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The Crystal and Molecular Structure of 1-Thia-4-selenacyclohexane 4,4-Dibromide, $C_4H_8SSeBr_2$

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1-Thia-4-selenacyclohexane 4,4-dibromide forms yellow crystals belonging to the monoclinic system with $a = 11.59$ A, $b = 6.49$ A, $c = 12.14$ A, and $\beta = 112.9°$. The space group symmetry is $P2_1/c$ with four molecules of $C_4H_8SSeBr_2$ in the unit cell. The trial structure was refined by use of three-dimensional, full-matrix, least-squares procedures based on 894 unique observed reflections. The molecular symmetry approximates m with the six-membered ring in the chair form. The bonding about selenium approximates a trigonal bipyramid with bromine atoms in the axial positions, two carbon atoms in equatorial positions, and the third equatorial position unoccupied. The observed bond distances (in A) are: Se–Br, 2.545 and 2.548 (esd 0.005); Se–C, 2.01 and 2.02 (esd 0.03); S–C, 1.83 and 1.79 (esd 0.03); and C–C, 1.50 and 1.54 (esd 0.04). The more interesting observed bond angles (in degrees) are: Br–Se–Br, 175.1 (esd 0.6); C–Se–C, 105 (esd 2); and C–S–C, 97 (esd 2.5). The plane of the Se–Br bonds is perpendicular to that of the Se–C bonds within the experimental limits of observation. The sulfur atom is not involved in bonding except to two carbon atoms in the same ring.

Introduction

Previous attempts to determine the structures of 1-thia-4-selenacyclohexane (1,4-thiaselenane)[1] and its derivatives[2,3] have involved compounds which proved to be disordered. The molecules in these cases were found to be crystallographically centrosymmetric, a requirement satisfied by random orientation of the sulfur and selenium ends of the ring. Thus it would have been difficult to have obtained good values for bond distances and angles in these compounds. However, a preliminary X-ray diffraction investigation of a number of 1,4-thiaselenane derivatives[3] indicated that the dibromide did not involve disorder. Its study was therefore undertaken, not only because of interest in the structure of the ring system, but also to study the heavy atom bonding in this new environment, the only previously reported structural studies of organoselenium dibromides having been on aromatic compounds.[4,5]

Experimental Section

1-Thia-4-selenacyclohexane was synthesized by the method of McCullough and Lefohn[6] and the dibromide prepared as described by McCullough.[3] Crystals suitable for the X-ray study were grown by slow evaporation of a solution in ethylene chloride. Most specimens showed a prismatic or lath-like development elongated on *b*, but some were polyhedra of roughly equal dimensions. Since there was some tendency to hydrolyze slowly in air, the specimens used for the intensity measurements were mounted in thin-walled Pyrex capillaries.

Weissenberg and precession photographs confirmed the monoclinic diffraction symmetry and the space group, $P2_1/c$, found in the preliminary study. The unit cell dimensions were redetermined with the aid of Weissenberg and precession photographs prepared with Cu Kα radiation and calibrated by use of the $hk0$ reflections of quartz.[7] On the basis of $a = 4.9131$ A for quartz, the parameters for 1,4-thiaselenane dibromide were found to be: $a = 11.59 \pm 0.01$ A, $b = 6.49 \pm 0.02$ A, $c = 12.14 \pm 0.01$ A, and $\beta = 112.9 \pm 0.1°$. The density calculated from these parameters is 2.577 g cm^{-3}, based on four $C_4H_8SSeBr_2$ per unit cell, while the density observed by flotation is 2.55 g cm^{-3}.

The intensity data were taken from multiple-film, integrated, Weissenberg photographs prepared with Cu Kα radiation. As in a number of similar cases involving selenium bromides, copper radiation was found to give photographs superior to those prepared with Mo Kα radiation. Although the absorption errors are greater with Cu radiation, the much denser background on the Mo photographs (probably caused by fluorescence) caused other problems. The main set of intensity photographs was taken about the *b* axis with a six-sided prismatic crystal. The cross-sectional dimensions between opposite pairs of faces were 0.12, 0.15, and 0.17 mm, respectively. With the average radius taken as 0.08 mm, the value of μR for Cu Kα radiation is 1.6. Although this is somewhat high, the intensity data were not corrected for absorption. Numerous unsuccessful attempts were made to find or prepare a crystal suitable for intensity measurements about the *a* or *c* axis for more completeness of data and for interlayer scaling. Ultimately a set of integrated Weissenberg photographs about [021] was prepared, but because of greater effects of absorption, these photographs were used only for interlayer scaling of the *b* axis data. The intensities on the integrated films were measured by means of a densitometer, corrected by the usual factors to give $k|F_o|$ values, and correlated by a least-squares method similar to that suggested by Rollett and Sparks.[8]

Determination and Refinement of the Structure

A two-dimensional Patterson summation was prepared by use of the $(h0l)$ data. This showed interactions characteristic of three heavy atoms in an equally-spaced linear arrangement and interpretation in these terms was straightforward. The resulting x and z parameters for Se, Br(1), and Br(2) were used to determine the phases for a two-dimensional Fourier summation which clearly revealed the positions of the sulfur and carbon atoms. Two-dimensional Fourier and least-squares refinement with individual isotropic temperature factors on all atoms gave x and z parameters which differed only slightly from the final three-dimensional values given in Table I.

Although a three-dimensional Patterson summation was prepared, it served merely to confirm the structure

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(1) J. D. McCullough and P. Radlick, *Inorg. Chem.*, **3**, 924 (1964).

(2) H. Hope and J. D. McCullough, *Acta Cryst.*, **15**, 806 (1962).

(3) J. D. McCullough, *Inorg. Chem.*, **3**, 1425 (1964).

(4) J. D. McCullough and G. Hamburger, *J. Am. Chem. Soc.*, **63**, 803 (1941).

(5) J. D. McCullough and R. E. Marsh, *Acta Cryst.*, **3**, 41 (1950).

(6) J. D. McCullough and A. Lefohn, *Inorg. Chem.*, **5**, 150 (1966).

(7) A. Pabst, *Am. Mineralogist*, **42**, 664 (1957).

