

**Cambridge International**

**AS and A Level Chemistry (9701)**

Practical booklet 11

Chemical properties of primary amines

**Introduction**

Practical work is an essential part of science. Scientists use evidence gained from prior observations and experiments to build models and theories. Their predictions are tested with practical work to check that they are consistent with the behaviour of the real world. Learners who are well trained and experienced in practical skills will be more confident in their own abilities. The skills developed through practical work provide a good foundation for those wishing to pursue science further, as well as for those entering employment or a non-science career.

The science syllabuses address practical skills that contribute to the overall understanding of scientific methodology. Learners should be able to:

1. plan experiments and investigations
2. collect, record and present observations, measurements and estimates
3. analyse and interpret data to reach conclusions
4. evaluate methods and quality of data, and suggest improvements.

The practical skills established at AS Level are extended further in the full A Level. Learners will need to have practised basic skills from the AS Level experiments before using these skills to tackle the more demanding A Level exercises. Although A Level practical skills are assessed by a timetabled written paper, the best preparation for this paper is through extensive hands-on experience in the laboratory.

The example experiments suggested here can form the basis of a well-structured scheme of practical work for the teaching of AS and A Level science. The experiments have been carefully selected to reinforce theory and to develop learners’ practical skills. The syllabus, scheme of work and past papers also provide a useful guide to the type of practical skills that learners might be expected to develop further. About 20% of teaching time should be allocated to practical work (not including the time spent observing teacher demonstrations), so this set of experiments provides only the starting point for a much more extensive scheme of practical work.

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**Practical 11 – Guidance for teachers**

**Chemical properties of primary amines**

**Aim**

To compare and contrast the properties and reactions of ammonia, an alkyl amine and an aromatic amine.

**Outcomes**

Syllabus section 20.1 and 12.2(a) as well as experimental skills 2 and 3

**Skills included in the practical**

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| --- | --- |
| **A Level skills** | **How learners develop the skills** |
| Evaluation | analyse qualitative data to draw appropriate conclusions  understand the significance of observations made in qualitative tests |
| Conclusions | make scientific explanations of the observations and data that they have described  make predictions about the results of further experiments |

This practical provides an opportunity to build on essential skills introduced at AS Level.

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| **AS Level skills** | **How learners develop the skills** |
| MMO collection | use apparatus to collect an appropriate quality of observations, including subtle difference of colour and solubility |
| PDO layout | choose a suitable and clear method of presenting the results obtained |
| PDO recording | record observations to the same level of fine discrimination |

**Method**

* **Learners must wear eye protection for these investigations.**
* Amines show basic properties because of the lone pair on the nitrogen atom in the –NH2 group. The properties of the -NH2 group are affected by the nature of the alkyl or aryl group attached to it. Some of the experiments carried out in this investigation will illustrate how the properties of the –NH2 group are affected. The availability of the lone pair to cause basic properties may either be increased by an alkyl group or reduced by an aryl group. See experiments 1 and 2.
* The presence of an -NH2 joined to a benzene ring enhances the reactivity of the benzene ring towards attack by electrophiles, such as bromine. This is because of the delocalisation of the lone pair on nitrogen into the ring. See experiment 3. Benzene itself does not react with aqueous bromine.
* The –NH2 group can be substituted to form a diazonium salt, with functional group –N2C*l*. Diazonium salts derived from alkyl amines are very unstable, but aryl diazonium salts can be prepared and stored at a low temperature of about 5 oC. See experiment 4.
* Aryl diazonium salts can be used in coupling reactions to prepare brightly coloured dyes, called azo dyes. See experiment 5. The discovery of these dyes revolutionised the clothing industry. Certain azo dyes can be used as indicators (e.g. methyl orange) because their colour changes according to whether or not a proton attaches to the molecule

* This experiment is suitable for learners to work in pairs or small groups.
* Learners should become familiar with working safely with hazardous chemicals.

**Results**

* Learners should note the colours and solubilities of reactants and products.
* They should record their observations using correct terminology (e.g. ‘cloudy solution’ is not acceptable for precipitate/ppt).

