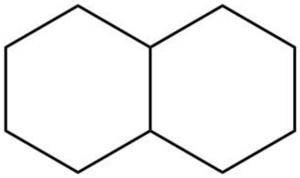
❖ Decalins

If two cyclic compounds are fused together, we will get a bicyclic system. These bicyclic compounds can be either bridged or fused systems. Two cycles share two adjacent C atoms in a fused system, whereas one or more carbon atoms act as a bridge between two non-adjacent carbon atoms in bridged systems. Here we will study one special kind of fused ring system called decalin or bicyclo-[4,4,0]-decane.

Fused bicyclo compound



Bicyclo-[4,4,0]-decane
(Decalin)

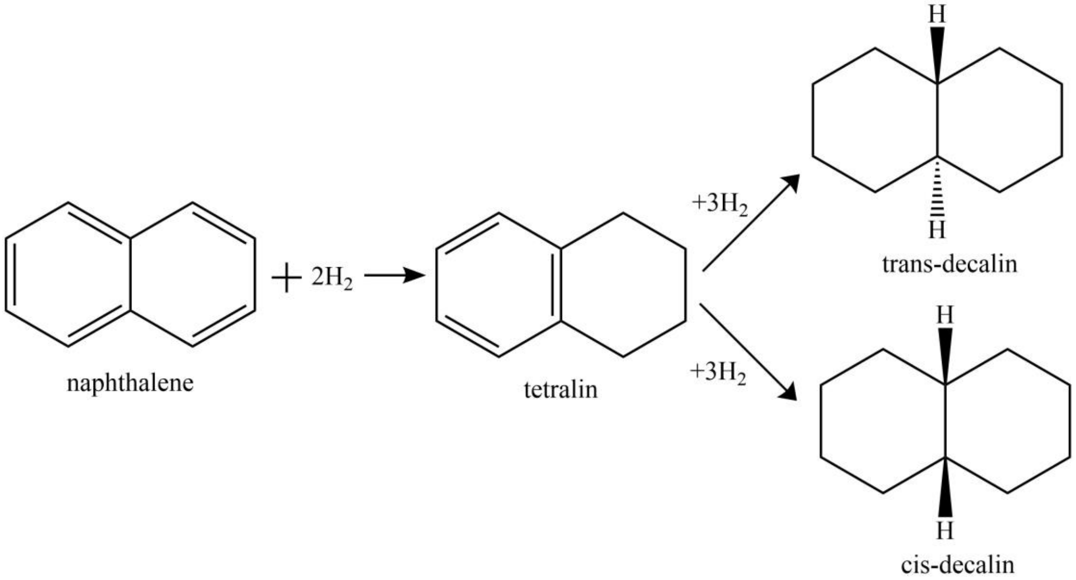
Bridged bicyclo compound

Bicyclo-[2,2,1]-heptane
(Norbornane)

Also, as far as the IUPAC name of decalin is concerned i.e. bicyclo-[4,4,0]-decane, the numbers 4, 4, 0 show the number of C atoms in each cycle (excluding the bridgehead carbon atoms).

