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Structural Studies of 1:1 Quinone-Hydroquinone Complexes

Gautam R. Desiraju [a] [b] , David Y. Curtin [a] & Iain C. Paul [a]
[a] Department of Chemistry and the Materials Research Laboratory, University of Illinois, Urbana, Illinois, 61801, U.S.A.
[b] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560012, India

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Structural Studies of 1:1 Quinone-Hydroquinone Complexes

GAUTAM R. DESIRAJU,† DAVID Y. CURTIN, and IAIN C. PAUL
Department of Chemistry and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, U.S.A.

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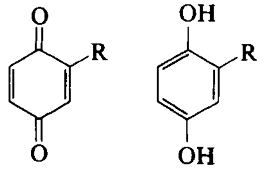
The structures of the 1 : 1 quinone-hydroquinone complexes of 2-phenyl and of 2-(4′-chloro) phenylbenzoquinone have been studied by X-ray methods. A superficial study would indicate that the quinhydrones are centrosymmetric and belong to the space group $P2_1/c$. However, other evidence indicates that the true crystal structure may belong to either the space group $P2_1$ or to Pc, or that the crystal may contain regions that would correspond to each of these two non-centrosymmetric space groups. Some possible consequences of such a structural arrangement are briefly discussed.

INTRODUCTION

Quinhydrones, which are the 1 : 1 molecular complexes of quinones and hydroquinones, have been known for some time[1] but X-ray structural studies of these compounds have been limited to the two forms of the unsubstituted complex **1**[2] and to the 1 : 1 naphthoquinone and hydroquinone complex.[3]



1. $R{=}H$
2. $R{=}C_6H_5$
3. $R{=}p\text{-}ClC_6H_4$

Complexes of the type **4** and **5** have been reported and shown to resist interconversion in the solid state even when heated to 140°.[4] It was suggested that the reason for this unusual thermal stability could lie in the fact that both hydrogen bonding and charge transfer interactions are involved here. To elucidate further the structural features of the quinhydrones, X-ray

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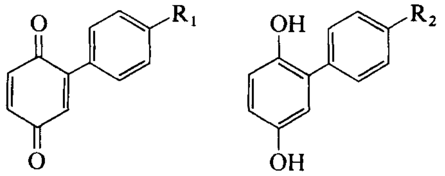
† Present address: Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India.

analyses of 2-phenylquinhydrone (**2**) and 2-(4′-chloro)phenylquinhydrone (**3**) were carried out.



4. R_1=H R_2=Cl
5. R_1=Cl R_2=H

RESULTS AND DISCUSSION

The apparent space group ($P2_1/c$ with $Z = 2$) observed in the X-ray study of single crystals of complexes **2** and **3** indicates that in both cases the quinone and hydroquinone molecules are related by a center, or pseudo-center of symmetry.

TABLE I

Atomic coordinates, in fractions of the unit cell edges, for the complex **2** in the crystal.[a,b]

Atom	x	y	z
C(1)	0.2006(8)	0.3466(5)	0.0219(2)
C(2)	0.0588(8)	0.2876(5)	0.0658(2)
C(3)	−0.1350(7)	0.1951(5)	0.0418(2)
C(4)	−0.2077(7)	0.1551(5)	−0.0290(2)
C(5)	−0.0700(7)	0.2153(5)	−0.0742(2)
C(6)	0.1277(8)	0.3070(5)	−0.0488(2)
C(7)	−0.1453(7)	0.1843(5)	−0.1483(2)
C(8)	0.0067(8)	0.1075(6)	−0.1842(2)
C(9)	−0.0635(10)	0.0857(7)	−0.2539(2)
C(10)	−0.2740(10)	0.1430(7)	−0.2878(3)
C(11)	−0.4258(10)	0.2191(8)	−0.2536(3)
C(12)	−0.3587(8)	0.2403(7)	−0.1824(2)
O(1)	0.3820(6)	0.4380(5)	0.0461(2)
O(2)	−0.3908(5)	0.0626(4)	−0.0507(2)
H(2)[c]	0.091(9)	0.326(7)	0.105(3)
H(3)	−0.256(6)	0.155(5)	0.072(2)
H(6)	0.231(9)	0.348(7)	−0.077(3)
H(8)	0.154(11)	0.080(8)	−0.158(3)
H(9)	0.084(9)	0.030(7)	−0.276(3)
H(10)	−0.371(6)	0.123(5)	−0.342(2)
H(11)	−0.614(8)	0.273(6)	−0.273(2)
H(12)	−0.465(6)	0.307(5)	−0.158(2)
OH(1)	0.43(2)	0.43(2)	0.013(6)
OH(2)	−0.50(1)	0.04(1)	−0.022(3)

