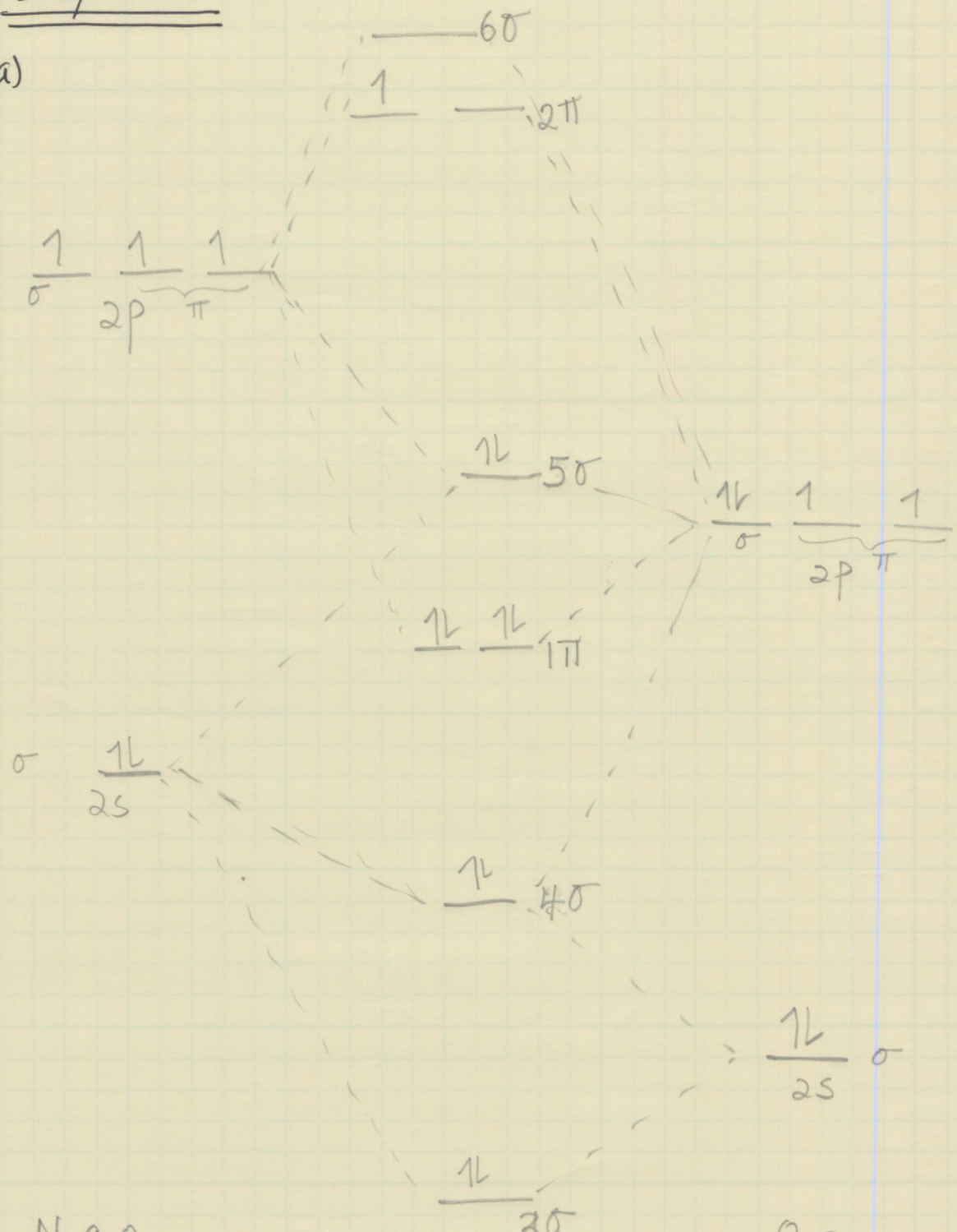
ADVANCED CHEMISTRY

INORGANIC CHEMISTRY H.W. – WEEK 8 – WINTER

Chapter 5

④ (a)



(b) Oxygen is more electronegative than N. Therefore the oxygen atom desires shared electrons more than the N atom. The shared electrons in 3σ, 1π and 5σ (all bonding orbitals) are closer to the oxygen atom indicating that they are centered closer to oxygen.

(c) # of unpaired electrons = 1

$$\text{bond order} = \frac{1}{2}(8-3) = \underline{\underline{2.5}}$$

(d) NO^+ (electron is removed from 2π).

