Tabelle 3. *Intramolekülare Abstände* (Å) *und Winkel* (°) *für* Cu(tsc)$_2$ *mit Standardabweichungen* (*e.s.d.*) *in Klammern*

Cu(1)–Se(2)	2,491 (4)	C(13)–N(7)	1,35 (3)
Cu(1)–Se(5)	2,508 (4)	N(6)—C(9)	1,47 (4)
Cu(1)–S(3)	2,354 (4)	N(6)—C(10)	1,48 (3)
Cu(1)–S(4)	2,339 (5)	N(7)—C(14)	1,49 (3)
Se(2)–C(8)	1,82 (2)	N(7)—C(15)	1,54 (3)
Se(5)–C(13)	1,82 (2)	C(9)—C(11)	1,52 (4)
S(3)—C(8)	1,82 (2)	C(10)–C(12)	1,56 (4)
S(4)—C(13)	1,84 (2)	C(14)–C(16)	1,52 (3)
C(8)—N(6)	1,37 (3)	C(15)–C(17)	1,52 (4)
Se(2)–Cu(1)–S(3)	78,3 (1)	Se(5)–C(13)–N(7)	120 (2)
S(4)—Cu(1)–Se(5)	77,6 (2)	C(8)—N(6)—C(10)	121 (2)
Cu(1)–Se(2)–C(8)	81,7 (6)	C(13)–N(7)—C(15)	123 (2)
Cu(1)–Se(5)–C(13)	82,8 (6)	C(8)—N(6)—C(9)	124 (2)
Cu(1)–S(3)—C(8)	85,8 (6)	C(13)–N(7)—C(14)	120 (2)
Cu(1)–S(4)—C(13)	87,4 (7)	C(9)—N(6)—C(10)	116 (2)
Se(2)–C(8)—S(3)	114 (1)	C(14)–N(7)—C(15)	117 (2)
S(4)—C(13)–Se(5)	112 (1)	N(6)—C(10)–C(12)	112 (2)
S(3)—C(8)—N(6)	125 (2)	N(7)—C(15)–C(17)	113 (2)
S(4)—C(13)–N(7)	128 (2)	N(6)—C(9)—C(11)	107 (2)
Se(2)–C(8)—N(6)	121 (2)	N(7)—C(14)–C(16)	114 (2)

niederen Wellenzahlen (907 cm^{-1}) gegenüber der im reinen Cu(dtc)$_2$ zu beobachtenden und für die (C=Se)-Bande eine Verschiebung nach höheren Wellenzahlen (840 cm^{-1}) gegenüber der im reinen Cu(dsc)$_2$ (830 cm^{-1}) gemessenen Wellenzahl. Jensen & Krishnan (1970) geben für die Lage der (C=S)- und (C=Se)-Bande vergleichbarer Verbindungen Werte von 910–915 cm^{-1} bzw. 820–830 cm^{-1} an. Die Bindungslängen zeigen, dass der Bindungsausgleich durch Delokalisierung im Chelatring behindert wird. Die Se–C-Bindung besitzt starken Doppelbindungs-, die S–C-Bindung Einfachbindungscharakter. Für die C–N-Bindung finden wir in Übereinstimmung mit einer Reihe von Dithiocarbamaten einen Wert von 1,36 Å.

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The Crystal Structure of Tetramethyl-*p*-phenylene Ditoluene-*p*-sulphonate

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A complete X-ray investigation was carried out for tetramethyl-*p*-phenylene ditoluene-*p*-sulphonate, $C_{24}H_{26}O_6S_2$. The compound crystallizes in the triclinic system with $a=8{\cdot}791_5$, $b=11{\cdot}109_1$, $c=7{\cdot}405_1$ Å, $\alpha=112{\cdot}53$, $\beta=120{\cdot}40$, $\gamma=86{\cdot}35°$, $V=568{\cdot}44$ Å^3, $\varrho_{\rm calc}=1{\cdot}393$, $\varrho_{\rm obs}=1{\cdot}381$ g cm^{-3}, $N=1$, space group $P\bar{1}$. X-ray data were obtained on an automatic four-circle Hilger–Watts diffractometer. Least-squares full-matrix refinement of the structure with the use of isotropic temperature factors led to $R=9{\cdot}0$%.

