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The Crystal and Molecular Structure of Sulfur Nitride, S_4N_4

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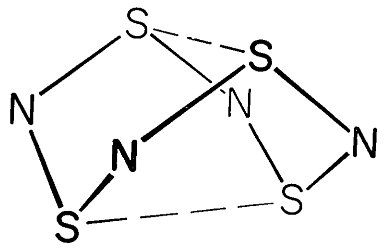
A three-dimensional refinement of crystalline S_4N_4 shows that molecule consists of a bisphenoid of sulfur atoms and a square of nitrogen atoms, in agreement with a previous electron diffraction investigation and a partial X-ray study. The inverse structure, *i.e.* a bisphenoid of nitrogen atoms and a square of sulfur atoms, which was supported by a different electron diffraction study and by spectroscopic investigations, is ruled out. The average S–N bond length is $1{\cdot}616 \pm 0{\cdot}010$ Å. The molecule may be described as a slightly elongated tetrahedron of sulfur atoms with nitrogen atoms added out from four of the edges.

Introduction

Numerous structures were proposed for the S_4N_4 molecule before the advent of diffraction and related methods of structure determination. These all were listed and discussed by Lu & Donohue (1944) in their report of an electron diffraction study in which they favored a structure (I) which had not been suggested previously. Just previously, Hassel & Viervoll (1943), also using the electron diffraction method, favored a different structure (II) which *prima facie* is more reasonable than (I) because sulfur and nitrogen show their expected ligancies of two and three. For both structures the molecular symmetry is $\bar{4}2m$ (D_{2d}). The agreement between observed and calculated scattering curves was apparently satisfactory in both investigations, and since the spectra of interatomic distances are quite different for the two structures, this conflict in the results is difficult to understand.



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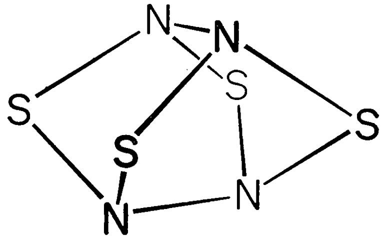

II

There have been three previous X-ray studies of S_4N_4. Jaeger & Zanstra (1931) reported that the crystals were orthorhombic with $a = 8{\cdot}87$, $b = 8{\cdot}47$, and $c = 7{\cdot}20$ (kX), and that the S_4N_4 molecule consisted of two interpenetrating bisphenoids of sulfur and nitrogen atoms with $S–N = 1{\cdot}2$ Å. These results are questionable not only because of the remarkably short S–N bond distance but also because it had been previously shown by goniometry that crystalline S_4N_4 is monoclinic (Artini, 1907; Smith, 1911). In a later X-ray study, Buerger (1936) verified that the crystals were monoclinic, with $a = 8{\cdot}74$, $b = 7{\cdot}14$, $c = 8{\cdot}645$ (kX), $\beta = 92^\circ\ 21'$, $Z = 4$, space group $P2_1/n$ (C_{2h}^5). Finally, Clark (1952) verified the unit cell and space group reported by Buerger, and by a Patterson & Fourier analysis of the three prism zones obtained satisfactory agreement ($R = 20\%$) assuming structure (I). He was apparently unaware of the work of Hassel & Viervoll.

Evidence favoring structure (II) was then presented by Lippincott & Tobin (1953), who studied the infrared and Raman spectra of both S_4N_4 and $S_4N_4H_4$. Their conclusion was based partly on indications of moderately high molecular symmetry together with the appearance of a Raman line at 888 cm^{-1} for S_4N_4, as compared with a line at 893 cm^{-1} from hydrazine corresponding to the N–N bond. They also concluded that the S_4N_4 and $S_4N_4H_4$ molecules were 'analogous in structure, except that in nitrogen hydrogen sulfide the two N–N bonds of nitrogen tetrasulfide have been broken to form N–H bonds.'

Both structures are nonpolar and therefore disagree with the dipole moment of $0{\cdot}72$ D reported by Phalnikar & Bhide (1939).

A recent evaluation of the parachor of S_4N_4 (Krylov, Patsuk & Podchainova, 1960) was said to be in good agreement with values calculated for both structures, and thus is of no aid in settling the controversy.

In the present paper we report the results of a three-dimensional X-ray study which show the S_4N_4 molecule to have structure (I).

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Table 1. *Observed and calculated structure factors*

Within each group the columns, reading from left to right, give the values of l, $10F_o$ and $10F_c$. Each group is headed by the values $h.k$. Reflections marked by an asterisk were given zero weight in the least-squares calculations. A minus sign on F_o denotes 'less than'

