

Lecture 7B • 10/11/11

We're going to see some practical consequences of how changing the position of different atoms in a molecule can change the energy that's present in that molecule. Since we're going to be talking about different forms of a molecule, we have some terminology – isomer. Conformers – those are different configurations of molecules; same molecule, but just different arrangement of atoms, for example, twisting around bonds in space. In that specific case of just rotating a bond, a rotational isomer, there is a shorthand term rotomer. When we're discussing rotomers, we use Newmann projections, because they allow us to understand what the angle relationships between different parts of a bond are. Hyperconjugation. Steric hinderance – this idea that different groups can bump into each other. The wrap-up is this rotational energy diagram, to how energy changes in a molecule simply by the rotation of a single bond.

What are isomers? Different shapes, but the molecules are related by having the same chemical formula. There's three main types. One would be in a situation like this, where you have the same number of different types of atoms, but you can see that I've swapped around the positions of a single and double bond. These would be functional isomers. Even more commonly, we're going to talk about a situation like this – the difference between butan-1-ol and butan-2-ol; very similar molecules, but the principal group, the alcohol group, is located somewhere else on the structure; these are known as structural isomers. A case where you have two molecules that are identical in nearly every way, except for how the atoms are arranged in 3D space. Dash and wedge bonds. These two molecules are, in fact, mirror images of each other. You could overlap all the carbon chains, one with the other, but the two substituents, the deuterium and the alcohol groups, would not be able to overlap, so they are two distinct molecules. Since it has only to do with the 3D structure, these are called stereoisomers.

Conformation – a specific geometric arrangement of the atoms in a molecule. As a little bit of shorthand, when we're comparing two molecules that differ only by their conformation, we call them conformers – conformational isomers. Different conformers can have different energies. The specific case we'll tackle today is rotational isomers or rotomers, which are identical molecules in which a single bond has been rotated. They're a subset of conformers – rotomers are a type of conformers, but we're going to learn of other conformers besides rotomers.

They're not stereoisomers since they're the same molecule, and they're not really structural isomers in the sense that bonds aren't hooked up in different places. All that's going on is, for example, a compound, if you invert the ring, or the case of a single bond, you just rotate it. So they are in fact identical molecules but they do differ in their structure.

Dash-wedge convention

What I've just written down are two versions of exactly the same molecule. You can imagine one can be turned into the other simply by taking the molecule and flipping it 180° on paper. How do these differ? The plain lines represent bonds that are in the plane of the paper. Whenever you see something plain like this, imagine that it's in this plane. A wedge, then, means that the group is going to pointed out towards you; however you are observing it, it's pointing up at you. The other way, doing this dash, that means that the group is pointed away from you. This one, which is the wedge, is pointed towards the observer, and the dash means pointed away from the observer. If you only use plain bonds, then what you're indirectly broadcasting is that you don't care what the geometry at that point is, you only care about what happens to be connected there. Some molecules, one form of which – if they're mirror images – one form might be a beneficial molecule, the other one might be harmful. There are many cases where that difference really does matter.

An inversion of a cyclohexane ring is a series of single bond rotations; they're another class of conformers.

There are different ways you can write structures, but the most commonly accepted way to visualize molecules on paper is as such: that in any tetrahedral structure, if you make two bonds be in the plane of the paper, then automatically one group is going to point out of the paper and one group is going to point in. That's just a consequence of having tetrahedral geometry. Notice that the two groups that are the plain bonds are both pointed in the opposite direction as the two groups that are written with the wedge and the dash. It's not that the plain lines have to be draw left/right or up/down, no matter what you do, no matter what orientation, it just needs to be so that the wedge and the dash are pointing in the other way. If you wrote a structure like this, for example, it's incorrectly drawn.

Let's take a simple molecule like ethane. If you notice the way that I'm drawing it, I'm doing it in such a way where whichever way that the single bonds that are the plain bonds are oriented, the wedge and the dash are pointed away from the point that those two plain bonds make. To distinguish the different hydrogens that are in ethane, I'm going to put arbitrary labels on them. Now, to make this projection, I need to visualize the molecule. Imagine that I my viewpoint oriented on the lefthand side and I was looking towards the right. To do the projection, it doesn't matter which way you do it, which direction you observe from, as long as you're consistent. If I'm looking along the bond here, I'm going to have three atoms, the ones labeled hydrogens A, B, C, closer to me, and I'll have the other ones D, E, F pointed away.