Introduction

Adams and co-workers (1940–1961) observed restricted rotation around the C–N bond in a series of suitably substituted aryl amines. Böhm & Zamłyński (1967) anticipated a similar phenomenon in the series of diesters of dihydroxybenzenes. On the basis of model considerations, they supposed that as for amines restricted rotation should lead to the occurrence of stable rotamers. However, despite very careful separation of the product by fractional crystallization and column chromatography, it was not possible to separate these rotamers. This anomaly was explained by the greater freedom of rotation around O–C as compared with N–C bonds.

The actual orientation of the OR group bonded to an aromatic ring is the result of a tendency of the molecule to achieve maximum conjugation of the oxygen lone pairs with an aromatic ring and the steric influence of *ortho* substituents. Böhm & Zamłyński considered the rapid interconversion of rotamers (from ultraviolet data and dipole moments) as the result of a considerable opening of the oxygen bond angle.

The present investigation is part of a structural study of dimethyl- and ditoluene-*p*-sulphonate derivatives of tetrasubstituted hydroquinones (Br, Cl, CH_3). The study was undertaken to confirm that rotation occurs around the bonds at oxygen and to determine the dependence of the molecular conformation on the nature of the substituent in the *ortho* position.

Experimental

The compound crystallizes in the form of triclinic prisms. Approximate values of the unit-cell parameters were determined from oscillation and rotation photographs taken with copper radiation.

The parameters were refined by least-squares calculations on the basis of ten high-angle reflexions measured with an automatic four-circle Hilger–Watts diffractometer controlled by a PDP-8I computer. Copper radiation with a graphite monochromator was used. These reflexions were scanned using the peak-finder program (Hilger & Watts, 1970) and parameters were calculated by Dobler & Duerr's (1968) program.

The investigation was performed in the X-ray laboratory of the Institute of Elemento-Organic Compounds of the Academy of Sciences, Moscow, U.S.S.R.

Crystal data

$a=8\cdot792\ (5)$, $b=11\cdot109\ (4)$, $c=7\cdot405\ (5)$ Å, $\alpha=112\cdot53\ (20)$, $\beta=120\cdot40\ (20)$, $\gamma=86\cdot35\ (20)^\circ$, $V=568\cdot44$ Å^3, $\varrho_{\rm calc}=1\cdot39_3$, $\varrho_{\rm obs}=1\cdot38_1$ g cm^{-3}, $N=1$, space group $P\bar{1}$.

The statistics of the normalized structure factors, E, indicated the space group to be $P\bar{1}$.

Reflexion intensities were measured for $\theta\le57^\circ$, using the ω scan according to Watson, Shotton, Cox & Muirhead's (1970) program (crystal dimensions were $0\cdot1\times0\cdot15\times0\cdot8$ mm; the crystal was elongated along the c axis). No absorption correction was applied. The structure was determined from 1363 significant reflexions with $F^2\ge5\sigma(F^2)$, out of a total 1600 reflexions.

Determination of the structure

The direct method was used. Triple products were formed with a probability $\ge0\cdot97$ using 191 normalized amplitudes with $|E|>1\cdot4$. The basic group contained seven reflexions. All possible combinations of signs ($2^7=128$ combinations) were assigned to these seven reflexions with high E values. Each of the combinations was used independently to define the signs of all the normalized amplitudes. Estimates of the three best sign combinations are given below (all computations were made using a program written by B. L. Tarnopolski, W. I. Andrianow and Z. S. Safina in 1969).

