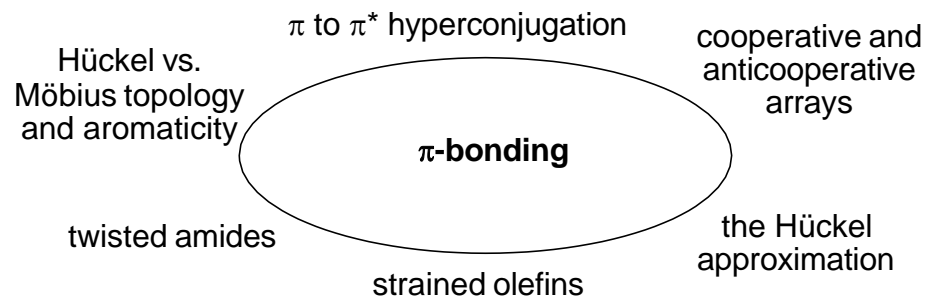


π -Bonding

Eugene E. Kwan

September 14, 2011

Scope of LectureHelpful References

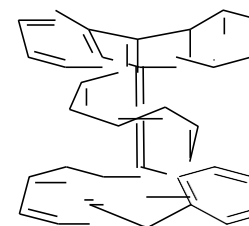
- Weinhold, F.; Landis, C. Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective Cambridge, Cambridge University Press, **2005**.
- Clayden, J.; Moran, W.J. "The Twisted Amide 2-Quinuclidone: 60 Years in the Making." *ACIE* **2006**, *45*, 7118-7120.
- Carroll, F.A. Perspectives on Structure and Mechanism in Organic Chemistry. Pacific Grove, California, Brookes/Cole Publishing Company, **1998**.

Key Questions

(1) Which is more stabilized by conjugation?

(2) Are there significant differences in the π -bonding of benzene and borazine?(3) Is this an amide? How do β -lactams work?

(4) Is this aromatic?



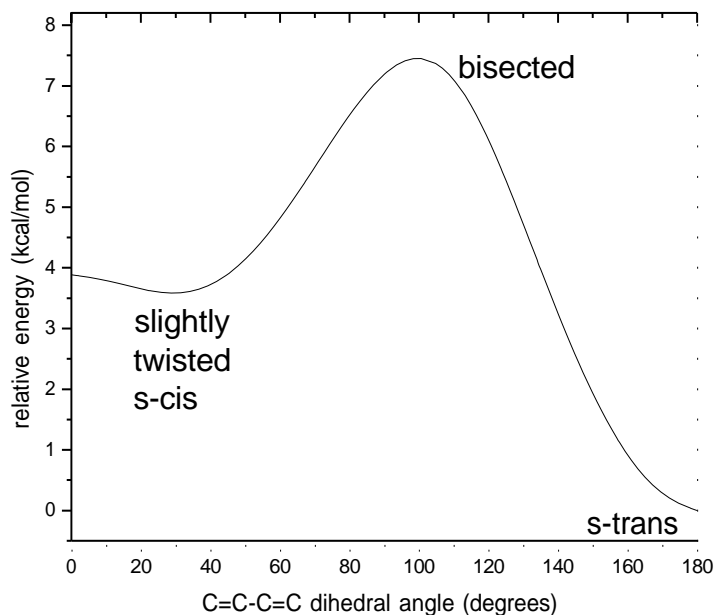
Conjugated Olefins

Consider butadiene. Please rank its conformers in terms of their stability:



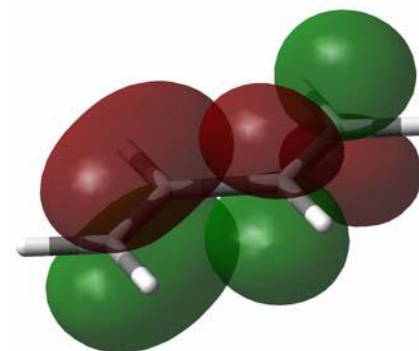
Of course, the bisected form is "not conjugated," and therefore quite unstable. In donor-acceptor terms, it does not possess complementary, bi-directional π to π^* interactions.

Here is butadiene's rotational energy profile (B3LYP/6-31g(d)). The C=C-C=C dihedral angle is incrementally frozen, and all the other geometric parameters are allowed to relax. This is sometimes called a "relaxed scan."



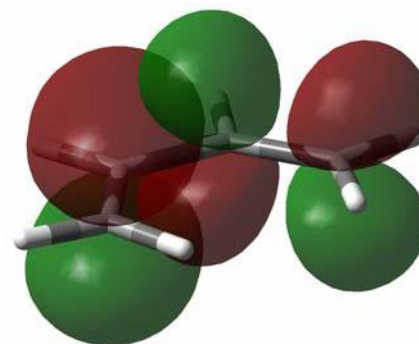
Thus, the ranking is s-trans (0 kcal/mol), slightly twisted s-cis (3.5 kcal/mol), bisected (7.6 kcal/mol). The twisting is due to the steric interaction between the in-plane C-Hs.

The π/π^* overlap in the s-trans conformation is a bit better than in the s-cis conformation, a general trend in dienes. Here are the PNBs:

**s-trans:**

$$S = 0.22$$

estimated energy/
interaction: 14.9
kcal/mol

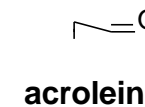
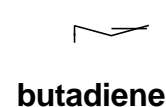
**s-cis:**

$$S = 0.20$$

estimated energy/
interaction: 12.8
kcal/mol

We can consider the perturbative estimates of the π to π^* donor-acceptor interactions a measure of the "conjugation energy." (Many complicated definitions of this exist, but we shall not trouble ourselves with such details.) Note that $(14.9 - 12.8) \times 2 = 4.2$, which is about the s-cis/s-trans difference.

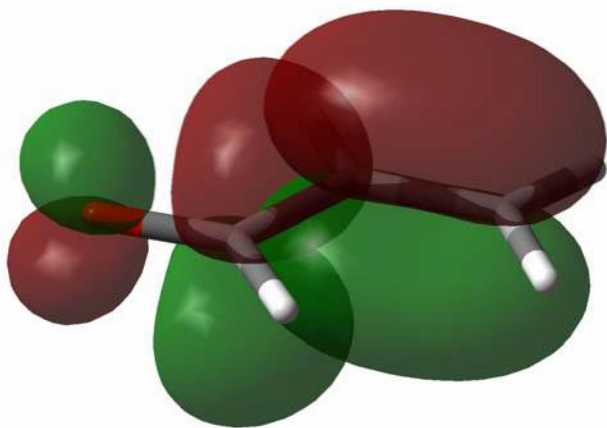
Do you think the stabilization in acrolein is bigger or smaller than in butadiene?



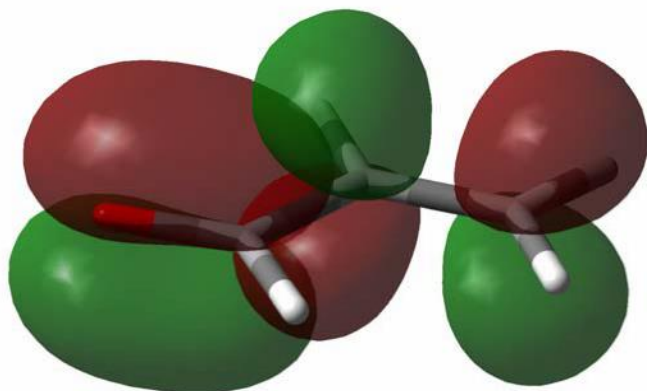
Conjugated Olefins

In acrolein, there are two donor-acceptor interactions (shown below as PNBOs):

(1) $\pi(\text{C}=\text{C})$ to $\pi^*(\text{C}=\text{O})$ ($S=0.26$, interaction energy: 20.4 kcal)



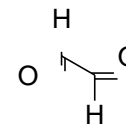
(2) $\pi(\text{C}=\text{O})$ to $\pi^*(\text{C}=\text{C})$ ($S=0.17$, interaction energy: 6.5 kcal)



