Orientation of Methanol enclathrated in the β-Hydroquinone Lattice: an X-Ray Crystallographic Study

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The crystal structure of a β-hydroquinone–methanol clathrate, $3C_6H_4(OH)_2 \cdot xCH_3OH$ ($x = 0.887$), has been determined. The encaged CH_3OH molecule has three preferred orientations related by three-fold rotation about the c axis. In each orientation, the C–O bond is tilted by 35° from c to facilitate interaction of the hydroxy-group with three phenolic oxygen atoms of a neighbouring $[OH]_6$ ring. Crystals are rhombohedral, space group $R3$, with $Z = 3$ in a hexagonal unit cell of dimensions $a = 16.621(2)$, $c = 5.562(1)$ Å. Refinement of 632 observed data yielded R 0.043.

The pioneering researches of Powell and his co-workers [1-5] have established that the β-hydroquinone (quinol, 1,4-dihydroxybenzene) host lattice gives rise to three crystallographically distinguishable types of clathrates of the same general formula, $3C_6H_4(OH)_2 \cdot xG(0 \leqslant x \leqslant 1)$, depending on the nature and size of the encaged guest species G as well as the conditions of preparation. In Type I clathrates, space group $R\bar{3}$, the guest molecules are fully disordered in their cavities and show little interaction with the host framework. Relaxation of the requirement of centrosymmetry at the cage centre gives rise to Type II clathrates belonging to space group $R3$. Further reduction in lattice symmetry from rhombohedral to trigonal leads to space group $P3$ for Type III clathrates.

The structure of the Type II hydroquinone–methanol clathrate was investigated over three decades ago by Palin and Powell [3] using two-dimensional photographic data. They concluded that it closely resembles that of the Type I hydroquinone–sulphur dioxide clathrate,[2] the imprisoned methanol molecules being ' arranged with their long axes parallel to the c direction '. This methanol clathrate has since been subjected to several physicochemical studies, much interest being centred on the preferred orientations and modes of reorientation of the encaged guest molecule. Based on heat capacity data, Matsuo [6] has suggested that the methanol molecule assumes an orientation in which a line joining the carbon atom to the centre of the O–H bond is aligned with the c axis. In another model, proposed by Gallier and Meinnel,[7] the CH_3 symmetry axis rotates about an axis perpendicular to c. More recently, Davidson and his co-workers [8] conducted very thorough dielectric and n.m.r. studies of methanol clathrate samples with two different degrees of cage occupancy over a wide temperature range. Their results are consistent with a model of six preferred orientations: three related by the C_3 axis, with the other three generated by further inversion through the cage centre.† On the assumption that the C–O–H plane is parallel to c, it was deduced that the C–O bond is inclined to c by 32° below 100 K and 40° at 300 K.

In the present work, which makes use of full three-dimensional diffractometer data, we attempted to define accurately the Type II β-hydroquinone host structure and to obtain, by means of Fourier and least-squares methods, information concerning the preferred orientations of the enclathrated methanol molecule.

Experimental

Commercial hydroquinone (Aldrich) was distilled and recrystallized from benzene. Suitable crystals for X-ray dif-

fraction were obtained by slow evaporation of a solution of hydroquinone in air-free methanol. A carefully chosen single crystal was ground to a sphere of diameter 0.42 mm with a Nonius crystal grinder and mounted on a glass fibre. Unit-cell dimensions were derived by least-squares fit of 25 high-order reflections measured with graphite-monochromated Mo-K_α radiation on a Nicolet R3m diffractometer.

Crystal Data.—$3C_6H_4(OH)_2 \cdot xCH_3OH$ ($x = 0.887$), $M = 358.75$. Rhombohedral, $a = 16.621(2)$, $c = 5.562(1)$ Å (hexagonal axes), $U = 1\,330.7$ Å^3, $D_m = 1.343(1)$ g cm^{-3}, $Z = 3$, $F(000) = 569.7$, D_c ($x = 0.945$) $= 1.350$ g cm^{-3}. Systematic absences: $-h + k + l \neq 3n$, space group $R3$ (No. 146) from intensity statistics and confirmed by structure analysis. Mo-K_α ($\lambda = 0.71069$ Å), $\mu = 0.96$ cm^{-1}.

