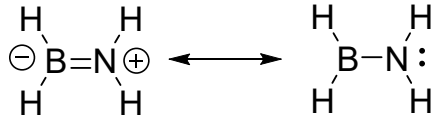
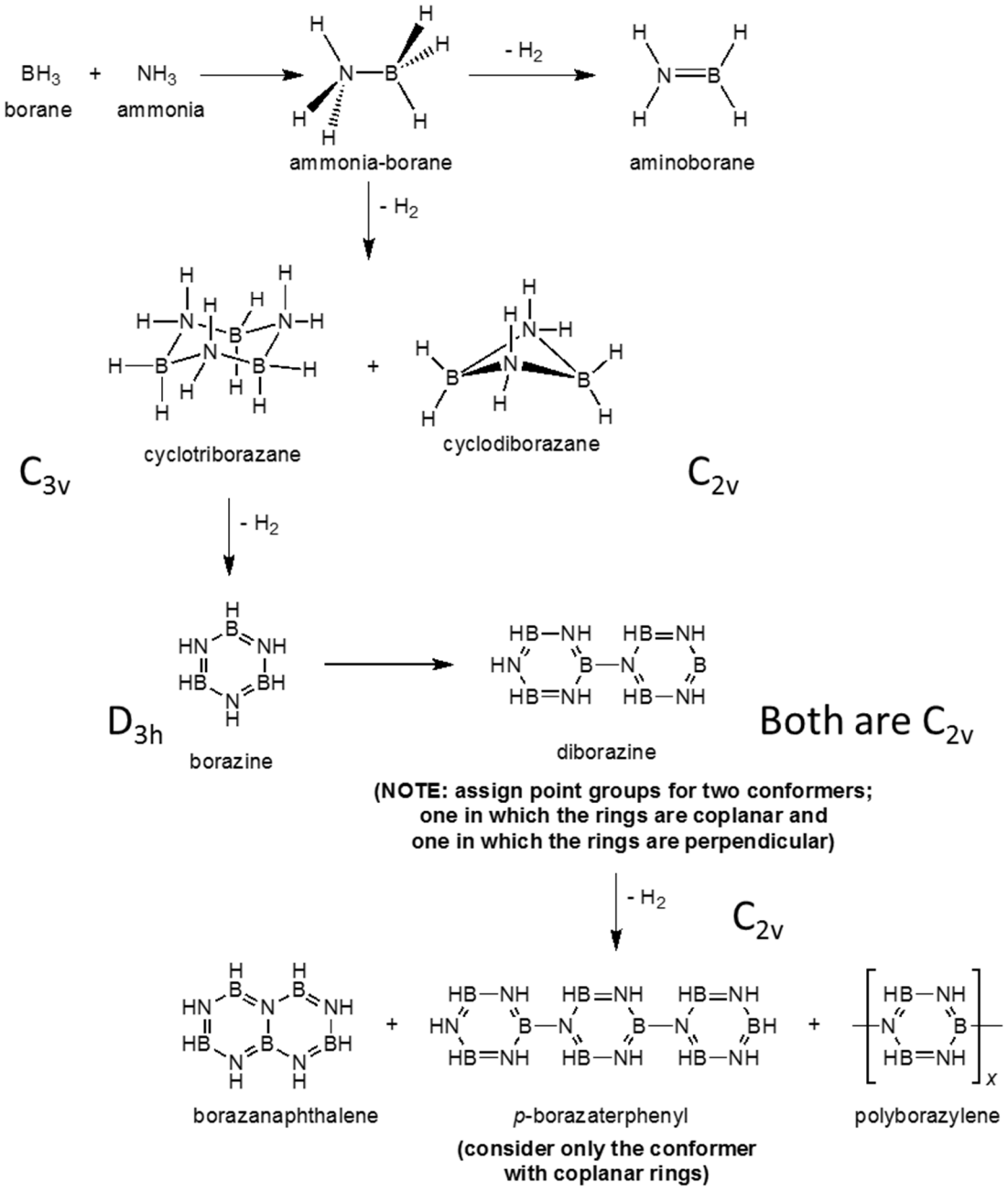
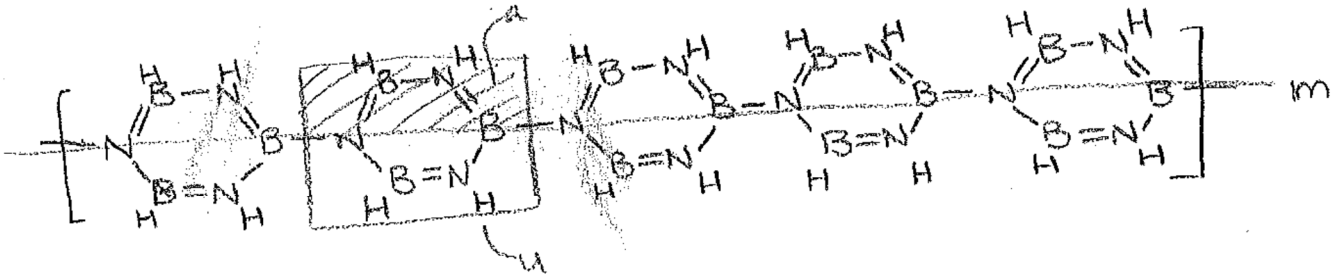
Problem 1 (2 points)

