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The Crystal Structure of Bis(diethylthiophosphoryl) Diselenide

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The crystal structure of bis(diethylthiophosphoryl) diselenide has been determined, and refined by means of three-dimensional X-ray analyses. The crystals are orthorhombic with $a = 9.41$ Å, $b = 12.04$ Å, $c = 14.19$ Å, $Z = 4$; space group D_{2h}^{10}—*Pccn*. The molecules possess twofold symmetry axes parallel with the c axis midway between the two selenium atoms. Some bond lengths and angles are: Se—Se = 2.33 Å, Se—P = 2.28 Å, P=S = 1.93 Å, ∠Se′—Se—P = 106.2°, ∠Se—P—S = 104.1°, and the dihedral angle P′Se′Se/Se′SeP = 104.5°.

Bis(diethylthiophosphoryl) diselenide was first reported by Kuchen and Knop [1] who from IR spectra assumed that it was the isomeric disulphide, bis(diethylselenophosphoryl) disulphide. Infrared spectra in the low frequency region obtained by the author [2] and the fact that sulphur has a greater tendency to form π-bonds and is more difficult to oxidize than selenium, led the author to doubt the correctness of the disulphide structure.

CRYSTAL DATA

Unit cell and space group data were derived from Weissenberg and oscillation photographs; the axial lengths are probably accurate to within 0.5 %. The density was determined in aqueous salt solutions.

Bis(diethylthiophosphoryl) diselenide, $(Et)_2P(S)Se—Se(S)P(Et)_2$. The crystals are yellow plates {010}, or truncated pyramids along b with {010} the dominant form. They are orthorhombic bipyramidal with $a = 9.41$ Å, $b = 12.04$ Å, $c = 14.19$ Å. There are four formula units in the unit cell; density, calc. 1.65, found 1.64 g/cm^3. The space group, from systematic absences, is D_{2h}^{10}—*Pccn*. With eight general positions in the unit cell, the molecule probably possesses a twofold axis of symmetry.

EXPERIMENTAL

The diselenide was prepared by oxidation of sodium diethylthioselenophosphinate with potassium triiodide in aqueous solution as described by Kuchen and Knop.[1,3] By

