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The Molecular Structure of *o*-Carboxyphenyl Methyl Sulphoxide and *o*-Carboxyphenyl Methyl Selenium Oxide

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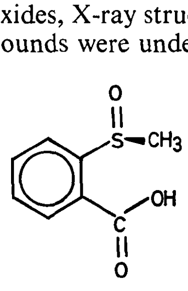
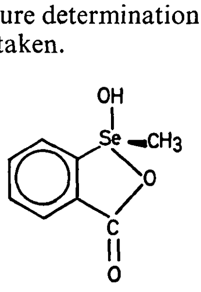
o-Carboxyphenyl methyl sulphoxide and *o*-carboxyphenyl methyl selenium oxide are monoclinic ($P2_1/c$) with cell dimensions $a=8{\cdot}979$, $b=11{\cdot}660$, $c=9{\cdot}554$ Å, $\beta=123{\cdot}62°$ and $a=8{\cdot}948$, $b=11{\cdot}445$, $c=9{\cdot}583$ Å, $\beta=122{\cdot}03°$ respectively. Although the two compounds show very similar atomic positions the molecular structures are essentially different. The hydroxyl hydrogen atom of the carboxyl group of the sulphur compound corresponds to the hydrogen atom attached to the selenium oxide oxygen, and there are several structural indications that there is ring closure by a Se–O bond. However, this bond is 2·378 Å which is 34% longer than a normal Se–O covalent bond. Both molecules are mainly planar except for the methyl group, which projects from the benzene ring plane. The molecules are linked together by a hydrogen bond from the hydroxyl oxygen to the oxygen attached to sulphur and selenium respectively in the adjacent molecule.

Introduction

Organic sulphoxides of the type RR'SO can be resolved into optical antipodes. In connection with work on (I) Professor A. Fredga of Uppsala University recently synthesized an analogous selenium oxide (report in preparation). As some spectral data indicated that there might be a difference in the structure of these oxides, X-ray structure determinations of the two compounds were undertaken.



(I)



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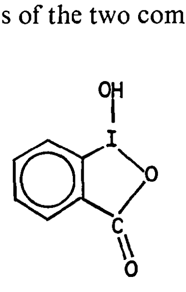


(III)

Experimental

Weissenberg photographs indicated that both compounds were monoclinic. The space group was determined as $P2_1/c$ from the systematic absences, $h0l$ for l odd and $0k0$ for k odd. The crystal data are as follows:

$C_8H_8O_3S$, *o*-Carboxyphenyl methyl sulphoxide
Molecular weight 184·21
Unit cell $a=8{\cdot}979$ (3), $b=11{\cdot}660$ (5), $c=9{\cdot}554$ (2) Å, $\beta=123{\cdot}62°(2)$
$V=832{\cdot}9$ Å^3
$Z=4$
$D_c=1{\cdot}469$ g cm^{-3}
$D_m=1{\cdot}469$ g cm^{-3}
$\mu=30{\cdot}73$ cm^{-1} for Cu $K\alpha$ radiation.

$C_8H_8O_3Se$, *o*-Carboxyphenyl methyl selenium oxide
Molecular weight 231·11
Unit cell $a=8{\cdot}948$ (5), $b=11{\cdot}445$ (6), $c=9{\cdot}583$ (6) Å $\beta=122{\cdot}03°(5)$.
$V=831{\cdot}9$ Å^3
$Z=4$
$D_c=1{\cdot}845$ g cm^{-3}
$D_m=1{\cdot}840$ g cm^{-3}
$\mu=65{\cdot}57$ cm^{-1} for Cu $K\alpha$ radiation.

Intensity data for both compounds were collected on a Picker FACS I automatic diffractometer using graphite monochromated Cu $K\alpha$ radiation. Reflexions up to $2\theta=124°$ were measured by scanning in the θ–2θ mode with a scan width of 2·0° and a scanning speed of 1° min^{-1}. 10 sec background counts were taken at both ends of the scan range for each reflexion.

Lorentz and polarization corrections were applied and the selenium compound data were also corrected for absorption and secondary extinction. Atomic scattering factors for carbon, oxygen, sulphur and selenium atoms were taken from *International Tables for X-ray Crystallography* (1962), while for hydrogen the values given by Stewart, Davidson & Simpson (1965) were used. Sulphur and selenium atoms were corrected for anomalous dispersion using the values given in Table ·3·3·2B of *International Tables for X-ray Crystallography* (1962). All calculations were performed on a Datasaab D21–PDP15 dual computer with a program system developed at this institute.

Structure determination and refinement

o-Carboxyphenyl methyl sulphoxide (OCSO)

A single crystal with dimensions 0·18×0·18×0·21 mm was mounted along the *b* axis. Of the measured intensities 1110 independent reflexions were used in the calculations. These intensities were more than 4 standard deviations above background and considered as observed. This limit was chosen as in this case most of the systematically absent reflexions were automatically excluded as unobserved by the data reduction programs.

For the structure solution a sharpened three-dimensional Patterson synthesis was calculated from which the coordinates of the sulphur atom could be determined. A sulphur-phased Fourier observation synthesis then made it possible to locate all carbon and oxygen atoms.