HOMO is 5σ, LUMO is 2π.

$$\text{bond order} = \frac{1}{2}(8-2) = 3$$

NO^- add one more electron to 2π

$$\text{bond order} = \frac{1}{2}(8-4) = 2$$

bond length $\longrightarrow$

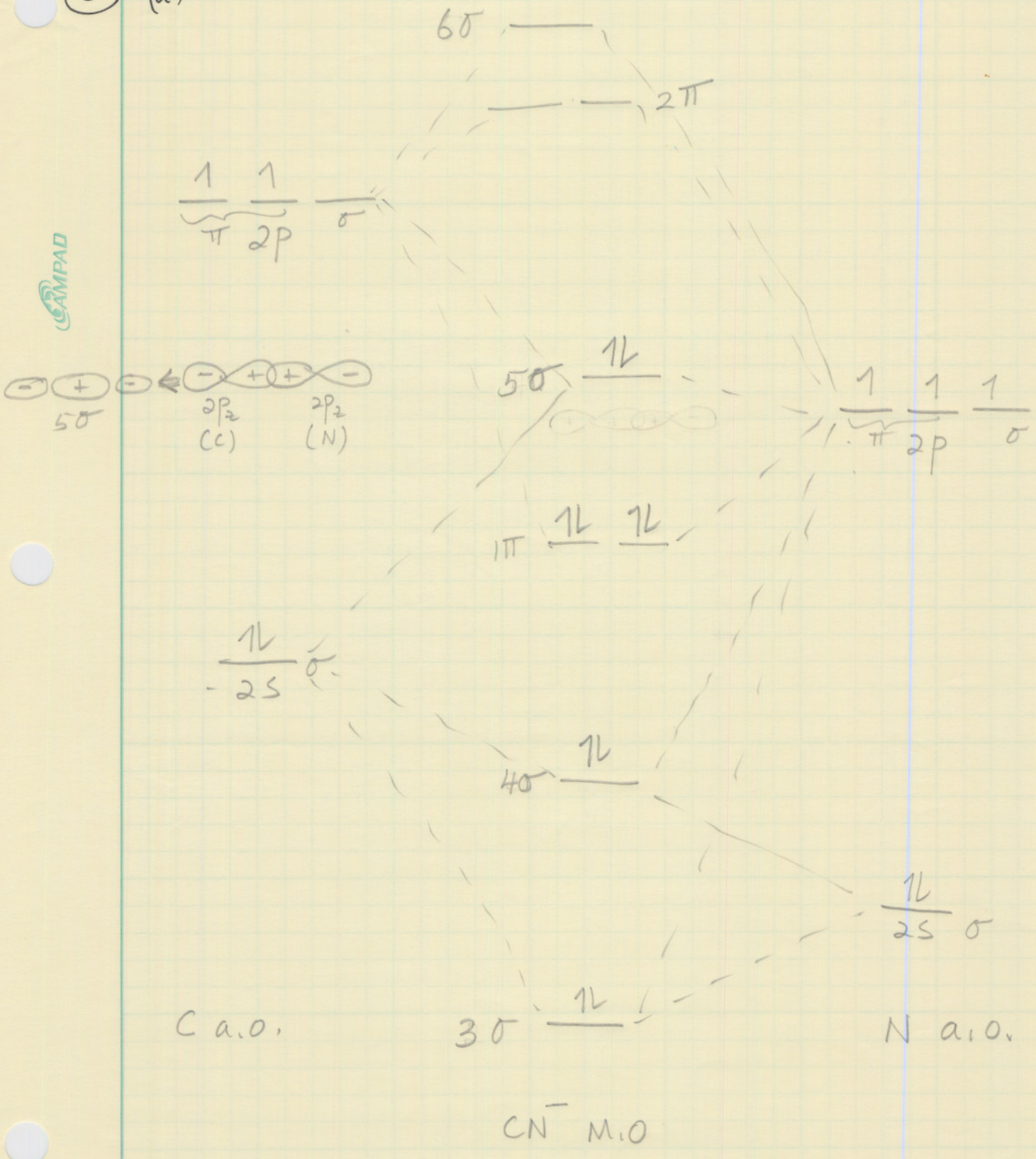
$$NO^+ < NO < NO^-$$

$\longleftarrow$

bond order
bond strength

Higher the bond order, stronger the bond and shorter the bond length.