	0.0	
2	421	-380
4	88	69
6	390	-331
8	180	-182
10	142	135
	0.1	
1	95	-51
2	484	501
3	210	186
4	540	500
5	-27	29
6	69	-71
7	109	-97
8	93	-88
9	-32	39
10	133	-120
11	43	-67
	0.2	
0	469	-510
1	46	26
2	*880	-1148
3	136	-125
4	504	441
5	124	85
6	229	217
7	206	174
8	-42	39
9	67	-66
10	-30	-00
	0.3	
1	75	-61
2	350	-391
3	205	-178
4	-42	49
5	-49	-45
6	281	-287
7	-57	64
8	269	258
9	-49	76
10	-35	33
	0.4	
0	234	251
1	-26	40
2	346	359
3	101	83
4	-53	20
5	226	-187
6	268	-264
7	-66	-33
8	-61	83
9	81	-84
10	-27	-15
	0.5	
1	149	129
2	135	-143
3	-51	13
4	243	283
5	129	108
6	247	-248
7	-51	-19
8	116	121
9	147	-129
10	122	-114
	0.6	
0	356	-369
1	193	-172
2	203	163
3	-59	59
4	59	-48
5	-59	07
6	141	-110
7	170	136
	0.7	
4	151	156
	0.8	
0	237	-238
	1.0	
1	508	479
3	678	735
5	388	-354
7	310	287
9	114	-105
	1.1	
0	-10	-17
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2	104	85
3	155	124
4	190	160
5	28	10
6	153	150
7	83	-83
8	209	-190
9	-32	-29
10	-26	32
	1.2	
0	73	57
1	410	-460
2	587	-548
3	25	15
4	268	229
5	338	-318
6	246	216
7	162	147
8	-42	-07
9	92	-83
10	-29	41
	1.3	
0	113	-132
1	464	496
2	210	-195
3	569	-547
4	547	-519
5	198	164
6	-54	50
7	-57	96
8	78	87
9	-48	-58
10	101	116
	1.4	
0	424	581
1	192	197
2	77	65
3	-46	06
4	122	-105
5	136	122
6	253	-237
7	-66	26
8	104	-132
9	-49	-52
10	-18	75
	1.5	
0	130	-135
	1.6	
0	323	-381
	1.7	
0	-59	-14
	1.8	
0	137	143
	-1.0	
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3	638	612
5	605	-544
7	-34	12
9	184	-206
11	88	102
	-1.1	
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2	39	35
3	450	428
4	258	-212
5	172	156
6	107	95
7	107	-94
8	92	-70
9	281	-293
10	-26	35
11	34	-33
	-1.2	
1	568	-690
2	325	318
3	61	67
4	-29	-02
5	152	-135
6	133	-121
7	415	420
8	-42	-55
9	80	-66
10	-30	42
	-1.3	
1	507	587
2	314	319
3	794	-750
4	170	141
5	97	-94
6	54	09
7	255	274
8	-55	-15
9	-49	11
10	62	16
	-1.4	
1	178	189
2	186	-158
3	226	182
4	121	122
5	86	-80
6	130	115
7	-66	-43
8	-61	15
9	63	-67
10	-22	29
	2.0	
0	*596	868
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4	559	535
6	185	160
8	201	189
10	-25	18
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1	359	-361
2	753	-812
3	479	434
4	124	-110
5	29	-53
6	177	-187
7	-34	-03
8	208	187
9	-30	27
10	77	81
	2.2	
0	320	415
1	219	-224
2	425	-408
3	78	-81
4	155	144
5	-36	16
6	390	-375
7	223	217
8	160	-136
9	76	-57
10	-27	36
	2.3	
0	86	-91
1	241	-245
2	-34	-27
3	357	-346
4	634	669
5	135	-134
6	223	-236
7	-51	38
8	-49	29
9	-46	47
10	63	-64
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2	108	-107
3	144	121
4	151	126
5	344	-327
6	-66	77
7	-65	15
8	130	124
9	78	-90
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	2.6	
0	242	-250
	2.7	
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	2.8	
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4	282	248
6	41	-55
8	195	-197
10	147	149
	-2.1	
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2	519	-572
3	382	-334
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5	138	-128
6	123	-116
7	-34	53
8	-34	-05
9	50	60
10	126	-117
	-2.2	
1	314	357
2	585	-582
3	151	134
4	215	189
5	347	-327
6	39	45
7	72	-69
8	-42	-13
9	-37	-33
10	-29	29
	-2.3	
1	162	173
2	178	-193
3	349	366
4	490	480
5	318	276
6	291	-294
7	114	-118
8	190	194
9	-48	-72
10	-34	16
	-2.4	
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2	86	60
3	-49	34
4	137	119
5	277	261
6	131	-131
7	208	191
8	-60	89
9	-49	16
10	-13	-31
	3.0	
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3	623	623
5	175	152
7	350	465
9	-30	-55
	3.1	
0	50	41
1	160	-175
2	214	198
3	617	-690
4	269	-265
5	300	-282
6	259	246
7	49	30
8	131	-121
9	102	95
10	64	74
	3.2	
0	55	47
1	450	467
2	233	-207
3	30	07
4	188	175
5	589	-548
6	183	-172
7	111	-119
8	-40	-13
9	71	-77
10	49	55
	3.3	
0	-35	-38
1	401	433
2	40	-28
3	76	67
4	-49	-57
5	339	356
6	-56	14
7	-56	-06
8	108	-89
9	102	-110
10	-18	07
	3.4	
0	324	333
1	-46	-19
3	147	-128
4	182	184
5	290	307
6	-66	-08
7	-63	94
8	-55	39
9	-39	-14
	3.5	
0	121	-126
	3.6	
0	-59	08
	3.7	
0	-59	-76
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7	375	463
9	136	-119
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1	272	-291
2	209	-185
3	535	-529
4	75	-80
5	230	-216
6	-32	10
7	-34	29
8	-34	36
9	-30	-24
10	-24	18
	-3.2	
1	262	265
2	215	207
3	292	259
4	57	-58
5	574	-612
6	222	-237
7	-42	26
8	-41	-34
9	62	-74
10	-26	18
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2	212	211
3	106	101
4	261	233
5	235	202
6	-56	-31
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8	-53	-60
9	122	-127
10	70	-68
	-3.4	
1	146	-131
2	-49	03
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4	-60	62
5	255	263
6	187	208
7	64	101
8	120	121
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0	78	74
2	575	-583
4	343	325
6	136	149
8	-33	36
10	35	49
	4.1	
0	87	-82
1	231	-233
2	493	-549
3	154	157
4	189	-197
5	261	-268
6	98	-82
7	99	110
8	46	47
9	65	63
10	28	-39
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2	179	-184
3	265	233
4	91	82
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2	182	175
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6	128	-124
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8	-48	84
9	97	-112
	4.4	
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2	-57	-29
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4	144	130
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6	-65	-46
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	4.5	
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	4.6	
0	233	-240
	-4.0	
2	396	-427
4	288	314
6	309	329
8	60	69
10	78	70
	-4.1	
1	162	143
2	694	-830
3	-69	-32
4	284	-286
