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The Refinement of the Structure of the Complex of Iodine with 1,4 Dithiane, $C_4H_8S_2 . 2 I_2$

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The structure of the molecular complex $C_4H_8S_2 . 2 I_2$ has been determined and refined by three-dimensional full-matrix least-squares procedures. There are two molecules of the complex in the monoclinic unit cell, for which

$$a = 6{\cdot}838 \pm 0{\cdot}006,\quad b = 6{\cdot}393 \pm 0{\cdot}006,\quad c = 16{\cdot}775 \pm 0{\cdot}010\ \text{Å};\quad \beta = 114^\circ\ 30' \pm 20'.$$

The space group is $P2_1/c$. Although the molecules are required only to be centrosymmetric, the actual molecular symmetry approximates $2/m$. The observed bond distances and angles are:

$$I_1\text{–}I_2 = 2{\cdot}787 \pm 0{\cdot}002,\quad I_2\text{–}S = 2{\cdot}867 \pm 0{\cdot}006,\quad S\text{–}C_1 = 1{\cdot}795 \pm 0{\cdot}024,\quad S\text{–}C_2 = 1{\cdot}825 \pm 0{\cdot}024,$$
$$C_1\text{–}C_2 = 1{\cdot}552 \pm 0{\cdot}032\ \text{Å},\ I_1\text{–}I_2\text{–}S = 177{\cdot}9 \pm 0{\cdot}4^\circ,\ I_2\text{–}S\text{–}C_1 = 100{\cdot}9 \pm 1{\cdot}0^\circ,\ I_2\text{–}S\text{–}C_2 = 96{\cdot}2 \pm 1{\cdot}0^\circ,$$
$$C_1\text{–}S\text{–}C_2 = 101{\cdot}5 \pm 1{\cdot}9^\circ,\quad S\text{–}C_1\text{–}C_2 = 110{\cdot}5 \pm 2{\cdot}4^\circ,\quad S\text{–}C_2\text{–}C_1 = 112{\cdot}8 \pm 2{\cdot}4^\circ.$$

The structure of the 1,4 dithiane part of the molecule is unaltered by complexing with iodine, which is attached to the ring in the equatorial positions. By contrast, the I–I bond in the iodine part of the complex is 0·11 Å longer than the value observed in solid I_2.

The temperature parameters for the iodine atoms are unusually high for heavy atoms but are understandable in terms of the observed structure and the high volatility of the solid. The packing distances are all reasonable.

Introduction

In a previous communication, (McCullough, Chao & Zuccaro, 1959) a preliminary study of the structures of the addition compounds of iodine with 1,4 dithiane and 1,4 diselenane was reported. In the present communication, the three-dimensional refinement and the details of the structure of $C_4H_8S_2 . 2 I_2$ are presented. The three-dimensional refinement of the similar (but not isostructural) selenium compound is in progress and will be reported later.

Experimental

The substance $C_4H_8S_2 . 2 I_2$ was first reported and characterized by Husemann (1863). The crystalline solid can be prepared by combining approximately stoichiometric amounts of the components in carbon tetrachloride or ethylene chloride. However, crystals better suited to X-ray diffraction studies may be prepared by permitting vapors of the two components to diffuse together slowly in a closed container. Grown in this manner, the crystals are fairly uniform in cross-section and are of suitable size. Analyses of two preparations indicated 80·50% and 80·74% of iodine respectively. The theoretical value for the formula $C_4H_8S_2 . 2 I_2$ is 80·85% iodine. In color and in luster, the crystals are similar to solid elementary iodine. Due to the high volatility of the solid (probably through dissociation into $C_4H_8S_2$ and I_2) the selected crystals were sealed in thin-walled X-ray capillaries.

Rotation and Weissenberg photographs about the *b* axis were prepared with Mo $K\alpha$ radiation. The intensity data were obtained by use of the multiple-film Weissenberg procedure, interleaving 0·0025 cm. brass foil between the films. Precession photographs of the *hk*0 and 0*kl* nets were also prepared with Mo $K\alpha$ radiation. On the precession camera, intensity data were obtained by making graduated sets of timed exposures of each net. The intensities were estimated visually by use of calibrated comparison strips and were corrected by application of the appropriate factors to give $|F_o|^2$ values.

The crystals used in the intensity measurements were close to 0·10 × 0·10 × 0·12 mm. in size. The calculated linear absorption coefficient for Mo $K\alpha$ radiation is 105 cm.$^{-1}$ which leads to a value of $\mu r = 0{\cdot}5$. Omission of absorption corrections was thus considered to be justified.

Measurement of the precession photographs indicated a monoclinic unit cell with the dimensions:

$$a = 6{\cdot}838 \pm 0{\cdot}006,\ b = 6{\cdot}393 \pm 0{\cdot}006,$$
$$c = 16{\cdot}775 \pm 0{\cdot}010\ \text{Å},\ \beta = 114^\circ\ 30' \pm 20'.$$

The above values are based on Mo $K\alpha = 0{\cdot}7107$ Å. (In the earlier communication, β was incorrectly reported as 117° 30′.) On the basis of two molecules in the unit cell, as found in the selenium analogue, the calculated density is 3·125 g.cm.$^{-3}$.

Determination of the structure

The only systematic extinctions are those for $h0l$ with l odd and for $0k0$ with k odd. The space group $P2_1/c$ is thus indicated. The presence of only two molecules $C_4H_8S_2.2\,I_2$ in the unit cell requires the molecules to be centrosymmetric. The asymmetric unit therefore consists of two I, one S, two C and four H atoms. However, no attempt was made to locate the hydrogen atoms. With the aid of Patterson summations on (010) and (100) the trial parameters for I and S listed as Set 1 in Table 1 were obtained. These parameters were then used in the preparation of Fourier summations on (010) and (100). Refinement by two-dimensional methods did not yield unambiguous carbon positions. A three-dimensional difference synthesis was accordingly carried out.

Table 1. *Atomic positional parameters in* $C_4H_8S_2.2I_2$

		Set 1	Set 2	Set 3	
		Patterson parameters	Fourier parameters	Final L.S. parameters	Standard deviation
I_1	x	0·825	0·825	0·8228	0·0003
	y	0·823	0·817	0·8163	0·0003
	z	0·185	0·183	0·1840	0·0001
I_2	x	0·526	0·525	0·5229	0·0002
	y	0·140	0·140	0·1389	0·0003
	z	0·144	0·147	0·1460	0·0001
S	x	0·183	0·208	0·2030	0·0009
	y	0·450	0·451	0·4611	0·0010
	z	0·095	0·100	0·1021	0·0003
C_1	x	—	0·233	0·2342	0·0032
	y	—	0·584	0·5853	0·0034
	z	—	0·017	0·0122	0·0016
C_2	x	—	0·967	0·9723	0·0031
	y	—	0·317	0·2911	0·0037
	z	—	0·041	0·0449	0·0016

In this procedure, refined Fourier parameters for I and S and some $1070|F_o|$ values derived from the observed reflections were employed. The resulting carbon positions are included in the Fourier parameters (Set 2) in Table 1. At this stage, the value of the residual, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ was 0·18.

Refinement of the structure

The structure was refined by use of the full-matrix least-squares routine written for SWAC by Sparks (Christofferson, Sparks & McCullough, 1958). Individual anisotropic temperature parameters were applied to each atom. The atomic scattering factors used for iodine were those of Thomas & Umeda (1957) corrected for dispersion for Mo $K\alpha$ radiation (Dauben & Templeton, 1955). For sulfur, the values were taken from the *Internationale Tabellen* (1935) and for carbon, the diamond values of McWeeney (1954) were used. The $|F_o|$ values used in the refinement were derived almost entirely from the b axis Weissenberg photographs, but were supplemented by the precession data. The latter served mainly for interlayer scaling of the Weissenberg data. After the first least-squares cycle, the calculated structure factors were used to refine the interlayer scale factors. The resulting changes in these factors were less than 5%. Five least-squares cycles were performed using the $|F_o|$ values for observed reflections in Table 3. The corresponding values of R (initially 0·181) were 0·119, 0·093, 0·085, 0·082 and 0·081.

Table 2. *Anisotropic temperature parameters* in $C_4H_8S_2.2\,I_2$

(Standard deviations in parentheses)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I_1	4·21	4·17	4·46	2·58	1·36	−1·09
	(0·07)	(0·08)	(0·08)	(0·16)	(0·11)	(0·39)
I_2	3·45	3·80	3·16	0·97	1·46	0·31
	(0·06)	(0·02)	(0·06)	(0·16)	(0·09)	(0·39)
S	2·95	3·79	2·37	1·53	0·55	−0·28
	(0·22)	(0·29)	(0·22)	(0·48)	(0·36)	(0·39)
C_1	0·5	2·4	6·5	1·4	4·7	−2·1
	(0·7)	(1·0)	(1·3)	(1·3)	(1·5)	(1·6)
C_2	1·5	3·3	4·5	2·2	1·2	1·0
	(0·7)	(1·1)	(1·1)	(1·4)	(1·4)	(1·6)

The final positional parameters are listed as Set 3 in Table 1, while the final anisotropic temperature parameters are given in Table 2. The observed structure factors are compared with those calculated on the basis of the final positional and temperature parameters in Table 3.

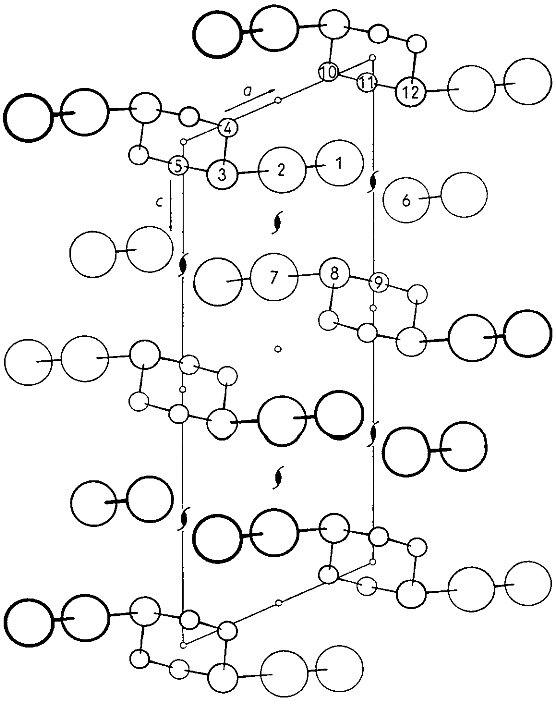

Fig. 1. Projection of the structure of $C_4H_8S_2.2\,I_2$ down the b axis.

Discussion of the structure

The molecular and crystal structures of $C_4H_8S_2.2\,I_2$ are shown in Figs. 1 and 2. The observed bond distances and bond angles are given in Table 4, where they are compared with the results of Marsh (1955) for 1,4 dithiane. All corresponding values in the two

Table 3. *Comparison of observed and calculated structure factors for* $C_4H_8S_2.2\,I_2$

The listed F_o and F_c values must be divided by 10 to put on an absolute scale. Unobserved reflections are indicated by means of asterisks. The F_o values given in these cases are the minimum observable values

h	k	l	F_o	F_c
00	00	2	1463	1500-
00	00	4	1942	2084-
00	00	6	2251	2269
00	00	8	443	432-
00	00	10	346	324-
00	00	12	208	221
00	00	14	• 98	24
00	00	16	•110	34
00	00	18	316	307-
00	00	20	217	271
01	00	20-	•130	10
01	00	18-	•122	28
01	00	16-	378	587
01	00	14-	789	710-
01	00	12-	224	233-
01	00	10-	2235	2264
01	00	08-	1989	1978-
01	00	06-	1743	1705-
01	00	04-	3864	3790
01	00	02-	985	1007-
01	00	00	776	724-
01	00	02	1418	1269
01	00	04	641	513-
01	00	06	252	191
01	00	08	617	540-
01	00	10	627	535
01	00	12	339	282
01	00	14	1080	1112-
01	00	16	385	388
01	00	18	379	448
01	00	20	318	377-
02	00	20-	333	354
02	00	18-	560	616-
02	00	16-	224	240-
02	00	14-	1424	1438
02	00	12-	950	927-
02	00	10-	1086	981-
02	00	08-	1191	1182
02	00	06-	839	730-
02	00	04-	• 56	5-
02	00	02-	258	68-
02	00	00	393	274
02	00	02	528	446
02	00	04	1984	1987-
02	00	06	1463	1416
02	00	08	969	953
02	00	10	1813	1864-
02	00	12	393	366
02	00	14	561	568
02	00	16	396	427-
03	00	20-	116	220-
03	00	18-	499	551
03	00	16-	• 99	181-
03	00	14-	314	267-
03	00	12-	• 90	49-
03	00	10-	164	221
03	00	08-	• 76	111-
03	00	06-	1219	1143-
03	00	04-	1464	1422
03	00	02-	648	655
03	00	00	2695	2963-
03	00	02	1818	1765
03	00	04	1405	1205-
03	00	06	1771	1755-
03	00	08	463	442
03	00	10	371	341
03	00	12	371	373-
03	00	14	•165	64
04	00	18-	•134	62
04	00	16-	•110	101-
04	00	14-	445	394
04	00	12-	• 88	64-
04	00	10-	1246	1285-
04	00	08-	1466	1517
04	00	06-	759	719
04	00	04-	2181	2440-
04	00	02-	1212	1186
04	00	00	957	933
04	00	02	895	921-
04	00	04	615	570
04	00	06	• 94	111
04	00	08	•102	84-
04	00	10	107	135-
04	00	12	•120	18
04	00	14	327	361
05	00	18-	442	461
05	00	16-	•104	13
05	00	14-	943	677-
05	00	12-	870	863
05	00	10-	541	526
05	00	08-	1061	1104-
05	00	06-	551	479
05	00	04-	194	153
05	00	02-	300	309-
05	00	00	208	211
05	00	02	• 92	75
05	00	04	477	469
05	00	06	561	562-
05	00	08	154	175-
05	00	10	717	738
05	00	12	327	321-
05	00	14	187	258-
06	00	18-	332	393-
06	00	16-	243	258
06	00	14-	198	215
06	00	12-	357	306-
06	00	10-	• 94	87
06	00	08-	• 92	26-
06	00	06-	• 88	23
06	00	04-	474	445-
06	00	02-	• 94	8
06	00	00	873	858
06	00	02	733	762-
06	00	04	357	363-
06	00	06	730	787
06	00	08	263	258-
06	00	10	176	186-
06	00	12	133	199
07	00	10-	197	236
07	00	08-	668	654-
07	00	06-	•100	121-
07	00	04-	822	002
07	00	02-	570	573-
07	00	00	318	319-
07	00	02	502	502
07	00	04	164	182-
08	00	14-	272	274
08	00	12-	420	390-
08	00	10-	•110	121-
08	00	08-	451	448
08	00	06-	303	272-
08	00	04-	154	126-
08	00	02-	223	209
08	00	00	•120	71-
00	01	01	439	512
00	01	02	429	371-
00	01	03	2068	1972-
00	01	04	1122	1125-
00	01	05	832	762
00	01	06	1590	1729
00	01	07	840	879
00	01	08	688	694-
00	01	09	912	851-
00	01	10	978	969-
00	01	11	374	349-
00	01	12	1229	1290
00	01	13	320	309
00	01	14	372	364-
00	01	15	277	294
00	01	16	342	399-
00	01	17	213	166-
00	01	18	405	459
00	01	19	178	142-
01	01	18-	166	154
01	01	17-	375	386
01	01	16-	665	653-
01	01	15-	• 84	16
01	01	14-	513	458
01	01	13-	754	790-
01	01	12-	307	271
01	01	11-	511	495
01	01	10-	514	496-
01	01	09-	504	446
01	01	08-	171	129
01	01	07-	1194	1229-
01	01	06-	161	176-
01	01	05-	1028	994
01	01	04-	1593	1753
01	01	03-	523	481
01	01	02-	755	769-
01	01	01-	1832	1967-
01	01	00	1478	1436-
01	01	01	308	283
01	01	02	2887	2947
01	01	03	1159	1050
01	01	04	1332	1350-
01	01	05	•106	74
01	01	06	1237	1207-
01	01	07	698	693-
01	01	08	1781	1828
01	01	09	228	191-
01	01	10	640	671-
01	01	11	691	702
01	01	12	507	492-
01	01	13	• 84	133-
01	01	14	476	495
01	01	15	160	201-
01	01	16	•122	13
01	01	17	256	259
02	01	18-	• 93	54
02	01	17-	357	361-
02	01	16-	121	111
02	01	15-	307	309
02	01	14-	221	187
02	01	13-	•148	113
02	01	12-	496	462-
02	01	11-	767	749-
02	01	10-	435	415-
02	01	09-	774	692
02	01	08-	1649	1801
02	01	07-	807	742
02	01	06-	1121	1155-
02	01	05-	724	659-
02	01	04-	901	900-
02	01	03-	635	620-
02	01	02-	2957	3037
02	01	01-	594	430
02	01	00	1496	1638-
02	01	01	1301	1262
02	01	02	961	925-
02	01	03	674	676-
02	01	04	1580	1720
02	01	05	602	564-
02	01	06	758	710-
02	01	07	895	921
02	01	08	356	326-
02	01	09	326	342-
02	01	10	• 78	37
02	01	11	201	197-
02	01	12	121	114
02	01	13	523	563
02	01	14	132	165
02	01	15	218	180-
02	01	16	349	322-
02	01	17	210	261-
03	01	18-	260	313
03	01	17-	• 88	102
03	01	16-	436	463-
03	01	15-	406	406-
03	01	14-	340	281-
03	01	13-	• 86	21
03	01	12-	1124	1133
03	01	11-	580	555
03	01	10-	1033	1064-
03	01	09-	398	358
03	01	08-	546	521-
03	01	07-	847	816-
03	01	06-	1683	1895
03	01	05-	273	234-
03	01	04-	1098	1129-
03	01	03-	1237	1302
03	01	02-	435	367-
03	01	01-	645	683-
03	01	00	795	788
03	01	01	433	410-
03	01	02	272	204-
03	01	03	940	1012
03	01	04	• 66	144
03	01	05	749	728-
03	01	06	771	740-
03	01	07	381	378-
03	01	08	366	297
03	01	09	695	713
03	01	10	361	374
03	01	11	• 88	5
03	01	12	662	696-
03	01	13	270	320-
03	01	14	222	283
03	01	15	145	51-
04	01	19-	135	103-
04	01	18-	130	105-
04	01	17-	234	273-
04	01	16-	515	557
04	01	15-	115	173
04	01	14-	587	597-
04	01	13-	525	502
04	01	12-	283	262-
04	01	11-	560	537-
04	01	10-	744	733
04	01	09-	292	245-
04	01	08-	396	362-
04	01	07-	793	777
04	01	06-	•122	70-
04	01	05-	760	751-
04	01	04-	255	247-
04	01	03-	169	195-
04	01	02-	474	429
04	01	01-	940	967
04	01	00	544	535
04	01	01	611	625-
04	01	02	1187	1207-
04	01	03	619	612-
04	01	04	739	660
04	01	05	314	300
04	01	06	432	435
04	01	07	319	294
04	01	08	884	1004-
04	01	09	• 88	109-
04	01	10	378	428
04	01	11	269	299-
04	01	12	221	251
04	01	13	144	127
04	01	14	319	360-
05	01	18-	161	163-
05	01	17-	202	243
05	01	16-	173	151-
05	01	15-	223	262-
05	01	14-	199	102
05	01	13-	• 78	59-
05	01	12-	152	122
05	01	11-	435	464
05	01	10-	• 72	40
05	01	09-	552	568-
05	01	08-	625	608-
05	01	07-	218	229-
05	01	06-	668	655
05	01	05-	647	623
05	01	04-	431	437
05	01	03-	• 70	29
05	01	02-	1107	1162-
05	01	01-	474	425-
05	01	00	902	928
05	01	01	289	294-
05	01	02	402	399
05	01	03	395	395
05	01	04	847	939-
05	01	05	86	135
05	01	06	393	431
05	01	07	382	372-
05	01	08	187	190
05	01	09	166	178
05	01	10	199	242-
05	01	11	146	59
06	01	16-	200	229
06	01	15-	214	255
06	01	14-	• 84	33
06	01	13-	166	159-
06	01	12-	532	515-
06	01	11-	264	263-
06	01	10-	544	536
06	01	09-	134	145
06	01	08-	152	179
06	01	07-	403	409
06	01	06-	791	818-
06	01	05-	• 76	72-
06	01	04-	678	730
06	01	03-	423	421-
06	01	02-	271	292
06	01	01-	354	361
06	01	00	543	516-
06	01	01	144	144
06	01	02	268	240
06	01	03	290	316-
06	01	04	90	66
06	01	05	262	327
06	01	06	•122	50
06	01	07	• 98	66
07	01	16-	247	277-
07	01	15-	130	130-
07	01	14-	298	291
07	01	13-	124	82-
07	01	12-	123	38
07	01	11-	257	318
07	01	10-	414	450-
07	01	09-	• 84	72
07	01	08-	265	274
07	01	07-	236	262-
07	01	06-	• 82	113
07	01	05-	315	299
07	01	04-	• 84	112-
07	01	03-	• 86	14
07	01	02-	• 88	12-
07	01	01-	265	292-
07	01	00	• 88	30-
07	01	01	275	312
07	01	02	265	267
07	01	03	136	138
07	01	04	197	219-
07	01	05	202	233-
07	01	06	146	116-
08	01	06-	159	180-
08	01	05-	244	254-
08	01	04-	• 94	35-
08	01	03-	• 94	70
08	01	02-	317	306
08	01	01-	• 96	127
08	01	00	261	245-
08	01	01	142	70-
08	01	02	145	63-
08	01	03	148	133-
08	01	04	308	290
00	02	00	1228	1218-
00	02	01	•148	68-
00	02	02	959	981
00	02	03	841	822-
00	02	04	•108	24
00	02	05	963	966
00	02	06	1102	1090-
00	02	07	596	578
00	02	08	879	812
00	02	09	1620	1673-
00	02	10	102	96
00	02	11	679	651
00	02	12	• 80	37-
00	02	13	768	754
00	02	14	• 88	58
00	02	15	705	840-
00	02	16	192	237-
00	02	17	•101	16
00	02	18	105	150
01	02	19-	529	489
01	02	18-	•102	51
01	02	17-	273	306-
01	02	16-	278	241-
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Table 3 (*cont.*)

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00	05	13	231	268-
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00	05	15	•114	16
00	05	16	333	326
01	05	16-	358	290
01	05	15-	266	276
01	05	14-	•104	3-
01	05	13-	141	139-
01	05	12-	163	227-
01	05	11-	•180	77-
01	05	10-	•170	31
01	05	09-	263	278
01	05	08-	234	223
01	05	07-	257	198-
01	05	06-	•128	106-
01	05	05-	421	425
01	05	04-	306	331-
01	05	00	• 76	33-
01	05	02	875	1087-
01	05	03	591	648-
01	05	04	651	684
01	05	05	218	71-
01	05	06	690	623
01	05	07	549	519
01	05	08	792	747-
01	05	09	476	461-
01	05	10	188	3
01	05	11	100	88
01	05	12	294	307
01	05	13	110	166
01	05	14	114	154-
02	05	12-	411	344
02	05	11-	• 86	107-
02	05	10-	143	155-
02	05	09-	531	503
02	05	08-	628	586-
02	05	07-	504	480-
02	05	06-	861	929
02	05	05-	172	170-
02	05	04-	243	257
02	05	03-	596	656
02	05	02-	931	1139-
02	05	01-	701	806-
02	05	00	447	462
02	05	01	121	81
02	05	02	597	556
02	05	03	397	364
02	05	04	525	482-
02	05	05	558	536-
02	05	06	•122	38-
02	05	07	176	132
02	05	08	131	176
02	05	09	167	8-
03	05	14-	174	112-
03	05	13-	320	332
03	05	12-	606	562-
03	05	11-	404	382-
03	05	10-	650	569
03	05	09-	• 80	56
03	05	08-	287	270
03	05	07-	382	412
03	05	06-	613	627-
03	05	05-	584	612-
03	05	04-	135	126
03	05	03-	283	234
03	05	02-	251	218
03	05	01-	138	137
03	05	00	141	131-
03	05	01	321	293-
03	05	02	154	125-
03	05	03	161	173
03	05	04	146	159
03	05	05	306	317-
03	05	06	207	153
03	05	07	97	174
03	05	08	462	423-
03	05	09	149	186
03	05	10	•110	1
03	05	11	228	269-
03	05	12	335	370
04	05	16-	291	311-
04	05	15-	184	220-
04	05	14-	177	149
04	05	13-	98	131
04	05	12-	134	127
04	05	11-	158	195
04	05	10-	124	159-
04	05	09-	323	257-
04	05	08-	• 82	87-
04	05	07-	279	247
04	05	06-	• 78	77
04	05	05-	• 78	54-
04	05	04-	• 76	86
04	05	03-	• 78	116
04	05	02-	473	426-
04	05	01-	228	231
04	05	00	262	202
04	05	01	523	499-
04	05	02	568	525
04	05	03	343	300
04	05	04	605	585-
04	05	05	99	141
04	05	06	102	142-

h	k	l	F_o	F_c
04	05	07	383	323-
04	05	08	493	460
04	05	09	255	256
05	05	12-	99	160-
05	05	11-	101	127
05	05	10-	188	150
05	05	09-	130	188-
05	05	08-	181	222
05	05	07-	295	300
05	05	06-	614	594-
05	05	05-	216	198
05	05	04-	153	129
05	05	03-	427	431-
05	05	02-	624	637
05	05	01-	380	347
05	05	00	492	440-
05	05	01	• 96	8-
05	05	02	141	145-
05	05	03	323	307-
05	05	04	395	348
05	05	05	243	254
05	05	06	113	69-
06	05	14-	110	164
06	05	13-	152	214-
06	05	12-	277	262
06	05	11-	178	203
06	05	10-	452	429-
06	05	09-	•100	57
06	05	08-	99	6
06	05	07-	144	250-
06	05	06-	427	362
06	05	05-	311	301
06	05	04-	140	203-
06	05	03-	100	117-
06	05	02-	101	41-
06	05	01-	206	205-
00	06	00	737	704
00	06	01	785	790
00	06	02	416	392-
00	06	03	198	213
00	06	04	294	333-
00	06	05	505	537-
00	06	06	499	439
00	06	07	164	190
00	06	08	197	218-
00	06	09	•186	100-
00	06	10	•200	88-
01	06	12-	150	113-
01	06	11-	302	282-
01	06	10-	486	414
01	06	09-	607	592
01	06	08-	562	398-
01	06	07-	110	4
01	06	06-	160	194-
01	06	05-	638	792-
01	06	04-	505	568
01	06	03-	281	453
01	06	01	262	318-
01	06	02	246	248
01	06	03	•182	109
01	06	04	190	160-
01	06	05	•156	86
02	06	15-	206	297-
02	06	14-	198	263
02	06	13-	377	376
02	06	12-	329	255-
02	06	11-	186	95
02	06	10-	176	71-
02	06	09-	484	454-
02	06	08-	275	258
02	06	07-	135	176
02	06	06-	147	165-
02	06	05-	138	39
02	06	04-	112	150
02	06	03-	139	157-
02	06	00	•122	59
02	06	01	119	120
02	06	02	294	232
02	06	03	157	203
02	06	04	364	354-
02	06	05	485	469-
02	06	06	265	246
02	06	07	171	112
02	06	08	209	179
02	06	09	501	482
02	06	10	380	341-
02	06	11	294	294-
03	06	08-	122	152
03	06	07-	•126	4
03	06	06-	349	273-
03	06	05-	280	277-
03	06	04-	322	291
03	06	03-	131	117
03	06	02-	170	154
03	06	01-	466	446
03	06	00	562	506-
03	06	01	646	628-
03	06	02	507	411
03	06	03	182	95-
03	06	04	135	116
03	06	05	670	562
03	06	06	455	403-
03	06	07	218	202-
03	06	08	228	189
04	06	10-	359	296-
04	06	09-	421	371-
04	06	08-	373	334
04	06	07-	120	182
04	06	06-	127	19-
04	06	05-	515	561
04	06	04-	482	465-
04	06	03-	516	486-
04	06	02-	411	371
04	06	01-	159	194-
04	06	01	453	379
04	06	02	264	265-
04	06	03	147	160-
04	06	04	108	134
05	06	09-	415	415
05	06	08-	250	258-
05	06	07-	225	230-
05	06	06-	200	184
05	06	05-	•188	63-
05	06	04-	141	91-
05	06	03-	142	175

studies are seen to agree within their respective standard deviations. The structurally significant nonbonded separations are given in Table 5.

Although the molecule $C_4H_8S_2.2\,I_2$ is required only to be centrosymmetric, it approximates the symmetry 2/*m*. Deviations from 2/*m* symmetry within the $C_4H_8S_2$ portion of the molecule are of the order of magnitude of the corresponding standard deviations. However, deviations involving the iodine atoms are of the order of several standard deviations (cf. the

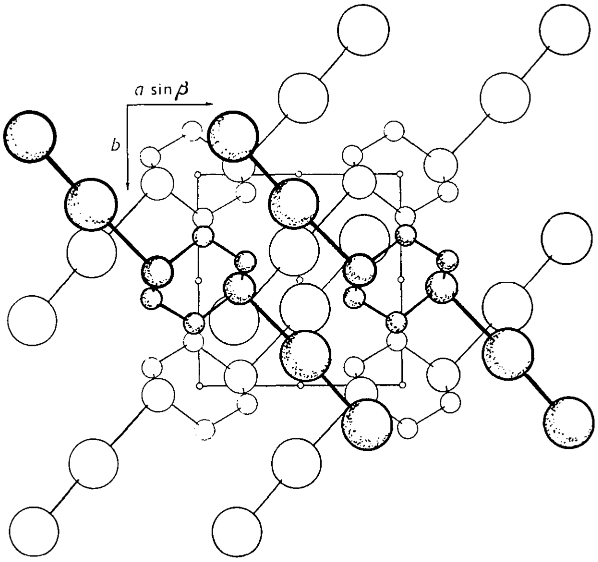

Fig. 2. Projection of the structure of $C_4H_8S_2.2\,I_2$ down the *c* axis.

non-bonded intramolecular separations I_2–C_1 and I_2–C_2, also the angles I_2–S–C_1 and I_2–S–C_2 in Tables 4 and 5).

Table 4. *Bond distances and angles in* $C_4H_8S_2.2\,I_2$ *compared with those in* $C_4H_8S_2$ (Marsh, 1955)

(*a*) Distances in Å. (Standard deviations in parentheses)

	$C_4H_8S_2.2\,I_2$	$C_4H_8S_2$
I_1–I_2	2·787 (0·0023)	—
I_2–S	2·867 (0·0062)	—
S–C_1	1·795 (0·024)	1·801 (0·013)
S–C_2	1·825 (0·024)	1·821 (0·011)
C_1–C_2	1·552 (0·032)	1·490 (0·018)
S · · · S	3·436 (0·012)	3·452 (0·007)

(*b*) Angles in degrees. (Standard deviations in parentheses)

	$C_4H_8S_2.2\,I_2$	$C_4H_8S_2$
I_1–I_2–S	177·9 (0·4)	—
I_2–S–C_1	100·9 (1·0)	—
I_2–S–C_2	96·2 (1·0)	—
I_2–S · · · S′	125·0 (0·6)	—
C_1–S–C_2	101·5 (1·9)	99·0 (0·6)
S–C_1–C_2	110·5 (2·4)	112·8 (0·9)
S–C_2–C_1	112·8 (2·4)	112·6 (0·9)

Table 5. *Shortest non-bonded interatomic separations in* $C_4H_8S_2.2\,I_2$

(Standard deviations: I–I, 0·002 Å; I–S, 0·006 Å; I–C, 0·023 Å)

(See Fig. 1 for identification numbers of atoms)

(*a*) Atoms within a given molecule

I–C	2–4	3·66 Å
	2–5	3·56

(*b*) Atoms in different molecules

I–I	1–2′	4·720 Å
	1–6	4·067
	1–7	4·536
	2–7	4·837
I–S	1–8	3·780
	1–12	4·090
	2–8	4·011
I–C	1–9	4·17
	1–10	4·32
	1–11	4·20
	2–10	4·07

The most interesting feature of the structure is the fact that the compound is a molecular complex. This result is in sharp contrast to those of previous studies in these laboratories on compounds of the types R_2SeX_2 and R_2TeX_2 where X is Cl or Br. The latter compounds have all been found to involve nearly linear X–Se–X and X–Te–X bonds with R groups in equatorial positions (see Christofferson, Sparks & McCullough, 1958, for references to the earlier studies). However, a study of (benzyl)$_2SI_2$ (Hassel, 1957) has shown that this substance is a molecular complex. Hassel (private communication, 1959) has also independently studied $C_4H_8S_2.2\,I$ and has found it to be a molecular complex, but the details of this study are not yet available to the present authors.

The fact that the intramolecular angle S · · · S–I is observed to be 125° indicates that the iodine molecules are bonded to the 1,4 dithiane ring in equatorial rather than in axial positions. By contrast, the angle Se · · · Se–I has been found to be 90° in the trial structure for the 1,4 diselenane-iodine complex.

The bonded distances involving iodine in the present study of the 1,4 dithiane-iodine complex are compared with corresponding distances in related complexes in Table 6.

Table 6. *Bond distances in* $C_4H_8S_2.2\,I_2$ *compared with those in related complexes*

Complex and reference	Bond	Obs. dist. (Å)	Radius sum (Å)	Diff. (Å)
$C_4H_8S_2.2\,I_2$	S–I	2·87	2·37	0·50
	I–I	2·79	2·66	0·13
$(C_6H_5CH_2)_2S.I_2$ (Hassel, 1957)	S–I	2·84	2·37	0·47
	I–I	2·81	2·66	0·15
$C_4H_8O_2.2\,ICl$ (Hassel & Hvoslef, 1956)	O–I	2·6	1·99	0·6
	I–Cl	2·3	2·32	0·0
$C_4H_8O_2.Br_2$ (Hassel & Hvoslef, 1954)	O–Br	2·71	1·80	0·91
	Br–Br	2·31	2·28	0·03

For reference to studies of other related complexes see Rømming (1958) and Mooney Slater (1959).

In most structures, the temperature parameters of heavy atoms tend to be smaller than those for lighter atoms. However, in $C_4H_8S_2.2\,I_2$, the temperature parameters for iodine are quite large and

$$B_{ii}(I_1) > B_{ii}(I_2) > B_{ii}(S)\,.$$

Although these values appear to be anomalous, they are actually understandable in terms of the nature of the structure of the complex. The sulfur atoms are part of a firmly bonded six-membered ring. The I_2 atoms are but loosely bonded to the sulfur atoms. The iodine molecule is thus relatively free to vibrate and the atom I_1, being at the unbonded end of the chain, would be expected to vibrate with an even greater amplitude than that of I_2. The high volatility of the complex, probably due to its ease of dissociation into volatile products, is also in keeping with the high observed temperature parameters for iodine. The vibrational parameters of the carbon atoms are erratic, as they often are in compounds containing ultra-heavy atoms, and are probably of little, if any, structural significance.

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References

Christofferson, G. D., Sparks, R. A. & McCullough, J. D. (1958). *Acta Cryst.* **11**, 782.

Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* **8**, 841.

Hassel, O. & Hvoslef, J. (1954). *Acta Chem. Scand.* **8**, 873.

Hassel, O. & Hvoslef, J. (1956). *Acta Chem. Scand.* **10**, 138.

Hassel, O. (1957). *Proc. Chem. Soc.* p. 250.

Hassel, O. (1959). Private communication.

Husemann, A. (1863). *Liebigs Ann.* **126**, 269.

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

McCullough, J. D., Chao, G. Y. & Zuccaro, D. E. (1959). *Acta Cryst.* **12**, 815.

McWeeny, R. (1954). *Acta Cryst.* **7**, 180.

Marsh, R. E. (1955). *Acta Cryst.* **8**, 91.

Mooney Slater, R. C. L. (1959). *Acta Cryst.* **12**, 187.

Rømming, C. (1958). *Acta Chem. Scand.* **12**, 668.

Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26**, 293.

Acta Cryst. (1960). **13**, 732

The Crystal Structure of 1-Naphthoic Acid

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Crystals of 1-naphthoic acid are monoclinic with four molecules in a unit cell of dimensions

$$a=31\cdot12,\ b=3\cdot87,\ c=6\cdot92\ \text{Å},\ \beta=92\cdot2^\circ,$$

space group $P2_1/a$; all the crystals examined, however, have been twinned on (100). The structure, which consists of centrosymmetrical dimers, has been determined from projections along the b and c axes, and values of the bond lengths, valency angles, and intermolecular distances have been obtained. The strain in a planar model for the molecule is relieved by an 11° twisting of the carboxyl group out of the plane of the aromatic rings, and by valency-angle distortions.

Introduction

The crystal structure of 1-naphthoic acid has been examined as part of a series of investigations of the structures of derivatives of naphthalene (Trotter, 1960).

Experimental

Crystals of 1-naphthoic acid, which were obtained by crystallization from aqueous ethanol, are colourless plates elongated along the b-axis, with (100) developed. The density was determined by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the b-axis, $h0l$ and $h1l$ Weissenberg films, and $hk0$ and $0kl$ precession films.

Crystal data

1-Naphthoic acid, $C_{11}H_8O_2$; $M=172\cdot2$; m.p. $=161$ °C.
Monoclinic, $a=31\cdot12\pm0\cdot10$, $b=3\cdot87\pm0\cdot01$, $c=6\cdot92\pm0\cdot02$ Å, $\beta=92\cdot2\pm0\cdot2^\circ$.
Volume of the unit cell $=832\cdot8$ Å^3.
Density, calculated (with $Z=4$) $=1\cdot373$, measured $=1\cdot380$ g.cm.$^{-3}$.
Absorption coefficients for X-rays, $\lambda=1\cdot542$ Å, $\mu=9\cdot04$ cm.$^{-1}$; $\lambda=0\cdot7107$ Å, $\mu=1\cdot12$ cm.$^{-1}$.