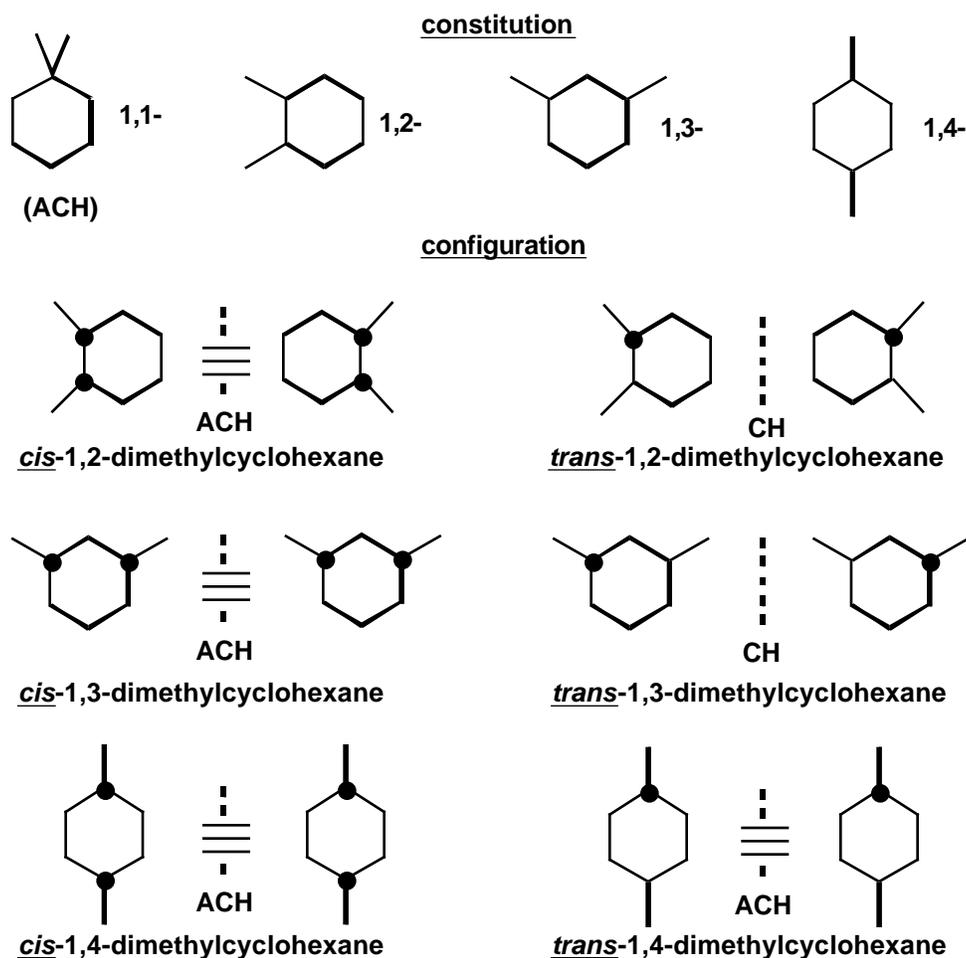


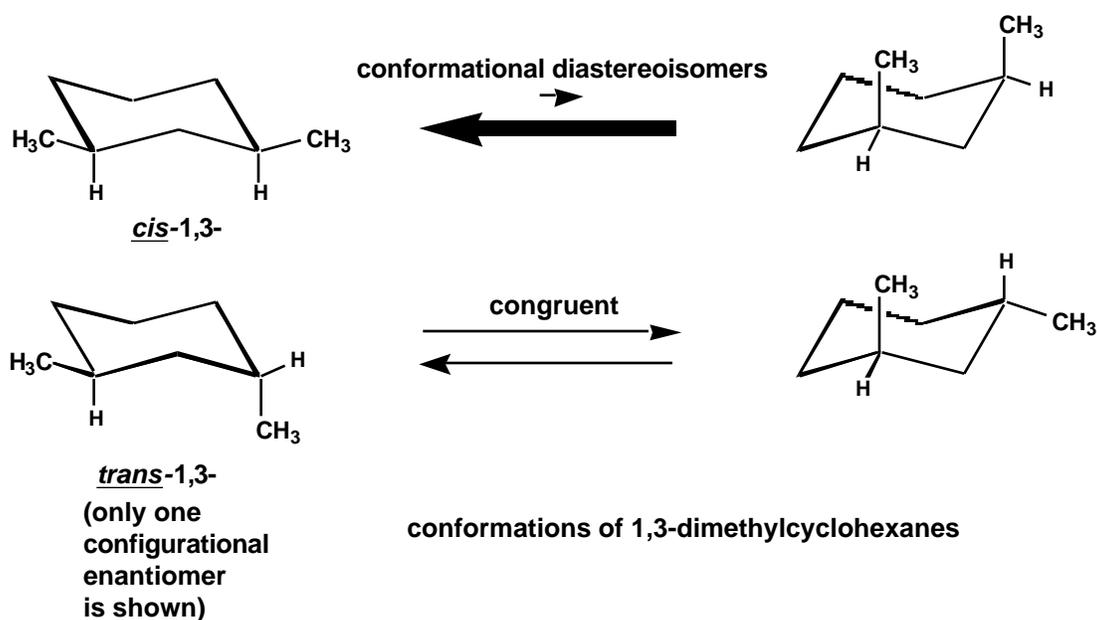
**Text Related to Segment 5.06 ©2002 Claude E. Wintner**

