ACTA CHEMICA SCANDINAVICA 25 (1971) 2507–2515

The Crystal and Molecular Structure of 6a-Selenaselenophthene

ASBJØRN HORDVIK and KÅRE JULSHAMN

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

6a-Selenaselenophthene crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions: $a = 7.842(3)$ Å, $b = 5.660(2)$ Å, $c = 16.749(5)$ Å, and $\beta = 98.39(3)°$. There are four molecules per unit cell.

The structure of 6a-selenaselenophthene has been solved by three-dimensional Patterson synthesis, and refined by least squares methods. The refinement comprises 984 $h0l - h3l$ reflections, including 290 unobserved.

The molecule is planar within the error, and the bond lengths are: Se(1) – Se(6a) = 2.586(3) Å, Se(6a) – Se(6) = 2.579(3) Å, Se(1) – C(2) = 1.856(29) Å, Se(6a) – C(3a) = 1.904(23) Å, Se(6) – C(5) = 1.811(26) Å, C(2) – C(3) = 1.374(31) Å, C(3) – C(3a) = 1.427(27) Å, C(3a) – C(4) = 1.395(30) Å, and C(4) – C(5) = 1.371(28) Å. The Se(1) – Se(6a) – Se(6) angle is 173.8(3)°.

In the crystals, Se(6a) of the reference molecule approaches the plane of a screw axis-related molecule at a distance of 3.55 Å. Other intermolecular atomic distances shorter than corresponding van der Waals distances are, Se(1)···H(5)′ = 3.08 Å, Se(1)···Se(6)′ = 3.92 Å, Se(6)···Se(6)′ = 3.87 Å, Se(6a)···Se(6a)′ = 3.83 Å, and Se(6)···Se(1)′ = 3.90 Å.

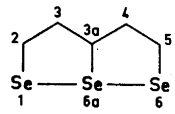
Structure investigations of potassium triselenocyanate hemihydrate, $K(SeCN)_3 \cdot \frac{1}{2}H_2O$, and of rubidium triselenocyanate hemihydrate, $Rb(SeCN)_3 \cdot \frac{1}{2}H_2O$, show that the selenium atoms of the triselenocyanate ion form an almost linear sequence.[1–3] The Se – Se bonds in the potassium salt are 2.689(4) Å and 2.648(4) Å,[3] respectively, and the Se – Se bonds in the rubidium salt are both 2.656(3) Å.[2]

An analogous linear three-selenium system occurs in the triselenourea ion. This has recently been shown by Hauge *et al.*[4] through structure studies of triselenourea dichloride hydrate, $[SeC(NH_2)_2]_3Cl_2.H_2O$, and triselenourea dibromide hydrate, $[SeC(NH_2)_2]_3Br_2.H_2O$. The Se – Se bonds are 2.60 and 2.72 Å in the dichloride, and 2.62 and 2.71 Å in the dibromide.

The bonding in these linear three-selenium systems may be described as three-center four-electron bonds.[5] One notes that the sum of the Se – Se bond lengths in the various compounds range from 5.31 to 5.34 Å; the average

Se – Se bond length is 2.66 Å, as compared with the Se – Se single bond length of 2.34 Å.[6]

In 6a-selenaselenophthene (I), a linear three-selenium sequence is built into an aromatic ring system. The three-selenium bonding in this compound, therefore, has some π-contribution, and it differs in this respect from the



(I)

three-selenium bonding in the compounds above. The present structure study of (I) has been carried out in order to find to which degree the Se – Se bonds in (I) are shortened through π-bonding.

STRUCTURE DETERMINATION

Crystals of 6a-selenaselenophthene (I) were generously supplied by Reid.[7] The crystals are very dark-purple and belong to the monoclinic space group $P2_1/c$.

The structure analysis is based on photographic data, taken with Weissenberg camera and Cu$K\alpha$ radiation. The data comprise 984 independent $h0l - h3l$ reflections, including 290 unobserved.

Approximate selenium positions were found from a three-dimensional Patterson map, and the carbon atoms revealed themselves during a subsequent Fourier synthesis.

The structure was refined by a full-matrix least squares procedure which minimizes the function.

$$r = \sum W(|F_o| - K|F_c|)^2$$

with $W = [(Ka_1)^2 + (a_2F_o)^2/4W_o]^{-1}$. W_o in the weighting scheme is an individual weight, which is estimated from the assumed reliability of the intensity measurement. The constants a_1 and a_2 were in the present case set equal to 1.0. Unobserved reflections with $K|F_c|$ greater than $F_c^{\text{threshold}}$ were included in the refinement with $F_o = F_o^{\text{threshold}}$. Anisotropic temperature factors were applied to selenium and carbon, and isotropic to hydrogen. Three low-order reflections, supposed to be affected by secondary extinction, were excluded from the least squares refinement. The final R factor is 9.4 % when unobserved reflections are included, and 9.7 % when they are omitted. For further details with respect to the structure determination, see Experimental.

DISCUSSION

Molecular shape and dimensions. Bond lengths and angles in the 6a-selenaselenophthene molecule, together with their standard deviations, are listed in Tables 1 and 2, and shown in Fig. 1.

Table 1. Bond lengths D(ij) in 6a-selenaselenophthene. The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	D(ij)
Se(1)	Se(6a)	2.586 (3) Å
Se(6a)	Se(6)	2.579 (3)
Se(1)	C(2)	1.856 (29)
Se(6a)	C(3a)	1.904 (23)
Se(6)	C(5)	1.811 (26)
C(2)	C(3)	1.374 (31)
C(3)	C(3a)	1.427 (27)
C(3a)	C(4)	1.395 (30)
C(4)	C(5)	1.371 (28)

