Solid-state Reactivity of Crystalline Hydroquinones with Quinone Vapour; Crystal Structures of 2,5-Dimethylhydroquinone and 2,3,5,6-Tetramethylhydroquinone[†]

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Use of single crystals of 2,5-dimethylhydroquinone and 2,3,5,6-tetramethylhydroquinone in studies of their reactions with 1,4-benzoquinone vapour has been found to give information not obtainable from previous studies of reactions of powders. Structures of the two crystalline hydroquinones were determined by *X*-ray analysis. Crystals of the dimethylhydroquinone are orthorhombic, $a = 13.256(2)$, $b = 4.5609(8)$, $c = 11.977(2)$ Å, $Z = 4$, space group $Pca2_1$; and the structure has been refined to an *R* factor of 0.0335 on 704 non-zero reflections. Molecules have an *anti*-arrangement of hydroxy groups and form hydrogen-bonded chains with a motif like that of γ-hydroquinone. Slight differences in the geometry of the hydrogen bonding at the two ends of the molecule are responsible for the polar nature of the structure. Results of both the test for second harmonic generation and a pyroelectric test for non-centrosymmetry are positive with these crystals. The pyroelectric test applied to crystals in which twinning is known to occur shows clear evidence of such twinning and might be useful in certain other cases as a test for twinning.

Crystals of the tetramethylhydroquinone are monoclinic, $a = 8.317(3)$, $b = 4.728(2)$, $c = 13.514(5)$ Å, $\beta = 125.85(2)°$, $Z = 2$, space group $P2_1/c$; the structure has been refined to an *R* factor of 0.0367 on 813 non-zero reflections. Microscopic studies show evidence that the reaction is initiated at nucleation sites on reactive faces and that both quinone and hydroquinone molecules migrate during reaction. The faster reaction occurs at those faces where hydroxy groups emerge.

It has been found that the shapes of the OH stretching regions of the Fourier transform i.r. spectra of these and other hydroquinones as well as the positions of the absorption maxima provide structural evidence useful for distinguishing among these compounds, and can be correlated with their crystal structures.

Among the most interesting of the many types of crystalline organic complexes which can be formed when the two components are ground together or placed in physical contact[1–3] are the quinhydrones, crystalline complexes of quinones with hydroquinones. It has been suggested[1,2][‡] that the mechanisms of such reactions involve at least two sorts of diffusional processes. One is diffusion of the vapour of at least one component, most importantly the quinone, through air and through cavities between microcrystalline particles. The other involves diffusion of one component over the surface and through interior defects of the other.

It was hoped that a study of the reaction of single crystals of hydroquinones with quinone vapours might provide insight into the nature of such reactions.

In the search for hydroquinones suitable for such studies we found literature reports of structures of only a very few simple hydroquinones of the type needed. The characteristic which seemed most desirable was a structure with well defined polar (hydroxy) and non-polar (hydrocarbon) regions which might lead to anisotropic behaviour in the reaction with gases, as had been found in the studies of the reactions of carboxylic acids and anhydrides with ammonia gas and amine vapours.[4]


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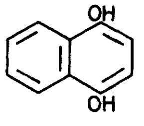
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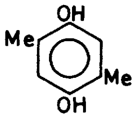
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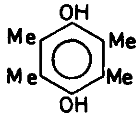
(4)

The parent compound, hydroquinone (**1**), has been found to exist in three crystalline forms, the structure of each of which has been determined. Unfortunately, the α-form, the one stable under ambient conditions, has a complex structure;[5a] the unit cell contains 54 molecules in a variety of orientations. This would be expected to complicate the correlation of reactivity with crystal structure. The β-form of hydroquinone (**1**) has been of unusual interest because of its propensity for clathrate formation; that is, it tends to crystallize in a structure with well defined cavities at least partially occupied by solvent molecules.[5b] Although the structure of the β-polymorph with its cavities unoccupied has been reported,[5c] its hexagonal symmetry and great tendency to crystallize with incorporation of solvent made it appear unpromising. The γ-form of hydroquinone, although with a structure[5d] which appeared to be suitable, had been reported[5e] to revert readily to the α-form at room temperature. Much more promising was 1,4-naphthohydroquinone (**2**), which crystallizes in hydrogen-bonded chains insulated from each other by non-polar regions made up of the naphthalene rings.[5f] However, initial difficulty in obtaining suitable crystals of this compound led us to consider 2,5-dimethylhydroquinone (**3**) and 2,3,5,6-tetramethylhydroquinone (**4**) for study. It was expected that the lateral methyl groups might provide hydrocarbon spacers between the polar regions containing hydrogen-bonded hydroxylic chains in the same way as does the second benzene ring in crystalline 1,4-naphthohydroquinone.[5f]

[†] *Supplementary data available* (SUP 56422, 3 pp.): thermal parameters. For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1986. Structure factor tables are available from the editorial office on request.

[‡] We regret that we were not aware of the existence of these papers and therefore did not refer to them in ref. 3*a*.

This paper reports the crystal structures of the dimethyl- **(3)** and the tetramethyl- **(4)** hydroquinone and a study of the reactions of these hydroquinones with quinone vapour.

Experimental

Preparation of 2,5-*Dimethyl*-1,4-*hydroquinone* **(3)** *and* 2,3,5,6-*Tetramethyl*-1,4-*hydroquinone* (*Durohydroquinone*) **(4)**.—Both hydroquinones were obtained by reduction of the corresponding quinone with aqueous sodium hydrosulphite. Purification of the dimethylhydroquinone by sublimation under vacuum at 0.01 mmHg pressure and crystallization of the tetramethyl compound from tetrahydrofuran gave thick 'hexagonal' plates, suitable in each case for *X*-ray structure determination but with imperfectly formed surfaces which made them unsuitable for studies under the microscope. Sublimation of the dimethylhydroquinone at atmospheric pressure with no cooling of the cold finger (where crystallization occurred) gave tiny needles, more perfectly formed. Sublimation of the tetramethyl compound also gave tiny needles. In each case these crystals were too small to give *X*-ray reflections but were suitable for studies of the reaction with benzoquinone under a microscope. The needles were related to the 'hexagonal' crystals by optical goniometry as described later. Solid–vapour reactions were carried out with these tiny needles in each case.

