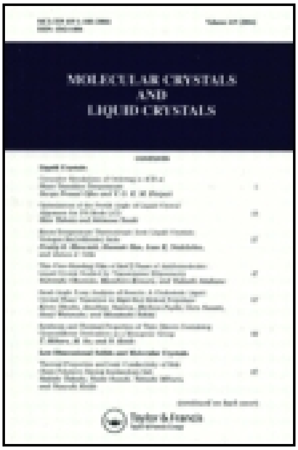

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Recent Studies on the Formation and Properties of Quinhydrone Complexes

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RECENT STUDIES ON THE FORMATION AND PROPERTIES OF QUINHYDRONE COMPLEXES

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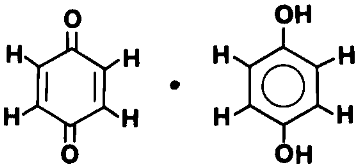
Department of Chemistry, University of Illinois, Urbana, Illinois 61801, USA

Abstract Several aspects of the structural and solid state chemistry of quinhydrones are described. Among the topics discussed are the preparation of isomeric quinhydrones, involving a solid state synthesis by grinding the components together, methods of interconversion of isomeric quinhydrones, and the use of spectroscopic methods including ^{13}C nmr to follow the interconversion. The important features of the crystal structures of several key complexes of quinones and hydroquinones are also described. Some rationalizations for the differences in ease of formation and in stoichiometry of complexes involving methyl substitutents are also presented.

Quinhydrones are 1:1 complexes of a quinone and a hydroquinone. These complexes exist in the solid state



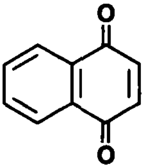
but are generally highly dissociated in solution. The emphasis in this paper will be on the solid state properties of quinhydrones including those of some other complexes of quinones and hydroquinones of stoichiometry other than 1:1.

HISTORICAL

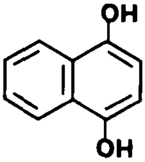
There are two crystallographic modifications of the parent or unsubstituted quinhydrone (1a:1b), the 1:1 complex of benzoquinone and benzohydroquinone (or simply quinone and hydroquinone). The first X-ray structural work on the monoclinic form of quinhydrone was carried out by Matsuda et al.[1] Subsequently Sakurai determined the structure of the triclinic form[2] and later carried out a much improved analysis of the monoclinic form.[3] The two forms of the unsubstituted quinhydrone display similar structural features. There are chains of alternating quinone and hydroquinone molecules linked by O-H---O hydrogen bonds. In the direction normal to the hydrogen-bonded chains and the molecular planes of the components there is a stacking of hydroquinone molecules over quinone molecules and vice-versa. The combination of hydrogen bonding and π-π interactions gives rise to an infinite two-dimensional layer-like structure (Figure 1). In both crystal modifications, the quinone and the hydroquinone molecules occupy crystallographic centers of symmetry. An interesting feature of the structure and the diffraction pattern of the triclinic modification was that there was an almost exact a/2 repeat relationship between quinone and hydroquinone molecules. In 1977, Thozet and Gaultier[4] published the structure of the quinhydrone formed by naphthoquinone (2a) and hydroquinone (1b). While this structure

1a

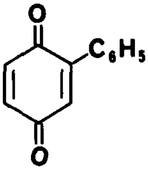
1b



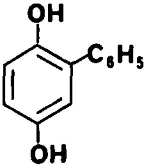
2a



2b



3a



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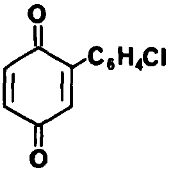
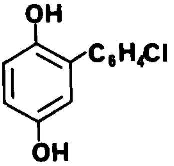


4a



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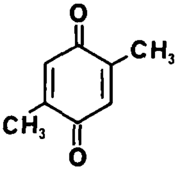
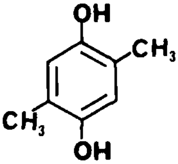
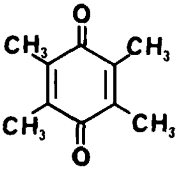


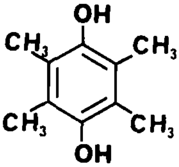
5a



5b



6a



6b

belonged to the space group $P2_12_12_1$ and the component molecules were in general positions, the previously noted features of hydrogen-bonded chains and π-π overlap were also present.

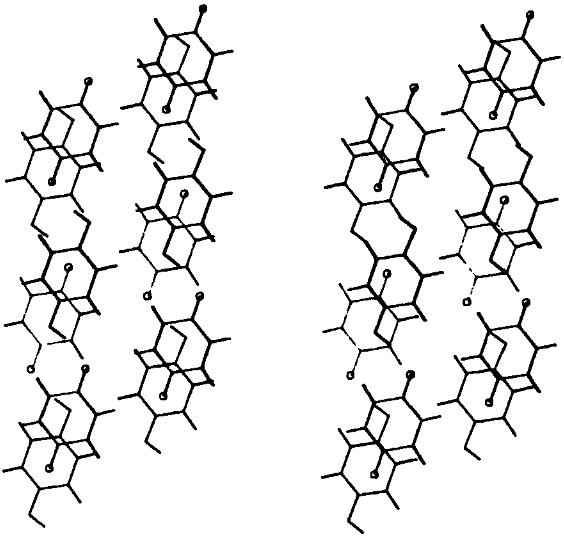


FIGURE 1. Stereoscopic view of the arrangement of the molecules in the triclinic form of quinhydrone. The hydrogen-bonded chains run vertically, while the next row of molecules is held by π-π interactions in a direction normal to the plane of the Figure. Parts of two layers are shown; there are no strong interactions in the horizontal direction of the Figure.