The structure was refined using block-diagonal least-squares treatment. When the R value was 0·069 a Fourier difference synthesis was calculated which revealed the positions of all hydrogen atoms. These were included in the refinement and given the same isotropic temperature factors as the parent atom. All atoms were then refined with four cycles of full matrix least-squares refinement using anisotropic temperature factors for the non-hydrogen atoms and isotropic for the hydrogen atoms. At this stage the average value of shift/standard deviation was 0·08. The final R value is 0·042. The weight assigned to each observation in the refinement was (Mills & Rollett, 1961)

$$w=(1+(|F_o|/6|F_{\min}|)^2)^{1/2}.$$

o-Carboxyphenyl methyl selenium oxide (OCSeO)

A crystal with the dimensions 0·08×0·12×0·30 mm was mounted along the *c* axis and used for the data collection. 1243 of the reflexions measured were more than 4 σ above background and included in the structure refinement. The limit value of 4σ between observed and unobserved reflexions was chosen for the same reason as in the sulphur-containing molecule.

As the two compounds belong to the same space-group and their unit cells are very similar the structures were assumed to be isotypical. Therefore all non-hydrogen atoms were assigned the same positional parameters as the corresponding atoms in OCSO. One cycle of block-diagonal refinement using isotropic temperature factors decreased the R value to 0·10. After another cycle of block-diagonal refinement a Fourier difference synthesis was calculated to obtain the hydrogen atom positions. All hydrogen atoms attached to carbon atoms could easily be located but the hydroxyl hydrogen did not show up at the expected position. In the sulphur compound the hydroxyl hydrogen takes part in an intermolecular hydrogen bond to oxygen O(1) in a symmetry-related molecule. However, the difference electron density map between these two oxygen atoms in the selenium compound only showed a well defined maximum about 0·9 Å from oxygen O(1).

The hydrogen atom was thus included in the calculations with the parameters from the difference syn-

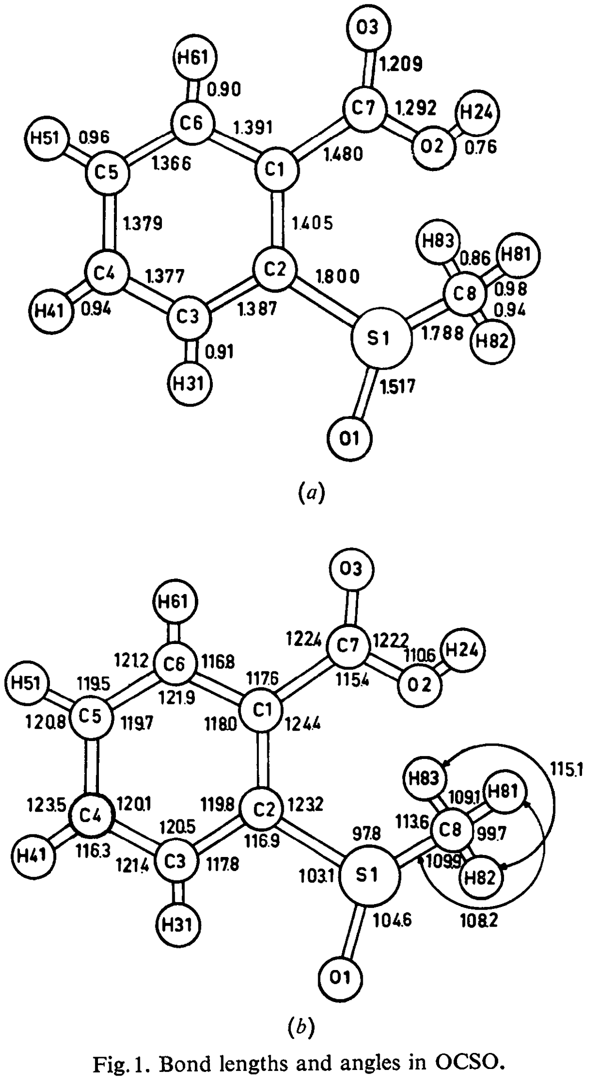


Fig. 1. Bond lengths and angles in OCSO.

thesis. The whole structure then refined very satisfactorily with full-matrix methods. The final R value is 0·039.

Table 1. *Fractional coordinates with standard deviations for the heavier atoms*

Values have been multiplied by 10^4.

$C_8H_8O_3S$	x	y	z
S(1)	751 (1)	3166 (1)	3833 (1)
C(1)	2570 (4)	1259 (3)	5925 (4)
C(2)	2298 (4)	2452 (3)	5790 (4)
C(3)	3336 (5)	3145 (3)	7186 (4)
C(4)	4611 (5)	2669 (4)	8712 (5)
C(5)	4894 (5)	1499 (4)	8856 (5)
C(6)	3888 (5)	813 (3)	7482 (4)
C(7)	1562 (5)	442 (3)	4514 (4)
C(8)	−1182 (5)	3080 (3)	3925 (5)
O(1)	1328 (3)	4412 (2)	4218 (3)
O(2)	86 (3)	830 (2)	3229 (3)
O(3)	2083 (5)	− 523 (2)	4561 (4)
$C_8H_8O_3Se$			
Se(1)	779 (0)	3085 (0)	3587 (0)
C(1)	2555 (4)	1206 (3)	5829 (4)
C(2)	2415 (4)	2420 (3)	5717 (4)
C(3)	3466 (5)	3130 (3)	7069 (5)
C(4)	4671 (5)	2611 (5)	8549 (5)
C(5)	4815 (5)	1416 (4)	8690 (5)
C(6)	3787 (5)	718 (4)	7352 (5)
C(7)	1418 (5)	463 (3)	4346 (4)
C(8)	−1346 (5)	3007 (4)	3658 (6)
O(1)	1380 (4)	4535 (2)	4335 (3)
O(2)	285 (4)	1045 (2)	3080 (3)
O(3)	1626 (4)	− 599 (2)	4391 (4)

