the boiling points of silicon tetramethyl and silicon tetrachloride.

3. Diethyl ether is a better solvent than dibutyl ether for the preparation of the dichloride. Although the greater yields of the trichloride were obtained with the ethyl ether, the pure trichloride could not be isolated from this solvent.

4. A satisfactory method for the complete analysis of small amounts of easily hydrolyzed volatile compounds containing carbon, hydrogen, silicon and chlorine has been devised.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Crystal Structure of Diphenylselenium Dibromide

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Introduction

The investigation of the crystal structure of diphenylselenium dibromide was undertaken for the purpose of studying the effect of the unshared electron pair on the bond orientations and interatomic distances. This subject has recently received attention in the investigations of the structures of the similar molecules, tellurium tetrachloride[1] by the electron diffraction method and the $IO_2F_2^-$ ion in potassium fluoroiodate[2] by means of X-rays. In both cases the evidence favored a trigonal bipyramidal structure with the unshared pair in one of the equatorial positions. This structure is also found in the present study, the bromine atoms forming opposed bonds with selenium, while the phenyl groups form bonds which are in a plane at right angles to the axis of the bromine atoms and making an angle of approximately 110° with each other.

Experimental

Diphenylselenium dibromide was prepared by mixing equimolar quantities of Eastman Kodak Co. diphenylselenium and purified bromine, both dissolved in carbon tetrachloride. The resulting precipitate was dissolved in carbon bisulfide and crystallized by slow evaporation of the solvent. The crystals varied from thin needles along the *b* axis of the unit to plates on (001). Goniometric measurements showed these crystals to be identical to those described by Groth[3] and by Gilta.[4] The crystals are described by both authors as being orthorhombic bipyramidal, the former giving axial ratios $a:b:c = 0.9023:1:0.3758$ and the latter $0.5543:1:0.8334$. These are consistent when the proper transformation is made.

Oscillation photographs were prepared about the three crystallographic axes using Cu-K_α radiation. The photographs about the *b* or needle axis were obtained from an approximately cylindrical crystal having 12 prism faces and a cross-sectional diameter of about 0.1 mm. These photographs were excellent for intensity estimations. The photographs about the *a* and *c* axes were poorer in the order named. This was due to the difficulty of cleaving the thin plates into small enough fragments so that absorption was not troublesome.

Measurements made on these photographs show the size of the unit cell to be $a_0 = 13.95 \pm 0.03$ Å., $b_0 = 5.78 \pm 0.03$ Å. and $c_0 = 15.40 \pm 0.03$ Å. The axial ratios of this cell, $a:b:c = 2.413:1:2.664$, are in excellent agreement with those given by Groth, which on interchange of *b* and *c* axes become $2.401:1:2.662$ and with those of Gilta which become $1:\frac{1}{2}(0.8334):2(0.5543)$ or $2.400:1:2.661$. All indices used in this paper are based on the X-ray unit shown above.

The photographs about all three axes show planes of symmetry as required by the orthorhombic system. The only regular absences found on indexing the photographs were $h0l$ with l odd, $0kl$ with k odd and $hk0$ with $(h + k)$ odd. The space group is accordingly uniquely determined as $D_{2h}^{14} - Pbcn$.

A rough density determination gave the value 2.09 g./cc. which corresponds to 3.98 molecules per unit cell. The calculated density for 4 molecules in the unit is 2.100 g./cc. The intensities used in this analysis were estimated visually with the aid of a calibrated comparison strip and were divided by the Lorentz and polarization factor to obtain values of $|F_{(hkl)}|^2$.

(1) D. P. Stevenson and Verner Schomaker, THIS JOURNAL, **62**, 1267 (1940).

(2) Lindsay Helmholz and M. T. Rogers, *ibid.*, **62**, 1537 (1940).

(3) P. Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, Vol. V, page 40.

(4) G. Gilta, *Bull. Soc. chim. Belg.*, **46**, 275 (1937).

With 4 molecules in the unit cell we must place 4Se, 8Br and 48C. The space group D_{2h}^{14} offers three possibilities for the 4Se. The 8Br are probably in one set of general positions (8 points to a set) and the 48C in six such sets. This would give 21 or 22 parameters to be evaluated. If the phenyl groups are assumed to have their usual structure, this number is reduced to 7 or 8, depending on the positions taken by selenium.