2-Phenylquinhydrones

Our group at the University of Illinois became interested in quinhydrones in the mid 1970's with a view to preparing "mixed" or isomerically-substituted quinhydrones and to examine the possibilities of interconversion. As a first step, the identically substituted 2-phenyl and

2-(p-chlorophenyl) quinhydrones (3a:3b) and (4a:4b) were prepared.[5] Large single crystals of these complexes were obtained by non-aqueous gel diffusion techniques.[6] X-ray investigations revealed that the crystals of 3a:3b and 4a:4b were isostructural and belonged to the space group $P2_1/c$ with two molecules of the complex in the crystal unit cell.[7] This situation requires a center of inversion in the complex which is not possible for an ordered hydrogen-bonded arrangement of the type found in the previous investigations. The general arrangement of the "averaged" phenyl quinhydrone molecules was quite consistent with the features of hydrogen-bonded chains and π-π overlap found previously (Figure 2). No evidence for a disordered proton, due either to statistical static disorder or to rapid exchange, could be found in the x-ray structural determination. Attempts to refine the structures either in the space group $P2_1$ or in Pc offered no improvement over the centrosymmetric solution. There were, however, two indications that the crystals may indeed be non-centrosymmetric.

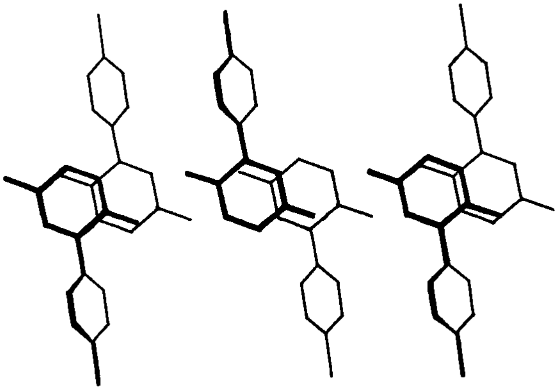


FIGURE 2: A view of two rows of the layer of the 2-phenylquinhydrone structure.

Crystals of 2-phenylquinhydrone gave a positive second harmonic generation test with a Nd-YAG laser,[8] while a morphological examination of crystals of both complexes suggested a polar axis in the b-direction, thus implying the space group $\underline{P}2_1$.[7] A possible explanation for these apparently contradictory results may be as follows. Based on the structural characteristics of the previously examined quinhydrones and the dispositions of the molecules in the phenylquinhydrone complexes, two-dimensional sheets of molecules would be formed by hydrogen-bonding and π-π overlap. However, there are no specific interactions, other than those involving space-filling protruding phenyl groups, to mesh one layer with its neighbor in such a way as to provide three-dimensional order in terms of distinguishing a phenylquinone molecule from a phenylhydroquinone molecule. If one constructs an ordered structure of the type shown in Fig.3a, the symmetry elements conform to the space group $\underline{P}2_1$. By merely switching the protons in the central row, one converts the space group to Pc (Fig 3b). There would seem to be little to favor one arrangement over the other and, in the process of crystal growth, regions of one arrangement could be perpetuated and then, due to some local disturbance, the alternate arrangement could form. Crystals, although not suitable for single crystal X-ray analysis, of the mixed or isomerically substituted quinhydrones (3a:4b) and (4a:3b) were prepared. They resisted interconversion in the solid state after heating at 140°C for several hours and were stable indefinitely at room temperature. However, there