(8) J. S. Rollett and R. A. Sparks, *Acta Cryst.*, **13**, 273 (1960).

TABLE I

FINAL ATOMIC POSITIONAL PARAMETERS IN $C_4H_8SSeBr_2$

Atom	x	y	z
Se	0.2893 (1)[a]	0.3788 (4)	0.2070 (1)
Br(1)	0.1500 (2)	0.6677 (4)	0.0843 (2)
Br(2)	0.4424 (2)	0.0991 (5)	0.3228 (2)
S	0.1545 (4)	0.3874 (11)	0.4223 (4)
C(1)	0.146 (2)	0.164 (4)	0.327 (2)
C(2)	0.143 (2)	0.211 (4)	0.206 (2)
C(3)	0.338 (2)	0.559 (4)	0.354 (2)
C(4)	0.315 (2)	0.450 (4)	0.457 (2)

[a] Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits.

already deduced on the basis of the following observations and assumptions: (1) In the range of $0k0$ reflections observable on Mo precession photographs, 040 was very strong and all others were absent. This suggested that the nearly linear Br–Se–Br system is centered at $y = n/8$, where n is an odd integer. (2) Previous studies suggested an Se–Br distance of 2.54 A. Taken into consideration with the projected Se–Br separations on the $(h0l)$ Fourier this gave the y parameters of the Br atoms relative to Se. (3) Packing considerations across the screw axes and centers of symmetry indicated which Br atom is above Se and which is below with respect to y parameters. (4) The nonbonded S···S distance in the 1,4-dithiane ring[9] is 3.45 A and the corresponding Se···Se distance in 1,4-diselenane[10] is 3.66 A. The average of these, 3.55 A, gives a value for the expected S···Se separation in the 1,4-thiaselenane ring. The observed S···Se separation on the $(h0l)$ Fourier is 3.52 A, and this suggested that the y parameter for S is close to that for Se.

The y parameters of the four heavy atoms deduced in this manner were each within 0.015 of the final refined values given in Table I.

After confirmation of the trial structure by means of a three-dimensional Patterson summation, the structure determination and refinement took the following steps: (1) The parameters of the four heavy atoms were refined by least-squares procedures with individual, isotropic temperature factors. (2) A three-dimensional difference Fourier synthesis was prepared in which the four heavy atoms used for phasing were subtracted at their refined positions. This synthesis clearly showed the carbon atom positions. (3) The parameters of all atoms (except hydrogen) were refined by the method of least-squares. Isotropic temperature factors were used on all atoms. (4) In order to check and adjust the interlayer scaling of the b axis data a series of independent least-squares refinements was carried out in which the data were used one level at a time. Isotropic temperature factors were used throughout and the y parameters were held constant on the zero and first level refinements. Thus a refined scale factor was obtained for each level. All scale factors, except that for the second level, $(h2l)$, were within 1% of their average, but an adjustment of 7% was required in that case. However, even including the second level, the positional and thermal parameters were in excellent agreement throughout. (5) With the scaling readjusted, a final series of least-squares refinement cycles was computed with anisotropic temperature parameters on the heavier atoms and isotropic parameters on carbon. In no case was the final shift in a parameter greater than 5% of the corresponding esd value. The final positional and temperature parameters, with their esd values, are listed in Tables I and II, respectively. (6) A final difference Fourier was computed in which all atoms except hydrogen were subtracted. The fluctuations in this summation were all within the range ± 1.5 e A^{-3} and the esd of the electron density was 0.5 e A^{-3}. Although there were some 20 maxima in the range between 1.0 and 1.5 e A^{-3}, these were located more or less at random and they could not be correlated with anticipated hydrogen positions. (7) A final set of structure factors was computed and listed in Table III. The final values of the usual index, R, were 0.084 for the 894 observed reflections and 0.114 for all 1272 reflections listed in Table III. In computing R, unobserved reflections were given the tabulated values of F_o.

TABLE II

FINAL THERMAL PARAMETERS IN $C_4H_8SSeBr_2$

(A) Anisotropic Parameters[a] for Heavy Atoms in A^2

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Se	1.6 (1)	2.0 (2)	1.7 (1)	0.0 (1)	0.9 (1)	0.0 (1)
Br(1)	3.0 (1)	2.4 (2)	3.0 (1)	0.1 (1)	0.5 (1)	0.6 (1)
Br(2)	3.1 (1)	3.2 (2)	4.7 (1)	1.3 (1)	1.9 (1)	1.0 (1)
S	2.3 (2)	3.4 (4)	2.1 (2)	−0.3 (2)	1.3 (1)	−0.8 (2)

(B) Isotropic Parameters for Carbon Atoms in A^2

Atom	C(1)	C(2)	C(3)	C(4)
B	2.6 (3)	2.1 (3)	2.6 (3)	2.1 (3)

[a] The relationships between the tabulated B values and the b values given in the anisotropic temperature factor expression are given by: $B_{11} = 4a^2(\sin^2 \beta)b_{11}$, $B_{22} = 4b^2b_{22}$, $B_{12} = 2ab(\sin \beta)b_{12}$, etc.

Computing Procedures

The Patterson, Fourier, and difference syntheses involved in this study were computed by use of UCLACFOUR written by P. K. Gantzel, H. Hope, and C. Knobler in these laboratories. The least-squares refinement was carried out by use of UCLALS4 written mainly by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood. The latter program minimizes the weighted sum of the quantity $(KF_o - GF_c)$ by a full-matrix routine, where K and G are scale factors. The program provides for several weighting options and for either isotropic or anisotropic temperature factors of the form: $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ on the individual atoms. The weighting scheme used for the observed reflections was that of Hughes[11] with $4F_o$ (min) = 40 and unobserved reflections were omitted in the refinement.

The atomic scattering factors used in the calculations were the neutral atom values given in the Inter-

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(9) R. E. Marsh, *Acta Cryst.*, **8**, 91 (1951)

(10) R. E. Marsh and J. D. McCullough, *J. Am. Chem. Soc.*, **73**, 1106 (1951).

(11) E. W. Hughes, *ibid.*, **63**, 1737 (1941).

