THIRD
EDITION

Solution manual
ORGANOMETALLIC
CHEMISTRY

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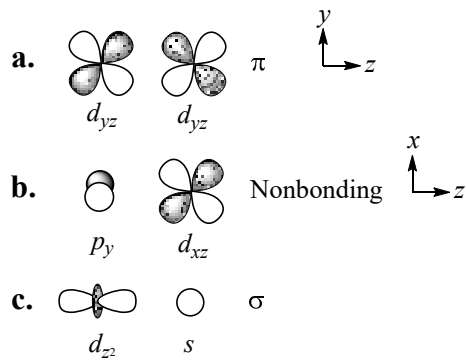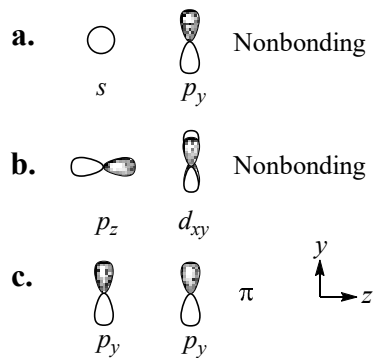GARY O. SPESSARD
GARY L. MIESSLER

Chapter 2:

2-1   **a.** For $n = 3$, quantum number l can have values of **0**, **1**, and **2**.

        b. One electron in the orbital must have $m_s = \dfrac{1}{2}$, the other $m_s = -\dfrac{1}{2}$

        c. p electrons have quantum number $l = 1$; m_l can have the values: **–1, 0, 1**

        d. In a d subshell ($l = 2$) m_l can have the values: **–2, –1, 0, 1, 2**

2-2

2-3

2-4 The molecular orbital diagram of NO is very similar to that of CO (Figure **2-5**).

In NO there is a single electron in a π_{2p}^* orbital. The bond order $= 2(10-5) = \mathbf{2.5}$.

(Alternatively one can count only valence electrons; in that case bond order $=$

$2(8-3) = \mathbf{2.5}$)

Bond orders for the three species:

	Bond order
NO^+	3
NO	2.5
NO^-	2

NO^+, with the highest bond order, has the shortest bond:

	Bond distance (pm)
NO^+	106
NO	115
NO^-	127

2-5

	π orbitals	π* orbitals
N₂		
CN⁻		
CO		
BO⁻		

Increasing difference in electronegativity

Increasingly concentrated on <u>more</u> electronegative atom. (Energy match of MO with *2p* orbital of more electronegative atom becomes better.)