Table 2. Bond angles ∠(ijk) in 6a-selenaselenophthene. The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	k	∠(ijk)°
C(2)	Se(1)	Se(6a)	88.4 (7)
Se(1)	Se(6a)	C(3a)	87.6 (6)
Se(1)	Se(6a)	Se(6)	173.8 (2)
C(3a)	Se(6a)	Se(6)	86.3 (6)
Se(6a)	Se(6)	C(5)	88.7 (5)
Se(1)	C(2)	C(3)	122.1 (1.7)
C(2)	C(3)	C(3a)	122.3 (2.0)
C(3)	C(3a)	C(4)	119.9 (1.9)
C(3)	C(3a)	Se(6a)	119.5 (1.5)
Se(6a)	C(3a)	C(4)	120.5 (1.5)
C(3a)	C(4)	C(5)	121.7 (2.1)
C(4)	C(5)	Se(6)	122.8 (1.6)

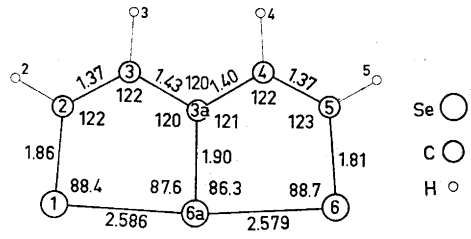


Fig. 1. Bond lengths (Å) and bond angles (°) in the 6a-selenaselenophthene molecule.

The molecule is presented in Fig. 1 in a projection onto its least squares plane. The equation for this plane, with weights equal to six for selenium, one for carbon, and zero for hydrogen, is,

$$0.83989\,X - 0.52836\,Y - 0.24545\,Z = 0.90772$$

with X, Y, and Z in Å units. Deviations, in Å units, from the plane are, Se(1) 0.003, Se(6a) −0.009, Se(6) 0.007, C(2) −0.015, C(3) 0.025, C(3a) 0.024, C(4) −0.023, and C(5) −0.015. Thus, the molecule is planar within the error.

The selenium−selenium bonds, Se(1)−Se(6a) = 2.586(3) Å and Se(6a)−Se(6) = 2.579(3) Å, are almost equal, and their average length, 2.58 Å, is 0.08

Å shorter than the average Se – Se bond length, 2.66 Å, in the triselenocyanate and triselenourea ions.[1-4]

*Comparison with the structure of thiothiophthene.** One notes from Fig. 1 that the 6a-selenaselenophthene molecule is nearly symmetric about a plane perpendicular to the molecular plane and passing through Se(6a) and C(3a). There are no significant differences between the dimensions of the two halves.

If one takes the average of corresponding bond lengths in the two halves of 6a-selenaselenophthene, one gets the values which are shown in Fig. 2, Ia. Furthermore, in Fig. 2, the bond lengths in thiothiophthene (II) are given. They are from a recent structure study, based on diffractometer data.[10] Results from a structure study of II on film data have been reported.[11]

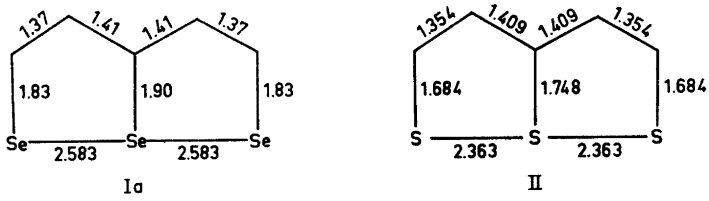


Fig. 2. Comparison of the average structure of 6a-selenaselenophthene (Ia) with the structure of thiothiophthene(II). Bond lengths in Å units.

The standard deviations of the bond lengths in II from the diffractometer study are, S – S ± 0.001 Å, S – C ± 0.003 Å, and C – C ± 0.003 Å. In crystals of thiothiophthene, the molecules lie across crystallographic mirror planes passing through the central sulphur and carbon atoms. The two halves of the molecule are therefore exactly equal.

From Fig. 2, the difference between the selenium – selenium bond length in Ia, and the sulphur – sulphur bond length in II, is 0.22 Å, or about two times the difference, 0.12 Å, between the covalent bond radii of selenium and sulphur.[6,12] It should be mentioned that the bond lengths in II, Fig. 2, have been corrected for libration, while the bond lengths in Ia have not been corrected. A rigid-body analysis of I is hardly warranted in view of the poor accuracy of the thermal parameters of the carbon atoms (*cf.* Table 5).

The terminal selenium – carbon bonds in Ia, 1.83(3) Å, are 0.07 Å shorter than the central one, 1.90(3) Å. In II, the terminal sulphur – carbon bonds, 1.684(3) Å, are 0.064 Å shorter than the central one, 1.748(3) Å. The difference between the terminal Se – C and S – C bond lengths, 0.15 Å, and the difference between the central ones, 0.15 Å, are somewhat greater than the difference between the covalent radii for selenium and sulphur.

The terminal and central carbon – carbon bonds in Ia are 1.37(3) Å and 1.41(3) Å, respectively, in agreement with the lengths of the corresponding bonds in II, 1.354(3) Å and 1.409 Å (*cf.* Fig. 2).

* Bezzi, Mammi and Garbuglio, who in 1958 studied the structure of the 2,5-dimethyl derivative of II (*cf.* Fig. 2), found II to be a new aromatic system, which they proposed to be named thiothiophthene.[8] Different names, *e.g.* 6a-thiothiophthene and trithiopentalene, have appeared later. A survey of nomenclatures is given by Klingsberg in Ref. 9, p. 544.

The crystal structure. The arrangement of 6a-selenaselenophthene molecules in the unit cell, as seen along the *b*-axis, is shown in Fig. 3. Intermolecular

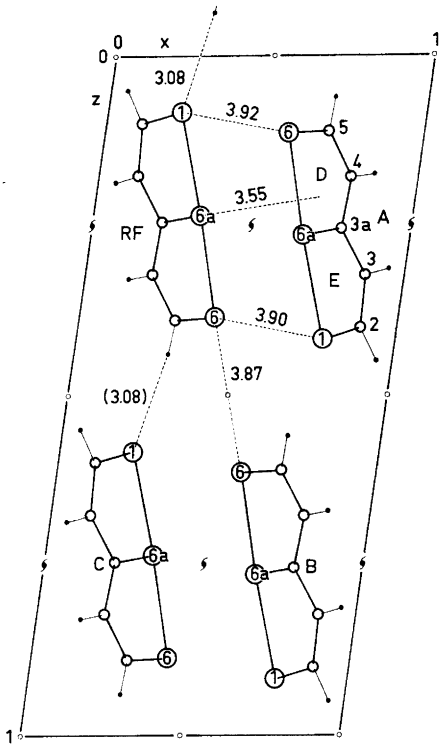


Fig. 3. The arrangement of 6a-selenaselenophthene molecules in the crystal as seen along the *b*-axis. Atomic distances are given in Å units.

atomic distances shorter than corresponding van der Waals distances are shown in the figure. The positions of the molecules $A-C$ relative to the position (x,y,z) of the reference molecule RF are the following.

