Crystal Structure of a Clathrate Inclusion Compound of Hydroquinone and Hydrogen Sulphide

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The crystal structure of a β-hydroquinone clathrate of stoicheiometry $3C_6H_4(OH)_2{\cdot}xH_2S$ ($x = 0.768$) has been determined from three-dimensional *X*-ray data. The hydrogen-bonded $[OH]_6$ hexagonal rings are nearly but not exactly planar, and a difference map revealed an ordered proton arrangement. The clathration cavity is roughly spherical with a free diameter of *ca.* 4.8 Å. Analysis of the thermal parameters showed that the hydroquinone molecule behaves as a rigid body, and that vibration of the S atom is very pronounced, particularly in the direction of the *c* axis.

The structure was refined by full-matrix anisotropic least-squares to *R* 0.089 for 635 visual reflections. Crystals are rhombohedral, space group $R\bar{3}$, with $Z = 3$ in a hexagonal unit cell of dimensions: $a = 16.67(1)$ and $c = 5.518(5)$ Å. Bond distances and angles are all as expected.

HYDROQUINONE (quinol) clathrates are molecular inclusion compounds of general formula $3C_6H_4(OH)_2{\cdot}xM$, where M is the encaged guest species and *x* is a site-occupancy factor between zero and one. The nature of molecular association in these compounds, and consequently the general concept of clathration, were clarified by Palin and Powell in their *X*-ray crystallographic investigation of the hydroquinone–sulphur dioxide molecular adduct.[1] Since then hydroquinone clathrates have been subjected to numerous physicochemical and theoretical studies, and there are extensive reviews of the results.[2-7]

In the present work we sought to define accurately the β-hydroquinone † host lattice and to obtain, by means of an electron-density distribution, information concerning the motional behaviour of the encaged guest molecules and the proton location in the $O \cdots O$ hydrogen bond. We have therefore determined the crystal structure of the hydroquinone–hydrogen sulphide clathrate, which was known to exist well over a century ago.[8] There are three good reasons for selecting H_2S as the guest species. First, the clathrate crystals are easily prepared, well formed, and stable at room temperature and pressure. Secondly, H_2S is small enough to be accommodated comfortably in its cage so that the resulting host lattice may be expected to approximate closely to the hypothetical empty β-hydroquinone structure. Thirdly, and most important of all, since H_2S can be treated essentially as a sulphur atom in structure-factor calculations, complications due to disorder as encountered in the early *X*-ray analyses of the SO_2,[1] MeOH,[9] and MeCN [10] clathrates cease to be a problem.

DISCUSSION

Description of the Structure.—Final positional parameters are listed in Table 1, and interatomic distances and bond angles in Table 2. The dimensions of hydroquinone in the present clathrate are in excellent agreement with those found for this molecule in other crystal structures.[11] The difference between the angles O–C(1)–C(2) and O–C(1)–C(3) is highly significant and in accord with the observation [12] that, for many phenols, the angle C–C–OH is somewhat larger on the side of the hydrogen atom. The hydroquinone molecule, with the exception of the hydroxy-hydrogen, is planar. The equation to the mean plane containing O, C(1)—(3), and atoms related to them by the symmetry centre at $(\frac{1}{6}, -\frac{1}{6}, \frac{1}{3})$ is $0.812\,0X - 0.119\,1Y - 0.571\,4Z = 1.398\,9$, where *X*, *Y*, and *Z* are Cartesian co-ordinates in Å referred to a set of axes directed along *a*, *b**, and *c*. The normal to the plane makes an angle of 55.2° with the *c* axis. The long axis of the hydroquinone molecule, which passes through the

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† For historical reasons molecular adducts of hydroquinone are referred to as β-hydroquinone clathrates since hydroquinone crystallized under normal conditions from solvents which cannot be enclathrated has a different structure known as α-hydroquinone. Sublimation of hydroquinone yields a monoclinic modification known as the γ-form.

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[9] D. E. Palin and H. M. Powell, *J. Chem. Soc.*, 1948, 571.

[10] S. C. Wallwork and H. M. Powell, *J. Chem. Soc.*, 1956, 4855.

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[12] F. L. Hirschfeld, *Israel J. Chem.*, 1964, **2**, 87.

