has a ring with two short carbon double bonds (1·322 Å) and four carbon single bonds (1·477 Å)].

To get an impression of how reliable the bond lengths were, a structure analysis of the dihydrate of chloranilic acid was made. Results from this determination are given in the next paper.

The perpendicular distances from the atoms in the molecule to a plane through C(1), C(3), and C(2′) are given in Table 3. From this Table it is concluded that the molecule is planar within our limits of accuracy.

Table 3. *Out-of-plane displacements*

	From plane through C(1), C(3), C(2′)	From plane through origin and parallel to the plane in the previous column
C(1)	0·000 Å	−0·007 Å
C(2)	0·014	0·007
C(3)	0·000	−0·007
C(1′)	0·014	0·007
C(2′)	0·000	−0·007
C(3′)	0·014	0·007
Cl	0·008	0·001
O(1)	−0·020	−0·027
O(2)	−0·024	−0·031
Cl′	0·006	−0·001
O(1′)	0·034	0·027
O(2′)	0·038	0·031

The crystal structure

The molecules are stacked in columns along the lines 0*y*0, $\frac{1}{2}y0$, *etc.* These columns are viewed end on in Fig. 2. The molecules within each stack are parallel, and the perpendicular distance between neighbour molecules is 3·26 Å. The closest approach of acid molecules belonging to different columns is the hydrogen bonds of 2·769 Å between, for example O(1) and O(2‴). The chloranilic acid molecules are linked by these bonds to ribbons extending throughout the structure. Other short contacts are found between O(1) molecules related by the screw axis and between chlorine atoms related by a symmetry centre. These and a few more intermolecular distances are given in Fig. 2.

It is a pleasure to thank P. Mondrup, Finn Larsen and J. Danielsen for providing structure-factor and Fourier programs and to acknowledge the constant encouragement of Prof. A. Tovborg Jensen (during very many years). Most calculations were made possible by a grant from the Carlsberg Foundation. The final calculations were carried out at NEUCC Lyngby.

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The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones. II. Chloranilic Acid Dihydrate

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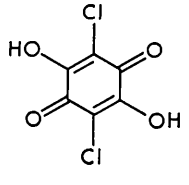
(*Received* 18 *July* 1966)

The structure of chloranilic acid dihydrate has been determined by use of three-dimensional data. The cell dimensions are $a=8{\cdot}617$, $b=10{\cdot}386$, $c=5{\cdot}203$ Å, $\beta=104{\cdot}8°$. The space group is $P2_1/c$ and $Z=2$. The geometry of the carbon ring system is similar to that of *p*-benzoquinone. There are, however, carbon–carbon single bonds of two lengths (1·446 and 1·512 Å), and there are two kinds of carbon–oxygen distance (1·229 and 1·317 Å) corresponding to C=O and C–OH bonds. The carbon ring is planar, but the chlorine and oxygen atoms are displaced from the ring plane by distances from 0·013–0·040 Å. The hydrogen atoms have been located.

Introduction

The structure determination of chloranilic acid dihydrate (I) was made to provide a check on the molecular structure found in the anhydrous acid.

(I)



, 2 H_2O

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Experimental

Chloranilic acid dihydrate was prepared by a method described by Graebe (1891). It was recrystallized from water. The crystals are short red needles, with the *c* axis along the needle direction.

The following lattice constants were determined from powder photographs taken in a Guinier–Hägg camera:

$$a=8·617,\ b=10·386,\ c=5·203\ \text{Å}\ (\sigma\ \text{all}\ 0·001\ \text{Å});$$
$$\beta=104·8°\ (\sigma\ 0·01°)\ .$$

The molecular weight of chloranilic acid dihydrate is 245·02. With the observed lattice constants, assuming two molecules per unit cell, the calculated density is 1·806 g.cm^{-3}. The observed density determined by flotation is 1·800 g.cm^{-3}.

From the crystals listed in Table 1 equi-inclination Weissenberg diagrams were taken. A long and a short exposure, using multiple-film technique, were taken of each layer. Intensities were estimated visually. Only film halves with extended spots were measured. The intensities were corrected for spot extension and converted to structure factors. No correction for absorption was made.