5	-31	34
6	215	-226
7	-35	-08
8	201	200
9	-29	13
10	89	92
	-4.2	
1	51	50
2	97	-99
3	325	-280
4	72	-60
5	111	105
6	228	-261
7	-42	-25
8	216	-182
8	-51	11
9	-33	-14
10	67	76
	-4.3	
1	95	91
2	-44	12
3	252	-245
4	651	748
5	96	90
6	198	-218
7	-56	-23
9	-40	-14
	-4.4	
1	282	331
2	78	-82
3	119	-115
4	126	125
5	102	86
6	93	93
7	-62	-19
8	-53	84
	5.0	
1	222	236
3	98	83
5	121	-111
7	-34	-49
9	58	-60
	5.1	
0	97	83
1	309	332
2	-29	-22
3	43	43
4	275	-273
5	-34	03
6	156	180
7	48	-64
8	102	-117
9	134	-150
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3	100	-110
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6	229	-205
7	168	161
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	5.3	
0	-49	-00
1	241	289
2	269	291
3	262	-288
4	194	190
5	-57	-09
6	-56	59
7	138	126
8	113	-107
9	24	42
	5.4	
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1	121	118
2	433	-455
3	91	96
4	324	318
5	-66	-12
6	-62	113
7	-54	-49
8	89	87
	5.5	
0	91	-87
	5.6	
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	-5.0	
1	268	-283
3	339	349
5	109	-115
7	282	372
9	-27	-38
	-5.1	
1	153	157
2	148	-153
3	168	-182
4	316	349
5	149	-162
6	109	-113
7	-34	18
8	-31	-02
9	-26	28
	-5.2	
1	108	-121
2	171	-188
3	181	187
4	110	102
5	330	-358
6	111	111
7	-41	-11
8	-37	24
9	79	-78
	-5.3	
1	275	321
2	224	-243
3	-51	-72
4	247	-237
5	-56	67
6	-56	-45
7	120	124
8	113	112
9	102	-118
	-5.4	
1	-60	-15
2	302	308
3	-64	16
4	147	-158
5	-66	79
6	156	-152
7	-58	79
8	-46	-26
9	-20	-31
	6.0	
0	804	959
2	-32	-17
4	70	-65
6	330	-253
8	90	-100
	6.1	
0	76	-60
1	351	-357
2	313	344
3	210	219
4	308	315
5	135	-150
6	-35	17
7	-30	18
8	150	-144
	6.2	
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1	204	227
2	354	-367
3	-41	-00
4	252	200
5	104	-96
6	189	167
7	108	101
8	69	72
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2	123	-143
3	196	200
4	151	-173
5	-56	-37
6	-51	-73
7	-45	68
8	104	118
	6.4	
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1	113	-125
2	187	185
3	-66	19
4	-65	02
5	-62	-83
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7	132	139
	6.5	
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	6.6	
0	187	-187
	-6.0	
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4	53	-52
6	-35	-11
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9	37	-42
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1	38	-21
2	312	-345
3	212	-218
4	101	94
5	207	242
6	175	152
7	-38	58
8	56	-59
9	-23	06
	-6.3	
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3	307	-334
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6	121	-96
7	-49	52
8	108	106
9	59	74
	-6.4	
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2	262	224
3	155	-105
4	-66	-39
5	-64	-23
6	145	-120
7	214	-206
8	35	37
	7.0	
1	437	454
3	138	148
5	232	-184
7	106	-98
	7.1	
0	163	157
1	304	321
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3	296	277
4	-34	17
5	116	112
6	107	106
7	90	-66
8	109	-130
	7.2	
0	210	230
1	255	-272
2	229	-255
3	104	-94
4	204	180
5	56	80
6	62	55
7	89	90
8	-17	10
	7.3	
0	-57	01
1	-57	-16
2	-57	-68
3	278	-264
4	174	-166
5	-51	-12
6	-45	42
7	-34	32
	7.4	
0	268	253
1	236	202
2	195	-172
3	-64	-12
4	-60	60
5	-54	27
6	171	-179
7	-23	-27
	7.5	
0	92	-85
	-7.0	
1	266	263
3	200	197
5	336	-307
7	90	-72
9	40	-61
	-7.1	
1	239	260
2	152	-151
3	309	322
4	140	143
5	119	127
6	73	-82
7	41	-41
8	-23	24
	-7.2	
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2	118	123
3	59	65
4	42	26
5	-41	48
6	-38	-28
7	202	198
8	63	66
	-7.3	
1	-57	59
2	-57	-45
3	302	-305
4	-56	42
5	161	-142
6	120	-85
7	189	176
8	75	83
	-7.4	
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2	101	118
3	65	69
4	-62	-02
5	121	-99
6	89	-89
7	-38	-31
	8.0	
0	210	216
2	-35	26
4	116	80
6	-27	36
	8.1	
0	-35	-05
1	242	-189
2	-34	-39
3	322	289
4	-32	62
5	103	-90
6	-25	-08
7	45	39
	8.2	
0	113	-110
1	-42	-48
2	82	-85
3	-40	-04
4	-38	05
5	-34	45
6	70	-82
7	119	144
	8.3	
0	-56	-29
1	192	-172
2	77	-63
3	169	-157
4	84	94
5	180	-140
6	-32	-26
	8.4	
0	-62	69
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3	-56	06
4	-50	25
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	-8.0	
2	160	139
4	53	-55
6	140	-112
8	158	-169
	-8.1	
1	209	166
2	49	42
3	138	-140
4	202	183
5	55	-63
6	-29	-08
7	82	73
8	65	-69
	-8.2	
1	135	254
2	178	-160
3	71	-75
4	-40	28
5	-37	-40
6	180	166
7	55	-46
	-8.3	
1	152	123
2	150	-144
3	131	123
4	-51	48
5	98	97
6	69	-78
7	-29	-33
	-8.4	
1	-62	-65
2	-61	75
3	149	-114
4	-54	01
5	232	201
6	-36	-60
	9.0	
1	226	-174
3	147	107
5	188	159
	9.1	
0	136	111
1	89	-90
2	-31	47
3	207	-203
4	-27	-18
5	112	-119
6	71	81
	9.2	
0	39	-55
1	148	132
2	181	-167
3	-34	-36
4	151	143
5	151	-153
	9.3	
0	-49	31
1	-49	45
2	180	-165
3	129	132
4	90	-86
5	85	88
	9.4	
0	290	285
1	-50	-06
2	-47	-49
3	-41	-51
4	-30	72
	-9.0	
1	264	-194
3	217	147
5	51	-55
7	43	46
	-9.1	
1	161	-115
2	274	-218
3	85	-76
4	62	52
5	46	-15
6	75	-68
7	-12	09
	-9.2	
1	-38	69
2	113	110
3	-36	44
4	-34	-26
5	115	-107
6	157	-149
	-9.3	
1	-49	63
2	131	115
3	79	90
4	229	208
5	-35	04
6	-21	-36
	-9.4	
1	-51	-68
2	-50	-54
3	-46	-20
4	39	76
5	76	89
	10.0	
0	234	-238
2	143	-117
4	74	67
	10.1	
0	-27	-09
1	92	-83
2	238	-217
3	123	109
4	169	-168
	10.2	
0	190	193
1	-30	04
2	97	93
3	51	40
4	64	-85
	10.3	
0	-38	07
1	-36	-58
2	111	119
3	34	63
	10.4	
0	82	-91
1	38	45
	-10.0	
2	130	-97
4	89	69
	-10.1	
1	-27	22
2	251	-233
3	-25	-23
4	186	-153
5	50	-49
	-10.2	
1	120	120
2	96	92
3	117	-114
4	91	-87
5	-14	27
	-10.3	
1	91	76
2	107	111
3	54	27
4	131	191
	-10.4	
1	66	66
2	-27	-27
	11.0	
1	58	-68
	11.1	
0	59	62
1	-15	-19
	11.2	
0	93	99
	-11.0	
1	128	-132
	-11.1	
1	41	-46
2	73	-84
	-11.2	
1	57	96