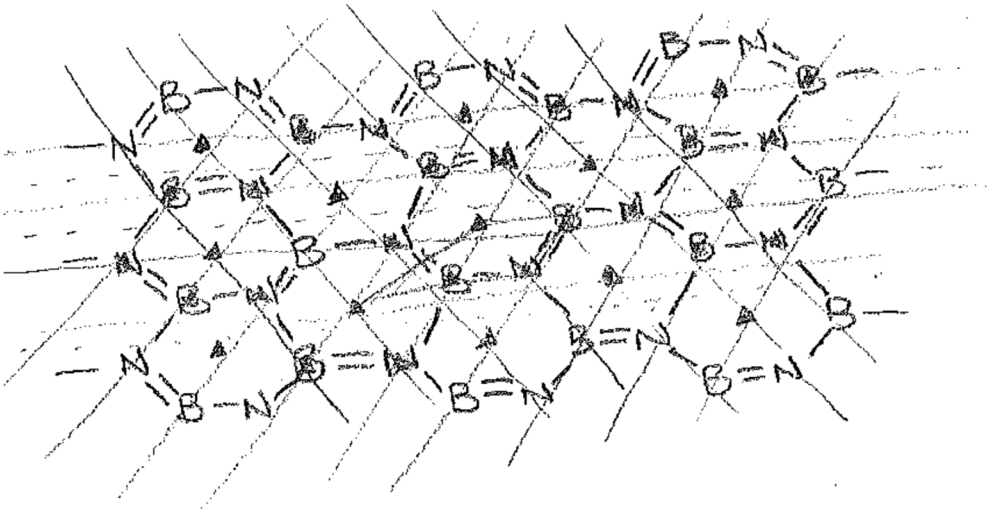


Lone pair on N may donate to an empty p orbital of B on another molecule of aminoborane, leading to oligomers.





CLASS Z



P3m1

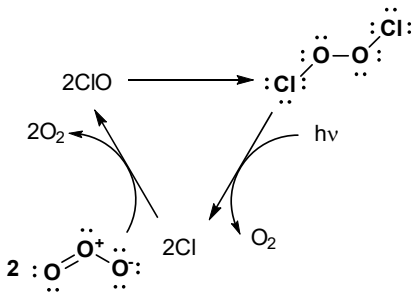
x $H_3B{-}NH_3$ → 3x H_2 + $(BN)_x$

MW($H_3B{-}NH_3$) = 30.87 g/mol

MW(H_2) = 2.02 g/mol

3(2.02)/30.87 = 19.6%

Problem 2



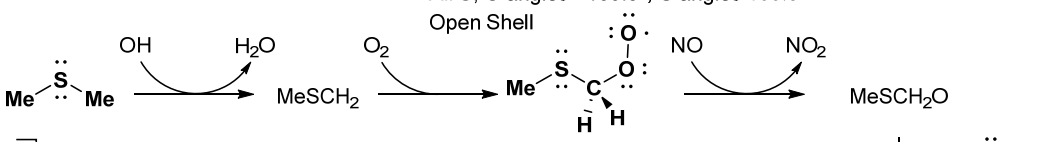
Oxidation States: O^0
C_{2v}, achiral
Bent, O-O-O angle <120°
Closed Shell

Oxidation States: O^{-I}, Cl^{I}
C_{2h}, achiral
Bent oxygens; Cl-O-Cl angle <109.5°
Closed Shell

Methyl is always C^{-II}, H^{I} with a tetrahedral configuration; bond angles each around 109.5°

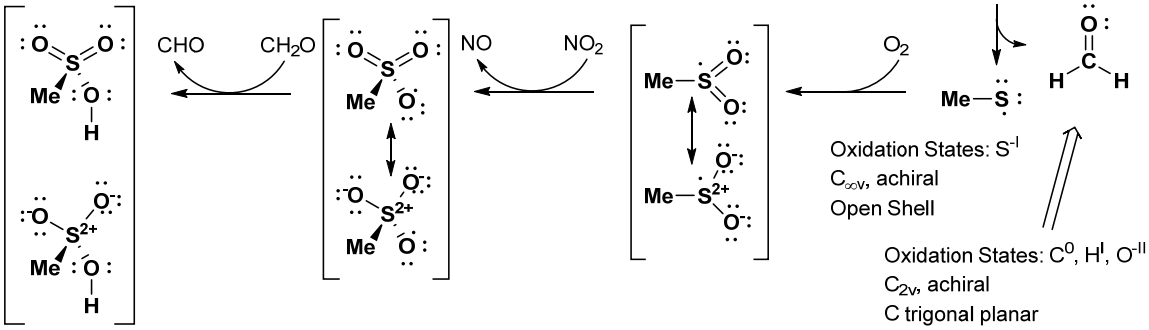
Oxidation States: S^{-II}
C_{2v}, achiral
Bent, O-S-O angle <120°
Closed Shell

Oxidation States: S^{-II}, C^{0}, H^{I}, bridging O^{-I}, terminal O^{0}
C_{v}, achiral
S, O bent; C tetrahedral
All S, O angles <109.5°, C angles 109.5°
Open Shell



Hypervalent structures -> on top

Octet rule structures -> below



Oxidation States: S^{-I}
$C_{\infty v}$, achiral
Open Shell

Oxidation States: C^{0}, H^{I}, O^{-II}
C_{2v}, achiral
C trigonal planar
All C angles 120°
Closed Shell

