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Refinement of the Crystal Structure of 3,5-Diamino-1,2,4-dithiazolium Iodide

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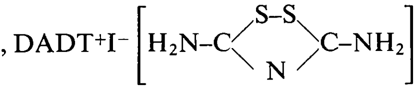
The crystal structure of 3,4-diamino-1,2,4-dithiazolium iodide ($S_2C_2N_3H_4I$) (thiouret hydroiodide) ($DADT^+I^-$) has been refined by full-matrix least-squares methods, including anisotropic temperature factors from counter data collected at room temperature, to a final R index of 0·032. The crystals are orthorhombic, space group *Pcmn*, $Z=4$, $a=14·025$ (6), $b=9·274$ (3), $c=5·349$ (1) Å. The structure is composed of molecular ions, $DADT^+$, and iodide ions with somewhat shorter than normal nonbonded distances between them. The $DADT^+$ ion, including hydrogen atoms, is planar well within experimental error. The S–S, C–S, C–N distances are 2·083 (3); 1·752 (5), 1·317 (7); 1·330 (6) Å, respectively. The shortest 'nonbonded' S···I distance is 3·746 (2) Å.

Introduction

Thiourea [$SC(NH_2)_2$] reacts with a number of oxidizing agents including some metal ions to form a disulfide linkage [$(NH_2)_2C–S–S–C(NH_2)_2$]$^{2+}$. Dithiobiuret, on the other hand, is a much stronger reducing agent than thiourea and can be oxidized by iodide ion. During a systematic investigation of thiourea and dithiobiuret metal complexes, we prepared 3,5-diamino-1,2,4-dithiazolium iodide, $DADT^+I^-$  I^-, the ring closure oxidation product of dithiobiuret. This particular ion is also known by the trivial name of the thiouret ion. We decided it would be of interest to examine the crystal structure of this compound to see the effect of the disulfide linkage and electron delocalization on the C–S and C–N bond lengths and to compare these distances with those found by us in the metal complexes of dithiobiuret and thiourea. An earlier single-crystal structure investigation was reported (Foss & Tjomsland, 1956, 1958) from two-dimensional data. Unfortunately, we were unaware of this work until our structure was completed. But since this earlier research was based on only two-dimensional data, we decided to report the structure solution based on three-dimensional counter data.

Experimental

3,5-Diamino-1,2,4-dithiazolium was prepared by dissolving dithiobiuret in an aqueous 20% hydroiodic-acid solution with a pinch of iodine. Single-crystals suitable for diffraction studies were grown by slow evaporation of the solution. Preliminary Weissenberg and precession photographs established the space groups as $Pc2_1n$ or *Pcmn* (*International Tables for X-ray Crystallography*, 1952). The latter was assumed and verified by the structure solution and refinement. A crystal specimen in the shape of a parallelepiped (0·22 × 0·16 × 0·36 mm) was mounted about the long direction (**c**) in a glass capillary and used for the collection of intensity data on a Picker automatic diffractometer utilizing Zr-filtered Mo $K\alpha$ radiation. A capillary was necessary because the crystal reacted with or dissolved in the common adhesives.

Ten general reflections were accurately centered and used as a basis for a least-squares refinement (Spofford, 1968) of the cell parameters at room temperature with Mo $K\alpha$ radiation ($\lambda=0·71068$ Å). The crystal data are: $a=14·025$ (6), $b=9·274$ (3), $c=5·349$ (1) Å, $D_{\rm calc}=2·47$ $D_{\rm obs}=2·48$ (1); $Z=4$, F.V. 261·0, $V=696·0$ Å^3, space group *Pcmn*. (Numbers in parentheses here and elsewhere in this paper are estimated standard deviations in the least significant digits.)

The crystal was accurately centered on the diffractometer by variations of well known methods (Furnas, 1957). Intensities of 1650 independent *hkl* reflections were measured by stationary-counting backgrounds and scanning peaks by the usual θ–2θ technique with Mo $K\alpha$ radiation. Reflections *hk*0 through *hk*3 were recorded for 108 seconds (1·8° in 2θ) and the backgrounds were measured at ±0·90° in 2θ from the peak maxima for 40 seconds. For *hk*4 through *hk*8 the reflections were recorded for 114 seconds (1·9°) and the backgrounds were measured at ±0·95° in 2θ from the peak maxima for 40 seconds. A random sampling of symmetry-related reflections gave agreement within less than a standard deviation and no systematic variation was detected; thereafter only the symmetry-independent data were collected. A standard reflection was measured after every tenth reflection to ensure stability of operation and check any crystal decomposition. The total variation in intensity of this standard peak during data collection was less than three standard deviations. But it showed a slow overall downward drift during the data-collection period, probably indicating some crystal decomposition by the X-ray beam. All the data were scaled to the original standard to correct for this decomposition. The integrated intensity was calculated from:

$$I(\text{net}) = I(\text{scan}) - \frac{t_s}{t_b}(B_1 + B_2)$$

where B_1 and B_2 are the background counts, t_s = scan time and t_b = sum of background counting times for each reflection. The standard deviation of I(net) was calculated from $\sigma[I(\text{net})] = [I(\text{scan}) + (t_s/t_b)^2(B_1+B_2)]^{1/2}$. A reflection was considered above background when I(net) was greater than $3{\cdot}49[B_1+B_2]^{1/2}$ for $hk0 \geq hk3$ and $3{\cdot}59[B_1+B_2]^{1/2}$ for $hk3 \geq hk8$. By this criterion 853 nonzero hkl reflections were retained. The calculated linear absorption coefficient (μ) was 54·7 cm^{-1} with Mo $K\alpha$ radiation. No absorption correction was made. Neglect of an absorption correction probably makes our error estimates somewhat optimistic and has some effect on the anisotropic temperature factors. The usual Lorentz–polarization corrections were applied to the intensities which were then reduced to structure factors.

