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Hexachlorocyclohexa-2,5-dienone

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Abstract. C_6Cl_6O, tetragonal $I4_1/a$, $a=21·796$ (3), $c=8·568$ (4) Å, $V=4070·36$ Å^3, $Z=16$, $D_x=1·96$ g cm^{-3}, λ(Mo $K\alpha_1$)$=0·7093$ Å. Final residual $R=0·049$ for 2218 observed reflexions. Molecules are arranged nearly at right angles to each other, and parallel to the *a* and *b* axes. The atoms of the molecule lie on a plane, except Cl(3) and Cl(4) which are 1·556 and 1·335 Å from the plane respectively. No significant molecular distortion due to the Cl atoms was observed.

Introduction. The present study was initiated in connexion with the chemistry and structure of some perchlorinated alkaromatic compounds.

Crystals were obtained as green prisms elongated along **c**, or as bipyramids, by slow evaporation of a hexane solution at room temperature. The dimensions of the selected crystal were 0·3 × 0·4 × 0·3 mm.

The unit-cell dimensions, space group and intensities were obtained on a Philips single-crystal diffractometer with Mo $K\alpha$ radiation, λ(Mo $K\alpha$)$=0·7093$ Å. 2·733 independent reflexions were measured, of which 470 were unobserved. No absorption corrections were made.

The structure was solved by direct methods, using *MULTAN* (Germain, Main & Woolfson, 1971). The normalization of F_o, the symbolic addition procedure, a Fourier E map and its automatic interpretation were applied by the programs of Declerq, Germain, Main & Woolfson (1973). An E map calculated with the set of signs with highest figures of merit revealed peaks for 11 atoms. A subsequent electron density synthesis revealed the positions of all atoms. After 11 cycles of block-diagonal least-squares calculation with individual isotropic and six cycles with anisotropic thermal parameters, the refinement was terminated at $R=0·049$ for 2218 reflexions. The final atomic and thermal parameters are listed in Table 1. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). Fig. 1 shows a view of the molecule, drawn by the *ORTEP* program (Johnson, 1965), and the numbering of atoms and some distances.†

Discussion. Intramolecular distances and angles are given in Table 2. The C(1)–O(1) distance is slightly shorter than in *p*-benzoquinone (Trotter, 1960) as an expected result of the electronegativity of the Cl substituents (Yates, Ardas & Fieser, 1956), while the C(2)–C(3) double bond is longer. These results are in good agreement with those obtained for tetrachloro-*p*-benzoquinone (chloranil) (Chu, Jeffrey & Sakurai, 1962). The shortest distance between Cl atoms is 2·898 Å for Cl(3)–Cl(4). C–Cl bond distances do not differ significantly from the usual values. Systematic differences between the bond lengths of C(3)–C(4), C(4)–C(5) and C(1)–C(2), C(6)–C(1) are due to the sp^3 character of C(4), which also gives rise to the differences observed between C(4)–Cl(3), C(4)–Cl(4) and other C–Cl bonds. The ring is planar with a C(6)–C(1)–C(2) angle less

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* This paper reports part of the research work undertaken to satisfy the requirements for a D. Sc. degree.

† The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31156 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final structure parameters* (*with standard deviations in parentheses*)