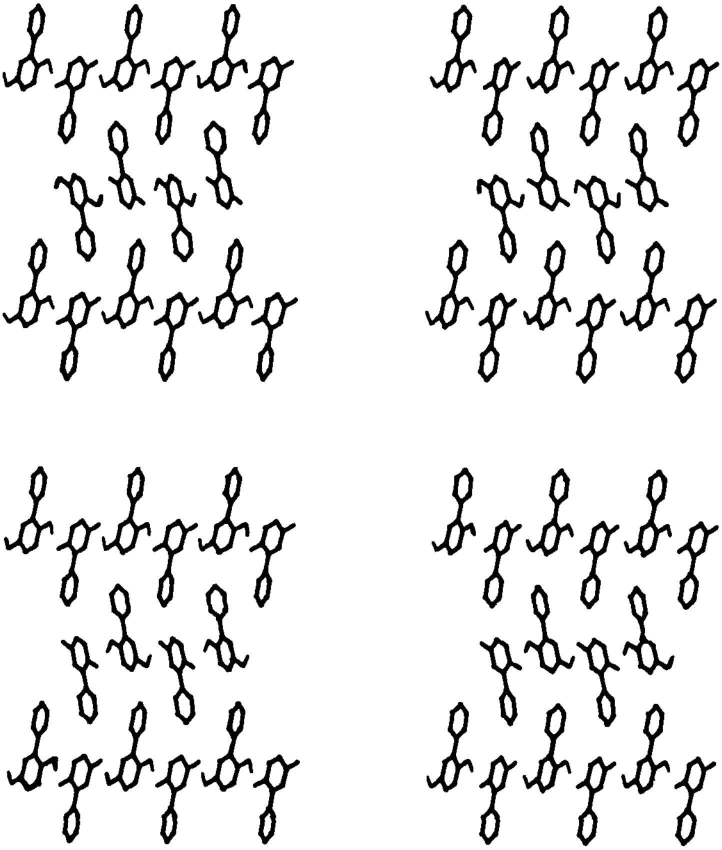
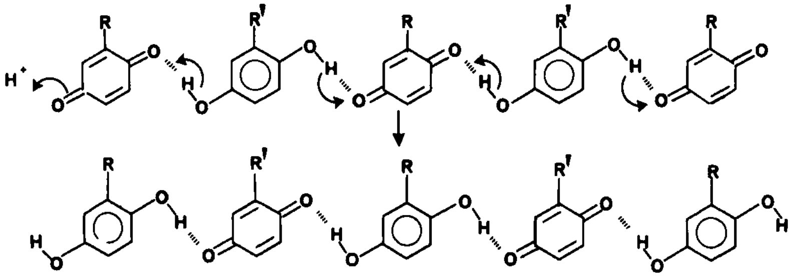


Figure 3: Stereoscopic views of the packing of the 2-phenylquinhydrone molecules in the crystal. (a) With the hydrogen atoms arranged so that the space group is $P2_1$ (b) With the hydrogen atoms arranged so that the space group is Pc.

was precedent for solid state interconversion of quinhydrones as Gragerov and coworkers[9] had succeeded in partially interconverting the ^1H and ^2H "isomeric" quinhydrones by heating powders at 107-120°.

General Methods for Preparation of Pairs of Isomeric Quinhydrones

In recent years, our group at Illinois has resumed work on quinhydrones with the object of finding a general method to prepare pairs of differently substituted, or isomeric quinhydrones, and to explore methods for interconversion of these isomeric pairs. Interconversion could be achieved conceptually, given the known crystal structures, by capture of a H^+ or H^- at the surface, followed by proton transfer along the hydrogen bonded row, as follows:



The interconversion was probed by various physical techniques in an attempt to obtain information on the mechanism, such as formation of intermediates.

A possible reason for the failure to effect interconversion between the 2-phenyl and 2-(p-chlorophenyl)-quinhydrones may be that that particular pair of quinhydrones are well-balanced thermodynamically. Interconversions may be more readily achieved if a pair of isomeric quinhydrones were prepared with a greater free energy difference between the isomers. The thermodynamic relationships used to select suitable compounds were those obtained from solution studies and involved the use of a greater variety of substituents than had been employed in the earlier work. Unfortunately this plan ran into the fairly immediate problem, that all efforts to prepare the less stable isomer by crystallization of the components led to crystals of the more stable complex due to fast exchange processes in solution prior to crystallization.

We resolved this difficulty by adopting a method used by Rastogi and co-workers[10] to form various complexes. They had achieved success in the preparation of several complexes, including unsubstituted quinhydrone, by grinding the components together. There was also in the literature another report[11] which indicated that the grinding reaction for quinhydrones did not go to completion. There was, however, no indication that the method had been used to prepare the thermodynamically less stable member of an isomeric pair. Thus no significantly differently-substituted pairs of quinhydrones had been obtained previously.

When a mixture of a quinone and a hydroquinone in equimolar amounts was ground in an agate mortar and pestle, the solid, which was initially light-yellow, quickly turned dark as the π-complexed quinhydrone formed. Grinding was continued for 5 minutes after no further color change was noted. Typical total grinding times were 15-25 minutes. Quinones and hydroquinones used in these experiments included the unsubstituted (1a,b), the 2-phenyl

(3a,b), the naphtho (2a,b), and a great many methyl-substituted compounds. The method was found to be of broad generality and to go to completion. The progress and the products of the reaction were followed by several techniques.

X-ray powder diffraction photographs are sensitive indicators of a difference in crystal structure. The powder photographs of the products of grinding the two sets of isomeric pairs of quinones and hydrogens were clearly distinct although generally similar (Fig. 4). The similarity in powder photographs of the two isomeric quinhydrones is not surprising in that the crystal structures should be similar in view of the expected common struc-

