

## The Crystal Structure of Selenium Bis(diethyl-dithiocarbamate)

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The structure of selenium bis(diethyldithiocarbamate),  $\text{Se}[\text{Et}_2\text{NCS}_2]_2$ , has been determined by means of three-dimensional X-ray methods. The yellow crystals are orthorhombic with  $a=9.711 \pm 0.005 \text{ \AA}$ ,  $b=25.533 \pm 0.010 \text{ \AA}$ ,  $c=6.655 \pm 0.005 \text{ \AA}$ ,  $Z=4$  and space group  $D_{2h}^4-P2_12_12_1$ . The density of the crystals is calc. 1.52, found 1.50 g/cm<sup>3</sup>.

Using  $\text{CuK}\alpha$  radiation and multiple-film Weissenberg techniques, 1236 intensities were estimated visually. The structure was refined by full-matrix least squares methods to a conventional  $R$  value of 6.2 %.

The molecules are monomeric, each selenium atom being bonded to all four sulphur atoms of the two ligands in the molecule, forming an asymmetric, planar complex. Some relevant bond lengths and angles are,  $\text{Se}-\text{S}_1=2.312 \pm 0.005 \text{ \AA}$ ,  $\text{Se}-\text{S}_2=2.719 \pm 0.005 \text{ \AA}$ ,  $\text{Se}-\text{S}_3=2.332 \pm 0.004 \text{ \AA}$ ,  $\text{Se}-\text{S}_4=2.779 \pm 0.005 \text{ \AA}$ ,  $\angle \text{S}_1-\text{Se}-\text{S}_2=70.9 \pm 0.2^\circ$ ,  $\angle \text{S}_1-\text{Se}-\text{S}_3=87.7 \pm 0.2^\circ$ ,  $\angle \text{S}_3-\text{Se}-\text{S}_4=70.9 \pm 0.2^\circ$  and  $\angle \text{S}_2-\text{Se}-\text{S}_4=131.5 \pm 0.2^\circ$ . The  $\text{C}_1-\text{N}_1$  and  $\text{C}_6-\text{N}_2$  bond lengths are 1.33 and 1.38  $\text{\AA}$ , respectively, indicating considerable double bond character for these bonds in accord with transfer of charge from nitrogen to sulphur atoms.

One of the four ethyl groups in a molecule seems to be oriented in two different ways, the result being a disordered structure with a statistical distribution of orientations.

The present structure investigation is part of the study undertaken in this laboratory of compounds of divalent tellurium and selenium with dithio and related anions.<sup>1-8</sup> The compounds whose structures have been determined so far,<sup>3,5-8</sup> all demonstrate the tendency of divalent tellurium and selenium to form planar four-coordinate structures. Only two of those structures, *viz.*, those of tellurium di(ethylxanthate)<sup>5</sup> and tellurium di(morpholylidithiocarbamate)<sup>8</sup> are four-coordinate complexes based on intramolecular bonds only. In the other structures, two weak intermolecular bonds complete the four-coordination. In the xanthate and dithiocarbamate, the average length of each of the two three-center systems S—Te—S consisting of two Te—S bonds *trans* ( $150^\circ$ ) to each other, was found to be 5.36  $\text{\AA}$ . Exactly the same length

has been found in centro-symmetrical *trans* tellurium complexes with thiourea or substituted thioureas as sulphur-containing ligands.<sup>9</sup>

For selenium, the data available from Se—Se—Se linear three-center systems found in triselenocyanate ions,<sup>9-12</sup> indicate a central selenium atom radius of 1.49 Å. It was expected that the structure of selenium bis(diethyl-dithiocarbamate) would be related to those of the analogous tellurium compounds,<sup>5,8</sup> and it would therefore be of interest to see if the length of the S—Se—S three-center system was close to that predicted (5.06 Å) from the selenium radius of 1.49 Å.

### EXPERIMENTAL

The preparation of selenium bis(diethyl-dithiocarbamate),<sup>13,14</sup>  $\text{Se}[\text{Et}_2\text{NCS}_2]_2$ , and its use in connection with analytical methods<sup>15</sup> have been reported. Crystals used in the present investigation were made by the procedure used to prepare divalent selenium bis(dialkyldithiophosphates) and bis(dialkyldithiophosphinates).<sup>1</sup> Russel also obtained selenium bis(diethyl-dithiocarbamate) by a similar method.<sup>13</sup> An aqueous solution of sodium diethyl-dithiocarbamate was added, with stirring, to selenious acid dissolved in 2 N hydrochloric acid, in the molar ratio 4:1. The resulting yellow oil was dissolved in warm benzene and cooled. The yellow crystals which formed, were dissolved in boiling alcohol. Upon cooling, yellow prisms crystallized out (m.p. 105°C).

The orthorhombic crystals are elongated along *c*. Unit cell data were computed from 62 high-order reflections, read from NaCl-calibrated Weissenberg *0kl* and *hk0* films, using a least squares program "CELLDIM". This program plus the other programs used in the computations were made available by the Weizmann Institute of Science, Rehovoth, Israel. They were modified for use on the IBM 360-50H computer at the University of Bergen, by Dr. Dove Rabinovich. The cell dimensions are,  $a = 9.711 \pm 0.005$  Å,  $b = 25.533 \pm 0.010$  Å and  $c = 6.655 \pm 0.005$  Å. There are four molecules per unit cell with density, calc. 1.52, found 1.50 g/cm<sup>3</sup>. From systematic extinctions, *h00*, *0k0*, and *00l* for *h*, *k*, and *l* odd, the space group is  $D_{2h}^4 - P2_12_12_1$ .

Integrated Weissenberg equi-inclination photographs were taken of the *0kl*, *1kl*, *hk0*, *hk1*, *hk2*, and *hk3* layers, using the multiple-film technique and Ni-filtered CuK radiation. Reflection intensities were estimated visually and 1236 out of 1471 independent reflections with  $\sin \theta \leq 0.985$  were observed and measured. (The reflection 020 was caught by the beam stop). The crystals used for the *a* and *c* axis photographs had cross-sections of  $0.10 \times 0.13$  and  $0.07 \times 0.09$  mm<sup>2</sup>, respectively. Usual Lorentz and polarization corrections were applied, but the intensities were not corrected for absorption ( $\mu = 78$  cm<sup>-1</sup>).

### STRUCTURE SOLVING

Patterson projections were computed along the *a* and *c* axes. From these, the *x* and *y* coordinates for the selenium and sulphur atoms were found; however, their *z* coordinates were difficult to ascertain. Fourier refinements and use of molecular models based upon assumed bond lengths and angles, enabled us to arrive at the proper solution. Further Fourier refinements gave all atomic positions except for the two carbon atoms of one of the four ethyl groups. The position of this group could therefore only be tentatively fixed.

At this stage of refinement, all reflections were brought to the same scale by comparison of reflections common to two layers. The structure was then further refined by means of full-matrix, least squares methods. The least squares program employed ("BDLS") minimizes the expression  $\sum w[|F_o| - |kF_c|]^2 / \sum wF_o^2$ , where *k* is a variable scale factor in the computation, and *w*, the relative weight assigned to a reflection, is equal to  $1/\sigma^2(F)$ .  $\sigma^2(F)$  is evaluated

as  $(ka_1)^2 + (a_2 F_o)^2 / 4w_o$ , where  $w_o$  is a weight factor related to the reliability with which the intensity of a given reflections is measured, and  $a_1$  and  $a_2$  are constants, here put equal to 2.0 and 1.0, respectively.