All values have been multiplied by 10^5. The temperature factor is in the form $\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
C(1)	10459 (12)	17541 (12)	17737 (32)	161 (6)	137 (5)	1212 (35)	68 (21)	−21 (21)	−12 (8)
C(2)	11788 (12)	13147 (12)	4956 (29)	144 (5)	171 (6)	965 (30)	122 (20)	16 (19)	−23 (8)
C(3)	11595 (12)	7122 (12)	7047 (30)	166 (6)	162 (6)	993 (30)	−100 (20)	−19 (20)	1 (9)
C(4)	9850 (13)	4269 (12)	22413 (29)	191 (6)	127 (5)	1056 (32)	44 (19)	−125 (21)	−35 (8)
C(5)	8719 (12)	8809 (12)	35290 (29)	170 (5)	166 (5)	848 (28)	76 (19)	−23 (19)	−18 (8)
C(6)	8979 (12)	14828 (12)	33036 (30)	138 (5)	158 (5)	1065 (32)	−94 (20)	1 (19)	−7 (8)
Cl(1)	13577 (5)	16361 (4)	−12602 (9)	339 (2)	272 (2)	1164 (10)	312 (7)	259 (8)	−70 (3)
Cl(2)	13114 (5)	2091 (4)	−7739 (10)	363 (2)	228 (2)	1252 (10)	−347 (7)	93 (8)	43 (3)
Cl(3)	3010 (4)	−99 (4)	19347 (10)	268 (2)	224 (2)	1560 (11)	−32 (7)	−98 (7)	−230 (3)
Cl(4)	15793 (4)	−845 (4)	28447 (10)	306 (2)	166 (2)	1664 (13)	35 (7)	−304 (8)	125 (3)
Cl(5)	6819 (5)	5748 (4)	52896 (9)	380 (2)	249 (2)	993 (9)	236 (6)	141 (8)	−83 (4)
Cl(6)	7544 (4)	19995 (4)	47645 (10)	288 (2)	208 (2)	1454 (11)	−349 (7)	162 (8)	44 (3)
O(1)	10651 (13)	22993 (10)	15704 (32)	358 (5)	140 (5)	1886 (40)	148 (21)	184 (28)	−28 (9)

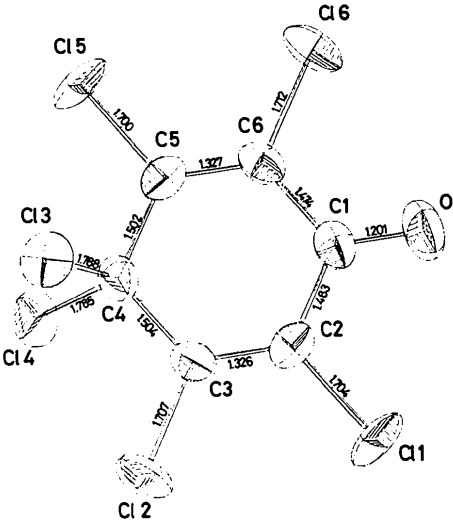

Fig. 1. Perspective view of the molecule showing thermal ellipsoids.

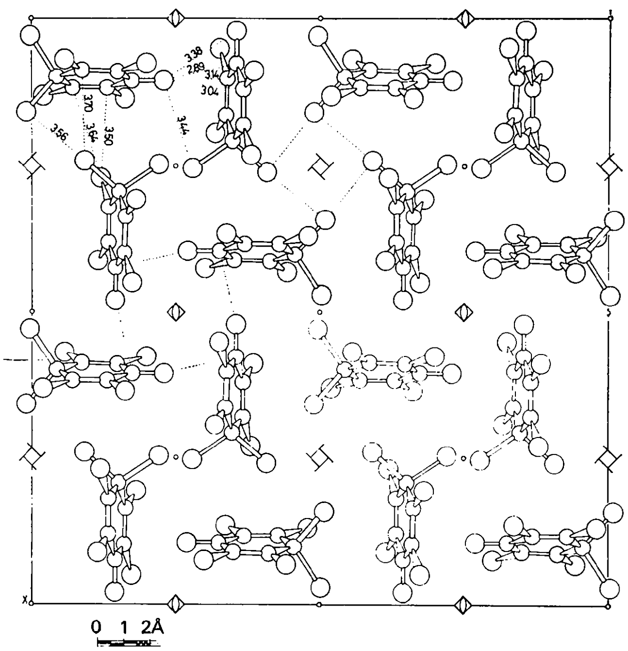

Fig. 2. Projection of one unit cell along the *c* axis, showing shortest intermolecular distances.