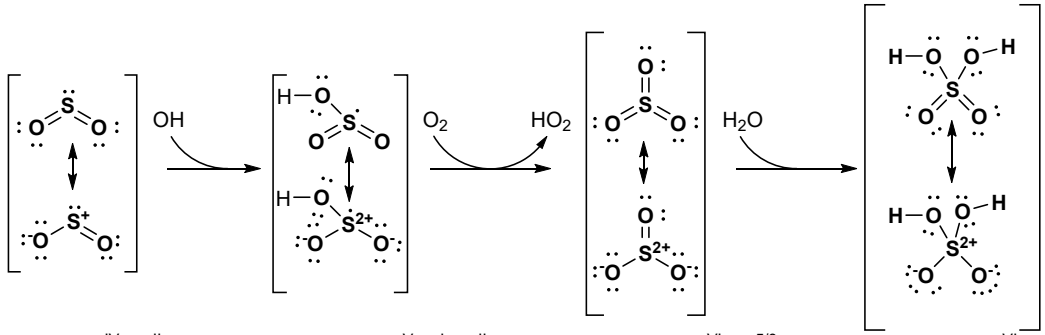
Oxidation States: S^{IV}, H^{I}, O^{-II}
C_{s}, achiral
S tetrahedral, O bent
All S angles 109.5°, O angle <109.5°
Closed Shell

Oxidation States: S^{IV}, $O^{-5/3}$
C_{3v}, achiral
S tetrahedral
All angles 109.5°
Open Shell

Oxidation States: S^{III} O^{-II}
C_{s}, achiral
S trigonal pyrimidal
All S angles 109.5°
Open Shell

Hypervalent structures -> on top

Octet rule structures -> below



Oxidation States: S^{IV}, O^{-II}
C_{2v}, achiral
S bent
O-S-O angle <120°
Closed Shell

Oxidation States: S^{V}, H^{I}, O^{-II}
C_{s}, achiral
S trigonal pyramidal, O bent
All angles <109.5°
Open Shell

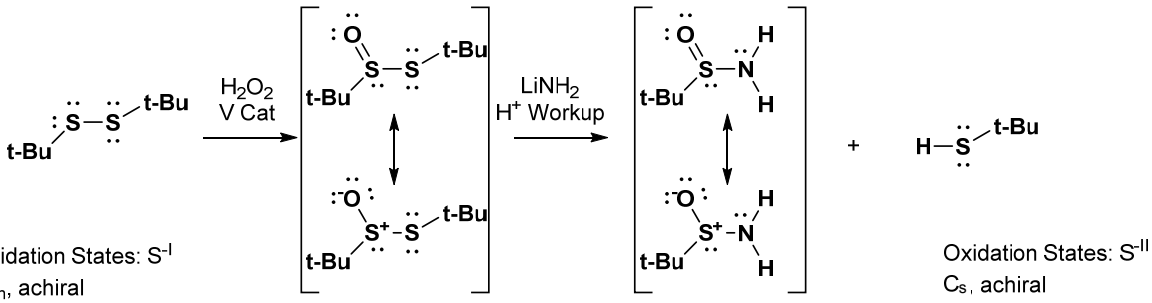
Oxidation States: S^{VI}, $O^{-5/3}$
D_{3h}, achiral
S tetrahedral
All angles 120°
Closed Shell

Oxidation States: S^{VI}, H^{I} O^{-II}
C_{2v}, achiral
S tetrahedral
All S angles 109.5°
All O angles <109.5°
Closed Shell

Tert butyl's is always center C^{I}, methyl-C^{-III}, H^{I} with a tetrahedral configuration on all C and bond angles each around 109.5°

Hypervalent structures -> on top

Octet rule structures -> below



Oxidation States: S^{-I}
C_{2h}, achiral
S bent
All S angles <109.5°
Closed Shell

Oxidation States: left S^{I}, right S^{-I}, O^{-2}
C_1, chiral
Left S trigonal pyramidal, right S bent
All S angles <109.5°
Closed Shell

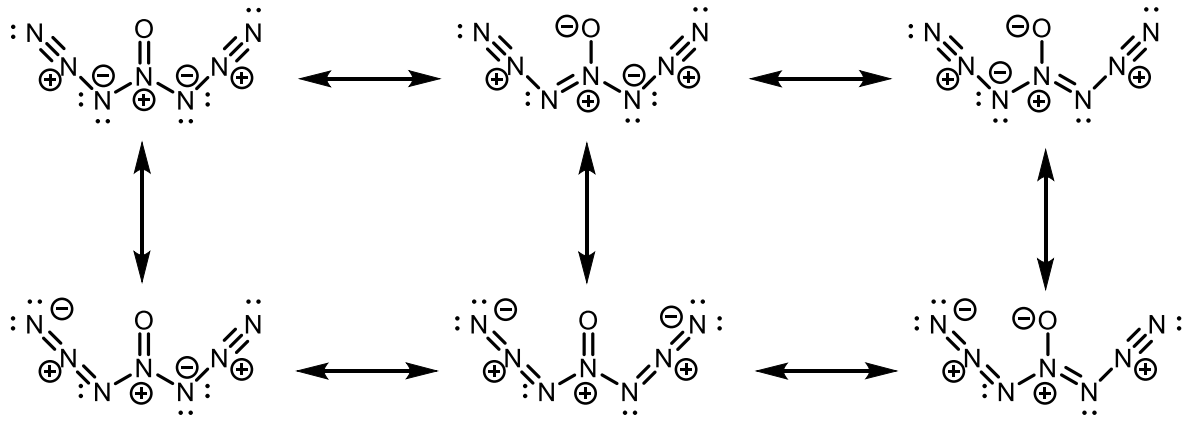
Oxidation States: S^{II}, N^{-III}, H^{I}
C_1, chiral
S, N both trigonal pyramidal
All S,N angles <109.5°
Closed Shell