**Interpretation and evaluation**

* The inductive effect of the alkyl group can be revised, and the overlap of the lone pair of electrons on the nitrogen atom with the delocalised system of the benzene ring can be introduced or revised.
* Discussion can take place on whether phenylamine is expected to be more or less basic than ethyl 4-aminobenzenecarboxylate (electron withdrawing effect of the carboxylate group).
* Complex formation can be revised. The availability of the nitrogen lone pair for forming a dative covalent/coordinate bond can be discussed. (Ethyl 4-aminobenzenecarboxylate may only form a complex with Cu2+ on heating.)
* Learners can be reminded that only chlorine and bromine (but not iodine) react with benzene and the reactions require a catalyst. The mechanism of the electrophilic substitution reaction can be revised. The reactivity of the benzene ring can be compared to that in phenol or phenylamine, in which the benzene ring is more reactive.
* The possible mechanisms for a reaction with bromine can be brainstormed or revised. The similarity of phenol and aminobenzene in activating the benzene ring can be introduced or revised. (The product of the electrophilic substitution reaction of ethyl 4‑aminobenzenecarboxylate with bromine is ethyl 4-amino-3,5- dibromobenzenecarboxylate.)
* When nitrous acid is added to the alkyl amine, the following reaction occurs during which bubbling should be observed.

RNH2 + HNO2 → ROH + H2O + N2

When the same reaction is carried out with the aryl amine at 5 oC, no nitrogen is given off, but the diazonium salt is produced instead. At higher temperatures the aryl amine behaves in the same way as the alkyl amine in this reaction.

* The stabilising effect of the ring preventing electrophilic substitution in benzene diazonium chloride can be discussed ( –N+≡N the positive charge can be delocalised in the ring with the 2, 4 and 6 positions becoming δ+). The reason why the atom closer to the benzene ring carries the positive charge can be discussed (due to dative bonding electrons).
* Diazonium salts readily undergo nucleophilic substitution reactions, due to the positive charge on the nitrogen atom joined to the benzene ring.

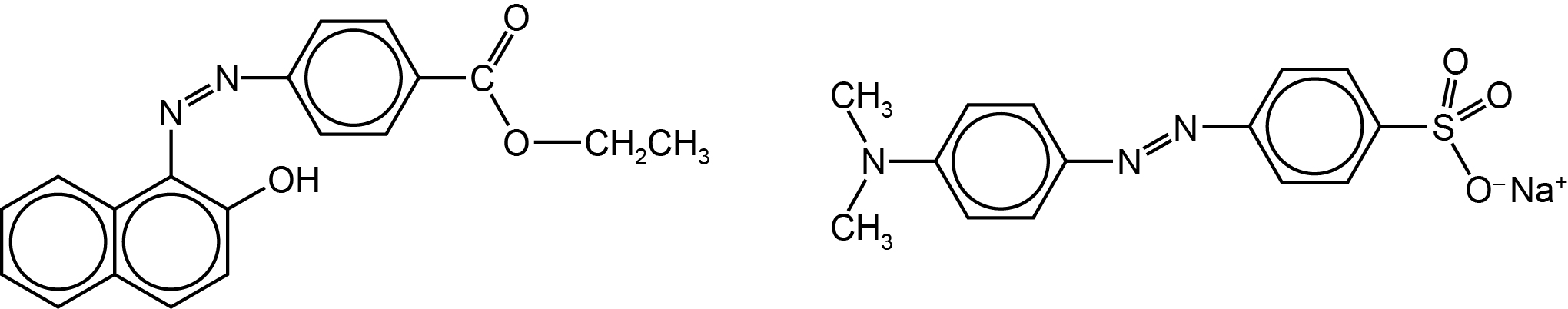
–N+≡N C*l*– + KI → –I + KC*l* + N2



–N+≡N + H2O → –OH + H+ + N2

* C10H7OH(s) + OH–(aq) → C10H7O–(aq) + H2O(l)