(5) (a)



(b) bond order = $\frac{1}{2}(8-2) = 3$

(c) When forming a bond with H^+, the electrons involved in the bond are donated by CN^- ion. Therefore these electrons come from the HOMO of the CN^- ion. The HOMO is the 5σ orbital.

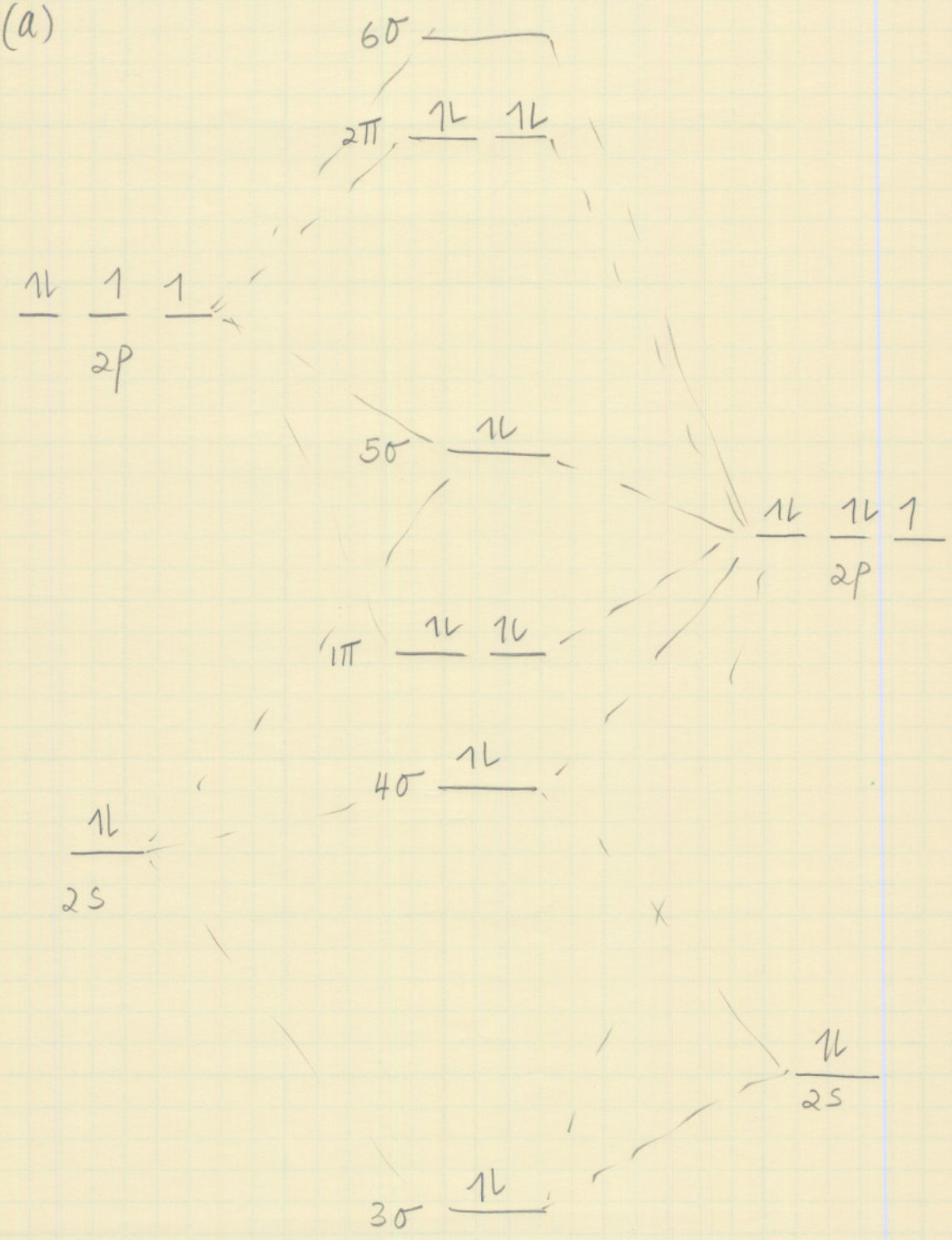
$$\psi_{5\sigma} = A_1 \psi_{2p_z}(N) + A_2 \psi_{2p_z}(C) + A_3 \psi_{2p_s}(C)$$

∴ HOMO has more C character than N character. (i.e. HOMO is centered more on the C atom)