Oxidation States: S^{-II}
C_s, achiral
S bent
S angle <109.5°
Closed Shell

Problem 3 (2 points)

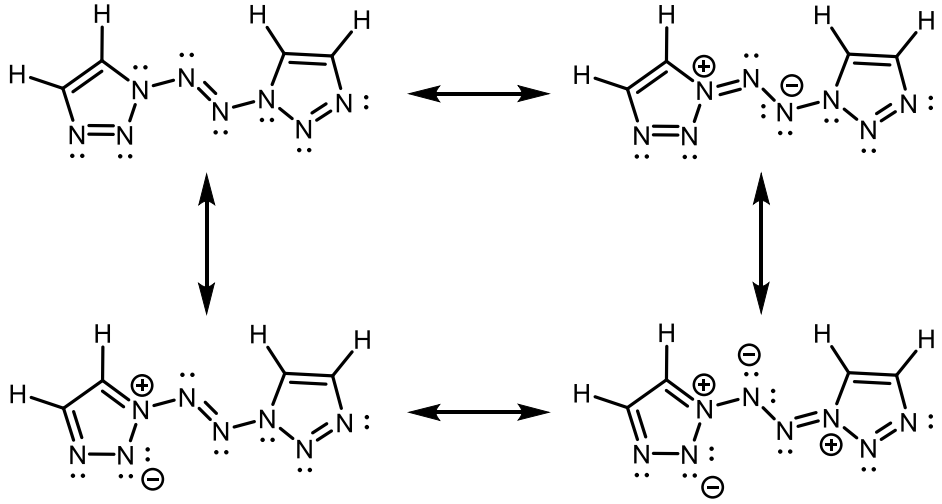
A) The synthesis of polynitrogen compounds is of particular interest towards the development of new high-energy materials. Nitrogen-nitrogen single and double bonds are significantly weaker in energy compared with the triple bond in N_2, leading to decomposition of polynitrogen compounds to N_2 to be very favorable. The N_7O^+ ion has C_{2v} symmetry and features an N_7 chain. Draw at least three Lewis dot structures. Compound $(C_2H_2N_3)NN(N_3C_2H_2)$ displays an N_8 chain and two five-membered rings. Draw at least two Lewis dot structures.

Lewis Dot Structures of $[N_7O]^+$



For more information, c.f. Christe et al. *Inorg. Chem.* **2010**, *49*, 1245.

Lewis Dot Structure of $(C_2H_2N_3)NN(N_3C_2H_2)$



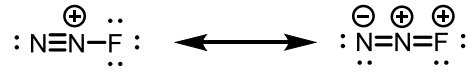
For more information, c.f. Pang and coworkers, *J. Am. Chem. Soc.* **2010**, *132*, 12172-12173.

B) The N_5^+ cation can be prepared using the reaction below:

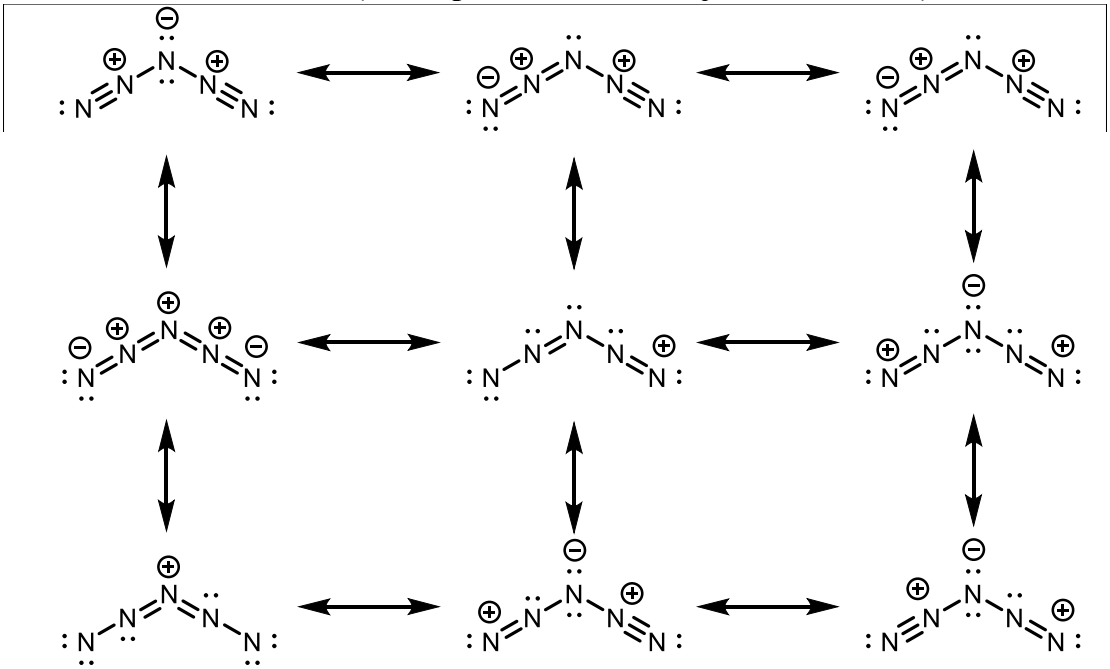
$$[N_2F][SbF_6] + HN_3 \rightarrow [N_5][SbF_6] + HF$$

