Homodesmotic reactions

Homodesmotic reactions are hypothetical reactions used to calculate strain energy. The technique involves setting up a reaction where a strained molecule is transformed into a molecule that has no strain. The standard enthalpy $\Delta H^{o}{}_{r}$ of a homodesmotic reaction is a measure of strain. A homodesmotic reaction has the following constraints:

(1) It must be stoichiometrically balanced.
(2) The molecule whose E_{strain} is being calculated must be the only strained species in the reaction.
(3) The number and type (e.g., Csp^3—Csp^3 σ, Csp^3—H1s σ, Csp^2—Csp^2 π, Csp^2—H1s σ, etc.) of all bonds must be conserved.
(4) The number of methyl (CH_3), methylene (CH_2) and methine (CH) groups must be conserved.

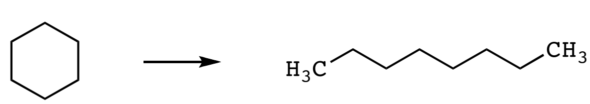
The constraints are enforced so that the quantity being calculated reflects strain energy only, and not bond energy.

Calculating the strain energy of monocyclic cycloalkanes

Let's set up a homodesmotic reaction to calculate the strain energy of cyclohexane. The basic idea is this:

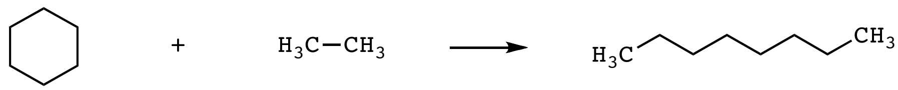
cyclohexane → something with no strain

A good choice for "something with no strain" would be a straight-chain alkane. Because cyclohexane has six CH_2 groups and because the number of CH_2 groups must be conserved, an appropriate choice of straight-chain alkane might be octane:



6 Csp^3—Csp^3 σ	7 Csp^3—Csp^3 σ
12 Csp^3—H1s σ	18 Csp^3—H1s σ
6 CH_2	6 CH_2
0 CH_3	2 CH_3

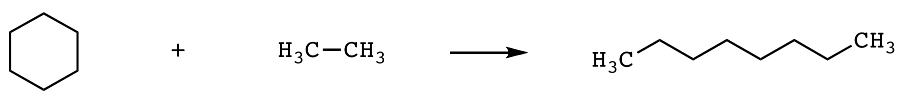
On the left-hand side of the equation we now need a molecule that has two strain-free CH_3 groups; a molecule of ethane fits the bill perfectly:



6 Csp^3—Csp^3 σ	1 Csp^3—Csp^3 σ	7 Csp^3—Csp^3 σ
12 Csp^3—H1s σ	6 Csp^3—H1s σ	18 Csp3—H1s σ
6 CH_2	0 CH_2	6 CH_2
0 CH_3	2 CH_3	2 CH_3

The reaction is now balanced and homodesmotic. It will truly calculate the strain of cyclohexane because cyclohexane is the only strained molecule in the reaction.

We perform a Hess's Law computation using standard enthalpy of formation $\Delta H^o{}_f$ values:



$\Delta H^o{}_f$ —123 kJ/mol —85 kJ/mol —208 kJ/mol

$\Delta H^o{}_r$ = (—208 kJ/mol) — (—123 kJ/mol) — (—85 kJ/mol) = 0 kJ

We arrive at the conclusion that cyclohexane has no strain! Cyclohexane puckers into the chair conformation because it is strain—free.

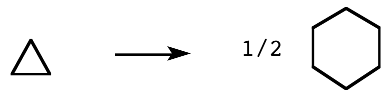
That cyclohexane has no strain will make setting up other homodesmotic reactions easier because we can use it as a strain-free target into which to transform other strained rings.

<u>Problem</u> Calculate the strain energy of cyclopropane ($\Delta H^o{}_f$ = 53 kJ/mol).

