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Bis[2-(diphenylphosphinoyl)benzene] disulfide

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The title compound, [2-$Ph_2P(O)C_6H_4S]_2$ or $C_{36}H_{28}O_2P_2S_2$, obtained by electrochemical oxidation of 2-(diphenylphosphino)benzenethiol, has twofold crystallographic symmetry. Principal dimensions include S—S 2.0212 (15) Å, S—C 1.786 (3) Å and C—S—S—C 81.34 (14)°.

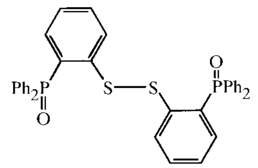
Comment

Metal phosphinothiolate complexes can be prepared easily by an electrochemical procedure starting from a sacrificial metal anode in a cell containing the ligand in an appropriate solvent. In this way, the synthesis of Co, Ni (Perez-Lourido *et al.*, 1998) and In (Perez-Lourido, Romero *et al.*, 1999) compounds with 2-(diphenylphosphino)benzenethiol and similar ligands have been reported. In attempts to prepare gallium complexes by electrochemical oxidation of a gallium anode in an acetonitrile solution of 2-(diphenylphosphino)benzenethiol, white crystals of [2–$Ph_2P(O)C_6H_4S]_2$, (I), suitable for X-ray diffraction studies were isolated and its crystal structure determined. The compound is the result of the electrochemical oxidation of [2-$Ph_2P—C_6H_4SH$] to gave the disulfide in a process such as:

$$\text{Cathode: } 2[2\text{-}Ph_2P{-}C_6H_4SH] + 2e^- \rightarrow H_2(g) + 2[2\text{-}Ph_2P{-}C_6H_4S]^-$$

$$\text{Anode: } 2[2\text{-}Ph_2P{-}C_6H_4S]^- \rightarrow [2\text{-}Ph_2PC_6H_4S]_2 + 2e^-.$$

The structure of the compound shows that oxidation has ocurred at the P atom, and the source of oxygen is surely oxygen dissolved in acetonitrile. Such a facile oxidation of phosphine to phosphine oxides has been observed already in similar complexes (Block, Kang *et al.*, 1989). The molecular structure is similar to related organic disulfide compounds such as bis(4,6-dimethylpyrimidyl) 2,2′-disulfide (Castro *et al.*, 1995) and bis[6-(*tert*-butyldimethylsilyl)-2-pyridyl] disulfide (Tallon *et al.*, 1995). The molecule shows a twofold axis through the S—S bond and it has an equatorial conformation with a torsion angle C2—S1—S1^i—C2^i of 81.34 (14)° [symmetry code: (i) $-x$, y, $\frac{3}{2}-z$]; this angle is within the 90±10° range found in most aromatic disulfides. In addition, the torsion angle C1—C2—S1—S1^i is −172.9 (2)°. This value corresponds with an equatorial conformation in the Shefter classification (Shefter, 1970). The S1—S1^i bond distance of 2.0212 (15) Å is close to the average value of 2.0 Å suggested for organic disulfides and almost equal to those found in bis[6-(*tert*-butyldimethylsilyl)-2-pyridyl] disulfide [2.032 (3) Å; Tallon *et al.* 1995] or in bis(4,6-dimethylpyrimidyl) 2,2′-disulfide [2.017 (1) Å; Castro *et al.* 1995]. In addition, the C2—S1 bond length, [1.786 (3) Å] is similar to those found in other disulfides with an equatorial conformation (Highasi *et al.*, 1978) and consistent with a C—S single bond. The P1—O1 bond distance [1.478 (2) Å] is almost equal to the distance observed in [$2Ph_2P(O)6–(Me_3Si)–C_6H_3SH$], [1.493 (3) Å; Perez-Lourido, Garcia-Vazquez *et al.*, 1999] and in agreement with the value proposed for a P═O bond (Allen *et al.*, 1987). The phenyl rings are practically flat with unremarkable bond distances and angles. Bond angles around the P atoms are in the range of 104.33 (12)–113.01 (12)° expected for a tetrahedral environment around a P atom.



(I)

Experimental

The synthesis of 2-(diphenylphosphino)benzenethiol was carried out using slight modifications of the standard literature procedure involving lithiation of benzenethiol (Block, Ofori-Okai & Zubieta, 1989) using Schlenk techniques and dry solvents. The electrochemical procedure used was similar to described (Highasi *et al.*, 1978). A solution containing 0.20 g of the ligand in 50 ml of acetonitrile and a few mg of tetramethylammonium perchlorate as electrolytic support was electrolyzed in a cell with a gallium anode and a platinum cathode over a period of 2 h using 20 mA of intensity. No metal was found to be dissolved from the anode. The resultant solution was filtered off and then air concentrated. White crystals of [2-$Ph_2P(O)C_6H_4S]_2$, suitable for X-ray diffraction studies were isolated.

Crystal data

$C_{36}H_{28}O_2P_2S_2$
$M_r = 618.64$
Monoclinic, $C2/c$
$a = 13.249$ (3) Å
$b = 10.801$ (2) Å
$c = 21.193$ (5) Å
$\beta = 104.50$ (2)°
$V = 2936.3$ (11) Å^3
$Z = 4$
$D_x = 1.399$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.54$–16.06°
$\mu = 0.324$ mm^{-1}
$T = 203$ (2) K
Plate, light brown
0.25 × 0.25 × 0.20 mm

Data collection

Nonius CAD-4 MACH-3 diffractometer
ω–2θ scans
2697 measured reflections
2575 independent reflections
1848 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 24.97°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 12$
$l = -25 \rightarrow 24$
6 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.091$
$S = 1.033$
2575 reflections
246 parameters
H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.9871P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.294$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.243$ e Å^{-3}

Data collection: Nonius CAD-4 software; cell refinement: Nonius CAD-4 software; data reduction: Nonius CAD-4 software; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

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