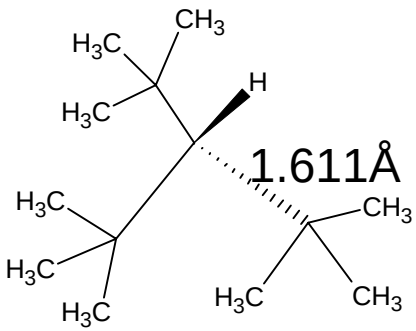
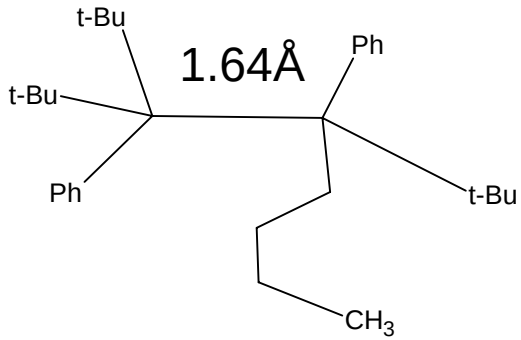
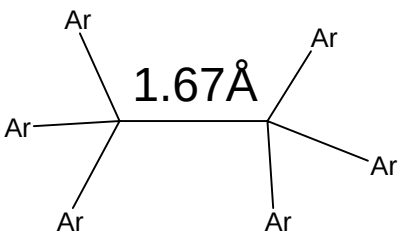
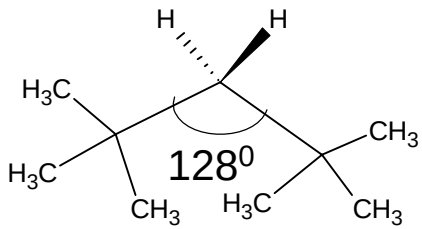
Highly-strained molecules

Longer bonds, larger bond angles

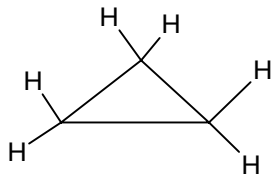




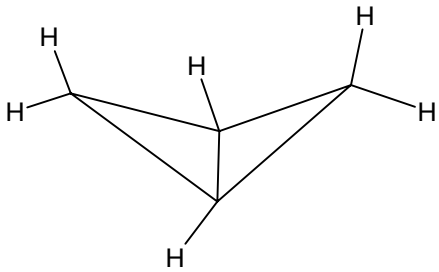




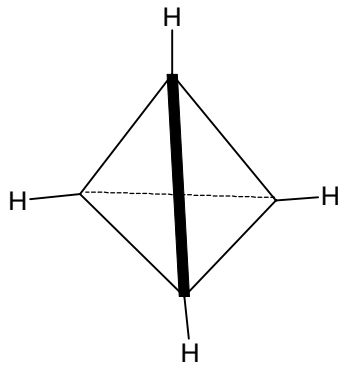
Small rings. Deviations to smaller bond angles