A	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
B	$1-x$	$-y$	$1-z$
C	x	$-\frac{1}{2}-y$	$\frac{1}{2}+z$

The angle between the plane of the reference molecule and the plane of molecule A is 63.8°. Intermolecular atomic distances, which show the way in which Se(6) of the reference molecule approaches the atoms of ring E in molecule A, and the way in which Se(6a) of RF approaches the atoms of ring D in A, are listed in Table 3.

$Se(6)_{RF}$ forms two close contacts with neighbouring molecules (*cf.* Fig. 3). The $Se(6)_{RF}\cdots Se(1)_A$ distance is 3.90 Å, and the $Se(6)_{RF}\cdots Se(6)_B$ distance is 3.87 Å, as compared with the corresponding van der Waals distance of 4.00 Å.[6]

Table 3. Intermolecular atomic distances D(ij) between Se(6) of molecule RF and the atoms of ring E in molecule A, and between Se(6a) of RF and the atoms of ring D in A.

i	j	D(ij)	i	j	D(ij)
$Se(6)_{RF}$	$Se(1)_A$	3.90 Å	$Se(6a)_{RF}$	$Se(6a)_A$	3.83 Å
$Se(6)_{RF}$	$Se(6a)_A$	4.22	$Se(6a)_{RF}$	$Se(6)_A$	4.06
$Se(6)_{RF}$	$C(2)_A$	3.83	$Se(6a)_{RF}$	$C(3a)_A$	3.71
$Se(6)_{RF}$	$C(3)_A$	3.94	$Se(6a)_{RF}$	$C(4)_A$	3.88
$Se(6)_{RF}$	$C(3a)_A$	4.09	$Se(6a)_{RF}$	$C(5)_A$	3.99

$Se(6a)_{RF}\cdots Se(6a)_A = 3.83$ Å is 0.17 Å shorter than the corresponding van der Waals contact. Furthermore, $Se(6a)_{RF}$ lies 3.55 Å only from the plane of molecule A. This distance is 0.15 Å shorter than the distance, 3.70 Å, one gets by adding the van der Waals radius of selenium to the half-thickness of an aromatic molecule.[6]

$Se(1)_{RF}$ forms a close contact of 3.92 Å to $Se(6)_A$, and another one of 3.08 Å to a neighbouring hydrogen atom (*cf.* Fig. 3). The latter contact is

Table 4. Atomic coordinates in fractions of corresponding cell edges. The standard deviations given in parentheses refer to the last digits of the respective values.

Atom	x	y	z
Se(1)	0.22946 (32)	0.08877 (54)	0.08148 (13)
Se(6a)	0.33396 (24)	0.11201 (46)	0.23502 (11)
Se(6)	0.42317 (29)	0.09101 (52)	0.38928 (12)
C(2)	0.1128 (26)	−0.1869 (55)	0.0997 (13)
C(3)	0.1216 (19)	−0.2850 (42)	0.1752 (12)
C(3a)	0.2144 (21)	−0.1766 (42)	0.2453 (11)
C(4)	0.2096 (24)	−0.2757 (42)	0.3212 (13)
C(5)	0.2982 (23)	−0.1779 (52)	0.3900 (10)
H(2)	0.051	−0.263	0.050
H(3)	0.047	−0.455	0.185
H(4)	0.136	−0.459	0.323
H(5)	0.297	−0.253	0.444

Table 5. Temperature parameters U_{ij} (Å²) for selenium and carbon. The expression used is $\exp[-2\pi^2(h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12}+\cdots)]$. All values are multiplied by 10^4. Standard deviations in parentheses refer to the last digits of the respective values. Isotropic temperature factors $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$ with $U = 0.0375$ Å² were used for the hydrogen atoms.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Se(1)	713 (15)	592 (30)	398 (10)	2 (15)	44 (13)	28 (10)
Se(6a)	435 (10)	294 (26)	432 (9)	−44 (12)	21 (12)	48 (7)
Se(6)	652 (14)	532 (30)	416 (11)	−73 (14)	−10 (13)	−21 (10)
C(2)	489 (110)	748 (252)	590 (129)	−40 (133)	40 (141)	−125 (99)
C(3)	206 (71)	268 (191)	574 (102)	95 (87)	78 (109)	−10 (68)
C(3a)	281 (77)	176 (185)	644 (119)	57 (98)	202 (118)	7 (75)
C(4)	526 (105)	21 (202)	617 (116)	72 (102)	94 (113)	108 (89)
C(5)	422 (96)	917 (234)	319 (83)	143 (122)	318 (115)	17 (72)

