

Isolation of Anhydrous Hydrazine as Stable Inclusion Complexes with Hydroquinone and *p*-Methoxyphenol, and their Solid State Reaction with Esters which gives Pure Hydrazides

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Anhydrous hydrazine is isolated in a pure state as a stable inclusion complex crystal with hydroquinone or *p*-methoxyphenol, the X-ray structures of which have been analysed; the solid-state reaction of the hydrazine inclusion complex and esters gives hydrazides which are virtually uncontaminated with acid hydrazine salt byproducts.

Because of their highly explosive nature, it is very difficult and dangerous to prepare anhydrous hydrazine by distillation of an aqueous hydrazine solution. The hydrazine hydrate, $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, is the most concentrated hydrazine which can be prepared safely. However, since it contains 32% water, reactions with the reagent are often affected by the water, and the reaction products are contaminated with byproducts produced by side reactions with water. For example, the reactions of esters with hydrazine hydrate give hydrazides which are contaminated by the hydrazine salt of the acid produced by hydrolysis of the ester. When anhydrous hydrazine becomes safely available, its various applications for organic synthesis can be developed.

We succeeded in isolating pure hydrazine **2** as stable inclusion complexes with hydroquinone **1** and *p*-methoxyphenol **7** from aqueous hydrazine. The inclusion complexes were also found to be useful reagents for reactions in the solid state. For example, reactions of esters with the hydrazine inclusion complex in the solid state give much more pure hydrazides than those obtained by solution reactions with hydrazine hydrate.

Hydroquinone **1** (220.22 g, 2 mol) was dissolved in 19.4% aqueous hydrazine (700.24 g, containing 136.16 g, 4 mol, of hydrazine) by heating to 80–90 °C. Cooling of the solution gave a 1 : 1 inclusion complex **3** of **1** and **2** as colourless crystals, after washing with water and drying (269.1 g, 94.7% yield, mp 158–159 °C). The 1 : 1 ratio was determined by microanalysis (found: C, 50.43; H, 19.87%, calc. for $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2$: C, 50.69; H, 19.71%). The ratio was also confirmed by a determination of the hydrazine content through a titration with HCl (found 22.47%, calc. 22.57%). The hydrazine complex **3** is thermally stable and melts at 158–159 °C without decomposition, and is also stable to shock. Although a 1 : 1 inclusion complex **6** of methylhydrazine **4** with 2,2-di(*p*-hydroxyphenyl)propane **5** has been prepared,¹ **6** is less important than **3**, because **4** is stable and can be obtained easily in a pure state by distillation of its aqueous solution.

However, *p*-methoxyphenol **7** formed a 2 : 1 inclusion complex **8** with **2**. When a solution of **7** (248.28 g, 2 mol) in a 9.8% aqueous solution of **2** (700.12 g, containing 68.8 g 2 mol, of hydrazine) was kept at room temp., a 2 : 1 inclusion complex of **7** and **2** was formed as colourless crystals, after washing with water and drying (250.8 g, 89.5% yield, mp 90–91 °C). The 2 : 1 ratio was determined by microanalysis (found: C, 60.02; H, 10.14%, calc. for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_4$: C, 59.99; H, 9.99%), and by determination of the content of **2** (found 10.92%, calc. 11.43%).

The structures of the 1 : 1 complex **3** of **1** and **2** and the 2 : 1 complex **8** of **7** and **2** were studied by X-ray analysis.[†] In the crystal of **3**, hydroquinone and hydrazine molecules lie on the crystallographic inversion centres and twofold axes, respectively. As shown in Fig. 1, the extensive hydrogen-bonding network between the NH_2 groups and the OH groups generates a layered packing of the molecules in the unit cell, stacked perpendicular to the *b* axis with alternating hydrophobic (benzene rings) and hydrophilic regions (OH groups and hydrazine molecules). One NH_2 group is bonded to three OH groups as two donors and one acceptor, indicating that each hydrazine molecule is tightly fixed by six hydrogen bonds in the crystal. The structure of **8** is closely related to that of the

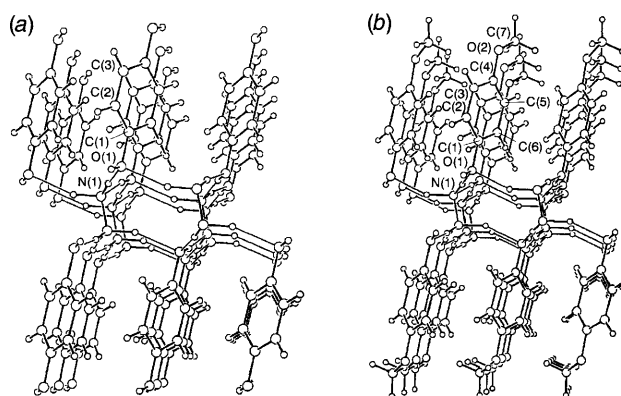
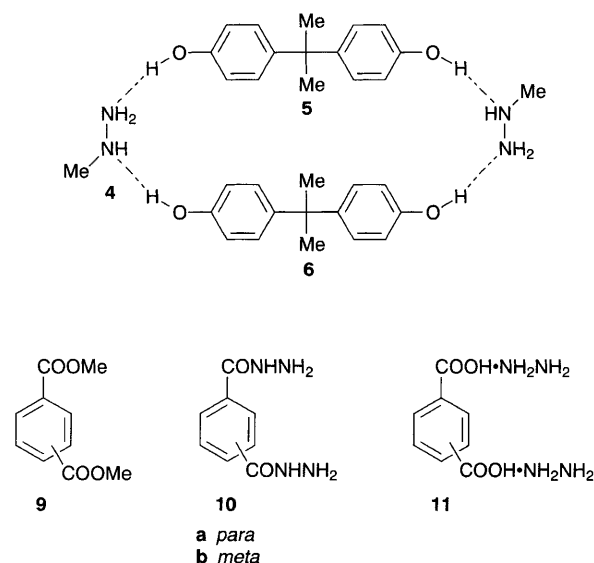
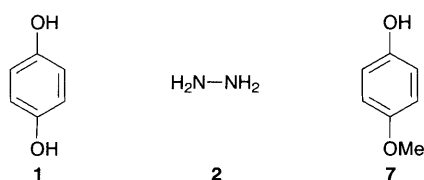