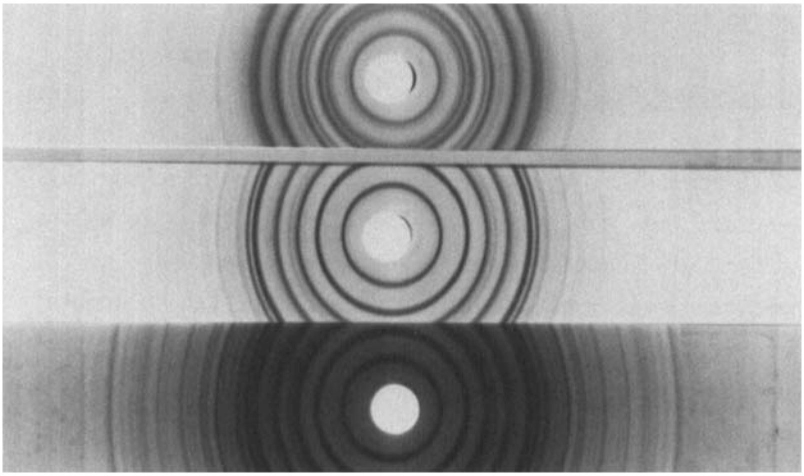


Figure 4: X-ray powder photographs of (top) the quinhydrone (3a:2b) prepared by grinding 2-phenylquinone (3a) with naphthohydroquinone (2b), (center) the quinhydrone (2a:3b) obtained by grinding naphthoquinone (2a) and 2-phenylhydroquinone (3b), and (bottom) the complex 2a:3b obtained by crystallizing a mixture of either 2a and 3b, or 3a and 2b.

tural characteristics, e.g., H-bonding and π-complexing. The powder photograph of the stable form was identical to the powder photograph of the complex grown from solution, a result that indicates that the crystal structures are identical. The powder photographs of the unstable form obtained by grinding was quite distinct from that of a mixture of starting quinone and hydroquinone (Fig. 4). It may be noted that the product of grinding a mixture of unsubstituted quinone and hydroquinone together was a mixture of the monoclinic and triclinic forms of quinhydrone.

It had previously been noted[11] that the carbonyl stretching frequency of the quinones shifts to lower frequency when the hydrogen-bonded quinhydrone is formed. The F.t.i.r. spectra (nujol mulls) of the complexes prepared by grinding were clearly distinct from a superposition of those of the components. The spectra of the isomeric quinhydrones were different from each other, while the spectra of the stable form prepared by grinding were identical to those of the complex prepared by crystallization (Fig. 5).[12] Differential scanning calorimetry also provided evidence for the completion of the grinding reaction. As the reaction progressed the endotherms corresponding to the reactants decreased to be replaced by gradually increasing endotherms for the products.

Interconversion of Isomeric Quinhydrones

It was noted[12] in the spectroscopic investigations discussed above that when the unstable quinhydrones were allowed to stand in nujol, spectra corresponding to the stable form began to appear. An investigation was carried out to examine the conditions for interconversion. Conant

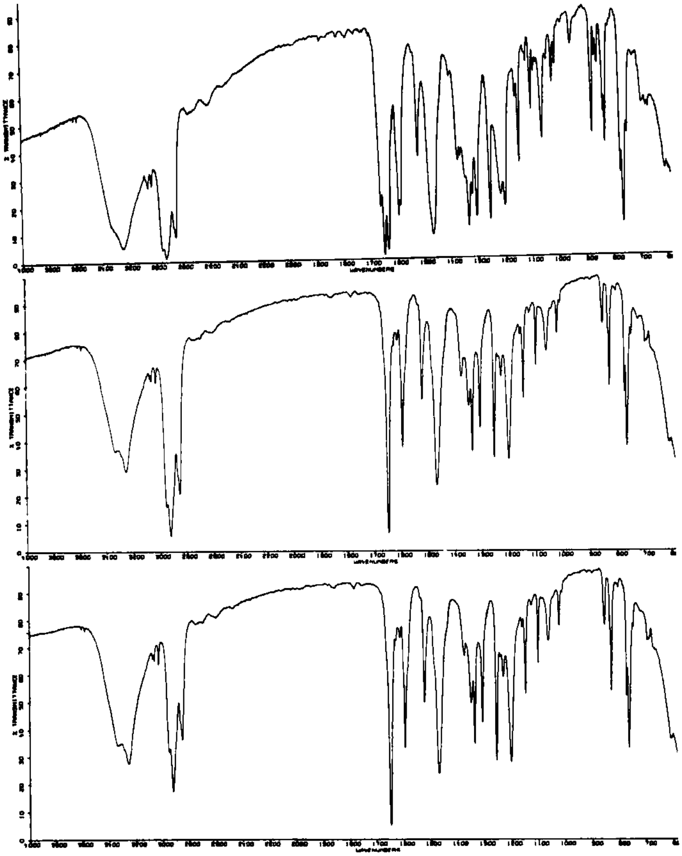
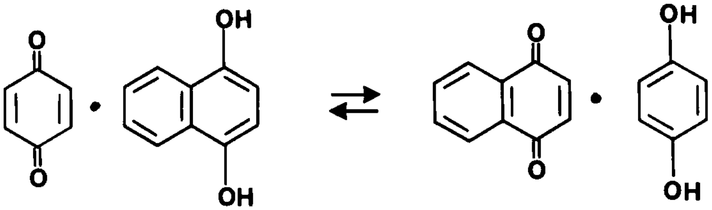


Figure 5: The Ftir spectra of, (top) the 1:1 complex of benzoquinone: naphthohydroquinone (1a:2b) prepared by grinding, (middle) the 1:1 complex of naphthoquinone: hydroquinone (2a:1b) prepared by grinding, (bottom) the complex 2a:1b prepared by crystallization. The latter two spectra are essentially identical, while the first spectrum is clearly different.

