Effect of Methyl Substitution on the Crystal Structures of Complexes of Quinones with Hydroquinones. Crystal Structures of the 1:1 Complex of 2,3,5,6-Tetramethyl-1,4-benzoquinone with 2,3,5,6-Tetramethylbenzohydroquinone and of the 1:2 Complex of 2,3,5,6-Tetramethylbenzoquinone with Hydroquinone.† Correlation of Fourier Transform Infrared Spectra with Structure

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The crystal structures of the 1:1 complex of 2,3,5,6-tetramethyl-1,4-benzoquinone with 2,3,5,6-tetramethyl-1,4-hydroquinone (duroquinhydrone), and of the 1:2 complex of 2,3,5,6-tetramethyl-1,4-benzoquinone with hydroquinone have been determined by X-ray methods. The structure of duroquinhydrone $(C_{10}H_{12}O_2 \cdot C_{10}H_{14}O_2)$ is monoclinic, space group $P2_1/c$ with $a = 8.006(2)$, $b = 6.574\ 6(8)$, $c = 17.056(4)$ Å, $\beta = 105.02(2)°$, $Z = 2$. It was solved by direct methods and refined to $R = 0.048$ for the 994 non-zero reflections recorded. The gross features of the structure are remarkably similar to those of monoclinic quinhydrone. The structure of the 1:2 complex of tetramethylbenzoquinone with hydroquinone is triclinic, space group $P\bar{1}$ with $a = 7.578(2)$, $b = 9.455(3)$, $c = 7.183(2)$ Å, $\alpha = 94.02(2)$, $\beta = 107.75(2)$, $\gamma = 88.59(2)°$. There is one 1:2 complex in the unit cell, with each of the three component molecules occupying a crystallographic centre of symmetry. The structure has been refined to an R-factor of 0.046 on 1 634 non-zero reflections. There are chains of alternating quinone and hydroquinone molecules with the other hydroquinone molecule lying between the chains. The structure is unusual in comparison with other complexes between quinones and hydroquinones in that the typical two-dimensional layers of molecules held together in one direction by hydrogen-bonding chains of nearly coplanar quinones and hydroquinones and in the other by π-complexing of overlapping quinone and hydroquinone molecules are absent in this crystal.

These structures, together with structures of other quinone–hydroquinone complexes recently reported, suggest generalizations which help to explain the stoicheiometry of such complex formation.

The implications for the Fourier transform i.r. spectra of the hydrogen bonding of quinone–hydroquinone complexes are discussed.

The structural chemistry of quinhydrones (1:1 complexes of quinones and hydroquinones) and of related complexes has been receiving considerable attention recently.[1] The structures of complexes of quinones with hydroquinones highly substituted with methyl groups are of particular interest because of the importance that has been attached to π-complexing as a factor stabilizing such complexes. Additional points of interest are the substantial variations in the hydroxy stretching frequency which have been found in the Fourier transform i.r. spectra, and the varied stoicheiometry shown by a number of these complexes.

The crystal structure of duroquinhydrone [(1)·(2)], the fully methylated relative of quinhydrone, is of particular interest since, as was mentioned earlier,[1b] the i.r. spectrum shows a significant difference from those of other previously studied 1:1 complexes of quinones with hydroquinones. The O–H stretching absorption is both sharper and at a higher frequency than has been found in the other quinhydrones thus far investigated. The present paper reports the determination of the structure by X-ray crystallography and discusses the unusual feature of the i.r. absorption in relation to the structure. In addition we report the crystal structure of the 1:2 complex of 2,3,5,6-tetramethylbenzoquinone (1) with hydroquinone (3) and discuss the correlation of the Fourier transform i.r. spectra with structures for these and other quinone–hydroquinone complexes.†

(1)   (2)   (3)
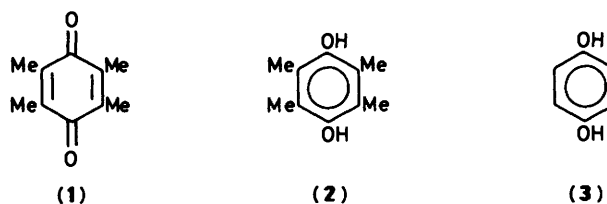
Experimental

Duroquinhydrone.—The 1:1 complex of duroquinone (1) with durohydroquinone (2) was prepared by the procedure of Michaelis and Granick.[2] Differential scanning calorimetry showed endotherms at 120 and 225 °C. When heated in a capillary tube the red needles of the complex became yellowish-white with partial melting and sublimation of the quinone (112—115 °C) but with retention of the shapes of the crystals; melting was complete at 230—235 °C. Attempts to prepare the complex by grinding the components together, even with seeding by the product complex or heating at 80 °C, were unsuccessful.

X-Ray Structure of Duroquinhydrone.—Single crystals suitable for X-ray crystallography were obtained by dissolving equimolar amounts $(2 \times 10^{-3}$ mol) of the quinone (1) and the hydroquinone (2) in acetone (50 ml). Slow evaporation gave thick flat red crystals, one of which (0.62 × 0.35 × 0.22 mm) was placed in a sealed capillary tube.

Crystal data. $C_{10}H_{12}O_2 \cdot C_{10}H_{14}O_2$, M 330.4, monoclinic, space group $P2_1/c$, $a = 8.006(2)$, $b = 6.574\ 6(8)$, $c = 17.056(4)$

Table 1. Final atomic co-ordinates for duroquinhydrone

	x	y	z
O(1)	0.681 3(2)	0.336 8(3)	0.035 3(1)
O(11)	0.204 6(3)	0.335 7(3)	0.046 9(1)
C(1)	0.596 4(3)	0.181 5(4)	0.018 7(1)
C(2)	0.582 1(3)	0.040 7(4)	0.085 0(1)
C(3)	0.492 1(3)	−0.132 7(4)	0.067 5(1)
C(4)	0.674 9(5)	0.109 7(5)	0.168 9(2)
C(5)	0.471 7(4)	−0.288 4(5)	0.128 3(2)
C(11)	0.100 2(3)	0.170 2(4)	0.021 2(1)
C(12)	0.082 7(3)	0.037 8(4)	0.081 9(1)
C(13)	−0.018 4(3)	−0.137 7(4)	0.061 0(1)
C(14)	0.171 5(4)	0.091 2(5)	0.169 0(2)
C(15)	−0.038 4(5)	−0.291 5(5)	0.123 6(2)
H(11)	0.205(4)	0.429(5)	0.009(2)
H(4A)	0.683(5)	0.001(6)	0.209(2)
H(4B)	0.805(5)	0.143(6)	0.173(2)
H(4C)	0.639(5)	0.263(6)	0.179(2)
H(5A)	0.538(5)	−0.249(6)	0.181(2)
H(5B)	0.516(3)	−0.418(6)	0.114(2)
H(5C)	0.345(5)	−0.300(6)	0.126(2)
H(14A)	0.171(5)	−0.026(6)	0.206(2)
H(14B)	0.301(5)	0.117(6)	0.176(3)
H(14C)	0.154(5)	0.251(6)	0.180(2)
H(15A)	0.031(5)	−0.257(6)	0.174(2)
H(15B)	0.002(6)	−0.415(6)	0.112(2)
H(15C)	−0.161(6)	−0.308(7)	0.123(2)