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

H= 0, K= 0		
2	89	-104
4	55	-49
6	20	-26
8	124	-129
10	67	71
12	4*	10
14	27	30
H= 1, K= 0		
-14	3*	3
-12	31	33
-10	31	30
-8	94	-93
-6	55	-58
-4	50	-50
-2	138	172
0	41	-38
2	71	76
4	3*	-2
6	164	-173
8	111	112
10	5*	-12
12	4*	14
H= 2, K= 0		
-14	23	-20
-12	43	49
-10	77	-85
-8	31	32
-6	57	56
-4	12	-13
-2	129	113
-0	97	-105
2	89	-94
4	59	-62
6	84	82
8	15	15
10	4*	-6
12	19	18
H= 3, K= 0		
-14	23	21
-12	94	-99
-10	4*	4
-8	55	55
-6	3*	-12
-4	226	273
-2	174	-181
0	124	-128
2	12	10
4	44	-50
6	122	124
8	28	26
10	4*	-8
12	43	-48
H= 4, K= 0		
-14	25	-21
-12	41	-40
-10	4*	-9
-8	4*	1
-6	169	182
-4	112	-112
-2	12	-12
-0	76	-76
2	128	-146
4	185	195
6	4*	-6
8	19	20
10	4*	4
12	37	-43
H= 5, K= 0		
-14	48	-43
-12	27	27
-10	4*	7
-8	29	29
-6	3*	5
-4	30	-32
-2	23	-21
-0	75	-78
2	121	123
4	36	-33
6	4*	-4
8	11	8
10	58	-49
H= 6, K= 0		
-14	50	42
-12	38	34
-10	44	-43
-8	95	94
-6	154	-153
-4	41	-41
-2	64	61
-0	67	66
2	85	81
4	28	-31
6	28	-25
8	68	-68
10	17	21
H= 7, K= 0		
-14	34	30
-12	4*	3
-10	100	106
-8	148	-154
-6	33	-31
-4	4*	15
-2	99	-94
-0	198	217
2	31	-28
4	27	-25
6	23	-21
8	38	-36
H= 8, K= 0		
-14	3*	-8
-12	30	27
-10	5*	5
-8	19	-17
-6	4*	-4
-4	60	-63
-2	133	133
-0	64	-59
2	18	-19
4	21	20
6	62	-60
8	44	46
H= 9, K= 0		
-14	38	-35
-12	27	29
-10	62	-67
-8	25	26
-6	56	57
-4	33	32
-2	4*	-1
-0	43	-38
2	16	-12
4	46	-45
6	56	52
H= 10, K= 0		
-14	26	29
-12	110	-88
-10	4*	7
-8	43	44
-6	28	-27
-4	121	117
-2	69	-67
-0	55	-56
2	4*	-5
4	4*	9
6	34	36
H= 11, K= 0		
-14	15	-19
-12	3*	-11
-10	4*	6
-8	29	-27
-6	102	100
-4	60	-64
-2	4*	-5
0	5*	4
2	53	-54
4	51	53
H= 12, K= 0		
-10	13	-13
-8	24	20
-6	26	-27
-4	4*	-12
-2	20	22
-0	25	-27
2	57	57
H= 13, K= 0		
-0	32	35
H= 0, K= 1		
1	49	-57
2	110	130
3	124	144
4	114	112
5	94	-96
6	41	-43
7	57	59
8	4*	5
9	4*	-10
10	79	-76
11	26	-26
12	4*	3
13	3*	11
14	29	32
H= 1, K= 1		
-14	21	-21
-13	17	17
-12	46	45
-11	5*	-3
-10	5*	-12
-9	38	35
-8	86	85
-7	4*	4
-6	53	-53
-5	3*	7
-4	137	-152
-3	129	-131
-2	93	87
-1	86	-76
-0	76	-77
1	93	114
2	113	142
3	35	-37
4	23	24
5	111	124
6	54	-57
7	22	-27
8	17	-16
9	55	-56
10	24	-25
11	25	25
12	32	29
13	18	-26
H= 2, K= 1		
-14	16	19
-13	30	-32
-12	4*	-1
-11	23	23
-10	14	17
-9	94	92
-8	23	-25
-7	39	-42
-6	86	-88
-5	3*	8
-4	110	106
-3	84	-78
-2	40	-41
-1	62	-60
-0	100	112
1	8	13
2	35	33
3	73	82
4	117	-132
5	20	21
6	19	22
7	49	-50
8	31	-31
9	9	5
10	39	39
11	31	-36
12	12	13
13	13	17
H= 3, K= 1		
-15	18	-20
-14	36	33
-13	4*	-7
-12	22	-22
-11	41	40
-10	20	-17
-9	73	-71
-8	61	-63
-7	110	108
-6	19	-15
-5	69	-67
-4	50	44
-3	93	-86
-2	177	163
-1	162	162
0	2*	13
1	61	-70
2	111	-134
3	57	57
4	3*	2
5	4*	-5
6	61	-64
7	23	-21
8	46	47
9	5*	-5
10	49	53
11	13	-10
12	12	-16
H= 4, K= 1		
-14	3*	-10
-13	24	21
-12	34	29
-11	27	-27
-10	61	-65
-9	4*	6
-8	65	-63
-7	70	-68
-6	93	91
-5	3*	3
-4	27	21
-3	132	130
-2	85	76
-1	120	-125
-0	21	-22
1	102	106
2	77	-81
3	43	-46
4	50	-54
5	71	-72
6	24	25
7	60	65
8	45	47
9	12	-15
10	8	-6
11	34	30
12	11	12
H= 5, K= 1		
-14	12	15
-13	25	21
-12	20	-19
-11	44	-45
-10	33	-36
-9	4*	-2
-8	71	71
-7	36	-32
-6	53	-49
-5	34	31
-4	105	97
-3	50	48
-2	30	-28
-1	69	75
-0	96	-101
1	65	-65
2	41	43
3	81	-86
4	17	-15
5	30	31
6	46	49
7	34	-36
8	9	-6
