

The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included in the calculation for the P atom (Cromer, 1974). Molecular graphics were produced using ORTEPII (Johnson, 1976). All calculations were carried out on an NEC ACOS 930S computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, Japan.

The authors thank Dr Hideo Imoto, Department of Chemistry, Faculty of Science, The University of Tokyo, Japan, for the least-squares program (ANYBLK). The Ministry of Education, Japan, is thanked for a Grant-in-Aid for Scientific Research. The Ciba-Geigy Foundation (Japan) is thanked for partial support of this work.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: OH1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Baker, J. M. & Pringle, P. G. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1292–1293.
- Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Gridunova, G. V., Furmanova, N. G., Shklover, V. E., Struchkov, Yu. T., Ezhkova, Z. I. & Chayanov, B. A. (1982). *Kristallografiya*, **27**, 477.
- Imoto, H. (1990). *ANYBLK. Program for Least-Squares Refinement*. Department of Chemistry, Univ. of Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kagan, H. B. (1985). *Asymmetric Catalysis*, Vol. 5, edited by J. D. Morrison, pp. 1–39.
- Kwok, T. J. & Wink, D. J. (1993). *Organometallics*, **12**, 1954–1959.
- Miyashita, A., Yasuda, A., Takaya, H., Toriumi, K., Ito, T., Souchi, T. & Noyori, R. (1980). *J. Am. Chem. Soc.* **102**, 7932–7934.
- Nugent, W. A., RajanBabu, T. V. & Burk, M. J. (1993). *Science*, **259**, 479–483.
- Richter, W. J. (1983). *J. Mol. Catal.* **18**, 145–148.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Tani, K., Yamagata, T. & Tashiro, H. (1994). *Acta Cryst.* **C50**, 769–771.
- Tani, K., Yamagata, T., Tatsuno, Y., Yamagata, Y., Tomita, K., Akutagawa, S., Kumobayashi, H. & Otsuka, S. (1985). *Angew. Chem.* **97**, 232–234; *Angew. Chem. Int. Ed. Engl.* **24**, 217–219.

Acta Cryst. (1994). **C50**, 1276–1279

Tris(2,6-dimethoxyphenyl)phosphine Sulfide Monohydrate

SHUICHI HAYASE, TATSUO ERABI AND
MASANORI WADA

*Department of Materials Science,
Faculty of Engineering, Tottori University,
Koyama, Tottori 680, Japan*

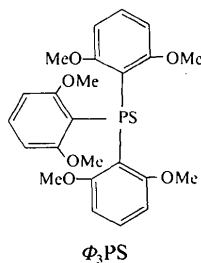
(Received 18 May 1993; accepted 8 November 1993)

Abstract

The title compound C₂₄H₂₇O₆PS.H₂O, or Φ_3 PS.H₂O [$\Phi = 2,6-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$], has an average P—C bond length of 1.840 Å, a P=S length of 1.971 (2) Å and an average C—P—C angle of 107.1°, which are considerably longer and wider than those of triphenylphosphine sulfide, with values of 1.817, 1.950 Å and 105.7°, respectively. Intramolecular distances between the six methoxy O atoms and the P atom are all shorter than the sum of van der Waals radii of O and P atoms, implying the presence of direct electron donation from the methoxy O atoms to the P atom.

Comment

Φ_3 PS [$\Phi = 2,6-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$] has been reported to have very high nucleophilicity (Wada, Kanzaki, Fujiwara, Kajihara & Erabi, 1991) and to form unusual 1:1 complexes with dimethyltin dihalides (Wada *et al.*, 1993). While the structure of tris(2,6-dimethoxyphenyl)phosphine (Φ_3 P) has been determined (Livant, Sun & Webb, 1991), that of Φ_3 PS was unknown; we report here the crystal structure of this compound in order to clarify the origin of these unusual properties.



