Acta Cryst. (1978). B**34**, 3631–3634

Hydroquinone–Acetonitrile (3:1) Clathrate

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(*Received* 18 *November* 1977; *accepted* 4 *July* 1978)

$3C_6H_4(OH)_2.CH_3CN$, $3C_6H_6O_2.C_2H_3N$, is trigonal, space group $P3$, with $a = 15{\cdot}982$ (8), $c = 6{\cdot}239$ (5) Å, $Z = 3$, $D_m = 1{\cdot}34$ (1) (by flotation in xylene/bromobenzene), $D_x = 1{\cdot}340$ g cm^{-3}. The structure was determined from new film data and refined by isotropic rigid-body least-squares calculations to $R = 0{\cdot}113$. The three symmetry-independent acetonitrile molecules fit snugly inside clathration cavities in the shape of prolate spheroids, with one guest molecule aligned in the opposite sense to the other two. The mean $O\cdots O$ hydrogen-bond length is significantly longer than the corresponding distances in the H_2S and HCl clathrates, in consonance with the relative stabilities of the three types of β-hydroquinone lattices.

Introduction

The classical studies of Powell and co-workers (Palin & Powell, 1947, 1948*a*,*b*; Wallwork & Powell, 1956) have established that the β-hydroquinone (quinol) host lattice gives rise to three crystallographically distinguishable types of clathrates of the same general formula, $3C_6H_4(OH)_2.xM$ ($0 < x \leq 1$), depending on the nature of the encaged guest species M.* Type I hydroquinone clathrates crystallize in space group $R\bar{3}$; to fit into a cavity, a non-linear molecule such as SO_2 must necessarily be disordered to achieve a centre of symmetry. Relaxation of the requirement of centrosymmetry for the guest species gives rise to type II clathrates belonging to space group $R3$. Further reduction in symmetry, from a rhombohedral lattice to a trigonal one, leads to space group $P3$ for type III clathrates.

The structure of the type III hydroquinone–acetonitrile clathrate was determined more than 20 years ago by Wallwork & Powell (1956) from two-dimensional X-ray data. They showed that the β-hydroquinone cage departs only slightly from rhombohedral symmetry, the hydrogen-bonded $[OH]_6$ ring is puckered, and the clathration cavity is considerably extended in the direction of the c axis in order to accommodate the acetonitrile guest molecule. Their rather limited data did not permit precise location of all the atoms in the asymmetric unit. In the present work, which makes use of the full three-dimensional diffraction data, we attempt to determine the nature of the distortion of the type III cagework from the idealized β-hydroquinone host lattice (Mak, Tse, Tse, Lee & Chong, 1976) for type I and type II clathrates and to obtain, by means of an electron-density distribution, information concerning the location and orientation of the imprisoned acetonitrile molecules.

Colourless prismatic crystals of the clathrate were obtained by slow evaporation of a saturated solution of hydroquinone in acetonitrile. The compound effloresces rapidly in air, and specimens for diffraction study were therefore sealed in glass capillaries filled with hexane. Individual specimens were kept for periods ranging from a few days to well over a month, and were discarded when deterioration became noticeable as judged from the appearance of streaks and the general increase in background on the photographs. Unit-cell dimensions were determined from high-angle reflections on an $h0l$ Weissenberg photograph calibrated with superimposed NaCl powder lines and refined by minimizing the sum of the residuals $|\sin^2\theta_m - \sin^2\theta_c|$. Four different crystals, all roughly spherical and of diameter 0·7 mm, were used in recording the intensities of the $h0l$–$h15l$ levels with Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation using the multiple-film Weissenberg technique. The visually estimated intensities were corrected for Lorentz and polarization factors but absorption was ignored ($\mu = 8{\cdot}39$ cm^{-1}). A set of scaled structure amplitudes was derived (Hamilton, Rollett & Sparks, 1965) which, after reduction, consisted of 855 independent observed and 1120 unobserved reflections.

The asymmetric unit consists of three hydroquinone molecules in general positions and three acetonitrile molecules in sites of threefold symmetry. The unfavourable data-to-parameter ratio necessitates the use of rigid-body (group) least-squares refinement (Doedens, 1970). Each hydroquinone molecule was fixed as a regular C_6 hexagon of side 1·390 Å with two *para* C–O bonds of the same length.

