Solid State Complexes of Polymethylated Quinones with Polymethylated Phenols. The Crystal Structure of the 2:1 Complex of 2,5-Dimethyl-1,4-benzoquinone with 2,5-Dimethyl-1,4-dihydroxybenzene

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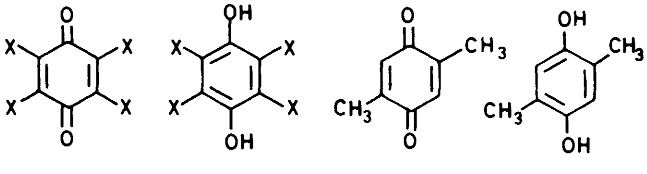
2,5-Dimethyl-1,4-benzoquinone and 2,5-dimethylhydroquinone have been found to form a 2 : 1 complex instead of the more usual 1 : 1 quinhydrone. The crystal structure and Fourier transform i.r. spectrum of this complex have been determined. The structure is monoclinic, space group $P2_1/c$, with a = 10.480(4), b = 12.344(3), c = 9.301(3) Å, β = 115.91(2)°, Z = 2, $(C_8H_8O_2)_2{\cdot}C_8H_{10}O_2$. The structure has been determined by direct methods and refined to R 0.051 for the 1 404 reflections recorded with an automatic single crystal diffractometer. Duroquinhydrone has been re-examined and the ^1H n.m.r. spectrum in solution as well as the Fourier transform i.r. spectrum of the solid (paraffin oil mull) have confirmed the previous assumption that, in spite of the steric crowding introduced by the eight methyl groups, this is a 1 : 1 complex, although the position of the oxygen–hydrogen stretching frequency, higher than is found with other quinhydrones, suggests that the hydrogen bonded structure in this complex is significantly affected by the presence of the methyl groups.

Quinones have long been known to form 1 : 1 complexes with hydroquinones; the prototype is quinhydrone, the complex of benzoquinone (1a) with hydroquinone (2a). These complexes have been of particular interest because of the structural problem they have posed. Those quinhydrones which have been submitted to *X*-ray structure determination have been found to be made up of chains of alternating quinone and hydroquinone molecules held together in the crystalline state by hydrogen bonding in one dimension and π-bonding in a second.[1]

In solution quinhydrones are largely dissociated [2] and unsymmetrically substituted quinhydrones have been shown [3,4a] to be capable in solution of a rapid redox reaction interchanging the quinone and hydroquinone structures. In contrast this exchange has been slow or non-existent in the crystalline state.[4,5]

Such complexes have generally been prepared by crystallization from a solvent [2] but, in a previous paper,[6] we have described the synthesis of a number of them by grinding together the two solid components. If the benzene rings are more highly substituted, reaction may become more difficult. For example, the complex of tetrachloro-1,4-hydroquinone (2b) with chloranil (tetrachloro-1,4-benzoquinone) (1b) has thus far not been prepared.[7]

In this paper we report the formation of a highly coloured complex resembling the quinhydrones in appearance. This complex, obtained by evaporation of the solvent from a solution of dimethylquinone (3) and dimethylhydroquinone (4), has been found by *X*-ray structure determination, its Fourier transform i.r. spectrum (Nujol mull), and the n.m.r. spectrum (solution) to be not the 1 : 1 quinhydrone but instead to contain two molecules of the quinone (3) to one of the hydroquinone (4).



(1) (2) (3) (4)

a; X = H
b; X = Cl
c; X = CH_3

The tetramethyl analogue, the complex of duroquinone (1c) and durohydroquinone (2c), was reported by Michaelis and Granick.[2] This complex subsequently assumed considerable importance when, appropriately substituted with ^{14}C, it was employed by Bothner-by [5b] to show that hydrogen-transfer between the quinone and hydroquinone of a quinhydrone, although rapid in solution, is slow in the crystalline state. Instrumental methods for the study of such a structure were very much more limited at the time of the original investigations and there seems to be no report in the literature of a direct demonstration that the complex has a stoicheiometry of 1 : 1. The discovery that the dimethyl compounds (3) and (4) form only a 2 : 1 complex has prompted a further examination of the complex of the tetramethyl compounds (1c) and (2c) with Fourier transform i.r. spectroscopy of the solid and n.m.r. (solution).