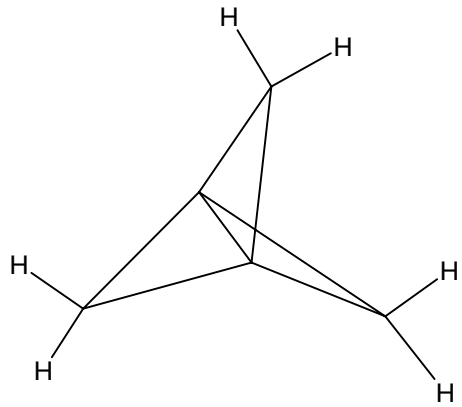
Cyclopropane
E_s = 27.5 kcal/mol



Bycyclobutane
E_s = 66.5 kcal/mol



Tetrahedrane
E_s = 140 kcal/mol

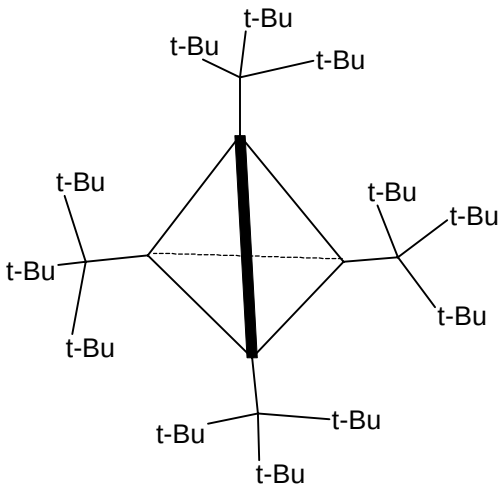


[1,1,1]-propellane
E_s = 66 kcal/mol

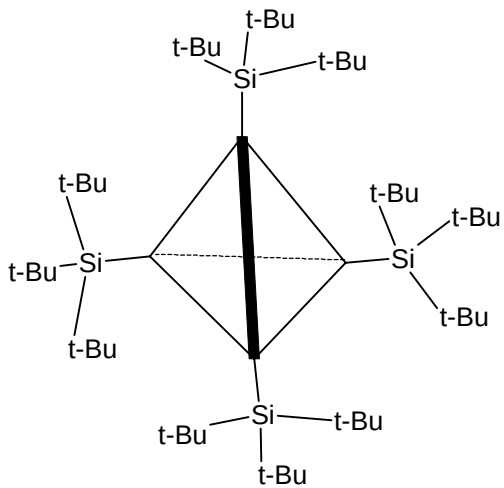
Bent bonds or Banana bonds

Bent bonds are a special type of bonding in which the ordinary hybridization state of two atoms making up a chemical bond are modified with increased or decreased s-orbital character in order to accommodate a particular molecular geometry. Bent bonds are found in strained organic compounds such as cyclopropane, oxirane and aziridine.

In these compounds it is not possible for the carbon atoms to assume the 109.5° bond angles with standard sp3 hybridization. Increasing the p character makes it possible to reduce the bond angles to 60°. At the same time the carbon to hydrogen bonds gain more s-character and shorten. In cyclopropane the maximum electron density between two carbon atoms does not correspond to the internuclear axis hence the name *bent bond*. In cyclopropane the **interorbital angle** is 104°. This bending can be observed experimentally by X-ray diffraction of certain cyclopropane derivatives: the **deformation density** is outside the line of centers between carbons. The carbon carbon bonds are unusually short: 1.51 Å versus 1.54 Å for a regular bond.



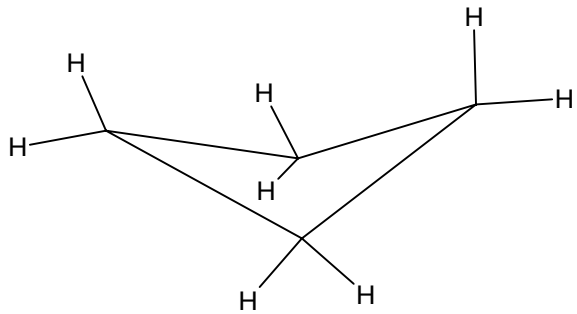
Corset effect

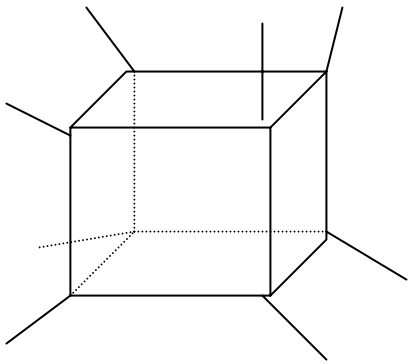


Banana bonds. Overlap of p-orbitals. The carbon atoms are high in s-character, almost sp. Si is a σ-donor to C.

Si-C bonds are longer- corset effect is smaller

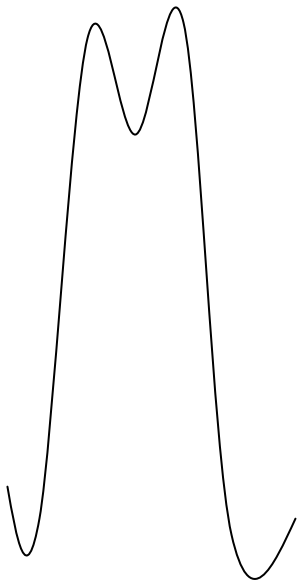
Cyclobutane is a larger ring but still has bent bonds. In this molecule the carbon bond angles are 90° for the planar conformation and 88° for the puckered one. Contrary to cyclopropane the CC bond lengths actually increase and not decrease and this is mainly due to 1,3-nonbonded steric repulsions. In terms of reactivity cyclobutane is relatively inert and behaves like ordinary alkanes.



