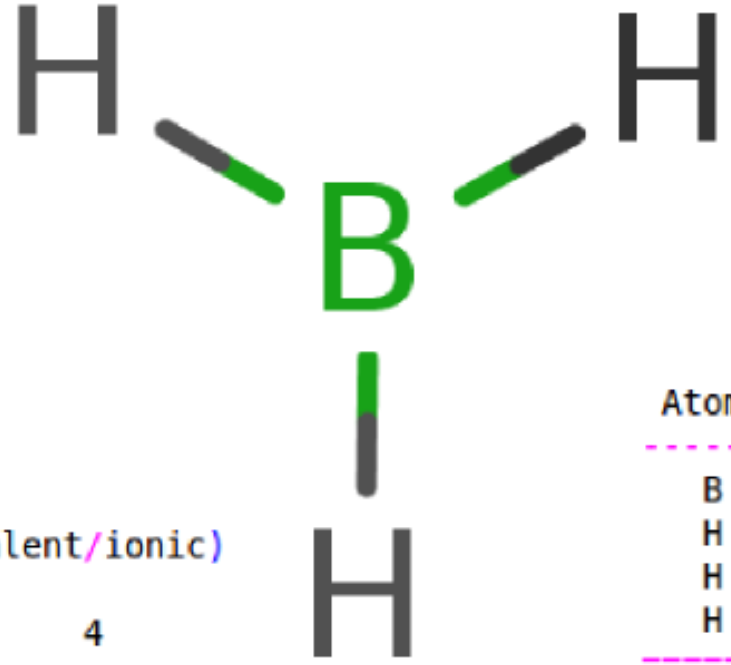
Electron-Deficient Molecules and the world of the Boranes

Properties of Borane, the BH_3 Molecule

Natural Bond Orbital (NBO) analysis following MO calculation

Natural Atomic Valencies:

	Atom	Valency	Co-Valency	Electro-Valency
1.	B	2.9923	2.6713	0.3210
2.	H	0.9974	0.8904	0.1070
3.	H	0.9974	0.8904	0.1070
4.	H	0.9974	0.8904	0.1070



Atom	No	Natural Charge
B	1	0.32164
H	2	-0.10721
H	3	-0.10721
H	4	-0.10721
* Total *		0.00000

Natural Bond Order: (total/covalent/ionic)

Atom		1	2	3	4
1. B	t	0.0038	0.9974	0.9974	0.9974
	c	---	0.8904	0.8904	0.8904
	i	---	0.1070	0.1070	0.1070

Wgt=99.62%

Borane Exists as a Dimer: Diborane

- Diborane, B_2H_6, is a colorless gas forming explosive mixtures with air
- Diborane is endothermic with $\Delta H_f^\circ = 36$ kJ/mol
- Despite this thermodynamic stability, diborane is kinetically not so reactive but takes place in many reactions involving loss of H_2
- Industrial synthesis: $8\ BF_3 + 6\ LiH \longrightarrow B_2H_6 + 6\ LiBF_4$
- Convenient laboratory synthesis: $2\ NaBH_4 + I_2 \longrightarrow 2\ NaI + B_2H_6 + H_2$

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Borane Exists as a Dimer: Diborane

- Alfred Stock pioneered the chemistry of the boron hydrides using vacuum-line techniques
- Stock proposed an ethane-like structure for diborane
- S. H. Bauer in 1937 reported electron diffraction measurements interpreted (DOI: 10.1021/ja01285a041) in support of the ethane-like structure
- The ethane-like structure required resonance structures with one-electron bonds

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Borane Exists as a Dimer: Diborane

- 1943 (DOI: 10.1039/JR9430000250) undergraduate student H. C. Longuet-Higgins (Balliol College, Oxford) and R. P. Bell proposed B-H-B bridge bonds instead with a D_{2h} symmetry structure
- In 1941 a U. of Chicago chemistry professor Schlesinger working on the Manhattan project wrote a letter to Linus Pauling suggesting the same structure with B-H-B bridge bonds (A Diborane Story, Pierre Laszlo, ACIE 2000, 39, 2071); Pauling responded unfavorably
- Mulliken weighed in (1947) with an MO analysis favoring the D_{2h} structure because of agreement with electronic absorption spectra
- Price interpreted the IR data in terms of the D_{2h} structure and gave assignments
- Shoolery reported clinching NMR data in 1955

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Structure for the B_2H_6 Molecule

Graphic from Price, 1948, DOI: 10.1063/1.1747028

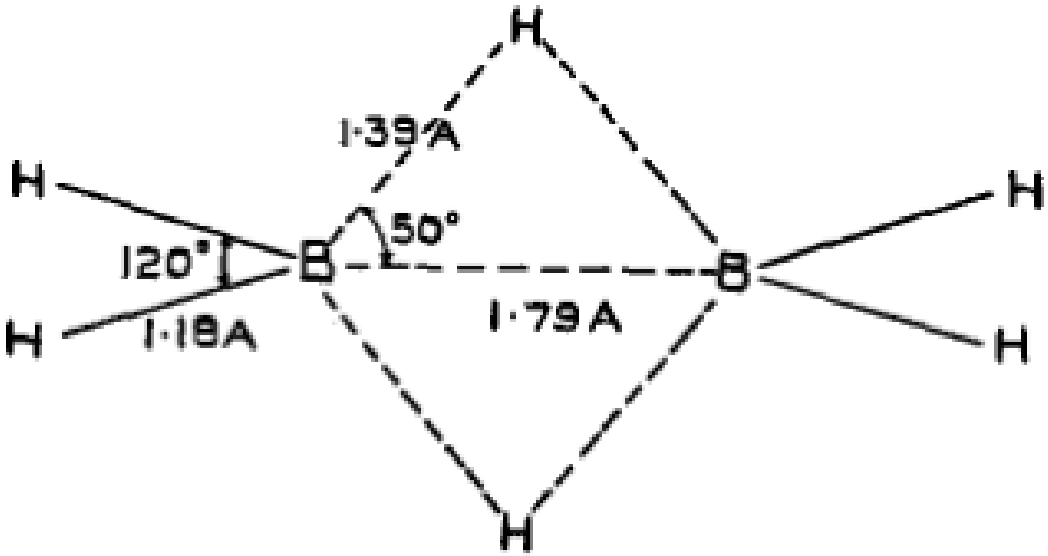

FIG. 3. Structure of diborane molecule according to the interpretation of the electron diffraction results in terms of a bridge model.