Experimental

Fourier transform i.r. spectra were obtained with a Nicolet 7000 spectrophotometer and differential calorimetry scans were recorded with a DuPont 900 thermal analyser.

Preparation and N.m.r. Spectrum of the 2 : 1 *Complex of* (3) *and* (4).—Equimolar amounts of 2,5-dimethylbenzoquinone (272.3 mg, 2 × 10^{-3} mol) and 2,5-dimethylhydroquinone (276.3 mg) were dissolved in ethyl acetate (50 ml) and the solution allowed to evaporate slowly until crystals appeared. The complex was obtained as blackish red crystals, m.p. (sealed capillary) 117—118 °C; δ (360 MHz; $[^2H_6]$-DMSO) 8.33 (s, 2 H), 6.72 (q, 4 H, J 1.5 Hz), 6.44 (s, 2 H), 1.98 (s, 6 H), and 1.94 (d, 12 H, J 1.5 Hz). Crystals of the complex were found to be unstable on standing due to loss of the quinone and formation of a residue of hydroquinone. From the original reaction mixture there were also obtained some yellow and white crystals of the quinone (3) and hydroquinone (4).

When equimolar amounts (10^{-3} mol) of the 2,5-dimethylquinone (3) and 2,5-dimethylhydroquinone (4) weighed to ± 0.1 mg were ground with an agate mortar and pestle for

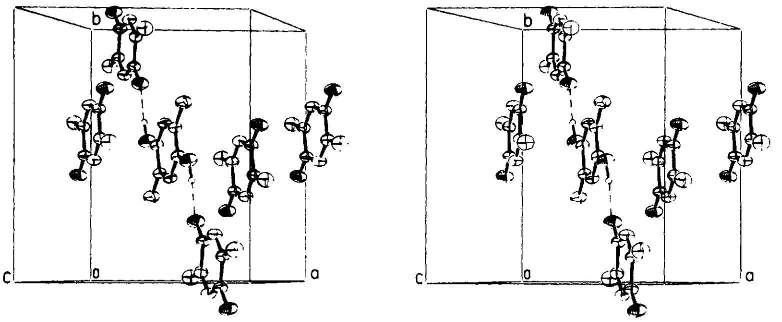


Figure 1. Stereoscopic view of some aspects of the packing in the complex. The reference dimethylquinone molecule is to the upper left rear of the unit cell, while the reference dimethylhydroquinone ' half-molecule ' is at the centre of the cell (about the centre of symmetry at 1/2, 1/2, 1/2) and is the half of the molecule to the rear of the cell. The dimethylhydroquinone molecule centred about 1/2,0,0 is not shown for the purposes of clarity. The O(9)–H ··· O(4) hydrogen bonds are shown by discontinuous lines

Final atomic co-ordinates, standard deviations in parentheses, as fractions of the unit cell edge

