The Crystal and Molecular Structure of 1-Thiocarbamoylimidazolidine-2-thione

By G. Valle, G. Cojazzi,* V. Busetti and M. Mammi†

Istituto di Chimica Organica dell'Università, 35100 *Padova, Italy*

The structure of 1-thiocarbamoylimidazolidine-2-thione, $C_4H_7N_3S_2$, has been determined from X-ray three-dimensional diffraction data. The crystals are monoclinic, space group $P2_1/c$, $a = 4·958 \pm 0·003$, $b = 10·092 \pm 0·005$, $c = 13·841 \pm 0·006$ Å, $\beta = 103·0 \pm 0·2°$, $Z = 4$. The structure has been determined by Patterson and direct methods and refined by full-matrix least squares ($R = 0·057$). The molecule is nearly planar, with an intramolecular N–H$\cdots$S hydrogen bond of 2·998 Å. Bond lengths and resonance in the dithiobiuret moiety are discussed. Two pairs of intermolecular N–H$\cdots$S hydrogen bonds of 3·409 and 3·449 Å bring molecules together across centres of symmetry and give rise to infinite chains which are superimposed on each other, by the a-axis repeat, at a perpendicular distance of 3·506 Å.

Introduction

1-Thiocarbamoylimidazolidine-2-thione (formula I) (hereinafter TIO), is obtained by reacting ethylene diisothiocyanate (II) with ammonia. The structure of this product of the reaction was uncertain and the heptatomic triazepinic ring (III) was suggested on chemical grounds (Thorn & Ludwig, 1954).
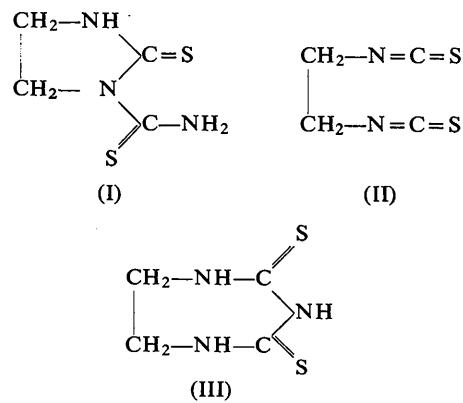
Further chemical investigations cast some doubt on this hypothesis (D'Angeli & Bandel, 1961; D'Angeli, Bandel & Giormani, 1963) and the X-ray analysis, also undertaken to elucidate the physico-chemical properties of the compound, definitely established the imidazolidine structure (I). While the chemical implications of this assignment have been reported in a preliminary account based on two-dimensional data (Valle, Cojazzi & Busetti, 1963; Mammi, D'Angeli & Bezzi, 1965), the crystal and molecular structures obtained by three-dimensional refinement are discussed here.

* Present address: Centro di Fisica Macromolecolare, Istituto Ciamician, 40100 Bologna, Italy.
† To whom enquiries should be addressed.

Experimental

Transparent colourless crystals were obtained by evaporating ethanolic solutions. They were spindle-shaped, with a nearly square cross-section and with elongation axis perpendicular to (100).

Crystal data

1-Thiocarbamoylimidazolidine-2-thione, $C_4H_7N_3S_2$, F.W. 161·1, m.p. 193°C.
Monoclinic, space group $P2_1/c$

$a = 4·958 \pm 0·003$ Å	$D_x = 1·57$ g.cm^{-3}
$b = 10·092 \pm 0·005$	$D_m = 1·53$ (by flotation)
$c = 13·841 \pm 0·006$	$\mu_{Cu\ K\alpha} = 63·2$ cm^{-1}
$\beta = 103·0 \pm 0·2°$	$\mu_{Mo\ K\alpha} = 7·4$
$V = 674·8$ Å^3	$F(000) = 336$
$Z = 4$	

$0kl$, $h0l$ and $hk0$ reflexions were first collected and used in a preliminary two-dimensional analysis. Three-dimensional data, $0kl$ to $4kl$, were then recorded in a Weissenberg camera (multiple-film technique, Ni-filtered Cu $K\alpha$ radiation) and 915 reflexions were observed, out of 1359 possible in the collected layers. Moreover, 82 $h0l$ reflexions (out of 103) and 64 $hk0$ (out of 74) were measured on Buerger precession photographs (Zr-filtered Mo $K\alpha$ radiation) and used for interlayer scaling.

Intensities were obtained by a Joyce Flying Spot Integrating Microdensitometer and the Lorentz, polarization and absorption correction were applied. The cross-dimensions of the crystal used were 0·25 × 0·30 mm.

Determination and refinement of the structure

The atomic positional parameters were first determined by two-dimensional analysis. The (100) Patterson synthesis allowed a direct localization of the sul-

phur atom S(1) only. As later ascertained, the S(2) rotational vector was in fact out of peak position, masked by a neighbouring larger peak. The S(2) atom was, however, easily localized on the first electron density map, and the R index decreased from 54 to 44%. The next Fourier synthesis showed an electron density distribution which was consistent with the imidazolidine structure (I), although the molecular model could fit with two different orientations. Only one of them significantly improved the R index (34%).

On account of the preliminary uncertainty on the chemical structure, a parallel attempt to derive the phases of the structure factors directly from the Sayre relationship (Woolfson, 1961) was successfully carried out, with the following simplified procedure. The $0kl$

reflexions having $|U(0kl)| \geq 1\cdot5 \ [\Sigma_j n_j^2]^{1/2} = 0\cdot17$ (63 reflexions out of 122 observed) (Zachariasen, 1952) were divided into four groups of 10, 16, 20 and 17 reflexions having $|U(0kl)| \geq 0\cdot35, 0\cdot25, 0\cdot20$ and $0\cdot17$ respectively. Arbitrary sign was given to the 0,2,15 and 0,9,2 reflexions and the sign of two others was expressed by letters; thus the four sign relationships found in the first group gave the sign to eight reflexions (just as sign or as letters).

By including the 16 reflexions of the next group (twelve new sign relationships found), the sign of all the 26 first reflexions was obtained, and so continuing the process, 60 structure factors were given a sign,

Table 1. *Atomic coordinates, vibrational parameters* ($\times 10^4$) *and e.s.d.'s* (*in parentheses*)