Table 6. Observed and calculated structure factors for 6a-selenaselenophthene. The values given are ten times the absolute values. Unobserved reflections are marked with a minus sign in front of F_o.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
1	0	0	1131	-1124	5	0	14	-53	10	1	1	14	121	76	3	1	-13	158	151	6	1	-10	271	252
2	0	0	1529	-1367	5	0	16	303	-349	1	1	15	178	-141	3	1	-14	481	457	6	1	-11	435	-428
3	0	0	305	288	5	0	-2	246	241	1	1	16	-63	58	3	1	-15	732	-663	6	1	-12	117	-119
4	0	0	111	-104	5	0	-4	115	-112	1	1	17	-59	-36	3	1	-16	400	-369	6	1	-13	-60	-15
5	0	0	335	305	5	0	-6	168	-167	1	1	18	149	138	3	1	-17	-60	11	6	1	-14	-57	36
7	0	0	135	-125	5	0	-8	79	98	1	1	19	153	148	3	1	-18	-55	-68	6	1	-15	122	-117
8	0	0	148	-151	5	0	-10	349	-336	1	1	20	-38	-35	3	1	-19	-48	39	6	1	-16	202	-194
9	0	0	431	379	5	0	-12	112	94	1	1	-1	2581	2342	3	1	-20	121	-113	6	1	-17	298	304
0	0	2	879	-727	5	0	-14	-63	-71	1	1	-2	326	268	4	1	1	426	462	6	1	-18	90	97
0	0	4	969	-756	5	0	-16	491	448	1	1	-3	371	336	4	1	2	148	132	7	1	1	420	-435
0	0	6	2517	-2311	5	0	-18	158	-162	1	1	-4	182	146	4	1	3	920	1007	7	1	2	473	471
0	0	8	817	706	6	0	2	783	-827	1	1	-5	-36	-24	4	1	4	956	-1066	7	1	3	484	470
0	0	10	524	470	6	0	4	515	496	1	1	-6	503	493	4	1	5	698	-871	7	1	4	146	-176
0	0	12	712	567	6	0	6	232	122	1	1	-7	854	-975	4	1	6	170	177	7	1	5	94	103
0	0	14	406	-394	6	0	8	353	341	1	1	-8	316	-292	4	1	7	305	-335	7	1	6	-61	23
0	0	16	-64	-19	6	0	10	389	-372	1	1	-9	97	78	4	1	8	-61	62	7	1	7	188	185
0	0	18	-58	60	6	0	12	-53	60	1	1	-10	-52	-15	4	1	9	340	-401	7	1	8	203	-207
0	0	20	143	-129	6	0	14	-41	7	1	1	-11	-56	70	4	1	10	615	632	7	1	9	368	-357
1	0	2	261	-156	6	0	-2	424	-410	1	1	-12	-59	43	4	1	11	622	596	7	1	10	112	89
1	0	4	231	-184	6	0	-4	1114	1157	1	1	-13	116	-102	4	1	12	333	-334	7	1	11	-43	14
1	0	6	163	-160	6	0	-6	-62	-63	1	1	-14	273	-275	4	1	13	-63	56	7	1	12	-36	-14
1	0	8	64	-75	6	0	-8	-64	-58	1	1	-15	167	130	4	1	14	-60	-53	7	1	-1	152	-157
1	0	10	119	133	6	0	-10	456	-466	1	1	-16	106	78	4	1	15	-55	45	7	1	-2	-65	11
1	0	12	997	942	6	0	-12	-63	37	1	1	-17	107	82	4	1	16	74	-85	7	1	-3	255	-223
1	0	14	374	-357	6	0	-14	-59	85	1	1	-18	-57	10	4	1	17	119	-133	7	1	-4	301	-252
1	0	16	251	-259	6	0	-16	-50	83	1	1	-19	202	189	4	1	-1	536	501	7	1	-5	416	357
1	0	18	480	-476	7	0	2	257	268	1	1	-20	193	185	4	1	-2	1038	1200	7	1	-6	-64	57
1	0	20	294	320	7	0	4	184	-191	1	1	-21	171	-186	4	1	-3	1012	-1038	7	1	-7	124	97
1	0	-8	1666	-1847	7	0	6	76	84	2	1	1	-33	-23	4	1	-4	517	-533	7	1	-8	-63	37
1	0	-10	486	-532	7	0	8	171	174	2	1	2	346	296	4	1	-5	212	-209	7	1	-9	-62	-15
1	0	-12	501	-514	7	0	10	67	-68	2	1	3	61	50	4	1	-6	243	-228	7	1	-10	167	127
1	0	-14	1066	1151	7	0	12	-39	-73	2	1	4	501	459	4	1	-7	-54	-2	7	1	-11	-59	-74
1	0	-16	124	141	7	0	-2	85	102	2	1	5	936	863	4	1	-8	218	-215	7	1	-12	-56	-50
1	0	-18	-59	0	7	0	-4	574	-580	2	1	6	492	-488	4	1	-9	262	293	7	1	-13	-53	-44
1	0	-20	353	-353	7	0	-6	375	336	2	1	7	96	-105	4	1	-10	136	106	7	1	-14	-48	-39
2	0	2	1136	-905	7	0	-8	-64	4	2	1	8	63	-73	4	1	-11	-62	93	7	1	-15	-43	43
2	0	4	1265	-1358	7	0	-10	541	521	2	1	9	-54	-13	4	1	-12	-64	91	8	1	1	326	305
2	0	6	1894	1940	7	0	-12	394	-422	2	1	10	-57	-39	4	1	-13	-65	-42	8	1	2	87	-70
2	0	8	455	556	7	0	-14	-50	-53	2	1	11	-60	43	4	1	-14	-64	-34	8	1	3	182	-163
2	0	10	478	443	7	0	-16	148	-160	2	1	12	104	71	4	1	-15	145	140	8	1	4	-55	14
2	0	12	1524	-1430	8	0	2	411	392	2	1	13	91	-102	4	1	-16	91	58	8	1	5	-53	31
2	0	14	-64	-11	8	0	4	-56	43	2	1	14	-65	-89	4	1	-17	148	-135	8	1	6	-50	-40
2	0	16	-62	57	8	0	6	103	104	2	1	15	149	-151	4	1	-18	-51	4	8	1	7	-46	-70
2	0	18	491	461	8	0	8	405	-445	2	1	16	-61	-29	5	1	1	-56	13	8	1	-1	-60	-48
2	0	-2	1716	1559	8	0	-2	106	-149	2	1	17	213	-179	5	1	2	394	-401	8	1	-2	-60	-68
2	0	-4	361	336	8	0	-4	129	-135	2	1	18	221	201	5	1	3	580	-660	8	1	-3	147	134
2	0	-6	48	-57	8	0	-6	73	94	2	1	19	263	251	5	1	4	961	-999	8	1	-4	290	270
