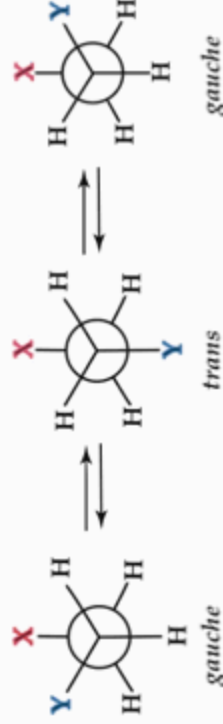


New Directions in Understanding Conformational Preferences of 1,2-Substituted Ethanes

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One of the very simplest of organic compounds is ethane, of formula C_2H_6 and structure, CH_3-CH_3 , with chemical bonds between the two carbon atoms and also between each carbon and three hydrogen atoms. The point of our interest is that ethane undergoes what can be regarded as the simplest of all organic reaction in that rotation occurs about the C-C bonds of ethane molecules causing the hydrogens to move past one another. Three interesting points about this rotation are; first, it is incredibly fast (more than a billion times per second) and second it is not wholly smooth, there being three points in the rotation in which it slows. This is best understood if we look at a drawing of an ethane of structure with two groups **X** and **Y** each replacing one hydrogen on one and the other end of the molecule as $X-CH_2-CH_2-Y$. Now if we look in three dimensions along the C-C bond we can visualize the three more stable way points in the rotation each at 120° steps as shown below.



Almost all of what we use to figure out whether the two gauche or the trans conformation should be more stable is how **X** and **Y** can interact with each other. A very simple example is how large the groups are, which you can visualize impact from the fact the **X** and **Y** groups are much closer together in the gauche conformations than they are in the trans. From this we can predict that, if **X** and **Y** are large groups, they will bump into one another and, as a result will on the average, favor the trans arrangement.

So now, suppose that we look another simple appearing example, where **X** and **Y** are both $-CO_2^-$ carboxylate groups each with a negative charge. The simple laws of electrostatics, suggest that the charges should repel each other and thus favor the trans conformation. Easy, but wrong! Actually, not in water nor in many other solvents, particularly ones that are not, or very weakly, acidic. Substantial amounts of the gauche conformation are observed experimentally and estimated to be on the order of from about 30% to 85%. The major problem here is to determine the structures of each of the conformers present in solution. Not an easy task at all for solutions. And the truth of what is happening requires experimental and theoretical verification, both of which are being vigorously pursued.