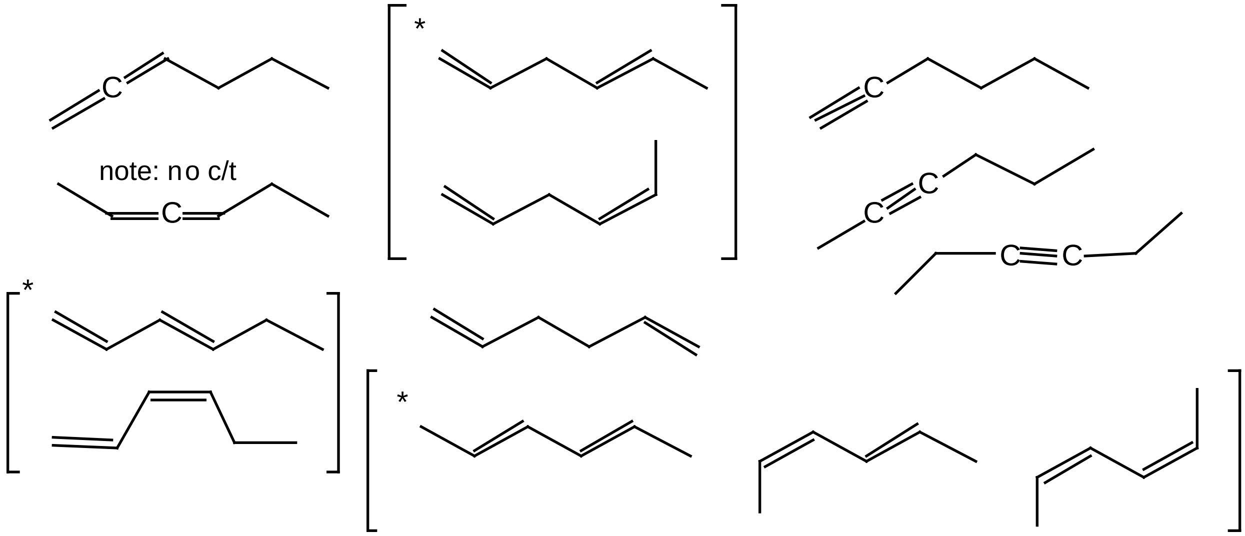
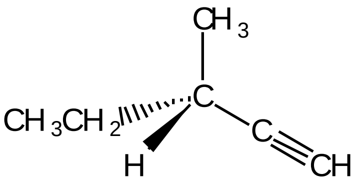
Answers to Hour Examination #1, Chemistry 301X-2005

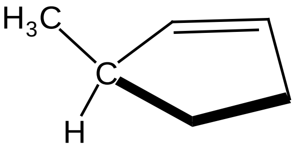
1.



There are, of course, many many possible answers to the second part. Here are two:



(*S*)



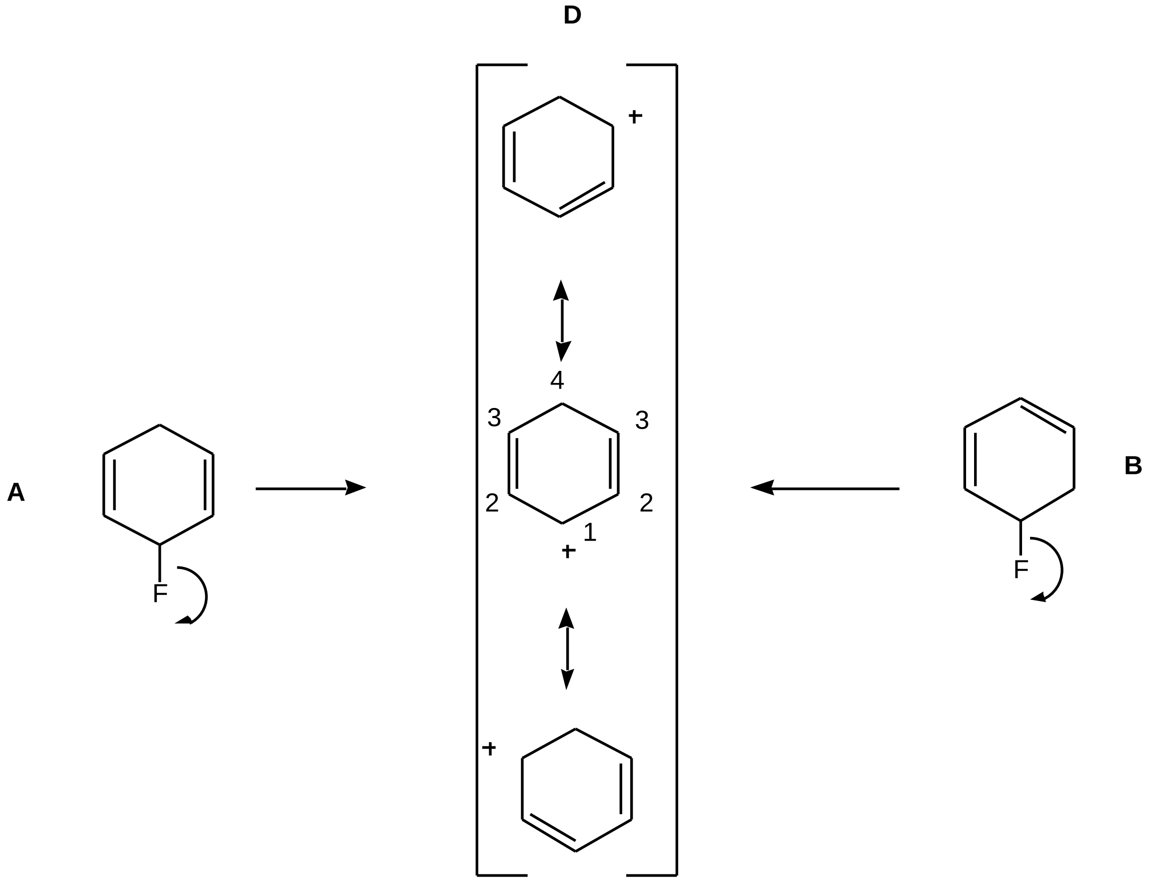
(*R*)