Table 1. *The size of crystals used for intensity data collection*

Crystal	Size	Data collected
c(2)	0·29 × 0·13 × 0·08 mm	*hk*0 → *hk*3
b(4)	0·13 × 0·10 × 0·08 mm	*h*0*l* → *h*4*l*
b(5)	*	*h*5*l*

* *b*(5) was about the same size as *b*(4). It was lost during experiments.

A total of 692 reflexions were estimated, of which 256 were observed from two crystals. Within the limiting sphere for copper radiation there are 1031 reflexions. Of the 339 unobserved reflexions, 180 were too weak to be observed and 159 were not covered by the experiments. The residual between the 256 structure factors estimated from two crystals was 0·076. This residual gives some measure of the reliability of the intensity estimates.

The trial structure

In the Weissenberg diagrams the following conditions were observed to limit the reflexions:

hkl	no conditions
*h*0*l*	$l=2n$
0*kl*	$k=2n$;

the space group $P2_1/c$ (no. 14) was therefore assumed.

Since there are two acid molecules in the unit cell, they must lie on special positions, and hence be centrosymmetric. The positions 0,0,0 and 0,$\frac{1}{2}$,$\frac{1}{2}$, were chosen.

The *x* and *y* coordinates of the chlorine atoms were easily found from the Patterson projection along [001]. With signs from these chlorine positions alone the electron density projected along the [001] direction was calculated. This and two subsequent projections revealed all the other atoms (except hydrogen atoms).

The *x* and *y* coordinates were refined by Bhuiya & Stanley's (1963) minimum residual method. Three calculations were made, the first with steps 0·01, the second with 0·005, and the third with steps 0·001. The *R* index was 0·30 before these calculations and 0·13 after. Fig. 1 is an electron-density projection based on signs from the third Bhuiya–Stanley calculation.

From the result of the [001] projection and from a knowledge of the approximate geometry of the chloranilic acid molecule a three-dimensional trial structure was worked out. The *z* coordinates of this structure were refined independently of all other parameters by Bhuiya & Stanley's method. Two calculations were made, the first with steps 0·01, the second with steps 0·005. The *R* index was 0·24 before and 0·17 after these calculations.

The final refinement

The structure was now refined by least squares with the Busing, Martin & Levy (1962) ORFLS program. The quantity minimized was $\Sigma\ w(F_o-F_c)^2$. The weighting scheme was that introduced by Hughes (1941) with

Table 2. *Final atomic parameters and standard deviations*

For the numbering of atoms see Figs. 1 and 2.

(*a*) Positional parameters (× 10^4)

	x	σ(*x*)	*y*	σ(*y*)	*z*	σ(*z*)
Cl	2188	2	1420	1	4972	2
C(1)	952	6	673	5	2262	10
C(2)	8290	6	133	5	9331	10
C(3)	9350	6	832	5	1679	10
O(1)	6832	4	278	4	8916	8
O(2)	8651	5	1578	4	3100	9
O(*w*)	5529	5	1843	4	2605	9

Table 2 (*cont.*)

(*b*) Thermal parameters (in the form $-\{\frac{1}{4}\ \Sigma\Sigma\ B_{ij}h_ih_ja_i{}^*a_j{}^*\}$)

	B_{11}	$\sigma(B_{11})$	B_{22}	$\sigma(B_{22})$	B_{33}	$\sigma(B_{33})$	B_{12}	$\sigma(B_{12})$	B_{13}	$\sigma(B_{13})$	B_{23}	$\sigma(B_{23})$
Cl	2·61	0·06	3·34	0·06	2·31	0·05	−0·55	0·04	0·36	0·04	−0·54	0·05
C(1)	2·70	0·19	2·42	0·20	2·28	0·19	−0·32	0·16	0·59	0·15	−0·24	0·17
C(2)	2·49	0·19	2·84	0·22	2·50	0·19	−0·15	0·16	0·50	0·16	0·31	0·18
C(3)	2·74	0·20	2·69	0·21	2·37	0·18	−0·08	0·16	0·82	0·16	0·22	0·18
O(1)	2·20	0·14	4·05	0·20	3·59	0·18	0·05	0·12	0·57	0·13	−0·76	0·16
O(2)	2·93	0·16	3·56	0·19	3·27	0·16	0·15	0·13	1·02	0·13	−1·06	0·16
O(*w*)	2·71	0·15	3·67	0·19	3·87	0·19	−0·23	0·13	1·31	0·13	−0·38	0·15