2	0	-8	204	155	8	0	-8	-57	89	2	1	-1	1968	-2127	5	1	5	237	230	8	1	-5	412	-445
2	0	-10	52	-68	8	0	-10	92	-114	2	1	-2	1664	-1748	5	1	6	93	-127	8	1	-6	246	-220
2	0	-12	-58	42	8	0	-12	162	159	2	1	-3	668	594	5	1	7	-63	-14	8	1	-7	179	121
2	0	-14	656	-647	9	0	2	330	-336	2	1	-4	244	-208	5	1	8	-64	39	8	1	-8	-56	19
2	0	-16	136	136	9	0	4	-40	48	2	1	-5	608	558	5	1	9	-65	33	8	1	-9	-54	3
2	0	-18	144	112	9	0	6	84	-125	2	1	-6	358	-340	5	1	10	-64	64	8	1	-10	-51	-85
2	0	-20	360	394	9	0	-2	-50	-16	2	1	-7	1332	1454	5	1	11	-63	21	8	1	-11	213	266
3	0	2	330	265	9	0	-4	148	156	2	1	-8	1013	1068	5	1	12	-60	-9	8	1	-12	109	106
3	0	4	1705	1829	9	0	-6	332	-309	2	1	-9	573	-777	5	1	13	110	86	8	1	-13	146	-109
3	0	6	921	-862	1	1	0	807	-726	2	1	-10	-54	12	5	1	14	-52	-28	1	2	0	600	-550
3	0	8	2032	-2225	2	1	0	1219	1263	2	1	-11	406	-445	5	1	-1	55	-81	2	2	0	65	31
3	0	10	420	-418	3	1	0	80	-93	2	1	-12	-60	15	5	1	-2	451	-493	3	2	0	135	94
3	0	12	179	176	4	1	0	54	55	2	1	-13	456	-480	5	1	-3	935	1068	4	2	0	128	94
3	0	14	-64	30	5	1	0	-56	-42	2	1	-14	542	-512	5	1	-4	542	603	5	2	0	213	214
3	0	16	87	42	6	1	0	98	-126	2	1	-15	519	439	5	1	-6	102	67	6	2	0	149	-116
3	0	18	109	106	7	1	0	121	-126	2	1	-16	123	125	5	1	-7	156	-169	7	2	0	-80	-14
3	0	-2	1996	-2028	8	1	0	90	92	2	1	-17	149	133	5	1	-8	348	371	8	2	0	-70	-53
3	0	-4	45	-20	9	1	0	-46	19	2	1	-18	-57	36	5	1	-9	717	-760	9	2	0	-50	26
3	0	-6	135	107	0	1	2	47	-38	2	1	-19	-51	45	5	1	-10	619	-671	0	2	2	313	280
3	0	-8	1605	1491	0	1	3	329	268	3	1	1	245	-222	5	1	-11	347	358	0	2	3	564	-517
3	0	-10	341	-359	0	1	4	39	-18	3	1	2	94	68	5	1	-12	-65	40	0	2	4	280	-253
3	0	-12	193	-234	0	1	5	505	430	3	1	3	240	-201	5	1	-13	156	171	0	2	5	796	-764
3	0	-14	252	-253	0	1	6	822	-709	3	1	4	405	368	5	1	-14	-62	-19	0	2	6	709	-610
3	0	-16	-63	-12	0	1	7	1212	-1144	3	1	5	831	870	5	1	-15	222	216	0	2	7	1155	1223
3	0	-18	109	74	0	1	8	445	375	3	1	6	263	-217	5	1	-16	246	222	0	2	8	145	122
3	0	-20	-42	-17	0	1	9	270	-257	3	1	7	205	205	5	1	-17	157	-149	0	2	9	187	179
4	0	2	105	104	0	1	10	206	165	3	1	8	188	-194	5	1	-18	-44	-17	0	2	10	185	184
4	0	4	118	98	0	1	11	97	-92	3	1	9	66	-11	6	1	1	-62	5	0	2	11	128	106
4	0	6	-55	-10	0	1	12	563	532	3	1	10	435	-434	6	1	2	253	-268	0	2	12	95	75
4	0	8	158	-122	0	1	13	1053	1050	3	1	11	896	-943	6	1	3	268	-277	0	2	13	372	-359
4	0	10	530	-529	0	1	14	454	-433	3	1	12	438	448	6	1	4	259	255	0	2	14	-81	65
4	0	12	174	179	0	1	15	-65	-41	3	1	13	79	114	6	1	5	102	-89	0	2	15	-80	-6
4	0	14	208	215	0	1	16	131	-116	3	1	14	105	107	6	1	6	107	96	0	2	16	-77	-46
4	0	16	365	375	0	1	17	140	-142	3	1	15	148	160	6	1	7	-64	9	0	2	17	-72	-13
4	0	18	249	-290	0	1	18	186	-174	3	1	16	168	144	6	1	8	267	245	0	2	18	-65	-20
4	0	-2	1088	1059	0	1	19	427	-442	3	1	17	396	425	6	1	9	420	442	0	2	19	84	-93
4	0	-4	648	-668	0	1	20	224	231	3	1	18	286	-271	6	1	10	365	-346	1	2	1	428	380
4	0	-6	241	-258	1	1	1	923	-806	3	1	19	148	-162	6	1	11	-56	-59	1	2	2	184	-134
4	0	-8	856	-920	1	1	2	330	-241	3	1	-1	89	-75	6	1	12	-52	-42	1	2	3	136	111
4	0	-10	761	643	1	1	3	960	-862	3	1	-2	388	362	6	1	13	-46	-84	1	2	4	-48	37
4	0	-12	207	249	1	1	4	553	-472	3	1	-3	222	-194	6	1	14	76	-55	1	2	5	171	136
4	0	-14	354	383	1	1	5	1698	-1902	3	1	-4	142	-138	6	1	-1	139	137	1	2	6	-56	-55
4	0	-16	545	-562	1	1	6	1088	1392	3	1	-5	98	-85	6	1	-2	87	44	1	2	7	104	72
4	0	-18	-52	-72	1	1	7	1260	1335	3	1	-6	-46	46	6	1	-3	183	-183	1	2	8	-64	-22
5	0	2	527	554	1	1	8	158	-150	3	1	-7	420	-429	6	1	-4	-62	-4	1	2	9	180	159
5	0	4	867	-917	1	1	9	573	572	3	1	-8	692	-734	6	1	-5	237	239	1	2	10	102	74
5	0	6	243	-237	1	1	10	-54	-18	3	1	-9	763	801	6	1	-6	84	72	1	2	11	314	334
5	0	8	248	-228	1	1	11	593	555	3	1	-10	374	361	6	1	-7	-64	-4	1	2	12	214	180
5	0	10	765	788	1	1	12	622	-540	3	1	-11	103	134	6	1	-8	120	-108	1	2	13	582	-581
5	0	12	-61	5	1	1	13	767	-724	3	1	-12	111	97	6	1	-9	285	293	1	2	14	-81	44

