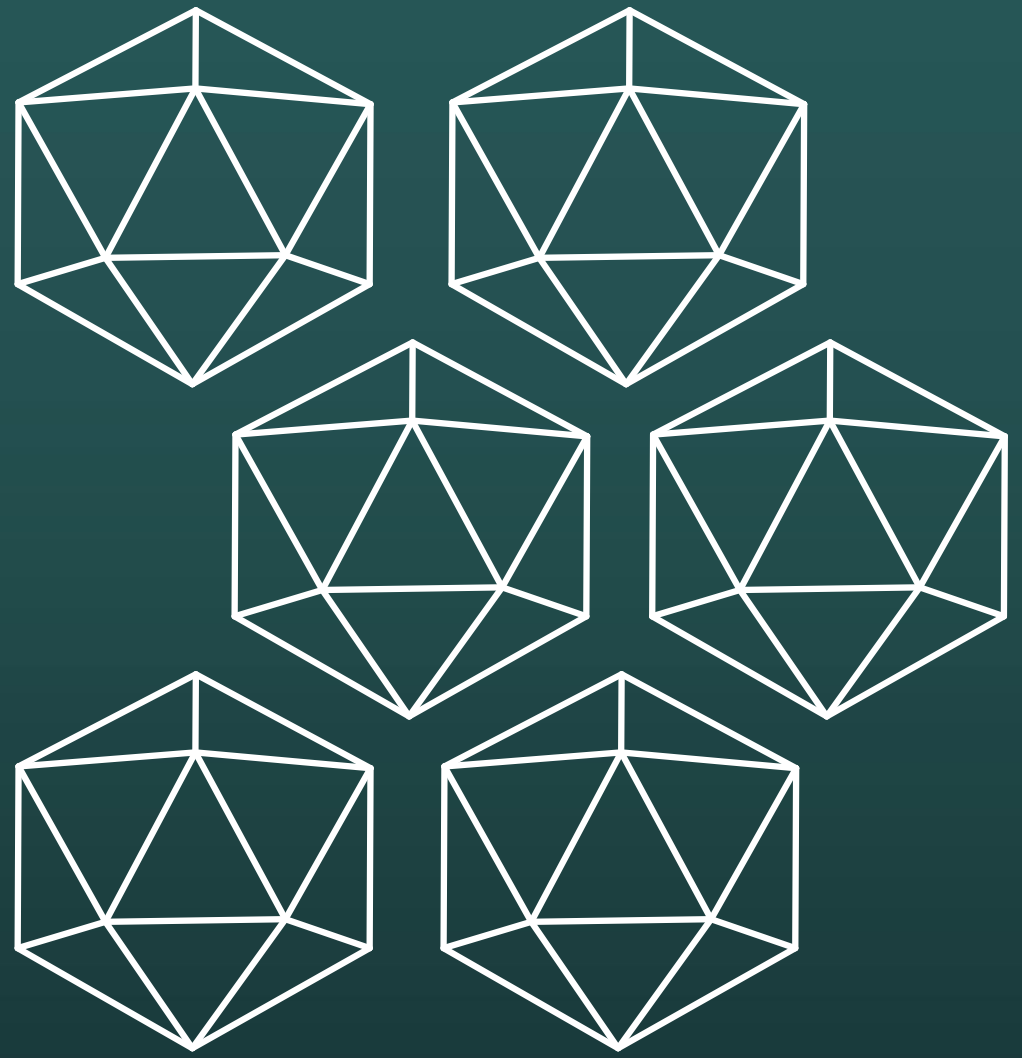
# Strukture i svojstva borana i karborana



09. siječnja 2025.

Nastupno predavanje u sklopu kolegija Anorganska kemija 1

dr. sc. Darko Vušak

# Sadržaj

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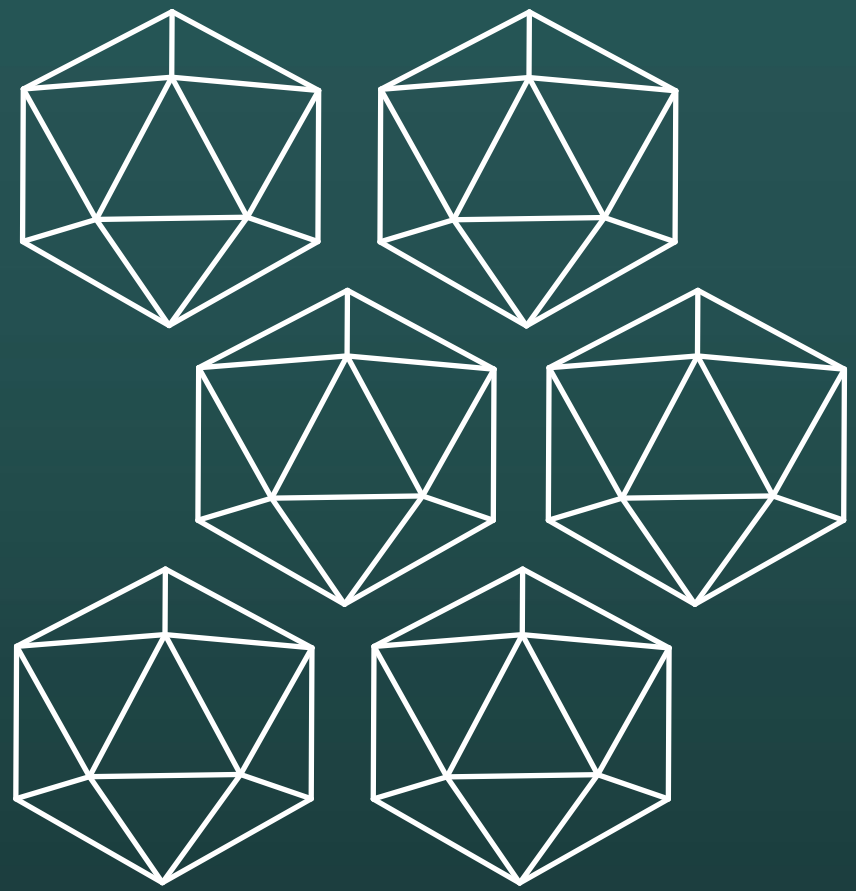


# 1. Bor i njegova svojstva

- Borovi spojevi korišteni još u drevnom Egiptu
- Trgovina boraksom u 8. st. (boraks)
- Najvažnije rude
  - kernit – $Na_2B_4O_6(OH)_2 \cdot 3H_2O$
  - boraks (tinkal) – $Na_2B_4O_5(OH)_4 \cdot 8H_2O$
- Elementarni bor neovisno su priredili H. Davy (30. lipnja 1808.) te J. L. Guy-Lussac i L. J. Thénard (21. lipnja 1808.)
- Esencijalan element za biljke – važan za izgradnju stanične stjenke

Uzorak amorfnog bora

https://en.wikipedia.org/wiki/Boron

# 2. Povijest otkrića borana i karborana

- Boran je generalni naziv za binarne spojeve bora i vodika, tj. borove hidride

Opća formula: $B_xH_y$

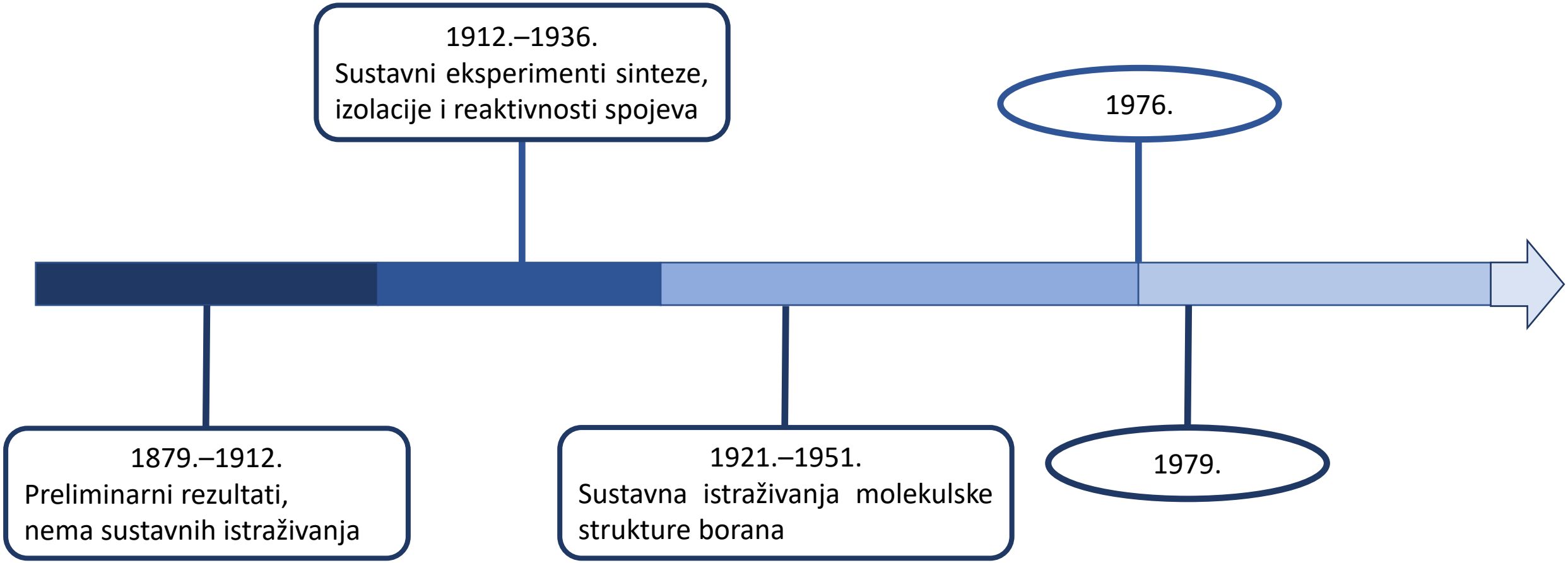
Moguće molekulske formule: $B_xH_{x+4}$, $B_xH_{x+6}$ (u neutralnim hidridima)

