

Lecture 7A • 10/10/11

We're going to move on to rotomers, rotational conformers.

First, what are isomers? Molecules that have the same molecular formula but different structures. Molecules with the same formula but different structures. There's a few major types of isomers. If you look at these two molecules, you would determine that they both have the same chemical formula, it's just that I've changed the position of the single and the double bond. These are functional isomers, which have different functional groups. If I had just an alcohol but I had it at the 1 position versus the 2 position, these are called structural isomers. They're at different positions. Then, there's the trickier class of molecules that have the same chemical formula, and everything is pretty much hooked up at the same positions, but, you have a different three-dimensional connectivity. Same substituents on that main, central carbon. You have a methyl, and ethyl, a deuterium, and an alcohol. But those are not the same molecule. You would not be able to take one molecule and stack it on top of the other and have it match, because they differ in 3D space. These are stereoisomers; they have different 3D connectivity.

Then we have what we're investigating today: not different molecules, but different forms of the same molecule. There the term conformation, which means the specific geometric arrangement of atoms in a molecule. From that, we get this sort of hybrid term, conformer, which is a shorthand meaning molecules that are identical molecules, but have different conformations. For example, you could rotate a single bond around, partway. Rotating the single bond doesn't change the molecule I've got, but it could change the energy, depending on how the different substituents are interacting with each other in that molecule. That's what the term conformer refers. Conformers are identical molecules with different conformations and, potentially, different energies.

The specific type of conformer we'll look at today is what is sometimes referred to as a rotational isomer, or rotomer. Rotomers are identical molecules in which a single bond has been rotated. They're a subset of conformers. We need a way of writing these structures down. What we're going to be doing is looking, examining some different bonds and seeing how the different groups that are part of that system are physically located relative to each other. This kind of structure writing is what is known as a Newmann projection. For our first Newmann projection, I'm going to use the molecule ethane. I'm going to label the six hydrogens in ethane A, B, C, D, E, F. In order to do this, though, we formally need the dash and wedge bond types. This is all about visualization.

The dash-wedge convention. If you write something with that wedge, that thick bond, that means that it's pointed out towards you. The simple bonds we have written, the thin lines, those are to represent that you've got a molecule sitting there in the plane of the paper. If I was looking down at the projector, it would be like the -OH group is pointed back up at me. From where you're sitting, the -OH group would then be pointed out the board towards you. This means pointed towards the observer. The opposite, if you were to turn this example molecule 180° and flip it over so that now the -OH group would be pointed away from you, either to the back of the board from where you're sitting or into this project from where I'm standing, that's what the dash represents: pointed away from the observer.

Properly-written tetrahedral structures will have no more than exactly one wedge and one dash. It doesn't matter which way that they're pointing, in a sense, except that, where you have the two plain bonds that come together and form a point, then notice the way I've done this: the wedge always points away from that point, the dash always points away from that point. This is related to tetrahedral symmetry. If you look at the way I've written ethane, then, you can see that I have the two simple bonds pointing in one direction; it's like they're making a point directed towards the lower lefthand corner of the page, so the dash and the wedge, I also wrote towards that direction. Then on the other side, I have the two plain bonds where they make a point that's pointed towards the upper right, and notice that the dash and the wedge are also written to the upper right. This is again related to what a tetrahedron looks like.

If you think that you're going to have difficulty visualizing these kinds of structures, then I highly recommend that you get one of the molecular modeling kits that's available. The bookstore should be carrying one type [name of model]. You will be allowed to use them on an exam. What kind of visualization are we going to do? Let me label the different hydrogens arbitrarily. To do visualization for a Newmann projection, it's all about focusing on what's around a particular single bond. I've written this single bond in a plain way to show that that bond's in the plane of the paper, to make it more apparent to a reader: which bond do I care about. There are seven single bonds in this molecule. But I'm going to visualize this one that's lined up for us already. I'm going to look down the bond so I can see is one hydrogen on one carbon possibly got a substituent on it that's pointed the same way as another carbon. Those two substituents, depending on how big they are, they're only one atom separated from each other, but what if they're really big, huge groups? They might physically bump into each other and, energetically, it might be preferable, then, if the bond was to rotate, to not have that bumping into each other. That's the whole point of this analysis. We're going to be doing what's called conformational analysis: figuring out what's the lowest-energy form of a molecule. If you're in the bio field, you'll eventually hear about that as well, since proteins and DNA, they fold to minimize energy as well.

