Fig. 3. A stereoscopic packing diagram for 5'-GMP.3H₂O.

solubility of the zwitterions in aqueous solution may have played an important role in the formation of the corresponding polymers under primordial conditions.

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# Structure of Tetrabromo-*p*-phenylene Bis(toluene-*p*-sulphonate)

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**Abstract.** $C_{20}H_{14}Br_4O_6S_2$, $M_r = 734 \cdot 1$, triclinic, $P\bar{1}$, $a = 7 \cdot 555$ (2), $b = 9 \cdot 396$ (2), $c = 10 \cdot 470$ (2) Å, $\alpha = 109 \cdot 71$ (1), $\beta = 112 \cdot 98$ (2), $\gamma = 101 \cdot 02$ (2)°, $Z = 1$, $D_c = 2 \cdot 04$, $D_m = 2 \cdot 00$ Mg m⁻³, $V = 597 \cdot 9$ (2) Å³. X-ray data were obtained on an automatic four-circle Syntex $P2_1$ diffractometer. The structure was refined to $R = 0 \cdot 046$. The dihedral angle between the planes of the first and second benzene rings is $48 \cdot 6$ (5)°.

**Introduction.** This work is part of a study on the conformation of bis(toluene-*p*-sulphonate) derivatives of tetrasubstituted (by Br, Cl, CH₃) hydroquinones. Results for tetramethyl- and tetrachloro-*p*-phenylene bis(toluene-*p*-sulphonate) (Wieczorek, Bokiy & Struchkov, 1975; Wieczorek & Gałdecki, 1978) have proved that toluene-*p*-sulphonate groups are in a *trans* orientation. Single crystals of tetrabromo-*p*-phenylene bis(toluene-*p*-sulphonate) were grown from chloroform/cyclohexane solutions. Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer. Measurements were carried out in the $\theta$–$2\theta$ scan mode

for $3 \cdot 5 \leq 2\theta \leq 50°$ and an absorption correction was applied $[\mu(\text{Mo } K\alpha) = 6 \cdot 78 \text{ mm}^{-1}]$. With the application of the acceptance criterion $F \geq 4 \cdot 0\sigma(F)$, 1399 unique reflections were retained for the refinement. The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976) and refined by blocked-full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms. The methyl H atoms were refined as part of rigid methyl groups. The remaining H atoms were subjected to the constraint $d(\text{C}-\text{H}) = 1 \cdot 08 \pm 0 \cdot 02$ Å, with individual isotropic temperature factors. The terminal value of $R_w$ was $0 \cdot 038$ with $R$ $0 \cdot 046$.* Weights were given by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, where $k$ and $g$ were refined to $1 \cdot 7559$ and $0 \cdot 0003$ respectively. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman,

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

| | $x$ | $y$ | $z$ | $B_{eq.}$ $(\text{Å}^2)$ |
|---|---|---|---|---|
| Br(1) | 7662 (1) | 1180 (1) | 7373 (1) | 3·42 (5) |
| C(1) | 8969 (10) | 3364 (6) | 8916 (7) | 2·4 (3) |
| C(2) | 8306 (10) | 4540 (7) | 8596 (6) | 2·4 (3) |
| Br(3) | 8501 (1) | 7722 (1) | 9084 (1) | 3·65 (5) |
| C(3) | 9320 (11) | 6160 (7) | 9646 (7) | 2·9 (3) |
| O(2) | 6643 (7) | 4078 (5) | 7134 (5) | 2·9 (2) |
| S | 4260 (3) | 3323 (2) | 6768 (2) | 2·99 (8) |
| O(1) | 3236 (8) | 2110 (5) | 5204 (5) | 3·9 (3) |
| O(3) | 4343 (8) | 2942 (6) | 7977 (6) | 4·7 (3) |
| C(4) | 3438 (10) | 4955 (7) | 6873 (7) | 2·6 (3) |
| C(5) | 2965 (11) | 5366 (8) | 5670 (8) | 3·6 (3) |
| C(6) | 2482 (12) | 6740 (9) | 5833 (9) | 4·5 (4) |
| C(7) | 2490 (11) | 7698 (8) | 7157 (9) | 3·7 (4) |
| C(8) | 2947 (12) | 7242 (9) | 8354 (9) | 4·1 (4) |
| C(9) | 3428 (12) | 5868 (8) | 8214 (8) | 4·0 (3) |
| C(71) | 1992 (15) | 9204 (9) | 7309 (11) | 5·9 (5) |