Structure determination

Four molecules of DADT$^+$I$^-$ can be accommodated in the general positions of $Pc2_1n$ or in $Pcmn$ with the ring nitrogen atom in the mirror plane and the iodine ions either on the mirror or on centers of symmetry. An unsharpened Patterson (Sly–Shoemaker–van den Hende) function was computed and the iodine atom was located on the mirror and the sulfur atoms were located in the general positions of $Pcmn$. A set of

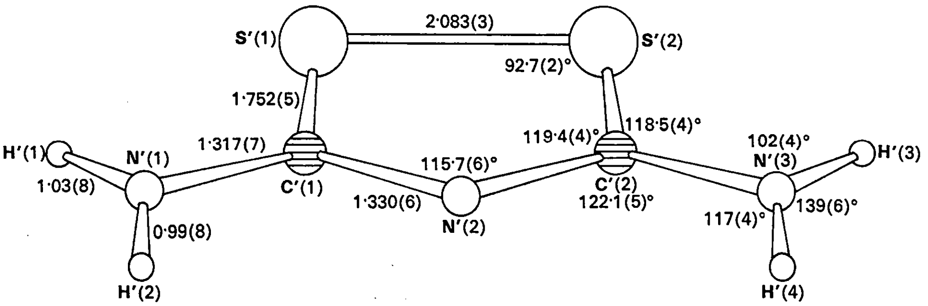


Fig. 1. Perspective view of the DADT$^+$ molecule with distances and angles indicated. The two halves of the molecular ion are related by a mirror plane and the angles are denoted on one half and the distances on the other half.

Table 1. *Structure factors*

(*a*) Observed and calculated (first column is h followed by F_o and F_c. $F_c/10$ is absolute).