The weighting scheme used in the refinement was

$$w = \{1 + [(|F_o| - 3|F_{\text{min}}|)/4{\cdot}5|F_{\text{min}}|]^2\}^{1/2}.$$

Results and discussion

The final atomic parameters are given in Tables 1–3. Lists of the final observed and calculated structure fac-

Table 3. *Fractional coordinates and isotropic temperature factors and standard deviations for the hydrogen atoms*

Fractional coordinates have been multiplied by 10^4.

$C_8H_8O_3S$	x	y	z	B (Å^2)
H(31)	3060 (43)	3908 (30)	7085 (40)	3·9 (0·7)
H(41)	5284 (58)	3184 (32)	9598 (58)	5·7 (0·9)
H(51)	5778 (60)	1158 (39)	9919 (58)	7·7 (1·1)
H(61)	4012 (49)	45 (34)	7558 (46)	5·2 (0·9)
H(81)	−2170 (59)	3473 (38)	2937 (57)	6·9 (1·0)
H(82)	−1042 (66)	3563 (46)	4774 (68)	8·8 (1·3)
H(83)	−1500 (55)	2388 (44)	3952 (54)	6·6 (1·0)
H(24)*	− 390 (54)	0365 (35)	2564 (49)	5·6 (1·0)
$C_8H_8O_3Se$				
H(31)	3411 (46)	3958 (37)	6974 (44)	2·2 (0·7)
H(41)	5247 (73)	3058 (36)	9333 (69)	3·9 (1·2)
H(51)	5608 (59)	1062 (38)	9694 (56)	3·7 (0·9)
H(61)	3766 (58)	−7 (45)	7320 (54)	3·7 (1·0)
H(81)	−2325 (97)	3155 (42)	2485 (94)	7·0 (1·8)
H(82)	−1192 (95)	3548 (62)	4498 (94)	9·1 (1·9)
H(83)	−1694 (61)	2384 (50)	3993 (57)	4·1 (1·0)
H(24)*	766 (83)	5038 (74)	3519 (77)	8·5 (2·1)

* Refers to the oxygen atom O(2).

Table 2. *Anisotropic thermal parameters in the form*

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lha^*c^*U_{31} + 2hka^*b^*U_{12})].$$

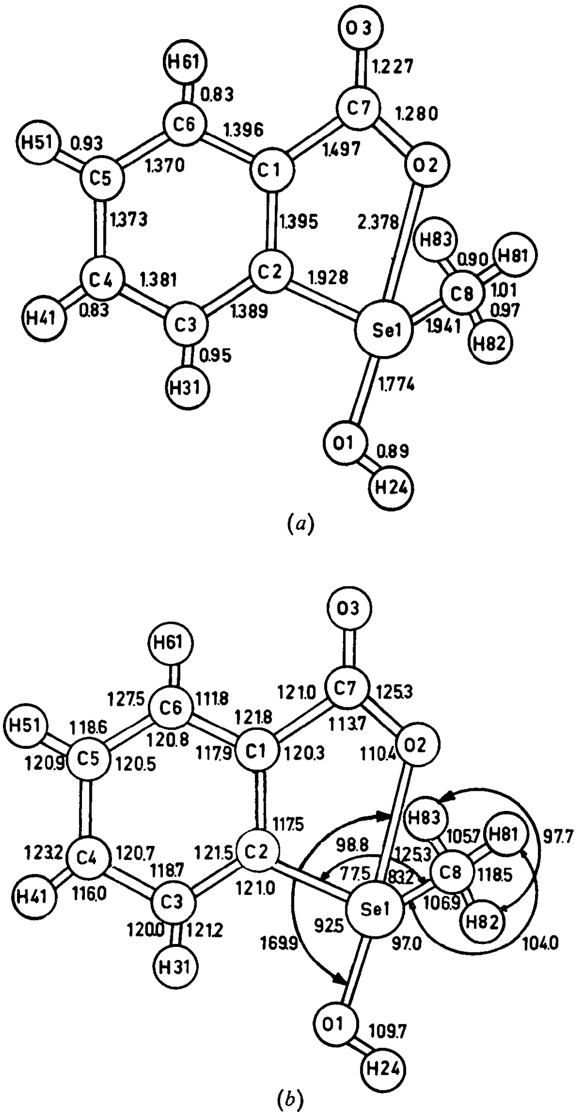
Standard deviations are given in parentheses. All values have been multiplied by 10^4.