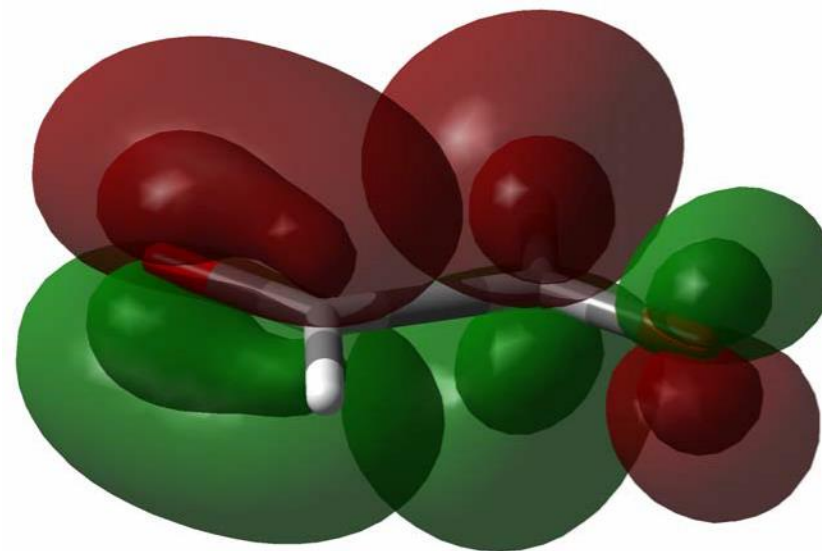
The overall estimate of resonance energy, 27.1 kcal/mol, is less than in butadiene, where it was 29.8 kcal/mol.

So, the electronegativity imbalance in the carbonyl group improves interaction (1) but makes interaction (2) worse. Overall, the stabilization is worse. This is a general feature of donor-acceptor interactions: equal, bidirectional interactions are better than unequal ones.

Given your knowledge, what can you predict about glyoxal?



$S=0.19$

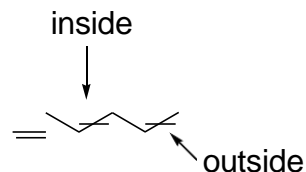


The directionality of the donor-acceptor interactions is once again matched (look at the higher isosurfaces on the inside). However, not all double bonds are created equal; these $\pi(\text{C}=\text{O})$ to $\pi^*(\text{C}=\text{O})$ interactions are only worth 7.7 kcal/mol.

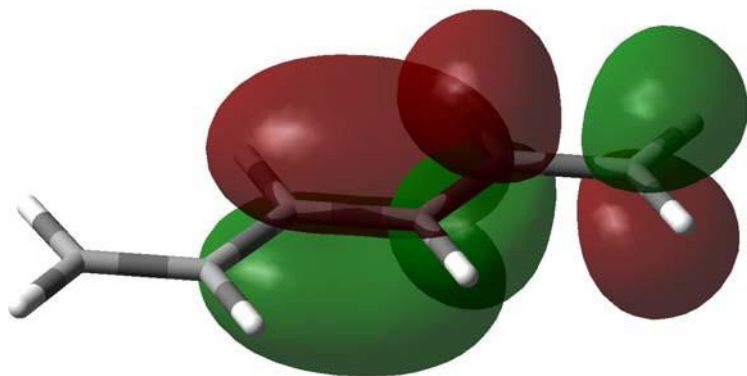
(All of these calculations were done at B3LYP/6-31g(d).)

Conjugated Olefins

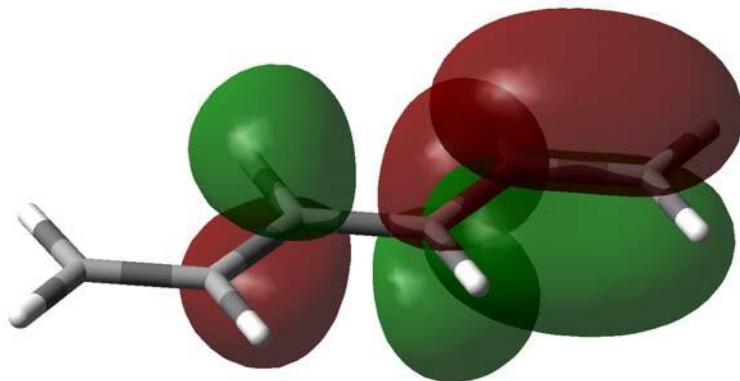
What do you think happens with all s-trans hexatriene? Will the resonance energy here just be _____ times the π to π^* interaction in butadiene?



(1) $\pi(\text{inside})$ to $\pi^*(\text{outside})$: $S=0.22$



(2) $\pi(\text{outside})$ to $\pi^*(\text{inside})$: $S=0.22$

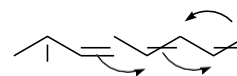


Evidently, the inside olefin is a bit different from the ones on the outside. Let's add up all the resonance stabilizations:



In butadiene, the resonance energy/olefin is 14.9 kcal/mol; here is 20.1 kcal/mol. So there is a *cooperative* benefit to having three olefins together.

