Å, and correspond to those of tetramethyl- and tetrachloro-*p*-phenylene bis(toluene-*p*-sulphonate): O(1) −0·052 (14), S 1·267 (14) Å and O(1) −0·050 (5), S 1·289 (5) Å, respectively. As a result of the interactions of Br(1) and Br(3) with C(2), O(2), O(3) and H(8) some distances are shorter than the sum of the van der Waals radii: Br(1)···C(2) 2·836, Br(3)···C(2) 2·822, Br(1)···O(2) 3·030, Br(3)···O(2) 3·012, Br(1)···O(3) 3·398, Br(3)···H(8) 3·199 Å.

Br atoms deviate from the least-squares plane of benzene ring *A* by 0·136 and 0·145 Å. The O—(O=)S-(=O)—C group is a distorted tetrahedron. Identical distortions of the sulphur tetrahedron were observed in other structures (Chandross, 1977; Kobelt & Paulus, 1974; Enkelmann, 1977). Additional results concerning the geometry of the molecule are given in the tables.

The author expresses his gratitude to W. S. Sheldrick and A. Borkenstein for valuable discussions and for making diffractometric measurements possible and to the directors of the Gesellschaft für Biotechnologische Forschung for the award of a guest fellowship, during the tenure of which this work was carried out.

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Structure of 2,3,5,6-Tetrachloro-1,4-dimethoxybenzene

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Abstract. $C_8H_6Cl_4O_2$, $M_r = 275{\cdot}9$, monoclinic, $P2_1/c$, $a = 4{\cdot}078\ (1)$, $b = 14{\cdot}506\ (5)$, $c = 9{\cdot}245\ (4)$ Å, $\beta = 104{\cdot}13\ (3)°$, $Z = 2$, $D_c = 1{\cdot}731$, $D_m = 1{\cdot}72$ Mg m^{-3}, $V = 530{\cdot}42\ (28)$ Å^3. The structure was refined by full-matrix least-squares calculations with anisotropic temperature factors to $R = 0{\cdot}049$. The dihedral angle between the mean plane through the benzene ring and the plane through C(3), O(1) and C(4) is 84·0 (3)°.

Introduction. Hydroquinone derivatives were used by Böhm & Zamłyński (1967*a*,*b*) as model substances for the investigation of hindered rotation around the C_{Ar}—O bond. The hindered rotation around C—N in a number of suitably substituted arylamines suggests the possible occurrence of the same phenomenon in a number of analogously substituted phenols, resorcinols and hydroquinones; this is because of the similarity of the simplest stereochemical features, *e.g.* valency angles and bond lengths formed by N and O (Böhm & Zamłyński, 1967*a*,*b*). The authors did not observe the occurrence of stereoisomerism caused by hindered rotation in the hydroquinone derivatives. They explained this fact by a facile rebuilding of the valency sphere of the O electrons. Structural investigations of 2-methyl derivatives of hydroquinone (Wieczorek, Bokiy & Struchkov, 1975; Wieczorek & Karolak-Wojciechowska, 1978) were carried out in order to determine the effect of Br and CH_3 substituents on the geometry of the benzene ring. The present work is part of a study of Cl substitution. 2,3,5,6-Tetrachloro-1,4-dimethoxybenzene crystallizes from a mixture of chloroform and benzene. It was difficult to obtain single crystals because of a tendency to form twins. The crystals were sealed in Lindemann-glass capillary tubes.

Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer by the use of graphite-monochromated Cu $K\alpha$ radiation. Measurements were carried out in the θ–2θ scan mode for $2\theta \le 135{\cdot}0°$. Lorentz, polarization and absorption [μ(Cu $K\alpha$) = 9·645 mm^{-1}] corrections were applied. With the application of the acceptance criterion $F \ge 3{\cdot}0\sigma(F)$, 861 of the 941 unique reflections measured were considered to be observed.

