The Crystal Structure of the α Form of Quinol

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The α form of quinol crystallises in the rhombohedral space group $R\bar{3}$ with 54 molecules in each unit cell of hexagonal dimensions $a = b = 38.46(2)$, $c = 5.650(3)$ Å, *i.e.* three times larger than the cell originally described by Caspari. There are therefore 3 molecules in each asymmetric unit. Two of these are involved in forming two interpenetrating, open, hydrogen-bonded cageworks similar to those found in the structure of β-quinol and capable of clathrating small molecules such as CO_2, N_2, and Ar, whereas the third forms double helices consisting of hydrogen-bonded chains of quinol molecules round three-fold screw axes. The cageworks and helices are hydrogen-bonded together in such a way that the interpenetrating cageworks are connected (unlike the β structure) and the two strands of the double helix are connected. The overall α structure is more dense than the β structure and is the stable form at room temperature.

QUINOL (1,4-dihydroxybenzene) is known to form three crystalline modifications, designated α, β, and γ. Of these α is the stable form at room temperature, β is the open cagework from which can clathrate many small molecules [1-3] when crystallised in their presence but which can also be obtained as an empty cagework [4] when crystallised from air-free ethanol,[5] and γ is the form produced by sublimation or by rapid evaporation of a solution in ether.[6] The β and γ forms both change spontaneously into the α form. Before the start of this work in 1946, the crystal structure of the β-quinol clathrates was known [1] and the density of the empty β structure had been calculated [7] as approximately 1.22 g cm^{-3}. It was also known [8] that the density of the α form was about 1.33 g cm^{-3} so it must have a less open structure. On the other hand, it soon became clear [7] that the α structure was also capable of clathrating certain small molecules, such as CO_2. This inter-relation between the α and β structures was emphasised by their common trigonal symmetry and by the similarity of their *c* unit cell dimensions (both *ca.* 5.62 Å). It was therefore possible to propose [7] a trial structure for the α form in which the OH at one end of each quinol molecule forms part of an open hydrogen-bonded cagework of the β type and the OH at the other end is directly hydrogen-bonded in a more compact way to another quinol molecule. Although it transpired, at an early stage in the investigation, that the unit cell was 3 times larger than that found in the early work by Caspari,[8] so that the crystal structure must be rather complex, having 54 molecules in the unit cell and 3 in the asymmetric unit, it was decided to pursue the structure determination in order to elucidate the similarities and differences between the α and β forms.

EXPERIMENTAL

Suitable crystals for *X*-ray diffraction were obtained by subliming a commercial sample of quinol. (The process of sublimation produces needles of the α form as well as plates of the γ form.) The space group and approximate unit cell dimensions and intensities for *hk*0 reflections were determined visually from oscillation and Weissenberg photographs taken with Cu-K_α radiation. A great deal of trial structure and optical diffraction work was carried out for the *c* axis projection using these data. Many years later, a crystal of approximate dimensions 0.6 × 0.2 × 0.1 mm in the form of a flattened, hexagonal prism, elongated along the *c* axis and with $(11\bar{2}0)$ as the most prominent face, was mounted on a Hilger and Watts, computer-controlled, four-circle diffractometer. The cell dimensions were then refined and complete intensity data were collected using Mo-K_α radiation, a scintillation counter, and a θ/2θ scan. The density of the crystals was measured by flotation in mixtures of xylene and bromobenzene.

Crystal Data: HOC_6H_4OH, $M = 110.1$. Rhombohedral. $a = b = 38.46(2)$, $c = 5.650(3)$ Å (hexagonal axes), $U = 7\,238$ Å^3, $D_m = 1.35(1)$ g cm^{-3}, $Z = 54$, $D_c = 1.364$ g cm^{-3}. $F(000) = 3\,132$. Mo-K_α ($\lambda = 0.71069$ Å), $\mu = 1.11$ cm^{-1}. Space group $R\bar{3}$ from systematic absences *hkl* when $-h + k + l \neq 3n$ (centre of symmetry assumed).