X-*Ray Structure Determination*.—Cell and intensity measurements were made with a Syntex $P2_1$ automated diffractometer with graphite-monochromated radiation. The atomic scattering factors for neutral atoms were those of Cromer and Waber;[6] all calculations were performed with the SHELX76 system of computer programs[7] and the direct methods package MULTAN80.[8]

Crystals of dimethylhydroquinone (3) from diethyl ether solution were found to be twinned. Crystals grown by slow sublimation as already described showed no evidence of twinning, however. Colourless crystals of dimethylhydroquinone (3) (0.78 × 0.35 × 0.25 mm) so obtained and of tetramethylhydroquinone (4) (1.1 × 1.0 × 0.25 mm from tetrahydrofuran) were mounted with epoxy cement on glass fibres for data collection. Cell parameters for each compound were obtained by a least-squares fit of the diffractometer setting angles of fifteen carefully centred high-order reflections. All scans were made in the θ—2θ mode at speeds ranging from 2.02 to 19.53° min^{-1}.

Dimethylhydroquinone (3). Crystal data: $C_8H_{10}O_2$, M_r = 138.2, orthorhombic, a = 13.256(2), b = 4.5609(8), c = 11.977(2) Å, V = 724.1(2) $Å^3$, D_c = 1.27 g cm^{-3}, Z = 4, $F(000)$ = 296, space group $Pca2_1$ or $Pcam$ (non-standard setting for $Pbcm$); the former was confirmed by refinement of the structure,* $\mu(\text{Cu-}K_\alpha, \lambda = 1.5418 \text{ Å}) = 7.0 \text{ cm}^{-1}$.

Two equivalent octants of data ($hk\bar{l}$, $\bar{h}k\bar{l}$) were collected to a 2θ value of 145°, resulting in a total of 1 796 measurements; the two octants were merged to give 753 unique reflections (R_{int} = 0.02), of which 704 had intensities greater than $3\sigma(I)$ and were considered observed. The data were corrected for Lorentz and polarization effects; a periodic measurement of the intensities of three check reflections over the 36.1 h of data collection indicated crystal and instrument stability. No absorption correction was made, in view of the lack of well developed faces on this crystal, the low μ value for this compound, and the shape of the crystal.

An analysis of the intensity statistics failed to resolve the space group ambiguity; however, packing considerations indicate the acentric space group $Pca2_1$. The successful solution (MULTAN80) and refinement of the structure in this space group and the failure of all efforts to solve the structure in $Pbcm$ verifies the selection. The hydroxy and phenyl hydrogen atoms as well as two equivalent sets of half-hydrogen atoms for each methyl group were located by difference-Fourier techniques and were included in the refinement (site occupancy factor = 0.5 for the methyl hydrogen atoms).

Table 1. Final atomic co-ordinates in fractions of the unit-cell edge for 2,5-dimethylhydroquinone

	x	y	z
O(1)	0.581 6(1)	0.269 6(4)	0.227 0[a]
O(2)	0.170 7(1)	0.229 0(4)	0.147 7(2)
C(1)	0.478 0(1)	0.260 4(5)	0.207 0(3)
C(2)	0.419 2(2)	0.090 5(6)	0.277 4(3)
C(3)	0.315 5(2)	0.083 8(8)	0.255 8(3)
C(4)	0.273 8(1)	0.235 4(5)	0.167 9(3)
C(5)	0.332 8(2)	0.406 5(6)	0.097 2(3)
C(6)	0.436 2(2)	0.417 3(8)	0.119 2(3)
C(7)	0.464 6(2)	−0.074 9(8)	0.374 2(4)
C(8)	0.288 2(2)	0.568 7(8)	0.000 7(4)
H(1)	0.605(2)	0.441(8)	0.175(2)
H(2)	0.136(2)	0.062(7)	0.167(2)
H(3)	0.272(2)	−0.044(7)	0.298(4)
H(6)	0.481(2)	0.532(7)	0.069(5)
H(7A1)	0.520	−0.219	0.346
H(7B1)	0.517	0.015	0.418
H(7C1)	0.421	−0.234	0.394
H(7A2)	0.542	−0.080	0.361
H(7B2)	0.462	0.057	0.444
H(7C2)	0.400	−0.099	0.424
H(8A1)	0.234	0.439	−0.047
H(8B1)	0.328	0.565	−0.078
H(8C1)	0.256	0.762	0.041
H(8A2)	0.209	0.636	0.001
H(8B2)	0.293	0.413	−0.078
H(8C2)	0.334	0.701	−0.041

[a] The z-co-ordinate of this atom was held constant to determine the origin in this direction.

The final cycle of full-matrix least-squares refinement included positional and anisotropic thermal parameters for the non-hydrogen atoms, positional and a group thermal parameter for the phenyl and hydroxy hydrogen atoms, and a single group thermal parameter for the methyl half-hydrogen atoms {which were constrained to their host atom at idealized positions [d(C–H) = 0.95 Å]}; reflection:parameter ratio = 6.8:1. No parameter shifted by more than 0.24σ and the final residual values were R = 0.0335, R_w = 0.0508, and GOF = 3.042. The weighting scheme was based on counting statistics $\{w = 1.000/[(\sigma|F|)^2 + 0.0002F^2]\}$ and showed no dependence on the value of θ or on the magnitude of F. The maximum and minimum peaks on the final difference map corresponded to 0.11 and -0.10 e/$Å^3$, respectively. The final values of the atomic co-ordinates are given in Table 1.

Tetramethylhydroquinone (4). Crystal data: $C_{10}H_{14}O_2$, M_r = 166.2, monoclinic, a = 8.317(3), b = 4.728(2), c = 13.514(5) Å, β = 125.85(2)°, V = 430.7(6) $Å^3$, D_c = 1.28 g cm^{-3}, Z = 2, $F(000)$ = 180, space group $P2_1/c$ (molecule sits on an inversion centre), $\mu(\text{Mo-}K_\alpha, \lambda = 0.710 73 \text{ Å}) = 0.8 \text{ cm}^{-1}$.

Of the 991 unique reflections measured (R_{int} = 0.01) out to 2θ = 55°, 813 had intensities greater than $3\sigma(I)$ and were considered observed. The data were corrected for Lorentz and polarization effects and a linear decay correction was applied based on a 3.8% decline in the intensities of three standard

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* In a preliminary investigation referred to in ref. 3*b* another crystal of 2,5-dimethylhydroquinone gave *X*-ray data which suggested a monoclinic space group and, in fact, the structure could be refined (although not very satisfactorily) in space group $P2_1/c$. Powder photographs of the two crystalline samples are identical, however. It is almost certain that the crystal referred to in ref. 3*b* exhibited some form of twinning.

