Refinement of the Crystal Structure of Tetrachloro-*p*-Benzoquinone (Chloranil) at 110°K

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The crystal structure of tetrachloro-*p*-benzoquinone (chloranil), space group $P2_1/a$ with $Z = 2$, has been refined with 4277 non-zero reflexions measured at low temperature (110°K). Average values for the bond lengths and angles, with estimated standard deviations for the individual values in units of the last decimal place in parentheses, are: C–C = 1·490 (2), C=C = 1·344 (2), C=O = 1·211 (1_5), C–Cl = 1·701 (1) Å, C–C–C = 117·4 (1), C=C–C = 121·2 (1), O=C–C = 121·3 (1), C–C–Cl = 115·9 (1), C=C–Cl = 122·9 (1)°. The values are not corrected for the errors due to thermal oscillations.

Introduction

Tetrachloro-*p*-benzoquinone (chloranil) forms molecular complexes with different molecules. Examples are given by Chu, Jeffrey & Sakurai (1962) (to be referred to as CJS). Due to complex formation small changes in the bond lengths and angles may occur which can be studied if both the structures of the complex considered and the parent compounds are known accurately. As the structure of chloranil determined by CJS at room temperature is not sufficiently accurate for such a study (de Boer & Vos, 1968), we decided to refine this structure with data collected at low temperature (110°K).

Refinement

After several attempts good crystals (yellow plates) could be grown from a solution in chloroform by slow evaporation of the solvent. The twinning described by CJS was not observed. Details of the experimental work are given in Table 1. The least-squares refinement of the structure was done with a program working in block-diagonal approximation (Cruickshank, 1961).

The scattering factors given by Doyle & Turner (1968) were used. In the final stages of the refinement all 4277 non-zero reflexions were considered. The weighting scheme is $w = [w_c^{-1} + P^2|F_o|^2]^{-1}$ with $P = 0·01$. The weights w_c were calculated from the relations $w_c =$

$$\frac{1}{[\sigma(F)]^2}, \quad \frac{[\sigma(F)]}{F} = \frac{[I(\text{net}) + \sigma\{I(\text{net})\}]^{1/2} - [I(\text{net})]^{1·2}}{[I(\text{net})]^{1/2}}$$

and $\sigma[I(\text{net})] = [I(\text{peak}) + I(\text{background})]^{1/2}$. The constant P was chosen so as to avoid systematic variations of $\langle w(\Delta F)^2 \rangle$ with $|F|$. Corrections for extinction according to Zachariasen (1968) were applied. For the strongest reflexions 003, 210 and 211 this correction amounted to 20% in F. Some of the strong reflexions appeared to be over corrected at the end of the refinement. In the final cycle all atomic shifts were smaller than 1/3 the respective estimated standard deviations. The weighted residual $R_w = [\sum w(F_o - F_c)^2 / \sum w|F_o|^2]^{1/2}$ decreased to 0·057 for all non-zero reflexions, $R = [\sum (F_o - F_c)^2 / \sum |F_o|^2]^{1/2} = 0·056$. The final parameters with standard deviations as calculated by the least-squares program, are given in Table 2. These standard deviations are lower estimates of the errors occurring

Table 1. *Crystal data and details of the experimental work*

Temperature	110°K
Space group	Monoclinic, $P2_1/a$, $Z = 2$*
Special position used	$\bar{1}$
Cell dimensions	$a = 8·664$ (4), $b = 5·658$ (3), $c = 8·532$ (4) Å, $\beta = 105·95$ (2)°
Determination of cell dimensions	Zero layer line Weissenberg photographs calibrated with NaCl reflexions: $\lambda(\text{Cu } K\alpha_1) = 1·54051$, $\lambda(\text{Cu } K\alpha_2) = 1·54433$ Å
Size of crystal used for collecting *I*'s	$0·63 \times 0·40 \times 0·23$ mm³
Method used	Diffractometer; Zr-filtered Mo radiation; θ–2θ scan, equal times used to measure *I* (peak) and *I* (background); reference reflexions
$\sin \theta/\lambda$ (max)	$1·11$ Å⁻¹
Number of reflexions	4593 independent reflexions
Number with *I* (net) > 0†	4277
F values	Correction for Lorentz and polarization effects and for absorption;‡ $\mu(\text{Mo}) = 14·1$ cm⁻¹

