20 題單選，每題 2.5 分，共五十分

For a tetragonal unit cell with a Laue symmetry of 4/mmm, answer Questions 1-3.

1. Select the appropriate point group:

(A) D_{4h}
(B) D_{4d}
(C) C_{4v}
(D) C_{4h}

2. What are the correct cell conditions:

(A) $a \neq b \neq c$; $\alpha = \gamma = 90^\circ \neq \beta$
(B) $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
(C) $a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
(D) $a = b = c$; $\alpha = \gamma = 90^\circ \neq \beta$

3. What is the number of Lattice point:

(A) 4 (*I*-centered)
(B) 2 (*F*-centered)
(C) 4 (*Primitive*)
(D) 2 (*I*-centered)

4. The IR stretching frequency of CO gas (ν_{CO}) is 2341 cm^{-1}. The IR stretching frequency of $R_1R_2C{=}O$ is around 1600 cm^{-1}. What would be the appropriate IR stretching frequency expected for $W(NH_3)_3(CO)_3$, where the metal to CO charge transfer is established.

(A) 2500 cm^{-1}
(B) 1950 cm^{-1}
(C) 1450 cm^{-1}
(D) 2300 cm^{-1}

5. Select the highest C-O stretching frequency:

(A) $Ni(CO)_3(PH_3)$
(B) $Ni(CO)_3(PF_3)$
(C) $Ni(CO)_3(PCl_3)$
(D) $Ni(CO)_3(PMe_3)$

6. For I = ionization energy, A = electron affinity, η = absolute hardness, χ = electronegativity, E_{HOMO} = HOMO energy and E_{LUMO} = LUMO energy, select the incorrect expressions:

(A) $\chi = \dfrac{A+I}{2}$
(B) $E_{HOMO} = -I$
(C) $\eta = \dfrac{A+I}{2}$
(D) $E_{LUMO} = -A$

7. A 2.00×10^{-4} M solution of $Fe(S_2CNEt_2)_3$ (Et = C_2H_5) in $CHCl_3$ at 25 °C has absorption bands at 350 nm (absorbance, A = 2.34) and 514 nm (A = 0.532). What are the molar absorptivity (ε) for this compound at each wavelength.

(A) 11,700 and 2,660 L $mol^{-1}cm^{-1}$
(B) 23,400 and 5,320 L $mol^{-1}cm^{-1}$
(C) 46,800 and 10,640 L $mol^{-1}cm^{-1}$
(D) 5,850 and 1,330 L $mol^{-1}cm^{-1}$

8. For the d^4-d^7 electron configurations of the metals with an octahedral ligand field select the correct order of degree of Jahn-Teller effect.
   (A) low spin d^4 > high spin d^4
   (B) low spin d^5 < high spin d^5
   (C) low spin d^6 > high spin d^6
   (D) low spin d^7 > high spin d^7

9. The correct order of bond angles for the hydrides of Group 15 (VA) element are:
   (A) $NH_3 > PH_3 > AsH_3 >$ and SbH_3
   (B) $NH_3 < PH_3 < AsH_3 <$ and SbH_3
   (C) $NH_3 > PH_3 > AsH_3 <$ and SbH_3
   (D) $NH_3 > PH_3 < AsH_3 >$ and SbH_3

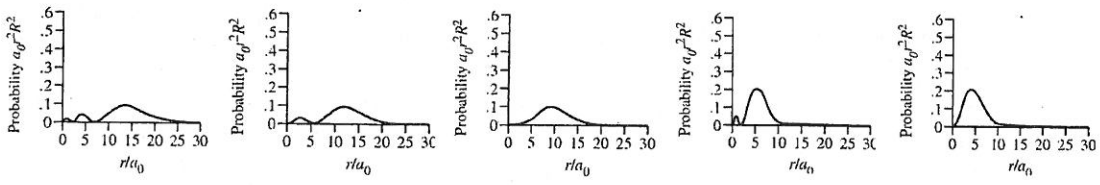
10. The correct order of bond distances of homonulcear diatomic molecules and ions is:
   (A) $B_2 > C_2 > N_2 > O_2$
   (B) $H_2^{-2} > H_2^{-1} > H_2 > H_2^{+}$
   (C) $F_2 > O_2 > N_2 > C_2$
   (D) $O_2^{-2} > O_2^{-1} > O_2 > O_2^{+}$

