*Data collection*

Stoe Stadi-4 diffractometer
$\omega/\theta$ scans
Absorption correction: none
2876 measured reflections
2795 independent reflections
2129 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.064$

$\theta_{\max} = 27.50°$
$h = -6 \rightarrow 0$
$k = 0 \rightarrow 25$
$l = -14 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.117$
$S = 1.033$
2795 reflections
160 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.8982P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.335$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.389$ e Å$^{-3}$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0073 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1—S1 | 1.595 (2) | S1—C1 | 1.755 (3) |
| N1—S2 | 1.600 (2) | S2—O4 | 1.4459 (19) |
| S1—O2 | 1.4445 (18) | S2—O3 | 1.4480 (19) |
| S1—O1 | 1.4486 (18) | S2—C2 | 1.751 (3) |
| S1—N1—S2 | 118.87 (13) | O4—S2—O3 | 115.95 (12) |
| O2—S1—O1 | 115.68 (11) | O4—S2—N1 | 113.11 (11) |
| O2—S1—N1 | 113.38 (11) | O3—S2—N1 | 106.28 (11) |
| O1—S1—N1 | 106.21 (11) | O4—S2—C2 | 107.11 (12) |
| O2—S1—C1 | 106.92 (12) | O3—S2—C2 | 106.75 (13) |
| O1—S1—C1 | 107.10 (12) | N1—S2—C2 | 107.15 (12) |
| N1—S1—C1 | 107.09 (13) | | |
| S2—N1—S1—O2 | −36.88 (19) | S1—N1—S2—O4 | −37.39 (19) |
| S2—N1—S1—O1 | −165.01 (14) | S1—N1—S2—O3 | −165.72 (14) |
| S2—N1—S1—C1 | 80.80 (17) | S1—N1—S2—C2 | 80.42 (17) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···N2$^{i}$ | 0.95 (3) | 1.87 (3) | 2.817 (3) | 177 (3) |
| C1—H1*C*···O4$^{ii}$ | 0.98 | 2.43 | 3.374 (3) | 162 |
| C2—H2*C*···O2$^{iii}$ | 0.98 | 2.41 | 3.360 (3) | 163 |
| C4—H4*A*···O1$^{iv}$ | 0.99 | 2.43 | 3.342 (3) | 152 |
| C4—H4*B*···O1$^{i}$ | 0.99 | 2.41 | 3.344 (3) | 157 |
| C5—H5*B*···O3$^{v}$ | 0.99 | 2.29 | 3.256 (3) | 164 |
| C6—H6*B*···O3 | 0.99 | 2.43 | 3.393 (3) | 165 |

Symmetry codes: (i) $x-1, y, z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $1-x, 1-y, -z$; (v) $1-x, 1-y, 1-z$.

Many pairs of atoms are related by a translation of *ca* $0,\frac{1}{2},0$; reflections with $k$ odd are thus weak. H-atom treatment: NH coordinates free, $U$ fixed; rigid methyl groups (allowed to rotate but not tip); others riding.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP*5 (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1353). Services for accessing these data are described at the back of the journal.

## References

Bakshi, P. K., Linden, A., Vincent, B. R., Roe, S. P., Adhikesavalu, D., Cameron, T. S. & Knop, O. (1994). *Can. J. Chem.* **72**, 1273–1293.
Bandrauk, A. D., Truong, K. D., Carlone, C. & Hanson, A. W. (1987). *J. Phys. Chem.* **91**, 2063–2069.
Blaschette, A., Wieland, E., Seurig, G., Koch, D. & Safari, F. (1983). *Z. Anorg. Allg. Chem.* **506**, 75–86.
Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
Głowiak, T., Sobczyk, L. & Grech, E. (1975). *Chem. Phys. Lett.* 36, 106–107.
Henschel, D. (1996). PhD thesis, Technical University of Braunschweig, Germany. [ISBN 3-931986-30-6]
Henschel, D., Blaschette, A. & Jones, P. G. (1997). *Acta Cryst.* C**53**, 1875–1877.
Petrusenko, S. R., Kokosay, V. N. & Fritzky, I. O (1997). *Polyhedron*, **16**, 267–274.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen.
Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments, Madison, USA.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.
Weitze, A., Henschel, D., Blaschette, A. & Jones, P. G. (1995). *Z. Anorg. Allg. Chem.* **621**, 1746–1754.
Zhao, D., Ladipo, F. T., Braddock-Wilking, J., Brammer, L. & Sherwood, P. (1996). *Organometallics*, **15**, 1441–1445.