Table 1. Observed and calculated *0kl*, *4kl*, and *h0l* structure factors for bis(diethylthiophosphoryl) diselenide. The absolute values are multiplied by a factor of five.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	2	0	< 94	- 11	0	5	12	247	243	4	6	4	428	- 423	4	1	11	248	- 227
0	4	0	1494	-1613	0	6	12	89	96	4	7	4	78	- 74	4	2	11	98	84
0	6	0	370	348	0	7	12	105	- 106	4	8	4	99	- 86	4	3	11	< 77	47
0	8	0	< 67	- 84	0	8	12	< 78	- 19	4	9	4	< 76	- 39	4	4	11	< 77	20
0	10	0	441	- 503	0	9	12	101	- 109	4	10	4	328	354	4	5	11	158	146
0	12	0	948	356	0	10	12	< 67	41	4	11	4	< 77	64	4	6	11	< 78	- 8
0	14	0	198	215	0	11	12	78	87	4	12	4	129	- 126	4	7	11	82	92
										4	13	4	86	- 102	4	8	11	< 76	- 7
0	0	2	642	- 763	0	0	14	175	- 141	4	14	4	104	- 138	4	9	11	< 71	24
0	1	2	890	-1011	0	1	14	99	92						4	10	11	< 63	- 37
0	2	2	462	- 433	0	2	14	155	143	4	1	5	60	- 49	4	11	11	49	- 51
0	3	2	243	- 210	0	3	14	87	62	4	2	5	61	56					
0	4	2	198	121	0	4	14	124	105	4	3	5	< 54	10	4	0	12	152	- 150
0	5	2	1078	1069	0	5	14	133	- 136	4	4	5	< 58	- 3	4	1	12	215	- 226
0	6	2	565	477	0	6	14	255	- 265	4	5	5	63	31	4	2	12	119	95
0	7	2	158	- 141	0	7	14	100	- 89	4	6	5	208	173	4	3	12	< 76	- 69
0	8	2	276	261	0	8	14	< 67	- 12	4	7	5	< 72	30	4	4	12	142	135
0	9	2	618	- 365	0	9	14	< 56	64	4	8	5	262	227	4	5	12	191	202
0	10	2	111	- 98						4	9	5	< 77	- 19	4	6	12	172	- 174
0	11	2	247	240	0	0	16	< 75	32	4	10	5	< 76	- 77	4	7	12	106	- 111
0	12	2	97	- 101	0	1	16	74	84	4	11	5	< 76	- 35	4	8	12	71	- 70
0	13	2	171	- 166	0	2	16	< 74	0	4	12	5	233	- 257	4	9	12	79	- 81
0	14	2	< 70	- 19	0	3	16	< 73	- 14	4	13	5	< 62	21	4	10	12	99	112
0	15	2	188	- 251	0	4	16	101	- 34										
					0	5	16	< 66	- 95	4	0	6	447	- 446	4	1	13	153	132
0	0	4	854	- 982	0	6	16	< 58	14	4	1	6	466	459	4	2	13	< 79	41
0	1	4	319	- 303	0	7	16	113	133	4	2	6	151	136	4	3	13	< 78	- 26
0	2	4	576	558						4	3	6	155	132	4	4	13	< 78	- 54
0	3	4	210	- 155	0	0	18	76	102	4	4	6	262	245	4	5	13	104	- 103
0	4	4	717	694	0	1	18	< 44	27	4	5	6	547	- 528	4	6	13	< 73	- 62
0	5	4	< 54	36						4	6	6	286	- 263	4	7	13	< 71	- 53
0	6	4	863	- 873						4	7	6	108	86	4	8	13	< 64	7
0	7	4	434	- 384	4	2	0	383	- 389	4	8	6	< 76	48	4	9	13	< 51	16
0	8	4	238	- 190	4	4	0	489	- 477	4	9	6	230	225					
0	9	4	173	- 149	4	6	0	736	670	4	10	6	190	184	4	0	14	222	- 211
0	10	4	492	512	4	8	0	208	203	4	11	6	165	- 172	4	1	14	77	69
0	11	4	353	357	4	10	0	384	- 391	4	12	6	115	- 127	4	2	14	< 76	47
0	12	4	165	- 138	4	12	0	112	105	4	13	6	< 57	40	4	3	14	< 76	32
0	13	4	227	247	4	14	0	95	115						4	4	14	153	139
0	14	4	149	- 165						4	1	7	154	- 142	4	5	14	< 71	- 64
0	15	4	< 41	10	4	1	1	436	- 561	4	2	7	94	108	4	6	14	77	- 105
					4	2	1	76	- 48	4	3	7	76	- 56	4	7	14	< 61	34
0	0	6	173	- 187	4	3	1	< 40	- 6	4	4	7	< 67	- 15	4	8	14	< 48	- 15
0	1	6	498	490	4	4	1	< 47	13	4	5	7	136	127					
0	2	6	101	129	4	5	1	450	382	4	6	7	182	- 164	4	1	15	< 72	- 18
0	3	6	< 54	62	4	6	1	163	132	4	7	7	166	144	4	2	15	86	- 60
0	4	6	229	214	4	7	1	313	271	4	8	7	189	- 155	4	3	15	< 70	- 24
0	5	6	423	- 396	4	8	1	< 72	46	4	9	7	< 76	1	4	4	15	< 67	20
0	6	6	250	- 235	4	9	1	< 76	31	4	10	7	< 77	25	4	5	15	< 63	40
0	7	6	596	561	4	10	1	77	- 69	4	11	7	< 73	- 44	4	6	15	54	59
0	8	6	119	- 132	4	11	1	102	- 79	4	12	7	177	182					
0	9	6	367	359	4	12	1	< 76	- 59	4	13	7	< 49	- 15	4	0	16	< 65	23
0	10	6	86	112	4	13	1	< 70	- 75						4	1	16	112	109
0	11	6	495	- 526	4	14	1	< 56	- 35	4	0	8	633	648	4	2	16	< 62	- 11
0	12	6	< 77	- 16						4	1	8	229	237	4	3	16	< 58	28
0	13	6	228	- 273	4	0	2	330	359	4	2	8	105	- 94	4	4	16	< 52	- 25
0	14	6	57	1	4	1	2	527	- 627	4	3	8	< 68	28	4	5	16	91	- 118
					4	2	2	< 36	13	4	4	8	400	- 411					
0	0	8	< 59	64	4	3	2	148	- 145	4	5	8	230	- 227	4	1	17	< 43	- 20
0	1	8	334	339	4	4	2	216	- 127	4	6	8	230	235					
0	2	8	349	- 322	4	5	2	646	599	4	7	8	214	189					
0	3	8	150	128	4	6	2	< 61	39	4	8	8	< 76	47	2	0	0	301	- 297
0	4	8	216	- 188	4	7	2	376	- 354	4	9	8	107	111	4	0	0	542	519
0	5	8	388	- 361	4	8	2	116	- 111	4	10	8	219	- 239	6	0	0	1203	-1175
0	6	8	539	541	4	9	2	321	- 308	4	11	8	174	- 174	8	0	0	290	271
0	7	8	< 76	- 34	4	10	2	94	- 98	4	12	8	82	87	10	0	0	221	- 248
0	8	8	207	204	4	11	2	383	403						12	0	0	219	282
0	9	8	< 79	27	4	12	2	110	93	4	1	9	255	234					
0	10	8	282	- 283	4	13	2	< 69	58	4	2	9	205	- 180	1	0	2	1080	-1214
0	11	8	< 78	- 68	4	14	2	< 54	44	4	3	9	< 72	12	2	0	2	714	- 686
0	12	8	< 72	2						4	4	9	< 74	30	3	0	2	884	816
0	13	8	159	184	4	1	3	306	297	4	5	9	201	- 173	5	0	2	1031	-1009
					4	2	3	69	- 28	4	6	9	127	106	6	0	2	459	344
0	0	10	689	684	4	3	3	46	49	4	7	9	185	- 163	7	0	2	555	494
0	1	10	324	- 312	4	4	3	< 52	- 16	4	8	9	< 79	33	8	0	2	337	296
0	2	10	98	60	4	5	3	268	- 215	4	9	9	< 77	- 17	9	0	2	273	- 270
0	3	10	161	- 163	4	6	3	290	- 215	4	10	9	< 74	25	10	0	2	113	- 79
0	4	10	373	- 352	4	7	3	246	- 219	4	11	9	78	68	11	0	2	272	283
0	5	10	304	274	4	8	3	179	- 155	4	12	9	< 51	- 46					
0	6	10	< 78	- 7	4	9	3	< 76	- 1						1	0	4	54	- 1
0	7	10	< 79	- 28	4	10	3	122	118	4	0	10	251	269	2	0	4	944	952
0	8	10	104	- 97	4	11	3	77	92	4	1	10	220	- 213	3	0	4	865	773
0	9	10	128	- 102	4	12	3	176	185	4	2	10	176	- 170	5	0	4	< 76	- 1
0	10	10	100	- 124	4	13	3	< 68	16	4	3	10	80	- 74	6	0	4	446	427
0	11	10	144	145	4	14	3	86	99	4	4	10	200	- 213	7	0	4	146	136
0	12	10	142	156						4	5	10	241	241	8	0	4	506	- 492
					4	0	4	715	- 835	4	6	10	264	294	9	0	4	267	- 240
0	0	12	399	- 386	4	1	4	88	- 89	4	7	10	79	- 58	10	0	4	226	222
0	1	12	167	- 152	4	2	4	202	191	4	8	10	< 77	67	11	0	4	< 79	- 41
0	2	12	94	- 92	4	3	4	117	83	4	9	10	136	- 155					
0	3	12	< 79	36	4	4	4	565	548	4	10	10	138	- 148	1	0	6	574	534
0	4	12	252	233	4	5	4	266	206	4	11	10	83	91	2	0	6	484	462