- Karborani (karbaborani) su derivati borana u kojima je jedan ili više borovih atoma zamijenjeno atomima ugljika

Opća formula: $C_xB_yH_z$

Najčešća molekulska formula: $C_2B_{x-2}H_x$ (u neutralnim hidridima)

# 2. Povijest otkrića borana i karborana



# 2. Povijest otkrića borana i karborana

1879.

- Prvi preliminarni rezultati s opisom fizikalnih i kemijskih svojstava borana (Francis Jones)
- Dobivanje „plina” reakcijom $MgB_2$ i klorovodične kiseline
- Opažanja: „Bezbojan plin, gori jarkim zelenim plamenom, vrlo neugodnog mirisa koji podsjeća na fosfin ili stibin.”

1881.

- 1881. objavljen rad *On boron hydride* (autori F. Jones i R. L. Taylor)
- Opažanja:
  - Nastaje borov hidrid uz veliki suvišak vodika
  - Izaziva mučninu i glavobolju kad se udahne u umjerenoj količini
- Istražene reakcije s $KMnO_4$, $NH_3$

# 2. Povijest otkrića borana i karborana

1909.–1936.

- 1909. Alfred Stock počinje raditi na boranima
- 1912. – 1936. sinteza i odjeljivanje niza borana
- Odvojio različite borane postupkom frakcijskog ukapljivanja plinova
- Najjednostavniji dobiveni boran $B_2H_6$


Medalja memorijalne nagrade Alfred Stock dodijeljivana 1950. – 2022. (od 2023. nagrada nosi ime Marianne Baudler)

# 2. Povijest otkrića borana i karborana

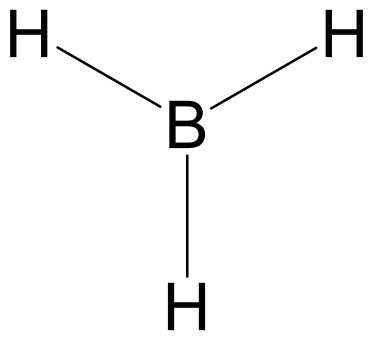
| Formula | Naziv spoja | Talište / °C | Vrelište / °C | Reakcija sa zrakom pri 25 °C | Reakcija s vodom |
|---|---|---|---|---|---|
| $B_2H_6$ | Diboran(6) | −165 | −93 | Spontano zapaljenje | Trenutna hidroliza |
| $B_4H_{10}$ | Tetraboran(10) | −120 | 18 | Zapaljiv | Hidroliza unutar 24 h |
| $B_5H_9$ | Pentaboran(9) | −47 | 48 | Spontano zapaljenje | Uz zagrijavanje |
| $B_5H_{11}$ | Pentaboran(11) | −123 | 63 | Spontano zapaljenje | Brza hidroliza |
| $B_6H_{10}$ | Heksaboran(10) | −62 | 108 | Stabilan | Uz zagrijavanje |
| $B_6H_{12}$ | Heksaboran(12) | −82 | 80–90 | - | Kvantitativni raspad na $B_4H_{10}$, $B(OH)_3$, $H_2$ |
| $B_{10}H_{14}$ | Dekaboran(14) | 100 | 213 | Vrlo stabilan | Spora hidroliza |

$B_xH_{x+4}$ $B_xH_{x+6}$

# 3. Struktura i priroda veze u boranima i karboranima

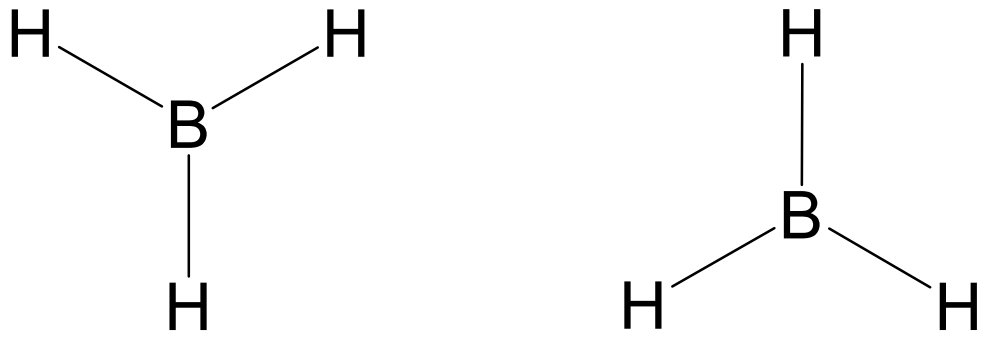
Najjednostavniji boran $BH_3$

- detektiran 1964., postojanje potvrđeno masenom spektrometrijom
- infracrveni spektri – pretpostavljena planarna struktura
- nedovoljno stabilan za opsežna ispitivanja kemijskih svojstava



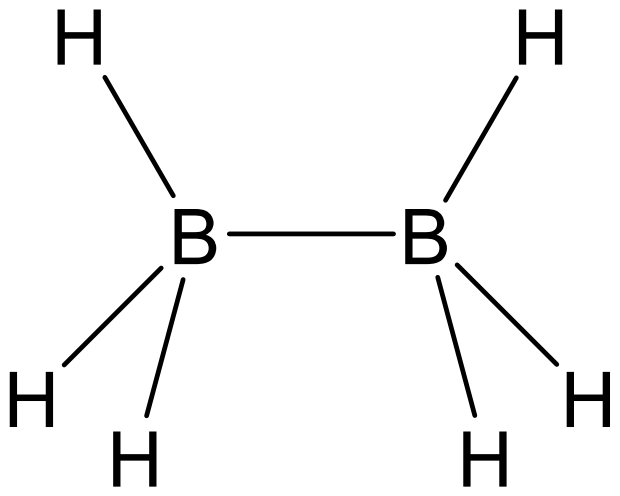
# 3. Struktura i priroda veze u boranima i karboranima

- Koliki je najmanji broj klasičnih kovalentnih veza potreban da bismo opisali strukturu molekule $B_2H_6$?