Intensity data were collected using the variable-speed θ–2θ scan technique in bisecting mode. Crystal orientation was monitored every 250 reflections. The intensities of three check reflections, measured every 50 data, fluctuated within ±2% and showed no systematic decline. Of the 759 unique reflections measured up to $2\theta \leqslant 55°$, 636 (83.8%) were considered observed at the $3\sigma(F)$ significance level.

The co-ordinates of the C and O atoms of the host hydroquinone molecule were deduced from those published for the H_2S [9] and HCl [10] clathrates. Refinement of these eight anisotropic atoms [the z co-ordinate of O(1) was fixed at zero], plus four isotropic riding aromatic hydrogen atoms with C–H bonds fixed at 0.96 Å, yielded a best R factor of 0.185. A difference Fourier map revealed the guest methanol molecule as two large peaks lying on the c axis and disposed unsymmetrically with respect to the geometrical centre of the cage. The methyl C(7) and hydroxy O(3) atoms were next introduced in Wyckoff position 3(*a*) of the type (0,0,z) and varied isotropically with a common site occupancy factor k. The R factor converged smoothly to 0.065, but the apparent C(7)–O(3) bond distance of 1.17 Å was much too short compared to the known distance of 1.425 Å.[11] The resulting difference map clearly showed that the phenolic hydrogen atoms are ordered in the $[OH]_6$ ring, and that the guest molecule is inclined to the c axis in a three-fold disordered arrangement. Further refinement based on this model yielded a final R of 0.043 for 632 observed data,‡ with no residual peaks higher than 0.35 e Å^{-3}. The final least-squares cycle gave 0.315(12) for the site occupancy factor k, which is in good agreement with the value $x/3 = 0.297$ calculated from the measured crystal density.

All computations were performed with the SHELXTL package of crystallographic programs on a Data General

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† This six-site model is based on the idealized β-hydroquinone lattice in space group $R\bar{3}$.[9]

‡ When both C(7) and O(3) were allowed to vary anisotropically, R converged to 0.054 and the resulting difference map was far less satisfactory.

Table 1. Fractional atomic co-ordinates,* with estimated standard deviations in parentheses

	x	y	z
O(1)	0.096 8(3)	−0.091 8(3)	0
C(1)	0.134 7(3)	−0.125 4(3)	0.166 7(11)
C(2)	0.111 5(4)	−0.217 6(3)	0.141 9(15)
C(3)	0.143 7(5)	−0.259 3(4)	0.299 2(12)
C(4)	0.198 9(3)	−0.207 1(3)	0.489 5(12)
C(5)	0.222 3(4)	−0.115 3(3)	0.521 3(13)
C(6)	0.190 6(4)	−0.075 3(4)	0.357 8(12)
O(2)	0.232 2(3)	−0.245 9(3)	0.654 0(5)
C(7)	0.004(8)	0.021(3)	0.524(3)
O(3)	−0.011(2)	−0.035(1)	0.314(3)
H(1)	0.124(4)	−0.029(1)	0.057(8)
H(2)	0.072 1	−0.253 4	0.011 2
H(3)	0.127 8	−0.322 9	0.278 2
H(4)	0.205(4)	−0.312(1)	0.672(8)
H(5)	0.260 2	−0.180 1	0.654 7
H(6)	0.207 3	−0.011 4	0.377 6

* The z co-ordinate of O(1) was fixed. The benzene-type H atoms have the same estimated standard deviations as the corresponding C atoms to which they are bonded.
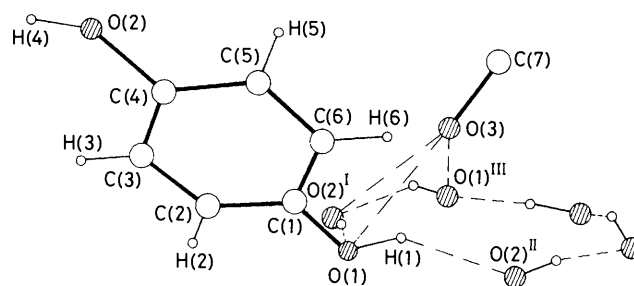