The expression for the temperature factor is

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right].$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0·2792 (2)	0·3437 (1)	0·5762 (0)	335 (8)	96 (2)	36 (1)	−44 (3)	5 (2)	−4 (1)
S(2)	−0·4869 (2)	0·0900 (1)	0·3557 (0)	280 (8)	85 (2)	45 (1)	−49 (3)	14 (2)	−5 (1)
N(1)	0·2228 (7)	0·4171 (4)	0·3901 (2)	284 (27)	79 (6)	45 (3)	−31 (10)	30 (7)	2 (4)
N(2)	−0·0848 (7)	0·2660 (3)	0·4016 (2)	218 (24)	69 (5)	34 (3)	−9 (8)	20 (6)	−2 (3)
N(3)	−0·1633 (9)	0·1358 (4)	0·5309 (2)	432 (32)	125 (8)	40 (3)	−96 (12)	22 (8)	12 (4)
C(1)	−0·1429 (10)	0·2984 (5)	0·2951 (3)	333 (33)	95 (8)	36 (3)	−22 (12)	14 (8)	12 (4)
C(2)	0·0622 (10)	0·4061 (5)	0·2878 (3)	353 (37)	124 (9)	45 (4)	−46 (14)	9 (9)	12 (5)
C(3)	0·1377 (8)	0·3425 (4)	0·4544 (3)	185 (27)	71 (6)	39 (3)	−2 (10)	15 (7)	−8 (4)
C(4)	−0·2295 (9)	0·1671 (4)	0·4366 (3)	231 (30)	75 (6)	41 (3)	0 (10)	33 (8)	−4 (4)

|				B					
H(1)	0·390 (3)	0·475 (2)	0·409 (1)	3·1 Å^2					
H(2)	−0·048 (3)	0·497 (2)	0·266 (1)	3·2					
H(3)	0·192 (3)	0·371 (2)	0·238 (1)	3·2					
H(4)	−0·348 (3)	0·332 (2)	0·271 (1)	3·9					
H(5)	−0·099 (3)	0·212 (2)	0·255 (1)	3·9					
H(6)	−0·005 (3)	0·189 (2)	0·576 (1)	4·0					
H(7)	−0·266 (3)	0·065 (2)	0·557 (1)	4·0					
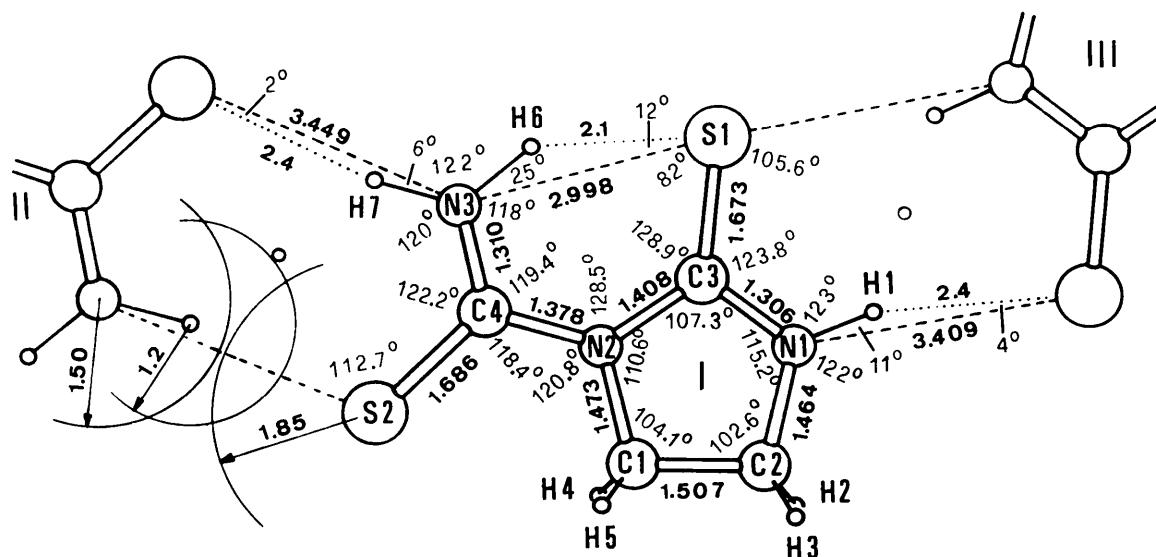
Fig. 1. Bond lengths and angles in the TIO molecule, and parameters of the hydrogen bridges.