After a few cycles of refinement with isotropic temperature factors, the reliability index,  $R = \sum ||F_o - |F_c|| / \sum |F_o|$  had decreased to 0.085. Nevertheless, the bond lengths, angles and temperature parameters of the  $C_4-C_5$  ethyl group were obviously in error. A three-dimensional Fourier synthesis, based on reflections with signs determined from a structure factor calculation excluding  $C_4$  and  $C_5$  was then computed for the part of space where  $C_4$  and  $C_5$  could possibly be located. Four peaks corresponding to ca.  $1.5 - 2 e^-/\text{\AA}^3$  each were found, three of them overlapping. Putting  $C_4$  and  $C_5$  in positions corresponding to the two highest peaks gave reasonable bond lengths and angles. All reflections were then given a common scale factor after being rescaled by comparison between observed and calculated structure factors.

Anisotropic temperature factors were introduced for the heavy atoms; however, by further refinement  $C_4$  and  $C_5$  ended up much as before. Difference maps were then computed for the  $a$  and  $c$  axes projections, excluding  $C_4$  and  $C_5$  from the corresponding structure factor calculations. Four peaks corresponding to  $2 e^-/\text{\AA}^2$  each were found in the  $hk0$  map, and a wide electron density maximum corresponding to  $3.1 e^-/\text{\AA}^2$  was found in the suspect ethyl group region in the  $0kl$  map. Use of the molecular model, the three-dimensional Fourier and the two-dimensional difference Fourier maps finally gave as a result that there are two types of molecules, due to two different configurations of the  $C_4-C_5$  ethyl group, statistically distributed in the crystals. The two ethyl group configurations are related by rotation around the  $N_1-C_4$  bond; however, due to interatomic repulsions not only the  $C_5$  but also the  $C_4$  atom occupy different positions in the two configurations. These are called A and B, respectively, and A and B have been added as indices to the two atoms. Based on a statistical (1:1) distribution of the two types of molecules the structure refined satisfactorily, the  $R$ -value converging to 0.062. A final three-dimensional difference synthesis of the section of space around the above ethyl group showed no maxima or minima larger than  $0.4 e/\text{\AA}^3$ .

Final observed and calculated structure factors are listed in Table 1. Atomic scattering factors for selenium, sulphur, nitrogen, and carbon listed in *International Tables*<sup>16</sup> were used. The atomic scattering factors for selenium and sulphur were corrected for anomalous dispersion according to Cromer,<sup>17</sup> using  $f'$  and  $f''$  values from the *International Tables*.<sup>18</sup> Final positional parameters are listed in Table 2, while the components of atomic vibration tensors are listed in Table 3. Interatomic distances and angles based on coordinates from Table 2 are listed in Tables 4-6.

#### THE STRUCTURE OF THE SELENIUM BIS(DIETHYLDITHIOCARBAMATE) MOLECULE

One molecule of selenium bis(diethyldithiocarbamate),  $\text{Se}[\text{Et}_2\text{NCS}]_2$ , represents an asymmetric unit. In Fig. 1 the molecules are viewed along the  $a$  axis, and in Fig. 2 along the  $c$  axis. In the latter figure, some intermolecular distances are indicated to illustrate the packing of the molecules in the crystals.

**Table 1.** Observed and calculated  $0kl$ ,  $1kl$ ,  $hk0$ ,  $hk1$ ,  $hk2$  and  $hk3$  structure factors ( $\times 10$ ). Negative  $F_o$  values indicate that the corresponding reflection is unobserved.

