was based on F with weights of the form $w^{-1} = [\sigma^2(F) + 0.00203(F^2)]$. Convergence to conventional R values of $R = 0.0442$ and $wR = 0.0574$ was obtained using 274 variables and 3919 unique reflections with $F^2 > 3\sigma(F^2)$. In the final cycle, the maximum shift/σ was 0.004 with maximum and minimum residual electron densities of $+1.57$ and -1.57 e Å^{-3} in the vicinity of the Hg atom. Goodness of fit indicator 1.052. Perspective views of the cation and anion are shown in Figs. 1 and 2, respectively. Atomic positional and equivalent isotropic thermal parameters are given in Table 1.* Bond lengths and angles are summarized in Table 2. Fig. 3 shows the packing.

Related literature. The structures of the [AuHg-$(C_{13}H_{12}PS)_2$]$^+$ cation and the [Au($C_4N_2S_2$)$_2$]$^-$ anion are similar to the corresponding ones in [AuHg-$(C_{13}H_{12}PS)_2$]PF$_6$ and [N(n-C_4H_9)$_4$][Au($C_4N_2S_2$)$_2$] reported previously.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53036 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
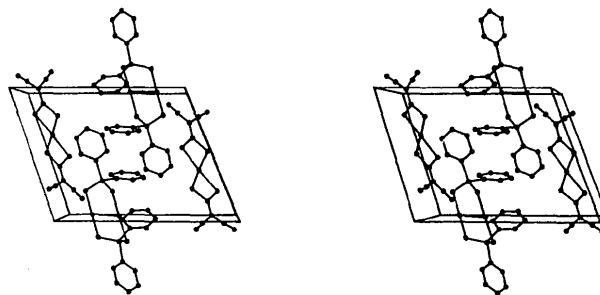

Fig. 3. A stereoview packing diagram of the unit-cell contents projected along the b axis.

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Tetraphenylarsonium Diisopropyldithiophosphinate

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Abstract. [As(C_6H_5)$_4$][PS$_2$(C_3H_7)$_2$], $M_r = 564.63$, triclinic, $P\bar{1}$, $a = 11.849$ (3), $b = 12.345$ (3), $c = 21.153$ (4) Å, $\alpha = 91.64$ (2), $\beta = 105.63$ (2), $\gamma = 102.78$ (2)°, $V = 2893.2$ Å^3, $Z = 4$, $D_x = 1.30$ g cm^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, $\mu = 13.8$ cm^{-1}, $F(000) = 1176$, $T = 294$ (1) K, $R_F = 0.034$ for 6201 observed unique reflections. There are two essentially identical molecules in the asymmetric unit. Both the cation and the anion have tetrahedral geometry. All P—S bond lengths are identical (1.989–1.995 Å) and significantly longer than observed for analogs with electron-withdrawing substituents at phosphorus.

Experimental. The title compound was obtained from NH$_4$[S$_2$P(C_3H_7)$_2$] and [As(C_6H_5)$_4$]Cl in ethanol, followed by evaporation, extraction with CH$_2$Cl$_2$, evaporation, and crystallization from 2-propanol/ ether as colorless rods. Colorless cuboid crystal, 0.26 × 0.19 × 0.17 mm, was mounted on a glass fiber. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, unit-cell constants from the setting angles of 25 reflections ($24 < 2\theta < 28°$). 10745 total reflections were collected, 10163 unique, 3962 unobserved, 6201 with $F_o^2 > 3.0\sigma(F_o^2)$, maximum $2\theta = 50.0°$, $0 < h < 14$, $-14 < k < 14$, $-25 < l < 25$, using θ–2θ scans. Corrections: Lorentz and polarization, linear decay (from 0.915–1.130 on I), reflection averaging (agreement on $I = 2.6\%$ for 815 reflections), empirical absorption (from 0.926 to 1.000 on I). Centrosymmetric space group judged correct based on successful refinement. Solution by Patterson and Fourier methods. Refinement by full-matrix least squares. H atoms refined as riding atoms (calculated with C—H = 0.95 Å and ideal