∴ the bond formed with H^+ is with the C atom of CN^-

$$H^+ + CN^- \longrightarrow H-CN$$

(6) (a)

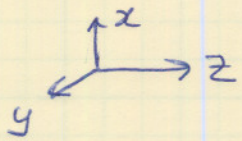


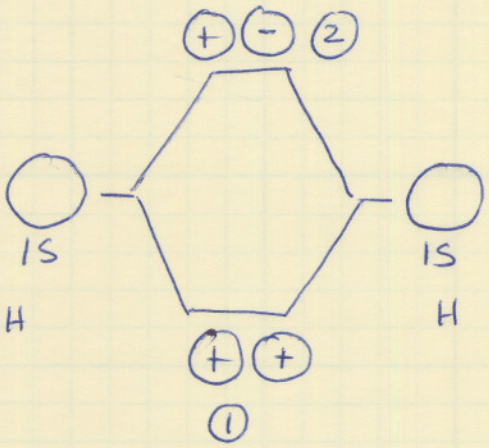
(b) No unpaired electrons. Bond order = $\frac{1}{2}(8-6) = 1$

to form HOF.

(9) Construct group orbitals to represent terminal atoms.

H – C – H $D_{\infty h}$ point group



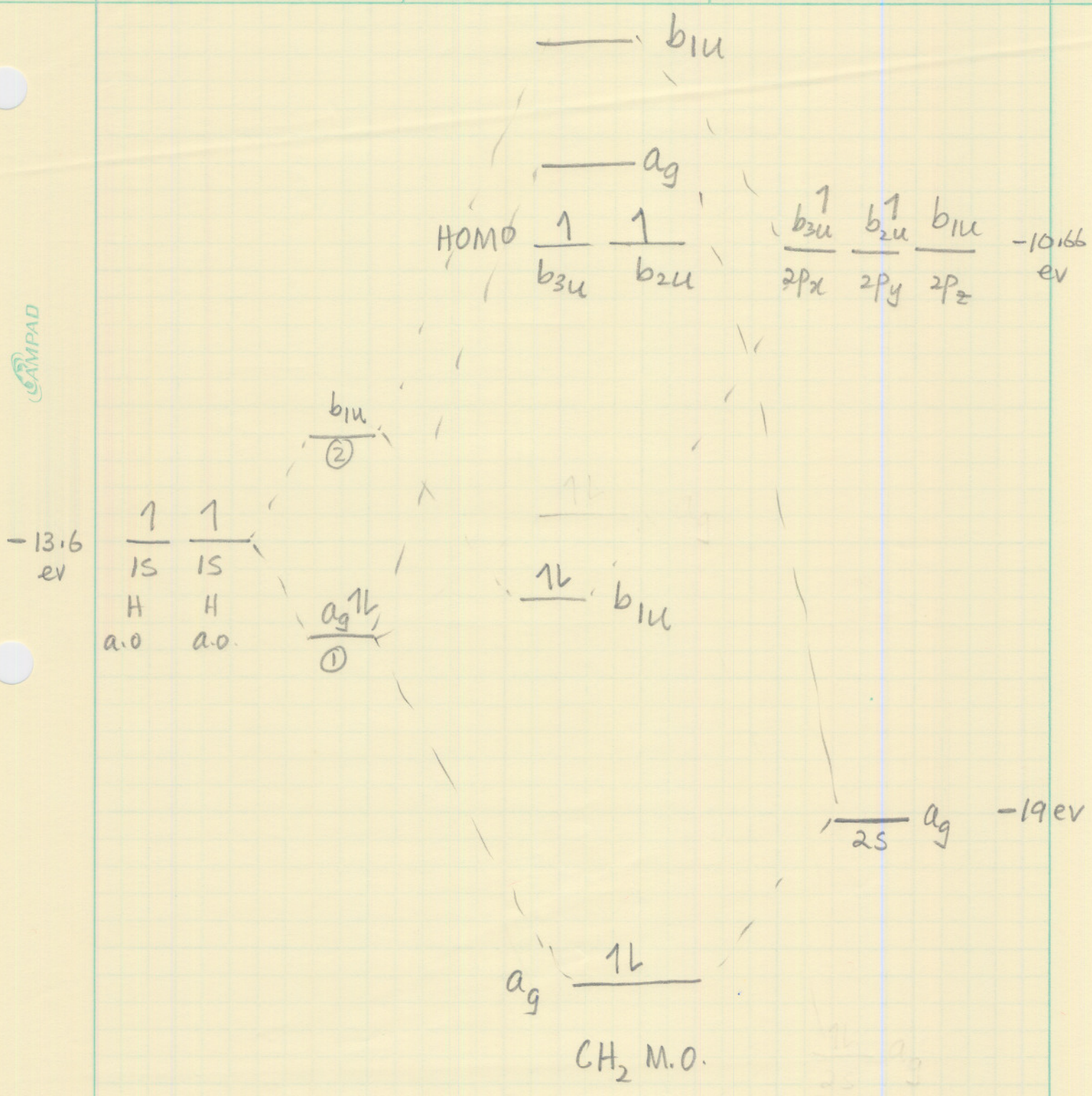


Two group orbitals are formed. Determine their symmetry in D_{2h} point group

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
group orb. ①	1	1	1	1	1	1	1	1	a_g
group orb. ②	1	1	−1	−1	−1	−1	1	+1	b_{1u}

C 2s	a_g
$2p_x$	b_{3u}
$2p_y$	b_{2u}
$2p_z$	b_{1u}

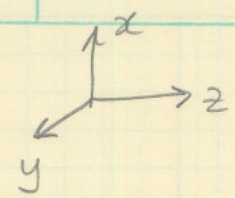
Use the SALC of the terminal atoms and valence orbitals of C to draw the MO diagram