	x/*a*	*y*/*b*	*z*/*c*
O(1)	0.030 1(2)	1.089 4(1)	−0.232 6(2)
O(4)	0.279 9(2)	0.774 4(1)	0.175 8(2)
O(9)	0.316 3(2)	0.547 9(2)	0.188 0(2)
C(1)	0.089 0(3)	1.016 3(2)	−0.139 9(3)
C(2)	0.063 3(2)	0.901 1(2)	−0.194 0(3)
C(3)	0.126 6(3)	0.824 1(2)	−0.086 5(3)
C(4)	0.222 2(2)	0.847 4(2)	0.081 3(3)
C(5)	0.247 3(3)	0.961 7(2)	0.135 9(3)
C(6)	0.184 7(3)	1.038 6(2)	0.028 8(3)
C(7)	−0.031 4(4)	0.879 4(3)	−0.365 7(3)
C(8)	0.341 1(4)	0.981 8(3)	0.308 9(3)
C(9)	0.407 2(2)	0.526 5(2)	0.343 8(2)
C(10)	0.432 8(2)	0.416 6(2)	0.386 9(3)
C(11)	0.526 2(2)	0.393 5(2)	0.544 6(3)
C(12)	0.361 1(4)	0.328 3(2)	0.268 5(4)
H(3)	0.111(3)	0.742(3)	−0.108(3)
H(6)	0.188(3)	1.121(2)	0.053(3)
H(71)	−0.099(4)	0.924(3)	−0.401(4)
H(72)	−0.060(4)	0.786(4)	−0.361(5)
H(73)	0.006(4)	0.914(3)	−0.420(4)
H(81)	0.309(3)	0.944(3)	0.365(4)
H(82)	0.404(4)	0.937(3)	0.333(5)
H(83)	0.364(4)	1.059(3)	0.327(4)
H(9)	0.300(3)	0.622(3)	0.181(3)
H(11)	0.539(2)	0.311(2)	0.566(2)
H(121)	0.283(5)	0.312(4)	0.248(5)
H(122)	0.368(4)	0.339(3)	0.179(5)
H(123)	0.390(4)	0.249(3)	0.330(4)

[a] Hydrogen atoms are given the number of the atom to which they are bonded. In the case where more than one hydrogen is bonded to a single atom, an extra digit is added at the end.

15 mins no colour change was observed, in contrast to the results with the quinones and hydroquinones discussed previously.[6]

X-*Ray Structure Determination of the* 2 : 1 *Complex of* (3) *and* (4).—Because of the ready loss of the quinone (3) from the complex the structure was determined with a crystal mounted in a closed capillary.

Crystal data. $(C_8H_8O_2)_2{\cdot}C_8H_{10}O_2$, *M* 410.5, monoclinic, $a = 10.480(4)$, $b = 12.344(3)$, $c = 9.301(3)$Å, $\beta = 115.91(2)°$, $U = 1082.1(5)$ Å^3, $\rho_{calc} = 1.258$ g cm^{-3}, $Z = 2$, space group $P2_1/c$; λ(Cu-K_α) = 1.54178 Å.

The data ($\bar{h}kl$ and hkl) collected on a Syntex $P2_1$ diffractometer to $2\theta = 130°$ (Cu-K_α) gave 1404 independent reflections with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors but no absorption correction was made.

The structure was solved with the program MULTAN 80. An *E* map revealed the positions of all the non-hydrogen atoms. Least squares refinement and difference Fourier synthesis yielded the rest of the structure. The final refinement cycle employed anisotropic thermal parameters for the non-hydrogen atoms, while hydrogen atoms had isotropic temperature factors. The final values of *R*, R_w, and ' goodness of fit ' are 0.051, 0.057, and 3.56, respectively.

The reflections were weighted as $4.42/[\sigma^2(F) + 0.0002\ F^2]$ and the scattering curves were taken from ref. 8 and included the anomalous dispersion corrections. The highest peak on a final difference map was 0.19 e Å^{-3}. The final atomic co-ordinates are given in the Table. The temperature factors and structure factors have been deposited in Supplementary Publications No. SUP 23887 (15 pp.).*

Preparation and Structure Investigation of Duroquinhydrone, the Complex from Duroquinone (1c) *and Durohydroquinone* (2c).—Equimolar amounts of duroquinone (328 mg, 2×10^{-3} mol) and durohydroquinone (332 mg) were dissolved in acetone (5 ml), distilled water (2—3 drops) was added, and the solution cooled in an ice–salt bath following the procedure in the literature.[2,5b] Filtration and drying under vacuum gave the complex as black needles, $\nu_{max.}$ (Fourier transform, Nujol mull) 3 495 (s, sharp), 1 628, 1 425, 1 312, 1 300, 1 268, 1 207, 1 182, 1 122, 1 080, 1 008, 840, and 698 (s) cm^{-1}; δ (100 MHz, [$^2H_6$]DMSO) 7.16 (s, 2 H), 2.04 (s, 12 H), and 1.94 (s, 12 H).