Table 2. Observed and calculated structure factors

Columns are L, $10|F_o|$, $10|F_c|$. Unobserved reflexions, which were given half the minimum observed intensity, are marked by an asterisk.

```
0,0,L
2  404  453
4  407 -490
6  438 -446
8  171 -168
10  81  -81
12  25*  -6
14 179  199
16  48  -58

0,1,L
1   93   80
2  480  546
3   93   82
4  436 -412
5  142 -148
6  140 -133
7  508 -521
8   20*  10
9  149  145
10 211  205
11 182  187
12  25*  -7
13  24* -30
14  81  -85
15  20*  -1
16  44  -52
17  30   40

0,2,L
0  377 -375
1  106  -89
2  265 -273
3  441 -493
4  138 -120
5  254  279
6  354  317
7  104   95
8  220  231
9   64   62
10 108 -110
11 418  418
12  77  -58
13  97   96
14  22*   7
15 145 -153
16  16*   5
17 127 -134

0,3,L
2  293 -274
2  371  368
3   86   80
4  291 -340
5  177  173
6  276 -300
7  325  340
8  196  185
9   23*   8
10 151  128
11 111 -103
12 152 -156
13  91  -89
14  37  -32
15  64  -60
16  31   33
17   4*  29

0,4,L
0  711 -772
1   79  -78
2  249 -255
3  189  208
4   93   81
5  323  323
6   19* -35
7  174 -153
8  104   96
9  277 -297
10 186  189
11  73  -71
12  24*  -4
13  59   53
14 127 -124
15  17*   0
16  12*  -1

0,5,L
1  240  241
2  443  441
3  189 -203
4  202  198
5   20*   8
6  117 -100
7  171  169
8  168 -156
9   92  -72
10  80  -72
11  87  -74
12  23*  -2
13  77   73
14  88   89
15  15*  29
16  79   95

0,6,L
0   52  -44
1  150  142
2  305  309
3  129  105
4  273  281
5   76  -64
6  259 -261
7   73  -69
8  326 -332
9  115 -108
10  25*  -8
11  62  -50
12  99   85
13  19* -21
14  16*  14
15  27   42

0,7,L
1  119  107
2  246 -273
3   47  -38
4   37   12
5  125 -116
6  192  173
7   25*  27
8   57   52
9  164 -152
10  24*  19
11  54  -41
12  50   57
13 142  134
14  50  -63

0,8,L
0   51  -45
1   51  -45
2   49   46
3  136 -116
4   50   45
5  241 -227
6   25*  -9
7  143  127
8   24*  10
9  260  286
10  21*   0
11  19*  -3
12  16*  -6
13  23  -33

0,9,L
1  114 -100
2  222 -230
3   25*  -3
4   40   36
5   50   42
6   34   34
7   23*  -7
8   34  -27
9   73   72
10 184  -25
11  15*  -1
12  50   59

0,10,L
0   24* -18
1   88   78
2  182 -170
3  114   98
4   66  -45
5   22*  -6
6  170  153
7   20* -12
8  118  109
9   16*   5
10  13*  -8
11  53  -47

0,11,L
1   76  -71
2   21*  15
3   76   70
4   20*  -3
5   66   57
6   17*  23
7   42  -45
8   51  -50
9   42   42

0,12,L
0  147  164
1   16* -14
2   44   44
3   15* -18
4   92  -95
5   39   42
6   46  -36

0,13,L
1   73   55
2   77   64

1,0,L
 1  225  227
 2  285 -262
-2  478  449
 4  294  261
-4  725  749
 6  336 -332
-6  232 -228
 8  127  113
-8  486 -479
10  487  559
-10  87  -32
12  267 -266
-12 173 -180
14  112 -109
-14 131  126

1,1,L
 0  111  -96
 1  352  324
-1  186  202
 2   86  -67
-2  261 -280
 3  564 -533
-3  482 -479
 4  334  328
-4   39   30
 5  142 -131
-5  221  216
 6  416  405
-6   45   36
 7   98  105
-7  298  278
 8  188 -176
 9  105   94
-9  105  -93
10   29* -50
-10  90   67
11   72  -69
-11 233 -235
12   29* -32
-12 220 -210
13   27*  24
-13  85   82
14   77  -80
-14  53  -55
15   21* -24
-15 108  124
16   34  -47
-16  22*   6
-17  17*   4

1,2,L
 0  409 -434
 1  282 -290
-1 1601 -1601
 2  346  353
-2  428 -466
 3   53   49
-3  470 -501
 4  375  366
-4   72   50
 5  194  181
-5  438  476
 6   23*   1
-6   20* -37
 7  362  346
-7  208  202
 8  256 -257
-8  186  181
 9  241  265
-9   26* -29
10   57  -50
-10 127  114
11   45  -37
-11  29*  15
12   29*  15
-12  29*  16
13  190 -183
-13  29*  20
14   25*   1
-14  27* -28
15   34   47
-15 134 -136
16   64   64
-16  22*  -9
-17  16*   6

1,3,L
 0  375 -372
 1  195  188
-1  229 -225
 2  380 -402
-2  463  545
 3  351  345
-3  114 -121
 4  195  195
-4  134  127
 5   76   63
-5  171 -158
 6  430  434
-6   64  -68
 7   68  -77
-7   52   41
 8  162 -151
-8  193  191
 9  193 -188
-9  172  165
10  163 -155
-10  73  -72
11   29* -14
-11  82   76
12  106  -98
-12  98  -83
13   55   58
-13  29* -10
14   43  -42
-14  27*  39
15   91  106
-15 108 -107
16   53  -57
-16  72   63
-17  53  -63

1,4,L
 0  219  213
 1  373  383
-1   42   38
 2   77  -61
-2  111 -110
 3  240  227
-3  321  325
 4  177 -178
-4  439 -443
 5  393 -373
-5  170  164
 6   26*  22
-6   24* -24
 7  196 -187
-7  178 -171
 8  197  176
 9   29* -21
-9  369 -387
10  222 -229
-10 174  173
11   29* -22
-11  64   63
12  199  183
13   42   33
-13 201  180
14   69   75
-14  26*  47
15   91   79
-15  23* -13
-16 101  -94
-17   7*  -7

1,5,L
0  185  213

1,6,L
 0  142  137
 1  159  152
-1  212  205
 2  241 -242
-2  229  210
 3   26*  12
-3   53   48
 4  298 -290
-4   62   54
 5   27*  10
-5   26*  -2
 6  173  168
-6  240  232
 7  163 -162
-7   63  -53
 8  241  247
-8  114 -104
 9   97  -95
-9   84   79
10   56  -47
-10 345 -353
11   26*  43
-11  29* -32
12   24*   6
-12 106  -98
13   20*  24
-13 148 -145
14   28   35
-14  60   63
-15  17*  28

1,7,L
 0   52  -50
 1  247 -241
-1   90  -84
 2   39   36
-2  236 -228
 3   28* -11
-3  329  344
 4   28*  -2
-4   60   62
 5   29*  -6
-5   79   76
 6   29*  14
-6  111  100
 7   29*  -3
-7  109 -110
 8  171  161
-8  129 -121
 9   28*  19
-9   67  -70
10   28*  -5
-10  28*  -5
11   78   83
-11  27*  -7
12  112 -128
-12  25*  22
13   37  -49
-13  22*  -6
14   18*  -3
-14  18*  -3
15    9*  18

1,8,L
 0   69   68
 1  345 -390
-1   28* -24
 2   47   45
-2   29*  30
 3  121 -113
-3   80  -71
 4   53  -55
 5   28*  -3
 6   37   24
-6   36  -36
 7  109  102
-7   53   49
 8   11* -15
 9   28*  19
-9   67  -70

1,9,L
 0   29* -40
-10 184  192
 1   73   69
 2  127  125
-2  134 -131
 3   69  -51
-3  115 -115
 4   29*   1
 5   28* -18
-5   52  -53
-6  164  152
 7   42  -40
-7   28*  31
 8  130  149
-8   26*   3
 9   48  -51
-9   79   74
10   19*  32
-10  23*  84
11   55  -33
-11  46   46
-12  16*  36
-13   6*  29

1,10,L
 0   91  -89
 1   52   49
-1  147  152
 2   64   62
-2  111 -106
 3   39  -43
-3   28*  -1
 4  175  175
-4   27*  -2
-5  136 -136
 6   68  -69
-6   26* -28
 7   54  -56
-7   29* -36
 8  100 -108
-8   23*  30
 9   38  -36
-9   38  -36
10   11*   3
-10 140  143
-11  13* -13

1,11,L
 0   84   82
 1   90   84
-1   25*   1
 2   68   64
 3   24* -16
-3  148 -145
 4   24*  40
 5   47   44
-5   23*  46
 6   57  -65
-6   47  -47
 7   51   57
-7   82   93
 8   11* -44
-8  207 -219
-9   13* -16

1,12,L
 0   56  -59
 1   60   62
-1   19*  28
 2   18* -13
-2   49   48
 3   17* -10
-3   19   42
 4   15*   0
-4  126   96
 5   12* -50
-5   15*  31
-6   13* -25
-7    6* -47

2,0,L
 1  194 -192
 2  357 -331
-2  675 -675
 4   39   42
-4  399 -366
 6  553  536
-6  385  351
 8  417  404
-8  347  154
-10 182 -179
-12  51  -40
-14  21*  22
-16  94  -90

2,1,L
 0  267  282
 1  317 -294
-1  374 -441
 2  457  428
-2  257 -282
 3  336  315
-3  247  283
 4   47   42
-4  158 -145
 5  380  337
-5  229  206
 6  170 -158
-6   93  -85
 7  169 -156
-7  131 -122
 8   21*  30
-8   58  -56
 9   21* -24
-9  134  130

2,2,L
 0  274  258
 1  242 -224
-1   10*   5
 2  140  138
-2  176 -165
 3   64  -65
-3  259 -277
 4  109 -121
-4  105  102
 5  328  316
-5  606 -636
 6   19* -27
-6   23*  85
 7   44  -45
-7   16*   1
 8  140 -142
-8   43   29
 9  349 -339
-9  428  420
10   57  -51
-10 164 -162
11   21* -20
-11 232  221
12   57   47
-12  22* -32
13   76   90
-13  80   85
14   67   93
-14 113  122
15    7*  66
-15  18*  38
16   15*   0
-16 168  180
17    7*   0
-17  77  -74

2,3,L
 0  303 -281
 1  139  123
-1  193  201
 2  365  343
-2   82 -104
 3  210 -192
-3   16* -90
 4   60  -54
-4  326  319
 5  243 -240
-5   15* -34
 6   52   41
-6   85   88
 7  115 -116
-7  148 -151
 8  170  145
-8  207 -219
 9   13* -16
10   38  -37
-10 104 -106
11  162  163
-11  52   56
12  130 -135
-12 230  229
13  123  132
-13  68   82
14   36  -34
-14  36  -34
15   17*  49
-15  99  -93
-17  10* -22

2,4,L
 0  173  170
 1  317 -304
-1  280  256
 2   16*  25
-2  486  523
 3  330 -315
-3  512  556
 4   93  -92
-4   44  -37
 5   63  -54
-5  135  152
 6  357 -364
-6  202 -211
