Acta Cryst. (1964). **17**, 937

The Crystal Structure of Trimethylenethiourea

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(*Received* 26 *August* 1963)

The crystal structure of trimethylenethiourea,

$$\mathrm{S\ =\ \underline{C{-}NH{-}CH_2{-}CH_2{-}CH_2{-}NH}}\ ,$$

at 140–150 °K, has been determined by three-dimensional methods. In an orthorhombic unit cell,

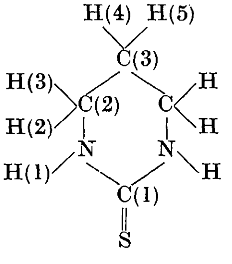
$$a=9{\cdot}240\pm0{\cdot}006,\ b=14{\cdot}793\pm0{\cdot}012,\ c=8{\cdot}276\pm0{\cdot}005\ \text{Å}\ ,$$

space group *Abam*, there are eight molecules which lie with the S = C bonds and the central methylene groups in mirror planes at $z/c=0$ or $z/c=\frac{1}{2}$. Refinement has been carried out by the method of least squares with allowance for anisotropic vibration for sulphur, carbon, and nitrogen atoms and isotropic vibration for hydrogen atoms. The final R value is 0·108. From coordinates corrected for rotational oscillation the bond lengths are S = C 1·722 ± 0·007 Å, C–N 1·334 ± 0·006 Å, N–C(methylene) 1·452 ± 0·007 Å and C–C 1·518 ± 0·007 Å, and the angles are S–C–N 119·8 ± 0·4°, N–C–N 120·5 ± 0·5°, C–N–C 122·9 ± 0·5°, N–C–C 109·0 ± 0·5° and C–C–C 109·7 ± 0·6°. The N–H and C–H bond lengths range from 0·91 to 1·03 Å, but, with standard deviations of 0·08 to 0·17 Å, none differs significantly from 1·0 Å.

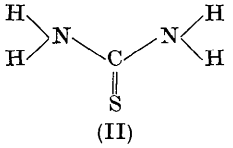
The thioamide group $\mathrm{S=C}\!\begin{smallmatrix}\diagup\mathrm{N}\\ \diagdown\mathrm{N}\end{smallmatrix}$ is planar, but the methylene carbon atoms do not lie in this plane so that the six-membered ring approximates to the chair form. The molecules are held in chains approximately parallel to the c axis by hydrogen bonds; each nitrogen atom is 3·30 Å from a sulphur atom, and each sulphur atom has two hydrogen bonds from nitrogen. The hydrogen atom does not lie along this bond, the N–H · · · S angle being 161 ± 8°.

Introduction

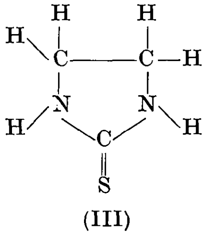
An accurate determination of the dimensions of trimethylenethiourea (I) was undertaken as part of a programme of study of sulphur compounds and is of particular interest for comparison with thiourea (II) and ethylenethiourea (III). The numbering of the atoms is also shown in (I).



(I)



(II)



(III)

Experimental

A sample of the compound was supplied by Prof. Kumler. Recrystallization from methanol, or from ethanol, produced specimens suitable for X-ray work. The colourless crystals showed cleavage parallel to (010) and were biaxial negative with the minimum refractive index parallel to the b axis.

Cu $K\alpha$ radiation was used for all diffraction measurements. At room temperature the unit-cell dimensions, measured approximately from oscillation photographs, are:

$$a=9{\cdot}23\pm0{\cdot}02,\ b=14{\cdot}93\pm0{\cdot}03,\ c=8{\cdot}39\pm0{\cdot}03\ \text{Å}.$$

Systematic absences (hkl with $k+l$ odd, $0kl$ with k odd and $h0l$ with h odd) corresponded to the space groups *Aba* or *Abam*. With 8 molecules in the unit cell the calculated density is 1·34 g.cm^{-3} compared 1·33 g.cm^{-3} measured by flotation.

For intensity measurements the crystal was cooled in a stream of nitrogen with an apparatus adapted from that described by Robertson (1960). It was necessary to keep the crystal in a glass capillary to prevent it from being blown off in the gas stream. No phase transformation took place on cooling. Periodically the temperature at the site of the crystal was measured and found to lie in the range 140 to 150 °K.

Unit-cell dimensions were obtained from Weissenberg photographs on which were superimposed patterns from a copper wire for calibration; the values obtained were:

$a = 9{\cdot}240 \pm 0{\cdot}006$, $b = 14{\cdot}79_3 \pm 0{\cdot}01$, $c = 8{\cdot}276 \pm 0{\cdot}005$ Å.

Equi-inclination Weissenberg photographs were taken about the three principal axes; the layers $0kl \ldots 5kl$ were obtained from a crystal 0·36 mm long and 0·18 × 0·54 mm in cross section, $h0l \ldots h6l$ from a crystal 0·2 mm long and 0·36 × 0·54 mm in cross-section and $hk0 \ldots hk5$ from a crystal 0·40 mm long and 0·27 × 0·27 mm in cross-section. A multiple-film technique was used and intensities estimated visually with the aid of a calibration strip. Lorentz and polarization factors were applied on the Leeds University Ferranti Pegasus computer (which will now be called the computer) with a program written by Mr J. G. F. Smith. The same program also enabled us to apply an absorption correction as for a cylinder with diameter equal to the average cross-section of the crystal, $\mu = 39{\cdot}1$ cm^{-1}, and to apply Phillips's (1954) corrections to the layers $3kl$, $h4l$, $hk2$, and all higher ones for which only the elongated spots had been measured.