H	K	L	$F_o$	$F_c$	H	K	L	$F_o$	$F_c$	H	K	L	$F_o$	$F_c$	H	K	L	$F_o$	$F_c$
0	4	0	1022	1330	0	20	3	-81	38	0	11	7	213	218	1	14	3	335	337
0	6	0	410	411	0	21	3	-81	0	0	12	7	-63	19	1	15	3	-65	63
0	9	0	113	117	0	22	3	133	133	0	13	7	61	66	1	16	3	371	397
0	10	0	319	319	0	23	3	-78	12	0	14	7	-58	11	1	17	3	113	111
0	12	0	215	251	0	24	3	189	183	0	15	7	167	160	1	18	3	280	280
0	18	0	466	466	0	25	3	-73	2	0	16	7	-50	43	1	19	3	155	155
0	16	0	305	287	0	26	3	-68	67	0	17	7	-45	45	1	20	3	133	133
0	18	0	940	877	0	27	3	133	126	0	18	8	105	124	1	21	3	165	181
0	20	0	-77	61	0	28	3	167	170	0	19	8	116	107	1	22	3	159	167
0	22	0	426	388	0	29	3	-50	8	0	20	8	-54	37	1	23	3	260	258
0	24	0	-91	7	0	30	3	87	99	0	21	8	-54	71	1	24	3	-65	39
0	26	0	212	220	0	30	4	377	313	0	22	8	91	100	1	25	3	126	116
0	28	0	105	109	0	31	4	541	566	0	23	8	-52	25	1	26	3	118	120
0	10	0	103	92	0	32	4	-64	47	0	24	8	83	93	1	27	3	115	119
0	32	0	60	79	0	33	4	712	675	0	27	8	-48	20	1	28	3	65	75
0	1	1	119	1242	0	34	4	-65	21	0	28	8	102	131	1	29	3	78	77
0	3	1	1319	1376	0	35	5	650	500	0	29	8	-13	16	1	30	3	86	107
0	3	1	956	956	0	36	5	22	67	0	30	9	120	120	1	30	4	381	358
0	9	1	91	79	0	37	4	432	408	0	31	1	155	203	1	14	4	615	592
0	5	1	574	480	0	38	4	364	345	1	1	1	527	531	1	12	4	111	108
0	6	1	156	156	0	39	4	661	632	1	2	1	425	412	1	3	4	783	769
0	7	1	85	63	0	40	4	307	299	1	3	1	105	112	1	4	4	372	353
0	9	1	457	445	0	41	4	286	277	1	4	1	1279	1308	1	5	4	343	331
0	9	1	184	197	0	42	4	178	180	1	5	1	1221	1239	1	6	4	348	336
0	10	1	299	293	0	43	4	182	202	1	6	1	257	199	1	7	4	389	405
0	11	1	295	364	0	44	4	206	189	1	7	1	588	611	1	8	4	322	326
0	12	1	464	450	0	45	4	358	340	1	8	1	368	335	1	9	4	193	191
0	13	1	262	263	0	46	4	-80	35	1	9	1	681	666	1	10	4	530	519
0	14	1	155	160	0	47	4	170	186	1	10	1	200	198	1	11	4	252	277
0	15	1	401	391	0	48	4	184	194	1	11	1	224	225	1	12	4	174	173
0	17	1	272	270	0	49	4	99	90	1	12	1	183	187	1	13	4	-67	47
0	17	1	-70	30	0	50	4	20	70	1	13	1	171	173	1	14	4	166	166
0	19	1	266	263	0	51	4	172	174	1	14	1	561	586	1	15	4	355	359
0	19	1	643	608	0	52	4	-75	64	1	15	1	220	176	1	16	4	121	125
0	20	1	-78	11	0	53	4	129	120	1	16	1	153	160	1	17	4	248	247
0	21	1	356	349	0	54	4	-68	55	1	17	1	467	432	1	18	4	-70	71
0	22	1	-90	32	0	55	4	25	41	1	18	1	352	329	1	19	4	187	198
0	23	1	304	298	0	56	4	-58	56	1	19	1	268	264	1	20	4	-69	79
0	24	1	-81	5	0	57	4	27	42	1	20	1	251	235	1	21	4	153	153
0	25	1	247	235	0	24	4	43	11	1	21	1	278	287	1	22	4	-65	15
0	26	1	-77	40	0	1	5	425	391	1	22	1	193	196	1	23	4	185	191
0	9	1	118	102	0	2	5	536	504	1	23	1	93	86	1	24	4	-59	37
0	24	1	-60	53	0	3	5	501	548	1	24	1	130	115	1	25	4	94	93
0	29	1	113	99	0	4	5	207	22	1	25	1	164	164	1	26	4	-50	111
0	30	1	-59	1	0	5	200	207	1	26	1	91	77	1	27	4	157	151	
0	31	1	61	71	0	6	5	461	403	1	27	1	140	142	1	28	4	-37	10
0	0	2	981	781	0	7	5	-78	17	1	28	1	60	59	1	0	5	358	329
0	1	2	203	199	0	8	5	-78	15	1	29	1	95	101	1	1	5	240	212
0	2	2	98	89	0	9	5	79	95	1	30	1	-49	48	1	2	5	154	130
0	3	2	169	155	0	10	5	259	242	1	31	1	119	132	1	3	5	314	338
0	4	2	-44	58	0	11	5	345	343	1	32	1	37	47	1	4	5	606	611
0	5	2	78	74	0	12	5	187	175	1	33	1	105	43	1	5	5	66	83
0	6	2	437	411	0	13	5	221	198	1	34	2	50	31	1	6	5	125	159
0	7	2	60	62	0	14	5	107	117	1	35	2	596	525	1	7	5	214	198
0	8	2	661	581	0	15	5	-81	43	1	36	2	610	578	1	8	5	503	498
0	9	2	1069	336	0	16	5	243	265	1	37	2	555	532	1	9	5	97	101
0	10	2	356	337	0	17	5	164	163	1	38	2	238	240	1	10	5	120	139
0	11	2	-59	76	0	18	5	196	176	1	39	2	75	175	1	21	5	236	235
0	12	2	661	646	0	19	5	-75	26	1	40	2	674	677	1	41	5	157	152
0	13	2	92	901	0	20	5	203	196	1	42	2	616	586	1	43	5	46	76
0	14	2	277	295	0	21	5	176	201	1	43	2	-46	12	1	44	5	171	183
0	15	2	226	213	0	22	5	-64	52	1	44	2	614	634	1	45	5	217	247
0	16	2	519	527	0	23	5	-60	2	1	45	2	711	703	1	46	5	109	121
0	17	2	390	372	0	24	5	199	207	1	47	2	368	346	1	47	5	68	72
0	18	2	311	298	0	25	6	198	177	1	48	2	195	182	1	48	5	214	224
0	19	2	184	187	0	1	6	191	194	1	49	2	541	528	1	5	129	141	141
0	20	2	231	273	0	2	6	114	111	1	50	2	537	542	1	20	5	-62	59
0	21	2	226	226	0	3	6	124	124	1	51	2	293	274	1	21	5	-59	35
0	22	2	150	155	0	4	6	81	43	1	52	2	277	258	1	22	5	189	213
0	23	2	-31	17	0	5	44	61	1	53	2	277	255	1	23	5	115	115	
0	24	2	-79	65	0	6	5	-81	19	1	54	2	275	228	1	24	5	50	80
0	25	2	-77	64	0	7	6	-81	25	1	55	2	215	228	1	25	5	70	81
0	26	2	231	218	0	8	6	97	72	1	56	2	241	247	1	26	5	76	93
0	27	2	133	190	0	9	6	180	195	1	57	2	234	222	1	27	5	-77	80
0	28	2	-65	34	0	10	6	62	72	1	58	3	555	519	1	11	6	99	80
0	29	2	-59	19	0	11	6	215	204	1	59	3	321	311	1	12	6	115	122
0	30	2	128	126	0	12	6	160	152	1	60	3	443	400	1	20	6	98	94
0	31	2	152	176	0	13	6	135	131	1	61	2	213	227	1	16	3	371	394
0	3	1	283	289	0	14	6	-75	73	1	62	2	213	227	1	17	3	371	394
0	2	1	-53	55	0	15	6	-73	57	1	63	2	214	205	1	18	2	101	131
0	3	1	372	284	0	16	6	113	129	1	64	2	212	202	1	19	2	222	236
0	4	1	373	371	0	17	6	185	195	1	65	2	210	207	1	20	2	106	116
0	5	1	421	376	0	18	6	149	149	1	66	2	207	202	1	21	2	95	105

Table 1. Continued.