[a] Estimated Standard Deviations are given in brackets.

[b] For labelling of atoms see Figure 1.

[c] Hydrogen atoms are given the numbers of the atoms to which they are attached.

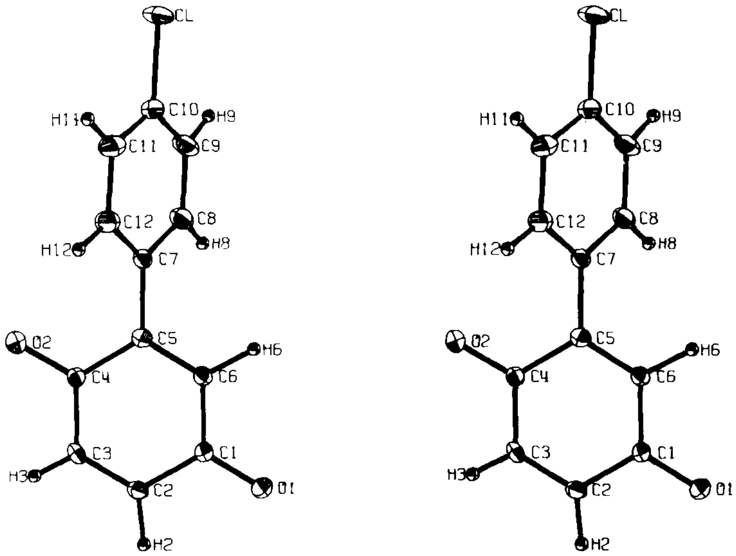


FIGURE 1 Stereoscopic view of the geometry of the "averaged" molecule of **3** resulting from the refinement in the space group $P2_1/c$.

The crystals of complex **2** are monoclinic, $a = 5.983(2)$, $b = 7.515(3)$, $c = 20.299(5)$ Å, $\beta = 102.5(2)°$ and the structure was refined to an R-factor of 0.092 in the space group $P2_1/c$ using 1251 observed reflections. The atomic coordinates are given in Table I.[†] Complex **3** is also monoclinic, $a = 5.980(1)$, $b = 7.446(1)$, $c = 22.916(7)$ Å, $\beta = 100.3(2)°$ and the structure was refined to an R-factor of 0.092 in $P2_1/c$ using 1516 observed reflections. A stereoscopic view of the molecular geometry resulting from this refinement is shown in Figure 1. The atomic coordinates are given in Table II.

Significantly, the structure of the unsubstituted complex, **1**, is ordered (the quinone and hydroquinone molecules can be distinguished).[2] In the unsubstituted quinhydrone (**1**), the constituent quinone and hydroquinone are themselves centrosymmetric and in both forms of the crystallographic complex, occupy distinct crystallographic sites with $\bar{1}$ symmetry (Figure 2). Hence the problems associated with a pseudo-center of symmetry that were encountered in the present analyses of **2** and **3** did not apply in the case of **1**. Although the X-ray results on the crystals of **2** and **3** might seem to point to

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[†] The atomic coordinates in this Table and in Table II correspond to refinements in $P2_1/c$. Refinements were also attempted in the space groups $P2_1$ and Pc; these refinements were not significantly better than that in $P2_1c$ on the basis of statistical arguments. Full details of this aspect of the work will be published at a later date.