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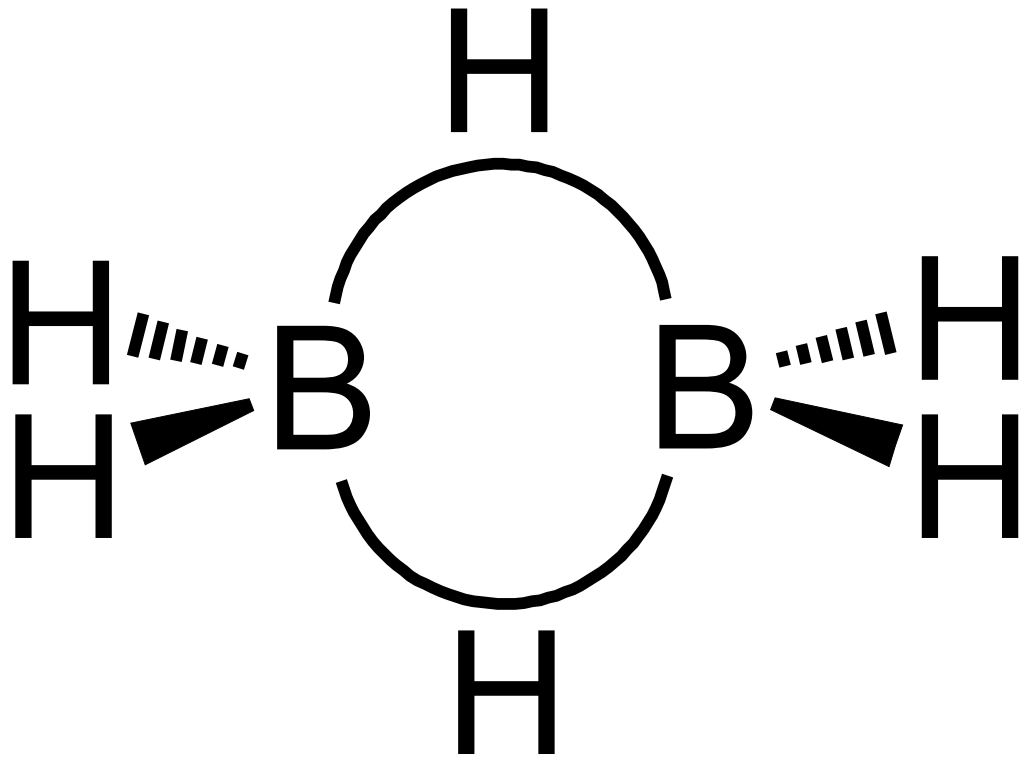
Structure for the B_2H_6 Molecule