Table 6. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
1	2	15	-79	-92	4	2	2	-67	55	7	2	7	-69	63	1	3-17	-58	61	4	3-10	161	163
1	2	16	130	-122	4	2	3	198	-173	7	2	8	-65	56	1	3-18	-50	-27	4	3-11	-72	-43
1	2	17	148	-115	4	2	4	111	-127	7	2	9	243	-242	1	3-19	-40	-48	4	3-12	123	82
1	2	18	177	-157	4	2	5	-72	26	7	2	10	-54	-4	2	3	1	273	-302	4	3-13	-69	26
1	2	19	405	405	4	2	6	-75	93	7	2	11	-46	-9	2	3	2	364	340	4	3-14	-66	-85
1	2	-1	1405	-1358	4	2	7	173	-151	7	2	-1	-80	-80	2	3	3	168	146	4	3-15	-62	-9
1	2	-2	400	330	4	2	8	-79	-69	7	2	-2	-80	11	2	3	4	670	622	4	3-16	228	175
1	2	-3	93	-65	4	2	9	179	-173	7	2	-3	268	222	2	3	5	71	-66	4	3-17	-48	40
1	2	-4	457	420	4	2	10	221	-178	7	2	-4	169	-128	2	3	6	511	-584	5	3	1	99	-124
1	2	-5	214	-184	4	2	11	424	389	7	2	-5	382	-343	2	3	7	-64	39	5	3	2	329	-322
1	2	-6	335	331	4	2	12	-78	52	7	2	-6	-79	53	2	3	8	-67	-19	5	3	3	209	162
1	2	-7	1443	1818	4	2	13	112	118	7	2	-7	-78	69	2	3	9	-69	-41	5	3	4	434	393
1	2	-8	356	-379	4	2	14	148	104	7	2	-8	108	71	2	3	10	-71	-1	5	3	5	153	-150
1	2	-9	437	-404	4	2	15	-63	54	7	2	-10	-72	66	2	3	11	-72	-24	5	3	6	-72	-22
1	2	-10	307	-340	4	2	16	115	101	7	2	-11	349	400	2	3	12	169	-171	5	3	7	-71	54
1	2	-11	206	-213	4	2	17	325	-369	7	2	-12	-65	-43	2	3	13	-70	46	5	3	8	-70	59
1	2	-12	128	-98	4	2	-1	476	-537	7	2	-13	-60	-85	2	3	14	-67	15	5	3	9	-68	20
1	2	-13	556	-543	4	2	-2	312	300	8	2	1	291	274	2	3	15	-63	5	5	3	10	-65	-59
1	2	-14	391	302	4	2	-3	913	1043	8	2	2	-67	78	2	3	16	-56	30	5	3	11	-61	-36
1	2	-15	466	423	4	2	-4	188	-156	8	2	3	150	-153	2	3	17	-48	48	5	3	12	-56	100
1	2	-16	134	108	4	2	-5	-68	-47	8	2	4	-63	65	2	3	18	214	232	5	3	13	-49	25
1	2	-17	178	160	4	2	-6	221	-232	8	2	5	-59	-15	2	3	-1	467	438	5	3	-1	147	156
1	2	-18	-66	-19	4	2	-7	252	266	8	2	6	-55	-2	2	3	-2	1420	-1256	5	3	-2	586	-681
1	2	-19	228	235	4	2	-8	312	-323	8	2	7	226	-251	2	3	-3	378	-328	5	3	-3	199	-177
1	2	-20	-46	-79	4	2	-9	937	-1129	8	2	8	-43	-57	2	3	-4	378	-388	5	3	-4	637	799
2	2	1	74	-73	4	2	-10	312	330	8	2	-1	-71	29	2	3	-5	234	232	5	3	-5	112	130
2	2	2	357	-346	4	2	-11	230	213	8	2	-2	-71	-50	2	3	-6	460	-443	5	3	-6	129	147
2	2	3	-51	16	4	2	-12	166	179	8	2	-3	-71	-6	2	3	-7	288	-315	5	3	-7	148	-159
2	2	4	378	-295	4	2	-13	-80	42	8	2	-4	-70	29	2	3	-8	1310	1396	5	3	-8	246	252
2	2	5	1366	1492	4	2	-14	-79	57	8	2	-5	-70	-94	2	3	-9	184	229	5	3	-9	208	224
2	2	6	428	429	4	2	-15	656	600	8	2	-6	-68	-41	2	3-10		-69	6	5	3-10	493	-570
2	2	7	383	-375	4	2	-16	212	-175	8	2	-7	-67	-39	2	3-11		112	-97	5	3-11	121	-157
2	2	8	248	318	4	2	-17	259	-225	8	2	-8	-64	26	2	3-12		119	-66	5	3-12	-68	-62
2	2	9	248	-260	4	2	-18	-57	-61	8	2	-9	-61	61	2	3-13		199	176	5	3-13	-64	69
2	2	10	-75	58	4	2	-19	106	-83	8	2	-10	-58	-5	2	3-14		572	-538	5	3-14	-60	-22
2	2	11	565	-576	5	2	1	-74	-44	9	2	1	266	-268	2	3-15		156	-162	5	3-15	-55	-60
2	2	12	360	-321	5	2	2	140	118	9	2	2	-46	16	2	3-16		-63	58	5	3-16	203	249
2	2	13	557	513	5	2	3	842	-1009	9	2	3	59	95	2	3-17		-57	29	6	3	1	-72	4
2	2	14	165	-141	5	2	4	301	-291	9	2	4	-69	-46	2	3-18		-49	82	6	3	2	214	-192
2	2	15	244	188	5	2	5	418	400	9	2	5	-22	-47	2	3-19		-38	-26	6	3	3	-71	27
2	2	16	-72	40	5	2	6	188	-188	1	3	0	1484	-1720	3	3	1	-57	2	6	3	4	150	113
2	2	17	297	274	5	2	7	238	199	2	3	0	733	761	3	3	2	181	146	6	3	5	-69	-49
2	2	18	178	147	5	2	8	-81	-33	3	3	0	79	-57	3	3	3	148	148	6	3	6	167	165
2	2	19	209	-233	5	2	9	572	664	4	3	0	205	242	3	3	4	518	555	6	3	7	-66	61
2	2	-1	860	-873	5	2	10	345	322	5	3	0	116	-105	3	3	5	320	-290	6	3	8	243	255
2	2	-2	-47	-68	5	2	11	528	-507	6	3	0	-72	-96	3	3	6	348	-315	6	3	9	-59	-66
2	2	-3	154	110	5	2	12	-71	16	7	3	0	77	-41	3	3	7	123	124	6	3	10	317	-304
2	2	-4	114	110	5	2	13	113	-103	8	3	0	199	184	3	3	8	247	-299	6	3	11	83	46
2	2	-5	115	111	5	2	14	-58	-59	0	3	2	59	-25	3	3	9	113	-97	6	3	12	70	-92
2	2	-6	-57	34	5	2	15	212	-190	0	3	3	59	52	3	3	10	487	-514	6	3	-1	-72	-52