---

*Acta Cryst.* (1997). C53, 1879–1881

# Tricyclohexylphosphoniodithioformate

JAGADESE J. VITTAL† AND PHILIP A. W. DEAN

*Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7. E-mail: chmjjv@leonis.nus.sg*

(*Received 21 October 1996; accepted 13 June 1997*)

## Abstract

The two molecules in the asymmetric unit of the title compound, $C_{19}H_{33}PS_2$, have similar conformations. The $PCS_2$ fragments are planar and the C—S distances are 1.669 (2) and 1.640 (2) Å in molecule *A*, and 1.672 (3) and 1.637 (3) Å in molecule *B*. The S—C—S angles are 130.2 (1) and 130.5 (1)° in molecules *A* and *B*, respectively.

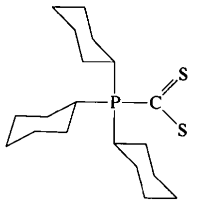
---

† Present address: Department of Chemistry, National University of Singapore, Singapore 119260.

© 1997 International Union of Crystallography
Printed in Great Britain – all rights reserved

## Comment

Triaryl- or trialkylphosphoniodithioformate ligands display a variety of coordination modes to metal atoms (for recent references see, for example, Carriedo *et al.*, 1996; Galindo *et al.*, 1996, and references therein). The structure of $Et_3PCS_2$ has been reported by Margulis & Templeton (1962). In our previous work, we have reported the chemistry and structure of a lead complex containing $Cy_3PCS_2$ (where Cy = $C_6H_{11}$) (Burnett, Dean & Vittal, 1994). The structure of the free ligand, (I), is reported in this paper.



(I)

The crystal structure contains two crystallographically independent molecules in the asymmetric unit. A view of one of the two independent molecules is shown in Fig. 1. Both molecules have similar conformations. The weighted r.m.s. deviation for the fit of the superimposed structures of these two molecules is 0.0356 Å. The $PCS_2$ fragments in both molecules are planar and all the cyclohexyl rings are in chair conformations. In each molecule there are two different C—S bond distances. The distances C1—S2 1.640 (2) Å and C2—S4 1.637 (3) Å are shorter than the distances C1—S1 1.669 (2) Å and C2—S3 1.672 (3) Å. Two different C—S distances were also reported previously for $Et_3PCS_2$ (Margulis & Templeton, 1962), however, the distances 1.677 and 1.693 Å are longer than the values observed here. The P—C distances, 1.863 (2) and 1.862 (2) Å, observed in (I) are longer than the 1.79 Å reported for $Et_3PCS_2$, indicating the substituent effects on these values.

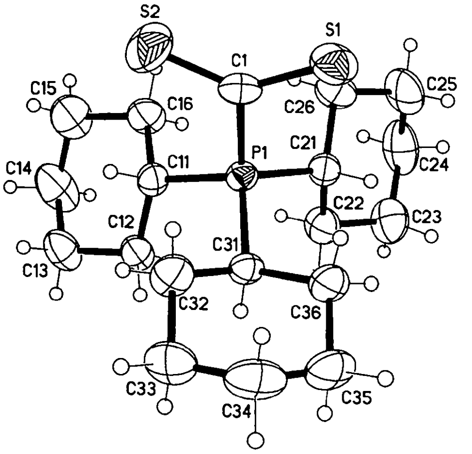


Fig. 1. A view of one of the molecules of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

