Carbanions

HA → $A^- + H^+$ ΔH= proton affinity

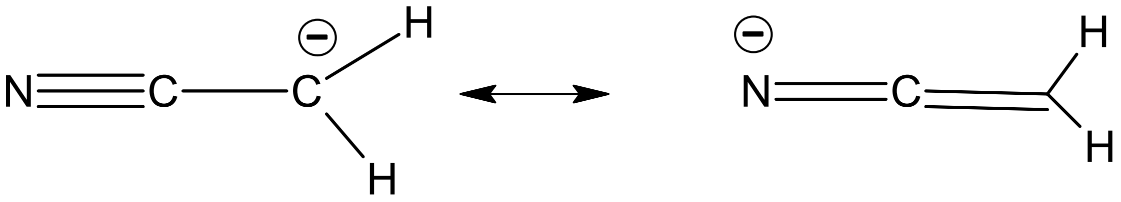
In solution: pK_a (negative log of K_a in water). Small pK_a- strong acid

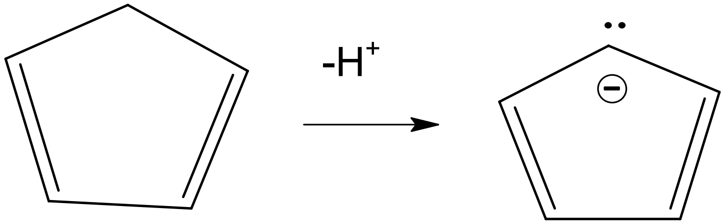
In the gas phase: ΔH

	Gas phase ΔH, kcal/mol
CH_4	416.6
C_2H_6	420.1
$H_2C{=}CH_2$	407.5
Propene	390.8
C_6H_6	400.7
FCH_3	409
$ClCH_3$	396
$BrCH_3$	392
ICH_3	386
Acetonitrile	373.5
Acetone	370
Toluene	377
Nitromethane	356.7

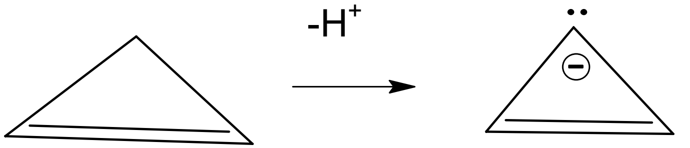
	pK_a
Ethane	50
Cyclohexane	45
$(CH_3)CH$	71
$H_2C{=}CH_2$	44
C_6H_6	43(37)
Acetylene	24
Phenylacetylene	19.9
$PhCH_3$	41.2
$CH_2{=}CHCH_3$	43
Ph_2CH_2	33
Cyclopentadiene	16
Acetone	20
CH_3NO_2	10.2
CH_3CN	25
CH_3SOCH_3	28.5

Deprotonation of sp^2 is favored over sp^3 (explain using electronegativities or hybridization)





6π-electron system like benzene- aromatic
pK_a= 16



4π-electron system like cyclobutadiene- antiaromatic; pK_a = 61

Stable media: For A^- to be persistent, the solvent should have greater pK_a than pK_a of AH.

In general, carbanions are less active than carbocations

The Group Increment Method for Heats of Formation and Strain Energy

ΔH_f^o, kcal/mol, for linear alkanes

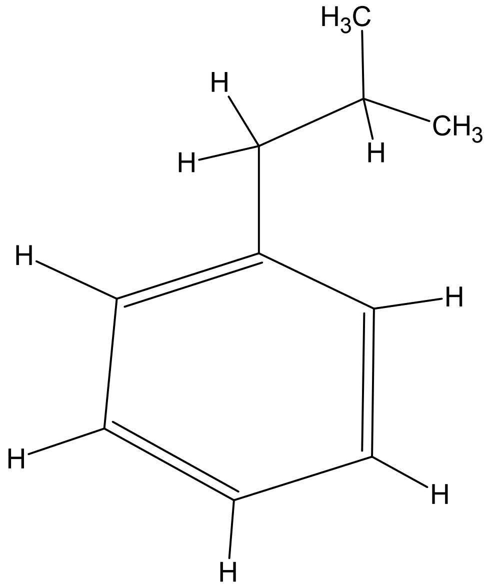
Structure	ΔH_f^o	$\Delta\ \Delta H_f^0$
CH_3-CH_3	-20.24	-
CH_3-CH_2-CH_3	-24.84	4.60
CH_3-$(CH_2)_2$-CH_3	-30.15	5.31
CH_3-$(CH_2)_3$-CH_3	-35.00	4.88