* H	0	0 *
2	211	242
6	466	501
8	243	236
10	400	401
12	158	152
14	172	171
16	129	133
* H	1	0 *
1	181	174
3	353	362
5	151	153
7	517	547
11	454	468
13	117	115
15	239	248
17	140	155
21	102	98
* H	2	0 *
0	743	874
2	305	312
4	615	700
6	508	540
8	330	337
10	413	424
12	66	65
14	229	238
* H	3	0 *
1	600	631
3	787	952
5	77	72
7	653	704
9	186	181
11	299	305
13	172	173
* H	4	0 *
0	517	501
2	120	110
4	432	435
8	301	308
10	225	229
12	143	145
* H	5	0 *
1	580	579
3	813	882
7	611	632
9	221	220
11	221	225
13	165	169
* H	6	0 *
0	390	377
2	94	85
4	381	376
6	211	211
8	302	290
10	268	258
12	129	126
14	190	212
* H	7	0 *
1	228	218
3	359	352
5	66	56
7	360	362
11	252	255
13	103	100
* H	8	0 *
0	724	742
2	117	115
4	521	522
6	253	252
8	137	138
10	217	215
12	70	64
14	87	107
* H	9	0 *
1	77	81
3	112	119
5	95	92
7	208	213
9	62	45
11	227	231
* H	10	0 *
0	402	395
2	130	126
4	300	295
6	256	256
8	110	104
10	197	196
14	91	88
* H	11	0 *
1	149	149
3	207	208
5	70	60
7	201	201
11	115	134
* H	12	0 *
0	162	166
4	140	142
8	92	86
10	86	85
* H	13	0 *
1	151	140
3	238	230
7	173	178
* H	14	0 *
4	82	74
* H	15	0 *
3	113	112
7	90	98
* H	16	0 *
0	133	128
4	102	99
* H	0	1 *
3	151	145
4	769	930
5	319	305
6	442	452
7	138	118
8	733	781
9	316	310
10	52	47
12	342	344
13	175	178
14	85	77
15	80	77
16	66	76
* H	1	1 *
1	386	382
2	571	594
3	451	455
4	130	117
5	350	343
6	305	296
7	262	260
8	152	148
9	364	361
10	74	77
13	267	269
15	141	140
17	100	113
19	118	124
* H	2	1 *
1	351	343
2	770	880
3	236	228
4	294	289
5	292	291
6	458	453
7	43	43
8	376	377
10	128	127
11	59	65
15	80	76
16	129	135
* H	3	1 *
1	726	764
2	298	286
3	359	340
4	116	107
6	189	185
7	104	110
8	177	171
9	376	371
10	75	72
11	245	240
12	164	162
13	126	126
15	163	164
19	95	71
* H	4	1 *
1	326	302
2	178	175
3	131	121
4	115	104
5	355	346
6	386	381
8	187	185
9	221	218
10	350	349
12	223	223
13	68	69
14	136	138
16	157	166
* H	5	1 *
2	204	193
3	280	268
4	89	86
5	642	658
6	147	141
7	181	175
8	151	148
9	324	316
10	74	66
11	270	265
12	148	150
15	148	147
16	94	100
* H	6	1 *
1	237	228
2	409	398
3	142	136
4	69	65
5	220	213
6	323	314
8	165	163
9	142	133
10	177	176
11	54	51
12	195	195
13	61	62
16	142	138
* H	7	1 *
1	313	311
2	263	261
3	218	213
4	73	64
5	305	305
6	166	163
7	65	56
8	95	89
9	229	229
11	67	61
12	79	73
13	130	131
15	91	93
* H	8	1 *
1	79	75
2	410	405
4	342	336
5	150	149
6	234	226
8	364	363
9	153	153
12	188	192
13	91	96
* H	9	1 *
1	110	111
2	219	211
3	158	158
4	61	58
5	114	119
6	129	123
7	140	135
8	65	71
9	162	165
13	140	147
* H	10	1 *
1	95	94
2	360	351
4	180	177
5	97	97
6	172	172
8	201	203
9	86	80
12	117	119
* H	11	1 *
1	158	161
2	92	99
3	105	100
5	167	171
6	69	63
8	67	64
9	131	135
13	72	77
* H	12	1 *
2	99	97
5	100	97
6	112	112
8	79	79
9	73	70
10	95	92
* H	13	1 *
1	183	183
3	69	69
5	180	181
9	95	94
* H	15	1 *
1	101	96
5	91	86
* H	0	2 *
1	613	615
2	281	265
3	496	490
4	548	528
5	419	404
6	495	498
7	328	318
10	348	345
11	214	210
12	161	154
13	129	125
14	122	124
15	100	104
16	92	89
17	124	127
* H	1	2 *
0	559	581
1	135	126
2	236	222
3	137	120
4	462	455
5	210	202
6	425	425
7	239	226
8	225	217
9	135	135
10	334	334
11	245	236
14	172	177
15	128	130
17	78	77
18	65	77
* H	2	2 *
0	477	489
1	311	311
2	134	131
3	479	478
4	376	371
5	81	74
6	277	257
7	441	447
8	153	147
9	68	69
10	228	220
11	272	276
13	116	112
14	125	126
15	107	110
17	87	91
* H	3	2 *
0	496	506
1	277	277
2	112	106
3	486	495
4	443	446
5	58	54
6	248	241
7	393	384
8	284	285
9	188	187
10	242	240
11	165	160
12	103	103
13	139	140
14	151	158
* H	4	2 *
0	241	224
1	441	433
2	115	112
3	491	490
4	257	244
5	121	122
6	141	138
7	322	317
8	244	242
9	134	130
11	156	155
12	143	140
13	167	168
14	132	123
15	74	77
* H	5	2 *
0	401	392
1	277	267
2	74	71
3	498	504
4	370	365
5	105	106
6	177	175
7	372	370
8	260	259
9	239	239
10	195	196
11	116	116
12	99	103
13	144	149
14	135	141
* H	6	2 *
0	181	174
1	237	228
3	368	361
4	186	183
6	58	56
7	330	325
8	158	157
9	74	77
10	116	112
11	182	188
12	73	75
13	88	89
14	112	117
15	68	74
* H	7	2 *
0	327	320
1	134	135
2	103	98
3	183	182
4	274	267
5	73	68
6	220	217
7	183	177
8	150	148
10	200	203
11	121	121
14	100	125
* H	8	2 *
0	379	375
1	251	253
2	107	107
3	230	237
4	251	249
5	166	166
6	225	224
7	174	176
10	171	176
11	113	116
12	70	69
13	63	71
* H	9	2 *
0	260	260
2	97	90
4	207	204
5	107	105
6	193	191
7	85	84
8	93	94
9	96	92
10	162	161
11	114	122
* H	10	2 *
0	244	246
1	107	111
2	85	83
3	162	162
4	173	168
6	169	166
7	172	172
10	120	122
11	120	125
* H	11	2 *
0	182	181
1	62	62
3	97	98
4	156	153
6	89	96
7	105	106
8	89	91
10	97	94
11	76	78
* H	12	2 *
0	90	89
1	121	118
3	134	139
4	86	85
7	100	102
8	69	65
* H	13	2 *
0	108	106
1	77	75
3	138	140
4	99	101
7	104	109
8	80	77
* H	14	2 *
1	64	58
3	97	97
7	85	88
* H	0	3 *