Table 2. Final atomic co-ordinates for $C_{10}H_{12}O_2 \cdot (C_6H_6O_2)_2$

	x	y	z
O(1)	0.678 3(2)	0.132 0(1)	0.410 3(2)
O(11)	0.055 5(2)	0.277 8(1)	0.152 2(2)
O(21)	0.429 1(2)	0.361 5(1)	0.296 5(2)
C(1)	0.828 2(2)	0.071 1(2)	0.454 6(2)
C(2)	0.836 1(2)	−0.083 1(2)	0.399 3(2)
C(3)	0.999 6(2)	−0.150 6(2)	0.438 3(2)
C(4)	0.653 2(3)	−0.153 5(2)	0.297 6(3)
C(5)	1.021 6(3)	−0.304 4(2)	0.383 4(3)
C(11)	0.032 3(2)	0.139 2(2)	0.078 3(2)
C(12)	0.177 1(2)	0.042 5(2)	0.110 4(2)
C(13)	0.144 7(2)	−0.096 2(2)	0.032 6(2)
C(21)	0.468 2(2)	0.430 0(1)	0.150 1(2)
C(22)	0.636 9(2)	0.415 5(2)	0.112 5(2)
C(23)	0.668 6(2)	0.484 3(2)	−0.037 0(2)
H(11)	0.169(4)	0.282(2)	0.214(3)
H(21)	0.517(5)	0.299(3)	0.341(5)
H(4A)	0.568(5)	−0.126(3)	0.358(5)
H(4B)	0.664(6)	−0.254(4)	0.280(5)
H(4C)	0.612(6)	−0.157(4)	0.142(6)
H(5A)	0.953(4)	−0.334(3)	0.263(4)
H(5B)	0.147(5)	−0.323(3)	0.372(5)
H(5C)	0.984(5)	−0.371(4)	0.460(5)
H(12)	0.304(3)	0.067(2)	0.194(3)
H(13)	0.239(3)	−0.163(2)	0.048(3)
H(22)	0.733(3)	0.354(2)	0.187(3)
H(23)	0.783(3)	0.476(2)	−0.068(3)

Å, $\beta = 105.02(2)°$, $V = 871(3)$ Å^3, $Z = 2$, $D_{calc.} = 1.265$ g cm^{-3}, $F(000) = 356$, $\mu(Cu\text{-}K_\alpha, \lambda = 1.541 78$ Å$) = 6.62$ cm^{-1}. Cell dimensions were determined by least-squares fit to the settings for fifteen carefully centred high-order ($54° < 2\theta > 86°$) reflections on a Syntex P2$_1$ diffractometer using Cu-K_α radiation. Intensity data (hkl and $hk\bar{l}$) were collected in the θ–2θ mode at scan speeds from 2.02 to 19.53 deg min^{-1}. Out of 1 918 measurements ($2\theta < 135°$), 994 independent reflections were considered significant at the $3\sigma(I)$ level. The data were corrected for Lorentz and polarization factors, and a linear decay correction was applied based on a 6.3% decline in the intensities of three standard reflections measured periodically during the 27.3 h of data collection. An analytical absorption correction based on a crystal bound by the forms $\{1\,0\,0\}$, $\{0\,1\,0\}$, and $\{0\,0\,1\}$, with dimensions 0.62 × 0.22 × 0.35 mm, respectively, resulted in transmission factors ranging from 0.75 to 0.87.

The structure was solved by direct methods using the MULTAN 80 package of programs.[3] The positions of the hydrogen atoms were determined by conventional difference Fourier and least-squares techniques. The duroquinone and durohydroquinone molecules all occupy crystallographic centres of symmetry.

The final least-squares refinement cycles employed positional and anisotropic thermal parameters for the non-hydrogen atoms; the hydrogen atoms had isotropic temperature factors. The final values of R, R_w, and 'goodness of fit' were 0.048, 0.064, and 2.97, respectively, based on 994 non-zero reflections. The reflections were weighted as $6.9046/[\sigma^2(F) + 0.002F^2]$ and the scattering curves were taken from ref. 4 and included the anomalous dispersion corrections. The range of electron density on a final difference map was from −0.19 to 0.17 e Å^{-3}. The final atomic co-ordinates are given in Table 1.

X-*Ray Structure of the* 1:2 *Complex of Duroquinone* (1) *with Hydroquinone* (3).—Crystals of the 1:2 complex were obtained as described in the preceding paper.[5] A red parallelepiped crystal of dimensions 0.43 × 0.25 × 0.92 mm, bound by the forms $\{1\,0\,0\}$, $\{0\,1\,0\}$, and $\{0\,0\,1\}$, was mounted in a glass capillary tube for data collection. All measurements were

performed at ambient temperature on a Syntex P2$_1$ diffractometer employing graphite-monochromated Cu-K_α radiation ($\lambda = 1.541 78$ Å).

All computations, other than structure solution, were performed with the SHELX 76 package of computer programs.[6]

Cell data. $C_{10}H_{12}O_2 \cdot (C_6H_6O_2)_2$, $M_r = 384.43$, triclinic, $P\bar{1}$, $Z = 1$, $a = 7.578(2)$, $b = 9.455(3)$, $c = 7.183(2)$ Å, $\alpha = 94.02(2)$, $\beta = 107.75(2)$, $\gamma = 88.59(2)°$, $V = 489.0(2)$ Å^3, $D_{calc.} = 1.30$ g cm^{-3}. Unit-cell parameters were determined by a least-squares fit to the setting angles for 15 carefully centred high-order reflections ($2\theta = 78$—$114°$). A total of 2 011 reflections was measured out to $2\theta = 140°$. Scans were made in the θ–2θ mode at speeds ranging from 2.02 to 19.53 deg min^{-1} with scan widths of 0.8° below K_{α_1} to 0.9° above K_{α_2}. Averaging of equivalent reflections ($R_{merge} = 0.016$) resulted in 1 829 unique reflections, of which 1 634 had intensities greater than $3\sigma(I)$ and were considered observed.

