Table 5. *Intermolecular contact distances* (Å) <3·3 Å

$F(4')\cdots F(4'^{i})$	$2{\cdot}77_5$	$O(2)\cdots C(4^{vii})$	3·06
$F(5)\cdots F(4'^{ii})$	2·88	$F(4')\cdots O(2^{ix})$	3·10
$F(5)\cdots F(6'^{iii})$.	2·89	$F(4)\cdots F(6'^{iii})$	3·10
$F(5)\cdots F(5'^{iii})$	2·96	$F(3')\cdots C(6^{v})$	3·14
$F(6)\cdots F(5^{iv})$	2·98	$F(3')\cdots O(2^{ix})$	3·14
$F(3')\cdots F(8^{v})$	3·00	$F(5')\cdots F(6'^{viii})$	3·15
$F(4')\cdots C(4'^{i})$	3·02	$F(3')\cdots C(5^{v})$	3·15
$F(4)\cdots F(3^{vi})$	3·02	$C(4')\cdots O(2^{ix})$	3·18
$O(2)\cdots F(4^{vii})$	3·04	$C(3')\cdots O(2^{ix})$	3·18
$C(5)\cdots F(4'^{ii})$	3·04	$O(1)\cdots F(3^{ix})$	3·26
$F(2')\cdots F(4^{v})$	3·04	$F(2')\cdots F(3^{vii})$	3·28
$F(5')\cdots F(2'^{ii})$	3·05	$F(4)\cdots F(4^{vi})$	3·28
$F(5')\cdots F(6^{viii})$	3·06		

Symmetry code

(i)	$\bar{x}$,	$2-y$,	$\bar{z}$	(vi)	$1-x$,	$\bar{y}$,	$1-z$
(ii)	x,	$1\frac{1}{2}-y$,	$\frac{1}{2}+z$	(vii)	$1-x$,	$1-y$,	$1-z$
(iii)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	(viii)	$\bar{x}$,	$1-y$,	$\bar{z}$
(iv)	$\bar{x}$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(ix)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
(v)	x,	$1+y$,	z				

standing the difference in inter-ring angle (59·6 and 59·5° in perfluoro- and 2*H*-nonafluorobiphenyl, compared with 85·5° in the present structure). This suggests that there is very little, if any, correlation between inter-ring bond length and inter-ring angle. However, in decachlorobiphenyl (Pedersen, 1975), where the dihedral angle between the rings is similar (86·7°), the C(1)—C(1′) bond length is significantly longer (1·514 Å).

Fig. 2 shows the packing in the crystal viewed along **b**. Many close intermolecular contacts occur (Table 5), but none of these is substantially shorter than the sum of the van der Waals radii of the atoms concerned.

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The Crystal and Molecular Structure of Tetrachloro-*o*-benzoquinone

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Crystals of tetrachloro-*o*-benzoquinone (TOB) are monoclinic, with a = 7·756 (8), b = 8·258 (8), c = 6·471 (5) Å, β = 90·3 (1)°, Z = 2, space group $P2/a$ (after structure analysis) with required molecular symmetry C_2. Intensity data were collected on a four-circle diffractometer with Mo $K\bar{\alpha}$ radiation. The structure was solved by direct methods and refined by full-matrix least squares to a final conventional R value of 0·047 (R_w = 0·049) for the 826 observed reflexions with $I > 3\sigma(I)$. The quinoid ring adopts a shallow boat conformation with the Cl and O atoms significantly displaced from its mean plane. The molecular dimensions are in agreement with those found in *o*-benzoquinone and analogous compounds. In the crystal the molecules form layers, approximately parallel to ($\bar{2}01$), whose mean separation is 3·33 Å.