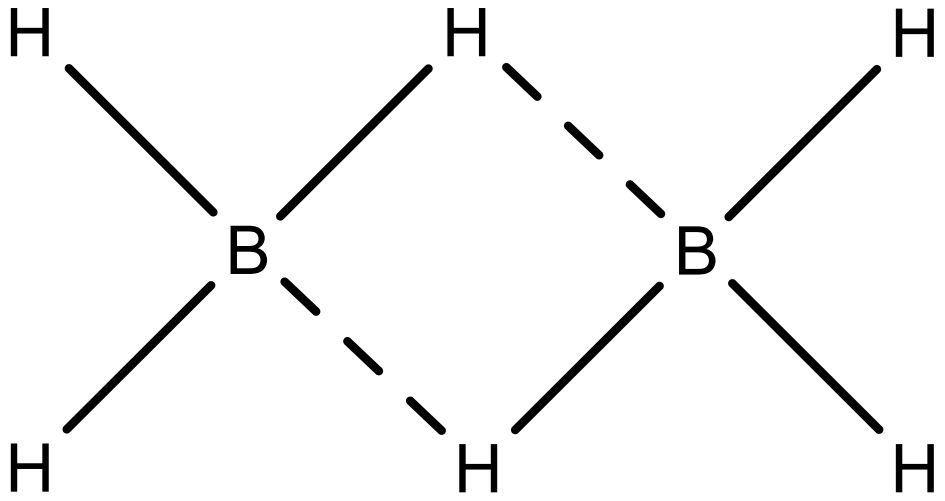


# 3. Struktura i priroda veze u boranima i karboranima

- Koliki je najmanji broj klasičnih kovalentnih veza potreban da bismo opisali strukturu molekule $B_2H_6$?
- Elektronima deficijentni (oskudni) spojevi, spojevi s *manjkom* elektrona
- Prijedlozi strukture diborana prije 1940.:




Prijedlog L. Paulinga



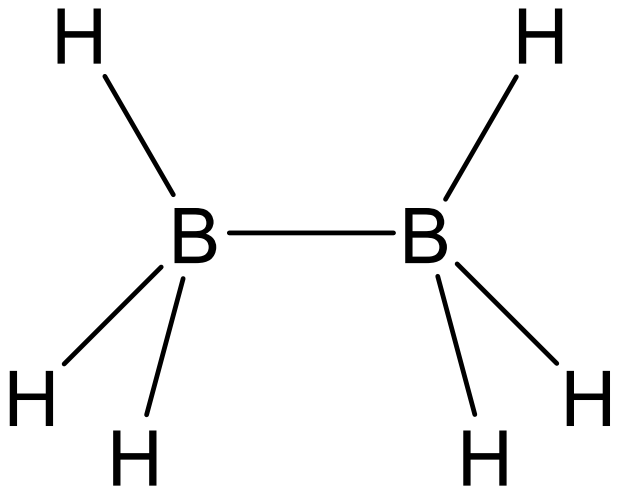

Prijedlog H. I. Schlesingera

# 3. Struktura i priroda veze u boranima i karboranima

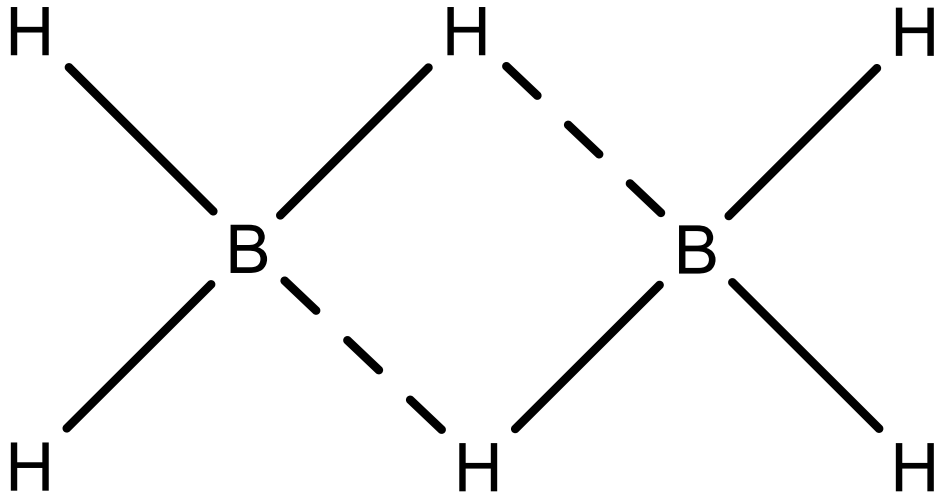
## A Reinvestigation of the Structures of Diborane and Ethane by Electron Diffraction[1,2]

BY KENNETH HEDBERG AND VERNER SCHOMAKER

The ethane-like model for diborane has been eliminated and the bridge model confirmed in an electron-diffraction reinvestigation of diborane and ethane which has led to the bond angle and bond distance values $\angle H_{bond}-B-H_{bond} = 121.5 \pm 7.5°$, $B-B = 1.770 \pm 0.013$ Å., $B-H_{bond} = 1.187 \pm 0.030$ Å., and $B-H_{bridge} = 1.334 \pm 0.027$ Å. for diborane, and $\angle C-C-H = 110.5 \pm 3.5°$, $C-H = 1.114 \pm 0.027$ Å., and $C-C = 1.536 \pm 0.016$ Å. for ethane. A reasonable combination of the values for ethane with the spectroscopic moments of inertia gives $\angle C-C-H = 110.4°$, $C-H = 1.110$ Å., and $C-C = 1.535$ Å., in excellent agreement with the purely electron-diffraction results and considerably more precise.




Prijedlog L. Paulinga



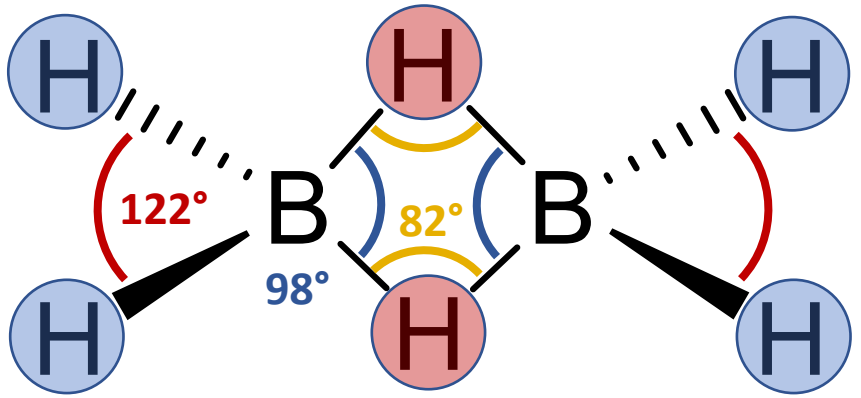

Prijedlog H. I. Schlesingera

# 3. Struktura i priroda veze u boranima i karboranima

- Iako je udaljenost B–B kraća od sume van der Waalsovih radijusa (1,74 Å), nije potvrđeno postojanje veze B–B, već su dva borova atoma premoštena vodikom s dva elektrona

$d(\mathrm{B}\cdots\mathrm{B}) = 1{,}74$ Å

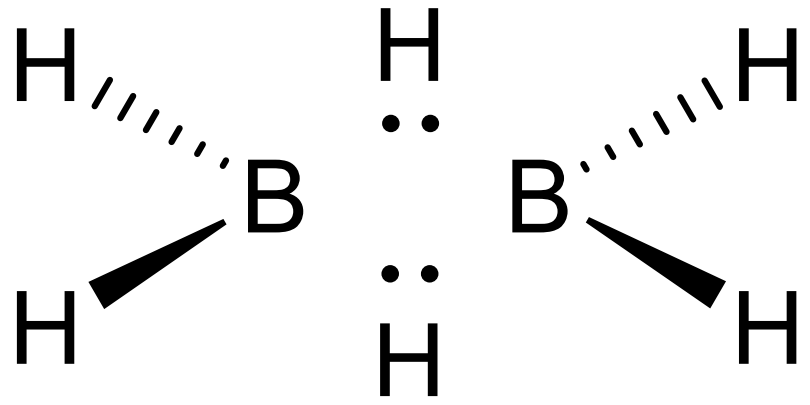
| |
|---|
| $d(\mathrm{B–H_t}) = 1{,}16–1{,}17$ Å |
| $d(\mathrm{B–H_b}) = 1{,}32–1{,}33$ Å |




*Z. Anorg. Allg. Chem.* **2004**, *630*, 1313–1316.

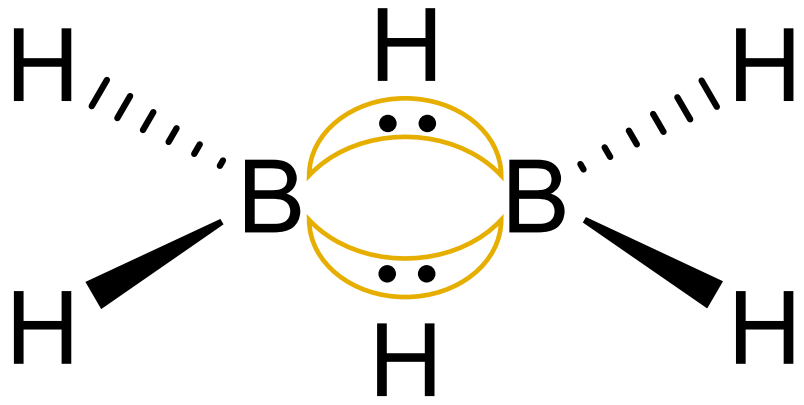
# 3. Struktura i priroda veze u boranima i karboranima

- Terminalne B–H veze mogu se opisati klasičnim kovalentnim vezama – 2c-2e



# 3. Struktura i priroda veze u boranima i karboranima

- Terminalne B–H veze mogu se opisati klasičnim kovalentnim vezama – 2c-2e
- Premošćujuće veze B–H–B sadrže dva elektrona koji su delokalizirani između tri centra – 3c-2e veze
- Koncept policentrične veze primjenjiv je i na drugim spojevima



# Kristalna struktura $B_6H_{10}$

„The preparation of $B_6H_{10}$ and the determination of the boron arrangement from 144 observed X-ray diffraction maxima were described in a preliminary communication. **The incompleteness of these early data, due to the termination of our low-temperature experiments by an electrician who accidentally cut off all electrical power in the building, precluded any complete structure determination and made necessary the present extension of that investigation.**”

F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert Jr., i W. N. Lipscomb, *J. Chem. Phys*., **1958**, *28*, 56–61.