$N_1=61$	$Q_1=191$	$R_1=0\cdot995$
$N_2=125$	$Q_2=191$	$R_2=0\cdot960$
$N_3=44$	$Q_3=191$	$R_3=0\cdot953$

N is the solution number,
Q the number of defined signs and

$$R=\frac{\sum^+|E_hE_{h'}E_{h''}|}{\sum|E_hE_{h'}E_{h''}|}$$

where $\sum^+$ is the sum of the triple products for which $S(E_h)\,.\,S(E_{h'})\,.\,S(E_{h''})>0$ and $\sum|E_hE_{h'}E_{h''}|$ is the sum of all the triple products. The E synthesis for the best solution revealed the positions of all the non-hydrogen atoms. These positions were refined by least-squares calculations; isotropic temperature factors were refined in the next stage. In the final stage of refinement the weights proposed by Cruickshank (1961) were used. The R value was 10·7%. The difference synthesis revealed the positions of all the hydrogen atoms. Their inclusion in a structure factor calculation (without refinement)

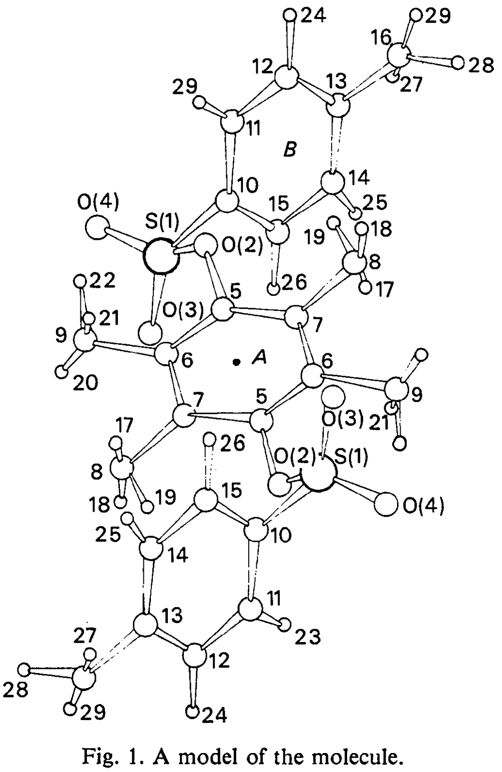


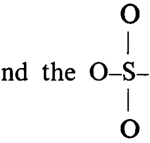
Fig. 1. A model of the molecule.

Table 1. *Atomic parameters*

	B_j (Å^2)	x	y	z
S(1)	3·068 (30)	0·8384 (21)	0·212 (2)	0·647 (2)
O(2)	3·11 (7)	0·936 (5)	0·223 (5)	0·904 (5)
O(3)	4·43 (9)	0·801 (6)	0·076 (6)	0·495 (7)
O(4)	5·13 (9)	0·694 (7)	0·285 (6)	0·622 (7)
C(5)	2·39 (9)	0·965 (7)	0·106 (7)	0·946 (8)
C(6)	2·67 (9)	0·829 (8)	0·038 (7)	0·929 (8)
C(7)	2·58 (9)	1·138 (7)	0·073 (7)	1·021 (8)
C(8)	3·55 (12)	1·282 (9)	0·157 (8)	1·047 (9)
C(9)	4·12 (12)	0·648 (9)	0·085 (9)	0·861 (10)
C(10)	3·20 (11)	0·999 (8)	0·300 (8)	0·655 (9)
C(11)	3·46 (11)	1·025 (8)	0·438 (8)	0·750 (9)
C(12)	3·87 (12)	1·159 (9)	0·506 (9)	0·764 (10)
C(13)	3·70 (12)	1·269 (8)	0·442 (8)	0·687 (9)
C(14)	3·99 (12)	1·241 (9)	0·303 (9)	0·589 (10)
C(15)	3·79 (12)	1·105 (9)	0·231 (9)	0·569 (10)
C(16)	5·38 (15)	1·416 (11)	0·520 (10)	0·708 (12)
H(17)		1·296	0·114	0·930
H(18)		1·303	0·216	1·160
H(19)		1·240	0·230	1·040
H(20)		0·587	0·030	0·738
H(21)		0·650	0·108	0·980
H(22)		0·654	0·186	0·863
H(23)		0·950	0·480	0·820
H(24)		1·180	0·610	0·850
H(25)		1·290	0·244	0·524
H(26)		1·084	0·129	0·496
H(27)		1·390	0·480	0·573
H(28)		1·550	0·490	0·773
H(29)		1·460	0·580	0·830