Introduction

Tetrachloro-*o*-benzoquinone, which is a well known strong electron acceptor, forms π-molecular compounds with various molecules which are electron donors (Herbstein, 1971). The ground states of most crystalline π-molecular compounds are non-ionic, but evidence has accumulated in recent years that crystals with ionic ground states also occur and that these often have particularly interesting physical properties. Owing to the interaction between the two components in a π-molecular compound small changes in the bond lengths and angles may occur which can be studied if the structures of both the complex and its parent components are known accurately. The molecular dimensions, therefore, should give an indication of the effects of complex formation on the components and in particular show whether the components are present as charged or uncharged species. The present analysis was undertaken to establish the geometry of the title compound, thus providing a basis of comparison for further studies of some of its π-molecular complexes.

Experimental

Crystals of tetrachloro-*o*-benzoquinone (TOB) were grown from a light petroleum/acetone solution, by evaporation of the solvent, as thick bright-red prisms.

The crystal data, obtained from single-crystal diffractometry, are presented in Table 1. The intensities were collected from an approximately spherical crystal (radius ~0·2 mm) on a Philips PW 1100 four-circle diffractometer, operating in the $\theta/2\theta$ scan mode (scan width = 1·2°, scan speed = 0·04° s^{-1}), with Mo $K\bar{\alpha}$ radiation monochromatized by a graphite crystal. 1211 independent reflexions up to $\theta = 30°$ were measured; of these, 826 had intensities greater than three times their standard deviations (σ), σ being calculated from the counting statistics of the measurements. During the data collection two standard reflexions were measured every 120 min to check the stability of the crystal and the electronics. It should be mentioned that all attempts to measure the intensity of the $\bar{2}01$ reflexion failed, since it was much stronger than the others. Intensities were corrected for Lorentz and polarization effects and were converted to an absolute scale by Wilson's method. An absorption correction was applied using the coefficients reported in *International Tables for X-ray Crystallography* (1959).

Table 1. *Crystal data*

$C_6Cl_4O_2$
$M_r = 245{\cdot}88$
$\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å
$a = 7{\cdot}756\ (8)$ Å
$b = 8{\cdot}258\ (8)$
$c = 6{\cdot}471\ (5)$
$\beta = 90{\cdot}3\ (1)°$
$V = 414{\cdot}46$ Å^3
Space group: $P2/a$
$Z = 2$
$D_c = 1{\cdot}97$ g cm^{-3}
$\mu(\text{Mo } K\bar{\alpha}) = 13{\cdot}65$ cm^{-1}
$F(000) = 240$

Structure determination and refinement

On the basis of reflexion symmetry and systematic absences there are two possible space groups, *i.e.* Pa and $P2/a$. The positional parameters of all atoms were determined by direct methods on the assumption of the noncentrosymmetric space group Pa. Normalized structure factors were calculated and the 200 reflexions with $|E(hkl)| > 1{\cdot}40$ were used in the phasing program *MULTAN* (Germain, Main & Woolfson, 1971). An E map was calculated and the structural solution was evident. The conventional R value was 0·20. The refinement of the positional parameters was carried out by full-matrix least-squares analysis, allowing the atoms to vibrate anisotropically. The correction for the real and imaginary parts of the anomalous dispersion was applied to Cl only (*International Tables for X-ray Crystallography*, 1974). The final R value for the 826 observed reflexions with $I > 3\sigma(I)$ was 0·042. Nevertheless, some of the bond lengths and angles were chemically implausible, and all standard deviations were unusually high for a rather low R value. In addition, inspection of the correlation matrix showed there to be large cross-terms (up to $|0{\cdot}90|$) between corresponding parameters of pairs of atoms, taken to be independent in Pa, but symmetry-related in $P2/a$. These large correlations and the intensity statistics suggested that the centrosymmetric structure was more probable (Parthasarathy, Sime & Speakman, 1969) and, therefore, a refinement was carried out on this basis. The final R value for all observed reflexions was $R = 0{\cdot}047$ ($R_w = 0{\cdot}049$).* The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 8[1 + (|F_o| - 10)/12]^{-2}$, to give average values of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) for groups of reflexions, independent of the value of $|F_o|$.

The calculations were carried out on the Cyber 76 computer of the Centro Inter-Universitario Italia Nord Orientale with the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). All atomic scattering factors were those of Cromer & Mann (1968).