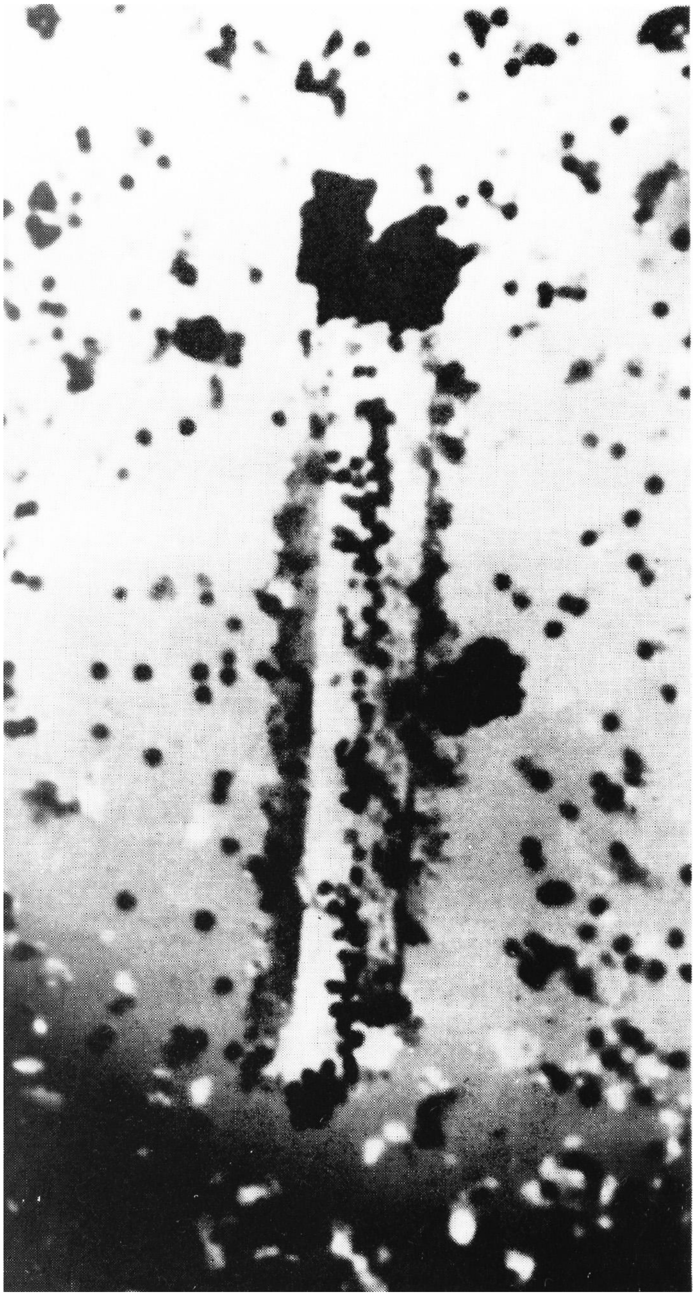

Plate 1. A twinned plate-like crystal of dimethylhydroquinone (**3**) looking down a direction parallel to the (0 0 1) face after spraying with a ground mixture of lycopodium powder, carmine, and sulphur. The major faces, shown edge-on, at the left and right sides of the crystal have become coated with the negatively charged particles of sulphur and carmine while a thin line of the positively charged lycopodium powder has formed approximately half-way between the (0 0 1) and (0 0 $\bar{1}$) faces.

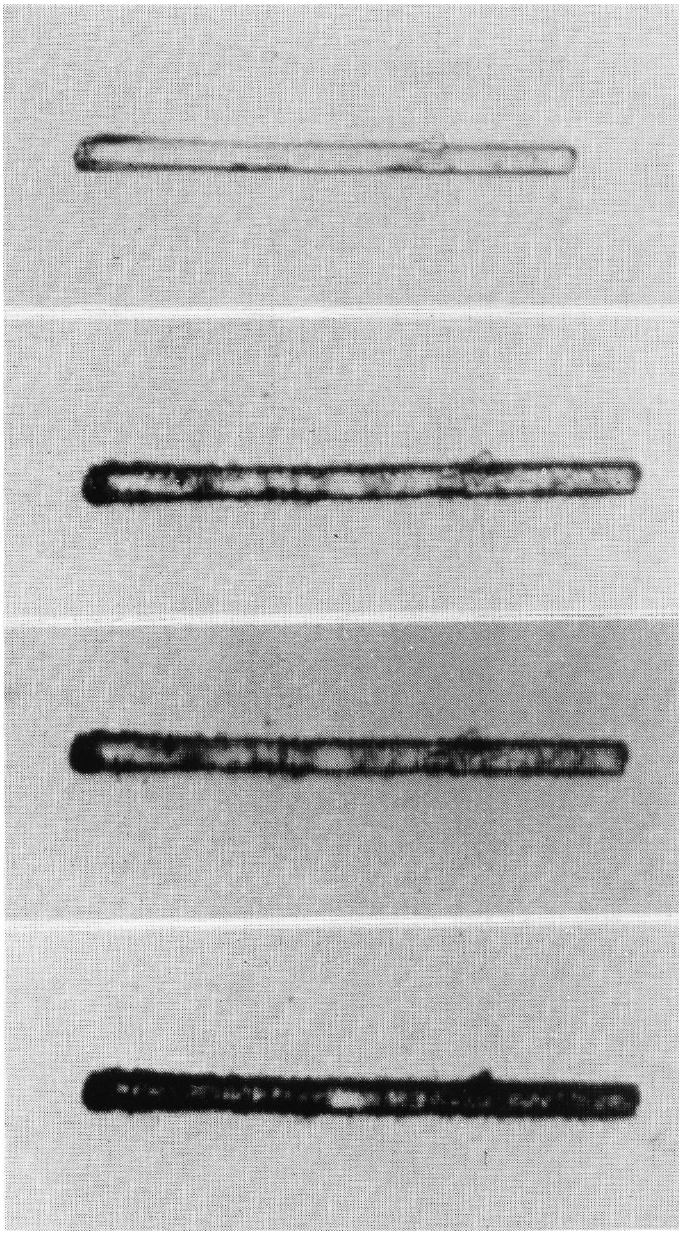

Plate 2. A needle of tetramethylhydroquinone (**4**) undergoing reaction with benzoquinone vapour. The major (top) face is $(1\ 0\ \bar{2})$. From top to bottom the photographs show reaction after 0, 3.5, 6, and 25 h.