Partial three-dimensional data were obtained by correlation of $hk0 \ldots hk5$ with $0kl$ and $1kl$. Later, a program written by Mr Smith was used to carry out a correlation for all the layer lines by the least-squares procedure of Rollett & Sparks (1960) and gave the complete set (660 out of a possible 671) of hkl structure amplitudes on an arbitrary scale.

Structure determination

There were two possible space groups, *Aba*, for which no molecular symmetry was required, or *Abam*, in which the molecules would have to occupy special positions on centres of symmetry, twofold axes, or mirror planes. The distribution test on the $0kl$ intensities showed dominance by a heavy atom and not whether the projection was centrosymmetric. Wilson's method gave a temperature factor, $B = 2{\cdot}5$ Å^2, and the scale factor for $0kl$.

Attempts to solve the structure in projection were unsuccessful and so the partial three-dimensional data were used for a three-dimensional Patterson synthesis; this was computed with a program written by Pilling, Lovell & Bujosa (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). Vectors for S–S, S–C and S–N showed clearly and there were two peaks on the line 0, 0, w corresponding to N–N′ and C(2)–C(2′) for atoms of the same molecule related to one another by a mirror plane at $w = 0$. The space group was thus established as *Abam* with the atoms S, C(1), C(3) (and H(4) and H(5)) lying in the mirror plane at $x, y, 0$. The coordinates from the Patterson synthesis were not sufficiently accurate for immediate refinement; two cycles were attempted but R remained at 0·40. It was necessary to carry out two cycles of

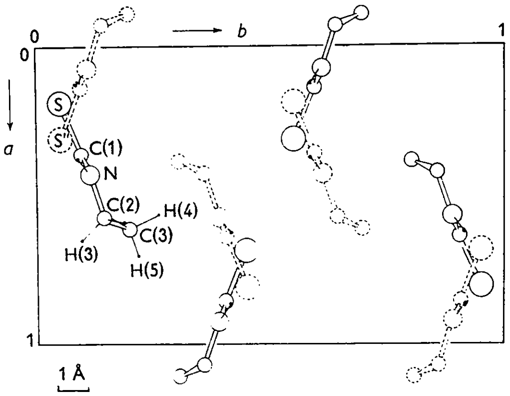


Fig. 1. Projection of the structure down [001]. Molecules shown with broken lines lie on the mirror plane at $z/c = \frac{1}{2}$, those with full lines at $z/c = 0$.

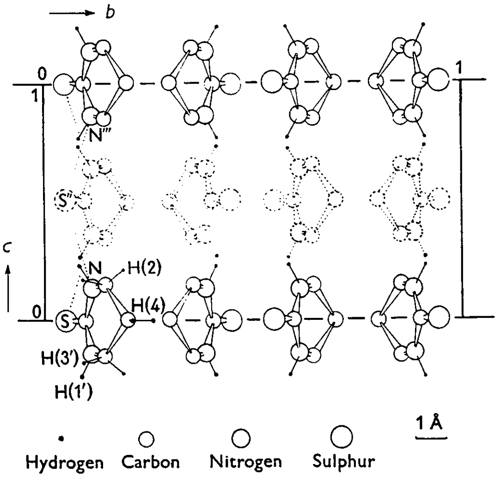


Fig. 2. Projection of the structure down [100]. Full lines and broken lines denote the same molecules as in Fig. 1. The dotted lines show hydrogen bonds with N ··· S = 3·30 Å.

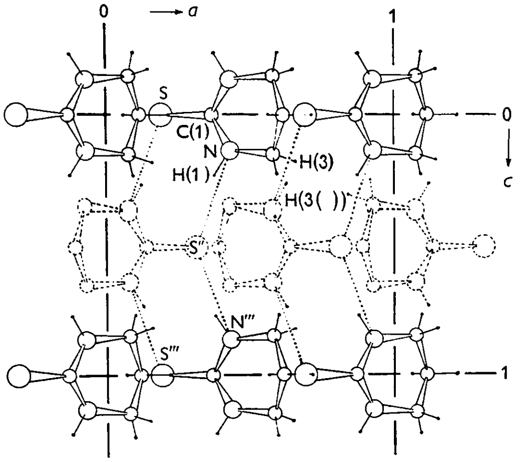


Fig. 3. Projection down [010] of half a unit cell, from $y/b = 0$ to $y/b = \frac{1}{2}$. The dotted lines show hydrogen bonds with N ··· S = 3·30 Å.