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„The accuracy of the present study would doubtless have been improved had the crystal used in our new series of experiments not **melted and then decomposed when an assistant, on his way to refill the liquid-nitrogen Dewar, tripped on a stairway and lay unconscious for about an hour,** thus bringing our photographic program to a premature end."

F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert Jr., i W. N. Lipscomb, *J. Chem. Phys*., **1958**, *28*, 56–61.

William Lipscomb
Nobelova nagrada 1976.

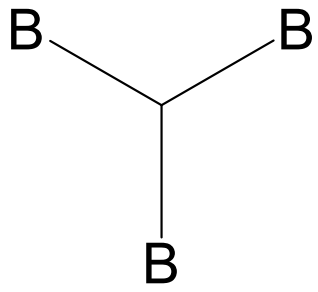
# 3. Struktura i priroda veze u boranima i karboranima

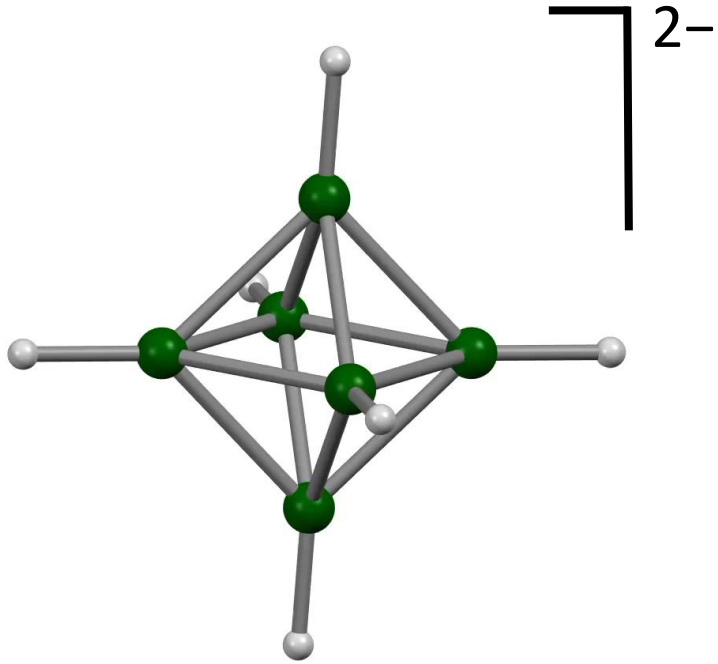
**Strukture ostalih borana (i karborana)**

- *closo* (zatvorena) – anioni opće formule $[B_xH_x]^{2-}$
- *nido* (gnjezdolika) – spojevi opće formule $B_xH_{x+4}$
- *arachno* (paučinasta) – spojevi opće formule $B_xH_{x+6}$

# 3. Struktura i priroda veze u boranima i karboranima

- *closo* (zatvorena) – anioni opće formule $[B_xH_x]^{2-}$
- Pr. $[B_6H_6]^{2-}$ u spoju $[Li(NH_3)_4]_2[B_6H_6]\cdot 2NH_3$
- Dodatne BBB 3c-2e veze između atoma bora



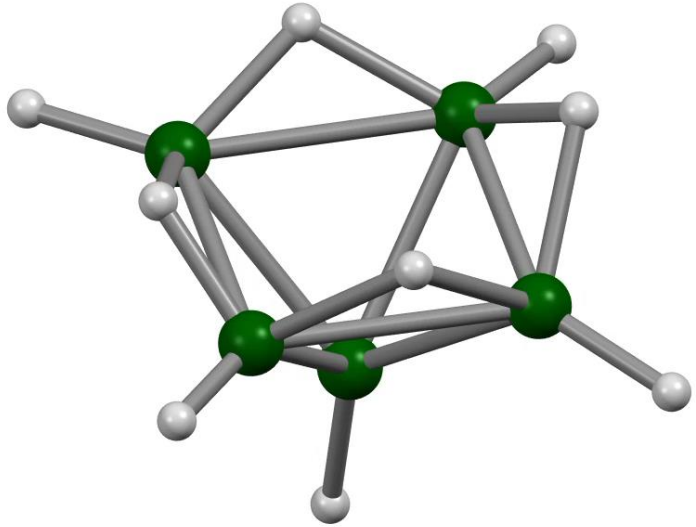

| | Udaljenosti atoma / Å |
|---|---|
| 3c-2e B–B–B | 1,72–1,73 |
| 2c-2e B–H | 1,09–1,10 |

# 3. Struktura i priroda veze u boranima i karboranima

- *nido* (gnjezdolika) – spojevi opće formule $B_xH_{x+4}$

Pr. $B_5H_9$

| | **Udaljenosti atoma / Å** |
|---|---|
| 2c-2e B–B | 1,66 |
| 3c-2e B–B–B | 1,66 i 1,77 |
| 2c-2e B–H | 1,20–1,21 |
| 3c-2e B–H–B | 1,35 |