A search of the April 1996 release of the Cambridge Structural Database (Allen & Kennard, 1993) produced 43 hits for the complexes of trisubstituted phosphoniodithioformates. Of these, 21 were tricyclohexylphosphoniodithioformate complexes. A comparison of the geometric parameters of the free ligand, (I), with those present in its complexes gave the following results: (i) the P—C bond distance in general decreases on complexation (range 1.752–1.866 Å). The lowest bond distance, 1.752 Å is observed in a dimanganese complex where the bonding of the ligand is $\eta^3$-(S,C,S′) mode (Miguel, Riera, Miguel, Gómez & Solans, 1991). (ii) Depending upon the coordination mode of the $Cy_3PCS_2$, the C—S distances vary from 1.643 to 1.828 Å. The shortest C—S bond distance in the compound *cis*-$[Pt(CO)(C_6F_5)_2(\eta^1\text{-}S_2CPCy_3)].CH_2Cl_2$, involves non-bonded sulfur (Uson *et al.*, 1986). A C—S bond lengthening is observed when the S atom involved is coordinated. (iii) The S—C—S angles vary over a wide range, 102.3–129.4°, again depending on how the ligand is bonded to the metal. For example, in *fac*-$[Mn(CO)_3(S_2CPCy_3)_2](ClO_4).H_2O$ (Miguel *et al.*, 1987), the angle for the phosphoniodithioformate involved in $\eta^1$-(S) bonding is 129.4°, which is close to that observed in (I). The smallest angle observed, 102.3°, occurs in $[Mn_2(\mu\text{-dppm})(CO)_4(S_2CPCy_3)].CH_2Cl_2$ [dppm is bis(diphenylphosphino)methane] where the bonding mode of the dithioformate ligand is $\eta^3$-(S,C,S′)$\eta^2$-(S,S′) (Miguel *et al.*, 1991).

## Experimental

The title compound was obtained commercially. Single crystals were grown from $CS_2$. The compound may also be prepared by crystallizing $PEt_3$ from $CS_2$.

### *Crystal data*

$C_{19}H_{33}PS_2$
$M_r = 356.54$
Triclinic
$P\bar{1}$
$a = 9.515 (1)$ Å
$b = 12.782 (1)$ Å
$c = 16.467 (2)$ Å
$\alpha = 83.94 (1)°$
$\beta = 88.95 (1)°$
$\gamma = 80.68 (1)°$
$V = 1965.2 (4)$ Å$^3$
$Z = 4$
$D_x = 1.205$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 6.27–13.13°$
$\mu = 0.349$ mm$^{-1}$
$T = 298 (2)$ K
Big block, cut
0.34 × 0.32 × 0.24 mm
Dark red–brown

### *Data collection*

Siemens *P*4 diffractometer
$2\theta/\omega$ scans

$R_{\rm int} = 0.029$
$\theta_{\rm max} = 25°$

Absorption correction: empirical *via* $\psi$-scan (*XSCANS*; Siemens, 1994)
$T_{\min} = 0.720$, $T_{\max} = 0.811$
7919 measured reflections
6927 independent reflections
5257 reflections with $I > 2\sigma(I)$
$h = -1 \rightarrow 11$
$k = -14 \rightarrow 15$
$l = -19 \rightarrow 19$
3 standard reflections every 297 reflections intensity decay: random 5.1%

*Refinement*

Refinement on $F^2$
$R(F)[F > 4\sigma(F)] = 0.044$
$wR(F^2)[F^2 > 2\sigma(F^2)] = 0.114$
$S(F^2)[F^2 > 2\sigma(F^2)] = 1.068$
6927 reflections
397 parameters
All H-atom positions were refined using a riding model
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.438$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.303$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—C1 | 1.669 (2) | S3—C2 | 1.672 (3) |
| S2—C1 | 1.640 (2) | S4—C2 | 1.637 (3) |
| P1—C11 | 1.829 (2) | P2—C41 | 1.832 (2) |
| P1—C21 | 1.833 (2) | P2—C51 | 1.837 (2) |
| P1—C31 | 1.838 (2) | P2—C61 | 1.842 (2) |
| P1—C1 | 1.863 (2) | P2—C2 | 1.862 (2) |
| C11—P1—C21 | 112.95 (10) | C41—P2—C51 | 113.33 (10) |
| C11—P1—C31 | 106.33 (9) | C41—P2—C61 | 106.49 (9) |
| C21—P1—C31 | 110.38 (9) | C51—P2—C61 | 109.90 (9) |
| C11—P1—C1 | 110.18 (10) | C41—P2—C2 | 109.89 (11) |
| C21—P1—C1 | 109.74 (10) | C51—P2—C2 | 109.82 (10) |
| C31—P1—C1 | 107.06 (9) | C61—P2—C2 | 107.18 (9) |
| S2—C1—S1 | 130.24 (14) | S4—C2—S3 | 130.46 (14) |
| S2—C1—P1 | 116.31 (13) | S4—C2—P2 | 116.78 (14) |
| S1—C1—P1 | 113.35 (12) | S3—C2—P2 | 112.69 (13) |
| C12—C11—P1 | 115.63 (14) | C42—C41—P2 | 115.35 (14) |
| C16—C11—P1 | 113.83 (15) | C46—C41—P2 | 113.6 (2) |
| C22—C21—P1 | 113.43 (15) | C52—C51—P2 | 112.93 (15) |
| C26—C21—P1 | 113.6 (2) | C56—C51—P2 | 114.36 (15) |
| C32—C31—P1 | 110.31 (14) | C62—C61—P2 | 110.42 (14) |
| C36—C31—P1 | 113.76 (15) | C66—C61—P2 | 114.26 (15) |