<u>Answer</u> The basic idea is

cyclopropane → something with no strain

The balanced homodesmotic reaction is



	Cyclopropane	Cyclohexane
	3 Csp^3–Csp^3 σ	3 Csp^3–Csp^3 σ
	6 Csp^3–H1s σ	6 Csp^3–H1s σ
	3 CH_2	3 CH_2
$\Delta H^o{}_f$	53 kJ/mol	–123 kJ/mol

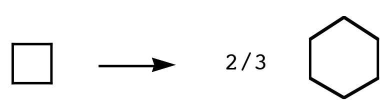
$$\Delta H^o{}_r = (1/2\ \text{mol})(-123\ \text{kJ/mol}) - (1\ \text{mol})(53\ \text{kJ/mol}) = -114\ \text{kJ}$$

The negative sign of $\Delta H^o{}_r$ is saying that cyclopropane is less stable than cyclohexane. This makes sense because cyclopropane has strain whereas cyclohexane is strain-free. The value of E_{strain} of cyclopropane is thus 114 kJ per mole of cyclopropane. We used 1/2 mole of cyclohexane in setting up the homodesmotic reaction because we want the final answer to correspond to the strain energy of one mole of cyclopropane.

Problem Calculate the strain energy of (a) cyclobutane ($\Delta H^o{}_f$ = 27 kJ/mol); (b) cyclopentane ($\Delta H^o{}_f$ = –77 kJ/mol); (c) cycloheptane ($\Delta H^o{}_f$ = –119 kJ/mol); (d) cyclooctane ($\Delta H^o{}_f$ = –126 kJ/mol). Express your answers in units of kilojoule per mole of cycloalkane.

Answer For the molecules in this problem, setting up the balanced homodesmotic reaction is simply a matter of getting the number of CH_2 on both sides of the equation to match.

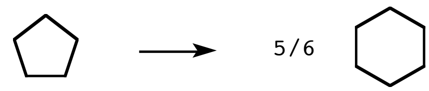
(a)



	Cyclobutane	Cyclohexane
	4 CH_2	4 CH_2
$\Delta H^o{}_f$	27 kJ/mol	–123 kJ/mol

$$\Delta H^o{}_r = (2/3\ \text{mol})(-123\ \text{kJ/mol}) - (1\ \text{mol})(27\ \text{kJ/mol}) = -109\ \text{kJ}$$

The strain energy of cyclobutane is 109 kJ/mol. Cyclobutane (E_{strain} = 109 kJ/mol) is a little less strained than cyclopropane (E_{strain} = 114 kJ/mol) because cyclobutane has less angle strain and because cyclobutane can pucker to relieve eclipsing (torsional) strain whereas cyclopropane cannot pucker.

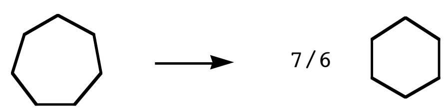
(b) 

5 CH_2 5 CH_2

ΔH°_{f} −77 kJ/mol −123 kJ/mol

$$\Delta H^{\circ}_{r} = (5/6\ \text{mol})(-123\ \text{kJ/mol}) - (1\ \text{mol})(-77\ \text{kJ/mol}) = -26\ \text{kJ}$$

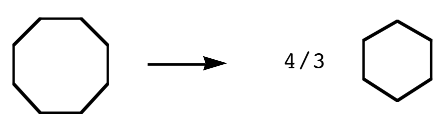
E_{strain} = 26 kJ/mol. Cyclopentane is markedly less strained than either cyclopropane or cyclobutane because cyclopentane has very little angle strain and can pucker into the envelope conformation to relieve eclipsing strain.

(c) 

ΔH°_{f} −119 kJ/mol −123 kJ/mol

$$\Delta H^{\circ}_{r} = (7/6\ \text{mol})(-123\ \text{kJ/mol}) - (1\ \text{mol})(-119\ \text{kJ/mol}) = -24\ \text{kJ}$$

E_{strain} = 24 kJ/mol.