A different way of writing the bridge bonds



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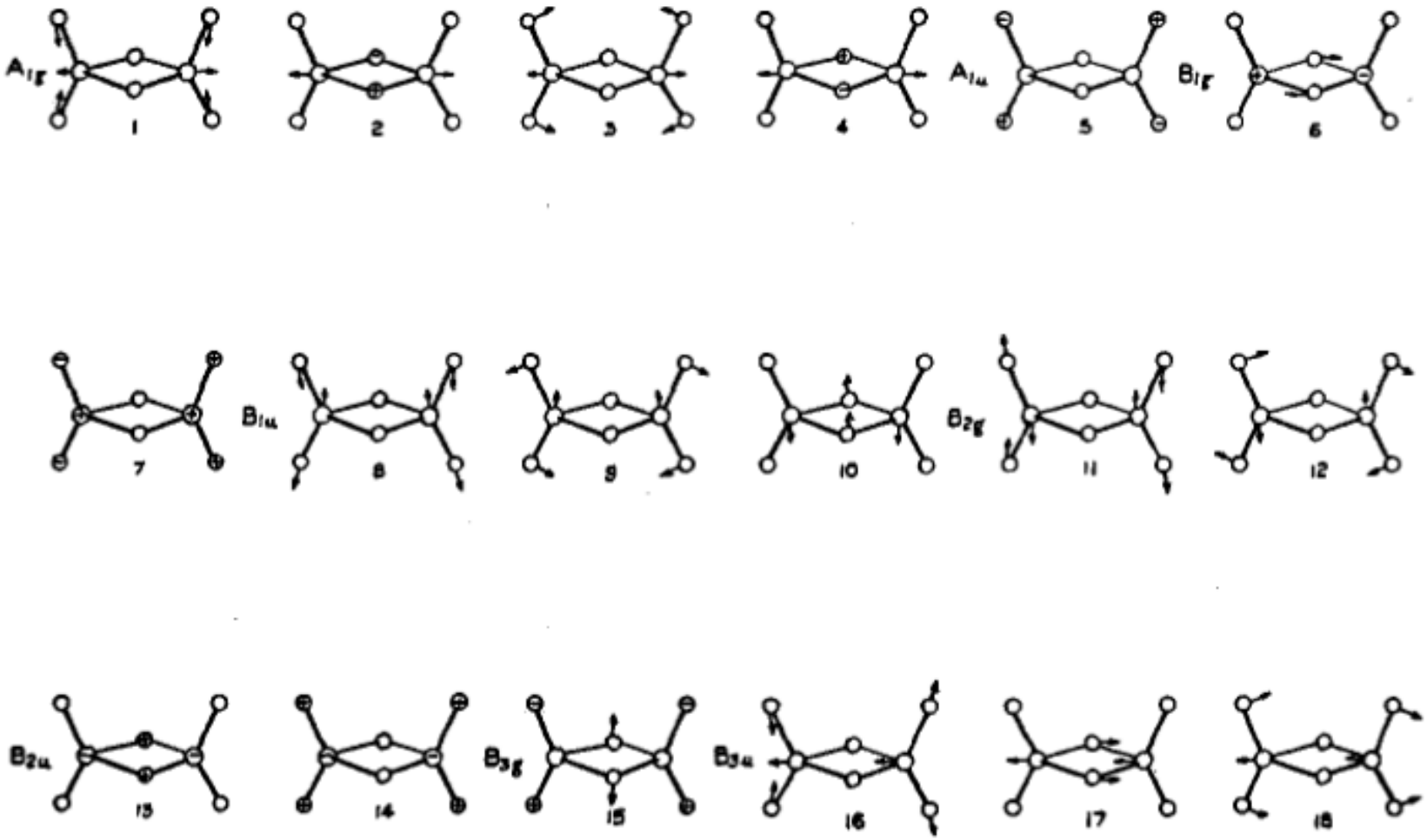
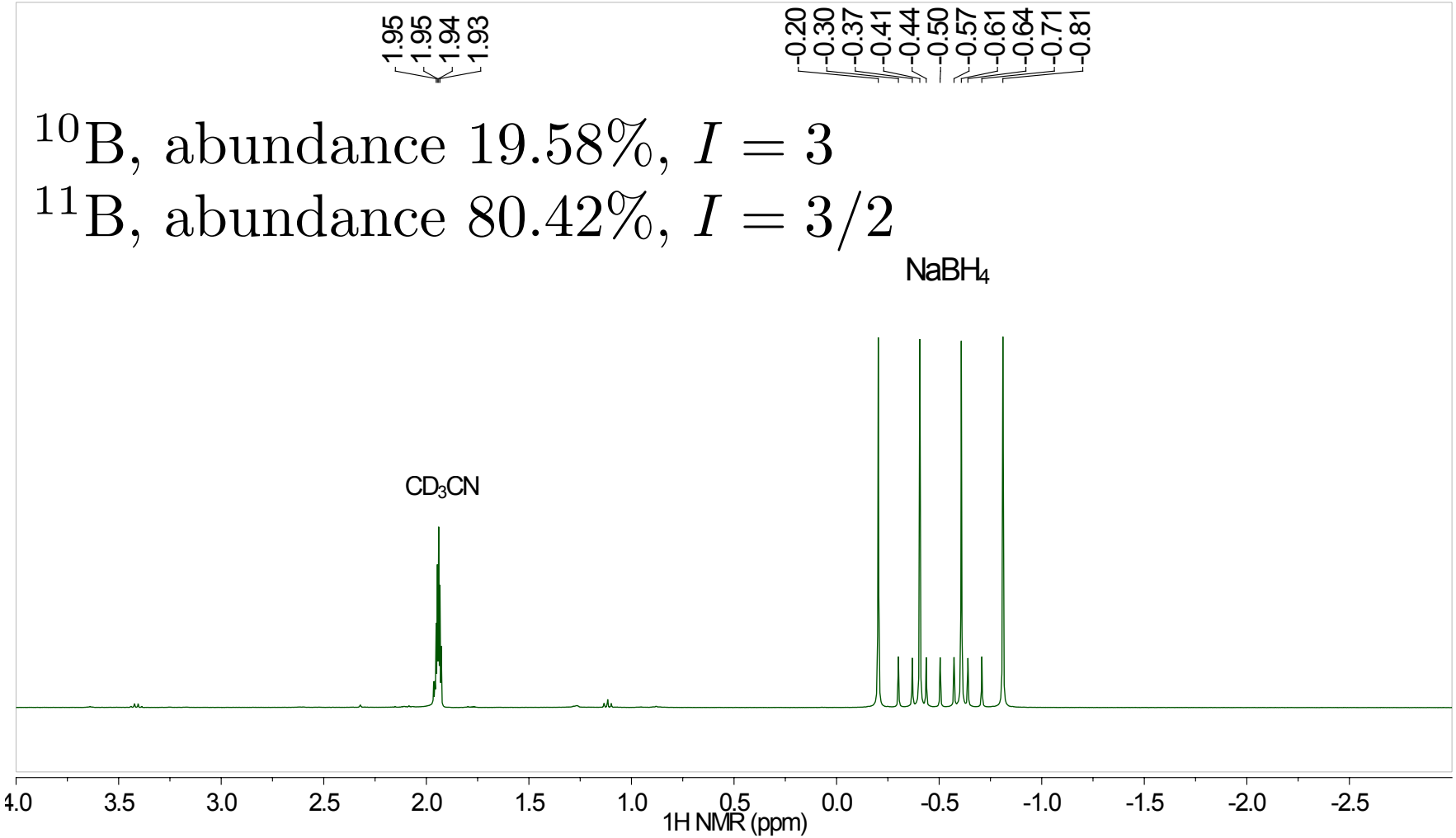


FIG. 4. The character of the normal vibrations of "bridge" diborane.
(After Bell and Longuet-Higgins.[2])

Borohydride Ion $[BH_4]^-$ has T_d Symmetry



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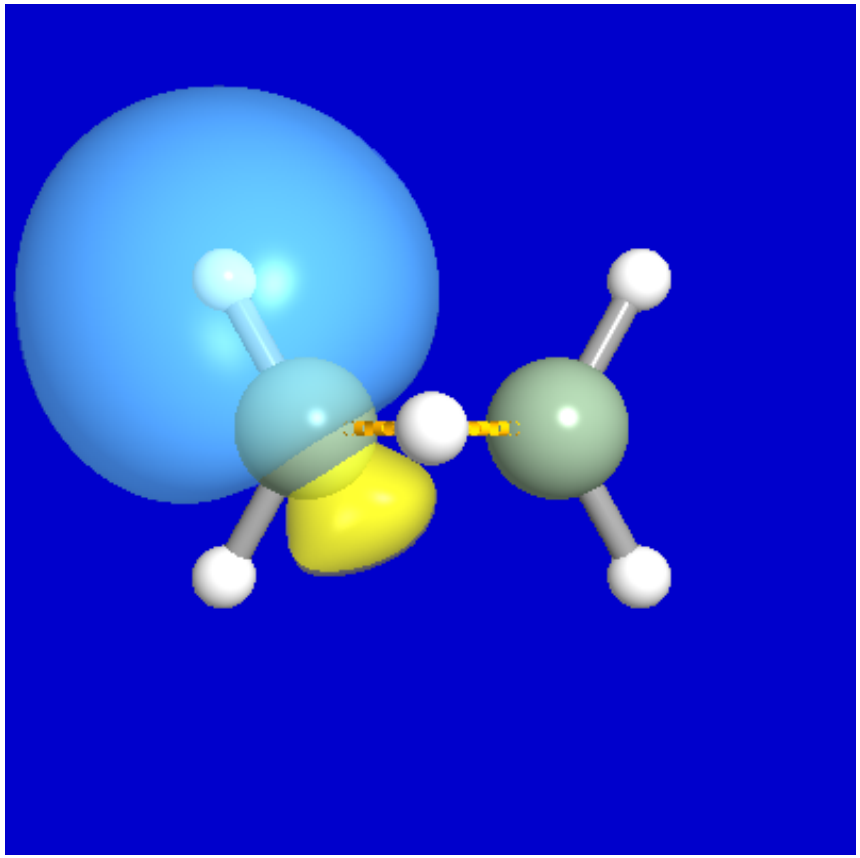
MO Calculations on the B_2H_6 Molecule