Table 1. *Positional parameters and their estimated standard deviations*

	x	y	z	B_{eq}* (Å²)
Anion I				
S1	0·27450 (8)	1·32729 (8)	0·82353 (5)	3·89 (2)
S2	0·48350 (8)	1·17132 (8)	0·84118 (5)	3·67 (2)
P1	0·36165 (8)	1·23856 (7)	0·78182 (4)	2·88 (2)
C1	0·2502 (3)	1·1246 (3)	0·7249 (2)	3·68 (9)
C2	0·1743 (4)	1·0523 (3)	0·7620 (2)	5·2 (1)
C3	0·1707 (4)	1·1630 (4)	0·6654 (2)	5·9 (1)
C4	0·4345 (3)	1·3274 (3)	0·7288 (2)	3·59 (9)
C5	0·5302 (4)	1·4273 (3)	0·7693 (2)	5·1 (1)
C6	0·4882 (3)	1·2639 (3)	0·6865 (2)	5·2 (1)
Anion II				
S3	0·72888 (9)	0·72883 (8)	0·62124 (5)	4·19 (2)
S4	0·8360 (1)	1·01001 (9)	0·65199 (5)	4·89 (3)
P2	0·69508 (8)	0·87934 (8)	0·62636 (5)	3·16 (2)
C7	0·5958 (3)	0·9013 (3)	0·5469 (2)	4·00 (9)
C8	0·4754 (4)	0·8157 (4)	0·5262 (2)	6·1 (1)
C9	0·6601 (4)	0·9042 (4)	0·4938 (2)	5·4 (1)
C10	0·6031 (3)	0·8794 (3)	0·6835 (2)	4·5 (1)
C11	0·5589 (4)	0·9862 (3)	0·6855 (2)	6·7 (1)
C12	0·6700 (4)	0·8571 (4)	0·7523 (2)	6·9 (1)
Cation I				
As1	0·15492 (3)	0·60723 (3)	0·64850 (2)	2·764 (7)
C13	0·1104 (3)	0·7137 (3)	0·5895 (2)	2·80 (8)
C14	0·1482 (3)	0·7216 (3)	0·5333 (2)	3·64 (9)
C15	0·1146 (4)	0·7987 (3)	0·4904 (2)	4·5 (1)
C16	0·0434 (3)	0·8651 (3)	0·5036 (2)	4·5 (1)
C17	0·0058 (3)	0·8574 (3)	0·5595 (2)	4·00 (9)
C18	0·0389 (3)	0·7815 (3)	0·6028 (2)	3·39 (8)
C19	0·2464 (3)	0·5272 (3)	0·6119 (2)	2·84 (8)
C20	0·3690 (3)	0·5697 (3)	0·6250 (2)	3·52 (9)
C21	0·4327 (3)	0·5198 (3)	0·5930 (2)	4·4 (1)
C22	0·3748 (3)	0·4297 (3)	0·5478 (2)	4·42 (9)
C23	0·2535 (3)	0·3860 (3)	0·5357 (2)	4·3 (1)
C24	0·1882 (3)	0·4350 (3)	0·5675 (2)	3·52 (9)
C25	0·0137 (3)	0·5035 (3)	0·6557 (2)	3·10 (8)
C26	−0·0991 (3)	0·5155 (3)	0·6240 (2)	4·6 (1)
C27	−0·1982 (4)	0·4359 (4)	0·6272 (2)	6·2 (1)
C28	−0·1855 (4)	0·3445 (4)	0·6602 (2)	6·3 (1)
C29	−0·0730 (4)	0·3331 (4)	0·6911 (2)	6·7 (1)
C30	0·0266 (4)	0·4119 (3)	0·6898 (2)	5·1 (1)
C31	0·2566 (3)	0·6816 (3)	0·7313 (2)	3·13 (8)
C32	0·2914 (3)	0·7965 (3)	0·7414 (2)	4·05 (9)
C33	0·3684 (4)	0·8459 (3)	0·8014 (2)	5·0 (1)
C34	0·4117 (4)	0·7817 (4)	0·8494 (2)	5·4 (1)
C35	0·3774 (4)	0·6688 (4)	0·8385 (2)	5·4 (1)
C36	0·3000 (3)	0·6169 (3)	0·7800 (2)	4·5 (1)
Cation II				
As2	0·13755 (3)	0·27157 (3)	0·00786 (2)	2·380 (9)
C37	0·2356 (3)	0·4149 (3)	0·0040 (2)	3·60 (9)
C38	0·3496 (4)	0·4480 (4)	0·0457 (2)	5·1 (1)
C39	0·4170 (4)	0·5554 (4)	0·0473 (2)	6·0 (1)
C40	0·3691 (4)	0·6270 (4)	0·0072 (2)	6·4 (1)
C41	0·2569 (4)	0·5946 (4)	−0·0355 (2)	6·2 (1)
C42	0·1879 (4)	0·4867 (3)	−0·0376 (2)	4·9 (1)
C43	−0·0001 (3)	0·2390 (3)	−0·0673 (2)	3·59 (9)
C44	−0·0922 (3)	0·2905 (3)	−0·0680 (2)	4·6 (1)
C45	−0·1914 (4)	0·2732 (4)	−0·1216 (2)	5·6 (1)
C46	−0·1965 (4)	0·2046 (4)	−0·1745 (2)	5·8 (1)
C47	−0·1052 (4)	0·1519 (4)	−0·1752 (2)	5·6 (1)
C48	−0·0054 (3)	0·1694 (3)	−0·1204 (2)	4·2 (1)
C49	0·0812 (3)	0·2744 (3)	0·0843 (2)	4·4 (1)
C50	−0·0152 (4)	0·1929 (4)	0·0880 (2)	6·4 (1)
C51	−0·0538 (5)	0·1920 (5)	0·1441 (2)	9·0 (2)
C52	0·0066 (5)	0·2673 (6)	0·1953 (3)	10·9 (2)
C53	0·1008 (5)	0·3492 (6)	0·1924 (3)	11·2 (2)
C54	0·1385 (4)	0·3550 (5)	0·1353 (2)	7·3 (1)
C55	0·2271 (3)	0·1597 (3)	0·0133 (2)	3·36 (8)
C56	0·2272 (3)	0·0886 (3)	0·0629 (2)	4·5 (1)
C57	0·2882 (4)	0·0047 (3)	0·0647 (2)	5·2 (1)
C58	0·3441 (4)	−0·0104 (4)	0·0176 (2)	5·2 (1)
C59	0·3442 (3)	0·0614 (3)	−0·0311 (2)	4·9 (1)
C60	0·2872 (3)	0·1477 (3)	−0·0330 (2)	3·99 (9)