In octatetraene, the effect is even stronger:

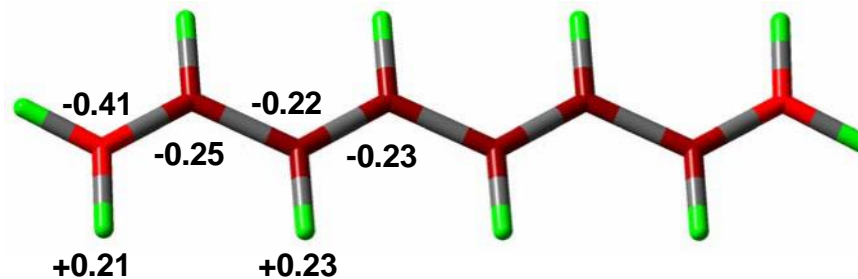


inside to outside: 2×15.9
 inside to inside: 2×16.4
 outside to inside: 2×14.6
 average: 15.6 kcal/mol

As the chain gets longer, there are more and more olefins on the inside and fewer terminal ones (by proportion). So the resonance stabilization/olefin levels out eventually.

Why are the hyperconjugations on the interior stronger?

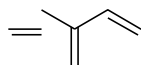
The polyolefins get slightly positively charged at the ends, as shown by the NBO charges below. Note the alternation:



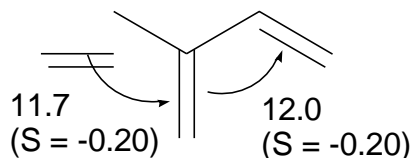
As noted above, this asymmetry reduces stabilization.

Cross-Conjugation

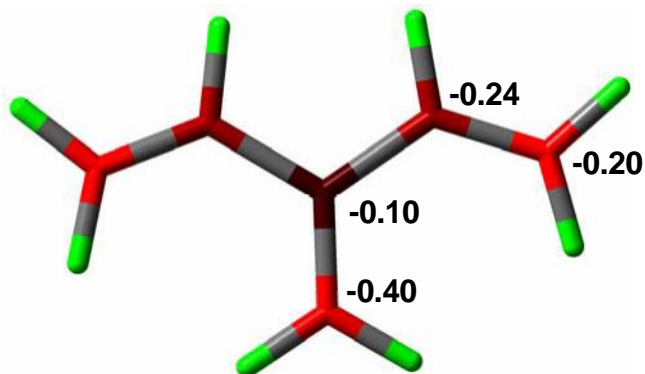
Sometimes, the olefins are not in a linear array, but are "cross-conjugated" like in the example below. Will this arrangement be more or less stable than the linear array in the hexatriene example given above?



The resonance energy is **less**. Here are the second-order perturbative estimates from the NBO program:

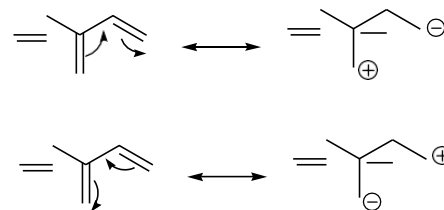


Certainly, overlap is reduced in this *s-cis* array, but the charge distribution shows an additional effect (in *s-cis*-butadiene, the estimate was 12.8 kcal/mol):

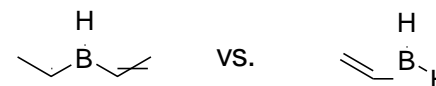


The chain is somewhat positively charged in its interior. This has an obvious polarizing disadvantage. Another way to think about it is that the central olefin is "busy" donating to two acceptors, and is not as good of a donor.

Note that typical resonance structures predict some sort of polarization, although they don't indicate its direction:



In general, cross-conjugated systems ("open charge transfer") are less stable than linearly-conjugated systems ("closed CT"). What can you predict about this system?



Same thing: the average donations are 24.2 kcal/mol (left) and 26.2 (right).

Now that you know about these "anticooperative effects," can you predict which of these will have more resonance stabilization?



The compound on the right is "borazine," the "inorganic benzene." See Pietro, *Inorg Chem* **1989** 28 544.

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