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The Crystal and Molecular Structure of the Iodine Monobromide Complex of 1,4-Dithiane, $C_4H_8S_2 \cdot 2IBr$

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The 2:1 complex of iodine monobromide with 1,4-dithiane forms red-orange needles with elongation along the a axis of the monoclinic unit cell for which $a = 5.994$ (1) Å, $b = 11.565$ (1) Å, $c = 8.448$ (2) Å, and $\beta = 99.78$ (3)°. The space group is $P2_1/c$ with two centrosymmetric molecules of $C_4H_8S_2 \cdot 2IBr$ in the unit cell. The calculated and observed densities are 3.072 (2) and 3.05 (3) g cm^{-3}, respectively. The intensities of 1773 unique reflections were measured on a Picker automated diffractometer with Nb-filtered Mo Kα radiation. The structure was determined and refined by use of Patterson, Fourier, and least-squares procedures with a final, conventional R index of 2.5% for the 1442 observed reflections. The dithiane ring is in the chair conformation with the IBr molecules attached to sulfur in *equatorial* positions. The observed bond distances (in ångströms) are as follows: S–I, 2.687 (2); I–Br, 2.646 (1); S–C(av), 1.816 (4); C–C, 1.523 (8); C–H (av), 0.94 (4). The observed bond angles (in degrees) are as follows: S–I–Br, 178.2 (4); C–S–C, 100.0 (3); I–S–C(1), 103.7 (3); I–S–C(2), 98.9 (3); S–C–C(av), 111.8 (3); S–C–H(av), 104 (2); C–C–H(av), 114 (2); H–C–H(av), 110 (4).

Introduction

In an earlier study, some halogen and interhalogen addition compounds of 1,4-thiaselenane were prepared and their unit cells and space groups were reported.[3] Among the compounds studied was $C_4H_8SSe \cdot 2IBr$, but a precise structural study was not attempted because of a type of disorder which requires the molecule to have a pseudo center of symmetry. This difficulty is not present in the isomorphous IBr complex of 1,4-dithiane, $C_4H_8S_2 \cdot 2IBr$. Interest in this structure is mainly in the S–I–Br bonding system, but secondary items of interest are the mode of attachment of IBr to sulfur in the ring (*equatorial* or *axial*) and the possibility of intermolecular bonding through the halogen atoms.

Experimental Section

The crystalline complex was prepared from resublimed 1,4-dithiane by the procedure described for the 1,4-thiaselenane complex.[3] Crystals suitable for the X-ray study were grown by slowly cooling a saturated solution of the complex in ethylene chloride. The fine, red-orange needles are elongated on the monoclinic a axis and are stable in air and on exposure to X-radiation.

The crystal selected for intensity measurements was a needle ($0.3 \times 0.06 \times 0.06$ mm along a, b, and c^*, respectively) mounted with a close to the φ axis of a Picker full-circle automated diffractometer. Crystal setting parameters and cell dimensions were obtained by a least-squares fit to 11 sets of measured diffractometer angles. The resulting cell dimensions are $a = 5.994$ (1) Å, $b = 11.565$ (1) Å, $c = 8.448$ (2) Å, and $\beta = 99.78$ (3)° at 23°, based on λ(Cu Kα_1) 1.54051 Å. The systematic extinctions ($h0l$ absent with l odd and $0k0$ absent with k odd) uniquely determine the space group to be $P2_1/c$. The density observed by flotation in a mixture of methylene iodide and chloroform is 3.05 (3) g cm^{-3}, which compares favorably with the value 3.072 (2) g cm^{-3} calculated from the above cell parameters with $Z = 2$. Thus, there is half of a molecule of $C_4H_8S_2 \cdot 2IBr$ in the asymmetric unit, and the molecule, as formulated, must be centrosymmetric.

The intensities of all 1773 unique reflections accessible with 2θ less than 62° were measured with the diffractometer in automatic mode. The radiation was Mo Kα filtered through Nb foil and counted with a scintillation detector. The 2θ–θ scan technique (scan speed 2°/min) was used with the scan range given by $[2\theta(\alpha_1) - 0.8°]$ to $[2\theta(\alpha_2) + 0.8°]$. Background counts were taken for 20 sec at each end of the scan range and the automatic attenuator mechanism was set to keep the count rate below 10,000 cps. The intensities of two reference reflections were measured at 6-hr intervals and no systematic drift was noted. By a procedure related to one used by previous workers,[4] each recorded number of counts, N, was assigned an estimated standard deviation, $\sigma(N) = [N + (0.01N)^2]^{1/2}$. A total of 1442 reflections for which the net intensity, I, was greater than $3\sigma(I)$ were recorded as "observed." The recorded value of F for an "unobserved" reflection was derived from the larger of I and $0.7\sigma(I)$. Only "observed" reflections were used in the least-squares refinement. Lorentz and polarization corrections were applied in the usual manner, but due to the small value of μR for the crystal orientation given ($\sim$0.4), no absorption corrections were considered necessary. It is estimated that the errors in KF_o (where K is the scale factor) caused by neglecting the effects of absorption are in the range $\pm 1.3\%$.

Structure Determination and Refinement

The structure was determined by the heavy-atom method, refined by the use of least-squares procedures, and the hydrogen atoms were located by means of a difference Fourier synthesis.[5] In the final stages, all observed reflections were corrected for the effects of secondary extinction.

A set of final structure factors for all measured reflections was calculated on the basis of the final positional and thermal parameters in Tables I and II. The resulting values of F_c for the 1442 observed reflections are listed with the respective values of $|F_o|$ in Table III. The final value of the R index for these reflections is 0.025 while that for all 1773 measured reflections is

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

[4] S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).

[5] Fourier summations were computed by use of UCLAFOUR written by Gantzel and Hope and the least-squares refinement was carried out by use of the full-matrix program ACA No. 317 (modified) written by Gantzel, Sparks, and Trueblood. This program minimizes $w(\Delta|F|)^2$, and the weights, w, in the earlier least-squares cycles were those of E. W. Hughes, *J. Amer. Chem. Soc.*, **63**, 1737 (1941), with $4|F_o|(\text{min}) = 30$. In the latter cycles, w was taken as $1/\sigma(|F_o|)$. The R index is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, and the esd values for the parameters were obtained from the inverse of the final least-squares matrix. Corrections for the effects of secondary extinction were calculated by use of Christensen's SECEXT program and the thermal ellipsoid plots were prepared by use of Johnson's ORTEP routine.

