side-chain conformations, especially on the O(6) acetyl conformation.

We thank Professor Nobuo Morimoto and Dr Katsutoshi Tomita, Institute of Geology and Mineralogy, Faculty of Science, Kyoto University, for the use of the Rigaku AFC5 diffractometer. All computations were performed on the Facom M190 computer at Data Processing Center, Kyoto University, using the *KPAX* program system.

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Tetraphenyldiphosphine Disulphide (Tetraphenyl-1,2-dithioxodi-λ^5-phosphane), $Ph_2P(S)P(S)Ph_2$*

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(*Received* 19 *September* 1980; *accepted* 22 *December* 1980)

Abstract. $C_{24}H_{20}P_2S_2$, monoclinic, $P2_1/c$, $a = 9{\cdot}628$ (3), $b = 15{\cdot}798$ (11), $c = 14{\cdot}304$ (4) Å, $\beta = 96{\cdot}29$ (3)°, $V = 2162{\cdot}6$ (17) Å^3, $D_o = 1{\cdot}38$ (displacement), $D_c = 1{\cdot}34$ Mg m^{-3}, $Z = 4$. The final R is 0·045 for 2259 reflections. The unit cell contains two independently oriented pairs of *trans*-$Ph_2P(S)P(S)Ph_2$ molecules in two sets of (C_i) special positions. The P–P bond [2·263 (4) Å (mean)] is significantly longer than that found (2·21 Å approximately) in corresponding alkyl compounds.

Introduction. The IR spectrum of tetraphenyldiphosphine disulphide contains only one identifiable SPPS stretching absorption, assigned to υ_{as}PS, and is consistent with a planar *trans* SPPS conformation similar to that found in various related tetraalkyl compounds (Cowley & White, 1966). The highest-symmetry conformation possible for an $R_2P(S)P(S)R_2$ molecule is C_{2h}, but in practice this appears to be achieved only in the tetramethyl compound (Pedone & Sirigu, 1967; Lee & Goodacre, 1971). In other compounds for which detailed structural information is available [tetraethyldiphosphine disulphide (Dutta & Woolfson, 1961); bis(cyclotetramethylene)diphosphine disulphide (Lee & Goodacre, 1969); bis(cyclopentamethylene)diphosphine disulphide (Lee & Goodacre, 1970)] the alkyl groups are not symmetrically oriented relative to the SPPS plane and the molecules belong to the C_i point group. The C_{2h} and C_i conformations cannot be distinguished reliably using vibrational data alone and crystallographic analysis of the tetraphenyl compound was therefore desirable in order to confirm the proposed *trans* structure, to determine the orientation of the phenyl groups and to provide information for a more detailed examination of the vibrational spectrum.

Tetraphenyldiphosphine disulphide was prepared as colourless square prismatic, almost cubic, crystals from the reaction of tetraphenyldiphosphine with sulphur

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* Diphosphine derivatives. VII. Part VI: Blake, McQuillan & Oxton (1980).

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under reflux in dry, oxygen-free toluene (Kuchen & Buchwald, 1958; Niebergall & Langenfeld, 1962). Preliminary cell constants were obtained from precession and de Jong–Bouman photographs taken about the long axis of a single crystal. The systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) identify the space group as $P2_1/c$; the long axis coincides with the crystallographic c axis. Precise unit-cell parameters were obtained by least-squares refinement of the indexed powder diffraction pattern, measured from standard Guinier–Hägg photographs with calcite as an internal calibrant, using a prototype Guinier microdensitometer developed by the late Mr B. G. Cooksley of this Department (Cu $K\alpha_1$ radiation, $\lambda = 1{\cdot}5406$ Å).

Intensity data were collected for a single crystal ($0{\cdot}8 \times 0{\cdot}5 \times 0{\cdot}5$ mm) mounted about **b**, using a Hilger & Watts Model Y190 automatic linear diffractometer with balanced filters and Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). A total of 7766 reflections were measured, with an ω scan of 2·5°, for $\sin^2\theta < 0{\cdot}30$. After equivalent reflections were averaged a total of 2259 Lp-corrected independent 'observed' reflections [$I > 3\sigma(I)$] were available for use in the structure determination.