Results and discussion

The geometry of the molecule and the numbering system are presented in Fig. 1(*a*), where the bond

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33610 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lengths and valence angles, not corrected for changes due to thermal vibration, are also given. The final positional parameters of all atoms with their e.s.d.'s are reported in Table 2. The molecules lie on twofold axes parallel to **b**. The equation of the best least-squares plane through the ring atoms, with the deviations of the substituents from it, is shown in Table 3. Small but significant deviations from planarity are observed in the molecule [Fig. 1(*b*)]. The ring has therefore adopted a shallow twist–boat conformation. As to the planarity of the molecule, it was noticed (van Weperen & Visser, 1972) that the chloro derivatives of *p*-benzoquinone also have a tendency to be nonplanar, the O and Cl atoms substituted at neighbouring atoms being alternately above and below the best plane through the C atoms. The non-planarity of the TOB molecule may be ascribed to steric interactions between the substituents. The non-bonded distances [Fig. 1(*b*)], which agree well with those observed in tetrachloro-*p*-benzoquinone, are appreciably shorter than the sum of the van der Waals radii (1·8, 1·4 and 1·7 Å 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 mainly be determined by the Cl⋯C and O⋯C repulsions.

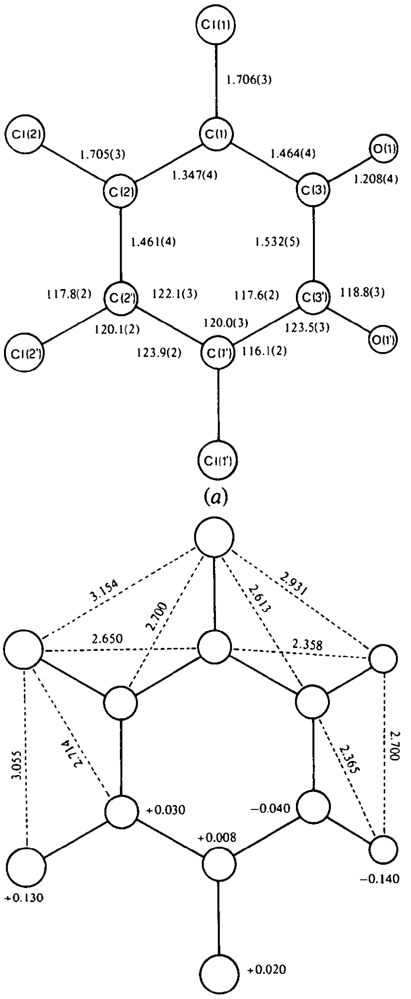

Fig. 1. Geometry of the tetrachloro-*o*-benzoquinone molecule. (*a*) Bond lengths (Å) and angles (°) not corrected for libration. (*b*) Deviations (Å) from the best plane through the C atoms and values for the most relevant intramolecular non-bonded distances.

The observed lengths of the C—Cl bonds, which are significantly shorter than the sum of the single-bond covalent radii (1·742 Å, Pauling, 1960), are in good agreement with values from tetrachloro-*p*-benzoquinone, the chloranil–1,5-diaminonaphthalene complex, chloroethylenes and other aromatic compounds (van Weperen & Visser, 1972; Tamura & Ogawa, 1977; Chu, Jeffrey & Sakurai, 1962).

A comparison of the remaining bond lengths and angles with those observed in *o*-benzoquinone by Macdonald & Trotter (1973) is presented in Fig. 2. The C(3)—C(3′) bond (1·532 Å) in TOB is yet another example of an abnormally long bond between (approximately) trigonally hybridized C atoms. It is similar in length to the bonds in diketonic groups (Karle, Britts & Brenner, 1964; Wong, Marsh & Schomaker, 1964; Allen & Trotter, 1970), and to those in oxalic acid and its derivatives (Delaplane & Ibers, 1969), but is much longer than the 1·48–1·51 Å normally accepted for $C(sp^2)$—$C(sp^2)$ bonds. The lengthening cannot simply be a result of steric interaction, since it is found equally in planar and non-planar molecules. The C=C double-bond length is longer in TOB than in *o*-benzoquinone but agrees well with the value found in tetrachloro-*p*-