Experimental

A sample of S_4N_4, prepared by the method described by Arnold, Hugill & Hutson (1936), was kindly supplied by Prof. N. Kharasch of this department, under whose directions our own preparations of some pure material had been discarded. Numerous attempts to obtain single crystals were unsuccessful, but an acicular twin, of approximately 0·1 mm radius, was finally obtained which gave a diffraction pattern which could be indexed unequivocally. Multiple film Weissenberg photographs (Cu $K\alpha$) about b, $k=0$ to 4, were taken, the intensities being estimated visually by means of an intensity strip. A total of 651 unique reflections was recorded. Correlation between the layers was effected with $(0kl)$ and $(hk0)$ precession photographs of the same crystal. After correction of the intensities for absorption with the powder rod formula, relative F values were calculated in the usual way. The final values of the interlayer scale factors were averages of the values obtained (a) with the precession photographs, (b) from application of Wilson's method to the individual layers, and (c) comparison of the F_o with those calculated using the parameters of Clark (1952). These last calculations, in addition to giving an isotropic B value of 2·67 Å^2, also suggested that Clark's structure was essentially correct, since for the layers $k=0$ to 4 the respective values of R were 24%, 28%, 22%, 21%, and 29%. The lattice constants $a=8·75$, $b=7·16$, $c=8·65$ Å, $\beta=92·5°$ (Clark) have been adopted in the present study.

Refinement

The structure was refined by both least-squares and Fourier methods. The parameters of Clark were used as the starting point in a least-squares treatment in which the positional parameters and individual isotropic B's were refined. The quantity minimized was $\Sigma w(F_o-F_c)^2$. The weighting scheme was that of Hughes (1941). The form factor curve for sulfur was that of Dawson (1961), and for nitrogen, that of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The resulting values were then subjected to further refinement by the use of three-dimensional difference maps (Leung, Marsh & Schomaker, 1957), from which anisotropic B_{ij} were evaluated. No spurious peaks were noted in the difference maps. The final values of the thermal and positional parameters were obtained from successive full matrix least squares. The shifts in the last cycle were all less than 10^{-4} (positional parameters as fractions of cell edges, B's as coefficients of h^2, *etc.*). During the above calculations R (absent reflections omitted) dropped steadily from 23·2% to 9·8%. Observed and calculated structure factors are presented in Table 1. The final parameters are presented in Table 2. The respective average and maximum changes from the starting positional parameters are, for the sulfur atoms, 0·032 and 0·055 Å, and, for the nitrogen atoms, 0·055 and 0·132 Å.

