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A Study of the Crystalline Environment of Some Dehydration Reactions That Take Place in the Solid State

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A Study of the Crystalline Environment of Some Dehydration Reactions That Take Place in the Solid State

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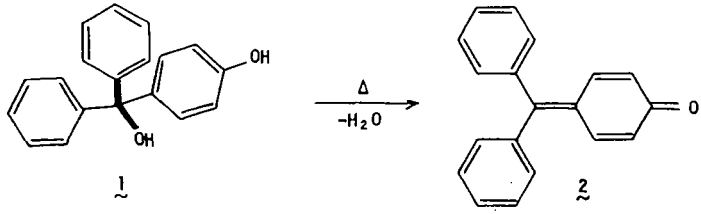
(p-Hydroxyphenyl)diphenylmethanol (**1**) undergoes dehydration to diphenylquinomethane, the fuchsone (**2**), both in solution and in the solid



1 **2**

state.[1] The crystal structure of the related (3,5-dibromo-4-hydroxyphenyl)-diphenylmethanol (**3**) was determined by Stora.[2] In this structure, the molecules form cross-linked double chains by hydrogen-bonding along the *z*-direction (see Figure 1). Two phenolic hydroxyl groups and two aliphatic hydroxyl groups from four separate molecules provide a centrosymmetric "square" of oxygen atoms held together by hydrogen bonds. The crystal structure of **1** has been determined in our laboratory. The crystals are monoclinic $a = 8.816$, $b = 15.379$, $c = 10.863$ Å, and $\beta = 101.4°$, and the space group is $P2_1/c$. The relative position of four molecules of **1** is not greatly different from that in **3**, but there is enough difference that only three hydrogen bonds can be formed among the four hydroxyl groups. Rather than a (phenol)O—H---(alcohol)O—H---(phenol)O—H---(alcohol)OH---(back to original phenol)O—H system of hydrogen bonds as in **3**, there is a (phenol)

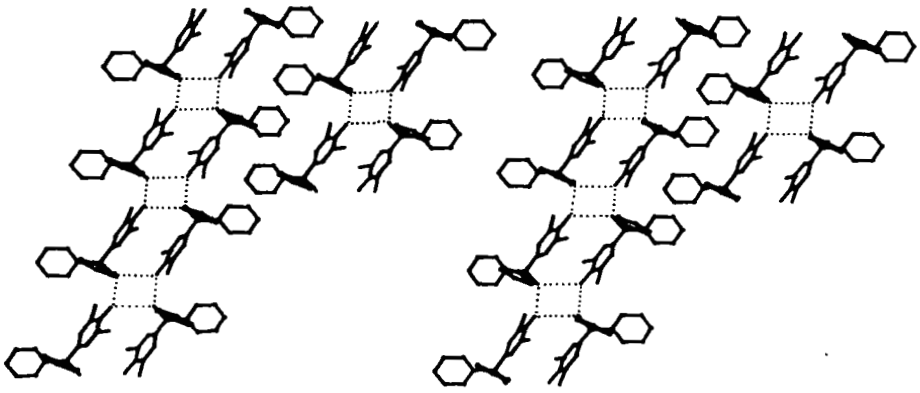
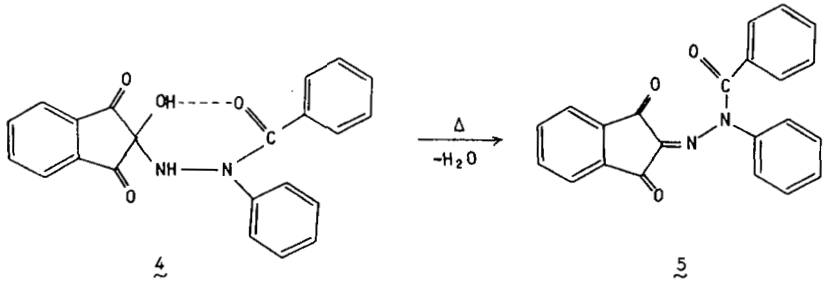


FIGURE 1 Stereoscopic view of the molecular packing in the crystal of **3** (after Stora[2]). Hydrogen bonds are shown by discontinuous lines.

O—H···(alcohol)O—H···(alcohol)O—H···(phenol)O—H hydrogen bonding system (Figure 2). As there is a center of symmetry between the two alcohol oxygen atoms, the crystal represents a statistical disorder of two



centrosymmetrical hydrogen-bonding assignments. Thus, only half of the phenolic hydrogen atoms participate in hydrogen bonding in the crystal.