After many unsuccessful attempts to solve the structure by the trial structure method (by comparison with the structure of β-quinol), optical diffraction tests seemed to confirm that the β-quinol cagework was an essential component of the α-quinol structure. However, they suggested the wrong orientation for this cagework round the *c* axis, and Fourier and difference Fourier syntheses phased on this suggestion did not show interpretable indications of the rest of the structure. Peaks near the origins of three-dimensional Patterson and sharpened Patterson syntheses calculated from the diffractometer intensity data suggested that there were only three different orientations of quinol molecules in the unit cell and even these were related by the three-fold symmetry axis of the space group. Higher peaks further from the origin were interpreted as representing the accumulations of several equal atom-atom vectors from centrosymmetrically related pairs of quinol molecules, and since one of these peaks in the asymmetric unit corresponded to the expected vector between a centrosymmetrically related pair of molecules across the hydrogen-bonded hexagon of the β-quinol structure, it was used as the basis for the superposition method of interpreting Patterson syntheses. Coincidences of peaks revealed the positions of the centres of all the quinol molecules in the unit cell. With these as a guide, it was possible to propose a reasonable trial structure which reproduced all the known and probable facts about the structure and involved every hydroxy-group in the formation of a hydrogen bond and acceptance of another. Structure factors based on this trial structure (carbon and oxygen atoms only) gave an *R* value of 0.52 which, after 2 cycles of full-matrix, isotropic, least-squares refinement, fell to 0.24. After 4 further cycles of isotropic refinement, a

Fourier difference map revealed the positions of all the hydrogen atoms so they were included in the subsequent refinement with isotropic thermal parameters. Refinement continued in block-diagonal form with anisotropic thermal parameters for non-hydrogen atoms and with a weighting scheme $1/w = 1 + [(|F_o| - B)/A]^2$ where $A = 16.0$, $B = 15.0$ and $|F_o|$ is on the absolute scale. The three strongest reflections were omitted from the least-squares calculations. Convergence occurred at a final R factor of 0.051 for all 1 660 reflections with no parameter shift greater than 0.25 times its standard deviation.

The structure is illustrated in Figures 1 and 2. The final atomic co-ordinates are given in Table 1 and the dimensions of the three independent molecules are shown in Figure 3, both uncorrected and corrected for libration. Averaged values for chemically similar bonds are given in Table 2, compared with earlier determinations of the dimensions of the quinol molecule. Details of the hydrogen bonds are shown in Figure 4. Information about the least-squares plane through each molecule is summarized in Table 3. Thermal parameters and the comparison of observed and final calculated structure factors are in Supplementary Publication No. SUP 22717 (18 pp.).*