2. (a)

Bonds broken = one methane C—H = 105 kcal/mol
Bonds made = one C—C = ~85 kcal/mol and one C—H = ~100 kcal/mol

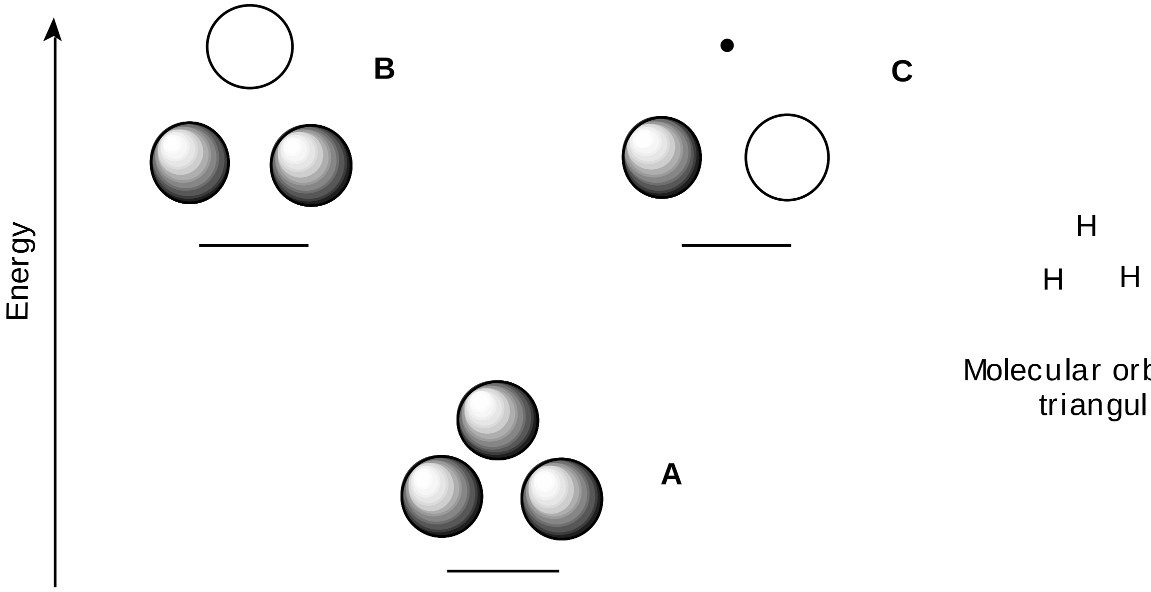
So, 185 minus 105 = 80 kcal/mol exothermic; $\Delta H = -80$ kcal/mol

(b) The two starting materials ionize to give exactly the same resonance-stabilized carbocation, **D**:



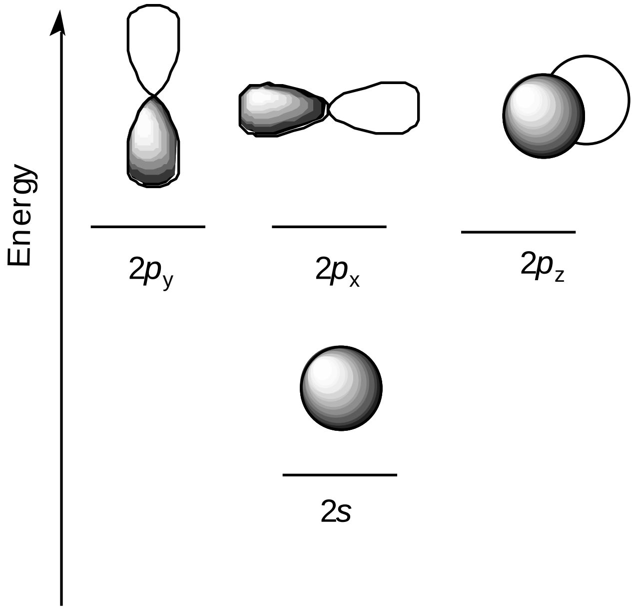
3.

(a)



Molecular orbitals for triangular H_3

orbitals for N



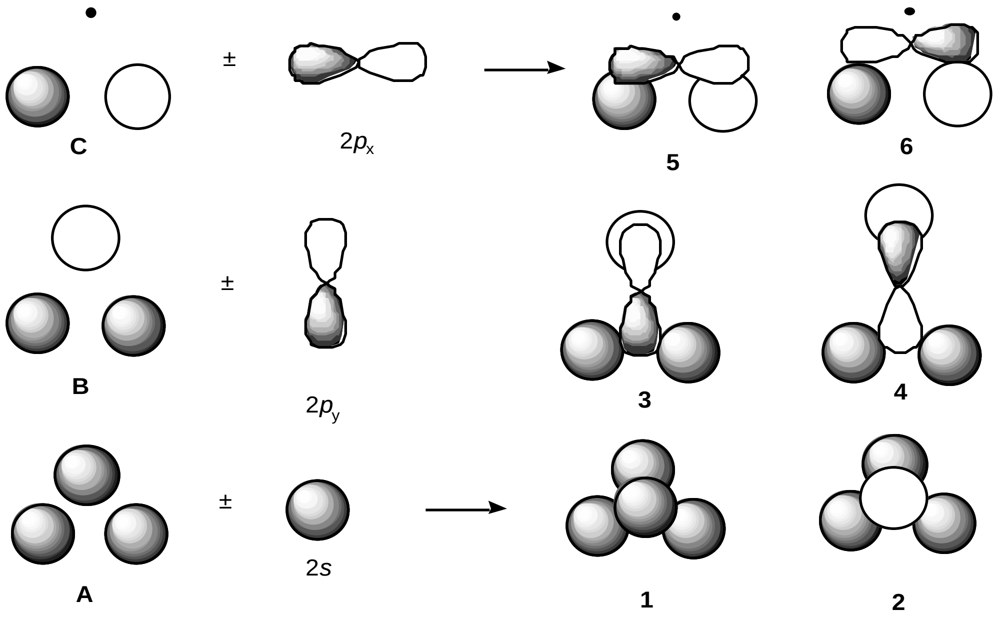
(b)

$2s \pm$ **A**

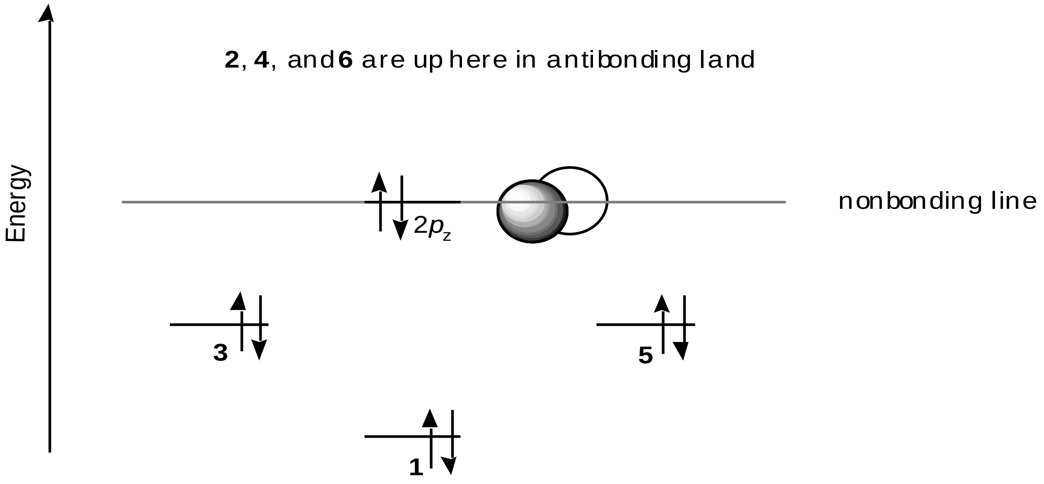
$2p_y \pm$ **B**

$2p_x \pm$ **C**

$2p_z$ does not interact.
Here are the new MOs:



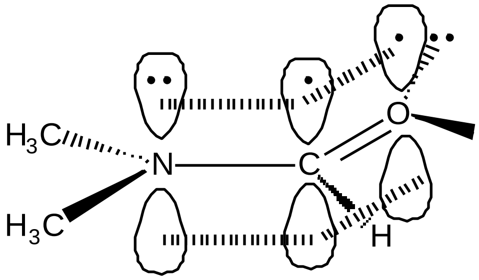
(c,d) Here is the ordering (count nodes) and the electron occupancy:



4.

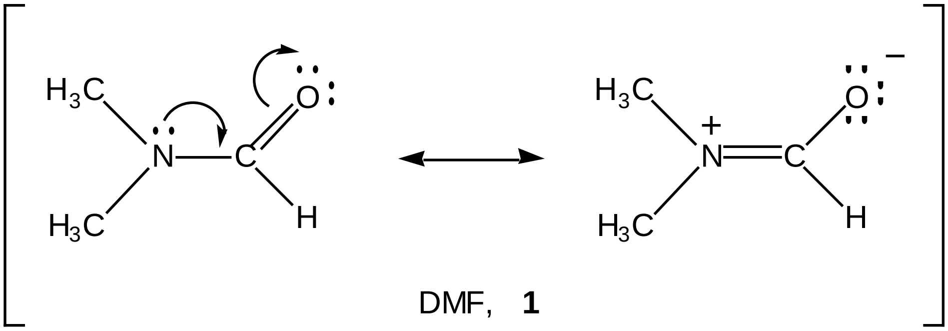
(a) 107° is very close to 109.5°, so ammonia is very close to sp^3 hybridized.

(b) If N is hybridized sp^2, the three 2*p* orbitals align perfectly in a flat structure, and delocalization of the lone pair on N is optimal.



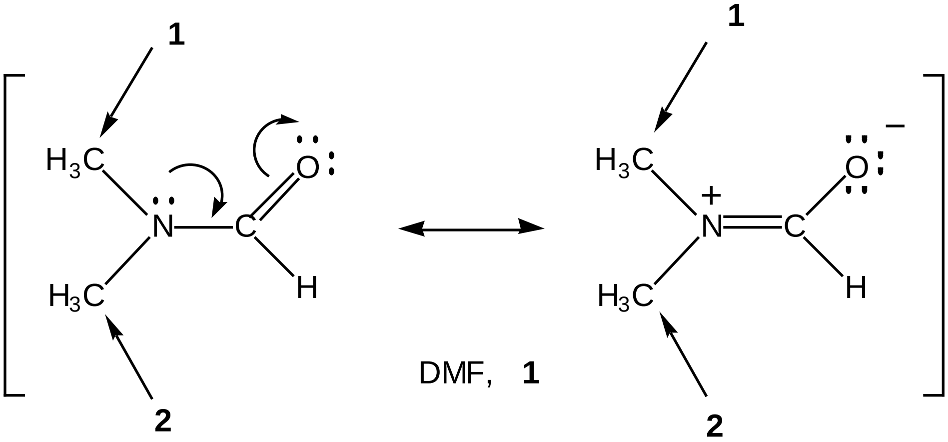
N, C, O all sp^2

Delocalization of electrons here is highly stabilizing (see resonance forms below).