1	331	321
2	461	448
3	160	158
4	235	232
5	489	481
6	130	123
7	61	56
8	199	195
9	458	451
10	114	106
13	251	250
14	110	107
15	112	96
19	96	86
* H	1	3 *
1	155	154
2	673	691
4	292	278
5	111	111
6	376	361
7	90	86
8	354	346
10	75	71
12	256	249
13	102	99
16	130	133
* H	2	3 *
1	462	467
2	101	99
3	292	282
5	481	475
7	50	44
8	102	101
9	338	335
11	112	107
13	170	170
15	133	127
19	79	84
* H	3	3 *
1	219	223
2	529	539
3	84	86
3	84	86
4	130	126
5	187	189
6	374	369
7	57	55
8	222	220
9	54	51
10	162	156
11	78	73
12	227	223
16	148	146
* H	4	3 *
1	406	404
2	192	186
3	77	72
4	123	124
5	528	530
7	138	141
8	72	70
9	369	371
10	89	91
11	147	145
12	55	53
13	148	154
14	64	69
15	84	83
16	89	88
* H	5	3 *
1	275	271
2	430	433
3	88	82
4	74	71
5	235	232
6	324	322
7	99	99
8	164	164
10	160	156
11	105	104
12	196	197
13	67	68
16	138	138
* H	6	3 *
1	371	370
3	196	195
5	372	372
9	238	239
11	100	100
13	106	108
15	91	92
* H	7	3 *
2	373	376
4	144	144
8	200	201
* H	8	3 *
1	176	177
2	182	192
3	90	88
4	102	99
5	248	256
6	63	62
8	85	91
9	235	243
* H	9	3 *
1	96	94
2	309	311
4	142	140
5	86	78
6	159	164
8	172	175
* H	10	3 *
1	164	162
2	96	100
3	105	116
4	86	89
5	175	173
* H	0	4 *
1	256	245
2	114	103
3	267	257
4	50	38
5	169	163
6	173	160
7	275	264
8	121	114
11	236	231
12	115	108
13	144	141
14	85	82
15	140	138
17	143	137
18	85	79
21	65	66
* H	1	4 *
0	537	563
1	178	177
2	166	159
3	299	288
4	441	434
6	328	316
7	206	197
8	194	187
9	117	111
10	249	235
13	78	70
14	101	100
* H	2	4 *
0	64	71
1	266	263
3	362	354
4	89	89
5	91	85
6	71	67
7	329	324
8	98	96
9	66	62
10	73	68
11	210	211
12	61	60
13	115	113
14	55	51
15	93	92
17	97	90
* H	3	4 *
0	295	289
2	90	84
4	279	272
5	68	68
6	210	209
7	69	60
8	203	198
9	58	62
10	233	235
11	98	89
12	86	82
14	170	174
18	84	86
* H	4	4 *
0	354	366
1	392	394
2	86	81
3	465	466
4	234	231
5	128	127
6	168	164
7	295	292
9	78	73
10	121	116
11	94	94
12	80	80
13	114	104
17	67	64
* H	5	4 *
0	189	199
2	60	54
3	56	57
4	207	211
5	90	86
6	152	153
8	189	189
9	103	101
10	200	203
11	89	92
12	97	91
14	164	167
15	74	81
18	82	85
* H	6	4 *
0	151	152
1	216	220
2	71	68
3	305	312
4	111	114
6	130	132
7	249	255
9	82	75
10	89	87
11	130	136
13	86	87
* H	7	4 *
0	304	312
1	59	72
2	72	76
3	103	108
4	244	256
6	164	167
7	92	94
8	134	136
10	134	151
* H	8	4 *
1	118	136
3	141	150
5	81	81
7	142	150
11	117	128
13	77	84
* H	9	4 *
0	277	282
1	101	99
2	82	82
3	157	163
6	159	165
7	109	109
8	65	89
10	129	120
* H	10	4 *
3	112	120
7	129	134
* H	11	4 *
0	131	138
* H	0	5 *
1	98	91
2	104	101
3	105	95
5	140	139
6	183	182
9	187	185
10	191	189
12	72	67
13	134	135
14	86	92
15	62	61
16	65	64
* H	1	5 *
1	290	290
2	328	326
3	111	108
4	175	168
5	305	300
6	148	144
7	88	83
8	200	189
9	179	175
11	143	137
12	115	112
13	59	61
15	89	86
* H	2	5 *
1	169	172
2	242	246
3	79	85
4	52	52
5	213	211
6	171	171
8	98	94
9	165	168
10	80	78
12	102	101
13	74	83
15	58	57
16	70	72
* H	3	5 *
1	147	147
2	200	202
3	133	138
5	141	139
6	158	160
7	84	86
8	78	80
9	122	124
10	78	81
12	102	105
13	86	89
16	75	77
* H	4	5 *
1	234	238
2	239	242
3	54	50
4	235	239
5	259	263
6	138	134
7	111	106
8	273	269
9	148	145
11	115	110
12	148	150
* H	5	5 *
1	85	84
2	147	146
3	118	121
5	78	77
6	135	144
7	112	112
9	104	101
10	91	92
12	91	96
13	89	95
16	82	80
* H	6	5 *
1	169	171
2	238	241
3	61	58
4	99	98
5	189	193
6	134	131
8	123	125
9	115	120
11	61	57
12	67	89
* H	7	5 *
1	135	141
2	172	177
3	66	70
4	77	79
5	144	152
6	102	101
8	101	106
9	111	112
11	58	58
12	77	83
13	67	60
* H	8	5 *
1	59	62
2	75	73
5	80	88
6	102	105
9	99	105
10	98	102
13	69	75
* H	9	5 *
1	159	157
4	65	94
5	168	164
8	78	104
* H	0	6 *
0	168	169
4	150	154
5	85	85
8	114	114
9	77	77
10	81	78
11	67	63
12	62	59
14	115	114
* H	1	6 *
0	127	128
1	194	198
2	72	71
3	299	300
4	68	72
6	139	136
7	251	252
9	75	71
10	87	85
11	126	120
13	69	75
* H	2	6 *
0	211	215
1	60	60
3	54	53
4	187	186
6	120	115
8	110	115
10	132	128
14	95	97
* H	3	6 *
1	90	93
3	140	144
7	161	163
8	61	58
11	133	133
15	68	74
* H	4	6 *
0	361	373
2	60	61
3	134	137
4	265	276
5	64	64
6	130	138
7	91	89
8	85	89
9	103	97
10	127	127
14	71	71
* H	5	6 *
3	85	90
7	126	126
8	62	69
11	120	124
* H	6	6 *
0	211	219
3	64	83
4	174	173
6	126	130
8	70	78
10	121	120
* H	7	6 *
7	144	148
11	70	90
* H	0	7 *
1	108	106
2	76	79
5	114	104
6	89	89
8	88	81
10	77	81
12	82	86
* H	1	7 *
1	190	200
3	107	106
5	197	197
9	113	120
11	75	73
* H	2	7 *
4	63	69
6	119	118
8	93	96
12	78	80
* H	3	7 *
5	112	113
9	92	95
* H	4	7 *
2	186	197
4	120	116
6	111	123
8	137	144
* H	5	7 *
9	73	77
* H	6	7 *
2	151	153
* H	0	8 *
1	100	99
3	126	130
4	82	84
* H	1	8 *
7	101	109
8	67	64
* H	2	8 *
0	100	105
3	71	71
4	83	83
* H	3	8 *
0	95	101
3	66	72
4	74	76
6	64	63
7	66	69
* H	4	8 *
0	108	111
4	80	85
6	71	82
* H	5	8 *
0	104	111
* H	6	8 *
0	96	100

