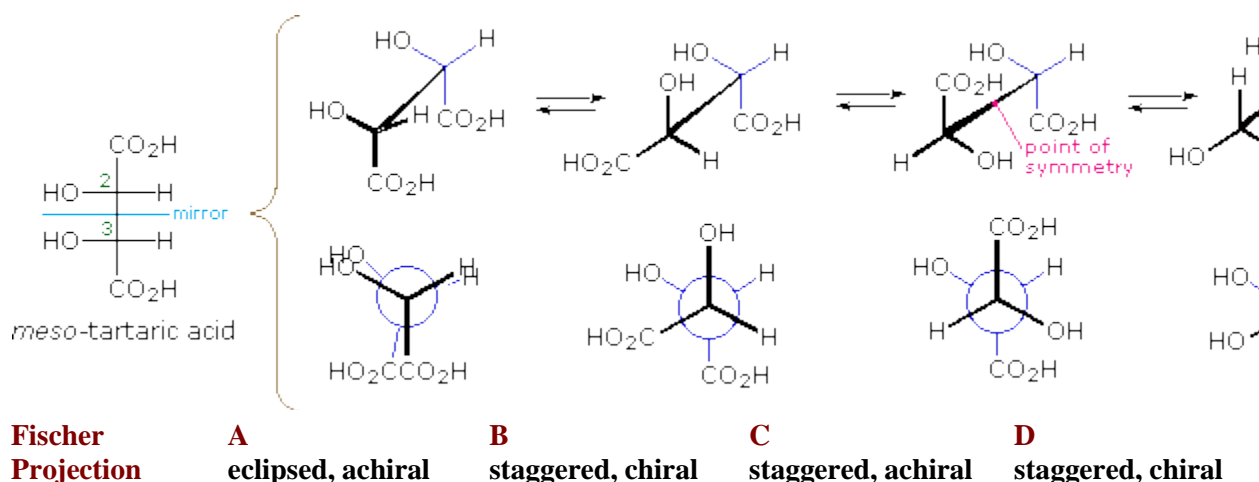


Conformational Enantiomorphism

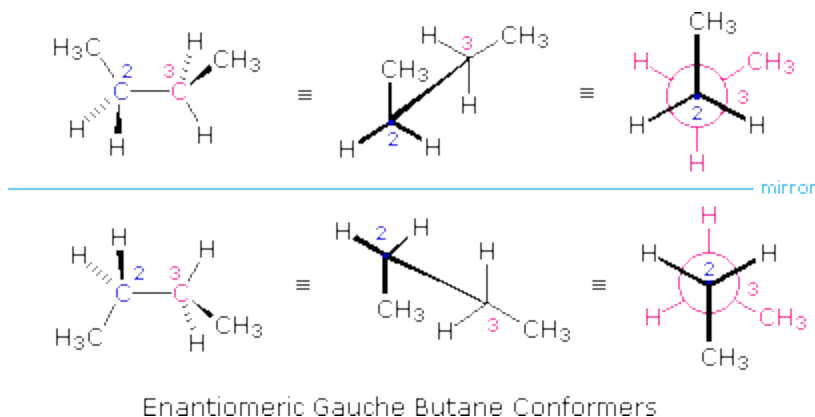
The Fischer projection formula of meso-tartaric acid has a plane of symmetry bisecting the C2–C3 bond, as shown on the left in the diagram below, so this structure is clearly achiral. The eclipsed orientation of bonds that is assumed in the Fischer drawing is, however, an unstable conformation, and we should examine the staggered conformers that undoubtedly make up most of the sample molecules. The four structures that are shown to the right of the Fischer projection consist of the achiral Fischer conformation (**A**) and three staggered conformers, all displayed in both sawhorse and Newman projections. The second and fourth conformations (**B & D**) are dissymmetric, and are in fact enantiomeric structures. The third conformer (**C**) has a center of symmetry and is achiral.