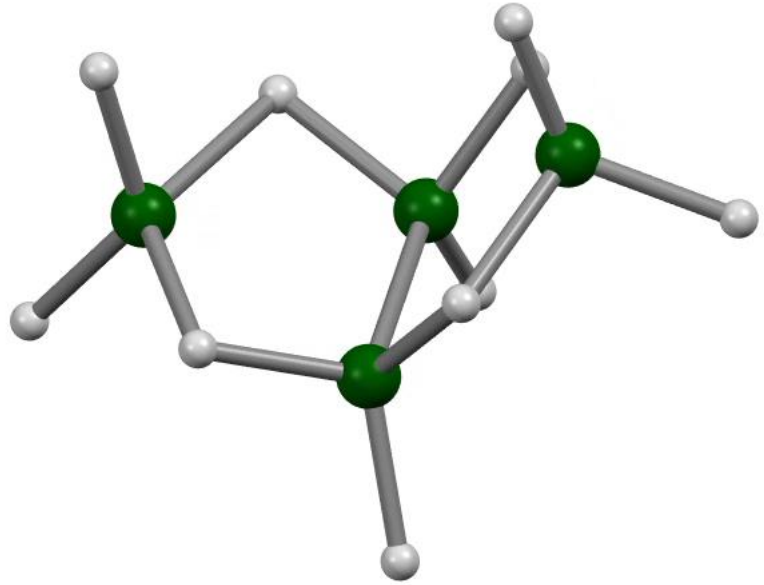


# 3. Struktura i priroda veze u boranima i karboranima

- *arachno* (paučinasta) – spojevi opće formule $B_xH_{x+6}$

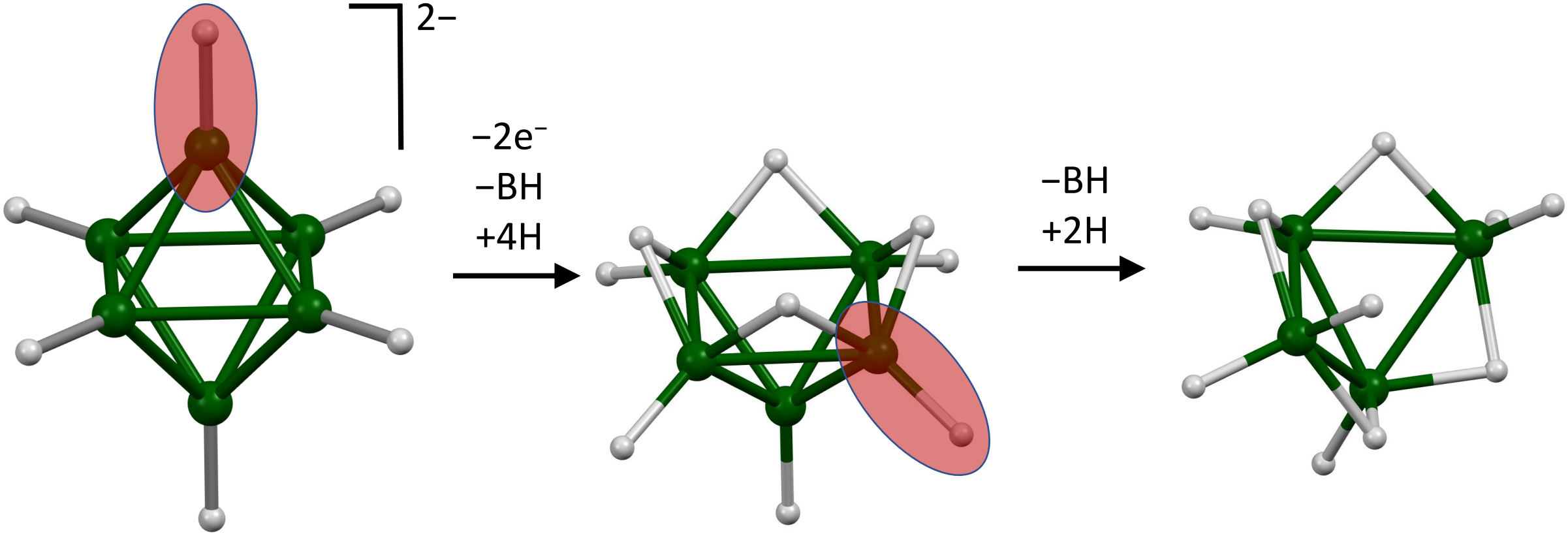
Pr. $B_4H_{10}$

| | **Udaljenosti atoma / Å** |
|---|---|
| 2c-2e B–B | 1,73 |
| 2c-2e B–H | 1,18 |
| 3c-2e B–H–B | 1,29–1,35 (B–$H_b$)<br>1,85–1,86 (B–B) |



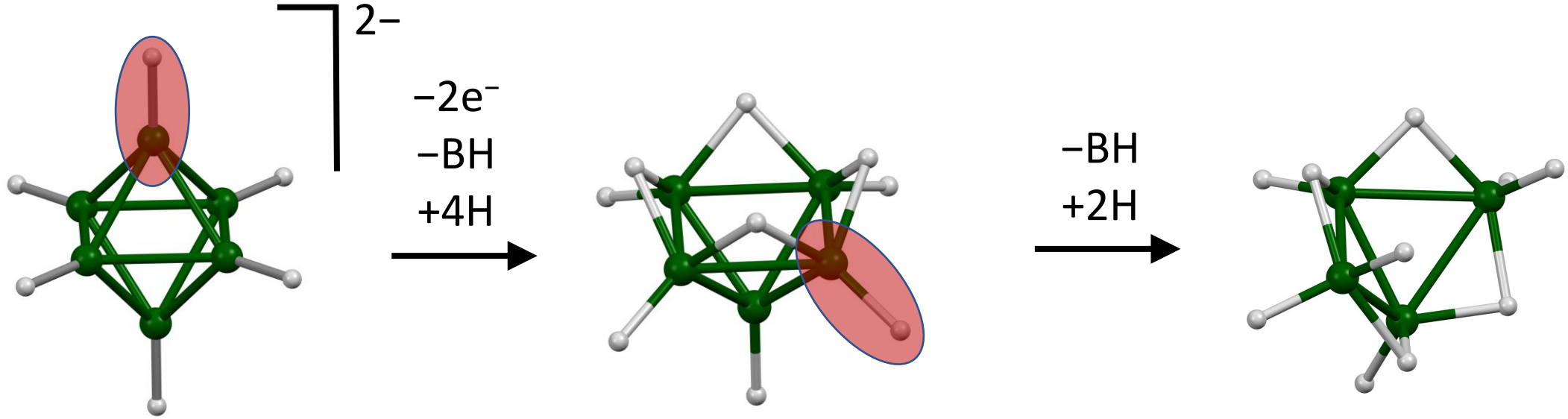
# 3. Struktura i priroda veze u boranima i karboranima

- Kako su strukturni tipovi međusobno povezani?




*closo*-$[B_6H_6]^{2-}$ *nido*-$B_5H_9$ *arachno*-$B_4H_{10}$

# 3. Struktura i priroda veze u boranima i karboranima




*closo*-$[B_6H_6]^{2-}$ *nido*-$B_5H_9$ *arachno*-$B_4H_{10}$

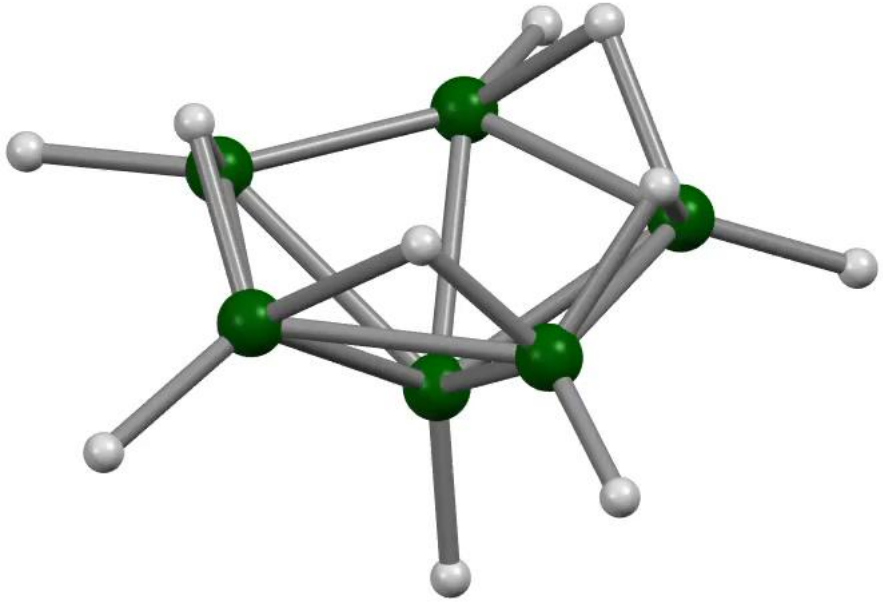
| Tip strukture | Broj vrhova deltaedra | Broj parova elektrona (u boranima) | Opća formula borana | Opća formula karborana |
|---|---|---|---|---|
| *closo* | $n$ | $n$+1 | $[B_nH_n]^{2-}$ | $C_mB_{n-m}H_n$ |
| *nido* | $n$−1 | $n$+1 | $B_{n-1}H_{n+3}$ | $C_mB_{n-m-1}H_{n+3}$ |
| *arachno* | $n$−2 | $n$+1 | $B_{n-2}H_{n+4}$ | $C_mB_{n-m-2}H_{n+4}$ |

# 3. Struktura i priroda veze u boranima i karboranima

| Tip strukture | Broj vrhova deltaedra | Broj parova elektrona (u boranima) | Opća formula borana | Opća formula karborana |
|---|---|---|---|---|
| *closo* | $n$ | $n$+1 | $[B_nH_n]^{2-}$ | $C_mB_{n-m}H_n$ |
| *nido* | $n$−1 | $n$+1 | $B_{n-1}H_{n+3}$ | $C_mB_{n-m-1}H_{n+3}$ |
| *arachno* | $n$−2 | $n$+1 | $B_{n-2}H_{n+4}$ | $C_mB_{n-m-2}H_{n+4}$ |

- Odredite tip strukture i osnovni deltaedar za $B_6H_{10}$.