Table 1 (*cont.*)

(*b*) Unobserved and calculated. These are on same scale as (*a*). The 400, 201, 531, 151 and 002 reflections listed here are in reality not unobserved but, in fact, not included in the refinement because of poor background measurements or equipment malfunctions.

$F_{\min} \leq |F(\text{calc})| < 2{\cdot}0 \times F_{\min}$ (8 0)

```
  L =  0  12  9  48   3 15  46   2  6  44   7  0  74   1  6  65   3  3  71
19  1  65   3 10  64    L =  2  10  6  63  11  2  45   2  6  58   1  4  66
 9  7  57  11 11  52   9  0  56   7  9  61   8  5  46   9  6  44   1  5  75
 0 14  60  12 11  58  12  1  47    L =  4   3  8  54   0  7  55   3  5  61
 1 15  69   1 12  80   5 10  47  19  0  46   3  9  52   6  7  58   4  5  52
  L =  1    4 12  50   6 13  48  11  1  49   6  9  72  10  7  49   5  5  78
 1  0  48   2 13  51    L =  3  15  3  66   7  9  57    L =  7     L =  8
11  0  87   7 13  51  16  0  58   6  8  69    L =  6   4  0  49   1  1  58
16  1  52   1 14  60  17  0  60   8  8  57   2  2  47   2  1  44   1  2  44
13  5  69   2 14  72  11  1  45  12  8  50   4  3  47  10  1  50   1  3  53
15  6  52   5 14  56   6  2  53   9  9  71   1  4  59   1  2  44   5  4  57
10  7  56   6 14  80  17  2  53   5 10  46  13  4  50  10  2  59
11  8  46   2 15  53   9  5  45    L =  5   1  5  59   2  3  81
```

$2{\cdot}0 \times F_{\min} \leq F(\text{calc}) < 3{\cdot}0 \times F_{\min}$ (1 0)

```
  L =  1  16  3 105    L =  4   1  7 111   2  5  95   3  1 110
12  1 106    L =  3   1 10  91    L =  7     L =  8
13  2  97   4  2 105    L =  6   1  3 108   0  0  95
```

$3{\cdot}0 \times F_{\min} \leq F(\text{calc})$ (1 2)

```
  L =  0   2  0 924   5  3 691   0  0 906    L =  4   2  9 175    L =  7
 4  01395   9  2 188   1  5 705    L =  3   4  9 215    L =  6   2  2 157
  L =  1  12  2 270    L =  2   6  7 231    L =  5   3  7 160
```

structure factors was calculated with these atomic coordinates using program *ORFLS* (Busing, Martin & Levy, 1962) with local modifications. The resultant reliability index, *R*, was 0·26. The remainder of the non-hydrogen atoms were located from three-dimensional electron density sections (Harris, 1964) computed with phases based on the sulfur and iodine positions. A full-matrix isotropic refinement for all non-hydrogen atoms converged to a conventional *R* value of 0·10. Refinement with anisotropic temperature factors for iodine converged to an *R* of 0·057 and refinement with anisotropic temperature factors for all non-hydrogen atoms converged to an *R* of 0·043. A difference Fourier map at this point clearly resolved the hydrogen atoms. The inclusion of variables for the two hydrogen coordinates and a constant isotropic temperature factor for hydrogen of 3·0 Å^2 further reduced *R* to 0·032. The least-squares refinement was performed with program *ORFLS*, modified locally for use on the on the IBM 7040 computer (Busing, Martin & Levy, 1962). Atomic scattering factors for the iodide ion, neutral carbon, nitrogen and sulfur (Cromer & Waber, 1965) were used. Real and imaginary dispersion corrections were applied to the iodine and the real correction was applied to sulfur (Cromer, 1965; Ibers & Hamilton, 1964); H-atom scattering factors were from Stewart (Stewart, Davidson & Simpson, 1965). We minimized the function $\sum w(|F_o|-|F_c|)^2$, and the observations were weighted on counting statistics and a 4% intensity factor (Busing & Levy, 1957). Atomic parameter shifts for the last cycle of refinement were less than 0·01σ. The final disagreement index $R(R=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$, weighted $R=[\Sigma w||F_o|-|F_c||^2/\Sigma w|F_o|^2]^{1/2}$ and standard error $[\Sigma w(F_o-F_c)^2/(NO\text{-}NV)]^{1/2}$, where $NO=852$ and $NV=46$, were found to be 0·032, 0·042 and 1·35, respectively. A final difference map was relatively featureless with the largest positive peak $\frac{1}{5}$ the peak height of the hydrogen peaks found earlier.