$$w = |F_o|^{-2} \quad \text{for} \quad |F_o| > 4|F_{\min}|$$

and

$$w = 0{\cdot}0625\ |F_{\min}|^{-2} \quad \text{for} \quad |F_o| < 4|F_{\min}|\ .$$

In the calculations the positional parameters, anisotropic temperature parameters, and one scale factor were adjusted. The hydrogen atoms were not included. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962).

Three cycles were carried out. The R index before the first cycle was 0·18, after the first cycle it was 0·078, and after the second and third cycles it was 0·074. In the last cycle the atomic parameters changed less than 0·00002. The final parameters are given in Table 2.

The hydrogen atoms

The position of the hydrogen atoms was found from a three-dimensional difference synthesis. This was calculated with the reflexions for which $\sin\theta/\lambda$ was smaller than 0·40. In Table 3, the coordinates and the electron densities of the three highest peaks in the difference Fourier are given. Besides the peaks in Table 3 there was one of 0·35 e.Å^{-3} halfway between two chlorine atoms. No other peak exceeded 0·25 e.Å^{-3}. When three hydrogen atoms were included in the structure factor calculations at the positions of Table 3 and with isotropic temperature factors of 3·6 Å^2, R fell to 0·068. A list of calculated and observed structure factors is available on request from the author.

Table 3. *The positions of hydrogen atoms, and the electron density at these positions*

	x	y	z	ϱ (e.Å^{-3})
H(1)	0·49	0·12	0·30	0·44
H(2)	0·54	0·22	0·42	0·48
H(3)	0·75	0·14	0·25	0·43

The standard deviations on bond lengths

The standard deviations on positional parameters in Table 2 are given in fractions of the cell edges. The average standard deviation in Å for carbon and oxygen atoms is $\sigma(\mathrm{C,O}) = 0{\cdot}005$ Å for all coordinates. This gives a standard deviation on bond lengths σ(C–C