The symbol for this CH_2 group is $–C(H)_2$-C_2 and the group increment is -4.93 kcal/mol

Group increments (in kcal/mol) for fundamental groupings

Group	ΔH_f^0	Group	ΔH_f^0	Group	ΔH_f^0
$C-(H)_3(C)$	-10.20	$C-(O)(C_d)(H)_2$	-6.5	$C-(O)_2(C)_2$	-18.6
$C-(H)_2(C)_2$	-4.93	$C_B-(O)$	-0.9	$C-(O)_2(C)(H)$	-16.3
$C-(H)(C)_3$	-1.90	$O-(C)_2$	-23.2	$C-(O)_2(H)_2$	-16.1
$C-(C)_4$	0.50	$O-(C)(H)$	-37.9	$C-(N)(H)_3$	-10.08
$C_d-(H)_2$	6.26	$O-(C_d)_2$	-33.0	$C-(N)(C)(H)_2$	-6.6
$C_d-(H)(C)$	8.59	$O-(C_d)(C)$	-30.5	$C-(N)(C)_2(H)$	-5.2
$C_d-(C)_2$	10.34	$O-(C_B)_2$	-21.1	$C-(N)(C)_3$	-3.2
$C_d-(C_d)(H)$	6.78	$O-(C_B)(C)$	-23.0	$C_B-(N)$	-0.5
$C_d-(C_d)(C)$	8.88	$O-(C_B)(H)$	-37.9	$N-(C)(H)_2$	4.8
$C_d-(C_B)(H)$	6.78	$C-(CO)(C)_3$	1.58	$N-(C)_2(H)$	15.4
$C_d-(C_B)(C)$	8.64	$C-(CO)(C)_2(H)$	-1.83	$N-(C)_3$	24.4
$C_d-(C_d)_2$	4.6	$C-(CO)(C)(H)_2$	-5.0	$N-(C_B)(H)_2$	4.8
$C_B-(H)$	3.30	$C-(CO)(H)_3$	-10.08	$N-(C_B)(C)(H)$	14.9
$C_B-(C)$	5.51	$C_B-(CO)$	9.7	$N-(C_B)(C)_2$	26.2
$C_B-(C_d)$	5.68	$CO-(C)_2$	-31.4	$N-(C_B)_2(H)$	16.3
$C_B-(C_B)$	4.96	$CO-(C)(H)$	-29.1	$N_I-(H)$	16.3
$C-(C_d)(C)(H)_2$	-4.76	$CO-(H)_2$	-26.0	$N_I-(C)$	21.3
$C-(C_d)_2(H)_2$	-4.29	$CO-(C_B)_2$	-25.8	$N_I-(C_B)$	16.7
$C-(C_d)(C_B)(H)_2$	-4.29	$CO-(C_B)(C)$	-30.9	$CO-(N)(H)$	-29.6
$C-(C_B)(C)(H)_2$	-4.86	$CO-(C_B)(H)$	-29.1	$CO-(N)(C)$	-32.8