$C_8H_8O_3S$	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
S(1)	589 (5)	298 (4)	471 (5)	9 (3)	311 (4)	30 (3)
C(1)	554 (16)	430 (16)	571 (17)	93 (13)	366 (14)	77 (13)
C(2)	501 (15)	426 (15)	463 (15)	18 (12)	302 (13)	−14 (12)
C(3)	577 (18)	538 (20)	594 (19)	−35 (15)	325 (16)	−107 (15)
C(4)	524 (18)	954 (29)	527 (20)	−36 (20)	241 (16)	−191 (20)
C(5)	532 (19)	967 (30)	603 (22)	244 (21)	281 (18)	29 (19)
C(6)	652 (20)	618 (22)	622 (20)	207 (17)	378 (18)	128 (17)
C(7)	756 (21)	330 (15)	628 (19)	63 (14)	430 (18)	103 (15)
C(8)	556 (18)	472 (19)	629 (20)	−12 (16)	324 (16)	18 (15)
O(1)	751 (14)	287 (11)	628 (13)	13 (9)	370 (12)	−34 (9)
O(2)	745 (16)	339 (12)	656 (15)	−100 (11)	296 (13)	63 (11)
O(3)	1312 (26)	458 (15)	846 (19)	43 (18)	405 (14)	348 (16)
$C_8H_8O_3Se$						
Se(1)	363 (3)	225 (3)	268 (3)	− 7 (1)	155 (2)	0 (1)
C(1)	362 (17)	318 (17)	368 (18)	19 (15)	205 (15)	33 (14)
C(2)	308 (15)	309 (17)	314 (17)	21 (14)	168 (14)	8 (13)
C(3)	370 (20)	379 (24)	379 (21)	−37 (14)	167 (17)	−80 (14)
C(4)	374 (20)	605 (28)	375 (22)	−65 (20)	122 (18)	−97 (19)
C(5)	373 (20)	637 (28)	388 (21)	134 (20)	131 (17)	70 (19)
C(6)	435 (21)	379 (22)	470 (22)	116 (18)	240 (18)	116 (17)
C(7)	464 (20)	290 (18)	390 (20)	8 (15)	266 (18)	16 (15)
C(8)	377 (20)	440 (24)	466 (24)	54 (17)	238 (19)	11 (15)
O(1)	526 (16)	235 (12)	376 (15)	−32 (11)	182 (13)	−28 (11)
O(2)	539 (15)	240 (13)	331 (13)	−25 (11)	120 (12)	9 (12)
O(3)	722 (20)	260 (15)	507 (17)	27 (12)	249 (15)	65 (12)

tors can be obtained from the research unit and as Supplementary Publication No. SUP 30041 (4pp.).* Interatomic distances and angles are shown in Figs. 1 and 2 and with standard deviations in Table 4. Correction for thermal motion has not been made. The equations for the least-squares planes through the benzene rings and the deviations from the planes are given in Table 5.

From the determination of the position of the hydroxyl hydrogen in OCSeO, it was evident that the sulphur and selenium compounds could not be completely isotypical, as the hydroxyl hydrogens were attached to non-corresponding atoms.

Furthermore the Se(1)···O(2) distance is 2·378 Å, which is well below the expected van der Waals distance of 3·4 Å. Even if the normal covalent Se–O bond is considerably shorter there are structural features that



(*a*)

(*b*)

Fig. 2. Bond lengths and angles in OCSeO.

Table 4. *Bond lengths and angles with their estimated standard deviations*

	$C_8H_8O_3S$	$C_8H_8O_3Se$
X(1)—C(2)	1·800 (3) Å	1·928 (3) Å
X(1)—C(8)	1·788 (5)	1·941 (6)
X(1)—O(1)	1·517 (2)	1·774 (3)
C(1)—C(2)	1·405 (4)	1·395 (5)
C(2)—C(3)	1·387 (4)	1·389 (5)
C(3)—C(4)	1·377 (5)	1·381 (5)
C(4)—C(5)	1·379 (7)	1·373 (7)
C(5)—C(6)	1·366 (5)	1·370 (6)
C(1)—C(6)	1·391 (4)	1·396 (5)
C(1)—C(7)	1·480 (4)	1·497 (5)
C(7)—O(2)	1·292 (3)	1·280 (4)
C(7)—O(3)	1·209 (4)	1·227 (4)
C(3)—H(31)	0·914 (35)	0·951 (43)
C(4)—H(41)	0·935 (39)	0·826 (47)
C(5)—H(51)	0·964 (41)	0·932 (40)
C(6)—H(61)	0·900 (40)	0·830 (52)
C(8)—H(81)	0·980 (38)	1·008 (65)
C(8)—H(82)	0·937 (64)	0·966 (86)
C(8)—H(83)	0·860 (52)	0·902 (62)
O(2)—H(24)	0·761 (38)	
O(1)—H(24)		0·889 (69)
X(1)—O(2)		2·378 (3)
C(2)—X(1)–C(8)	97·8 (2)°	98·8 (2)°
C(2)—X(1)–O(1)	103·1 (1)	92·5 (1)
C(8)—X(1)–O(1)	104·6 (2)	97·0 (2)
C(2)—X(1)–O(2)		77·5 (2)
C(8)—X(1)–O(2)		83·2 (2)
O(1)—X(1)–O(2)		169·9 (2)
X(1)—C(2)–C(1)	123·2 (2)	117·5 (2)
X(1)—C(2)–C(3)	116·9 (2)	121·0 (3)
C(1)—C(2)–C(3)	119·8 (2)	121·5 (3)
C(2)—C(3)–C(4)	120·5 (3)	118·7 (4)
C(3)—C(4)–C(5)	120·1 (3)	120·7 (4)
C(4)—C(5)–C(6)	119·7 (3)	120·5 (4)
C(1)—C(6)–C(5)	121·9 (4)	120·8 (4)
C(2)—C(1)–C(6)	118·0 (3)	117·9 (3)
C(2)—C(1)–C(7)	124·4 (2)	120·3 (3)
C(6)—C(1)–C(7)	117·6 (3)	121·8 (3)
C(1)—C(7)–O(2)	115·4 (3)	113·7 (3)
C(1)—C(7)–O(3)	122·4 (3)	121·0 (3)
O(2)—C(7)–O(3)	122·2 (3)	125·3 (3)
X(1)—O(2)–C(7)		110·4 (3)
C(2)—C(3)–H(31)	117·8 (17)	121·2 (19)
C(4)—C(3)–H(31)	121·4 (18)	120·0 (19)
C(3)—C(4)–H(41)	116·3 (23)	116·0 (30)
C(5)—C(4)–H(41)	123·5 (23)	123·2 (31)
C(4)—C(5)–H(51)	120·8 (27)	120·9 (27)
C(6)—C(5)–H(51)	119·5 (27)	118·6 (27)
C(1)—C(6)–H(61)	116·8 (20)	111·8 (27)
C(5)—C(6)–H(61)	121·2 (21)	127·5 (27)
X(1)—C(8)–H(81)	108·2 (38)	104·0 (61)
X(1)—C(8)–H(82)	109·9 (37)	106·9 (53)
X(1)—C(8)–H(83)	113·6 (38)	125·3 (36)
H(81)–C(8)–H(82)	99·7 (42)	118·5 (57)
H(81)–C(8)–H(83)	109·1 (35)	105·7 (49)
H(82)–C(8)–H(83)	115·1 (56)	97·7 (66)
C(7)—O(2)–H(24)	110·6 (28)	
X(1)—O(1)–H(24)		109·7 (47)