Observed, unobserved and calculated structure factors are listed in Table 1. Final atomic coordinates and thermal parameters are given in Table 2. Interatomic distances, angles and errors, which were computed with the *ORFFE* program with local modifi-

Table 2. *Final atomic positional parameters, thermal parameters and e.s.d.'s**

Anisotropic temperature factors of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}kh+2\beta_{13}hl+2\beta_{13}kl)\times 10^4]$

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	0·6074 (0)	0·7500 (–)	0·3252 (1)	40 (0)	56 (1)	184 (2)	0 (–)	7 (1)	0 (–)
S(1)	0·4151 (1)	0·6377 (2)	–0·2294 (3)	39 (1)	58 (1)	159 (4)	3 (1)	–20 (1)	4 (2)
N(1)	0·3376 (4)	0·5006 (5)	0·1540 (10)	48 (3)	56 (5)	224 (17)	–2 (3)	26 (7)	14 (9)
N(2)	0·3347 (5)	0·7500 (–)	0·1788 (12)	31 (3)	59 (6)	157 (19)	0 (–)	7 (7)	0 (–)
C(1)	0·3572 (3)	0·6286 (6)	0·0604 (9)	21 (2)	62 (6)	136 (15)	1 (3)	2 (5)	–1 (8)
H(1)	0·355 (5)	0·433 (7)	0·008 (16)	0 (–)	0 (–)	0 (–)	0 (–)	0 (–)	0 (–)
H(2)	0·301 (6)	0·498 (8)	0·313 (14)	0 (–)	0 (–)	0 (–)	0 (–)	0 (–)	0 (–)

* Numbers in parentheses here and in succeeding tables are e.s.d.'s in the least significant digits. (–) indicates a fixed parameter.

Table 3. *Equations of least-squares plane of the type* $AX+BY+CZ-D=0$†

$A=-0{\cdot}8856$, $B=0{\cdot}0001$, $C=-0{\cdot}4644$, $D=-4{\cdot}5855$

Deviations of atoms from the least-squares plane (Å):

S(1)	0·000 (1)	S(2)	0·000 (1)	N(1)	0·010 (4)
N(2)	–0·016 (5)	N(3)	0·010 (4)	C(1)	–0·002 (3)
C(2)	–0·002 (3)				

Deviation of atoms from the least-squares plane that were not considered in the plane (Å):

I(1)	–3·767 (4)	H(1)	0·15 (5)	H(2)	0·07 (6)
H(3)	0·15 (5)	H(4)	0·07 (6)		

† *X*, *Y*, and *Z* refer to atom positional parameters in Å. All atoms across the mirror plane were considered and they were equally weighted in the least-squares plane (Rollett, 1965).

cations on the IBM 7040 (Busing, Martin & Levy, 1964), are shown in Figs. 1, 2 & 3. Table 3 contains the least-squares plane (Spofford, 1967).

Results and discussion

The crystal structure may be described as 3,5-diamino-1,2,4-dithiazolium (DADT)$^+$ ions and iodide ions separated by normal nonbonded distances (Figs. 1, 2 & 3). Bond lengths and angles in the isolated (DADT)$^+$ ions are shown in Fig. 1. The overall agreement with the results of Foss & Tjomsland (1958) is surprisingly good considering the authors' analysis was made with two-dimensional photographic data. Table 3 reveals that the (DADT)$^+$ ion is planar and well within experimental error. It is noteworthy that the (DADT)$^+$ ion in (DADT)$^+$Br$^-$ (Hordvik & Joys, 1965), (DADT)$^+$ Cl.$\frac{1}{2}$H$_2$O (Hordvik & Sletten, 1966) is planar as is the related 1,2-dithiolium ion in 4-phenyl-1,2-dithiolium iodide [bromide, chloride.H$_2$O, thiocyanate] (Hordvik & Kjøge, 1969), 3,5-diacetamido-1,2-dithiolium bromide (Hordvik & Kjøge, 1966) and 3-phenyl-1,2-dithiolium iodide (Hordvik & Kjøge, 1965).

A considerable amount of structure data of varying degrees of accuracy on five-membered conjugated cyclic disulfides, of which DADT$^+$ is a representative now exists (Table 4). Much has been said in the literature concerning the lengthening of the S–S bond and short intermolecular S–X distances. Note that in Table 4 one of the shortest S–S distances (3-Ph-1,

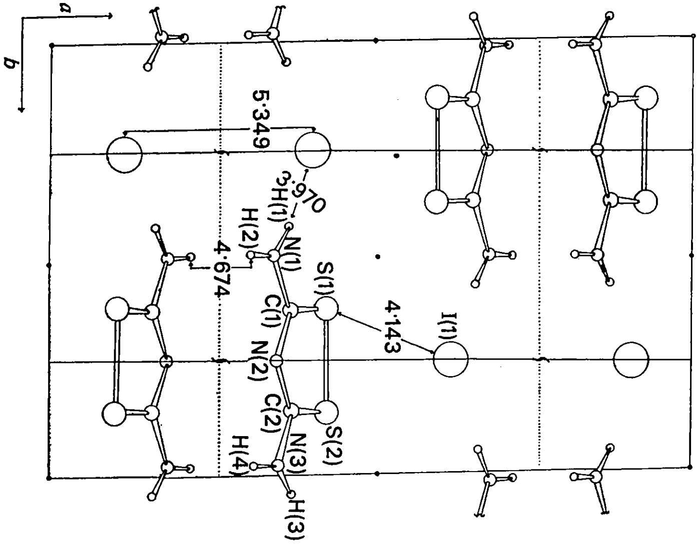


Fig. 2. Perspective view of the molecular packing down the *c* axis. The e.s.d.'s of S–I, I–I, H–I and H–H are 0·002, 0·001, 0·07 and 0·1 Å, respectively.

