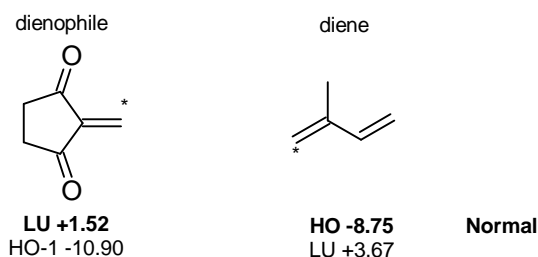


SELECTED ANSWERS

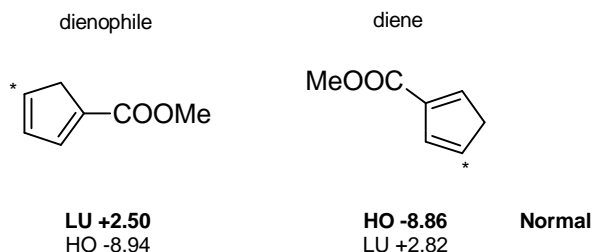
Main comments:

- First rxn – dienophile orbital is HOMO-1, not HOMO
- Second rxn – convert E_{rel} into K_{eq} or concentrations
- Second rxn – using FMO to determine orientation of reactants is rather ambiguous. Don't worry if that part didn't make sense.

1. Frontier orbital energies shown in eV (**bold = MO for dominant interaction, * marks reacting atom that makes largest contribution to dominant MO**). Each reaction is “normal” because $HO_{diene}-LU_{dienophile}$ is the dominant interaction (normal) and $HO_{dienophile}-LU_{diene}$ (inverse electron demand) is less important.



Notice that you should give HOMO-1 energy for the dienophile above (not HOMO) because HOMO-1 is the CC pi bonding MO



The observed product is not consistent with the orbital coefficients in the dominant MOs (notice that the difference between the terminal atoms in the diene HOMO is very small and it is necessary to consult the table of mixing coefficients).

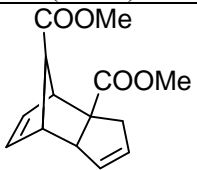
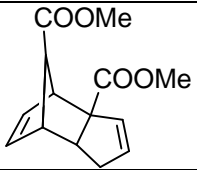
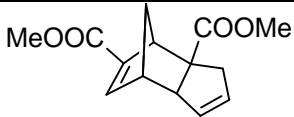
2.

a.

Isomer	E_{total} (au) (kcal/mol)	Rel E_{total} (kcal/mol)	[diene]/[3b]
3a	-417.092011 (-261729.408)	+6.13	0.00003
3b	-417.101778 (-261735.537)	$\equiv 0$	$\equiv 1$
3c	-417.099702 (-261734.234)	+1.30	0.11

Use ΔE_{total} in place of ΔG° to estimate relative equilibrium concentrations. The values indicate that **3b** and **3c** will co-exist with **3b** as the major isomer, but **3a** will be an insignificant part of the mixture. *If* the isomers are in rapid equilibrium (and if HF/3-21G ΔE_{total} values are reliable), reactions should be limited to **3b/3b**, **3b/3c**, **3c/3c**.

b.

Isomer	HO (eV)	LU (eV)	Pairing	Dominant LU-HO (eV)	Fastest (FMO)	Product (FMO)
3a	-8.77	3.49	3a-3b	11.27 LU(3b)-HO(3a)	←	
3b	-8.94	2.50	3a-3c	11.59 LU(3c)-HO(3a)		
3c	-8.86	2.82	3b-3c	11.36 LU(3b)-HO(3c)	(←)	
			3a-3a	12.46		
			3b-3b	11.44		
			3c-3c	11.68		

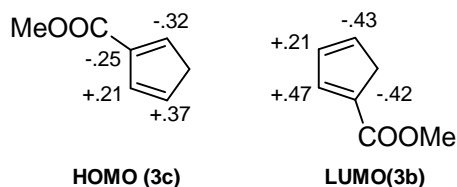
The smallest HOMO-LUMO gap is predicted for **3a** + **3b**. This reaction is probably not observed because the concentration of **3a** is so small.