 7  195  210
-7   35   28
 8  116 -106
-8  206 -201
 9   66  -73
-9  108 -107
10  161   63
-10 140  143
11   58   55
-11 262 -265
12   51   56
-12 155 -153
13   15* 107
-13  66  -64
14   25  -31
-14  23*  11
15   42   43
-15  13*  34
16   13*  34
-16  11*   8
17   71   73

2,5,L
 0   52  -55
 1  104  106
-1  280  278
 2   83  -93
-2   17*  30

2,6,L
 0  472 -461
 1  129  120
-1  103  107
 2   28  -24
-2  137 -132
 3   31  -28
-3   19*  -6
 4  325  321
-4   20* -37
 5   37  -41
-5  149  142
 6  102   95
-6   21*  -4
 7   22* -17
-7   95   85
 8   64   60
-8  112  117
 9  103  105
-9   57  -63
10   48   56
-10 168  180
11   17*   0
-11  47  -44
12   42  -40
-12  98 -107
13    9* -10
-13  49  -49
-14  21*  31
-15  12*  -8

2,7,L
 0   21*  29
 1   83   91
-1   76  -75
 2  156 -148
-2   44   44
 3   49  -40
-3  178 -183
 4  110  103
-4  128 -115
 5   54   53
-5   21*  16
 6   22*  16
-6   56  -67
 7  189  187
-7  224  214
 8  128 -135
-8   52   56
 9   19* -10
-9   66   64
10   23*  -5
-10 359  356
11   56  -54
-11  25*  35
12   13* -15
-12  86  -90
13   22* -18
-13  22*  18
14   40   47
-14   4* -25

2,8,L
 0   22*  24
 1  140  141
-1  241 -233
 2   44  -42
-2   44   66
 3  224  215
-3  237 -240
 4   44  -37
-4   42   37
 5   72  -72
-5   22*  38
 6   41   32
-6  128 -129
 7   55  -56
-7   21*  17
 8   18*   7
-8   21* -38
 9   16*  10
-9   20*  16
10   44   43
-10 120 -121
11   25* -15
-11  82  -77
12  161  165
-12  25* -15
13  168  157
-13 168  157

2,9,L
 0   68   61
 1   21* -13
-1   66   71
 2   21*  11
-2   40   33
 3   50  -42
-3  134  136
 4   88   88
-4  174 -188

2,10,L
 0  176  177
 1   37   34
-1   50   47
 2   19*  12
-2   60   60

2,11,L
 0   27   23
 1   26  -36
-1   71  -70
 2   22* -17
-2   23   27
 3  110  108
 4   13* -28
-4   49   49
 5   44   48
-5   35   36
 6    8*  33
-6   41   49
 7   98  104
-7   72   68
-8   58   56
-12  48   56

2,12,L
 0   11*  -4
 1   52  -52
-1   45   41
 2  140 -136
 3  103 -106
-3  134  130
 4   58  -51
-4  113 -120
 5   20* -24
 6   46   78
-6   78   74
 7  102   97
-7   85 -107
 8   59  -58
-8  113 -118
 9   20* -29
-9   54  -57
10   12* -19
-10  22* -19
11   98  107
-11  24* -27
12   14* -36
-12  14*  14
13   56   43

3,0,L
 1  356 -386
 2   24*   9
-2   92  -93
 3  205  204
-3   63  -59
 4  155  155
-4  141 -149
 5  206  218
-5   59  -58
 6   88  -93

3,1,L
 0  229  255
 1  242  276
-1   94  111
 2  220 -225
-2  385 -373
 3   96  -91
-3  144 -180
 4  212 -212
-4  168 -163
 5  125  125
-5   71  -67
 6  209 -206
-6  123  123
 7  113 -112
-7  131 -123
 8  172  155
-8  117 -113
 9   17* -27
-9   15* -23
10   38  -43
-10  15*  38
11  150 -139
-11  16*  11

3,2,L
 0   75  -72
 1  272  278
-1  140  145
 2   40   33
-2   30   27
 3   50  -42
-3  150  153
 4   88   88
-4  174 -188

3,3,L
 0   17*  27
 1  167 -174
-1   95  -97
 2  163 -157
-2  291  298
 3  147 -143
-3   74   80
 4   34  -56
-4  141 -149
 5   24* -15
-5  206  218
 6  221  217
-6  200 -203
 7   45   41
-7   21*  16
 8   59   54
-8  113 -118
 9  136  138
-9   24* -27
10   84  -78
-10  84  -78
11   35   36
-11  72   68
12   98  104
-12  14*  14
13   54  -57
-13  54  -57
-14   8*  34

3,4,L
 0  185  173
 1   45   41
-1  159 -383
 2  140 -136
-2  221  223
 3  153  148
-3   58  -61
 4  222 -215
-4  106  105
 5   24*   9
-5   92  -93
 6   25*  26
-6  246 -252
 7  157  150
-7   59   56
 8  170  168
-8   41  -37
 9   65  -67
-9   25*   6
10   29* -28

3,5,L
 0  229  255
 1  171 -166
-1   22* -13
 2   23*   4
-2   53  -45
 3  204  205
-3  135  133
 4  162 -153
-4   77   77
 5   96  -94
-5   24* -24
 6  131 -123
-6  131 -123
 7  155 -140
-7  131 -123

3,6,L
 0  187  130
 1   82  -76
-1   42   37
 2  216  222
-2  237 -292
 3   50  -42
-3  150  153

3,7,L
 0   44  -40
 1   65   62
-1   36  -29
 2   25* -18
-2   90  -85
 3  205  204
-3   63  -59
 4   88  -88
-4  155  155
 5   83   84
-5  102 -106
 6  137 -124
-6  153  145
 7  140 -147
-7   59  -58
 8   59   54
-8  113 -118
 9  136  138
-9   24* -27
10   11*  53
-10  84  -78
11    7* 138
-11  72   68
12   19*  32
-12  19*  32
13   18* -36
-13  18* -36
-14  85  -36
-15  13* -28
-16   7*  -8

3,8,L
 0   25*  11
 1   43  -42
-1  194  192
 2   24*  -9
-2   63  -62
 3  103 -106
-3  134  130
 4   20*  -4
-4  113 -120
 5   20* -24
-5   35   31
 6   46   78
-6   24*  18

3,9,L
 0   23*  11
 1   53  -50
-1   42  -34
 2  214  211
-2  189 -206
 3  103  102
-3  170 -176
 4   62  -51
-4  113  125
 5  159  150
-5   17*  -5
 6  116 -115
-6  133 -135
 7   18*  12
-7   39  -32
 8   56   54
-8   93  104
 9   39  -80
-9   81   84
10   69   73
-10  90  -83
11   20*  15
-11  58  -59

3,10,L
 0   85  -85
 1   18* -26
-1   19*  19
 2   17* -23
-2  106  102
 3   16* -20
-3   60  -56
 4   14*   9
-4  149  151
 5   53   55
-5   15*  11
 6   20* -37
-6   25* -42
 7   18*  -4
-7   53   62
 8   11* 110
-8   19*  19
 9   20* -42
-9   83  -90
10   12* -31
-10  20*  15
-11  58  -59

3,11,L
 0   48  -52
 1   48   49
-1   30   27
 2   10*  33
-2   41   49
 3   44  -43
-3   35  -37
 4   13* -27
-4    9*  26
 5    9*  26
-5    6*   6

4,0,L
 1  236  257
 2   72  -65
-2  133  134
 4  435 -453
-4   10* -27
 6   20* -34
-6   59  -49
 7   23*  20
-7   25* -27
 8   58  -56
10   13* -17
-10 189 -179
-12 181  174
-14 218  202
-16   9*  11

4,1,L
 0  139 -131
 1  113  -93
-1   20   27
 2   45  -41
-2   18  -17
 3   18* -18
-3  145  149
 4   85   76
 5   20* -20
-5   85  -77
 6   88  -77
-6  147  149
 7   81  -85
-7  186 -199
 8  196  184
-8   51  -47
 9   47   42
-9   65   62
10   93   85
-10 145  149
11    7* 138
-11  63  -73
12  115 -137
-12  85   90
13   76   88
-13  76   88
-14  10*  -8

4,2,L
 0  103  112
 1  196 -194
-1  226  248
 2   55   47
-2  166 -166
 3  207 -205
-3  226  233
 4   20*  -4
-4  113 -120
 5   20* -24
-5   35   31
 6   46   78
-6   93   93
 7  104  -95
-7   41  -34
 8   39   37
-8   22* -17
 9   20* -29
-9   20* -29
10   12* -19
-10  22* -17
11   98  107
-11  72   68
12   98  104
-12  14*  14
-13  56   43

4,3,L
 0  121 -118
 1   31   30
-1   42  -34
 2  214  211
-2  189 -206
 3  103  102
-3  170 -176
 4   62  -51
-4  113  125
 5  159  150
-5   17*  -5
 6  116 -115
-6  133 -135
 7   18*  12
-7   39  -32
 8   93  104
-8   93  104
 9  102  -85
-9   88  -96
10   10*  19
-10  19*  -5
-11  58  -59

4,4,L
 0  218 -215
 1   97   90
-1   52   51
 2    4*  53
-2   18*  -5
 3   14*  -5
-3  152 -162
 4  229  213
-4  110  110
 5  103  100
-5  285 -288
 6   81   78
-6   19*  14
 7    9*   1
-7   20* -25
 8   35  -37
-8   19*  13
 9  137  151
10    6* -12
-10  34   30

4,5,L
 0  124  121
 1   20*   2
-1   20*   9
 2  196  198
-2   19*  -1
 3  137 -124
-3   96  -94
 4   40   42
-4   85  -86
 5   94  -90
-5   70   72
 6  102 -100
-6  131 -137
 7  109  120
-7  145  149
 8   61  -60
-8   52  -53
 9   10*   6
-9  108 -113
-10  81   87
-11  63  -73
-12  85   90
-13  76   88
-14  10*  -8

4,6,L
 0   62  -65
 1   54   53
-1   20* -13
 2   20*   1
-2  137  142
 3   41   41
-3  113 -114
 4   51   46
 5   17* -23
-5   71  -68
 6  163 -163
-6  101 -104
 7   13*  17
-7   40  -38
 8  108 -106
-8   78  -79
-9   85  -90
-10  62   61
-11  54   65
-12  13*  15
-13  10*  32

4,7,L
 0   78  -73
 1  102   97
 2  157 -159
-2   60   60
 3   47   47
-3   88  -93
 4   63   61
-4   28   23
 5   98 -107
-5   48   48
 6   96   93
-6   15*  38
 7    9* -18
-7   18* -24
 8   93  104
-9  102  -85
-10  15*  11
-11  22  -31
-12  56  -65

4,8,L
 0   17* -27
 1   17* -17
-1   91  -92
 2   52  -54
-2   18*  17
 3   41  -39
-3  107  113
 4   18*  -1
 5   61  -59
-5  257  257
 6    4*  10
-6   16*  -1
 7    9* -18
-7   16*  -1
 8   93  104
-9   88  -96
10   10*  19
-11  58  -59

4,9,L
 0   14*  32
 1   20   22
-1   58  -59
 2  146 -155
-2   84   87
 3  107  107
-3   14* -22
 4    4* -53
-4   14*   9
 5   14*  -5
-5   52 -162
 6  229  213
-7   11* -16
-8   12* -10
-9    4*  -2

4,10,L
 0    6* -25
 1    8* -11
-2   60  -63
 3    9   13
-4   63  -75
-5    6*   6
```