9	48	42
10	9	-9
11	23	18
H= 6, K= 1		
-15	27	30
-14	3*	-1
-13	45	-37
-12	30	-27
-11	38	36
-10	53	54
-9	55	-56
-8	4*	-0
-7	34	-31
-6	65	61
-5	109	104
-4	52	-46
-3	36	-33
-2	132	-139
-1	51	45
-0	74	75
1	4*	-8
2	36	-36
3	32	-30
4	78	80
5	20	-16
6	40	37
7	8*	15
8	49	-48
9	16	14
10	3*	-4
H= 7, K= 1		
-15	20	-23
-14	38	-34
-13	33	28
-12	4*	-0
-11	12	-18
-10	67	70
-9	5*	-4
-8	4*	6
-7	67	65
-6	21	18
-5	103	-110
-4	83	-80
-3	62	68
-2	36	-37
-1	43	-43
-0	27	-23
1	49	-42
2	70	67
3	80	84
4	58	53
5	23	-22
6	43	-41
7	21	18
8	4*	10
9	3*	-9
H= 8, K= 1		
-15	16	-20
-14	27	-24
-13	4*	6
-12	53	47
-11	5*	5
-10	34	-33
-9	57	59
-8	50	50
-7	12	-15
-6	23	-23
-5	26	24
-4	67	-67
-3	73	-72
-2	52	53
-1	55	-52
0	4*	-10
1	66	65
2	48	43
3	30	-31
4	15	-14
5	48	51
6	20	-16
7	4*	-7
8	3*	-8
H= 9, K= 1		
-14	31	30
-13	30	-29
-12	23	-24
-11	4*	4
-10	5*	8
-9	48	50
-8	17	-20
-7	5*	-7
-6	61	-67
-5	4*	2
-4	83	86
-3	36	-35
-2	14	-11
-1	5*	7
-0	46	39
1	5*	-7
2	5*	3
3	31	34
4	62	-55
5	4*	7
6	3*	6
H= 10, K= 1		
-14	22	25
-13	8	-11
-12	4*	-9
-11	36	37
-10	19	-20
-9	64	-70
-8	41	-46
-7	43	48
-6	27	25
-5	12	-15
-4	5*	0
-3	29	-27
-2	60	60
-1	43	47
-0	18	14
1	21	-22
2	69	-64
3	18	15
4	4*	6
H= 11, K= 1		
-13	22	24
-12	19	23
-11	36	-39
-10	21	-26
-9	19	21
-8	21	-25
-7	29	-31
-6	26	29
-5	18	-15
-4	17	13
-3	74	78
-2	19	21
-1	47	-44
-0	26	-25
1	20	21
2	4*	-4
3	21	-21
4	16	-15
5	16	-24
H= 12, K= 1		
-13	11	13
-12	3*	-6
-11	11	-18
-10	23	-19
-9	4*	-13
-8	52	51
-7	15	-16
-6	36	-30
-5	36	34
-4	19	16
-3	4*	-7
-2	4*	-14
-1	36	35
-0	15	-23
1	3*	-5
2	32	15
3	28	-36
H= 13, K= 1		
-7	20	-20
-6	22	24
-5	21	21
-4	4*	-11
-3	4*	-7
-2	48	-58
-1	3*	6
0	31	30
1	2*	-7
H= 14, K= 1		
-7	30	39
-6	3*	10
-5	39	-50
-4	24	-31
H= 0, K= 2		
1	45	-38
2	27	-25
3	92	-86
4	16	16
5	77	66
6	50	46
7	9	-9
8	5*	-3
9	5*	-2
10	13	-14
11	55	50
12	12	-11
13	48	-48
H= 1, K= 2		
-13	50	-44
-12	5*	-8
-11	5*	-7
-10	5*	3
-9	18	18
-8	40	40
-7	48	-44
-6	4*	-6
-5	213	222
-4	15	-12
-3	97	-96
-2	56	-50
-1	98	-88
0	72	-84
1	19	-18
2	74	76
3	128	-132
4	43	40
5	107	97
6	4*	4
7	52	45
8	5*	2
9	35	35
10	15	-22
11	51	-37
12	4*	-2
13	21	-19
H= 2, K= 2		
-13	48	-43
-12	5*	6
-11	5*	-7
-10	5*	18
-9	43	-45
-8	34	33
-7	154	162
-6	9	8
-5	3*	-6
-4	68	-60
-3	17	12
-2	43	-33
-1	11	-4
0	24	23
1	217	-267
2	3*	9
3	137	148
4	39	36
5	25	21
6	5*	-6
7	35	29
8	51	-46
9	34	34
10	5*	0
11	70	-57
12	4*	8
H= 3, K= 2		
-13	4*	4
-12	5*	-4
-11	5*	-14
-10	5*	19
-9	5*	4
-8	5*	2
-7	47	44
-6	41	-39
-5	3*	2
-4	3*	2
-3	3*	-8
-2	28	-20
-1	158	-141
0	68	68
1	110	114
2	53	48
3	25	-26
4	33	-31
5	12	12
6	16	-13
7	84	76
8	22	-17
9	86	-84
10	5*	-2
11	28	25
H= 4, K= 2		
-13	30	28
-12	5*	17
-11	28	-35
-10	5*	-4
-9	100	104
-8	42	-39
-7	105	-97
-6	4*	-11
-5	58	-52
-4	24	-21
-3	28	21
-2	51	42
-1	34	-32
0	41	38
1	101	102
2	30	-28
3	11	13
4	4*	-1
5	5*	-4
6	28	-26
7	79	-74
8	5*	10
9	5*	7
10	16	22
11	9	13
H= 5, K= 2		
-13	4*	-12
-12	5*	1
-11	106	99
-10	5*	3
-9	65	-63
-8	43	-36
-7	64	-57
-6	4*	-2
-5	4*	13
-4	52	47
-3	151	-134
-2	21	20
-1	199	203
0	4*	1
1	35	32
2	41	-38
3	4*	-9
4	42	-41
5	15	-16
6	5*	10
7	88	-81
8	18	19
9	16	17
H= 6, K= 2		
-13	28	27
-12	5*	-4
-11	5*	12
-10	28	-33
-9	5*	-15
-8	5*	7
-7	5*	-10
-6	23	18
-5	140	-129
-4	25	20
-3	138	136
-2	46	40
-1	4*	-5
0	43	-38
1	4*	-0