The difference in acid behaviour of alcohols, phenols and carboxylic acids can be revised.



|  |  |
| --- | --- |
| ethyl 4-[2-(2-hydroxy-1-naphthyl)hydrazine]  benzenecarboxylate  (systematic names not needed) | methyl orange  sodium 4-[(4-dimethylamine) phenyldiazenyl]  benzenesulfonate |

* The reasons why chemicals are coloured can be discussed and colour in complexes may be revised. The red form (acidic) of methyl orange absorbs light of a shorter wavelength (more energetic transition). (The anion is protonated at the –N=N– group allowing a different pattern of delocalisation. The reason why conjugated and delocalised organic systems are chromophores is not required for this syllabus.)

**Practical 11 – Information for technicians**

**Chemical properties of primary amines**

**Each learner will require:**

|  |  |  |
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|  | (a) | Eye protection |
|  | (b) | Gloves (nitrile) may be worn |
|  | (c) | 2 x 250 cm3 beaker |
|  | (d) | 1 x 25 cm3 measuring cylinder |
|  | (e) | 1 x 100 cm3 beaker |
|  | (f) | 8 x test-tube (these may be rinsed and re-used but more tubes should be available) |
|  | (g) | 3 x boiling tube |
|  | (h) | 1 x Bunsen burner (placed away from the ethylamine or 1-aminobutane) |
|  | (i) | 1 x heat proof mat |
|  | (j) | 1 x tripod and gauze |
|  | (k) | 1 x thermometer (–10 ºC to +110 ºC at 1 ºC) |
|  | (l) | 4 x teat/dropping pipette |
|  | (m) | 1 x glass rod |
|  | (n) | 3 x weighing boat or container for weighing small masses of solid |
|  | (o) | 10 cm3 2.0 mol dm–3 ammonia |
| **[F][C]** | (p) | 10 cm3 aqueous ethylamine (70% solution) **or** 1-aminobutane (butylamine) supplied in a stoppered test-tube **or** in the fume cupboard |
| **[H]** | (q) | 1 g ethyl 4-aminobenzenecarboxylate (benzocaine) |
| **[N]** | (r) | 5 cm3 0.1 mol dm–3 copper(II) sulfate |
| **[H]** | (s) | 10 cm3 aqueous bromine (0.02 mol dm–3 is a suitable concentration) |
| **[H]** | (t) | 15 cm3 2.0 mol dm–3 hydrochloric acid |
| **[O][T]**  **[N]** | (u) | 2 g sodium nitrite |
| **[H]** | (v) | 0.5 g naphthalen-2-ol (β-naphthol) |
| **[C]** | (w) | 5 cm3 2.0 mol dm–3 sodium hydroxide |
|  | (x) | 15 cm3 distilled water |
|  | (y) | ice |
|  | (z) | access to balance weighing to at least 1 dp |
|  | (aa) | pen suitable for marking glassware |
|  | (bb) | paper towel |

**Additional instructions**

A simple ice bath is made by placing (crushed) ice in a 250 cm3 beaker. If a freezing mixture is required then sodium chloride salt is added to the ice.

Good ventilation of the laboratory or use of a fume cupboard is needed.

**Hazard symbols**

|  |  |
| --- | --- |
| **C** = corrosive substance | **F** = highly flammable substance |
| **H** = harmful or irritating substance | **O** = oxidising substance |
| **N** = harmful to the environment | **T** = toxic substance |

**Practical 11 – Worksheet**

**Chemical properties of primary amines**

**Aim**

To compare and contrast the properties and reactions of ammonia, an alkyl amine and an aromatic amine.