Table 1. *Observed and calculated structure factors* (× 10)

h	k	l	$\lvert F_o \rvert$	F_c
0	0	2	1074	1238
0	0	4	390	373
0	0	6	987	1144
0	0	8	700	744
0	0	10	163	139
0	2	0	527	589
0	2	2	554	573
0	2	4	405	423
0	2	6	352	342
0	2	8	280	268
0	2	10	222	201
0	4	0	1229	−1402
0	4	2	512	475
0	4	4	759	771
0	4	6	201	−226
0	4	8	120	−121
0	4	10	246	220
0	6	0	452	−487
0	6	2	395	−414
0	6	4	314	−309
0	6	6	218	−193
0	6	8	210	−170
0	6	10	115	−135
0	8	0	139	−114
0	8	2	632	−639
0	8	4	736	−837
0	8	6	200	−208
0	8	8	193	−161
0	10	0	221	−184
0	10	2	248	−223
0	10	4	189	−194
0	10	6	228	−211
0	10	8	135	−120
0	12	0	418	−383
0	12	2	281	−224
0	12	4	98	−87
0	12	6	336	−209
0	12	8	204	−178
0	14	0	105	−93
0	14	2	117	−76
0	14	4	73	−55
0	14	6	29	−33
0	16	0	73	66
0	16	2	61	52
0	16	4	43	31
0	18	0	117	117
0	18	2	117	102
1	1	1	615	−677
1	1	3	802	831
1	1	5	204	169
1	1	7	199	−186
1	1	9	101	108
1	2	0	640	−724
1	2	2	637	−678
1	2	4	410	−412
1	2	6	284	−293
1	2	8	280	−266
1	2	10	188	−174
1	3	1	1029	1102
1	3	3	316	−311
1	3	5	166	166
1	3	7	428	406
1	3	9	88	47
1	4	0	1421	−1561
1	4	2	881	−962
1	4	4	659	−703
1	4	6	546	−591
1	4	8	434	−422
1	4	10	248	−228
1	5	1	386	393
1	5	3	488	−475
1	5	5	94	−106
1	5	7	194	188
1	5	9	62	−24
1	6	0	275	−318
1	6	2	380	−376
1	6	4	370	−367
1	6	6	320	−292
1	6	8	185	−186
1	6	10	127	−150
1	7	1	263	−257
1	7	3	330	303
1	7	5	56	21
1	7	7	196	−196
1	7	9	46	24
1	8	0	32	23
1	8	2	299	−240
1	8	4	247	−275
1	8	6	107	−62
1	8	8	59	−57
1	9	1	434	−434
1	9	3	65	−64
1	9	5	152	−127
1	9	7	272	−242
1	9	9	122	−111
1	10	0	37	14
1	10	2	67	76
1	10	4	102	93
1	10	6	56	39
1	10	8	69	14
1	11	1	177	−153
1	11	3	350	−308
1	11	5	184	−185
1	11	7	72	−51
1	12	0	93	79
1	12	2	254	218
1	12	4	284	267
1	12	6	94	81
1	12	8	67	74
1	13	1	51	43
1	13	3	42	−52
1	13	5	46	−43
1	13	7	24	24
1	14	0	217	194
1	14	2	187	152
1	14	4	129	110
1	14	6	175	131
1	15	1	48	23
1	15	3	37	42
1	15	5	36	27
1	16	0	351	260
1	16	2	249	168
1	16	4	127	108
1	17	1	113	78
1	17	3	88	83
1	18	0	78	67
1	18	2	111	85
2	0	0	195	214
2	0	2	805	−897
2	0	4	899	−958
2	0	6	194	−185
2	0	8	147	−150
2	0	10	299	−307
2	1	1	432	−445
2	1	3	255	−225
2	1	5	263	−261
2	1	7	132	−134
2	1	9	34	−40
2	2	0	657	−703
2	2	2	500	−521
2	2	4	405	−419
2	2	6	302	−315
2	2	8	217	−215
2	2	10	156	−147
2	3	1	162	166
2	3	3	199	−207
2	3	5	165	−170
2	3	7	44	−34
2	3	9	39	−63
2	4	0	784	−817
2	4	2	67	26
2	4	4	303	279
2	4	6	249	−228
2	4	8	172	−157
2	4	10	70	62
2	5	1	417	−388
2	5	3	541	−566
2	5	5	310	−289
2	5	7	197	−173
2	5	9	240	−228
2	6	0	242	257
2	6	2	146	163
2	6	4	188	172
2	6	6	150	151
2	6	8	75	80
2	6	10	32	52
2	7	1	796	−788
2	7	3	282	−254
2	7	5	304	−320
2	7	7	365	−394
2	7	9	208	−186
2	8	0	641	642
2	8	2	293	283
2	8	4	95	82
2	8	6	300	306
2	8	8	237	230
2	9	1	158	−143
2	9	3	74	71
2	9	5	72	−46
2	9	7	121	−118
2	10	0	311	312
2	10	2	320	307
2	10	4	229	254
2	10	6	208	187
2	10	8	194	175
2	11	1	242	236
2	11	3	143	−101
2	11	5	51	32
2	11	7	201	179
2	12	0	107	71
2	12	2	212	171
2	12	4	229	207
2	12	6	119	86
2	12	8	62	52
2	13	1	351	350