Since the host lattice is pseudo-rhombohedral (reflections with $-h + k + l \neq 3n$ either weak or absent) and closely related to the idealized β-hydroquinone struc-

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* An alternative but different classification of the host lattice into three types on the basis of the quinol Raman bands around 470 cm^{-1} has been given by Davies & Wood (1975).

ture, an initial set of group parameters was derived in the following way. The six parameters [see note (*b*) in Table 1] defining the location and orientation of one of the hydroquinone molecules were deduced from atomic coordinates given in the earlier work (Wallwork & Powell, 1956;* Mak *et al.*, 1976). The other two hydroquinone molecules were then generated from the first one by applying the rhombohedral translations $(\frac{1}{3},\frac{2}{3},-\frac{1}{3})+$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$. An acetonitrile guest molecule, composed of atoms C(19), C(20) and N(1), with C—C and C—N distances fixed at 1·466 and 1·154 Å respectively, was also introduced into the subsequent refinement. Three cycles of least-squares refinement with an overall isotropic thermal parameter for each group yielded an *R* factor of 0·19. A Fourier map revealed the remaining atomic positions and gave unequivocal indication that one acetonitrile guest molecule was not related to the other two by simple rhombohedral translations and had in fact the reverse orientation. In the next stage of refinement, one acetonitrile molecule was held stationary, the other two were allowed to shift along the *z* direction, the three hydroquinone molecules were varied as rigid groups, and individual isotropic temperature factors were used for all atoms. Thus the total number of parameters, including an extinction parameter (Zachariasen, 1967, 1968) and a scale factor, was 55, as opposed to the 114 parameters which would have been required for individual-atom isotropic refinement. Convergence was reached in three cycles, and the final *R* index for 855 observed reflections was 0·113.† A difference Fourier map based on the last set

Table 1. *Atomic and rigid-group parameters and, in parentheses, estimated standard deviations*

	x	*y*	*z*	*B* (Å²)
Acetonitrile *a*				
C(19)	0	0	0·615 (1)	4·20 (6)
C(20)	0	0	0·380 (1)	6·30 (9)
N(1)	0	0	0·195 (fixed)	4·90 (6)
Acetonitrile *b*				
C(21)	$\frac{1}{3}$	$\frac{2}{3}$	0·280 (1)	5·82 (8)
C(22)	$\frac{1}{3}$	$\frac{2}{3}$	0·045 (1)	4·10 (6)
N(2)	$\frac{1}{3}$	$\frac{2}{3}$	−0·140 (1)	4·97 (6)
Acetonitrile *c*				
N(3)	$\frac{2}{3}$	$\frac{1}{3}$	1·100 (1)	7·80 (9)
C(23)	$\frac{2}{3}$	$\frac{1}{3}$	0·915 (1)	5·35 (8)
C(24)	$\frac{2}{3}$	$\frac{1}{3}$	0·680 (1)	8·70 (12)
Hydroquinone *a* [x_g = 0·1645 (3), y_g = −0·1697 (4), z_g = 0·317 (2), φ = 152·6 (4)°, θ = 149·8 (3)°, ρ = 122·6 (3)°]				
O(1)	0·1075 (7)	−0·0896 (7)	−0·007 (2)	3·56 (3)
C(1)	0·1360 (5)	−0·1297 (5)	0·155 (2)	5·63 (5)
C(2)	0·1156 (7)	−0·2248 (5)	0·139 (2)	3·45 (4)
C(3)	0·1441 (7)	−0·2648 (4)	0·301 (2)	3·28 (4)
C(4)	0·1930 (5)	−0·2098 (5)	0·479 (2)	3·97 (4)
C(5)	0·2134 (7)	−0·1146 (5)	0·495 (2)	3·07 (3)
C(6)	0·1849 (7)	−0·0746 (5)	0·333 (2)	4·25 (4)
O(2)	0·2215 (7)	−0·2498 (7)	0·642 (2)	4·98 (3)
Hydroquinone *b* [x_g = 0·4988 (4), y_g = 0·4983 (5), z_g = −0·018 (2), φ = 153·2 (3)°, θ = 150·6 (2)°, ρ = 121·2 (2)°]				
O(3)	0·4441 (6)	0·5767 (6)	−0·350 (2)	2·77 (2)
C(7)	0·4715 (5)	0·5375 (5)	−0·184 (2)	3·85 (4)
C(8)	0·4509 (6)	0·4422 (5)	−0·195 (2)	4·62 (5)
C(9)	0·4782 (6)	0·4030 (5)	−0·029 (2)	2·29 (3)
C(10)	0·5262 (5)	0·4591 (5)	0·149 (2)	1·32 (2)
C(11)	0·5467 (6)	0·5544 (6)	0·160 (2)	3·16 (3)
C(12)	0·5194 (6)	0·5936 (5)	−0·006 (2)	5·22 (5)
O(4)	0·5535 (6)	0·4199 (6)	0·315 (2)	4·76 (3)
Hydroquinone *c* [x_g = 0·8341 (4), y_g = 0·1677 (5), z_g = 0·654 (2), φ = 149·4 (3)°, θ = 153·0 (2)°, ρ = 123·8 (2)°]				
O(5)	0·7767 (6)	0·2448 (6)	0·324 (2)	3·80 (3)
C(13)	0·8054 (5)	0·2062 (5)	0·489 (2)	3·00 (3)
C(14)	0·7803 (6)	0·1095 (5)	0·484 (2)	3·73 (4)
C(15)	0·8090 (6)	0·0709 (5)	0·649 (2)	3·55 (4)
C(16)	0·8628 (5)	0·1292 (5)	0·819 (2)	2·32 (3)
C(17)	0·8879 (6)	0·2259 (5)	0·824 (2)	4·02 (4)
C(18)	0·8592 (7)	0·2645 (5)	0·659 (2)	3·95 (4)
O(6)	0·8915 (6)	0·0907 (7)	0·984 (2)	4·24 (3)