Increasingly concentrated on <u>less</u> electronegative atom. (Energy match of MO with less electrongative atom becomes better.)
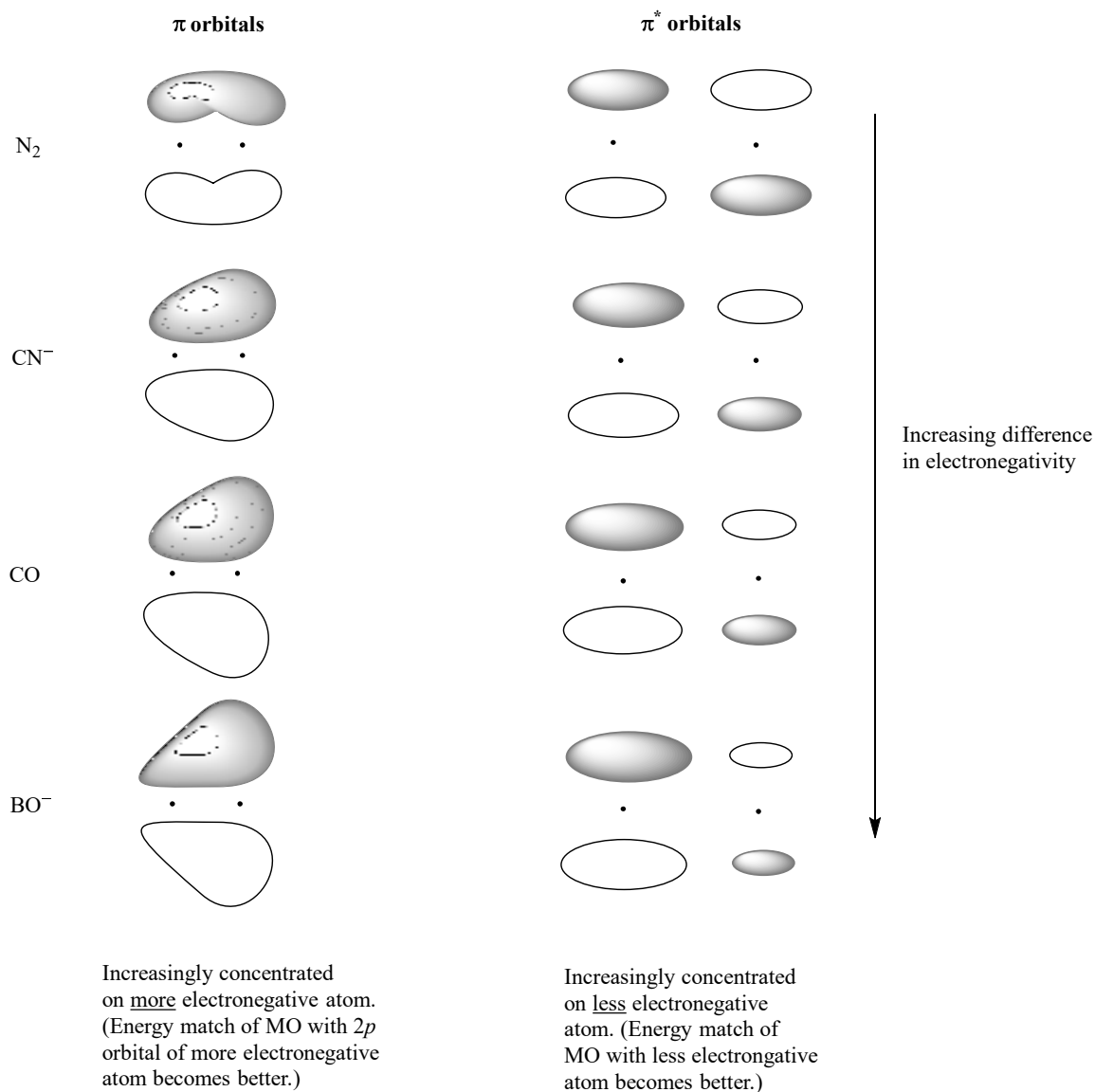
2-6   Calculations should give similar results to problem **2-5**: as the difference in electronegativity of the atoms increases, the lobes of the π orbitals should become increasingly concentrated on the more electronegative atom, and the lobes of the π* orbitals should become more concentrated on the less electronegative atom.

2-7   **a. H₂** (bond order $= 1$; bond order of $H_2^+ = 0.5$)

b. NO⁺ (bond order $= 3$; bond orders of NO and NO^- are 2.5 and 2, respectively)

c. CO (bond order $= 3$; bond order of $CO^+ = 2.5$)

