

The conformation of acetaldehyde: a simple molecule, a complex explanation?

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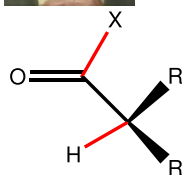
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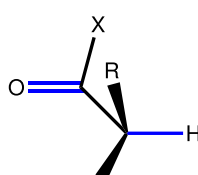
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Consider acetaldehyde (ethanal for progressive nomenclaturists). What conformation does it adopt, and why? This question was posed of me by a student at the end of a recent lecture of mine. Surely, an easy answer to give? Read on ...

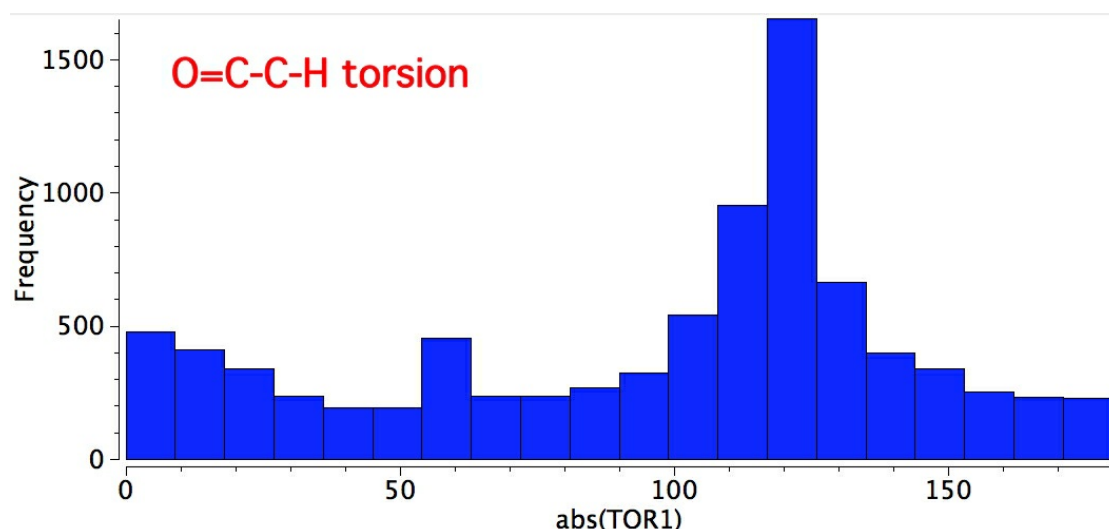


syn



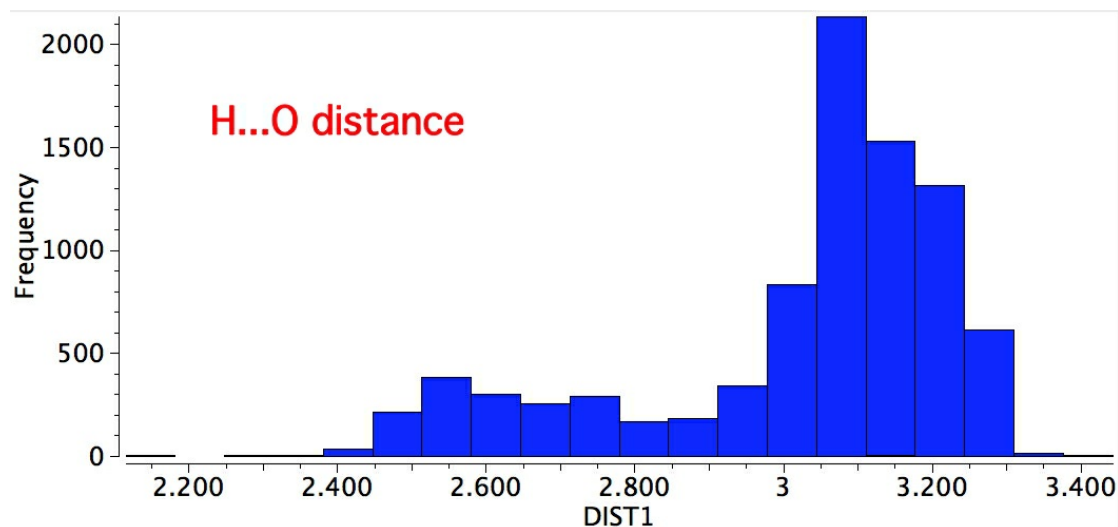
anti

There really are only two possibilities, the **syn** and **anti**. Well, I have discovered it is useful to start with a search of the Cambridge data base. With R=H or C, X unspecified, acyclic and $T \leq 175\text{K}$, two searches were performed. The first identified the torsion around $\text{O}=\text{C}-\text{C}-\text{H}$. This clearly shows a maximum at 120° (with twice the probability), and a smaller one at 0° . This matches **syn**; the **anti** conformation above would be expected to have peaks at 60° and 180° ; the latter in particular is singularly missing.