2	2	-7	266	-240	5	2	-1	-73	5	0	3	4	141	-121	3	3	11	273	248	6	3	-2	102	117
2	2	-8	175	159	5	2	-2	205	188	0	3	5	205	-187	3	3	12	512	514	6	3	-3	114	105
2	2	-9	287	374	5	2	-3	523	535	0	3	6	822	-839	3	3	13	173	-180	6	3	-4	235	-203
2	2	-10	-72	27	5	2	-4	199	-182	0	3	7	366	281	3	3	14	213	189	6	3	-5	119	-101
2	2	-11	-75	73	5	2	-5	-75	-9	0	3	8	460	435	3	3	15	84	56	6	3	-6	134	100
2	2	-12	-78	-63	5	2	-6	93	-65	0	3	9	182	-155	3	3	16	145	164	6	3	-7	-71	79
2	2	-13	368	380	5	2	-7	150	-152	0	3	10	346	304	3	3	17	93	-91	6	3	-8	-70	-87
2	2	-14	310	-294	5	2	-8	-79	56	0	3	11	140	150	3	3	-1	126	102	6	3	-9	119	-125
2	2	-15	550	-553	5	2	-9	124	104	0	3	12	716	672	3	3	-2	159	127	6	3-10		312	317
2	2	-16	-77	86	5	2-10		99	-109	0	3	13	285	-255	3	3	-3	257	-48	6	3-11		101	145
2	2	-17	-72	-72	5	2-11		151	-142	0	3	14	549	-590	3	3	-4	113	-89	6	3-12		128	-163
2	2	-18	98	100	5	2-12		-80	4	0	3	15	144	134	3	3	-5	129	-126	6	3-13		-56	-89
2	2	-19	120	-111	5	2-13		-78	32	0	3	16	231	-201	3	3	-6	-62	60	6	3-14		-50	-12
2	2	-20	110	96	5	2-14		-75	11	0	3	17	-57	-43	3	3	-7	129	127	6	3-15		-43	80
3	2	1	443	356	5	2-15		268	-242	0	3	18	188	-176	3	3	-8	570	-709	7	3	1	182	164
3	2	2	373	365	5	2-16		-64	100	0	3	19	113	118	3	3	-9	-69	-89	7	3	2	454	471
3	2	3	729	735	5	2-17		289	245	1	3	1	492	410	3	3-10		206	295	7	3	3	224	-210
3	2	4	504	467	6	2	1	352	-323	1	3	2	424	-378	3	3-11		113	114	7	3	4	108	-104
3	2	5	1302	-1553	6	2	2	365	-318	1	3	3	198	-196	3	3-12		156	147	7	3	5	-60	90
3	2	6	165	-117	6	2	3	751	745	1	3	4	329	-273	3	3-13		164	-136	7	3	6	-57	-20
3	2	7	112	63	6	2	4	240	170	1	3	5	587	574	3	3-14		478	492	7	3	7	-53	-57
3	2	8	209	-230	6	2	5	195	-124	1	3	6	1189	1543	3	3-15		139	118	7	3	8	312	-350
3	2	9	-76	-58	6	2	6	-80	71	1	3	7	592	-559	3	3-16		330	-324	7	3	9	104	108
3	2	10	229	-153	6	2	7	118	91	1	3	8	-63	17	3	3-17		-54	-76	7	3	-1	-68	-70
3	2	11	498	504	6	2	8	-77	55	1	3	9	145	152	3	3-18		127	-123	7	3	-2	-68	-10
3	2	12	225	202	6	2	9	346	-325	1	3	10	109	-115	4	3	1	157	164	7	3	-3	107	109
3	2	13	137	-107	6	2	10	-70	-2	1	3	11	164	-170	4	3	2	257	205	7	3	-4	394	-412
3	2	14	-76	-11	6	2	11	158	139	1	3	12	772	-788	4	3	3	179	-166	7	3	-5	115	-96
3	2	15	-72	-20	6	2	12	-58	-36	1	3	13	267	249	4	3	4	1221	-1202	7	3	-6	149	126
3	2	16	-65	-32	6	2	13	-50	-40	1	3	14	251	208	4	3	5	207	181	7	3	-7	-64	11
3	2	-1	1439	1587	6	2	-1	-79	-21	1	3	15	-66	-74	4	3	6	154	148	7	3	-8	108	109
3	2	-2	860	-986	6	2	-2	-79	52	1	3	16	84	93	4	3	7	143	-143	7	3	-9	-60	-24
3	2	-3	1100	-1287	6	2	-3	708	-819	1	3	17	-54	15	4	3	8	108	93	7	3-10		-57	19
3	2	-4	-58	-47	6	2	-4	255	202	1	3	18	136	110	4	3	9	139	134	7	3-11		-53	55
3	2	-5	412	-445	6	2	-5	580	557	1	3	-1	672	-595	4	3	10	627	581	7	3-12		-48	42
3	2	-6	284	278	6	2	-6	139	87	1	3	-2	947	882	4	3	11	132	-123	7	3-13		-42	-10
3	2	-7	673	-727	6	2	-7	156	119	1	3	-3	207	185	4	3	12	199	-163	8	3	1	103	-90
3	2	-8	312	250	6	2	-8	-81	-38	1	3	-4	576	462	4	3	13	-60	80	8	3	2	254	-274
3	2	-9	833	954	6	2	-9	342	326	1	3	-5	168	-162	4	3	14	-54	-82	8	3	3	85	80
3	2-10		-75	38	6	2-10		275	-210	1	3	-6	422	431	4	3	15	-46	-45	8	3	4	-46	98
3	2-11		128	118	6	2-11		341	-315	1	3	-7	434	410	4	3	16	124	-152	8	3	5	-42	-40
3	2-12		148	-126	6	2-12		-75	37	1	3	-8	329	-300	4	3	-1	271	-257	8	3	6	-36	-39
3	2-13		-80	39	6	2-13		-71	-87	1	3	-9	197	-190	4	3	-2	627	808	8	3	-1	-55	82
3	2-14		150	-90	6	2-14		-67	55	1	3-10		117	-109	4	3	-3	247	250	8	3	-2	-56	-1
3	2-15		217	-153	7	2	1	-79	91	1	3-11		-70	-36	4	3	-4	290	-283	8	3	-3	153	-155
3	2-16		-75	30	7	2	2	-79	-30	1	3-12		-72	13	4	3	-5	105	-117	8	3	-4	230	243
3	2-17		-70	-35	7	2	3	-78	-36	1	3-13		-72	-10	4	3	-6	201	-232	8	3	-5	197	197
3	2-18		-62	-9	7	2	4	-76	33	1	3-14		151	-130	4	3	-7	-69	62	8	3	-6	217	-249
4	2	1	80	44	7	2	5	129	118	1	3-15		-68	-4	4	3	-8	270	-309	8	3	-7	107	-115
					7	2	6	-72	23	1	3-16		-64	-38	4	3	-9	-71	-23	8	3	-8	-48	-14