Conformations of meso-Tartaric Acid



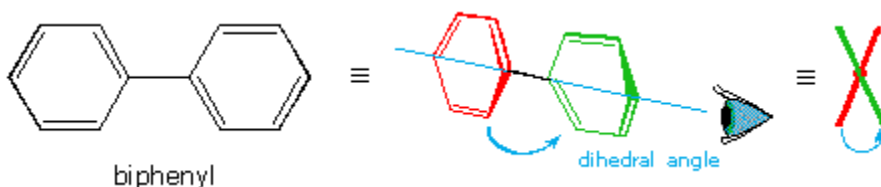
Since a significant proportion of the meso-tartaric acid molecules in a sample will have chiral conformations, the achiral properties of the sample (e.g. optical inactivity) should not be attributed to the symmetry of the Fischer formula. Equilibria among the various conformations are rapidly established, and the proportion of each conformer present at equilibrium depends on its relative potential energy (the most stable conformers predominate). Since enantiomers have equal potential energies, they will be present in equal concentration, thus canceling their macroscopic optical activity and other chiral behavior. Simply put, any chiral species that are present are racemic.

It is interesting to note that chiral conformations are present in most conformationally mobile compounds, even in the absence of any chiral centers. The gauche conformers of butane, for example, are chiral and are present in equal concentration in any sample of this hydrocarbon. The following illustration shows the enantiomeric relationship of these conformers, which are an example of a chiral axis rather than a chiral center.

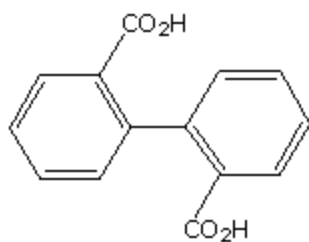


Conformations of Biphenyls

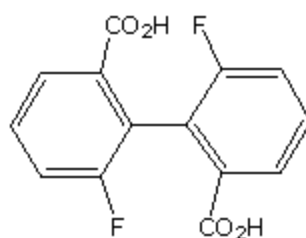
Another class of compounds that display conformational enantiomorphism are the substituted biphenyls. As shown in the following diagram, biphenyl itself is not planar, one benzene ring being slightly twisted or canted in relation to the other as a consequence of steric crowding. **This crowding will be demonstrated by clicking on the diagram.** The resulting chiral conformation, having a dihedral angle of about 45° , equilibrates rapidly with its enantiomer by rotation about the connecting single bond. Note that a conformation having a 90° dihedral angle is achiral, as a consequence of a plane of symmetry.



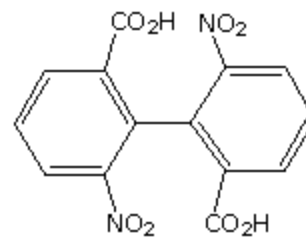
If each of the phenyl rings of a biphenyl has two different ortho or meta substituents (one may be hydrogen), even the twisted 90° dihedral angle conformer becomes chiral. In order to interconvert such conformers with their mirror image structures, a rotation through the higher energy coplanar form must be made. The ease with which this interconversion occurs will depend on the size of the ortho substituents, since these groups must slide past each other. The 2,2'-dicarboxylic acid on the left below cannot be resolved at room temperature, since thermal (kinetic) energy is sufficient to provide the necessary activation energy for racemization. The two additionally substituted diacids to its right have a higher activation energy for racemization, and can be resolved if care is taken to avoid heating them. **As a rule, an activation energy barrier of 16 to 19 kcal/mole is required to prevent spontaneous room temperature racemization of substituted biphenyls.** Since fluorine is smaller than a nitro group, the center compound racemizes more rapidly on heating than does the nitro compound to its right. Conformational isomers that are isolable due to high energy barriers are called **atropisomers**.



not resolved at room temperature



resolved at room temperature
racemizes easily



resolved at room temperature
racemizes slowly

Source : <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/sterism3.htm#isom13>