Table 2. Final atomic co-ordinates for tetramethylhydroquinone

	x	y	z
O(1)	0.401 3(1)	0.071 3(2)	0.178 84(8)
C(1)	0.198 4(2)	0.042 8(2)	0.089 0(1)
C(2)	0.143 0(2)	−0.141 6(2)	−0.006 5(1)
C(3)	−0.060 0(2)	−0.186 1(2)	−0.097 8(1)
C(4)	0.299 4(2)	−0.290 0(3)	−0.010 9(1)
C(5)	−0.127 9(2)	−0.382 4(3)	−0.203 2(1)
H(1)	0.430(3)	0.237(4)	0.215(2)
H(4A1)	0.250(5)	−0.309(8)	−0.101(3)
H(4B1)	0.316(6)	−0.484(8)	0.020(3)
H(4C1)	0.423(5)	−0.163(7)	0.033(3)
H(4A2)	0.422(5)	−0.334(8)	0.070(3)
H(4B2)	0.266(5)	−0.486(8)	−0.039(3)
H(4C2)	0.331(6)	−0.201(8)	−0.064(4)
H(5A1)	−0.081(6)	−0.316(7)	−0.252(3)
H(5B1)	−0.240(6)	−0.458(8)	−0.232(3)
H(5C1)	−0.051(6)	−0.576(7)	−0.168(3)
H(5A2)	−0.243(5)	−0.288(7)	−0.287(3)
H(5B2)	−0.039(6)	−0.414(7)	−0.218(4)
H(5C2)	−0.158(6)	−0.575(7)	−0.190(3)

reflections. Owing to the low value of μ for this compound no absorption correction was made.

The structure was solved by direct methods (MULTAN80). All hydrogen atoms were found by difference-Fourier techniques. Two equivalent sets of hydrogen atoms were found for each methyl group, indicating disorder; both sets were included in the model with site occupancy factors of 0.5.

The final cycle of full-matrix least-squares refinement (maximum parameter shift = 0.06σ) included positional parameters for all the atoms, anisotropic thermal parameters for the non-hydrogen atoms, an isotropic thermal parameter for the hydroxy hydrogen atom, and a group thermal parameter for the methyl half-hydrogen atoms for a reflection-to-parameter ratio of 8.5:1. The weighting scheme $\{w = 2.97/[(\sigma|F|)^2 + 0.0006F^2]\}$ was based on counting statistics and resulted in final residual values of $R = 0.0367$, $R_w = 0.0518$, and GOF = 1.73. The final difference map was essentially featureless, with peaks ranging from 0.25 to −0.16 e/Å^3. The final atomic co-ordinates are given in Table 2.

Orientation of Molecules in Single Crystals of Dimethylhydroquinone (**3**).—The 'hexagonal' crystals were plates (point group *mm*2) shown by orientation on the *X*-ray diffractometer and also by measurement of interfacial angles with an optical goniometer to have as the major faces (0 0 1) and (0 0 $\bar{1}$) with sides {2 0 1}, and {1 1 1} [Figure 1(a)]. The presence of a polar axis was indicated by the upward-inclined faces of form {1 1 1} and the absence of those of form {1 1 $\bar{1}$}. The thin needles along *b* showed as the same major faces (0 0 1) and (0 0 $\bar{1}$) bounded by {2 0 1} as indicated by the agreement of the measured angle of 61° with the calculated value. The faces at the ends of the needle gave reflections too poor to permit assignment by optical goniometry.

Second Harmonic and Pyroelectric Tests with Dimethylhydroquinone (**3**).—A second-harmonic experiment similar to that described by Dougherty and Kurtz[9] was employed to test the effect of crystals with this weakly polar structure. A microcrystalline sample of the hydroquinone placed in a 1 064 nm beam (200 mJ) from a Q-switched, 20 ns, Nd-YAG laser gave a weak but definite second harmonic signal at 532 nm.

Application of the pyroelectric test described elsewhere[10] showed clear evidence of the polar axis. Since the major faces were (0 0 1) and (0 0 $\bar{1}$) the polar *c* axis passes through the thin direction of the crystal. In spite of this, and the weak polarity as judged from the crystal structure, untwinned crystals showed good discrimination between (0 0 1) and (0 0 $\bar{1}$) faces. The twinned crystals obtained from diethyl ether gave an interesting result on application of the pyroelectric effect test. When viewed down the *a* axis the two major faces were found to be coated with sulphur-carmine, and a thin line of lycopodium powder was observed approximately midway between these two faces. Such a result would be expected if there were twinning on (0 0 1) with reversal of the *c* direction at the interface of the twins (Plate 1).

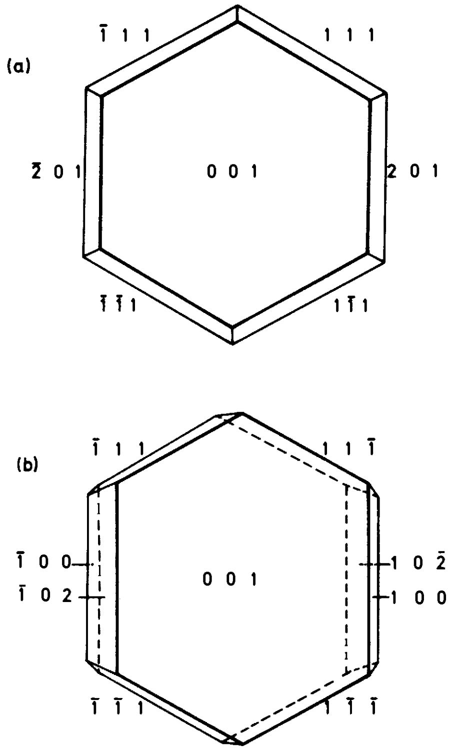

Figure 1. Sketches showing faces of the plates of (a) dimethylhydroquinone (**3**) and (b) tetramethylhydroquinone (**4**). Note that the polar axis of (**3**) is indicated by the absence of side faces pointing downward

Orientation of Molecules in Single Crystals of Tetramethylhydroquinone (**4**).—The 'hexagonal' plates (point group 2/*m*) on {0 0 1} were bounded by {1 0 0}, {1 0 2}, and {1 1 1} [Figure 1(b)]. The thin needles showed as the major faces {1 0 2} bounded by {1 0 0} and with the ends of the needle formed by {1 1 1}.