Figure 1. Guest–host interactions. The labelled atoms correspond to the positional parameters in Table 1; for symmetry code, see Table 2

Table 1. Bond distances and angles are listed in Table 2. Thermal parameters and comparison of observed and calculated structure factors are available as Supplementary Publication No. SUP 23422 (7 pp.).†

The present analysis confirmed that the β-hydroquinone–methanol adduct is a Type II clathrate belonging to the non-centrosymmetric space group $R3$.[3] As prepared under ordinary

Table 2. Bond lengths (Å) and angles (°) *

(a) Hydroquinone and methanol molecules

O(1)–C(1)	1.386(7)		C(1)–C(2)	1.387(7)
C(1)–C(6)	1.383(8)		C(2)–C(3)	1.379(11)
C(3)–C(4)	1.385(8)		C(4)–C(5)	1.385(7)
C(4)–O(2)	1.384(8)		C(5)–C(6)	1.377(10)
C(7)–O(3)	1.43(4)			
O(1)–C(1)–C(2)	116.6(5)		O(1)–C(1)–C(6)	125.1(5)
C(2)–C(1)–C(6)	118.3(6)		C(1)–C(2)–C(3)	121.9(6)
C(2)–C(3)–C(4)	118.2(6)		C(3)–C(4)–C(5)	121.3(6)
C(3)–C(4)–O(2)	120.5(5)		C(5)–C(4)–O(2)	118.1(5)
C(4)–C(5)–C(6)	118.9(6)		C(1)–C(6)–C(5)	121.3(5)

(b) Hydrogen bonding and guest–host interactions

O(1) · · · O(2)ᴵ	2.653(5)		O(3) · · · O(1)	2.98(3)
O(1) · · · O(2)ᴵᴵ	2.779(5)		O(3) · · · O(2)ᴵ	2.87(2)
			O(3) · · · O(1)ᴵᴵᴵ	3.13(3)
O(1) · · · O(2)ᴵ · · · O(1)ᴵᴵᴵ	119.9(2)		C(1)–O(1) · · · O(3)	101.8(6)
C(1)–O(1) · · · O(2)ᴵ	113.1(2)		C(1)ᴵᴵᴵ–O(1)ᴵᴵᴵ · · · O(3)	103.3(5)
C(1)–O(1) · · · O(2)ᴵᴵ	112.6(2)		C(4)ᴵ–O(2)ᴵ · · · O(3)	177.1(7)
C(4)ᴵ–O(2)ᴵ · · · O(1)	116.0(2)		C(7)–O(3) · · · O(1)	138(6)
C(4)ᴵ–O(2)ᴵ · · · O(1)ᴵᴵᴵ	110.1(2)		C(7)–O(3) · · · O(2)ᴵ	162(3)
			C(7)–O(3) · · · O(1)ᴵᴵᴵ	120(6)

* Symmetry code: I $-1/3 - y$, $-2/3 + x - y$, $-2/3 + z$; II $2/3 - x + y$, $1/3 - x$, $-2/3 + z$; III $y - x$, $-x$, z.

Corporation Nova 3 minicomputer. By the method of additional observational equations, interatomic distance constraints of 1.385 ± 0.005 Å* were applied to all C–C and C–O bonds in the hydroquinone molecule, 1.43 ± 0.01 Å to the C(7)–O(3) bond in the methanol molecule, and 0.98 ± 0.02 Å to the two phenolic O–H bonds. The weighting scheme employed for the blocked-cascade least-squares refinement and analysis of variance was $w = [\sigma^2(F) + 0.001|F|^2]^{-1}$. Four of the strongest reflections were omitted from the least-squares calculations.