TABLE I

ATOMIC POSITIONAL PARAMETERS IN $C_4H_8S_2 \cdot 2IBr$[a]

	x	y	z
I	0.92340 (6)	0.23240 (3)	0.50276 (4)
Br	1.25809 (9)	0.10417 (5)	0.43118 (7)
S	0.5771 (2)	0.3623 (1)	0.5655 (2)
C(1)	0.7114 (10)	0.4968 (5)	0.6409 (8)
C(2)	0.4596 (11)	0.4055 (5)	0.3617 (7)
H(1)	0.823 (11)	0.510 (6)	0.583 (8)
H(2)	0.774 (11)	0.474 (6)	0.744 (8)
H(3)	0.394 (10)	0.334 (6)	0.312 (7)
H(4)	0.584 (11)	0.426 (6)	0.314 (7)

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

0.035. All 331 of the "unobserved" reflections have values of $|F_c| < 8$, and 257 have values of $|F_c| \leqslant |F_o|$. In no case is $|F_c| > 2|F_o|$; for 10 reflections, $2|F_o| > |F_c| > 1.5|F_o|$, and for 64, $1.5|F_o| > |F_c| > |F_o|$.

The atomic scattering curve used for iodine was based on the I^0 values of Doyle and Turner,[6] that for carbon was based on the diamond values of McWeeny,[7] and the curve for hydrogen was based on the bonded values of Stewart, Davidson, and Simpson.[8] The curves for bromine and sulfur were based on the neutral atom values given in Table 3·3·1A of ref 9. The real part of the anomalous scattering correction was applied to the curves for I, Br, and S by use of the $\Delta f'$ values of Templeton and Dauben for Mo $K\alpha$ radiation given in Table 3·3·2C of ref 9.

TABLE II

ANISOTROPIC THERMAL PARAMETERS ($Å^2$)[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	2.74 (1)	1.70 (1)	2.28 (1)	0.09 (1)	0.38 (1)	−0.06 (1)
Br	3.03 (3)	2.49 (2)	3.62 (3)	0.50 (2)	0.90 (2)	−0.21 (2)
S	2.90 (6)	1.73 (5)	2.67 (5)	0.34 (5)	0.65 (4)	0.20 (4)
C(1)	3.1 (2)	2.1 (2)	2.9 (2)	0.3 (2)	−0.1 (2)	0.0 (2)
C(2)	3.4 (3)	1.8 (2)	2.3 (2)	0.6 (2)	0.3 (2)	−0.2 (2)

[a] The anisotropic temperature factor in the least-squares program has the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$. The relationships between the tabulated B values and the b parameters are given by $B_{11} = 4a^2(\sin^2 \beta)b_{11}$, $B_{22} = 4b^2b_{22}$, $B_{12} = 2ab(\sin \beta)b_{12}$, etc.

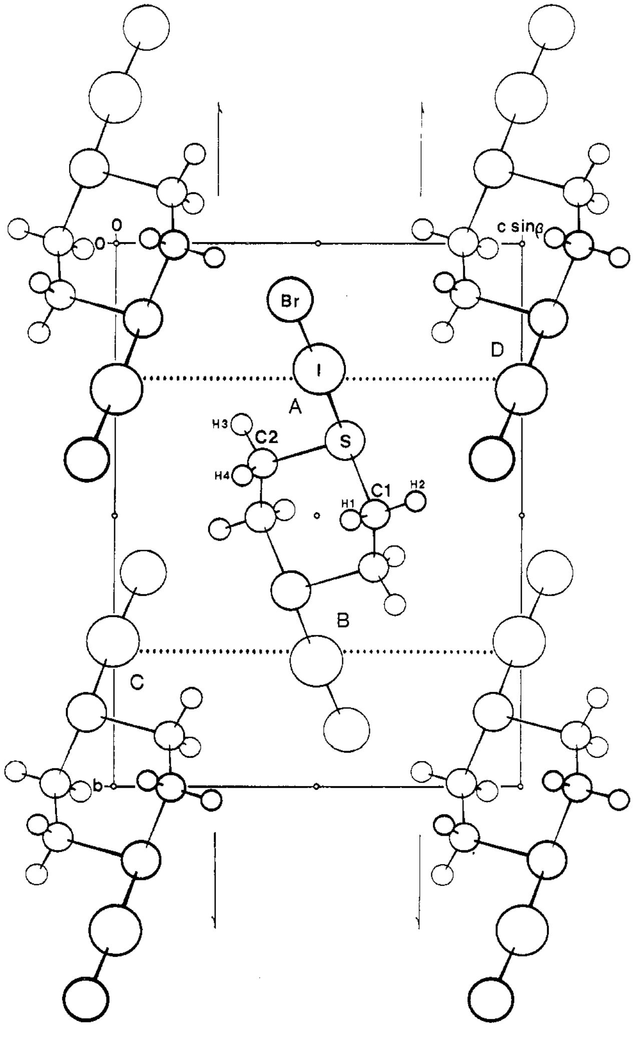

Figure 1.—Projection of the structure of $C_4H_8S_2 \cdot 2IBr$ down the crystallographic a axis. The rectangle outlines one unit cell.

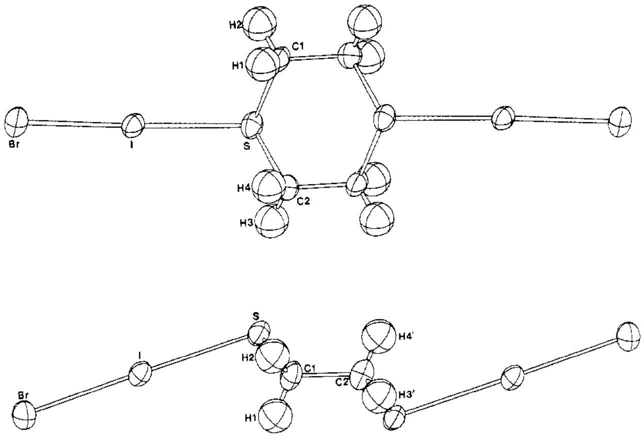

Figure 2.—Two ORTEP plots of the $C_4H_8S_2 \cdot 2IBr$ molecule. The thermal ellipsoids are at the 50% probability level.