TABLE II

Atomic coordinates, in fractions of the unit cell, for the complex **3** in the crystal.[a,b]

Atom	*x*	*y*	*z*
Cl	0.8195(3)	0.1457(2)	0.3291(1)
C(1)	0.3003(7)	0.3490(6)	−0.0201(2)
C(2)	0.4455(8)	0.2878(6)	−0.0595(2)
C(3)	0.6370(7)	0.1934(6)	−0.0379(2)
C(4)	0.6997(7)	0.1556(5)	0.0240(2)
C(5)	0.5558(7)	0.2175(6)	0.0647(2)
C(6)	0.3634(7)	0.3088(6)	0.0417(2)
C(7)	0.6238(7)	0.1896(5)	0.1291(2)
C(8)	0.4690(9)	0.1204(7)	0.1630(2)
C(9)	0.5316(10)	0.1060(7)	0.2243(2)
C(10)	0.7408(10)	0.1612(7)	0.2524(2)
C(11)	0.8980(10)	0.2278(9)	0.2198(2)
C(12)	0.8380(9)	0.2396(7)	0.1589(2)
O(1)	0.1203(5)	0.4407(5)	−0.0410(1)
O(2)	0.8825(6)	0.0628(5)	0.0440(2)
H(2)[c]	0.41(1)	0.329(10)	−0.100(3)
H(3)	0.75(1)	0.159(5)	−0.061(2)
H(6)	0.25(1)	0.369(7)	0.071(2)
H(8)	0.32(1)	0.082(8)	0.142(3)
H(9)	0.42(1)	0.044(9)	0.251(3)
H(11)	1.02(1)	0.242(9)	0.239(3)
H(12)	0.95(1)	0.297(6)	0.137(2)
OH(1)	0.17(4)	0.442(3)	−0.114(8)
OH(2)	0.08(1)	−0.046(10)	−0.016(3)

[a] Standard deviations are indicated in brackets.

[b] Atom labelling is shown in Figure 1.

[c] Hydrogen atoms are given the numbers of the atoms to which they are attached.

centrosymmetry there are two indications that the crystals are not centrosymmetric. Second harmonic generation with a Nd-YAG laser has given an indication of non-centrosymmetry[5],† while morphological examination of a number of crystals of **2** and **3** has shown indication of a polar axis (Figures 3 and 4).

The common feature in the structures of **1**, **2** and **3**, (and indeed of the napthoquinone-hydroquinone complex) seems to be that each of them is held together by π-complexing in one direction and by hydrogen bonding in a second. Thus it is possible to build ordered layers of molecules in which

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† We are indebted to Dr. G. Tsoucaris for assistance and to Dr. J. Jerphagnon for the SHG measurements. In addition we thank Dr. M. Delfino for recording further SHG measurements on **2** at the poster sessions of the 5th International Symposium on the Chemistry of the Organic Solid State, Brandeis University, June 1978.

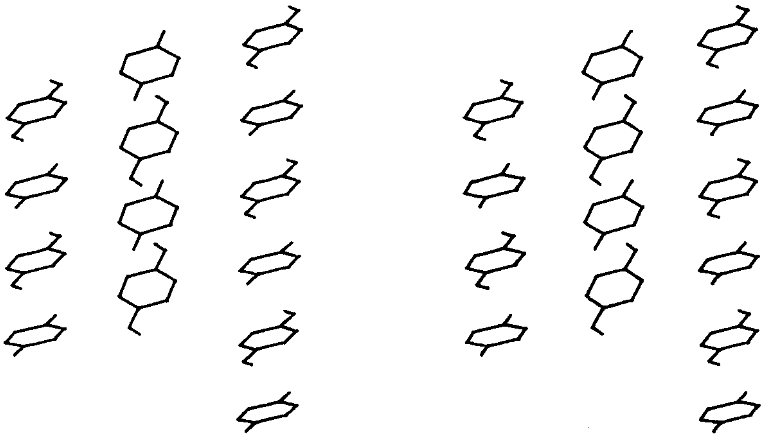

FIGURE 2 Stereoscopic view of some aspects of the packing of the monoclinic form of the unsubstituted complex **1**.