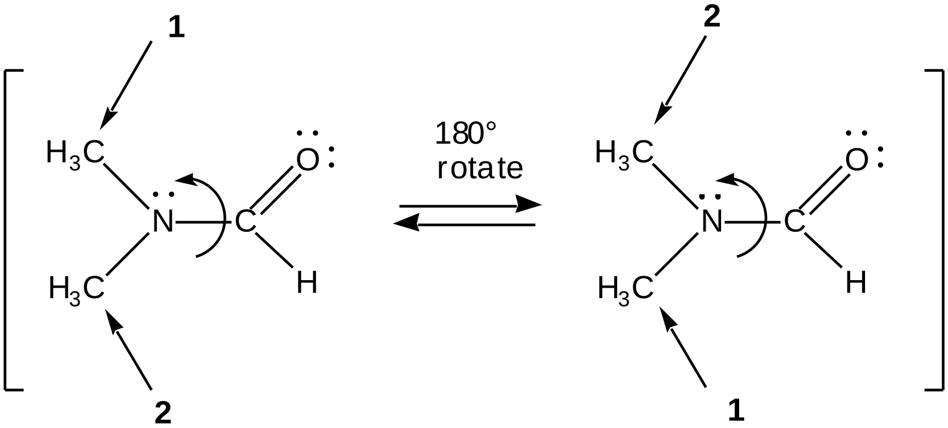
DMF, **1**

(c) Unless rotation is fast, there will be two different methyls in the flat structure. Note the “double bond character” to the C—N bond - that partial double bond will make rotation difficult. At room temperature, rotation must be slow. Of course, higher temperature means more energy and eventually rotation becomes possible. At 111° C the two methyls become equivalent through rotation.



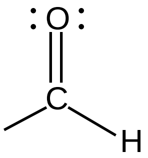
DMF, **1**

at high temperature:



5.

(a)

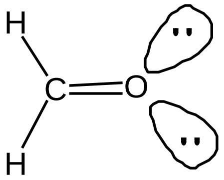


Formaldehyde, **2**

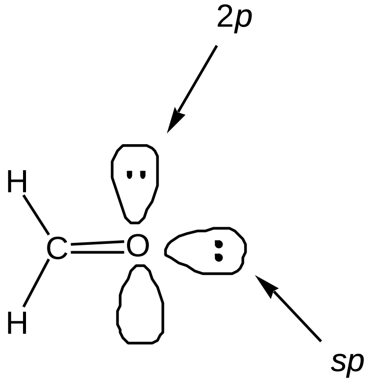
(b) *sp*^{2}

(c) *sp*^{2} or *sp* pictures below

(d)



top view of O = *sp*^{2}

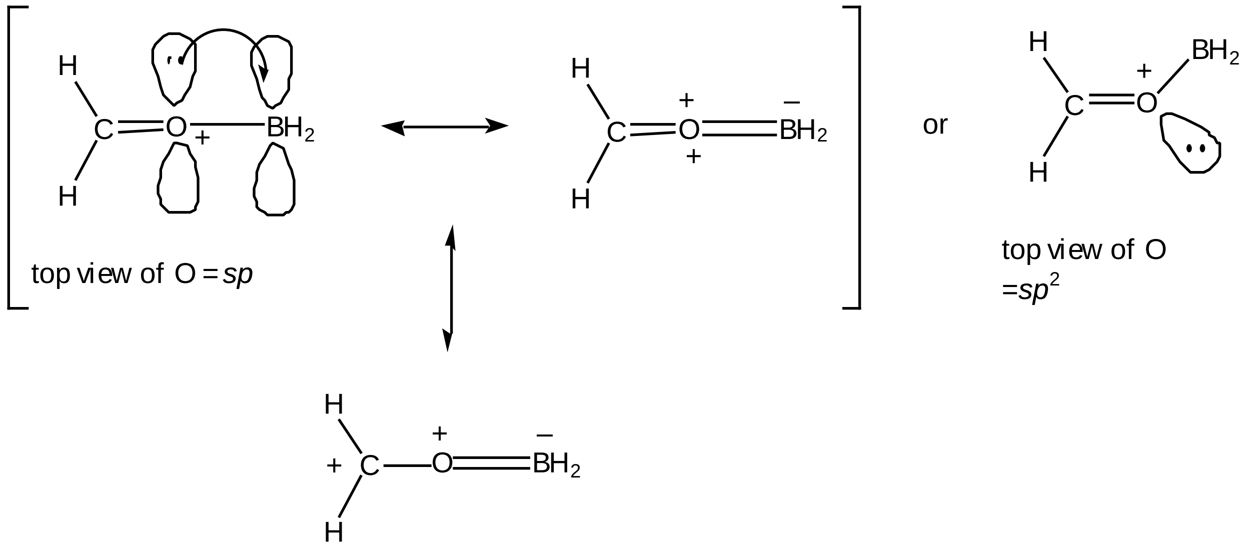


top view of O = *sp*

There are two different lone pairs in the *sp* hybridized structure, but only one in the *sp*^{2} version. Oxygen must be *sp*.

(e) Oxygen is hybridized *sp*^{2} in the bent form, *sp* in the linear one.

Note how in the *sp* version the empty 2*p* orbital in the BH$_2$-substituted molecule can delocalize = stabilize the lone pair in the filled 2*p* orbital.



The linear form is better (lower energy). Those other forms are not great, that's for sure, but they still help (lowers energy of the resonance hybrid) a little. In the bent form there is not much overlap between the boron 2*p* and the oxygen *sp*^{2}.