Periodic measurement of three standard reflections revealed only minor fluctuations in intensity ($\pm 4.3\%$) which were attributed to electronic instability. Corrections were made for Lorentz and polarization effects, and an analytical absorption correction ($\mu_{Cu\text{-}K_\alpha} = 7.41$ cm^{-1}) was applied which resulted in transmission factors ranging from 0.66 to 0.84.

The structure was solved by direct methods using MULTAN 80.[3] Each of the three rings of the complex lies about an independent inversion centre: the tetramethylquinone ring is situated about an inversion centre at (0.0, 0.0, 0.5), and the hydroquinone rings lie about centres at (0.0, 0.0, 0.0) and (0.5, 0.5, 0.0). All hydrogen atoms were found by conventional difference Fourier and least-squares techniques.

Full-matrix least-squares refinement included positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms for a reflection to parameter ratio of 9.3:1. In the final cycle no parameter shifted by more than 0.003σ. The final residuals were $R = 0.046$, $R_w = 0.074$, and 'goodness of fit' = 2.65. The weighting scheme was based on counting statistics $\{1.000/[\sigma^2(F) + 0.006(F^2)]\}$ and showed no system-
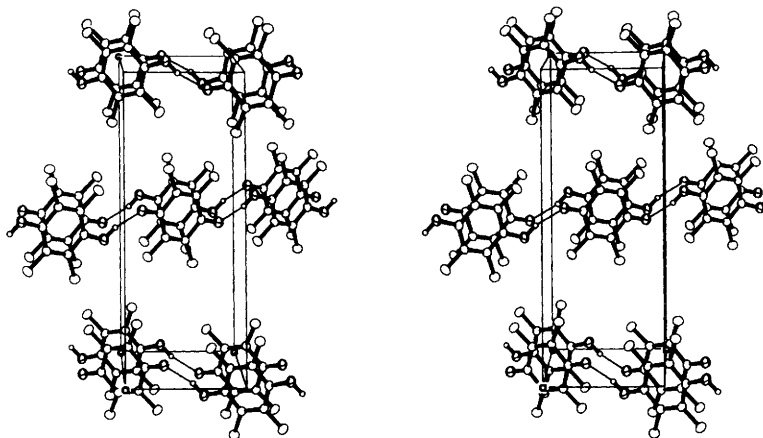
Figure 1. Stereoscopic view of the structure of the 1:1 duroquinhydrone complex; the hydrogen bonds are shown by thin lines

atic variation with the magnitude of F or with the value of θ. The final difference map was featureless with peaks ranging from 0.23 to -0.18 e Å^{-3}.

The atomic scattering curves were taken from ref. 4. Atomic co-ordinates are given in Table 2.

Spectroscopic Measurements.—Fourier transform i.r. spectra were obtained with a Nicolet 7000 Ftir spectrophotometer.

Results and Discussion

Crystal and Molecular Structure of Duroquinhydrone [(1)·(2)].—The crystal structure (Figure 1) of duroquinhydrone was found, in spite of the steric interference of the eight methyl groups, to be composed of chains of alternating, nearly coplanar (2.17°) duroquinone and durohydroquinone molecules held together by hydrogen bonds. The O(11) – – – O(1) distance is 2.846(3) Å with an H – – – O(1) distance of 2.03(3) Å and an O(11)–H(11) – – – O(1) angle of 157(3)°. The π overlap of quinone with hydroquinone rings of adjacent chains is very similar to that found in the unsubstituted quinhydrone,[7a–c] as might be expected from the characteristically deep colour of this quinhydrone complex. However, the overlapping chains are pushed apart somewhat by the methyl groups; the distances of the quinone ring atoms and oxygen atoms from the plane of the hydroquinone are in the range 3.38—3.50 Å; cf. 2.88—3.27 Å for the unsubstituted quinhydrones.[7a–c]

The component duroquinone and durohydroquinone molecules all occupy crystallographic centres of symmetry at 0.5,0,0 and 0,0,0, respectively. Bond lengths and angles in the complex are shown in Table 3. Comparison of the geometry of duroquinone in this complex with that of the uncomplexed molecule,[8] which crystallizes with two independent centrosymmetric molecules in the asymmetric unit, reveals no major differences. In each crystal, the C(=O)–C–CH₃ angles are much less than 120°, being 114.8(2) and 115.3(2)° in the complex and 116.7 and 117.0° in the quinone crystal, with a concomitant increase in the C(CH₃)–C–CH₃ angles. The six-membered ring in the duroquinone molecule of the complex is very close to being planar (± 0.004 Å), with the adjacent methyl groups on one side of the molecule lying 0.017(4) and $-0.029(3)$ Å out of the plane and the methyl groups on the other side of the molecule at equal but opposite distances from the plane; the carbonyl oxygen atom [O(1)] lies very close (-0.021 Å) to the molecular plane.

The structure of uncomplexed tetramethylhydroquinone has been described;[9] in that crystal, the molecule sits on a crystallographic centre of symmetry. The geometries of the

Table 3. Intramolecular distances (Å) and angles (°) for duroquinhydrone

Distances

O(1)–C(1)	1.219(3)	O(11)–C(11)	1.373(3)
C(1)–C(2)	1.448(3)	C(11)–C(12)	1.388(3)
C(2)–C(3)	1.341(3)	C(12)–C(13)	1.401(3)
C(1)–C(3′)	1.492(3)	C(11)–C(13′)	1.401(3)
C(2)–C(4)	1.501(4)	C(12)–C(14)	1.513(4)
C(3)–C(5)	1.496(4)	C(13)–C(15)	1.508(4)
C(4)–H(4A)	0.98(4)	O(11)–H(11)	0.90(3)
C(4)–H(4B)	1.05(4)	C(14)–H(14A)	0.99(4)
C(4)–H(4C)	1.08(4)	C(14)–H(14B)	1.03(4)
C(5)–H(5A)	0.95(4)	C(14)–H(14C)	1.08(4)
C(5)–H(5B)	0.97(4)	C(15)–H(15A)	0.92(4)
C(5)–H(5C)	1.01(4)	C(15)–H(15B)	0.91(4)
		C(15)–H(15C)	0.98(4)

