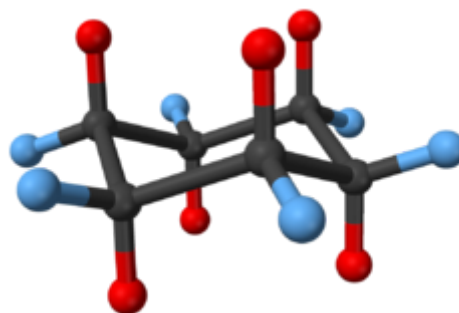


# Cyclohexane conformation

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In organic chemistry, **cyclohexane conformations** are any of several three-dimensional shapes adopted by molecules of cyclohexane. Because many compounds feature structurally similar six-membered rings, the structure and dynamics of cyclohexane are important prototypes of a wide range of compounds.<sup>[1][2]</sup>

The internal angles of a regular, flat hexagon are  $120^\circ$ , while the preferred angle between successive bonds in a carbon chain is about  $109.5^\circ$ , the tetrahedral angle. Therefore, the cyclohexane ring tends to assume certain non-planar (warped) conformations, which have all angles closer to  $109.5^\circ$  and therefore a lower strain energy than the flat hexagonal shape. The most important shapes are *chair*, *half-chair*, *boat*, and *twist-boat*. Their relative stabilities are: chair > twist boat > boat > half-chair. All relative conformational energies are shown below.<sup>[3][4]</sup> The molecule can easily switch between these conformations, and only two of them—*chair* and *twist-boat*—can be isolated in pure form.



A cyclohexane molecule in *chair* conformation. Hydrogen atoms in axial positions are shown in red, while those in equatorial positions are in blue.

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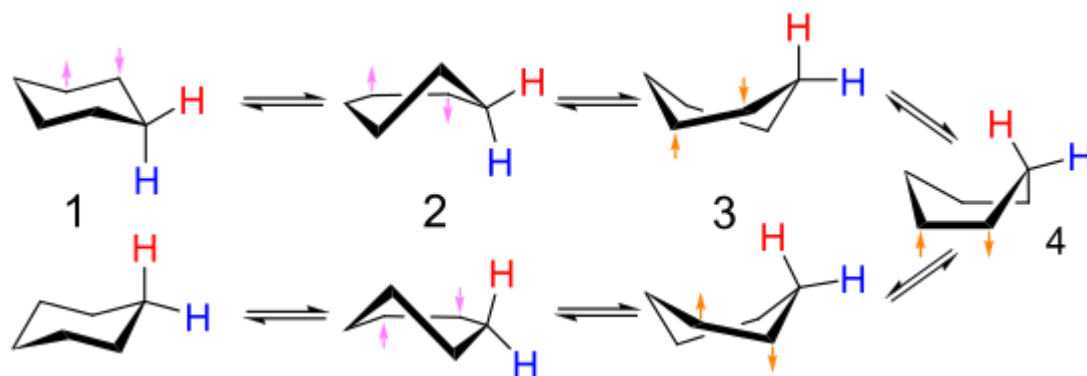
## Principal conformers

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### Chair conformation

The chair conformation is the most stable conformer. At 25 °C, 99.99% of all molecules in a cyclohexane solution adopt this conformation.

The symmetry is  $D_{3d}$ . All carbon centers are equivalent. Six hydrogen centers are poised in axial positions, roughly parallel with the  $C_3$  axis. Six hydrogen atoms are poised nearly perpendicular to the  $C_3$  symmetry axis. These H atoms are respectively referred to as axial and equatorial.



Cyclohexane chair flip (ring inversion) reaction via boat conformation (4). Structures of the significant conformations are shown: chair (1), half-chair (2), twist-boat (3) and boat (4).

When ring flip happens completely from chair-to-chair, hydrogens that were previously axial (blue H in upper-left structure) turn equatorial and equatorial ones (red H in upper-left structure) turn axial.<sup>[3]</sup>

Each carbon bears one "up" and one "down" hydrogen. The C-H bonds in successive carbons are thus staggered so that there is little torsional strain. The chair geometry is often preserved when the hydrogen atoms are replaced by halogens or other simple groups.

## Boat and twist-boat conformations

The boat conformations have higher energy than the chair conformations. The interaction between the two flagpole hydrogens, in particular, generates steric strain. Torsional strain also exists between the C2–C3 and C5–C6 bonds, which are eclipsed. Because of this strain, the boat configuration is unstable (i.e. is not a local energy minimum).