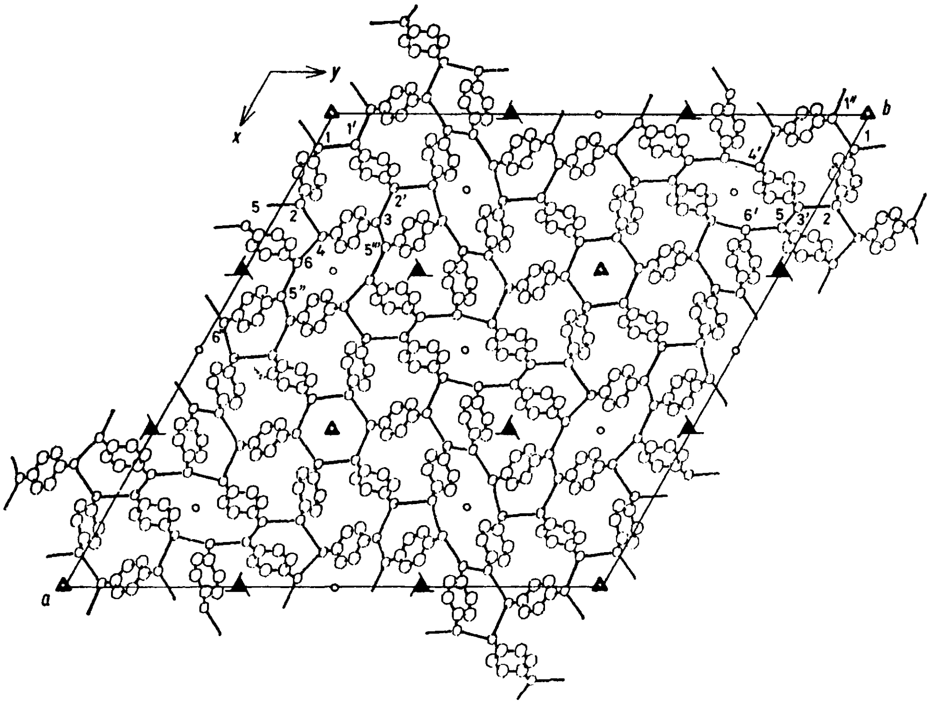

FIGURE 1 Projection of the structure along the z axis, showing the symmetry elements and omitting the hydrogen atoms. The longer lines represent hydrogen bonds and the numbers refer to the oxygen atoms

DISCUSSION

The structure is built up from two units: (a) an open cagework, round the centres of symmetry on the $\bar{3}$ axes, of the same type as that found in β-quinol, and (b) a double helix of chains of quinol molecules round the three-fold screw axes. The cagework can be seen by comparing the heavily outlined portion on the right of Figure 2(b) with the β-quinol cagework drawn in the same orientation in Figure 2(a). As in the β-quinol structure, two such cageworks interpenetrate, and this is shown in Figure 2(b) by the interpenetration of the cageworks drawn with full and broken lines. Each cagework is made up from the quinol molecules containing O(1), O(2) and O(3), O(4), and their symmetry-related molecules. Atoms of the type O(1) form a slightly puckered, hydrogen-bonded hexagon round the origin, each atom being 0.059(3) Å out of the plane in the direction which increases the C–O ··· O angles [to 116.1(3)° on the side where the hydrogen atom is and to 110.9(3)° on the other side] and the O(1)–O(2) axis of the molecule makes an angle of 41.5° with (001), the mean plane of the hexagon. Atoms of the type O(2) do not form complete hexagons, as in the β-quinol structure, but are part of open units consisting of four hydrogen bonds [O(6) ··· O(4) ··· O(2) ··· O(3') ··· O(5)] and a quinol molecule, stretching from O(5) to a repeat of O(6) one unit cell below. The quinol molecules containing O(3) and O(4) complete the sides of the β-quinol-type cagework and their O–O axes are tilted at 43.8° to the (001) plane. Since this cagework has approximately the same dimensions as the β-quinol cagework, it must be capable of clathrating the same small molecules but, since there are 54 quinol molecules per unit cell and the position 0,0,½ (which corresponds to the centre of the cage) is three-fold, the maximum stoicheiometry for α-quinol clathrates must be 1 guest molecule to 18 quinol molecules (compared with 1 : 3 in the β-quinol clathrates). It is known that α-quinol can clathrate CO_2, N_2, and Ar,

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but the stoicheiometries of these complexes are not known. Because of the possibility that the crystal studied might have contained some clathrated air, a Fourier difference synthesis was computed after the refinement had converged. The largest peak had a height of 0.28 electrons Å^{-3} which is about one half of the heights of peaks representing hydrogen atoms in an earlier difference synthesis. Also this peak was at the origin and therefore in the plane of the hydrogen-bonded hexagons at the extremity of the cage and not in a suitable position to represent a clathrated molecule. It can therefore be concluded that the crystal contained a negligible amount of clathrated air.