Angles

O(1)–C(1)–C(2)	119.5(2)	O(11)–C(11)–C(12)	115.4(2)
O(1)–C(1)–C(3′)	120.2(2)	O(11)–C(11)–C(13′)	122.0(2)
C(2)–C(1)–C(3′)	120.3(2)	C(12)–C(11)–C(13′)	122.6(2)
C(1)–C(2)–C(3)	120.2(2)	C(11)–C(12)–C(13)	119.4(2)
C(1)–C(2)–C(4)	114.8(2)	C(11)–C(12)–C(14)	118.3(2)
C(3)–C(2)–C(4)	125.0(2)	C(13)–C(12)–C(14)	122.3(2)
C(2)–C(3)–C(1′)	119.5(2)	C(12)–C(13)–C(11′)	118.0(2)
C(2)–C(3)–C(5)	125.2(2)	C(12)–C(13)–C(15)	122.2(2)
C(1′)–C(3)–C(5)	115.3(2)	C(11′)–C(13)–C(15)	119.8(2)
C(2)–C(4)–H(4A)	112(2)	C(11)–O(11)–H(11)	115(2)
C(2)–C(4)–H(4B)	111(2)	C(12)–C(14)–H(14A)	111(2)
C(2)–C(4)–H(4C)	110(2)	C(12)–C(14)–H(14B)	110(2)
H(4A)–C(4)–H(4B)	103(2)	C(12)–C(14)–H(14C)	110(2)
H(4A)–C(4)–H(4C)	124(3)	H(14A)–C(14)–H(14B)	103(3)
H(4B)–C(4)–H(4C)	95(3)	H(14A)–C(14)–H(14C)	129(3)
C(3)–C(5)–H(5A)	109(2)	H(14B)–C(14)–H(14C)	89(3)
C(3)–C(5)–H(5B)	108(2)	C(13)–C(15)–H(15A)	110(3)
C(3)–C(5)–H(5C)	109(2)	C(13)–C(15)–H(15B)	109(3)
H(5A)–C(5)–H(5B)	109(3)	C(13)–C(15)–H(15C)	111(2)
H(5A)–C(5)–H(5C)	111(3)	H(15A)–C(15)–H(15B)	105(4)
H(5B)–C(5)–H(5C)	110(3)	H(15A)–C(15)–H(15C)	113(3)
		H(15B)–C(15)–H(15C)	108(4)

hydroquinone molecules in the two crystals are quite similar; the most noteworthy common feature is the nonequivalence of the two external C–C–O(H) angles: 115.4(2) and 122.0(2)° in the complex and 116.3(1) and 121.1(1)° in the parent compound. The six-membered ring in the tetramethylhydroquinone molecule in the complex is close to planar, with some bending of the substituents out of the plane, C(14), C(15), O(11), and H(11)
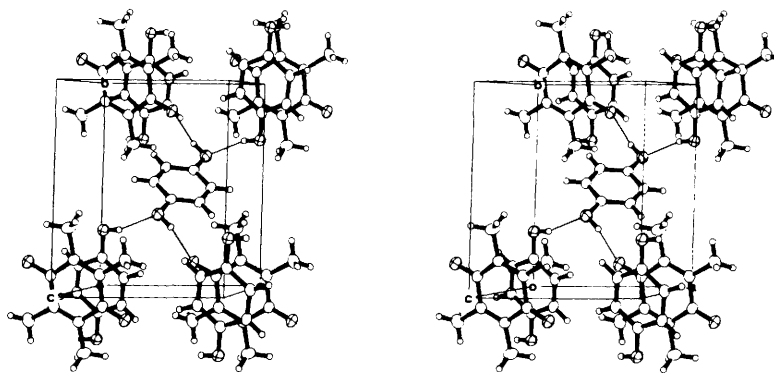
Figure 2. Stereoscopic view of the 1:2 duroquinone–hydroquinone complex; hydrogen bonds are shown by thin lines

being 0.045, −0.041, −0.026, and 0.076 Å from the plane. In the uncomplexed molecule, the central ring is close to planar, but only the oxygen atoms lie a significant distance (0.045 Å) from the plane.

Crystal and Molecular Structure of the 1:2 Complex of Duroquinone (1) *with Hydroquinone* (3).—A view of the packing is shown in Figure 2. This complex is atypical in that the usual two-dimensional layers of alternating quinone and hydroquinone molecules held together in one direction by hydrogen-bonding between essentially coplanar quinone and hydroquinone molecules and in the other by π-bonding of parallel alternating stacks of quinone and hydroquinone molecules are absent. There are chains of essentially planar (5.44°) quinone and hydroquinone molecules that have the π-interactions in a direction normal to the chain, but these chains are held together by a system of hydrogen bonds with the 'extra' out-of-plane hydroquinone in the structure acting as a bridge between the adjacent quinone and hydroquinone molecules. These chains run horizontally in Figure 2. Alternatively, the structure can be thought of as consisting of alternating quinone and hydroquinone molecules held together by direct quinone–hydroquinone hydrogen bonds, but the planes of these molecules are inclined at an angle of 74.14° to each other. The extremely non-planar character of this chain prevents any possibility of π–π overlap of quinone and hydroquinone molecules. For the purposes of the present discussion the essentially planar chain of quinone and hydroquinone molecules, but without direct hydrogen-bonding between adjacent molecules in the chain, will be considered as the primary chain. The dimensions of the hydrogen bond between the in-plane hydroquinone molecule [C(11)–C(13), O(11)] and the out-of-plane hydroquinone molecule [C(21)–C(23), O(21)] are: O(11)– – –O(21) 2.815(2); H(11)– – –O(21) 2.02(3) Å; C(11)–H(11)– – –O(21) angle 156(2)°. The dimensions of the hydrogen bond from the out-of-plane hydroquinone molecule to the quinone molecule [C(1)–C(3), O(1)] are: O(21)– – –O(1) 2.837(2); H(21)– – –O(1) 1.97(3) Å; O(21)–H(21)– – –O(1) angle 169(3)°. As is the case with all other quinhydrone or quinhydrone-like complexes, there is π–π overlap between adjacent chains. However, the overlap pattern is different from those found in the 1:1 quinhydrones (see later). The arrangement of the molecules in the cell of the 1:2 complex of (1) and (3) is similar in many respects to that of the 1:2 complex of 2,5-dimethylquinone and hydroquinone.[1c] However, in that complex, there is direct bonding between the in-plane quinone and hydroquinone components in the primary chain. In both 1:2 complexes, the 'extra' hydroquinone molecule serves to link chains together in a direction normal to both hydrogen-bonding and π-complex interactions.

