Acta Cryst. (1978). B**34**, 3785–3787

Triphenylphosphine Sulfide[*]

By Penelope W. Codding and K. Ann Kerr

Department of Chemistry, The University of Calgary, Calgary, Alberta T2N 1N4, Canada

(*Received* 30 *March* 1978; *accepted* 3 *August* 1978)

Abstract. $C_{18}H_{15}PS$, monoclinic, $a = 18{\cdot}314\,(4)$, $b = 9{\cdot}640\,(2)$, $c = 18{\cdot}013\,(4)$ Å, $\beta = 105{\cdot}99\,(2)^\circ$, $P2_1/c$, $Z = 8$; $\rho_c = 1{\cdot}279$, $\rho_o = 1{\cdot}22\,(3)$ g cm^{-3}. The dimensions of the two molecules in the asymmetric unit are very similar. The geometry at the P atom is approximately tetrahedral with an average P=S distance of 1·950 (3) Å and an average P—C distance of 1·817 Å. The bond angles around the P atom range from 103·7 (3) to 113·9 (2)° with an average C—P—S angle of 113·1 (6)° and an average C—P—C angle of 105·7 (16)°.

Introduction. This study is part of a structural investigation of phosphine chalcogenide ligands of the type $R_3M{=}Y$, directed at a better understanding of the factors that influence bonding in these molecules. The structure of tricyclohexylphosphine sulfide, TCyPS, has been reported (Kerr, Boorman, Misener & van Roode, 1977) and structure determinations are in progress on other members of the isostructural series $(C_6H_5)_3M{=}Y$ with M = P or As and Y = S or Se.

Weissenberg and precession photographs exhibited systematic absences of the type $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$, thus confirming the space group, $P2_1/c$. A crystal of dimensions 0·010 × 0·009 × 0·037 cm was used for intensity-data collection on a Picker FACS-1 diffractometer with Ni-filtered, Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The data were collected in the θ–2θ scan mode at a scan rate of 1° min^{-1} with a scan width of $\Delta 2\theta = (1{\cdot}6 + 0{\cdot}285 \tan\theta)^\circ$. Background counts were measured for 40s at either end of the scan. Of the 3987 reflections measured to a maximum $\sin\theta/\lambda$ of 0·53 Å^{-1}, 1669 had intensities greater than $3\sigma(I)$ where $\sigma(I) = [T + B + (0{\cdot}02I)^2]^{1/2}$ and T is the total peak count and B is the total background count normalized to the time interval of the scan.

Data were corrected for absorption [μ(Cu $K\alpha$) = 26·73 cm^{-1}] by analytical methods. The value of the correction ranged from 1·22 to 1·49. Structure solution by *MULTAN* (Germain, Main & Woolfson, 1971) was followed by least-squares refinement. Owing to the low ratio of observations to parameters, positions and thermal parameters of the heavy atoms were refined in large blocks (1 block/molecule). Positions of H atoms were calculated after isotropic refinement and confirmed in a difference Fourier synthesis. Although these atoms were included in the model, they were not refined. The final R values are $R_w = [\sum w^2(|F_o| - |F_c|)^2/\sum w^2|F_o|^2]^{1/2} = 0{\cdot}0517$ for the 1669 observed reflections; conventional $R = 0{\cdot}0457$ for these 1669 reflections and 0·1433 for all 3987 reflections. The $\sqrt{w} = [\sigma^2(F) + 0{\cdot}0008\,F^2]^{1/2}$ where $\sigma(F)$ was derived from counting statistics. The standard deviation of an observation of unit weight is 1·10. The final atomic coordinates for the non-hydrogen atoms are given in Table 1 with the atoms labelled according to Fig. 1. The scattering factors were taken from *International Tables for X-ray Cyrstallography* (1974). Computer programs used include *MULTAN* (Germain, Main & Woolfson, 1971), *CUDLS* (John Stephens), *ORTEP* (Johnson, 1965), *ANABS* (L. Templeton & D. Templeton), and several programs from the Los Alamos Scientific Laboratory system of programs (A. C. Larson).[†]