Notes: (*a*) N(1) was held stationary in the least-squares refinement. The same standard deviation of 0·001 is presumed for the *z* coordinates of all other atoms of the guest molecules. (*b*) The internal orthogonal axial system *X,Y,Z* for each hydroquinone group is defined as follows: The origin is at the molecular centre; the +**X** directions are the O(1)—O(2), O(3)—O(4), O(5)—O(6) vectors for groups *a*, *b*, *c* respectively; the corresponding +**Y** directions are the vectors from the molecular centres to the midpoints of the C(5)—C(6), C(11)—C(12), and C(17)—C(18) bonds; and **Z** is the vector product **X** × **Y**. For definition of the three angular parameters φ, θ, and ρ, see Doedens (1970). The fractional coordinates of the centroid of each group are denoted by x_g, y_g and z_g.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *in hydrogen-bonded* $[OH]_6$ *rings, with estimated standard deviations in parentheses*

Ring *A*, *z* of O(1) − *z* of O(6)$^{\mathrm{i}}$ = +0·009			
O(1)···O(6)$^{\mathrm{i}}$	2·749 (14)	O(6)$^{\mathrm{ii}}$···O(1)···O(6)$^{\mathrm{i}}$	121·0 (5)
O(1)···O(6)$^{\mathrm{ii}}$	2·745 (13)	O(1)···O(6)$^{\mathrm{i}}$···O(1)$^{\mathrm{iii}}$	118·9 (5)
Ring *B*, *z* of O(3) − *z* of O(2)$^{\mathrm{iv}}$ = +0·008			
O(3)···O(2)$^{\mathrm{iv}}$	2·693 (13)	O(2)$^{\mathrm{ii}}$···O(3)···O(2)$^{\mathrm{iv}}$	117·5 (5)
O(3)···O(2)$^{\mathrm{ii}}$	2·805 (13)	O(3)···O(2)$^{\mathrm{iv}}$···O(3)$^{\mathrm{v}}$	122·4 (5)
Ring *C*, *z* of O(5) − *z* of O(4)$^{\mathrm{vi}}$ = +0·009			
O(5)···O(4)$^{\mathrm{vi}}$	2·729 (12)	O(4)$^{\mathrm{vii}}$···O(5)···O(4)$^{\mathrm{vi}}$	120·6 (4)
O(5)···O(4)$^{\mathrm{vii}}$	2·798 (12)	O(5)···O(4)$^{\mathrm{vi}}$···O(5)$^{\mathrm{vii}}$	119·3 (4)

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

(i)	$-y, -1+x-y, -1+z$	(v)	$-x+y, 1-x, z$
(ii)	$1-x+y, 1-x, -1+z$	(vi)	$1-y, x-y, z$
(iii)	$-x+y, -x, z$	(vii)	$1-x+y, 1-x, z$.
(iv)	$-y, x-y, -1+z$		

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* Wallwork & Powell indexed the reflections such that those with $h - k + l \neq 3n$ were weak or absent. Their C and O coordinates (x',y') and the corresponding set (x,y) used here are related by $x \simeq -x' + y'$ and $y \simeq -x'$.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33808 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of parameters contained no peaks higher than 0·7 e Å^{-3}.