R	K	L	T(0)	T(C)	R	K	L	T(0)	T(C)	R	K	L	T(0)	T(C)	R	K	L	T(0)	T(C)
3	4	0	381	328	6	19	0	-70	26	11	11	0	59	60	5	1	1	447	440
3	5	0	208	339	6	20	0	-89	23	11	12	0	55	51	5	2	1	882	871
3	6	0	106	164	6	21	0	-46	3	11	13	0	196	180	5	3	1	263	261
3	7	0	421	410	6	22	0	16	150	11	14	0	65	85	5	4	1	63	18
3	9	0	493	555	6	17	0	-50	42	12	12	0	-53	38	5	5	1	576	605
3	10	0	851	888	6	24	0	-75	7	12	12	0	-53	41	5	6	1	571	572
3	11	0	272	254	6	25	0	-70	12	12	2	0	52	12	5	7	1	449	460
3	12	0	315	304	6	26	0	101	103	12	3	0	125	138	5	8	1	189	212
3	13	0	1094	1067	7	2	0	523	544	12	5	0	-48	23	5	10	1	196	198
3	14	0	334	319	7	3	0	289	286	12	6	0	61	58	5	11	1	578	571
3	15	0	228	238	7	4	0	-43	72	12	7	0	151	158	5	12	1	260	264
3	16	0	-80	27	7	5	0	111	105	2	0	1	369	348	5	13	1	312	326
3	17	0	512	496	7	6	0	711	611	2	1	1	507	494	5	14	1	187	163
3	18	0	298	298	7	7	0	165	132	2	2	1	416	429	5	15	1	321	342
3	19	0	-80	30	7	8	0	211	189	2	3	1	324	265	5	16	1	322	313
3	20	0	296	303	7	9	0	47	89	2	12	1	175	219	5	17	1	212	217
3	21	0	159	353	7	10	0	275	265	5	5	1	188	185	5	18	1	159	148
3	22	0	-21	7	11	0	126	122	5	6	1	177	201	5	19	1	120	120	
3	23	0	-90	68	7	12	0	440	426	2	7	1	1012	1044	5	20	1	277	293
3	24	0	109	97	7	13	0	180	179	2	8	1	1205	1230	5	21	1	156	168
3	25	0	231	238	7	14	0	-21	26	2	9	1	510	511	5	22	1	152	158
3	26	0	93	95	7	15	0	157	144	2	10	1	372	407	5	23	1	112	123
3	27	0	221	241	7	16	0	228	243	2	11	1	909	878	5	24	1	209	223
3	28	0	-73	4	17	0	-89	48	2	12	1	727	707	5	25	1	-71	17	
3	29	0	-66	38	7	18	0	-88	7	2	13	1	190	172	5	26	1	111	123
3	30	0	118	11	7	19	0	105	88	2	14	1	430	410	5	27	1	-60	28
3	31	0	112	222	7	20	0	102	91	2	15	1	252	257	5	28	1	107	117
4	0	0	646	446	7	21	0	-76	24	2	16	1	304	300	5	29	1	54	71
4	1	0	317	409	7	22	0	-75	10	2	17	1	75	75	6	0	1	-69	18
4	2	0	250	261	7	23	0	-70	37	2	18	1	225	212	6	1	1	201	216
4	3	0	853	854	7	24	0	130	149	2	19	1	170	170	6	2	1	166	167
4	4	0	161	195	9	0	0	683	663	2	20	1	317	308	6	3	1	308	324
4	5	0	301	309	9	1	0	360	144	2	21	1	103	106	6	4	1	296	282
4	6	0	373	413	8	2	0	-89	0	2	22	1	210	208	6	5	1	316	319
4	7	0	639	621	9	3	0	118	126	2	23	1	112	98	6	6	1	398	412
4	8	0	610	357	9	4	0	507	899	2	24	1	229	242	6	7	1	570	579
4	9	0	98	71	9	5	0	100	171	2	25	1	136	134	6	8	1	340	350
4	10	0	308	258	9	6	0	-90	53	2	26	1	200	210	6	9	1	392	402
4	11	0	320	304	9	7	0	159	137	2	27	1	92	99	6	10	1	145	143
4	12	0	74	65	9	8	0	206	192	2	28	1	99	116	6	11	1	490	478
4	13	0	123	121	9	9	0	111	50	2	29	1	85	89	6	12	1	188	197
4	14	0	-79	2	10	0	-91	5	2	30	1	93	105	6	13	1	159	159	
4	15	0	207	624	9	11	0	129	130	2	31	1	143	143	6	14	1	255	255
4	16	0	-84	31	9	12	0	101	121	2	32	1	112	98	6	15	1	341	400
4	17	0	122	113	9	13	0	167	177	3	1	1	371	355	6	16	1	161	155
4	18	0	-93	38	9	14	0	165	163	3	2	1	1102	1195	6	17	1	-85	15
4	19	0	604	580	8	15	0	-88	24	3	1	1	535	521	6	18	1	201	200
4	20	0	187	167	8	16	0	-56	23	3	4	1	220	188	6	19	1	207	222
4	21	0	206	215	8	17	0	185	155	3	5	1	785	932	6	20	1	116	125
4	22	0	172	165	8	18	0	197	219	3	6	1	1016	1057	6	21	1	218	218
4	23	0	165	175	8	19	0	-77	13	3	7	1	421	425	6	22	1	163	167
4	24	0	-74	22	8	20	0	73	61	3	8	1	548	504	6	23	1	97	104
4	25	0	214	214	8	21	0	-69	23	3	9	1	302	261	6	24	1	139	145
4	26	0	148	135	8	22	0	230	217	3	10	1	567	552	6	25	1	90	110
4	27	0	74	85	9	1	0	128	114	3	11	1	461	425	6	26	1	100	100
4	28	0	-67	11	9	2	0	209	399	3	12	1	663	657	6	27	1	125	117
4	29	0	120	112	9	3	0	-91	17	3	13	1	534	525	6	28	1	56	56
5	1	0	744	742	9	4	0	262	224	3	14	1	109	201	7	0	1	588	604
5	2	0	467	458	9	5	0	296	264	3	15	1	474	432	7	1	1	124	95
5	3	0	356	355	9	6	0	111	92	3	16	1	314	318	7	2	1	124	98
5	4	0	147	141	9	7	0	-110	81	3	17	1	191	182	7	3	1	237	234
5	5	0	558	544	9	8	0	155	156	3	18	1	178	187	7	4	1	526	490
5	6	0	69	107	9	9	0	156	137	3	19	1	267	275	7	5	1	311	325
5	7	0	70	48	9	10	0	88	80	3	20	1	244	256	7	6	1	-80	44
5	8	0	-72	29	9	11	0	87	42	3	21	1	-85	23	7	7	1	190	175
5	9	0	324	324	9	12	0	111	93	3	22	1	259	250	7	8	1	255	257
5	10	0	335	324	9	13	0	138	137	3	23	1	111	104	7	9	1	594	584
5	11	0	103	101	9	14	0	100	73	3	24	1	219	216	7	10	1	93	123
5	12	0	160	159	9	15	0	79	53	3	25	1	200	74	7	11	1	36	36
5	13	0	409	162	9	16	0	173	166	3	26	1	76	83	7	12	1	206	207
5	14	0	519	519	9	17	0	155	154	3	27	1	-72	7	7	13	1	382	382
5	15	0	192	122	9	18	0	62	63	3	28	1	134	166	7	14	1	-85	83
5	16	0	116	129	9	19	0	-64	1	3	29	1	104	116	7	15	1	-85	18
5	17	0	348	343	9	20	0	232	241	3	30	1	-52	33	7	16	1	-84	77
5	18	0	195	163	9	21	0	105	104	3	31	1	1338	1528	7	17	1	263	265
5	19	0	120	136	9	22	0	122	116	3	32	1	547	527	7	18	1	172	160
5	20	0	354	342	9	23	0	-86	15	3	33	1	272	295	7	19	1	-75	25
5	21	0	129	129	9	24	0	-78	37	3	34	1	107	93	7	20	1	272	273
5	22	0	-26	10	3	25	0	100	124	4	21	1	788	805	7	21	1	136	146
5	23	0	66	57	4	22	0	100	172	5	21	1	284	254	7	22	1	21	21
5	24	0	184	190	5	23	0	55	59	4	22	1	1372	380	8	5	1	199	206
5	25	0	75	60	5	24	0	114	104	4	23	1	249	227	8	6	1	164	141
5	26	0	-73	32	5	25	0	167	162	4	24	1	181	192	8	7	1	-50	19
5	27	0	29	27	5	26	0	65	40	4	25	1	359	389	7	8	1	86	88
5	28</td																		

Table 1. Continued.

