Extension 18: Unusual Alkanes

1. Prerequisites

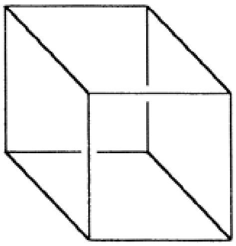
The key ideas required to understand this section are:

Topic	Book page
Alkanes	318
Percentage composition	127
Enthalpy of combustion	228
Concentration as percentage composition	151
NMR	409

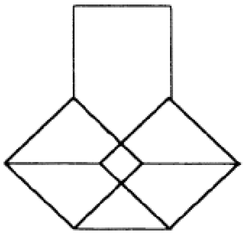
2. Organic compounds

Organic compounds have been made in a number of weird and wonderful shapes. Cubane and basketane have been given trivial names that exactly describe their structures:

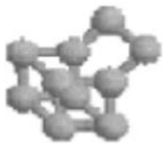
cubane



basketane



In the following ball and stick models of cubane and basketane hydrogen atoms have been omitted for clarity.



Cubane (first made in 1964) is a strained molecule, because the geometry around each carbon atom is very far from the idealized tetrahedral angle of 109½°. However, cubane has been shown to be stable to air water and most common reagents (Table 1).

Table 1 Properties of cubane

Property	*Value*
Toxicity	Non-toxic
Decomposition	> 220°C
Density	1.29 g cm^{-3}
Melting point	130-131°C
Boiling point	133°C
Solubility at 25°C	18% w/w (in hexane)
Enthalpy of formation	602 kJ mol^{-1}

Cubane-type molecules have potential applications as propellants and explosives, and derivatives of cubane might have applications in fighting the AIDS virus.

Revision questions

1. What is the molecular formula of cubane?

2. What is the percentage composition of carbon in the molecule?

3. What is an approximate C–C–C bond angle in cubane?

4.

- **(i)** Write a balanced equation for the complete combustion of cubane.
- **(ii)** How much heat is released by the combustion of exactly 5 g of cubane? (Use p. 225 for additional data.)

5. If the density of hexane is 0.660 g cm^{-3} at 25°C, what mass of cubane could you dissolve in 150 cm^3 hexane?

6. What would you expect the ^{1}H–NMR of cubane to look like?

Answers

1. C_8H_8

2. 92.3%

3. 90°

4.

(i) $C_8H_8(s) + 10O_2(g) \rightarrow 8CO_2(g) + 4H_2O(l)$

(ii) Using Hess's law:

$8C(s) + 4H_2(g) \rightarrow C_8H_8(s)$ $\Delta H^\ominus = 602$ kJ mol^{-1} (1)
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\ominus = 393.51$ kJ mol^{-1} (2)
$H_2(g) + \frac{1}{2}O_2 \rightarrow H_2O(l)$ $\Delta H^\ominus = -285.83$ kJ mol^{-1} (3)
$C_8H_8(s) + 10O_2(g) \rightarrow 8CO_2(g) + 4H_2O$ $\Delta H^\ominus = ?$
Multiply equation (2) by 8, multiply equation (3) by 4 and add both:
$8C(s) + 8O_2(g) \rightarrow 8CO_2(g)$
$4H_2(g) + 2O_2 \rightarrow 4H_2O(g)$
$8C(s) + 8O_2(g) + 4H_2(g) + 2O_2 \rightarrow 8CO_2(g) + 4H_2O(g)$ (1) $\Delta H^\ominus$
$= (8 \times -393.51) + (4 \times -285.83)$
$= -4291.4$ kJ
For
$C_8H_8(s) \rightarrow 8C(s) + 4H_2(g)$ $\Delta H^\ominus = 602$ kJ mol^{-1}
Add these two equations and simplify:
~~$8C(s)$~~ $+ 8O_2(g) +$ ~~$4H_2(g)$~~ $+ 2O_2 + C_8H_8(s) \rightarrow 8CO_2(g) + 4H_2O(g) +$ ~~$8C(s)$~~ $+$ ~~$4H_2(g)$~~
Then
$C_8H_8(s) + 10O_2(g) \rightarrow 8CO_2(g) + 4H_2O(l)$ $\Delta H^\ominus$
$= -4291.4 + (-602)$
$= -4.89 + 10^3$ kJ mol^{-1}
This value is for 1 mol (or 104 g) C_8H_8
For 5 g, enthalpy change is $5/104 \times -4.89 \times 10^3 = -235$ kJ

5. 150 cm^3 hexane has a mass of 150×0.660 g. It will dissolve a maximum of 18% w/w or $150 \times 0.660 \times 0.18 = 17.8$ g C_8H_8.

6. A single absorption at δ 4.0 (all protons are in the same chemical environment).