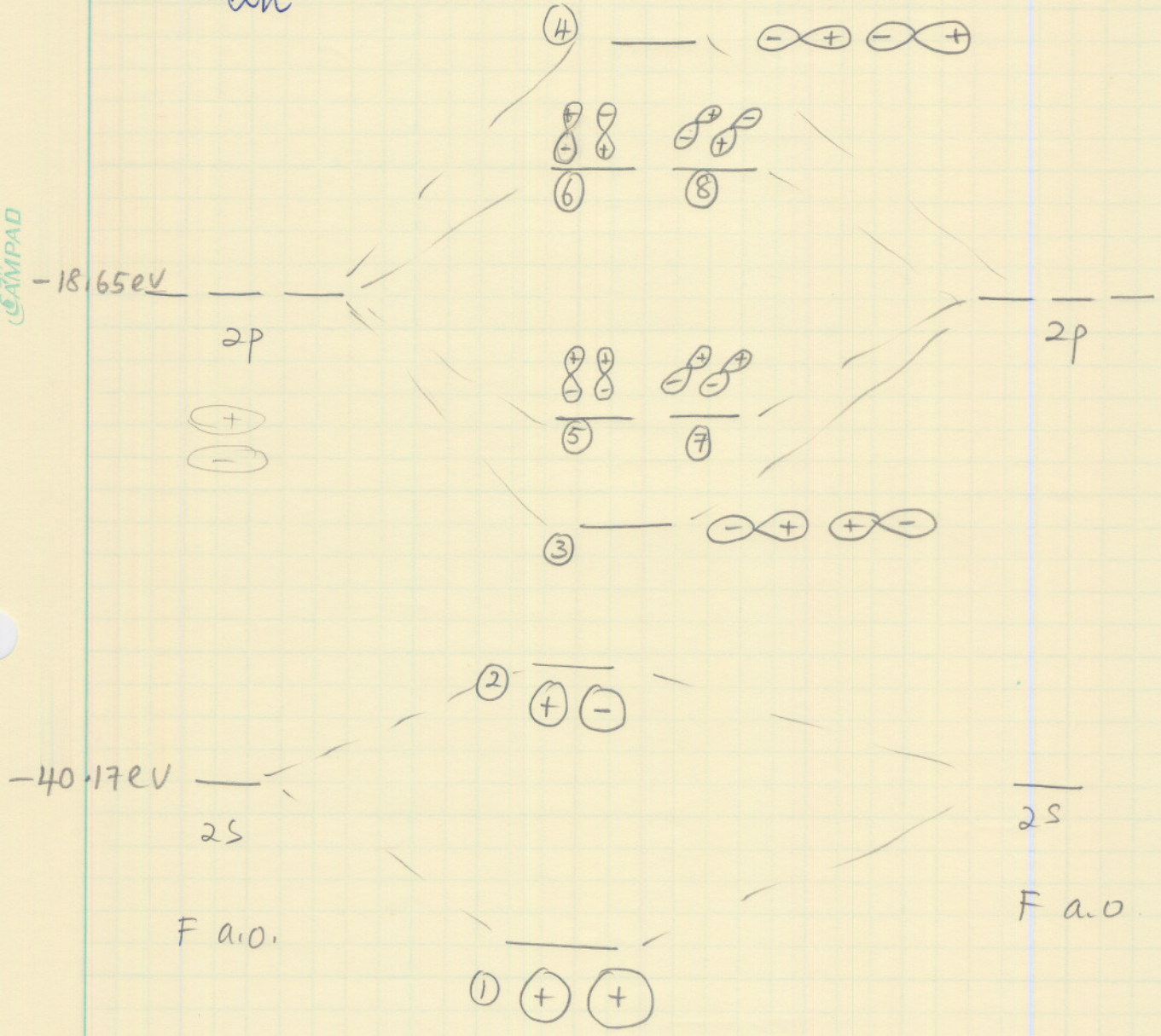


(b) Paramagnetic

(10) F — Be — F

$D_{\infty h}$





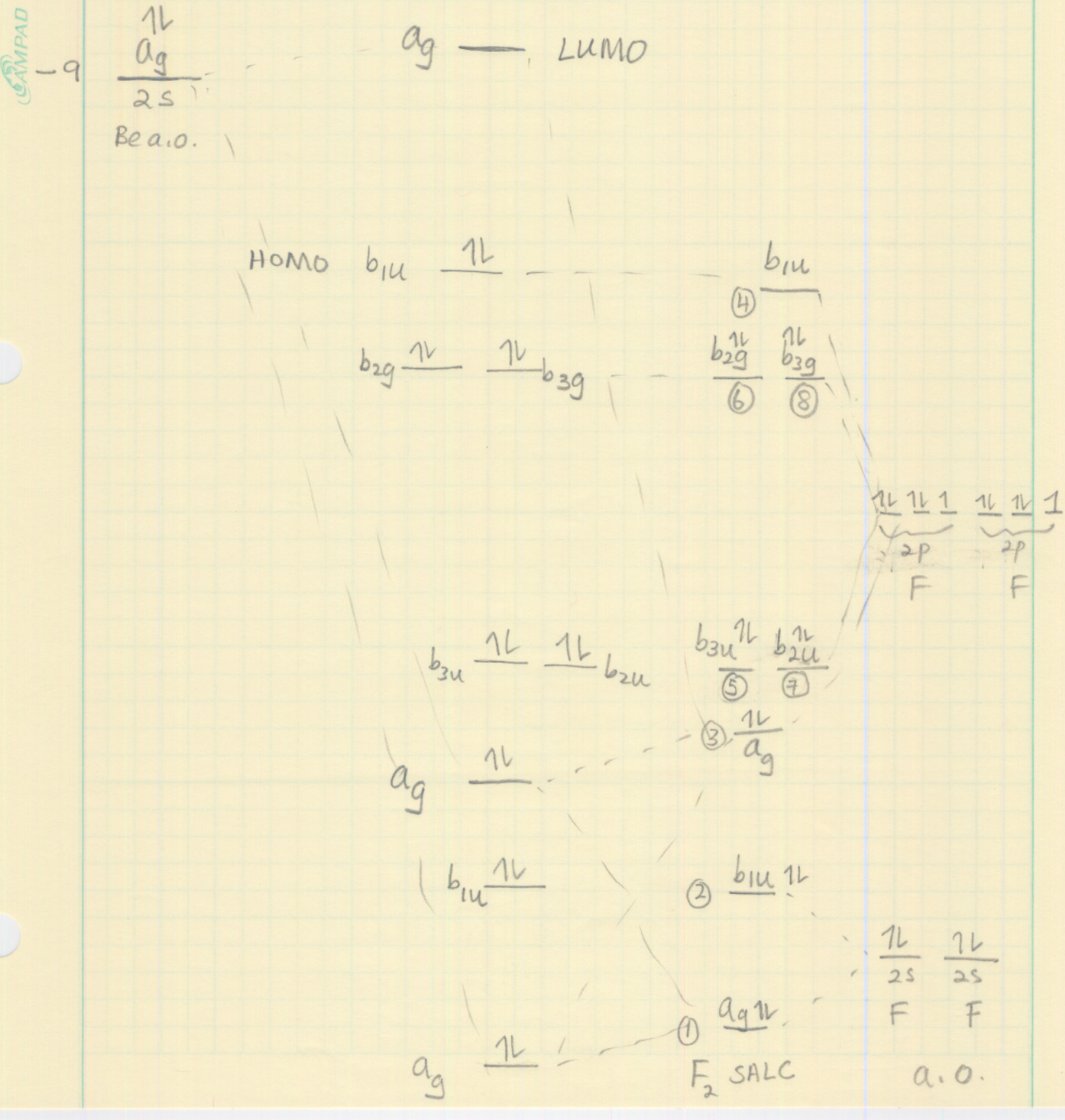
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	symm
①	1	1	1	1	1	1	1	1	a_g
②	1	1	−1	−1	−1	−1	1	1	b_{1u}
③	1	1	+1	1	1	1	1	1	a_g
④	1	1	−1	−1	−1	−1	1	1	b_{1u}
⑤	1	−1	−1	1	−1	1	1	−1	b_{3u}
⑥	1	−1	−1	1	−1	1	−1	+1	b_{3g}