2	13	3	231	193
2	13	5	261	218
2	13	7	253	228
2	14	0	56	27
2	14	2	60	32
2	14	4	51	42
2	14	6	64	37
2	15	1	111	95
2	15	3	350	280
2	15	5	178	164
2	16	0	53	−44
2	16	2	65	−57
2	16	4	65	−63
2	17	1	37	−21
2	17	3	46	43
2	18	0	91	−80
2	18	2	98	−88
3	1	1	563	−550
3	1	3	363	−357
3	1	5	327	−309
3	1	7	318	−319
3	1	9	197	−200
3	2	0	110	193
3	2	2	138	139
3	2	4	292	271
3	2	6	161	158
3	2	8	39	19
3	2	10	37	39
3	3	1	568	−510
3	3	3	557	−535
3	3	5	397	−361
3	3	7	230	−209
3	3	9	204	−179
3	4	0	415	−403
3	4	2	264	228
3	4	4	265	247
3	4	6	57	−15
3	4	8	59	12
3	4	10	95	123
3	5	1	47	39
3	5	3	60	−54
3	5	5	54	−42
3	5	7	55	33
3	5	9	50	4
3	6	0	559	593
3	6	2	370	378
3	6	4	218	230
3	6	6	223	217
3	6	8	282	231
3	7	1	157	163
3	7	3	244	256
3	7	5	178	172
3	7	7	121	118
3	7	9	76	112
3	8	0	556	560
3	8	2	54	37
3	8	4	119	−118
3	8	6	191	234
3	8	8	142	141
3	9	1	453	456
3	9	3	463	469
3	9	5	336	381
3	9	7	249	249
3	9	9	129	188
3	10	0	158	−127
3	10	4	62	61
3	10	6	52	−16
3	10	8	61	−49
3	11	1	406	419
3	11	3	337	337
3	11	5	261	305
3	11	7	243	240
3	12	0	325	−353
3	12	2	61	−42
3	12	4	95	105
3	12	6	196	−189
3	13	1	110	98
3	13	3	72	57
3	13	5	64	51
3	13	7	65	66
3	14	0	112	−115
3	14	2	208	−177
3	14	4	197	−204
3	14	6	102	−97
3	15	1	48	−78
3	15	3	47	−64
3	15	5	52	−60
3	16	0	124	104
3	16	2	80	−67
3	16	4	113	−140
3	17	1	136	−150
3	17	3	117	−123
3	18	0	55	−44
4	0	0	817	−841
4	0	2	166	−154
4	0	4	84	−81
4	0	6	219	−229
4	0	8	152	−137
4	0	10	18	9
4	1	1	220	185
4	1	3	113	118
4	1	5	41	43
4	1	7	110	94
4	1	9	118	117
4	2	0	144	138
4	2	2	115	111
4	2	4	80	81
4	2	6	55	62
4	2	8	55	47
4	2	10	15	22
4	3	1	801	745
4	3	3	281	287
4	3	5	321	317
4	3	7	371	378
4	3	9	219	234
4	4	0	492	401
4	4	2	32	25
4	4	4	77	−47
4	4	6	95	135
4	4	8	65	77
4	5	1	683	644
4	5	3	417	392
4	5	5	457	463
4	5	7	352	388
4	5	9	164	174
4	6	0	67	64
4	6	2	59	55
4	6	4	78	66
4	6	6	51	25
4	6	8	44	13
4	7	1	217	207
4	7	3	572	615
4	7	5	352	359
4	7	7	94	100
4	7	9	98	172
4	8	0	40	−28
4	8	2	81	50
4	8	4	114	110
4	8	6	55	−23
4	8	8	38	−7
4	9	1	50	41
4	9	3	232	241
4	9	5	74	79
4	10	0	193	−204
4	10	2	194	−185
4	10	4	177	−184
4	10	6	100	−111
4	10	8	60	−80
4	11	1	53	−27
4	11	3	329	−352
4	11	5	213	−178
4	11	7	36	20
4	12	0	50	−18
4	12	2	49	−29
4	12	4	59	−47
4	12	6	61	−12
4	13	1	178	−190
4	13	3	323	−310
4	13	5	190	−191
4	13	7	50	−93
4	14	0	42	22
4	14	2	44	26
4	14	4	44	33
4	14	6	25	12
4	15	1	268	−293
4	15	3	68	−71
4	15	5	88	−135
4	16	0	37	43
4	16	2	33	35
4	16	4	24	27
4	17	1	95	−112
4	17	3	23	−37
4	18	0	14	34
5	1	1	927	901
5	1	3	294	299
5	1	5	434	433
5	1	7	457	502
5	1	9	228	219
5	2	0	97	74
5	2	2	211	180
5	2	4	329	271
5	2	6	137	131
5	2	8	44	23
5	3	1	50	−27
5	3	3	489	457
5	3	5	223	182
5	3	9	136	132
5	4	0	155	139
5	4	2	413	336
5	4	4	391	350
5	4	6	148	114
5	4	8	130	104
5	5	1	121	−124
5	5	3	213	190
5	5	5	56	47
5	5	7	105	−101
5	5	9	33	20
5	6	0	186	147
5	6	2	48	35
5	6	4	62	−45
5	6	6	46	28
5	6	8	94	82
5	7	1	270	−250
5	7	3	512	−502
5	7	5	304	−299
5	7	7	94	−104
5	8	0	240	171
5	8	2	88	−87
5	8	4	180	−168