Fig. 1 Molecular packings of the complexes **3** (a) and **8** (b) viewed along the *b* axis with *c* horizontal. Hydrogen bonds are illustrated by thin lines.



complex **3** as is inferred from the lattice constants and the space groups (Fig. 1). The 2:1 complex **8** may be formed by the replacement of one of the hydrophilic regions located on both sides of the hydrophobic regions of the complex **3** by the *p*-methoxy groups which protrude from the benzene rings. The hydrogen-bonding network around the hydrazine molecules with crystallographic twofold axes is quite similar to that in the complex crystal **3**.

The structures of **3** and **8** which are constructed by a complex hydrogen-bonding network (Fig. 1) are completely different from the cyclic structure of **6** which has been analysed by an X-ray study.¹

It is valuable to be able to isolate anhydrous hydrazine in a pure state as a stable inclusion complex solid with a simple organic host compound such as hydroquinone **1** or *p*-methoxyphenol **7**. Since the complex solid is stable, very reactive hydrazine can be stored safely under usual conditions. Furthermore, the inclusion complex of **2** was found to be useful as a reagent in the solid state. For example, the solid state reaction of **3** with esters gives hydrazides. Some hydrazides are used as the hardener in epoxy resins. However, when a hydrazide contaminated with a carboxylic acid hydrazine salt is used, the epoxy resin is partly decomposed and coloured. Since hydrazide is prepared by the reaction of an ester with hydrazine hydrate, the ester is partly hydrolysed to its acid and is converted to its hydrazine salt. When the anhydrous hydrazine reagents **3** or **8** are used instead of the hydrazine hydrate, the pure hydrazide would be obtained.

A mixture of powdered dimethyl terephthalate **9a** (19.4 g, 0.1 mol) and **3** (58.5 g, 0.4 mol) was kept under a nitrogen atmosphere at 100–125 °C for 25 h. To the reaction mixture was added MeOH and MeOH insoluble terephthalic acid dihydrazide **10a** was obtained by filtration (17.1 g, 88.1% yield). The amount of terephthalic acid hydrazine salt **11a** contaminant in **10a** was determined to be 25.7 ppm by GC analysis of the acetone hydrazone produced by the reaction of **11a** in **10a** with acetone. When the reaction of **9a** with hydrazine hydrate was carried out, **10a** which was much more contaminated with **11a** was produced. A solution of **9a** (155 g, 0.8 mol) in hydrazine hydrate (800 g, 16 mol) was stirred under a nitrogen atmosphere at 70 °C for 9 h. The reaction product, formed as colourless crystals, was filtered, washed with water, and dried to give **10a**

(140 g, 90% yield) which was contaminated with **11a** (144 ppm).

Similar treatment of dimethyl isophthalate **9b** with **8** gave pure isophthalic acid dihydrazide **10b**. A mixture of powdered **9b** (19.4 g, 0.1 mol) and **8** (89.92 g, 0.3 mol) was kept under a nitrogen atmosphere at 110–120 °C for 5 h. To the reaction mixture was added MeOH and MeOH-insoluble **10b** was isolated by filtration (13.6 g, 70% yield). The amount of isophthalic acid hydrazine salt **11b** contaminant in **10b** was determined to be 81 ppm by the same GC analysis as that employed for **10a**. On the other hand, **10b** which had been prepared by the reaction of **9b** with hydrazine hydrate was contaminated with 195 ppm of **11b**.

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Footnotes

† Crystal data for C₆H₆O₂·N₂H₄ **3**: monoclinic, space group C2/c, *a* = 17.277(2), *b* = 5.193(3), *c* = 8.142(2) Å, β = 96.49(2)°, *U* = 725.8(5) Å³, *Z* = 4, *D_c* = 1.30 g cm⁻³. For 2C₇H₈O₂·N₂H₄ **8**: monoclinic, space group C2/c, *a* = 34.333(2), *b* = 5.251(3), *c* = 8.152(4) Å, β = 93.23(2)°, *U* = 1467.3(8) Å³, *Z* = 8, *D_c* = 1.12 g cm⁻³. 722 (**3**) and 145 (**8**) independent reflections (2θ < 50°, Mo-Kα radiation, graphite monochromator) on a Rigaku AFC7R diffractometer on a rotating anode were obtained. Of these, 587 (**3**) and 903 (**8**) were judged as observed. Solution and refinement with the TEXSAN package of the Molecular Structure Corporation (direct methods); full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic hydrogens converged to *R* = 0.050 and *R_w* = 0.067 for **3**, and *R* = 0.051 and *R_w* = 0.058 for **8**, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

Reference

- 1 F. Toda, K. Tanaka, T. Hyoda and T. C. W. Mak, *Chem. Lett.*, 1988, 107.