Table 2. *Bond lengths* (Å)

| | | | |
|---|---|---|---|
| C(1)–Br(1) | 1·881 (5) | C(2)–C(1) | 1·384 (10) |
| C(3)–C(2) | 1·371 (7) | O(2)–C(2) | 1·397 (7) |
| C(3)–Br(3) | 1·879 (7) | S–O(2) | 1·637 (6) |
| O(1)–S | 1·412 (4) | O(3)–S | 1·409 (7) |
| C(4)–S | 1·748 (8) | C(5)–C(4) | 1·376 (12) |
| C(9)–C(4) | 1·380 (11) | C(6)–C(5) | 1·381 (12) |
| C(7)–C(6) | 1·371 (13) | C(8)–C(7) | 1·398 (14) |
| C(71)–C(7) | 1·505 (12) | C(9)–C(8) | 1·384 (12) |
| H(5)–C(5) | 1·07 (7) | C(1)–C(3') | 1·394 (10) |

Table 3. *Bond angles* (°)

| | | | |
|---|---|---|---|
| C(2)–C(1)–Br(1) | 119·8 (4) | C(3)–C(2)–C(1) | 121·5 (5) |
| O(2)–C(2)–C(1) | 119·2 (4) | O(2)–C(2)–C(3) | 119·2 (6) |
| Br(3)–C(3)–C(2) | 119·7 (5) | S–O(2)–C(2) | 120·2 (5) |
| O(1)–S–O(2) | 103·2 (3) | O(3)–S–O(2) | 107·6 (3) |
| O(3)–S–O(1) | 121·5 (3) | C(4)–S–O(2) | 102·9 (3) |
| C(4)–S–O(1) | 109·7 (3) | C(4)–S–O(3) | 110·1 (4) |
| C(5)–C(4)–S | 119·2 (6) | C(9)–C(4)–S | 118·8 (6) |
| C(9)–C(4)–C(5) | 121·9 (7) | C(6)–C(5)–C(4) | 118·2 (8) |
| C(7)–C(6)–C(5) | 121·9 (9) | C(8)–C(7)–C(6) | 118·8 (8) |
| C(71)–C(7)–C(6) | 120·6 (9) | C(71)–C(7)–C(8) | 120·6 (8) |
| C(9)–C(8)–C(7) | 120·4 (8) | C(8)–C(9)–C(4) | 118·9 (8) |
| C(2)–C(1)–C(3') | 119·1 (5) | C(2)–C(3)–C(1') | 119·5 (5) |
| C(3')–C(1)–Br(1) | 121·1 (4) | Br(3)–C(3)–C(1') | 120·7 (5) |
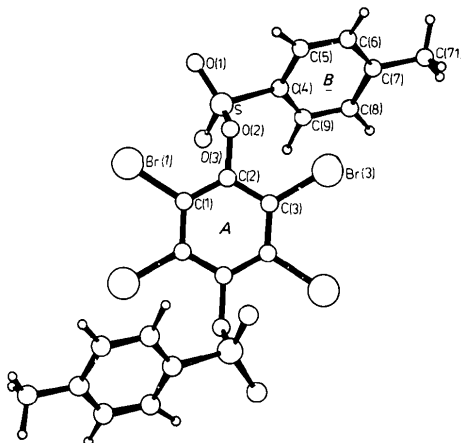


Fig. 1. Perspective view of a molecule of $C_{20}H_{14}Br_4O_6S_2$.