Initial parameters for all 28 non-hydrogen atoms in the asymmetric unit were found using *MULTAN* (Germain, Main & Woolfson, 1971) and the structure was refined by block-diagonal least-squares methods, with anisotropic thermal vibrational parameters in the later stages, until the value of $R = \sum |F_o - F_c|/\sum F_o$ converged at 0·057. At this point, the H atom positions were calculated and in most cases coincided with small peaks on a difference map. The refinement was continued including the H atoms with isotropic temperature factors until the parameter shifts were negligible (<0·2 e.s.d.) and the value of R had fallen to 0·045. A final difference map showed no significant features. The weighting scheme used throughout was of the form $\omega = [1 + (0{\cdot}067|F_o| - 1{\cdot}67)^2]^{-1}$. Computer programs apart from *MULTAN* were based on those of Ahmed, Hall, Pippy & Huber (1966) and neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

The final parameters are listed in Table 1 and bond length and angle data in Table 2.*

Table 1. *Final fractional coordinates* (*e.s.d. refers to last significant figure*) *and isotropic thermal parameters*

$B_{\rm eq}$ (non-H atoms) and $B_{\rm iso}$ (H atoms) are given (Å^2) ($B_{\rm eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$).

	*A**					*B*†			
	x	y	z	$B_{\rm eq}/B_{\rm iso}$		x	y	z	$B_{\rm eq}/B_{\rm iso}$
P(1)	0·0929 (1)	0·5357 (2)	0·5361 (1)	2·70	P(2)	0·5065 (1)	0·5417 (1)	0·0646 (1)	2·91
S(1)	0·0445 (1)	0·6015 (1)	0·6435 (1)	3·85	S(2)	0·3767 (1)	0·6366 (1)	0·0484 (1)	4·29
C(1)	0·1505 (4)	0·6006 (3)	0·4439 (3)	3·04	C(13)	0·6880 (4)	0·5737 (3)	0·0797 (3)	3·28
C(2)	0·1413 (5)	0·6871 (3)	0·4516 (4)	4·10	C(14)	0·7167 (5)	0·6589 (3)	0·0636 (3)	4·30
C(3)	0·1721 (7)	0·7398 (3)	0·3785 (4)	5·68	C(15)	0·8517 (6)	0·6869 (4)	0·0677 (4)	5·62
C(4)	0·2145 (6)	0·7042 (4)	0·2977 (4)	5·16	C(16)	0·9588 (6)	0·6318 (5)	0·0899 (4)	6·66
C(5)	0·2260 (5)	0·6190 (3)	0·2896 (3)	4·39	C(17)	0·9341 (5)	0·5469 (5)	0·1039 (4)	5·75
C(6)	0·1927 (5)	0·5655 (3)	0·3607 (3)	3·55	C(18)	0·7982 (5)	0·5166 (4)	0·0995 (4)	4·36
C(7)	0·2175 (4)	0·4524 (3)	0·5697 (3)	2·96	C(19)	0·4697 (4)	0·4681 (3)	0·1563 (3)	3·13
C(8)	0·3382 (5)	0·4374 (3)	0·5255 (3)	3·82	C(20)	0·5683 (5)	0·4434 (3)	0·2280 (3)	4·15
C(9)	0·4275 (5)	0·3731 (3)	0·5578 (4)	4·47	C(21)	0·5302 (6)	0·3885 (4)	0·2982 (4)	5·04
C(10)	0·3997 (5)	0·3224 (3)	0·6304 (4)	4·56	C(22)	0·3942 (7)	0·3598 (3)	0·2951 (3)	5·15
C(11)	0·2812 (5)	0·3370 (4)	0·6746 (4)	4·59	C(23)	0·2959 (6)	0·3867 (3)	0·2234 (4)	4·67
C(12)	0·1909 (5)	0·4015 (3)	0·6440 (3)	3·65	C(24)	0·3339 (5)	0·4403 (3)	0·1543 (3)	3·82
H(2)‡	0·119 (4)	0·713 (3)	0·508 (3)	1·8	H(14)	0·634 (5)	0·702 (3)	0·051 (3)	1·6
H(3)	0·159 (6)	0·803 (4)	0·393 (4)	4·7	H(15)	0·878 (6)	0·754 (4)	0·063 (4)	4·0
H(4)	0·233 (6)	0·742 (4)	0·245 (4)	3·8	H(16)	1·054 (7)	0·655 (4)	0·091 (5)	6·2
H(5)	0·261 (6)	0·597 (4)	0·229 (4)	4·8	H(17)	1·003 (6)	0·499 (4)	0·115 (4)	4·4
H(6)	0·190 (5)	0·503 (3)	0·352 (3)	1·2	H(18)	0·773 (5)	0·459 (3)	0·103 (3)	1·7
H(8)	0·361 (4)	0·473 (2)	0·479 (3)	0·8	H(20)	0·670 (5)	0·470 (3)	0·237 (3)	2·4
H(9)	0·505 (6)	0·357 (4)	0·531 (4)	4·4	H(21)	0·611 (6)	0·363 (4)	0·347 (4)	4·2
H(10)	0·463 (6)	0·278 (4)	0·649 (4)	3·5	H(22)	0·360 (5)	0·319 (3)	0·345 (3)	2·1
H(11)	0·267 (5)	0·299 (3)	0·727 (4)	3·0	H(23)	0·193 (6)	0·360 (4)	0·216 (4)	5·0
H(12)	0·101 (5)	0·411 (3)	0·675 (4)	3·3	H(24)	0·262 (5)	0·463 (3)	0·107 (3)	2·3

* Coordinates *A* generate molecules with centres of symmetry at $0,\frac{1}{2},\frac{1}{2}$; 0,0,0.

† Coordinates *B* generate molecules with centres of symmetry at $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$.

‡ Hydrogen atoms are numbered in the same way as carbon atoms to which they are attached.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35872 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and selected bond angles* (°) (*e.s.d.'s in parentheses*)

	Molecule *A*		Molecule *B*
P(1)–P(1′)	2·266 (2)	P(2)–P(2′)	2·261 (2)
P(1)–S(1)	1·952 (2)	P(2)–S(2)	1·950 (2)
P(1)–C(1)	1·805 (4)	P(2)–C(13)	1·810 (4)
P(1)–C(7)	1·810 (4)	P(2)–C(19)	1·816 (4)
C(1)–C(2)	1·374 (7)	C(13)–C(14)	1·399 (7)
C(2)–C(3)	1·393 (8)	C(14)–C(15)	1·368 (7)
C(3)–C(4)	1·386 (8)	C(15)–C(16)	1·360 (9)
C(4)–C(5)	1·357 (8)	C(16)–C(17)	1·381 (10)
C(5)–C(6)	1·387 (7)	C(17)–C(18)	1·388 (7)
C(6)–C(1)	1·412 (6)	C(18)–C(13)	1·398 (7)
C(7)–C(8)	1·403 (6)	C(19)–C(20)	1·376 (6)
C(8)–C(9)	1·377 (7)	C(20)–C(21)	1·405 (7)
C(9)–C(10)	1·361 (7)	C(21)–C(22)	1·382 (9)
C(10)–C(11)	1·383 (7)	C(22)–C(23)	1·384 (8)
C(11)–C(12)	1·380 (7)	C(23)–C(24)	1·380 (7)
C(12)–C(7)	1·378 (6)	C(24)–C(19)	1·377 (6)
P(1′)P(1)S(1)	112·3 (1)	P(2′)P(2)S(2)	112·0 (1)
P(1′)P(1)C(1)	103·9 (1)	P(2′)P(2)C(13)	103·1 (1)
P(1′)P(1)C(7)	103·1 (1)	P(2′)P(2)C(19)	102·7 (1)
S(1)P(1)C(1)	113·1 (1)	S(2)P(2)C(13)	113·4 (1)
S(1)P(1)C(7)	112·7 (1)	S(2)P(2)C(19)	113·9 (1)
C(1)P(1)C(7)	111·1 (2)	C(13)P(2)C(19)	110·8 (2)
P(1)C(1)C(2)	118·6 (3)	P(2)C(13)C(14)	117·1 (3)
P(1)C(1)C(6)	122·2 (2)	P(2)C(13)C(18)	123·1 (3)
P(1)C(7)C(8)	124·2 (3)	P(2)C(19)C(20)	123·2 (3)
P(1)C(7)C(12)	117·1 (3)	P(2)C(19)C(24)	116·7 (3)