Provide at least two Lewis dot structures for ions $[N_2F]^+$ and $[N_5]^+$. Note that $[N_5]^+$ consists of an N_5 chain. Provide an example of an abundant and stable neutral molecule isoelectronic to $[N_2F]^+$.

Lewis Dot Structures of $[N_2F]^+$

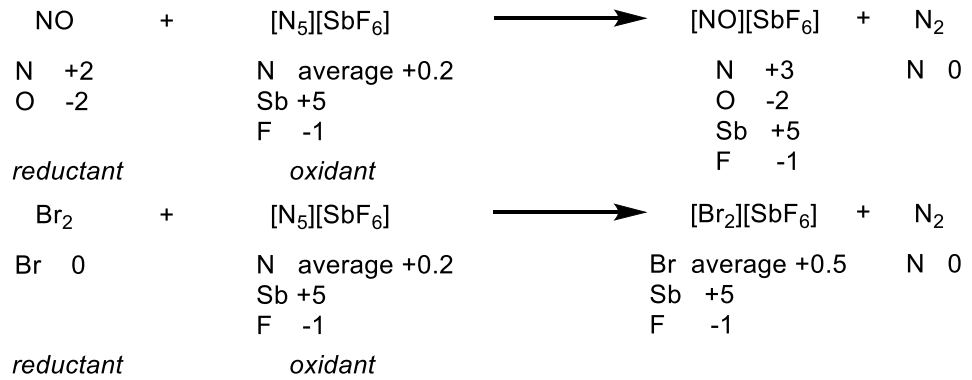


Lewis Dot Structures of $[N_5]^+$ (The top three are the major contributors):