# 3. Struktura i priroda veze u boranima i karboranima

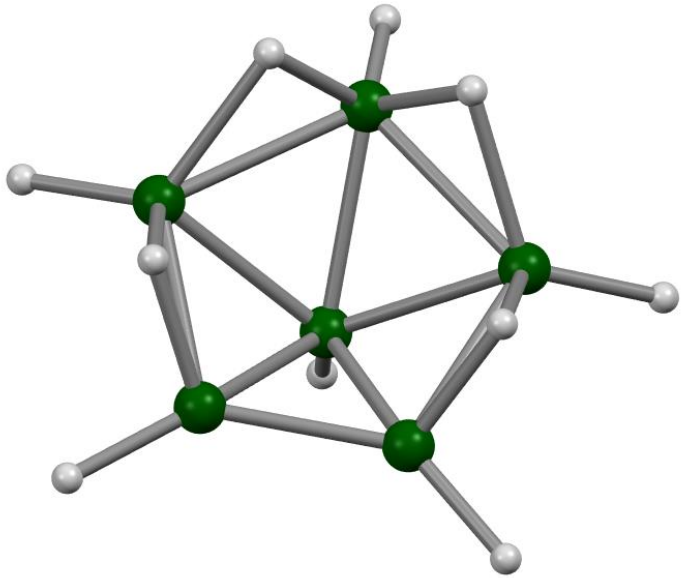


*nido*-heksaboran(10)

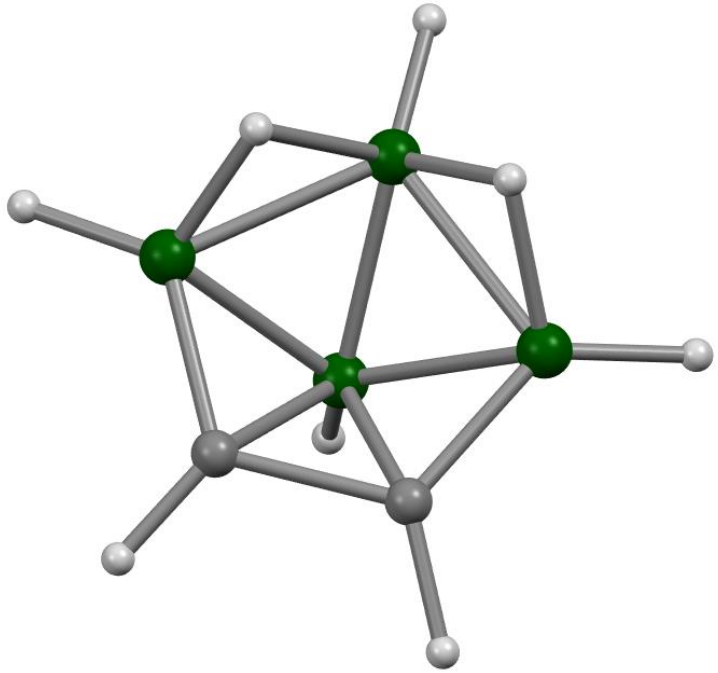
- Odredite tip strukture i osnovni deltaedar za $B_6H_{10}$.

# 3. Struktura i priroda veze u boranima i karboranima

- Karborani imaju strukturne tipove ekvivalentne boranima



*nido*-$B_6H_{10}$



*nido*-$C_2B_4H_8$

# 4. Kemijska svojstva borana i karborana

**Diboran**

$$3Na[BH_4](sln) + 4Et_2O \cdot BF_3(sln) \rightarrow 2B_2H_6(g) + 3Na[BF_4](sln) + 4Et_2O(l)$$

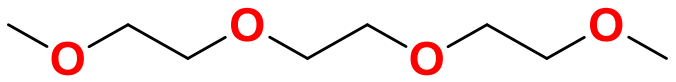
(uz diglim, 298 K; Et = $C_2H_5$)

$$3Na[BH_4](sln) + 4\,triglim \cdot BF_3(sln) \rightarrow 2B_2H_6(g) + 3Na[BF_4](sln) + 4triglim(l)$$

- Industrijski dobiva se reakcijom:

$$2BF_3(s) + 6NaH(s) \rightarrow B_2H_6(g) + 6NaF(s)$$

(pri 450 K)




Trietilenglikol dimetileter – triglim

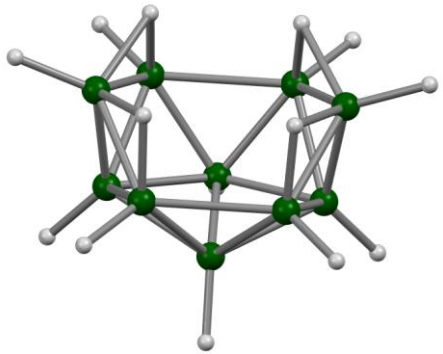
- Viši borani dobivaju se termičkim raspadom diborana, ovisno o uvjetima sinteze.

# 4. Kemijska svojstva borana i karborana

**Karborani**

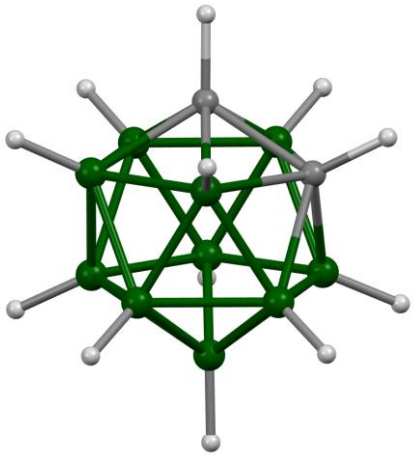
$$B_{10}H_{14} + 2R_2S \rightarrow B_{10}H_{12}(R_2S)_2 + H_2$$

$$B_{10}H_{12}(R_2S)_2 + RC \equiv CR' \rightarrow B_{10}H_{10}C_2RR' + 2R_2S + H_2$$