Reaction of Benzoquinone Vapour with Single Crystals of Dimethylhydroquinone (**3**).—Very thin needles (surface dimensions *ca.* 0.4 × 0.01 mm), enclosed in a covered crystallizing dish and surrounded by benzoquinone powder, were set aside at room temperature. Periodic observation with a microscope (magnification × 100) showed that after *ca.* 2 h the dark colour of the quinhydrone began to appear. In the early stages of reaction there was a clear preference for attack on the side {2 0 1} and {1 1 1} faces of the crystal leaving the top and bottom {0 0 1} faces clear. On continuation of the reaction for 24 h the crystals became completely coated with the dark-coloured quinhydrone complex. After 1 week small reddish-orange microcrystals had begun to grow out from the surface of the parent crystal. These microcrystallites showed extinction under crossed polarizing filters. After 2 months the crystal appeared completely black but examination of a Nujol mull by Fourier transform i.r. spectroscopy showed a spectrum

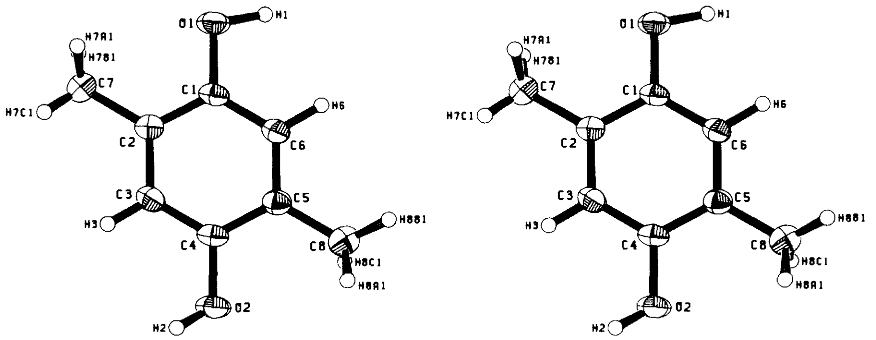

Figure 2. A stereoscopic view of a single molecule of dimethylhydroquinone (**3**) showing the atomic numbering system employed. Note the difference in the angle of twist of the hydroxy groups at the two ends of the molecule (a major source of crystal polarity)

similar to that of the unchanged hydroquinone but with small additional peaks at 1 630, 1 218, 1 080, 950, and 870 cm^{-1} characteristic of the 1:1 complex of benzoquinone with 2,5-dimethylhydroquinone. Examination of a larger crystal cut by a razor blade after reaction for 80 days showed that a major central portion of the crystal was colourless and apparently unchanged by reaction. Reactions which had been allowed to proceed for extended periods (2 months) showed the formation of small crystals of unmethylated monoclinic quinhydrone (identified by its Fourier transform i.r. spectrum) on the sides of the cell at sites remote from the parent crystal.

Reaction of Benzoquinone Vapour with Single Crystals of Tetramethylhydroquinone (**4**).—(*a*) The reaction was carried out with the tiny needles in the same manner as that of (**3**). As with the dimethyl compound initial attack was on the side faces {1 0 0} and {1 1 1} leaving the top and bottom face {$\bar{1}$ 0 2} clear. After 2 months the Fourier transform i.r. spectrum (Nujol mull) was similar to that of tetramethylhydroquinone (**4**) with additional peaks at 3 200, 1 630, 1 512, 945, 870, and 760 cm^{-1}, characteristic of the 2:1 complex of benzoquinone with (**4**).[3d]

(*b*) The reaction was much accelerated when a few single crystals of the hydroquinone (**4**) surrounded by a large excess of benzoquinone powder was placed in a closed cell formed from two microscope slides separated by a circular metal band 4 mm thick. The assembly placed on a microscope stage was photographed at regular intervals.

Fourier Transform I.r. Spectrum and Stability of γ-Hydroquinone γ-(**1**).—Very thin plate-like crystals of γ-(**1**) were obtained from the α-form by sublimation. The Fourier transform i.r. spectra of α- and γ-(**1**) showed, in addition to the difference in the O–H stretching region discussed in this paper, other marked differences. Thus α-(**1**) (Nujol mull) showed peaks at 3 220vbr, 1 515, 1 350, 1 257, 1 240, 1 220, 1 208, 1 190, 1 095, 825, 803, and 756 cm^{-1}; γ-(**1**) (Nujol mull) showed peaks at 3 375, 3 330, 1 515, 1 238, 1 211, 1 095, 830, and 755 cm^{-1}. In contrast to an earlier report,[5e] the γ-polymorph showed almost no change to the α-form even after 17 days in a Nujol mull. (After 2 months the change was substantial: the peak at 3 330 cm^{-1} became broader and new absorptions at 1 257, 1 190, and 830 cm^{-1} were evident.) A Fourier transform i.r. spectrum of γ-(**1**) which had been kept under ambient conditions (*ca.* 25 °C) showed somewhat more change than the sample which had been kept for the same length of time in Nujol.

Table 3. Bond lengths (Å) and angles (°) in 2,5-dimethylhydroquinone (**3**) and in tetramethylhydroquinone (**4**)

(**3**)		(**4**)	
O(1)–C(1)	1.396(2)	O(1)–C(1)	1.393(1)
C(1)–C(2)	1.385(4)	C(1)–C(2)	1.394(2)
O(2)–C(4)	1.388(3)	C(2)–C(3)	1.406(2)
C(2)–C(3)	1.401(3)	C(1)–C(3′)	1.399(2)
C(3)–C(4)	1.377(4)	C(2)–C(4)	1.510(2)
C(4)–C(5)	1.392(4)	C(3)–C(5)	1.506(2)
C(1)–C(6)	1.387(4)	O(1)–H(1)	0.88(2)
C(5)–C(6)	1.395(3)		
C(2)–C(7)	1.508(5)		
C(5)–C(8)	1.494(6)		
O(1)–H(1)	1.05(4)		
O(2)–H(2)	0.92(3)		
C(3)–H(3)	0.95(3)		
C(6)–H(6)	1.01(3)		
O(1)–C(1)–C(2)	117.7(2)	C(1)–O(1)–H(1)	111(1)
O(1)–C(1)–C(6)	120.6(2)	O(1)–C(1)–C(2)	116.3(1)
C(2)–C(1)–C(6)	121.7(2)	O(1)–C(1)–C(3′)	121.1(1)
C(1)–C(2)–C(3)	116.9(3)	C(2)–C(1)–C(3′)	122.6(1)
C(1)–C(2)–C(7)	121.6(2)	C(1)–C(2)–C(3)	118.8(1)
C(3)–C(2)–C(7)	121.5(3)	C(1)–C(2)–C(4)	120.2(1)
C(2)–C(3)–C(4)	121.6(3)	C(3)–C(2)–C(4)	121.0(1)
O(2)–C(4)–C(3)	121.2(2)	C(2)–C(3)–C(1′)	118.6(1)
O(2)–C(4)–C(5)	117.4(2)	C(2)–C(3)–C(5)	121.0(1)
C(3)–C(4)–C(5)	121.4(2)	C(5)–C(3)–C(1′)	120.5(1)
C(4)–C(5)–C(6)	117.2(3)		
C(4)–C(5)–C(8)	121.7(2)		
C(6)–C(5)–C(8)	121.2(3)		
C(1)–C(6)–C(5)	121.2(3)		
C(1)–O(1)–H(1)	102(1)		
C(4)–O(2)–H(2)	116(2)		
C(2)–C(3)–H(3)	120(2)		
C(4)–C(3)–H(3)	117(2)		
C(1)–C(6)–H(6)	120(2)		
C(5)–C(6)–H(6)	118(2)		

