

Crystal Structure of the (1:1) Addition Compounds of Diiodoacetylene with 1,4-Dithiane and 1,4-Dieselenane, Respectively

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Crystals of the (1:1) compounds formed by diiodoacetylene and 1,4-dithiane resp. 1,4-diselenane have been investigated by X-ray methods. The space groups are both $P2_1/c$, the unit cell of the dithiane compound contains 4 formula units whereas the corresponding number for the diselenane compound is 2. In both cases molecules are linked together by charge transfer bonds to form endless chains of alternating donor and acceptor molecules. The S...I and Se...I charge transfer bonds were found equal to 3.27 Å and 3.34 Å, respectively.

Several years ago the structure of some charge-transfer complexes formed by 1,4-dioxan and halogen molecules were investigated by Hassel *et al.*¹ Later on it has been shown that thio- and seleno ethers form corresponding addition compounds with halogen. The structure of these^{2,3} display the same features as the ether compounds, *i.e.* a linear donor-halogen-halogen arrangement in which the donor-halogen distance is shorter than the corresponding van der Waals' separation and the halogen-halogen bond length larger than in the free halogen molecule.

The present report deals with the structure determination of crystals in which 1,4-dithiane and 1,4-diselenane act as electron donors and di-iodoacetylene as the electron acceptor molecule. Diiodoacetylene was expected to possess weaker electron acceptor properties than iodine, and it was felt to be of interest to examine the charge-transfer bond lengths as well as the general geometry of the complexes as compared to the corresponding iodine compounds.

EXPERIMENTAL

The compounds were prepared by evaporation of the solvent from solutions of equimolecular mixtures of diiodoacetylene and 1,4-dithiane or 1,4-diselenane in light petroleum ether at room temperature. The crystals grown from this solvent are needleformed;

they sublime and decompose in air and were therefore mounted in sealed-off thin-walled pyrex capillary tubes during the X-ray exposures. The dimensions of the crystals used in the experiments were about $0.07 \times 0.07 \times 0.15 \text{ mm}^3$.

Precession diagrams showed that both compounds form monoclinic crystals. The systematic absence of the reflections $h0l$ when l is odd and $0k0$ when k is odd uniquely determined the space groups to be $P2_1/c$. The compounds are not isomorphous, however.

Intensities were determined from precession films ($\mu = 30^\circ$, $\text{MoK}\alpha$ -radiation) and integrated Weissenberg diagrams ($\text{CuK}\alpha$ -radiation) by microphotometrical measurements and, for the weakest reflections, by visual estimates by comparison with a calibrated scale. For the dithiane compound 140 $h0l$ and 96 $h,k,-h$ reflections were measured from precession films and 76 $0kl$ reflections from Weissenberg films. The maximum number obtainable under actual conditions are 176, 147, and 126, respectively. For the diselenane compound 84 $0kl$ and 71 $h0l$ reflections were measured on precession films; the corresponding maximum numbers are 142 and 88.

The $0kl$ intensities of the dithiane compound obtained with $\text{CuK}\alpha$ -radiation were corrected for absorption effects.

CRYSTAL DATA

Diiodoacetylene-1,4-dithiane, $\text{C}_2\text{I}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$.

Monoclinic, space group $P2_1/c$.

$a = 10.25 \text{ \AA}$; $b = 9.47 \text{ \AA}$; $c = 12.50 \text{ \AA}$; $\beta = 109.7^\circ$.

Calculated density 2.31 gcm^{-3} . $Z = 4$.

Diiodoacetylene-1,4-diselenane, $\text{C}_2\text{I}_2 \cdot \text{C}_4\text{H}_8\text{Se}_2$.

Monoclinic, space group $P2_1/c$.

$a = 5.51 \text{ \AA}$; $b = 9.24 \text{ \AA}$; $c = 13.15 \text{ \AA}$, $\beta = 123.2^\circ$.