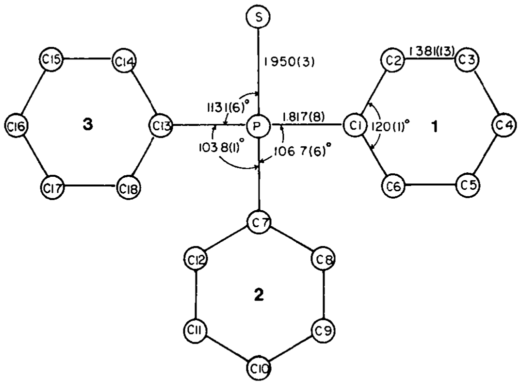

Fig. 1. The labelling scheme and average interbond distances (Å) and angles for triphenylphosphine sulfide. The second molecule in the asymmetric unit has the same numbering scheme and is differentiated by a prime in the text and tables. The value in parentheses is the e.s.d. of the mean. There are two significantly smaller C—P—C angles, one per molecule, due to intramolecular contacts which have been averaged separately to give the two values for the C—P—C angle shown here.

[†] Lists of structure factors, anisotropic thermal parameters and hydrogen positional and isotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33748 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[*] Crystal Structure Studies of Group V Chalcogenide Compounds. II.

Table 1. *Fractional coordinates for the non-hydrogen atoms of triphenylphosphine sulfide*

The estimated standard deviation of the last digit is in parentheses.

	x	*y*	*z*
P	0·9397 (1)	0·1588 (2)	0·8228 (1)
S	0·8989 (1)	0·0018 (2)	0·8670 (1)
C(1)	1·0423 (3)	0·1628 (7)	0·8523 (4)
C(2)	1·0787 (4)	0·1486 (7)	0·9304 (4)
C(3)	1·1569 (4)	0·1470 (7)	0·9568 (4)
C(4)	1·2004 (4)	0·1590 (8)	0·9049 (4)
C(5)	1·1653 (4)	0·1716 (7)	0·8280 (4)
C(6)	1·0865 (4)	0·1736 (7)	0·8011 (4)
C(7)	0·9091 (3)	0·3250 (6)	0·8499 (3)
C(8)	0·9583 (4)	0·4298 (7)	0·8844 (4)
C(9)	0·9296 (4)	0·5537 (8)	0·9007 (4)
C(10)	0·8539 (4)	0·5776 (7)	0·8860 (4)
C(11)	0·8036 (4)	0·4741 (8)	0·8514 (4)
C(12)	0·8302 (3)	0·3487 (8)	0·8339 (4)
C(13)	0·9093 (3)	0·1617 (7)	0·7174 (3)
C(14)	0·9220 (4)	0·2765 (7)	0·6767 (4)
C(15)	0·8972 (5)	0·2796 (8)	0·5969 (5)
C(16)	0·8595 (5)	0·1647 (10)	0·5583 (4)
C(17)	0·8477 (4)	0·0499 (9)	0·5983 (5)
C(18)	0·8714 (4)	0·0469 (7)	0·6779 (4)
P′	0·5578 (1)	0·5768 (2)	0·6688 (1)
S′	0·5955 (1)	0·7280 (2)	0·6177 (1)
C(1′)	0·4545 (3)	0·5743 (7)	0·6450 (4)
C(2′)	0·4138 (4)	0·5848 (8)	0·5683 (4)
C(3′)	0·3363 (4)	0·5891 (8)	0·5465 (4)
C(4′)	0·2969 (4)	0·5877 (8)	0·6023 (4)
C(5′)	0·3372 (4)	0·5753 (8)	0·6780 (4)
C(6′)	0·4152 (4)	0·5696 (7)	0·7007 (4)
C(7′)	0·5873 (4)	0·4059 (7)	0·6445 (3)
C(8′)	0·5385 (4)	0·3020 (8)	0·6133 (4)
C(9′)	0·5666 (5)	0·1743 (8)	0·5965 (4)
C(10′)	0·6422 (5)	0·1525 (9)	0·6125 (4)
C(11′)	0·6926 (4)	0·2571 (10)	0·6444 (4)
C(12′)	0·6655 (4)	0·3842 (8)	0·6603 (4)
C(13′)	0·5916 (3)	0·5823 (7)	0·7733 (4)
C(14′)	0·5832 (4)	0·4692 (7)	0·8170 (4)
C(15′)	0·6085 (4)	0·4733 (8)	0·8975 (4)
C(16′)	0·6440 (5)	0·5923 (10)	0·9335 (4)
C(17′)	0·6545 (4)	0·7031 (9)	0·8907 (5)
C(18′)	0·6286 (4)	0·6989 (7)	0·8106 (4)