gave a final R value of 0·090. The atomic coordinates and the temperature factors are given in Table 1.*

Results and discussion

The model of the molecule is shown in Fig. 1 with bond lengths and angles in Tables 2 and 3. The average C_{Ar}–C_{Ar} bond lengths in benzene rings A and B are 1·393 and 1·396 Å respectively; the C_{Ar}–C_{Me} and C_{Ar}–S bond lengths are 1·515 and 1·736 Å respectively. These values and the C–O length of 1·429 Å are consistent with the literature data (Berthou, Jéminet & Laurent, 1972; Baenziger & Schultz, 1973; Sato, Shiro & Koyama, 1968). The toluene-*p*-sulphonate groups are *trans* and the  $O{-}\overset{O}{\underset{O}{S}}{-}C$ group is a distorted tetrahedron with S–O 1·602 and S=O 1·426 and 1·431 Å.

An identical distortion of the sulphur tetrahedron is reported by Sato *et al.* (1968).

Table 2. *Bond distances* (Å)

S(1)—O(2)	1·602 (8)	C(9)—H(20)	0·78 (6)
S(1)—O(3)	1·431 (9)	C(9)—H(21)	0·80 (12)
S(1)—O(4)	1·426 (8)	C(9)—H(22)	1·12 (9)
S(1)—C(10)	1·736 (11)	C(10)-C(11)	1·396 (11)
O(2)—C(5)	1·429 (10)	C(10)-C(15)	1·410 (14)
C(5)—C(6)	1·375 (10)	C(11)-C(12)	1·380 (15)
C(5)—C(7)	1·408 (10)	C(11)-H(23)	1·00 (10)
C(6)—C(7)	1·394 (12)	C(12)-C(13)	1·399 (14)
C(6)—C(9)	1·530 (12)	C(12)-H(24)	1·07 (8)
C(7)—C(8)	1·504 (14)	C(13)-C(14)	1·398 (11)
C(8)—H(19)	0·89 (10)	C(13)-C(16)	1·511 (16)
C(8)—H(18)	0·78 (7)	C(14)-C(15)	1·393 (16)
C(8)—H(17)	0·88 (10)	C(14)-H(25)	0·88 (10)
C(16)-H(29)	0·82 (7)	C(15)-H(26)	1·04 (8)
C(16)-H(28)	1·10 (8)		
C(16)-H(27)	0·83 (9)		

The deviations of the atoms from the least-squares planes of the benzene rings A and B are given in Table 4.

The C–H bond lengths are within the usual range of 0·75–1·12 Å. As for the conformation of the molecule the most interesting data are the angles between the planes of benzene rings A and B and the plane defined by S(1), O(2) and C(5). The respective values are 42° 58′ and 98° 14′.