➢ *Synthesis of Decalin*

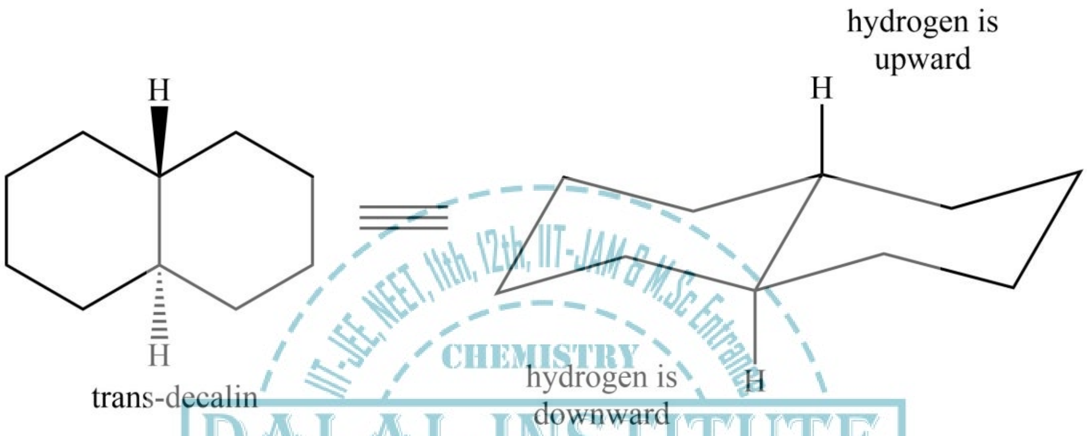
One of the most popular names of Decalin is decahydronaphthalene because it is a saturated counterpart of naphthalene molecule, and can also be obtained from the same by simple hydrogenation in a fused state.



The preparation gives two stereoisomers of decalin; where the first have both the hydrogens at the bridgehead carbons at ‘cis’ arrangement and trans hydrogens in the second one.

➢ *Geometrical Isomerism in Decalin*

Since there are two cyclohexane rings fused in decalin, and those cyclohexenes are most stable in their chair form; it is reasonable to think that most stable should also have them in chair form. Using the same rationale, Sachse and Mohr proposed the decalin should be a puckered structure with no strain which exists as two isomers that cannot be interconverted without any bond-breaking. And therefore, they must be treated as diastereomers or configurational isomers. Both the puckered structures of decalin (cis and trans isomers) are shown below.



trans-decalin

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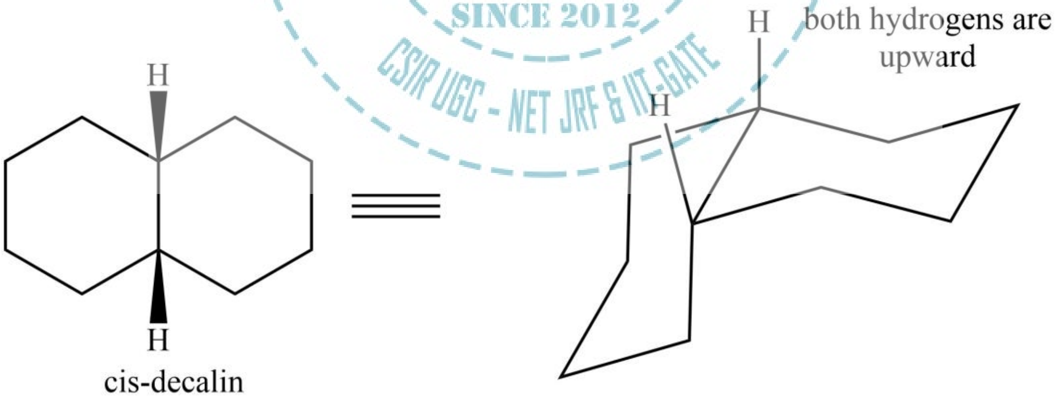

cis-decalin

Now because both the stereoisomers have cyclohexane chairs, there should be no torsional or angle strain in either decalin molecule. It is also obvious that the two bridgehead hydrogens in trans decalin are directed in opposite directions, and therefore, both are axial hydrogens. Conversely, the two bridgehead hydrogens in cis decalin are pointing in the same direction with one axial and other of equatorial nature.