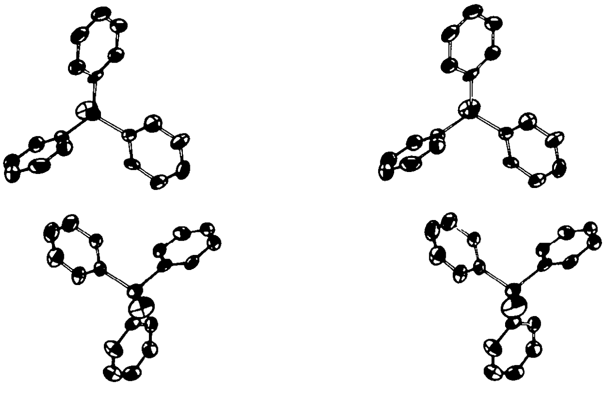

Fig. 2. A stereodrawing of the two molecules in the asymmetric unit of triphenylphosphine sulfide. The drawing was made with the computer program *ORTEP*. The boundary ellipse is drawn at the 50% probability level.

Average values of interatomic distances and angles are given in Fig. 1. Fig. 2 is a stereodrawing of the two molecules in the asymmetric unit. Both the dimensions and the conformation of the two molecules are very similar. The numbering scheme is such that equivalent atoms in the two molecules have the same number but they are primed in one molecule. In each molecule, one phenyl ring (ring 3) is nearly parallel with the corresponding S–P–C(13) plane. This conformation produces short intramolecular contacts from ring (1) to each of the other two rings: C(1)···H(8) 2·66, H(6)···C(14) 2·67, C(1′)···H(8) 2·70, H(6′)···C(14) 2·64 Å. These short contacts are probably responsible for the observed variation in the C–P–C angles in TPPS. The C–P–C angles involving rings (2) and (3) are 103·8 (3) and 103·7 (3)°; significantly smaller than 106·7°, the average value of the C(1)–P–C angles.

Table 2 compares the dimensions of TPPS with similar molecules in the literature.

Discussion. The behavior of phosphorus ligands depends greatly on the characteristics of the substituents on the P atom. Bulky substituents on the P atom should expand the C–P–C angles closer to tetrahedral values and lengthen the P–S bond (Tolman, 1977). Increasing the electronegativity of the substituents in R_3P=S enhances $d\pi$–$p\pi$ back donation from the filled orbitals of S and shortens the P=S bond. Thus it is not unexpected that the P=S bond in TPPS is shorter than that found in TCyPS and the average C–P–C angle is smaller.

The similarity in the dimensions of the three substituted-phenyl-ring compounds in Table 2 is striking. The P=S bonds and the C–P–C angles are the same within the error of the determination for all four structures. This suggests that electronic effects are less important than steric effects for these compounds and that the difference in steric requirements for phenyl and *o*-tolyl groups is small enough to be masked by such crystal effects as packing and thermal motion.

Table 2. *Average dimensions of* R_3P = S *structures*

Molecule	P=S (Å)	P–C (Å)	C–P–C (°)	S–P–C (°)
TPPS[a]	1·950 (3)	1·817 (8)	105·7 (16)	113·1 (6)
Br-TPPS[b]	1·950 (2)	1·816 (3)	105·7 (1)	113·1 (1)
Cl-TPPS[c]	1·949 (2)	1·807 (2)	105·9 (1)	112·9 (1)
ToTPS[d]	1·947 (4)	1·818 (7)	106·3 (5)	112·5 (3)
TCyPS[e]	1·966 (2)	1·839 (3)	108*	111·2 (1)

References: (*a*) Triphenylphosphine sulfide, this work. (*b*) *p*-Bromophenyldiphenylphosphine sulfide (Dreissig, Plieth & Zäske, 1972). (*c*) *p*-Chlorophenyldiphenylphosphine sulfide (Dreissig & Plieth, 1972). (*d*) Tri-*o*-tolylphosphine sulfide (Cameron, Howlett, Shaw & Woods, 1973). (*e*) Tricyclohexylphosphine sulfide (Kerr, Boorman, Misener & van Roode, 1977).