R	K	L	T(0)	F(C)	R	K	L	T(0)	F(C)	R	K	L	T(0)	F(C)	R	K	L	T(0)	F(C)
3	9	2	465	366	6	10	2	205	186	10	1	2	196	202	3	26	3	58	62
3	10	2	274	272	6	11	2	180	168	10	2	2	170	179	3	27	3	64	61
3	11	2	243	239	6	12	2	281	276	10	3	2	234	228	3	28	3	71	62
3	12	2	127	121	6	13	2	165	156	10	4	2	61	52	3	29	3	48	57
3	13	2	309	293	6	14	2	249	272	10	5	2	113	120	4	0	3	289	277
3	14	2	232	229	6	15	2	176	178	10	6	2	266	257	4	1	3	835	861
3	15	2	195	196	6	16	2	214	212	10	7	2	140	151	4	2	3	190	182
3	16	2	169	162	6	17	2	93	111	10	8	2	71	71	4	3	3	348	356
3	17	2	235	279	6	18	2	171	160	10	9	2	69	75	4	4	3	262	246
3	18	2	322	306	6	19	2	134	143	10	10	2	117	128	4	5	3	441	449
3	19	2	201	198	6	20	2	250	269	10	11	2	108	111	4	6	3	168	172
3	20	2	68	88	6	21	2	162	175	10	12	2	95	113	4	7	3	278	265
3	21	2	201	201	6	22	2	73	103	10	13	2	49	54	4	8	3	406	400
3	22	2	234	210	5	23	2	124	146	10	14	2	75	73	4	9	3	526	505
3	23	2	164	175	5	24	2	111	120	10	15	2	74	71	10	3	260	250	
3	24	2	65	70	5	25	2	128	150	10	16	2	43	48	4	11	3	135	146
3	25	2	148	151	6	26	2	59	70	10	17	2	68	79	4	12	3	547	540
3	26	2	-59	46	6	27	2	*1	152	11	9	2	240	259	4	13	3	498	495
3	27	2	82	87	7	2	2	265	247	11	1	2	95	113	4	14	3	177	170
3	28	2	-50	29	7	1	2	171	175	11	2	2	57	74	4	15	3	209	188
3	29	2	54	46	7	2	2	103	*2	11	3	2	117	126	4	16	3	241	265
3	30	2	41	59	7	3	2	274	273	11	4	2	141	144	4	17	3	204	193
3	31	2	173	175	7	4	2	131	136	11	5	2	103	106	4	18	3	66	90
4	1	2	885	878	7	5	2	-65	46	11	6	2	-48	37	4	19	3	120	119
4	2	2	458	456	7	6	2	133	134	11	7	2	80	78	4	20	3	118	127
4	3	2	765	765	7	7	2	141	126	11	8	2	74	74	4	21	3	158	150
4	4	2	176	173	7	8	2	94	104	11	9	2	76	76	4	22	3	166	164
4	5	2	500	514	7	9	2	-67	67	11	10	2	-40	35	4	23	3	66	68
4	6	2	543	519	7	10	2	269	257	11	11	2	50	44	4	24	3	62	63
4	7	2	475	506	7	11	2	76	79	11	12	2	-34	21	4	25	3	106	125
4	8	2	832	802	7	12	2	209	195	11	13	2	49	67	4	26	3	61	85
4	9	2	107	79	7	13	2	97	114	12	1	2	65	75	4	27	3	72	75
4	10	2	395	367	7	14	2	315	332	12	1	2	68	80	4	28	3	50	70
4	11	2	234	260	7	15	2	302	282	12	2	2	42	88	5	0	2	229	215
4	12	2	393	370	7	16	2	142	165	12	3	2	49	63	5	1	3	185	172
4	13	2	104	178	7	17	2	-65	34	2	0	3	594	622	5	2	3	113	109
4	14	2	98	113	7	18	2	191	187	2	1	3	774	937	5	3	3	257	248
4	15	2	164	110	7	19	2	255	269	2	2	3	655	712	5	4	3	431	426
4	16	2	318	300	7	20	2	102	123	2	3	3	473	478	5	5	3	336	308
4	17	2	296	296	7	21	2	79	92	2	3	3	412	437	5	6	3	178	192
4	18	2	96	117	7	22	2	97	100	2	4	3	53	62	5	7	3	131	122
4	19	2	167	165	7	23	2	72	73	2	6	3	293	279	5	8	3	596	595
4	20	2	63	69	7	24	2	112	122	2	7	3	810	374	5	9	3	85	86
4	21	2	166	172	7	25	2	90	102	2	8	3	385	361	5	10	3	343	323
4	22	2	-57	49	8	2	2	90	85	2	9	3	226	217	5	11	3	345	339
4	23	2	152	152	8	10	2	161	160	2	10	3	226	202	5	12	3	319	299
4	24	2	-62	65	8	2	2	107	97	2	11	3	237	244	5	13	3	134	128
4	25	2	88	92	8	3	2	96	67	2	12	3	163	152	5	14	3	258	249
4	26	2	-55	30	8	4	2	277	267	2	13	3	260	257	5	15	3	245	227
4	27	2	91	111	8	5	2	232	234	2	14	3	309	311	5	16	3	104	91
4	28	2	87	106	8	6	2	214	213	2	15	3	225	218	5	17	3	94	105
4	29	2	15	37	8	7	2	68	27	2	16	3	251	247	5	18	3	78	100
4	30	2	-51	5	8	8	2	243	260	2	17	3	240	226	5	19	3	145	166
5	1	2	278	303	8	9	2	155	224	2	18	3	182	172	5	20	3	-57	30
5	2	2	164	178	8	10	2	240	238	2	19	3	155	153	5	21	3	78	86
5	3	2	477	503	8	11	2	-69	51	2	20	3	236	228	5	22	3	59	44
5	4	2	379	376	8	12	2	184	177	2	21	3	270	284	5	23	3	118	149
5	5	2	310	296	8	13	2	327	320	2	22	3	72	82	5	24	3	46	58
5	6	2	215	206	8	14	2	289	279	2	23	3	242	257	5	25	3	104	116
5	7	2	425	421	8	15	2	63	72	2	24	3	62	81	5	26	3	79	97
5	8	2	408	415	8	16	2	125	139	2	25	3	178	191	5	27	3	85	97
5	9	2	124	139	8	17	2	132	146	2	26	3	50	58	6	0	3	145	138
5	10	2	252	240	8	18	2	180	146	2	27	3	42	101	6	1	3	438	445
5	11	2	372	364	8	19	2	54	67	2	28	3	50	45	6	2	3	315	329
5	12	2	371	363	8	20	2	80	99	2	29	3	42	100	6	3	3	312	319
5	13	2	160	152	8	21	2	64	65	3	0	3	184	181	6	4	3	161	152
5	14	2	279	276	8	22	2	59	71	3	1	3	633	704	6	5	3	322	299
5	15	2	-67	5	8	23	2	67	44	3	2	3	154	153	6	6	3	503	510
5	16	2	206	200	9	0	2	101	96	3	1	3	700	717	6	7	3	119	98
5	17	2	268	270	9	1	2	117	104	3	4	3	337	320	6	8	3	114	117
5	18	2	-97	105	9	2	2	166	170	3	5	3	294	257	6	9	3	91	85
5	19	2	131	139	9	3	2	83	103	3	6	3	294	243	6	10	3	259	242
5	20	2	106	129	9	4	2	211	216	3	7	3	556	544	6	11	3	163	144
5	21	2	211	244	9	5	2	136	126	3	8	3	310	319	6	12	3	179	184
5	22	2	78	87	9	6	2	67	94	3	9	3	125	136	6	13	3	94	107
5	23	2	144	165	9	7	2	339	320	3	10	3	224	220	6	14	3	128	123
5	24	2	-59	23	9	8	2	254	246	3	11	3	234	238	6	15	3	-59	51
5	25	2	121	131	9	9	2	138	139	3	12	3	517	500	6	16	3	142	118
5	26	2	119	122	9	10	2	127	135	3	13	3	52	53	6	17	2	224	226
5	27	2	70	85	9	11	2	167	160	3	14	3	371	364	6	18	3	122	109
5	28	2	38	61	9	12	2	136	140	3	15	3	404	394	6	19	3	122	135
5	29	2	125	156	9	13	2	94	120	3	16	3	201	186	6	20	3	136	146
6	1	2	142	159	9	14	2	91	105	3	17	3	220	208	6	21	3	158	154
6	2	2	190	203	9	15	2	-55	63	3	18	3	323	306	6	22	3	67	65
6																			

Table 2. Final coordinates in fractions of cell edges for selenium bis(diethyldithiocarbamate). Origin halfway between three mutually perpendicular and non-intersecting screw axes. Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Se	0.4312 (2)	0.1154 (1)	-0.0561 (3)
S <sub>1</sub>	0.2778 (4)	0.0946 (2)	-0.3096 (7)
S <sub>2</sub>	0.2165 (5)	0.0609 (2)	0.1026 (7)
S <sub>3</sub>	0.5627 (4)	0.1588 (2)	-0.2972 (7)
S <sub>4</sub>	0.6630 (5)	0.1592 (2)	0.1216 (7)
N <sub>1</sub>	0.0534 (14)	0.0420 (5)	-0.2111 (22)
N <sub>2</sub>	0.7887 (11)	0.2095 (4)	-0.1790 (20)
C <sub>1</sub>	0.1687 (15)	0.0621 (5)	-0.1373 (24)
C <sub>2</sub>	0.0161 (16)	0.0436 (5)	-0.4295 (28)
C <sub>3</sub>	-0.0617 (19)	0.0928 (6)	-0.4799 (29)
C <sub>4A</sub>	-0.0687 (44)	0.0287 (15)	-0.0727 (68)
C <sub>4B</sub>	-0.0203 (35)	-0.0030 (14)	-0.0816 (64)
C <sub>5A</sub>	-0.0754 (41)	-0.0308 (14)	-0.0751 (65)
C <sub>5B</sub>	-0.1472 (49)	0.0296 (17)	-0.0143 (77)
C <sub>6</sub>	0.6828 (14)	0.1779 (5)	-0.1143 (24)
C <sub>7</sub>	0.8058 (15)	0.2251 (5)	-0.3956 (26)
C <sub>8</sub>	0.7416 (17)	0.2780 (6)	-0.4407 (32)
C <sub>9</sub>	0.8908 (14)	0.2295 (5)	-0.0308 (26)
C <sub>10</sub>	1.0143 (19)	0.1923 (7)	-0.0230 (31)

A and B indicate atoms in the two ethyl group configurations resulting from disorder.