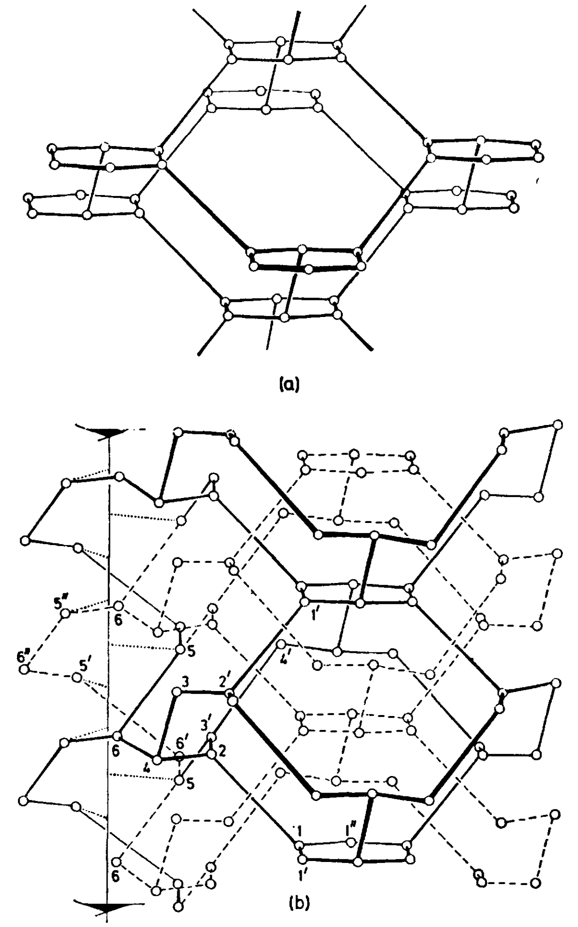

FIGURE 2 Part of the structure viewed approximately along the y axis, showing two interpenetrating cageworks (each $2c$ in height) on the right and the double helix round the three-fold screw axis on the left in (b) compared with the β-quinol cagework in the same orientation in (a). Longer lines represent the O–O molecular axes and shorter lines are hydrogen bonds. Numbers refer to the oxygen atoms

The double helix is formed by the repetition round the three-fold screw axis of molecules containing O(5) and O(6). One continuous chain of hydrogen-bonded quinol molecules stretches from O(6) in one unit cell, through O(5), O(6′), O(5′), O(6″), O(5″) to O(6) two unit cells above the first O(6). Another hydrogen-bonded chain is intertwined with this, separated from it by the c translation and not linked to it at any point on the spiral. Each quinol molecular axis O(6)–O(5) is tilted at 35.8° to the (001) plane. Successive O(5) atoms, or successive O(6) atoms, of each hydrogen-bonded spiral of quinol molecules constitute *alternate* points generated by the 3_1 axis [see Figure 2(b)] and therefore correspond to a 3_2 axis of opposite chirality. Because of this, each quinol spiral has the opposite chirality to the 3_1 screw axis which generates it. There are three left-handed and three right-handed spirals in each unit cell.

In the β-quinol structure, the two interpenetrating cageworks are not linked at any point but, in the α-quinol structure, the two similar cageworks are linked by means of the quinol molecule O(5)O(6). Thus, starting from the point labelled O(3′) in Figure 2(b), on the cagework shown in full lines, the hydrogen bond O(3′) · · · O(5), which, in the β-quinol cagework would continue in the same plane as O(6)O(4)O(2)O(3′) to form a hydrogen-bonded hexagon, here slopes down and, with the quinol molecule sloping down further from O(5) to O(6), links to the incomplete hydrogen-bond hexagon attached to the cagework shown in broken lines. Just as segments of the spirals of quinol molecules link the other-

TABLE 1

Final fractional atomic co-ordinates (with standard deviations in parentheses)