*Reaction of γ-Hydroquinone γ-(**1**) with Benzoquinone Vapour.*—Very thin freshly sublimed crystals when treated with benzoquinone vapour in a closed cell as just described showed a bluish tinge due to the beginning of formation of quinhydrone within 10 min. The reaction showed no sign of anisotropy. The product crystals rotated between crossed polarizers showed dramatic interference colours, particular regions of the crystals changing between red and blue as the stage was rotated.

Results and Discussion

*Crystal Structure of Dimethyl- (**3**) and Tetramethyl- (**4**) hydroquinone.*—The molecular structure of dimethylhydroquinone (**3**) is shown in Figure 2. Bond lengths and angles are given in Table 3. The molecule displays a high degree of centrosymmetric character although crystallizing in a non-centrosymmetric space group. The alternative space group (*Pcam*, non-standard setting for *Pbcm*) is quite inconsistent with the packing arrangement of the molecule. The principal deviation from a centrosymmetric molecule is in the disposition of the hydroxy hydrogen atoms, one lying −0.19 Å from the best plane through the hydroquinone ring, the other 0.38 Å from that plane; the corresponding distances for the hydroxy oxygen atoms are 0.015 and −0.016 Å.

The molecular dimensions are in agreement with those found in the 2:1 complex of 2,5-dimethyl-1,4-benzoquinone with dimethylhydroquinone (**3**).[3b] A notable feature is a bending of the CO(H) bonds *towards* the adjacent methyl groups, caused presumably by the steric requirements of the hydroxy hydrogen atom which participates in intermolecular hydrogen bonding; the values for the two $C(CH_3)$–C–O(H) bond angles are 117.4(2) and 117.7(2)°. In addition, the internal ring angles at the methyl-bonded carbon atoms are significantly less than 120°, being 116.9(3) and 117.2(3)°, respectively.

A view of the arrangement of the molecules in the unit cell is shown in Figure 3. Translationally related hydroquinone molecules are stacked along the *b*-axis with the plane of the benzene ring making an angle of 38° with the (0 1 0) plane. Adjacent stacks in the *a*-direction are linked by O–H - - - O hydrogen bonding to form a unimolecular layer in the *ab*-plane. These adjacent stacks are arranged such that one hydroxy oxygen from one stack lies approximately equidistant from two hydroxy oxygens in the other stack, and the resulting hydrogen-bonded chains extend in the *b*-direction. The O(1)–H(1) - - - O(2) ($\frac{1}{2} + x$, $1 - y$, z) distance is 2.744(2) Å, the H(1) - - - O(2) distance is 1.77(3) Å, and the O(1)–H(1) - - - O(2) angle is 153(2)°. The O(2)–H(2) - - - O(1) ($-\frac{1}{2} + x$, $-y$, z) distance is 2.732(2) Å; the H(2) - - - O(1) distance is 1.82(3) Å, and the O(2)–H(2) - - - O(1) angle is 170(2)°. Additional layers in the *c*-direction are arranged such that the relatively bulky methyl groups point towards a hydrogen atom attached to the hydroquinone ring. As the arrangement of hydrogen atoms in the methyl groups is disordered, there are presumably no very specific interactions. The crystal has a polar axis in the *c*-direction. All the O(1)–H(1) bonds have a component in the −*c*-direction (as defined in Figure 3), whereas all the O(2)–H(2) bonds have a component in the +*c*-direction.

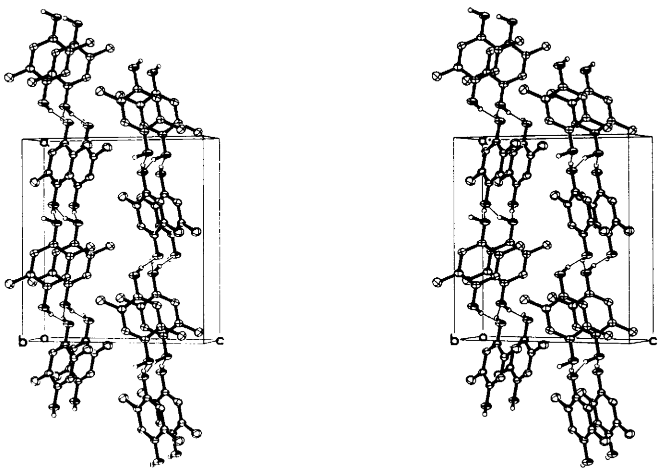

Figure 3. A stereoscopic view showing the packing of dimethylhydroquinone (**3**) in the unit cell. The hydrogen bonds are shown by thin lines. The reference molecule is in the left centre of the cell

The molecular structure of tetramethylhydroquinone (**4**) is shown in Figure 4. Bond lengths and angles are given in Table 3. The molecule sits on a crystallographic centre of symmetry at 0,0,0. Features of the molecular dimensions commented upon in the case of the dimethylhydroquinone molecule are also evident in that of the tetramethyl derivative. Bending of the C–O(H) bond due to overcrowding of the hydrogen atom is shown by the $C(2)(CH_3)$–C–O(H) angle of 116.3(1)°; the internal angles at the $C(-CH_3)$ atoms are 118.6(1) and 118.8(1)°. The methyl groups are disordered with one methyl hydrogen atom in each orientation pointing almost perpendicular to the plane of the ring. The aromatic ring is accurately planar, with one methyl carbon in the plane of the ring and the other lying 0.005 Å from it. The hydroxy oxygen atom lies very significantly (0.045 Å) out of the plane of the ring while the hydroxy hydrogen is 0.324 Å on the other side of the plane.

