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The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones. I. Chloranilic Acid

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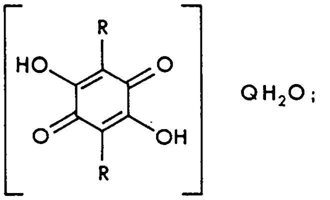
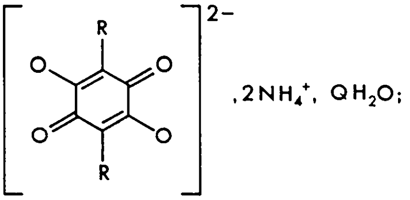
The structure of chloranilic acid has been determined by use of three-dimensional data. The cell dimensions are: $a=10{\cdot}025$, $b=5{\cdot}544$, $c=7{\cdot}566$ Å, $\beta=104{\cdot}8°$. The space group is $P2_1/a$ and $Z=2$. The geometry of the carbon-ring system is similar to that of *p*-benzoquinone. There are, however, carbon–carbon single bonds of two lengths (1·445 and 1·501 Å), and there are two kinds of carbon–oxygen distance (1·222 and 1·322 Å) corresponding to C=O and C–OH bonds. The carbon ring is planar and the chlorine and oxygen atoms lie very close (largest deviation 0·03 Å) to the ring plane. The hydrogen atom has been located.

Introduction

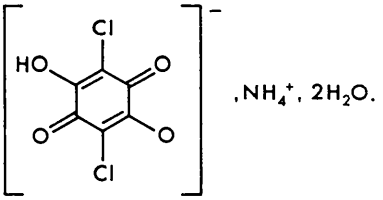
This paper is the first of a series describing the crystal and molecular structure of six compounds with the following general formulae:



(*a*)



(*b*)



(*c*)

The compounds are:

Chloranilic acid [R=Cl, Q=0 in formula (*a*)]; this paper.

Chloranilic acid dihydrate [R=Cl, Q=2 in formula (*a*)]; part II.

Ammonium chloranilate monohydrate [R=Cl, Q=1 in formula (*b*)]; part III.

Ammonium hydrogen chloranilate dihydrate [formula (*c*)]; part VI.

Ammonium nitranilate [R=NO_2, Q=0 in formula(*b*)]; part IV.

Nitranilic acid hexahydrate [R=NO_2, Q=6 in formula (*a*)]; part V.

The formulae above have all been written in quinoidal form. In fact, of the compounds described, only chloranilic acid and its dihydrate (see part II) have a quinoidal structure.

The compounds were investigated in order to see what happens to the molecular structure of the compounds (*a*), the quinones, when they form salts, *i.e.* compounds (*b*) or (*c*). The character of the carbon-ring system has particularly attracted my interest.

Experimental

Chloranilic acid was prepared as the dihydrate by a method described by Graebe (1891). It was dried over silica gel, and recrystallized from absolute ethyl alcohol.

The crystals are short red needles with the *b* axis along the needle direction.

Accurate lattice constants were determined from indexed powder photographs taken in a Guinier–Hägg camera with quartz as internal standard. The camera was calibrated by means of the observed quartz lines and lattice constants for quartz ($a=4{\cdot}913$, $c=5{\cdot}405$ Å) recorded by Swanson & Fuyat (1954). In this calculation and in the calculation of lattice constants the weighted mean of α_1 and α_2 wave-lengths for copper radiation, 1·5418 Å, has been used. In the final calculations the reciprocal lattice constants were adapted by the least-squares method to the observed $\sin^2\theta$ values. The lattice constants are:

$$a=10{\cdot}025\,(0{\cdot}002),\ b=5{\cdot}544\,(0{\cdot}001),\ c=7{\cdot}566\text{ Å}\,(0{\cdot}002);$$
$$\beta=122{\cdot}9°\ (0{\cdot}01)$$

(Values in brackets are standard deviations.) They are in good agreement with the constants found from single-crystal exposures.

The molecular weight of chloranilic acid is 208·99. With the observed lattice constants, assuming two molecules per unit cell, the calculated density is 1·963 g.cm^{-3}. The observed density determined by flotation in a bromoform–benzene mixture is 1·957g.cm^{-3}.

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From the crystals listed in Table 1 equi-inclination Weissenberg diagrams were taken. The crystals have been given names corresponding to the axis they were rotated about. The first entry in the size column is the length of the crystal along this axis.