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* This table has been deposited with the National Lending Library, England. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

seem to favour structure (II) for OCSeO, *i.e.* that a five-membered ring has been formed with a bond between the Se and O atoms.

The angles in the five-membered ring are smaller than the corresponding angles at C(2), C(1) and C(7) in OCSO. In OCSeO the angles are 117·5, 120·3 and 113·7° compared with 123·2, 124·4 and 115·4° respectively in OCSO. The large angles in the sulphur compound are no doubt due to the short non-bonded interaction between S(1) and O(2) of 2·777 Å. This has also resulted in the carboxyl group being twisted 17·1° out of the benzene ring plane.

OCSeO on the other hand is almost planar except, of course, for the methyl group which as in OCSO is pointing out of the plane of the benzene ring. None of the other heavier atoms deviates more than 0·13 Å from the plane. The mean deviations for the carbon

Table 5. *Least-squares planes*

The least-squares plane through the carbon atoms in the benzene ring for the sulphoxide is $0\cdot7754X+0\cdot1058Y-0\cdot6225Z+0\cdot1560=0$. The corresponding plane in the selenium oxide is $0\cdot7820X+0\cdot0295Y-0\cdot6225Z+0\cdot1597=0$. The equation is expressed in terms of the crystal axes.

	Deviations from the plane	
	$C_8H_8O_3S$	$C_8H_8O_3Se$
	X=S	X=Se
C(1)	−0·003	0·002
C(2)	−0·003	−0·002
C(3)	0·007	−0·001
C(4)	−0·006	0·006
C(5)	0·001	−0·006
C(6)	0·004	0·003
C(7)	0·009	0·015
O(2)	−0·331	−0·074
O(3)	0·314	0·130
X(1)	0·102	0·071
O(1)	0·483	0·123
C(8)	−1·650	−1·824