Table 4. *Summary of relevant distances in related molecules* (Å)

	S–S	S–C	C–N$_{int(C-C)}$	C–N$_{ext}$	X–S	Reference
DADT$^+$I$^-$	2·083 (3)	1·752 (5)	1·330 (6)	1·317 (7)	3·746 (2) I–S	This work
DADT$^+$Br$^-$	2·081 (8)	1·72 (3), 1·74 (3)	1·35 (3), 1·33 (3)	1·32 (4), 1·37 (3)	3·38 Br–S	Hordvik & Joys (1965).
DADT$^+$Cl$^-$. $\frac{1}{2}$H$_2$O	2·063 (4)	1·767 (7), 1·756 (7)	1·34 (1), 1·345 (9)	1·310 (9), 1·30 (1)	3·27 Cl–S	Hordvik & Sletten (1966), Furnas (1957).
4-Ph+,2-DT$^+$SCN$^-$	2·004 (5)	1·678 (8)	1·39 (1), 1·50 (1)		2·87 (1) N–S	Hordvik & Kjøge (1969).
4-Ph+,2-DT$^+$I$^-$	2·03 (1)	1·67 (2)	1·40 (3)		3·503 (8) I–S	Hordvik & Sletten (1966), Knox (1967).
4-Ph-1,2-DT$^+$Br$^-$	2·008 (8)	1·70 (1)	1·37 (2)			Hordvik & Sletten (1966), Knox (1967).
3-Ph-1,2-DT$^+$I$^-$	2·00 (1)	1·67 (3), 1·71 (3)	1·39 (5), 1·39 (4)		3·37 (1) I–S	Hordvik & Kjøge (1965).
4-Ph-1,2DT$^+$Cl$^-$. H$_2$O	2·021 (6)	1·673 (9)	1·38 (1)			Hordvik & Sletten (1966), Knox (1967).
3,5-DA-1,2 . DT$^+$I$^-$	2·08 (2)					Hordvik & Joys (1965).
3,5-DAc-1,2-DT$^+$Br$^-$	2·075 (5)	1·74 (1), 1·75 (1)	1·36 (2), 1·39 (2)		3·11 (1) O–S	Hordvik & Kjøge (1966).
DTBH	>4	1·678 (4), 1·707 (4)	1·388 (5), 1·375 (5)	1·344 (6), 1·317 (6)	2·621 N–S	Spofford & Amma (1970).
Pd(DTB)$_2$	3·169 (2), 3·319 (2)	1·712 (7), 1·743 (7)	1·335 (8), 1·350 (8)	1·34 (1), 1·322 (9)	2·584 (7) N–S	Girling & Amma (1968).
Ni(DTB)$_2$	2·895 (6), 3·220 (6)	1·720 (8), 1·728 (8)	1·32 (1), 1·34 (1)	1·31 (1), 1·34 (1)	2·561 (6) N–S	Lüth, Hall, Spofford & Amma (1969).

Nomenclature:
DADT$^+$ = 3,5-diamino-1,2,4-dithiazolium ion
Ph = phenyl
1,2 DT$^+$ = 1,2 dithiolium ion
3,5 DA-1,2-DT$^+$ = 3,5-diamino-1,2-dithiolium ion
3,5 DAc-1,2-DT$^+$ = 3,5-diacetamido-1,2-dithiolium ion
C–N$_{int(C-C)}$ = carbon to ring (internal) nitrogen
C–N$_{ext}$ = carbon to terminal (external) nitrogen
C–C = in the dithiolium ion the ring N is replaced by C.
X–S = shortest 'nonbonded' respective distance
DTBH = dithiobiuret
M(DTB)$_2$ = bis-(dithiobiuret) M(II)

2-DT$^+$) is accompanied by one of the shortest I–S intermolecular distances (3·37 Å). A similar situation exists for 4-Ph-1, 2-DT$^+$SCN$^-$. Therefore, it seems unlikely that charge is simply transferred from X to the sulfur and in particular to an antibonding S–S σ molecular orbital as has been postulated. If, indeed, charge is accepted by DADT$^+$, it would go into a relatively low lying π^* molecular orbital (Rodesiler & Amma, 1970). The acceptance of electronic charge into a delocalized π^* molecular orbital would also make the S–S difference not as sensitive to intermolecular interactions as would otherwise seem. It is worthy of note that 'short' nonbonded S–S distances exist, intrachelate and interchelate, in both Ni(DTB)$_2$ (Lüth, Hall, Spofford & Amma, 1969) and Pd(DTB)$_2$ (Girling & Amma, 1968). It is unfortunate that the 3,5 DA-1,2-DT$^+$I$^-$ structure is not complete since this would give a measure of the effect of the ring nitrogen atom and the external amide group on the S–S and C–S distances. At this point the S–S distances seem to be more readily rationalized in terms of electron-attracting groups relative to sulfur, *e.g.* –NH$_2$ and –CO–NH$_2$, rather than intermolecular sulfur-halogen interactions.