with no uncertainty. Moreover, several coincidences indicated the sign, as + or −, of the two letters: the process was therefore extended to all the 122 observed reflexions, all of which were given an appropriate sign.

Fourier syntheses confirmed the Patterson hypothesis, with an R index of 22% and, at the end of the refinement, only three of the weakest reflexions had their sign changed. Analysis and refinement of the (010) pro-

Table 3. *Principal axes of the vibration ellipsoids*

Root-mean-square displacements U_i and angles θ with the crystallographic axes.

	Axis (i)	U_i	θ_{ia}	θ_{ib}	θ_{ic}
S(1)	1	0·1658 Å	56·2	68·6	41·6
	2	0·2023	54·9	61·2	131·4
	3	0·2396	126·9	37·1	86·7
S(2)	1	0·1575	39·4	57·8	69·8
	2	0·2094	71·7	81·1	159·6
	3	0·2274	123·6	33·7	92·8
N(1)	1	0·1655	32·9	57·6	95·1
	2	0·2045	99·9	83·8	168·3
	3	0·2144	121·0	33·1	79·5
N(2)	1	0·1588	12·9	79·0	83·3
	2	0·1771	80·5	104·9	162·2
	3	0·1911	98·7	18·7	106·4
N(3)	1	0·1697	128·6	125·4	58·3
	2	0·1957	119·6	103·2	147·0
	3	0·2940	127·3	38·5	81·8
C(1)	1	0·1713	91·0	114·0	23·1
	2	0·1922	152·9	114·4	101·2
	3	0·2386	117·1	34·7	70·0
C(2)	1	0·1903	42·7	81·3	48·6
	2	0·1989	59·4	58·7	133·3
	3	0·2731	116·6	32·8	72·3
C(3)	1	0·1477	13·6	87·7	76·6
	2	0·1755	78·8	134·2	133·6
	3	0·2059	97·7	135·7	46·7
C(4)	1	0·1582	166·5	84·4	77·8
	2	0·1888	102·9	129·6	137·5
	3	0·2030	86·4	139·8	50·0

Table 4. *Intramolecular distances and angles with e.s.d.'s (in parentheses)*

The calculated double bond characters are reported in square brackets.

