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The Crystal Structures of the 1:1 Complexes Formed by Hexamethylenetetramine with Hydroquinone and Resorcinol

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Abstract

Structural results for the hydroquinone complex ($C_6H_6O_2.C_6H_{12}N_4$) are compared with those already published. The differences between corresponding atomic fractional coordinates are normally distributed but the e.s.d.'s of these differences appear to have been underestimated by a factor of about 1·6. The resorcinol complex ($C_6H_6O_2.C_6H_{12}N_4$) is structurally closely related to the hydroquinone complex in spite of the fact that it crystallizes in a different crystal system. It has an orthorhombic cell, space group $C2cm$, with a = 10·344 (9), b = 7·080 (3), c = 16·835 (8) Å, Z = 4. The structure was solved by comparison with that of the hydroquinone complex but could only be refined below $R \simeq 0{\cdot}28$ for 398 reflexions by applying constraints to the dimensions of both types of molecule, when R fell to 0·11. Either the structure is disordered or the cell is a subcell corresponding to the superposition of portions of a larger true cell. The resorcinol and hexamethylenetetramine molecules are connected by O—H···N hydrogen bonds of length about 2·7 Å.

Introduction

Polyhydric phenols form complexes with a wide variety of other molecules and ions. Some of these are clathrates in which there is no direct interaction between the phenol and the other molecule but, in most complexes, there is direct interaction in the form of hydrogen-bonding. Some complexes of the latter type formed by hydroquinone (*p*-dihydroxybenzene) have had their crystal structures determined in this laboratory (Lee & Wallwork, 1958; Mahmoud & Wallwork, 1975, 1976). As a continuation of this work we studied (Mahmoud, 1974) two complexes of 1:1 stoichiometry with hexamethylenetetramine (hexamine), one formed by hydroquinone and the other by resorcinol (*m*-dihydroxybenzene) in order to determine the relationship between the hydrogen-bond systems formed by *para*- and *meta*-hydroxyl groups. Although they crystallize in different crystal systems (monoclinic for the hydroquinone and orthorhombic for the resorcinol complex) it was found that these complexes have closely related structures. After the completion of the work, but before its publication, an independent determination of the structure of the hydroquinone complex was published by Mak, Tse, Chong & Mok (1977; henceforward MTCM) based on visual intensities. Our results for the hydroquinone complex are therefore only reported briefly in the form of a comparison with the less precise results of MTCM but the main emphasis in this paper is on the comparison of the structures of the complexes formed by hydroquinone and resorcinol. Crystal data for the resorcinol complex have also been published by Tse, Wong & Mak (1977) but no structural details were given.

Experimental

Transparent plates of the hydroquinone complex were formed when 0·2 g of hexamine in 0·7 ml of ethanol plus 0·3 ml of water were added to 0·15 g of hydroquinone in 0·4 ml of ethanol plus 0·2 ml of water. Similarly shaped crystals of the resorcinol complex were deposited when a solution of 1·5 g of resorcinol in 7 ml of water was mixed, without stirring, with 1·0 g of hexamine in 7 ml of water. In each case the space group and approximate cell dimensions were found from oscillation and Weissenberg photographs and the cell dimensions were refined and intensities measured on a Hilger & Watts, four-circle, computer-controlled diffractometer with Mo $K\alpha$ radiation. Both crystals were mounted so as to rotate about **b** in the plane of the plate. For the hydroquinone complex this corresponded to the longer diagonal (*ca* 0·7 mm) of a parallelogram with the plate face $(10\bar{1})$ having an acute angle of about 85° and bounded by (021), $(0\bar{2}1)$, $(0\bar{2}\bar{1})$ and $(02\bar{1})$ but for the resorcinol complex it corresponded to the longest (*ca* 0·6 mm), unique side of an isosceles triangle opposite an angle of about 80° (bisected by **c**).

On photographs of the resorcinol complex a few weak intermediate spots having $k \simeq n \pm \frac{1}{3}$ occurred

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between the layers or festoons of integral k. However, when a search was made on the diffractometer for these reflexions on the basis of a b cell dimension three times that deduced from the main reflexions, they were found at somewhat different positions from those predicted. It was therefore concluded that the true cell was not related in a simple way to the pseudo cell giving the main reflexions and the extra reflexions were ignored in the subsequent data collection and structure solution and refinement.