Imagine if I took a molecule that was with the two plain bonds oriented in the plane in the paper like this and I tilted the whole molecule towards you. You technically, then, could represent both of those bonds as being wedges, plus the one that's being drawn even more towards you that's tipping forward because of that tetrahedral geometry. All three could be written with wedge, technically, with the one written as a dash, but that makes it more difficult to interpret. If you drew a wedge one way and a dash another way, that is an incorrect representation. You really need to make sure the two points are pointed away from the line.

If I put the wedge and the dash in opposite positions, that isn't actually ambiguous. That would be if you're looking at it a little bit from this side versus this side, but you're still representing the same thing. Whether the dash is in between the plain and the wedge or whether the wedge is in between the plain and the dash, that's kinda personal preference. But the two of them combined have to point away from the way that the two plain lines are pointing.

To complete this projection, what I'm going to do is put this disc in between the atoms. Three of them are going to be closer to me and three of them are going to be further away; to highlight that difference, we put a disc that's going to partially block the view of the back bonds. Of course, this doesn't really exist in the molecule, it's just a way of doing the projection. This is called a Newmann projection. The projection would look like this: you start with a circle, which represents that disc. Everything that's on the front, to your perspective, you're going to draw with lines that cut all the way through to the center of this disc, because this disc is behind the front bonds. If I was looking from this perspective, looking from the side, and the eyebrow means that I am standing up this way looking at it, where does it appear that H_a is located? Straight up. From that same viewpoint position, where would it appear that H_c is located? Down and to the right. What kind of angle would that H_c make with H_a from that perspective? 120°, because even though in a tetrahedron you have 109.5° angles, you're visualizing it in such a way where you're only seeing the triangular aspect of the pyramid; if you're looking at a triangle, that's 120° angle. H_c would be on my right, because if I was looking along the molecule and that wedge means it's out towards you, out towards you is on my right, so H_c is on the right. That's going to make H_b be on the left, and it's also going to be a 120° angle. {suggestion to get molecular models}

What about the back carbon? We're not going to draw the bonds all the way through because that's the point of putting this disc here, to show which is the front, which is the back. So we'll draw the lines but stop the lines at the disc itself. Which of the atoms in the back would be pointed either straight up or straight down? Which one's in the plane of the paper? H_f. If it's in the plane of the paper, and I'm looking like this along the paper, that means it's straight up or down. Technically, because of the 109.5° angle, it's going to be pointed away from me in that direction, but I won't necessarily see that from this perspective; all I can tell is that it's going to be pointed straight down, so we would write it like this. Then, H_d would be pointed out and to the right, similar to how H_c was pointed to the right, except that it's oriented up, so we'll write it this way. Then, last one, H_e, is in the back.

Because the drawing make depends on what perspective point you choose, this is not the correct answer, it's a correct answer. I tend to have this habit from visualizing from left to right. You're free to do it however you want to. The one conditions is that you must, for a Newmann projection, be looking along the bond itself.

This angle, instead of comparing atoms attached to the same atom, what if I compare one of the groups that is attached to the front position, relative to the back position? When you do project and squish it like this, you see that this is some kind of bond angle there. But it's not a normal bond angle because again, it's not two things attached to the same position. We refer to this as a dihedral angle, which is technically an angle made between two planes. Imagine that you had two bonds at some arbitrary angle but separate by one position. This first bond could be said to be in a plane, and the other could be said to be in a plane. How those two planes are oriented anglewise with each other, that's the dihedral angle.

Right now, if you look from front to back along this bond, it looks like all the groups are at 60° angles to each other. This is what is known as the staggered conformation, because from this perspective it looks like everything is nicely between each other. This is the staggered case; let's make the opposite case of this. What we're going to do is take the front carbon and keep it still, by arbitrary choice, and I'm going to take the back carbon and rotate it by 60°. Let's say that I rotate it in such a way where I'm going to make H_d rotate back into the paper. This little curly arrow that I've written is not a reaction arrow; it's sometimes used in text to show writing of equivalent structures, but without implying anything else going on. If I take H_d, which is currently out of the plane but pointed upwards, and I rotate it 60°, it's now going to be pointed straight up. What is that going to mean for H_e? It's going to rotate down because it used to be up, but it's still going to be in the back of the paper, because you only rotated it 60°. What about H_f that's pointed straight down? If you rotate the same direction as the other two, that means it has to rotate out towards you, which means it's now going to be a wedge.

If I rotate 60°, I haven't broken any bonds, so I haven't changed the molecule, but, it will have energetic consequences. Again, D went from out of it into the plane, the one that was behind and up is now behind and down, and the one that was down in the plane is now down but pointed outwards. If we were to view the Newmann projection, visualize along the bond, the front is going to look the same as the previous projection, because I didn't rotate that front carbon and I kept my same perspective. In the back, though, since we've rotate by 60°, from front to back it's going to look like the different groups overlap each other.