*nido*-$B_{10}H_{14}$

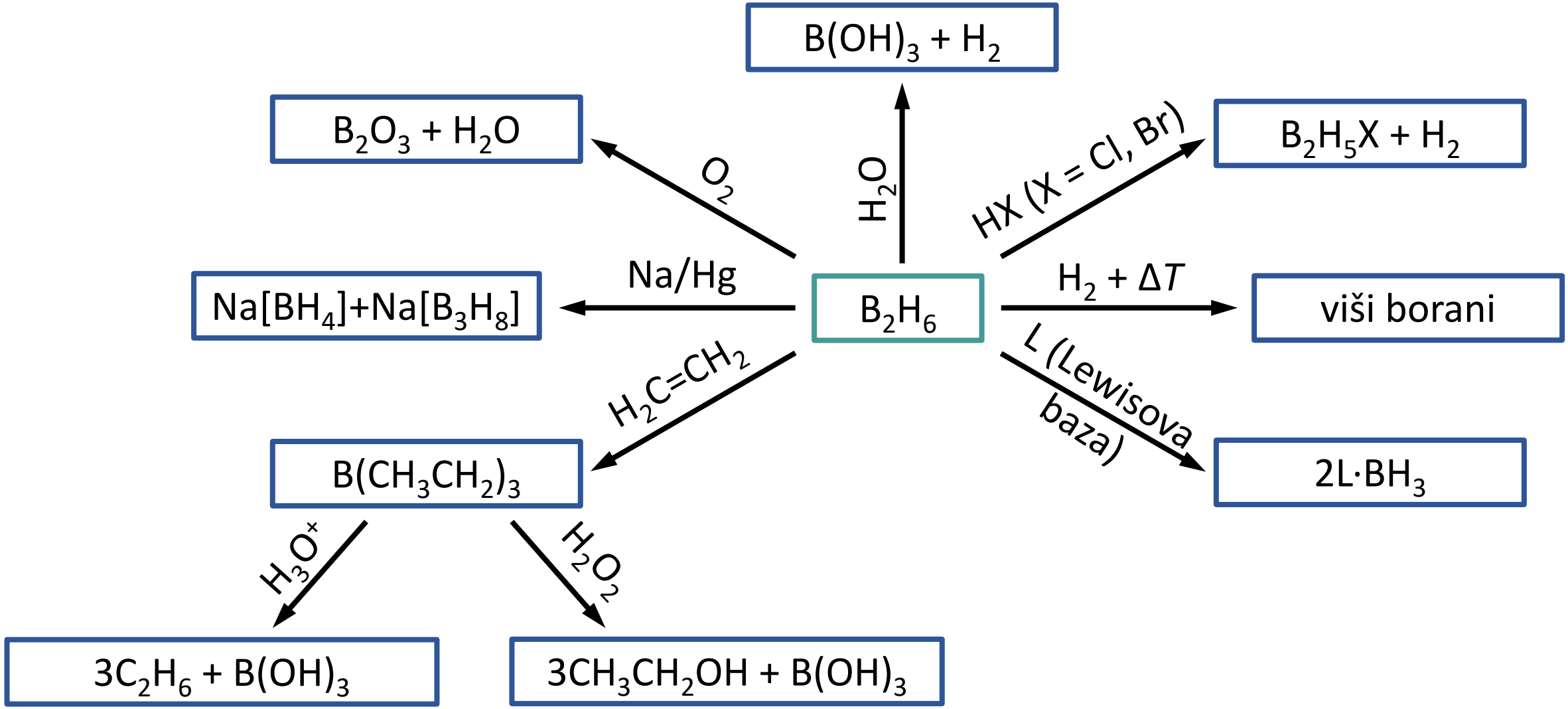
$HC \equiv CH$



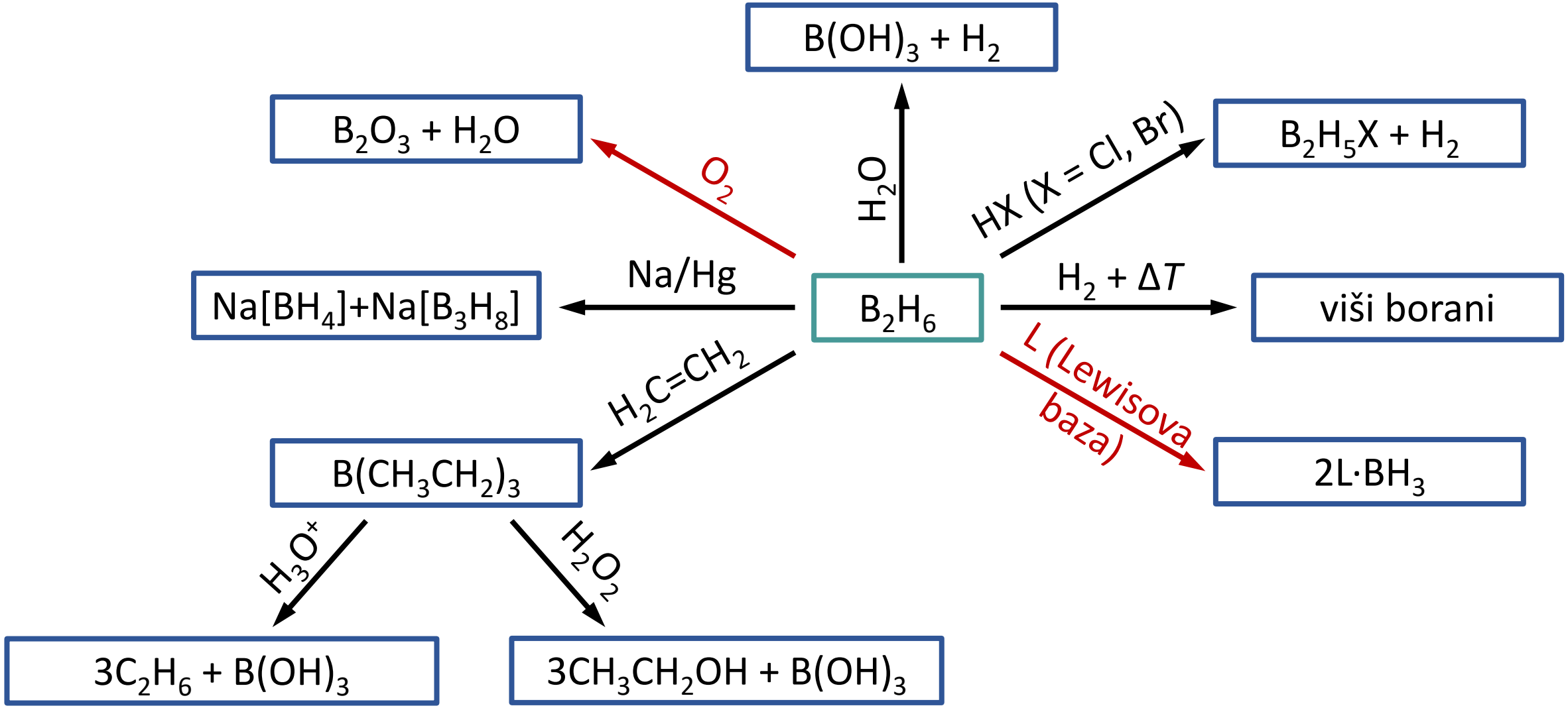
*closo*-$C_2B_{10}H_{12}$

- Moguća je funkcionalizacija klastera

# 4. Kemijska svojstva borana i karborana

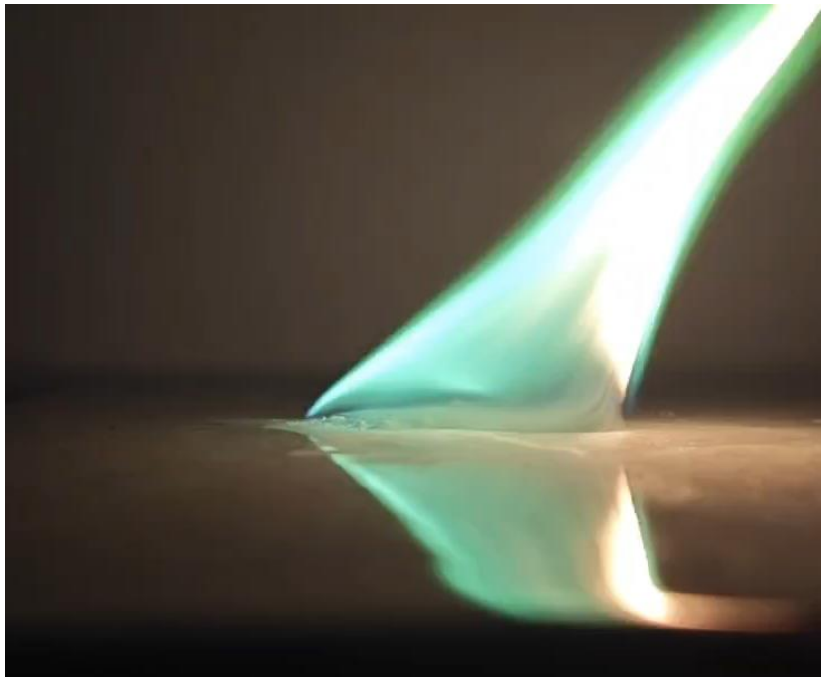


# 4. Kemijska svojstva borana i karborana

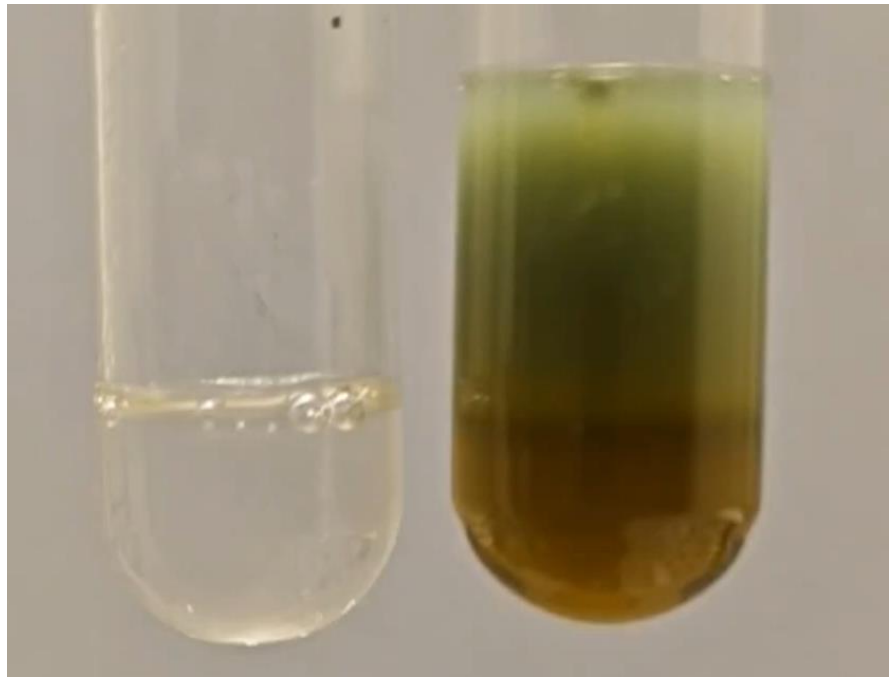


# 4. Kemijska svojstva borana i karborana

Herbert C. Brown
Nobelova nagrada 1979.



$$(CH_3)_3N \cdot BH_3(s) + O_2(g)$$



$$(CH_3)_3N \cdot BH_3(s) + (CH_3)_2CO(l) + H_2SO_4(aq)$$

# 5. Primjena borana i karborana

- 1940.-ih do 1960.-ih istraživani kao potencijalno raketno gorivo
- Diboran ima vrlo veliku molarnu entalpiju sagorijevanja i među najvećim energijama sagorijevanja po masi tvari

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g) \;\; ; \Delta_r H° = -2138 \text{ kJ mol}^{-1}$$