That's a more complicated case of conformational analysis, but same purpose: to look and see how things bumping into each other will affect the shape of a molecule.

If we're analyzing this bond, we have to decide: are we going to look from this side and look at the bond this direction, or are we going to look from this side and look at the bond from this direction. It doesn't matter which we do, so let's look at it from left to right. This is where that eyebrow thing comes in, because, am I going to look at the molecule like this, or am I going to fall over and look at the molecule like that? It matters, because we want to make sure that we're accurately representing the diagram, the relative position of all of the atoms, so it matters which way we do it. I will go ahead and put my eyebrow up, so I'm going to visualize the molecule this direction. I'm going to put something into the molecule that doesn't exist: a disc. We're going to see which things will be in front of that disc and which things will be partly obscured by this disc. This was created by Newmann to try to show: what is the relative position of all of these hydrogen or other groups, relative to each other.

Let's try to translate this into the projection. Here's the way the projection's going to be written. We'll start out with that disc. What we see in front of that disc, we'll write bonds that go all the way through to the different atoms, because they're not being blocked by that disc. What do I see in front of me in this diagram? I see [hydrogens] A, B, C. If I'm looking this way, which way is A? Straight up; that's what this plain bond means. It is tilted towards me a little bit because this is a 109.5° angle. From this perspective, I can't tell, necessarily, that it's pointed towards or away from me. All I know is that it's straight up. What about B? From my position, it's on my left, because the dash means into the plane of the board. If I'm looking this way, but that dash means into the board, that means I'm looking over here which is my left. Between A and B, what will be the apparent angle? Not 109.5° , not if I'm viewing it from this direction. 120° , because I have this circle I'm looking at, and angle this way or that I can't tell from this perspective, I'm not visualizing that way. All I can see is that I've got something pointed up, something pointed to the left, and we're going to come to C here that's pointed to the right. It's one of those geometrical coincidences: when you look along a bond of a tetrahedron like imagine it wasn't a tetrahedron. Imagine it really is like we're going to call it tetrahedral in shape, but if I took this off and put a lone pair, what shape would I call it? Trigonal, means 120° , which means when I look at that pyramid from it's bottom, you're going to see 120° angles there, not 109.5° .

What I'm going to see in front of the molecule is this: the hydrogen pointed straight up (Ha). I'm going to see Hb down and to the left. It's going to be at 120° on this diagram. Then Hc will be equivalently point 120° the other direction on this diagram. That's for the front carbon. I'm writing virtual disc, because it's not really that the molecule has some disc in the middle of it, it's the way we can tell front and back apart. How? The things in back, I'm not going to connect the lines all the way to the center, because that disc effectively blocks it. Hf, which way is it pointing? Straight down. Ignore the fact that it's really leaning off to the right; if I'm looking like this at this board, can I tell if anything is pointing towards or away from me? Not unless I'm looking in 3D, off to the side, but if I'm just visualizing this way, then you can't tell. It doesn't matter that Hf is really pointed that direction, it's pointed straight down from my perspective because it's in the plane of the paper, because it's written with a plain bond. So Hf will be pointed this direction. Hd. To my left or right? It's to the right, because it's a wedge; wedge means out of the paper; I'm looking along the paper; the wedge being out this way is my right. So there's Hd. Then, we have He in back.