Discussion

Molecular structure

Table 3. *Intramolecular distances and angles*

The standard errors in the distances have been multiplied by 10^3

Distance		(σ)	Angle		(σ)
S(1)–N(4)	1·631 Å	(13)	N(2)–S(1)–N(4)	103·3°	(1·6°)
S(2)–N(4)	1·605	(19)	N(3)–S(3)–N(1)	104·9	(1·6)
S(2)–N(1)	1·621	(14)	N(1)–S(2)–N(4)	105·1	(1·5)
S(3)–N(1)	1·616	(17)	N(2)–S(4)–N(3)	104·6	(1·3)
S(3)–N(3)	1·596	(14)			
S(4)–N(3)	1·617	(22)	S(2)–N(1)–S(3)	112·3	(0·6)
S(4)–N(2)	1·610	(14)	S(4)–N(2)–S(1)	112·8	(0·7)
S(1)–N(2)	1·634	(18)	S(3)–N(3)–S(4)	113·6	(0·7)
S(1) · · · S(3)	2·586	(8)	S(1)–N(4)–S(2)	112·6	(0·7)
S(2) · · · S(4)	2·576	(8)			
S(1) · · · S(2)	2·693	(8)			
S(1) · · · S(4)	2·702	(10)			
S(3) · · · S(4)	2·689	(8)			
S(2) · · · S(3)	2·688	(6)			

The intramolecular distances and angles are shown in Table 3 and Fig. 1. The molecular symmetry is $\bar{4}2m$ within the limits of error. The average S–N bond distance is $1·616\pm0·010$ Å. The previously reported values of $1·60\pm0·04$ Å (Clark, 1952) and $1·62\pm0·02$ Å (Lu & Donohue, 1944) are not significantly different from this value. All of these disagree with value 1·74 Å reported by Hassel & Viervoll (1943). The intramolecular distances S(1) · · · S(3) and S(2) · · · S(4) are much shorter than would be expected on the basis of the van der Waals diameter of *ca* 3·3 Å, but are much longer than the S–S single bond distance of 2·05 Å. The S–N bond distance corresponds to about

Table 2. *Final parameters and their standard errors*

All values have been multiplied by 10^4

Atom	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	$b_{11}(\sigma_{b_{11}})$	$b_{22}(\sigma_{b_{22}})$	$b_{33}(\sigma_{b_{33}})$	$b_{12}(\sigma_{b_{12}})$	$b_{13}(\sigma_{b_{13}})$	$b_{23}(\sigma_{b_{23}})$
S(1)	106(4)	9260(6)	2996(4)	118(4)	156(12)	135(5)	19(12)	−6(6)	−157(13)
S(2)	1500(3)	7088(5)	943(4)	66(3)	97(11)	128(4)	37(9)	17(5)	−18(10)
S(3)	−1488(3)	7951(6)	652(4)	66(3)	112(12)	133(4)	47(9)	−27(5)	0(11)
S(4)	−353(4)	5535(6)	2787(4)	126(5)	137(13)	135(5)	−10(12)	21(7)	116(12)
N(1)	70(12)	7587(17)	−238(12)	115(13)	116(30)	105(13)	112(35)	−20(20)	−79(35)
N(2)	−172(14)	7309(21)	3923(13)	156(18)	278(47)	116(14)	−11(48)	24(26)	10(46)
N(3)	−1761(11)	6075(19)	1597(14)	87(13)	91(32)	185(19)	13(34)	23(24)	85(41)
N(4)	1663(11)	8851(19)	2083(13)	83(11)	114(32)	156(16)	−12(33)	−33(21)	−141(38)

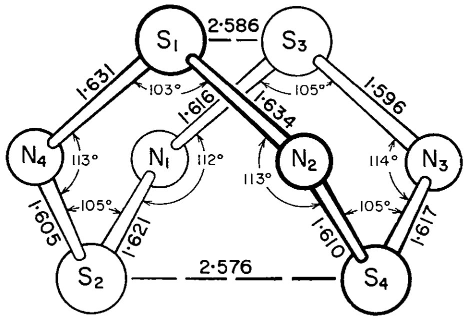
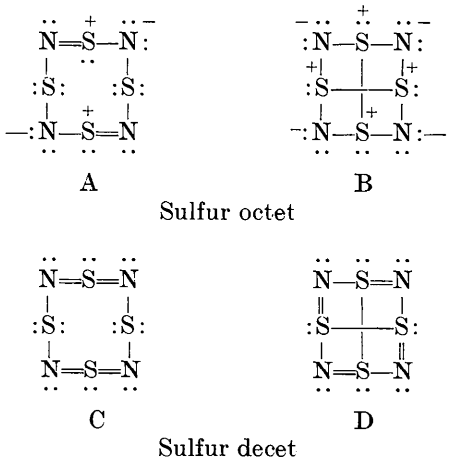


Fig. 1. Bond distances and angles.

one-third double bond character. The bond angles of 105° at a sulfur atom and 113° at a nitrogen atom, on the other hand, do not imply very much, if any, double bond character. This paradox scarcely seems resolved on consideration of what are probably the most important of the many possible resonance structures:



While these considerations allow a discussion of the results, they scarcely can be said to explain why the S_4N_4 molecule assumes the unusual structure that it does. It seems likely that the geometrical restraints