and Fieser[14] and Hunter and Kvalnes[15] had measured the reduction potentials of several quinones and these data indicated the probable stable quinhydrone of an isomeric pair. Of the quinones studied in our investigations, naphthoquinone was the most stable, followed by multiply-substituted methylquinones, while there was little difference between phenylquinone and hydroquinone. Thus, an equilibrium of the type shown:



1a 2b

2a 1b

would be expected to lie well to right on the basis of the reduction potential data, and in fact the quinhydrone 2a:1b has been shown to be the more stable isomer.[16]

We found that when the thermodynamically less stable complexes, such as 1a:2b and 3a:2b, were heated at 70-80° for 3 hours they were converted quantitatively to 2a:1b and 2a:3b. The products of the reaction were microcrystalline and were determined to be identical to those prepared either by grinding the components together or by crystallization from solution on the basis of X-ray powder photographs and Ftir spectra. In all cases examined, it was found that the complex that is more stable in solution is also the product of the heating reaction and therefore the more stable in the solid state.

Anomalous behavior was found in the case of the unsubstituted quinone (1a) and 2,5-dimethylhydroquinone (5b) complex. When the 1:1 complex prepared by grinding these components together is heated, the resulting product is a 1:2 complex of dimethylquinone (5a) and hydroquinone (1b) with excess 2,5-dimethylquinone being produced. When a mixture of 5a and 1b is crystallized, the same 1:2 complex is obtained.

The conversion of 1a:5b (1:1) to 5a:1b (1:2) was followed by CPMAS ^{13}C NMR solid state spectroscopy.[17] Before the reaction was studied, the solid state spectra of representative quinones, hydroquinones and quinhydrones were obtained. The solid state NMR spectra of the quinones are quite similar to those reported in solution if due allowance is made for differences in chemical equivalence between the crystalline and solution environments. Quinones in which one carbon atom is involved in C-H---O interactions show doubling of the signals from otherwise chemically equivalent carbon atoms. The ^{13}C solid state spectra of hydroquinones are also rather similar to the solution spectra, despite the possible influences of differences in hydrogen bonding, rapid O-H proton shifts in solution, and ring current effects of aromatic rings. Comparison of quinhydrone spectra between solution and the solid state media are not possible because of the tendency for dissociation in solution. The solid state spectra of the monoclinic and triclinic forms of quinhydrone are shown in Figure 6. The spectra are quite similar to each other. Complexation has the effect of shifting the carbonyl carbon resonance 3-4 ppm upfield, although the phenolic carbon resonance in the complex is at the same position as one of the phenolic carbon resonances in solid

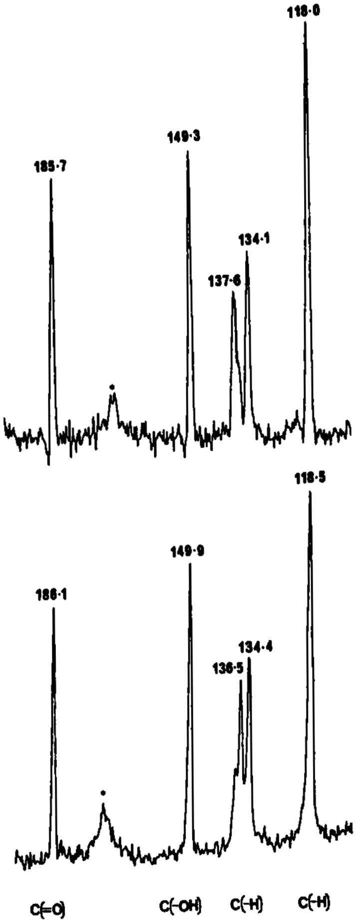


Figure 6: Solid state ^{13}C NMR spectra of (top) monoclinic quinhydrone and (bottom) triclinic quinhydrone.

α-hydroquinone. Similar upfield shifts are encountered in other quinhydrone complexes involving benzoquinone, but down-field shifts are observed when tetramethylquinone complexes with tetramethylhydroquinone.

While the direct conversion of the complex 1a:5b to 5a:1b was studied by solid state ^{13}C NMR, there were complications due to the formation of the excess quinone, 5a. It was found[17] that the best approach to follow the conversion was to examine the reaction:

1a:1b (1:1) + 5b → 5a:1b (1:2)

When a solid mixture of the 1:1 complex of benzoquinone: hydroquinone and 2,5-dimethylhydroquinone was heated at 85° and ^{13}C NMR spectra recorded at various times, the results shown in Figure 7 were obtained.[17] The starting mixture gave a spectrum identical to that expected for a mixture of 1a:1b and 5b, while after heating for 4 hours the final spectrum is essentially identical to that of the pure 5a:1b (1:2) complex. The intermediate spectra show a gradual diminution of some signals and the appearance and growth of others. There is no evidence for the presence of any intermediates in the reaction.