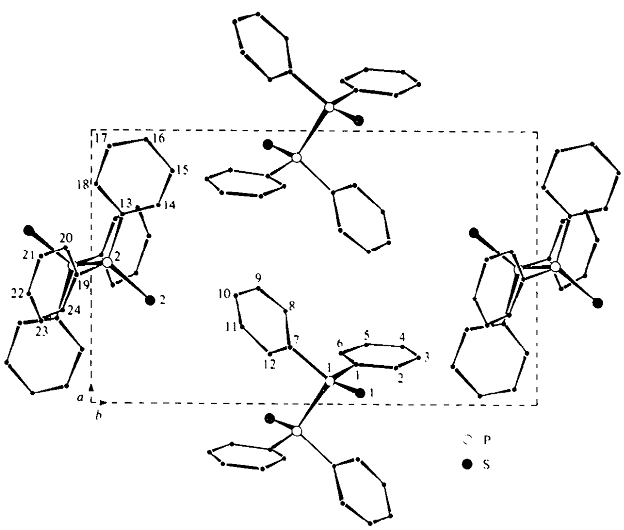

Fig. 1. $Ph_2P(S)P(S)Ph_2$ unit cell at $z = \frac{1}{2}$, showing molecules (*A*) with centres at $0,\frac{1}{2},\frac{1}{2}$ and (*B*) with centres at $\frac{1}{2},0,\frac{1}{2}$. Other molecules of type (*A*) have centres at 0,0,0 and type (*B*) at $\frac{1}{2},\frac{1}{2},0$.

Discussion. The asymmetric unit identified by *MULTAN* consists of two chemically distinct $Ph_2P(S)$ half-molecules. Operation of the crystallographic centres of symmetry generates two independent, differently oriented pairs of $Ph_2P(S)P(S)Ph_2$ molecules, occupying two separate sets of special positions in the unit cell (Fig. 1). The two sets of molecules differ only in orientation: all of them have the same symmetry and all bond lengths and angles are identical to within the limits of experimental error.

The tetraphenyldiphosphine disulphide molecule has the centrosymmetric *trans* structure and the SPPS skeleton is strictly planar. Within each Ph_2P grouping, the phenyl rings are inequivalently rotated about the P–C bonds and thus make unequal dihedral angles [110·5 and 88·2° (mean values)] with the SPPS plane: the overall molecular symmetry is therefore C_i rather than C_{2h}.

The P–P bond distance of 2·263 Å is appreciably longer than the corresponding bonds in related compounds which [with the exception of $Me_2P(S)P(S)Me_2$] are consistently in the range 2·21 ± 0·01 Å (Table 3). Even allowing for the lower accuracy of some of the earlier determinations, the difference appears to be significant.* In the case of tetramethyldiphosphine disulphide, two substantially different P–P bond lengths (2·161, 2·245 Å, mean value 2·203 Å) are reported for two sets of nonequivalent molecules in the unit cell. There is also a corresponding, smaller, difference in the P–S bond lengths (Lee & Goodacre, 1971). However, although the reported variation in the P–P bond length in particular appears to be large enough to have a detectable effect on the vibrational spectrum of the solid compound, the IR and Raman spectra of $Me_2P(S)P(S)Me_2$ in the P–P and P–S stretching-frequency regions are very simple and although not conclusive seem to be more consistent with a structure in which all the $Me_2P(S)P(S)Me_2$ molecules have identical geometry (McQuillan & Oxton, 1977).

