

TEST OF CHEMISTRY

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化 学 専 攻

November 24, 2008 (平成 20 年 11 月 24 日) 9 : 00 ~ 11 : 00

General Directions (注 意 事 項)

1. Answer all problems in English or in Japanese. (すべての問題に英語または日本語で解答せよ。)
2. Check the number of sheets. (以下の用紙の枚数を確認せよ。)

Problem Sheets (問題用紙) 4 枚

Answer Sheets (解答用紙) 3 枚

[I] Answer the following problems (a) – (c). (次の問(a)~(c)に答えよ。)

- (a) The table below shows first ionization energies of the second period elements, which in general increase with the atomic number. Suggest a reason for the irregularity exhibited by N and O. (下の表は第二周期の元素の第一イオン化エネルギーで、一般に原子番号とともに増加する。NとO元素が示す異常を説明せよ。)

Elements	First ionization energies (eV)
B	8.30
C	11.26
N	14.53
O	13.61
F	17.42

- (b) Name the complexes (i) and (ii) and count the number of the total valence electrons around each metal center. (i) *cis*-[PtCl₂(NH₃)₂] and (ii) [Ni(CO)₃(py)]. (py = pyridine) ((i), (ii)の錯体を命名し、金属中心まわりの総価電子数を答えよ。(py = ピリジン))
- (c) Draw the shapes of (i) H₂Se, (ii) P₂H₄, and (iii) H₃O⁺, using Lewis structures and the VSEPR model. (Lewis 構造および VSEPR 則を用いて(i)~(iii)の化合物の分子またはイオンの安定構造を描け。)

[II] Read the following sentences and answer the problems (a) – (d). (次の文を読み、問(a)～(d)に答えよ。)

The electron configuration of a carbon atom in the ground electronic state is $1s^2 2s^2 2p_x^1 2p_y^1$. This expression seems to imply that carbon should be divalent instead of [A], and does not lead to the tetrahedral bonding in methane and other hydrocarbons. The [B] of carbon is explained by the [C] of one of the 2s electrons to the $2p_z$ orbital, giving an electron configuration of $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$. This configuration gives four singly occupied orbitals so that the carbon atom becomes [A]. The hydrocarbon molecules have various structures by forming the bonds between the orbitals constructed by appropriate linear combinations of the singly occupied orbitals of the carbon atoms and the 1s orbitals of the hydrogen atoms. Acetylene has the linear structure, ethylene has the planar structure, and methane has the tetrahedral structure.

(a) Insert appropriate words in [A], [B] and [C], respectively.

([A], [B], [C] それぞれにあてはまる適当な語句を書け。)

(b) In the underlined sentence, how are the constructed atomic orbitals called ?

(下線部のようにして作られた軌道は何と呼ばれるか。)

(c) In ethylene, a carbon atom forms a double bond with the other carbon atom, and forms two single bonds with two hydrogen atoms. As seen in Figure 1, three of the four bonds are in the $x-z$ plane and each bond angle is approximately 120° . The three orbitals of the carbon atom are expressed as, (エチレンの炭素は、隣の炭素と2重結合を結び、また2つの水素と単結合を結ぶ。3つの結合は同じ平面内にありお互いに 120° の角度をもつ。炭素の3つの軌道は以下の式で表される。)

$$\psi_1 = a s + b p_z,$$

$$\psi_2 = a s + b (p_x \sin\theta + p_z \cos\theta),$$

$$\psi_3 = a s + b (-p_x \sin\theta + p_z \cos\theta).$$

Here, $\theta = 120^\circ$, s refers to the 2s orbital, and p_x and p_z refer to the 2p orbitals. a and b are the coefficients. Obtain the coefficients a and b by knowing that these orbitals are normalized

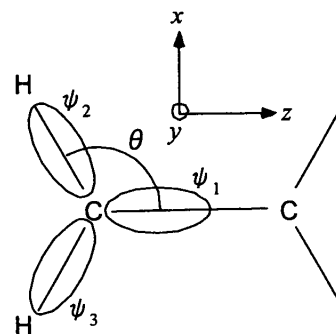


Figure 1

and orthogonal with each other. (ここで θ は 120° , s , p_x , p_z はそれぞれ炭素の2s軌道, 2p軌道であり, a , b は各係数である。それぞれの軌道が規格・直交化されていることを使って係数 a , b を求めよ。)

(d) The tetrahedral structure of methane is shown in Figure 2. Here, the carbon is located in the middle of the cube and four hydrogen atoms are located at the corners. We can obtain the $H(1)-C-H(2)$ bond angle from this figure. We let the coordinates of the middle carbon, $H(1)$, and $H(2)$ be $(0,0,0)$, $(-1,-1,1)$, and $(1,1,1)$, respectively in Cartesian coordinates. Obtain the cosine of the $H(1)-C-H(2)$ bond angle.

(メタンの正四面体構造を図 2 に示した。炭素は立方体の中心に位置し、水素はかどに位置している。この図を使い、 $H(1)-C-H(2)$ 結合角を求めることができる。中心炭素 C、水素 $H(1)$, $H(2)$ の座標をそれぞれ、 $(0,0,0)$, $(-1,-1,1)$, $(1,1,1)$ として $H(1)-C-H(2)$ 結合角の余弦を求めよ。)

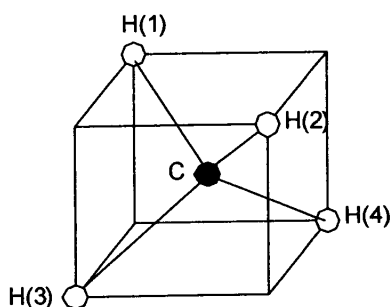
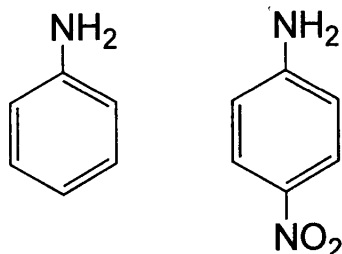


Figure 2

[III] Answer the following problems (a) and (b). (次の問(a)と(b)に答えよ。)

(a) Which of the following two anilines do you expect to be more basic? Explain your answer.

(次の2つのアニリン誘導体のうち、塩基性度が大きいのはどちらか。また、理由も説明せよ。)



(b) Give the structures of the major organic products (**1**, **2**, **3**) expected in the following reactions.

For the reactions (i) and (ii), propose each mechanism with an arrow formalism (↷). (次の反応における主生成物(有機化合物)(**1**, **2**, **3**)の構造を記せ。その際、(i), (ii)に関しては、反応機構を電子の動きがわかるように矢印(↷)で図示せよ。)