Natural Bond Orbital (NBO) analysis following MO calculation



- This is one of the four terminal 2c-2e B-H bonds

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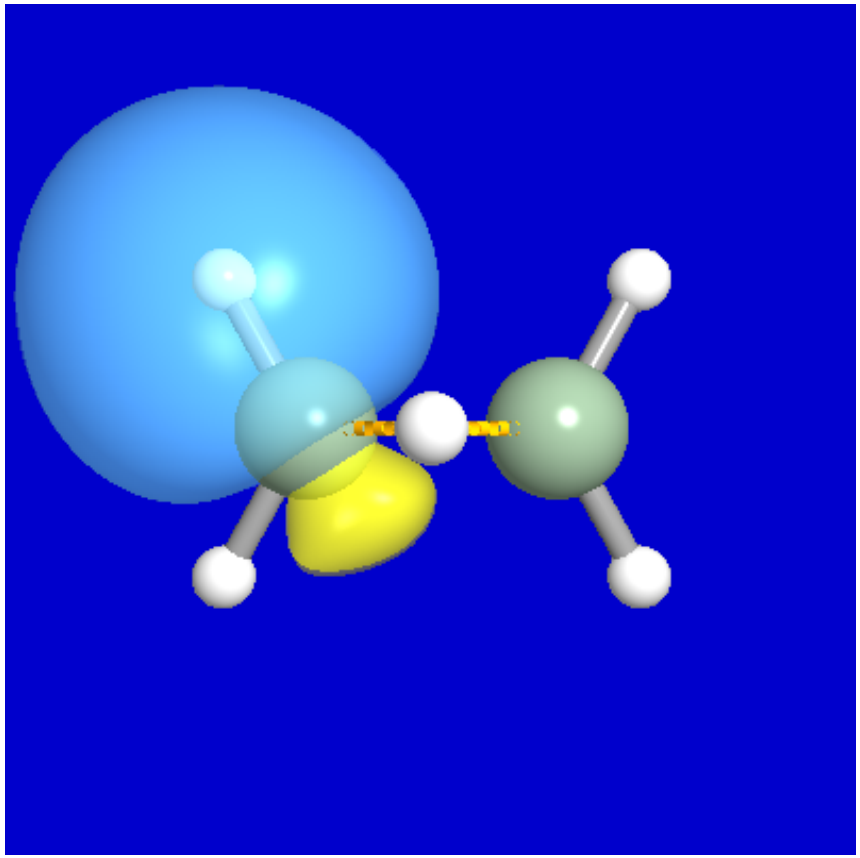

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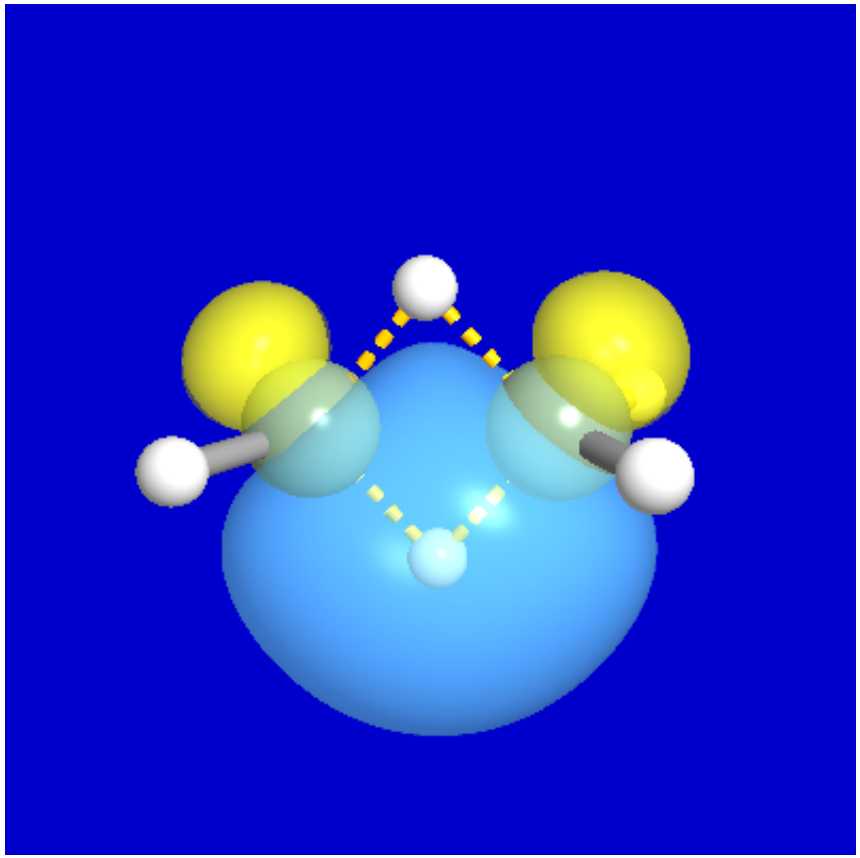