Crystal Structures of Several Complexes of Quinones with Hydroquinones

Crystal structures have been determined for the 1:1 complex of 2,3,5,6-tetramethylquinone (6a) with 2,3,5,6-tetramethylhydroquinone (6b),[18] the 2:1 complex of 2,5-dimethylquinone (5a) with 2,5-dimethylhydroquinone (5b),[19] and the 1:2 complexes of 2,5-dimethylquinone (5a)[13] with unsubstituted hydroquinone (1b) and of

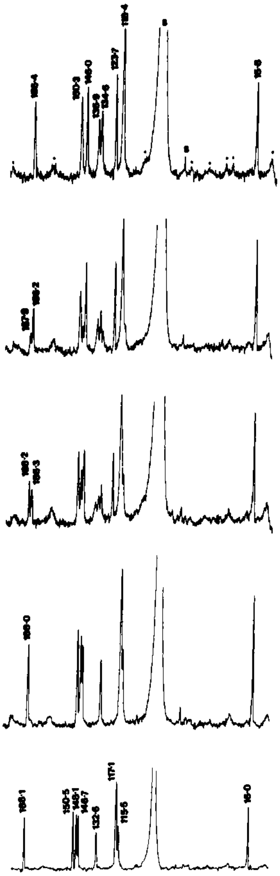


Figure 7: A series of solid state ^{13}C NMR spectra measured when a mixture of 2,5-dimethylhydroquinone and the 1:1 complex of benzoquinone and hydroquinone was heated at 85°C. Spectra were recorded at 0 min, 70min, 230 min, and 500 min. At the bottom is the solid state ^{13}C NMR spectrum of the 1:2 complex of 2,5-dimethylquinone and hydroquinone.

2,3,5,6-tetramethylquinone (6a) with hydroquinone (1b).[18] The 1:1 complex of tetramethylquinone and tetramethylhydroquinone (duroquinhydrone) was first reported by Michaelis and Granick.[2] The Ftir shows a single hydroxyl stretching absorption at 3495 cm^{-1} which is significantly higher than those (3220-3330 cm^{-1}) found in other 1:1 quinhydrones.[18,19] The crystal structure was carried out to confirm definitely the stoichiometry and to seek explanations for the variation of the hydroxyl stretching frequency. The crystal structure is shown in Fig 8.[18] The

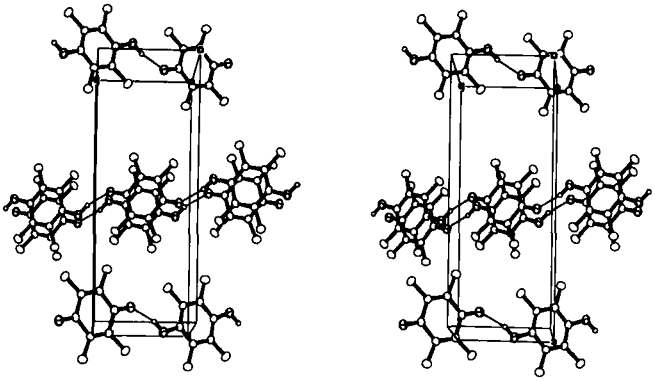


Figure 8: Stereoscopic view of the structure of the 1:1 complex of tetramethylquinone with tetramethylhydroquinone (6a:6b).

space group is $P2_1/c$ with two formula units ($C_{10}H_{12}O_2 \cdot C_{10}H_{14}O_2$) in the cell. The component duroquinone and durohydroquinone molecules each occupy crystallographic centers of symmetry. In many ways, the crystal structure resembles closely that of monoclinic unsubstituted quinhydrone, but with the intermolecular dimensions significantly increased. The ring-ring distances between the overlapping rings are in the range 3.38-3.50Å compared to 2.88-3.27Å for the unsubstituted quinhydrones while the intermolecular O---O hydrogen bonding distance in the chain is 2.846(3)Å as compared to 2.737(6)Å in monoclinic quinhydrone.

Crystals of the 2:1 complex of 2,5-dimethylquinone (6a) with 2,5-dimethylhydroquinone (6b) are most reliably obtained by nucleating a mixture of the components with a crystal of the 2:1 complex. It is also obtained in small amounts by crystallization from an ethyl acetate solution along with a different complex of 6a and 6b which has the 1:1 stoichiometry.[20] These two complexes have different Ftir spectra and X-ray powder patterns. Crystals of the 1:1 complex suitable for single crystal X-ray studies have not yet been obtained. The structure of the 2:1 complex has been determined.[19] The crystals belong to the space group $P2_1/c$ with two formula units $((C_8H_8O_2)_2 \cdot C_8H_{10}O_2)$ in the cell. The structure is shown in Figure 9.[19] The 2,5-dimethylhydroquinone molecule occupies a crystallographic center of symmetry with each hydroxyl group hydrogen bonded to a 2,5-dimethylquinone molecule. The overall structure does not consist of hydrogen-bonded chains but has "triplets" of quinone-hydroquinone-quinone molecules,