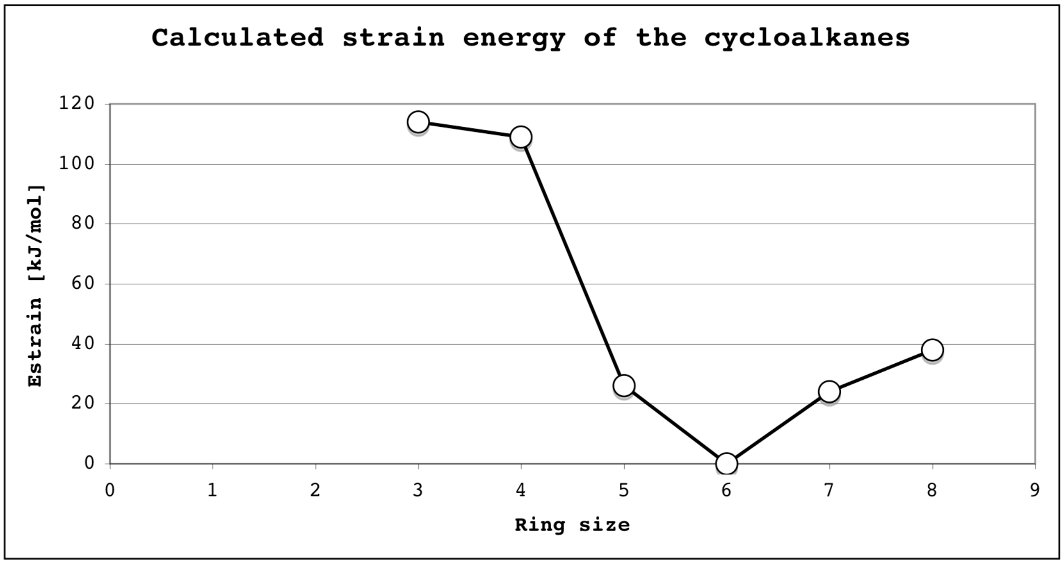
(d) 

ΔH°_{f} −126 kJ/mol −123 kJ/mol

$$\Delta H^{\circ}_{r} = (4/3\ \text{mol})(-123\ \text{kJ/mol}) - (1\ \text{mol})(-126\ \text{kJ/mol}) = -38\ \text{kJ}$$

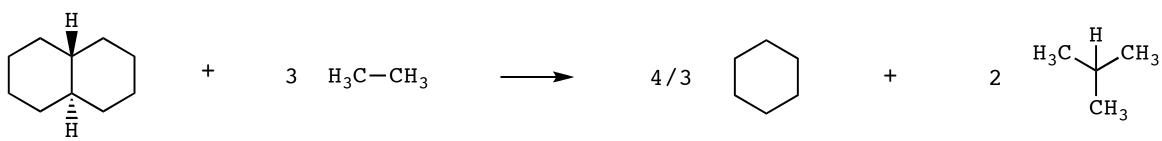
E_{strain} = 38 kJ/mol.

We collect our results in the form of a plot:



Calculating the strain energy of polycyclic cycloalkanes

Consider the following homodesmotic reaction in which the bicyclic molecule *trans*-decalin is transformed into products with no strain:

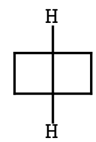


	11 Csp^3—Csp^3 σ	3 Csp^3—Csp^3 σ	8 Csp^3—Csp^3 σ	6 Csp^3—Csp^3 σ
	18 Csp^3—H1s σ	18 Csp^3—H1s σ	16 Csp^3—H1s σ	20 Csp^3—H1s σ
	2 CH	0 CH	0 CH	2 CH
	8 CH_2	0 CH_2	8 CH_2	0 CH_2
	0 CH_3	6 CH_3	0 CH_3	6 CH_3
ΔH^{o}_{f}	–182 kJ/mol	–85 kJ/mol	–123 kJ/mol	–136 kJ/mol

$$\Delta H^{o}_{r} = (4/3\ \text{mol})(-123\ \text{kJ/mol}) + (2\ \text{mol})(-136\ \text{kJ/mol}) - (1\ \text{mol})(-182\ \text{kJ/mol}) - (3\ \text{mol})(-85\ \text{kJ/mol}) = 1\ \text{kJ}$$

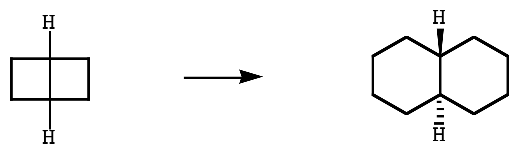
Although the result is not exactly the 0 kJ/mol figure that was much to be desired, the calculation suggests that *trans*-decalin is almost strain-free; thus, we can use *trans*-decalin as a strain-free target into which to transform strained rings that have a methine (CH) carbon.