Table 3. Components of atomic vibration tensors,  $U \times 10^3$  in  $\text{\AA}^2$  with standard deviations, referred to crystallographic axes. For Se and S the expression is  $\exp\{-2\pi^2[U_{11}(ha^{-1})^2 + U_{22}(kb^{-1})^2 + U_{33}(lc^{-1})^2 + 2U_{12}hka^{-1}b^{-1} + 2U_{23}klb^{-1}c^{-1} + 2U_{13}hla^{-1}c^{-1}]\}$ . For the N and C atoms, the expression is  $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$ .

	<i>U</i> <sub>11</sub> ( <i>U</i> )	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>
Se	48.31 (0.69)	46.63 (0.64)	53.95 (1.05)	- 2.96 (0.70)	4.45 (0.77)	- 0.37 (1.06)
S <sub>1</sub>	51.81 (1.84)	57.35 (1.86)	54.66 (2.58)	- 9.16 (1.68)	6.15 (1.93)	5.22 (2.39)
S <sub>2</sub>	66.84 (2.35)	76.96 (2.44)	53.94 (2.79)	- 10.32 (2.12)	14.17 (2.25)	- 5.76 (3.11)
S <sub>3</sub>	51.24 (1.92)	68.13 (2.07)	54.84 (2.53)	- 13.09 (1.97)	2.72 (2.03)	- 4.46 (2.72)
S <sub>4</sub>	67.43 (2.36)	71.51 (2.34)	46.56 (2.48)	- 8.12 (2.05)	8.34 (2.10)	- 6.32 (2.81)
N <sub>1</sub>	65.27 (3.53)					
N <sub>2</sub>	45.30 (2.76)					
C <sub>1</sub>	50.56 (3.66)					
C <sub>2</sub>	58.61 (3.82)					
C <sub>3</sub>	80.24 (4.93)					
C <sub>4A</sub>	77.63 (10.13)					
C <sub>4B</sub>	69.96 (9.47)					
C <sub>5A</sub>	82.63 (10.31)					
C <sub>5B</sub>	110.83 (15.35)					
C <sub>6</sub>	46.59 (3.40)					
C <sub>7</sub>	52.57 (3.68)					
C <sub>8</sub>	73.24 (4.76)					
C <sub>9</sub>	54.88 (3.76)					
C <sub>10</sub>	81.91 (5.44)					

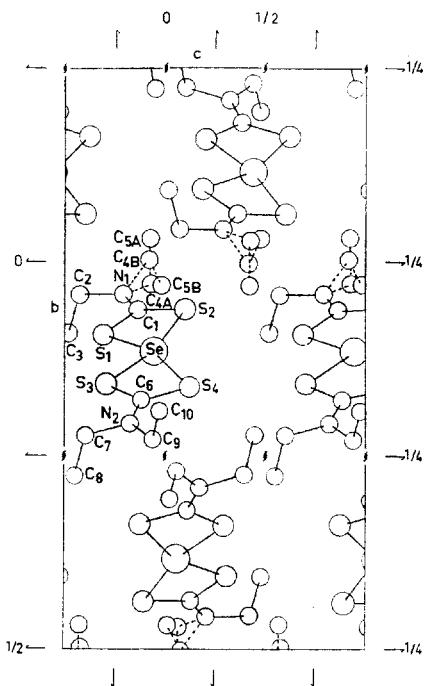
Table 4. Bond lengths and angles in selenium bis(diethyldithiocarbamate) with standard deviations in brackets.

Se—S <sub>1</sub>	2.312(5) Å	∠S <sub>1</sub> —Se—S <sub>2</sub>	70.9 (2)°
Se—S <sub>2</sub>	2.719(5)	∠S <sub>1</sub> —Se—S <sub>3</sub>	87.7 (2)
Se—S <sub>3</sub>	2.332(4)	∠S <sub>1</sub> —Se—S <sub>4</sub>	157.7 (2)
Se—S <sub>4</sub>	2.779(5)	∠S <sub>2</sub> —Se—S <sub>3</sub>	158.5 (2)
S <sub>1</sub> —C <sub>1</sub>	1.77(2)	∠S <sub>2</sub> —Se—S <sub>4</sub>	131.5 (2)
S <sub>2</sub> —C <sub>1</sub>	1.66(2)	∠S <sub>3</sub> —Se—S <sub>4</sub>	70.0 (1)
S <sub>3</sub> —C <sub>6</sub>	1.75(2)	∠Se—S <sub>1</sub> —C <sub>1</sub>	91.2 (5)
S <sub>4</sub> —C <sub>9</sub>	1.65(2)	∠Se—S <sub>2</sub> —C <sub>1</sub>	80.4 (5)
C <sub>1</sub> —N <sub>1</sub>	1.33(2)	∠Se—S <sub>3</sub> —C <sub>6</sub>	91.1 (5)
C <sub>6</sub> —N <sub>2</sub>	1.38(2)	∠Se—S <sub>4</sub> —C <sub>9</sub>	78.8 (5)
N <sub>1</sub> —C <sub>2</sub>	1.50(2)	∠S <sub>1</sub> —C <sub>1</sub> —S <sub>2</sub>	117.6 (9)
C <sub>2</sub> —C <sub>3</sub>	1.50(2)	∠S <sub>1</sub> —C <sub>1</sub> —N <sub>1</sub>	116.6(12)
N <sub>1</sub> —C <sub>4A</sub>	1.54(5)	∠S <sub>2</sub> —C <sub>1</sub> —N <sub>1</sub>	125.8(12)
C <sub>4A</sub> —C <sub>5A</sub>	1.52(5)	∠S <sub>3</sub> —C <sub>6</sub> —S <sub>4</sub>	120.1 (8)
N <sub>1</sub> —C <sub>4B</sub>	1.60(4)	∠S <sub>3</sub> —C <sub>6</sub> —N <sub>2</sub>	116.3(11)
C <sub>4B</sub> —C <sub>5B</sub>	1.55(6)	∠S <sub>4</sub> —C <sub>6</sub> —N <sub>2</sub>	123.6(11)
N <sub>2</sub> —C <sub>7</sub>	1.50(2)	∠C <sub>1</sub> —N <sub>1</sub> —C <sub>2</sub>	123.5(13)
C <sub>7</sub> —C <sub>8</sub>	1.52(2)	∠C <sub>1</sub> —N <sub>1</sub> —C <sub>4A</sub>	120.9(20)
N <sub>2</sub> —C <sub>9</sub>	1.49(2)	∠C <sub>1</sub> —N <sub>1</sub> —C <sub>4B</sub>	117.0(18)
C <sub>9</sub> —C <sub>10</sub>	1.53(2)	∠C <sub>2</sub> —N <sub>1</sub> —C <sub>4A</sub>	113.6(19)
		∠C <sub>2</sub> —N <sub>1</sub> —C <sub>4B</sub>	115.7(17)
		∠N <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	111.2(13)
		∠N <sub>1</sub> —C <sub>4A</sub> —C <sub>5A</sub>	104.2(29)
		∠N <sub>1</sub> —C <sub>4B</sub> —C <sub>5B</sub>	97.3(26)
		∠C <sub>6</sub> —N <sub>2</sub> —C <sub>7</sub>	122.5(12)
		∠C <sub>6</sub> —N <sub>2</sub> —C <sub>9</sub>	119.4(13)
		∠C <sub>7</sub> —N <sub>2</sub> —C <sub>9</sub>	118.1(11)
		∠N <sub>2</sub> —C <sub>7</sub> —C <sub>8</sub>	112.3(13)
		∠N <sub>2</sub> —C <sub>9</sub> —C <sub>10</sub>	109.4(12)