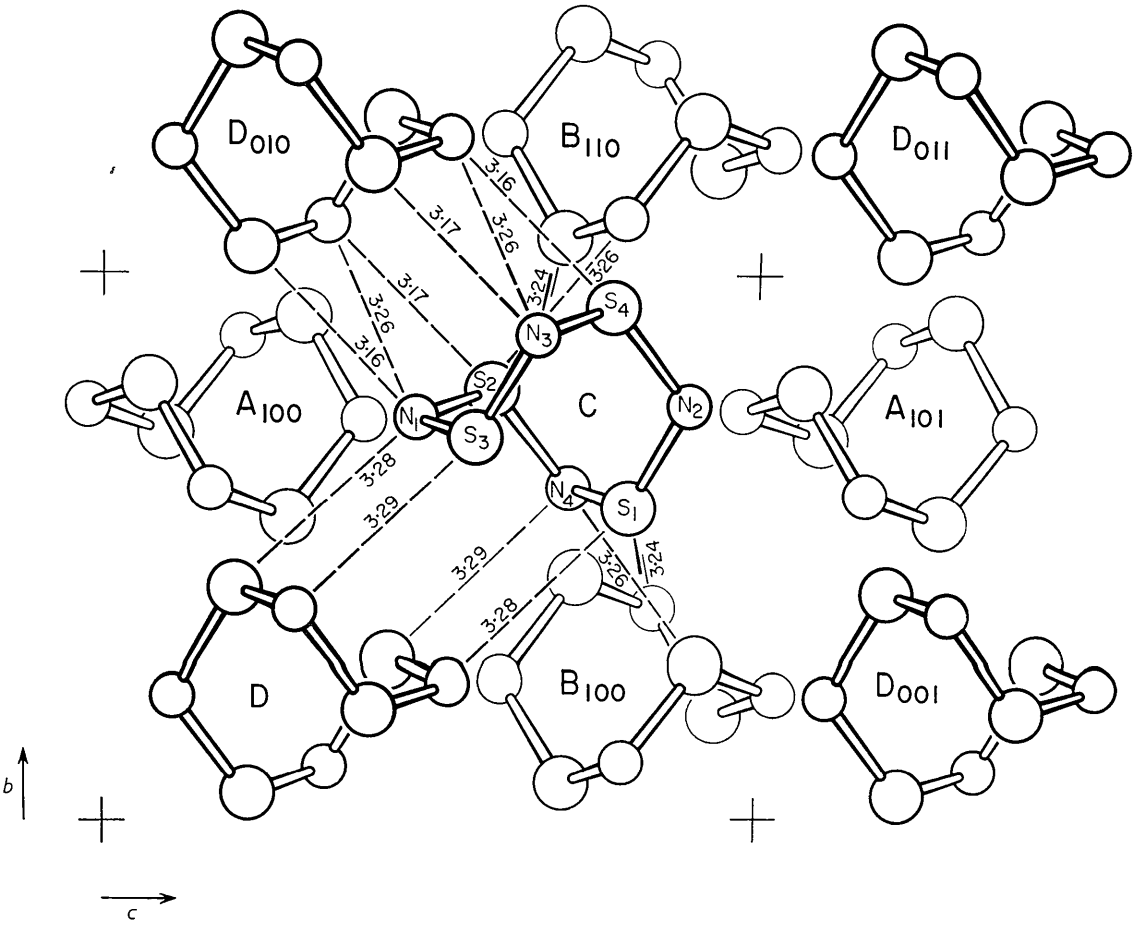


Fig. 2. The structure viewed down the a axis.

imposed by the molecular symmetry may well result in some strain, a conclusion not in disagreement with the rather unstable nature of the substance.

A somewhat different interpretation has been proposed by Lindquist (1958), who suggested, partly on the basis of the geometry of the $\genfrac{}{}{0pt}{}{N\diagdown}{N\diagup}\!S\cdots S$ groupings (the eight different N–S · · · S angles are all within 2° of 90°), that the S · · · S distances of 2·58 Å corresponded to pure $p\sigma$ bonds, and that only structure B was important. While this explanation has its attractions, it does not appear to account for the short S–N bond length. Other molecules in which the S–N bond is formally single include sulfamic acid, $H_3\overset{+}{N}\text{–}\overset{-}{S}O_3$ (Sass, 1960) and $(SNH)_4$ (Sass & Donohue, 1958) in which the respective bond distances are 1·764 ± 0·020 Å and 1·674 ± 0·004 Å; the former is probably a pure single (sp^3) bond, and the latter then corresponds to some double ($p\pi$) bond character, a situation also suggested by the bond angles, as discussed by Sass & Donohue. The single-bond radius sum is 1·74 Å (Schomaker & Stevenson, 1941).

A reinterpretation of the spectroscopic data reported by Lippincott & Tobin in terms of structure (I), rather than structure (II) favored by them, is to be desired. The same suggestion applies to their spectral data for $(SNH)_4$, since that molecule is a staggered ring with symmetry $4mm$, which is hardly 'analogous' to the $\bar{4}2m$ symmetry of the S_4N_4 molecule. Similarly, a redetermination of the dipole moment is desirable.

