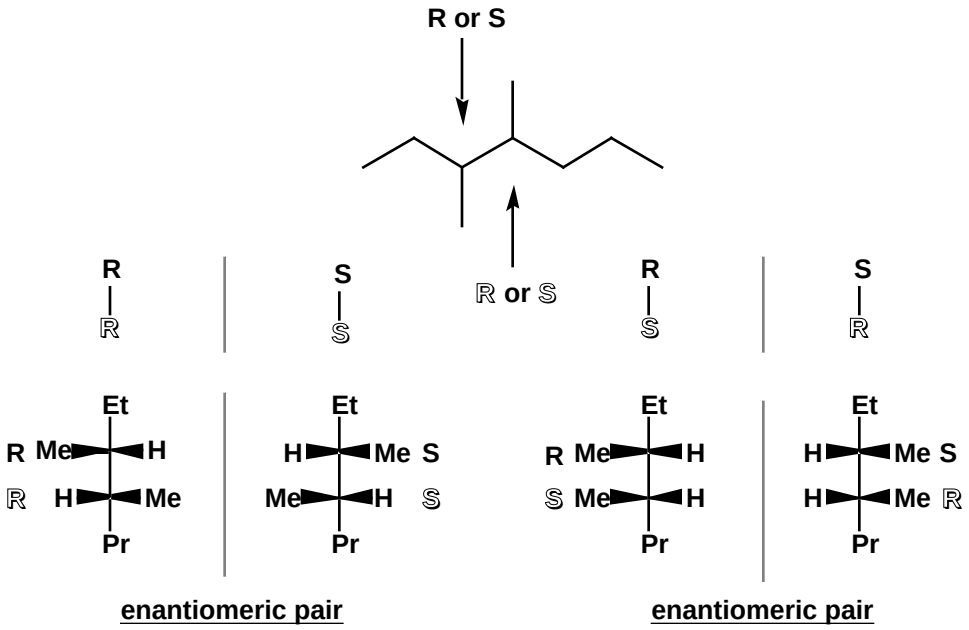
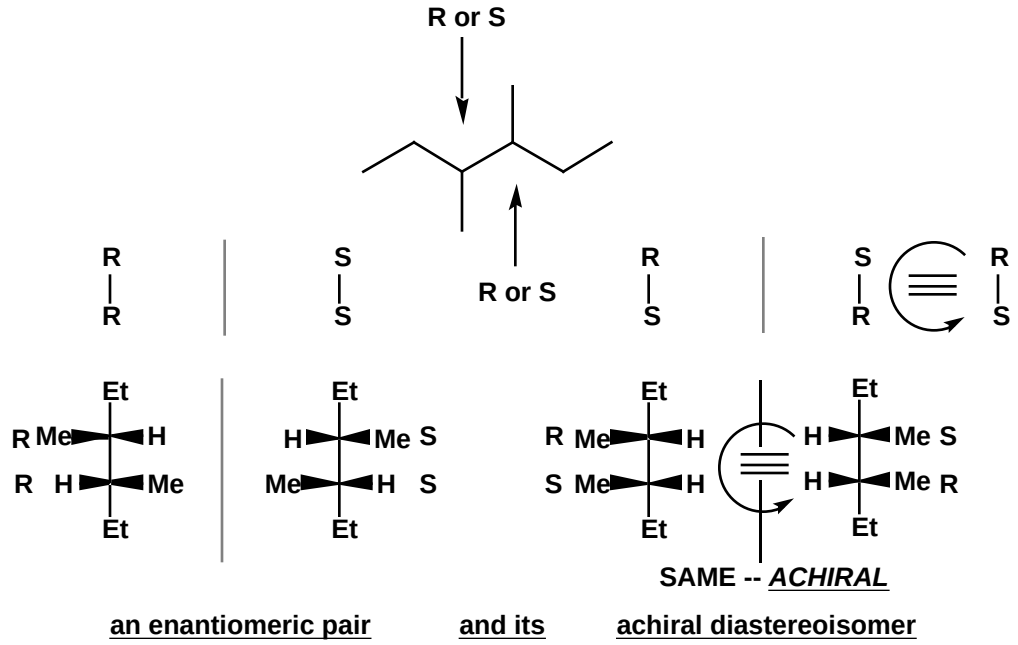
Text Related to Segment 4.05 ©2002 Claude E. Wintner

Consider now what happens with 3,4-dimethylhexane, by comparing the case with 3,4-dimethylheptane, as it was treated in the previous segment:



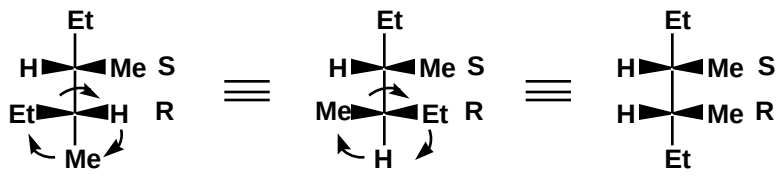


configurational isomers of 3,4-dimethylheptane and of 3,4-dimethylhexane

In any stereoisomer of 3,4-dimethylhexane the two stereogenic carbon atoms are *equivalently* substituted, as regards *constitution,* by hydrogen, a methyl group, an ethyl group, and a secondary butyl group. For 3,4-dimethylheptane it was necessary to use the labels R_{shadow} and S_{shadow}, as well as the labels R and S, in order to differentiate the non-equivalently substituted centers. For 3,4-dimethylhexane, in contrast, we must use only the labels R and S. What *were* four possible combinations now collapse to only three, as the figure makes clear: just as the combination R—S is identical with the combination S—R, so the corresponding molecules are congruent. Furthermore, while the R—R combination still represents a molecule which is enantiomeric with the S—S case, the diastereoisomeric R—S case is *achiral* (not chiral): its image in a plane mirror *can* be made congruent with itself. The Fischer projection formulae tell the same story, of an enantiomeric pair and its achiral diastereoisomer. Again, a model should be consulted! It must be remembered that, while a Fischer projection formula cannot be "flipped like a pancake" to establish congruence (for then the bonds coming out of the paper would be going in, and those going in would be coming out), it *can* be rotated in the plane of the paper without this problem arising. In the case of the Fischer projection formulae for the achiral stereoisomer of 3,4-dimethylhexane, when one draws the mirror image, one can rotate it by 180° and achieve congruence with the original, because there are ethyl groups on both ends of the molecule, as opposed to an ethyl group and a propyl group, as in 3,4-dimethylheptane.