In order to locate the heavier selenium and bromine atoms, Patterson projections were made upon (010) and (100). The summations were carried out only along the lines shown in Figs. 1 and 2 which include all peaks due to interaction of the heavier atoms. The Patterson function for

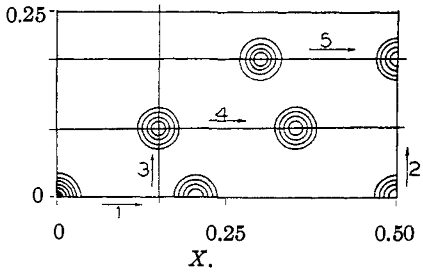


Fig. 1.—Patterson projection on (010).

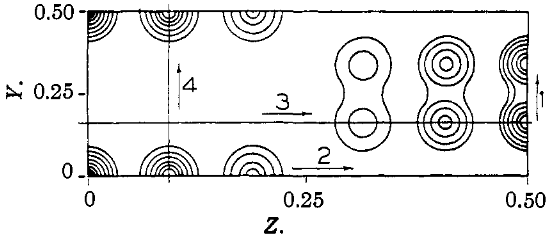


Fig. 2.—Patterson projection on (100).

the projection on (010) consists of the double summation: $P(X, Z) = \Sigma h \Sigma l \, |F_{(h0l)}|^2 \cos 2\pi(hX + lZ)$. Examination of the plots shows that they are consistent with 4Se in the positions $\pm\ 0y\frac{1}{4};\ \frac{1}{2}, \frac{1}{2} + y, \frac{1}{4}$ and 8Br in the positions $\pm\ xyz;\ \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z;\ \frac{1}{2} + x, \frac{1}{2} - y, \bar{z};\ \bar{x}, y, \frac{1}{2} - z$, with parameters shown in Tables I and II.

The averages for the bromine parameters are $x = 0.149$, $y = 0.078$, $z = 0.157$, and for selenium $y = 0.080$. It is interesting that the y parameters are practically equal, indicating that the bond angle Br–Se–Br is 180°.

As a check on these important parameters and in order to locate the phenyl groups, Fourier projections on (010) and (100) were computed, the sign of $|F_{hkl}|$ being taken as that resulting from the contribution of selenium and bromine with

TABLE I

PARAMETERS FROM PATTERSON PROJECTION ON (010)

Summation number	x_{Br}	z_{Br}
1	0.150	
2		0.154
3		0.158
4a	.148	
4b	.148	
5	.150	

TABLE II

PARAMETERS FROM PATTERSON PROJECTION ON (100)

Summation number	y_{Se}	y_{Br}	z_{Br}
2a			0.156
2b			.158
3a			.159
3b			.157
1 and 4	0.080	0.080	
5 (at Z = 0.32)		0.075	

the average parameters obtained from the Patterson projections. The projection on (010) is given by the double summation: $\rho(x, z) = \Sigma h \Sigma l \, |F_{h0l}| \cos 2\pi(hx + lz)$. The results of these summations are shown in Figs. 3 and 4.

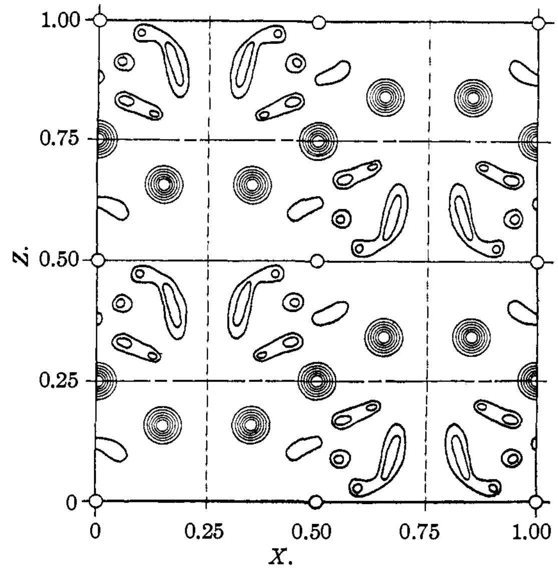


Fig. 3.—Fourier projection on (010).

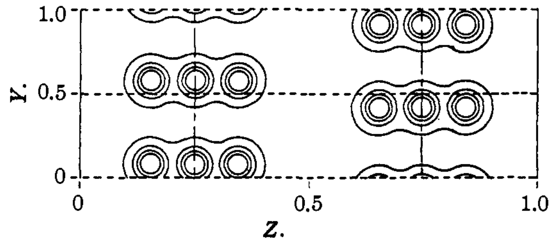


Fig. 4.—Fourier projection on (100).