Table 1 (*cont.*)

h	k	l	$\lvert F_o \rvert$	F_c
5	8	6	46	70
5	8	8	35	29
5	9	1	301	−256
5	9	3	380	−358
5	9	5	253	−268
5	9	7	148	−144
5	10	0	118	−99
5	10	2	46	−21
5	10	4	47	32
5	10	6	49	−22
5	11	1	271	−260
5	11	3	116	−131
5	11	5	128	−157
5	11	7	141	−184
5	12	0	209	−183
5	12	2	44	11
5	12	4	69	86
5	12	6	97	−91
5	13	1	141	−155
5	13	3	108	−114
5	13	5	73	−96
5	14	0	41	47
5	14	4	37	−33
5	15	1	69	48
5	15	3	34	28
5	16	0	33	35
5	16	2	76	−71
5	17	1	37	65
6	0	0	277	−261
6	0	2	517	459
6	0	4	609	637
6	0	6	71	24
6	0	8	56	41
6	1	1	54	−59
6	1	3	147	−129
6	1	5	133	−114
6	1	7	36	−41
6	2	0	395	374
6	2	2	337	290
6	2	4	279	260
6	2	6	255	217
6	2	8	195	151
6	3	1	424	−421
6	3	3	528	−497
6	3	5	402	−391
6	3	7	271	−226
6	3	9	177	−173
6	4	0	525	468
6	4	2	94	−91
6	4	4	304	−295
6	4	6	231	183
6	4	8	157	121
6	5	1	411	−404
6	5	3	363	−355
6	5	5	277	−267
6	5	7	249	−227
6	6	0	225	−209
6	6	2	111	−115
6	6	4	123	−112
6	6	6	152	−131
6	6	8	73	−71
6	7	1	155	−163
6	7	3	45	−32
6	7	5	61	−60
6	8	0	362	−418
6	8	2	139	−133
6	8	4	46	28
6	9	1	96	−71
6	9	3	44	−37
6	9	5	56	−62
6	10	0	154	−156
6	10	2	210	−185
6	10	4	122	−167
6	11	1	148	152
6	11	3	56	44
6	11	5	74	64
6	12	0	41	23
6	12	2	109	−74
6	12	4	75	−120
6	13	1	84	93
6	13	3	54	58
6	13	5	58	71
6	14	0	34	−36
6	14	2	46	−27
6	14	4	25	−27
6	15	1	39	73
6	15	3	95	125
6	16	0	21	20
7	1	1	119	−116
7	1	3	542	−529
7	1	5	304	−278
7	1	7	38	−14
7	2	0	333	−331
7	2	2	276	−255
7	2	4	194	−179
7	2	6	222	−184
7	2	8	181	−165
7	3	1	290	−266
7	3	3	208	175
7	3	5	53	−31
7	3	7	246	−208
7	4	0	235	−202
7	4	2	307	−269
7	4	4	255	−230
7	4	6	207	−170
7	4	8	164	−133
7	5	1	93	−66
7	5	3	249	237
7	5	5	121	103
7	5	7	106	−82
7	6	0	349	−355
7	6	2	408	−359
7	6	4	333	−352
7	6	6	304	−249
7	6	8	89	−167
7	7	1	273	275
7	7	3	44	−27
7	7	5	125	100
7	8	0	175	−164
7	8	2	113	−100
7	8	4	74	−77
7	9	1	148	182
7	9	5	50	48
7	10	0	42	25
7	10	2	38	31
7	10	4	71	46
7	11	3	105	107
7	11	5	39	38
7	12	0	148	146
7	12	2	105	113
7	12	4	74	83
7	13	1	45	35
7	13	3	68	85
7	14	0	158	184
7	14	2	171	173
7	15	1	27	35
8	0	0	424	−556
8	0	2	185	−182
8	0	4	40	9
8	0	6	344	−306
8	1	1	114	112
8	1	3	42	48
8	1	5	74	61
8	1	7	79	69
8	2	0	321	−318
8	2	2	354	−316
8	2	4	280	−269
8	2	6	276	−212
8	3	1	54	42
8	3	3	106	82
8	3	5	82	45
8	3	7	33	26
8	4	0	116	128
8	4	2	214	−177
8	4	4	317	−299
8	4	6	61	17
8	5	1	76	21
8	5	3	129	126
8	5	5	60	55
8	6	0	80	92
8	6	2	101	109
8	6	4	80	79
8	6	6	48	52
8	7	1	59	61
8	7	3	50	−45
8	7	5	48	13
8	8	0	63	43
8	8	2	231	225
8	8	4	269	289
8	9	3	104	−90
8	9	5	39	−29
8	10	0	291	311
8	10	2	306	287
8	10	4	191	270
8	11	1	47	−14
8	11	3	69	87
8	12	0	171	199
8	12	2	125	119
8	12	4	28	65
8	13	1	34	−34
8	14	0	20	2
9	1	1	59	−24
9	1	3	186	−165
9	1	5	101	−89
9	1	7	14	3
9	2	0	136	126
9	2	2	144	143
9	2	4	102	112
9	2	6	73	79
9	3	1	69	−36
9	3	3	78	89
9	3	5	44	24
9	4	0	358	325
9	4	2	193	192
9	4	4	145	133
9	4	6	247	207
9	5	1	128	−98
9	5	3	70	35
9	6	0	274	264
9	6	2	271	262
9	6	4	282	241
9	6	6	191	199
9	7	1	90	116
9	7	3	35	28
9	7	5	63	58
9	8	0	74	51
9	8	2	212	203
9	8	4	168	240
9	9	1	70	72
9	9	3	29	−13
9	10	0	74	−2
9	10	2	26	−28
9	10	4	45	−38
9	11	3	18	33
9	12	0	25	−28
9	12	2	77	−150
10	0	0	240	209
10	0	2	212	204
10	0	4	189	197
10	1	1	74	35
10	1	3	38	19
10	1	5	46	47
10	2	0	145	120
10	2	2	148	131
10	2	4	143	120
10	3	1	161	138
10	3	3	248	198
10	3	5	180	156
10	4	0	121	110
10	4	2	122	93
10	4	4	96	70
10	5	1	132	114
10	5	3	201	180
10	5	5	89	99
10	6	0	41	−9
10	6	2	34	−37
10	6	4	41	−46
10	7	1	95	85
10	7	3	36	−49
10	8	0	147	−174
10	9	1	32	51
10	10	0	115	−159
11	1	1	187	174
11	1	3	257	232
11	2	0	33	−22
11	2	2	26	−36
11	2	4	41	−69
11	3	1	132	114
11	3	3	24	22
11	4	0	92	−93
11	4	2	147	−150
11	5	1	37	−39
11	5	3	37	−72
11	6	0	85	−92
11	6	2	47	−69
11	7	1	82	−133