2-8

a. Linear:
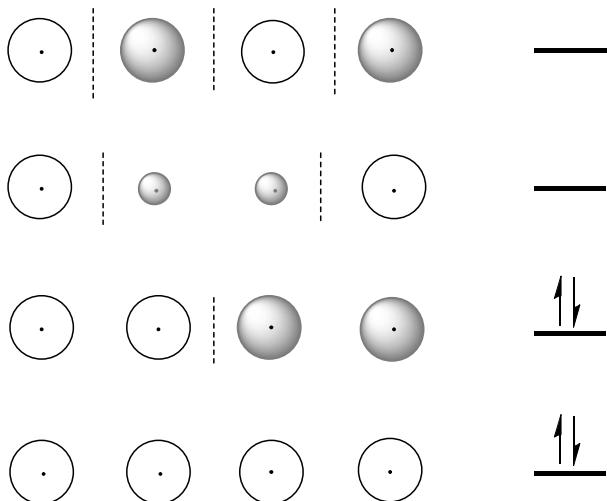
b. Square:
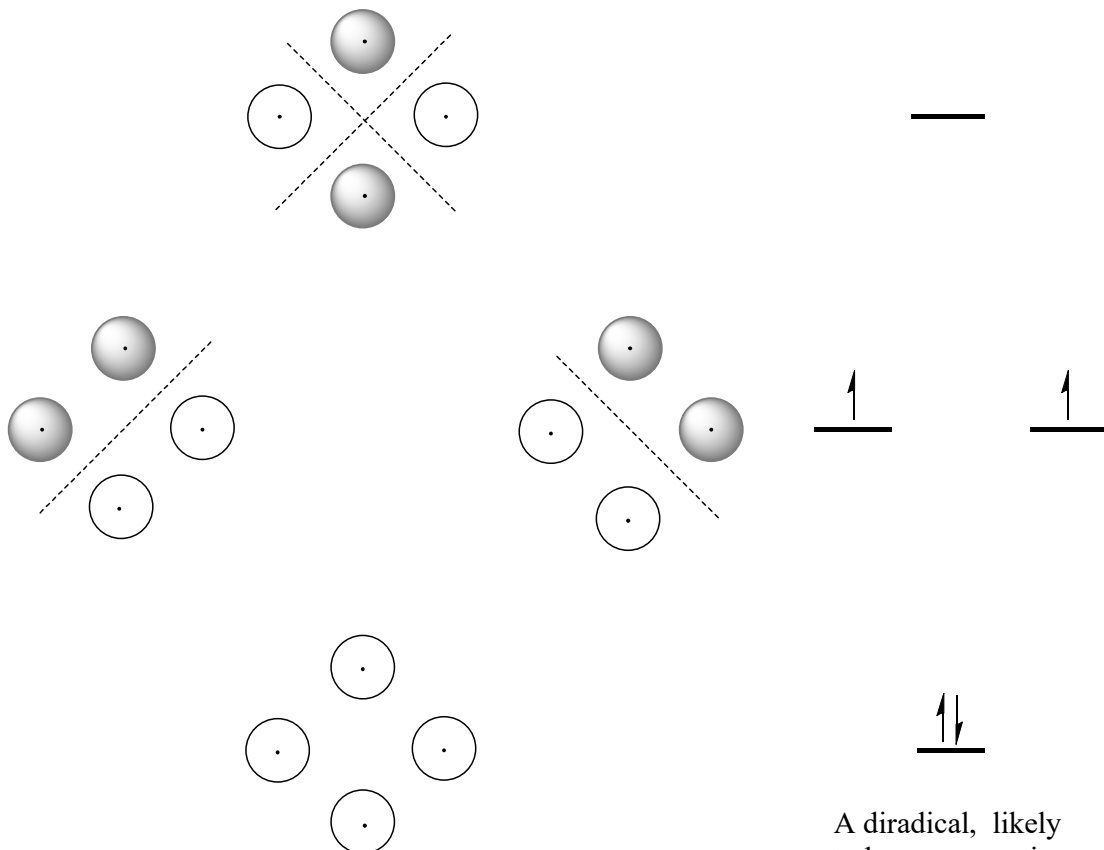
A diradical, likely to be more reactive than linear case.

2-9

N_3^-	Central Atom Orbitals Suitable for Interaction	Group Orbitals	Type of Interaction
	s		Sigma
			Sigma
	p_z		Sigma
			Sigma
	p_x		Pi
			No interaction
	p_y		Pi
			No interaction
	N	N · N	