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

Crystal	Size (mm)	Data collected
b(1)	0·50 × 0·15 × 0·15	$h0l \rightarrow h3l$
a(1)	0·096 × 0·11 × 0·14	$0kl \rightarrow 6kl$

A long and a short exposure were taken of each layer by the multiple-film technique. Intensities were estimated visually by comparison with an intensity scale prepared for each crystal. Only film halves with extended spots were used. The intensities were corrected for spot extension and converted to structure factors. No correction for absorption was made. A total of 622 independent reflexions were estimated, of which 258 were observed from both crystals. Within the limiting sphere for copper radiation there are 812 reflexions. Of the 190 non-observed reflexions, 60 were not covered by the experiments. The residual between the 258 structure factors estimated from both crystals was 0·117 [the intensities for several of the strongest reflexions were estimated much lower from crystal *b*(1) than from crystal *a*(1)].

The trial structure

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

hkl	no conditions
$h0l$	$h=2n$
$0k0$	$k=2n$;

hence the space group $P2_1/a$ (no. 14 with change of *a* and *c*) was assumed.

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

From the Patterson projection along [010] it was possible to set up a two-dimensional trial structure. This was refined by Bhuiya & Stanley's (1963) minimum residual method. The final residual for this projection was $R=0{\cdot}12$ (omitting non-observed reflexions). From the result of this projection and from a knowledge of the approximate geometry of the chloranilic acid molecule a three-dimensional trial structure was worked out.

Refinement of the structure

The *y* coordinates were first refined independently of all other parameters except one scale factor by Bhuiya & Stanley's method. Three cycles of calculations were carried out, two of them with steps $0{\cdot}01 \times b$ and one with steps $0{\cdot}005 \times b$. The *R* index was 0·37 before these calculations and 0·18 after. All positional parameters and isotropic temperature factors were now refined by diagonal least-squares (not block-diagonal) calculations. The result of these calculations has been reported (Andersen, 1964). They agree roughly with the final results, which are reported below (deviations in bond lengths up to 0·04 Å).

The refinement of the structure was finished with three cycles of least-squares calculations. These were carried out with the Busing, Martin & Levy (1962) ORFLS program. The hydrogen atom was not included. The scattering factors used were those selected by *International Tables for X-ray Crystallography* (1962).

The quantity minimized in the calculations was $\Sigma\, w(F_o-F_c)^2$. The weighting scheme was that introduced by Hughes (1941) with

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

and

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

In the calculations positional parameters, anisotropic temperature parameters and one scale factor were adjusted.

Three cycles were calculated. The *R* index was 0·24 before and 0·118 after the first cycle. After the second and third cycle *R* was 0·113. It was now observed that the calculated structure factors for 22 strong reflexions

Table 2. *Final atomic parameters and standard deviations*

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

(*a*) Positional parameters (× 10^4)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cl	4414	1	8583	2	2747	2
C(1)	4714	5	6670	8	1209	6
C(2)	5834	4	4718	8	2238	5
C(3)	6100	5	3051	8	895	6
O(1)	6612	4	4395	6	4141	4
O(2)	7155	4	1312	6	1883	5
H*	7400		1000		3200	

* The hydrogen atom was not included in the refinements.

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	2·71	0·06	3·20	0·07	1·66	0·07	0·33	0·03	1·28	0·04	−0·59	0·03
C(1)	2·22	0·14	2·65	0·16	1·53	0·16	0·14	0·12	1·12	0·12	−0·36	0·11
C(2)	1·96	0·13	2·57	0·15	1·32	0·15	−0·24	0·13	0·79	0·12	−0·39	0·11
C(3)	1·96	0·14	2·71	0·16	1·65	0·15	−0·25	0·12	1·05	0·12	−0·18	0·12
O(1)	2·97	0·11	3·23	0·13	1·34	0·12	0·18	0·11	1·06	0·09	−0·07	0·10
O(2)	3·07	0·14	2·86	0·14	1·55	0·13	0·98	0·09	1·14	0·10	0·28	0·08

were much higher than the observed values. One cycle of least squares with these 22 structure factors left out gave $R=0{\cdot}092$.

The final parameters are given in Table 2.

The hydrogen atom

The position of the hydrogen atom was found from a three-dimensional difference synthesis. This was calculated with the reflexions for which $\sin\theta/\lambda$ was smaller than 0·40 and the 22 strong reflexions mentioned above were left out. There was a prominent peak at (0·74, 0·10, 0·32), but there were also strong peaks at other positions, especially near the chlorine atom. When one hydrogen atom was included in structure factor calculations at the position mentioned above, and with an isotropic temperature factor of 3·6 Å^2, R was 0·089 (the 22 strong reflexions still left out). The observed and calculated structure factors are available on request from the author.

Standard deviations of bond lengths

The standard deviations of positional parameters in Table 2 are given in fractions of the cell edges. The average standard deviation is for carbon and oxygen atoms $\sigma(\text{O,C})=0{\cdot}004$ Å. This gives a standard deviation for bond lengths $\sigma(\text{C–C, C–O})=0{\cdot}006$ Å [$\sigma(\text{C–Cl})$ will be lower], and hence differences in bond lengths greater than 0·02 Å are significant.