2	21	-20
3	63	65
4	5*	1
5	114	-104
6	5*	3
7	34	31
8	21	19
H= 7, K= 2		
-13	47	43
-12	5*	-8
-11	52	-48
-10	5*	1
-9	5*	0
-8	5*	-6
-7	34	27
-6	26	26
-5	20	17
-4	4*	7
-3	4*	9
-2	42	-38
-1	4*	-12
0	5*	-13
1	5*	-2
2	5*	0
3	100	-84
4	5*	17
5	55	50
6	25	20
7	15	14
H= 8, K= 2		
-13	75	-65
-12	5*	-6
-11	5*	-13
-10	5*	7
-9	39	37
-8	46	44
-7	46	-38
-6	5*	-11
-5	144	144
-4	23	-19
-3	27	-25
-2	5*	-12
-1	61	-55
0	40	-34
1	41	-36
2	29	26
3	28	-26
4	5*	18
5	45	40
6	4*	-3
7	10	10
H= 9, K= 2		
-13	25	-27
-12	4*	6
-11	5*	3
-10	5*	6
-9	68	-65
-8	5*	11
-7	130	124
-6	5*	9
-5	28	-24
-4	34	-28
-3	16	-20
-2	5*	-14
-1	32	33
0	34	28
1	116	-101
2	5*	10
3	59	51
4	5*	4
5	13	12
H= 10, K= 2		
-14	2*	6
-13	21	20
-12	4*	-3
-11	4*	-12
-10	5*	10
-9	5*	16
-8	5*	-8
-7	5*	-12
-6	34	-30
-5	5*	-11
-4	5*	10
-3	29	25
-2	5*	-4
-1	78	-77
0	5*	15
1	76	69
2	22	17
3	4*	-4
4	10	-9
H= 11, K= 2		
-13	23	29
-12	11	9
-11	18	-20
-10	4*	-2
-9	61	52
-8	5*	-16
-7	71	-56
-6	5*	2
-5	26	-24
-4	5*	-8
-3	5*	-2
-2	16	20
-1	5*	21
0	5*	10
1	41	33
2	27	-22
3	4*	-5
4	3*	-3
H= 12, K= 2		
-12	5	-3
-11	77	68
-10	4*	-2
-9	34	-34
-8	14	-14
-7	34	-32
-6	4*	5
-5	11	13
-4	24	22
-3	70	-51
-2	4*	4
-1	81	63
H= 13, K= 2		
-7	30	28
-6	4*	4
-5	78	-60
-4	4*	2
-3	58	48
-2	9	9
-1	8	-10
0	9	-13
H= 14, K= 2		
-5	28	29
H= 0, K= 3		
1	69	100
2	44	47
3	71	-70
4	16	15
5	4*	5
6	4*	-6
7	58	-57
8	37	37
9	5*	9
10	48	-48
11	25	22
12	4*	3
13	3*	5
H= 1, K= 3		
-10	49	-52
-9	56	-58
-8	76	74
-7	37	-40
-6	4*	7
-5	4*	1
-4	62	-68
-3	68	67
-2	75	77
-1	81	90
0	80	-112
1	43	-53
2	3*	15
3	14	-14
4	36	32
5	89	-96
6	4*	-1
7	5*	8
8	5*	11
9	70	64
10	13	-17
11	4*	5
12	3*	0
H= 2, K= 3		
-14	2*	8
-13	24	25
-12	39	-33
-11	42	-35
-10	13	15
-9	58	-56
-8	21	-18
-7	18	16
-6	4*	-3
-5	10	12
-4	127	135
-3	132	134
-2	135	-135
-1	2*	-4
0	56	61
1	39	-47
2	3*	-3
3	82	-91
4	69	-68
5	38	-43
6	79	83
7	65	69
8	43	-40
9	5*	2
10	11	12
11	27	29
12	3*	-8
H= 3, K= 3		
-14	10	17
-13	4*	-3
-12	39	-37
-11	67	-55
-10	5*	0
-9	27	25
-8	15	-16
-7	36	-34
-6	4*	12
-5	88	91
-4	19	-17
-3	56	53
-2	76	72
-1	86	-89
0	19	-20
1	3*	-1
2	62	-68
3	49	-52
4	72	77
5	37	44
6	57	-61
7	28	24
8	31	28
9	5*	7
10	16	22
11	3*	-11
H= 4, K= 3		
-14	23	-25
-13	30	-30
-12	50	44
-11	5*	10
-10	13	-19
-9	5*	10
-8	51	-50
-7	44	41
-6	78	75
-5	37	34
-4	69	-63
-3	107	-110
-2	34	27
-1	3*	0
0	33	31
1	62	-63
2	14	-17
3	55	56
4	34	-34
5	70	82
6	5*	-9
7	25	-25
8	14	17
9	4*	3
10	4*	-11
11	33	-35
H= 5, K= 3		
-14	10	16
-13	4*	-13
-12	4*	7
-11	46	41
-10	12	-14
-9	17	21
-8	69	65
-7	65	65
-6	118	-117
-5	75	-66
-4	67	60
-3	61	-56
-2	33	32
-1	56	-49
0	66	-61
1	4*	8
2	94	95
3	95	103
4	51	-51
5	5*	-12
6	5*	-10
7	5*	4
8	4*	-4
9	37	-34
10	3*	-1
H= 6, K= 3		
-14	3*	9
-13	33	26
-12	4*	-2
-11	5*	-8
-10	32	32
-9	47	47
-8	29	-28
-7	5*	8
-6	25	21
-5	83	-76
-4	45	-42
-3	4*	-11
-2	52	-49
-1	4*	-2
0	92	101
1	68	67
2	61	-60
3	5*	10
4	39	37
5	5*	2
6	15	20
7	26	-25
8	35	-36
9	26	-27
H= 7, K= 3		
-14	9	-14
-13	4*	-4
-12	4*	-6
-11	5*	20
-10	40	40
-9	5*	-3
-8	5*	-10
-7	71	-73
-6	5*	9
-5	38	33
-4	5*	-9
-3	26	-24
-2	4*	-16
-1	50	49
0	41	-41
1	51	46
2	33	31
3	45	-43
4	14	12
5	13	-13
6	14	-16
7	23	-21
8	31	30
H= 8, K= 3		
-14	18	-21
-13	3*	-3
-12	26	28
-11	5*	12
-10	55	-57
-9	55	-56
-8	50	51
-7	5*	-2
-6	22	21
-5	5*	-6
-4	36	-30
-3	52	50