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

The financial support of the Natural Sciences and Engineering Research Council of Canada, in the form of an Individual Research Grant to PAWD and an equipment grant that allowed the purchase of the diffractometer, is gratefully acknowledged. We thank the Co-editor for bringing the program *BUNYIP* (Hester & Hall, 1996) to our attention.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1026). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Burnett, T. R., Dean, P. A. W. & Vittal, J. J. (1994). *Can. J. Chem.* **72**, 1127–1136.

Carriedo, G. A., Pérez-Martínez, J. A., Miguel, D., Riera, V., García-Granda, S. & Pérez-Carreño, E. (1996). *J. Organomet. Chem.* **511**, 77–84.

Galindo, A., Mealli, C., Cuyás, J., Miguel, D., Riera, V., Pérez-Martínez, J. A., Bois, C. & Jeannin, Y. (1996). *Organometallics*, **15**, 2735–2744.

Hester, J. & Hall, S. R. (1996). *J. Appl. Cryst.* **29**, 474–478.

Margulis, T. N. & Templeton, D. H. (1962). *J. Chem. Phys.* **36**, 2311–2319.

Miguel, D., Riera, V., Miguel, J. A., Bois, C., Philoche-Levisalles, M. & Jeannin, Y. (1987). *J. Chem. Soc. Dalton Trans.* pp. 2875–2880.

Miguel, D., Riera, V., Miguel, J. A., Gómez, M. & Solans, X. (1991). *Organometallics*, **10**, 1683–1692.

Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Uśon, R., Forniés, J., Uśon, M. A., Yagüe, J. F., Jones, P. G. & Meyer-Bäse, K. (1986). *J. Chem. Soc. Dalton. Trans.* pp. 947–952.

---

*Acta Cryst.* (1997). **C53**, 1881–1883

# Methyl 3$\beta$-Bromine-7$\alpha$-hydroxy-5$\beta$-cholan-24-oate

ANGEL DAGO MORALES,[a] RAMÓN POMÉS HERNÁNDEZ,[a] FRANCISCO COLL MANCHADO,[b] ROXANA PÉREZ GIL,[b] GRACIELA PUNTE[c] AND GUSTAVO ECHEVERRÍA[c]

[a]*Dirección de Química, Centro Nacional de Investigaciones Científicas, Apartado 6990, Ciudad de la Habana, Cuba,* [b]*Facultad de Química, Universidad de la Habana, Ciudad de la Habana 10400, Cuba, and* [c]*PROFIMO, Departamento de Física, Facultad de Ciencias Exactas, UNLP, CC 67, (1900) La Plata, Argentina. E-mail: xray@infomed.sld.cu*

*(Received 21 February 1997; accepted 19 May 1997)*

## Abstract

In the title compound, $C_{25}H_{41}BrO_3$, the Br atom bonded to C3 is $\beta$-axially oriented and is (−)-synclinal to the C4—C5 bond. The six-membered rings (*A*, *B* and *C*) have chair conformations as expected. The five-membered ring (*D*) adopts a distorted 13$\beta$-envelope conformation. The *A*/*B* ring junction is *cis* and the *B*/*C* and *C*/*D* ring junctions are both *trans*.

## Comment

Elimination reactions of 3-halogenated steroids yield steroidal alkenes, key intermediates in the synthesis of biologically active steroids such as ecdysteroids and brassinosteroids. We report here the crystal structure

© 1997 International Union of Crystallography
Printed in Great Britain – all rights reserved

*Acta Crystallographica Section C*
ISSN 0108-2701 ©1997