Calculated density 2.91 gcm^{-3} . $Z = 2$.

Table 1. Final atomic coordinates with standard deviations. 1,4-dithiane-diiodoacetylene.

	x	y	z
I(1)	-0.0468 (.0004)	0.4367 (.0005)	0.2534 (.0003)
I(2)	-0.3629 (.0003)	0.3173 (.0004)	0.4950 (.0003)
S(1)	0.1517 (.0013)	0.4747 (.0013)	0.0984 (.0013)
S(2)	0.4204 (.0014)	0.2420 (.0020)	0.1313 (.0013)
C(1)	0.241 (.006)	0.230 (.007)	0.015 (.004)
C(2)	0.146 (.006)	0.297 (.005)	0.062 (.005)
C(3)	0.326 (.005)	0.481 (.006)	0.207 (.004)
C(4)	0.439 (.008)	0.426 (.005)	0.161 (.005)
C(5)	-0.137 (.010)	0.365 (.010)	0.367 (.006)
C(6)	-0.224 (.009)	0.377 (.011)	0.407 (.007)

Table 2. Final atomic coordinates with standard deviations. 1,4-diselenane-diiodoacetylene.

	x	y	z
I	0.8744 (.0008)	0.0695 (.0006)	0.1563 (.0003)
Se	0.7619 (.0019)	0.1255 (.0007)	0.3780 (.0005)
C(1)	0.806 (.012)	0.124 (.007)	0.507 (.004)
C(2)	0.813 (.025)	-0.077 (.008)	0.380 (.006)
C(3)	0.974 (.013)	0.017 (.007)	0.036 (.004)

Table 3. Observed and calculated structure factors. 1,4-dithiane-diiodoacetylene.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
1	0	0	50	45	9	0	4	44	- 33
2	0	0	90	95	10	0	4	26	- 22
3	0	0	167	168	12	0	4	21	- 17
4	0	0	115	-131	-14	0	6	19	17
5	0	0	97	89	-12	0	6	8	10
6	0	0	34	23	-11	0	6	83	81
7	0	0	66	- 62	-10	0	6	8	9
8	0	0	3	1	- 9	0	6	73	76
9	0	0	60	- 45	- 8	0	6	72	66
10	0	0	78	- 73	- 7	0	6	47	- 38
11	0	0	15	- 15	- 6	0	6	79	65
12	0	0	18	- 15	- 5	0	6	31	24
-14	0	2	15	19	- 4	0	6	72	- 68
-13	0	2	13	11	- 3	0	6	48	38
-11	0	2	38	37	- 1	0	6	209	-216
-10	0	2	21	18	0	0	6	6	- 6
- 9	0	2	42	37	1	0	6	203	-194
- 8	0	2	150	151	2	0	6	48	- 65
- 7	0	2	33	- 33	4	0	6	111	-110
- 6	0	2	49	51	5	0	6	27	27
- 5	0	2	32	26	6	0	6	8	- 7
- 4	0	2	263	-268	7	0	6	31	- 28
- 3	0	2	83	74	8	0	6	49	44
- 2	0	2	195	-203	9	0	6	9	8
- 1	0	2	200	-223	10	0	6	11	12
0	0	2	29	27	11	0	6	14	15
1	0	2	329	-389	-13	0	8	17	- 24
2	0	2	177	-193	-12	0	8	12	- 14
3	0	2	66	- 63	-10	0	8	65	- 67
4	0	2	98	-100	- 9	0	8	57	- 48
5	0	2	47	47	- 8	0	8	17	- 20
6	0	2	60	65	- 7	0	8	95	-103
7	0	2	41	- 33	- 6	0	8	8	8
8	0	2	61	55	- 5	0	8	53	53
9	0	2	21	20	- 4	0	8	74	- 63
11	0	2	59	52	- 3	0	8	121	130
12	0	2	8	7	- 2	0	8	12	11
-13	0	4	16	- 20	- 1	0	8	7	8
-12	0	4	50	- 54	0	0	8	172	169
-10	0	4	68	- 74	1	0	8	7	6
- 9	0	4	32	- 27	2	0	8	83	80
- 8	0	4	26	25	3	0	8	75	65
- 7	0	4	167	-181	4	0	8	27	- 24
- 6	0	4	38	32	5	0	8	27	24
- 5	0	4	25	- 18	7	0	8	12	- 13
- 4	0	4	59	- 56	8	0	8	9	8
- 3	0	4	270	261	9	0	8	8	- 7
- 2	0	4	114	119	-13	0	10	10	11
- 1	0	4	92	100	-12	0	10	14	13
0	0	4	221	223	-11	0	10	44	43
1	0	4	28	22	- 9	0	10	40	31
2	0	4	47	40	- 8	0	10	93	72
3	0	4	210	205	- 7	0	10	31	- 27
5	0	4	50	47	- 6	0	10	80	77
6	0	4	27	22	- 5	0	10	18	16
8	0	4	8	10	- 4	0	10	80	- 69