Crystal data

Hydroquinone complex: p-HO–C_6H_4–OH.-$(CH_2)_6N_4$, $M_r = 250{\cdot}3$. Monoclinic, $a = 6{\cdot}0362$ (7), $b = 16{\cdot}667$ (2), $c = 6{\cdot}6140$ (6) Å, $\beta = 110{\cdot}79$ (1)°; $U = 622{\cdot}1$ Å^3, $D_m = 1{\cdot}34$ (2), $Z = 2$, $D_c = 1{\cdot}334$ (1) Mg m^{-3}; $F(000) = 268$, Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 0{\cdot}102$ mm^{-1}. Space group $P2_1$ or $P2_1/m$ from systematic absences. Resorcinol complex: m-HO–C_6H_4–OH.$(CH_2)_6N_4$, $M_r = 250{\cdot}3$. Orthorhombic, $a = 10{\cdot}344$ (9), $b = 7{\cdot}080$ (3), $c = 16{\cdot}835$ (8) Å; $U = 1232{\cdot}9$ Å^3, $D_m = 1{\cdot}35$ (1), $Z = 4$, $D_c = 1{\cdot}348$ (3) Mg m^{-3}; $F(000) = 536$, Mo $K\alpha$, $\mu = 0{\cdot}102$ mm^{-1}. Space group $Cmc2_1$, $C2cm$, or $Cmcm$ from systematic absences.

Data were collected for the hydroquinone complex for $\theta \leq 30°$ with a $\theta/2\theta$ scan and a scintillation counter. Of the 1873 reflexions measured, 1475 had significant intensities [$I > 3\sigma(I)$]. The same conditions were used for the resorcinol complex except that the θ limit was 27° and in this case there were only 398 significant intensities out of about 700 measured. Both sets of intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

The solution of both structures was attempted by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). The statistical distribution of E values suggested a centrosymmetric structure for each complex (space groups $P2_1/m$ and $Cmcm$, respectively). For the hydroquinone complex the set of signs having the highest figure of merit gave rise to an E map showing all the non-hydrogen atoms in reasonable positions. For the resorcinol complex a pattern of atoms that was approximately correct was found among the E maps from the five sets of signs with the highest figures of merit but it was not recognized because of the disorder (described below).

The atomic positions and thermal parameters for the hydroquinone complex were refined by full-matrix least-squares analysis. In the later stages the non-hydrogen atoms were assumed to vibrate anisotropically, H atoms were introduced with isotropic temperature factors at positions found from a difference map and a weighting scheme was used, in the form $1/w = 1 + [(|F_o| - B)/A]^2$ with $A = 6{\cdot}0$, $B = 2{\cdot}0$ and $|F_o|$ on the absolute scale. The refinement converged with $R = 0{\cdot}057$ for 1475 reflexions.

After the apparent failure to solve the structure of the resorcinol complex by direct methods, a solution was attempted by the Patterson method, still assuming the space group to be $Cmcm$. Although a possible orientation of the hexamine molecule was found (which later proved to be approximately correct) the possible position deduced for this molecule did not lead to an encouraging R or Fourier synthesis. At this stage, a probable trial structure in the space group $C2cm$ was suggested by Professor D. Rogers on the basis of a comparison with the structure of the hydroquinone complex. This comparison is shown in Fig. 1 in which the hydroquinone complex is redrawn on the basis of an almost orthogonal cell, diagonally related to the true cell, with $\mathbf{a}'(10{\cdot}42$ Å$) = \mathbf{a} - \mathbf{c}$, $\mathbf{b}'(7{\cdot}20$ Å$) = \mathbf{a} + \mathbf{c}$, and $\mathbf{c}'(16{\cdot}67$ Å$) = -\mathbf{b}$ and the origin has been shifted through $-\mathbf{a}'/2 - \mathbf{b}'/4$ in order to bring a centre of symmetry to $x' = \frac{1}{4}$, $y' = 0$, $z' = 0$. If the hexamine molecules are kept in the same positions and the centrosymmetric hydroquinone molecules are replaced by resorcinol molecules lying on twofold axes a satisfactory trial structure is produced which is hydrogen-bonded in a similar way to the hydroquinone complex. The hexamine orientation is consistent with the Patterson function.