-2	46	43
-1	66	64
0	49	-45
1	59	-57
2	5*	-0
3	12	-13
4	9	6
5	26	-38
6	4*	10
7	3*	6
H= 9, K= 3		
-13	21	21
-12	48	-46
-11	24	-28
-10	12	16
-9	33	-34
-8	5*	-12
-7	5*	8
-6	28	-28
-5	14	17
-4	89	90
-3	63	64
-2	69	-63
-1	26	-25
0	27	25
1	5*	-0
2	5*	2
3	37	-34
4	32	-28
5	16	-17
6	31	30
H= 10, K= 3		
-12	3*	-9
-11	38	-36
-10	4*	-5
-9	32	35
-8	23	-23
-7	21	-23
-6	31	30
-5	31	29
-4	34	-33
-3	5*	10
-2	35	34
-1	41	-40
0	5*	8
1	5*	-3
2	50	-40
3	4*	-5
4	31	29
5	26	30
H= 11, K= 3		
-12	30	34
-11	22	26
-10	4*	0
-9	4*	7
-8	34	-29
-7	14	21
-6	15	19
-5	12	16
-4	12	-13
-3	65	-65
-2	11	15
-1	4*	5
0	4*	0
1	13	-17
2	9	13
3	15	21
H= 12, K= 3		
-10	11	-18
-9	4*	9
-8	52	48
-7	39	34
-6	61	-59
-5	44	-39
-4	4*	8
-3	4*	-5
-2	11	15
-1	11	-13
0	11	-14
1	3*	1
H= 13, K= 3		
-8	25	-24
-7	3*	-5
-6	11	19
-5	9	-16
-4	3*	-8
-3	3*	-0
-2	31	-39
H= 0, K= 4		
1	13	14
2	55	58
3	63	69
4	5*	7
5	51	48
6	6*	4
7	42	-39
8	71	68
9	28	-30
10	34	-36
11	5*	-3
12	4*	-2
H= 1, K= 4		
-12	5*	-13
-11	18	22
-10	16	-15
-9	38	41
-8	37	35
-7	33	-33
-6	6*	6
-5	5*	-8
-4	41	36
-3	53	-54
-2	91	-87
-1	20	-20
0	28	33
1	80	103
2	30	-35
3	5*	-3
4	18	-22
5	25	-22
6	100	97
7	19	-21
8	52	-50
9	17	-24
10	22	24
11	5*	10
12	3*	-9
H= 2, K= 4		
-12	37	-30
-11	6*	8
-10	57	55
-9	7*	-11
-8	44	-41
-7	18	-18
-6	6*	-11
-5	57	-51
-4	13	18
-3	50	45
-2	32	-31
-1	69	73
0	38	38
1	12	-11
2	12	-11
3	17	23
4	43	42
5	55	-53
6	55	-55
7	38	-37
8	7*	4
9	29	30
10	5*	11
11	4*	5
H= 3, K= 4		
-12	62	56
-11	6*	2
-10	30	-26
-9	39	-40
-8	35	-32
-7	51	-46
-6	36	32
-5	18	23
-4	135	-132
-3	41	31
-2	129	113
-1	62	58
0	37	34
1	5*	-1
2	5*	-0
3	74	-78
4	29	28
5	6*	-4
6	65	-61
7	7*	18
8	6*	-2
9	6*	17
10	19	-17
H= 4, K= 4		
-13	10	16
-12	18	27
-11	28	-26
-10	14	-13
-9	23	-20
-8	7*	16
-7	6*	4
-6	109	-102
-5	17	17
-4	68	59
-3	81	65
-2	5*	-7
-1	24	-14
0	5*	-8
1	63	-62
2	110	111
3	19	-23
4	94	-93
5	7*	-15
6	17	15
7	23	32
8	6*	-12
9	24	29
10	10	-11
H= 5, K= 4		
-13	12	-16
-12	16	-26
-11	6*	4
-10	15	13
-9	19	-25
-8	7*	8
-7	34	35
-6	6*	-11
-5	61	57
-4	16	18
-3	31	-28
-2	26	-23
-1	8*	-4
0	49	47
1	46	-42
2	71	-67
3	6*	-11
4	18	24
5	47	41
6	6*	11
7	6*	5
8	29	-27
9	4*	-5
H= 6, K= 4		
-13	9	-16
-12	16	-21
-11	6*	-13
-10	35	33
-9	35	36
-8	54	-48
-7	17	20
-6	93	88
-5	6*	-15
-4	6*	4
-3	6*	-7
-2	32	-30
-1	71	-68
0	6*	-12
1	17	18
2	32	-33
3	47	46
4	16	17
5	6*	10
6	6*	-1
7	16	15
8	39	37
H= 7, K= 4		
-10	59	-58
-9	7*	19
-8	73	73
-7	21	29
-6	7*	4
-5	28	-29
-4	6*	-16
-3	61	-59
-2	63	57
-1	6*	-2
0	110	-104
1	20	21
2	18	19
3	23	25
4	6*	8
5	12	15
6	5*	9
H= 8, K= 4		
-11	5*	14
-10	6*	3
-9	30	30
-8	7*	5
-7	44	-40
-6	7*	-13
-5	7*	0
-4	57	52
-3	7*	-3
-2	79	-71
-1	7*	-6
0	41	35
1	41	48
2	6*	-3
3	6*	1
4	26	-26
5	19	-19
6	43	39
H= 9, K= 4		
-11	5*	-4
-10	34	36
-9	15	-20
-8	29	-32
-7	6*	-5
-6	7*	-9
-5	37	-33
-4	18	-15
-3	21	25
-2	7*	13
-1	52	48
0	35	26
1	6*	-16
2	6*	-14
3	5*	-1
4	32	33
5	9	-13
H= 10, K= 4		
-11	4*	2
-10	14	-15
-9	25	-23
-8	31	-31
-7	16	-23
-6	20	23
-5	17	26
-4	66	-66
-3	6*	12
-2	41	41
-1	6*	7
0	6*	16
1	5*	-1
2	12	12
3	36	-34
H= 11, K= 4		
-10	4*	-10
-9	5*	-5
-8	36	37
-7	5*	8
-6	64	-65
-5	6*	7
-4	31	32
-3	33	29
-2	5*	1
-1	5*	-5
0	16	-20
1	27	-29
2	36	40
H= 12, K= 4		
-8	4*	-5
-7	3*	15
-6	5*	17
-5	6*	17
-4	5*	10
-3	13	-21
-2	13	-28
-1	4*	1
0	26	29