As you can see, on the front carbon, you have a bond that's a plain line and the back carbon, a plain line, pointed in the same direction, up. We don't write them exactly on top of each other in the Newmann projection, though, because that would be a bit difficult to read. What we do is we put on off to the side. It doesn't really matter which way you do it, as long as you're consistent. You don't want to show it too far off to the side because someone might misinterpret that as being the staggered conformation. So up top we have Hd, then the left, cause that's the back, we have He, and then the front, we have Hf. Since they are right on top of each other, this is known as an eclipsed conformation.

It is higher in energy. Can you guess why it might be higher in energy? You've got these two objects that are pointed kinda towards each other and they've both got clouds of electrons associated with them. What if we made this a more extreme case; what if we had methyl groups instead of the hydrogens? Then you have a lot of space that these electrons are taking up, and you end up with a space problem. Two clouds of electrons are trying to occupy the same point in space, that's not going to really happen. If you imagine some kind of balloons, you can squish two balloons together, but that takes effort, that takes energy. That's something known as steric hinderance. Steric, the term, has to do with shape or volume or size. It is related to the term stereo. Steric hinderance is this: when two clouds of electrons attempt to occupy the same space, they will repel. In some cases, this causes the molecular structure to distort, usually resulting in a higher potential energy. For every other case of rotomers we study, this is going to be the principal reason why having things eclipsed is higher in energy, because things are bumping into each other. But for ethane, it's not the case, because the hydrogens are small enough that they don't really particularly bump into each other. What is the one-word answer that explains why the eclipsed form of ethane is higher in energy than the staggered form? Torsional energy is something that has to do with the angle that something's at; there can be multiple factors that contribute to torsional strain. This is something a little different: hyperconjugation. That's where you have an interaction between two different orbitals that could, for example, between two different bonds. We have so far been talking about orbitals as being just between two atoms, but if you had two orbitals that had the right geometry, they may have some secondary interaction with each other. In ethane, the eclipsed conformation is higher in energy due to hypercojugation.

Let's see how the energy would change as we took the dihedral angle and we didn't just look at 0° or 60° , we allow the molecule to rotate a full 360° around. For ethane's case, it's not going to generate anything too interesting, because it's such a symmetric molecule. It just has hydrogens at every location from to back. This is a general technique that we could use. We'll look at the extremes between eclipsed and staggered. Molecules can adopt angles other than these simple angles, it's just that these are the maxima, the highest- and lowest-energy points, which is why we care about them. Let's say I call the eclipsed form, where the two groups are on top of each other, as 0° , and then I rotate around 60° at a time. That means I'm going to go back and forth between eclipsed and staggered. Since the molecule is so symmetric, all of the eclipsed forms have the same energies as each other, and the staggered forms have the same energies. It is 12kJ/mol difference between these two energy forms, which has a consequence for equilibrium. Since this is an energy diagram, we should always make sure to show energy as an axis. In between, this will look much like a smooth sine wave; energy oscillates up and down, up and down as you rotate. This has a real-life consequence. What this means is there is a barrier to rotation about a single bond. Even though single bond are rotatable because they have only one point of contact, that doesn't mean there isn't some cost in energy to rotate, because there will be these points when they go through eclipsed conformations that they're higher in energy. At room temperature, there's usually enough thermal energy for single bonds to rotate freely, assuming that they're not ring structures, or that there's not something else in the molecule preventing that rotation. If you cool a molecule down enough, you'll come to a point where rotation is not possible because they're not enough thermal energy to get over this rotational energy barrier. At room temperature, there's usually enough thermal energy to overcome the rotational energy barrier in a single bond, meaning the bond can rotate freely. However, at low temperature, rotation would cease. At low enough temperature, because of the energy barrier, rotation would cease. It would get stuck in the staggered conformation. If it was in the eclipsed, any movement at all and it would just slip into the staggered conformation. There are quantized energy levels to rotation. There are vibrational, rotational, and translational motions in any system. It can have all three forms, each each form has its own energy states. I tend to do the eclipsed form at 0° because I like to start my diagrams at the highest energy. There's different forms of potential energy. Because you could have a steric effect from things bumping into each other, if you force the molecule into the eclipsed conformation, that interaction between electrons would be itself a form of potential energy, because that energy would be released by allowing those electrons to no longer bump into each other. Bonds themselves have a form of potential energy.