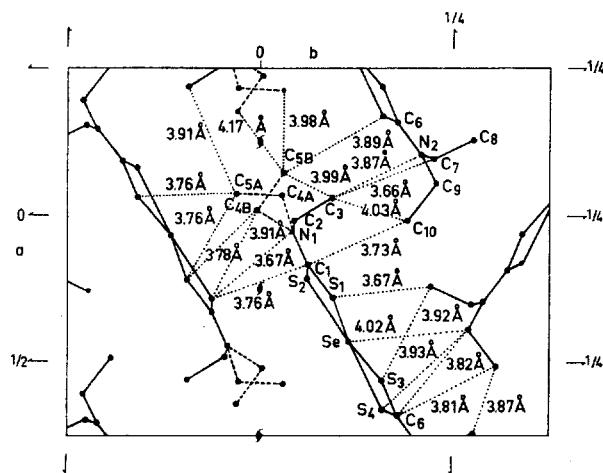
As mentioned before, there are two different configurations of the C<sub>4</sub>—C<sub>5</sub> ethyl group. They correspond to a rotation of about 150° around the N<sub>1</sub>—C<sub>4</sub> bond. Due probably to steric effects (Fig. 2, Table 5), both carbon atoms of this ethyl group occupy different positions in the two configurations. In the configuration A, the molecules nearly have mirror plane symmetry, the mirror plane passes through the selenium atom at right angles to the SeS<sub>4</sub> plane. There are probably a 1:1 mixture of A and B molecules statistically distributed in the crystals.

The molecules are approximately planar, apart from the disordered ethyl group, the methyl groups and the hydrogen atoms. The least squares plane through this roughly planar part of the molecule is within 0.12 Å of any of the atoms defining it. The atoms C<sub>4A</sub> and C<sub>4B</sub> are —0.56 and 0.37 Å, respectively, away from this plane. For the normal to the least squares plane through the SeS<sub>4</sub> group with all atoms given equal weight, the equation 0.500  $x$ —0.849  $y$ —0.165  $z$ =0 referred to the crystal axes, is found. The plane is —0.369 Å from the origin, while Se, S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, and S<sub>4</sub> are 0.022, 0.007, —0.014, 0.016, and 0.001 Å, respectively, away from the plane.

In Fig. 3 the nearly planar part of the molecule is shown projected into the SeS<sub>4</sub> plane with bond lengths and angles included. The configuration



*Fig. 1.* The arrangement of the molecules in the unit cell as seen along the  $\alpha$  axis. Dashed lines indicate the bonds in the disordered ethyl group.



**Fig. 2.** The packing of the molecules viewed down the *c* axis. Dashed lines indicate bonds in the disordered ethyl group, while dotted lines indicate intermolecular distances according to Table 6 which should be consulted with regard to *z* coordinates.

Table 5. Intramolecular contacts.

Se—C <sub>1</sub>	2.94 Å	C <sub>1</sub> —C <sub>4A</sub>	2.50 Å
Se—C <sub>6</sub>	2.94	C <sub>1</sub> —C <sub>4B</sub>	2.50
S <sub>1</sub> —S <sub>2</sub>	2.94	C <sub>1</sub> —C <sub>6A</sub>	3.38
S <sub>1</sub> —S <sub>3</sub>	3.22	C <sub>1</sub> —C <sub>6B</sub>	3.28
S <sub>1</sub> —N <sub>1</sub>	2.64	C <sub>2</sub> —C <sub>4A</sub>	2.54
S <sub>1</sub> —C <sub>2</sub>	2.97	C <sub>2</sub> —C <sub>4B</sub>	2.63
S <sub>1</sub> —C <sub>3</sub>	3.49	C <sub>2</sub> —C <sub>6A</sub>	3.16
S <sub>2</sub> —N <sub>1</sub>	2.67	C <sub>2</sub> —C <sub>6B</sub>	3.21
S <sub>2</sub> —C <sub>4A</sub>	3.12	C <sub>3</sub> —C <sub>4A</sub>	3.17
S <sub>2</sub> —C <sub>4B</sub>	3.07	C <sub>3</sub> —C <sub>4B</sub>	3.63
S <sub>2</sub> —C <sub>6A</sub>	3.86	C <sub>3</sub> —C <sub>6A</sub>	4.15
S <sub>2</sub> —C <sub>6B</sub>	3.70	C <sub>3</sub> —C <sub>6B</sub>	3.59
S <sub>3</sub> —S <sub>4</sub>	2.95	C <sub>4</sub> —C <sub>7</sub>	2.53
S <sub>3</sub> —N <sub>2</sub>	2.67	C <sub>6</sub> —C <sub>8</sub>	3.40
S <sub>3</sub> —C <sub>7</sub>	2.98	C <sub>6</sub> —C <sub>9</sub>	2.48
S <sub>3</sub> —C <sub>8</sub>	3.63	C <sub>6</sub> —C <sub>10</sub>	3.30
S <sub>4</sub> —N <sub>2</sub>	2.67	C <sub>7</sub> —C <sub>9</sub>	2.57
S <sub>4</sub> —C <sub>9</sub>	3.02	C <sub>7</sub> —C <sub>10</sub>	3.31
S <sub>4</sub> —C <sub>10</sub>	3.64	C <sub>8</sub> —C <sub>9</sub>	3.33
N <sub>1</sub> —C <sub>3</sub>	2.48		
N <sub>1</sub> —C <sub>6A</sub>	2.42		
N <sub>1</sub> —C <sub>6B</sub>	2.37		
N <sub>2</sub> —C <sub>8</sub>	2.51		
N <sub>2</sub> —C <sub>10</sub>	2.46		
C <sub>1</sub> —C <sub>2</sub>	2.49		
C <sub>1</sub> —C <sub>3</sub>	3.29		

Table 6. Intermolecular distances in Å.