refinement for the sulphur position only, followed by a three-dimensional Fourier synthesis. This showed the sulphur, carbon and nitrogen positions, close to those deduced from the Patterson synthesis. The coordinates of the atomic centres were found by the parabola method and used to calculate structure factors for the full three-dimensional data. An R value of 0·32 was obtained and subsequent refinement proceeded smoothly. The structure is shown in Figs. 1, 2 and 3.

Refinement

Refinement was carried out by the method of least squares with a program written by Cruickshank & Pilling (Cruickshank *et al.*, 1961). The function minimized was $R' = \Sigma w(|F_o| - |F_c|)^2$ where the weighting factor w was $1/|F_o|$. For sulphur the scattering factor of Tomiie & Stam (1958) was used, for carbon and nitrogen those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

Two cycles of anisotropic refinement reduced R to 0·18 (from 0·32) and at this stage the most significant shift in a coordinate was 2·8 times the corresponding standard deviation. The hydrogen atoms, H(2), H(3), H(4) and H(5) were now added in positions calculated to make the C–H bond lengths 1·0 Å and to complete tetrahedra around the methylene carbon atoms. Because the C–N–C angle was 122°, we chose the position for H(1) on the assumption that the bonds round nitrogen were planar and that N–H was 1·0 Å. Isotropic temperature factors ($\overline{U}$) of 0·06 Å^2 were assigned to the hydrogen atoms; in subsequent refinement both the coordinates and the isotropic temperature factors of the hydrogen atoms were refined. After three cycles of refinement R fell to 0·12;

the largest shift was equal to the corresponding standard deviation, and the temperature factors of the hydrogen atoms were less than 0·06 Å^2.

An empirical extinction correction was applied for reflexions with $\sin\theta \leq 0{\cdot}25$; from the equation $I_o = I_{\text{true}} \exp(-\alpha I_c)$, the coefficients α were found graphically as $6{\cdot}6 \times 10^{-6}$, $1{\cdot}0 \times 10^{-5}$ and $4{\cdot}3 \times 10^{-6}$ for observations made about the a, b and c axes respectively; these values vary reasonably with the cross-sections of the crystals. Only for 002, 040, 140 and 131 were the corrections large, being 14, 16, 22 and 13% of the original $|F_o|$ respectively.

Three more cycles completed the refinement, the largest shift in any parameter ($\bar{U}$ for H(3)) being 0·25 of the corresponding standard deviation and the value of R 0·108. Table 1 shows the final observed and calculated structure factors.

In Table 2 the atomic coordinates and their standard deviations are given. Table 3 shows the final values for the tensor components describing the anisotropic vibrations of the atoms; the standard deviations calculated in the least-squares refinement are also shown. The tensor components U_{ij} are those occurring in the temperature factor:

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \ldots)\right],$$

so that, for instance, U_{11} is the mean square amplitude of vibration of the atom parallel to the a^* axis.

Table 2. *Fractional coordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
S	0·1906	0·0521	0	0·002	0·002	—
N	0·4287	0·1135	0·1391	0·004	0·005	0·005
C(1)	0·3628	0·0962	0	0·007	0·006	—
C(3)	0·6139	0·1978	0	0·009	0·009	—
C(2)	0·5777	0·1436	0·1491	0·005	0·006	0·005
H(1)	0·375	0·085	0·236	0·10	0·10	0·13
H(2)	0·596	0·184	0·231	0·07	0·07	0·09
H(3)	0·652	0·097	0·170	0·08	0·07	0·09
H(4)	0·569	0·260	0	0·13	0·17	—
H(5)	0·710	0·213	0	0·14	0·14	—

Table 3. *Thermal parameters*

($\times 10^3$ Å^2)

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	σ
S	30	0·9	43	1	22	0·9	−2	0·6	0	—	0	—
N	36	2	49	2	27	2	2	2	−4	2	−5	2
C(1)	37	3	28	3	33	3	8	2	0	—	0	—
C(3)	40	4	56	4	37	4	−14	3	0	—	0	—
C(2)	35	2	53	3	25	2	1	2	1	2	−4	2

	U	σ
H(1)	64	28
H(2)	25	18
H(3)	31	20
H(4)	71	52
H(5)	56	41

An analysis of the vibrational motion was carried out with a program written by Bujosa & Cruickshank (Cruickshank, 1956; Cruickshank *et al.*, 1961). The results showed that the assumption that the molecule moved as a rigid body was justified within experimental error; the root mean square standard deviation of the radial tensors, for all the atoms, was 0·003 Å^2. The principal axes of the translational and rotational tensors are shown in Table 4 with, for comparison, the direction cosines of the S=C bond and of the axis with the minimum moment of inertia. Although the smallest rotational oscillation is calculated to be negative, it is not significantly different from zero. The largest oscillation is approximately about the axis with the minimum moment of inertia, close to the direction of the S=C bond, and the zero oscillation is approximately about the normal to the S, C(1), N,N′ plane.