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Table 1. *Positional parameters* ($\times 10^4$) *and* $B_{eq.}$ *values for the non-hydrogen atoms*

	x	y	z	$B_{eq.}$ (Å^2)
Cl(1)	41 (3)	3594 (1)	2539 (1)	4·50 (8)
Cl(2)	−4090 (3)	3184 (1)	−733 (1)	4·28 (8)
O(1)	3770 (7)	5331 (2)	2864 (3)	3·71 (12)
C(1)	8 (10)	4369 (2)	1128 (4)	3·06 (15)
C(2)	−1826 (9)	4190 (2)	−315 (4)	3·04 (15)
C(3)	1829 (9)	5183 (2)	1448 (3)	3·09 (12)
C(4)	2221 (16)	5890 (4)	3797 (5)	4·52 (20)

Table 2. *Hydrogen-atom positional parameters* ($\times 10^3$) *with isotropic temperature factors* (Å^2 $\times 10^2$)

	x	y	z	U
H(1)	2 (8)	576 (5)	374 (8)	13 (3)
H(2)	224 (8)	652 (5)	338 (7)	12 (2)
H(3)	386 (9)	592 (4)	482 (7)	12 (2)

Table 3. *Bond lengths* (Å)

C(1)–Cl(1)	1·719 (4)	C(2)–Cl(2)	1·720 (4)
C(3)–O(1)	1·371 (4)	C(4)–O(1)	1·437 (5)
C(2)–C(1)	1·386 (4)	C(3)–C(1)	1·389 (5)
H(1)–C(4)	0·91 (8)	H(2)–C(4)	0·99 (7)
H(3)–C(4)	1·02 (7)	C(3)–C(2′)	1·387 (5)

Table 4. *Bond angles* (°)

C(4)–O(1)–C(3)	115·2 (3)	C(2)–C(1)–Cl(1)	120·7 (3)
C(3)–C(1)–Cl(1)	119·3 (2)	C(3)–C(1)–C(2)	120·0 (3)
C(1)–C(2)–Cl(2)	120·6 (3)	C(1)–C(3)–O(1)	119·4 (3)
C(1)–C(3)–C(2′)	119·7 (3)	C(3′)–C(2)–C(1)	120·3 (3)
O(1)–C(3)–C(2′)	120·8 (3)	Cl(2)–C(2)–C(3′)	119·1 (3)

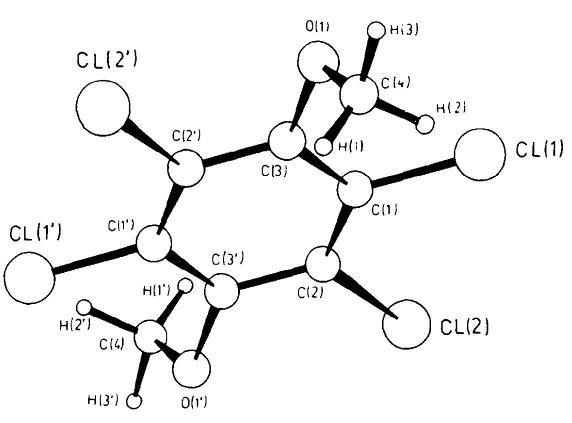

Fig. 1. Perspective view of a molecule of $C_8H_6Cl_4O_2$.

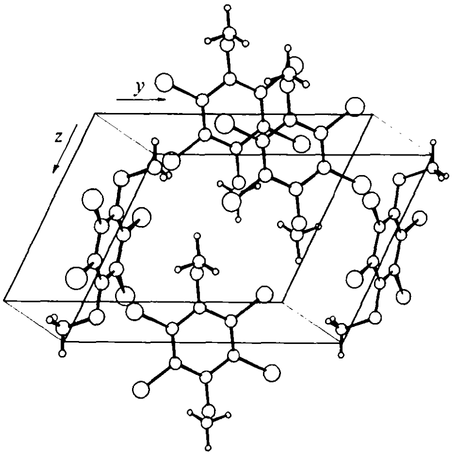

Fig. 2. A perspective view showing the unit-cell packing.