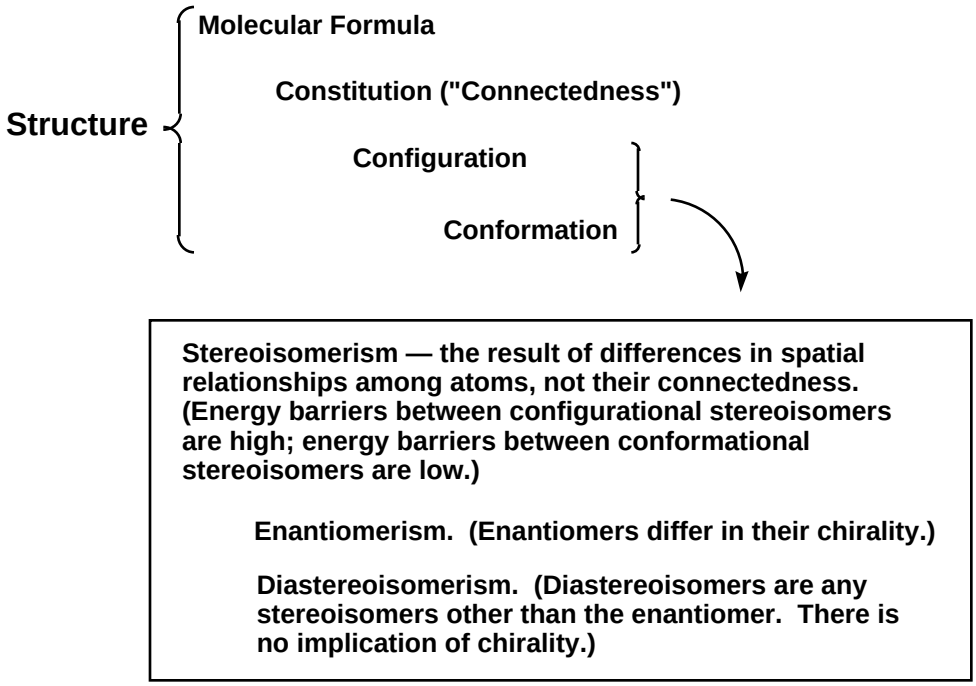
The underlying idea is one with which we are all, in fact, familiar. We have a (chiral) right hand and a (chiral) left hand, a (chiral) right foot and a (chiral) left foot; yet we are, taken as a whole, (formally) achiral objects, as a result of a (formal) internal plane of symmetry. A person with two right hands, or two left hands, would be, taken as a whole, chiral! In the 3,4-dimethylhexane stereoisomers the same circumstances are operative: the achiral case, and only the achiral case, has an internal

plane of symmetry. To recapitulate, there are four molecules, all with the constitution 3,4-dimethylheptane but differing in their configuration, each of which we can place in a separate bottle, to speak colloquially, and each of which, being chiral, will rotate a beam of plane polarized light. On the other hand, we can have only three bottles of different 3,4-dimethylhexane configurational isomers, and one of the bottles will contain an achiral molecule, showing no rotation of plane polarized light. A final point is worthy of note: the three Fischer projection formulae shown below do not correspond to configurationally different molecules, but rather to the same molecule, achiral-(R,S)-3,4-dimethylhexane, in three different conformations. The lesson here is that, in order to discover configurational achirality conveniently using a Fischer projection, one should use symmetry of representation to one's advantage!



three configurationally equivalent Fischer projection formulae (the last being the most useful)

The following summary of terms now should prove helpful:



summary of terms

A few amplifying notes are in order here:

1. The word *structure*, in its preferred present usage, most properly is invoked only in a situation where molecular formula, constitution, configuration (if relevant) and conformation are *all* defined. This is, for example, what one learns from an X-ray crystallographic analysis.
2. The words *stereoisomer, enantiomer, diastereoisomer* generally are used to refer to *configurational* stereoisomers, *configurational* enantiomers, *configurational* diastereoisomers. However, strictly speaking, one always must be clear as to whether it is configurational stereoisomerism or conformational stereoisomerism that is the issue at hand.

3. There is no difference in geometrical principle between the concepts of configurational isomerism and conformational isomerism. In each case one is considering entities which have the same "connectedness" but which differ in the spatial relationships among the atoms. The difference between configuration and conformation is associated with "high" versus "low" energy barriers between the entities being considered. Generally we feel we know what "high" and "low" mean, but there are, in fact, numerous gray areas that appear as soon as one advances in the subject.
4. Beware the word *isomer!* It always should be accompanied by a modifier. Thus:
    a. Constitutional isomers have the same molecular formula, but differ in their constitution ("connectedness").
    b. Configurational isomers have the same molecular formula and constitution, but differ in their configuration (spatial arrangement of the atoms, ignoring simple torsion).
    c. Conformational isomers have the same molecular formula, constitution, and (if relevant) configuration, but differ in their conformation (spatial arrangement of the atoms resulting from simple torsion).