Table 4. *Principal axes of the translational and rotational tensors with respect to the crystallographic axes*

Mean square amplitude of translation	Direction cosines		
0·037 ± 0·004 Å^2	0·751	0·660	0·000
0·028 ± 0·002 Å^2	−0·660	0·751	0·000
0·027 ± 0·002 Å^2	0·000	0·000	1·000
Root mean square angular oscillation			
6·2 ± 1·2°	0·965	0·262	0·000
3·1 ± 1·0°	0·000	0·000	1·000
−1·3 ± 1·2°	−0·262	0·965	0·000
S–C(1)	0·926	0·379	0·000
Axis with minimum moment of inertia	0·910	0·414	0·000

Corrections for the systematic error caused by rotational oscillation about the two axes with positive values were calculated by hand from Cruickshank's (1961) formulae; the most significant change in any coordinate was 1·7 times the corresponding standard deviation (−0·0029 Å in y for sulphur) while the largest change in a heavy atom coordinate was +0·0068 Å in z for C(2). The corrected coordinates are given in Table 5.

Table 5. *Corrected atomic coordinates with respect to the crystal axes*

	x	y	z
S	1·759 Å	0·768 Å	0·000 Å
N	3·962	1·678	1·158
C(1)	2·251	1·422	0·000
C(3)	5·675	2·932	0·000
C(2)	5·341	2·125	1·241
H(1)	3·47	1·26	1·96
H(2)	5·51	2·73	1·93
H(3)	6·03	1·42	1·42
H(4)	5·25	3·85	0·00
H(5)	6·56	3·16	0·00

Interatomic distances and angles

From the corrected coordinates (to 4 decimal places) the bond lengths and angles within the molecules and all intermolecular distances of less than 3·5 Å were calculated with a program written by one of us (Cruickshank *et al.*, 1961). A program written by Mr J. G. F. Smith was used to compute the standard deviations in all the distances and angles.

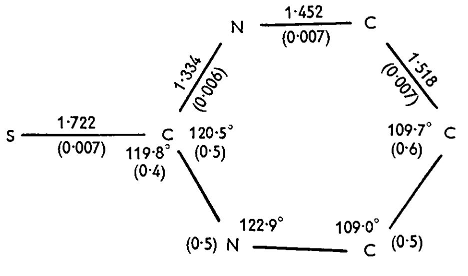


Fig. 4. The bond lengths (Å) and angles for the heavy atoms; the numbers in parentheses are the standard deviations.

For the heavy atoms the bond lengths and angles, together with their standard deviations, are shown in Fig. 4 while those involving hydrogen atoms are shown in Table 6.

Table 6. *Bond lengths and angles involving hydrogen atoms*

N–H(1)	1·03 ± 0·11 Å	C(1)–N–H(1)	112 ± 6°
C(2)–H(2)	0·93 ± 0·08	C(2)–N–H(1)	122 ± 6
C(2)–H(3)	1·00 ± 0·08		
C(3)–H(4)	1·01 ± 0·17	N–C(2)–H(2)	115 ± 4
C(3)–H(5)	0·91 ± 0·14	N–C(2)–H(3)	117 ± 4
		C(3)–C(2)–H(2)	102 ± 5
		C(3)–C(2)–H(3)	112 ± 5
		H(2)–C(2)–H(3)	102 ± 7
		C(2)–C(3)–H(4)	113 ± 4
		C(2)–C(3)–H(5)	110 ± 4
		H(4)–C(3)–H(5)	100 ± 15

From Fig. 1 it appears that the atoms S, C(1), N, N′, C(2) and C(2′) might be coplanar. However, the deviations of these atoms from the best plane through them are −0·019, +0·046, +0·028 and −0·031 Å for S, C(1), N and C(2) respectively and vary from 10 to 5 times the corresponding standard deviation. The plane of the thioamide group, S, C(1), N and N′ was calculated; its equation is

$$0·3816x - 0·9247y + 0·0390 = 0$$

with the maximum deviation of 0·003 Å for C(1). Distances of other atoms from this plane are

0·20 Å for H(1) (this is probably not significant),
0·112 Å for C(2) (this is highly significant, $\Delta/\sigma = 20$),

and

−0·507 Å for C(3).

The only intermolecular distance of less than 3·5 Å between atoms other than hydrogen atoms is 3·30 Å from N to S″; this and the corresponding separations for molecules related by the mirror planes and by the c-glide at $x/a = \frac{1}{4}$, are shown in Figs. 1, 2 and 3. This distance is characteristic for N ··· S hydrogen bonds and further support for this interpretation is the H(1) ··· S″ distance of 2·31 Å, which is much smaller than the sum of the van der Waals radii. As usual in hydrogen-bonded structures the hydrogen atom does not lie directly on the N ··· S line, with the result that the N–H ··· S″ angle is 161 ± 8°. Each nitrogen atom has one hydrogen bond, the direction of which is not quite in the thioamide plane, S″ being 0·421 Å from this plane. Each sulphur atom takes part in two hydrogen bonds and these, with the S–C bond, form a pyramidal arrangement; the angle N″ ··· S–C is 101·7 ± 0·2°, and N″ ··· S ··· N‴ is 128·8 ± 0·1°, or in terms of the hydrogen atoms, H ··· S–C = 99 ± 2° and H ··· S ··· H = 140 ± 4°. The shortest intermolecular contact of any kind (Fig. 3) is 2·23 Å from H(3) to H(3( )).

