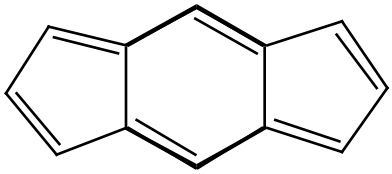
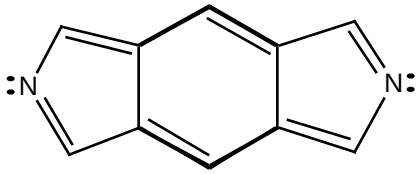
Examination 1 **November 15, 1994**

Chemistry 262 **Dr. Jay H. Baltisberger**

Name: _____

1. Describe the Hückel approximations used in molecular orbital calculations and apply these to derive a determinant for the electronic energy in $C_{12}H_8$. Note where improvements could be made in this simple theory by changing terms in the determinant if the molecule was $C_{10}N_2H_6$. Describe what each integral (α, β) used in this determinant indicates in both words and symbols. (25 points, note that these molecules are fully conjugated, planar and sp^2 hybridized at each atom. Be sure to number the atoms relative to secular determinant columns.)





2. Classify the point group of the following molecules. (A) B_2H_6 (note 2 hydrogen atoms are bridging) (B) Staggered-C_2H_6 (C) HCN (D) Fe(C_5H_5)Cl (E) 1-chloro-2-bromobenzene. In each case indicate the allowed symmetry operations. (15 points)

3. A ClO_2 molecule is of the point group C_{2v} and has a ground electronic state of symmetry B_1. When a molecule is trapped in a solid (to prevent motion) and light of *y* polarization falls on it (relative to the molecular axis frame) the molecule is excited to an upper electronic state. What symmetry types would be allowed for the final state (test all symmetry species)? (10 points)

4. Construct a complete molecular orbit wavefunction description of the π bonding in CO_3^{2-}. Note that you should demonstrate how you arrive at each of the π orbits from the four $2p_z$ orbits on the atoms (you need not expand p_z functions). Assume the molecule is planar and that each is sp^2 hybridized. Be sure to include proper irreducible representations for each orbit. (15 points)

5. Using Einstein extinction coefficients, explain why a population difference between energy levels is required for a net absorption of resonant photon energy. A laser requires the populations of two energy levels be inverted. Explain what happen when the resonant photon density increases when the population of a pair of energy levels is exchanged ($N_L \rightarrow N_U$ and $N_U \rightarrow N_L$). (8 points)

6. Describe in a short answer what is required of a molecule to show pure rotational transitions. Which of the following molecules may show a pure microwave rotational spectrum: (A) H_2 (B) HCl (C) CH_4 (D) CH_2Cl_2 (E) H_2O (F) NH_3? (12 points)

7. For $^{63}Cu^{79}Br$ the J=13–14, 14–15 and 15–16 pure rotational transitions occured at 84 421.34, 90 449.25, and 96 476.72 Mhz. Calculate the rotational constant (*B*) in cm^{-1} and the bond length of CuBr. ($I = \mu r^2$, $\mu = m_1 m_2 / (m_1 + m_2)$, $B = h / 8 \pi^2 c I$, $E = h c B J (J + 1)$, $h = 6.626 \times 10^{-34}$ J s, $c = 2.99 \times 10^8$ m/s, 1 amu = 1.6605×10^{-27} kg, 10 points)