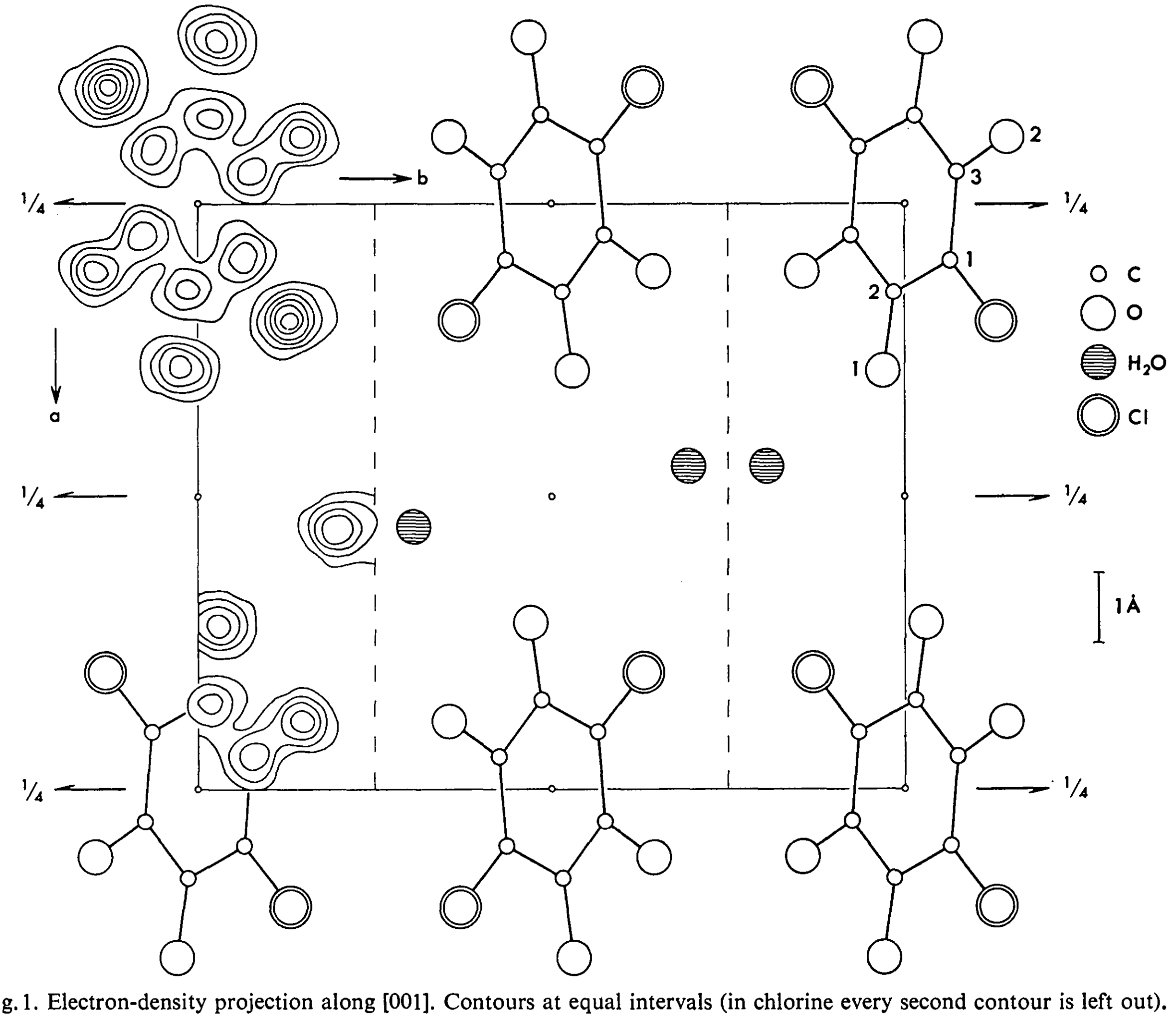


Fig. 1. Electron-density projection along [001]. Contours at equal intervals (in chlorine every second contour is left out).

C–O) = 0·007 Å [σ(Cl–C) will be lower], hence differences in bond lengths greater than 0·02 Å should be significant.

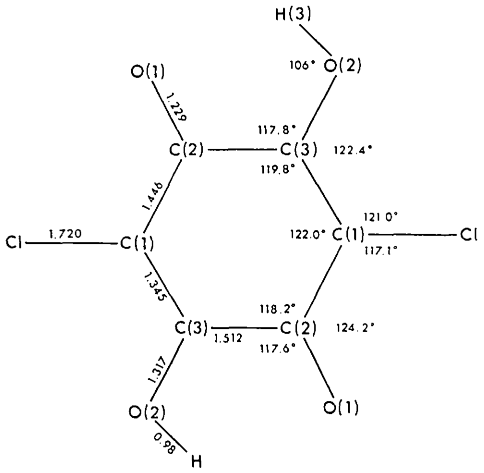


Fig. 2. Intramolecular distances (Å) and angles in the chloranilic acid molecule.

The molecular structure

The intramolecular distances and angles are shown in Fig. 2, and in Table 4 they are compared with the corresponding set of distances and angles determined from crystals of the anhydrous acid (part I). The agreement between the two sets is good. The two determinations show with certainty that the carbon–carbon single bonds differ in length.

Before the molecular geometry is discussed in detail attention is drawn to a point on which the two determinations do not agree, *viz.* with respect to planarity. The out-of-plane displacements for atoms in the molecule are given for both determinations in Table 5. While the carbon atoms within the limits of accuracy are in the same plane, most exocyclic atoms are out of this plane, and it will be seen that these deviations are not similar for the two determinations. A better agreement on this point would have been expected (we believe) if these displacements were typical for the chloranilic acid molecule.