The white crystals of 2-hydroxy-2-(*β*-benzoyl-*β*-phenylhydrazyl)-indane-1,3-dione (**4**) also undergo dehydration to the red product, indanetrione 2-(N-benzoyl-N-phenylhydrazone) (**5**). The molecule of **4** represents an example of the carbinol hydrazines that are thought to be intermediates in many carbonyl addition reactions. The white crystals of **4** are monoclinic with $a = 10.069(5)$, $b = 9.205(5)$, $c = 24.913(16)$ Å and $\beta = 124.2(1)°$, the space group is $P2_1/c$ and there are four molecules of **4** in the unit cell. The crystal structure of **4** is shown in Figure 3. The molecular packing is characterized by a chain of molecules arranged along the *b*-axis, held by intermolecular N—H···O=C (carbonyl) hydrogen bonding. The hydroxyl group partici-

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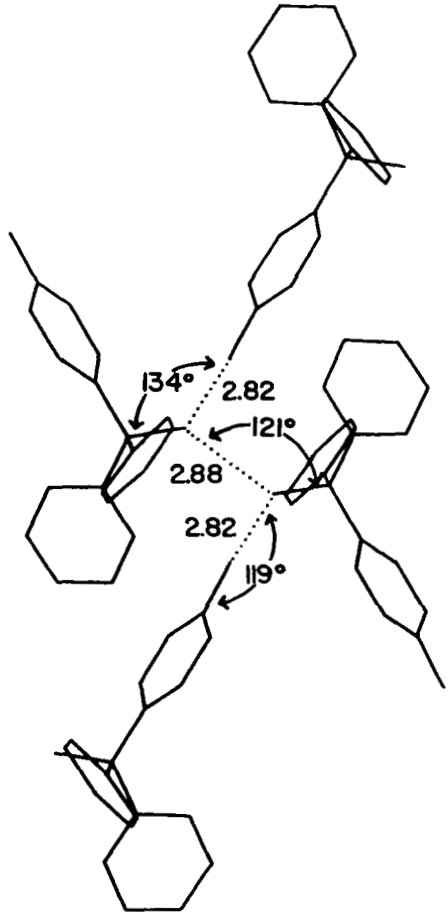

FIGURE 2 The hydrogen bonding in the crystals of **1**.

pates in an intramolecular O—H···O=C (amide). In the crystal the hydroxyl group that is eliminated is about 3.0 Å from the amine proton on the adjacent molecule and a possible chain mechanism can be put forward to describe the dehydration process in the solid state.

Examination of the crystals of **4** when heated under a microscope suggests that there is a directional preference for red color to spread along the *b*-axis (Figure 4).

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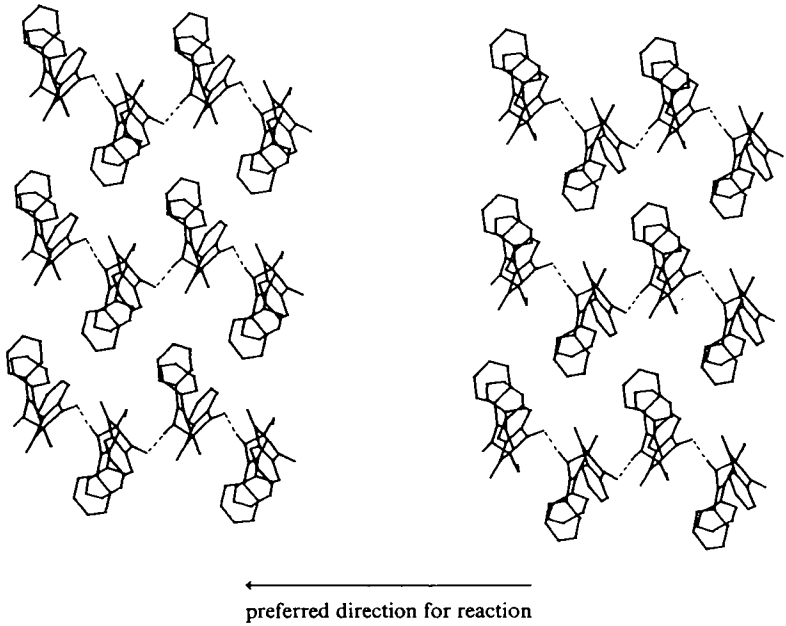

FIGURE 3 Stereoscopic view of the molecular packing of **4** looking onto the (001) layer plane. The apparently favored direction of dehydration is shown.

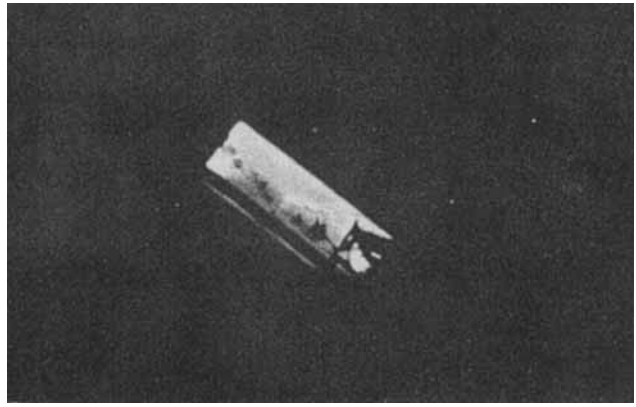

FIGURE 4 A single crystal of **4** undergoing reaction to **5**. The long axis of the crystal corresponds to the crystallographic *b*-axis.

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