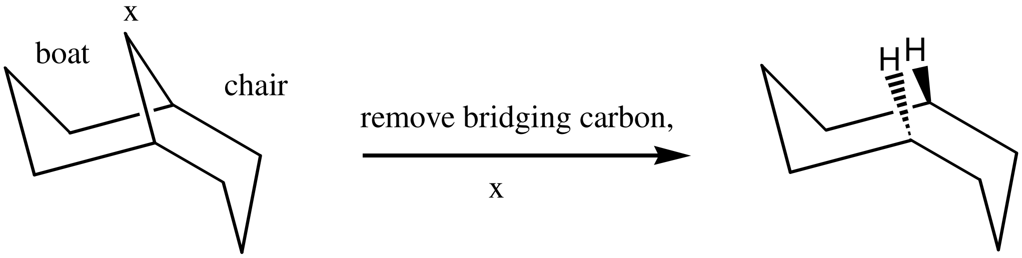
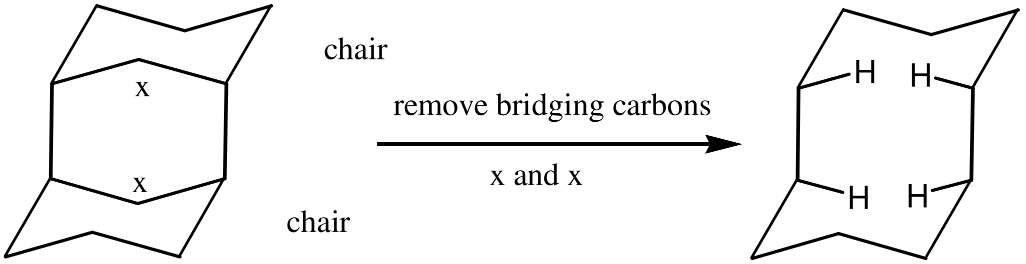
Alicyclic Chemistry. Lecture 2

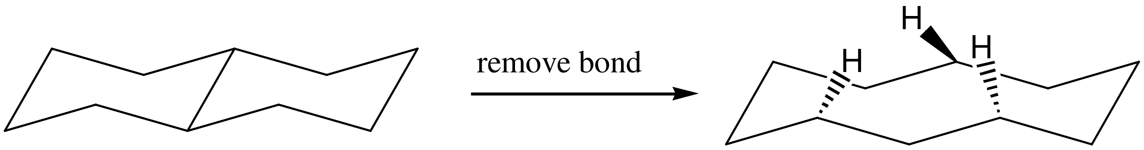
3. Transannular Strain (Medium, 8 – 11 membered, rings)

In cyclooctane the preferred conformation is the boat-chair, constructed from the boat and the chair conformations of two six-membered rings as follows:



On removal of the bridging carbon, x, from the bicyclo-nonane on the left, the resultant cyclooctane has two hydrogens, one either side of the ring, which point towards the space originally occupied by x. They, therefore, come within van der Waals radii of one another and this raises the energy of this conformation. Since this extra energy comes from the interaction of groups (hydrogens here) across the ring, it is known as Transannular Strain. The same is true in other medium rings as can be seen in cyclodecane, which exists in either the chair-chair conformation or the crown conformation:





Crown

In the former case two pairs of hydrogens get close to one another but the resultant strain is not as high as in cyclooctane, despite double the number of repulsive interactions, because cyclodecane is bigger and can flex slightly to pull the hydrogens apart. Likewise in the crown conformation some hydrogens interact across the ring.

The total strain energy in rings is reflected in their heats of combustion relative to that of cyclohexane, which is generally regarded as totally strain free:

The differences (Δ) in heat of combustion of cycloalkanes relative to that of cyclohexane in kJ mole^{-1} per CH_2

Ring Size (n):	3	4	5	7	8	9	10	11	12
Δ:	39	27	5.4	3.8	5.0	5.8	5.0	4.2	1.2
Δ x n:	117	108	27	27	40	52	50	46	14

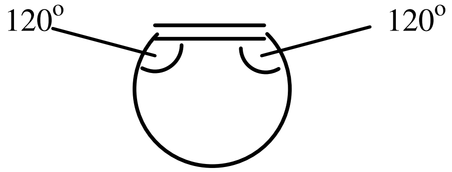
For comparison, the heats of combustion for oxiranes (114 kJ mole^{-1}) and aziridines (113 kJ mole^{-1}) suggest that these molecules also show the same bonding effects as cyclopropanes.