C <sub>2</sub> —C <sub>5B</sub>	3/2—x, —y, —1/2+z	4.08	C <sub>6</sub> —C <sub>10</sub>	»	3.81
C <sub>3</sub> —C <sub>5A</sub>	»	3.91	C <sub>9</sub> —C <sub>10</sub>	»	4.18
C <sub>5B</sub> —C <sub>5B</sub>	»	4.17	C <sub>8</sub> —C <sub>10</sub>	»	3.87
S <sub>1</sub> —C <sub>3</sub>	—1/2+x, 1/2—y, 1—z	3.67	C <sub>3</sub> —C <sub>4B</sub>	x, y, —1+z	3.99
S <sub>3</sub> —C <sub>8</sub>	»	3.92	S <sub>1</sub> —C <sub>4B</sub>	1/2—x, —y, —1/2+z	3.78
S <sub>2</sub> —C <sub>10</sub>	—1+x, y, z	3.98	S <sub>1</sub> —C <sub>5A</sub>	»	3.76
C <sub>1</sub> —C <sub>10</sub>	»	3.73	S <sub>3</sub> —C <sub>6A</sub>	»	3.76
C <sub>3</sub> —C <sub>6</sub>	»	4.10	S <sub>2</sub> —C <sub>1</sub>	1/2—x, —y, 1/2+z	3.76
C <sub>3</sub> —C <sub>7</sub>	»	3.66	S <sub>1</sub> —C <sub>2</sub>	»	3.73
C <sub>3</sub> —C <sub>10</sub>	»	4.03	S <sub>2</sub> —C <sub>4B</sub>	»	3.91
C <sub>3</sub> —N <sub>2</sub>	»	3.87	S <sub>2</sub> —N <sub>1</sub>	»	3.67
C <sub>5B</sub> —C <sub>5B</sub>	3/2—x, —y, 1/2+z	4.17	S <sub>4</sub> —C <sub>6A</sub>	»	3.94
C <sub>5A</sub> —C <sub>5B</sub>	»	3.98	C <sub>10</sub> —N <sub>2</sub>	1/2+x, 1/2—y, —z	3.90
Se—C <sub>9</sub>	—1/2+x, 1/2—y, —z	4.02	S <sub>2</sub> —C <sub>2</sub>	x, y, 1+z	3.70
S <sub>3</sub> —C <sub>9</sub>	»	3.96	S <sub>2</sub> —C <sub>3</sub>	»	3.96
S <sub>4</sub> —C <sub>9</sub>	»	3.93	S <sub>4</sub> —C <sub>7</sub>	»	3.88
C <sub>6</sub> —C <sub>9</sub>	»	3.82	S <sub>4</sub> —C <sub>5B</sub>	1+x, y, z	3.89

The left column represents distances from an atom in the original molecule (Table 2) to an atom in a molecule whose transformation from the original one is listed in the next column.

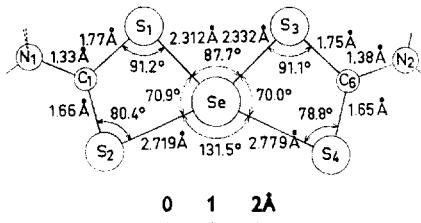


Fig. 3. The projection of the central part of the molecule as seen along the normal to the least squares plane through the nearly planar  $\text{SeS}_4$  group.

around the central selenium atom resembles that found for divalent tellurium in tellurium di(ethylxanthate)<sup>5</sup> and tellurium di(morpholylidithiocarbamate).<sup>8</sup> However, in the two tellurium compounds, there are short intermolecular  $\text{Te}\cdots\text{S}$  contacts. No corresponding  $\text{Se}\cdots\text{S}$  contact is found in the present structure.

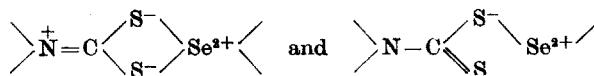
There are two long and two short  $\text{Se}-\text{S}$  bonds, the bond lengths being  $\text{Se}-\text{S}_1=2.312 \pm 0.005$  Å,  $\text{Se}-\text{S}_2=2.719 \pm 0.005$  Å,  $\text{Se}-\text{S}_3=2.332 \pm 0.004$  Å, and  $\text{Se}-\text{S}_4=2.779 \pm 0.005$  Å. These values are all significantly larger than the covalent radii sum of 2.21 Å.<sup>18</sup> The inter-ligand  $\text{Se}-\text{S}$  bond angles are  $\angle \text{S}_1-\text{Se}-\text{S}_3=87.7 \pm 0.2^\circ$  and  $\angle \text{S}_2-\text{Se}-\text{S}_4=131.5 \pm 0.2^\circ$ . The corresponding angles in the two tellurium analogs<sup>5,8</sup> are close to 82 and 145°, respectively, reflecting the greater size of the tellurium atom as compared to selenium. Replacing tellurium by selenium in these compounds results in shorter central atom to  $\text{S}_1$  and  $\text{S}_3$  bond lengths. The inter-ligand  $\text{S}_1\cdots\text{S}_3$  contact therefore becomes too short unless the  $\text{S}_1-\text{Se}-\text{S}_3$  angle opens up. As a consequence of this effect and a similar increase in the intra-ligand sulphur to central atom bond angles from about 66° to close to 70°, the other, large inter-ligand bond angle is then reduced as found above. Another result of replacing tellurium by selenium is that the *trans* three-center  $\text{S}_1-\text{Se}-\text{S}_4$  and  $\text{S}_3-\text{Se}-\text{S}_2$  systems become less bent, both angles being close to 158° as compared to values between 147.4 and 149.8° found in their tellurium counterparts.<sup>5,8</sup>

The lengths of the nearly linear three-center  $\text{Se}-\text{Se}-\text{Se}$  systems in potassium and rubidium triselenocyanate, 5.34 and 5.30 Å, respectively,<sup>9-12</sup> assuming single covalent radii for the outer selenium atoms, give an average bonding radius of 1.49 Å for the central selenium atom. The *trans* three-center  $\text{S}-\text{Se}-\text{S}$  systems in the present structure have an average length of 5.072 Å, which, with single covalent radii for the ligand sulphur atoms, corresponds to a bonding radius of 1.496 Å for selenium. This value is thus close to that found for selenium in the triselenocyanate ion.<sup>9-12</sup> A corresponding agreement has been found between the tellurium radius in linear three-center systems and in the non-linear three-center systems in tellurium di(ethylxanthate)<sup>5</sup> and tellurium di(morpholylidithiocarbamate).<sup>8</sup> As in the tellurium analogs, *p*-orbitals probably play an important role in the bonding in the  $\text{SeS}_4$  group.

The recent structure determination of phenylarsenic bis(diethyldithiocarbamate)<sup>20</sup> shows that apart from the phenyl group, the configuration around the central arsenic atom is very close to that found for selenium in the present work, except that the  $\text{AsS}_4$  group is slightly pyramidal. This similarity is perhaps not so surprising taking into account that arsenic(III) with a phenyl

substituent is isoelectronic with selenium(II). The structure of arsenic tris(diethyldithiocarbamate)<sup>21</sup> is distorted trigonal antiprismatic. The short and long As—S bonds of average lengths 2.35 Å and 2.8–2.9 Å appear not to be significantly different from those found in phenylarsenic bis(diethyldithiocarbamate).<sup>20</sup> In both arsenic compounds and in selenium bis(diethyldithiocarbamate), the bond angles between the short As—S or Se—S bonds are all close to 90°. This supports the idea that the sulphur to central atom bonding in such compounds is based mainly on *p*-orbitals, perhaps with some *s*-orbital contribution. Each long sulphur to central atom bond might be pictured as part of a non linear (145–160° angle), asymmetric three-center system, each long bond being *trans* to a short one.

The short and long C—S bond lengths in selenium bis(diethyldithiocarbamate) have average values of 1.66 and 1.76 Å, respectively, while the C≡N bond lengths have an average value of 1.35 Å. These bond lengths are normal for dithiocarbamates<sup>22</sup> and imply that the canonical forms indicated



above are the most important ones. The angles at the N<sub>1</sub>, N<sub>2</sub>, C<sub>1</sub>, and C<sub>6</sub> atoms correspond to *sp*<sup>2</sup> hybridization in agreement with the above. Other N—C and C—C bond lengths correspond to normal, covalent bond lengths within the error limits.

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