In Fig. 3, mean bond lengths from the two structure determinations of chloranilic acid are compared with bond lengths in some related molecules. The ring

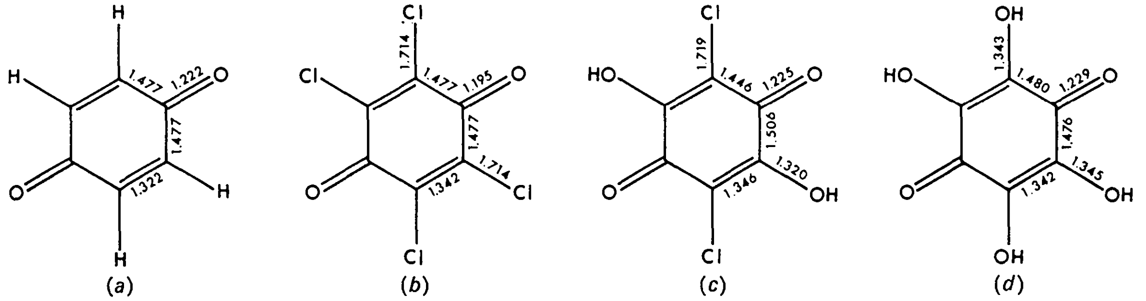


Fig. 3. Bond lengths in (*a*) *p*-benzoquinone (Trotter, 1960), (*b*) chloranil (Chu, Jeffrey & Sakurai, 1962), (*c*) chloranilic acid (mean values from the anhydrous acid and from the dihydrate) and (*d*) tetrahydroxy-*p*-benzoquinone (Klug, 1965).

Table 4. *Bond lengths and angles in the chloranilic acid molecule, with standard deviations in brackets*

Bonds and angles	From this determination the dihydrate	From the anhydrous acid	Mean
C(1)—Cl	1·720 (0·005) Å	1·717 (0·005) Å	1·719 Å
C(1)—C(2)	1·446 (0·008)	1·445 (0·006)	1·446
C(2)—C(3)	1·512 (0·007)	1·501 (0·007)	1·506
C(1)=C(3)	1·345 (0·008)	1·346 (0·006)	1·346
C(2)=O(1)	1·229 (0·006)	1·222 (0·004)	1·225
C(3)—O(2)	1·317 (0·007)	1·322 (0·005)	1·320
O(2)—H(3)	0·98	0·90	
O(*w*) -H(1)	0·92		
O(*w*) -H(2)	0·94		
Cl——C(1) -C(2)	117·1° (0·4°)	117·9° (0·3)	117·5°
Cl——C(1) -C(3)	121·0 (0·4)	120·9 (0·4)	120·9
C(2)—C(1) -C(3)	122·0 (0·5)	121·2 (0·5)	121·6
C(1)—C(2) -O(1)	124·2 (0·4)	123·8 (0·4)	124·0
C(1)—C(2) -C(3)	118·2 (0·5)	117·9 (0·3)	118·1
C(3)—C(2) -O(1)	117·6 (0·5)	118·2 (0·4)	117·9
C(1)—C(3) -C(2)	119·8 (0·4)	120·6 (0·4)	120·2
C(2)—C(3) -O(2)	117·8 (0·5)	116·6 (0·4)	117·2
C(1)—C(3) -O(2)	122·4 (0·5)	122·7 (0·4)	122·5
C(3)—O(2) -H	106	114	
H(1)—O(*w*)-H(2)	83		

Table 5. *Out-of-plane displacements* (Å)