* Only the modification studied by CJS was observed; no phase transition was found between room temperature and 110°K.
† Calculated value for *I* (net) = *I* (peak) − *I* (background) larger than zero.
‡ Busing & Levy (1957).

in the parameters (Visser & Vos, 1971). In the discussion given in the next section the standard deviations in the atomic coordinates are assumed to be 1·5 times the values given in Table 2. An analysis of the thermal vibrations according to Cruickshank (1956) showed that the molecule is not a rigid body, the root-mean square value $\langle\{[U_{ii}(o)-U_{ii}(c)]/\sigma[U_{ii}(o)]\}^2\rangle^{1/2}=4\cdot5$. The distances and angles given in Fig. 1(a) and (b) are therefore not corrected for libration effects. The observed and calculated structure factors are compared in Table 3.
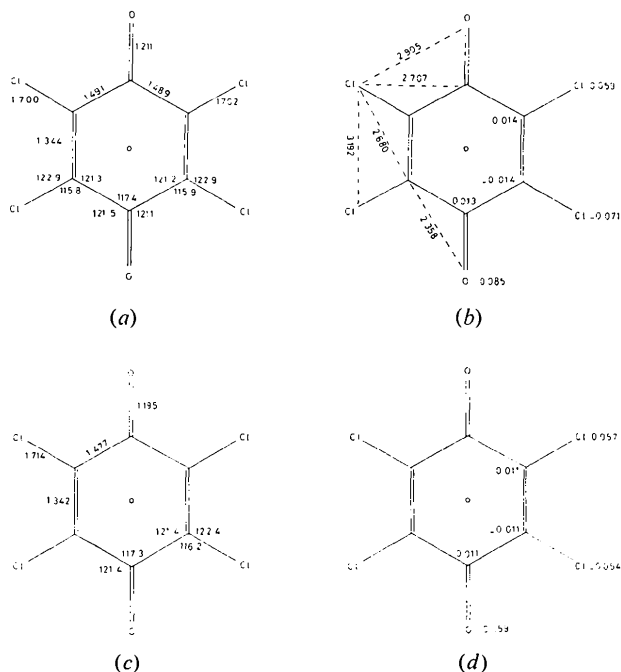

(a)　　　　　　　(b)

(c)　　　　　　　(d)

Fig. 1. Geometry of the chloranil molecule. (a) 110°K. Bond lengths and angles, not corrected for libration, σ(C–Cl) = 0·0012, σ (remaining bonds) = 0·0015 – 0·0017 Å, σ (angles) = 0·09 – 0·12°. (b) 110°K. Deviations from the best plane through the carbon atoms (right hand side), and average values for some non-bonded distances (left hand side). (c) CJS. Average bond lengths and angles corrected for libration, σ(C–Cl) = 0·008, σ (remaining bonds) = 0·011 Å, σ (angles) = 0·6 – 0·7°. (d) CJS. Deviations from the best plane through the carbon atoms.
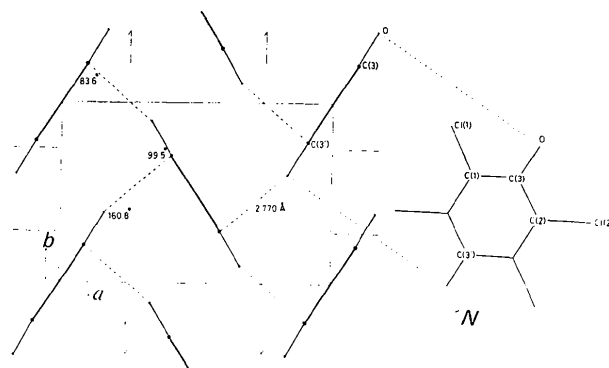

Fig. 2. Schematic drawing of the projection of one layer of the structure along the normal N of (001) onto (001), with a perpendicular view of the molecule. The best plane through the carbon atoms makes an angle of 89·5° with (001) and is indicated by the thick line C(3)–C(3'). The bond C(3)–O which approximately lies in (001) is given by a thinner line and the short intermolecular C···O distances by dashed lines.

Discussion

The geometries of the chloranil molecule at 110°K and at room temperature are given in Fig. 1. The two structures do not show significant differences.

