O—O distance), there is a tendency for both the C(1) and C(5) carboxyl groups in these dicarboxylic acid zwitterions to become more nearly alike ($\Delta 3$ approaches zero). A fundamental question still remains: why in such similar compounds does the O—H···O hydrogen-bond distance vary so much?

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Triphenylphosphine Selenide*

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Abstract. $C_{18}H_{15}PSe$, monoclinic, $P2_1/c$, a = 18·471 (3), b = 9·667 (1), c = 18·120 (3) Å, β = 106·87 (1)°, $Z = 8$, ρ_c = 1·46 Mg m^{-3}. The dimensions of the two molecules in the asymmetric unit are the same within the error of the determination. The coordination geometry of the P atom is nearly tetrahedral with an average P=Se distance of 2·106 (1) Å and an average P—C distance of 1·826 (13) Å. The bond angles around the P atom range from 103·4 (4) to 113·8 (3)° with an average Se—P—C angle of 113·1 (8)° and average C—P—C angle of 106 (2)°.

Introduction. This study is a continuation of the investigation of an isostructural series of chalcogenide ligands of the type $(C_6H_5)_3M{=}Y$. The triphenylphosphine sulfide (TPPS) structure (M = P, Y = S) has been reported (Codding & Kerr, 1978) and the determinations of the arsine sulfide and stibine sulfide structures are in progress.

Crystals were obtained as colorless laths from acetone. Weissenberg photographs indicated that they were isostructural with TPPS and that the space group was $P2_1/c$ (systematic absences of the type $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$). A crystal of dimensions 0·20 × 0·16 × 0·27 mm was coated with epoxy resin to prevent the loss of elemental Se and used for intensity data collection on a Picker FACS-1 diffractometer with Ni-filtered Cu $K\alpha$ radiation (λ = 1·5418 Å). The data were collected in the θ–2θ scan mode at a scan rate of 1° min^{-1} with a scan width of $\Delta 2\theta$ = (1·6 + 0·285 tan θ)°. Background counts were measured for 20 s at either end of the scan. The data were measured to a maximum $\sin\theta/\lambda$ of 0·562 Å^{-1}; of the 4119 reflections measured, 2481 had intensities greater than $3\sigma(I)$ where $\sigma(I) = [T + k^2B + (0{\cdot}02I)^2]^{1/2}$ and T is the total peak count, B is the total background count, and k is the time factor to normalize B to the time interval of the scan.

Data were corrected for absorption [μ(Cu $K\alpha$) = 4·498 mm^{-1}] by analytical methods. The value of the correction ranged from 1·77–2·96. Since the structure is isomorphous with TPPS, the TPPS coordinates were used to start the refinement. The positions and thermal parameters of the heavy atoms were refined in large blocks (1 molecule/block). Positions of the H atoms

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* Crystal Structure Studies of Group V Chalcogenide Compounds. III.

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were calculated after isotropic refinement using a C—H distance of 1·0 Å; although these atoms were included in the model, they were not refined. The final R values are $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}0701$ for the 2481 observed reflections and 0·0956 for all reflections. The value of $w = [\sigma^2(F) + 0{\cdot}005F^2]^{-1}$ where $\sigma(F)$ was derived from counting statistics; the standard deviation of an observation of unit weight is 1·17. A final difference Fourier map showed no significant peaks. 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 Crystallography* (1974). Computer programs used include *CUDLS* (J. Stevens), *ORTEP* (Johnson, 1965), *ANABS* (L. Templeton and D. Templeton) and several programs from the Los Alamos Scientific Laboratory System of Programs (A. C. Larson).

Table 1. *Atomic coordinates* (×10⁴) *of the non-hydrogen atoms in triphenylphosphine selenide*

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

	x	y	z
P	9390 (1)	1620 (2)	8194 (1)
Se	8967·1 (6)	−84·6 (12)	8662·5 (7)
C(1)	10415 (4)	1659 (8)	8498 (5)
C(2)	10787 (5)	1527 (10)	9288 (5)
C(3)	11549 (5)	1526 (10)	9536 (5)
C(4)	11994 (5)	1654 (11)	9029 (6)
C(5)	11632 (5)	1764 (10)	8256 (6)
C(6)	10846 (5)	1791 (10)	7974 (5)
C(7)	9085 (4)	3300 (9)	8470 (4)
C(8)	9571 (5)	4341 (10)	8817 (5)
C(9)	9289 (5)	5554 (11)	9000 (6)
C(10)	8551 (6)	5767 (10)	8854 (5)
C(11)	8025 (5)	4740 (11)	8518 (6)
C(12)	8302 (4)	3477 (10)	8324 (5)
C(13)	9074 (4)	1663 (9)	7133 (5)
C(14)	9208 (5)	2819 (10)	6749 (5)
C(15)	8976 (6)	2855 (12)	5948 (6)
C(16)	8591 (6)	1684 (12)	5546 (6)
C(17)	8458 (5)	540 (11)	5932 (6)
C(18)	8712 (5)	554 (10)	6734 (5)
P′	5571 (1)	5770 (2)	6700 (1)
Se′	5960·9 (6)	7424·5 (12)	6161·3 (7)
C(1′)	4540 (4)	5706 (9)	6452 (5)
C(2′)	4130 (5)	5826 (11)	5669 (5)
C(3′)	3354 (5)	5865 (11)	5451 (5)
C(4′)	2962 (5)	5829 (10)	6020 (6)
C(5′)	3368 (5)	5742 (11)	6777 (6)
C(6′)	4156 (5)	5688 (10)	7009 (5)
C(7′)	5873 (5)	4100 (9)	6452 (4)
C(8′)	5390 (5)	3018 (10)	6142 (5)
C(9′)	5678 (6)	1809 (11)	5990 (6)
C(10′)	6436 (8)	1618 (12)	6152 (6)
C(11′)	6936 (6)	2619 (12)	6447 (6)
C(12′)	6666 (5)	3892 (10)	6608 (5)
C(13′)	5924 (4)	5804 (10)	7756 (5)
C(14′)	5840 (5)	4661 (9)	8174 (5)
C(15′)	6109 (6)	4717 (11)	8983 (6)
C(16′)	6458 (5)	5851 (12)	9346 (5)
C(17′)	6548 (5)	7004 (11)	8922 (6)
C(18′)	6271 (5)	6989 (9)	8114 (6)

Discussion. Molecular dimensions and conformations are very similar in the two molecules of the asymmetric unit. Average values for bond distances and bond angles are shown in Fig. 1 and a stereodrawing of the asymmetric unit is shown in Fig. 2. The molecules are significantly distorted from the trigonal propeller-like structures usually assumed to be the ground-state conformation of molecules of this type. In each molecule, the angle C(7)—P—C(13) is markedly smaller than the other two C—P—C angles. The variation appears to depend on the relative orientation of the phenyl rings. Similar trends are shown in other phenyl-substituted phosphine sulfides and selenides such as *p*-chlorophenyldiphenylphosphine sulfide (Dreissig & Plieth, 1971) and triphenylphosphine selenide–mercury(II) chloride (Dent Glasser, Ingram, King & McQuillan, 1969).

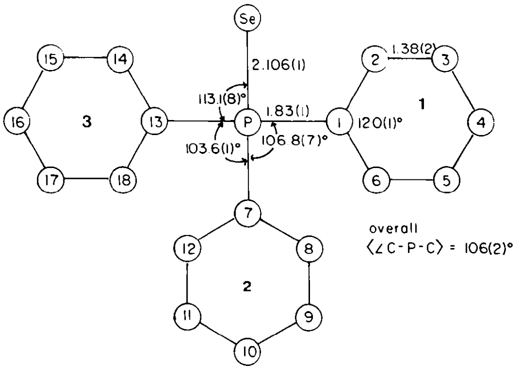

Fig. 1. The mean bond distances (Å) and bond angles for TPPSe averaged over two molecules in the asymmetric unit. In each molecule the angle C(7)—P—C(13) is significantly smaller than the other C—P—C angles and was averaged separately.

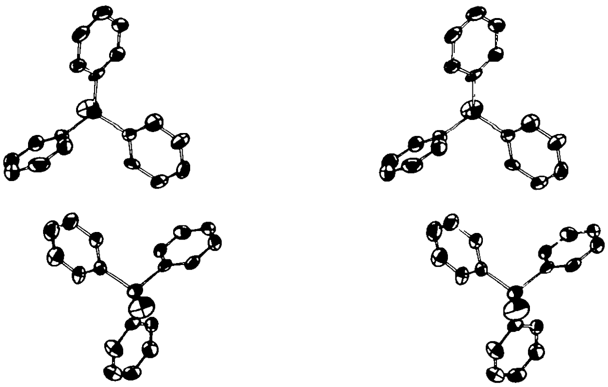

Fig. 2. Stereoscopic view of the asymmetric unit. The thermal ellipsoids correspond to 50% probability.

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* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34170 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Inter-plane angles*

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

Plane	σ(plane)	Atoms in plane	Angle to Se—P—C	Angle to hub*
Phenyl 1	0·006 Å	C(1), C(2), C(3), C(4), C(5), C(6)	50·8 (5)°	44·1 (9)°
Phenyl 2	0·008	C(7), C(8), C(9), C(10), C(11), C(12)	54·4 (5)	42·5 (9)
Phenyl 3	0·005	C(13), C(14), C(15), C(16), C(17), C(18)	9·8 (5)	79·6 (9)
Phenyl 1′	0·008	C(1′), C(2′), C(3′), C(4′), C(5′), C(6′)	50·9 (5)	41·7 (9)
Phenyl 2′	0·006	C(7′), C(8′), C(9′), C(10′), C(11′), C(12′)	56·4 (5)	41·6 (9)
Phenyl 3′	0·007	C(13′), C(14′), C(15′), C(16′), C(17′), C(18′)	12·5 (5)	78·4 (9)

* The hub is the plane formed by the three lead atoms: C(1), C(7) and C(13).

The average P=Se distance of 2·106 (1) Å falls within the range of values observed for similar compounds; for example, tri-*m*-tolylphosphine selenide 2·109 (5) Å (Cameron, Howlett & Miller, 1978) and others listed in Table 5 of Gałdecki, Główka, Michalski, Okruszek & Stec (1977). The average P—C distance is somewhat longer than that observed in TPPS although the average values of both the X—P—C and C—P—C angles [in TPPS 113·1 (6) and 105·7 (16)° respectively] are affected by the conformation and bulk of the R group rather than by the electronic effect of the atom bonded to P.

The conformation of TPPSe is the same as that observed in the sulfide structure. The conformational angles listed in Table 2 indicate that one phenyl ring lies almost parallel to the P=Se bond. This conformation seems to facilitate efficient packing of the molecules while producing some variation in the individual C—P—C bond angles as noted in Fig. 1.

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Methyl 6α-Ethoxyformamido-6β-phenoxyacetamidopenicillanate

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Abstract. $C_{20}H_{25}N_3O_7S$, $M_r = 451{\cdot}5$, tetragonal, $P4_1$, $a = b = 11{\cdot}943$ (1), $c = 16{\cdot}597$ (1) Å, $U = 2367{\cdot}3$ Å^3, $Z = 4$, $D_m = 1{\cdot}25$, $D_c = 1{\cdot}27$ Mg m^{-3}, $F(000) = 952$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo $K\alpha$) $= 0{\cdot}183$ mm^{-1}. The analysis confirms that the reaction of methyl 6α-phenoxyacetamidopenicillanate (I) with *N*-chloro-*N*-sodiourethane in acetonitrile at room temperature proceeds with retention of the stereochemistry at C(6), yielding as major product (80–90%) methyl 6α-ethoxyformamido-6β-phenoxyacetamidopenicillanate (II). The absolute stereochemistry of (II), although not determined from the present analysis, is inferred from the known absolute stereochemistry at C(3) of the starting material (I).

Introduction. Exposure of a small crystal to graphite-monochromated Mo radiation on a Hilger & Watts Y290 diffractometer yielded 1975 independent reflexions [$I \geq 2\sigma_I$, $\sigma_I = (I + B_1 + B_2)^{1/2}$] (measured by the θ,ω-scan technique in the range $2\theta = 0$–54°). The

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