Table 2. *Atomic coordinates with their e.s.d.'s in parentheses*

	x	*y*	*z*
Cl(1)	0·4723 (1)	0·7061 (1)	0·4094 (1)
Cl(2)	0·3447 (1)	1·0328 (1)	0·2076 (2)
C(1)	0·3524 (4)	0·7123 (3)	0·1878 (5)
C(2)	0·2990 (4)	0·8503 (3)	0·0968 (5)
C(3)	0·3092 (4)	0·5556 (3)	0·0951 (5)
O(1)	0·3605 (4)	0·4277 (3)	0·1619 (4)

Table 3. *Deviations* (Å) *of atoms from the least-squares plane of the* C_6 *ring*

The equation of the plane is in the form $AX + BY + CZ = D$, in orthogonal Å space with X parallel to a, Z perpendicular to a in the ac plane and Y perpendicular to the ac plane. Asterisks denote atoms not used in the plane calculation.

$$0·8359X - 0·5489Z = 1·6208$$

C(1)	−0·008	C(1′)	0·008
C(2)	−0·03	C(2′)	0·03
C(3)	0·04	C(3′)	−0·04
Cl(1)*	−0·02	Cl(2)*	−0·13
O(1)*	0·14		

benzoquinone (van Weperen & Visser, 1972). The C=O bond length (1·208 Å) is very close to that found in *o*-benzoquinone and tetrachloro-*p*-benzoquinone. The remaining C–C bond lengths of the quinoid ring are the same [C(2)–C(2′) = 1·461 (4), C(3)–C(1) = 1·464 (4) Å] in TOB, whilst in *o*-benzoquinone C(3)–C(1) is longer by 0·015 Å than C(2)–C(2′); this difference has been attributed to greater electron localization in the C=O bond than in C=C, as a result of the electronegativity of the O.

As expected, the mean value of the angles in the ring is 120° both in TOB and *o*-benzoquinone and the small but significant differences from this value can be regarded as characteristic of the quinoid ring.

Presumably the deviations of the O atoms from the ring plane both in TOB and *o*-benzoquinone arise as a result of steric repulsion, since the O(1)···O(1′) distance (2·700 and 2·693 Å in TOB and *o*-benzoquinone respectively) is less than the sum of the appropriate van der Waals radii. In benzocyclobutenedione, cyclohexenylbutenedione and phenylcyclobutenedione (Karle, Britts & Brenner, 1964; Wong, Marsh & Schomaker, 1964; Allen & Trotter, 1970), where the geometry is such as to allow the O atoms to be more than 3·0 Å apart, planarity of the cyclobutenedione system is observed. In contrast, the O atoms are significantly displaced from the ring plane in catechol (Brown, 1966). However, alloxan and the nitranilate anion have also been found to be planar (Bolton, 1964; Jensen & Anderson, 1964).

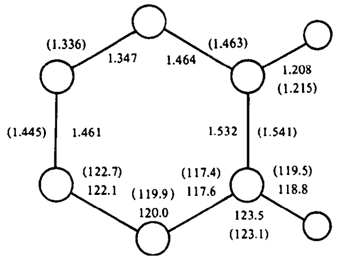

Fig. 2. Bond lengths (Å) and angles (°), not corrected for libration, in tetrachloro-*o*-benzoquinone and *o*-benzoquinone (values in parentheses).

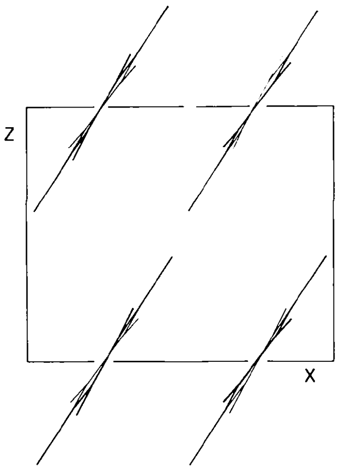

Fig. 3. Crystal structure viewed down **b**.