<u>Problem</u> Calculate the strain energy of bicyclo[2.2.0]hexane:



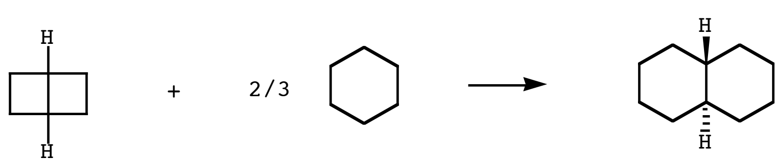
$\Delta H^o{}_f$ = 125 kJ/mol

<u>Answer</u> We wish to transform this strained molecule into molecules that have no strain, but the reaction we write must be balanced and homodesmotic. Because the molecule has methine (CH) carbons, an appropriate choice of product is (almost strain-free) *trans*-decalin:



2 CH	2 CH
4 CH_2	8 CH_2

The reaction must now be balanced and made homodesmotic. We need to add four CH_2 on the left-hand side of the equation, but they must come from a strain-free molecule otherwise the reaction will not render the strain energy of bicyclo[2.2.0]hexane. Two-thirds of a mole of cyclohexane accomplishes the balancing:

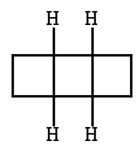


	2 CH	0 CH	2 CH
	4 CH_2	4 CH_2	8 CH_2
$\Delta H^o{}_f$	125 kJ/mol	–123 kJ/mol	–182 kJ/mol

$\Delta H^o{}_r$ = (1 mol)(–182 kJ/mol) – (1 mol)(125 kJ/mol) – (2/3 mol)(–123 kJ/mol)
= –225 kJ

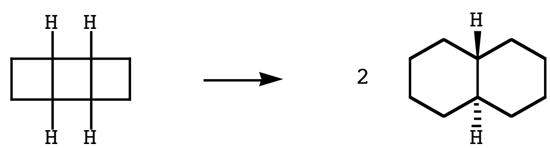
The strain energy of bicyclo[2.2.0]hexane is 225 kJ/mol. Given that E_{strain} of cyclobutane worked out to 109 kJ/mol, we might conclude that strain energy is approximately additive: bicyclo[2.2.0]hexane, which is two cyclobutanes fused together, is about as strained as two cyclobutanes. In the next problem, we calculate E_{strain} of three fused cyclobutanes. Will we get a value close to 3 × 109 = 327 kJ/mol? Stay tuned.

<u>Problem</u> Calculate the strain energy of:



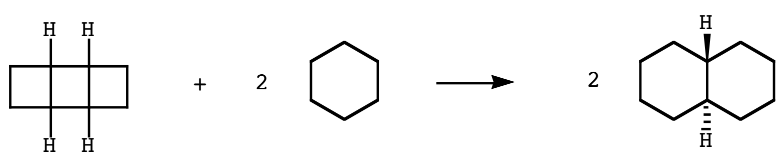
ΔH°_f = 235 kJ/mol

<u>Answer</u> First balance methine (CH) carbons by using the appropriate number of *trans*-decalins:



4 CH	4 CH
4 CH_2	16 CH_2

Now we need 12 strain-free CH_2 on the left-hand side of the equation, that is, two cyclohexanes:

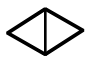


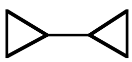
ΔH°_f	235 kJ/mol	–123 kJ/mol	–182 kJ/mol

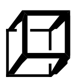
ΔH°_r = (2 mol)(–182 kJ/mol) – (1 mol)(235 kJ/mol) – (2 mol)(–123 kJ/mol)
= –353 kJ

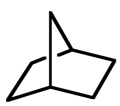
The strain energy of the molecule is 353 kJ/mol, which is close to the expected value of 327 kJ/mol. We conclude that strain is approximately additive.