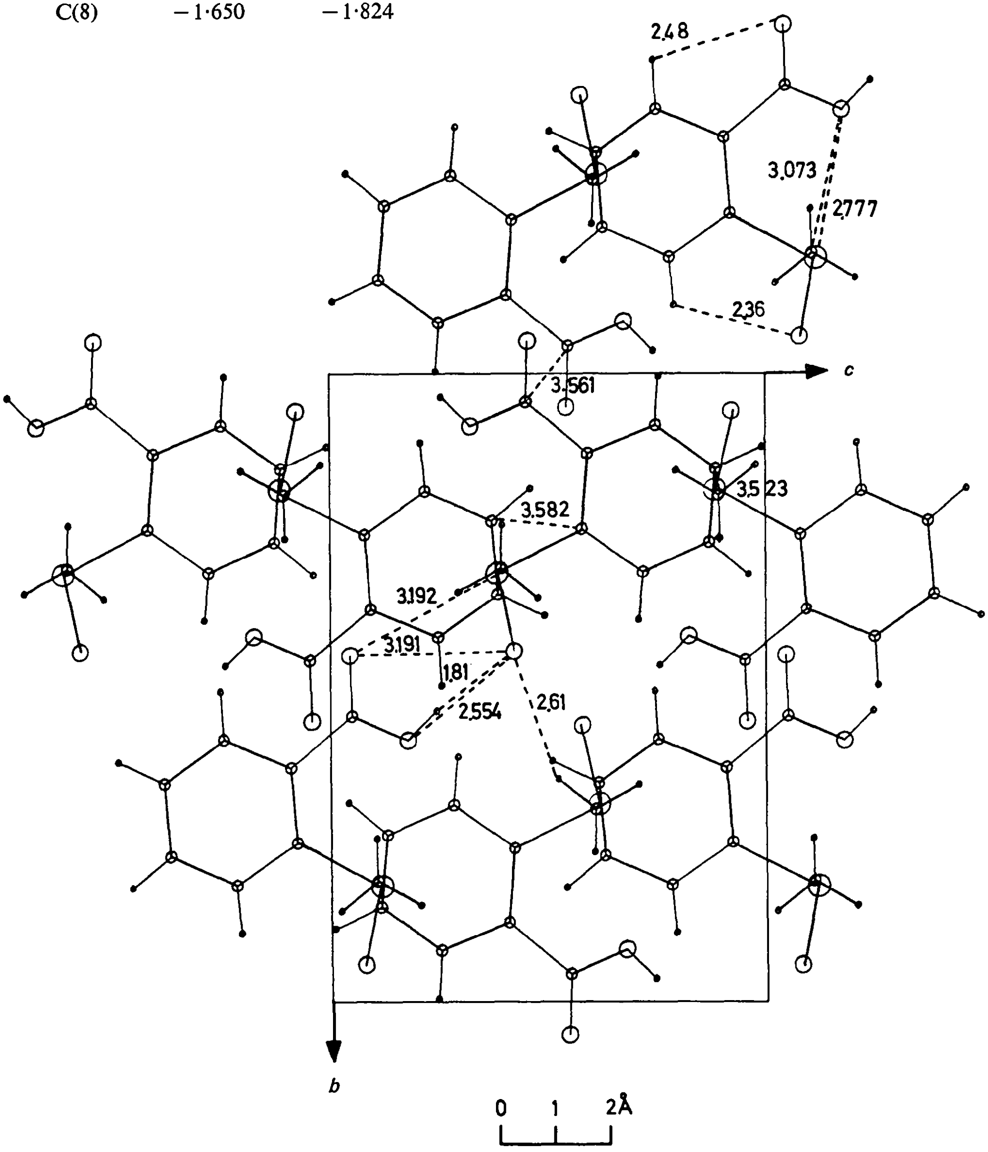

Fig. 3. The molecular arrangement in OCSO as seen along the *a* axis.

Table 6. *Comparison of sulphur-atom environments in several compounds*

Compound	C–S	S–O	C–S–O	C–S–C	Reference
Dimethyl sulphoxide	1·775* (0·008) Å 1·821* (0·011)	1·531* (0·005) Å	106·7° (0·4) 106·8 (0·4)	97·4° (0·4)	Thomas, Shoemaker & Eriks (1966)
Diphenyl sulphoxide	1·76 (0·015)	1·47 (0·016)	106·2 (0·7)	97·3 (0·9)	Abrahams (1957)
(+)-*S*-Methyl-L-cystein sulphoxide	1·814 (0·017) 1·833 (0·022)	1·488 (0·012)	107·5 (0·7) 104·4 (0·8)	96·7 (1·0)	Hine (1962)
(+)-Methyl *p*-tolyl sulphoxide	1·809* (0·003–0·006) 1·804* (0·003–0·006)	1·505* (0·003–0·006)	105·5 (~0·3) 106·5 (~0·3)	97·6 (~0·3)	De la Camp & Hope (1970)
o-Carboxyphenyl methyl sulphoxide	1·788 (0·005) 1·800 (0·003)	1·517 (0·002)	103·1 (0·1) 104·6 (0·2)	97·8 (0·2)	Present work

* After correction for thermal motion.