$\mathrm{C{-}(C_d)(C)_2(H)}$	-1.48	$\mathrm{CO{-}(O)(C)}$	-35.1	$\mathrm{N{-}(CO)(H)_2}$	-14.9
$\mathrm{C{-}(C_B)(C)_2(H)}$	-0.98	$\mathrm{CO{-}(O)(H)}$	-32.1	$\mathrm{N{-}(CO)(C)(H)}$	-4.4
$\mathrm{C{-}(C_d)(C)_3}$	1.68	$\mathrm{CO{-}(O)(C_d)}$	-32.0	$\mathrm{N{-}(CO)(C)_2}$	-
$\mathrm{C{-}(C_B)(C)_3}$	2.81	$\mathrm{CO{-}(O)(C_B)}$	-36.6	$\mathrm{N{-}(C)(C_B)(H)}$	0.4
$\mathrm{C{-}(O)(C)_3}$	-6.6	$\mathrm{CO{-}(C_d)(H)}$	-29.1	$\mathrm{N{-}(CO)_2(H)}$	-18.5
$\mathrm{C{-}(O)(C)_2(H)}$	-7.2	$\mathrm{O{-}(CO)(C)}$	-43.1	$\mathrm{N{-}(CO)_2(C)}$	-5.9
$\mathrm{C{-}(O)(C)(H)_2}$	-8.1	$\mathrm{O{-}(CO)(H)}$	-58.1	$\mathrm{N{-}(CO)_2(C_B)}$	-0.5
$\mathrm{C{-}(O)(H)_3}$	-10.08	$\mathrm{C_d(CO)(C)}$	7.5		
$\mathrm{C{-}(O)(C_B)(H)_2}$	-8.1	$\mathrm{C_d{-}(CO)(H)}$	5.0		



$C_B(H)$:	5x (+3.3)= 16.50
C_B-(C):	1x5.51= 5.51
C-(C_B)(C)(H_2):	1x(-4.86)= -4.86
C-(H)$(C)_3$:	1x(-1.90)= -1.90
C-$(H)_3$(C):	2x(-10.20)= -20.40
	ΔH_f^0= -5.15 kcal/mol

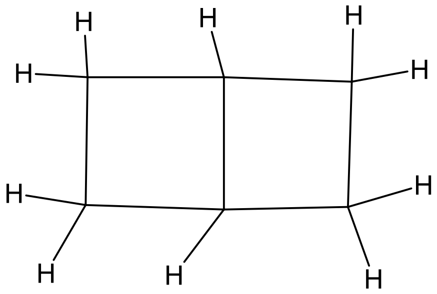
Exp. ΔH_f^0= -5.15 ±0.34 kcal/mol

Calculated and observed ΔH_f^0 values in kcal/mol

	calculated	observed
Cyclohexane	-29.6	-29.9
Cyclopentane	-24.7	-18.3
Cyclobutane	-19.7	+6.7
Cyclopropane	-14.8	+12.7

Strain energy is the difference between the experimental ΔH_f^0 value and the value calculated using strain-free group increments

Example:



Exp. ΔH_f^0= +25.63 kcal/mol

Increments:

$C\text{-}(H)_2(C)_2$: 4x(-4.93) = -19.7

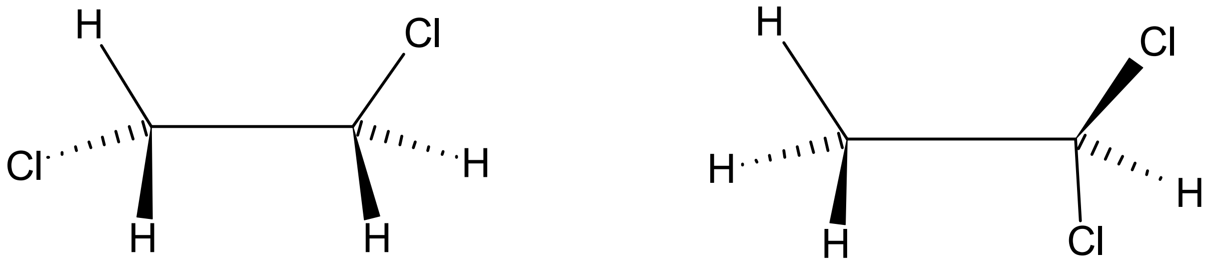
$C\text{-}(H)(C)_3$: 2x(-1.9) = - 3.8

-23.5

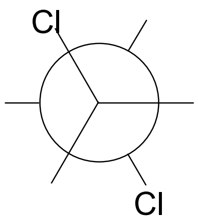
Strain energy: 25.63 + 23.5= 49.13 kcal/mol