Thus the O(2)–S bond is not coplanar with benzene ring A, in accordance with ultraviolet and dipole moment data. The C–O–S bond angle is 120·1°, *i.e.* close to experimental data on other hydroxybenzene derivatives (116–123°; Gaultier & Hauw, 1969; McGregor & Speakman, 1968; McKechnie & Paul, 1969; Andrianow, Tarnopolski & Szibaewa, 1969). Analysis of non-bonded intramolecular distances

Table 3. *Bond angles* (°)

O(2)-S(1)-O(3)	108·66 (53)	C(5)—C(7)—C(6)	117·4 (8)
O(2)-S(1)-O(4)	105·3 (5)	C(5)—C(7)—C(8)	120·6 (7)
O(2)-S(1)-C(10)	102·4 (5)	C(6)—C(7)—C(8)	122·0 (7)
O(3)-S(1)-O(4)	119·2 (5)	S(1)—C(10)-C(11)	119·7 (8)
O(3)-S(1)-C(10)	111·1 (5)	S(1)—C(10)-C(15)	119·2 (6)
O(4)-S(1)-C(10)	108·7 (4)	C(11)-C(10)-C(15)	121·0 (9)
S(1)-O(2)-C(5)	120·1 (5)	C(10)-C(11)-C(12)	118·7 (9)
O(2)-C(5)-C(6)	118·8 (7)	C(11)-C(12)-C(13)	121·9 (8)
O(2)-C(5)-C(7)	116·8 (8)	C(12)-C(13)-C(14)	118·5 (9)
C(6)-C(5)-C(7)	124·3 (8)	C(12)-C(13)-C(16)	120·3 (8)
C(5)-C(6)-C(7)	118·3 (7)	C(14)-C(13)-C(16)	121·2 (9)
C(5)-C(6)-C(9)	121·1 (8)	C(13)-C(14)-C(15)	121·1 (9)
C(7)-C(6)-C(9)	120·6 (8)	C(10)-C(15)-C(14)	118·6 (7)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31080 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Deviations from the benzene ring planes*

Benzene ring *A*	C(5)	0·0091 Å	C(6)	−0·0089 Å
	C(7)	−0·0087	C(5)	−0·0091
	C(6)	0·0089	C(7)	0·0087
	O(2)	0·063	C(9)	−0·074
	C(8)	−0·063		
Benzene ring *B*	C(10)	−0·0105 Å	C(11)	0·0012 Å
	C(12)	0·0077	C(14)	−0·0025
	C(13)	−0·0069	C(15)	0·0111
	S(1)	−0·0925	C(16)	−0·0158

shows that there is no serious overcrowding (the shortest distances are S···C 3·36, S···H 2·88, C···C 3·48, C···O 2·77, C···H 3·07, H···H 2·65 Å) which might hinder the rotation around the C–O bond. This is an obvious conclusion in view of the impossibility rotamer separation (Fig. 2).

Analysis of the intermolecular distances in the structure indicated no contacts shorter than the sum of the van der Waals radii.

X-ray investigations of the other derivatives of hydroquinone to evaluate the influence of the size of *ortho* substituents on the molecular conformation are in progress.

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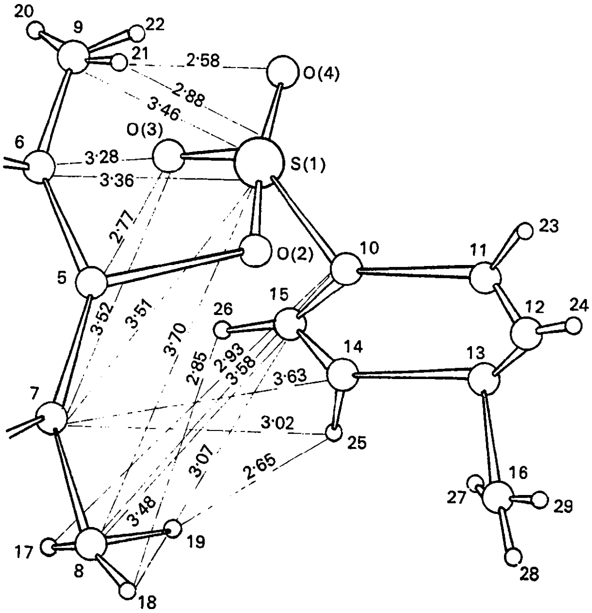

Fig. 2. Intermolecular distances.

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