H	K	L	FO	FC
3	0	6	1078	-1145
5	0	6	257	212
6	0	6	< 91	49
7	0	6	347	- 332
8	0	6	240	- 226
9	0	6	448	447
10	0	6	154	154
11	0	6	< 68	- 51
1	0	8	597	622
2	0	8	648	- 679
3	0	8	141	54
5	0	8	513	490
6	0	8	96	- 95
7	0	8	293	- 262
8	0	8	305	318
9	0	8	< 93	24
10	0	8	162	- 165
1	0	10	491	- 459
2	0	10	122	- 123
3	0	10	178	147
5	0	10	294	- 294
6	0	10	380	- 403
7	0	10	231	216
8	0	10	< 94	56
9	0	10	91	- 95
10	0	10	72	- 103
1	0	12	350	- 357
2	0	12	< 97	82
3	0	12	165	166
5	0	12	236	- 246
6	0	12	252	234
7	0	12	175	178
8	0	12	< 80	- 7
9	0	12	67	- 94
1	0	14	191	183
2	0	14	209	250
3	0	14	< 99	59
5	0	14	165	167
6	0	14	88	91
7	0	14	78	- 89
1	0	16	91	80
2	0	16	< 89	- 68
3	0	16	223	- 271
5	0	16	< 66	51
1	0	18	< 53	25

recrystallization from ligroin, yellow plates were obtained. By very slow evaporation from more dilute ligroin solutions, truncated prisms were obtained.