[a] The data are separated into groups having common values of h and k. The three columns in each group list values of l, F_o, and F_c, in that order. Unobserved reflections are indicated by * and the values of F_o given correspond to $\sqrt{2}/2$ times the minimum observable values.

national Tables for X-Ray Crystallography.[12] The factors for S, Se, and Br were corrected for dispersion for Cu Kα radiation.

Discussion of the Structure

A projection of the crystal structure of $C_4H_8SSeBr_2$ down the crystallographic *b* axis is shown in Figure 1, and the structurally interesting bond distances, bond angles, dihedral angles, intramolecular nonbonded separations, and intermolecular packing distances are given in Tables IV, V, VI, VII, and VIII, respectively. Although the molecule is not required crystallographically to have symmetry above the identity operation, the symmetry m is closely approximated. Small deviations from mirror symmetry are indicated by the differences in corresponding pairs of bond distances, bond angles, dihedral angles, and intramolecular separations listed in the tables. Figure 2 shows two views of the molecule idealized to the symmetry m.

The 1,4-thiaselenane ring has the expected chair conformation. However, the presence of two different, heavy, heteroatoms causes some marked deviations from the usual shape of a cyclohexane ring. These deviations are apparent in Figure 2.

The four carbon atoms are coplanar within the ex-

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[12] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1 A.

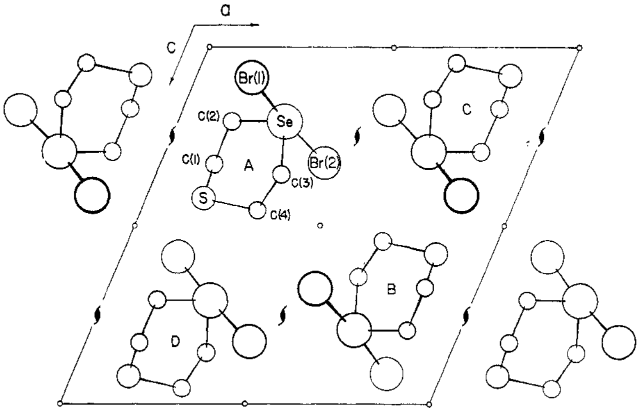

Figure 1.—Projection of the structure of $C_4H_8SSeBr_2$ down the *b* axis.

TABLE IV

BOND DISTANCES IN $C_4H_8SSeBr_2$

Bond	Distance, A	Bond	Distance,
Se–Br(1)	2.545 (5)	S–C(1)	1.83 (3)
Se–Br(2)	2.548 (5)	S–C (4)	1.79 (3)
Se–C(2)	2.01 (3)	C(1)–C(2)	1.50 (4)
Se–C(3)	2.02 (3)	C(3)–C(4)	1.54 (4)

TABLE V

BOND ANGLES IN $C_4H_8SSeBr_2$

Atoms	Angle, deg	Atoms	Angle, deg.
Br(1)–Se–Br(2)	175.1 (6)	C(2)–Se–C(3)	105 (2)
Br(1)–Se–C(2)	93 (1)	Se–C(3)–C(4)	112 (2)
Br(1)–Se–C(3)	89 (1)	C(3)–C(4)–S	114 (3)
Br(2)–Se–C(2)	91 (1)	C(4)–S–C(1)	97 (3)
Br(2)–Se–C(3)	92 (1)	S–C(1)–C(2)	116 (3)
Br(1)–Se···S	93.4 (8)	C(1)–C(2)–Se	114 (2)
Br(2)–Se···S	91.0 (8)		

TABLE VI

DIHEDRAL OR TORSION ANGLES IN 1,4-THIASELENANE RING IN $C_4H_8SSeBr_2$ (esd ~3°)

Atoms	Angle, deg
Se–C(2)–C(1)–S	57
Se–C(3)–C(4)–S	62
C(2)–Se–C(3)–C(4)	33
C(3)–Se–C(2)–C(1)	31
C(1)–S–C(4)–C(3)	76
C(4)–S–C(1)–C(2)	74

TABLE VII

NONBONDED INTRAMOLECULAR DISTANCES IN $C_4H_8SSeBr_2$

Atoms	Distance, A	Atoms	Distance, A
Br(1)–C(2)	3.33	Se–C(4)	2.96
Br(1)–C(3)	3.25	S–C(2)	2.82
Br(2)–C(2)	3.25	S–C(3)	2.77
Br(2)–C(3)	3.29	C(1)–C(3)	3.34
Br(2)–C(1)	3.49	C(2)–C(4)	3.29
Br(2)–C(4)	3.44	C(1)–C(4)	2.73
Se–S	3.52	C(2)–C(3)	3.20
Se–C(1)	2.96		

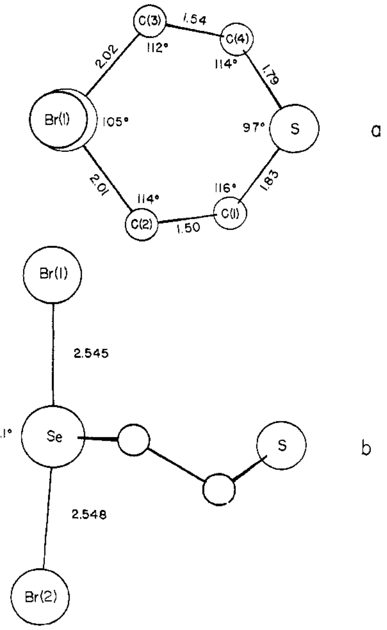

Figure 2.—Two views of the molecular structure of $C_4H_8SSeBr_2$. (a) A projection of the molecule perpendicular to the plane of the C–Se–C bonds. (b) A projection of the molecule parallel to the plane of the carbon atoms and perpendicular to the plane of the Br–Se–Br bonds.