Be valence orbitals 2s = a_g −9.32 eV

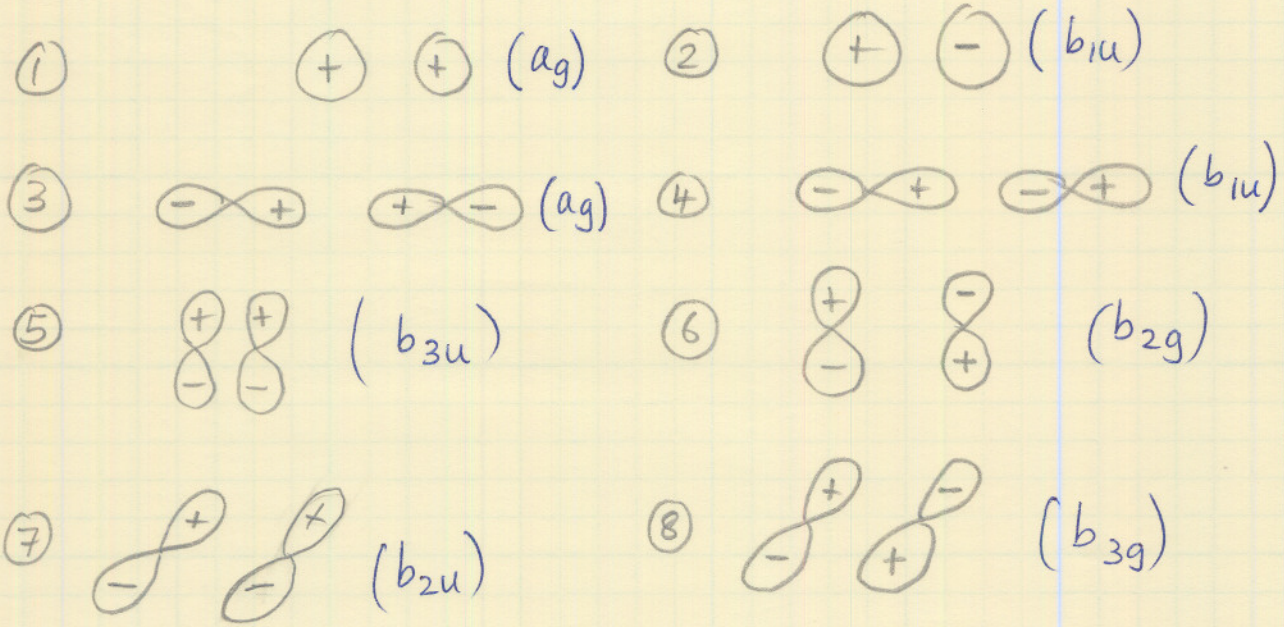
2p_x = b_{3u}

2p_y = b_{2u}

2p_z = b_{1u}



(11) (a) Very similar to the previous problem. Group orbitals are sketched here, with their symmetries



(b) Xe valence orbitals are 5s 5p 5d

	symmetry	can overlap w/ group orbitals if they have similar energy
5s =	a_g	①, ③
$5p_x$ =	b_{3u}	⑤
$5p_y$ =	b_{2u}	⑦
$5p_z$ =	b_{1u}	②, ④
$5d_{z^2}$ =	a_g	①, ③
$5d_{x^2-y^2}$		
$5d_{xy}$ =	b_{1u}	②
$5d_{xz}$ =	b_{2g}	⑥
$5d_{yz}$ =	b_{3g}	⑧