Basic conformational analysis- relationship between structure and energetics

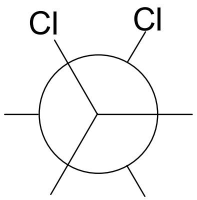
Constitutional isomers



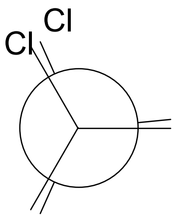
Conformational isomers- rotation about a single bond



Anti-

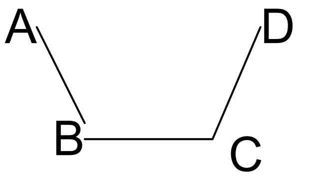


gauche

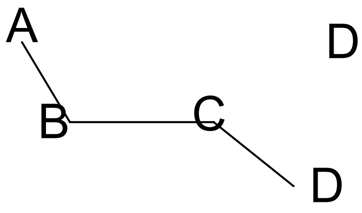


eclipsed

Dihedral angle, ABCD,- angle between the ABC and BSD planes



D=0^{o}



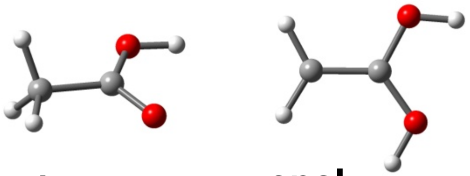
D=180^{o}

Anti: D=180^{o}
Eclipsed- 0^{0}
Gauche 60^{o}

STEREOCHEMISTRY

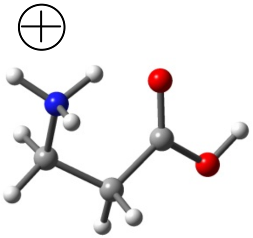
ISOMERS- same formula, different structure

**Constitutional isomers
Different connectivity**

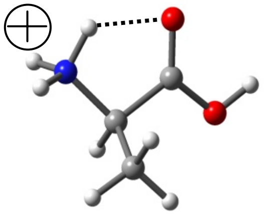


keto- **enol-**
tautomers

(Functional group isomers)



β-alanine

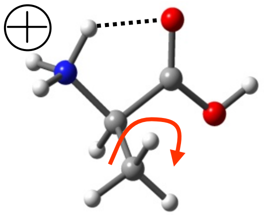


α-alanine

Positional isomers

**Stereoisomers: same connectivity,
different spatial orientation**

2



α-alanine

1

configurational

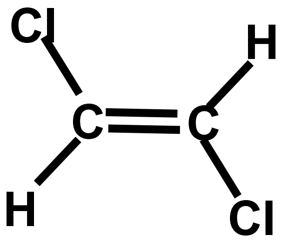
Cannot be made identical by rotation about single bond. Need break the bond.

conformational

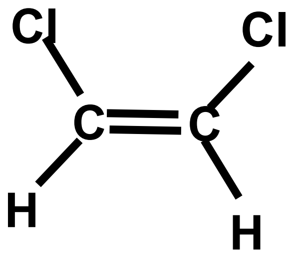
Rotation about a single bond

configurational

Cis-trans

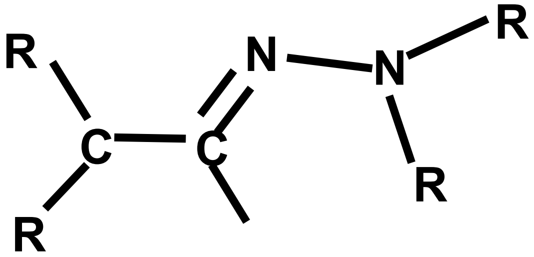


Trans-



Cis-

Z-E isomerisation about the C=N double bond



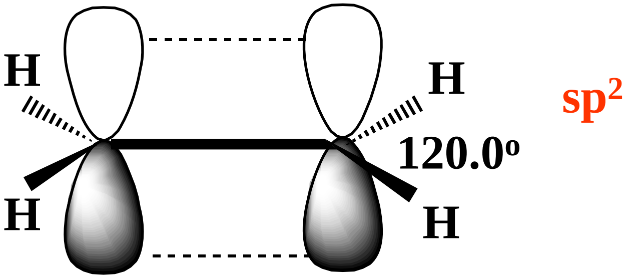
conformational

The barrier to the rotation about single bond is ca. 3-7kcal/mol.