TABLE VIII

SHORTEST INTERMOLECULAR PACKING DISTANCES IN $C_4H_8SSeBr_2$

First atom (position A)	Second atom, position,[a] and lattice translation			Distance, A
Se	Br(2)	C	000	3.56
Se	S	D	$00\bar{1}$	3.63
Se	C(4)	D	$00\bar{1}$	3.80
Br(1)	Br(1)	B	$\bar{1}0\bar{1}$	3.93
Br(1)	S	D	$01\bar{1}$	3.50
Br(1)	S	C	$\bar{1}00$	3.77
Br(1)	C(1)	D	$00\bar{1}$	3.77
Br(1)	C(1)	C	$\bar{1}00$	3.94
Br(1)	C(2)	A	010	3.83
Br(1)	C(2)	B	$\bar{1}0\bar{1}$	3.91
Br(1)	C(4)	D	$01\bar{1}$	3.80
Br(2)	Br(2)	C	000	4.15
Br(2)	Br(2)	B	$0\bar{1}0$	4.18
Br(2)	C(3)	A	$0\bar{1}0$	3.80
Br(2)	C(3)	C	$0\bar{1}0$	3.93
S	C(1)	C	$\bar{1}00$	3.99
S	C(2)	D	000	3.54
S	C(2)	C	$\bar{1}00$	3.81
C(3)	C(3)	B	000	4.06
C(3)	C(4)	B	000	3.77
C(4)	C(4)	B	000	4.06

[a] Positions: A = (x, y, z); B = $(1 - x, 1 - y, 1 - z)$; C = $(1 - x, {}^1/_2 + y, {}^1/_2 - z)$; D = $(x, {}^1/_2 - y, {}^1/_2 + z)$.

perimental errors of the determination. The displacements (in A) of the six ring atoms from the least-squares plane fit to the four carbon atoms are: C(1), −0.018; C(2), 0.015; C(3), −0.015; C(4), 0.018; Se, 0.612; S, −0.063. The plane of the C–Se–C bonds makes a diehdral angle of only 30° with the least-squares plane of the carbon atoms, while the corresponding dihedral angle for the C–S–C bonds is 63°. This situation brings the sulfur atom close to the plane of the C–Se–C bonds. The calculated distance of sulfur from the plane is 0.051 A (esd 0.05 A).

A comparison of the C–Se–C bond angle of 105° (esd 2°) with the C–S–C bond angle of 97° (esd 3°) is of interest in view of the expectation that the bond at Se should be smaller than that at S. The observed difference of 8° is approximately three times the standard deviation of the angles and may therefore be considered to be significant. It is suggested that the bond angle at Se may be enlarged by the bonding with bromine. However, this is not certain since the structure of uncombined 1,4-thiaselenane has not yet been determined. With respect to the bond angles at the heteroatoms, the 1,4-thiaselenane ring in the dibromide is different from the 1,4-oxaselenane ring in its iodine complex.[13] In the latter case the C–Se–C angle is 94° (esd 2°) and the C–O–C angle is 111° (esd 3°).

The bonding about selenium is the same as that observed in diphenylselenium dibromide[4] and di-*p*-tolylselenium dibromide.[5] The observed bond distances and angles at selenium in the three dibromides are compared in Table IX. With the exception of the Se–C distances, the differences are probably not significant. The Se–C distances observed in the dibromide of 1,4-thiaselenane compare favorably with the values 1.99 and 2.04 A (av 2.02 A, esd 0.03 A) observed in 1,4-diselenane[10].

TABLE IX

COMPARISON OF BOND DISTANCES AND ANGLES ABOUT SELENIUM IN THREE ORGANOSELENIUM DIBROMIDES; ESD IN PARENTHESES[a]

	Bond distance, A		Bond angle, deg	
Compound	Se–Br	Se–C	Br–Se–Br	C–Se–C
$C_4H_8SSeBr_2$	2.546 (3)[b]	2.01 (2)[b]	175.1 (6)	105 (2)
$(C_6H_5)_2SeBr_2$[4]	2.52 (1)	1.91 (3)	180 (3)	110 (10)
$(p\text{-}CH_3C_6H_4)_2SeBr_2$[5]	2.55 (2)	1.95 (3)	177 (1)	108 (1)

[a] The esd values for $(C_6H_5)_2SeBr_2$ and $(p\text{-}CH_3C_6H_4)_2SeBr_2$ were rough estimates based on two-dimensional Fourier refinement. [b] Average of two independent observed values.

The Br–Se–Br bond angle of 175.1° deviates from a straight line by 4.9°, a value which is eight times the esd of 0.6°. From a consideration of the various Br–Se–C and Br–Se···S angles in Table V, it is evident that the bromine atoms are bent away from the methylene groups to which selenium is bonded. The shortness of the four Br–CH_2 intramolecular nonbonded separations (3.25–3.33 A) suggests that the bromine atoms may be pushed outward by these contacts. A similar situation appears to exist in di-*p*-tolylselenium dibromide, but in diphenylselenium dibromide the structure determination was not accurate enough to permit definite conclusions in this regard. Apparently, in the present case, the repulsion[14] of the lone pair on selenium is insufficient to overcome the repulsion of the bromine atoms by the methyl groups. In some other related examples, however (*i.e.*, $(CH_3)_2TeCl_2$[15] and ClF_3[16]), the repulsion of the lone pair(s) appears to predominate.

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