The smallest HOMO-LUMO gap involving **3b** and **3c**, the only species present in significant concentration, is **3b** + **3c**. Dimerizations involve slightly weaker FMO interactions.

I regret asking you to predict the 'FMO Product'. ☹ Since both reactants are dienes, there are two possibilities: diene #1 acts as diene and diene #2 acts as dienophile, or the reverse. Since the "dienophile" diene can use either of its CC double bonds, this doubles the possibilities again.

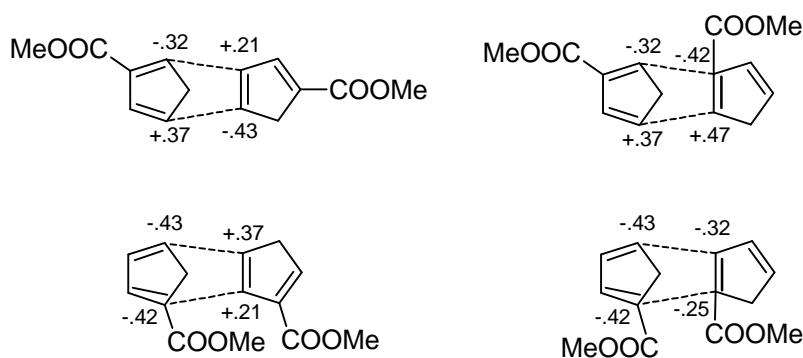
And since there are two regioisomers for each pair of reactants, this doubles the possibilities yet again. In other words, there are 8 possible cross-products for **3b** + **3c**.

Rather than work through all 8 possibilities for the 3 different cross-reactions, I'll just kind of point you in the right direction. First, remember that we are interested only in the dominant MO interaction. For **3b** + **3c**, this is LUMO(**3b**) + HOMO(**3c**). Next, we obtain the orbital mixing coefficients for these orbitals. They are shown below:

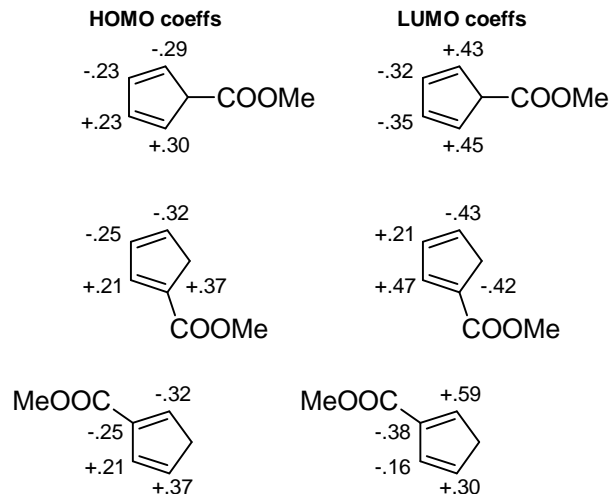


Next, we decide on *roles* for the two reactants. The roles are usually obvious, but since each molecule can be a diene or a dienophile, we have to consider both possibilities. A *normal* cycloaddition would be diene(**3c**) + dienophile(**3b**). An *inverse electron demand* addition would be diene(**3b**) + dienophile(**3c**).

The following figure shows two *normal* possibilities (top) and two *inverse electron demand* possibilities (bottom). Again, the reason for so many possibilities is because either CC double bond in a diene can function as a dienophile.



The combination in the upper right produces the best overall combination of coefficients: $(.47)(.37)+(-.32)(-.42)$ (multiply the coefficients to estimate overlap between MOs). Similar reasoning was used to predict the structures of the other two cross-products listed in the 'Product (FMO)' column. The relevant MO coefficients are shown in the next figure.



Of course, most Diels-Alder reactions are not so complicated.

- Usually we know immediately which molecule is the diene and which is the dienophile.
- Usually there is a clear-cut dominant FMO interaction, so the analysis is not so convoluted.

That said, it must be admitted that the FMO model of transition states is very simplistic and often gives wrong answers for Diels-Alder reactions. Serious computational chemists rely on model transition state energies, not FMO interactions, to predict the outcome of a chemical reaction.