S(1)–C(3)	1·674 (4) Å	[1·40]	S(1)–C(3)–N(1)	123·8 (3)°
S(2)–C(4)	1·687 (4)	[1·35]	S(1)–C(3)–N(2)	128·9 (3)
N(1)–C(3)	1·306 (6)	[1·48]	S(2)–C(4)–N(3)	122·2 (3)
N(2)–C(3)	1·409 (5)	[1·12]	S(2)–C(4)–N(2)	118·4 (3)
N(1)–C(2)	1·464 (5)		N(3)–C(4)–N(2)	119·4 (4)
N(2)–C(1)	1·474 (5)		N(2)–C(3)–N(1)	107·3 (3)
N(3)–C(4)	1·311 (5)	[1·46]	C(4)–N(2)–C(3)	128·5 (3)
N(2)–C(4)	1·379 (6)	[1·19]	C(4)–N(2)–C(1)	120·8 (3)
C(1)–C(2)	1·507 (7)		C(3)–N(2)–C(1)	110·6 (3)
			N(2)–C(1)–C(2)	104·1 (3)
			C(1)–C(2)–N(1)	102·6 (3)
			C(2)–N(1)–C(3)	115·2 (4)

Values involving hydrogen atoms

H(1)–N(1)	1·00 (2) Å	H(1)–N(1)–C(3)	122 (1)°
H(2)–C(2)	1·08 (2)	H(1)–N(1)–C(2)	122 (1)
H(3)–C(2)	1·10 (2)	H(2)–C(2)–H(3)	115 (1)
H(4)–C(1)	1·05 (2)	H(2)–C(2)–N(1)	109 (1)
H(5)–C(1)	1·08 (2)	H(2)–C(2)–C(1)	109 (1)
H(6)–N(3)	1·04 (2)	H(3)–C(2)–N(1)	111 (1)
H(7)–N(3)	1·00 (2)	H(3)–C(2)–C(1)	108 (1)
		H(4)–C(1)–H(5)	113 (1)
		H(4)–C(1)–C(2)	111 (1)

jection were then straightforward (Valle *et al.*, 1963; Mammi *et al.*, 1965).

The three-dimensional refinement was carried out later, on an IBM 7094/7040 DCS computer, using the *ORFLS* full-matrix least-squares program of Busing, Martin & Levy (1962), as adapted in the *X-ray* 63 *Program System* (1965). The weighting scheme of Mills & Rollett (1961), $w = 1/(1 + [(k|F_o| - b)/a]^2)$, with $a = 8|F_{min}| = 24$, $b = 5|F_{min}| = 15$ and $k = 0.7$, was applied. The R index decreased from 14 to 10.5% in two cycles, with isotropic thermal parameters, and was improved to 5.9% in three further cycles, allowing for anisotropic vibrations. All the final shifts in atomic parameters were less than one tenth the estimated standard deviations.

During refinement, which was carried out with the observed reflexions only, the H atom coordinates calculated from a model were kept constant. Almost the same coordinates were then obtained by a difference synthesis, that showed peaks in the expected H atom positions, of heights 0.45 to 0.60 e.$Å^{-3}$, on maximum background fluctuations of ± 0.20 e.$Å^{-3}$. A final least-squares cycle was calculated to refine these H atom coordinates only, using the reflexions up to sin $\theta = 0.5$ and unitary weighting scheme. The final R index for all the observed reflexions was 5.7%.

The atomic coordinates and vibrational parameters, with their estimated standard deviations, are reported in Table 1, the observed and calculated structure factors in Table 2, and the parameters of the principal axes of the vibrational ellipsoids in Table 3. The scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962).

Fig. 2. View of the structure along the *a* axis. The electron density at the H atom positions is also reported, as found on sections of a difference map at the *x* levels of each H atom. Contours are at intervals of 0.1 e.$Å^{-3}$, starting from 0.2 e.$Å^{-3}$. (For molecule numbering, see Table 6).

Molecular structure

Bond lengths and angles in the molecule are listed in Table 4 and shown in Fig. 1. The estimated standard deviations have been calculated according to Ahmed & Cruickshank (1953) and Darlow (1960).

Table 5. *Distances of atoms from the planes*

(a) Mean molecular plane, π_1,

$$-0.1842X + 0.1815Y + 0.0392Z = 1$$

(b) Mean ring plane, π_2,

$$-0.1781X + 0.1822Y + 0.0395Z = 1$$

Equations refer to the orthogonal axes X, Y, Z (Å) coincident with $\mathbf{a}, \mathbf{b}, \mathbf{c}^*$. Distances of centres of symmetry and of atoms not included in calculations are given in parentheses.

	(a)	(b)
S(1)	+0.041 Å	(+0.048)
S(2)	+0.017	(−0.067)
N(1)	−0.047	−0.020
N(2)	+0.029	+0.004
N(3)	−0.048	(−0.110)
C(1)	+0.002	−0.015
C(2)	+0.001	+0.020
C(3)	+0.007	+0.010
C(4)	−0.004	(−0.059)
$\bar{1}(-\frac{1}{2}, 0, \frac{1}{2})$	(+0.054)	(−0.056)
$\bar{1}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	(+0.029)	(+0.085)

Fig. 3. Perspective view of the structure, showing the packing of chains of hydrogen-bonded molecules. (For molecule numbering, see Table 6.)

The molecule is planar, on the whole, but a detailed analysis indicates (Table 5) that some of the deviations from the best molecular plane are very significant (Δ/σ up to 10 and more). A more strict planarity is shown by the five atoms of the imidazolidine ring; the S(1) and C(4) atoms are significantly out of this plane, with the C(3)–S(1) and N(2)–C(4) bonds bent on opposite sides by 1·3 and 2·6° respectively. The thio-carbamoyl group S(2)C(4)N(3) is tilted from the ring plane 2·8°.

The molecular parameters in the ethylenethiourea moiety compare with those reported by Wheatley (1953) for the unsubstituted ethylenethiourea. The main differences are observed in the C=S (1·708 Å) and C–N (1·322 Å) bond lengths, and appear to be due to the effect of the bonded thiocarbamoyl group on the thiourea resonance system. The same considerations apply to trimethylenethiourea (Dias & Truter, 1964) and to tetramethylenethiourea (Mammi, Del Pra & Di Bello, 1967), in which, however, the ring valence angles are obviously much larger. In these compounds, the

bending of the C–S bond out of the $\underset{\diagdown}{\overset{N-C}{\diagup}} C \underset{N-C}{\diagup}$ plane
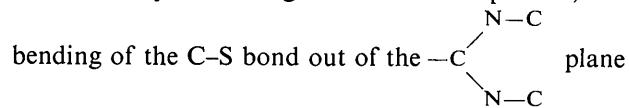
increases with the ring size, being 1, 3·8 and 5°, for the five-, six- and seven-membered ring molecules respectively. (The 3·8° value has been calculated using the parameters reported by Dias & Truter, 1964.) The unsubstituted thiourea is fairly planar (Kunchur & Truter, 1958). The rather small value of the C(1)–C(2) bond length in the ring is also worth noting. It is comparable with those found in trimethylenethiourea (1·518 Å) and tetramethylenethiourea (1·50–1·51 Å).