Table 4. *Least-squares planes of benzene rings A and B and deviations of atoms* (Å) *from the planes*

Plane $A$    $-0·5973X_o + 0·1316Y_o + 0·7911Z_o = 1·0815$
Plane $B$    $0·9667X_o + 0·2063Y_o - 0·1512Z_o = 2·1629$

| Plane $A$ | | Plane $B$ | |
|---|---|---|---|
| C(1) | −0·005 (8) | C(4) | 0·005 (8) |
| C(2) | 0·005 (7) | C(5) | −0·001 (8) |
| C(3) | 0·005 (8) | C(6) | −0·007 (9) |
| C(1') | 0·005 (8) | C(7) | 0·009 (9) |
| C(2') | −0·005 (7) | C(8) | −0·004 (9) |
| C(3') | −0·005 (8) | C(9) | −0·003 (9) |
| O(2)* | −0·058 (5) | C(71)* | 0·026 (11) |
| S* | 1·296 (2) | S* | 0·152 (2) |
| Br(1)* | −0·136 (2) | | |
| Br(3)* | 0·145 (2) | | |

$\chi^2 = 0·41; 0·5 < p < 0·9$    $\chi^2 = 0·28; 0·90 < p < 0·95$
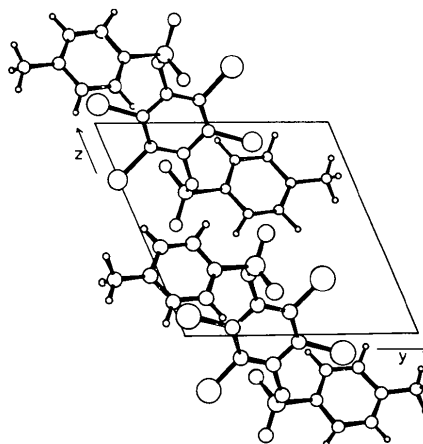
* Not included in the calculation of the plane.



Fig. 2. The unit-cell contents.

1970). Table 1 gives the final positional parameters, Tables 2 and 3 the bond lengths and angles. Table 4 gives least-squares-planes data. Fig. 1 is a perspective view of the molecule with the numbering scheme and Fig. 2 shows the unit-cell contents.

**Discussion.** The dihedral angle between the planes of benzene rings $A$ and $B$ is 48·6 (5)°. Analogous angles for the tetramethyl and tetrachloro derivatives are 43·0 and 46·4° respectively (Wieczorek, Bokiy & Struchkov, 1975; Wieczorek & Gałdecki, 1978). The most interesting results concern the angles between the plane of benzene ring $A$ and the plane defined by SO(2) and C(2) and between benzene ring $B$ and the plane SO(2), C(2): these are 100·3 (4) and 79·5 (4)° respectively. The deviations of O(2) and S from the mean plane of benzene ring $A$ are $-0·058$ (5) and 1·296 (2)

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.

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

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**Abstract.** $C_8H_6Cl_4O_2$, $M_r = 275·9$, monoclinic, $P2_1/c$, $a = 4·078$ (1), $b = 14·506$ (5), $c = 9·245$ (4) Å, $\beta = 104·13$ (3)°, $Z = 2$, $D_c = 1·731$, $D_m = 1·72$ Mg m$^{-3}$, $V = 530·42$ (28) Å$^3$. The structure was refined by full-matrix least-squares calculations with anisotropic temperature factors to $R = 0·049$. 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 ex-

plained 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 _Kα_ radiation. Measurements were carried out in the $\theta$–$2\theta$ scan mode for $2\theta \leq 135·0°$. Lorentz, polarization and absorption [$\mu$(Cu _Kα_) = 9·645 mm$^{-1}$] corrections were applied. With the application of the acceptance criterion $F \geq 3·0\sigma(F)$, 861 of the 941 unique reflections measured were considered to be observed.