Molecular packing

The arrangement of the molecules in the crystal roughly approximates cubic close packing, as may be seen from Figs. 2 and 3. All intermolecular distances less than 3·30 Å are indicated in Fig. 2, and all those less than 3·50 Å listed in Table 4. These are all seen to be S · · · N distances; the shortest S · · · S distance is 3·64 Å, a value greater than the numerous van der Waals contacts of 3·50–3·53 Å observed in S_6 (Donohue, Caron & Goldish, 1961). It thus seems likely that in S_4N_4 the molecular packing is determined by intermolecular S · · · N contacts. The shortest S · · · N contacts of 3·16 Å are 0·2 Å shorter than the sum of the van der Waals radii (Pauling, 1960)

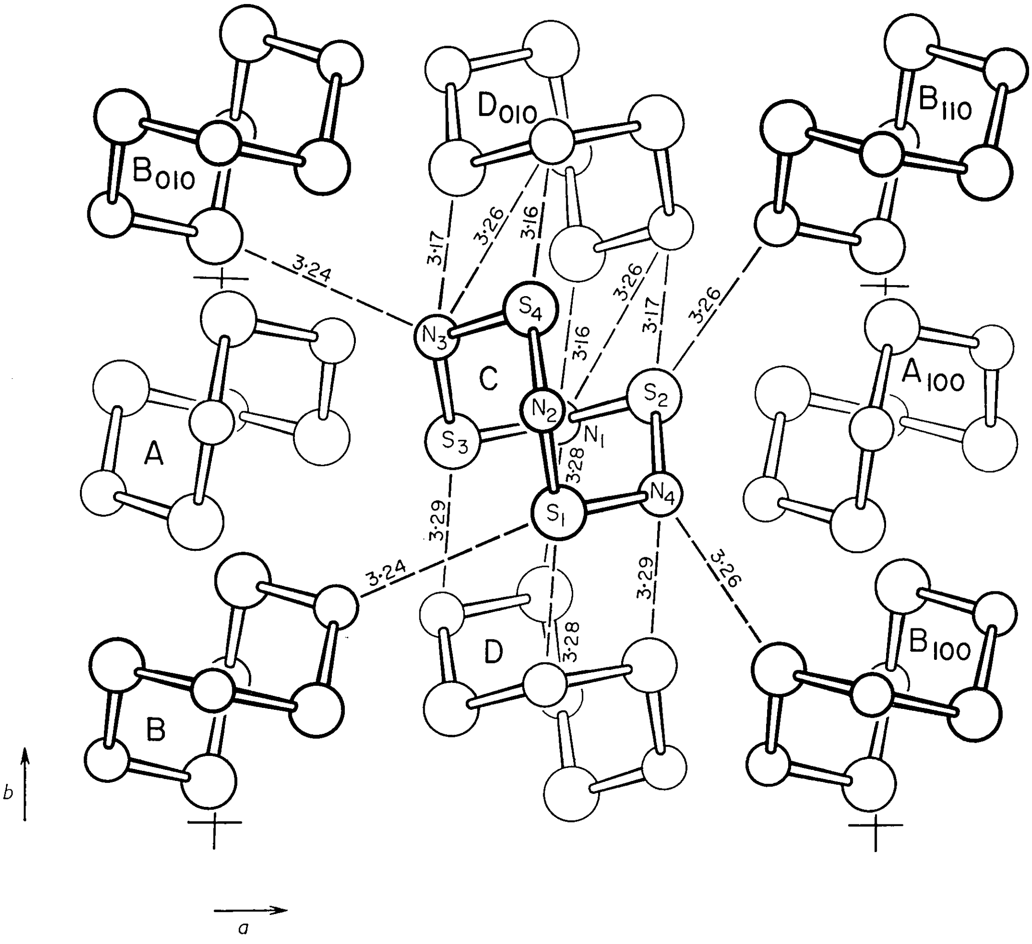


Fig. 3. The structure viewed down the c axis.

Table 4. *Intermolecular distances*

Molecular designations are $A(x, y, z)$, $B(-x, 1-y, 1-z)$, $C(\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z)$, $D(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$; subscripts give lattice translations from these

From atom in molecule C	To atom	in molecule	Distance	Equivalent distance Atom in C	to atom	in molecule
S(1)	N(3)	B	3·235 Å	N(3)	S(1)	B_{010}
S(1)	N(1)	D	3·283	N(1)	S(1)	D
S(2)	N(2)	A_{100}	3·487	N(2)	S(2)	A_{001}
S(2)	N(4)	B_{110}	3·260	N(4)	S(2)	B_{100}
S(2)	N(3)	D_{010}	3·170	N(3)	S(2)	D_{010}
S(3)	N(2)	A	3·498	N(2)	S(3)	A_{101}
S(3)	N(1)	D	3·452	N(1)	S(3)	D
S(3)	N(4)	D	3·291	N(4)	S(3)	D
S(4)	N(4)	B_{110}	3·444	N(4)	S(4)	B_{100}
S(4)	N(1)	D_{010}	3·157	N(1)	S(4)	D_{010}
N(1)	N(3)	D_{010}	3·255	N(3)	N(1)	D_{010}
N(1)	N(4)	D	3·338	N(4)	N(1)	D
N(1)	N(1)	D	3·482	N(1)	N(1)	D_{010}

Table 5. *R.M.S. amplitudes* $(\overline{u^2})^{\frac{1}{2}}$ *and direction cosines q relative to a*bc of the principal axes of the temperature factor ellipsoids*