For the structure determination, the intensities of the $0kl$, $h0l$, and $4kl$ reflections were estimated visually from zero-layer and equi-inclination Weissenberg photographs. Cu$K\alpha$ radiation with $\lambda = 1.5418$ Å was used, and 292 out of 397 reflections within the range $\sin\theta \leq 0.985$ were observed and measured. The least squares refinements were carried out on an IBM 1620 computer. Mair's program [4] with weighting scheme No. 3 was used.

STRUCTURE ANALYSIS

Patterson projections along the *a* and *b* axes gave the position of the selenium atom, and indicated the positions of the phosphorus and sulphur atoms in the asymmetric unit. Subsequent Fourier refinements gave the positions of all atoms.

All reflections were then brought to a common scale by comparison between reflections common to two and two layers. The structure was then further refined by means of least squares syntheses. The unobserved reflections were removed from the least squares data, and likewise, the $h0l$ reflections also occurring among the $0kl$ and $4kl$ data, as those had the lowest observed intensities. Anisotropic temperature factors were applied to selenium, sulphur, and phosphorus.

One of the carbon atoms at an early stage had an abnormally high temperature factor, but after the atom had been moved to a new position based on rotation of the P—C bond, in accordance with the last Fourier maps, the structure rapidly improved. After eight least squares cycles, the structure factors from the three layers were rescaled in relation to each other by comparison of the observed structure factors with the calculated ones. The reflections 0146, 104, 308, and 442, which had very low calculated structure factors, were removed from the data after the twelfth cycle. After the fifteenth and final least squares refinement, the reliability index $R = \sum||F_o| - |F_c||/\sum|F_o|$ had converged to 0.082 for the material used.

A final structure factor calculation based on the parameter output from the last refinement was then made for all reflections. The *R*-value for this material, with non-observed reflections included only when F_c exceeds the observable limit, is 0.087. The final observed and calculated structure factors are listed in Table 1. The calculated values are based on atomic scattering factors for selenium and phosphorus by Freeman and Watson,[5] for sulphur by Dawson,[6] and for oxygen and carbon by Hoerni and Ibers.[7] The atomic parameter output from the final least squares refinement is listed in Tables 2 and 3.

Table 2. Atomic coordinates for bis(diethylthiophosphoryl) diselenide, in fractions of cell edges. Origin at a centre of symmetry.

	x	y	z
Se	0.2538	0.1531	0.1123
S	0.0798	−0.0641	0.1993
P	0.0724	0.0960	0.2066
C_1	0.103	0.160	0.325
C_2	−0.011	0.127	0.394
C_3	−0.085	0.164	0.162
C_4	−0.135	0.119	0.063

Table 3. Final temperature parameters $\beta_{ij} \times 10^3$. The expression used is exp $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + kl\beta_{23} + hl\beta_{13} + hk\beta_{12})$.

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Se	7.92	4.01	5.41	−2.10	1.47	−1.14
S	10.84	2.29	6.97	1.97	−0.65	0.51
P	8.98	2.44	4.10	−0.26	−0.71	−2.27

For the carbon atoms a temperature factor exp$-B(\sin^2\theta/\lambda^2)$ was used, with $B = 3.74$, 5.35, 3.04, and 4.34 for C_1, C_2, C_3, and C_4, respectively.

THE BIS(DIETHYLTHIOPHOSPHORYL) DISELENIDE MOLECULE

The crystals are built up of discrete diselenide molecules. Each molecule possesses an exact twofold symmetry axis parallel with c, halfway between the two selenium atoms. A prime is used in the following to denote the equivalent of an atom produced by the operation of this axis.

The bond lengths and angles calculated from the coordinates in Table 2 are shown in Table 4 together with some other interatomic distances. The

Table 4. Bond lengths and angles in bis(diethylthiophosphoryl) diselenide.