- This is one of the two 3c-2e B-H bridge bonds

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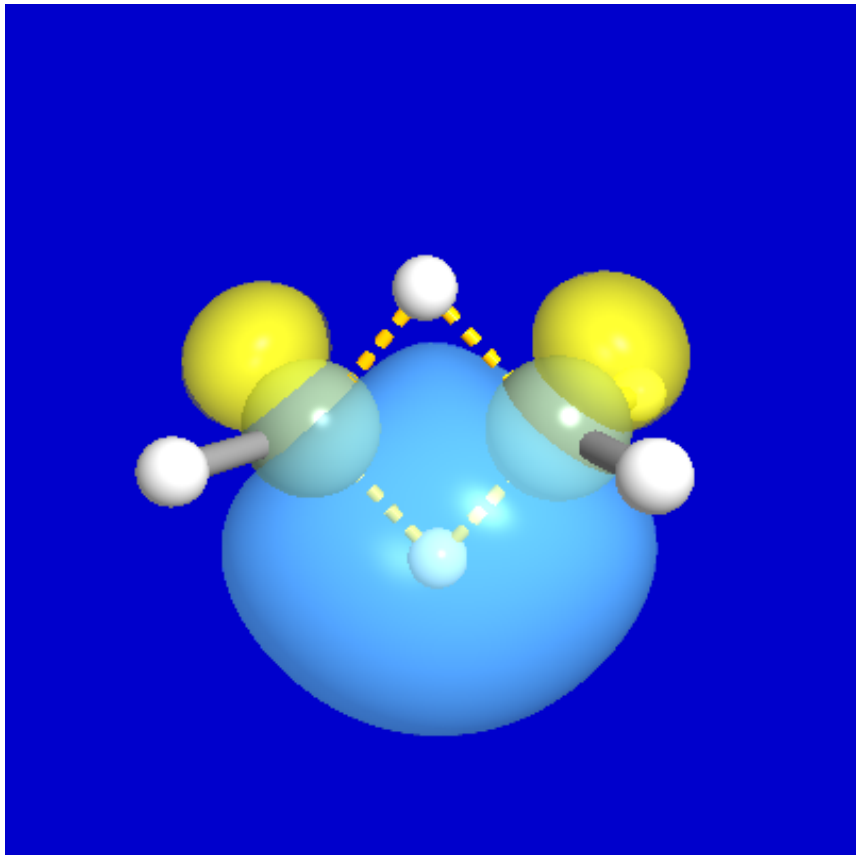

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Resonance Structures for the B_2H_6 Molecule

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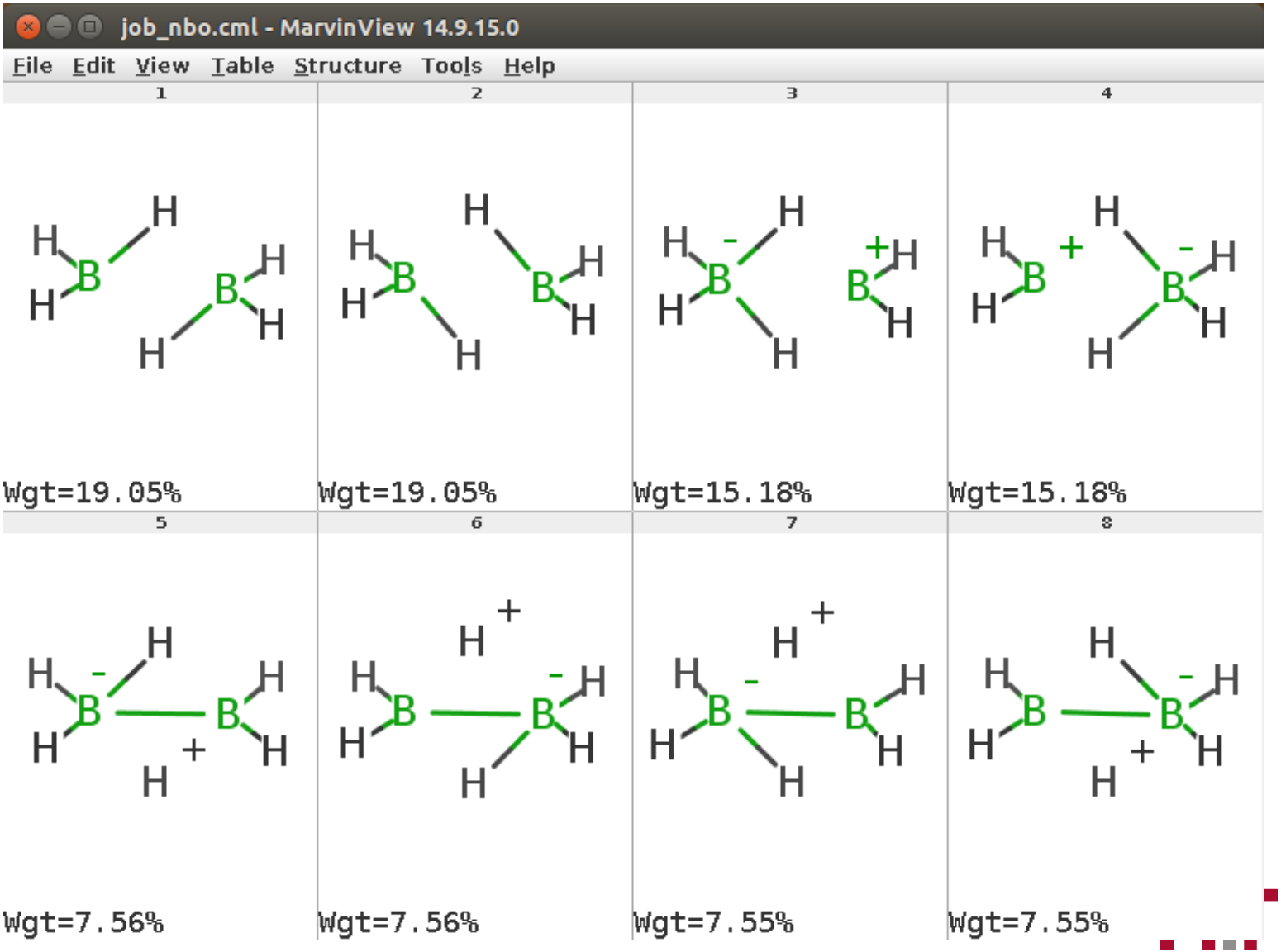
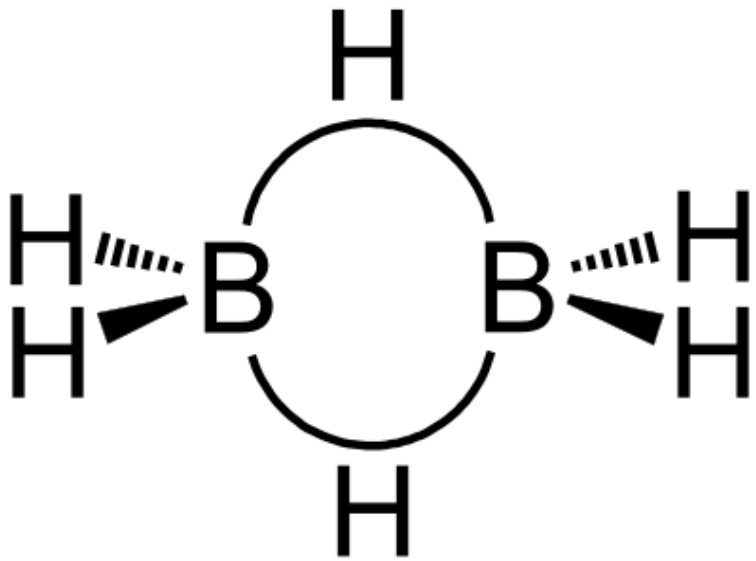