The bond lengths in chloranil at 110°K may be compared with the values calculated from the bond length–bond order curves recently obtained by Rees (1970b) in a discussion of the room temperature structures of the monochloro-, dichloro- and tetrachloro-derivatives of p-benzoquinone. By use of the bond orders given by Rees we obtain for chloranil C–C = 1·482 (0·006), C=C = 1·348 (0·008), C=O† = 1·223 (0·004), C–Cl† = 1·719 (0·005) Å. The numbers in parentheses are the r.m.s. values of the differences between the experimental and expected lengths for the bonds considered by Rees. Comparison of the calculated bond lengths for chloranil with the experimental values of Fig. 1(a) shows that the differences are quite large, but that only for C–Cl is the deviation larger than three times the

† Length independent of bond order; the calculated value is the weighted average value of the bonds considered by Rees.

Table 2. *Final parameters* ($\times 10^5$) *with in parentheses the standard deviations calculated by the least-squares program in units of the last decimal place.*

The formula for the temperature factor is

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{13})\right].$$

For numbering of atoms, see Fig. 2.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl(1)	2708 (3)	23004 (5)	−32586 (3)	2238 (9)	2543 (10)	2068 (8)	288 (15)	1454 (14)	1550 (13)
Cl(2)	19354 (3)	22379 (5)	33245 (3)	1836 (8)	2620 (10)	2050 (8)	−599 (14)	−1716 (14)	395 (12)
O	16498 (8)	39686 (12)	488 (9)	1502 (21)	1381 (22)	3301 (32)	−708 (37)	−229 (44)	1682 (41)
C(1)	572 (9)	9880 (14)	−15382 (9)	1267 (22)	1451 (26)	1786 (25)	123 (40)	224 (43)	945 (38)
C(2)	8461 (9)	9509 (14)	15641 (9)	1163 (21)	1493 (26)	1778 (25)	−112 (40)	−513 (43)	663 (37)
C(3)	9305 (8)	21280 (10)	296 (10)	1017 (21)	1188 (24)	2153 (28)	−101 (36)	−176 (43)	1048 (38)

r.m.s. value. Further low temperature studies must be done to check whether C–Cl in chloranil is significantly different from the C–Cl bonds in the other chloro-derivatives of p-benzoquinone.

As to the planarity of the molecules, Rees noticed that the chloroderivatives of p-benzoquinone have a tendency to be non-planar, the oxygen and chlorine atoms substituted at neighbouring carbon atoms being alternately above and below the best plane through the carbon atoms. This feature of the molecule, as well

Table 3. *Observed and calculated structure factors*

The columns are H, F_o, F_c. The structure factors are on 10 times the absolute scale.

Table 3 (cont.)

as the fact that the carbon atoms 'follow' the deviations of their substituents, is clearly shown for chloranil in Fig. 1(b). Similar deviations are indicated by the study of CJS [Fig. 1(d)], but in this case as well as for most of the p-benzoquinone derivatives, the standard deviations are so large that the deviations of the carbon atoms from their best plane are not significant. The non-planarity of the chloranil molecule may be ascribed to steric interaction between the substituents (see also CJS and Rees, 1970b). The non-bonded distances given in Fig. 1(b) are appreciably shorter than the sum of the van der Waals radii (1·8, 1·4 and 1·7 for Cl, O and C respectively; Nyburg, 1961). As the Cl···C and O···C distances are even shorter in comparison with the sum of the relevant van der Waals radii than Cl···O and Cl···Cl, the values of the exocyclic angles will be determined most by the Cl···C and O···C repulsions. Fig. 1(b) shows that the angles at

C–Cl are such that all Cl···C distances are approximately the same. Moreover it appears that the O···C and Cl···C distances are approximately equally short relative to the van der Waals distances.

The packing of the chloranil molecules in the crystal has been discussed by CJS (see their Figs. 4 and 5) and by Rees (1970a, b). The most interesting feature of the crystal structure is the existence of strong C=O···C=O interactions between neighbouring molecules. Owing to this interaction the reare two-dimensional layers perpendicular to the c* axis. One layer with the values of some interesting distances and angles observed at 110°K is shown in Fig. 2. The C=O···C=O network lies approximately in the plane (001), the atoms C(3) and O being at distances of 0·024 and 0·040 Å from this plane. A comparison with related structures and a discussion of the intermolecular forces can be found in CJS and in Rees (1970a, b).