The water molecule of crystallization was detected by IR bands at 3400 and 1630 cm⁻¹, and the amount was estimated from weight reduction at 373 K. The calculated density (D_x) was also consistent with the

measurement, assuming that the crystal contained one water molecule per molecule of $\Phi_3\text{PS}$. Fig. 1 shows an *ORTEP* plot (Johnson, 1976) of $\Phi_3\text{PS}\cdot\text{H}_2\text{O}$. The average P—C bond lengths ($\langle d \rangle$), average C—P—C bond angles ($\langle \beta \rangle$) and the P=S bond lengths for this and some related compounds are shown in Table 3. $\Phi_3\text{PS}\cdot\text{H}_2\text{O}$ has $\langle d \rangle$ and $\langle \beta \rangle$ values larger than those of Ph_3PS , as is consistent with the bulkiness of the Φ group. The larger $\langle \beta \rangle$ value of $\Phi_3\text{PS}\cdot\text{H}_2\text{O}$ than that of $\Phi_3\text{P}$ (Livant *et al.*, 1991) can be attributed to reduction of electron-pair repulsion by P=S bond formation. The P=S bond length [1.971 (2) Å] is also larger than that of Ph_3PS [1.950 (3) Å] (Coddling & Kerr, 1978). This elongation can be understood by the weaker $d\pi-p\pi$ back bonding between P and S in $\Phi_3\text{PS}$ than in Ph_3PS , as is consistent with the higher nucleophilicity of $\Phi_3\text{PS}$.

Intramolecular distances between methoxy O atoms and the P atom are all shorter than the sum of the van der Waals radii of O and P atoms, 3.3 Å (Table 2). Analogous results are also found for $\Phi_3\text{PO}$ coordinated to Me_2SnCl_2 (Wada *et al.*, 1993), for $[\text{Ph}_2(\text{C}_6\text{H}_5\text{CH}_2)(2\text{-CH}_3\text{OC}_6\text{H}_4)\text{P}]\text{Br}$ (Wood, Wikholm & McEwen, 1977), for $[\Phi_6\text{P}_4][\text{Me}_3\text{SnF}_2]_2$ (Heuer, Ernst, Schmutzler & Schomburg, 1989), for $(\Phi\text{PCl})_2$ (Heuer, Schomburg & Schmutzler, 1989), for $\Phi_3\text{P}$ [our calculation from the data set of Livant *et al.* (1991)], and for $[2,4,6\text{-(CH}_3\text{O)}_3\text{C}_6\text{H}_2]_3\text{P}$ [our calculation from the data set of Nemeth, Pinkerton, Stowe & Ogle (1992)]. These observations can be understood by the presence of direct electron donation from each methoxy O atom to the P atom in these compounds. It should be noted that one of the methoxy O atoms in each Φ group of the title compound (O1, O3 and O5) is located closer to the P atom (2.80–2.88 Å) than the others (3.06–3.19 Å). Two of them (O1 and O3) are also located close to the S atom.

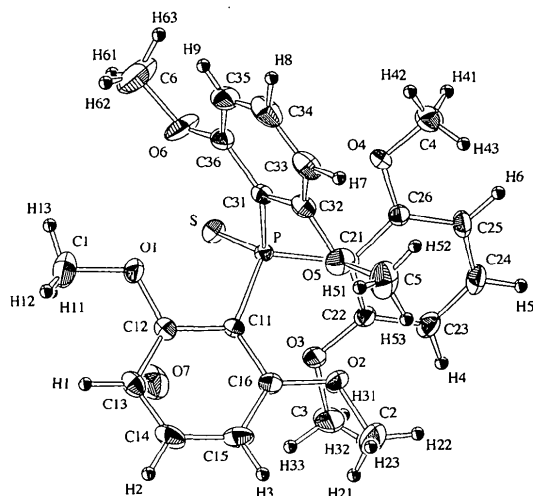


Fig. 1. *ORTEP* plot of $\Phi_3\text{PS}\cdot\text{H}_2\text{O}$ with atomic labelling scheme.

Distances between O7 of the water molecule and its neighbours are: O7...S 3.365 (6), O7...O3 3.358 (7), O7...C12 3.446 (8) and O7...C11 3.594 (8) Å. The O7...S distance is slightly longer than the typical hydrogen-bond length, O—H...S, of 3.31 Å (Kuleshova & Zorkii, 1981).