The molecular symmetry is  $C_{2v}$ .

The boat conformations spontaneously distorts to twist-boat conformations. Here the symmetry is  $D_2$ , a purely rotational point group. This conformation can be derived from the boat conformation by applying a slight twist to the molecule so as to remove eclipsing of two pairs of methylene groups.

The concentration of the twist-boat conformation at room temperature is less than 0.1%, but at 1073 kelvins it can reach 30%. Rapid cooling of a sample of cyclohexane from 1073 K to 40 K will freeze in a large concentration of twist-boat conformation, which will then slowly convert to the chair conformation upon heating.<sup>[5]</sup>

## Dynamics

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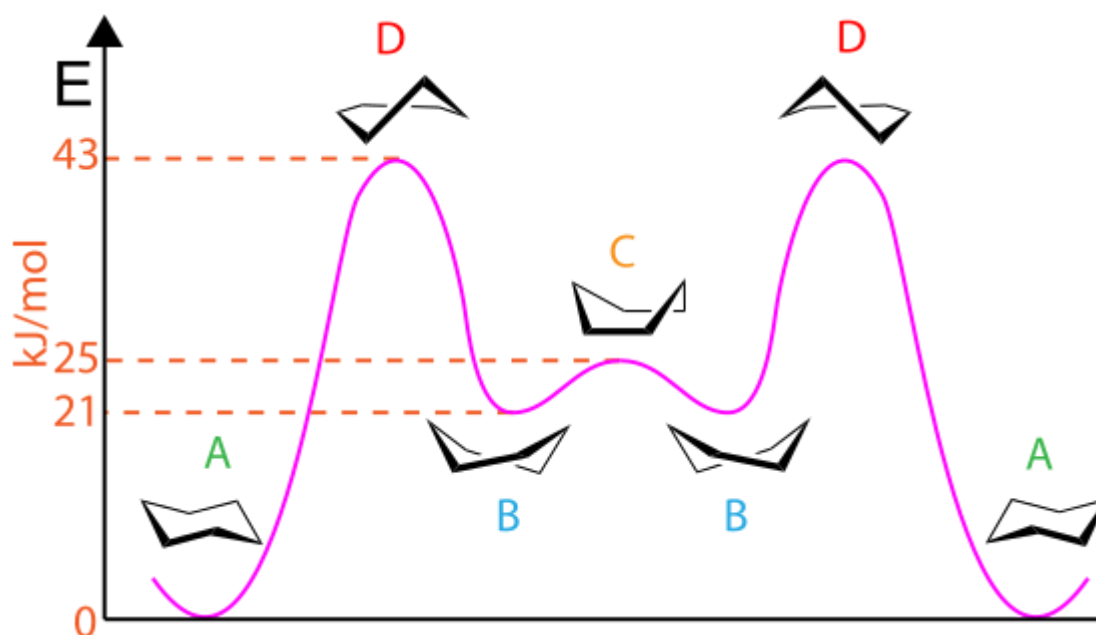
### Chair-chair

The interconversion of chair conformers is called **ring flipping** or **chair-flipping**. Carbon-hydrogen bonds that are axial in one configuration become equatorial in the other, and vice versa. At room temperature the two chair conformations rapidly equilibrate. The proton NMR spectrum of cyclohexane is a singlet at room temperature.

The detailed mechanism of the chair-to-chair interconversion has been the subject of much study and debate.<sup>[6]</sup> The **half-chair state (D)**, in figure below) is the key transition state in the interconversion between the chair and twist-boat conformations. The half-chair has  $C_2$  symmetry. The interconversion between the two chair conformations involves the following sequence: chair  $\rightarrow$  half-chair  $\rightarrow$  twist-boat  $\rightarrow$  half-chair'  $\rightarrow$  chair'.

## Twist-boat - twist-boat

The boat conformation (C, below) is a transition state, allowing the interconversion between two different twist-boat conformations. While the boat conformation is not *necessary* for interconversion between the two chair conformations of cyclohexane, it is often included in the reaction coordinate diagram used to describe this interconversion because its energy is considerably lower than that of the half-chair, so any molecule with enough energy to go from twist-boat to chair also has enough energy to go from twist-boat to boat. Thus, there are multiple pathways by which a molecule of cyclohexane in the twist-boat conformation can achieve the chair conformation again.