Table 2. *Intramolecular distances and angles*

C(1)–C(2)	1·483 (3)	C(1)–C(2)–C(3)	122·2 (1)
C(2)–C(3)	1·326 (3)	C(2)–C(3)–C(4)	122·3 (1)
C(3)–C(4)	1·504 (3)	C(3)–C(4)–C(5)	114·3 (1)
C(4)–C(5)	1·502 (3)	C(4)–C(5)–C(6)	122·4 (1)
C(5)–C(6)	1·327 (3)	C(5)–C(6)–C(1)	122·3 (1)
C(6)–C(1)	1·474 (3)	C(6)–C(1)–C(2)	116·1 (1)
C(1)–O(1)	1·201 (3)	C(1)–C(2)–Cl(1)	115·5 (1)
C(2)–Cl(1)	1·704 (2)	Cl(1)–C(2)–C(3)	122·2 (1)
C(3)–Cl(2)	1·707 (2)	C(2)–C(3)–Cl(2)	121·9 (1)
C(4)–Cl(3)	1·788 (2)	Cl(2)–C(3)–C(4)	115·6 (1)
C(4)–Cl(4)	1·785 (2)	C(3)–C(4)–Cl(3)	107·5 (1)
C(5)–Cl(5)	1·700 (2)	C(3)–C(4)–Cl(4)	109·1 (1)
C(6)–Cl(6)	1·712 (2)	Cl(3)–C(4)–Cl(4)	108·3 (1)
Cl(1)–Cl(2)	3·139 (1)	Cl(3)–C(4)–C(5)	108·7 (1)
Cl(2)–Cl(3)	3·234 (1)	Cl(4)–C(4)–C(5)	108·5 (1)
Cl(2)–Cl(4)	3·219 (1)	C(4)–C(5)–Cl(5)	115·6 (1)
Cl(3)–Cl(4)	2·897 (1)	Cl(5)–C(5)–C(6)	121·8 (1)
		C(5)–C(6)–Cl(6)	122·4 (1)
		Cl(6)–C(6)–C(1)	115·2 (1)
		C(6)–C(1)–O(1)	122·2 (1)
		O(1)–C(1)–C(2)	121·6 (1)

Table 3. *Least-squares planes and atom deviations* ($\times 10^3$ Å)

Plane 1: $0{\cdot}9687x+0{\cdot}0038y+0{\cdot}2482z-2{\cdot}6034=0$

C(1)	−3 (2)	C(5)	−4 (2)
C(2)	1 (2)	C(6)	7 (2)
C(3)	0 (2)	O(1)	−1 (2)
Other atoms			
C(4)	−43 (2)	Cl(4)	1335 (1)
Cl(1)	8 (1)	Cl(5)	−34 (1)
Cl(2)	2 (1)	Cl(6)	19 (1)
Cl(3)	−1556 (1)		

Plane 2: $-0{\cdot}2588x+0{\cdot}1448y+0{\cdot}9550z-1{\cdot}4102=0$

C(4)	2 (2)	Cl(4)	−0 (1)
Cl(3)	−0 (1)	O(1)	−0 (2)

Dihedral angle between the two planes is 90·7°.

Table 4. *Intermolecular distances less than* 3·75 Å

(i) (ii)		(i) (iii)	
O(1)–C(1)	2·896 (3)	C(2)–Cl(2)	3·508 (2)
O(1)–C(2)	3·040 (3)	C(3)–Cl(2)	3·640 (2)
O(1)–C(6)	3·143 (3)	C(5)–Cl(4)	3·707 (2)
O(1)–O(1)	3·385 (3)	Cl(4)–Cl(4)	3·565 (1)
O(1)–Cl(3)	3·442 (2)		

Symmetry code

(i)	x,y,z
(ii)	$\frac{1}{4}-y,\frac{1}{4}+x,\frac{1}{4}-z$
(iii)	$\frac{1}{4}+y,\frac{1}{4}-x,\frac{1}{4}+z$

than 120°, characteristic of a quinonoid structure. All the atoms of the molecule except Cl(3) and Cl(4) lie on a plane. The deviation of C(4) from the ring is significant (Table 3).

