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The Crystal Structure of Diphenyl Diselenide

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The crystal structure of diphenyl diselenide has been determined by analysis of rotation and Weissenberg photographs about the b and c axes. The space group is D_2^4–$P2_12_12_1$; the unit cell dimensions are: $a = 24{\cdot}07$, $b = 8{\cdot}27$, $c = 5{\cdot}64$ Å. There are four molecules in the unit cell. Positional parameters for the selenium and carbon atoms were assigned from Fourier projections on (001) and (010); the selenium parameters were then refined by least-squares calculations. The observed Se–Se distance is $2{\cdot}29 \pm 0{\cdot}01$ Å, which is 0·05 Å shorter than twice the normal single-bond radius for selenium. The selenium–carbon distances are close to the predicted value of 1·94 Å.

Introduction

The crystal-structure investigation of diphenyl diselenide was undertaken as part of a program of studies on organoselenium compounds initiated by McCullough in 1940. Structures previously reported include those of diarylselenium dihalides (McCullough & Hamburger, 1941; McCullough & Hamburger, 1942; McCullough & Marsh, 1950*a*), triphenylselenonium chloride (McCullough & Marsh, 1950*b*), and 1,4-diselenane (Marsh & McCullough, 1951); in these compounds the selenium–carbon distances were found to vary from 1·94 to 2·01 Å. The current value for the normal single-bond radius of selenium—1·17 Å—was assigned from the selenium–selenium distance found in elementary hexagonal selenium (Pauling, 1948, p. 164) and recently confirmed in the crystal-structure investigation of α-monoclinic selenium (Burbank, 1951). The present study of diphenyl diselenide was undertaken in order to determine the selenium–selenium distance in an organic molecule, giving a check on the single-bond radius, as well as to obtain further information on selenium–carbon distances and selenium bond angles.

Experimental

A sample of diphenyl diselenide, which was prepared by Dr Tod Campbell, was recrystallized from ethylene chloride; the resulting yellow needles were elongated in the c direction. Rotation as well as zero- and first-layer Weissenberg photographs about the b and c axes were prepared, using unfiltered copper X-radiation. Measurements on these photographs indicated an orthorhombic unit cell with the following cell dimensions (using Cu $K\alpha = 1{\cdot}5418$ Å):

$$a = 24{\cdot}07 \pm 0{\cdot}05,\ \ b = 8{\cdot}27 \pm 0{\cdot}02,\ \ c = 5{\cdot}64 \pm 0{\cdot}02\ \text{Å}\,.$$

These values are in fair agreement with those reported by Egartner, Halla & Schacherl (1932):

$$a = 23{\cdot}70 \pm 0{\cdot}15,\ \ b = 8{\cdot}255 \pm 0{\cdot}005,\\ c = 5{\cdot}645 \pm 0{\cdot}005\ (\text{kX.})\,,$$

Absent reflections are $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd; the space group is thus D_2^4–$P2_12_12_1$, which has fourfold general positions. An assumption of four molecules of $C_{12}H_{10}Se_2$ per unit cell leads to a calculated density of 1·84 g.cm.$^{-3}$; the density observed by Egartner, Halla & Schacherl is 1·782 g.cm.$^{-3}$. Although this space group possesses no center of symmetry, projections of the structure on the three crystallographic faces are centro-symmetric. The general atomic coordinates (with the origin placed on the axis of symmetry of the (001) projection) are:

$$(x, y, z);\ (\bar{x}, \bar{y}, \tfrac{1}{2}+z);\ (\tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}-z);\ (\tfrac{1}{2}-x, \tfrac{1}{2}+y, \bar{z})\,.$$

The cell dimensions indicated that projections along the b and c axes might show good resolution of the molecules, and it was decided to undertake the structure investigation using only zero-layer Weissenberg data of the type $h0l$ and $hk0$. For these reflections, it is necessary only to determine the signs of the structure factors, the phase angles being either 0 or 180°. Intensity data were collected by visual comparison with a calibrated strip, averaging the readings obtained from four separate photographs for each zone. Of these four photographs, two were prepared from the same exposure, and a film factor of 3·7 was used to relate their intensities. No correction for absorption was considered necessary.