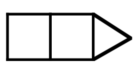
<u>Problem</u> Calculate the strain energy of the polycyclic molecules below; express your answers in units of kilojoule per mole of polycyclic cycloalkane.

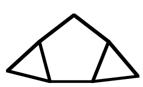
(a)  ΔH°_{f} = 217 kJ/mol

(b)  ΔH°_{f} = 130 kJ/mol

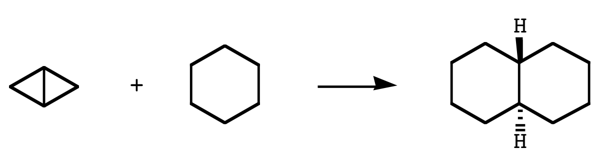
(c)  ΔH°_{f} = 622 kJ/mol

(d)  ΔH°_{f} = 55 kJ/mol

(e)  ΔH°_{f} = 235 kJ/mol

(f)  ΔH°_{f} = 149 kJ/mol

<u>Answer</u> Balance the number of CH using the appropriate number of *trans*-decalin molecules, then balance the CH_2 using the appropriate number of cyclohexane molecules.

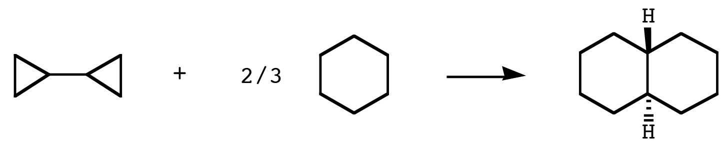


(a)

ΔH°_{r} = (1 mol)(−182 kJ/mol) − (1 mol)(217 kJ/mol) − (1 mol)(−123 kJ/mol)
= −276 kJ

E_{strain} = 276 kJ/mol

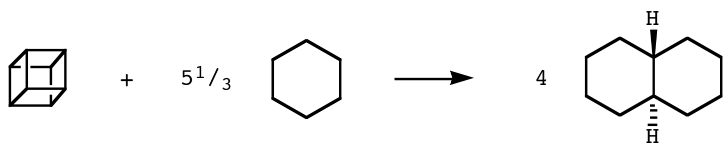
(b)



ΔH°_{r} = (1 mol)(−182 kJ/mol) − (1 mol)(130 kJ/mol) − (2/3 mol)(−123 kJ/mol)
= −230 kJ

E_{strain} = 230 kJ/mol

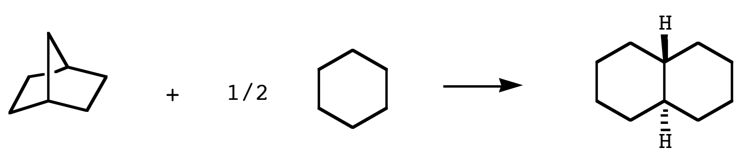
(c)



ΔH°_{r} = (4 mol)(−182 kJ/mol) − (1 mol)(622 kJ/mol) − (16/3 mol)(−123 kJ/mol)
= −694 kJ

E_{strain} = 694 kJ/mol

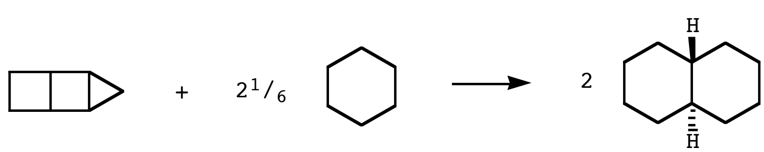
(d)



ΔH°_{r} = (1 mol)(−182 kJ/mol) − (1 mol)(55 kJ/mol) − (1/2 mol)(−123 kJ/mol)
= −176 kJ

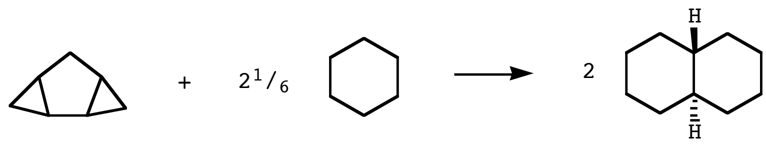
E_{strain} = 176 kJ/mol

(e)