The structure was solved by direct methods. Initial coordinates of two atoms [Cl(1), Cl(2)] were obtained from the E map calculated from phases developed by weighted multisolution tangent refinement (*SHELX* 76; Sheldrick, 1976). Several difference syntheses were carried out to find the positions of the other non-hydrogen atoms ($R = 0{\cdot}16$). Refinement by full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms converged to an R factor of 0·0663. The positions of the H atoms were found from a difference map. Full-matrix least-squares refinement with anisotropic temperature factors for all the non-hydrogen atoms and isotropic temperature factors for the H atoms reduced R to 0·049, R_w to 0·050 and R_G to 0·056; $w = 7{\cdot}1450/[\sigma^2(F) + 0{\cdot}0001F^2]$.*

Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Tables 1 and 2 give the final positional parameters. Fig. 1 is a perspective view of the molecule and Fig. 2 shows the unit-cell contents. The bond lengths and angles are listed in Tables 3 and 4.

Discussion. The valence angles at C(3) have values of 120·8 (3), 119·4 (3) and 119·7 (3)°. The small difference between exocyclic angles may be the result of the interaction between substituents in the *ortho* positions. The differences for the compounds with H as the *ortho* substituent are 6–12° (Ahmed, 1978; Cody & Mukherjee, 1975; Farnum, Neuman & Suggs, 1974; Hecht & Luger, 1974; Sletten, 1974; Irngartinger & Jäger, 1978; Valle, Zanotti & Busetti, 1977; Colapietro

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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 35061 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Least-squares plane of the benzene ring and deviations of atoms* (Å) *from the plane*

Equation of the plane in the standard orthogonal system

$$0{\cdot}87282X - 0{\cdot}45256Y - 0{\cdot}19075Z - 3{\cdot}2835 = 0$$

C(1)	0·002	Cl(1)*	0·003
C(2)	−0·002	Cl(2)*	0·006
C(3)	−0·002	O(1)*	0·070
C(3')	0·002	C(4)*	−1·190
C(1')	−0·002	Weighted standard deviation of plane: 0·003 Å.	
C(2')	0·002		

$\chi^2 = 2{\cdot}67$ $\alpha = 0{\cdot}5$

The benzene ring is nearly ideally planar within experimental error.

* Not included in the calculation of the plane.

& Domenicano, 1978); differences for those with a non-hydrogen *ortho* substituent are 1·4–3·0°.

The dihedral angle between the mean plane through the benzene ring and the plane through C(3), O(1) and C(4) is 84·0 (3)°. The differences in angles for the compounds with and without H as the *ortho* substituent are 0·5–12·0 and 84–88° respectively.

Deviations of atoms from the mean plane of the benzene ring are given in Table 5.

The angle C(3)—O(1)—C(4) is 115·2 (3)°. Analogous angles for the tetramethyl and tetrabromo derivatives are 114·7 (16) and 114·5 (7)° respectively.

Intermolecular distances do not indicate any interactions stronger than normal van der Waals.

The author expresses his gratitude to W. S. Sheldrick and A. Borkenstein for valuable discussions and for making diffractometric measurements possible and to the directors of the Gesellschaft für Biotechnologische Forschung for the award of a guest fellowship, during the tenure of which this work was carried out.

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Anhydrous (+)-Lupanine Perchlorate

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Abstract. $C_{15}H_{25}N_2O^+.ClO_4^-$, $M_r = 348{\cdot}9$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}551$ (2), $b = 10{\cdot}332$ (1), $c = 12{\cdot}369$ (1) Å, $Z = 4$, $d_x = 1{\cdot}44$ Mg m^{-3}. The structure was solved by the heavy-atom method and refined by full-matrix least squares to an R_F of 0·035 for 1249 observed reflections. Unlike lupanine, lupanine hydrochloride dihydrate and lupanine perchlorate monohydrate the lupanine cation in the anhydrous perchlorate has the *trans–cis* configuration and a significantly different conformation. Rings *A*, *B*, *C* and *D* have chair forms. The lupanine cation and perchlorate anion are linked by a weak hydrogen bond: $N(16)^+\cdots OClO_3^- = 3{\cdot}026$ (4) Å.

Introduction. This work is a continuation of an X-ray investigation of the structures of lupanine derivatives.

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