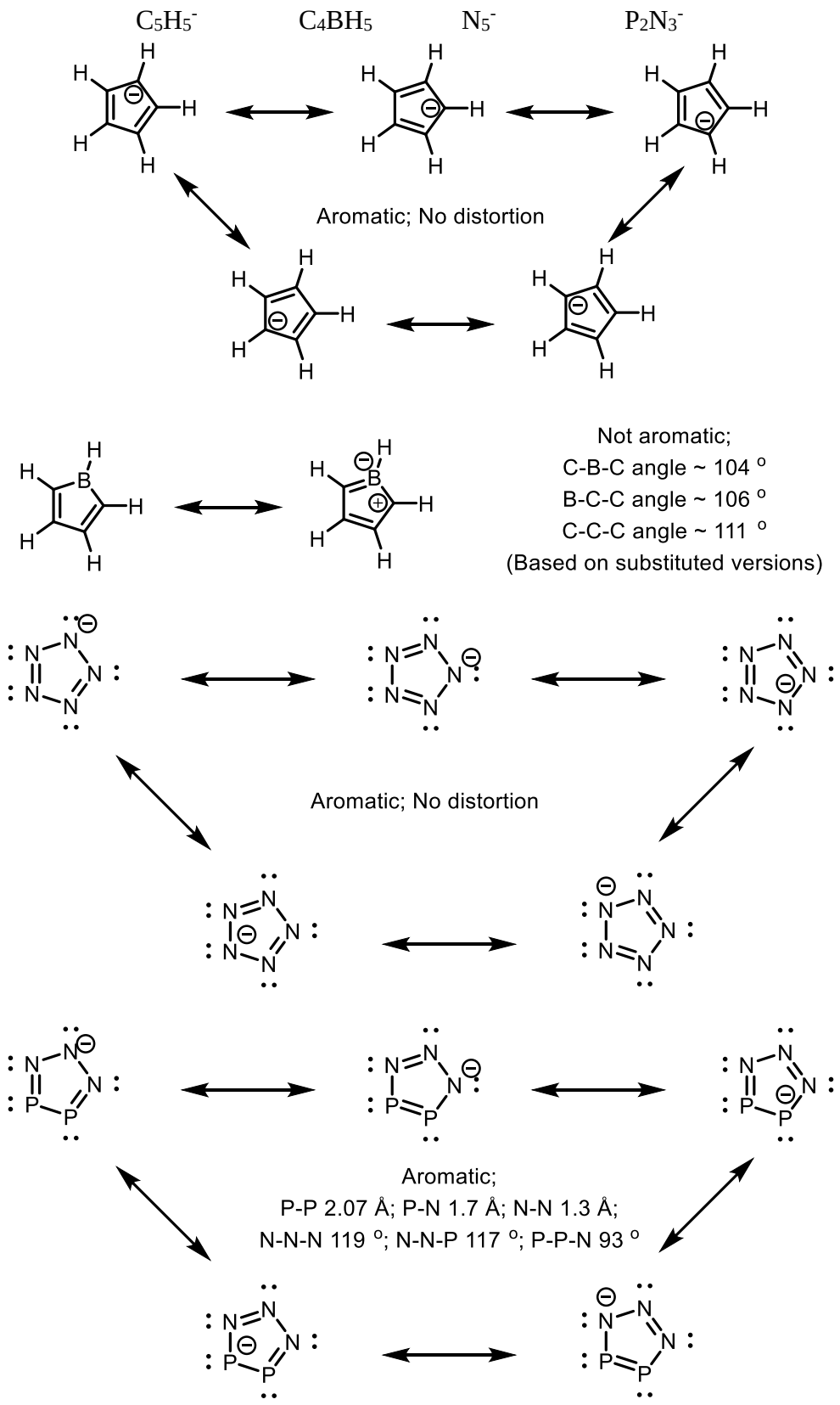


Example of stable, neutral molecules isoelectronic to $[N_2F]^+$: CO_2

C) The crystal structure of $[N_5][Sb_2F_{11}]$ was reported in 2001 by Christe and coworkers (*JACS*, **2001**, 6308). The $[N_5]^+$ ion reacts with reagents such as NO, NO_2, and Br_2, as shown below. For each of the following reactions assign the oxidation states of each atom and indicate which is the oxidant and which is the reductant.



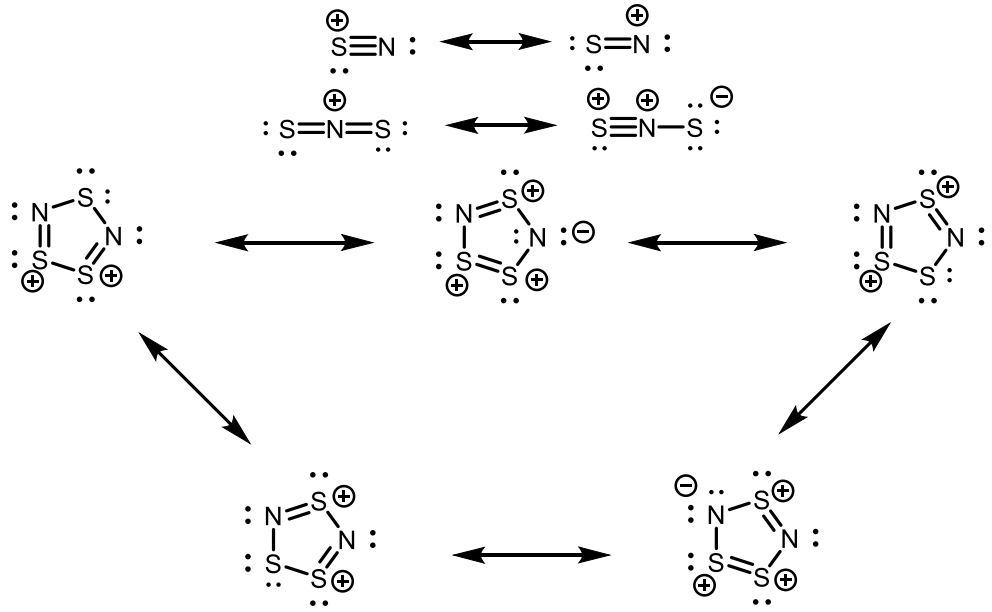
D) One very high energy target molecule is N_5N_5, a theoretical salt consisting of the N_5^+ cation and the cyclic N_5^- anion. Similar five-membered cyclic species, such as the cyclopentadienyl anion, are common ligands in organometallic chemistry. While N_5^- has only been detected in the gas phase, from high energy electrospray ionization of 4-pentazolyl-phenol, solid state-characterization of the corresponding $P_2N_3^-$ anion was reported by Velian and Cummins in 2015 (*Science*, **2015**, 1001). For each of the following cyclic compounds, draw at least two Lewis dot structures, predict if aromatic, and describe distortion from the idealized pentagonal geometry.


$C_5H_5^-$
C_4BH_5
N_5^-
$P_2N_3^-$
Aromatic; No distortion
Not aromatic;
C-B-C angle ~ 104 °
B-C-C angle ~ 106 °
C-C-C angle ~ 111 °
(Based on substituted versions)
Aromatic; No distortion
Aromatic;
P-P 2.07 Å; P-N 1.7 Å; N-N 1.3 Å;
N-N-N 119 °; N-N-P 117 °; P-P-N 93 °

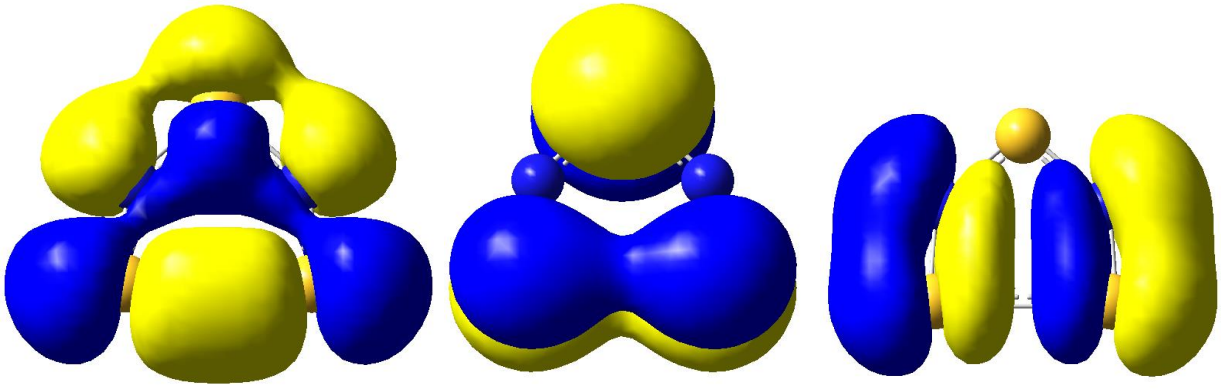
E) Also related to $C_5H_5^-$, $N_2S_3^{2+}$ and $N_2Se_3^{2+}$ have been structurally characterized. $N_2S_3^{2+}$ is prepared in the following reaction, in which none of the original N-S linkages are completely broken:

$$[SNS][AsF_6] + [NS][AsF_6] \rightarrow [N_2S_3][AsF_6]_2$$

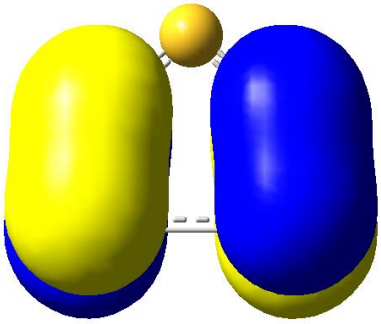
For each of the cations in the equation above provide at least two Lewis dot structures.



MOs from Gaussian (B3LYP) (S at top and bottom)



HOMO HOMO -1 HOMO -2



HOMO -3

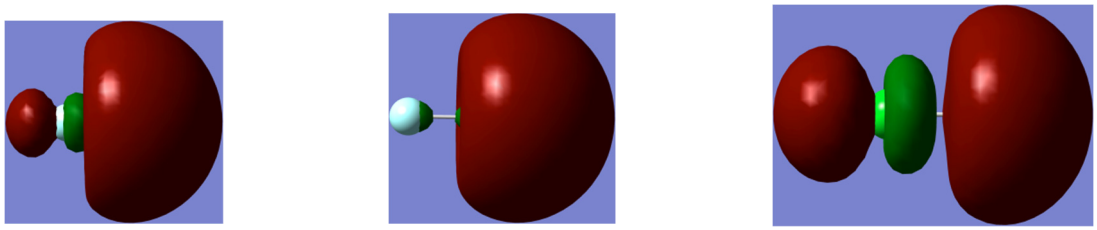
For more information on this compound c.f.

Reference: Brooks et al. *Inorg. Chem.* 1994, 33, 6230

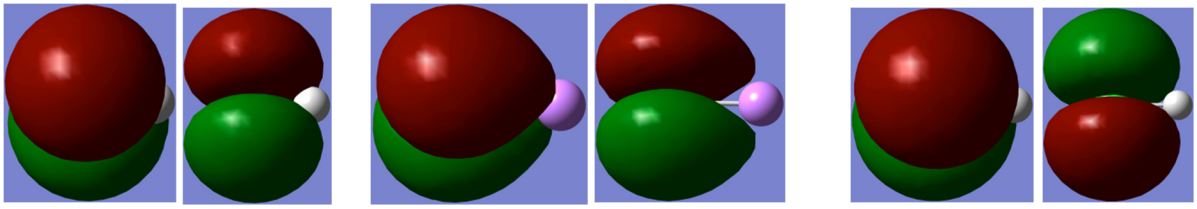
Problem 4 (2 points)

i) F−H **ii) F−Li** **iii) Cl−H**

LUMO* **(σ)**

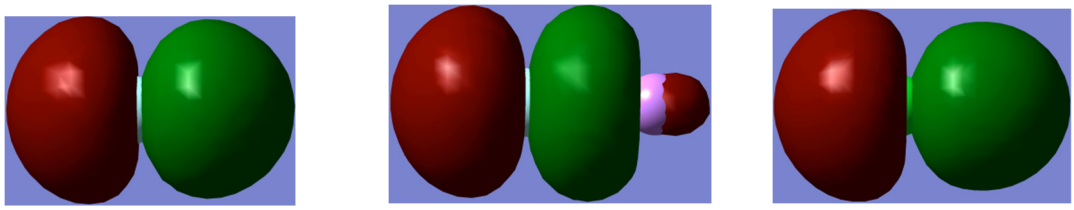


HOMO* **(π)**

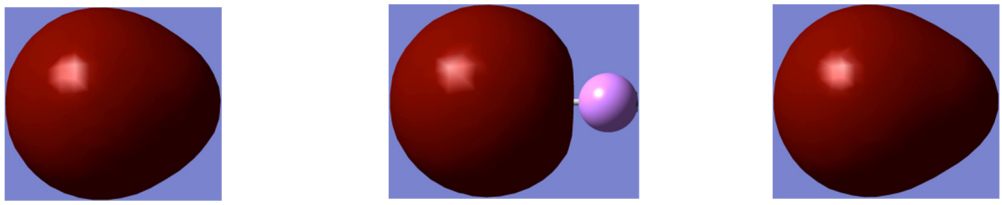


(degenerate set of two molecular orbitals)