Table 4. Intramolecular distances (Å) and angles (°) for $C_{10}H_{12}O_2$·$(C_6H_6O_2)_2$

Distances

O(1)–C(1)	1.223(2)	C(4)–H(4A)	0.91(4)
C(1)–C(2)	1.489(2)	C(4)–H(4B)	0.95(4)
C(2)–C(3)	1.340(2)	C(4)–H(4C)	1.06(4)
C(1)–C(3')	1.488(2)	C(5)–H(5A)	0.89(3)
C(2)–C(4)	1.503(2)	C(5)–H(5B)	0.99(4)
C(3)–C(5)	1.498(2)	C(5)–H(5C)	0.97(3)
O(11)–C(11)	1.373(2)	O(11)–H(11)	0.84(3)
O(21)–C(21)	1.381(2)	O(21)–H(21)	0.88(3)
C(11)–C(12)	1.385(2)	C(12)–H(12)	0.99(2)
C(21)–C(22)	1.387(2)	C(22)–H(22)	0.97(2)
C(12)–C(13)	1.386(2)	C(13)–H(13)	0.93(2)
C(22)–C(23)	1.377(2)	C(23)–H(23)	0.96(2)
C(11)–C(13')	1.390(2)		
C(21)–C(23')	1.389(2)		

Angles

O(1)–C(1)–C(2)	119.2(1)	C(11)–O(11)–H(11)	103(1)
O(1)–C(1)–C(3')	120.3(1)	C(21)–O(21)–H(21)	109(2)
C(2)–C(1)–C(3')	120.5(1)	C(2)–C(4)–H(4A)	111(2)
C(1)–C(2)–C(3)	120.2(1)	C(2)–C(4)–H(4B)	113(2)
C(1)–C(2)–C(4)	115.9(1)	C(2)–C(4)–H(4C)	115(2)
C(3)–C(2)–C(4)	123.9(1)	C(3)–C(5)–H(5A)	115(2)
C(2)–C(3)–C(1')	119.2(1)	C(3)–C(5)–H(5B)	110(2)
C(2)–C(3)–C(5)	124.0(1)	C(3)–C(5)–H(5C)	116(2)
C(1')–C(3)–C(5)	116.8(1)	C(11)–C(12)–H(12)	122(1)
O(11)–C(11)–C(12)	122.8(1)	C(13)–C(12)–H(12)	117(1)
O(11)–C(11)–C(13')	117.8(1)	C(12)–C(13)–H(13)	123(1)
C(12)–C(11)–C(13')	119.5(1)	C(11')–C(13)–H(13)	117(1)
C(11)–C(12)–C(13)	120.0(1)	C(21)–C(22)–H(22)	121(1)
C(12)–C(13)–C(11')	120.5(1)	C(23)–C(22)–H(22)	119(1)
O(21)–C(21)–C(22)	122.5(1)	C(22)–C(23)–H(23)	123(1)
O(21)–C(21)–C(23')	118.0(1)	C(21')–C(23)–H(23)	117(1)
C(22)–C(21)–C(23')	119.5(1)	H(4A)–C(4)–H(4B)	113(3)
C(21)–C(22)–C(23)	120.5(1)	H(4A)–C(4)–H(4C)	118(3)
C(22)–C(23)–C(21')	120.0(1)	H(4B)–C(4)–H(4C)	85(3)
		H(5A)–C(5)–H(5B)	100(3)
		H(5A)–C(5)–H(5C)	100(3)
		H(5B)–C(5)–H(5C)	113(3)

All three molecules in the cell occupy crystallographic centres of symmetry; the quinone is at 1,0,0.5, the in-plane hydroquinone at 0,0,0, and the out-of-plane hydroquinone at 0.5,0.5,0. Bond lengths and angles are given in Table 4. The ring atoms in the duroquinone molecule in the 1:2 complex are significantly non-planar with deviations of ±0.011 Å from the best plane; the adjacent methyl carbon atoms lie +0.029 and −0.035 Å from this plane while the oxygen atom lies 0.048 Å from the plane, on
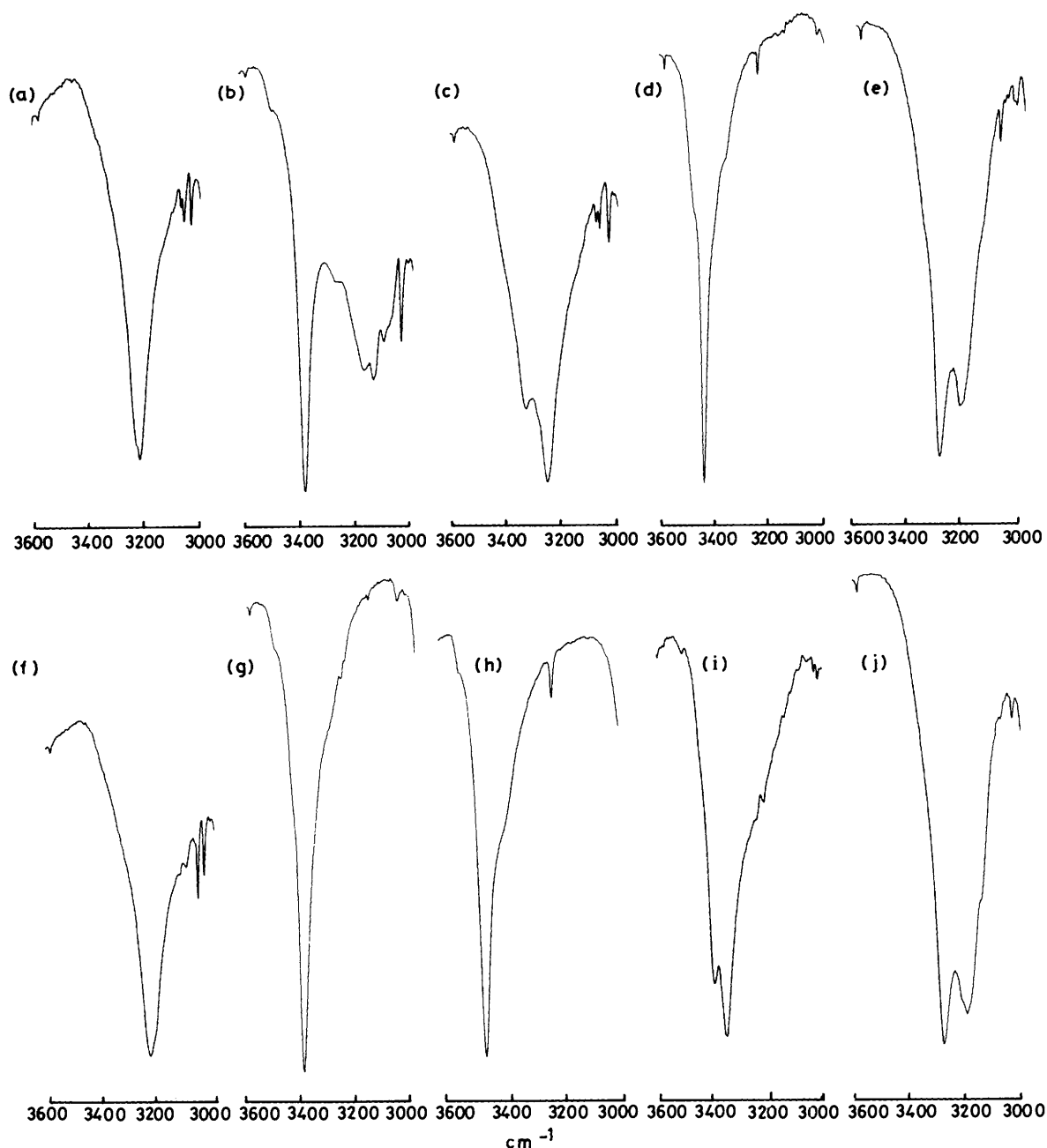
Figure 3. Hydroxy stretching frequency range of Fourier transform i.r. spectra for a series of complexes of quinones and hydroquinones: (a) monoclinic quinhydrone, (b) 2,5-dimethylquinone-hydroquinone (1:2), (c) naphthoquinone-hydroquinone (1:1), (d) tetramethylquinone-hydroquinone (1:1), (e) 2-phenylquinone-2-phenylhydroquinone (1:1), (f) triclinic quinhydrone, (g) 2,5-dimethylquinone-2,5-dimethyl-hydroquinone (2:1), (h) tetramethylquinone-tetramethylhydroquinone (1:1), (i) tetramethylquinone-hydroquinone (1:2), (j) 2-(p-chloro-phenyl)quinone-2-(p-chlorophenyl)hydroquinone (1:1)

the opposite side from the adjacent methyl carbon atoms. As in the duroquinhydrone structure and the uncomplexed duro-quinone, the C(=O)–C–CH₃ angles are less than 120°, being 115.9(1) and 116.8(1)°; the CH₃–C–C(CH₃) angles are 123.9(1) and 124.0(1)°. The ring atoms of both hydroquinone molecules are close to planar, but whereas the hydroxy oxygen and hydrogen of the in-plane hydroquinone lie −0.005 and +0.013 Å from the plane, those of the out-of-plane hydroquinone molecule lie −0.017 and −0.174 Å from the plane. It therefore appears that a significant twist is required of the hydroxy groups of the out-of-plane hydroquinone molecule to accommodate the hydrogen-bonding arrangements.

Hydroxy Stretching Absorptions and Crystal Structure.—The hydroxy stretching frequency as measured by Fourier transform i.r. methods has proved an extremely valuable method for following the formation and rearrangement of quinone:hydro-quinone complexes.[1a-c] The appearance of the hydroxy region provides some interesting correlations with crystal structure. For example, the monoclinic[7a,c] and triclinic[7b] forms of the unsubstituted quinhydrone duroquinhydrone, and the 2:1 complex 2,5-dimethylquinone with 2,5-dimethylhydro-quinone,[1b] all show single absorptions in the OH stretch region (Figure 3). In these four structures the hydroquinone molecule occupies a crystallographic centre of inversion and there is only

Table 5. Structural information on quinhydrone and related complexes

	M.p. (°C)	Density (g cm⁻³)	v_{OH}/ cm⁻¹	d(O - - - O)/ Å	d(H - - - O)/ Å	d(H - - - O) (corr.)/Å
Monoclinic quinhydrone	168—170	1.45	3 220	2.737(6)	2.05(8)	1.74
Triclinic quinhydrone	168—170	1.48	3 230	2.739(5)	1.85(4)	1.78
Duroquinhydrone		1.265	3 495	2.846(3)	2.03(2)	1.94
Naphthoquinone–hydroquinone		1.392	3 250	2.726(4)	1.81(5)	1.82
			3 330	2.740(4)	1.74(5)	1.76
Dimethylquinone–dimethylhydroquine (2:1)	117—118	1.258	3 300	2.818(3)	1.89(3)	1.82
Dimethylquinone–hydroquinone (1:2)	166—168	1.34	3 150	2.732(2)	1.77(2)	1.73
			3 380	2.775(2)	1.95(3)	1.795
Tetramethylquinone–hydroquinone (1:2)		1.30	3 360	2.815(2)	1.97(3)	1.85
			3 405	2.837(2)	2.02(3)	1.875
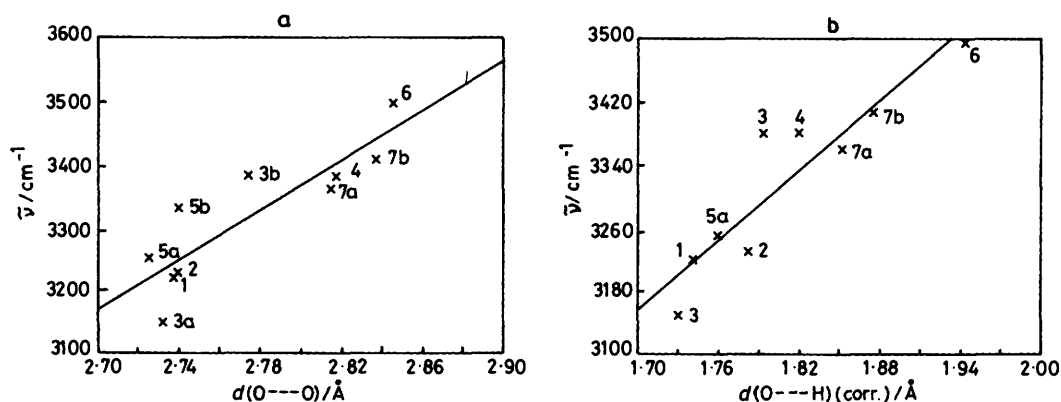
Figure 4. Plots of hydrogen-bonded distances (Å) vs. OH stretching frequencies (cm⁻¹): 1, monoclinic quinhydrone; 2, triclinic quinhydrone; 3, dimethylquinone–hydroquinone (1:2); 4, dimethylquinone–dimethylhydroquinone (2:1); 5, naphthoquinone–hydroquinone (1:1); 6, duroquinhydrone; 7, tetramethylquinone–hydroquinone (1:2)

one independent O–H group in the crystal. The 1:2 complex of 2,5-dimethylquinone with hydroquinone, the 1:2 complex of duroquinone with hydroquinone, and the 1:1 naphthoquinone–hydroquinone complex show more complex spectra, from which two main absorption lines can be recognized. In these three crystals, there are two crystallographically independent hydroxy groups.

It has been known for some time that a correlation can be expected between the O–H stretching frequency and the O - - - O distances for compounds containing hydrogen-bonded hydroxy groups.[10] Table 5 contains data for several complexes. A plot of OH stretching frequency versus O - - - O distances is given in Figure 4(a). If the positions of the hydrogen atoms were known accurately, a more valid comparison might be found with H - - - O distance. Figure 4(b) shows a plot with 'corrected' H - - - O distances, i.e. the hydrogen atom was fixed at 1.0 Å along the experimentally determined O–H vector. The two plots show a clear correlation of stretching frequency with O - - - O and O - - - H distances, respectively. In each case, the 1:2 complex of 2,5-dimethylquinone with hydroquinone deviates most from the best straight line.

As discussed in the preceding paper,[5] tetramethylquinone forms a 1:1 complex with hydroquinone in addition to the 1:2 complex discussed here. Crystals of the 1:1 complex suitable for X-ray structure analysis have not yet been obtained. The Fourier transform i.r. spectrum of this 1:1 complex is included in Figure 3. It shows a single sharp absorption in the hydroxy stretching range at 3 440 cm⁻¹. On the basis of the foregoing comparisons, it is conjectured that the component molecules all occupy centres of symmetry in the crystal, and that the O - - - O and H(corr.) - - - O distances are approximately 2.82 and 1.89 Å, respectively.

The OH stretching frequencies in quinhydrones undoubtedly are affected by aspects of the geometry of the O–H - - - (O=)C region of the complex other than the O - - - O distance. The hydroxylic hydrogen atom, which lies approximately in the plane of the benzene ring in most of the complexes and also in structures of phenols without ortho-substituents, in duroquinhydrone is forced out of the plane of the durohydroquinone ring by 0.08(3) Å, and in the out-of-plane hydroquinone molecule of the 1:2 tetramethylquinone–hydroquinone complex by 0.17(3) Å.

Fourier transform i.r. spectra of 2-phenyl- and 2-(p-chlorophenyl)-quinhydrone are worthy of note. The best refinement for these structures was in the space group $P2_1/c$ with a disordered arrangement of hydrogen-bonded quinone and hydroquinone molecules.[7e] However, it was recognized that there were problems with this interpretation as there was considerable evidence that the crystals as a whole were non-centrosymmetric. The Fourier transform i.r. spectra for these crystals show two OH absorptions (Figure 3), suggesting two independent O–H groups, a result inconsistent with the $P2_1/c$ formulation. These structures are not included in the plots since the disorder obscures the true distances.

Overlap Patterns in Quinhydrones and Related Complexes.— Figure 5 shows the overlap patterns in the quinhydrones that have been studied by X-ray diffraction and also for the 2:1 dimethylquinone–dimethylhydroquinone, for the 1:2 dimethylquinone–hydroquinone, and for the 1:2 tetramethylquinone–hydroquinone complexes. These drawings were obtained by projecting the atoms of the quinone molecule onto the best plane defined by the hydroquinone molecule (including the hydroxy oxygen atoms).
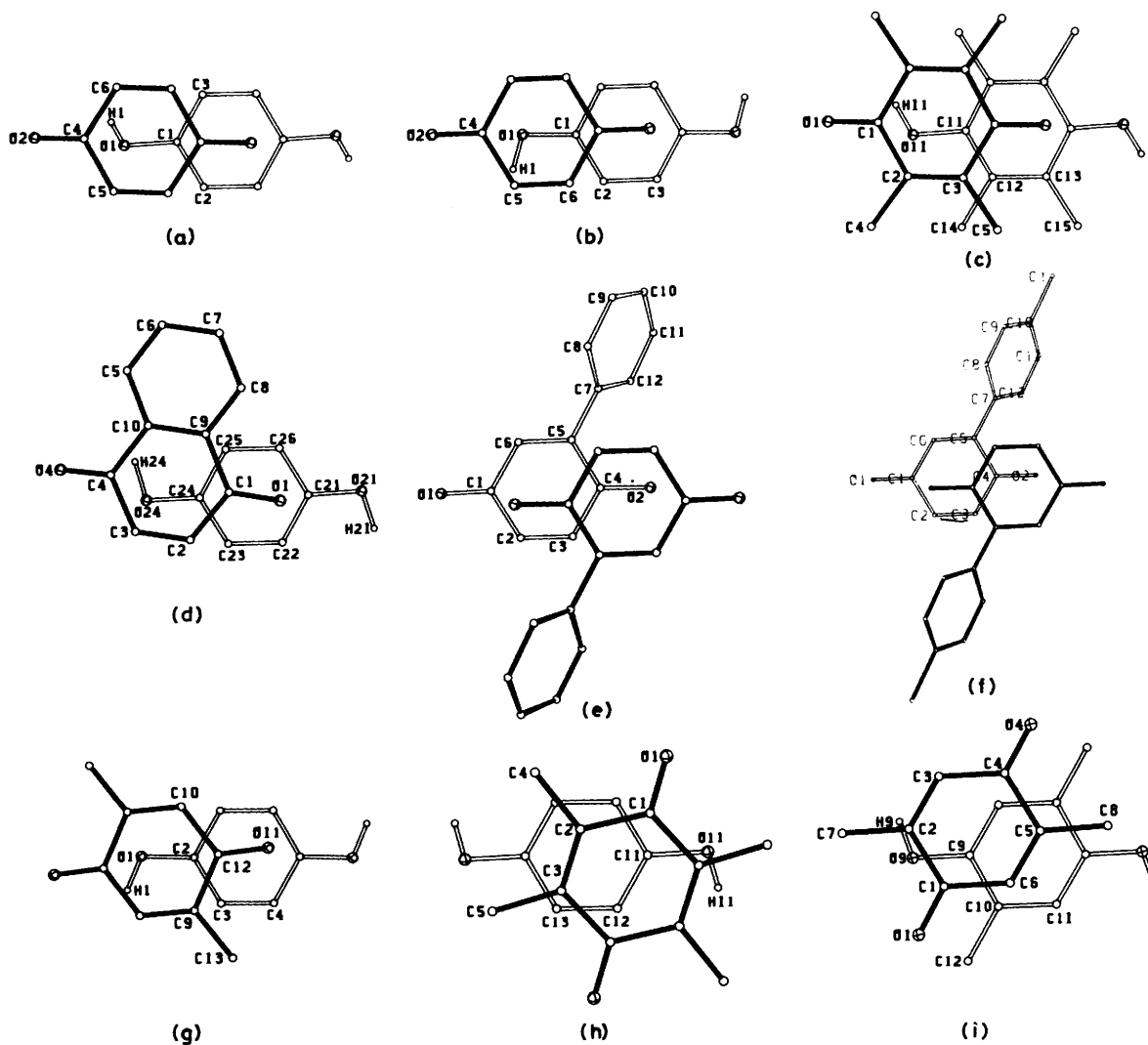
Figure 5. Overlap patterns in complexes of quinones with hydroquinones; drawings obtained by projecting the atoms of the quinone molecule onto the best plane defined by the six ring atoms and two oxygen atoms of the hydroquinone molecule: (a) monoclinic quinhydrone, (b) triclinic quinhydrone, (c) duroquinhydrone, (d) naphthoquinone–hydroquinone (1:1), (e) 2-phenylquinone–2-phenylhydroquinone (1:1), (f) 2-(p-chlorophenyl)quinone–2-(p-chlorophenyl)hydroquinone (1:1), (g) 2,5-dimethylquinone–hydroquinone (1:2), (h) 2,3,5,6-tetramethylquinone–hydroquinone (1:2), (i) 2,5-dimethylquinone–2,5-dimethylhydroquinone (2:1)

In the 1:1 quinhydrones, there is a small amount of ring–ring overlap and one of the quinone C=O bonds lies over the plane of the hydroquinone ring. The overlap patterns of the monoclinic and triclinic quinhydrones, and of duroquinhydrone, are virtually identical; the overlap of the naphthoquinone–hydroquinone complex has the projections of the C=O and C–O(H) bonds inclined at an angle of about 10°. The patterns of the 2-phenyl- and 2-(p-chlorophenyl)-quinhydrone show a slight displacement sideways so that the projections of the C=O and C–O(H) bonds (ignoring disorder) are not collinear.

In the two forms of unsubstituted quinhydrone, in duroquinhydrone, and in the 1:1 naphthoquinone–hydroquinone complex, the quinone ring is inclined at an angle to the reference hydroquinone ring, such that the quinone oxygen that lies over the hydroquinone ring is 0.1—0.4 Å further away from the plane defined by the hydroquinone ring than is the quinone oxygen that does not overlap. The co-ordinates from the disordered $(P2_1/c)$ structures for 2-phenyl- and 2-(p-chlorophenyl)-quinhydrone show no such tilt between the rings.

The overlap pattern of the quinone with one of the hydroquinone molecules in the 2,5-dimethylquinone–hydroquinone (1:2) complex is very similar to that found in the

unsubstituted 1:1 quinhydrones (Figure 5). However, the corresponding overlap in the tetramethylquinone–hydroquinone (1:2) complex is quite different. In this case, the overlap of the rings is greater, the projection of the quinone oxygen atom lies beyond the hydroquinone ring, and the relative orientation of the rings is different from that in any of the other complexes discussed in this section; the projections of the C=O and C–O(11) bonds are rotated ca. 70° from the parallel position.

There is significant ring–ring overlap of the quinone and hydroquinone rings in the dimethylquinone–dimethylhydroquinone (2:1) complex, but, as was the case with the tetramethylquinone–hydroquinone structure (1:2), the rings are rotated such that the C=O and C–O(H) projections are inclined at ca. 60° to each other. In this structure, the two quinone C=O bonds lie outside the plane of the hydroquinone molecule although one of the C–O (hydroxy) bonds lies under the quinone ring.*

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* In ref. 1b, there is an error in the Figure illustrating the overlap, which shows incorrectly that the C=O and C–O(4) bonds are almost parallel.

Table 6. Ranges of distances (Å) of atoms of quinone molecule from best plane through hydroquinone molecule
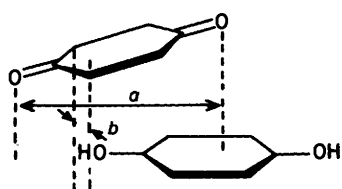
	Elongated range (all atoms) *a*	Sideways range of closest two atoms *b*
Monoclinic quinhydrone	2.857—3.267	3.100—3.101
Triclinic quinhydrone	2.972—3.232	3.099—3.141
Duroquinhydrone	3.387—3.496	3.445—3.446
Phenylquinhydrone	3.230—3.254	3.252—3.261
p-Chlorophenylquinhydrone	3.200—3.216	3.207—3.218
Naphthoquinone-hydroquinone (1:1)	3.039—3.337	3.231—3.367
Dimethylquinone-hydroquinone (1:2)	2.878—3.391	3.118—3.301
Tetramethylquinone-hydroquinone† (1:2)	3.280—3.536	3.370—3.554
Dimethylquinone-dimethylhydroquinone† (2:1)	3.297—3.375	3.279—3.383

† In these structures the projections of the O–O vectors of the quinone and hydroquinone are rotated *ca.* 60—70° from collinearity.

Table 6 lists the ranges of distances of the atoms of the quinone molecule from the best plane used to define the overlap. As one might expect, the unsubstituted quinhydrones have the closest quinone oxygen–hydroquinone plane distance (3.232 and 3.267 Å); duroquinhydrone has the greatest (3.496 Å).

Crystal Packing of Quinhydrones and Related Complexes.— The two structures described in this paper, taken together with previously determined structures, give some clues as to the ease of formation and the stoicheiometry of the complexes obtained when quinones and hydroquinones are brought together either in solution or in the solid state.[1a] The standard feature of a 1:1 quinhydrone is the formation of a two-dimensional layer of molecules, held together in one direction by O–H - - - O hydrogen bonding and in the other by π-complex formation. The manner in which these layers can be assembled to form a three-dimensional structure may be a major factor in determining the ease of crystal formation and the stoicheiometry. The unsubstituted quinhydrone and duroquinhydrone complexes are symmetrical, both in terms of substitution patterns within the individual molecules and also in the identical substitution patterns of the two complexing molecules. These complexes may be considered to represent the normal quinhydrone structure. Adjacent layers of the duroquinhydrone structure are built up with the methyl groups from one layer pointing into the hollows provided by the O–H - - - O hydrogen bond regions in the adjoining layer. Although bulky, the phenyl, *p*-chlorophenyl, and naphtho substituents are efficient packing groups and interleave with each other to form good crystals of a 1:1 quinhydrone.

However, the various mono-, di-, and tri-methyl substituents present a more difficult stacking problem; good quality crystals are generally difficult to obtain.[5] The surface of the layers that would be formed with these substituent patterns will provide bumps and hollows that are not readily filled in an efficient manner. When a methyl-substituted quinone complexes with unsubstituted hydroquinone, an unusual situation pertains. The bumps (methylquinone substituents) and hollows (unsubstituted hydroquinone) are more distinct than those to be encountered in the isomerically symmetrical methylquinhydrones, and, with the smallest hydroquinone available, opportunities exist for additional hydroquinone molecules to fill the hollows by forming hydrogen bonds to the hydroquinone molecules in the normal layer. This arrangement is typified by the 2,5-dimethylquinone–hydroquinone (1:2) complex. This out-of-plane hydroquinone molecule offers such stability that it is present in the tetramethylquinone–hydroquinone (1:2) complex in such a way that direct in-plane hydroquinone–quinone hydrogen-bonding is not found in the complex, but instead the out-of-plane hydroquinone provides a hydrogen-bonding bridge. Such 1:2 complexes would not be possible with a more bulky hydroquinone. Lacking a hydrogen-bonding donor capability, an unsubstituted quinone is unable to play the same role. The relatively few 2:1 quinone–hydroquinone complexes undoubtedly have a totally different structural arrangement.[1b]

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