The molecular structure

The detailed discussion of the molecular structure of chloranilic acid will be given in part II; only carbon–carbon bonds will be discussed here.

Fig. 1 shows that there are three types of bond in the carbon ring. There are two bonds of length 1·346 Å, two of length 1·445 Å, and two of length 1·501 Å. These bonds show that the molecule is in quinone form, although it is somewhat distorted [pure quinone

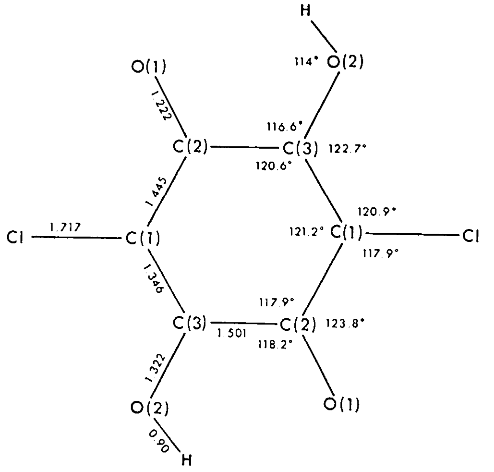

Fig. 1. Intramolecular distances (Å) and angles in the chloranilic acid molecule.

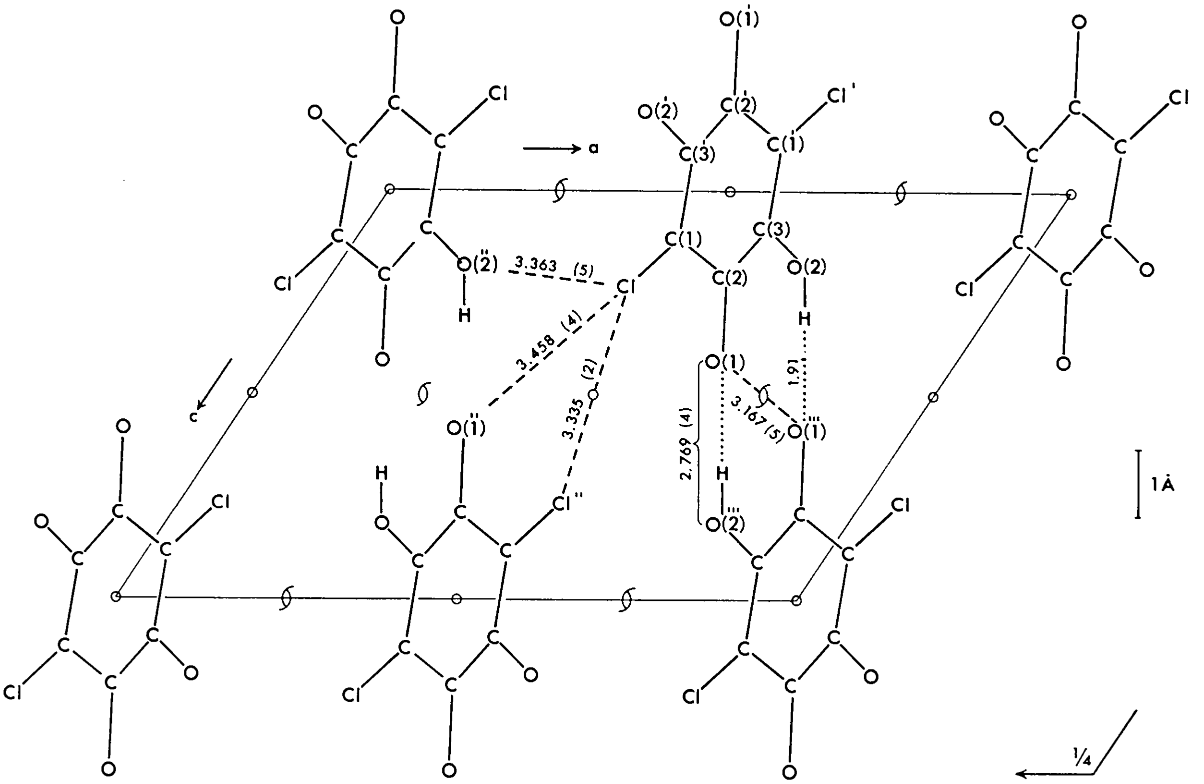

Fig. 2. Intermolecular distances (Å) in chloranilic acid. Values in brackets are standard deviations (third decimal place).

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 $0y0$, $\frac{1}{2}y0$, *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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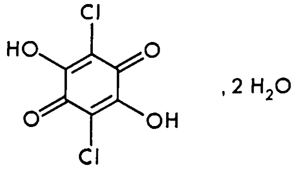
(*Received* 18 *July* 1966)

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)



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