Discussion of the Structure

A projection of the crystal structure of $C_4H_8S_2 \cdot 2IBr$ down the a axis is shown in Figure 1 and two views of the molecular structure of the complex are displayed in Figure 2. The more interesting bond distances and angles are indicated in Figure 3 and more complete listings are given in Tables IV and V. Table VI lists the torsion angles around the dithiane ring, while the

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(6) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 392 (1968).

(7) R. McWeeny, *ibid.*, **7**, 180 (1954).

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3178 (1965).

(9) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_4H_8S_2 \cdot 2IBr$[a]

H= 0, K= 0		
2	2411	2826
4	1004	1036
6	392	391
8	246	253
10	263	262
H= 0, K= 1		
1	527	-503
2	317	316
3	549	-546
4	106	103
6	73	-71
7	207	196
8	125	-123
10	107	-96
H= 0, K= 2		
0	1403	-1306
1	555	-537
2	1501	-1608
3	1157	-1197
4	1391	-1436
5	820	-813
6	981	-988
7	91	-71
8	658	-650
9	270	268
10	446	-437
11	216	198
H= 0, K= 3		
1	708	677
2	770	758
3	385	383
4	579	577
5	299	300
6	237	222
7	288	284
9	201	192
11	127	110
H= 0, K= 4		
0	211	205
1	112	-116
2	576	573
3	286	-292
4	1194	1207
5	261	-264
6	1309	1323
7	67	-60
8	927	922
10	461	443
H= 0, K= 5		
1	83	-62
2	134	121
3	502	-495
4	115	115
5	771	-769
7	667	-655
8	73	-57
9	370	-359
10	109	-98
11	154	-143
H= 0, K= 6		
0	1535	-1487
1	361	346
2	1286	-1263
3	754	751
4	775	-772
5	549	545
6	443	-443
7	122	113
8	322	-305
9	122	-114
10	265	-262
11	100	-84
H= 0, K= 7		
1	1276	1235
2	515	-509
3	864	846
4	426	-418
5	471	469
6	81	-86
7	257	260
8	74	86
9	171	179
10	136	116
H= 0, K= 8		
0	1357	1319
1	98	91
2	994	985
3	263	251
4	447	438
5	192	184
6	180	181
8	135	134
9	143	-142
10	145	141
H= 0, K= 9		
1	1223	-1217
2	394	-386
3	914	-909
4	368	-363
5	432	-432
6	185	-163
7	187	-180
9	202	-208
H= 0, K= 10		
1	132	-133
2	208	-201
3	205	-206
4	430	-439
5	72	-81
6	362	-355
8	226	-223
9	117	102
H= 0, K= 11		
1	364	364
2	258	256
3	452	451
4	268	274
5	644	656
6	112	103
7	651	651
H= 0, K= 12		
0	126	130
1	97	-90
2	74	88
3	191	-196
4	113	112
5	165	-159
6	193	192
8	124	139
H= 0, K= 13		
1	355	-361
2	296	299
3	501	-509
4	283	298
5	514	-525
6	108	118
7	402	-410
H= 0, K= 14		
0	121	-117
2	86	-81
H= 0, K= 15		
1	680	706
3	463	480
4	87	-108
5	234	236
H= 0, K= 16		
0	115	-135
2	113	-110
H= 1, K= 0		
-12	345	326
-10	646	625
-8	790	775
-6	684	674
-4	355	352
-2	41	-11
0	863	860
2	2223	2446
4	2095	2161
6	1254	1251
8	642	621
10	297	290
H= 1, K= 1		
-12	194	181
-10	366	349
-9	144	-136
-8	557	551
-6	646	647
-5	426	418
-4	552	556
-3	487	490
-2	419	424
-1	428	-433
0	288	280
1	661	-662
2	512	511
3	589	-599
4	790	799
5	434	-433
6	634	628
8	296	290
9	124	121
H= 1, K= 2		
-10	320	-308
-9	206	-199
-8	580	-572
-7	669	-668
-6	851	-856
-5	867	-873
-4	1176	-1217
-3	183	-176
-2	1621	-1718
-1	1011	982
0	1670	-1608
1	1047	1052
2	1000	-1023
3	485	477
4	901	-918
5	177	-178
6	834	-839
7	457	-446
8	588	-584
9	313	-304
10	383	-372
11	91	-74
H= 1, K= 3		
-11	90	90
-10	150	-138
-9	73	75
-8	82	-86
-7	112	94
-6	223	-224
-5	158	156
-4	654	-656
-3	236	241
-2	1271	-1269
-1	575	561
0	1741	-1663
1	1021	993
2	1149	-1158
3	703	703
4	199	-206
5	281	279
6	100	93
7	85	87
9	85	73
10	108	-110
H= 1, K= 4		
-8	221	219
-6	823	827
-5	168	135
-4	1587	1635
-3	513	510
-2	2092	2050
-1	882	831
0	1857	1756
1	585	576
2	779	773
3	215	217
4	196	185
6	297	284
8	474	471
10	410	409
H= 1, K= 5		
-10	168	163
-9	112	-106
-8	314	313
-7	363	-351
-6	508	506
-5	858	-873
-4	682	689
-3	1292	-1297
-2	727	715
-1	975	-954
0	572	552
1	110	-119
2	252	233
3	50	43
4	154	153
5	144	-147
6	182	174