The function minimized was $\sum w(|F_o| - |F_c|/\mathrm{ZACH})^2$, with ZACH $= \{C\beta I_o + [1 + (C\beta I_o)^2]^{1/2}\}^{1/2}$, where I_o is the measured integrated intensity on the right scale, and β is Zachariasen's (1963) angular-dependent function evaluated for a crystal sphere with $\mu r = 0{\cdot}30$ (*International Tables for X-ray Crystallography*, 1959). The weighting scheme used was of the form $w = (2A + |F_o| + 2|F_o|^2/B)^{-1}$ with A and B taken as 4·0 and 200·0 respectively. Scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974), and that for H from Stewart, Davidson & Simpson (1965). Calculations were carried out on an ICL-1904A computer with *NUCLS*4 (Ibers, 1969), a highly modified version of *ORFLS* (Busing, Martin & Levy, 1962) permitting the refinement of rigid groups.

The final positional and thermal parameters are listed in Table 1, and hydrogen-bond distances and angles in Table 2. The guest–host van der Waals contacts less than 4 Å are shown in Table 3. The value obtained for the extinction parameter C was 86 (3) × 10^{-7}.

Discussion

An *ORTEP* (Johnson, 1965) plot of the three acetonitrile molecules trapped inside their respective cages is shown in Fig. 1. Electron-density sections through the three guest molecules are shown in Fig. 2.

The main point that emerged from the present analysis is that one of the three symmetry-independent acetonitrile guest molecules points in the opposite direction from the other two as suggested, but not substantiated, by Wallwork & Powell (1956), and is displaced from its 'idealized' position along the z axis. In fact, the disposition of guest molecule c relative to the top $[\mathrm{OH}]_6$ ring of its cage is virtually the same as

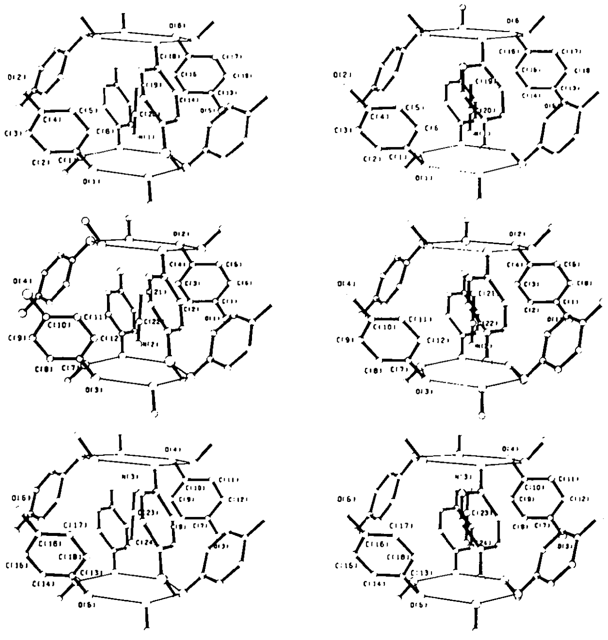

Fig. 1. *ORTEP* plot showing the guest acetonitrile molecules trapped inside their respective cages. For comparison all three cages are viewed in equivalent directions, which are approximately parallel to a vector along a^* towards the cell origin. For each cage the labelled atoms in the guest molecule and the hydroquinone molecule at the lower left corner correspond to the positional parameters in Table 2.

Table 3. *Close guest–host van der Waals separations less than* 4·00 Å

M stands for a hypothetical guest atom located at the centre of the cage. The estimated standard deviations of individual guest–host contacts have the same value of 0·01 Å.