<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c
- 3	0	10	45	37	0	9	3	21	- 23
- 2	0	10	96	- 93	0	10	3	18	18
- 1	0	10	63	- 51	0	11	3	14	18
0	0	10	11	12	0	4	4	38	- 34
1	0	10	89	- 76	0	5	4	23	- 21
2	0	10	35	- 26	0	6	4	25	22
3	0	10	9	- 9	0	8	4	94	- 84
4	0	10	49	- 38	0	1	5	75	79
8	0	10	12	13	0	2	5	83	94
- 12	0	12	30	- 25	0	3	5	70	- 80
- 10	0	12	57	- 54	0	4	5	59	57
- 9	0	12	15	- 14	0	5	5	76	88
- 7	0	12	79	- 59	0	6	5	51	45
- 6	0	12	17	19	0	9	5	15	- 19
- 5	0	12	12	- 11	0	10	5	9	- 12
- 4	0	12	31	- 23	0	11	5	9	11
- 3	0	12	53	41	0	1	6	43	35
- 1	0	12	41	25	0	2	6	153	- 163
0	0	12	70	53	0	4	6	12	- 15
2	0	12	21	16	0	5	6	17	19
3	0	12	30	24	0	6	6	66	63
5	0	12	14	13	0	9	6	10	9
- 11	0	14	29	24	0	1	7	43	41
- 9	0	14	41	32	0	2	7	35	- 49
- 8	0	14	34	26	0	3	7	79	- 81
- 7	0	14	8	- 8	0	4	7	86	- 84
- 6	0	14	34	27	0	5	7	62	73
- 4	0	14	27	- 22	0	6	7	28	- 36
- 3	0	14	19	16	0	8	8	29	- 40
- 2	0	14	21	- 19	0	1	9	24	27
- 1	0	14	27	- 22	0	2	9	51	49
1	0	14	39	- 30	0	3	9	65	- 58
2	0	14	8	- 9	0	4	9	32	30
- 10	0	16	16	- 17	0	5	9	33	31
- 7	0	16	29	- 24	0	7	9	11	- 14
- 3	0	16	26	19	0	2	10	28	- 43
0	0	16	19	15	0	3	10	16	16
0	1	1	47	43	0	5	10	16	- 13
0	2	1	162	183	0	6	10	36	45
0	3	1	192	- 199	0	3	11	30	- 42
0	4	1	143	149	0	4	11	22	- 30
0	5	1	75	71	0	2	14	25	- 24
0	6	1	70	62	0	2	13	14	22
0	7	1	21	- 19	0	1	13	10	15
0	11	1	15	16	0	8	0	83	- 74
0	1	2	52	- 49	- 1	1	1	44	- 43
0	2	2	244	- 256	- 1	2	1	15	16
0	3	2	47	35	- 1	3	1	63	57
0	5	2	68	- 63	- 1	4	1	192	- 193
0	6	2	138	124	- 1	5	1	107	- 113
0	9	2	11	- 15	- 1	6	1	10	- 10
0	10	2	24	27	- 1	7	1	15	- 13
0	1	3	83	85	- 1	8	1	23	22
0	2	3	68	- 60	- 1	9	1	3	3
0	3	3	99	- 105	- 1	10	1	8	- 5
0	4	3	97	- 111	- 1	11	1	17	- 13
0	5	3	90	86	- 1	12	1	23	21
0	6	3	40	- 35	- 1	13	1	10	7