**Method**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Safety:   * Wear eye protection. * Do not work close to the Bunsen flame in any of these experiments. * Gloves (nitrile) may be worn. * aqueous ethylamine or 1-aminobutane **[F] [H]** * ethyl 4-aminobenzenecarboxylate **[H]** * aqueous bromine **[H]** * 2.0 mol dm–3 hydrochloric acid **[H]** * sodium nitrite **[O] [T] [N]** * naphthalen-2-ol **[H]** * 2.0 mol dm–3 sodium hydroxide **[C]**   **Hazard symbols**   |  |  | | --- | --- | | **C** = corrosive substance | **F** = highly flammable substance | | **H** = harmful or irritating substance | **O** = oxidising substance | | **N** = harmful to the environment | **T** = toxic substance | |

* Approximately half-fill a 250 cm3 beaker with (tap) water and heat it over a Bunsen flame. This will be your hot water bath. When the water starts boiling switch off the Bunsen burner.

**Experiment 1: solubility and pH**

1. Test a 1 cm depth of aqueous solutions of ammonia and ethylamine (or 1-aminobutane) in separate test-tubes with one drop of universal indicator solution. If universal indicator solution is not available, use a glass rod to transfer 1 drop of solution onto narrow range universal indicator papers.
2. Transfer a **small** spatula measure of ethyl 4-aminobenzenecarboxylate (benzocaine) into a test-tube. Add a 2 cm depth of distilled water and heat the mixture in your hot water bath. Carefully pour about a 1 cm depth of the solution formed into a test-tube and add one drop of universal indicator solution. Cool the remaining solution.

**Experiment 2: reaction with copper(II) ions** .

1. To a 1 cm depth of 0.1 mol dm–3 copper(II) sulfate in a test-tube add aqueous ammonia drop by drop with shaking until no further change takes place.
2. Repeat step 1 but use aqueous ethylamine (or 1-aminobutane) in place of aqueous ammonia.
3. To a 1 cm depth of 0.1 mol dm–3 copper(II) sulfate in a test-tube add a **small** spatula measure of ethyl 4-aminobenzenecarboxylate and heat the mixture in your hot water bath (re-heat if necessary). Then allow the contents of the tube to cool.

**Experiment 3: reaction with aqueous bromine [H]**

1. To a 1 cm depth of aqueous ammonia in a test-tube add a 2 cm depth of hydrochloric acid followed by a 2 cm depth of aqueous bromine. Carefully shake the contents of the tube.
2. Repeat step 1 but use aqueous ethylamine (or 1-aminobutane) in place of aqueous ammonia.
3. To a **small** spatula measure of ethyl 4-aminobenzenecarboxylate in a test-tube add a 2 cm depth of hydrochloric acid. Warm the tube in your hot water bath (re-heat if necessary) to dissolve the solid then add a 2 cm depth of aqueous bromine.

**Experiment 4: reaction with aqueous sodium nitrite [O] [T] [N]**

Gloves may be worn. Switch off the Bunsen burner while carrying out this test

1. Use a measuring cylinder to transfer 10 cm3 of distilled water into a boiling tube. Add 2 g of sodium nitrite and shake the tube carefully to form a solution. Label the tube NaNO2. Place the tube in an ice bath or freezing mixture.
2. To a 1 cm depth of aqueous ammonia in a test-tube add a 2 cm depth of dilute hydrochloric acid. Label the tube NH3. Use a dropper to transfer about a 1 cmdepth of aqueous sodium nitrite into the tube. Let the test-tube stand at room temperature. If no change is observed, place the tube in the hot water bath.
3. Repeat step 2 but use aqueous ethylamine (or 1-aminobutane) in place of aqueous ammonia. Label the tube RNH2.
4. Dissolve 0.5 g of ethyl 4-aminobenzenecarboxylate in a 2 cm depth of dilute hydrochloric acid in a boiling tube. Label the tube NH2 and place it in the ice bath or freezing mixture. Half of this solution will be needed for experiment 5.

5. Use a dropper to transfer a 1 cm depth of solution from step 4 into a test-tube. Add about a 1 cmdepth of aqueous sodium nitrite into the tube. Let the test-tube stand at room temperature. If no change is observed, place the tube in the hot water bath.

**Experiment 5: a diazonium coupling reaction**

Gloves may be worn.