The conformers usually are close in energy.

Cannot separate them experimentally

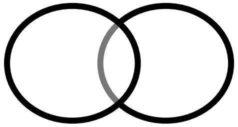
Double bond



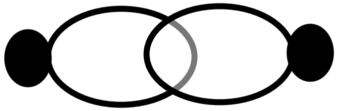
Rotation is a high-energy process

-Break the π-bond
- change electronic state from singlet to singlet biradical

Single bond

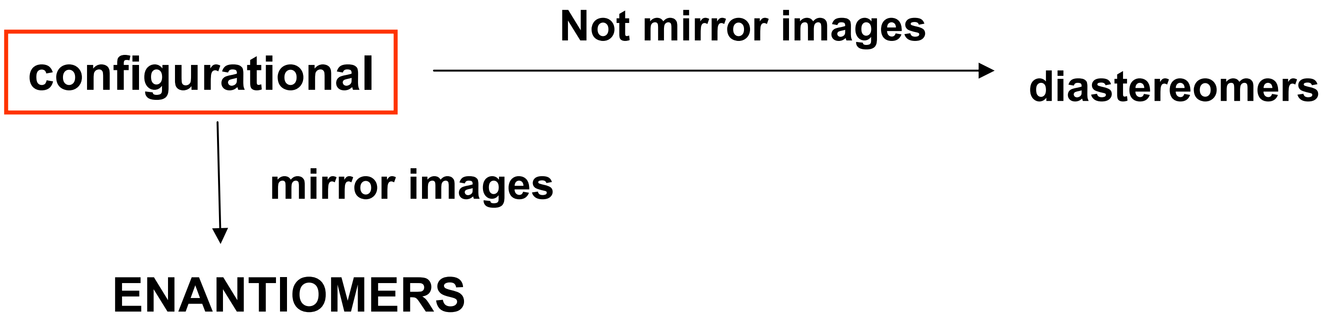


or



Rotation is a low-energy process

Stereoisomers



configurational

Not mirror images

diastereomers

mirror images

ENANTIOMERS

The necessary and sufficient condition:

A chiral molecule is one that is not superimposable on its mirror image.

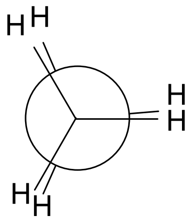
chiral molecule – may rotate plane-polarized light

Clockwise rotation- dextrorotatory *d*

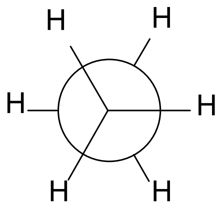
Anticlockwise rotation – levorotatory *l*

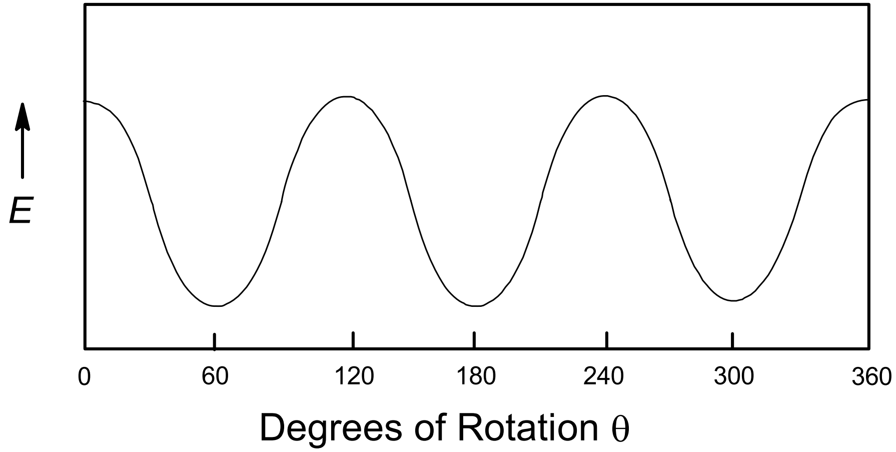
Conformers of ethane

A Eclipsed



B Staggered





For ethane, the rotation barrier is 3 kcal/mol

$k=Ae^{-Ea/RT}$ For unimolecular processes, $A=10^{13}$

$k= 10^{13}s^{-1}\ e^{(-3000cal/mol)/1.987\ cal/molK\ x298K} = 10^{13}s^{-1}\ e^{-5.066} = 6x10^{10}\ s^{-1}$