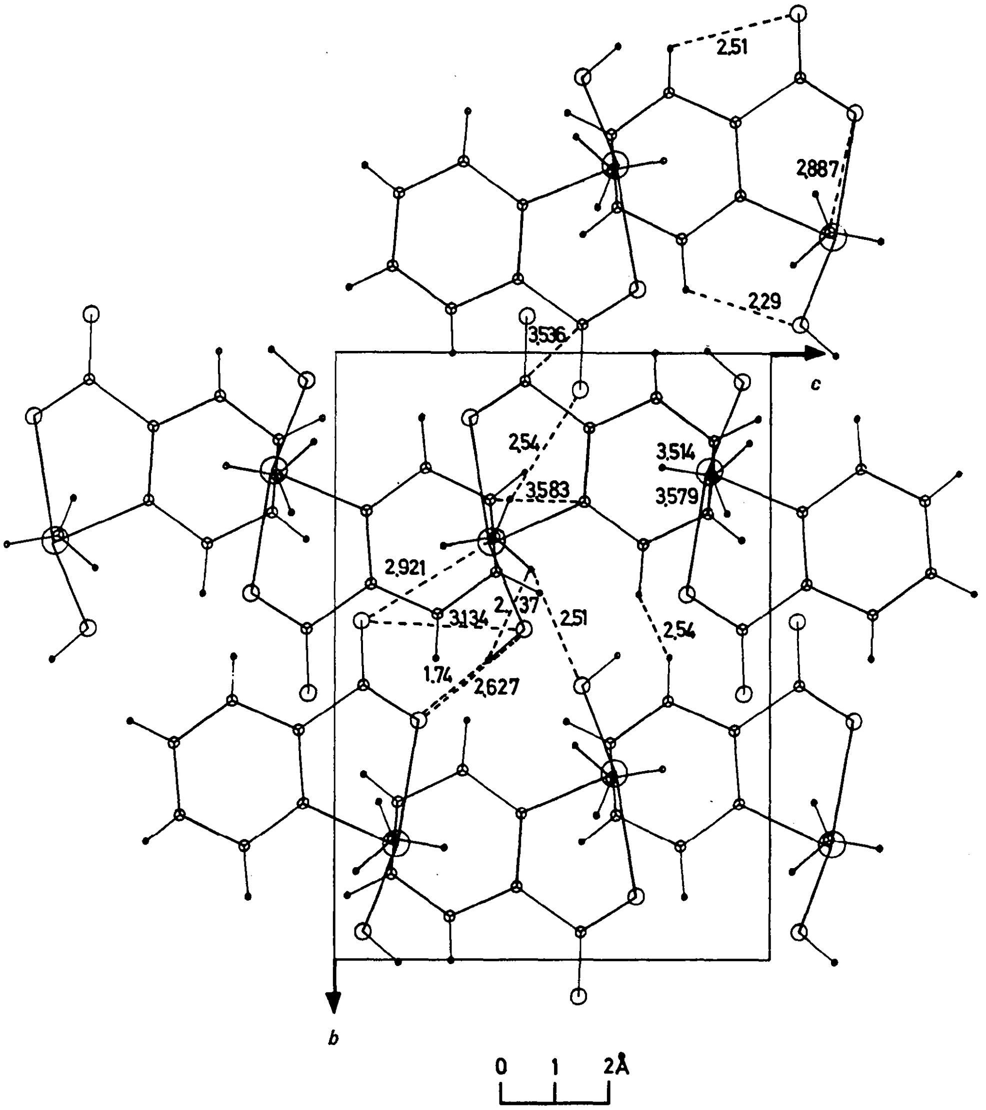

Fig. 4. The molecular arrangement in OCSeO viewed along the *a* axis.

and hydrogen atoms in the ring are 0·004 and 0·03 Å respectively for both the sulphur and the selenium compounds.

A similar observation has been made in an X-ray examination of *o*-iodosobenzoic acid (III) (Shefter & Wolf, 1965) where an analogue interaction was found to exist between the iodine and the carboxyl-oxygen. In that case the I–O distance is 2·30 Å as compared with the normal covalent bond of 2·00 Å. The I–O distance is thus 15% larger than the normal bond while the present Se–O distance exceeds the normal bond by 34%.

OCSO

The conformation around the sulphur atom is similar to that found for other organic sulphoxides, shown in Table 6. The geometry in the carboxyl group is normal (Nardelli, Fava & Giraldi, 1962; Sundaralingam & Jensen, 1965; Sakore, Tavale & Pant, 1967). As mentioned above there is a short intramolecular contact between S(1) and O(2) of 2·777 Å. The sum of their van der Waals radii would be about 3·2 Å (Pauling, 1961). However, such short S···O non-bonding interactions have been reported by Gilardi & Karle (1971), Lynch, Mellor & Nyburg (1971) and Johnson, Reid & Paul (1971).

The molecular packing projected on to the (100) plane is shown in Fig. 3, where some close intermolecular contacts are also given. The packing viewed along the *b* axis is illustrated in Fig. 5 for the selenium compound, and the sulphur compound looks very much the same in the latter projection.

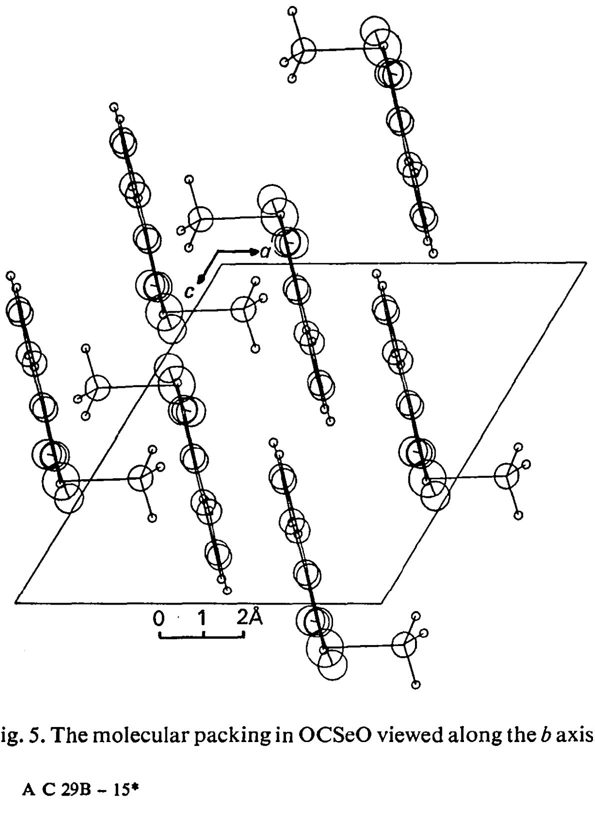

Fig. 5. The molecular packing in OCSeO viewed along the *b* axis.