Experimental

$\Phi_3\text{PS}$ was synthesized from $\Phi_3\text{P}$ and elemental sulfur (Wada *et al.*, 1991). Single crystals of $\Phi_3\text{PS}\cdot\text{H}_2\text{O}$ were obtained by slow cooling of its toluene solution.

Crystal data

$\text{C}_{24}\text{H}_{27}\text{O}_6\text{PS}\cdot\text{H}_2\text{O}$

$M_r = 492.52$

Orthorhombic

Pbca

$a = 17.765$ (3) Å

$b = 17.940$ (2) Å

$c = 15.390$ (2) Å

$V = 4905$ (1) Å³

$Z = 8$

$D_x = 1.33$ Mg m⁻³

$D_m = 1.37$ Mg m⁻³

D_m measured by flotation in a Wadon-type pycnometer

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 24

reflections

$\theta = 31.95\text{--}32.40^\circ$

$\mu = 2.071$ mm⁻¹

$T = 298$ K

Polygon

$0.4 \times 0.3 \times 0.3$ mm

Colourless

Data collection

Rigaku AFC-5R diffractometer

$2\theta/\omega$ scans

Absorption correction:

empirical

$T_{\min} = 0.91$, $T_{\max} = 1.00$

4087 measured reflections

4087 independent reflections

2968 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 60^\circ$

$h = 0 \rightarrow 20$

$k = 0 \rightarrow 20$

$l = 0 \rightarrow 17$

3 standard reflections

monitored every 150

reflections

intensity variation:

–2.20%

Refinement

Refinement on F

$R = 0.054$

$wR = 0.083$

$S = 5.48$

2968 reflections

334 parameters

$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = 0.05$

$\Delta\rho_{\max} = 0.32$ e Å⁻³

$\Delta\rho_{\min} = -0.61$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from Cromer (1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
S	0.31482 (9)	0.20173 (8)	0.5380 (1)	2.76 (7)
P	0.24078 (8)	0.13347 (8)	0.4854 (1)	1.89 (6)
O1	0.3724 (2)	0.0940 (2)	0.3962 (3)	3.5 (2)
O2	0.1723 (2)	–0.0242 (2)	0.5398 (3)	3.8 (2)
O3	0.2304 (2)	0.0753 (2)	0.6596 (3)	3.4 (2)
O4	0.0912 (2)	0.2146 (2)	0.4583 (3)	3.3 (2)
O5	0.1259 (3)	0.0559 (2)	0.3943 (3)	4.1 (2)

O6	0.2993 (3)	0.2482 (3)	0.3515 (3)	5.6 (3)
O7	0.4184 (3)	0.0700 (3)	0.6376 (4)	6.7 (3)
C1	0.4480 (4)	0.0992 (5)	0.3722 (6)	6.6 (5)
C2	0.1400 (5)	-0.0909 (5)	0.5742 (7)	8.0 (6)
C3	0.2348 (5)	0.0287 (5)	0.7352 (5)	6.9 (5)
C4	0.0220 (4)	0.2384 (4)	0.4231 (5)	4.8 (4)
C5	0.0671 (4)	0.0077 (5)	0.3678 (6)	6.0 (5)
C6	0.3372 (6)	0.2995 (6)	0.3010 (7)	9.8 (7)
C11	0.2763 (3)	0.0372 (3)	0.4758 (4)	2.1 (2)
C12	0.3471 (3)	0.0305 (3)	0.4345 (4)	2.5 (3)
C13	0.3855 (4)	-0.0368 (4)	0.4302 (4)	3.4 (3)
C14	0.3514 (5)	-0.0992 (4)	0.4615 (5)	4.3 (4)
C15	0.2798 (5)	-0.0971 (4)	0.4973 (5)	4.1 (4)
C16	0.2424 (4)	-0.0288 (3)	0.5053 (4)	2.9 (3)
C21	0.1575 (3)	0.1376 (3)	0.5564 (4)	2.2 (3)
C22	0.1634 (3)	0.1071 (3)	0.6397 (4)	2.7 (3)
C23	0.1034 (4)	0.1112 (4)	0.6978 (5)	3.7 (4)
C24	0.0394 (4)	0.1473 (4)	0.6750 (5)	3.9 (4)
C25	0.0327 (4)	0.1815 (4)	0.5950 (5)	3.5 (3)
C26	0.0922 (3)	0.1777 (3)	0.5361 (4)	2.6 (3)
C31	0.2115 (3)	0.1523 (3)	0.3733 (4)	2.3 (3)
C32	0.1528 (4)	0.1082 (3)	0.3385 (4)	3.0 (3)
C33	0.1256 (4)	0.1175 (4)	0.2554 (5)	4.1 (4)
C34	0.1579 (5)	0.1721 (5)	0.2052 (5)	5.1 (5)
C35	0.2150 (5)	0.2150 (5)	0.2344 (5)	4.6 (4)
C36	0.2427 (4)	0.2064 (4)	0.3190 (4)	3.3 (3)