TABLE 1

Final positional parameters and, in parentheses, estimated standard deviations of those varied in the least-square refinement

Atom	Equivalent set	Point symmetry	x	y	z
S	3(b)	$\bar{3}$	0	0	$\frac{1}{2}$
O	18(f)	1	0.097 3(2)	−0.089 6(2)	0.007 5(5)
C(1)	18(f)	1	0 133 9(2)	−0.126 0(2)	0.171 8(6)
C(2)	18(f)	1	0.111 0(2)	−0.217 8(2)	0.140 2(6)
C(3)	18(f)	1	0.189 3(2)	−0.074 7(2)	0.366 0(6)
H(1)	18(f)	1	0.130	−0.020	0.002
H(2)	18(f)	1	0.067	−0.258	−0.011
H(3)	18(f)	1	0.206	−0.003	0.389
Group of atoms					
$[OH]_6$ ring	3(a)	$\bar{3}$	0	0	0
Hydroquinone	9(e)	$\bar{1}$	1/6	−1/6	1/3

two C–O bonds, is inclined at an angle of 40.2° to the (0001) plane.

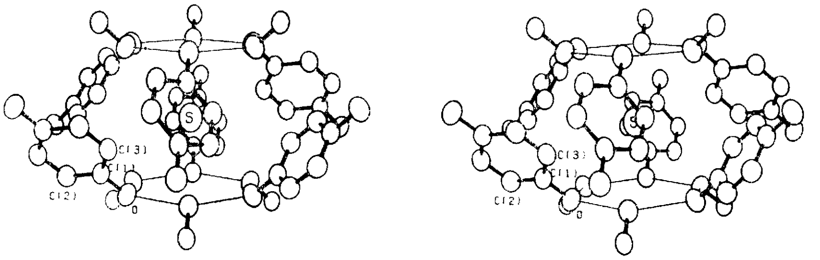

FIGURE 1 Stereo drawing showing the guest molecule (S) trapped inside a cage. For clarity all hydrogen atoms have been omitted. The labelled atoms correspond to the positional parameters in Table 1

As described by Palin and Powell,[1] the β-hydroquinone structure is composed of two interlocking three-dimensional hydrogen-bonded networks of rhombohedral symmetry. The oxygen atoms are grouped into hexagonal $[OH]_6$ rings normal to the c axis, and the guest molecule is sandwiched between two such $[OH]_6$ rings and surrounded by six C_6H_4 groups, three of which originate from the top $[OH]_6$ ring, the remaining three from the bottom (Figure 1). As indicated by the shorter guest-host interactions (Table 2), the clathration cavity is roughly spherical with a 'free diameter' of *ca.* 4.8 Å. For guest species not exceeding this limiting size, partial occupancy appears to be sufficient to stabilize the β-hydroquinone cagework.[13] The z parameter of the oxygen atom is different from zero; consequently the hydrogen-bonded $[OH]_6$ ring deviates slightly but significantly from exact planarity. The O · · · O bond length [2.700(3) Å] falls in the medium range, and the protons are ordered as revealed by a difference map (Figure 2).

TABLE 2

Interatomic distances (Å) and bond angles (°), with estimated standard deviations in parentheses

(a) Hydroquinone molecule			
O–C(1)	1.390(4)	O–C(1)–C(2)	117.4(3)
C(1)–C(2)	1.391(4)	O–C(1)–C(3)	122.3(3)
C(1)–C(3)	1.394(5)	C(2)–C(1)–C(3)	120.3(3)
C(2)–C(3)^{I}	1.388(4)	C(1)–C(2)–C(3)^{I}	120.1(3)
O–H(1)	1.00(3)	C(1)–C(3)–C(2)^{I}	119.6(3)
C(2)–H(2)	1.09(3)	C(1)–O–H(1)	115(2)
C(3)–H(3)	1.09(3)	C(1)–C(2)–H(2)	120(2)
		C(1)–C(3)–H(3)	119(2)
		C(3)^{I}–C(2)–H(2)	120(2)
		C(2)^{I}–C(3)–H(3)	121(2)
(b) Hydrogen-bonded $[OH]_6$ ring			
O · · · O^{II}	2.700(3)	O · · · O^{II} · · · O^{III}	119.9(3)
(c) Close guest-host van der Waals separations			
S · · · O	3.83	S · · · C(1)	4.17
S · · · O^{II}	3.89	S · · · C(3)	4.00

Roman numerals refer to the following equivalent positions relative to the atom at x, y, z:

I $1/3 - x, -1/3 - y, 2/3 - z$
II $y, -x + y, -z$
III $-x + y, -x, z$

Thermal parameters of the atoms are listed in Table 3. The thermal motion of the hydroquinone molecule (with omission of its hydrogen atoms) has been analysed in terms of the rigid-body modes of translation (T) and libration (R) using the method of Cruickshank.[14] The results of this analysis are summarized in Table 4. The root-mean-square ΔU_{ij} value of 0.001 7 Å^2 indicates a good fit of the rigid-body model. The translational motion is relatively small and not appreciably anisotropic, nor is there any apparent correlation with the inertial axes of the molecule. On the other hand, the libration is quite anisotropic, the principal motion corresponding to an amplitude of *ca.* 6° about an axis not too far (deviating by 24°) from the molecular axis through the C–O bonds. The thermal parameters found for the S atom (Table 3) are consistent with the experimental evidence for practically random motion of small guest molecules inside their cavities.[15,16] The unusually large vibrational

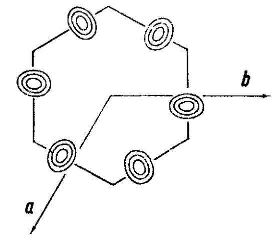

FIGURE 2 Section of three-dimensional difference map at $z = 0$. Electron-density contours are drawn at 0.1 eÅ^{-3} intervals starting at 0.2 eÅ^{-3}. The corners of the hexagon represent O atoms projected onto (0001)

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[13] D. E. Palin and H. M. Powell, *J. Chem. Soc.*, 1948, 815.
[14] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754.
[15] J. P. McTague, *J. Chem. Phys.*, 1969, **50**, 47.
[16] Ref. 6, pp. 240—241.

TABLE 3

Final anisotropic thermal parameters * ($Å^2 \times 10^4$), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B_{eq.}$†
S	880(39)	880	1 210(46)	440	0	0	7.81
O	475(14)	433(14)	732(18)	203(9)	−69(11)	49(10)	4.40
C(1)	368(15)	401(16)	580(19)	177(12)	18(12)	16(12)	3.60
C(2)	432(17)	433(17)	596(19)	166(13)	−21(13)	−48(13)	4.02
C(3)	475(18)	358(16)	649(21)	188(13)	−1(14)	−30(13)	3.97

* Anisotropic temperature factor expression: $T = \exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_ja_i^*a_j^*)$. † Equivalent isotropic temperature factor evaluated from the formula (W. C. Hamilton, *Acta Cryst.*, 1959, **12**, 609): $B_{eq.} = 8\pi^2/3[\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i \cdot a_j)]$.

TABLE 4

Rigid-body thermal parameters * of hydroquinone

$$\boldsymbol{T} = \begin{pmatrix} 356(14) & -39(9) & 66(11) \\ & 365(9) & -5(9) \\ & & 543(11) \end{pmatrix} \times 10^{-4}\ Å^2$$

$$\boldsymbol{R} = \begin{pmatrix} 182(30) & -39(10) & 155(24) \\ & 175(23) & -77(15) \\ & & 223(31) \end{pmatrix} \times 10^{-1}\ (°)^2$$

Principal axes of $\boldsymbol{T}$

R.m.s. amplitude/Å	Direction cosines (×10⁴)		
0.24	3 149	−839	9 454
0.20	5 118	−8 239	−2 436
0.18	7 993	5 605	−2 165

Principal axes of $\boldsymbol{R}$

R.m.s. amplitude/°	Direction cosines (×10⁴)		
6.3	5 979	−3 617	7 153
3.8	3 805	9 135	1 438
2.1	7 055	−1 862	−6 838

Root-mean-square (r.m.s.) discrepancy between observed and calculated U_{ij}: $17 \times 10^{-4}\ Å^2$.

* Axes of reference are *a*, *b**, *c*. Estimated standard deviations of components of $\boldsymbol{T}$ and $\boldsymbol{R}$ are given in parentheses.

amplitude in the *z* direction (Figure 1) is a consequence of the fact that the H_2S molecule has more freedom of movement in the direction of the open centres of the $[OH]_6$ rings.

EXPERIMENTAL

Crystals of hydroquinone–H_2S were formed as an opaque mass by passing hydrogen sulphide into a saturated aqueous solution of hydroquinone in a test tube, which was subsequently stoppered and sealed with adhesive tape. The test tube was then gently heated (water bath) to *ca.* 60 °C when all but a tiny fraction of the solid had dissolved. The water bath was then allowed to cool to room temperature. Colourless prismatic crystals began to appear after *ca.* ½ h, and a good crop could usually be obtained within a day or two.

Unit-cell dimensions were determined from high-angle reflections on a *h0l* Weissenberg photograph calibrated with superimposed NaCl powder lines and refined by minimizing the sum of the residuals $|\sin^2\theta_m - \sin^2\theta_c|$.