<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c
- 2	1	2	171	-189	- 6	2	6	21	- 20
- 2	2	2	2	3	- 6	3	6	98	-103
- 2	3	2	45	- 44	- 6	4	6	25	- 24
- 2	4	2	10	- 11	- 6	5	6	68	- 64
- 2	5	2	8	- 8	- 6	6	6	12	10
- 2	6	2	59	64	- 6	8	6	26	- 24
- 2	7	2	93	- 94	- 6	9	6	12	- 11
- 2	8	2	40	38	- 7	1	7	67	- 71
- 2	9	2	38	31	- 7	2	7	26	- 29
- 2	10	2	20	13	- 7	3	7	41	42
- 3	1	3	77	- 77	- 7	4	7	26	- 24
- 3	2	3	121	134	- 7	5	7	19	- 19
- 3	3	3	152	-161	- 7	6	7	5	- 8
- 3	4	3	8	6	- 7	7	7	28	27
- 3	5	3	88	99	- 7	9	7	29	24
- 3	6	3	73	72	- 7	10	7	15	9
- 3	7	3	27	28	- 8	1	8	34	- 36
- 3	8	3	14	13	- 8	2	8	55	- 55
- 3	11	3	25	18	- 8	3	8	42	37
- 4	1	4	52	61	- 8	4	8	20	- 13
- 4	2	4	83	83	- 8	5	8	25	22
- 4	3	4	92	87	- 8	6	8	31	32
- 4	4	4	19	25	- 8	7	8	10	- 11
- 4	5	4	16	15	- 9	1	9	27	26
- 4	6	4	76	- 74	- 9	2	9	64	58
- 4	7	4	34	27	- 9	3	9	5	6
- 4	8	4	31	28	- 9	6	9	25	26
- 4	9	4	33	- 31	- 9	9	9	7	- 5
- 4	10	4	19	- 18	-10	2	10	26	25
- 4	11	4	14	- 14	-10	6	10	32	- 30
- 5	1	5	130	131	-10	7	10	10	- 10
- 5	2	5	66	- 67	-11	1	11	17	20
- 5	3	5	21	14	-11	2	11	22	- 21
- 5	4	5	94	95	-11	3	11	8	- 12
- 5	5	5	7	- 6	-11	4	11	9	- 8
- 5	6	5	24	- 21	-11	5	11	9	12
- 5	7	5	39	- 37	-11	6	11	13	- 13
- 5	9	5	23	- 21	-12	1	12	8	11
- 5	10	5	24	19	-12	2	12	7	- 6
- 5	12	5	5	- 4	-12	3	12	12	- 11
- 6	1	6	49	49					

STRUCTURE DETERMINATION

The diiodoacetylene-1,4-dithiane compound crystallizes with *four* molecules in the unit cell. No symmetry requirements are therefore imposed upon the molecules in the present space group ($P2_1/c$). In the 1,4-diselenane compound the number of formula units per unit cell is *two*, however, and the molecules must be situated on centres of symmetry.

The structures were determined using standard Patterson methods and the parameters refined, first by successive Fourier calculations and then by least-squares methods; the heavy atoms (I, S, Se) were assumed to have anisotropic thermal vibrations. The final atomic parameters obtained are

Table 4. Observed and calculated structure factors. 1,4-diselenane-diiodoacetylene.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
1	0	0	189	172	-4	0	10	55	52
2	0	0	93	-90	-3	0	10	23	18
3	0	0	78	-79	-2	0	10	24	24
4	0	0	19	-17	-1	0	10	<12	15
5	0	0	<26	-9	0	0	10	44	-46
-6	0	2	24	22	1	0	10	57	-59
-5	0	2	59	56	2	0	10	14	-15
-4	0	2	12	15	3	0	10	11	11
-3	0	2	102	-107	-6	0	12	<13	-6
-2	0	2	121	-120	-5	0	12	53	-47
-1	0	2	13	-15	-4	0	12	75	-71
0	0	2	27	-30	-3	0	12	<13	-4
1	0	2	33	-31	-2	0	12	72	72
2	0	2	86	84	-1	0	12	51	52
3	0	2	106	105	0	0	12	<13	4
4	0	2	23	26	-7	0	14	16	21
5	0	2	16	-16	-6	0	14	23	19
6	0	2	<14	-10	-5	0	14	<13	-4
-6	0	4	<13	-4	-4	0	14	10	-14
-5	0	4	<25	-8	-3	0	14	18	-18
-4	0	4	<23	8	-2	0	14	39	-38
-3	0	4	113	123	-1	0	14	28	-32
-2	0	4	198	203	0	0	14	<16	5
-1	0	4	3	7	-7	0	16	9	-12
0	0	4	196	-200	-6	0	16	12	-10
1	0	4	111	-124	-5	0	16	23	20
2	0	4	4	-3	-4	0	16	52	45
3	0	4	<25	12	-3	0	16	23	20
4	0	4	<13	6	-2	0	16	16	-15
5	0	4	<12	11	-1	0	16	18	-17
-7	0	6	15	11	-6	0	18	5	-13
-6	0	6	17	-17	-4	0	18	4	-7
-5	0	6	71	-71	-2	0	18	8	12
-4	0	6	62	-59	0	1	1	15	27
-3	0	6	22	20	0	1	2	3	2
-2	0	6	36	32	0	1	3	82	-90
-1	0	6	33	33	0	1	4	53	48
0	0	6	112	108	0	1	5	76	72
1	0	6	100	95	0	1	6	33	-32
2	0	6	<24	-11	0	1	7	48	41
3	0	6	52	-51	0	1	8	43	-42
4	0	6	18	-20	0	1	9	86	-82
-7	0	8	<13	6	0	1	10	40	31
-6	0	8	12	12	0	1	11	<14	0
-5	0	8	49	44	0	1	12	18	13
-4	0	8	46	45	0	1	13	38	34
-3	0	8	78	-84	0	1	14	16	-17
-2	0	8	177	-189	0	1	15	13	-13
-1	0	8	80	-80	0	2	0	156	147
0	0	8	59	58	0	2	1	175	-186
1	0	8	53	54	0	2	2	31	-27
2	0	8	14	15	0	2	3	88	-89
3	0	8	<13	17	0	2	4	64	-64
-7	0	10	27	-26	0	2	5	118	139
-6	0	10	10	-8	0	2	6	74	66
-5	0	10	46	44	0	2	7	<11	2

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
0	2	8	<11	3	0	5	12	<14	11
0	2	9	55	— 48	0	5	13	16	— 17
0	2	10	41	— 35	0	6	0	76	— 69
0	2	11	13	13	0	6	2	34	31
0	2	12	<14	13	0	6	3	26	30
0	3	1	99	98	0	6	4	50	45
0	3	2	77	— 77	0	6	5	<11	— 2
0	3	3	64	— 59	0	6	6	50	— 46
0	3	4	81	82	0	6	7	43	— 42
0	3	5	31	— 29	0	6	8	<14	0
0	3	6	<10	— 7	0	6	9	<14	1
0	3	8	74	— 72	0	6	10	25	24
0	3	9	<14	11	0	6	11	25	24
0	3	10	43	36	0	7	1	58	— 56
0	3	11	18	— 13	0	7	2	40	— 39
0	3	12	21	21	0	7	3	74	72
0	3	13	<13	— 3	0	7	4	<11	0
0	3	14	21	— 25	0	7	5	<13	10
0	4	0	125	—116	0	7	6	27	26
0	4	1	83	— 98	0	7	7	48	— 42
0	4	2	5	5	0	7	8	<14	— 4
0	4	3	16	— 16	0	7	9	<16	8
0	4	4	83	81	0	7	10	12	— 14
0	4	5	88	87	0	8	0	<13	1
0	4	6	<11	— 12	0	8	1	12	11
0	4	7	52	— 46	0	8	2	24	21
0	4	8	49	— 41	0	8	3	<14	— 4
0	4	9	37	— 31	0	8	4	<14	— 2
0	4	10	<14	— 3	0	8	5	<14	— 14
0	4	11	35	35	0	8	6	25	— 27
0	4	12	<14	9	0	8	7	<16	9
0	5	1	23	22	0	8	10	17	18
0	5	2	118	—132	0	9	1	22	— 27
0	5	3	24	26	0	9	2	39	42
0	5	4	44	40	0	9	3	25	33
0	5	5	42	— 37	0	9	4	<14	— 13
0	5	6	61	59	0	9	5	<16	8
0	5	7	<11	— 3	0	9	6	22	— 22
0	5	8	45	— 36	0	9	7	22	— 23
0	5	9	42	39	0	10	7	17	19
0	5	10	<14	— 8	0	11	1	18	11
0	5	11	<14	— 9	0	11	6	16	— 14

listed in Tables 1 and 2 and the observed and calculated structure factors in Tables 3 and 4. The overall *R*-factors are 9.2 % for the data from the 1,4-dithiane compound and 9.3 % from the 1,4-diselenane compound.

DISCUSSION OF THE STRUCTURES

Owing to the presence of heavy atoms the accuracy in the determination of carbon coordinates is rather poor. It is sufficient, however, for indicating the orientation of the dithiane and diselenane rings and thus for the differentiation between axial and equatorial directions on the sulphur resp. selenium atoms.

The *diiodoacetylene-1,4-dithiane* crystals contain chains of alternating donor and acceptor molecules as shown in Fig. 1 a. Two successive charge-

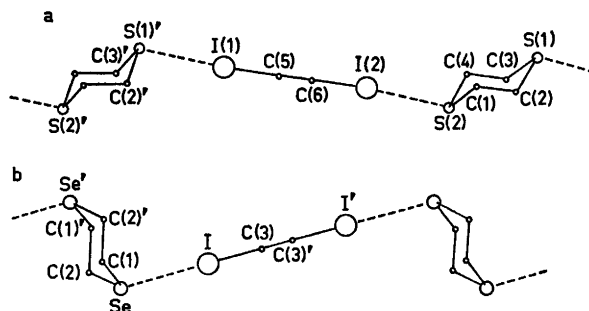


Fig. 1. Structure of the (a) 1,4-dithiane-diiodoacetylene and (b) 1,4-diselenane-diiodoacetylene chains.

transfer bonds along a chain are not crystallographically equivalent; the unit of one molecule of each kind is related to the next by a glide plane c . The two non-equivalent S—I bonds are of equal length, 3.27 Å, their directions correspond roughly to *equatorial* bonds of the dithiane ring and the S(1)'—I(1)—I(2)—S(2) arrangement is approximately linear. Interatomic distances and bond angles in this crystal are listed in Table 5. The intermolecular

Table 5. Interatomic distances and bond angles in diiodoacetylene-1,4-dithiane.