11. How many possible isomers are there for $[Co(dien)_2]^{3+}$ without considering ring conformations? (dien = diethylenetriamine)
   (A) 2
   (B) 3
   (C) 4
   (D) 5

12. The metallocene complexes MCp_2 (M = V, Cr, Mn, Fe, Co, Ni; Cp^- = cyclopetadienyl, $C_5H_5^-$, a very strong field ligand) are known to adopt an octahedral geometry with a very slight distortion on the d_π orbitals. Which of the following metallocene is diamagnetic?
   (A) $NiCp_2$
   (B) $CoCp_2^+$
   (C) $MnCp_2$
   (D) $CrCp_2$

13. What are the possible values for all four quantum numbers for a 4*f* electron?
   (A) $n = 4, l = 4, m_l = -4, m_l = -\frac{1}{2}$
   (B) $n = 4, l = 3, m_l = -3, m_l = +\frac{1}{2}$
   (C) $n = 4, l = 3, m_l = +4, m_l = +\frac{1}{2}$
   (D) $n = 4, l = 4, m_l = +3, m_l = -\frac{1}{2}$

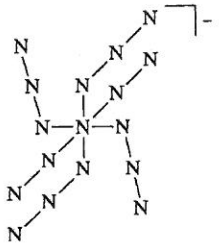
14. The following diagrams show the radial probability functions of 2*s*, 2*p*, 3*s*, 3*p*, and 3*d* orbitals. Assign the appropriate orbital to each of the diagram.



   (A) 3*d*, 3*p*, 3*s*, 2*p*, and 2*s*
   (B) 3*d*, 2*p*, 2*s*, 3*p*, and 3*s*
   (C) 2*s*, 2*p*, 3*s*, 3*p*, and 3*d*
   (D) 3*s*, 3*p*, 3*d*, 2*s*, and 2*p*

15. Assign the appropriate point group to the following compound.

(A) C_4
(B) D_{4d}
(C) D_{2h}
(D) C_{4v}



16. Based on the concept of VSEPR, select the one from each pair with the larger bond angle:

(i) CH_4 and NH_3　　(ii) OF_2 and OCl_2　　(iii) NH_3 and NF_3

(A) (i) NH_3 (ii) OF_2 (iii) NH_3
(B) (i) CH_4 (ii) OCl_2 (iii) NF_3
(C) (i) CH_4 (ii) OCl_2 (iii) NH_3
(D) (i) NH_3 (ii) OF_2 (iii) NF_3

17. Select the reasonable electron-dot structures for each of the following compounds.

(A) :N≡N–Ö:
(B) N̈–N̈≡Ö
(C) :N=N=Ö
(D) :N=N=Ö:

N̈=N̈=Ö　:N̈=N=O:　:N≡N–Ö:

N̈–N̈≡Ö　:N=N=Ö　:N=N=Ö:

18. Which of the following is correct?

(i) $C_2^2 = S_4^2$　　(ii) $S_2 = i$　　(iii) $S_1 = \sigma$　　(iv) $C_4 \times \sigma_v = S_4$
(v) $C_2\sigma_v\,(xz) = \sigma_v'\,(yz) \times h$

(A) (ii), (iii), (iv)
(B) (i), (iii), (v)
(C) (ii), (iii), (v)
(D) (i), (ii) (iv)