The Fourier summations confirm in every detail the previous findings regarding the location of selenium and bromine. The x and z parameters indicated by the Fourier projections are identical to the average values from the Patterson projections. The y parameters from the Fourier projection on (100) are 0.080 for both selenium and bromine, only slightly different from the previous average value of 0.078. The locations of the phenyl groups are also rather clearly indicated in the projection on (010) but the projection on (100) is of little help in this regard.

In discussing the positions of the phenyl groups, it is convenient to do so in terms of three angles, φ, θ and ω, where φ is the C–Se–C bond angle, θ is the angle between the plane of the C–Se–C bonds and the Br–Se–Br axis and ω is the angle between the plane of a phenyl group and the plane of the C–Se–C bonds. The positions of the phenyl groups are controlled entirely by the above angles and the Se–C bond distance, giving four parameters in all.

From packing considerations alone we may eliminate values of φ in the region near 180° since this would bring the para carbon atoms within 2.4 Å. of the bromine atoms of neighboring molecules and the para hydrogen atoms would be still closer. Examination of the Fourier projection on (010) shows that θ is 90° or very close to this value. Furthermore, it seems likely from steric considerations that the angle ω must be well removed from 90°. If this were not the case, the ortho hydrogen atoms would be too close to the bromine atoms of the same molecule. Taking the Se–C bond distance as 1.94 Å., the Se–Br bond distance as 2.52 Å. as calculated from the parameters in this analysis, and giving the distances within the phenyl group their customary values, the calculated non-bonded H–Br separation is only 2.1 Å. The sum of the van der Waals radii[5] for hydrogen and bromine is 3.15 Å. It appears also that ω must be greater than 0° since if the phenyl groups were parallel to the b axis, the length of this edge of the unit could not be less than 7 Å. The value observed for b is 5.78 Å.

Although no set of values for φ, θ, ω and the Se–C distance could be found which would satisfy all of the smaller peaks on the Fourier projection on (010) exactly, the fit is fairly good when the Se–C distance is taken as 1.91 Å., φ as 110°, θ as 90° and ω as 60°. These chosen values are admitted to be somewhat arbitrary and the calculated intensities are in general not very sensitive to small changes in them. The projection on (010), the reasonable structure which results and the general improvement in the calculated intensities on adding the contribution due to the phenyl groups are strong points in favor of values close to those chosen.

Since we have been considering a projection in the above discussion, we must still decide in which direction along the b axis the phenyl groups will point. The projection on (100) is of no help here. The decision as to which of the two possibilities is correct was made by comparing calculated with observed intensities for each possibility, and by examination of the packing in each case with the aid of scale models. Carbon parameters corresponding to the above angles and distances are shown in Table III. More accuracy is indicated

TABLE III

PARAMETER VALUES FOR DIPHENYLSELENIUM DIBROMIDE

	x	y	z
Se	0	0.080	$^1/_4$
Br	0.149	.080	0.157
C_I	.062	.274	.332
C_{II}	.126	.461	.304
C_{III}	.172	.601	.368
C_{IV}	.155	.545	.454
C_V	.090	.354	.482
C_{VI}	.044	.219	.422

in the carbon parameters than is justified by the present work. This was done in order to retain the proper size and shape of the phenyl group. In no case does the contribution from the phenyl groups change the sign of any F_{hkl} value used in the summations. Accordingly no second approximation was necessary. F_{hkl} values were calculated making use of the tabulated parameter values and Pauling–Sherman atomic scattering factors. No temperature factor was introduced. The calculated values are compared with the observed values in Table IV. The general agreement is considered good enough to confirm the structure reported.

Discussion of the Structure

Projections of the structure of diphenylselenium dibromide on (010) and (100) are shown in Fig. 5. It is seen that the molecule has a two-fold axis as its only symmetry element. There are actually two different kinds of molecules present, one being

(5) Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 176.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED AMPLITUDES

(hkl)	F_{hkl} Calcd.	Obsd.
002	−102	63
004	− 34	45
006	77	74
008	34	33
0·0·10	−148	105
0·0·12	115	95
0·0·14	− 13	0
0·0·16	− 33	32
102	48	51
104	− 57	71
106	− 55	63
108	80	92
1·0·10	− 46	32
1·0·12	− 55	62
200	43	48
202	− 48	62
204	97	80
206	− 92	88
208	45	66
2·0·10	− 18	0
2·0·12	50	45
302	− 11	26
304	− 23	35
306	− 41	63
308	28	46
3·0·10	− 9	0
3·0·12	− 35	43
400	− 84	87
402	− 25	48
404	115	93
406	−160	109
408	61	71
4·0·10	23	36
4·0·12	2	0