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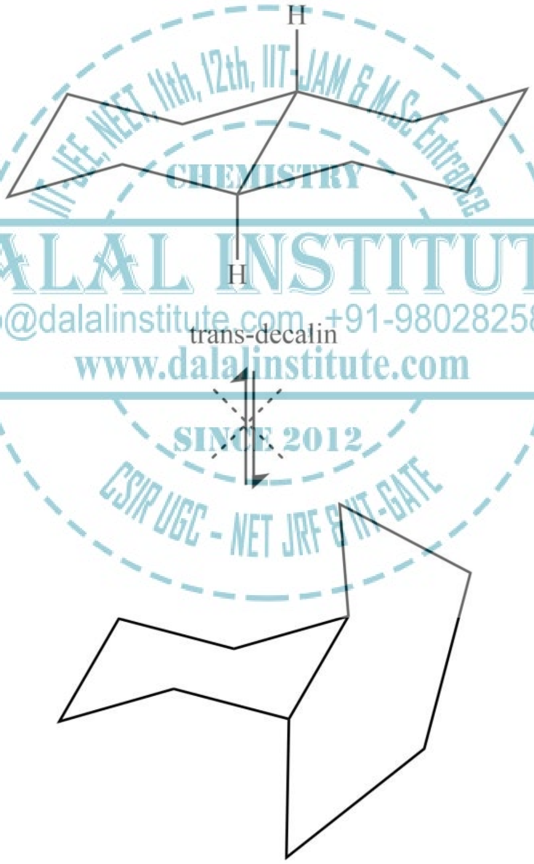
➢ *Conformational Analysis of Decalin*

After studying the geometrical isomerism in decalin, we need to discuss the conformational behavior of the same in a more comprehensive and sophisticated way. To do so, we will first discuss the ring flipping in trans and cis-decalin one by one.

1. Ring flipping in trans-decalin: The two cyclohexane rings in trans decalin are connected via equatorial positions. Since we know that the flipping of the ring in cyclohexane converts all the axial bonds to equatorial bonds and the vice-versa is also true, the flipping of the ring in trans-decalin would give a conformation where the two cyclohexane units would be connected via axial bonds. Nevertheless, this ring flipping is strongly forbidden because it is not conceivable to build a 6-membered ring with two diagonally opposite bonds. We are bound to fail if we attempt to build a molecular model in which the cyclohexane units are connected via axial bonds.



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Hence, we may conclude that the trans-decalin is actually ‘conformationally locked’ making ring flipping impossible. So, it keeps its equatorial confirmation for both the rings. Also, e,e-trans-decalin has an inversion center, and therefore, it is an optically inactive or achiral compound. In other words, trans-decalin is superimposable on its mirror image. There are also two C_2 symmetry axes, the first one through the equator and the other one passes through the axis.

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2. Ring flipping in cis-decalin: Unlike trans-decalin, which is relatively flat, the cis-decalin resembles a tent-like geometry with less hindered (convex)and more hindered (concave) sides. Though in both cases the cyclohexanes are stable chair-like conformations, the cis decalin has them with equatorial and axial bond joining. The flipping of the ring is allowed in this situation which changes one cis form into another one and translates the equatorial bonds to axial ones.

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The conformational study of cis-decalin also proved that it is an optically active or chiral molecule even if it has no chiral center. In other words, the cis-decalin cannot be superimposed on its mirror image. Nevertheless, a rapid flipping of the ring system cancels its optical activity and changes it into its mirror image. Consequently, we can not resolve the two chiral forms due to this rapid ring inversion, and it exists as a racemic mixture. The flipping of the ring in cis-decalin has also been supported by the NMR studies proving that only one peak H-NMR spectra; whereas, two proton peaks are observed in trans decalin. Two H-NMR peaks in the spectra of trans-decalin can be credited to its inflexibility. The equatorial and axial hydrogens are present in different chemical, as well as magnetic environments, and therefore, show the different magnitude of chemical shifts. On the other hand, the cis-decalin is able of very fast interconversion resulting in a single chemical shift for all the hydrogens.