19. For NH_3, $(CH_3)_2NH$, $(CH_3)_3P$ and $(CH_3)_2S$. Give the order of decreasing basicity toward BEt_3.

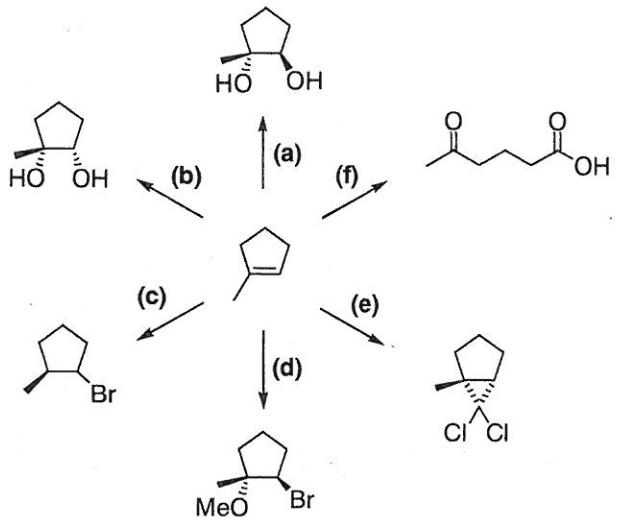
(A) $(CH_3)_2NH > NH_3 > (CH_3)_2S > (CH_3)_3P$
(B) $NH_3 > (CH_3)_2NH > (CH_3)_2S > (CH_3)_3P$
(C) $(CH_3)_2S > (CH_3)_3P > NH_3 > (CH_3)_2NH$
(D) $(CH_3)_3P > (CH_3)_2S > (CH_3)_2NH > NH_3$

20. The step-wise addition of pyridine (py, 2 eq.), NH_3 (1 eq.) and Br^- (1 eq.) to the starting compound $[PtCl_4]^{2-}$ gave the following product. Predict the *trans effect* of the ligand being added.

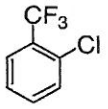
(A) py > Br^- > Cl^- > NH_3
(B) Br^- > Cl^- > NH_3 > py
(C) Cl^- > Br^- > py > NH_3
(D) NH_3 > py > Br^- > Cl^-

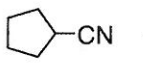
『有機化學』部份　總分 50 分

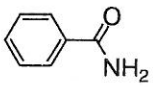
1. Suggest a reagents (or a series of reagents) that can be used to accomplish the following transformation. (2 pts each, 12 pts)

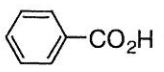


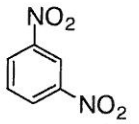
2. Give the expected major product of the following reactions. (2 pts each, 14 pts)

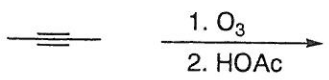
(1)  $NaNH_2$, NH_3 →

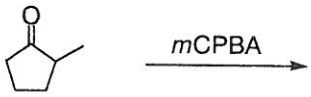
(2)  1. DIBAL-H, 2. H_2O →

(3)  P_2O_5 →

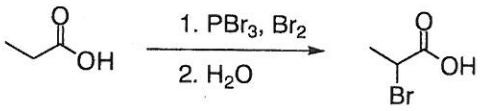
(4)  1. Ag_2O, H_2O; 2. Br_2, Δ →

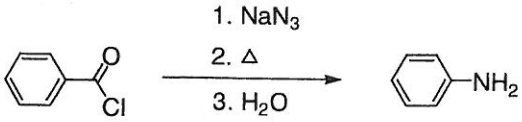
(5)  H_2S, NH_3 →

(6) 

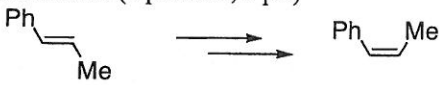
(7) 

3. Propose a mechanism for the following reactions. (5 pts each, 10 pts)

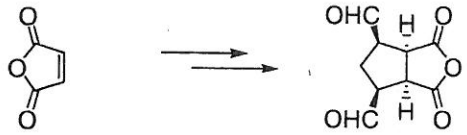
(1) 

(2) 

4. Propose a synthetic scheme for each of the following compounds from the readily available starting materials. (3 pts each, 9 pts)

(1) 

(2) 

(3) 

5. Deduce the structure of the compound that gives the following ^{1}H and ^{13}C spectra.
^{1}H NMR ($CDCl_3$): δ 6.5 (t, 1H), 3.0 (t, 2H), 2.2 (t, 2H), 1.9 (s, 3H).
^{13}C NMR ($CDCl_3$): δ 207 (C), 145 (CH), 139 (C), 37 (CH_2), 25 (CH_2), 16 (CH_3).
The mass spectrum of this compound shows the molecular ion at *m/z* 96. (5 pts)