The TIO molecule may also be regarded as the 1,3-ethylene derivative of dithiobiuret,

$$H_2N–CS–NH–CS–NH_2\ ;$$

its structure and resonance are therefore quite similar to those found in biuret (Hughes, Yakel & Freeman, 1961) which has a *trans* conformation and a strong internal N–H$\cdots$O hydrogen bond (Kogon, 1957; Kumler & Lee, 1960). In the TIO molecule, the intra-molecular N(3)---S(1) distance is 2·998 Å, with the

H(6) atom at 2·1 Å from S(1) and with an N–H$\cdots$S angle of 143° (for other angular values, see Fig. 1). The H(6) atom thus forms a nearly planar six-membered ring with the S(1), C(3), N(2), C(4) and N(3) atoms, deviations from planarity being in the range 0·01–0·02 Å. In this ring, besides the S$\cdots$H positive interaction, a repulsion between S(1) and N(3) is likely to occur, as suggested by the large N(2) and C(3) valence angles.

One may think of the dithiobiuret moiety as made up by two thiourea molecules, sharing one nitrogen atom, N(2), which is itself in sp^2 hybridization, coplanar (0·027 Å) with the three bonded atoms, C(1), C(3) and C(4). Each of the two thiourea fragments, N–CS–N, is planar (maximum deviation 0·0003 Å) and they are inclined to each other by 4·2° (5°33' in biuret). Three resonance structures can be written for each thiourea fragment:
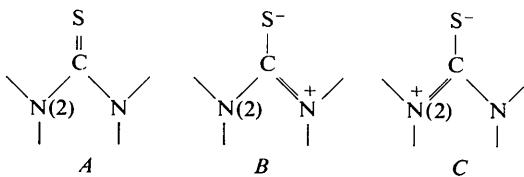
Their contributions may be estimated to about 40, 48 and 12% respectively, for the ring thiourea fragment N(1)–C(3)S(1)–N(2), and 35, 46 and 19% for the outer one, N(3)–C(4)S(2)–N(2). These amounts correspond to the double bond characters of Table 4, which have been computed by Pauling's (1948) equation using the values C–N, 1·475; C=N, 1·265; C–S, 1·81 and C=S, 1·59 Å, corrected by ±0·03 Å for negatively or positively charged atoms, according to Hahn (1957). The contribution of the resonance structure C, with a positive charge on the central N(2) atom, is therefore greatly decreased in both the thiourea groups with respect to symmetrical thioureas (where the values are about 20, 40 and 40%, respectively), and the decrease is mainly in favour of the unpolar structure A. The lengthening of the central bonds N(2)–C(3) and N(2)–C(4) corresponds quantitatively to the shortening of the C–S bonds, as indicated by the value of 4·00 for
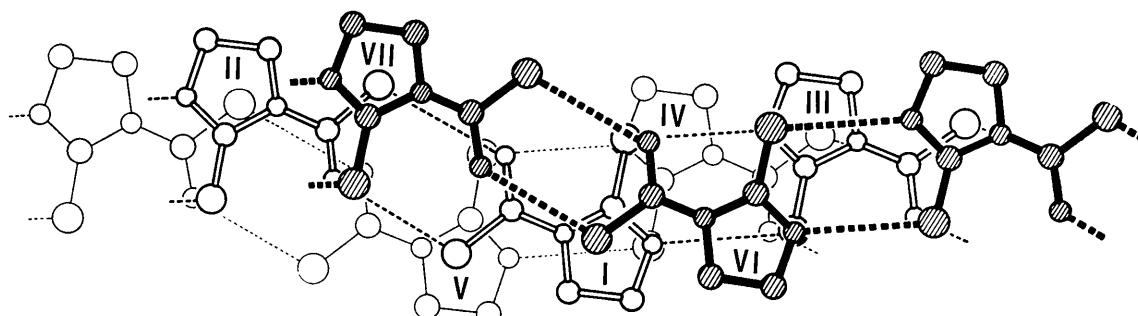
Fig. 4. Projection of three consecutive chains on to the molecular plane.

the total bond order of both C(3) and C(4). The formal charges on the atoms would be: S(1), -0.60; S(2), -0.65; N(1), $+0.48$; N(2), $+0.31$; N(3), $+0.46$; C(3), 0.00; C(4), 0.00 electrons. The two thiourea fragments, each with its three resonance structures A, B and C, combine in the dithiobiuret system to give the nine following resonance structures, whose estimated contributions are indicated in parentheses. The last structure has been excluded from consideration, as being impossible.

not exist or that there is no real evidence for its presence (Wheatley, 1953; Kunchur & Truter, 1958; Pimentel & McClellan, 1960). It must be pointed out, however, that there is some uncertainty in the reported values of the van der Waals radii. For instance, a radius in the range $1.6-1.7$ Å has been suggested for nitrogen by a detailed analysis of hydrogen bond distances (Pimentel & McClellan, 1960). Similarly, sulphur radii as high as 2.0 Å and more have been used by Kitaigorodskii (1961a) for crystal packing considera-

$$
\begin{array}{ccc}
\overset{\displaystyle NH_2}{\underset{\displaystyle |}{}} \quad \overset{\displaystyle S}{\underset{\displaystyle \|}{}} & \overset{\displaystyle {}^+NH_2}{\underset{\displaystyle \|}{}} \quad \overset{\displaystyle S}{\underset{\displaystyle \|}{}} & \overset{\displaystyle NH_2}{\underset{\displaystyle |\;+}{}} \quad \overset{\displaystyle S}{\underset{\displaystyle \|}{}} \\
S{=}C{-}N{-}C{-}NH \;(13\%) & {}^-S{-}C{-}N{-}C{-}NH \;(17\%) & {}^-S{-}C{=}N{-}C{-}NH \;(10\%)
\end{array}
$$

$$
\begin{array}{ccc}
\overset{\displaystyle NH_2}{\underset{\displaystyle |}{}} \quad \overset{\displaystyle S^-}{\underset{\displaystyle |\;+}{}} & \overset{\displaystyle {}^+NH_2}{\underset{\displaystyle \|}{}} \quad \overset{\displaystyle S^-}{\underset{\displaystyle |\;+}{}} & \overset{\displaystyle NH_2}{\underset{\displaystyle |\;+}{}} \quad \overset{\displaystyle S^-}{\underset{\displaystyle |\;+}{}} \\
S{=}C{-}N{-}C{=}NH \;(17\%) & {}^-S{-}C{-}N{-}C{=}NH \;(22\%) & {}^-S{-}C{=}N{-}C{=}NH \;(10\%)
\end{array}
$$

$$
\begin{array}{ccc}
\overset{\displaystyle NH_2}{\underset{\displaystyle |\;+}{}} \quad \overset{\displaystyle S^-}{\underset{\displaystyle |}{}} & \overset{\displaystyle {}^+NH_2}{\underset{\displaystyle \|\;+}{}} \quad \overset{\displaystyle S^-}{\underset{\displaystyle |}{}} & \overset{\displaystyle NH_2}{\underset{\displaystyle |\;++}{}} \quad \overset{\displaystyle S^-}{\underset{\displaystyle |}{}} \\
S{=}C{-}N{=}C{-}NH \;(6\%) & {}^-S{-}C{-}N{=}C{-}NH \;(6\%) & {}^-S{-}C{=}N{=}C{-}NH \;(0\%)
\end{array}
$$

The above reasoning, fairly common and useful in organic chemistry (Pauling, 1948; Streitwieser, 1961), gives a qualitative indication of the resonance in the TIO molecule.