This trial structure gave an encouraging R but a Fourier synthesis phased on the corresponding structure factors showed that the resorcinol molecule was disordered by reflexion about a plane perpendicular to x at $x \simeq \frac{1}{4}$. During the subsequent refinement of this structure, monitored by difference syntheses, it became clear that the hexamine molecule was also disordered by approximate reflexion across the same pseudo mirror plane. The refinement was therefore continued

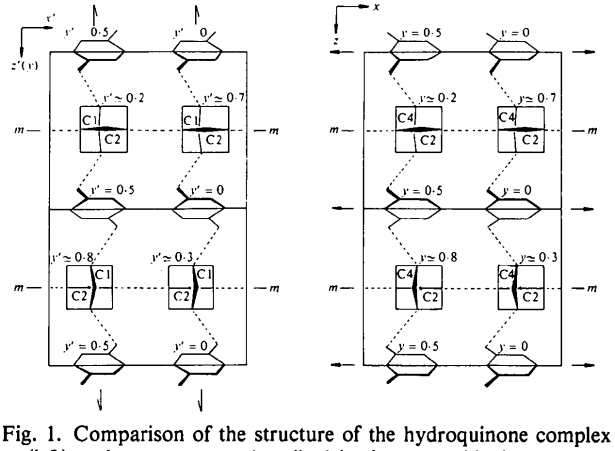

Fig. 1. Comparison of the structure of the hydroquinone complex (left), redrawn on axes described in the text, with the structure proposed for the resorcinol complex (right).

with two half-weight molecules of each type but R would not drop below 0·26 and the resultant molecules were rather distorted. Because of the approximate reflexion of both molecules in the pseudo mirror plane, an attempt was made to refine the structure in the space group *Cmcm* with half-weight molecules related exactly by the true mirror plane perpendicular to x (which takes the place of the pseudo mirror plane in *C*2*cm*) but poorer R factors were obtained. Eventually a satisfactory refinement of two half-weight molecules in *C*2*cm* was achieved by applying constraints to the dimensions of both molecules. The two half-weight resorcinol molecules were constrained to have C–C = 1·40 Å with an e.s.d. of 0·02 Å, C–C–C = 120° with an e.s.d. of 2°, the two C–O distances equal to each other within 0·02 Å and C–C–O angles equal to each other within 2°. For hexamine, all C–N distances and C–N–C and N–C–N angles were constrained to their separate means with e.s.d.'s of 0·02 Å, 2° and 2°, respectively. With these constraints, the refinement continued (with isotropic thermal parameters and unit weights throughout) and converged at R = 0·11 for 398 reflexions. Finally, the occupation factors of the atomic positions, previously assumed to be all equal to 0·5, were refined, but the final values did not differ significantly from 0·5 and there was an insignificant change in R. A difference synthesis calculated from the final structure factors showed seven small residual peaks but they did not form a chemically significant pattern and must be ascribed to errors in the observations and in the model.

The computer programs used were the XRAY system edited by J. M. Stewart, F. A. Kundell and J. C. Baldwin and the *CRYSTALS* system by J. R. Carruthers and J. S. Rollett. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates for the resorcinol complex are listed in Table 1.*

Projections of the structure of the resorcinol complex along x and y are shown in Fig. 2 and approximate bond lengths and angles for the resorcinol complex in Fig. 3.

Comparison of the structural results for the hydroquinone complex with the previous determination and with those for the resorcinol complex

The atomic coordinates, bond lengths and bond angles for the hydroquinone complex obtained in the present

* The atomic coordinates, bond lengths and angles for the hydroquinone complex and the thermal parameters for both complexes have been deposited, together with the comparison of observed and final calculated structure factors for both structures, with the British Library Lending Division as Supplementary Publication No. SUP 34553 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates in the resorcinol–hexamine complex*