7	292	-302
8	203	195
9	329	-327
10	171	160
11	247	-232
H= 1, K= 6		
-11	102	-183
-10	311	-307
-9	114	-106
-8	348	-353
-7	112	112
-6	301	-297
-5	138	144
-4	350	-350
-3	326	-319
-2	683	-657
-1	962	-921
0	997	-976
1	1092	-1062
2	1229	-1214
3	668	-664
4	1106	-1105
5	157	-153
6	626	-620
7	114	110
8	264	-260
9	88	95
10	171	-172
H= 1, K= 7		
-10	226	-219
-9	343	326
-8	441	-434
-7	460	453
-6	556	-547
-5	453	459
-4	419	-420
-3	327	327
-1	375	368
0	323	314
1	695	668
2	90	87
3	750	757
4	379	-380
5	686	681
6	480	-484
7	537	531
8	267	-264
9	315	313
10	108	-92
H= 1, K= 8		
-10	284	274
-9	276	269
-8	385	380
-7	461	459
-6	388	386
-5	458	458
-4	201	202
-3	136	118
-2	60	58
-1	123	-118
0	385	374
1	56	51
2	786	785
3	306	302
4	780	788
5	404	397
6	547	539
7	348	340
8	317	307
9	168	159
10	150	142
H= 1, K= 9		
-10	104	84
-9	366	-362
-7	359	-364
-5	173	-167
-3	191	-186
-2	260	251
-1	552	-543
0	586	581
1	874	-866
2	594	592
3	957	-958
4	287	284
5	783	-785
6	69	46
7	441	-434
9	193	-178
H= 1, K= 10		
-9	196	-194
-8	200	-206
-7	351	-353
-6	364	-370
-5	474	-481
-4	524	-521
-3	470	-468
-2	581	-576
-1	271	-266
0	268	-276
1	82	-76
2	106	91
3	104	-115
5	209	-210
6	217	-220
7	198	-202
8	251	-246
9	145	-139
H= 1, K= 11		
-9	105	96
-7	247	248
-6	101	95
-5	626	641
-3	899	906
-2	252	-285
-1	830	834
0	441	-441
1	645	643
2	336	-333
3	401	403
4	79	-81
5	198	198
7	159	204
H= 1, K= 12		
-7	97	102
-5	210	210
-4	161	186
-3	458	466
-2	212	211
-1	609	627
0	214	208
1	457	474
2	205	202
3	190	193
4	86	81
H= 1, K= 13		
-7	268	-262
-6	193	191
-5	420	-438
-4	158	153
-3	620	-635
-1	652	-663
0	271	-270
1	448	-457
2	271	-272
3	287	-302
5	297	-297
6	114	123
H= 1, K= 14		
-6	106	88
-5	173	-175
-4	131	128
-3	150	-157
-1	167	-164
0	90	-95
1	222	-234
2	167	-176
3	230	-230
4	137	-143
5	143	-156
H= 1, K= 15		
-5	174	186
-3	96	98
-1	188	198
0	110	120
1	393	415
3	487	507
H= 1, K= 16		
1	123	112
2	100	-110
H= 2, K= 0		
-10	143	135
-8	530	524
-6	916	932
-4	1009	1053
-2	768	791
0	110	102
4	516	524
6	716	711
8	526	525
10	324	315
H= 2, K= 1		
-12	156	166
-10	264	260
-9	218	-210
-8	586	578
-7	437	-430
-6	1143	1162
-5	362	-359
-4	1545	1673
-3	325	324
-2	1495	1651
-1	948	915
0	1153	1150
1	593	593
2	515	530
4	333	335
5	338	-353
6	475	478
7	367	-366
8	529	525
9	171	-162
10	375	364
H= 2, K= 2		
-10	131	-121
-9	107	103
-8	174	-180
-7	57	51
-6	355	-357
-5	405	-404
-4	585	-601
-3	1037	-1066
-2	927	-933
-1	1117	-1068
0	1303	-1265
1	231	-228
2	951	-972
3	203	201
4	562	-571
5	204	197
6	367	-372
7	61	67
8	306	-307
9	72	-45
10	230	-219
11	94	-88
H= 2, K= 3		
-11	97	101
-10	547	-533
-9	231	229
-8	591	-588
-7	275	280
-6	352	-362
-5	229	226
-4	209	-206
-2	582	-566
-1	436	-412
0	1237	-1195
1	220	-207
2	1536	-1594
3	334	336
4	1381	-1419
5	486	490
6	743	-752
7	311	311
8	235	-228
9	145	142
10	114	-90
H= 2, K= 4		
-11	195	191
-10	234	234
-9	238	233
-8	77	78
-7	217	218
-5	83	85
-4	230	230
-2	775	763
-1	297	290
0	1126	1104
1	803	783
2	1230	1247
3	770	778
4	819	823
5	455	457
6	307	307
7	216	204
8	132	137
10	144	157
H= 2, K= 5		
-10	319	311
-9	81	82
-8	367	364
-7	182	169
-6	420	418
-5	102	96
-4	559	550
-3	442	-444
-2	821	802
-1	1293	-1255
0	1101	1080
1	1234	-1201
2	1127	1121
3	386	-387
4	783	792
6	422	423
8	212	206
10	143	117
H= 2, K= 6		
-11	210	-205
-10	186	-182
-9	412	-397
-8	463	-454
-7	525	-523
-6	575	-574
-5	396	-393
-4	324	-319
-3	136	-134
-1	200	-192
0	98	-76
1	507	-488
2	198	-195
3	667	-666
4	446	-447
5	583	-576
6	621	-617
7	381	-370
8	438	-427
9	186	-181
10	165	-162
H= 2, K= 7		
-10	78	-64
-9	93	64
-8	241	-236
-7	149	135
-6	667	-663
-5	376	373
-4	1055	-1055
-3	607	527
-2	1106	-1082
-1	507	499
0	691	-669
1	339	332
2	170	-157