Natural Bond Order: (total/covalent/ionic)

Atom		1	2	3	4	5	6	7	8
1. B	t	0.0002	0.3148	0.0000	0.0000	0.9937	0.9937	0.4244	0.4242
	c	---	0.0329	0.0000	0.0000	0.9836	0.9836	0.2850	0.2849
	i	---	0.2819	0.0000	0.0000	0.0101	0.0101	0.1394	0.1393



Natural Atomic Valencies:

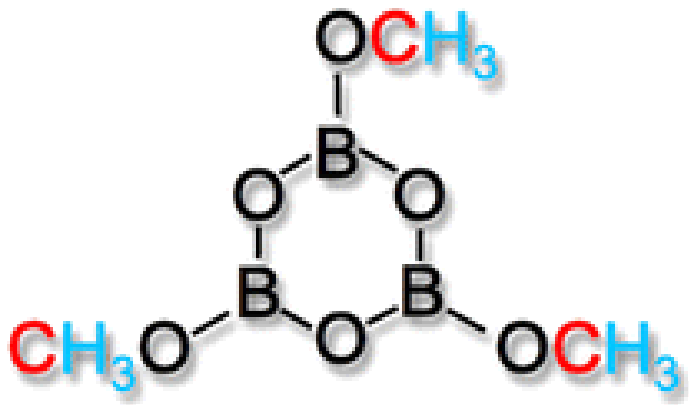
	Atom	Valency	Co-Valency	Electro-Valency
1.	B	3.1508	2.5700	0.5808
2.	B	3.1508	2.5700	0.5808
3.	H	0.9937	0.9836	0.0101
4.	H	0.9937	0.9836	0.0101
5.	H	0.9937	0.9836	0.0101
6.	H	0.9937	0.9836	0.0101
7.	H	0.8486	0.5699	0.2786
8.	H	0.8486	0.5699	0.2786

Reaction of Borane THF Adduct with CO_2

Mizuta et al. Organometallics, 2014, 33, pp 6692–6695 DOI: 10.1021/om5008488

$BH_3 \cdot THF$
(Commercially available)
or
$BH_3 \cdot THF$
+ 0.5 mol% $NaBH_4$

CO_2
1 atm, r.t.
THF



- The reaction between commercially available borane solutions and CO_2 had not been reported!
- The product of this reaction is called trimethoxyboroxine, with CO_2 reduced to the level of methanol

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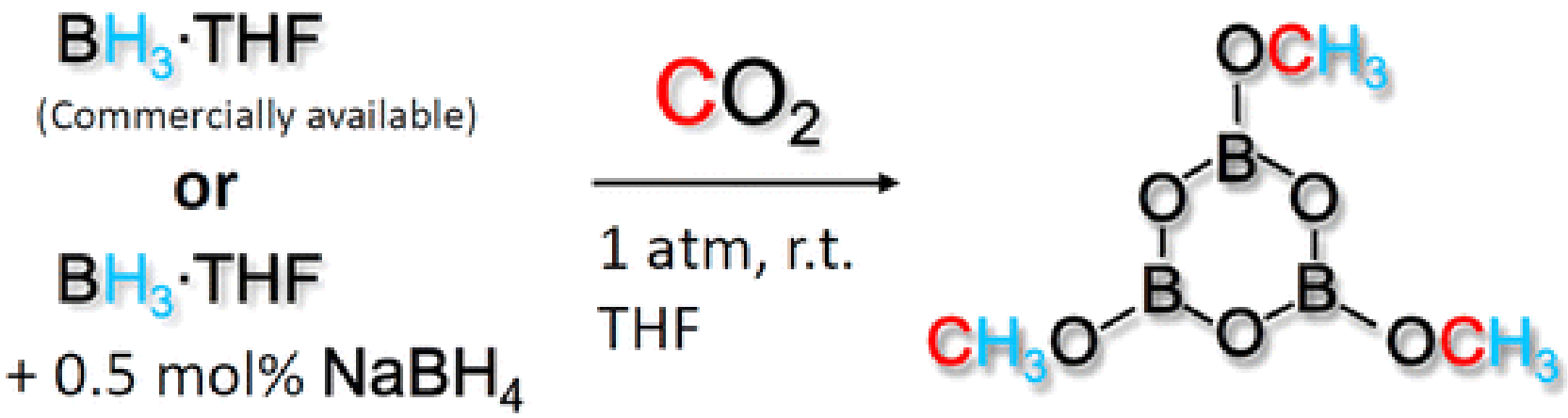