Results and Discussion

When dimethylquinone (3) and dimethylhydroquinone (4) were placed in contact in a capillary tube there was no indication of the formation of a coloured interlayer characteristic of complex formation although the dimethylquinone (3) rapidly formed such a coloured layer with unsubstituted hydroquinone (2a) and, similarly the unsubstituted quinone (1a) formed a coloured complex with the dimethylhydroquinone (4). Evaporation of a solution of equimolar amounts of dimethylquinone (3) and dimethylhydroquinone (4) gave, as shown by n.m.r. examination, not a 1 : 1 complex but a complex of quinone and hydroquinone in a ratio of 2 : 1. No indication of the formation of a 1 : 1 complex could be found.

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* For details of Supplementary Publications see Instructions to Authors in *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

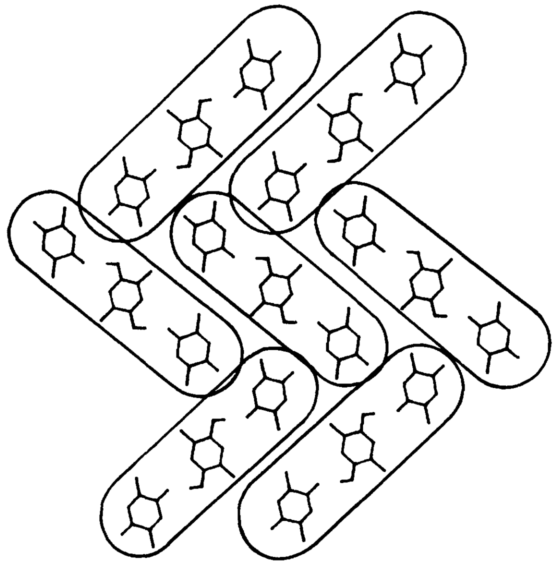

Figure 2. A view of a sheet of molecule lying in the $(\bar{3}02)$ plane. The hydrogen-bonded triplets are enclosed by heavy lines

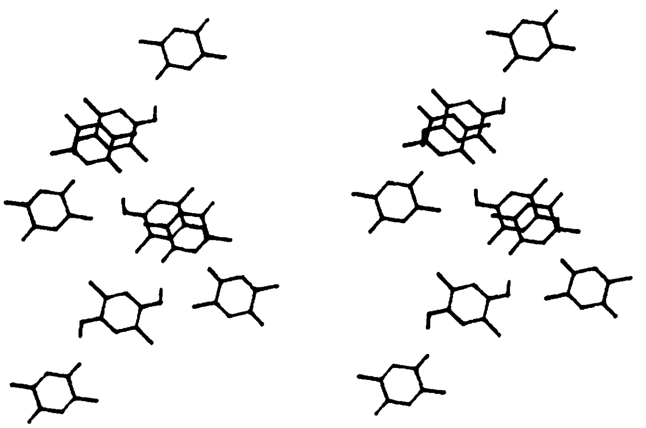

Figure 3. A stereoscopic view illustrating the overlap pattern of the $(\bar{3}02)$ sheets. Two triplets are shown in the nearer sheet

The crystal structure of the 2 : 1 complex of (3) with (4), determined by *X*-ray crystallography, is shown in Figure 1. In the crystal, the quinone molecules (3) occupy general positions while the hydroquinone molecules (4) sit on centres of symmetry at 1/2,0,0 and 1/2,1/2,1/2. The structure is composed of sheets of molecules lying in the $(\bar{3}02)$ plane (Figure 2). The basic structural unit consists of a triplet made up of one molecule of hydroquinone (4) forming hydrogen-bonded bridges to two molecules of quinone (3), one to each hydroxy-group. The quinone (3) is accordingly hydrogen-bonded by one carbonyl group to a hydroxy-group of the neighbouring hydroquinone (4) but the other carbonyl group is directed towards an aromatic C–H of a neighbouring triplet. The Fourier transform i.r. of the crystalline solid is consistent with this structure since it shows, in addition to the principal carbonyl stretching frequency at 1 628 cm^{-1}, a second less intense carbonyl absorption at 1 663 cm^{-1} which can be attributed to the non-hydrogen-bonded carbonyl groups terminating the triplet at each end.