3	316	311
5	206	205
6	169	-165
7	132	135
8	299	-302
9	175	176
H= 2, K= 8		
-9	217	214
-8	167	163
-7	454	457
-6	354	351
-5	853	858
-4	531	528
-3	1120	1113
-2	441	430
-1	827	802
0	134	127
1	239	241
2	93	85
4	211	210
5	144	157
6	224	227
7	257	256
8	206	192
9	254	260
H= 2, K= 9		
-10	198	185
-9	204	-195
-8	294	281
-7	432	-434
-6	321	314
-5	508	-516
-4	301	304
-3	246	-245
-2	261	249
0	200	193
2	253	257
3	257	-260
4	358	356
5	424	-423
6	307	307
7	405	-407
8	192	194
9	250	-248
H= 2, K= 10		
-9	209	-197
-8	130	128
-7	270	-263
-6	86	66
-5	406	-417
-4	183	-195
-3	608	-612
-2	538	-536
-1	750	-747
0	718	-715
1	690	-686
2	475	-479
3	480	-477
5	298	-299
6	124	121
7	204	-210
H= 2, K= 11		
-8	178	-174
-6	77	-79
-3	226	232
-1	437	447
0	141	-133
1	506	511
2	323	-321
3	471	472
4	330	-336
5	346	363
6	191	-194
7	208	209
H= 2, K= 12		
-8	99	99
-7	251	255
-5	157	152
-3	113	124
-1	374	377
1	703	716
2	98	104
3	723	737
4	161	158
5	476	474
6	125	114
7	218	222
H= 2, K= 13		
-7	81	-81
-5	103	-101
-4	145	150
-3	210	-208
-2	202	197
-1	388	-393
0	180	182
1	445	-461
3	326	-334
4	78	-71
5	206	-206
H= 2, K= 14		
-6	142	-146
-5	383	-388
-3	429	-445
-2	205	209
-1	369	-380
0	223	232
1	245	-256
2	119	118
3	230	-238
5	238	-256
H= 2, K= 15		
-3	265	277
-1	133	127
3	133	150
H= 2, K= 16		
-1	287	307
H= 3, K= 0		
-10	116	-106
-8	120	-118
-6	102	108
-4	446	449
-2	546	555
0	250	234
2	107	-102
4	121	-106
6	61	57
8	139	135
10	126	121
H= 3, K= 1		
-11	170	158
-10	358	348
-9	209	202
-8	307	306
-6	387	383
-5	471	-473
-4	889	910
-3	783	-803
-2	1582	1682
-1	473	-458
0	1044	1963
1	184	182
2	1497	1582
3	550	555
4	895	916
5	387	396
6	416	414
7	66	67
8	224	227
9	93	-99
10	214	212
H= 3, K= 2		
-11	110	-87
-6	59	60
-4	103	112
-3	191	-197
-2	137	139
-1	677	-648
0	122	-116
1	736	-745
2	371	-371
3	331	-335
4	338	-333
6	195	-190
8	105	-110
H= 3, K= 3		
-11	133	-134
-10	409	-398
-9	129	-133
-8	859	-862
-6	1222	-1272
-5	247	253
-4	1099	-1130
-3	497	504
-2	587	-572
-1	478	461
0	335	-322
1	118	-116
2	520	-500
3	377	-374
4	753	-763
5	198	-199
6	829	-840
8	637	-628
10	314	-308
H= 3, K= 4		
-11	135	132
-9	314	316
-8	128	133
-7	484	489
-5	550	553
-4	289	-287
-3	404	403
-2	148	-145
-1	115	112
0	135	124
2	246	240
3	253	254
4	323	318
5	427	428
6	249	256
7	333	336
9	210	197
H= 3, K= 5		
-11	147	-143
-10	336	330
-9	151	-138
-8	582	583
-6	804	813
-5	343	348
-4	876	879
-3	658	644
-2	783	755
-1	503	476
0	573	575
1	309	-297
2	555	550
3	691	-699
4	635	634
5	402	-393
6	589	591
7	92	-79
8	431	422
H= 3, K= 6		
-11	146	-143
-10	131	130
-9	246	-253
-8	130	122
-7	435	-435
-6	211	-208
-5	606	-613
-4	577	-576
-3	628	-616
-2	468	-468
-1	470	-455
0	101	-93
1	376	-371
2	114	114
3	429	-432
4	206	204
5	422	-426
6	124	123
7	315	-308
8	88	-87
9	170	-185
H= 3, K= 7		
-10	200	-204
-8	97	-90
-6	69	-72
-5	105	-114
-4	421	-427
-3	127	-135
-2	982	-972
0	1223	-1207
1	121	82
2	943	-942
3	137	128
4	492	-490
5	206	211
6	152	-157
7	154	141
H= 3, K= 8		
-9	131	123
-7	118	109
-5	251	257
-3	659	662
-2	183	179
-1	1117	1111
0	169	167
1	1159	1148
3	685	697
5	271	268
6	83	81
7	117	127
H= 3, K= 9		
-9	132	129
-8	197	193
-6	272	274
-5	237	-236
-4	315	311
-3	423	-425
-2	366	363
-1	292	-281
0	439	437
2	428	424
3	178	184
4	301	305
5	107	117
6	200	210
8	127	143
H= 3, K= 10		
-9	313	-313
-8	82	-98
-7	392	-394
-6	130	129
-5	440	-444
-4	365	373
-3	487	-500
-2	360	-361
-1	554	-553
1	555	-561
2	326	-328
3	507	-516
4	361	-370
5	421	-423
6	185	-191
7	299	-310
H= 3, K= 11		
-8	204	-201
-6	308	-314
-4	259	-261
-2	90	-80
1	107	102
3	113	114
4	158	-151
5	85	87
6	198	-201
H= 3, K= 12		
-7	518	532
-6	93	81
-5	592	604
-4	109	105
-3	449	463
-2	78	72
-1	185	188
1	116	108
3	295	304