$t_{1/2}= 0.693/6x10^{10} = 10ps$

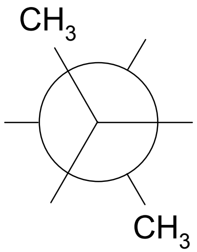
Rotation about a C-C bond at room temperature is extremely rapid!

3 kcal/mol –where is it come from?

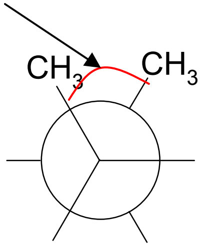
Collisions between ethane molecules and redistribution of various vibrational modes → stored as potential energy
in TS potential energy is stored as a strain energy- C-C and C-H bonds elongate

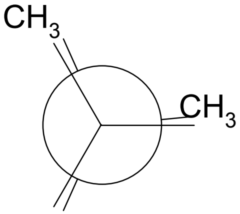
Conformers of Butane

Gauche is ca. 0.9 kcal/mol higher than anti- gauche effect

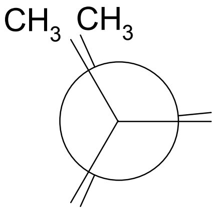


Vicinal repulsion





H/CH_3 eclipsed

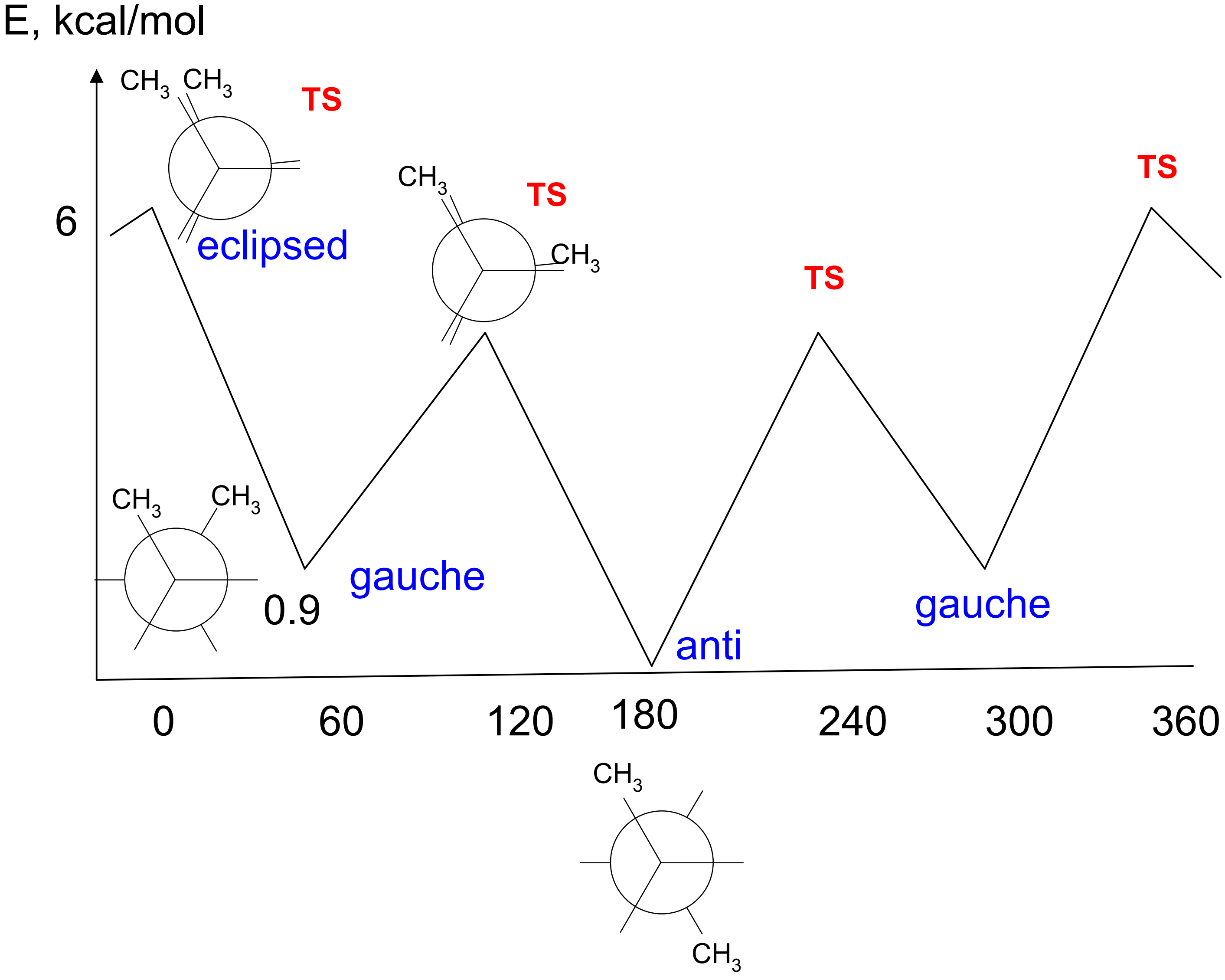