(hkl)	F_{hkl} Calcd.	Obsd.
502	−114	96
504	78	90
506	48	64
508	−104	86
5·0·10	67	51
600	150	107
602	− 95	88
604	− 21	28
606	12	39
608	48	61
6·0·10	−126	100
702	12	36
704	− 32	49
706	− 2	0
708	25	39
7·0·10	− 2	0
800	75	84
802	− 78	75
804	43	64
806	− 23	36
808	37	60
902	87	80
904	− 71	59
906	− 32	39
908	87	50
10·0·0	− 63	68
10·0·2	− 12	26
10·0·4	118	100
10·0·6	−140	92
10·0·8	65	41
11·0·2	− 55	45
11·0·4	55	48
11·0·6	35	30

(hkl)	F_{hkl} Calcd.	Obsd.
12·0·0	72	62
12·0·2	− 43	49
110	108	83
112	−120	91
114	− 3	10
116	− 8	0
118	61	66
1·1·10	−120	108
1·1·12	110	100
310	− 57	38
312	− 11	0
314	152	123
316	−172	140
318	55	61
510	75	104
512	− 65	79
514	82	75
516	− 56	50
518	50	54
710	160	112
712	− 99	100
714	− 20	31
716	50	54
718	70	65
910	6	12
912	− 23	23
914	90	77
916	−102	85
111	−128	83
113	12	15
115	3	16
117	− 10	21
119	− 65	68

(hkl)	F_{hkl} Calcd.	Obsd.
311	− 6	11
313	18	42
315	−102	88
317	70	61
319	− 2	0
511	− 18	33
513	41	63
515	− 45	50
517	48	52
711	− 77	52
713	34	54
715	28	45
717	11	00
911	4	0
913	40	39
915	− 67	71
917	55	52
212	−184	106
214	98	94
216	19	20
218	−128	100
2·1·10	29	34
412	95	90
414	− 45	48
416	− 31	45
418	68	78
612	84	84
614	− 55	52
616	− 1	0
618	62	73
812	−116	100
814	77	76
816	34	50

(hkl)	F_{hkl} Calcd.	Obsd.
10·1·4	19	0
10·1·6	− 7	0
211	− 20	24
213	80	73
215	9	0
217	− 57	50
219	48	52
411	82	83
413	− 56	73
415	12	0
417	40	30
611	41	31
613	− 47	62
615	1	0
617	26	46
811	− 38	52
813	48	60
815	− 20	20
10·1·1	0	0
10·1·3	− 2	0
020	62	58
021	− 86	105
022	− 42	58
023	34	28
024	− 7	0
025	27	26
040	− 35	40
041	− 73	84
042	20	31
043	23	26
060	− 76	56
061	− 14	0

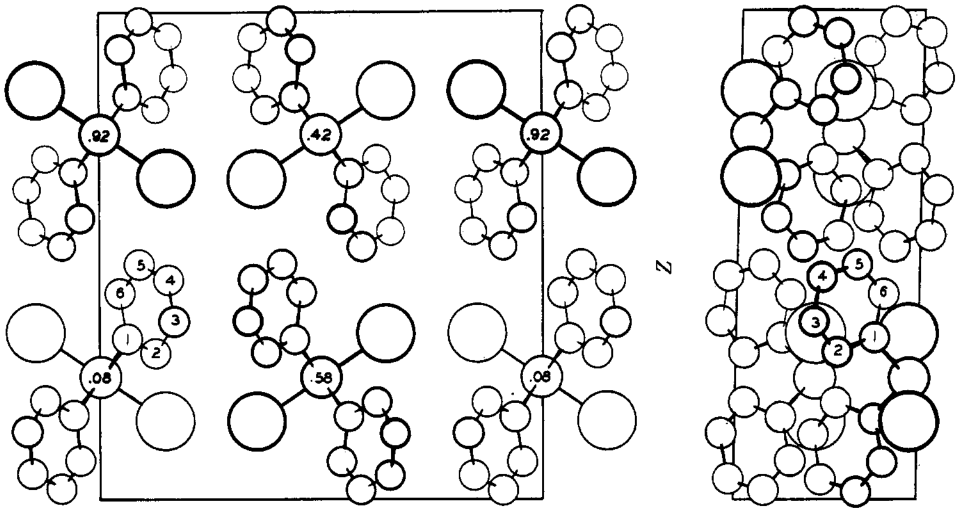
the mirror image of the other. In solution there would be little or no barrier involved in going from one form to the other since only rotation of the phenyl groups about the Se–C bond is needed, hence there would be no chance of resolving the mixture into two isomers. If the molecular structure in solution is the same as that in the crystal, we would expect a low electric dipole moment for the substance. This is interesting in view of the recent findings of Smyth, Grossman and Ginsburg[6] who found a rather large electric dipole moment of 3.47*D* for diphenylselenium dichloride in benzene solution. Work is now well under way in this Laboratory on the crystal structure of the dichloride and it is apparent already that the structures are quite different in spite of similar axial ratios (0.4986:1:0.8531) as given by Gilta[4] and an identical point group. The dichloride has an 8 molecule unit and the space group is $D_{2h}^{15} - Pbca$.