Atom	x/a	y/b	z/c
C(1)	0.102 1(1)	0.013 9(1)	0.174 0(7)
C(2)	0.140 7(1)	0.045 4(1)	0.138 4(7)
C(3)	0.171 0(1)	0.053 0(1)	0.297 7(7)
C(4)	0.162 4(1)	0.028 8(1)	0.494 5(7)
C(5)	0.124 0(1)	−0.003 3(1)	0.529 2(7)
C(6)	0.093 9(1)	−0.010 7(1)	0.369 0(7)
O(1)	0.073 4(1)	0.008 6(1)	0.010 4(5)
O(2)	0.191 20(9)	0.034 25(9)	0.659 4(5)
H(1)	0.053(1)	−0.012(2)	0.022(8)
H(2)	0.146(1)	0.063(1)	0.004(7)
H(3)	0.197(1)	0.076(1)	0.277(6)
H(4)	0.213(1)	0.059(2)	0.637(8)
H(5)	0.118(1)	−0.020(1)	0.676(8)
H(6)	0.067(1)	−0.032(1)	0.397(7)
C(7)	0.237 0(1)	0.174 5(1)	0.128 3(6)
C(8)	0.273 0(1)	0.174 7(1)	0.135 9(7)
C(9)	0.281 3(1)	0.153 8(1)	−0.033 4(7)
C(10)	0.253 5(1)	0.132 6(1)	−0.208 0(6)
C(11)	0.218 1(1)	0.133 2(1)	−0.217 7(7)
C(12)	0.209 8(1)	0.154 2(1)	−0.049 6(7)
O(3)	0.230 06(9)	0.195 21(9)	0.302 2(5)
O(4)	0.259 39(9)	0.109 67(8)	−0.374 1(5)
H(7)	0.209(1)	0.195(1)	0.283(7)
H(8)	0.292(1)	0.187(1)	0.268(7)
H(9)	0.304(1)	0.155(1)	−0.031(6)
H(10)	0.280(2)	0.107(2)	−0.340(9)
H(11)	0.199(1)	0.119(1)	−0.344(8)
H(12)	0.185(1)	0.155(1)	−0.054(6)
C(13)	0.257 5(1)	−0.010 0(1)	0.201 2(6)
C(14)	0.255 9(1)	0.024 2(1)	0.249 7(8)
C(15)	0.275 6(1)	0.057 8(1)	0.106 5(8)
C(16)	0.296 8(1)	0.056 8(1)	−0.088 3(7)
C(17)	0.297 9(1)	0.022 1(1)	−0.137 8(7)
C(18)	0.278 7(1)	−0.010 8(1)	0.008 3(7)
O(5)	0.238 22(9)	−0.043 56(8)	0.340 6(5)
O(6)	0.314 96(9)	0.090 50(8)	−0.229 3(5)
H(13)	0.224(2)	−0.040(2)	0.434(9)
H(14)	0.243(1)	0.025(1)	0.383(8)
H(15)	0.277(1)	0.083(1)	0.145(7)
H(16)	0.334(1)	0.092(1)	−0.295(7)
H(17)	0.314(1)	0.023(1)	−0.275(7)
H(18)	0.278(1)	−0.035(1)	−0.028(6)