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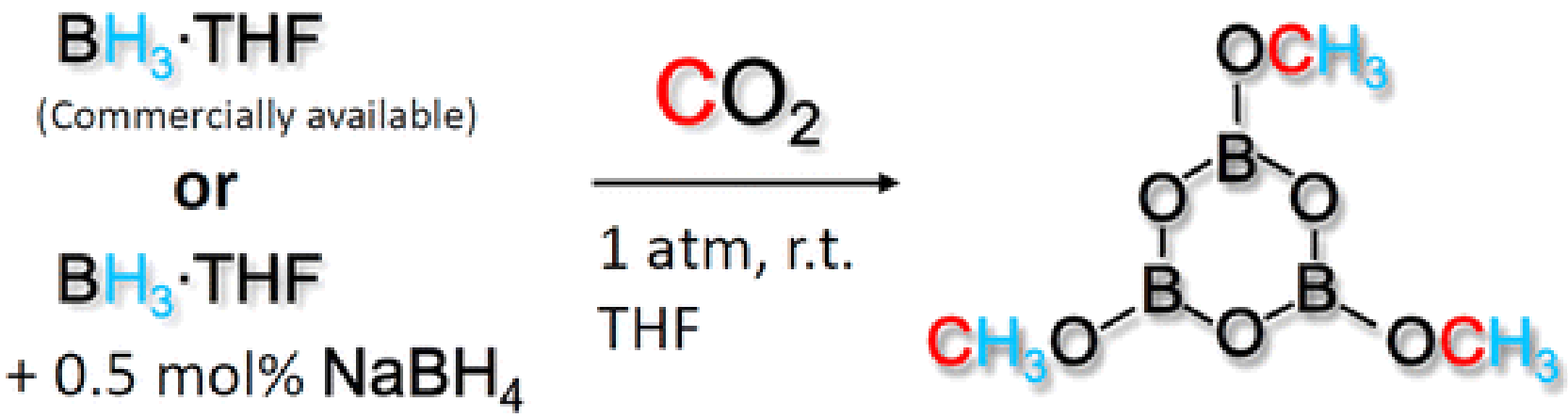

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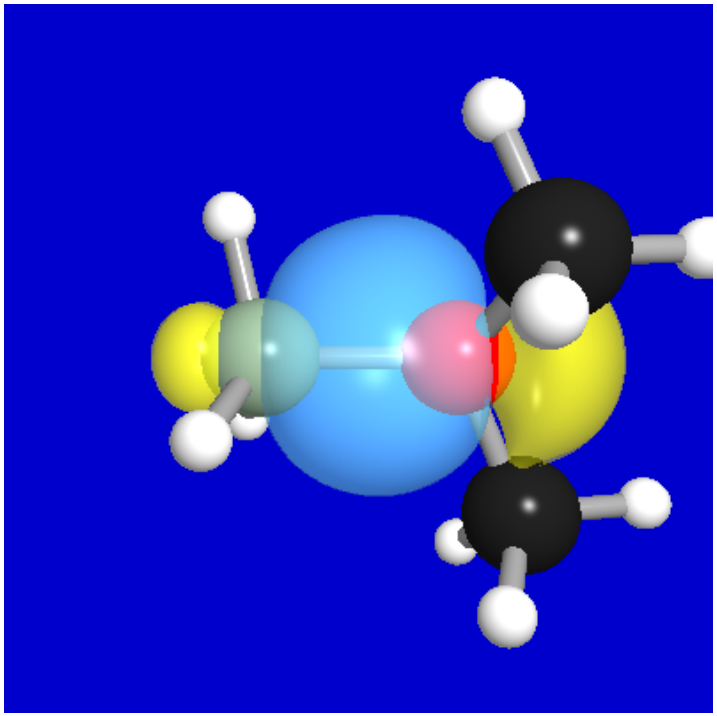
Donor-Acceptor Bonds

Typically written with an arrow or with a line and formal charges



- A donor-acceptor bond can be written this way: $Me_2O{:}\rightarrow BH_3$
- Alternatively it can be written this way: $Me_2O^{+}\text{–}B^{-}H_3$
- A donor-acceptor complex forms with a Lewis base donating an electron pair to a Lewis acid

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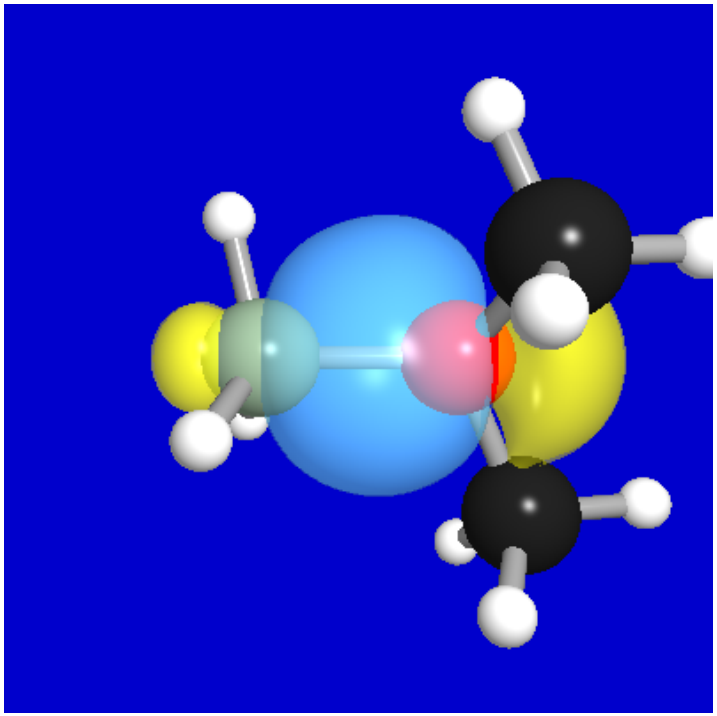