Distances (Å)	e.s.d.	
S(1)' — I(1)	3.27	(.01)
S(2) — I(2)	3.27	(.01)
I(1) — I(2)	5.243	(.004)
S(1) — S(2)	3.44	(.02)
S(1) — C(2)	1.73	(.05)
S(1) — C(3)	1.84	(.05)
S(2) — C(1)	1.93	(.05)
S(2) — C(3)	1.79	(.05)
C(1) — C(2)	1.45	(.07)
C(3) — C(4)	1.54	(.07)
C(5) — C(6)	1.17	(.10)

Angles (°)		
S(2)' — S(1)' — I(1)	119.4	(0.5)
S(1)' — I(1) — I(2)	173.9	(0.3)
I(1) — I(2) — S(2)	175.4	(0.3)
I(2) — S(2) — S(1)	134.8	(0.6)
C(1) — S(2) — C(4)	103	(3)
C(2) — S(1) — C(3)	99	(3)
I(1) — S(1)' — C(2)'	94	(2)
I(1) — S(1)' — C(3)'	102	(2)
I(2) — S(2) — C(1)	104	(2)
I(2) — S(2) — C(2)	104	(2)

contacts are normal except for an S(1)—S(1)' distance passing through a centre of symmetry of only 3.29 Å. This is shorter than the generally accepted van der Waals' separation and an interaction between these atoms may explain the fact that the S(2)—S(1)—I angle is about 15° smaller than the corresponding angle on the S(2) atom which has no such short interatomic contacts.

The *diiodoacetylene-1,4-diselenane* crystals are also built up of chains of alternating acceptor and donor molecules linked together by charge-transfer bonds. The situation is shown schematically in Fig. 1 b. Since all molecules

Table 6. Distances and angles involving the heavy atoms in diiodoacetylene-1,4-diselenane.

	e.s.d.
Se — I	3.336 Å (.007)
I — I'	5.167 Å (.006)
Se — Se'	3.65 Å (.01)
Se' — Se — I	106.3° (0.2)
Se — I — I'	173.1° (0.2)

are situated on centres of symmetry all charge-transfer bonds are crystallographically equivalent. The Se—I bond length is 3.34 Å and its direction corresponds closely to an *axial* bond relative to the selenane ring. The Se—I—I—Se arrangement is nearly linear.

A comparison of the geometry of the compounds examined in the present investigation with those of corresponding compounds with other acceptor molecules containing iodine may be of interest. Results from various structure determinations are listed in Table 7, and it is evident that the diiodoacetylene

Table 7. Charge-transfer bond lengths (in Å) in complexes of dithiane and diselenane with various molecules containing iodine atoms.

Donor	Acceptor			
	I ₂	C ₂ I ₂	C ₂ I ₄	CHI ₃
1,4-Dithiane	2.84 ²	3.27		3.32 ⁴
1,4-Diselenane	2.83 ³	3.34	3.40 (<i>equatorial</i>) 3.43 (<i>axial</i>) ⁵	3.47 (<i>axial</i>) 3.51 (<i>equatorial</i>) ⁶

molecule exhibits poorer electron acceptor properties than iodine itself. Thus, the charge-transfer bond length is greater in the present compounds than in the iodine complexes of dithiane and diselenane by 0.4 Å and 0.5 Å, respectively. Judging from the lengths of the charge-transfer bonds diiodoacetylene appears to be a better acceptor than tetraiodoethylene which in turn forms shorter charge-transfer bonds than aliphatic iodides.

That one iodine atom in a diiodoacetylene molecule is already engaged in a charge-transfer bond does not, apparently, seriously influence the ability of the other iodine atom to form a similar bond. Similar observations are made in weak charge-transfer interactions when the acceptor molecule contains more than one halogen atom. It has, however, never been observed in the case of very strong interactions like those between amines, thio- and selenoethers and halogen molecules.

The finding that the charge-transfer bonds have a direction roughly corresponding to an *equatorial* direction in the dithiane complex and to an *axial* direction in the diselenane complex is in full agreement with observations reported for the corresponding iodine complexes.^{2,3}

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