Butane. You have one methyl group on the front of the molecule and one methyl group on the back. There are going to be four distinct cases for butane. Ethane only had two because whether it's eclipsed or staggered. Now that we have a methyl group, what if the methyl group on the front or the back carbon are the groups that are bumping into each other in that eclipsed form? Or what of, instead, we had just a hydrogen and a methyl group? That would be different amounts of the steric hinderance, so they're going to be different energies. Let's start by writing out the line structures for the four unique forms of butane. By arbitrary choice, I'm going to set my viewpoint on the lefthand side of the paper, and I'm going to leave that carbon closest to the viewpoint alone as I rotate the back carbon. Let me draw that visualization point in. Let's draw the four line structures.

I'm going to start with an eclipsed case where the methyl groups are the ones bumping into each other. Rotating the back carbon, leaving the front carbon alone, let's say I move the methyl group towards us this time. If I move it 60° out, that's going to make it pointed towards us but still pointed up.

The hydrogen that was in back, because it's now rotating out, it will rotate up but still be in back, and then the hydrogen that was in the front, if I'm rotating something towards you, that means it's now rotating away from you, so it's going to be pointed down in the plane of the paper. Rotate it another 60°. That methyl group that is now pointed out at you is going to rotate down but still be pointed at you. The hydrogen that was in the plane of the paper just a moment ago continues to rotate back, which means it's going to be down and in the back of the paper, and then the hydrogen that was in back pointed up, since you're rotating it forward, is now going to be pointed straight up. Then, the last case, will be rotating that methyl group the last 60° so it's now completely opposite of the first methyl group. That's going to make both of the hydrogens point up, one out, and one in.

Let's draw the Newmann projections for these four cases. The front, because I never rotate it, will look the same each time. Since this is not a line structure we're drawing, you should always write in what time of atom you have; I explicitly wrote the methyl group in. What do we see in back? The first case is eclipsed, the next case is staggered, the case after that is again eclipsed, and the last case is also staggered. On the first eclipsed form, the methyl groups bump into each other. Then that back carbon is rotating, so the methyl group rotates to the right. As it continues to rotate to the right, it enters another eclipsed form, but now it's just a hydrogen and methyl group interacting. The last one is where the methyl groups are completely opposite each other. There are special terms for a few of these forms. These names generally pop up when we have something that's relatively symmetric like this, having only one substituent that's in the front and the back. When they're completely opposite of each other, that is called the anti form, meaning opposite. [When the methyl groups coincide with each other,] that is the syn form. The gauche form {explanation of word} is not as good as the anti form, because you're going to have a methyl group that's going to have some interaction with this first methyl group; it's a local minimum, it's not the best form, but it's close.

What would this look like on an energy diagram, since these are not all the same like they were with ethane? I'll draw the diagram out through 360°, but more commonly I just have you do it to 180°, because butane is symmetric so one half of this diagram is just going to be a mirror image of the other. The eclipsed form, the syn form, is the highest energy, because the methyl groups are the things interacting. The second-highest energy will be the next eclipsed form, where methyl and hydrogen interact. The third-highest will be that gauche form, where it's staggered, but it's not the lowest-energy staggered. The anti form will be the very lowest in energy. Your curve will look something like this. {warning that entire problem will be on the test}

isomers, conformers, rotomers, Newmann projections, hyperconjugation, steric hinderance, rotomer energy diagrams

isomers – molecules with the same chemical formula but different structures

conformation – specific geometric arrangement of atoms in a molecule

conformers – identical molecules that differ in their conformations (and possibly energy)

rotomers – identical molecules in which a single bond has been rotated (subset of conformers)

Dihedral angle – an angle made between two different planes

In ethane, the eclipsed conformation is higher in energy due to hyperconjugation.

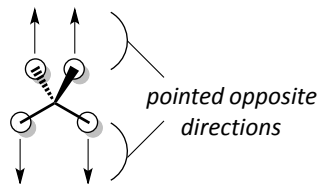
Steric hinderance – steric = shape/volume/size

When two clouds of electrons attempt to occupy the same space, they will repel, which in some cases causes a distortion in molecular structure, usually resulting in higher potential energy.

At room temperature, there is usually enough thermal energy to overcome the rotational energy barrier in a single bond, meaning the bond can freely rotate. At low enough temp, because of the energy barrier, rotation would cease.

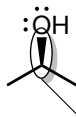
Structures (remaining structures identical to lecture 7A)

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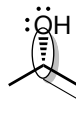


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dash-wedge convention



pointed towards the observer



pointed away from the observer