The relative positions of the molecules in hexachlorocyclohexa-2,5-dienone are similar to those in chloranil and the principal planes form an angle of 86·4° with each other. Intermolecular distances between atoms less than 3·75 Å are listed in Table 4, and shown in Fig. 2. The $O(1)^{i}$, distances to $C(1)^{ii}$, $C(2)^{ii}$, and $C(6)^{ii}$ are very short (2·89, 3·04, 3·14 Å, coinciding with the corresponding values for chloranil: 2·85, 3·06, 3·14 Å). The intermolecular O–C bonds form a square with an inversion tetrad symmetry axis relating four molecules. The shortest Cl–Cl intermolecular distance (3·56 Å) is between the Cl(4) atoms related by the tetragonal screw axis.

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3,9,9-Tribromocamphor

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Abstract. $C_{10}H_{13}Br_3O$, monoclinic, $P2_1$, $a=8{\cdot}949$ (5), $b=7{\cdot}712$ (7), $c=8{\cdot}996$ (9) Å, $\beta=93{\cdot}33$ (5)°, $Z=2$, $D_x=2{\cdot}08$ g cm^{-3}, μ(Mo $K\alpha$) = 102·8 cm^{-1}. The norbornane skeleton is undistorted, with close to normal bond lengths and angles. The C–C–C bridge angle is 95°. The molecules are linked by C–H···O hydrogen bonds in the solid state.

Introduction. The colourless crystals were small and poorly formed. Unit-cell and intensity data were measured on a Datex-automated G. E. XRD 6 diffractometer with Mo $K\alpha$ radiation and the θ–2θ scan technique. A standard reflexion monitored periodically throughout data collection decreased in intensity by 40% and the data were accordingly scaled. Of 1181 independent reflexions with $2\theta \le 50°$, 507 had intensities greater than 2σ above background [$\sigma^2(I)=S+B+(0{\cdot}09S)^2$, where $S=$ scan and $B=$ background count]. Absorption corrections were not made in view of the irregular crystal surface. The structure was solved by Patterson and Fourier syntheses. Refinement was by full-matrix least-squares techniques in which the function minimized was $\sum w(F_o-F_c)^2$ with weights w derived from counting statistics. The scattering factors for bromine were corrected for the real and imaginary parts of anomalous dispersion, and each bromine was refined with anisotropic thermal parameters. An attempt to refine all atoms with anisotropic thermal parameters resulted in non-positive-definite tensors for two of the carbon atoms and so the light atoms were refined with isotropic thermal parameters. Hydrogen atoms were included in the structure-factor calculations with fixed positional and thermal parameters. The correct absolute configuration has been determined (it is in any case determined from the chemical preparation), and the final R and R' $(=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2})$ for the 507 reflexions with $I \ge 2\sigma(I)$ are 0·066 and 0·076 [the opposite enantiomorph has $R=0{\cdot}067$ and $R'=0{\cdot}078$, and hence may be rejected at the 0·5% significance level (Hamilton, 1965)]. Three low-angle reflexions 020, 040, and 021 were given zero weight in the last two cycles of refinement because of suspected extinction effects. For all 1181 data R was 0·148 and R' 0·088.*

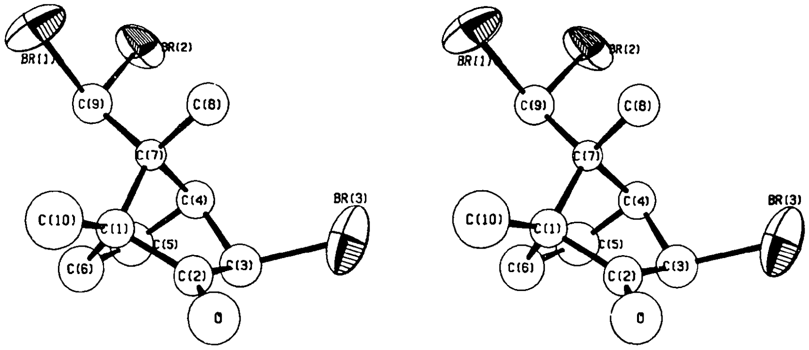

Fig. 1. Stereo diagram of 3,9,9-tribromocamphor showing the absolute configuration of the molecule.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31169 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.