ΔH°_{r} = (2 mol)(−182 kJ/mol) − (1 mol)(235 kJ/mol) − (13/6 mol)(−123 kJ/mol)
= −332 kJ

E_{strain} = 332 kJ/mol

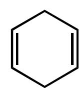
(f) 

ΔH°_r = (2 mol)(–182 kJ/mol) – (1 mol)(149 kJ/mol) – (13/6 mol)(–123 kJ/mol)
= –246 kJ

E_{strain} = 246 kJ/mol

Calculating the strain energy of cycloalkenes

Let's conclude our discussion of homodesmotic reactions by introducing another almost strain-free molecule: 1,4-cyclohexadiene (ΔH°_f = 105 kJ/mol).

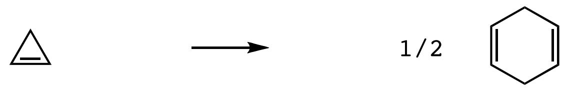


1,4-cyclohexadiene
ΔH°_f = 105 kJ/mol

1,4-Cyclohexadiene is used to balance homodesmotic reactions in which the molecule whose strain we wish to calculate has alkene methine (CH) groups just like *trans*-decalin is used to balance homodesmotic reactions in which the molecule whose strain we wish to calculate has alkane methine groups. We will not prove that 1,4-cyclohexadiene is almost strain-free because that demonstration requires a quantum mechanical technique beyond the scope of this course.

Problem Set up a homodesmotic reaction for calculating the strain energy of cyclopropene (ΔH°_f = 277 kJ/mol).

Answer



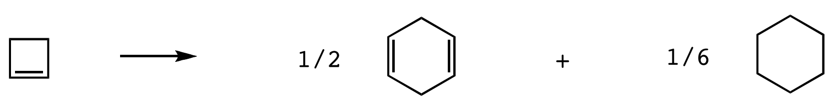
	2 Csp^3–Csp^2 σ	2 Csp^3–Csp^2 σ
	1 Csp^2–Csp^2 σ	1 Csp^2–Csp^2 σ
	1 Cp–Cp π	1 Cp–Cp π
	2 Csp^3–H1s σ	2 Csp^3–H1s σ
	2 Csp^2–H1s σ	2 Csp^2–H1s σ
	1 CH_2	1 CH_2
	2 alkene CH	2 alkene CH
$\Delta H^o{}_f$	277 kJ/mol	105 kJ/mol

$$\Delta H^o{}_r = (1/2 \text{ mol})(105 \text{ kJ/mol}) - (1 \text{ mol})(277 \text{ kJ/mol}) = -224 \text{ kJ}$$

The value of E_{strain} of cyclopropene is thus 224 kJ per mole. Note that cyclopropene has significantly more strain than cyclopropane (E_{strain} = 114 kJ/mol): the result reflects the high price of angle strain that must be paid when sp^2 hybridized carbon is confined to a small ring.

Problem Calculate E_{strain} of cyclobutene ($\Delta H^o{}_f$ = 157 kJ/mol).

Answer

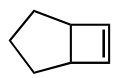


	2 alkene CH	2 alkene CH	0 alkene CH
	2 CH_2	1 CH_2	1 CH_2
$\Delta H^o{}_f$	157 kJ/mol	105 kJ/mol	–123 kJ/mol

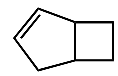
$$\Delta H^o{}_r = (1/2 \text{ mol})(105 \text{ kJ/mol}) + (1/6 \text{ mol})(-123 \text{ kJ/mol}) - (1 \text{ mol})(157 \text{ kJ/mol}) = -125 \text{ kJ}$$

It comes as no surprise that cyclobutene is less strained than cyclopropene: the ring carbons in cyclobutene are allowed to more closely approach their ideal bond angles.

<u>Problem</u> Calculate the strain energy of the molecules below; express your answers in units of kilojoule per mole of cycloalkene.