* TCyPS has mirror symmetry. The C–P–C angle bisected by the mirror is 113·2 (1)°, the other angles are 105·4 (1)°.

Table 3. *Inter-plane angles*

The angles refer to the angle between the normals of the respective planes. The P—S—C plane includes the lead C atom of the corresponding phenyl ring.

Plane	σ(plane)	Atoms in plane	Angle to P—S—C	Angle to hub*
Phenyl 1	0·003 Å	C(1),C(2),C(3),C(5),C(6)	50·3°	43·9°
Phenyl 2	0·006	C(7),C(8),C(9),C(10),C(11),C(12)	55·2	42·1
Phenyl 3	0·005	C(13),C(14),C(15),C(16),C(17),C(18)	10·6	79·4
Phenyl 1′	0·009	C(1′),C(2′),C(3′),C(4′),C(5′),C(6′)	50·0	43·4
Phenyl 2′	0·005	C(7′),C(8′),C(9′),C(10′),C(11′),C(12′)	57·5	40·0
Phenyl 3′	0·010	C(13′),C(14′),C(15′),C(16′),C(17′),C(18′)	12·2	78·1

* The hub is the plane through the three C atoms bonded to the P atom.

The conformational angles listed in Table 3 indicate a distinct departure from the C_3 symmetry normally assumed to be the ground-state conformation of molecules of this type. However, calculations performed by Andose & Mislow (1974) in their investigation of the 'two-ring flip' mechanism for stereoisomerization of trimesitylmethane suggest that the observed conformation is easily accessible from the ground state. It is interesting to note that their calculations show large variations in the central C(phenyl)—C—C(phenyl) bond angles in the transition conformations although the average angle is the same as in the ground-state conformation. These results are consistent with the idea that the average value of the C—P—C angle in phosphine sulfides is characteristic of the bulk of the substituents on the central atom, while the variation in C—P—C angles is a function of the conformation of the molecule.

The authors would like to thank Dr P. M. Boorman for providing the sample and for helpful discussions and Mr B. S. Misener for technical assistance. This work was supported by the National Research Council of Canada (Grant A5881 to K. A. Kerr).

References

Andose, J. D. Mislow, K. (1974). *J. Am. Chem. Soc.* **96**, 2168–2176.

Cameron, T. S., Howlett, K. D., Shaw, R. A. & Woods, M. (1973). *Phosphorus*, **3**, 71–73.

Dreissig, W. & Plieth, K. (1972). *Acta Cryst.* B**28**, 3478–3483.

Dreissig, W., Plieth, K. & Zäske, P. (1972). *Acta Cryst.* B**28**, 3473–3477.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory Tennessee.

Kerr, K. A., Boorman, P. M., Misener, B. S. & van Roode, J. G. H. (1977). *Can. J. Chem.* **55**, 3081–3085.

Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.

Acta Cryst. (1978). B**34**, 3787–3790

N,N′-Bis(3,4-dichlorophenyl)urea

By S. Stanković

Institute of Physics, University of Novi Sad, Dr Ilije Djuričića 4, 21000 *Novi Sad, Yugoslavia*

and G. D. Andreetti

Istituto di Strutturistica Chimica dell'Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, 43100 *Parma, Italy*

(*Received* 9 *January* 1978; *accepted* 14 *July* 1978)

Abstract. $C_{13}H_8Cl_4N_2O$, monoclinic, $P2_1/n$, a = 11·713 (3), b = 25·499 (7), c = 9·391 (5) Å, β = 92·13 (4)°, V = 2802·87 Å^3, Z = 8 (there are two molecules in the asymmetric unit), D_c = 1·66 g cm^{-3}. The structure consists of discrete molecules, linked together by hydrogen bonds and stacked in columns along the c axis. The columns are connected by van der Waals forces.