Magnetic shieldings were computed for the optimised geometries by employing gauge–including atomic orbitals (GIAOs)[86,87] using the same functional, and for comparison both pc-2 basis set and pcS-2 basis set, optimised for this type of calculations[88].

ESI-MS

Performed on a Thermo–Finnigan LCQ–Fleet ion trap instrument with electrospray ionization (ESI) and detection of negative ions. Samples dissolved in ethanol (concentrations approximately 100 ng/ml) were introduced to the ion source by infusion (15 µl/min) with the following setup: sheath gas flow 14.98 µl/min, source voltage 4.98 kV, capillary temperature 274 °C, capillary voltage −34.92 V, tube lens voltage −109.95 V, and mass range set from 90 to 2000.

IR Spectroscopy

The IR spectra of the new bifunctional isomers were measured on a Nicolet Nexus 670 FT-Infrared Spectrometer in KBr tablet in a range of 4000–200 cm^{-1}.

Acid-Base Titration

The samples (50 – 100 mg) were dissolved in 50 ml of EtOH (Penta, p.a. grade) and mixed with 50 g of deaerated distilled water. The mixtures were stirred and titrated with an ethanol/water (1:1) solution of NaOH (0.1 M). This blend of solvents was necessary for dissolving the samples that are otherwise not dissoluble in pure H_2O.

Melting Point Determination

Melting points were determined in sealed capillaries on BŰCHI Melting Point B-545 apparatus and are uncorrected.

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