HOMO-1 **(σ)**



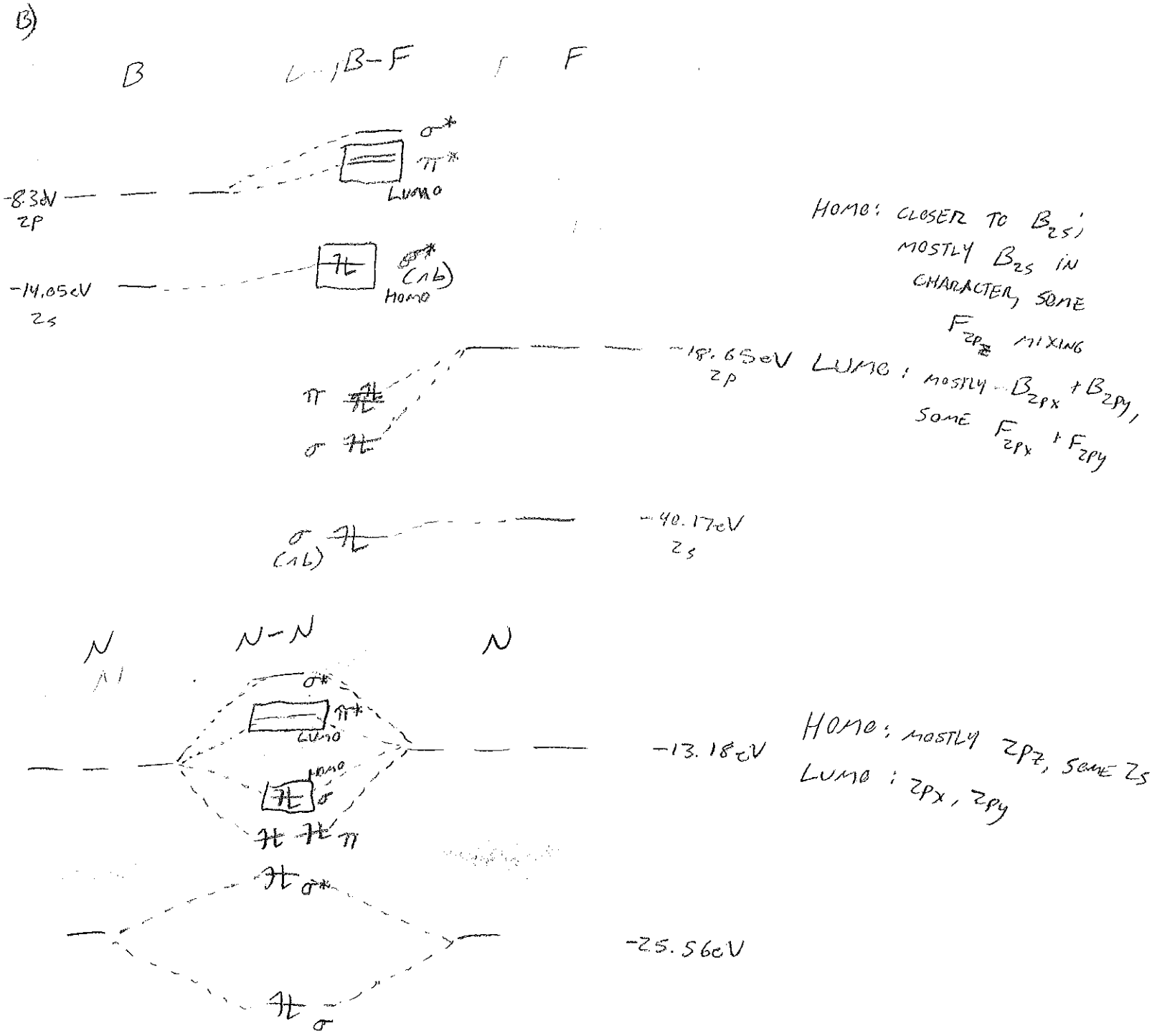
HOMO-2 **(σ)**



Bonding in LiF is ionic due to the large energy difference between Li orbitals (−5.39 eV, 2s) and F orbitals (−40.17 eV, 2s and −18.65 eV, 2p). The lowest energy MOs contain contribution from the most electronegative atom F, while the highest energy MOs contain contributions from Li, the least electronegative atom.

Bonding in HF is more covalent due to the closer energy difference between H orbitals (−13.61 eV, 1s) and F orbitals: hence, there is more mixing in the MOs. In HCl, bonding is even more covalent that in HF, as the Cl orbitals (−25.23 eV, 3s, and −13.67 eV, 3p) are closer in energy to the H orbitals. While there is more mixing, the lowest energy orbitals still contain a larger contribution from the more electronegative atom Cl and the higher energy orbitals contain more contribution from H.

B)



c) HOMO IN N_2 IS LOWER ENERGY THAN IN BF
ALSO, HOMO'S ARE SIMILAR TO B, N AO'S SO TREND IN DIATOMICS' IE SHOULD BE SIMILAR TO TREND IN IE FOR ELEMENTS

d) i IS N_2 ii IS BF_3

FOR ii, LOWER ENERGY MOs CONTAIN MOSTLY CONTRIBUTION FROM ELECTRONEG. F WHILE HIGHER MOs CONTAIN CONTRIBUTION FROM LESS ELECTRONEG. B.

e) HOMO IN BF HAS A LARGE LOBE ON B, WHERE N_2 HAS HOMO THAT IS MORE DELOCALIZED ⇒ HOMO OF BF WILL BETTER OVERLAP WITH BH_3, BF HOMO IS ALSO HIGHER ENERGY AND MORE REACTIVE.