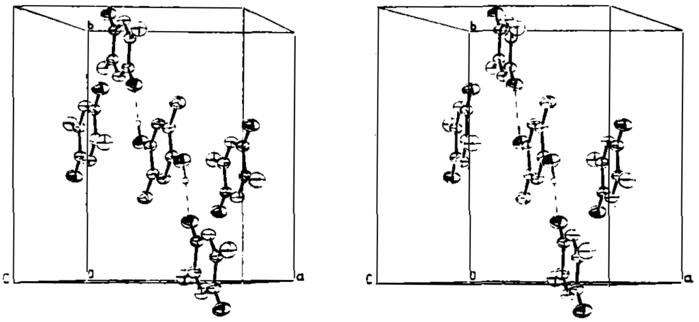


Figure 9: Stereoscopic view of the 2:1 complex of dimethylquinone (6a) and dimethylhydroquinone (6b).

with one of the carbonyl groups of each quinone not participating in O-H---O hydrogen bonding, although it is involved in a C-H---O contact. There is π-π overlap between the hydroquinone and quinones but the overlapping molecules do not have the -OH and C=O groups aligned in a parallel fashion, but instead they are rotated at an angle of ~60°.[18]

The crystal structures of the two 1:2 complexes, 2,5-dimethylquinone (5a) with hydroquinone (1b)[13] and tetramethylquinone (6a) with 1b,[18] are somewhat similar. Both crystals belong to the triclinic space group $P\bar{1}$ with one formula unit (Q:2HQ) in the unit cell. All the component molecules occupy crystallographic centers of symmetry. The crystal structures are shown in Figures 10 and 11. In each crystal, there is a chain of alternating

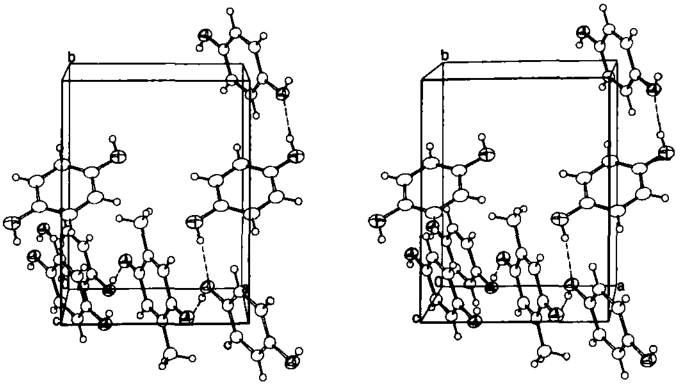


Figure 10: View of the packing of the 1:2 complex of dimethylquinone (6a) and hydroquinone (1b).

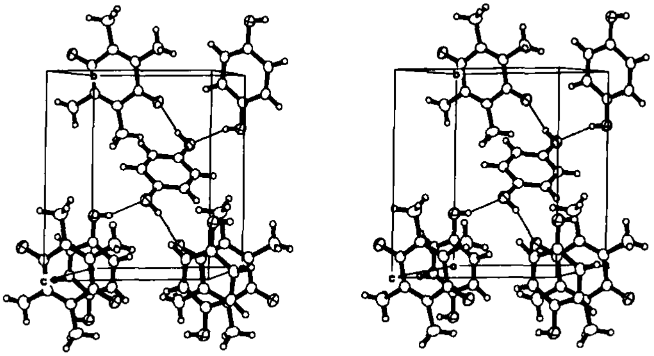


Figure 11: Stereoscopic view of the structure of the 1:2 complex of tetramethylquinone (6a) with hydroquinone (6b).

quinone and hydroquinone molecules held together by rather different forms of hydrogen bonds. The "extra" hydroquinone serves to cross-link the chains also by hydrogen bonding. In the 1:2 dimethylquinone:hydroquinone complex, the hydrogen-bonded chain is essentially the same as that found in most 1:1 quinhydrones with direct hydroquinone to quinone (O-H---O) linkages.[13] The additional hydroquinone molecule forms hydrogen bonds to the hydroxyl groups of the hydroquinone molecules that participate in the chain formation. The in-chain O---O distance is 2.732(2)Å, while the cross-linking O---O distance is 2.775(2)Å. The π-π overlap between adjacent chains is very similar to that found in 1:1 quinhydrones. By contrast, there is a "chain" of alternating quinone and hydroquinone molecules in the 1:2 complex of tetramethylquinone with hydroquinone, but there are no direct O-H---O hydrogen bonds between adjacent quinone and hydroquinone molecules. Instead, the "extra" hydroquinone, which still plays the role of a cross-link, has the hydroxyl groups fully interposed in the chain; the hydrogen bonding arrangement is OH(Chain HQ)--- O-H (Link HQ) --- O(=C) (Quinone). The O-H---O(H) distance is 2.815(2) and the O-H---O(=C) distance is 2.837(2)Å. There is also π-π overlap in the structure, but the interposition of the extra hydroquinone hydroxyl groups has the consequence that the adjacent overlapping quinone and hydroquinone molecules are rotated at ~70° from parallelism of the C=O and C-OH bonds.