* Anisotropic refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $8\pi^2/3 \times$ trace of the orthogonalized U tensor.

Table 2. *Selected bond distances (Å) and angles (°)*

Numbers in parentheses are estimated standard deviations in the least significant digits.

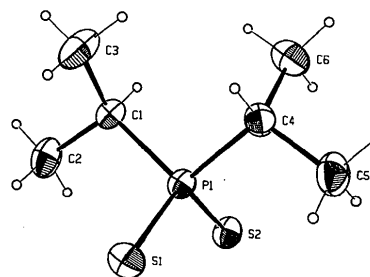|				
As1—C13	1·900 (3)		As2—C37	1·908 (3)
As1—C19	1·906 (4)		As2—C43	1·904 (3)
As1—C25	1·914 (3)		As2—C49	1·911 (4)
As1—C31	1·909 (3)		As2—C55	1·908 (4)
S1—P1	1·995 (2)		S3—P2	1·991 (1)
S2—P1	1·991 (1)		S4—P2	1·989 (1)
P1—C1	1·844 (3)		P2—C7	1·840 (4)
P1—C4	1·838 (4)		P2—C10	1·832 (5)
C1—C2	1·512 (6)		C7—C8	1·521 (5)
C1—C3	1·513 (5)		C7—C9	1·514 (6)
C4—C5	1·528 (4)		C10—C11	1·527 (6)
C4—C6	1·519 (6)		C10—C12	1·523 (5)
C13—As1—C19	107·4 (2)		C37—As2—C43	109·2 (1)
C13—As1—C25	110·1 (1)		C37—As2—C49	109·1 (2)
C13—As1—C31	110·0 (1)		C37—As2—C55	111·0 (2)
C19—As1—C25	108·3 (1)		C43—As2—C49	107·6 (2)
C19—As1—C31	107·6 (1)		C43—As2—C55	111·3 (2)
C25—As1—C31	113·2 (1)		C49—As2—C55	108·6 (2)
S1—P1—S2	117·66 (6)		S3—P2—S4	117·36 (7)
S1—P1—C1	108·9 (1)		S3—P2—C7	109·8 (1)
S1—P1—C4	108·2 (1)		S3—P2—C10	107·8 (1)
S2—P1—C1	107·5 (1)		S4—P2—C7	107·8 (1)
S2—P1—C4	108·9 (1)		S4—P2—C10	109·5 (1)
C1—P1—C4	104·9 (2)		C7—P2—C10	103·8 (2)
P1—C1—C2	109·8 (3)		P2—C7—C8	113·3 (3)
P1—C1—C3	114·3 (3)		P2—C7—C9	110·2 (3)
C2—C1—C3	110·6 (3)		C8—C7—C9	110·9 (3)
P1—C4—C5	111·3 (3)		P2—C10—C11	112·7 (3)
P1—C4—C6	113·0 (3)		P2—C10—C12	111·2 (3)
C5—C4—C6	110·4 (3)		C11—C10—C12	111·0 (4)