5	433	449
H= 3, K= 13		
-2	115	137
0	102	105
1	88	-91
2	82	69
3	145	-164
5	117	-107
H= 3, K= 14		
-5	311	-327
-4	258	-277
-3	396	-416
-2	214	-234
-1	490	-505
1	477	-500
2	119	116
3	331	-352
4	183	183
H= 3, K= 15		
-1	114	113
H= 4, K= 0		
-10	268	-267
-8	441	-434
-6	538	-543
-4	378	-384
0	246	242
2	90	-73
4	380	-380
6	325	-326
8	161	-153
H= 4, K= 1		
-10	448	440
-9	114	115
-8	648	640
-7	392	395
-6	629	632
-5	436	438
-4	406	407
-3	75	81
-2	372	380
-1	352	-337
0	691	695
1	476	-484
2	357	371
3	291	-297
4	919	940
6	688	687
7	189	187
8	412	400
9	106	105
H= 4, K= 2		
-11	135	-136
-10	145	147
-9	156	-152
-8	156	165
-6	197	202
-5	187	193
-4	255	263
-3	185	188
-2	401	393
-1	64	-58
0	549	545
1	426	-432
2	402	406
3	542	-559
4	178	173
5	314	-318
6	85	85
8	87	57
H= 4, K= 3		
-10	113	-117
-9	101	-107
-8	206	-217
-7	278	-277
-6	614	-622
-5	380	-383
-4	1221	-1244
-3	333	-332
-2	1482	-1441
0	1014	-1003
1	289	293
2	480	-484
3	169	164
4	276	-279
6	248	-257
7	87	-90
8	274	-277
H= 4, K= 4		
-10	101	-99
-7	201	200
-5	436	445
-4	289	-287
-3	607	607
-2	703	-691
-1	603	581
0	669	-651
1	351	349
2	322	-323
3	107	105
7	132	130
9	143	129
H= 4, K= 5		
-10	148	143
-8	194	194
-7	184	-181
-6	384	379
-5	144	-132
-4	670	673
-3	121	128
-2	949	921
-1	572	554
0	944	919
1	744	732
2	682	677
3	370	374
4	399	398
5	63	-47
6	261	261
7	112	-114
8	206	209
H= 4, K= 6		
-10	93	107
-9	155	-156
-8	293	282
-7	323	-327
-6	504	498
-5	530	-535
-4	400	399
-3	630	-628
-1	522	-507
0	154	-148
1	292	-292
3	178	-172
5	214	-215
6	117	130
7	255	-258
8	165	155
H= 4, K= 7		
-10	306	-293
-9	180	-193
-8	395	-385
-7	92	-120
-6	284	-283
-1	134	-142
0	400	-391
1	207	-206
2	684	-692
3	265	-264
4	639	-640
5	274	-271
6	416	-429
8	211	-208
H= 4, K= 8		
-9	362	356
-8	144	-153
-7	331	323
-6	145	-157
-5	177	170
-4	141	-133
-3	100	94
-2	65	-65
-1	203	200
1	452	451
2	80	-63
3	633	637
4	181	-167
5	543	542
6	133	-131
7	303	301
H= 4, K= 9		
-9	181	185
-8	245	251
-7	355	364
-6	342	340
-5	394	396
-4	378	379
-3	181	181
-2	286	287
0	144	142
1	119	-119
2	129	130
4	210	218
5	144	141
6	229	235
7	170	177
H= 4, K= 10		
-7	276	-275
-6	187	-183
-5	358	-356
-4	121	-122
-3	416	-412
-2	184	180
-1	476	-466
0	427	421
1	498	-493
2	329	325
3	428	-424
4	89	95
5	294	-299
H= 4, K= 11		
-7	83	-80
-6	143	-152
-5	213	-220
-4	325	-334
-3	336	-349
-2	364	-360
-1	302	-312
0	201	-200
1	183	-185
3	82	-79
H= 4, K= 12		
-5	425	434
-4	79	-56
-3	613	675
-1	628	647
1	426	429
3	186	185
5	125	122
H= 4, K= 13		
-3	126	124
-1	236	231
0	156	157
1	231	253
2	168	173
3	117	125
H= 4, K= 14		
-4	119	117
-3	252	-257
-1	264	-279
0	158	-170
1	303	-308
2	138	-154
H= 5, K= 0		
-10	106	-77
-8	317	-327
-6	668	-681
-4	590	-1008
-2	1012	-1053
0	561	-574
6	202	-198
8	231	-230
H= 5, K= 1		
-10	107	113
-9	139	-124
-8	282	275
-7	74	-79
-6	513	508
-5	211	214
-4	643	643
-3	405	406
-2	504	508
-1	304	295
0	298	298
1	104	107
2	246	252
4	303	301
5	142	-133
6	296	292
7	80	-68
8	234	231
H= 5, K= 2		
-10	278	272
-9	220	-211
-8	344	338
-7	399	-404
-6	409	410
-5	290	-294
-4	461	468
-3	98	107
-2	445	432
-1	408	392
0	461	454
1	319	323
2	516	524
4	434	431
5	227	-227
6	252	250
7	247	-241
8	164	165
H= 5, K= 3		
-10	159	-144
-8	82	-93
-5	102	-101
-4	138	-144
-3	255	-257
-2	539	-525
-1	423	-401
0	839	-813
1	303	-307
2	690	-700
3	113	-112
4	386	-391
6	159	-207
8	131	-132
H= 5, K= 4		
-10	322	-311
-8	336	-334
-6	198	-203
-3	184	180
-2	125	-112
-1	317	311
0	515	-499
1	329	327
2	693	-605
3	254	253
4	569	-551
5	126	128
6	304	-307
8	103	-110
H= 5, K= 5		
-10	203	201
-9	305	295
-8	249	242
-7	244	242
-6	213	207
-4	173	165
-3	103	-77
-2	207	195
0	316	307
1	225	223
2	398	401
3	407	403
4	385	390
5	340	337