Cage A containing acetonitrile a							
C(19)···O(6)^{ii}	3·59	C(20)···O(1)	3·65	N(1)···O(1)	3·01	$M(A)$···C(6)	3·82
C(19)···O(1)^{i}	3·61	C(20)···O(6)^{iv}	3·71	N(1)···O(6)^{iv}	3·06	$M(A)$···C(15)^{ii}	3·88
C(19)···C(15)^{ii}	3·76	C(20)···C(6)	3·71	N(1)···C(1)	3·69		
C(19)···C(16)^{ii}	3·90	C(20)···C(1)	3·94	N(1)···C(6)	3·80		
Cage B containing acetonitrile b							
C(21)···O(2)^{iii}	3·53	C(22)···O(2)^{v}	3·70	N(2)···O(2)^{v}	3·04	$M(B)$···C(12)	3·82
C(21)···O(3)^{i}	3·62	C(22)···C(12)	3·71	N(2)···O(3)	3·08	$M(B)$···C(3)^{iii}	3·82
C(21)···C(3)^{iii}	3·70	C(22)···O(3)	3·72	N(2)···C(7)	3·71		
C(21)···C(4)^{iii}	3·86	C(22)···C(7)	3·97	N(2)···C(12)	3·79		
Cage C containing acetonitrile c							
C(24)···O(5)	3·54	C(23)···C(9)^{i}	3·71	N(3)···O(4)^{i}	3·08	$M(C)$···C(9)^{i}	3·82
C(24)···O(4)	3·59	C(23)···O(4)^{i}	3·73	N(3)···O(5)^{i}	3·09	$M(C)$···C(18)	3·88
C(24)···C(18)	3·75	C(23)···O(5)^{i}	3·75	N(3)···C(10)^{i}	3·70		
C(24)···C(13)	3·87	C(23)···C(10)^{i}	3·97	N(3)···C(9)^{i}	3·78		

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

(i) $x, y, 1 + z$
(ii) $-1 + x, y, z$
(iii) $x, 1 + y, z$
(iv) $-1 + x, y, -1 + z$
(v) $x, 1 + y, -1 + z$.

that of molecules *a* and *b* with respect to their bottom rings (Fig. 1), and the guest–host contacts are very similar (Table 3). In the recently published X-ray and neutron study of the type II HCl clathrate (Boeyens & Pretorius, 1977), the guest molecule was found to be oriented within the clathration cavity due to weak host–guest interaction, which is unsymmetrical when sampled along [001]. The opposed alignment of the guest molecules in the present type III clathrate is mainly responsible for further lowering of the symmetry of the β-hydroquinone lattice from rhombohedral to trigonal. As compared to the type I and type II lattices, the type III lattice is considerably extended (by *ca* 0·7 Å) in the direction of the *c* axis, thereby resulting in a contraction in the girdle of each cage. If hypothetical guest atoms were to be located at the centres of the three cages, their closest neighbours would be C atoms at distances in the range 3·82–3·88 Å (Table 3). In comparison, the guest S atom in the type I H_2S clathrate is surrounded by O atoms at 3·83 and 3·89 Å, and by C atoms at 4·00 and 4·17 Å (Mak *et al.*, 1976). The acetonitrile molecules thus fit snugly inside the clathration cavities, which are more like prolate spheroids than spheres. Although anisotropic refinement was not carried out, the electron-density distributions (Fig. 2) suggest that the guest molecules have more freedom of movement in the direction of the open centres of the $[OH]_6$ rings.

Since the fixed dimensions of the hydroquinone molecules are based on those found in the H_2S clathrate and in many other crystal structures (Mahmoud & Wallwork, 1975), the positions of the O atoms as deduced from the group refinement may be regarded as reasonably accurate. The hexagonal $[OH]_6$ rings, which involve hydrogen bonding between O(1) and O(6), O(3) and O(2), O(5) and O(4), are puckered in the same way and deviate slightly from exact planarity (Table 2 and Fig. 1). The mean O···O hydrogen-bond length of 2·753 (6) Å is significantly longer than the corresponding distances of 2·700 (3) Å in the H_2S clathrate and 2·70 Å in the HCl clathrate, in accord with the relative stabilities of the three types of β-hydroquinone lattices.

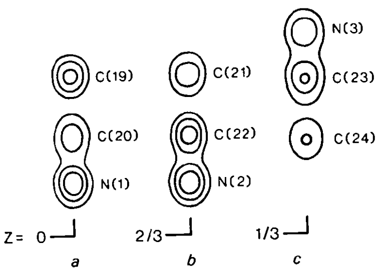

Fig. 2. Electron density sections through the guest molecules *a* at $(0,0,z_a)$, *b* at $(\frac{1}{3},\frac{2}{3},z_b)$, and *c* at $(\frac{2}{3},\frac{1}{3},z_c)$. Contours are drawn at 2·0, 4·0, and 6·0 e $Å^{-3}$. Molecule *c* has the opposite orientation to molecules *a* and *b*. Note that $z_b \simeq \frac{2}{3} + z_a$, and that molecule *c* is displaced from its 'idealized' position at $\frac{1}{3} + z_a$.

We thank Kwok-Cheung Fung for collecting part of the X-ray data.

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