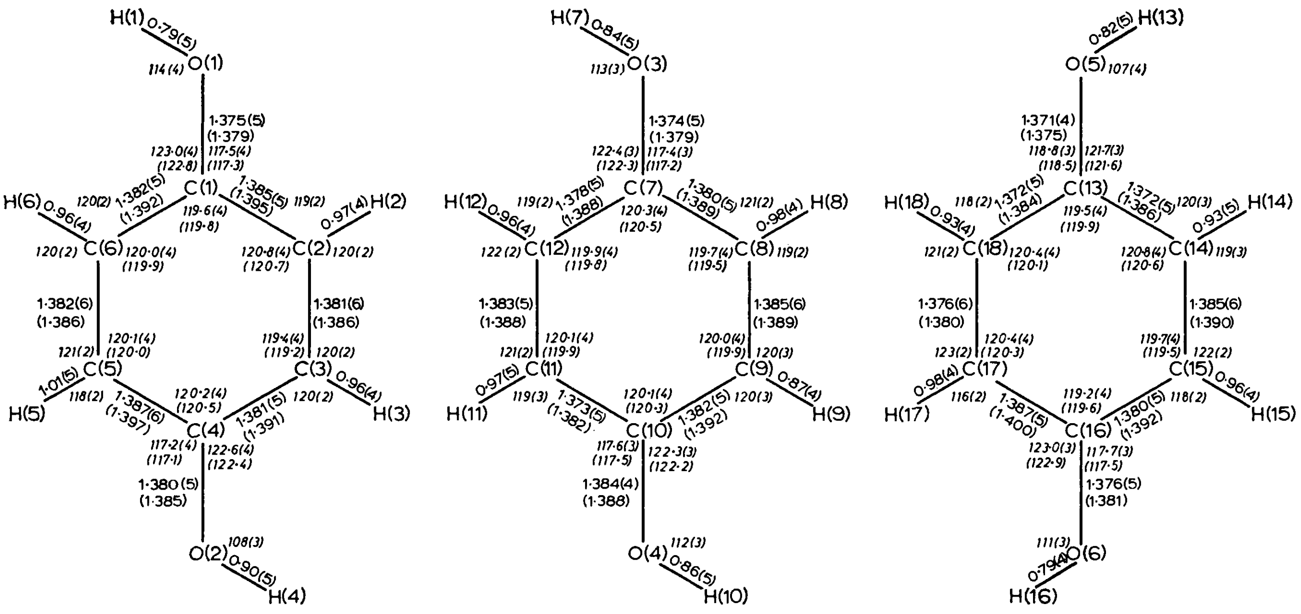

FIGURE 3 Molecular dimensions in Å and degrees before (upper line, with e.s.d.s in parentheses) and after (lower line) correction for librational motion

wise independent cageworks in this way, so the incomplete hexagons of the cagework link the otherwise independent spirals. Thus the spiral represented by broken lines in Figure 2(b) is linked by the incomplete hexagon of hydrogen bonds O(5)O(3′)O(2)O(4)O(6) to the spiral shown in full lines.

Of the three quinol molecules in each asymmetric unit of the structure, two are involved in forming the β-quinol-type cagework and one in forming the double helix. To a rough approximation, then, two-thirds of the structure is cagework of density[7] about 1.22 g cm^{-3} and one-third is helix. The overall density is about 1.36 g cm^{-3} so the density of the helical region must be about 1.43 g cm^{-3}. This is very high for an organic structure consisting only of light atoms (the calculated[8] density for γ-quinol is 1.38 g cm^{-3}) and confirms that this