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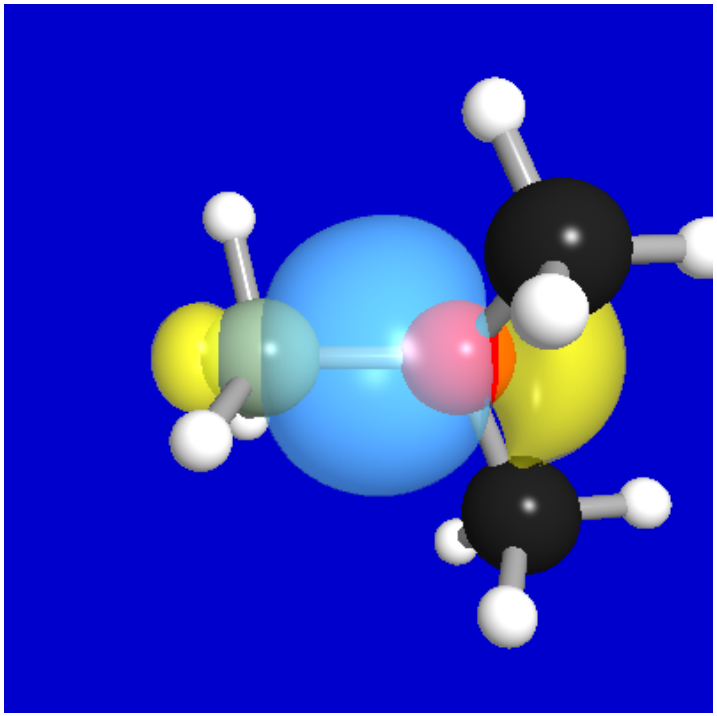

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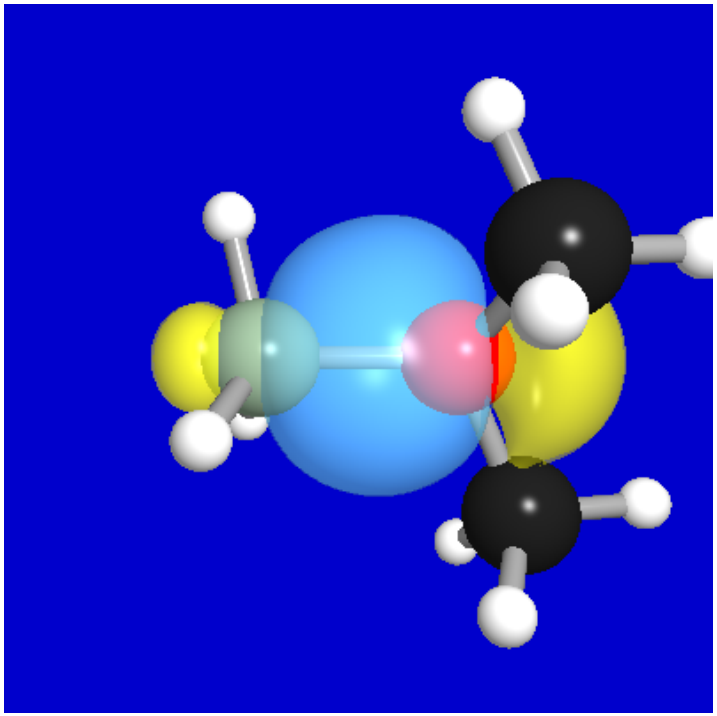

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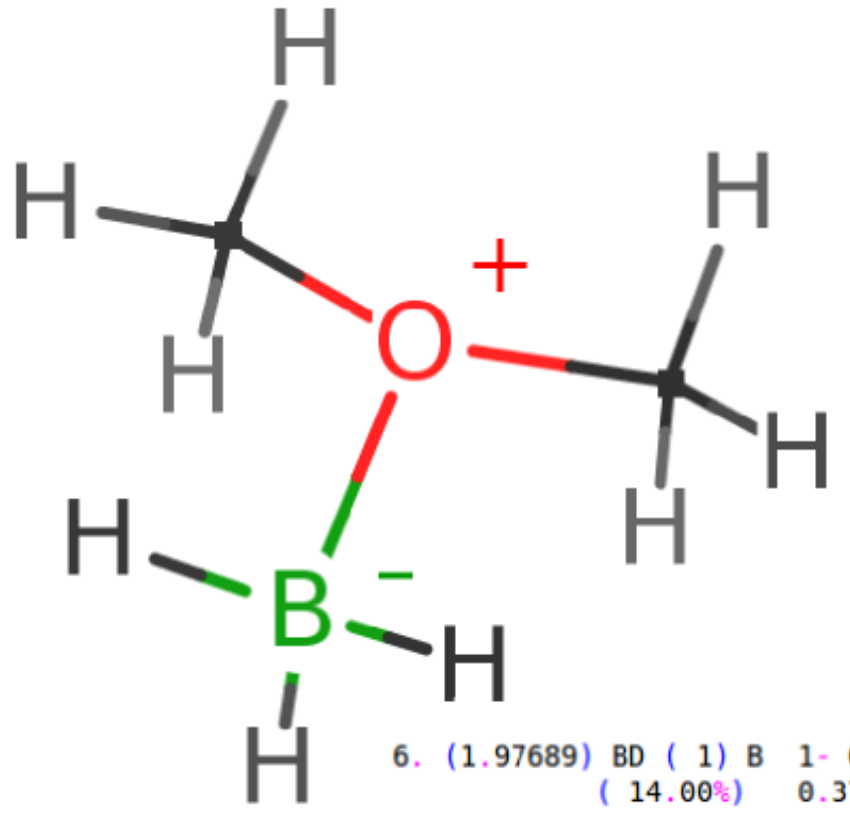
Atom	No	Natural Charge
B	1	-0.06306
O	2	-0.40329
H	3	-0.06664
H	4	-0.08184
H	5	-0.06663
C	6	-0.24858
H	7	0.21806
H	8	0.18833
H	9	0.18292
C	10	-0.24858
H	11	0.18837
H	12	0.18291
H	13	0.21803
* Total *		0.00000



6. (1.97689) BD (1) B 1- O 2
(14.00%) 0.3741* B 1 s(11.96%)p 7.35(87.88%)
0.0000 0.3455 0.0128 -
-0.0119 0.0067 0.0032
-0.0055 0.9363 0.0312 -
-0.0006 -0.0035 -0.0068
0.0002 -0.0003 0.0373 -
(86.00%) 0.9274* O 2 s(32.90%)p 2.04(67.05%)
0.0000 0.5733 0.0189
0.0130 -0.0020 0.0012 -
-0.0021 -0.8182 -0.0199
-0.0012 0.0079 -0.0003 -
0.0028 -0.0007 0.0146 -

Wgt=93.37%