	x	y	z
C(1)	0·169 (3)	0·173 (4)	0·177 (1)
C(2)	0·300 (*)	0·400 (4)	0·25
C(3)	0·407 (4)	0·146 (5)	0·178 (1)
C(4)	0·280 (5)	−0·082 (2)	0·25
C(5)	0·429 (5)	0·5	0
C(6)	0·362 (5)	0·640 (3)	0·039 (2)
C(7)	0·227 (4)	0·631 (3)	0·045 (1)
C(8)	0·159 (5)	0·5	0
C(11)	0·131 (4)	0·140 (3)	0·180 (1)
C(12)	0·247 (3)	0·390 (3)	0·25
C(13)	0·369 (4)	0·158 (2)	0·177 (1)
C(14)	0·256 (6)	−0·093 (4)	0·25
C(15)	0·099 (5)	0·5	0
C(16)	0·167 (4)	0·646 (3)	0·037 (2)
C(17)	0·303 (4)	0·652 (2)	0·034 (1)
C(18)	0·372 (5)	0·5	0
N(1)	0·173 (2)	0·297 (4)	0·25
N(2)	0·282 (4)	0·040 (2)	0·178 (1)
N(3)	0·413 (3)	0·267 (5)	0·25
N(11)	0·131 (3)	0·262 (3)	0·25
N(12)	0·253 (4)	0·029 (3)	0·178 (1)
N(13)	0·371 (3)	0·280 (3)	0·25
O(1)	0·155 (4)	0·758 (3)	0·086 (1)
O(11)	0·375 (4)	0·793 (2)	0·067 (1)

* The x coordinate of C(2) was fixed, in order to fix the origin in the non-centrosymmetric space group, so it has no e.s.d.

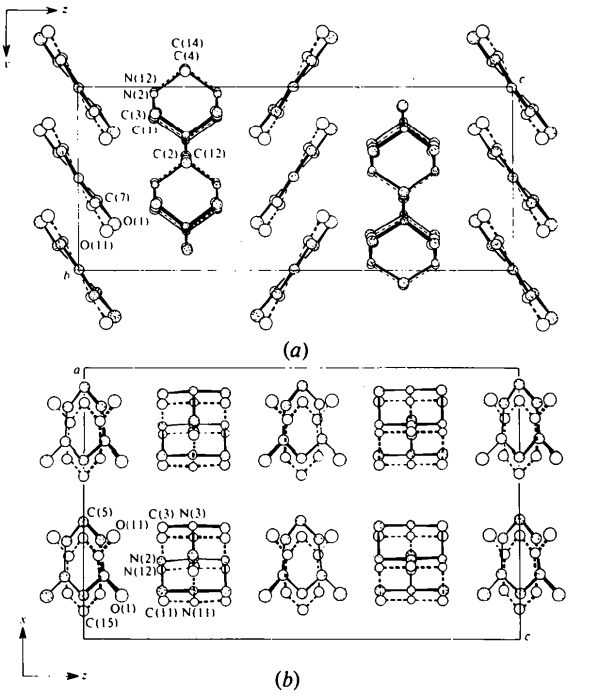

Fig. 2. Projection of the structure of the resorcinol complex along (*a*) x and (*b*) y. Open and stippled circles represent the two disordered positions for each molecule.

work are generally in good agreement with those obtained by MTCM. A quantitative comparison has been carried out by plotting against u the proportion P of deviates $\leq u$ (*i.e.* the empirical distribution function), where the deviate in each case is the algebraic difference between the values obtained in the two independent determinations divided by the e.s.d. of that difference, *i.e.*

$$\text{deviate} = (q_1 - q_2)/[\sigma^2(q_1) + \sigma^2(q_2)]^{1/2},$$

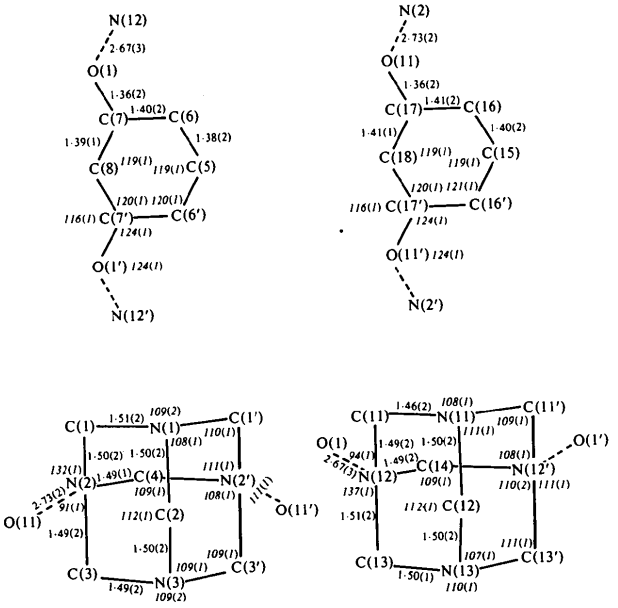

Fig. 3. Bond lengths (Å) and angles (°) for the resorcinol–hexamine complex. Angles not shown are: C(4)–N(2)···O(11) = 101 (1)°, C(14)–N(12)···O(1) = 94 (1)°.

where q_1 is the fractional atomic coordinate or bond length or bond angle found in the present work, q_2 is the same quantity found by MTCM, $\sigma(q_i)$ is the e.s.d. of q_i derived from the least-squares matrix.

