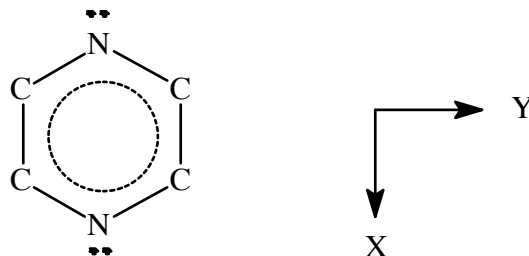
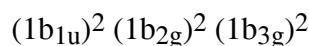


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PROBLEMS

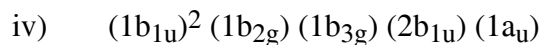
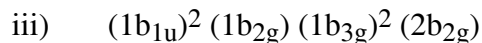
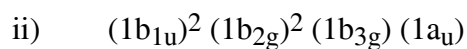
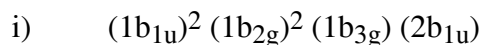
26. For the molecule pyrazine



(a) The π -electron ground state of pyrazine has the following configuration:



Are electronic transitions to the following excited states allowed, and if so, what are the polarizations with respect to the molecule?



(b) Combinations of the lone-pair sigma orbitals on the nitrogens are required to make non-bonding (n) molecular orbitals.

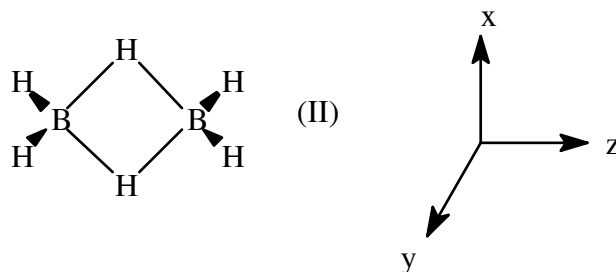
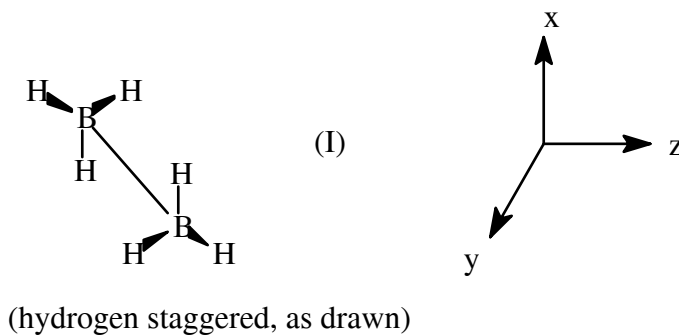
i) Sketch the two symmetry orbitals resulting from these combinations.

ii) Using the coordinate axis convention above, what are the symmetries of these non-bonding m.o.'s?

iii) Would there be an allowed $n \rightarrow \pi^*$ electronic transition from either of the lone pair m.o.s to the $b_{1u}\pi^*$ orbital? What is the polarization of this transition relative to the molecular plane?

(c) Sketch the $1b_{2g}$ and $1b_{3g}$ π -m.o.s. These two m.o.s are correlated with the e_{1g} degenerate pair in benzene. Why, in pyrazine, does the b_{2g} have a lower energy than the b_{3g} ?

27. How would one use vibrational spectroscopy based on $\text{C}\equiv\text{O}$ stretches to distinguish between cis- and trans- $[\text{M}(\text{CO})_4(\text{X})_2]^{+n}$ octahedral coordination complexes.
28. In the late 1940's there was a great deal of interest in the structure of diborane, B_2H_6 . Two of the most reasonable structures were an ethane-like structure (I) and a protonated bridged ethylene-like structure (II).



- (a) What are the point groups of each of the structures?
- (b) *Explicitly* state how an analysis of the infra-red and Raman spectra of B_2H_6 could distinguish between the two structures.
29. Benzene is a good example of an important molecule with relatively high symmetry. (a) Determine the symmetry type of the genuine vibrations. (b) Determine the infra-red and Raman activities of each vibrational mode. (c) Classify all in-plane vibrations as to whether they involve C—H stretching or angle bending. (d) Which vibrations involve out-of-plane C—H wagging? [Cotton (10.2, p. 347, parts a, b, c, d)]

FINIS