eclipsed

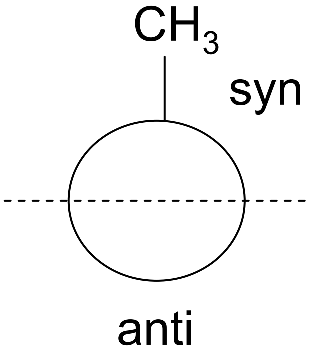
Gauche-gauche; TS=6 kcal/mol

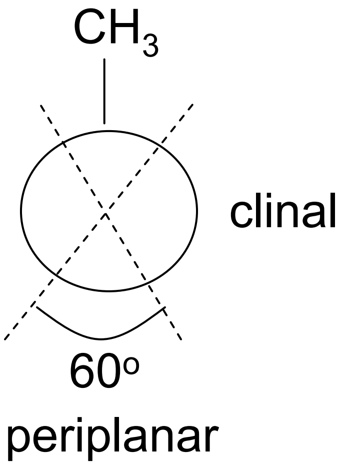
Gauche-anti-gauche; TS=3.5 kcal/mol – easier pathway

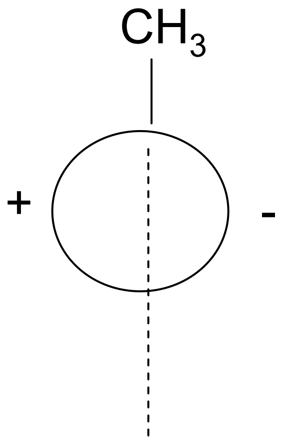
Butane

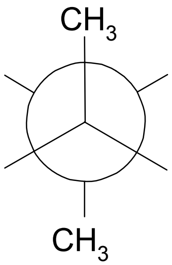

E, kcal/mol
6
0.9
CH3 CH3
TS
eclipsed
CH3
TS
CH3
TS
TS
CH3
CH3
gauche
anti
gauche
0
60
120
180
240
300
360
CH3
CH3

Nomenclature: Klyne-Prelog system

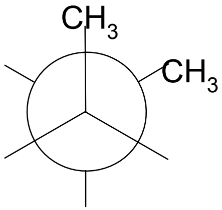




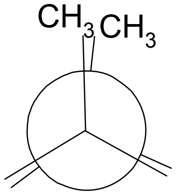




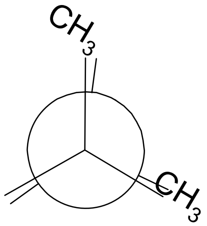
antiperiplanar



Synclinal(-)



synperiplanar

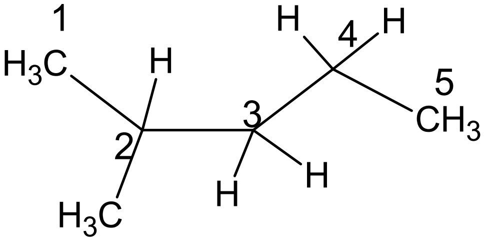


anticlinal(-)