**2-10** The MO diagram of O_3 will be similar to that for CO_2 (Figure **2-7**). However, the two degenerate π bonding and the two π antibonding MOs will convert to π-type bonding and antibonding MOs (resulting from interaction of the central oxygen atom's $2p_y$ atomic orbital and the group orbital composed of the $2p_y$ atomic orbitals from the outer oxygen atoms) and σ-type bonding and antibonding MOs (involving the combination of the $2p_x$ orbital of oxygen with the group orbital involving the $2p_x$ orbitals from the outer two oxygen atoms). These interactions are shown below:
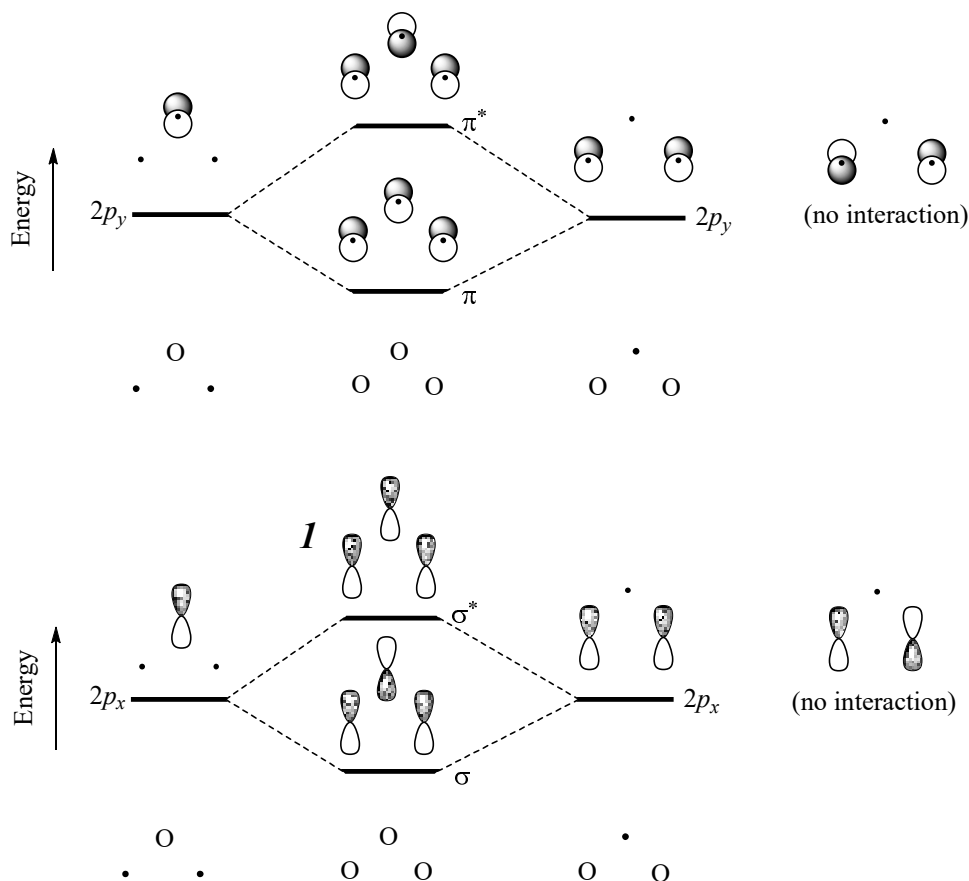
MOs resulting from combination of the $2s$ and $2p_z$ orbitals from the central oxygen atom and group orbitals comparable to 1 and 2 in Figure **2-7** yield the following MOs:
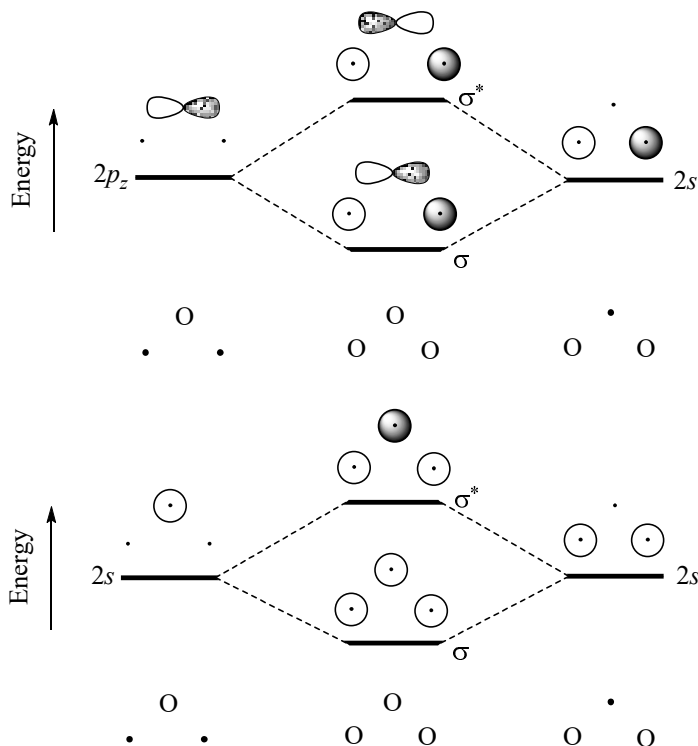
The remaining MOs of O_3 can be generated using the same procedure as above.