Determination of the structure

The intensities of all observed reflections were corrected for Lorentz and polarization effects, and the resultant F^2's were used to construct partial Patterson projections on (001) and (010). The resultant maxima, which correspond to Se–Se interactions, indicated

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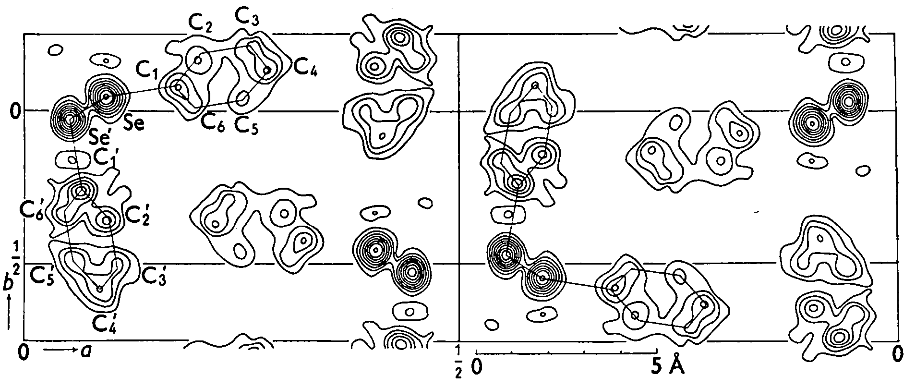

Fig. 1. Fourier projections of the structure on (001). Contours are drawn at intervals of approximately 2 e.Å^{-2} for the carbon atoms and 8 e.Å^{-2} for the selenium atoms, beginning with the 1-electron contour.

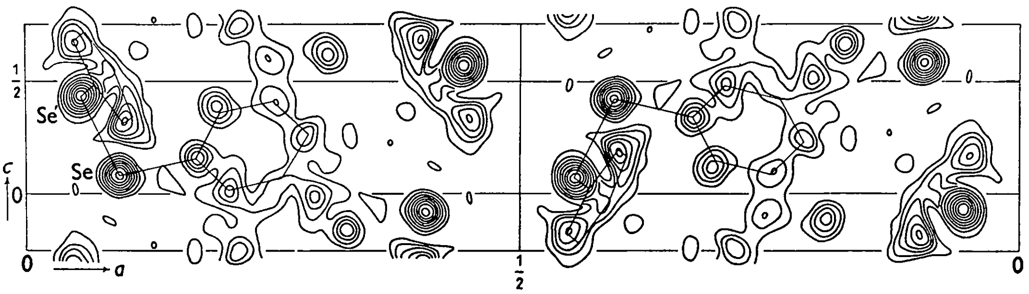

Fig. 2. Fourier projections of the structure on (010). Contours are drawn at intervals of approximately 2 e.Å^{-2} for the carbon atoms and 8 e.Å^{-2} for the selenium atoms, beginning with the 1-electron contour.

preliminary parameters for the selenium atoms. These parameters were used to assign signs to the F values for all observed reflections, and series of Fourier refinements, including the carbon contributions, were undertaken. The third and final projection on (001) is shown in Fig. 1, and the second and final projection on (010) in Fig. 2. Summations were calculated at intervals of $\frac{1}{100}a$ (0·24 Å), $\frac{1}{36}b$ (0·23 Å), and $\frac{1}{36}c$ (0·16 Å).

The centers of the peaks representing the selenium atoms were determined by fitting Gaussian curves to the nine electron-density points surrounding the peaks (Carpenter & Donohue, 1950); these parameters were refined by least-squares calculations using all observed $h0l$ and $hk0$ data. The F_o and F_c values were adjusted by empirical scale and temperature factors, and the observational equations were appropriately weighted according to the method of Hughes (1941). The results for the selenium atoms are summarized in Table 1.