Se−Se	2.334 ± 0.012 Å	∠Se′−Se−P	106.2 ± 0.5°
Se−P	2.275 ± 0.011	∠Se−P−S	104.1 ± 0.5
P−S	1.932 ± 0.011	∠Se−P−C_1	106.9 ± 1.3
P−C_1	1.87 ± 0.04	∠Se−P−C_3	106.0 ± 1.1
P−C_3	1.80 ± 0.04	∠S−P−C_1	116.9 ± 1.3
C_1−C_2	1.51 ± 0.06	∠S−P−C_3	117.5 ± 1.3
C_3−C_4	1.59 ± 0.05	∠C_1−P−C_3	104.7 ± 1.7
		∠P−C_1−C_2	111.8 ± 2.9
		∠P−C_3−C_4	113.6 ± 2.5

Other interatomic distances.

Se−S	3.324 Å
P−C_2	2.80
P−C_4	2.84
C_1−C_3	2.91
C_1−C_1′	4.30

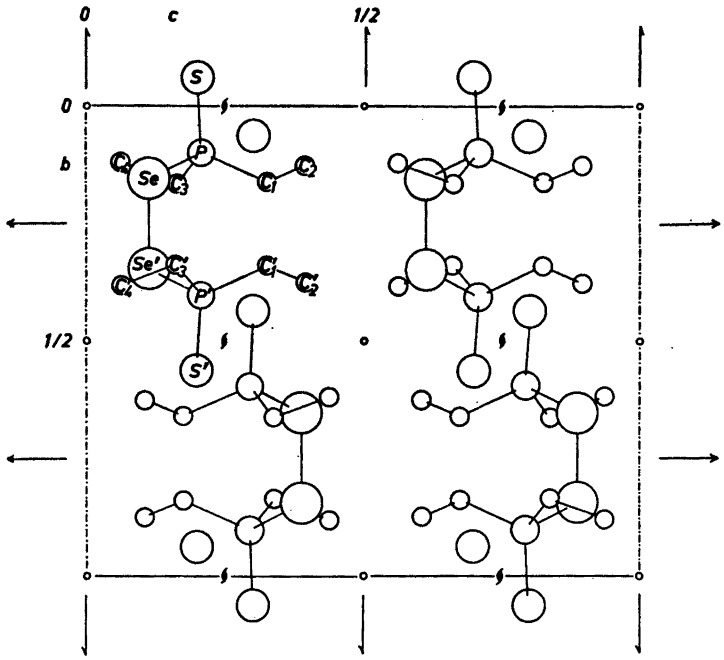

Fig. 1. The molecular arrangement of bis(diethylthiophosphoryl) diselenide seen along the *a*-axis.

uncertainties in cell edges add to the quoted standard deviations. The shape of the molecule with numbering of atoms is found in Fig. 1.

The Se—Se bond length is 2.33 Å as compared to 2.34 Å, twice the covalent radius of selenium according to Pauling.[8] The Se—P bond length is 2.28 Å which is close to the sum, 2.27 Å, of the covalent radii [8] for selenium and phosphorus. For the P=S double bond length, a value of 1.93 Å is found. This is not significantly different from the P=S bond lengths of 1.92 Å and 1.945 Å found in tellurium bis(dimethyldithiophosphate)[2] and methyl metadithiophosphonate,[9] respectively. The $P—C_1$ bond length is 1.87 Å while the $P—C_2$ bond length is 1.80 Å. The C—C bonds are also found to be different, the lengths being 1.51 Å and 1.59 Å. However, the large standard deviations for the P—C and C—C bond lengths show that the differences in the respective bond lengths are insignificant. Within the limit of error, the bonds are of the same length as the respective single bonds.

The $—C_1—P—C_3—C_4$ group is nearly planar, with C_4 being 0.06 Å away from the plane through the other three atoms. C_2 is 1.32 Å away from this plane and the interplanar angle $SePS/C_1PC_3$ is 88.1°. The angle Se'—Se—P is 106.2° and the dihedral angle PSeSe'/SeSe'P' is 104.5°. Both these angles are in good agreement with corresponding selenium valence angles and —Se—Se— dihedral angles cited in a review by Abrahams.[10]

There is no especially short intermolecular contacts. The closest Se—Se, S—S, S—P, and P—P approaches occur across a twofold screw axis and are 6.19, 5.16, 4.84, and 5.39 Å, respectively. The shortest Se—Se contact across a centre of symmetry is 6.72 Å. The packing of the molecules along the *a* axis is visualized in Fig. 1. The molecules are related through twofold screw axes, centres of symmetry and glide planes.

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