These plots of P (on a probability scale, which gives a linear plot for a normal distribution) are shown separately for fractional atomic coordinates, bond lengths and bond angles in Fig. 4(*a*), (*b*) and (*c*), respectively. In each case the corresponding linear plot for a standard normal distribution is also shown. The plots are all approximately linear but the slope is less than that for a standard normal distribution suggesting that the e.s.d.'s have been underestimated (by a factor of ~1·62 for coordinates, ~1·2 for lengths and ~1·3 for angles).* This underestimation is unexpected, since in each case the refinement used a full-matrix procedure. Even so, it is encouraging that none of the differences $(q_1 - q_2)$ falls outside the range -3σ to $+3\sigma$. The linear plots for coordinates and angles pass nearly through the expected median point for $u = 0$, but for bond lengths the median point occurs at about $u = -1{\cdot}0$, indicating a consistent tendency for MTCM bond lengths to be 1σ greater than those found in the present work. This is due to the larger cell dimensions reported by MTCM, which differ from the dimensions found in the present work by about the same proportion as a typical e.s.d. bears to a typical bond length.

One interesting feature of the hydroquinone molecule emerges as a result of the greater precision of the present determination. It appears to be not quite planar.

* *Note added in proof:* Replotting according to the method in *International Tables for X-ray Crystallography* (1974) gives similar results except that the factor for angles is ~1·5.

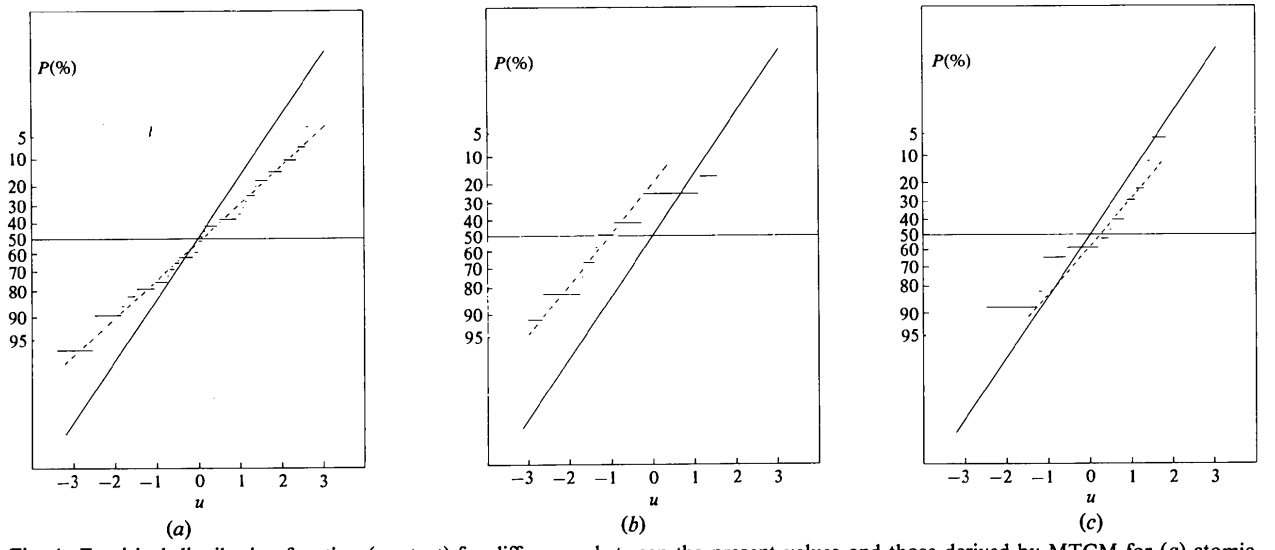

Fig. 4. Empirical distribution function (see text) for differences between the present values and those derived by MTCM for (*a*) atomic coordinates, (*b*) bond lengths and (*c*) bond angles for the hydroquinone complex. Full line = standard normal distribution; broken line = best linear plot for the observed distribution.