The parameters for the carbon atoms were assigned with the assumptions that the benzene rings are regular, plane hexagons with edges of 1·39 Å, and that the axis of each benzene ring is colinear with the corresponding selenium–carbon bond. These hexagons were adjusted by least-squares fits to the indicated peaks on the Fourier projection on (001). (The (010) projection was not used because of the poor resolution of the carbon atoms.) Thus, for each hexagon there are four positional parameters which were assigned so as to give a best fit with the six x and y values observed for the maxima on the projection. One of the positional parameters was the Se–C bonded distance; values for this distance of 1·965 and 1·891 Å were obtained for the two benzene rings, and an average value of 1·93 Å was finally used for both rings. The assigned carbon parameters are in good agreement with the observed maxima on the two projections.

Table 1. *Parameters of selenium atoms*

Parameter		Fourier on (001)	L. S. ($hk0$)	Fourier on (010)	L. S. ($h0l$)	Final
Se	x	0·0964	0·0961	0·0959	0·0964	0·0962
	y	0·041	0·041	—	—	0·041
	z	—	—	0·075	0·075	0·075
Se′	x	0·0546	0·0545	0·0557*	0·0544	0·0545
	y	0·972	0·972	—	—	0·972
	z	—	—	0·428*	0·425	0·425

* Unreliable owing to proximity of benzene ring on this projection.

Table 2. *Atomic parameters in diphenyl diselenide*

	Se	C_1	C_2	C_3	C_4	C_5	C_6
x	0·0962	0·1730	0·2057	0·2610	0·2835	0·2508	0·1955
y	0·041	0·079	0·178	0·206	0·134	0·035	0·007
z	0·075	0·157	0·016	0·075	0·276	0·417	0·358
x'	0·0545	0·0683	0·0973	0·1072	0·0881	0·0591	0·0492
y'	0·972	0·745	0·655	0·492	0·418	0·507	0·671
z'	0·425	0·478	0·310	0·348	0·553	0·721	0·683

Table 3. *Calculated and observed F values for diphenyl diselenide*

h	F_c	F_o
	*h*00	
0	600	—
2	104	57
4	−36	50
6	−244	182
8	−124	116
10	13	15
12	10	12
14	−47	59
16	−11	< 8
18	58	69
20	109	109
22	42	43
24	−26	24
26	−76	63
28	−35	32
30	4	< 5
	*h*10	
1	159	89
2	8	9
3	−2	9
4	50	50
5	−50	53
6	51	52
7	−91	81
8	19	24
9	−54	61
10	10	22
11	24	32
12	−55	57
13	−29	36
14	−26	30
15	−21	23
16	−17	26
17	12	23
18	20	19
19	68	76
20	11	13
21	70	69
22	8	< 9
23	8	< 9
24	−3	< 9
25	−43	40
26	−1	< 8
27	−52	45
28	5	< 7
29	−13	14
30	1	< 5
	*h*20	
0	231	140
1	−91	81
2	105	94
3	9	18
4	−69	76
5	2	8
6	−114	110
7	55	52
8	−71	70
9	36	42
10	5	< 6
11	−35	40
12	5	7
13	−59	66
14	−47	47
15	−26	27
16	−4	< 8
17	24	26
18	46	55
19	28	32
20	84	84
21	4	9
22	38	41
23	−6	< 9
24	−21	22
25	−10	< 8
26	−60	47
27	17	10
28	−32	29
29	6	< 6
30	−2	6
	*h*30	
1	143	113
2	−65	66
3	20	22
4	−12	13
5	−61	68
6	69	68
7	−98	90
8	79	88
9	−31	30
10	25	29
11	−5	< 7
12	−73	68
13	−12	12
14	−83	73
15	−27	26
16	−7	16
17	15	20
18	24	20
19	53	55
20	34	27
21	64	56
22	1	< 9
23	11	< 9
24	−4	< 8
25	−34	35
26	4	8
27	−39	36
28	17	14
29	−17	14
	*h*40	
0	128	118
1	−8	7
2	66	74
3	−8	< 6
4	−14	20
5	65	63
6	−78	69
7	83	76
8	−52	53
9	39	43
10	−30	32
11	−36	38
12	−6	11
13	−103	91
14	−16	16
15	−43	43
16	28	32
17	10	9
18	30	33
19	33	30
20	51	45
21	18	20
22	7	< 9
23	−2	< 8
24	−24	22
25	2	< 8
26	−25	23
27	19	16
28	−23	16
	*h*50	
1	48	46
2	−45	46
3	11	17
4	9	16
5	−11	16
6	81	71
7	−46	47
8	90	74
9	−19	19
10	−2	< 8
11	−8	8
12	−94	77
13	−11	9
14	−89	77
15	15	17
16	−6	11
17	−5	< 9
18	48	37
19	26	27
20	36	32
21	20	18
22	4	8
23	6	< 8
24	−17	11
25	−11	13
26	7	6
27	−17	14
	*h*60	
0	50	54
1	−27	25
2	20	26
3	−3	< 8
4	12	13
5	34	36
6	−20	23
7	87	75
8	−27	24
9	35	30
10	−19	19
11	−32	31
12	−34	30
13	−90	71
14	−1	< 9
15	−38	36
16	16	14
17	3	< 9
18	22	23
19	42	33
20	31	27
21	11	15
22	0	< 7
23	2	< 6
24	−9	11
25	0	< 4
	*h*70	
1	−4	< 9
2	−15	14