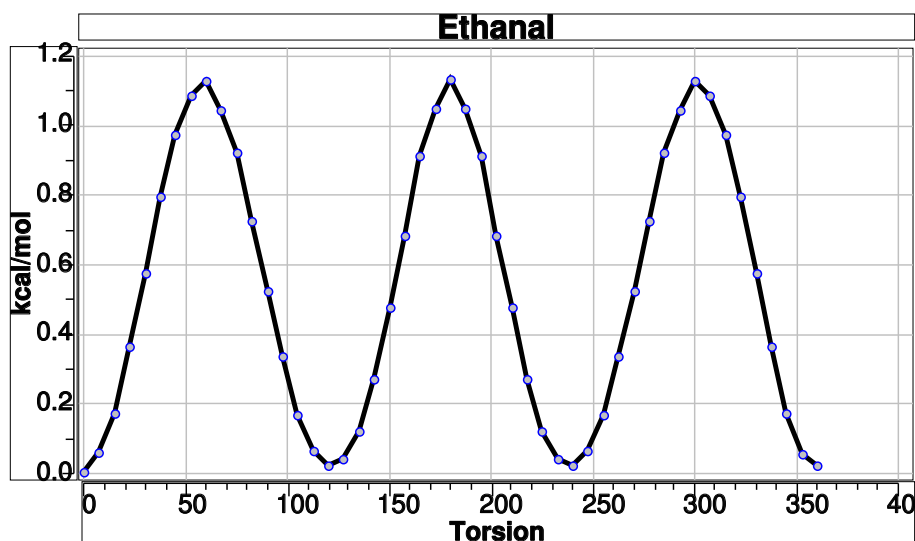


An alternative search is to define the distance between the oxygen and the H. For the **syn** conformer,

distances of ~ 2.5 and 3.1 \AA are expected; for the **anti** conformer, 2.7 and 3.3 \AA . Again, **syn** matches better. Remember, searches based on the position of a hydrogen are less reliable than most, so these distributions provide only a statistical indication.



Now for a (ω B97XD/6-311G(d,p) calculation of the rotational barrier. The minima occur at torsions of 0 , 120 and 240° , matching **syn**, although the barrier is very low.



Now to try to find explanations. The standard one finds this in three effects:

1. Donation from two C-H bonds ($R=H$ above) into the $\pi^*C=O$ NBO orbital (in the manner that was used to explain the cis-orientation of the two methyl groups in *cis*-butene).
2. Donation from the single co-planar C-H bond into the $\sigma^*C=O$ NBO orbital (blue bonds above)
3. Pauli bond-bond repulsions between two filled NBOs.

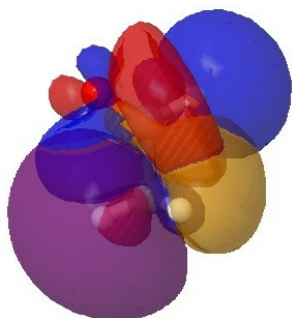
Effect 1 has an NBO perturbation energy $E(2)$ of 7.0 kcal/mol for the **syn** conformer and 6.45 for the **anti**. The explanation is the $\pi^*C=O$ NBO "leans outward", overlapping better with the C-H bonds in the **syn** than in the **anti**. The One up to the **syn**! Effect 2 has values of 1.3 for the **syn** and 4.1 for the **anti**. The latter now has the edge. But wait, there are other (smaller) interactions. The **syn** has an antiperiplanar orientation of the two C-H bonds shown above ($X=H$, red), $E(2) = 3.3$ vs 0.6 for the corresponding **syn**-planar orientation in the **anti**-conformation. It's now a tie; neck-and-neck.

Effect three suggests that the disjoint NLMO steric exchange energy is 54.34 for the **anti** and 53.88 (i.e. lower) for the **syn**. It is vaguely disappointing that no absolutely clear-cut explanation emerges. But then the difference (in total free energy) is only 1.4 kcal/mol. But even this small difference in

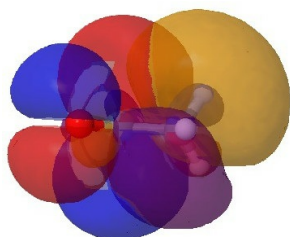
energy can manifest in fairly clear-cut conformational preferences obtained from crystal structures. Ultimately of course, all effects in chemistry are reducible to the sum of lots of small effects (in other words unpredictable until one does the sum).

I cannot end without mentioning the largest of all the NBO interactions, namely the in-plane lone pair on the oxygen as donor and the aldehyde proton C-H as acceptor (X=H). This has values of 29.3 for **syn** and 28.8 kcal/mol for **anti**. This manifest (*inter alia*) in a greatly reduced C-H vibrational wavenumber (ν 2982 for **syn**, 2900 cm^{-1} for **anti**) compared to the methyl C-H values (~3043-3164).

So this tiny little molecule ended up a little less obvious than might have seemed at the outset. One can find interesting things in even the tiniest of things!



HC...C-H alignment. Click
for 3D.



O=C*...C-H alignment.
Click for 3D.