We can review the concepts we have dealt with above by considering as a final exercise the dimethylcyclohexanes. First treating the problem as regards constitution and configuration, we find (in addition to the 1,1- case) *cis*- and *trans*- 1,2-, 1,3-, and 1,4- isomers. Both of the 1,4- diastereoisomers are achiral, the symmetry being the same as for the 1,3-dimethylcyclobutanes:



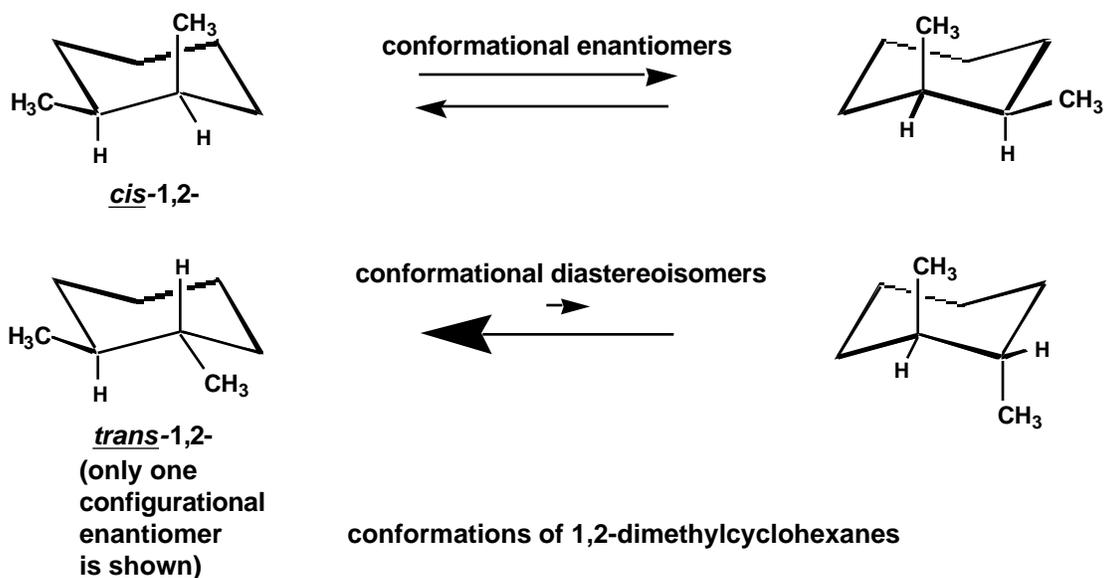
A conformational analysis of the dimethylcyclohexanes brings out several further interesting points. We already have stressed that "up" and "down" relative to the plane of the ring remain usable concepts, regardless of the conformation. Hence,

we did not mishandle the configurational problem by solving it, as we did above, using the conformationally unrealistic, but configurationally sound, platform of a planar cyclohexane ring. In the preceding segment we saw that when two methyl groups are attached *cis*-1,3- on the framework of the chair form of the cyclohexane ring, both will be equatorial. Note that in this case the diequatorial and the diaxial forms are *conformational diastereoisomers*, each of which is *achiral*. On the other hand, when the two methyl groups are fixed *trans*-1,3- on the same framework, it is apparent that if one methyl group is set in the favored equatorial position, the other must needs be axial. We know from our configurational analysis that *trans*-1,3-dimethylcyclohexane is *configurationally chiral*, but it is noteworthy that when the conformer of either configurational enantiomer is flipped, the starting conformational structure is precisely regenerated, as can be seen by rotating the formula of the "product" in space, to achieve congruence:

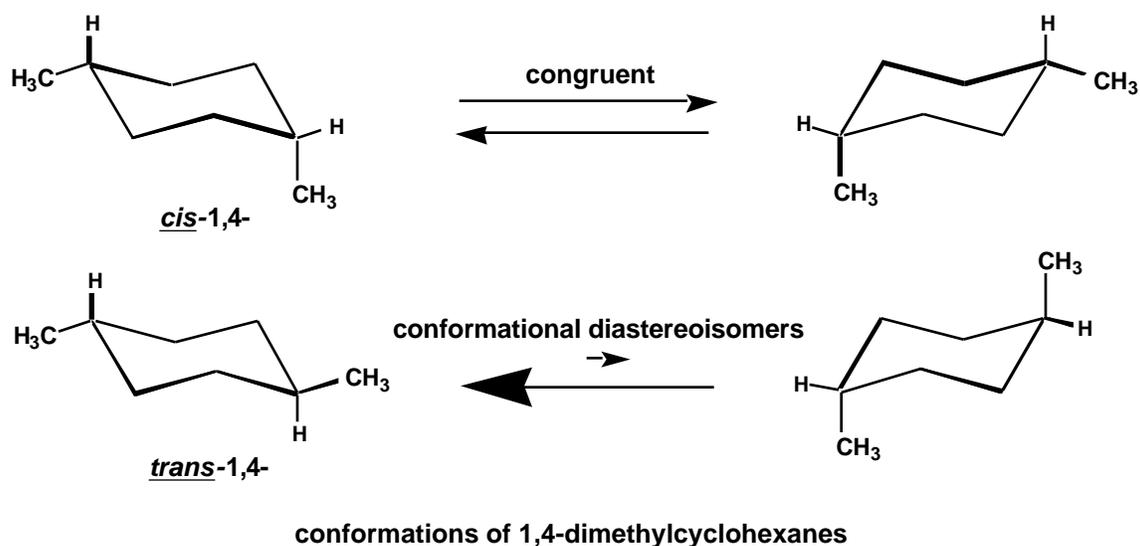


If the two methyl groups are incorporated in a *cis*-1,2- relationship, again it is necessary that one be equatorial and the other axial. The previous figure revealed

*cis*-1,2-dimethylcyclohexane as *configurationally achiral*. However, examination of the two conformers drawn for this molecule reveals that each is *conformationally chiral*, and that each is the *conformational enantiomer* of the other. The result is that *cis*-1,2-dimethylcyclohexane exists as a racemic mixture of conformational enantiomers. Remember, however, that the flipping among cyclohexane conformations occurs at the rate of  $10^5$  per second at room temperature. When a beam of plane polarized light is passed through *cis*-1,2-dimethylcyclohexane, no rotation of the plane of the beam is observed, any sample having, on average in the dynamic equilibrium, equal numbers of molecules in each conformation at any given moment. Although, in principle, resolution of such a racemate should be possible at very low temperatures — when the rate of flipping would be greatly diminished — the experiment has not been carried out. Two methyl groups set *trans*-1,2- on the framework of chair cyclohexane may be either both equatorial or both axial. As we already have seen for the conformational diastereoisomers of *cis*-1,3-dimethylcyclohexane, also here the equilibrium lies well on the side of the diequatorial form, although in this diaxial case the methyl groups, since they are on *opposite* sides of the ring, do not suffer a *cis*-1,3-diaxial methyl interaction. Furthermore, since *trans*-1,2-dimethylcyclohexane is *configurationally chiral*, each configurational enantiomer exists, separately, as either diequatorial or diaxial, and cannot be converted into the opposing configurational enantiomer:



Finally, *cis*-1,4-dimethylcyclohexane presents a single configurationally and conformationally achiral form, with one equatorial and one axial substituent, and congruent with the "product" obtained when the ring flips. The likewise configurationally achiral *trans*-1,4-dimethylcyclohexane exists as two achiral conformational diastereoisomers, of which the diequatorial again is favored heavily over the diaxial.



©2002 Claude E. Wintner