The Stoichiometry of Complexes of Polymethylated Quinones and Hydroquinones

It has already been noted that stoichiometries other than 1:1 are sometimes found when either the quinone or the hydroquinone has methyl substituents. We undertook a more systematic examination of the effect of methyl substitution in quinones and hydroquinones on the ease of formation and on the stoichiometry of the products.[20] Complexes prepared are shown in Figure 12. In the cases where the quinone and hydroquinone have identical substituents (left column), 1:1 complexes are found except in the case of the 2,5-dimethylquinone: 2,5-dimethylhydroquinone system where both 1:1 and 2:1 stoichiometries are found. In the examples where the quinone is unsubstituted but the hydroquinone has methyl substituents (center column), 1:1 stoichiometry is usually found, with the exception of the 2:1 complex of unsubstituted quinone (1a) with tetramethylhydroquinone (6b). If the quinone molecule has methyl substituents and the hydroquinone is unsubstituted (right column), the complexes are 1:2, with the exceptions of

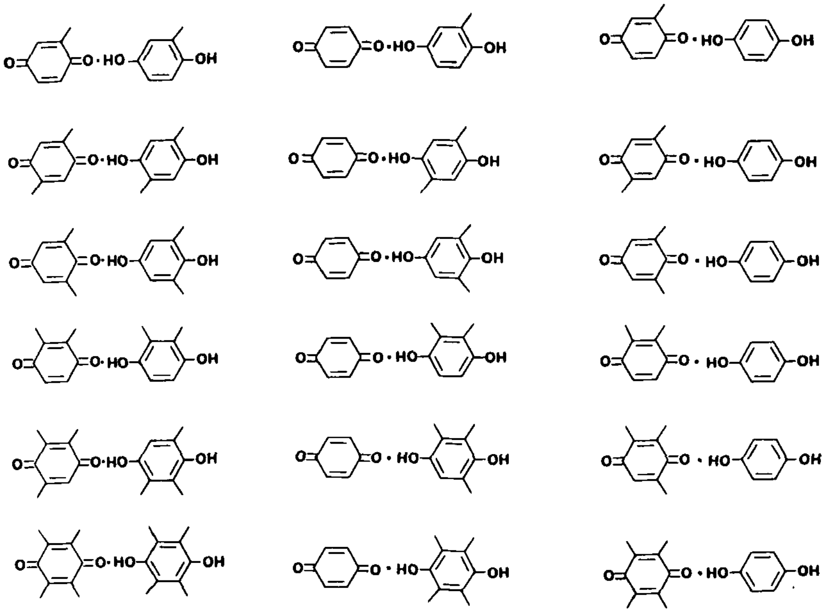


Figure 12: Complexes involving unsubstituted and methyl-substituted quinones and hydroquinones.

2,3-dimethylquinone: hydroquinone, which is 1:1, and tetramethylquinone: hydroquinone (6a:1b) which forms both a 1:1 and a 1:2 complex.

The tetramethylquinone (6a) and hydroquinone (1b) system provides an example of the role of nucleation in complex formation. Attempts at crystallization of equimolar amounts of 6a and 1b or grinding 6a and 1b together failed to give any complex of the two components. However, if the ground mixture was heated for 2 hours, a red 1:1 complex of 6a and 1b was formed. Also, if a mixture of 6a and 1b was nucleated with a few crystals of the 1:1 complex, then grinding at room temperature resulted in complete reaction to give the 1:1 complex. If a saturated ethyl acetate solution of 6a and 1b containing an excess of each of the solid compounds was nucleated with crystals of the 1:1 (or the 1:2) complex, well-formed crystals of the 1:2 complex of 6a and 1b were obtained.

Examination of the crystal structures described in this paper, and of those reported previously, [1-4,7] gives some clues as to why the methyl-substituted quinhydrones are sometimes difficult to prepare and often form with stoichiometries other than 1:1. The standard feature of the crystal packing of 1:1 quinhydrones is the presence of two-dimensional layers of molecules held together in one-direction by quinone-hydroquinone hydrogen bonding and in the other by π-π overlap of alternating quinone and hydroquinone rings. There are no strong packing interactions holding these layers together in the third direction. These two-dimensional layers are exemplified in the unsubstituted quinhydrones [1-3] and in duroquinhydrone. These complexes are "symmetrical" both in terms of having identical substitution patterns and having the component molecules centrosymmetric. Although less "symmetrical", the 1:1 naphthoquinone: hydroquinone (2a:1b) complex and the 2-phenyl quinhydrones (3a:3b) amd (4a:4b) are efficient packing groups and 1:1 complexes are readily obtained. However, methyl groups, especially when the rings are not fully substituted present a less favorable packing situation. The methyl goup is relatively bulky and occupies an essentially spherical shape. Unless there are complementary spherical shapes on adjacent sheets, an unfavorable packing arrangement will result. Complementary spherical shapes will most likely be encountered with identically substituted and fully substituted quinones and hydroquinones. Thus, duroquinhydrone is obtained with good crystals as a 1:1 complex. Also, most identically substituted methylquinones and methylhydroquinones give 1:1 complexes. When a methylquinone complexes with unsubstituted hydroquinone, the small size of the hydroquinone molecule provides the opportunity for an additional hydroquinone molecule to play the role of a bridge or link between the two-dimensional layers by acting as a hydrogen bonding donor. The result is a 1:2 complex, as shown by the structures of 5a:1b and 6a:1b. The unsubstituted quinone molecule, lacking a hydrogen bonding donor capability, is unable to play the bridging or linking role, so 1:1 complexes are normally obtained although often with difficulty and poor crystal quality.

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