Atom	Axis i	$(\overline{u^2})^{\frac{1}{2}}$	q_i^1	q_i^2	q_i^3
S(1)	1	0·268	−0·196	−0·620	0·760
	2	0·212	−0·980	0·090	−0·179
	3	0·144	−0·043	0·780	0·625
S(2)	1	0·221	0·019	−0·114	0·993
	2	0·177	0·723	0·688	0·065
	3	0·138	0·691	−0·717	−0·096
S(3)	1	0·229	−0·292	−0·093	0·952
	2	0·185	−0·537	−0·808	−0·243
	3	0·138	−0·792	0·582	−0·186
S(4)	1	0·251	−0·013	−0·551	−0·835
	2	0·221	−0·993	0·104	−0·054
	3	0·152	−0·116	−0·828	0·548
N(1)	1	0·252	−0·696	−0·555	0·456
	2	0·190	−0·557	0·015	−0·831
	3	0·124	−0·454	0·832	0·319
N(2)	1	0·269	0·137	−0·990	−0·041
	2	0·246	0·977	0·128	0·171
	3	0·208	0·164	0·064	−0·985
N(3)	1	0·271	0·042	0·259	0·965
	2	0·183	0·996	0·067	−0·061
	3	0·141	0·080	−0·964	0·255
N(4)	1	0·269	0·187	0·449	−0·874
	2	0·182	0·934	−0·357	0·016
	3	0·127	0·305	0·819	0·486

of 1·5 for N and 1·85 for S. It is interesting that an anomalously short S · · · S distance (of 3·37 Å) also occurs in orthorhombic S_8 (Donohue *et al.*, 1961).

Thermal vibrations

The atom vibration ellipsoids corresponding to the thermal parameters of Table 2 are presented in Table 5. Unfortunately, there does not appear to be much correlation of these anisotropies with the symmetry axes of the molecule, so it seems quite possible that the B_{ij} either do not correspond to a physically significant situation or that the thermal motions arise in no small part from the nature of the packing and are therefore difficult to untangle from the motions of the individual molecules. In fact, calculation of the $\mathbf{T}, \boldsymbol{\omega}$ tensor (Cruickshank, 1956) gives a result which suggests that the interpretation of the thermal vibrations of Table 5 in terms of rigid body motions is a rather dubious procedure. Accordingly, the evaluation of six B_{ij} per atom was, in the present case, probably merely a device for reducing the residual. The present example is doubtless not unique in this regard.

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The Crystal and Molecular Structure of Taurine

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The structure of taurine, $NH_2[CH_2]_2HSO_3$, has been determined by Patterson superposition and Fourier methods. The crystals are monoclinic with space group $P2_1/c$. The unit-cell dimensions are,

$$a=5{\cdot}30,\ b=11{\cdot}65,\ c=7{,}94\ \text{Å},\ \beta=94°\ 17'.$$

The structure was refined by least-squares methods using three-dimensional data. The final R-factor, 0·11, was obtained using individual isotropic temperature factors for the heavier atoms and an over-all isotropic temperature factor for the hydrogen atoms. The bond lengths, bond angles and inter-molecular contacts were found to be normal.

Introduction

The X-ray investigation of several related compounds is at present being undertaken by the authors, to obtain structural information on the sulphonate and sulphuric radicals, taurine being the first of the series.

Taurine, $NH_2[CH_2]_2HSO_3$, occurs in the combined state in ox-gall and many other animal secretions. In the animal organism taurine is formed from cysteine by decarboxylation followed by oxidation. It can be obtained synthetically by the addition of sodium bisulphite to nitroethylene and the subsequent reduction of the nitroethane sulphonic acid. It forms colourless crystals, and melts and decomposes at about 328 °C; it is readily soluble in water but insoluble in alcohol and is quoted as forming tetragonal crystals (*Handbook of Chemistry and Physics*, 1961).

Experimental

A sample of taurine was recrystallized from water, the form of the resulting crystals depending on the rate of evaporation of the solution. With rapid evaporation, needle-shaped crystals were formed—the length of the needle being parallel to the a-axis—whereas with slow evaporation the crystals adopted a tabular appearance, the greatest length being along the a-axis. Both crystal types possessed identical space groups and unit-cell dimensions.

The space group and unit-cell dimensions were obtained from Weissenberg films using Cu $K\alpha$ radiation; the systematic absences,

$$0k0 \text{ with } k=2n+1 \quad\text{and}\quad h0l \text{ with } l=2n+1$$

uniquely determined the space group as $P2_1/c$; the unit-cell dimensions were:

$$a=5{\cdot}30\pm0{\cdot}01,\ b=11{\cdot}65\pm0{\cdot}01,$$
$$c=7{\cdot}94\pm0{\cdot}01\ \text{Å};\ \beta=94°\ 17'\pm5'.$$

The density measured at 20 °C by the method of flotation, using a benzene-tetrabromoethane mixture, was $1{\cdot}70\pm0{\cdot}02$ g.cm^{-3}. The calculated value, assuming four molecules to the unit cell, was 1·71 g.cm^{-3}.

The intensity data were measured visually from sets of multiple-film equi-inclination Weissenberg photographs (Robertson, 1943) taken with Cu $K\alpha$ radiation. 850 independent reflexions were measured from the $0kl$, $hk0$, $h0l$ and hkh zones and upper layers ($h=1$ to 5) taken with the a-axis as rotation axis. The intensities were corrected for Lorentz and polarization factors, but since the crystals were needle-shaped no attempt was made to apply absorption corrections. A correction for the variation in the area of the reflexions occurring in the upper-level Weissenberg photographs was made by the method of Phillips (1954). It was found that when the Phillips correction factor was applied to the extended reflexions, there was a difference in scale factor between the reflexions on both halves of the film, the scale factor appearing to vary with the Bragg angle, θ. An empirical correction curve was calculated for the contracted reflexions

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