Since O_3 has two more electrons than CO_2, these extra electrons would likely reside in an MO that is antibonding (perhaps orbital *1* above). By placing two electrons in an antibonding orbital, the bond order of O_3 is decreased by one compared to CO_2. Thus, one would expect fewer than four bonds distributed among the three oxygen atoms, which is consistent with the Lewis structure of O_3.

2-11

(side view)   Relative energy*

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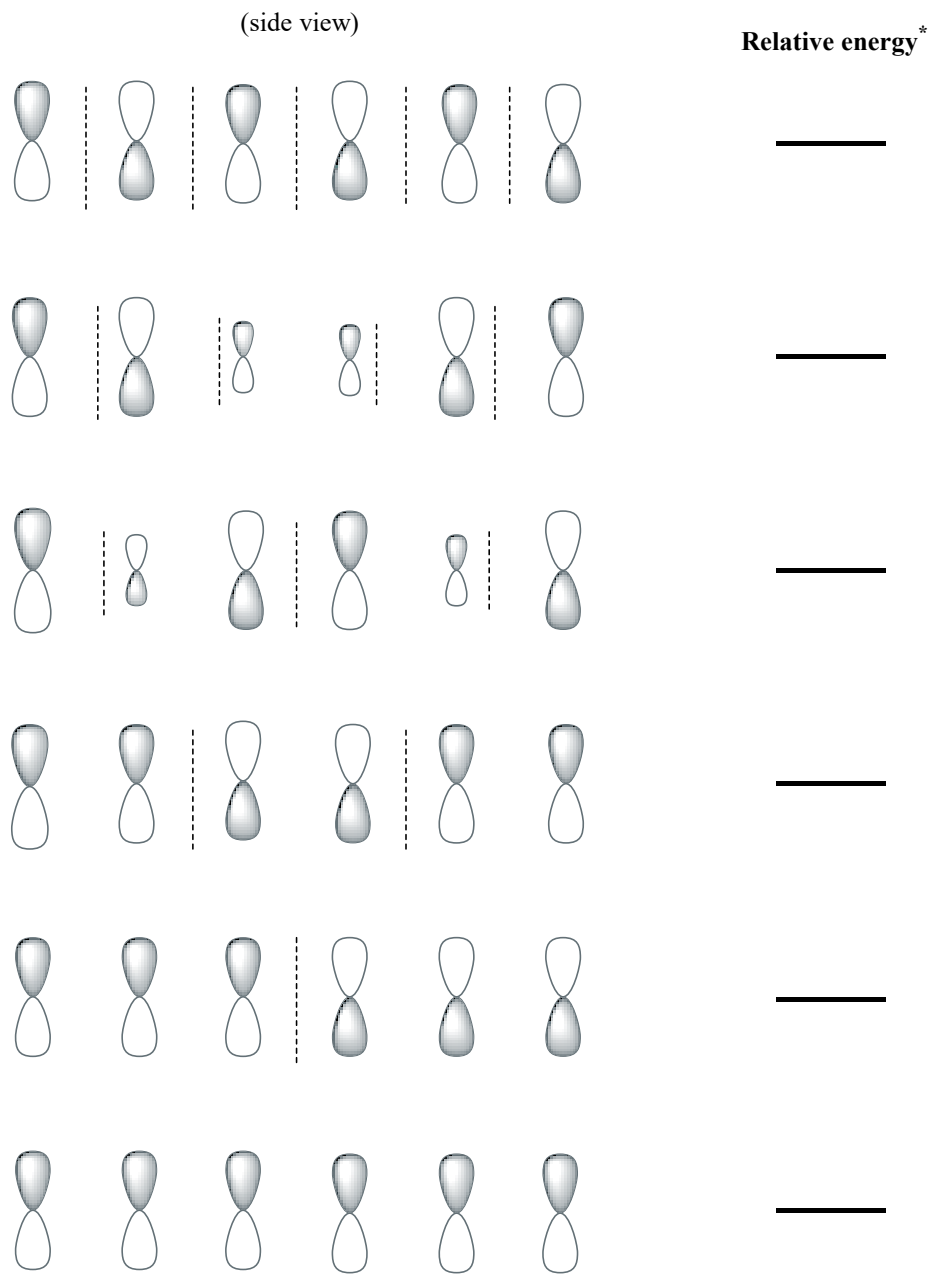
*Not all to scale; all are non-degenerate

2-12

Relative energy