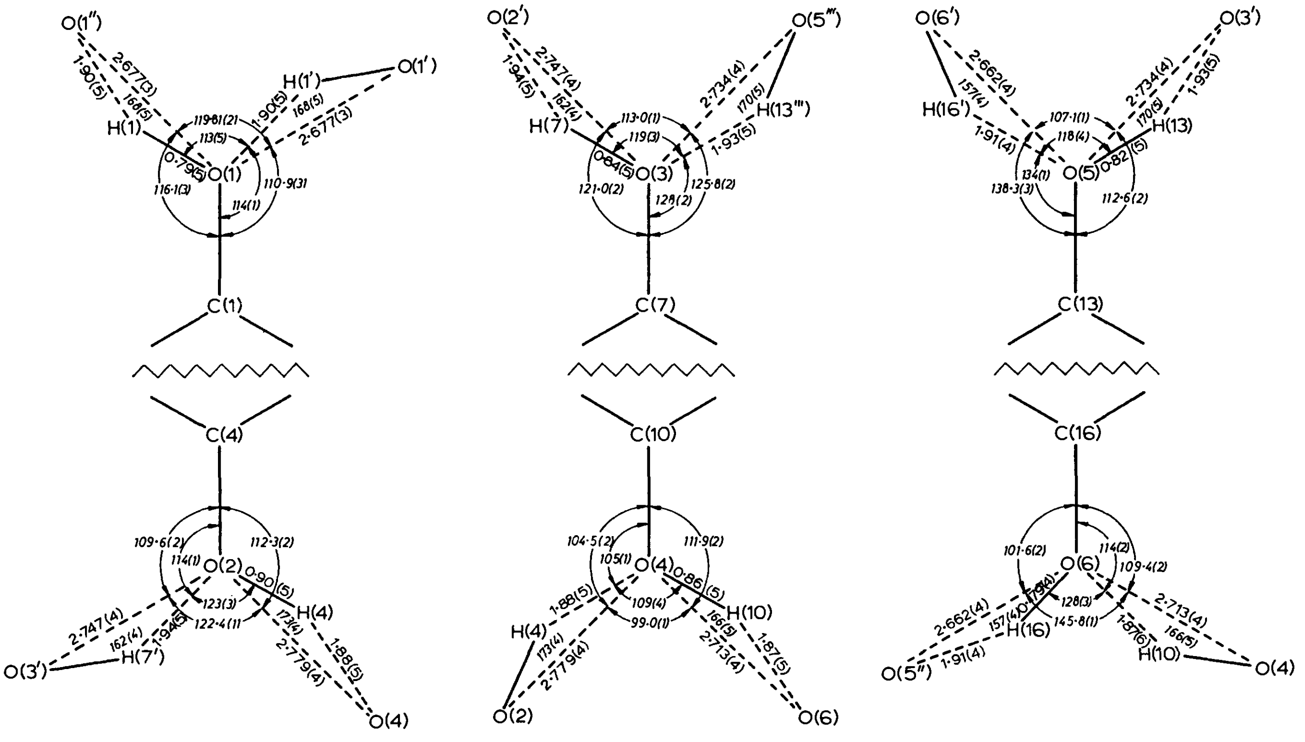

FIGURE 4 Details of the hydrogen-bonding geometry. Distances in Å, angles in degrees and e.s.d.s in parentheses

part of the structure cannot clathrate any guest molecules.

The dimensions of the three separate molecules in the asymmetric unit, shown in Figure 3, differ insignificantly from each other and from previous reasonably accurate determinations of the dimensions of quinol molecules shown in Table 2. The C–C–O angles show the well established inequality due to the steric effects of the phenolic hydrogen atom on one side of the molecule.

TABLE 2

Comparison of average quinol dimensions with previously determined values (Å and degrees). (Figures in parentheses are average standard deviations of single dimensions. Asterisks indicate dimensions corrected for librational motion)

C–C adjacent to C–O	C–C parallel to C–O	C–O	∠CCC at C–O	∠CCC not at C–O	Large ∠CCO	Small ∠CCO	Ref.
1.381(8)	1.387(8)	1.385(8)	120.8(5)	119.6(5)	121.3(5)	117.9(5)	*a*
1.375(6)	1.401(6)	1.392(5)	120.9	119.6	120.5	118.6	6
1.373(6)	1.401(6)	1.394(5)	121.1	119.5	121.4	117.5	
1.391(8) *	1.403(8) *	1.381(7) *	120.5(5)	119.8(5)	122.3(5)	117.2(5)	*b*
1.382(5)	1.382(5)	1.369(5)	120.2(5)	119.8(5)	121.4(5)	118.4(5)	*c*
1.385(5)	1.375(5)	1.373(5)	119.5(5)	120.3(5)	122.5(5)	118.0(5)	
1.378(9)	1.384(9)	1.384(8)	120.2(6)	119.9(6)	121.7(6)	118.3(6)	*d*
1.369(9)	1.397(9)	1.393(7)	121.0(6)	119.5(6)	120.9(6)	118.1(6)	
1.380(3)	1.392(3)	1.383(2)	120.2(2)	119.9(2)	122.1(2)	117.7(2)	*e*
1.387(3)	1.390(3)	1.378(2)	119.7(2)	120.1(2)	122.7(2)	117.6(2)	
1.387(4)	1.386(5)	1.364(4)	119.9(3)	120.1(3)	122.4(3)	117.8(3)	*f*
1.393(4)	1.388(4)	1.390(4)	120.3(3)	119.8(3)	122.3(3)	117.4(3)	*g*
1.388(5)	1.379(5)	1.371(5)	118.9(3)	120.5(3)	123.3(3)	117.8(3)	*h*
1.384(5)	1.382(6)	1.377(5)	119.9(4)	120.1(4)	122.8(4)	117.4(4)	*i*
1.394(5) *	1.386(6) *	1.382(5) *	120.1(4) *	119.9(4) *	122.6(4) *	117.2(4) *	*i*
1.378(5)	1.384(6)	1.379(5)	120.2(4)	119.9(4)	122.4(3)	117.5(3)	*i*
1.390(5) *	1.389(6) *	1.384(5) *	120.4(4) *	119.8(4) *	122.3(3) *	117.3(3) *	*i*
1.378(5)	1.381(6)	1.374(5)	119.4(4)	120.3(4)	122.4(3)	118.2(3)	*i*
1.388(5) *	1.385(6) *	1.378(5) *	119.7(4) *	120.1(4) *	122.3(3) *	118.0(3) *	*i*