Discussion

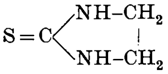
The structure consists of molecules held in chains approximately parallel to the *c* axis by hydrogen bonds, as depicted in Figs. 1, 2 and 3. The existence of hydrogen bonding explains the comparatively high melting point (213–215 °C), while the orientation of the molecules (Fig. 1) is consistent with cleavage parallel to (010) and a minimum refractive index parallel to the *b* axis. In ethylenethiourea (Wheatley, 1953) the individual molecules have a similar system of N ··· S hydrogen bonds but the packing of the structure is different so that the hydrogen bonding holds the molecules in puckered layers.

The advantage of low temperature work is not immediately apparent in the quoted figures for the standard deviation; they are little better than those obtained recently for *S*-methylthiourea sulphate (Stam, 1962) and thiourea dioxide (Sullivan & Hargreaves, 1962) by partial anisotropic refinement on observations collected at room temperature. But the statistical standard deviation does not allow for systematic errors, and bond lengths determined at room temperature may require corrections for rotational oscillation of the order of 0·02 Å (with some uncertainty in the correction) as found, for example, in thiourea (Kunchur & Truter, 1958) and thioacetamide (Truter, 1960). The correction in this work is only one-third of that required for room temperature investigation, and the uncertainty in the correction is very small (< 0·001 Å) compared with the statistical standard deviation which should now be a true representation of the accuracy.

The bond angles round the methylene carbon atoms C(2) and C(3) do not differ significantly from those of a regular tetrahedron; it is therefore reasonable to suppose that the observed C–C bond length, 1·518 ± 0·007 Å, represents a single bond between two sp^3 hybridized carbon atoms. It is, however, shorter

Table 7. *Bond lengths and angles in other molecules*

All the structures were determined at room temperature by three-dimensional methods

Compound	Rotational correction	N–Ĉ–N	N–C	C–S	Reference
$S=C(NH_2)_2$	*	115·6 ± 1·1°	1·33 ± 0·02 Å	1·72 ± 0·02 Å	Kunchur & Truter, 1958
$S=C(NH_2)CH_3$	*	117·7 ± 0·6 (N–Ĉ–C)	1·324 ± 0·008	1·713 ± 0·006	Truter, 1960
$[CH_3\text{–}S=C(NH_2)_2{}^+]_2SO_4{}^=$	†	122·5 ± 0·6	1·308 ± 0·009 1·333 ± 0·009	1·74 ± 0·007	Stam, 1962
$O_2S\text{–}C(NH_2)_2$	†	124·5 ± 0·7	1·310 ± 0·008	1·851 ± 0·016	Sullivan & Hargreaves, 1962
	†	110·2 ± 1·4	1·322 ± 0·008	1·708 ± 0·008	Wheatley, 1953

* Applied. † Not applied.

than the accepted length by 0·022 Å, which, at three times the standard deviation, is statistically significant at the 0·3% level. It is improbable that this has any chemical significance; it is another example of the caution required in the interpretation of molecular dimensions.

Both the C–N–C angle and the position of the atom H(1) indicate that the nitrogen atom is trigonally hybridized. The length N–C(2) represents a single bond, N(sp^2)–C(sp^3), and is slightly but not significantly shorter than the N(sp^3)–C(sp^3) distance (1·472 ± 0·005 Å) quoted in *Tables of Interatomic Distances* (1958). Round the carbon atom, C(1), the bond angles correspond to trigonal hybridization with the hybridization ratio the same for the carbon–sulphur and carbon–nitrogen bonds. Thioamide derivatives are known in which the angles range from N–C–X of 110·2 ± 1·4°, in ethylenethiourea, to 124·5 ± 0·7° in thiourea dioxide, as shown in Table 7. Bond angles are little affected by corrections for rotational oscillation so that the quoted standard deviations in the bond angles are comparable whether corrections have or have not been applied. Although the bond angles differ from compound to compound by amounts which are highly significant statistically the C–N and C–S bond lengths are the same within experimental error; only a change in the oxidation state of the sulphur atom, to IV, in thiourea dioxide produces a significant change in the carbon–sulphur bond lengths. Before we can be certain whether the variation in angles is correlated with a change in hybridization ratio and hence bond length, it will be necessary to determine several structures at reduced temperatures. The difference in the N–C–N angle between ethylenethiourea and trimethylenethiourea is reflected in a measurable difference in their electric dipole moments (Loader & Sutton, 1962).

We are grateful to Prof. Kumler for the crystals, Dr L. E. Sutton for informing us of his investigations on this compound and the Director and staff of the Leeds University Computing laboratory for computing facilities. One of us (H. W. D.) thanks the University of Ceylon (Peradeniya) for leave of absence during which this work was performed. Some of the equipment used was provided by the Royal Society and by Imperial Chemical Industries Ltd.

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