The only important bond distances determined in the present study of the dibromide are the Se–Br distance of 2.52 ± 0.01 Å. and the Se–C distance of 1.91 ± 0.03 Å. The sums of the single bond radii are 2.31 Å. for selenium and bromine and 1.94 Å. for selenium and carbon. The observed Se–Br separation is only 0.02 Å. less than that found in K_2SeBr_6,[7] another structure involving an unshared pair, hence the effect of the unshared pair in lengthening the bond seems to be about the same in the two cases.

The non-bonded separation of bromine atoms in neighboring molecules is 4.04 Å., just slightly

(6) C. P. Smyth, A. J. Grossman and S. R. Ginsburg, THIS JOURNAL, 62, 192 (1940).

(7) J. L. Hoard and B. N. Dickinson, *Z. Krist.*, 84, 436 (1933).



X. *Y.*

Fig. 5.—Projections of the structure of diphenylselenium dibromide on (010) and (100) of the unit cell. The circles, in order of decreasing size, indicate bromine, selenium and carbon atoms. The numbers on selenium indicate the fractional displacements from the plane (010) along the *b* axis.

greater than twice the van der Waals radius for bromine, 1.95 Å. Other packing distances are shown in Table V, the position of the hydrogen atoms being calculated on the assumption that they are in the plane of the phenyl group at a distance of 1.08 Å. from the carbon atom of the same number.

TABLE V

PACKING DISTANCES IN DIPHENYLSELENIUM DIBROMIDE

Closest distances only are given

Br–Br	4.04
Br–C_{II}	3.16
Br–C_{IV}	3.77
Br–C_{V}	3.76
Br–H_{II}	2.75
Br–H_{IV}	3.33
Br–H_{V}	3.05
C_{III}–C_{III}	3.61
C_{V}–C_{V}	3.10
C_{V}–C_{VI}	3.44

The authors wish to thank the National Youth Administration for providing the assistance of Miss Roxie Wittenberg, who carried out some of the calculations. We are also indebted to Professor Linus Pauling for reading and criticizing the manuscript.

Summary

An X-ray investigation of orthorhombic crystals of diphenylselenium dibromide shows a unit cell containing four molecules with a_0 = 13.95 Å., b_0 = 5.78 Å. and c_0 = 15.40 Å., all ± 0.03 Å. The space group was found to be D_{2h}^{14} – *Pbcn*. With the aid of Patterson and Fourier projections on (010) and (100), the complete structure was determined, the parameters being listed in Table III. Calculated amplitudes based on these parameters are compared satisfactorily with observed amplitudes in Table IV.

The diphenylselenium dibromide molecule was found to have a structure approximating very closely a trigonal bipyramid with selenium at the center, bromine atoms at the apices and the three equatorial positions occupied by the two phenyl groups and the unshared pair. The molecular symmetry is that of C_2 – 2, a possible mirror plane being eliminated by rotation of the phenyl groups about the axes of the Se–C bonds.

The observed bond angles and distances are: Br–Se–Br = 180° ± 3°, C–Se–C = 110° ± 10°, Se–Br = 2.52 Å. ± 0.01 Å. and Se–C = 1.91 Å. ± 0.03 Å.

LOS ANGELES, CALIFORNIA RECEIVED NOVEMBER 18, 1940