The S–C distance in DADT$^+$ is definitely longer than in DTBH (Spofford & Amma, 1970) as one would expect from delocalization of the π electrons involved in the C–S bond. Unfortunately, owing to the magnitude of the standard deviations, little comparison can be made of the C–S distances in the compounds listed except to note that in the dithiolium salts this distance is ~1·68 Å and in the dithiazolium salts it is ~1·75 Å.

The C–N internal distances in DADT$^+$ have also been elongated over those of free dithiobiuret and this also can be understood in terms of electron delocalization. On the other hand, the terminal C–N distances found in DADT$^+$ and dithiobiuret do not seem to differ significantly.

The angles in DADT$^+$ (Fig. 1) are somewhat different from those of dithiobiuret simply because of the ring closure and the C–S–S angle of 92·7 (2)°. This may also contribute to some of the differences in distances between dithiobiuret and DADT$^+$.

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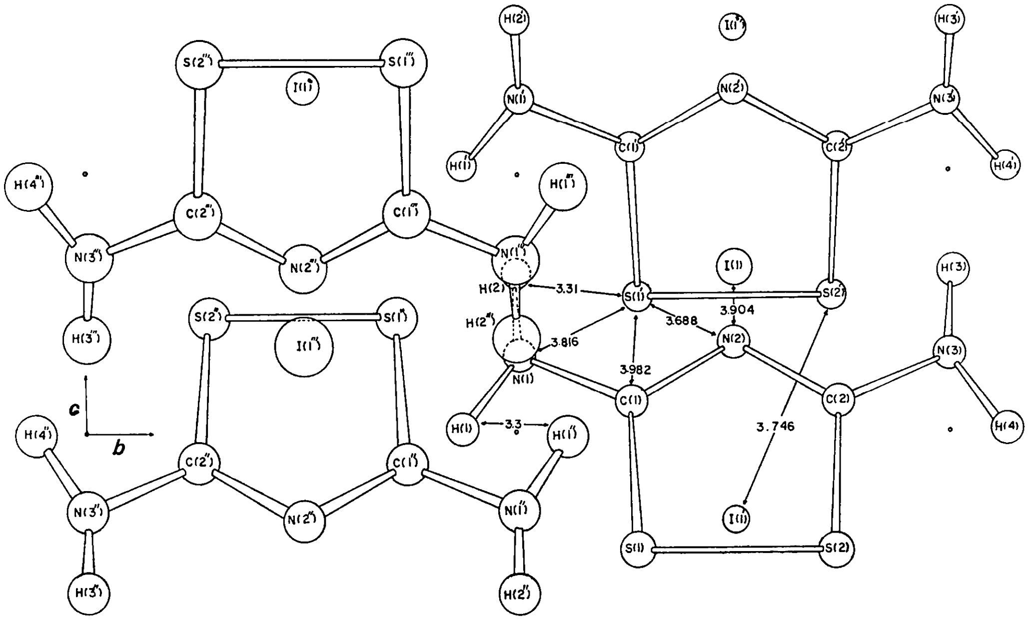

Fig. 3. Perspective view of the molecular packing down the *a* axis. The e.s.d's of I(1′)–S(2′), I(1)–N(2), N(2)–S(1′), S(1′)–C(1), S(1′)–N(1), S(1′)–H(2) and H(1)–H(1″) are 0·002, 0·007, 0·006, 0·005, 0·006, 0·08 and 0·1 Å, respectively,

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An Electron Diffraction Study of the Structures of Thiophene, 2-Chlorothiophene and 2-Bromothiophene. A Note

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The conclusions from the electron diffraction study of Harshbarger & Bauer are discussed. It is thought that they have not established that the thiophene ring deviates from C_{2v} symmetry.

Introduction

In their investigation of the molecular structures of thiophene, 2-chlorothiophene and 2-bromothiophene, Harshbarger & Bauer (1970) (hereafter to be abbreviated to HB for convenience), made the attempt to establish whether the thiophene ring geometry is immutable upon substitution, as it must be assumed to be in benzene and *s*-triazene. To this end HB determined the structures of 2-chlorothiophene and 2-bromothiophene by gas-phase electron diffraction. They concluded that their investigation clearly shows that in these compounds the thiophene ring deviates from C_{2v} symmetry when halogen atoms are attached to the 2 position, and that, although their diffraction analyses did not distinguish between two slightly different molecular models, other physical and chemical evidence favoured one of these.

However, a careful comparison of these two models, *A* and *B*, and of the standard deviations of the geometry parameters (see Tables 1 and 2) suggests that a symmetric C_{2v} structure which is an 'average' of *A* and *B* or even a completely undistorted thiophene ring might also fit nicely in with the electron diffraction data, the more so as the convergence difficulties involved in the greatly correlated parameter set in the unrestrained unsymmetrical refinement as described by HB, might decrease considerably by introducing parameter constraints *via* a symmetrical ring. At least, one could investigate quantitatively the significance of the unsymmetric ring used by HB in relation to a C_{2v} ring or a thiophene ring by least-squares refinements of all these structures, and subsequent comparison of residuals, standard deviations *etc.*

In this note the results of such a comparison are presented.

Results

The HB procedure was followed as closely as possible (Bonham & Bartell, 1959). Their observed intensities were reproduced by careful reading of their photographically enlarged Figs. 5 and 7 for integral *q* values. This of course introduces additional, though small, random errors compared with HB's data. Scattering factors for Br were taken from Cromer, Larson & Waber's (1964) tables, and those for C, H, S and Cl from Hanson, Herman, Lea & Skillman's (1964) data. All refinements were carried out with our ALGOL-60