Table 3. Average P—C bond lengths $\langle d \rangle$ (Å), average C—P—C angles $\langle \beta \rangle$ (°) and P=S bond lengths (Å) for Φ_3 PS.H₂O and some related compounds

	$\langle d \rangle$	$\langle \beta \rangle$	P=S	References
Ph ₃ P	1.831 (2)	102.8 (1)	—	Dunne & Orpen (1991)
Ph ₃ PS	1.817 (8)	105.7 (16)	1.950 (3)	Codding & Kerr (1978)
Φ_3 P	1.844 (3)	104.4 (1)	—	Livant <i>et al.</i> (1991)
Φ_3 PS.H ₂ O	1.840 (6)	107.1 (3)	1.971 (2)	This work

The crystal used for measurement was mounted on a glass fibre. The non-H atoms were refined anisotropically, aromatic H atoms were refined isotropically, methoxy H atoms were fixed and no H atoms of the water molecule were included in the refinement. All calculations were performed using the TEXSAN package (Molecular Structure Corporation, 1985). The structure was solved by direct methods (Beurskens, 1984; Gilmore, 1984) and refined by full-matrix least squares.

This work was supported by Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 04217218 from the Ministry of Education, Science and Culture. The authors thank all the staff of the Physical Chemistry Chair, Faculty of Engineering, Osaka University, for fruitful discussions.

Table 2. Selected interatomic distances (Å) and angles (°)