The O atom is 0·037 Å out of the plane of the ring, in a direction away from the hexamine molecule to which it is hydrogen-bonded.

The structure of the resorcinol complex is closely related to that of the hydroquinone complex, as may be seen from the confirmation in Fig. 2(*b*) of the comparison between the two structures shown in Fig. 1. In each case, both hydroxyl groups of the phenolic molecules are hydrogen-bonded to N atoms of hexamine molecules on either side. In the hydroquinone complex the hydrogen bonds are of length 2·738 (2) Å [present determination; 2·734 (4) Å, MTCM] and the C—O···N angle is 122·1 (2)° (present determination; not quoted by MTCM). This O···N distance is less than the average (2·78 Å) found for O—H···N hydrogen bonds (Wallwork, 1962). In the resorcinol complex there is some ambiguity as to which of the two disordered resorcinol molecules is hydrogen-bonded to which of the two disordered hexamine molecules. On the basis that the hydrogen bonds are expected to be similar in length to those in the hydroquinone complex the most likely pairing is O(1)···N(12) at 2·67 (3) Å with the C—O···N angle 124 (1)° and O(11)···N(2) at 2·73 (2) Å with the C—O···N angle 124 (1)°. [The alternative would be O(1)···N(2) = 2·85 (3) Å, C—O···N = 119 (1)° and O(11)···N(12) = 2·81 (2) Å, C—O···N = 117 (1)°.] In the hydroquinone complex the O···N line is 22° from being perpendicular to the C(1), C(3), C(4) plane and the H···N is 15° from this perpendicular, so the hydrogen bond is almost collinear with the lone-pair sp^3 hybrid orbital of the N atom. In both structures, the hydrogen bonds link alternate phenolic and hexamine molecules into zigzag chains along *y* in the hydroquinone and along *z* in the resorcinol complex. Another fairly short contact in the hydroquinone complex is H(9)···O(1) = 2·36 (2) Å between hydroquinone molecules adjacent in the *z* direction. This may represent a C—H···O hydrogen bond because it is appreciably less than the sum (2·6 Å) of the van der Waals radii for H and O and the angle at H is 157 (3)°. The C···O distance is 3·305 (3) Å and the corresponding contacts in the resorcinol complex are C(5)···O(1) = 3·24 (3) and C(15)···O(11) = 2·96 (3) Å which are also short enough to represent C—H···O hydrogen bonds. The only difficulty in ascribing these contacts to hydrogen bonds in the resorcinol complex is that the C—H bonds involved both lie on a twofold axis and so make two equal contacts each. This would mean that the hydrogen bonds are bifurcated unless the twofold axis corresponds to an average of two further disordered molecules which are orientated away from, and on either side of, this axis so as to point each C—H bond more directly towards one O atom. Apart from the possible C—H···O hydrogen bonds the zigzag chains of alternate hexamine and phenolic molecules are held together by van der Waals forces.

The dimensions of the hexamine molecules in the resorcinol complex, though only approximately determined, appear to be normal. The geometry of the resorcinol molecules cannot be discussed since their dimensions were so closely determined by the constraints applied during the refinement, apart from the C—O distances (1·36 Å) and the C(6)—C(7)—O(1) and C(16)—C(17)—O(11) angles (124°) which were merely constrained to be equal between the two disordered molecules. These may be compared with C—O distances 1·359 (5) and 1·370 (4) Å in a neutron study of resorcinol itself (Bacon & Jude, 1973), 1·378 (8) Å in the *p*-benzoquinone complex (Ito, Minobe & Sakurai, 1970) and 1·351 and 1·403 Å (σ = 0·005 to 0·009) in the progesterone complex (Dideberg, Dupont & Campsteyn, 1975) and the corresponding CCO angles 123·3 (6) (Ito, Minobe & Sakurai, 1970) and 117·9 and 123·2° (Dideberg, Dupont & Campsteyn, 1975). The atoms of the resorcinol molecules are not located with sufficient accuracy to permit discussion of their planarity but they are approximately planar in both disordered orientations. The maximum deviation from the average molecular planes is 0·06 Å for C(6).

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