	I From plane through C(1), C(2), C(3′)	II From plane through origin and parallel to the plane in column I	III Similar to column II but from anhydrous chloranilic acid
C(1)	0·000	−0·005	−0·007
C(2′)	0·009	0·005	0·007
C(3′)	0·000	−0·005	−0·007
C(1′)	0·009	0·005	0·007
C(2)	0·000	−0·005	−0·007
C(3)	0·009	0·005	0·007
Cl	−0·036	−0·040	0·001
O(1)	−0·028	−0·033	−0·027
O(2)	0·018	0·013	−0·031
Cl′	0·045	0·040	−0·001
O(1′)	0·038	0·033	0·027
O(2′)	−0·008	−0·013	0·031

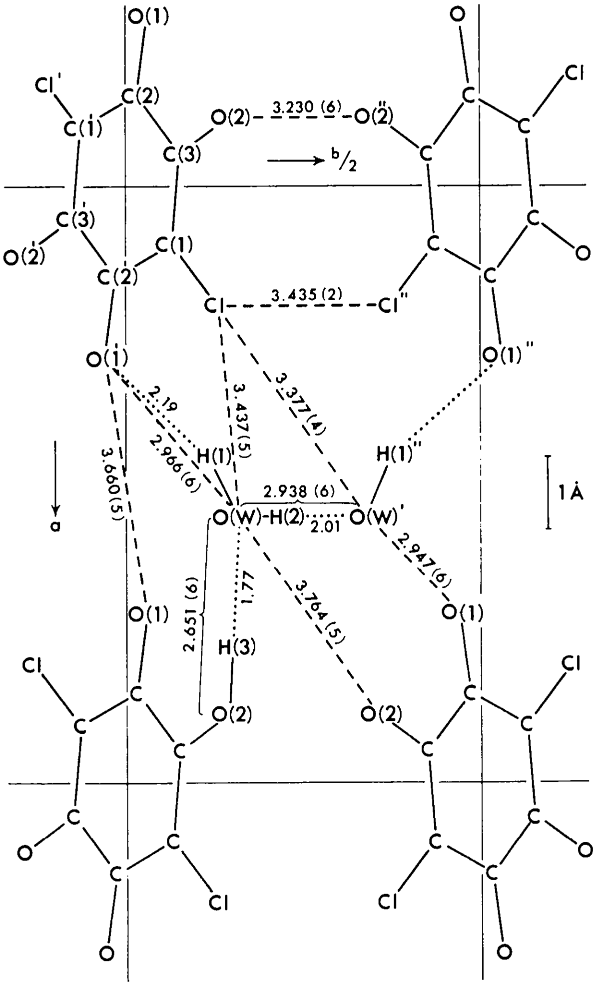
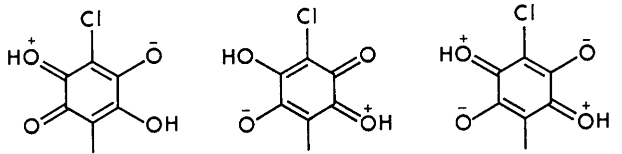


Fig. 4. Intermolecular distances in chloranilic acid dihydrate. Values in brackets are standard deviations (third decimal place).

systems in all four compounds and the C–Cl, C=O, and C–OH lengths are much alike (the bond angles, which are not given here, agree just as well); therefore the molecular structure of chloranilic acid is quinoidal.

The chloranilic acid molecule is, however, on two points different from the other molecules. The C–C bonds parallel to the C–OH bonds are significantly shorter than the C–C bonds parallel to the C–Cl bonds; and the C–OH bonds are short. This is in accordance with the rather strong acidity of the substance ($pK_1 =$ 0·58, $pK_2 = 3·18$) and resonance theory, which taken together would suggest contributions from structures such as:



the positive charge being responsible for the increased acidity (as compared with other hydroxyl compounds). These valence structures also account for the distribution of the C–C bonds in short and long pairs, and for the C–OH bonds being shorter than the usual 1·34 Å. One might expect a lengthening of the C=C and C=O bonds by conjugation, but such lengthenings are held to be extremely small for C=C bonds (Lide, 1962) and between 0·01 and 0·02 Å for C=O bonds (Bak & Hansen-Nygaard, 1960).