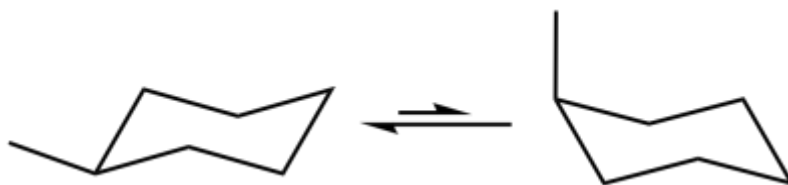
Conformations: chair (A), twist-boat (B), boat (C) and half-chair (D). Energies are 43 kJ/mol (10 kcal/mol), 25 kJ/mol (6 kcal/mol) and 21 kJ/mol (5 kcal/mol).<sup>[3]</sup>

## Substituted derivatives

In cyclohexane, the two chair conformations have the same energy. The situation becomes more complex with substituted derivatives. In methylcyclohexane the two chair conformers are not isoenergetic. The methyl group prefers the equatorial orientation. The preference of a substituent towards the equatorial conformation is measured in terms of its A value, which is the Gibbs free energy difference between the two chair conformations. A positive A value indicates preference towards the equatorial position. The magnitude of the A values ranges from nearly zero for very small substituents such as deuterium, to about 5 kcal/mol (21 kJ/mol) for very bulky substituents such as the tert-butyl group.

## Disubstituted cyclohexanes

For 1,2- and 1,4-disubstituted cyclohexanes, a *cis* configuration leads to one axial and one equatorial group. Such species undergo rapid, degenerate chair flipping.



The conformer of methylcyclohexane with equatorial methyl is favored by 1.74 kcal/mol (7.3 kJ/mol) relative to the conformer where methyl is axial.

For 1,3-disubstituted cyclohexanes, the *cis* form is diequatorial and the flipped conformation suffers additional steric interaction between the two axial groups. *trans*-1,3-Disubstituted cyclohexanes are like *cis*-1,2- and *cis*-1,4- and can flip between the two equivalent axial/equatorial forms.<sup>[2]</sup>

*Cis*-1,4-Di-*tert*-butylcyclohexane has an axial *tert*-butyl group in the chair conformation and conversion to the twist-boat conformation places both groups in more favorable equatorial positions. As a result, the twist-boat conformation is more stable by 0.47 kJ/mol (0.11 kcal/mol) at 125 K as measured by NMR spectroscopy.<sup>[6]</sup>

## Heterocyclic analogs

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Heterocyclic analogs of cyclohexane are pervasive in sugars, piperidines, dioxanes, etc. They exist generally follow the trends seen for cyclohexane, i.e. the chair conformer being most stable. The axial-equatorial equilibria (A values) are however strongly affected by the replacement of a methylene by O or NH. Illustrative are the conformations of the glucosides.<sup>[2]</sup> 1,2,4,5-Tetrathiane ((SCH<sub>2</sub>)<sub>3</sub>) lacks the unfavorable 1,3-diaxial interactions of cyclohexane. Consequently its twist-boat conformation is populated; in the corresponding tetramethyl structure, 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane, the twist-boat conformation dominates.

## Historical background

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In 1890, Hermann Sachse, a 28-year-old assistant in Berlin, published instructions for folding a piece of paper to represent two forms of cyclohexane he called *symmetrical* and *unsymmetrical* (what we would now call *chair* and *boat*). He clearly understood that these forms had two positions for the hydrogen atoms (again, to use modern terminology, *axial* and *equatorial*), that two chairs would probably interconvert, and even how certain substituents might favor one of the chair forms (Sachse–Mohr theory). Because he expressed all this in mathematical language, few chemists of the time understood his arguments. He had several attempts at publishing these ideas, but none succeeded in capturing the imagination of chemists. His death in 1893 at the age of 31 meant his ideas sank into obscurity. It was only in 1918 when Ernst Mohr, based on the molecular structure of diamond that had recently been solved using the then very new technique of X-ray crystallography,<sup>[7][8]</sup> was able to successfully argue that Sachse's chair was the pivotal motif.<sup>[9][10][11][12][13][14]</sup> Derek Barton and Odd Hassel shared the 1969 Nobel Prize for work on the conformations of cyclohexane and various other molecules.

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## External links

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- [Java applets of all conformations \(http://wetcbe.cmbi.ru.nl//organic/cyclohexane/jm/chxjmol.html\)](http://wetcbe.cmbi.ru.nl//organic/cyclohexane/jm/chxjmol.html) from the [University of Nijmegen](#)
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