The molecular packing is characterized by a hydrogen bond between oxygen O(2) and oxygen O(1) in the molecule symmetry related by a twofold screw axis. Thus two hydrogen bonded molecular chains run almost parallel to the *b* axis. The contacts O(1)···O(2) and O(1)···H(24) are 2·554 and 1·80 Å respectively and the angle O(1)···H(24)–O(2) is 168°.

OCSeO

The selenium–carbon bonds of 1·928 and 1·941 Å are normal. Aleby (1972) reports Se–C bonds ranging from 1·87 to 2·01 Å. Comparable data for the Se–O bond are rare. In benzeneseleninic acid (Bryden & McCullough, 1954) the Se–O bonds are 1·707 and 1·765 Å respectively and in the approximate structure of *p*-chlorobenzeneseleninic acid (Bryden & McCullough, 1956) the Se–O bonds are 1·70 and 1·79 Å. The value obtained in this structure is 1·774 Å for the 'normal' Se–O single bond.

Consistent with the ring closure in OCSeO the carboxyl group has the same bond character as in OCSO with C(7)–O(2) remaining a single bond (1·280 Å) and C(7)–O(3) a double bond (1·227 Å). The molecular packing is shown in Figs. 4 and 5. As in the sulphur compound the molecules are connected by an O–H···O hydrogen bond forming two chains running in the **b** direction. However, in this case the donor and acceptor roles of O(1) and O(2) are exchanged. The contacts O(1)···O(2) and O(2)···H(24) are 2·627 and 1·74 Å respectively. The angle O(1)–H(24)···O(2) is 175°.

There is also a very short contact of 2·921 Å between the two hydrogen-bonded molecules from the selenium atom to oxygen O(3). The sum of the van der Waals radii would be about 3·4 Å (Pauling, 1960).

As in OCSeO the atoms (except for the methyl group) lie in the same plane [due to the Se(1)–O(2) interactions], and there is no possibility for oxygen O(3) to bend away from the selenium atom. In the sulphur compound on the other hand the carboxyl group is twisted from the plane and too close a contact can be avoided. The corresponding distance in OCSO is 3·197 Å which is approximately the sum of the van der Waals radii. The more planar OCSeO molecules can obviously pack better, as the volume of OCSeO is smaller than that of OCSO despite of the larger Se atom.

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Structure Cristalline de Trois Phénols Encombrés: le Diméthyl-2,3 Phénol, le Méthyl-2 Bromo-3 Phénol et le Ditertiobutyl-2,6 Méthyl-4 Phénol

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The crystal structures of 3 hindered phenols have been solved. These phenols are: (1) 2,3-dimethylphenol $[C_6H_3(CH_3)_2(OH)]$ with cell parameters: $a=24{\cdot}62$, $b=5{\cdot}905$, $c=4{\cdot}808$ Å, space group $P2_12_12_1$, solved by means of 726 reflexions ($R=0{\cdot}09$); (2) 2-methyl-3-bromophenol $[C_6H_3(CH_3)Br(OH)]$ with cell parameters: $a=12{\cdot}13$, $b=12{\cdot}44$, $c=4{\cdot}67$ Å, space group $Pna2_1$, solved by means of 659 reflexions ($R=0{\cdot}09$); (3) 2,6-di-t-butyl-4-methylphenol $\{C_6H_2(CH_3)[C\text{–}(CH_3)_3]_2\}$ with cell parameters: $a=10{\cdot}38$, $b=15{\cdot}58$, $c=8{\cdot}822$ Å, space group $P2_12_12_1$, solved by means of 1140 reflexions ($R=0{\cdot}10$). These structures seem to show that the effect of alkylated *ortho* substituents on the conjugation between the aromatic ring and the (OH) group, depends on the nature of the substituents rather than on their bulk.

Introduction

Les phénols encombrés sont des phénols substitués en *ortho* par un ou plusieurs groupements hydrocarbonés volumineux. Les propriétés phénoliques de ces phénols sont perturbées et ces perturbations vont parfois jusqu'à masquer complètement la fonction phénol. Pour expliquer ce phénomène, différentes hypothèses structurales ont été émises:

(1) Les groupements encombrants repoussent l'hydrogène phénolique hors du plan du noyau ce qui rend difficile la conjugaison entre le groupement hydroxyle et le noyau (Rumpf & Lumbroso, 1950).

(2) Les substituants encombrants agissent en déformant le noyau benzénique, ce qui se répercute sur la conjugaison entre le groupement hydroxyle et le noyau (Demerseman *et al.*, 1966).

(3) Les substituants encombrants agissent stériquement en masquant la fonction phénol, c'est-à-dire en empêchant l'approche d'éventuels réactifs et le départ du proton (Bellamy & Williams 1960*a*,*b*; Ingold & Taylor, 1961).

L'étude structurale suivante a pour but de vérifier la présence ou l'absence de déformation dans quelques phénols encombrés: le diméthyl-2,3 phénol, le méthyl-2 bromo-3 phénol et le ditertiobutyl-2,6 paracrésol.

Structure du diméthyl-2,3 phénol

Les cristaux de diméthyl-2,3 phénol (ou xylénol vicinal) se présentent sous forme d'aiguilles parallélépipédiques de dimensions variables. Ils se subliment facilement (f=75°C). Leurs caractéristiques cristallines sont résumées dans le Tableau 1.