The authors thank Dr J. L. de Boer for suggesting the problem and Professor Aafje Vos for helpful discussions. Thanks are also due to Mr F. van Bolhuis and Mrs S. C. Swen-Walstra for valuable assistance during the experimental work. The calculations were carried out at the Computing Centre of the University of Groningen.

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The Crystal and Molecular Structure of 1,2,3,4-Tetrachlorobutadiene

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The crystal and molecular structure of a crystalline isomer of 1,2,3,4-tetrachlorobutadiene (m.p. 51 °C) was determined by the heavy-atom method. The crystals are monoclinic with the space group $P2_1/n$. The lattice constants are $a=3\cdot872$, $b=9\cdot087$, $c=10\cdot061$ Å and $\beta=101\cdot2°$, and two molecules are contained in the unit cell. The structure was refined by the least-squares method, to give the final R value of $0\cdot11$ for the 355 observed reflexions. The molecule is planar and the carbon skeleton takes *trans* configuration. The Cl atoms are attached in the *cis, cis* positions. The bond lengths are in good agreement with those observed in the other butadiene derivatives. The bond angle C=C–Cl (122°) also agrees with that of chloroprene.

Introduction

1,2,3,4-Tetrachlorobutadiene, $C_4H_2Cl_4$, is one of the starting materials for the synthesis of an organic semiconductor, 1,2,3,4-tetracyanobutadiene (Miura & Haga, 1969). It is obtained in either oily form (b.p. 173 °C) or crystalline form (m.p. 51 °C) through dehydrochlorination of 1,2,2,3,3,4-hexachlorobutane with potassium hydroxide. The crystalline tetrachlorobutadiene shows only one nuclear magnetic resonance peak at $\tau=2\cdot88$ ppm, which agrees with neither of the two peaks of the oily tetrachlorobutadiene ($\tau=2\cdot23$, and 3·51 ppm). Although this fact indicates that the crystal is either the *cis, cis*-tetrachloro- or the *trans, trans*-tetrachloro form, it is difficult to say which is the case. Miura & Haga inferred that it may be the *cis, cis* form, in view of the fact that the 1,2,3,4-tetrachlorobutadiene from hydrolysis of hexachlorotellurophene has a melting point of 51 °C (Mack, 1965). The present author attempted an X-ray structural analysis of the crystalline 1,2,3,4-tetrachlorobutadiene, in order to confirm their conclusion.

Experimental

The crystals were grown from a methanolic solution by slow evaporation. They were colourless transparent needles about 5 mm in length and 0·5 mm in thickness. Because the crystal is so volatile that it sublimes completely in air within an hour, the crystals with dimensions of $0\cdot1\times0\cdot1\times0\cdot3$ mm were sealed in Lindemann glass capillaries for the X-ray work. One crystal specimen was consumed per one layer, as they are unstable to X-rays and decompose after two days irradiation. The Cu $K\alpha$ radiation was used throughout the experiment. The cell constants were obtained from equatorial Weissenberg photographs about the a and b axes, on which powder diffraction lines of copper were superposed for the calibration purpose.

Crystal data

$C_4H_2Cl_4$, M.W. 191·86, Monoclinic, $a=3\cdot872\pm 0\cdot005$, $b=9\cdot087\pm 0\cdot002$, $c=10\cdot061\pm 0\cdot004$ Å, $\beta=101\cdot22\pm 0\cdot08°$, $U=347\cdot2$ Å³, $D_m=1\cdot817$ g.cm⁻³, $Z=2$, $D_x=1\cdot835$ g.cm⁻³, $F(000)=188$. Linear absorption coefficient for Cu $K\alpha$ radiation $\mu=146$ cm⁻¹, Absent reflexions, $0k0$ for $k=$ odd, $h0l$ for $h+l=$ odd, Space group $P2_1/n$.

Intensity data were collected for the layers $0kl$–$2kl$ about the a axis and $h0l$–$h2l$ about the b axis, by the multiple film equi-inclination method. The intensities were estimated visually by comparison with a standard scale. Non-zero independent reflexions 355 in total,