0.12 Å shorter than the sum of the covalent radii for selenium and hydrogen.[6]

It is interesting to note (*cf.* Fig. 3) that the environment of each of the three selenium atoms is roughly square planar.

EXPERIMENTAL

The unit cell dimensions for crystals of 6a-selenaselenophthene were determined from high-order reflections on *h0l* and *0kl* Weissenberg photographs, where sodium chloride powder lines had been superimposed for reference ($a_{NaCl} = 5.6394$ Å). A least squares procedure on 39 measured 2θ-values gave $a = 7.842(3)$ Å, $b = 5.660(2)$ Å, $c = 16.749(5)$ Å, and $\beta = 98.39(3)°$.

Four molecules per unit cell give a calculated density of 2.717 g/cm³ as compared with the density, 2.70–2.75 g/cm³, found by flotation.

The intensities of the *h0l*–*h3l* and *0kl* reflections were estimated visually from Weissenberg photographs taken with Ni-filtered Cu$K\alpha$ radiation ($\mu = 200.9$ cm^{-1}). *0kl* reflections from the zero layer about *a* were used for scaling only.

The crystals were rather irregularly shaped. One with dimensions roughly about $0.01 \times 0.4 \times 0.01$ mm in the three axial directions was used for the intensity data collection. Lp corrections were applied, but absorption corrections were not carried out.

The scattering factors used for selenium, carbon, and hydrogen in the structure factor calculations were those given in the *International Tables*.[13] The selenium scattering curve was corrected for anomalous dispersion, using the $\Delta f'$ and $\Delta f''$ values, given by Cromer.[14]

The hydrogen atoms in the molecule are bonded to sp^2-hybridized carbon, and their positions could therefore be estimated by assuming a C–H distance of 1.05 Å and C–C–H angles of 120°. The hydrogen positions were not refined.

The final atomic coordinates are listed in Table 4, and the temperature parameters are listed in Table 5. The final list of structure factors is given in Table 6.

Acknowledgements. The authors are indebted to Dr. D. H. Reid, Department of Chemistry, The University, St. Andrews, Scotland, for providing a sample of 6a-selenaselenophthene.

REFERENCES

1. Foss, O. and Hauge, S. *Acta Chem. Scand.* **17** (1963) 1807.
2. Hauge, S. *Acta Chem. Scand.* **25** (1971) 1134.
3. Hauge, S. and Sletten, J. *Acta Chem. Scand. To be published.*
4. Hauge, S., Opedal, D. and Aarskog, J. *Acta Chem. Scand.* **24** (1969) 1107.
5. Foss, O. In Anderson, P., Bastiansen, O. and Furberg, S. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 145.
6. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
7. Jackson, M. G. and Reid, D. H. *J. Chem. Soc. To be published.*
8. Bezzi, S., Mammi, M. and Garbuglio, C. *Nature* **182** (1958) 247.
9. Klingsberg, E. *Quart. Rev. (London)* **23** (1969) 537.
10. Hansen, L. K. and Hordvik, A. *Acta Chem. Scand. To be published.*
11. Hansen, L. K. and Hordvik, A. *Acta Chem. Scand.* **24** (1970) 2246.
12. Hordvik, A. *Acta Chem. Scand.* **20** (1966) 1885.
13. *International Tables for X-Ray, Crystallography*, Kynoch Press Birmingham 1962, Vol. III, p. 202.
14. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.

Received December 9, 1970.