Results and Discussion

Numbering of the atoms in the asymmetric unit is shown in Figure 1, and the final positional parameters are displayed in

conditions of temperature and pressure, the clathrate is non-stoicheiometric. The imprisoned methanol molecule exhibits three preferred orientations related by the C_3 symmetry axis along c (Figure 2). In each orientation, the C(7)–O(3) bond is tilted by 35° from the c axis such that O(3) is brought into closer contact with three O atoms of the basal [OH]₆ ring (Figure 1). Geometrical considerations indicate that these attractive guest–host interactions, though undoubtedly significant, cannot be described as conventional O–H · · · O hydrogen bonds involving the hydroxy-group and lone pairs of the closest phenolic O atoms. A more complex hydrogen-bonding scheme, perhaps a bi- or tri-furcated arrangement, seems more likely. The inclination angle of 35° is in remarkable agreement with the values of 32° below 100 K and 40° at 300 K deduced from dielectric studies.[8]

The C_6O_2 skeleton of the hydroquinone molecule is planar

* This is a very good averaged value based on a survey of the molecular dimensions of hydroquinone in its crystalline adducts.[12]

† For details, see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.
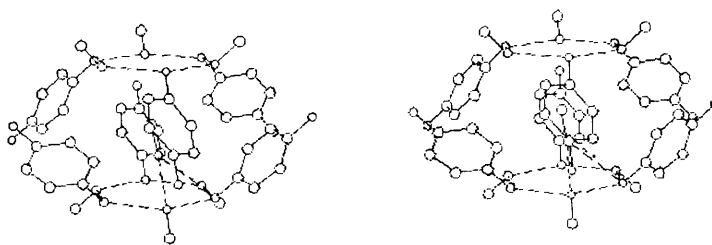
Figure 2. Stereodrawing showing a guest CH_3OH molecule trapped inside a cage. For clarity two of the three preferred molecular orientations and all hydrogen atoms have been omitted

within experimental error (r.m.s. Δ 0.011, max. Δ 0.020 Å); the equation to the mean plane is $0.8121X - 0.1339Y - 0.5679Z = 1.463\,0$, where X, Y, and Z are Cartesian co-ordinates in Å referred to a set of orthogonal axes directed along a, $b*$, and c. The C–C–O angles (Table 2) show the well established inequality due to the steric effects of the phenolic hydrogen atom on one side of the molecule.[12] It is interesting to note that the angle $C(6)$–$C(1)$–$O(1)$ is considerably larger than $C(3)$–$C(4)$–$O(2)$, so that the $C(1)$–$O(1)$ bond makes an angle of 4.3° with the long molecular axis passing through $C(1)$, $C(4)$, and $O(2)$. Furthermore, $C(2)$–$C(1)$–$C(6)$ is significantly smaller than $C(3)$–$C(4)$–$C(5)$, and the bond angles within the aromatic ring show an alternating pattern (Table 2). These distortions can be rationalized by the fact that $C(6)$ has closer contacts (3.71—3.75 Å), and hence stronger steric repulsion, with the guest molecule than $C(3)$ (3.79—3.85 Å). It is also conceivable that the balance between the attractive and repulsive guest–host interactions leads to unequal $O \cdots H$–O hydrogen bonds in the $[OH]_6$ ring.

In the published structure of the Type II HCl clathrate,[10] guest–host interactions of the type $^-OH \cdots Cl$–$H \cdots \overset{|}{O}H$ exist, and the $O \cdots H$–O distances alternate around the $[OH]_6$ ring. It was proposed that the HCl molecule lies preferentially on the surface of a cone, with its generator inclined by 33° to c and its apex at the Cl position. These features have much in common with those observed for the CH_3OH clathrate. It seems reasonable, therefore, to conclude that the formation of Type II β-hydroquinone clathrates is favoured by guest molecules of appropriate sizes which can

interact appreciably with specific sites in the walls of a clathration cavity.

It has been shown that the hydroquinone molecule executes rigid-body motion in the H_2S clathrate.[9] A similar TLS analysis [13] of the present hydroquinone thermal parameters gave a relatively poor fit. This difference further substantiates the thesis that Type I and II clathrates are distinguished mainly by the extent of guest–host interaction.

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