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TABLE 3

Details of molecular planes. Δ are deviations from the planes in Å

Plane	Atoms defining plane	Equation of the plane	Mean Δ for atoms defining the plane	Max. Δ for atoms defining the plane
(1)	C(1)—C(6), O(1), O(2)	$23.30x - 31.58y - 2.96z = 1.423$	0.008	−0.016 for O(1)
(2)	C(7)—C(12), O(3), O(4)	$-1.00x - 26.54y + 3.30z = -4.448$	0.021	0.046 for O(4)
(3)	C(13)—C(18), O(5), O(6)	$-29.06x + 3.22y - 3.16z = -8.151$	0.008	0.016 for O(6)
(4)	C(1)—C(6)	$23.45x - 31.63y - 2.94z = 1.453$	0.006	−0.009 for C(4)
(5)	C(7)—C(12)	$-0.89x - 26.69y + 3.27z = -4.457$	0.007	0.011 for C(10)
(6)	C(13)—C(18)	$-29.05x + 3.29y - 3.17z = -8.153$	0.005	0.009 for C(17)

Plane	Significant Δ values for atoms not defining the plane
(1)	C(4) −0.013(4); O(1) −0.016(4); H(4) −0.21(6)
(2)	C(9) −0.025(5); C(11) −0.022(4); O(3) 0.034(3); O(4) 0.046(3); H(10) 0.20(6)
(3)	O(5) 0.011(3); O(6) 0.016(3); H(16) −0.32(5)
(4)	O(1) −0.034(4); H(4) −0.20(6)
(5)	O(3) 0.032(3); O(4) 0.075(3); H(10) 0.24(6)
(6)	O(6) 0.027(3); H(16) −0.31(5)

Dihedral angles (degrees) between planes

(1)–(2)	80.6	(4)–(5)	80.2	(1)–(4)	0.3
(1)–(3)	87.7	(4)–(6)	88.1	(2)–(5)	0.3
(2)–(3)	91.8	(5)–(6)	91.9	(3)–(6)	0.2

It is interesting that the indications, from all the quinol dimensions listed, are that there is no significant difference between the C–C distances parallel to and adjacent to the C–O bond and the ring angles differ only slightly from 120°. This may be due to a combination of the tendency for O to enlarge the ring angle at the point of attachment with the tendency for conjugation to reduce the ring angle.[9,10]

None of the quinol molecules is accurately planar. When least-squares planes are calculated through all the non-hydrogen atoms for each molecule (Table 3), it is found that some of these atoms deviate significantly from their planes. If the ring carbon atoms only are used to define the planes none of them deviates significantly from its plane but most of the oxygen atoms show significant deviations. Each oxygen atom appears to be pulled slightly towards the oxygen atoms to which it is hydrogen-bonded.

The hydrogen-bonded O · · · O distances vary from 2.662(4) Å for O(5) · · · O(6) to 2.779(4) Å for O(2) · · · O(4), with an average of 2.719 Å which is slightly shorter than the average[11] of 2.76 Å for O–H · · · O(H) hydrogen bonds. The H · · · O hydrogen-bond distances vary from 1.87(5) Å for H(10) · · · O(6) to 1.94(5) for H(7) · · · O(2′) with an average of 1.91 Å. The average O–H · · · O angle is 166° and the maximum deviation from linearity (157°) occurs for O(6)–H(16) · · · O(5) suggesting that there might be some steric hindrance between the three quinol molecules related by the three-fold screw axis. This is supported by the fact that O(5) makes the two shortest non-bonded contacts in the structure, 3.234 Å with C(16′) and 3.290 Å with C(17′), and is also consistent with the high density calculated for this region of the structure. Other short contacts are: O(2) · · · C(10′) = 3.399 Å, C(7) · · · C(13′) = 3.360 Å, and O(3) · · · C(18′) = 3.359 Å

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