Crystal Data.—$3C_6H_4(OH)_2 \cdot xH_2S$ ($x = 0.768$), $M = 356.4$, rhombohedral, $a = 16.67(1)$, $c = 5.518(5)$ Å, $U = 1\,328.0$ Å^3, $D_m = 1.337(2)$ g cm^{-3} (by flotation hexane–carbon tetrachloride), $Z = 3$, $D_c = 1.367$ g cm^{-3} for $x = 1$, $F(000) = 563.5$. Space group $R\bar{3}$ (No. 148)* from systematic absences: $-h + k + l \neq 3n$ and intensity statistics. $\mu = 16.1$ cm^{-1} for Cu-K_α radiation, $\lambda = 1.5418$ Å.

For the collection of intensity data a roughly spherical crystal of diameter 0.3 mm was mounted along the *b* axis, and the zero through seventeenth levels were recorded with nickel-filtered Cu-K_α radiation on a Weissenberg camera using the multiple-film technique. Although the crystal eventually turned slightly yellowish, there was no detectable deterioration in the quality of the diffraction data. The intensities of the individual reflections were estimated visually by comparison with a calibrated strip. Data were corrected as usual for Lorentz and polarization factors and for spot-shape variations,[18] but not for absorption. Finally, a set of scaled structure amplitudes were derived by correlating equivalent reflections by a least-squares procedure.[19] The data after reduction consisted of 635 independent reflections of measurable intensity and 32 unobserved reflections.

Structure factors were calculated with the published positional parameters † for the hydroquinone–sulphur dioxide host structure, an occupancy factor $x = 0.768$ for the S atom in positions 3(*b*), and a uniform isotropic temperature factor *B* 4.0 Å^2. The initial agreement index *R* was 0.305 for observed reflections. Successive cycles of full-matrix isotropic and anisotropic refinement reduced *R* to 0.141, *x* being treated as a variable parameter in the least-squares calculation. A plot of $\ln(|F_o|/|F_c|)$ *vs.* $|F_c|^2$ indicated that there were large extinction effects on strong reflections with low $\sin\theta$ values. Inclusion of a secondary extinction parameter *C* as an additional variable in two further cycles of anisotropic refinement [20] lowered *R* to 0.113. A difference-Fourier map gave well-resolved peaks of 0.50, 0.65, and 0.80 eÅ^{-3} in reasonable positions for hydrogen atoms H(1)—(3); all other peaks in the map were <0.25 eÅ^{-3}. Inclusion of these three hydrogen atoms with *B* 4.0 Å^2 in a final least-squares cycle gave *R* 0.089. The refinement gave 0.747(15) for the site-occupancy factor *x*, which is in good agreement with the value of 0.768 calculated from the measured crystal density. The value obtained for the extinction parameter *C* was 0.000 15(1).

The function minimized was $\Sigma w(|F_o| - |F_c|/ZACH)^2$, with $ZACH = [C\beta I_0 + \{1 + (C\beta I_0)^2\}^{\frac{1}{2}}]^{\frac{1}{2}}$, where I_0 is the measured integrated intensity in approximately the right scale, and β is Zachariasen's angular dependent function [21] evaluated for a crystal sphere with $\mu R = 4.5$ cm^{-1}.[22] The weighting scheme used was that of Cruickshank *et al.*[23] with $w = (2F_{min.} + |F_o| + 2|F_o|^2/F_{max.})^{-\frac{1}{2}}$, where $F_{min.}$ and $F_{max.}$ were taken as 4.0 and 200.0 respectively. *X*-Ray scattering factors for nonhydrogen atoms were taken from ref. 24, whereas for H the form factor for a bonded hydrogen in the

* The corresponding primitive rhombohedral unit cell, with $a_{rh} = 9.799$ Å, $\alpha = 116.6°$, and $Z = 1$, is in the observe setting adopted as standard in ref. 17. Powell and co-workers [1,9,10] used the reverse setting with systematic absences: $h - k + l \neq 3n$ for reflections indexed on a hexagonal triply-primitive unit cell.

† The C and O co-ordinates in hydroquinone–SO_2 (x', y', z') (ref. 1) and the present clathrate (x, y, z) are related by $x \simeq y'$, $y \simeq -x' + y'$, and $z \simeq z' - \frac{1}{2}$.

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[17] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1952, p. 20.

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[24] Ref. 17, vol. III, 1962, pp. 202—207.

hydrogen molecule[25] was used. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21699 (5 pp., 1 microfiche).*

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

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