The six-membered rings of decalin, like those of cyclohexane, are expected to be most stable in the chair form. However, there are two possible ways in which two chairs can be joined (Figure 12-21). The ring-junction hydrogens may be either on the same side of the molecule (cis-decalin) or on opposite sides (trans-decalin). When the two rings are joined through two equatorial-type bonds, trans-decalin results, whereas an axial-equatorial union gives cis-decalin. Both isomers are known, and the trans isomer is about \(2 \text{ kcal mol}^{-1}\) more stable than the cis isomer, largely because of relatively unfavorable nonbonded interactions within the concave area of cis-decalin (see Figure 12-22).

**Figure 12-21:** Chair conformations of the decalins. The two drawings of the cis conformation represent the same arrangement of atoms but different perspectives.

**Figure 12-22:** Representation of cis-decalin showing nonbonded interactions (shaded areas). The numbering of the decalin ring is the currently accepted convention, which is not the same as the numbering system used generally for bicyclic systems, as described in Section 12-8.

It is of historical interest to note that the Baeyer strain theory with its planar rings predicts only one form of decalin with the ring-junction hydrogens on the same side of the molecule (Figure 12-23). The Sachse-Mohr concept of puckered strain-free rings allows for two isomers. In fact, Mohr predicted that the two isomers of decalin should exist before W. Hückel (1925) succeeded in preparing them. Both isomers occur in petroleum.

**Figure 12-23:** Baeyer formulation of decalin which, with planar rings, allows for only the cis configuration at the ring conjunction.

At this point, it probably will be helpful to construct models of cis- and trans-decalins to appreciate the following: (a) The two compounds cannot interconvert unless \(\text{C-C}\) or \(\text{C-H}\) bonds first are broken. (b) trans-Decalin is a relatively rigid system and, unlike cyclohexane, the two rings cannot flip from one chair form to another. Accordingly, the orientation of the substituent is fixed in the chair-chair conformation of trans-decalin. (c) The chair-chair forms of cis-decalin are relatively flexible, and inversion of both rings at once occurs fairly easily (the barrier to inversion is about \(14 \text{ kcal mol}^{-1}\)). A substituent therefore can interconvert between axial and equatorial conformations (Figure
Figure 12-24: Ring inversion in cis-decalin, which takes a substituent from the equatorial to the axial position. In both conformations, each ring is a chair form. You should check this process with ball-and-stick models.

The ramifications of conformational analysis of flexible and rigid ring systems are of considerable importance to the understanding of stability and reactivity in polycyclic systems. This will become increasingly evident in later discussions.

Contributors