- Danas potencijalni materijali za skladištenje vodika u sklopu zelene energetske tranzicije

$$NH_3BH_3(s) + NaH(s) \rightarrow NaNH_2BH_3(s) + H_2(g)$$

$$NaNH_2BH_3(s) \rightarrow NaNBH(s) + 2H_2(g)$$

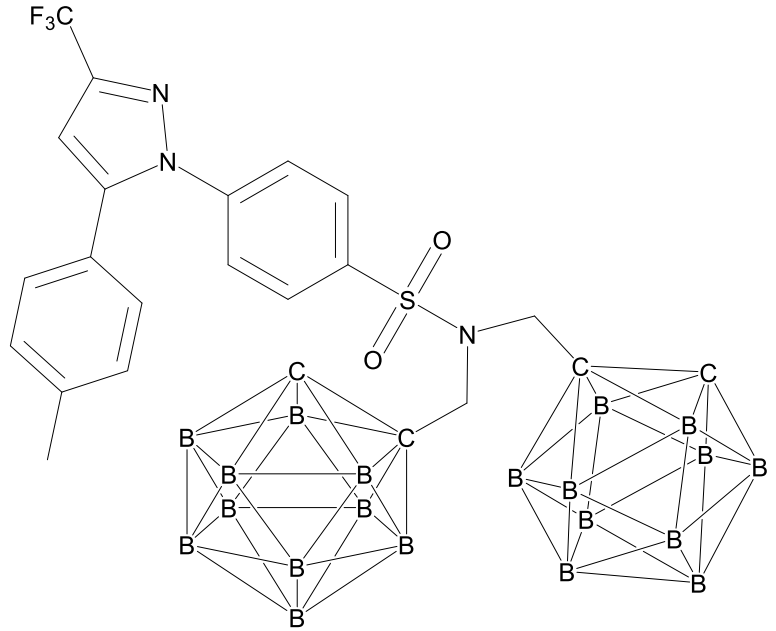
# 5. Primjena borana i karborana

- $^{10}B$ – efikasno apsorbira neutrone niske energije

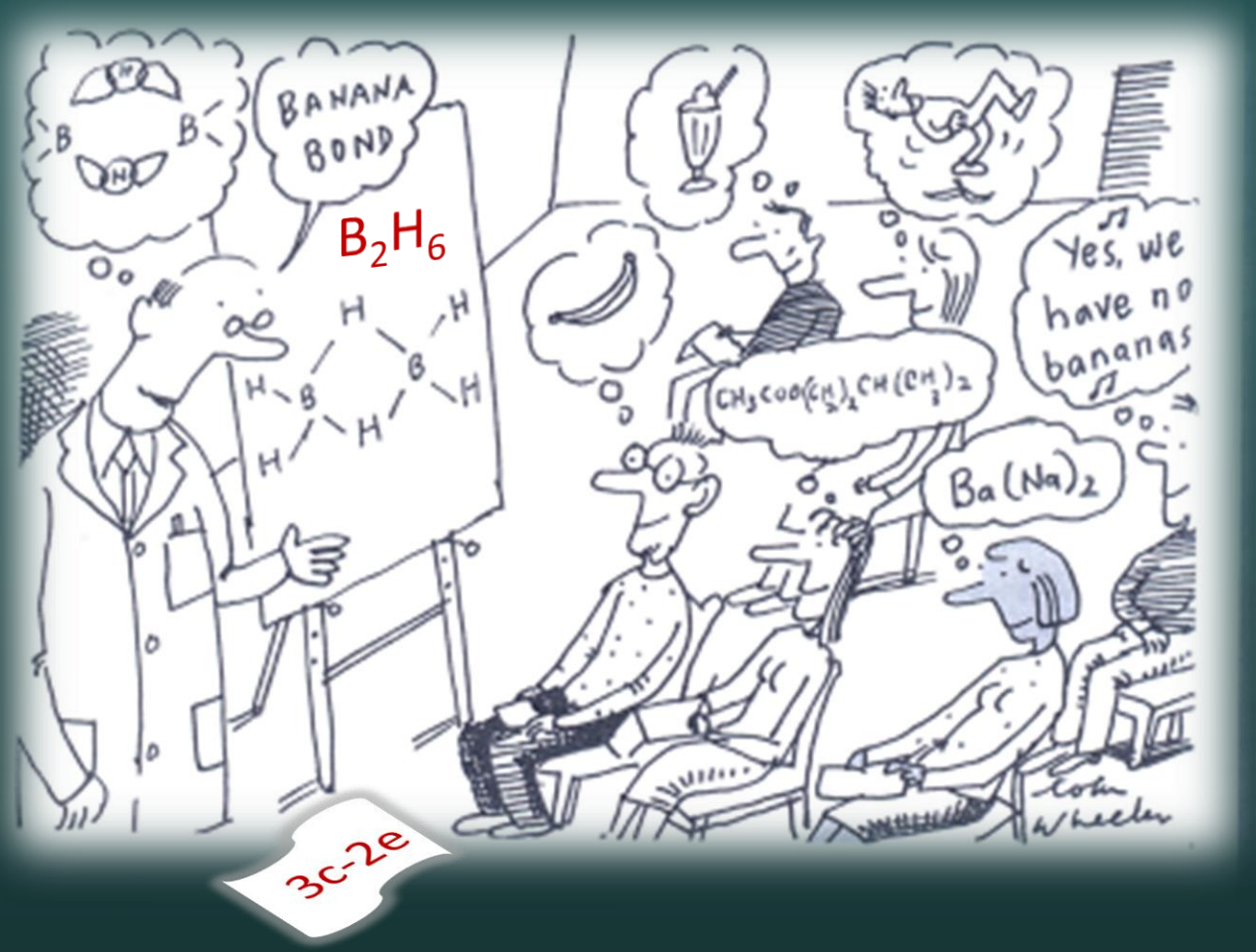
| | *x* / % |
|---|---|
| **$^{10}B$** | 19,6 |
| **$^{11}B$** | 80,4 |

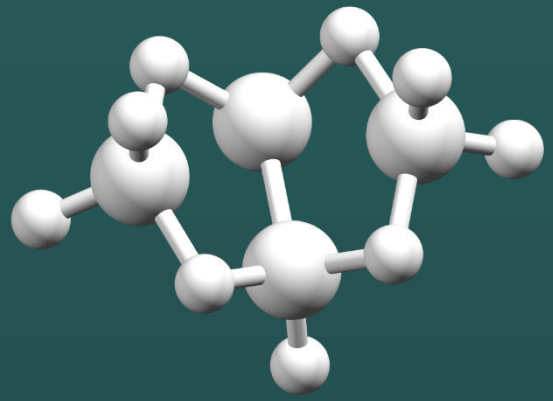
$$^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \rightarrow [{}^{11}_{5}\mathrm{B}]^{*} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{7}_{3}\mathrm{Li} + \gamma$$

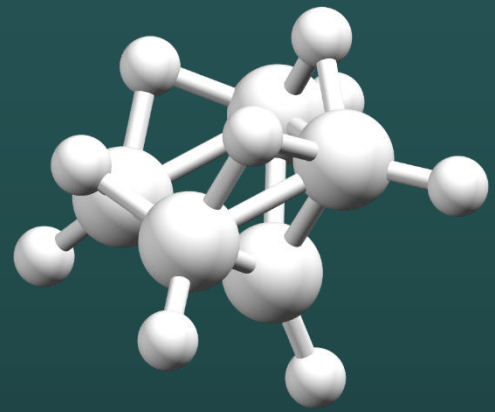
- Antitumorska terapija temeljena na apsorpciji neutrona i nuklearnom raspadu – engl. *boron neutron capture therapy* (BNCT)
- Selektivno uništenje tumorskih stanica
- Odobrena u Japanu 2020.

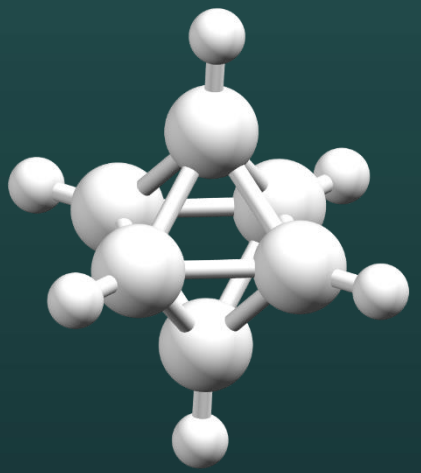



*ChemistrySelect* **2020**, 5, 14652–14660.


BANANA BOND
$B_2H_6$
$CH_3COO(CH_2)_2CH(CH_3)_2$
Yes, we have no bananas
$Ba(Na)_2$
3c-2e







# 6. Literatura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- D. Grdenić, *Molekule i kristali*, 5. izdanje, Školska knjiga, Zagreb, 2005.
- https://www.nobelprize.org/prizes/chemistry/1976/lipscomb/lecture/ (pristupljeno 7. siječnja 2025.)
- O povijesti: P. Laszlo, *A diborane story*, *Angew. Chem. Int. Ed*. 2000, **39**, 2071–2072.
- Tko želi znati više:
  - Wadeova pravila za predviđanje strukture borana, karborana i ekvivalentnih struktura drugih spojeva na temelju formule spoja