Common corrections to standard group increments, in kcal/mol

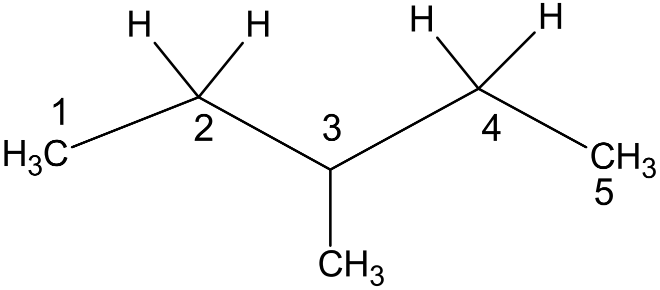
Gauche alkane	**0.8**
Cis-alkene	**1.0**
Ortho correction	**0.6**

Which isomer is lower in energy?



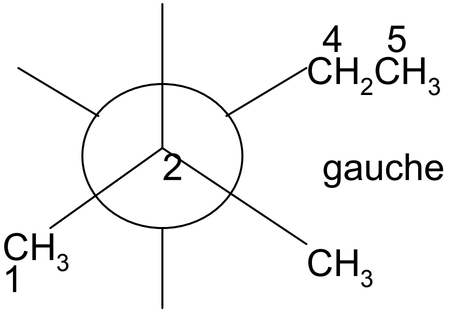
2-methylpentane

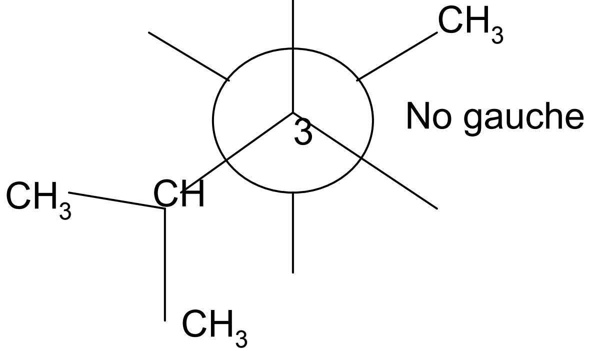
$C(H)_3C$: 3x (-10.2)
$C(H)(C)_3$: 1 x (-1.90)
$C(H)_2(C)_2$: 2x(-4.93)
-42.36



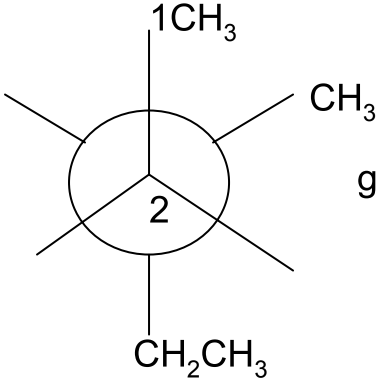
3-methylpentane

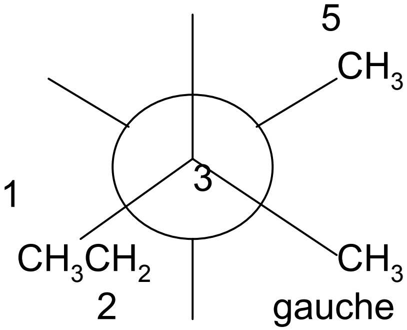
$C(H)_3C$: 3x (-10.2)
$C(H)(C)_3$: 1 x (-1.90)
$C(H)_2(C)_2$: 2x(-4.93)
-42.36





-42.36+0.8= **-41.56**.





-42.36+2x0.8= **-40.04**.

2-methyl pentane is 0.8 kcal/mol lower in energy than 3-methylpentane

Experimentally- lower by 0.66 kcal/mol

Group increment method is a very crude estimate. Correction to strain energy improves the method