Table 3 (*cont.*)

h	F_c	F_o
3	14	17
4	23	25
5	14	9
6	59	62
7	−5	10
8	67	64
9	−22	21
10	−4	< 9
11	−24	19
12	−63	57
13	1	< 9
14	−59	51
15	19	23
16	−25	30
17	9	11
18	25	17
19	−8	< 7
20	16	18
21	5	< 6
22	9	9
23	−6	8
	*h*80	
0	−10	< 9
1	−13	15
2	2	< 9
3	−4	< 9
4	13	9
5	26	35
6	11	< 9
7	57	62
8	−12	10
9	30	30
10	−19	16
11	−33	37
12	−17	16
13	−54	50
14	15	15
15	−36	37
16	20	21
17	7	< 6
18	8	13
19	32	29
20	−8	< 4
	*h*90	
1	−20	23
2	10	25
3	7	< 8
4	18	26
5	27	20
6	41	47
7	13	11
8	26	31
9	−16	14
10	−10	16
11	−15	16
12	−37	39
13	−4	< 9
14	−33	33
15	14	13
16	−8	10
	h,10,0	
0	−23	22
1	0	< 6
2	−14	10
3	13	12
4	14	10
5	16	20
6	22	18
7	31	33
8	0	< 9
9	8	9
10	−12	8
	*h*01	
1	5	9
2	−106	85
3	58	49
4	51	52
5	−119	102
6	26	28
7	117	92
8	−35	38
9	−49	46
10	37	40
11	−83	82
12	44	40
13	132	116
14	−2	< 11
15	−83	90
16	−29	31
17	−23	28
18	31	33
19	50	58
20	−1	< 9
21	−35	41
22	−35	40
23	4	13
24	26	31
25	−3	< 8
26	−2	< 8
27	17	21
28	−18	19
29	−12	< 6
30	11	15
	*h*02	
0	111	89
1	12	< 5
2	−47	42
3	−48	42
4	−19	18
5	52	51
6	87	75
7	21	24
8	−31	39
9	−84	69
10	0	< 6
11	102	79
12	17	20
13	−21	23
14	13	8
15	−69	66
16	−3	< 8
17	72	70
18	−8	10
19	−18	25
20	45	47
21	−7	< 9
22	−16	10
23	27	25
24	−8	18
25	7	< 8
26	27	32
27	0	< 7
28	−18	17
29	−15	19
	*h*03	
1	26	26
2	−136	123
3	−2	< 6
4	125	92
5	2	9
6	−52	46
7	23	21
8	−40	39
9	−15	< 8
10	37	36
11	−35	36
12	−7	< 8
13	7	9
14	28	21
15	−4	< 9
16	−45	38
17	−13	18
18	51	48
19	19	26
20	19	13
21	11	11
22	−53	50
23	−5	< 8
24	57	59
25	0	< 7
26	−5	8
27	1	< 5
28	−22	17
	*h*04	
0	−38	36
1	9	< 8
2	14	21
3	−52	50
4	14	< 8
5	65	63
6	−18	14
7	20	18
8	4	17
9	−106	100
10	1	11
11	106	89
12	−8	< 9
13	−5	14
14	−27	18
15	−59	54
16	−1	< 9
17	75	69
18	6	< 8
19	−15	11
20	−21	16
21	−16	13
22	11	14
23	7	8
24	6	7
25	2	< 5
	*h*05	
1	−11	< 9
2	−39	52
3	18	25
4	60	71
5	18	20