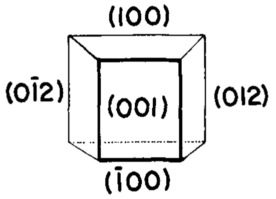

FIGURE 3 Schematic diagram of a single crystal of **2**. The polar axis is along *b*. The faces $(0\bar{1}2)$ and (012) are present, the faces $(01\bar{2})$ and $(0\bar{1}\bar{2})$ are not present.

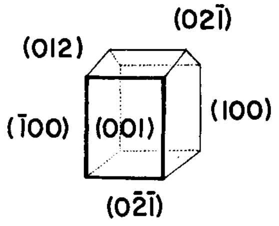

FIGURE 4 Schematic diagram of a single crystal of **3**. The polar axis is along *b*. The faces (012) and $(02\bar{1})$ are present, the faces $(0\bar{1}\bar{2})$ and (021) are not present.

neighbors are related by one of these two interactions (Figure 5). The complete structure is generated by a piling up of the layers. However, there are no strong specific interactions between molecules in different layers. The crystal structures of **2** and **3** may be analyzed in terms of two closely-related, ordered (and non-centrosymmetric) structures: a $P2_1$ structure with adjacent layers related by screw axes (Figure 6) and a *Pc* structure with adjacent layers related by glide planes (Figure 7). Inspection of these two diagrams shows that while the top and bottom rows of molecules are identical in both arrangements, the middle row differs in the two arrangements by having the hydroxyl hydrogen atoms moved to adjacent molecules. Thus, a concerted hydrogen transfer in every second row would convert the structure belonging to one space group into the structure that belongs to the other space group. The X-ray results then require that the differences between the quinone and hydroquinone molecules are obscured by the great similarities in the two molecular structures.

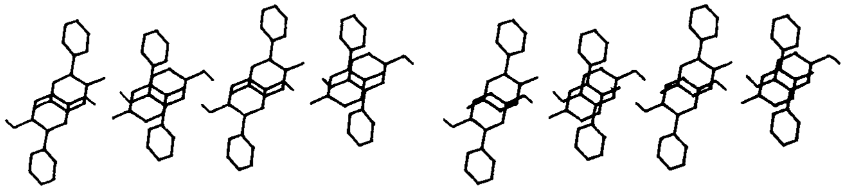

FIGURE 5 Stereoscopic drawing of the packing of **2**. The hydrogen bonding chains (hydroxyl hydrogen atoms included in the hydroquinone molecules) run horizontally, while the charge transfer interaction is in the direction normal to the plane of the paper. The two dimensional layers (horizontal and in a direction normal to the plane of the paper) would be formed by building up additional rows of molecules by the charge-transfer interaction.

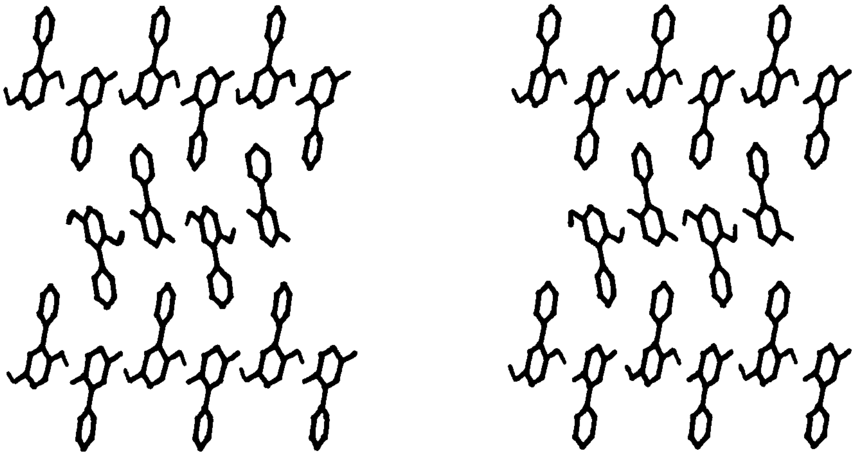

FIGURE 6 The crystal structure of **2** with the layers (running horizontally and in a direction normal to the plane of paper) related to each other by a two-fold screw axis ($P2_1$).