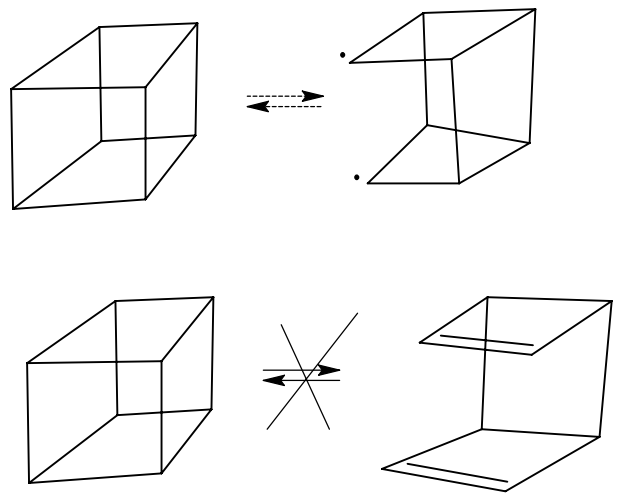


Cubane

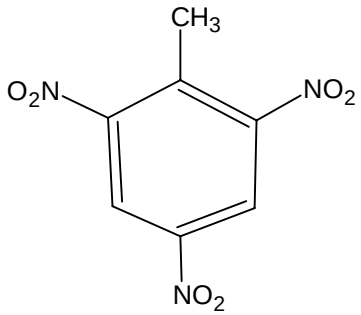
E_s = 166 kcal/mol



There is NO way to go!

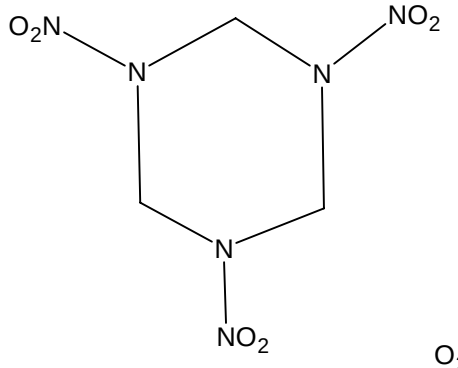


New explosive materials (energy storage)



2-methyl-1,3,5-trinitrobenzene

TNT

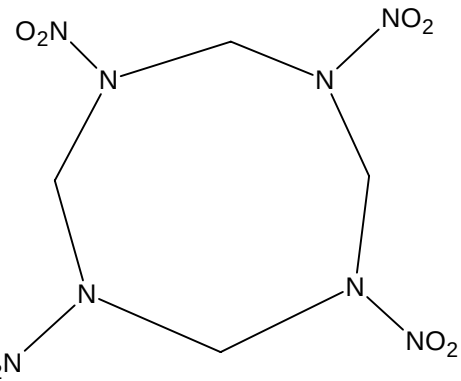


1,3,5-trinitro-1,3,5-triazinane

RDX

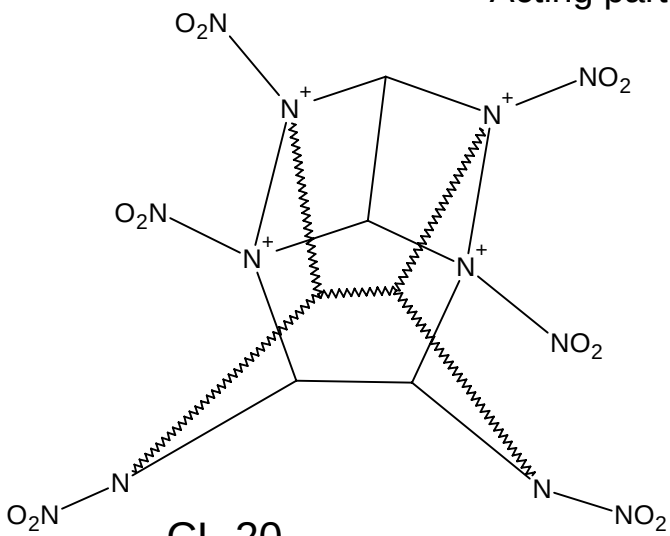
Research Department Explosive:

Acting part of C4- plastic explosive



1,3,5,7-tetranitro-1,3,5,7-tetrazocane

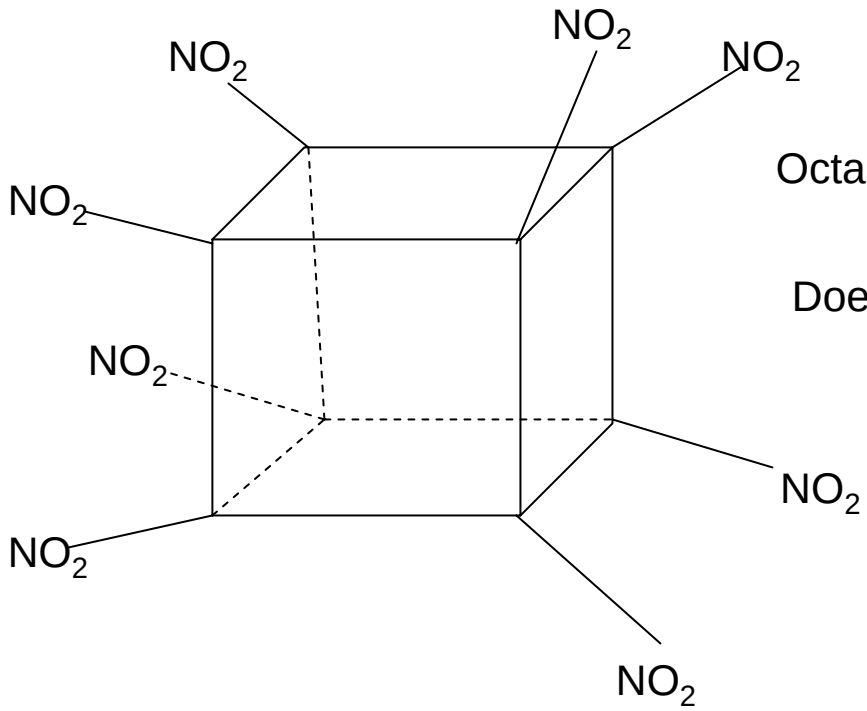
HMX



CL-20

Most powerful non-nuclear explosive known

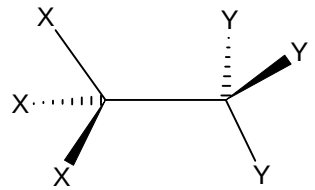
Large NO_2/C ratio



Octanitrocubane- potentially better than CL-20

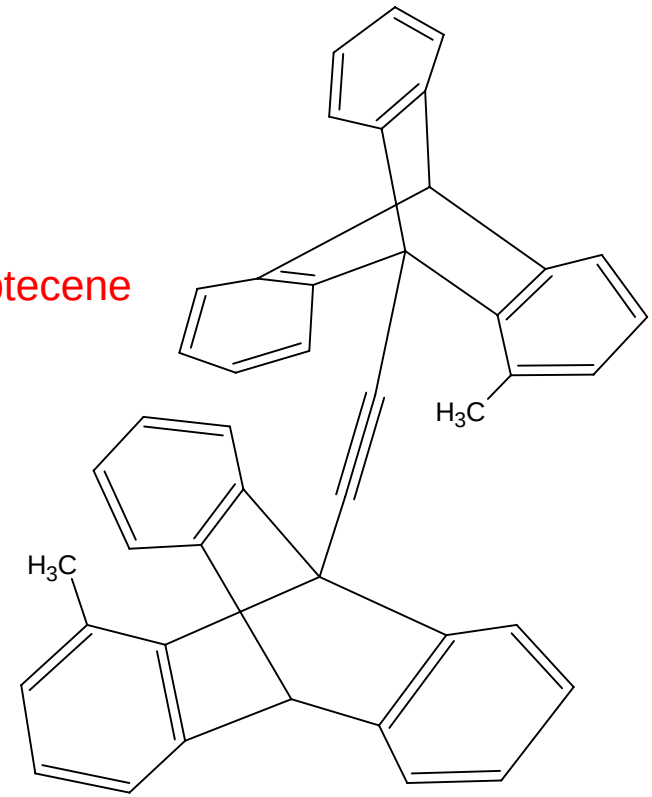
Does not make crystals with high enough density

Very large rotation barriers



X	Y	Rotational barrier , kcal/mol
H	H	3.0
H	CH_3	4.8
CH_3	CH_3	8.6
CH_2Cl	CH_2Cl	16
$C(CH_3)_2$ CN	$C(CH_3)_2CN$	37