This is a simple Newmann projection. Between every one of these, we have a 60° angle. Because we have them nice and evenly spaced, if we were to squish this molecule flat, from front to back there is no direct overlap between one group and another. Even if these were large groups, they'd still be kinda in between each other. We call this the staggered conformation. Let's do an exercise. What if, on this original line structure, I rotated the back carbon 60° ? Let's say I took the Hd that's pointed out towards you at the moment and rotated it so that's pointed straight up? It will overlap now. What's going to happen to He? It will line up with Hb, because if you take Hd, which is pointed out this way, and I turn it 60° so it's pointed straight up and down, that means that a group was pointed up and 60° this way will turn 60° and now be pointed down and in the back of the page. That means the group that was pointed straight down will also rotate 60° this way so now it will be pointed down but out of the page. In other words, if I rotate by 60° ... I've got an arrow wrapped about that bond to show I'm going to be rotating. Since arrows mean something specific, I've got this little loop arrow that doesn't mean chemical reaction, it just means you're rewriting the molecule.

{out of place} I'm rotating it 60° into the plane of the paper. Hd was pointed out and now I'm making it up; to the left.

I'm rotating it 60° , and the front carbon I'm going to leave along, the back carbon will now look like this. If you didn't follow how these different hydrogens end up in the different places, this is why you need models. For some of you, until you do it yourself and see it yourself, it isn't going to click, no matter how many times I say it. Let's take the same fixed position for our viewpoint, and let's see what kind of Newmann projection we'll get from that. The front's going to stay the same, cause I didn't rotate it, and I'm observing from the same place. Again, the front, because it's in front of this virtual disc that we insert there, we write the bonds all the way through. But in the back, what are we going to get now? If you look from front to back, Ha and Hd, they're both pointed the same way, they're both pointed straight up, so they're going to line up with each other now. You don't write them on top of each other cause that's hard to interpret. You're going to write the group in back just one side, just slightly, or the other. Whichever side you right it to, you should do the same for all three positions.

Because they exactly coincide, I'm going to decide to write it a little bit off to the right. I say a little bit, because if I wrote it in between A and C, then it looks like I'm trying to write something that's staggered. So I'm going to write it pretty darn close. By having it that close overlap, you're trying to show they're overlapped, but you're spreading it out just to take it easy on the reader.

If you observe Hc, which hydrogen is going to overlap with it? Hf, because they're both wedges, so they're both pointed out towards you. Because I wrote D a little bit to one side, specifically the right side, I'm going to do the same thing for my Hf. He will be similarly written. Notice the key feature, the three bonds, the ones I just wrote, do not go through to the center of the diagram. That's again the purpose of this disc we're putting in.

Can there be a bond angle somewhere in between the two? Could there be something between this staggered conformation I've shown you or this eclipsed conformation, where overlap occurs from front to back? The answer is yes, you can have angles anywhere in between, but these are the two extremes. One is going to be lowest possible energy for this particular molecule, and the other one is going to be the highest possible energy, in terms of what happens just as you rotate these things around. But that is the point, that you're going to rotate these things around. That's where this rotational energy diagram, this rotomer diagram, is going to come from.

Imagine that I had a bond that was pointed straight up on the front carbon, but was point at a 60° relative to that same axis on the back position. There's a term for that kind of angle: a dihedral angle, an angle created by two different planes. Here's one plane that contains that front hydrogen, and here's another plane that contains that back hydrogen. The two bonds to the two different hydrogens, they're not on the same carbon, so I can't just say what's the bond angle there, because they're not located on the same position. But if I use the term dihedral angle, built into that is the idea they're not on the same carbon, they're separated by one, and that's the angle that we're looking at. One more time: if you look at the Newmann projections, and you see the label showing a 60° angle, there isn't really a 60° angle here because you've got a bond separating the two carbons. Again, this refers to the relative position of these two things, but separated.

Why do I point out the dihedral angle? Because, in these rotational energy diagrams, we start with two of the atoms right on top of each other, and we see what happens as we rotate the atom 360° around. I'll define this staggered conformation that we got to be 0° . If I then write out a diagram, it's going to look like a sine wave. We only care about the 60° marks, because those are when the extremes, the staggered or eclipsed conformations, occur. Energy here because it's an energy diagram. Zero's going to be high, 60° low; 120° the same as 0° ; 180° the same as 60° . It just goes back and forth and back and forth. That energy difference is 2.9 kcal/mol or 12 kJ/mol difference. Which means, you cool this molecule down enough, and it won't rotate any more. This is what is called a rotational energy barrier. In this case, the staggered conformations are each the same energy lower than each of the eclipsed conformations. Things fall down, not up, so when possible, the molecules will try to be this staggered conformation. If there's enough energy around due to temperature, then that temperature provides the energy necessary to get over this hump, because you're going to be clashing, you're going to be rising in energy trying to get these things lined up with each other. Then, if you pass that boundary, it will continue to rotate until the next staggered position. At room temperature, there's usually enough energy for the rotation of a single bond to occur rapidly. However, at low enough temperature, this rotational energy barrier will prevent rotation from occurring.

Why is it that the staggered configuration of ethane is lower in energy than the eclipsed conformation? An educated guess would be that electrons repel each other. We have this term: steric hinderance. Steric refers to shape, size, or volume. The idea that there's space involved. Steric hinderance is this situation: if you had two methyl groups next to each other, one thing that is deceptive from the way we write structures is we draw these thin little lines connecting atoms to each other. But it totally ignores the fact that there's really a much larger cloud of electron density that really extends further away from the atoms than we indicate with these diagrams. Where the electron clouds bump into each other, that's negative charge bumping into negative charge, which is not favorable. Steric hinderance is this: it is energy strain caused by two clouds of electrons trying to occupy the same physical space. It won't happen. The structure of the molecule has to distort, and it's that distortion that's called steric hinderance. When two clouds of electrons attempt to occupy the same space, they will repel and/or the molecular structure will distort. That is steric hinderance. My o-chem instructor lovingly referred to it as the spaghetti effect. Two clumps of spaghetti to close to each other, you just can't squish them. If you did, you could squish them together, but something has to give, has to distort. That's steric hinderance.

Steric hinderance is not the answer to why having these hydrogens lined up with each other causes an energetic effect. It is the answer for any other problem like this we do. What really happens: hyperconjugation.

Tortional strain – that having this angle between atoms that are separated can have an influence on structure.

Butane is one of the classic problems for rotomer diagrams. We're going to draw the line structures for the unique forms of butane; we're going to draw the Newmann projections for the unique forms of butane; and then show how those forms are related energetically on a rotomer energy diagram. Butane has the central carbon-carbon bond and then one methyl group on either side. Let's draw four different line structures.

In each case, I'm going to keep a methyl group in the same place on the front position and visualize all of these from the lefthand side. If I wanted to rotate the back carbon – it doesn't matter which way I do it, but let's say I choose to rotate it so that it's now 60° out towards us compared to what it used to be. What would that mean for the hydrogens on the back carbon? Where will they be located? So the front hydrogen on the back carbon – if I rotate the methyl group, which is pointed up at the moment, but turn it 60° towards you, then that means that this group that was pointed down but towards you will rotate 60° as well. Well, 60° will bring it where? Straight down, back into the plane of the paper. The back hydrogen, it was point 60° away from you. If I turn it 60° , it's still pointed away from you, but now it's pointed up. Notice that everything I've drawn so far, every single carbon, has no more than one wedge, one dash, and two plain lines, and the two plain lines are always in opposition to the wedge and the dash.

What if I turned it another 60° , again keeping the front position the same. I'm rotating the methyl group another 60° , so it's pointed like the front hydrogen, it's pointed down towards you. What's that going to mean for the hydrogens? One hydrogen will move in back, so the hydrogen that was in the plane of the paper is going to move 60° now, so it's going into the back of the back. Then the last hydrogen, the one that was in back but pointed up away from you, it's going to rotate 60° and come straight up and down. The last case is the other case that's easier to draw, because if the two methyl groups are in the plane of the paper, that means the two hydrogens aren't. Now let's make Newmann projections for each of these. The front is always the same. We have the methyl group up top every single time because that's the way I've set my viewpoint. We have hydrogens on the left and the right on that front carbon. It is the back carbon that rotates, so let's see how it changes. The first form is an eclipsed conformation. The second, staggered. The next, eclipsed again. And the last, staggered again. One set of terms that we'll associate with these are eclipsed (E), staggered (S). Once you get past ethane, any larger group you start substituting on here, in terms of it's energetic effect, it's going to be sterics. The methyl group is big and bulky, and so it bumps into whatever is on the front carbon.

It might make sense that a methyl group bumping into a hydrogen is not going to have as much steric hinderance as a methyl group bumping into another methyl group. Two methyl groups experience more steric hinderance than a methyl and a hydrogen. Because of that, we worry about the relative position of the methyl groups to each other. We call the one where the two are as far away from each other as possible the anti conformation, anti meaning opposite. When it's the same, it's called the syn conformation. There is no commonly used name for the third form, but there is one for this staggered conformation, the non-lowest energy staggered conformation. That is called gauche {anecdote about left in Indo-European having the connotation of bad; sinister; right = correct}. Let me put a degree symbol along with this as well. If I define the one where the groups are on top of each other as 0° dihedral angle, then every time I rotate it is by 60° , so I'll get up to 180° . If I keep on rotating, since the molecule is perfectly symmetric, then, when you get to 240° , it's the same as 120° ; when you get to 300° , it's the same as 60° . Often, only half of the diagram is written [in these cases]. I'll show what happens energetically as we go from 0° to 60° to 120° to 180° . This is dihedral angle, and this is energy. Eclipsed is going to be higher than staggered, but the gauche form is going to be higher than the anti form, so the energy curve will look like this. Gauche is like a local minimum. The syn – when the two main groups are right on top of each other – most steric hinderance. The anti, furthest from each other, least steric hinderance. {admonition to study}

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

isomers – molecules with the same formula but different structures

conformation – specific geometric arrangement of atoms in a molecule

conformers – identical molecules with different conformations (and, potentially, different energies)

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

Dihedral angle – an angle created by two different planes

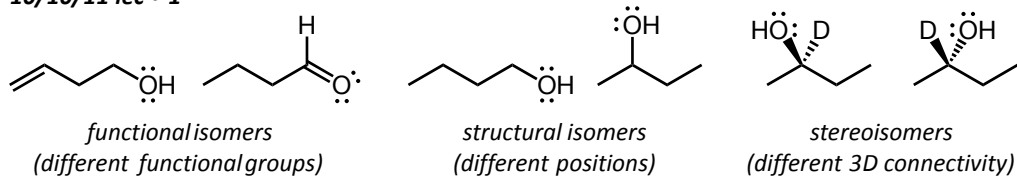
At room temperature, there is usually enough thermal energy to overcome the rotational energy barrier, so sigma bonds usually rotate. However, at low enough temp, rotation would cease.

steric hinderance; steric – refers to shape/size/volume – when two clouds of electrons attempt to occupy the same space, they will repel and/or the molecular structure will distort – steric hinderance

Two methyl groups experience more steric hinderance than a methyl & hydrogen

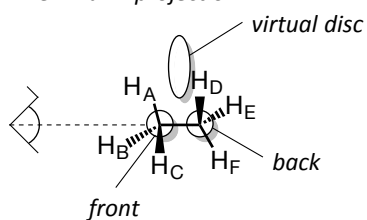
Structures

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Newmann projection

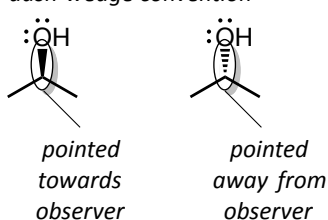


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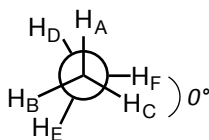
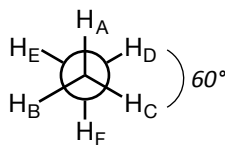
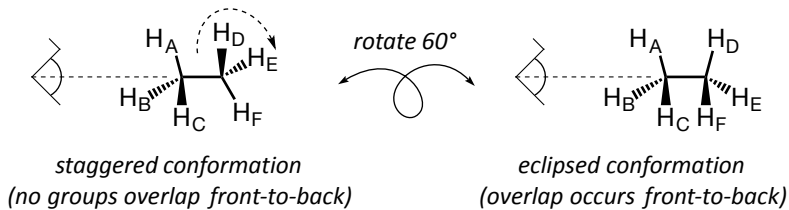


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dash-wedge convention



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