The hydroquinone of each triplet lies at a crystallographic centre of symmetry. Although such a layered structure superficially resembles the layered structure of triclinic quinhydrone it differs in the symmetry. Thus a single sheet is constructed not only of triplets related by translation but also of those related by operation of glide planes. A single layer of this complex thus is made up of triplet units arranged in a herring-bone structure (Figure 2). The hydrogen-bonding arrangement within the triplet is reminiscent of the hydrogen-bonded chains of, for example, triclinic quinhydrone which, however, has infinite chains of alternating quinone and hydroquinone molecules instead of triplets. Adjacent sheets in the 2 : 1 complex of (3) and (4) are derived by a translation of [102] (Figure 3).

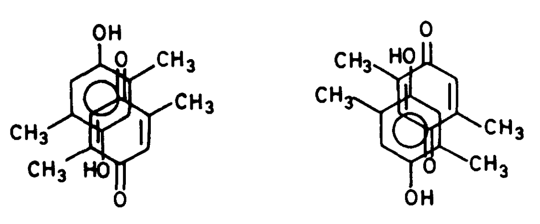

Figure 4. The two overlap patterns found in the structure (*cf.* ref. 9)

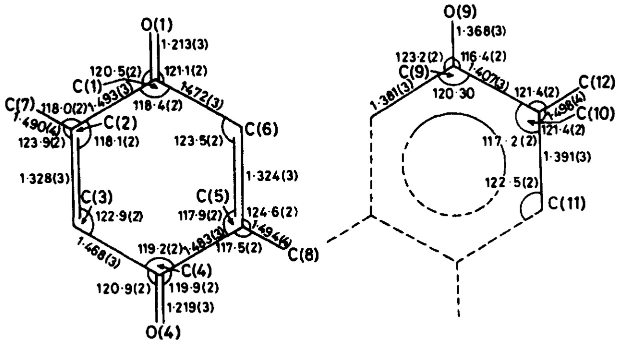

Figure 5. Bond lengths (Å) and angles (°) in the complex. Standard deviations in parentheses

The overlap of molecules with those in adjacent layer planes (Figure 4) is not unlike that of other complexes of quinone with phenols.[9] However, in this case the hydroquinone and quinone rings are slightly shifted to relieve interference of the methyl groups. The interplanar spacing of 3.30 Å can be compared with the values of 3.19 for α-quinhydrone and 3.22 Å for β-quinhydrone.[9]

The packing efficiency is less than that of either the component quinone (3) or hydroquinone (4). Herbstein[9] has pointed out that triclinic and monoclinic quinhydrone (without substituents on the rings) show decreases in molecular volume from that calculated from the starting materials of −9.0 and −6.7%. The 2 : 1 complex of (3) and (4), on the other hand, shows an increase in volume of 1.4% over that calculated from the molecular volumes of (3) and (4).[10]

The bond lengths and angles of the quinone (Figure 5) are in general agreement with those compiled in the survey by Bernstein *et al.*,[11] and with those reported by Rabinovich and Schmidt[12] for 2,5-dimethylquinone where the molecules sit on centres of symmetry. The greatest difference in the dimensions involves the C=C length which is 1.324(3) Å in the present structure as compared to an average of 1.334 (or 1.344 Å, if corrected for libration) in the quinone crystal. In the present study, the 2,5-dimethylquinone molecule has non-crystallographic C_i symmetry within the precision of the analysis. The carbonyl group [C(4)=O(4)] involved in the O–H···O intermolecular hydrogen bond is 0.006 Å (2σ) longer than the other [C(1)=O(1)] but the difference is of marginal significance. The C–C bonds between a C(–CH$_3$)

group and a C(=O) group are 0.02 Å longer than those between a C(−H) group and a C(=O) group and the internal ring (C−C(−CH_3)−C angles are 118° compared with the value of 123° for the C−C(−H)−C angles. These features are also apparent in the molecules in the 2,5-dimethylquinone crystal.[12]