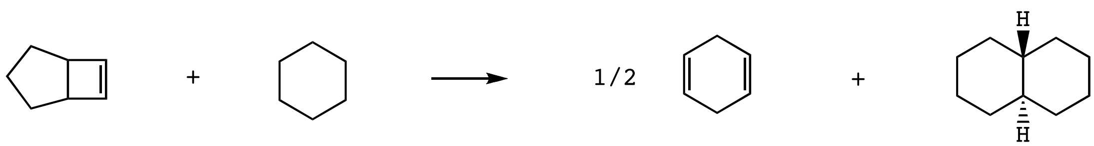


bicyclo[3.2.0]hept-6-ene
ΔH°_f = 140 kJ/mol



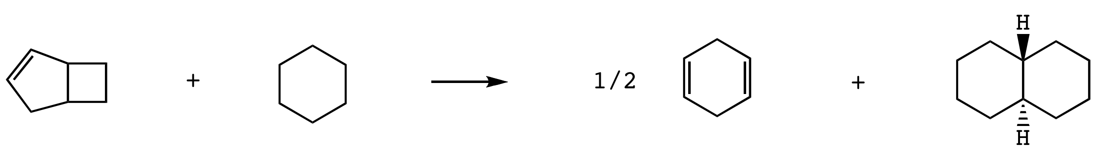
bicyclo[3.2.0]hept-2-ene
ΔH°_f = 119 kJ/mol

<u>Answer</u>



$$\Delta H^\circ_r = (1/2 \text{ mol})(105 \text{ kJ/mol}) + (1 \text{ mol})(-182 \text{ kJ/mol}) - (1 \text{ mol})(140 \text{ kJ/mol}) - (1 \text{ mol})(-123 \text{ kJ/mol})$$
$$= -146 \text{ kJ}$$

E_{strain} = 146 kJ/mol

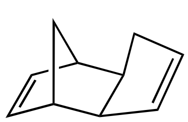


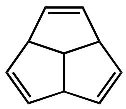
$$\Delta H^\circ_r = (1/2 \text{ mol})(105 \text{ kJ/mol}) + (1 \text{ mol})(-182 \text{ kJ/mol}) - (1 \text{ mol})(119 \text{ kJ/mol}) - (1 \text{ mol})(-123 \text{ kJ/mol})$$
$$= -126 \text{ kJ}$$

E_{strain} = 126 kJ/mol

The results seem reasonable because we expect an alkene to be more strained when it is trapped in a four-membered ring.

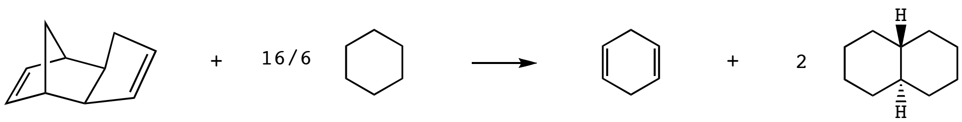
<u>Problem</u> Calculate the strain energy of the molecules below; express your answers in units of kilojoule per mole of polycyclic cycloalkene.

(a)  ΔH°_f = 117 kJ/mol

(b)  ΔH°_{f} = 224 kJ/mol

<u>Answer</u>

(a)

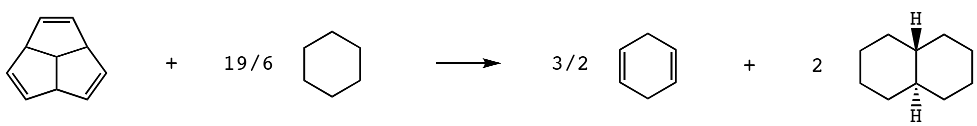


$$\Delta H^{\circ}_{r} = (1\text{ mol})(105\text{ kJ/mol}) + (2\text{ mol})(-182\text{ kJ/mol}) - (1\text{ mol})(117) - (16/6\text{ mol})(-123\text{ kJ/mol})$$

$$= -48\text{ kJ}$$

E_{strain} = 48 kJ/mol

(b)



$$\Delta H^{\circ}_{r} = (3/2\text{ mol})(105\text{ kJ/mol}) + (2\text{ mol})(-182\text{ kJ/mol}) - (1\text{ mol})(224) - (19/6\text{ mol})(-123\text{ kJ/mol})$$

$$= -41\text{ kJ}$$

E_{strain} = 41 kJ/mol