The P–S and P–C bond lengths in $Ph_2P(S)P(S)Ph_2$, unlike the P–P bond length, are very similar to those in other diphosphine disulphides. The bond angles at the P atoms are normal, with ∠PPS, ∠SPC and ∠CPC slightly greater, and ∠PPC slightly less, than the tetrahedral value. ∠CPC is a few degrees larger than in the tetraalkyl compounds, presumably to accommodate the phenyl groups. The mean C–C bond length is 1·383 Å and all C–C–C angles lie between 118·5 and 121·8°, with no evidence of any systematic variation around the ring. The phenyl rings are slightly displaced relative to the PC bonds, so that the PC bond does not exactly bisect the ring: the PCC angles in each case are about 117 and 123° and the P atoms lie 0·075 Å (average) away from the best planes through the rings. There are substantial residual uncertainties in the H atom positions and the measured C–H bond lengths vary from 0·92 to 1·09 Å. The average value of 1·01 Å represents the usual underestimate of the true CH bond distance.

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* *Note added in proof:* Recently, Troy, Galy & Legros (1980) have reported the structure of *trans*-$(Et_2N)(C_6H_{11})P(S)P(S)(Et_2N)(C_6H_{11})$ in which the P–P bond length of 2·254 (1) Å is close to that in the tetraphenyl compound.

Table 3. *Bond lengths* (Å) *and angles* (°) *in tetraphenyldiphosphine disulphide and related molecules*

Molecule	P–P	P–S	P–C	∠PPS	∠PPC	∠SPC	∠CPC	Reference
$Ph_2P(S)P(S)Ph_2$*	2·263 (4)	1·951 (3)	1·81 (1)	112·1	103·2	113·3	111·0	This work
$Me_2P(S)P(S)Me_2$	2·245 (6) 2·161 (4)	1·951 (3) 1·970 (4)	1·80 (1) 1·82 (1)	111·8	104·7	115·0	104·7	Lee & Goodacre (1971)
MePhP(S)P(S)MePh	2·21	1·98	1·88 (Ph) 1·82 (Me)	111·8				Wheatley (1960)
$Et_2P(S)P(S)Et_2$	2·22 (1)	1·94 (1)	1·83 (1)	112·8	102·2	115·4	107·3	Dutta & Woolfson (1961)
$(C_4H_8)P(S)P(S)(C_4H_8)$	2·21 (1)	1·95 (1)	1·82 (1)	111·1				Lee & Goodacre (1969)
$(C_5H_{10})P(S)P(S)(C_5H_{10})$	2·21 (1)	1·95 (1)	1·81 (1)	112·7				Lee & Goodacre (1970)

* Average values.

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Bortrichlorid–Pyridin

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(*Eingegangen am* 30. *Juli* 1980; *angenommen am* 12. *November* 1980)

Abstract. $C_5H_5N.BCl_3$, monoclinic, $a = 6·168$ (1), $b = 15·327$ (1), $c = 9·741$ (1) Å, $\beta = 115·22$ (3)°, $P2_1/c$, $Z = 4$, $D_x = 1·569$ (3), $D_o = 1·57$ (1) Mg m^{-3}. $C_5H_5N.BCl_3$ has been prepared from a solution of BCl_3 in cyclohexane by adding pyridine. Single crystals were obtained by sublimation at 333 K and $0·7 \times 10^2$ Pa. The crystal structure has been refined to $R = 0·019$ (1596 reflections). Its main structural features are a planar pyridine ring and a distorted tetrahedral coordination for boron ($d_{B-N} = 1·592$ Å).

Einleitung. Im Zusammenhang mit der Untersuchung von BX_3-Additionsverbindungen (X = F,Cl,Br,J) mit tertiären Aminen (Hess, 1969; Clippard, Hanson & Taylor, 1971; Geller & Hoard, 1951) sind die Pyridin-Addukte von Interesse, zumal für $C_5H_5N.BF_3$ über einen der kürzesten B—N-Bindungsabstände berichtet worden ist (Zvonkova, 1956). Unterstellt man einen Zusammenhang zwischen Bindungslänge und Bindungsstärke, so müsste auf Grund der Komplexstabilität sowie anderer thermodynamischer Daten

0567-7408/81/040969-03$01.00