S—P	1.971 (2)	O1—C1	1.397 (8)
P—C11	1.845 (5)	O1—C12	1.358 (7)
P—C21	1.842 (6)	O2—C2	1.429 (8)
P—C31	1.833 (6)	O2—C16	1.356 (7)
C11—C12	1.413 (8)	O3—C3	1.436 (8)
C12—C13	1.389 (8)	O3—C22	1.355 (7)
C13—C14	1.36 (1)	O4—C4	1.409 (8)
C14—C15	1.39 (1)	O4—C26	1.367 (7)
C15—C16	1.398 (8)	O5—C5	1.415 (8)
C16—C11	1.405 (8)	O5—C32	1.359 (7)
C21—C22	1.398 (8)	O6—C6	1.379 (9)
C22—C23	1.392 (8)	O6—C36	1.350 (8)
C23—C24	1.36 (1)	P...O1	2.802 (4)
C24—C25	1.38 (1)	P...O2	3.190 (4)
C25—C26	1.394 (8)	P...O3	2.883 (4)
C26—C21	1.401 (8)	P...O4	3.058 (4)
C31—C32	1.415 (8)	P...O5	2.841 (4)
C32—C33	1.378 (9)	P...O6	3.092 (5)
C33—C34	1.37 (1)	S...O1	3.090 (5)
C34—C35	1.35 (1)	S...O3	3.300 (4)
C35—C36	1.40 (1)	S...O6	3.002 (5)
C36—C31	1.396 (8)		
S—P—C11	112.7 (2)	P—C21—C22	118.0 (4)
S—P—C21	105.5 (2)	P—C21—C26	123.6 (4)
S—P—C31	117.5 (2)	C21—C22—C23	120.8 (6)
C11—P—C21	111.1 (3)	C22—C23—C24	120.1 (7)
C21—P—C31	108.9 (3)	C23—C24—C25	121.0 (7)
C31—P—C11	101.2 (3)	C24—C25—C26	119.6 (7)
C1—O1—C12	119.3 (6)	C25—C26—C21	120.5 (6)
C2—O2—C16	117.5 (5)	C26—C21—C22	117.9 (5)
C3—O3—C22	118.4 (5)	O3—C22—C21	115.9 (5)
C4—O4—C26	119.6 (5)	O3—C22—C23	123.3 (6)
C5—O5—C32	119.9 (6)	O4—C26—C21	117.0 (5)
C6—O6—C36	121.7 (6)	O4—C26—C25	122.5 (6)
P—C11—C12	114.8 (4)	P—C31—C32	117.5 (5)
P—C11—C16	128.1 (4)	P—C31—C36	125.3 (5)
C11—C12—C13	122.1 (6)	C31—C32—C33	122.8 (7)
C12—C13—C14	118.7 (7)	C32—C33—C34	117.6 (7)
C13—C14—C15	121.7 (7)	C33—C34—C35	122.3 (8)
C14—C15—C16	119.7 (7)	C34—C35—C36	120.7 (8)
C15—C16—C11	120.4 (6)	C35—C36—C31	119.6 (7)
C16—C11—C12	117.1 (5)	C36—C31—C32	117.1 (6)
O1—C12—C11	114.7 (5)	O5—C32—C31	114.0 (5)
O1—C12—C13	123.1 (6)	O5—C32—C33	123.2 (7)
O2—C16—C11	118.0 (5)	O6—C36—C31	117.5 (6)
O2—C16—C15	121.6 (6)	O6—C36—C35	123.0 (7)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: OH1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures - an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Codding, P. W. & Kerr, K. A. (1978). *Acta Cryst.* **B34**, 3785–3787.
- Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Dunne, B. J. & Orpen, A. G. (1991). *Acta Cryst.* **C47**, 345–347.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Heuer, L., Ernst, L., Schmutzler, R. & Schomburg, D. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1507–1509.
- Heuer, L., Schomburg, D. & Schmutzler, R. (1989). *Phosphorus Sulfur Silicon*, **45**, 217–222.
- Johnson, K. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kuleshova, L. N. & Zorkii, P. M. (1981). *Acta Cryst.* **B37**, 1363–1366.
- Livant, P., Sun, Y. J. & Webb, T. R. (1991). *Acta Cryst.* **C47**, 1003–1005.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nemeth, G., Pinkerton, A. A., Stowe, J. A. & Ogle, C. A. (1992). *Acta Cryst.* **C48**, 2200–2203.

- Wada, M., Fujii, T., Iijima, S., Hayase, S., Erabi, T. & Matsubayashi, G. (1993). *J. Organomet. Chem.* **445**, 65–70.
 Wada, M., Kanzaki, M., Fujiwara, M., Kajihara, K. & Erabi, T. (1991). *Bull. Chem. Soc. Jpn.* **64**, 1782–1786.
 Wood, J. S., Wikholm, R. J. & McEwen, W. E. (1977). *Phosphorus Sulfur*, **3**, 163–169.