The crystal structure of 2,5-dimethylhydroquinone has been studied in our laboratory.[10] In that crystal, there are two independent molecules, each sitting on a centre of symmetry. The C−O(H) length in the complex [1.368(3) Å] is somewhat shorter than those found in the hydroquinone crystal (average value 1.389 Å), while the adjoining C−C ring bonds are slightly different; $C(CH_3)$−C(OH) 1.407(3) Å *versus* 1.392 Å and C(H)−C(OH) 1.381(3) *versus* 1.387 Å. In both crystals the $C(CH_3)$−C−O(H) angles are much less than 120° [116.4(2) in the complex and 116.9 and 118.0 in the parent compound]. Thus the angle distortion patterns of the 2,5-dimethylhydroquinone molecule in the complex are different from those of the 2,5-dimethylquinone molecule where the C−C−O angles are close to 120° (Figure 5). The bending of the C−O(H) bond towards the methyl group probably arises from steric interference between the hydroxy hydrogen and the aromatic hydrogen *ortho* to it.

Both rings are close to being planar; however, the hydroquinone ring (maximum deviation of a ring atom 0.001 Å) is more planar than the quinone ring (maximum deviation 0.008 Å). In the quinone (3), the members of each pair of adjacent quinone oxygen and methyl carbon atom substituents are disposed on opposite sides of the plane of the ring [C(8) 0.045, O(4) −0.019, C(7) −0.022, O(1) 0.037 Å]. A similar effect, but with distances −0.012 to 0.015 Å is noted for the hydroquinone ring. The best planes through the respective quinone and hydroquinone rings are inclined 2.5° to each other. The quinone and hydroquinone ring are inclined 6.8 and 4.8° to the $(\bar{3}02)$ plane. The details of the best plane calculations have been deposited.

The triplets are held together by O(9)−H ··· O(4) hydrogen bonding; the O(9) ··· O(4) distance is 2.818(3) Å, the H(9) ··· O(4) distance is 1.89(3) Å and O(9) − H(9) ··· O(4) angle is 176(2)°. Within the sheets (Figure 2), the C(3)−H(3) bond points towards O(1), the quinone oxygen not involved in hydrogen bonding; the H(3) ··· O(1) $(-x, -1/2 + y, -1/2 - z)$ distance is 2.45(3) Å and the corresponding C(3)−H(3) ··· O(1) angle is 151(2)°.

The discovery that the dimethylated compounds (3) and (4) formed a 2 : 1 complex rather than the anticipated 1 : 1 quinhydrone together with the previously noted reluctance of the components to form a complex suggested the desirability of re-examining the structure of the complex from the more highly methyl-substituted duroquinone (1c) and durohydroquinone (2c).

Repetition of the synthetic method employed by Michaelis and Granick [2] and by Bothner-by [5b] gave, as shown by n.m.r. analysis, the 1 : 1 complex previously assumed. Fourier transform i.r. again is a useful tool in confirming the structure since it shows only a single (hydrogen-bonded) carbonyl group and a relatively sharp O−H stretching absorption as would be expected in a 1 : 1 but not in a 1 : 2 complex. Again there was no indication of the formation of any other complex.

It is thus confirmed that Bothner-by's elegant demonstration of slow redox hydrogen exchange in ^{14}C-labelled duroquinhydrone was performed with the assumed 1 : 1 quinhydrone.

However the shape and position of the hydroxy OH stretching absorption at 3 495 cm^{-1} are remarkable since the absorption band is sharper and at a higher frequency than the corresponding absorptions of either crystalline phenols or quinhydrones. This suggests that the hydrogen bonding interaction in duroquinhydrone differs substantially from that in other less substituted quinhydrones.

Acknowledgements

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