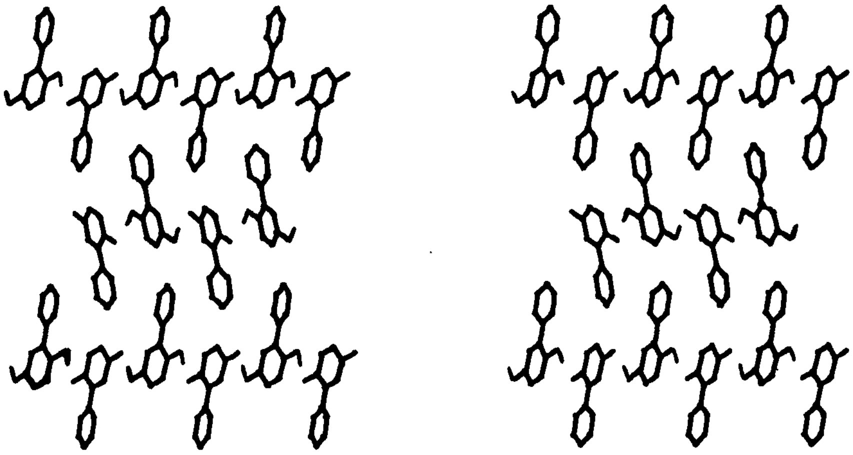

FIGURE 7 Crystal structure of **2** with the layers related to each other by a glide plane (Pc). Note that b (horizontal in the plane of the page) is non-polar here but polar in Fig. 6.

A crystal structure with a random distribution of *Pc* and $P2_1$ regions is another possible explanation for our otherwise seemingly conflicting results. This follows because averaging these symmetry relationships over the whole crystal would result in apparent centrosymmetric character and a space group of $P2_1/c$. Also this model requires that the specificity of interactions, albeit weak, between quinone and hydroquinone molecules in adjacent layers, found in the crystals of **1**, has been lost in complexes **2** and **3**.

The quinone and hydroquinone molecules in **2** and **3** are chiral in the solid-state because of the substitution pattern in the six-membered rings. It is significant to note that, in the ordered model, the chiralities of all the hydroquinone molecules are the same and opposite that of all the quinone molecules if the space group is $P2_1$ (enantiomeric). However, quinone and hydroquinone molecules of both chiralities are found in the space group *Pc* (racemic). We have previously[4] discussed the synthesis of quinhydrones with different substituted quinone and hydroquinone components, that is, "substituent-labelled" quinhydrones which can, in principle, be interconverted by hydrogen-transfer and might therefore act as a memory device. The present structures introduce the further possibility of "symmetry-labelling;" that is, the preparation of two crystalline forms of, for example, the phenylquinone-phenylhydroquinone complex, **2** which are distinguished by their chirality differences. Using the designations *R* and *S* to indicate absolute configuration, we get

$$\underset{P2_1}{\text{Quinone }(R)\text{. Hydroquinone }(S)} \rightleftharpoons \underset{P2_1}{\text{Quinone }(S)\text{. Hydroquinone }(R)}$$

One can conceive of other quinhydrone pairs where hydrogen exchange would result in a change of direction of the polar axis, thus making the pair of complexes "symmetry labelled" (see Fig. 6 and 7). Experiments are planned to try to achieve hydrogen exchange in these complexes.

EXPERIMENTAL SECTION

The preparation of the complex and the crystals has been described previously.[4,6] Preliminary X-ray studies were carried out photographically. Accurate cell data were obtained by a least squares analysis of the settings for 15 high order reflections at ambient room temperature (20–23°C) using CuK_α ($\lambda = 1.5418$ Å) on a Syntex $P2_1$ diffractometer. Intensity data were obtained on the Syntex diffractometer (CuK_α) at ambient room temperature. Crystallographic calculations were carried out on a Syntex EXTL structure determination system. Optical goniometric data were recorded on a Tecam two-circle optical goniometer.[4]

Acknowledgment

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