The crystal structure

The molecules are stacked in columns along the lines 00*z*, 0½*z* *etc.* Four such columns are viewed end on in Fig. 4. The molecules are parallel within each stack, and the perpendicular distance between neighbouring molecules is 3·23 Å, a value very close to the separation 3·26 Å found in the structure of the anhydrous acid. The closest approach of acid molecules belonging to different columns is the 3·23 Å between O(2) atoms across the glide plane.

A short contact of 3·435 Å is also found between chlorine atoms. This is comparable to the Cl···Cl distance in solid chlorine, which is 3·34 Å (Collin, 1952).

The water molecules are arranged in hydrogen bonded zigzag chains running along the *c* axis. Each of these chains is encircled by four columns of acid molecules.

The oxygen atoms in the water molecules are acceptors in two hydrogen bonds, one from a water molecule [O(*w*)···O(*w*′)] and another from an OH group [O(2)···O(*w*)]. The water molecules are also donors in two hydrogen bonds, the one going to another water molecule, the other going to O(1).

The surroundings of the water molecule are nearly tetrahedral. The angles between the bonds are H(1)–

O(*w*)–H(2) 83°, H(2)–O(*w*)–H(2) 126°, H(2)–O(*w*)–H(3) 117°, and H(3)–O(*w*)–H(1) 116°.

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The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones. III. Ammonium Chloranilate Monohydrate

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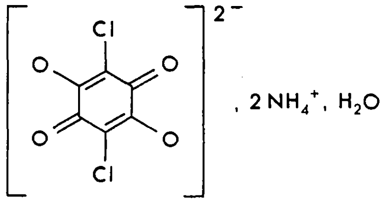
(*Received* 18 *July* 1966)

The structure of ammonium chloranilate monohydrate has been determined with three-dimensional data. The cell dimensions are $a=16{\cdot}988$, $b=4{\cdot}780$, $c=14{\cdot}101$ Å, $\beta=118{\cdot}01°$. The space group is $C2/c$ and $Z=4$. The carbon ring system is not in quinoidal form. It is planar and contains four carbon–carbon bonds of equal length (1·404 Å) and two considerably longer carbon–carbon bonds (1·535 Å). The C–O bonds are of equal length (1·248 Å). The chlorine and oxygen atoms are within the accuracy of the determination in the ring plane.

The structure determination of ammonium chloranilate monohydrate (I) was made in order to find what the molecular rearrangement is when chloranilic acid forms salts.



(I)

Experimental

Ammonium chloranilate monohydrate was prepared by slow evaporation of an aqueous chloranilic acid solution supersaturated with ammonia. The crystals are dark red violet needles with the *b* axis along the needle direction.

The following lattice constants were determined from indexed powder photographs taken in a Guinier–Hägg camera:

$$a=16{\cdot}988\ (0{\cdot}003),\ b=4{\cdot}780\ (0{\cdot}001),$$
$$c=14{\cdot}101\ (0{\cdot}003)\ \text{Å};$$
$$\beta=118{\cdot}01°\ (0{\cdot}02°)$$

(Values in brackets are standard deviations.)

The molecular weight of ammonium chloranilate monohydrate is 261·07. With the observed lattice constants, assuming 4 molecules per unit cell, the calculated density is 1·718 g.cm^{-3}. The observed density determined by flotation is 1·718 g.cm^{-3}.

From the crystals listed in Table 1 equi-inclination Weissenberg diagrams were taken. A long and a short exposure were taken of each layer, using the multiple-film technique. Intensities were estimated visually. Only film halves with extended spots were measured. The intensities were corrected for spot extension and converted to structure factors. The intensities measured from crystal *b*(2) were not corrected for absorption, but those measured from crystal *k*(1), which was ground to a sphere, were corrected with the aid of the tables in *International Tables for X-ray Crystallography* (1959). The data from crystal *b*(2) were put on the same relative scale by data from crystal *c*(1). The data from the [010] and [101] setting of crystal *k*(1) were also put on the same relative scale. The data from *k*(1) were finally combined into one set with which the final refinement of the structure was made. Within the limiting sphere

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