4. Cycloalkenes

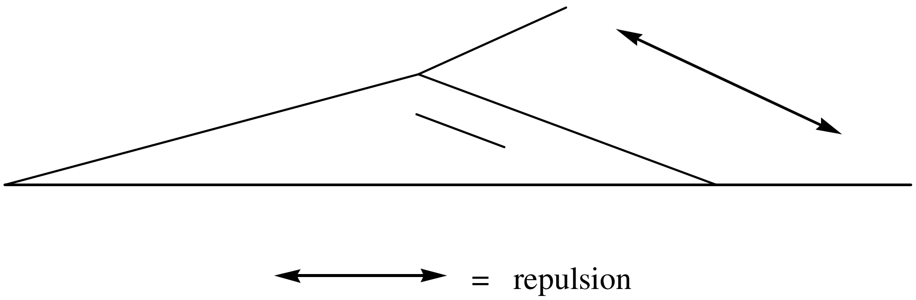
Alkenes add an extra parameter when considering the strain in rings, namely, their geometry.

i. cis –Cycloalkenes

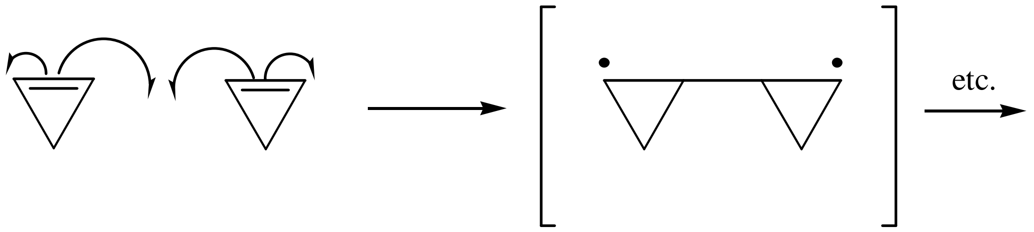
In these compounds we are trying to introduce two sp^2 angles into the ring and hence angle strain will go up for small rings:



In contrast, the torsional strain goes down slightly since we have removed two hydrogens e.g. in cyclopropene:

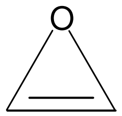


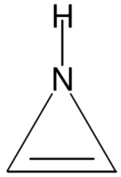
However, angle strain is much the larger force and thus the overall strain goes up on the introduction of a *cis* double bond. This is illustrated by the properties of cyclopropene itself which slowly polymerises at room temperature:



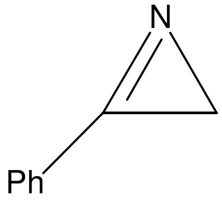
Naturally, the angle strain in the resultant polymer is lower since it is a poly-cyclopropANE.

2-Oxirenes and 2-Azirines (more commonly called 1H-azirines) are additionally unstable because they are both anti-aromatic and are transient species (4 electrons in the ring, one lone pair and one π-pair):



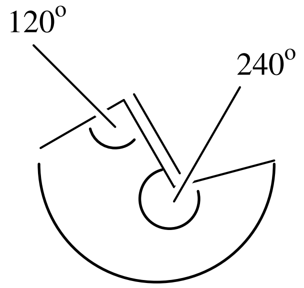


1-Azirines (more commonly called 2H-azirines) are known, the parent is unstable above liquid nitrogen temperatures but many substituted examples are isolable liquids or low-melting solids, e.g.:

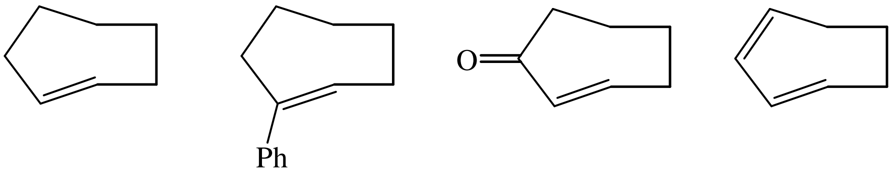


ii. trans-Cycloalkenes

Now we are trying to fit one 120° angle and one 240° angle into the ring and so the angle strain increases enormously:

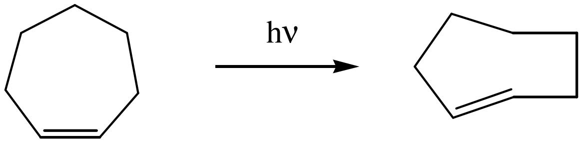


Indeed, it is not now possible to isolate compounds with rings smaller than eight which can accommodate a *trans*-double bond and remain stable at room temperature. *Trans*-cycloheptenes are known but they have short lifetimes:

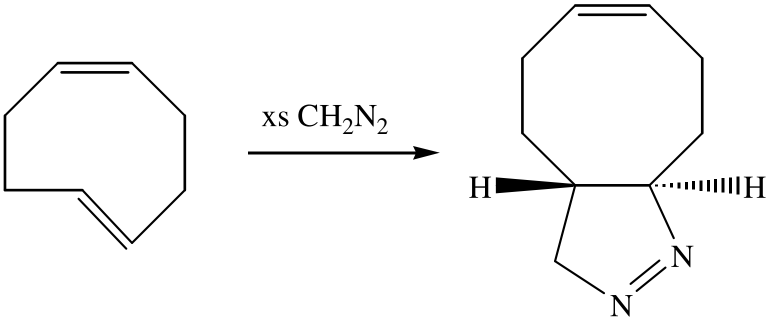


Half-life at room temperature	45s	4.2min	>17min	7.1min (-78°)

Many such short-lived species (and also stable compounds) can be made at low temperature by photolysis of the corresponding *cis*-isomer:

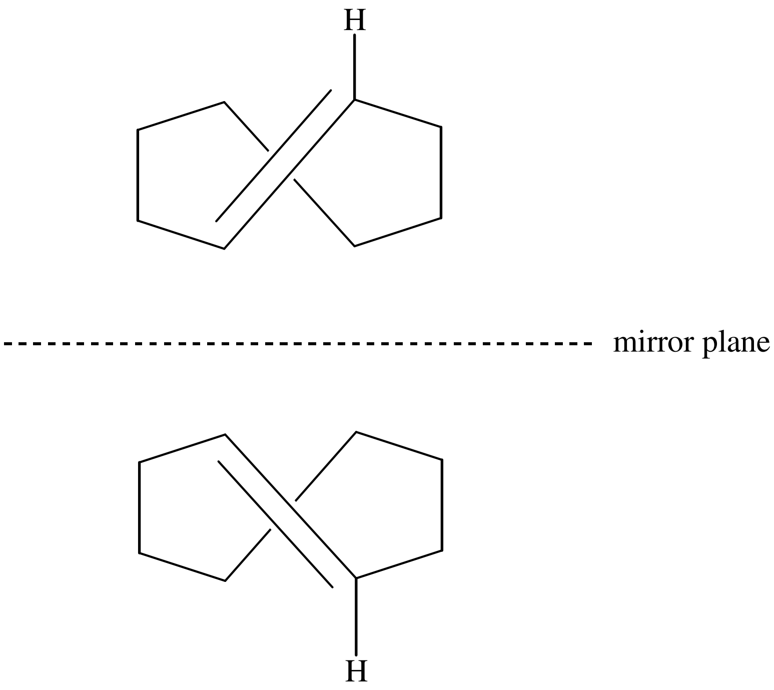


The extra strain of a *trans*-double bond in a ring can have interesting consequences. First, the *trans*-double bond is much more reactive as illustrated by the following case:

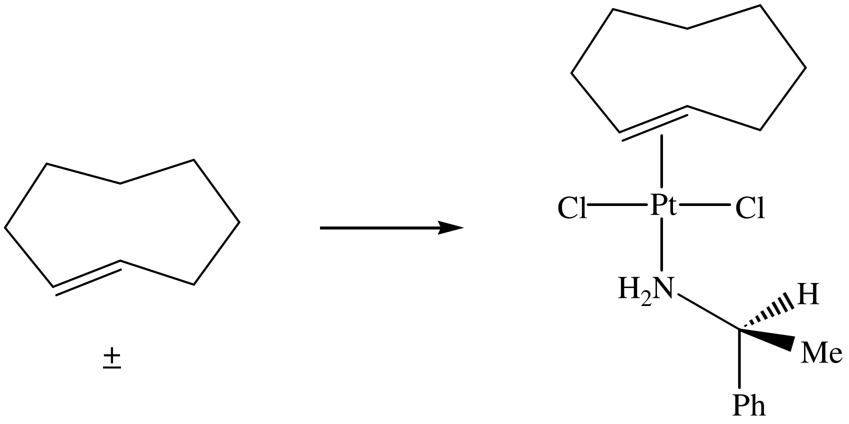


Note that the *cis*-double bond does not react even though an excess of reagent is used.

Second, the ring becomes dissymmetric e.g. in *trans*-cyclooctene we have a molecule with a C_2 proper axis of rotation which, therefore, can exist as two enantiomers:



Trans-Cyclooctene was first separated into its two enantiomers by Cope's group in 1963 by the formation of diastereoisomeric Pt complexes:



+.+ and +.−

Cope and his group found that the enantiomers only interconverted on heating. In contrast, *trans*-cyclononene racemised at much lower temperature and *trans*-cyclodecene racemised at below room temperature:

Ring Size:	8	9	10
Energy of racemisation ($kJ\ mol^{-1}$):	153	84	42

The reason for this trend relates to the physical mechanism of racemisation; the two enantiomers can be interconverted by rotation about two single bonds and consequent passage of one of the vinylic hydrogens through the centre of the ring. Obviously the bigger the ring, the easier it is to do this: