

4. This question is about bombardier beetles

Bombardier beetles get their name from the defence mechanism that they have when attacked, whereby they shoot a hot chemical spray at their attackers. In their abdomen they have two separate chambers, one containing an aqueous solution of hydrogen peroxide and the other an aqueous solution of an organic compound, denoted here as **A**.

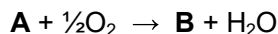


When the beetle is attacked, fluid from both chambers is squirted into a mixing chamber which contains enzymes. One of these enzymes, *catalase*, catalyses the breakdown of hydrogen peroxide into oxygen and water.

- (a) (i) Write a balanced equation for this reaction.
- (ii) How would you classify this reaction? Circle one of the following answers in the answer booklet.

Oxidation Reduction Disproportionation Hydrolysis Dehydration

Some of the intermediates produced during the breakdown of hydrogen peroxide react with the organic compound, **A**, to give a product **B**. The overall equation for the reaction can be considered as the result of **A** reacting with all of the oxygen produced by the equation in part (a)(i) as in the equation below.



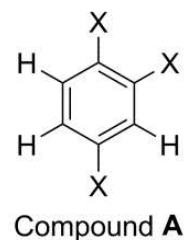
- (b) Write an overall equation for the reaction of hydrogen peroxide with **A** to form **B**.

The temperature of the mixture ejected from bombardier beetles has been measured to reach the boiling point of water, considerably hotter than the beetle's body temperature, which matches the surroundings (20 °C).

- (c) (i) Calculate the amount of energy needed to heat 1 dm³ of this mixture by this amount. Assume the specific heat capacity of the mixture is the same as that of pure water, 4.18 J g⁻¹ K⁻¹ and that the density of the mixture is the same as that of pure water, 1.00 g cm⁻³.
- (ii) Assuming equal volumes of the two solutions are mixed, what is the minimum concentration of the hydrogen peroxide solution in the beetle's hydrogen peroxide chamber?

The standard enthalpy change for the overall reaction (your answer to part (b)) per mole of **A** is -203 kJ mol⁻¹.

Compound **A** is a 1,2,4-trisubstituted benzene, shown on the right, where there are substituents present at the positions labelled with an X.



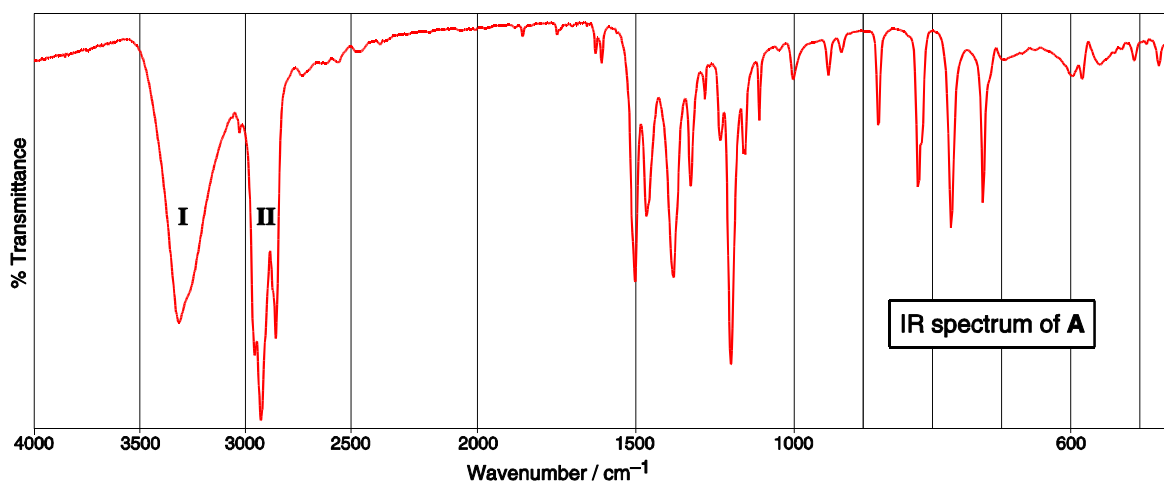
- (d) How many possible structures are there of this 1,2,4-trisubstituted benzene when:
- All of the X substituents are different from each other?
 - Two of the X substituents are identical?

Combustion analysis of Compound **A** indicates that it contains only carbon, hydrogen and oxygen.

In compound **A**, stretching in some of the bonds contained in the X substituents contributes to characteristic peaks in the IR spectrum of this compound (shown below).

These characteristic peaks are marked **I** and **II** on the spectrum.

- (e) Suggest which bond stretches are responsible for **I** and **II**.

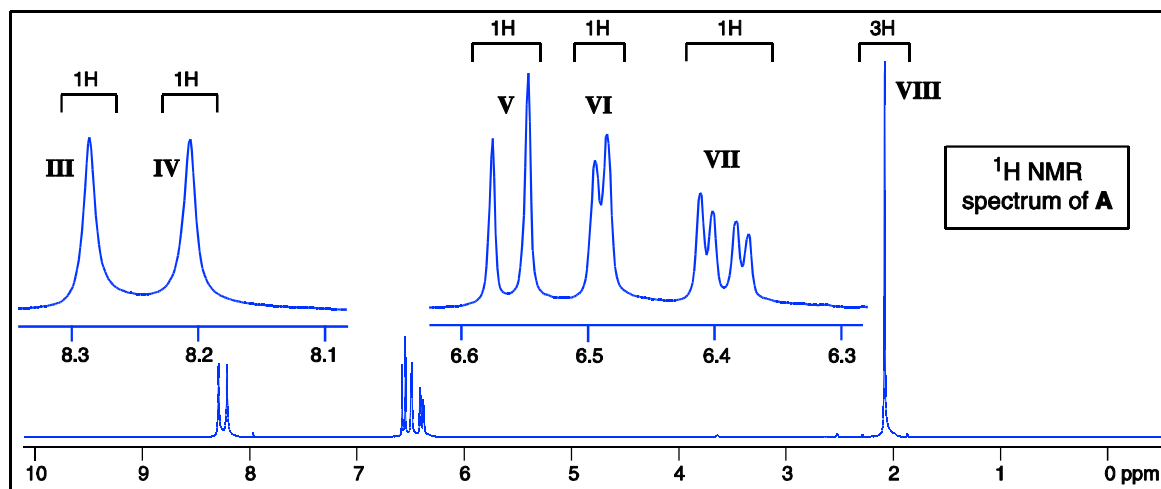


In compound **A**, two of the three X substituents are the same (i.e. the substituents are X_a , X_a and X_b).

The ^{13}C NMR spectrum of compound **A** contains seven signals.

The ^1H NMR spectrum of compound **A** is shown below.

Peaks III and IV in the ^1H NMR spectrum disappear on addition of D_2O to the sample.

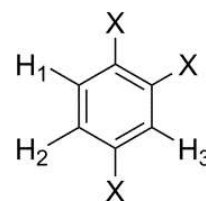


- (f) (i) Suggest an identity for the two identical substituents (X_a and X_a).
- (ii) Suggest an identity for the other substituent (X_b).

The protons on the benzene ring in compound **A** (H_1 , H_2 and H_3) can be assigned by analysis of their coupling constants in the ^1H NMR spectrum.

The splitting that is observed in the spectrum due to coupling between two non-equivalent benzene ring protons in a 1,2-relationship to each other, is considerably larger than the splitting observed due to coupling between two non-equivalent benzene ring protons in a 1,3-relationship.

The splitting due to coupling between two non-equivalent benzene ring protons in a 1,4-relationship is generally too small to be observed.



- (g) Assign one of the signals III-VIII in the ^1H NMR spectrum of **A** to each of the protons H_1 , H_2 and H_3 .

Bombardier beetles also use a simpler organic compound, **C** for the same purpose.

Compound **C** is a relative of compound **A** where one of the X substituents is replaced by a hydrogen atom, making a disubstituted benzene.

The ^1H NMR spectrum of compound **C** only contains two signals.

- (h) Suggest a structure for compound **C** and hence also a structure for compound **A**.

Compound **C** is oxidised to **D** in the same way that compound **A** is oxidised to **B**.

The ^1H NMR spectrum of compound **D** only contains one signal.

- (i) Suggest a structure for compound **B** and a structure for compound **D**.