Fig. 1. The diisopropyldithiophosphinate anion (50% probability ellipsoids).

geometries). 613 variable parameters, $R_F = 0·034$, $wR = 0·041$, e.s.d. of an observation of unit weight = 1·21, largest shift = 0·01σ. Minimization function $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o^2)$, instrument instability factor 0·040, maximum $\Delta\rho = 0·27$ (6), minimum $\Delta\rho = -0·06$ (6) e Å^{-3}. *MOLEN* program package (Fair, 1989). Atomic parameters are given in Table 1, selected bond lengths and angles in Table 2.* The anion structure is shown in Fig. 1. Atomic scattering factors and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Related literature. We have been concerned with the chemistry of molecules containing the S_2PR_2 moiety and have reported the chemistry and structures of molecules where this group is bound to a metal ion (Pinkerton, Schwarzenbach & Spiliadis, 1987) and on the dimers formed when the anion is oxidized (Gallacher, 1989; Gallacher & Pinkerton, 1989). As we have indicated previously (Pinkerton & Terrill, 1988), there are few reported structures of the parent dithio acids or of the uncomplexed salts, which makes discussion of small variations in the geometry of metal compounds difficult.

The current structure contains two molecules in the asymmetric unit; however, they are essentially identical. The phosphorus atoms are tetrahedral with identical P—S bond distances as expected for a delocalized anion. The P—S bond lengths [1·989 (1)–1·995 (2) Å] are significantly longer than the analogous values for the few known structures: 1·96(1)Å (identical by symmetry) in $KS_2P(OMe)_2$ (Coppens, McGillavry, Hovenkamp & Douwes, 1962); 1·965 (6), 1·974 (6) Å in $[Me_2NH_2][S_2P(OC_3H_7)_2]$ (Kalinin, Andrianov & Struchkov, 1979); 1·945 (2), 1·969 (2) Å in $KS_2P(CH_2Ph)_2$ (Hazel & Collin, 1972); 1·944 (3), 1·954 (3) Å in $[Ph_4As][S_2P(OMe)_2]$ (Pinkerton & Terrill, 1988). This is easily attributed to the inductive effect of the substituents at phosphorus, alkyl *versus* alkoxy or aromatic. The latter two structures indicate a possible small asymmetry in the PS_2 moiety, but much less than that expected for P—S and P=S bonds, *e.g.* P—SH =

2·077 (1) and P=S = 1·954 (1) Å in $Ph_2P(S)SH$ (Krebs & Henkel, 1981); P—S = 2·076 (2)–2·158 (2), P=S = 1·900 (2)–1·940 (3) Å for a series of thiophosphoryl disulfides (Gallacher, 1989). The S—P—S valence angle is larger than ideal [117·66 (6), 117·36 (7)°] owing to S···S steric interactions in agreement with a range of 116·6 (3)–120·1 (1)° for the anions cited above. The disulfides have a wider range of S—P—S angles [103·8 (1)–115·96 (4)°]; however, these are additional steric considerations here because of the variety of torsion angles about the disulfide bond.

The geometry of the tetraphenylarsonium cations is unremarkable.

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Stereochemical Studies of Oligomers. XXVII.*
Reinvestigation of the Structure of 4,4′-Diaminodiphenyl Sulfone

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Abstract. $C_{12}H_{12}N_2O_2S$, $M_r = 248·30$, orthorhombic, $P2_12_12_1$, $a = 8·078$ (2), $b = 25·589$ (3), $c = 5·772$ (1) Å, $V = 1193·1$ Å^3, $Z = 4$, $D_x = 1·38$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1·5418$ Å, $\mu = 23·01$ cm^{-1}, $F(000) = 520$, room temperature, $R = 0·046$ for 1252 reflections with $I \geq 2\sigma(I)$. The structure of the title compound, which plays an important role in the synthesis of epoxide resins, was redetermined in order to provide more precise geometrical information than available in Dickinson, Stewart & Ammon [*J. Chem. Soc. Chem. Commun.* (1970), pp. 920–921] ($R = 0·12$, with average e.s.d.'s in bond lengths and angles of 0·01 Å and 0·8°, respectively).

Experimental. Specimen approximately 0·2 × 0·8 × 0·9 mm, Siemens AED single-crystal diffractometer equipped with an IBM PS2/30 personal computer, unit cell from a least-squares fit to 28 reflections

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* Part XXVI: Bocelli & Cantoni (1989).