The packing of the molecules in the unit cell is shown in Figure 5. The hydrogen-bonding scheme is very similar to that found in 2,5-dimethylhydroquinone. The molecules stack above each other and the adjacent stacks in the *a*-direction are linked by intermolecular O–H - - - O hydrogen bonding. However, the directionality of the adjacent O–H - - - O bonding columns is reversed; there is no polar direction in this crystal. The O(1)–H(1) - - - O(1) ($1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) distance is 2.878(1) Å; the H(1) - - - O(1) distance is 2.04(2) Å, and the O(1)–H(1) - - - O(1) angle is 158(2)°. It may be noted that the hydrogen-bonding motif of γ-hydroquinone[5d] is similar to those of the dimethyl- and tetramethyl-hydroquinones described here. In each case the hydroxy hydrogen atoms at opposite ends of the molecule are *anti* to each other. The structure[5f] of naphthohydroquinone (**2**) shows a similar motif except that the two hydroxy protons are *syn* to one another, since they are constrained to point away from the 5- and 8-hydrogen of the adjacent ring.

Reaction of Single Crystals of Dimethyl- (**3**) *and Tetramethyl-* (**4**) *hydroquinone with Benzoquinone Vapour.*—Thin single

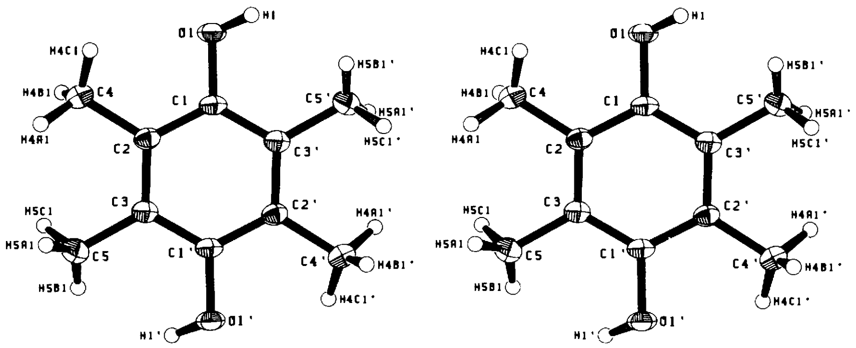

Figure 4. A stereoscopic view of a single molecule of tetramethylhydroquinone (**4**) showing the numbering of atoms

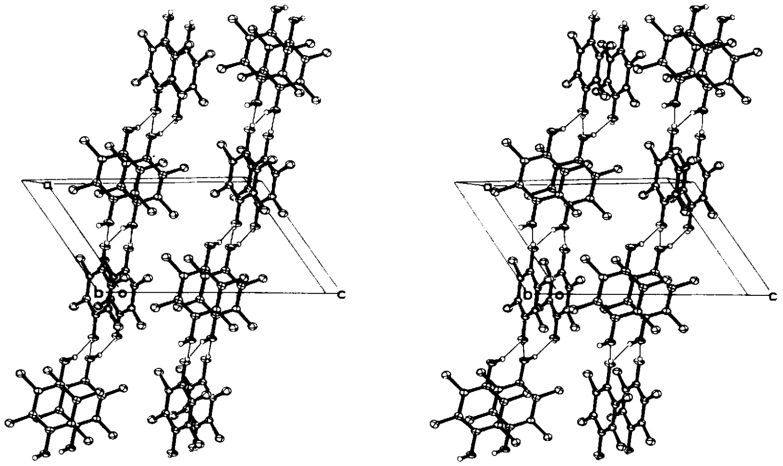

Figure 5. Stereoscopic view of the packing of tetramethylhydroquinone (**4**) in the unit cell. The two molecular layers shown going into the plane of the page and held together by hydrogen bonds lie in the ($\bar{1}$ 0 2) plane

crystals (the needle form) of tetramethylhydroquinone (**4**) surrounded by powdered 1,4-benzoquinone (not in direct contact) were observed on microscopic examination to react slowly and, in the initial stages, selectively at the side (1 0 0) and ($\bar{1}$ 0 0) faces rather than at the major ($\bar{1}$ 0 2) face of the crystal as shown by the formation on the surfaces of the deeply coloured quinhydrone complex (Plate 2). The reactive faces did not become coated evenly, however; instead reaction showed evidence of selective attack at nucleation sites at the reactive surfaces. As reaction continued, dark-coloured microcrystals grew on the surface of the parent crystal; hydroquinone molecules must, therefore, have diffused out of the parent crystal in order to react with quinone vapour. The structural feature of interest in the present context is the hydrogen-bonded chains running in both [2 0 1] and [0 1 0] directions. Comparison of the structure (Figure 5) with photographs of reacting crystals (see Plate 2) indicates that, in the early stages of the reaction at least, the faces most readily attacked are those containing the emerging hydroxy groups while the top face with its more hydrocarbon-like structure is attacked more slowly. Formation of crystallites of monoclinic quinhydrone could later be observed to have occurred on the glass surfaces of the reaction cell; the hydroquinone (**1**) needed for the reaction must have been formed by a redox reaction between benzoquinone and tetramethylhydroquinone (**4**). It is of interest that only the more volatile hydroquinone (**1**) rather than tetramethylhydroquinone (**4**) migrated to sites remote from the surfaces of the original tetramethylhydroquinone crystal. It is clear from these observations that not only the quinone molecules but also the less mobile hydroquinone molecules can migrate in the process of complex formation. This observation is in agreement with the conclusion of earlier workers[1,2] that solid–solid reactions of this kind can involve migration of one solid over the surface of another as well as migration by vapourization. In agreement with these observations the plate-like 'hexagonal' crystals of (**4**) showed immediate preferential attack by quinone vapour on the major face, in this case (0 0 1), rather than on the side faces.

Dimethylhydroquinone crystals when treated with benzoquinone vapour in the same way showed similar behaviour although the anisotropy was less pronounced. The crystal's upper surface, formed by the chains running from the bottom to the top of Figure 3, is corrugated with ridges and valleys running parallel to the *b*-axis. The ridges contain methyl groups and at the bottoms of the valleys are hydrogen-bonded chains parallel to *b*. Since this face is more open to penetration of quinone molecules to the hydroquinone hydroxy groups than was the case with the tetramethyl structure, it is not surprising that reaction is less selective in its anisotropy.