1. Dissolve 0.5 g naphthalen-2-ol **[H]** in 5 cm3 aqueous sodium hydroxide **[C]** in a boiling tube. Place the tube in the ice bath.
2. Add the remaining cold acidified solution of ethyl 4-aminobenzenecarboxylate to the tube containing the aqueous sodium nitrite. Keep the tube in the ice bath.
3. When the temperature of the solution from step 1 is ≤ 5 ºC transfer all of it into a 100 cm3 beaker. Add the mixture from step 2 to the contents of the beaker with stirring. Record what you observe.

Dispose of the contents **[H]** of the beaker carefully down the sink with plenty of water. This is an azo dye and most azo dyes are irritant, harmful or toxic.

**Results**

Record **all** your observations.

**Interpretation and evaluation**

1. List ammonia, ethylamine (or 1-aminobutane) and ethyl 4-aminobenzenecarboxylate in order of their basic strength.

(i) Explain in terms of structure why they are in this order.

(ii) Would you expect phenylamine to be a stronger or weaker base than ethyl 4‑aminobenzenecarboxylate? Explain your answer.

2. Explain fully your observations in experiment 2.

3. Draw the displayed formula of ethyl 4-aminobenzenecarboxylate, H2NC6H4COOC2H5.

The product of the reaction between aqueous bromine and ethyl 4-aminobenzenecarboxylate is a dibromo- compound.

Indicate on your displayed formula where you would expect the bromine atoms to be found.

Suggest a mechanism for the reaction between aqueous bromine and ethyl 4-aminobenzenecarboxylate.

4. When sodium nitrite reacts with hydrochloric or sulfuric acid the sodium salt of the acid and nitrous (nitric(III)) acid is formed.

NaNO2(aq) + HC*l*(aq) → NaC*l*(aq) + HNO2(aq)

(If the solutions are cold and sufficiently concentrated the resulting solution will be blue.)

Nitrous acid can react with amines to form a gas.

(i) Suggest the identities of the products of the reaction between RNH2 and HNO2.

RNH2 + HNO2 →

(ii) When the solutions are kept below 5 ºC any diazonium compound formed is more stable.

Suggest a reason for the lower stability of the diazonium compound formed by an alkyl amine, RNH2, compared with that formed by an aromatic amine, NH2.

Aromatic diazonium compounds are useful in organic syntheses as the diazo group can be replaced by a halogen atom, a nitrile group or a hydrogen atom.



(iii) Using to represent a phenyl (C6H5–) or substituted phenyl group, write an equation for the likely reaction between an aromatic diazonium chloride and potassium iodide.

5. Naphthalen-2-ol, C10H7OH, reacts in a similar way to phenol with aqueous sodium hydroxide.

(i) Write the ionic equation for the reaction between naphthalen-2-ol and sodium hydroxide. Include state symbols.

(ii) What type of behaviour is naphthalen-2-ol showing in this reaction?

(iii) In the coupling reaction with the diazonium compound (formed in step 2 of experiment 5) the 1 position of naphthalen-2-ol is used. Using to represent the substituted phenyl group, –C6H4COOC2H5, draw the displayed formula of the diazonium compound formed in step 2.



(iv) Using to represent the substituted phenyl group, write the equation for the reaction that occurs when the diazonium compound is warmed in aqueous solution.

(v) Draw the structure of the azo dye formed in step 3.

(vi) When 4-aminobenzenesulfonic acid (sulfanilic acid), H2NC6H4SO3H, reacts with nitrous acid and an alkaline solution of naphthalen-2-ol (instead of ethyl 4-aminobenzenecarboxylate) then a water soluble azo dye is formed, called orange II.

If N,N-dimethyphenylamine, C6H5N(CH3)2 (instead of naphthalen-2-ol) is added to 4-aminosulfonic acid, methyl orange indicator is the product.

Draw the structure of methyl orange, which is another azo dye.

(vii) Methyl orange is red in acidic solution and yellow in alkaline solution. Which form absorbs energy of shorter wavelength?