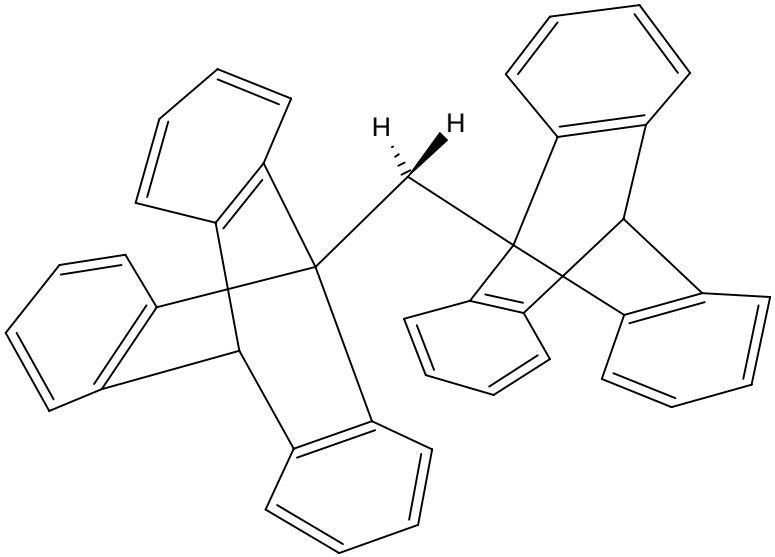
dimethyltriptecene



$E_{barrier}$ > 54 kcal/mol

Dibiptecene acetylene gives rotation about a triple bond (15 kcal/mol)

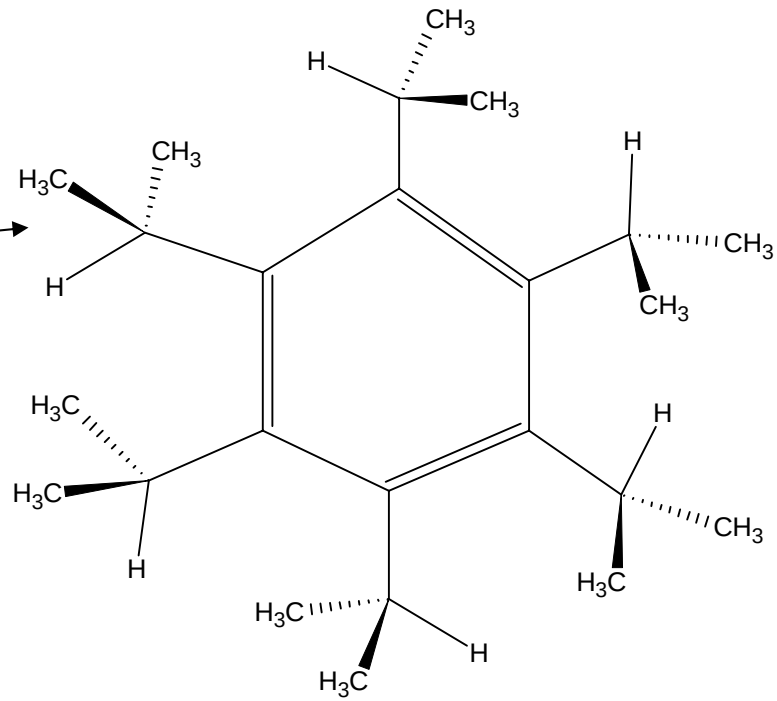
Conceptually new stereochemical phenomenon - rotation of one group causes rotation of another: molecular gears



Ditriptocene methane: Rotation of one triptocene causes rotation of another one

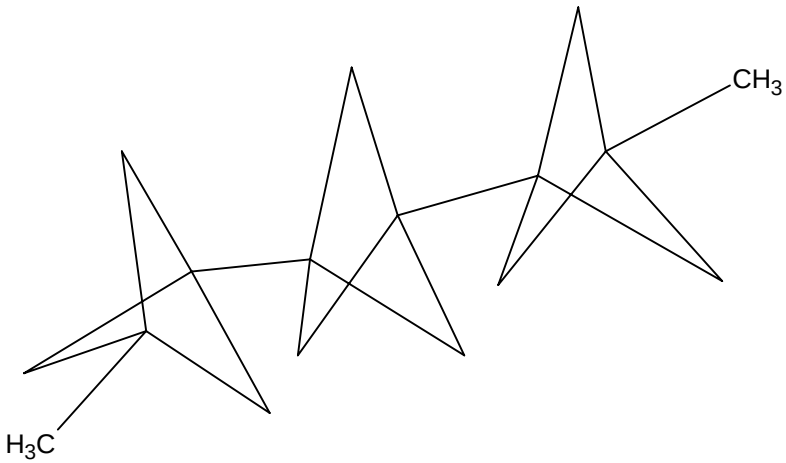
Molecular gear

Cogs of a gear



Simultaneous rotation of all isopropyl groups is ca. 35 kcal/mol (MM prediction)

Molecular “rod” composed from [1,1,1]propellane



Very rigid system. Rigid linear systems are called staffanes