A particular point of interest is that the polar *c*-axis emerges from the major face of the 'hexagonal' form of this crystal so that the crystals are pyramidal, the morphology indicating the direction of the polar axis [see Figure 1(a)]. The polarity had too little effect on the reaction with quinone vapour to show any difference in the rates of reaction in the two directions along the polar axis. In spite of the slight degree of polarity suggested by the crystal structure, the pyroelectric test[10] was decisive. More interesting was the fact that crystals apparently twinned, when treated with a mixture of positively and negatively charged powder, showed coating of both the (0 0 1) (0 0 $\bar{1}$) faces with negatively charged particles, while a thin line of positively charged powder formed in the middle of the crystal (see Plate 1). This suggests that the pyroelectric test may have some general utility for detecting twinning in certain types of polar crystals. A test for second harmonic generation[9] showed a weak but definite signal in spite of the low degree of polarity of these crystals.

In the reaction of both the dimethyl- and the tetramethylhydroquinone the quinone molecules seem to initiate reaction by undergoing preferential reaction with hydroquinone faces containing hydroxy groups. It may be that these faces contain more defects which permit escape of hydroquinone molecules to form the quinhydrone complex.

I.r. Spectrum, ^{13}C N.m.r. Spectra, and Crystal Structure.—A comparison of the hydroxy stretching frequencies in the Fourier transform i.r. spectra of Nujol mulls of the methylated hydroquinones with those of the hydroquinone (**1**) and naphthohydroquinone (**2**) has shown interesting differences. β-Hydroquinone β-(**1**), naphthohydroquinone (**2**), and tetramethylhydroquinone (**4**) show the O–H stretching absorptions as relatively narrow, as would be expected from the crystal structures which in all these cases[5b,c,f] contain hydroquinone molecules lying at crystallographic symmetry elements which equilibrate the hydroxy groups at opposite ends of an aromatic ring. The spectra of the dimethyl compound (**3**) and γ-hydroquinone γ-(**1**) show an incompletely resolved but pronounced doublet as would be expected for structures[5d] with non-equivalent hydroxy groups at the two ends of the molecule (Figure 6), in agreement with the crystal structures. The O–H stretching region of the α-form of hydroquinone (**1**) is much

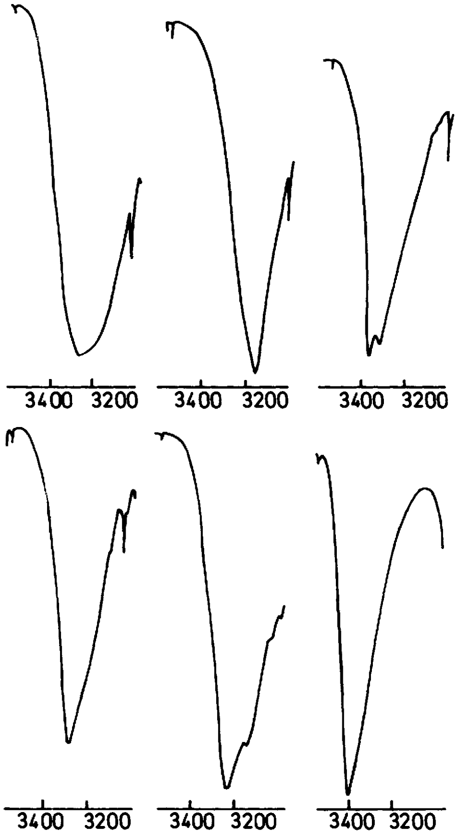

Figure 6. The O–H stretching regions of Fourier transform i.r. spectra of (top left) α-, (top middle) β-, and (top right) γ-hydroquinone (**1**), (bottom left) naphthohydroquinone (**2**), (middle) dimethylhydroquinone (**3**), and (bottom right) tetramethylhydroquinone (**4**)

broader as would be expected for a structure with six different kinds of hydroxy group taking part in hydrogen bonding.[5a]

It has been proposed previously that a reasonable correlation can exist between the O–H stretching frequency and O - - - O distance in hydrogen-bonded solids of the type being considered here.[11] The hydroxy groups of the dimethyl compound (**3**) are distorted by overcrowding from the normal positions nearly coplanar with the benzene ring and those of the tetramethyl compound by interference with the *ortho*-methyl groups with the consequent out-of-plane displacements and relatively long hydrogen bonds already described. These compounds provide an interesting test of the proposed linear correlation. In Figure 7 these frequencies, plotted against the measured O - - - O hydrogen-bond distances, give a reasonably linear plot. The fit must be regarded as somewhat coincidental since the hydrogen-bonding geometry is affected by a number of factors such as the extent of out-of-plane twisting of the phenolic hydroxy groups and the O–H - - - O, angle both of which vary from one case to the next. Neverthless the correlation with O - - - O distance seems to be better than those with other geometric parameters.

The ^{13}C n.m.r. spectrum of dimethylhydroquinone has been reported[3d] to show only four carbon resonances, as would be expected if the compound occupied a crystallographic centre of symmetry. Although the space group $Pca2_1$ precludes this occurence, the molecule does, as already mentioned, have opposite carbon atoms with similar crystallographic environments so that such a spectrum is not unexpected. The ^{13}C n.m.r. spectrum of the tetramethylhydroquinone has been discussed previously.[3d]

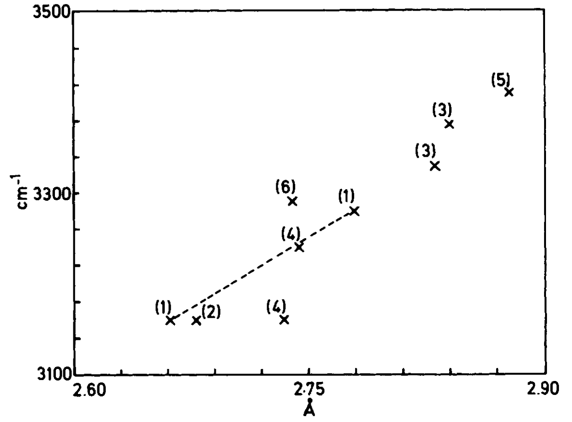

Figure 7. Plot of absorption maxima of the O–H stretching regions of several hydroquinones against the O - - - O distances: (1) α-, (2) β-, (3) γ-hydroquinone (**1**), (4) dimethylhydroquinone (**3**), (5) tetramethylhydroquinone (**4**), and (6) naphthohydroquinone (**2**). The dashed line indicates the range of values calculated from the several independent molecules of α-hydroquinone

Acknowledgements

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