6	281	284
7	147	149
H= 5, K= 6		
-8	146	146
-6	291	292
-4	527	530
-3	344	-334
-2	620	601
-1	555	-545
0	428	412
1	499	-495
2	220	217
3	268	-267
4	145	141
6	120	110
H= 5, K= 7		
-9	178	-182
-8	260	-257
-7	352	-354
-6	416	-414
-5	444	-447
-4	421	-412
-3	384	-362
-2	190	-175
-1	257	-253
1	126	-126
3	92	-81
4	186	-139
5	135	-133
6	238	-236
7	161	-163
H= 5, K= 8		
-8	150	-141
-7	310	306
-6	276	-278
-5	371	367
-4	392	-390
-3	252	249
-2	408	-401
-1	133	124
0	255	-248
1	92	88
3	108	114
5	182	177
6	126	-104
H= 5, K= 9		
-7	170	174
-6	76	80
-5	409	423
-4	226	231
-3	564	570
-2	379	372
-1	463	463
0	392	388
1	275	272
2	224	220
3	109	117
H= 5, K= 10		
-7	184	-197
-6	126	126
-5	234	-224
-3	217	-215
-2	80	-86
-1	160	-170
1	153	-163
2	195	196
3	217	-217
4	204	203
5	230	-236
H= 5, K= 11		
-3	106	-110
-2	155	-164
-1	304	-311
0	265	-272
1	386	-390
2	204	-214
3	328	-335
H= 5, K= 12		
-3	157	155
-1	267	278
0	85	-88
1	338	342
3	282	297
H= 5, K= 13		
-3	132	140
-2	98	-112
-1	126	132
0	141	-147
1	206	214
H= 6, K= 0		
-8	82	-73
-6	95	-100
-4	331	-329
-2	675	-684
0	939	-967
2	804	-826
4	380	-388
6	132	-124
H= 6, K= 1		
-7	69	-77
-6	76	65
-5	118	-117
-4	157	155
-2	228	221
-1	233	229
0	181	188
1	172	170
2	95	91
3	81	87
6	82	81
H= 6, K= 2		
-9	173	171
-8	351	354
-6	415	420
-5	281	-281
-4	469	475
-3	495	-493
-2	522	503
-1	319	-308
0	431	431
2	366	366
3	218	219
4	367	365
5	186	170
6	286	293
H= 6, K= 3		
-9	101	-109
-8	117	-97
-7	119	-123
-5	124	-133
-4	85	84
-3	114	-117
-2	106	104
-1	143	-135
1	184	-180
2	215	-213
3	136	-144
4	239	-246
5	95	-86
6	139	-138
H= 6, K= 4		
-8	449	-451
-6	635	-641
-4	567	-575
-3	105	-95
-2	278	-280
0	81	-79
1	92	96
2	130	-124
3	108	108
4	254	-260
6	309	-313
H= 6, K= 5		
-9	152	172
-7	327	326
-6	135	116
-5	383	384
-4	163	161
-3	264	259
-2	155	143
-1	68	71
0	107	96
3	95	104
5	173	176
H= 6, K= 6		
-8	155	145
-6	179	179
-5	118	127
-4	291	292
-3	257	256
-2	441	430
-1	146	135
0	466	463
1	90	-72
2	363	368
3	214	-216
4	237	237
5	182	-188
H= 6, K= 7		
-7	110	-107
-5	194	-197
-4	218	-222
-3	328	-324
-2	296	-285
-1	426	-416
0	181	-184
1	404	-393
3	271	-264
5	135	-137
H= 6, K= 8		
-5	126	124
-4	130	-125
-3	210	207
-2	284	-272
-1	127	121
0	419	-409
2	374	-364
4	189	-182
H= 6, K= 9		
-5	108	99
-4	102	-105
-3	274	276
-2	102	-74
-1	434	431
1	409	405
2	135	149
3	298	305
4	173	169
H= 6, K= 10		
-5	83	-76
-4	172	163
-3	147	-141
-2	124	121
-1	158	-152
1	81	-87
H= 6, K= 11		
-3	212	-214
-2	100	107
-1	95	-97
1	130	-133
H= 7, K= 0		
-8	370	-377
-6	295	-282
-4	140	-144
-2	82	-90
0	176	-172
2	353	-357
4	422	-426
H= 7, K= 1		
-8	162	-152
-6	154	-165
-4	85	-96
-3	140	-141
1	120	124
3	118	120
4	77	-62
H= 7, K= 2		
-8	217	216
-7	200	197
-6	314	324
-5	284	283
-4	324	323
-3	135	137
-2	402	383
-1	135	-128
0	358	364
1	221	-228
2	285	273
3	107	-125
4	198	204
H= 7, K= 3		
-3	94	-84
-2	208	191
-1	132	-110
0	236	224
1	155	-146
2	147	156
3	148	-151
H= 7, K= 4		
-6	220	-222
-4	470	-469
-3	84	-76
-2	578	-556
-1	133	-148
0	442	-437
1	115	-118
2	251	-253
4	115	-120
H= 7, K= 5		
-7	121	114
-6	108	-103
-5	245	242
-4	118	-114
-3	348	339
-2	98	-95
-1	291	295
1	120	125
H= 7, K= 6		
-6	135	129
-5	125	-121
-4	93	91
-2	182	167
-1	135	134
0	274	268
1	206	200
2	275	281
3	141	133
H= 7, K= 7		
-6	178	173
-5	159	-164
-4	112	107
-3	123	-143
-1	124	-115
1	145	-157
2	95	-73
H= 7, K= 8		
-5	122	-129
-4	116	-114
2	164	-147
H= 7, K= 9		
-1	133	121
0	66	-80
H= 8, K= 0		
-6	276	-274
-4	285	-289
-2	214	-213
0	108	-118
H= 8, K= 1		
-6	212	-207
-5	102	104
-4	286	-295
-2	279	-270
-1	103	-110
0	161	-162
1	82	-97
H= 8, K= 2		
-4	164	170
-3	152	150
-2	224	209
-1	175	177
0	228	221
2	201	201
H= 8, K= 3		
-5	93	-77
0	158	137