Table 3 (*cont.*)

h	F_c	F_o
6	−13	< 9
7	−50	52
8	− 9	20
9	25	26
10	14	16
11	21	20
12	− 8	< 8
13	−45	45
14	11	9
15	29	35
16	−14	18
17	14	10
18	21	18
19	−15	16
20	4	< 6
21	11	10
22	−22	23
	*h*06	
0	−58	48
1	− 4	< 8
2	30	31
3	−10	9
4	7	10
5	4	< 8
6	−48	40
7	− 6	< 8
8	12	8
9	−17	13
10	− 9	< 7
11	12	9
12	− 6	< 7
13	2	6
14	−10	6
15	− 6	8
16	4	6
17	13	9
	*h*07	
1	− 1	< 5
2	−10	7
3	2	< 5
4	3	< 5
5	22	11
6	− 2	< 4
7	−35	23
8	− 7	< 4

The final parameters for the selenium and carbon atoms are given in Table 2; the probable errors in these parameters are 0·005 Å for the selenium atoms (from least-squares residuals) and 0·05 Å for the carbon atoms (estimated).

In the final temperature factor, $B=2{\cdot}32\times10^{-16}$ cm.$^{-2}$ was used. As an indication of the agreement between calculated and observed structure factors, reliability factors, $R=\Sigma||F_o|-|F_c||\div\Sigma|F_o|$, were calculated. The values obtained were 0·155 for *hk*0 data and 0·162 for *h*0*l* data, using all observed reflections. These values are close to those found in other organoselenium structure determinations. Values of calculated and observed structure factors are given in Table 3.

Discussion of the results

The important bond distances and angles, together with estimated probable errors (obtained from least-squares residuals for the Se–Se distances) are given in Table 4.

Table 4. *Bond distances and angles in diphenyl diselenide*

Distances (Å)		Angles (degrees)	
Se–Se′	2·29±0·01	Se–Se′–C_1'	107·5±2·0
Se–C_1	1·93±0·05	Se′–Se–C_1	104·6±2·0
Se′–C_1'	1·93±0·05	'Dihedral'	82·0±3·0
Se–Se′ (non-bonded)	3·73±0·01		
Se′–Se′ (non-bonded)	3·88±0·01		

The selenium–selenium bonded distance of 2·29 Å is 0·05 Å shorter than twice the assigned single-bond radius for selenium, and compares with the values of 2·32 Å found in hexagonal selenium and 2·34 Å found in α-monoclinic selenium; it is the author's belief that the shortening is significantly greater than the experimental error in the present determination. On the other hand, the average selenium–carbon distance of 1·93 Å is in close agreement with the value of 1·94 Å predicted from the sum of the single-bond radii for carbon and selenium, although the relatively large experimental error in the carbon parameters introduces a corresponding uncertainty in the observed bond lengths. In 1,4-diselenane, carbon–selenium distances of 2·01±0·05 Å were observed, which represents an increase of 0·07 Å above the predicted value; in diarylselenium dihalides, values of about 1·94 Å were observed. It is apparent that the single-bond radius of selenium is rather fluid, and further investigations are necessary for a true understanding of the situation.

The non-bonded selenium–selenium distances of 3·73 and 3·88 Å, although significantly less than twice the assigned van der Waals radius of 2·0 Å, are in agreement with the values found in α-monoclinic selenium; these values ranged from 3·53 to 3·99 Å. The dihedral angle between the C_1–Se–Se′ and Se–Se′–C_1' planes is close to the predicted value of 90° (Pauling, 1949).

I should like to express my thanks to Prof. J. D. McCullough for his interest in and criticism of this work, as well as for providing the impetus for the undertaking.

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