Acta Cryst. (1994). **C50**, 1279–1281

A Dimeric (Phenylsulfonyl)oxazolidine

JOACHIM HIRSCHLER, BERND BERGER AND
 MICHAEL BOLTE*

*Institut für Organische Chemie der Universität
 Frankfurt, Marie-Curie-Strasse 11,
 D-60439 Frankfurt am Main, Germany*

(Received 18 August 1993; accepted 4 January 1994)

Abstract

We report the crystal structure of (1*R*,3*R*)-2[(2*R*,4*R*,5*R*)-3-(*p*-chlorophenylsulfonyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-yl]-5-{2-(1*R*,2*S*)-[(2*R*,4*R*,5*R*)-3-(*p*-chlorophenylsulfonyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-yl]-1-hydroxycyclopentyl}-1-cyclopentanone, C₄₂H₄₄Cl₂N₂O₈S₂ (1). The chlorophenyl-sulfonyl substituent is *cis* to the phenyl ring on each oxazolidine heterocycle. Each chlorophenyl-sulfonyl substituent adopts a folded conformation by which the aromatic ring shields the heterocycle. The oxazolidine rings have envelope conformations with C(3) and O(17) out of their respective planes. An intramolecular hydrogen bond exists between the hydroxyl group O(11) and the ketone O(7) [O(11)⋯O(7) 2.840 Å, O(11)—H(11)⋯O(7) 134.0°].

Comment

The title compound (I) is the product of a diastereoselective side reaction occurring during the preparation of the trimethylsilyl enol ether from the corresponding 2-(2-oxocyclopentyl)-5-phenyl-1,3-oxazolidine (Conde-Frieboes & Hoppe, 1992). It is generated as a pure diastereomer bearing ten stereogenic centres, whose relative configuration was determined using NOE derived distance restraints and distance–geometry calculations (Crippen & Havel, 1988; Mierke & Reggelin, 1992; Reggelin, Köck, Conde-Frieboes & Mierke, 1994). The X-ray structure analysis was carried out in order to confirm the stereochemical results from these calculations.

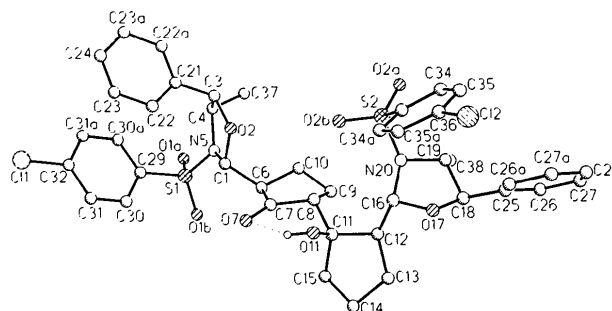
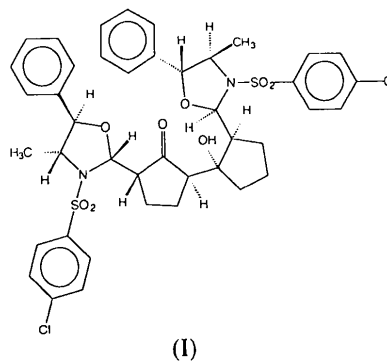


Fig. 1. Perspective view of the title compound with the atom-numbering scheme (only the hydroxy H atom is shown).

Experimental

Crystal data

C₄₂H₄₄Cl₂N₂O₈S₂
M_r = 839.8
 Monoclinic
 C2
a = 30.314 (4) Å
b = 7.372 (1) Å
c = 23.336 (4) Å
 β = 126.31 (1)°
V = 4202 (1) Å³
Z = 4
D_x = 1.327 Mg m⁻³

Cu K α radiation
 λ = 1.5418 Å
 Cell parameters from 25 reflections
 θ = 30–40°
 μ = 2.76 mm⁻¹
T = 293 K
 Transparent block
 0.3 × 0.3 × 0.1 mm
 Colourless
 Crystal source: from methanol/chloroform

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: empirical
 T_{\min} = 0.75, T_{\max} = 1.00
 4993 measured reflections
 3342 independent reflections
 3144 observed reflections
 $[F > 4\sigma(F)]$

R_{int} = 0.020
 θ_{max} = 60°
 $h = -34 \rightarrow 11$
 $k = -8 \rightarrow 0$
 $l = -24 \rightarrow 26$
 3 standard reflections
 frequency: 92 min
 intensity variation: none

Refinement

Refinement on *F*
 R = 0.038
 wR = 0.048
 S = 1.86

Extinction correction: empirical
 $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$