[a] The data are separated into groups having common h and k values. The three columns in each group list values of l, $10|F_o|$, and $10F_c$ in that order.

TABLE IV

BOND DISTANCES IN $C_4H_8S_2 \cdot 2IBr$ COMPARED WITH THOSE IN $C_4H_8S_2 \cdot 2I_2$[a]

	$C_4H_8S_2 \cdot 2IBr$	$C_4H_8S_2 \cdot 2I_2$
I–I	. . .	2.787 (2)
I–Br	2.646 (1)	. . .
S–I	2.687 (2)	2.867 (6)
S–C(1)	1.816 (6)	1.80 (2)
S–C(2)	1.816 (6)	1.83 (2)
C(1)–C(2)′	1.523 (8)	1.55 (3)
C(1)–H(1)	0.91 (7)	
C(1)–H(2)	0.92 (6)	
C(2)–H(3)	0.98 (6)	
C(2)–H(4)	0.94 (7)	
S· · ·S′	3.446 (4)	3.436 (12)

[a] G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, **13**, 727 (1960).

shortest intermolecular packing distances are given in Table VII.

The 1,4-dithiane ring is in the chair conformation and

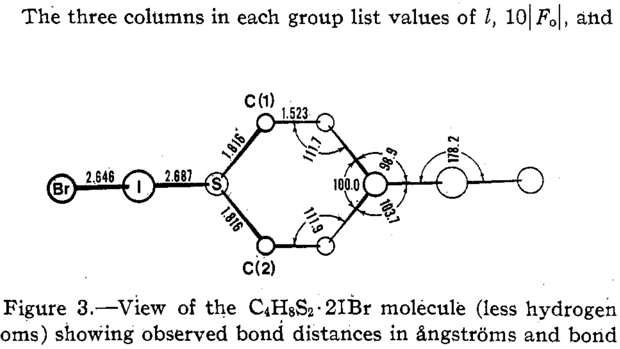

Figure 3.—View of the $C_4H_8S_2 \cdot 2IBr$ molecule (less hydrogen atoms) showing observed bond distances in ångströms and bond angles in degrees.

the IBr molecules are bonded *equatorially* to sulfur to give nearly linear S–I–Br groups. The $C_4H_8S_2 \cdot 2IBr$ molecule is required crystallographically to have only a center of inversion but, within the small errors involved, the 1,4-dithiane moiety has $2/m$ (C_{2h}) symmetry. The molecule as a whole, however, deviates significantly from mirror symmetry because of small displacements of the I and Br atoms from the pseudomirror. The

TABLE V

BOND ANGLES IN $C_4H_8S_2\cdot 2IBr$ COMPARED WITH THOSE IN $C_4H_8S_2\cdot 2I_2$

	$C_4H_8S_2\cdot 2IBr$	$C_4H_8S_2\cdot 2I_2$
I–I–S	. . .	177.9 (4)
Br–I–S	178.2 (4)	. . .
I–S–C(1)	103.7 (3)	101 (1)
I–S–C(2)	98.9 (3)	96 (1)
I–S···S′	128.9 (2)	125.0 (6)
C(1)–S–C(2)	100.0 (3)	102 (2)
S–C(1)–C(2)′	111.9 (4)	111 (2)
S–C(2)–C(1)′	111.7 (4)	113 (2)
S–C(1)–H(1)	106 (4)	
S–C(1)–H(2)	100 (4)	
S–C(2)–H(3)	104 (4)	
S–C(2)–H(4)	106 (4)	
S–C–H(av)	104 (2)	
C(2)′–C(1)–H(1)	115 (4)	
C(2)′–C(1)–H(2)	113 (4)	
C(1)′–C(2)–H(3)	113 (4)	
C(1)′–C(2)–′H(4)	113 (4)	
C–C–H(av)	114 (2)	
H(1)–C(1)–H(2)	110 (6)	
H(3)–C(2)–H(4)	109 (6)	
H–C–H(av)	110 (4)	

TABLE VI

TORSION ANGLES IN THE 1,4-DITHIANE RING (ESD ∼0.50°)

Atom	Angle, deg
S–C(1)–C(2)′–S′	68.8
C(2)–S–C(1)–C(2)′	61.6
C(1)–S–C(2)–C(1)′	61.4

TABLE VII

SHORTEST INTERMOLECULAR PACKING DISTANCES IN $C_4H_8S_2\cdot 2IBr$

First atom (position A)	Second atom, position,[a] and lattice translation			Distance, Å	Sum of van der Waals radii, Å
I	Br	B	$(1\bar{1}0)$	4.105 (1)	4.10
I	S	D	$(00\bar{1})$	4.068 (2)	4.00
I	H(2)	D	$(00\bar{1})$	3.26 (6)	3.4
Br	S	A	(100)	3.621 (3)	3.80
Br	H(3)	A	(100)	3.00 (6)	3.2
Br	H(2)	C	$(1\bar{1}1)$	3.17 (6)	
Br	H(4)	D	(100)	3.17 (7)	
Br	H(2)	D	$(00\bar{1})$	3.19 (6)	

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

magnitude of the displacement in the case of iodine is indicated by the I–S–C bond angles in Table V.

The four carbon atoms are required by the molecular center of symmetry to be coplanar. The displacements of the heavy atoms from the plane of the carbons are as follows: S, 0.952 Å; I, 0.143 Å; Br, −0.681 Å. The dihedral angle between the plane of the carbon atoms and the plane of the C–S–C bonds is 54.7 (2)°.

It is of interest to compare the present structure with that of the iodine complex of 1,4-dithiane, $C_4H_8S_2\cdot 2I_2$.[10] Although both complexes crystallize in the same space group ($P2_1/c$) with two centrosymmetric molecules per unit cell, the crystals are not isomorphous. The shapes of the unit cells and the molecular packing differ greatly. On the other hand, the molecular structures of the two complexes are closely similar. The comparison is facilitated by inclusion of bond distances and angles for the iodine complex with those of the IBr complex in Tables IV and V. The S–I bond distance of 2.687 (2) Å in the IBr complex is significantly shorter (0.180 Å) than that of 2.867 (6) Å in the I_2 complex. This is reasonable, in view of the greater acceptor strength of IBr relative to I_2 in complexes of this type.[11,12] While the observed S–I distance in $C_4H_8S_2\cdot 2IBr$ is 0.32 Å longer than the sum of the single-bond, covalent radii (2.37 Å), it is among the shortest S–I bonds reported to the time of this writing. As a result of the S–I bonding, the I–Br bond is lengthened from the value of 2.470 (5) Å observed in the vapor[13] to 2.646 (1) Å. In solid IBr, the observed intramolecular distance is 2.521 (4) Å,[14] but this is also lengthened from the value in the isolated gas molecule through the effects of self-complexing or intermolecular (secondary) bonding.

It is interesting to note that in the structures investigated to date, halogens and interhalogens bond to sulfur in six-membered ring systems in *equatorial* positions while the bonding to selenium in these situations is usually *axial*.[15-18] The one known exception is $C_4H_8SSe\cdot 2I_2$[19] where both iodine molecules are bonded equatorially.

An inspection of the shortest intermolecular atomic separations (Table VII) in relationship to the van der Waals radii involved reveals no case where a significant secondary bond is indicated. The tabulated Br···S separation of 3.62 Å is shorter than the sum of the van der Waals radii, 3.80 Å, but the difference is not considered large enough to affect other bond distances. Accordingly, the observed bond distances in the S–I–Br group may be considered reasonably unperturbed.

As usual in compounds of this type, the terminal atom (Br in the present study) has the highest thermal parameters in the molecule.

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