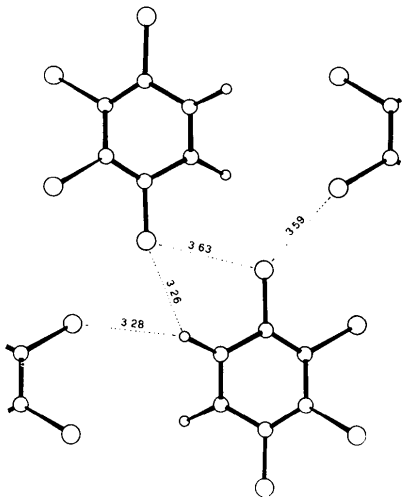

Fig. 4. Section of the crystal structure through ($\bar{2}01$).

Packing of the molecules

The packing is due solely to van der Waals interactions and the TOB crystal structure viewed down **b** is presented in Fig. 3. The molecules lie very nearly in the ($\bar{2}01$) plane, which has an interplanar spacing of 3·33 Å. The shortest intermolecular distances are marked in Fig. 4, which also shows the arrangement of the molecules on the ($\bar{2}01$) plane. The remaining contact distances are as expected for standard van der Waals values.

Finally, Fig. 4 shows that in the crystal the dipoles of all molecules are parallel to **b**. In addition, each ($\bar{2}01$) layer can be divided in alternating strips, again parallel to **b**. Within each strip the dipoles have the same direction, which is opposite to that of the dipoles in the neighbouring strips. This packing probably minimizes the potential energy between the permanent dipoles in the molecules.

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Contact Twinning of Embedded Polymorphs: The Crystal and Molecular Structures of Two of the Polymorphs of Tri-*tert*-butylmethyl *p*-Nitrobenzoate

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Clusters of twins of the title compound are deposited from acetone solution. Any one such twin, separated from the cluster, can be cleaved. The two fragments thus obtained are not homogeneous individual crystals for they all show two superimposed reciprocal lattices. They consist of two embedded closely-related polymorphic structures of which one is present (in the sample examined) to about 90% extent. Both components belong to space group $P2_1/c$ with their y and their z axes antiparallel. Major component data are: a = 11·541 (9), b = 8·161 (7), c = 21·289 (7) Å, β = 107·39 (1)°, Z = four molecules per cell; minor component: $\mathbf{a}' = \mathbf{a} + \frac{1}{2}\mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = -\mathbf{c}$, $\sin\beta'/\sin(\beta + \beta') = -2|\mathbf{a}|/|\mathbf{c}|$, $Z = 4$. The structure of the major component was refined to a conventional R of 0·104. Embedding causes reflections with l even from both components to overlap. Approximate atomic coordinates were found for the minor component but its low contribution to the intensities of the overlapped reflections made refinement impracticable.

Introduction

We report here X-ray structural analyses of two closely-related polymorphic forms of the title compound. These polymorphic forms are embedded in fragments which have been cleaved from twins. A brief report on the molecular structure of the molecule in the major component has been published elsewhere (Cheng, Nyburg, Thankachan & Tidwell, 1977).

Experimental

Crystals of the title compound were kindly supplied by Professor T. T. Tidwell and had been prepared according to the method of Bartlett & Stiles (1955). The first crystals obtained from acetone–water solutions are single colorless needles; crystals from the mother liquor appear as pale-yellow clusters. The structure of the latter crystals is reported here; the structure of the colorless needles (yet a third polymorph) will be reported later.

All crystals broken from the clusters were suspected to be twinned because they had re-entrant angles at their broken ends. X-ray photographs showed, in fact, that either of two types of contact twinning were involved: block (I) + block (II), twinned on (001), or block (I) + block (III), twinned on ($\bar{1}02$), shown schematically in Fig. 1. Such twins can be separated by