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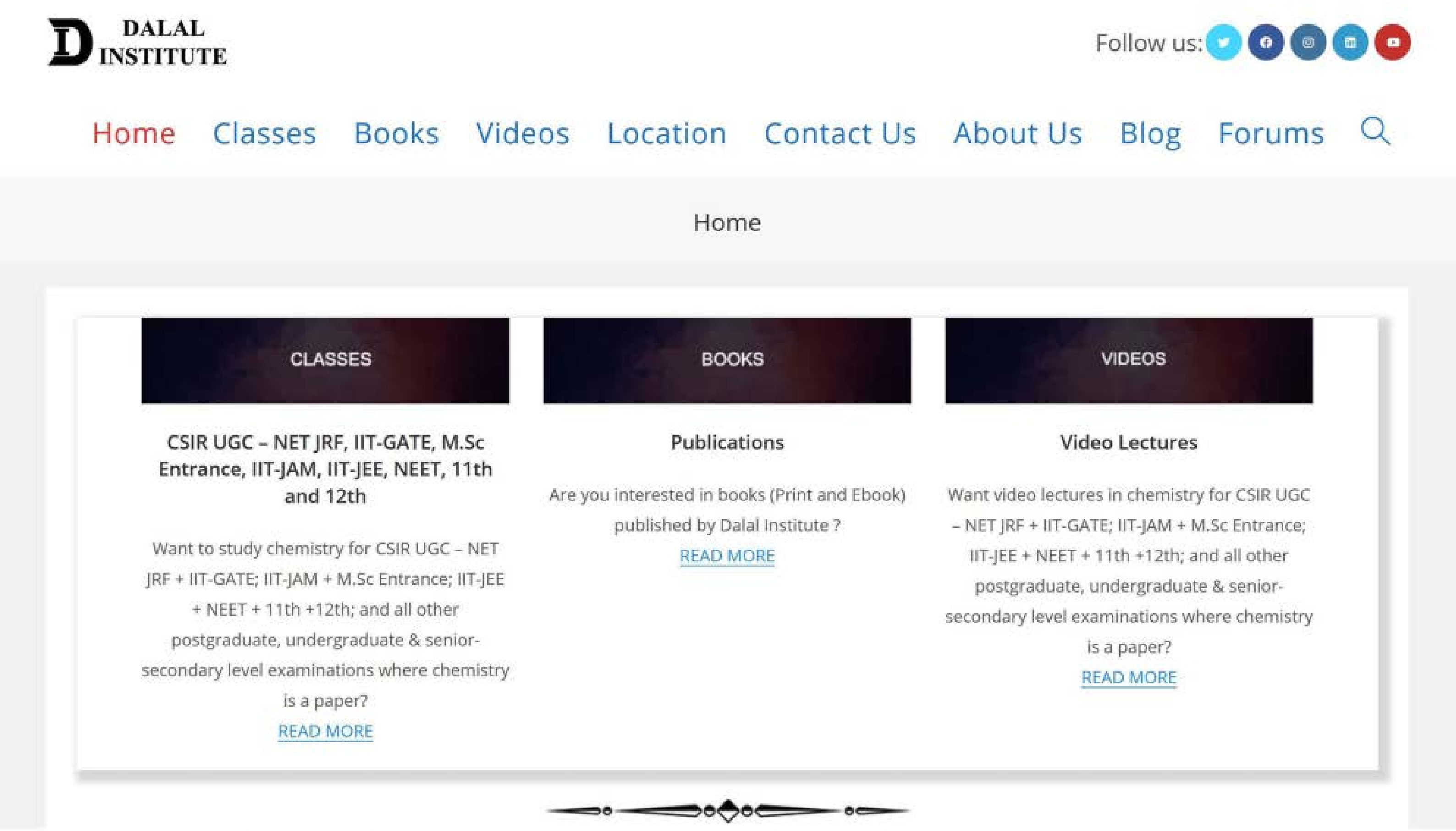

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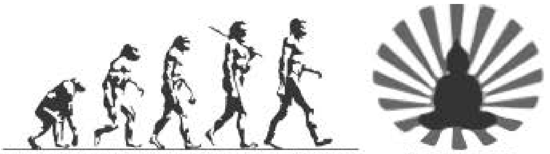

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