Hydrogen bonding

As shown in Figs. 1 and 2, the molecule is hydrogen bonded to the two neighbouring molecules II and III, across centres of symmetry at $-\frac{1}{2},0,\frac{1}{2}$ and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The bridging atoms, H(1) and H(7), whose observed positions agree with the resonance-required sp^2 hybridization of the nitrogen atoms, are almost collinear with N$\cdots$S, the N–H$\cdots$S angles being $165°$ and $172°$ respectively.

Each of the two resulting eight-membered rings, as a whole, is approximately planar, the small deviations from planarity being not unexpected (Jeffrey & Sax, 1963; Robertson, 1964). The displacements of the two centres of symmetry from the planes of the corresponding fairly planar thiourea groups, S(2)N(3)N(2)-C(4) and S(1)N(1)N(2)C(3), are $+0.114$ and $+0.082$ Å respectively; their displacements from the imidazolidine ring plane are -0.056 and $+0.085$ Å. It means that the hydrogen bond formation does not account for the observed molecular deviations from planarity and particularly for the bending and rotation of the thiocarbamoyl group C(4)N(3)S(2) from the ring plane. Other packing considerations are more likely to interfere.

The N$\cdots$S distances of 3.409 and 3.449 observed in the hydrogen bridges are slightly longer than the sum of the van der Waals radii reported by Pauling (1948) (N, 1.50; S, 1.85 Å), as shown in Fig. 1. Such cases (that is, A–H$---B$ with $d_{AB} > r_A + r_B$) have often been considered as indicating that the hydrogen bond does

tions. However, S$\cdots$S contacts of $3.4-3.5$ Å observed in several structures (Marsh, 1955; Van der Helm, Lessor & Merritt, 1962; Walker, Folting & Merritt, 1969; Andreetti, Cavalca, Manfredotti & Musatti, 1969; Valle, Busetti, Mammi & Carazzolo, 1969) suggest the reduction of the value for the sulphur atom to about 1.75 Å (Donohue, 1950; Walker et al., 1969). Such discrepancies might be tentatively accounted for by a non-spherical symmetry of the sulphur radius, with shortening in the valence-bond direction (Kitaigorodskii, 1961b).

Beyond the above speculations, the point is that in the present structure the hydrogen atoms have been located by the refinement, at an H$\cdots$S distance much smaller than the sum of the van der Waals radii (H radius, 1.2 Å); their position thus indicates that they do interact significantly with the sulphur atoms, with a hydrogen bond contraction of $0.6-0.7$ Å (see Fig. 1). Furthermore, it should be noted that almost all the N–H$\cdots$S distances observed in crystal structures with geometry compatible with hydrogen bonding, range from 3.3 to 3.5 Å (Wheatley, 1953; Kunchur & Truter, 1958; Truter, 1960; Dias & Truter, 1964; Braibanti, Manotti Lanfredi, Tiripicchio & Logiudice, 1969; Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1969). Hydrogen bond interaction in the TIO structure is also supported by the formation of infinite chains of nearly coplanar molecules and by the rather high melting point of the crystals ($193°$C). Some differences observed in the infrared spectra of the compound in the crystalline state and in solution (shift of the ν NH and amide II bands to lower and higher frequencies, respectively) (Giormani & Di Bello, 1969a,b) seem to agree with the hydrogen bond formation, though their interpretation is not certain (Mecke & Mecke, 1956; Rao, 1963; Bellamy, 1968).

Molecular packing

The molecular plane is tilted by only $3 \cdot 3°$ from the crystallographic plane ($\bar{1}21$). The corresponding reflexion amplitude is the strongest in the structure (Table 2) and the calculated value was used instead of the observed value, which was unreliable because of uncertainty in its original estimates or because of extinction.

Two equivalent orientations of the molecules occur by symmetry operations, at $88 \cdot 6°$ to each other, as shown in Figs. 2 and 3. Few intermolecular contacts occur between molecules in the two different orientations and all the distances less than 4 Å involve the methylene carbon atoms C(1) and C(2), except two S···S contacts at $3 \cdot 838$ Å (Table 6).

Table 6. *Intermolecular contacts less than* 4.0 Å

	x	y	z
I	x	y	z
II	$-1-x$	$-y$	$1-z$
III	$1-x$	$1-y$	$1-z$
IV	$-x$	$1-y$	$1-z$
V	$-1+x$	y	z
VI	$1+x$	y	z
VII	$-x$	$-y$	$1-z$
VIII	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
IX	$-1+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
X	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
XI	$-1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

Table 6 (*cont.*)

Contacts between chains with different orientations

$C(1^I) \cdots N(3^{VIII})$	$3 \cdot 696$ Å
$C(2^I) \cdots N(3^{VIII})$	$3 \cdot 504$
$S(2^I) \cdots S(1^{IX})$	$3 \cdot 838$
$C(1^I) \cdots S(1^{IX})$	$3 \cdot 942$
$C(2^I) \cdots S(2^X)$	$3 \cdot 701$
$C(1^I) \cdots S(2^{XI})$	$3 \cdot 829$
$C(2^I) \cdots S(2^{XI})$	$3 \cdot 602$

Contacts between parallel chains

$N(1^I) \cdots S(1^{IV})$	$3 \cdot 572$ Å
$C(2^I) \cdots S(1^{IV})$	$3 \cdot 773$
$C(3^I) \cdots S(1^{IV})$	$3 \cdot 752$
$C(3^I) \cdots N(1^{IV})$	$3 \cdot 929$
$C(3^I) \cdots C(3^{IV})$	$3 \cdot 785$
$N(3^I) \cdots S(1^V)$	$3 \cdot 635$
$C(4^I) \cdots S(1^V)$	$3 \cdot 868$
$S(2^I) \cdots N(1^V)$	$3 \cdot 676$
$N(2^I) \cdots N(1^V)$	$3 \cdot 727$
$C(1^I) \cdots N(1^V)$	$3 \cdot 862$
$C(4^I) \cdots N(1^V)$	$3 \cdot 658$
$S(2^I) \cdots N(2^V)$	$3 \cdot 633$
$S(2^I) \cdots C(1^V)$	$3 \cdot 805$
$S(2^I) \cdots C(2^V)$	$3 \cdot 886$
$S(2^I) \cdots C(3^V)$	$3 \cdot 603$
$N(3^I) \cdots C(3^V)$	$3 \cdot 980$
$C(4^I) \cdots C(3^V)$	$3 \cdot 661$
$N(1^I) \cdots S(2^{VI})$	$3 \cdot 675$
$N(2^I) \cdots S(2^{VI})$	$3 \cdot 632$
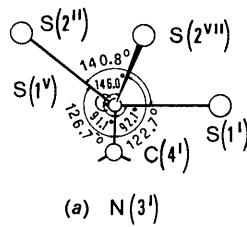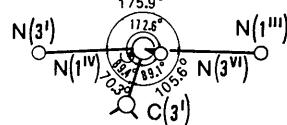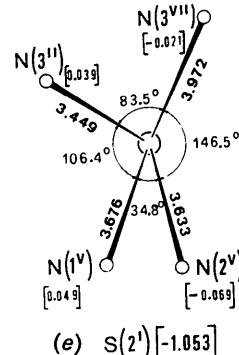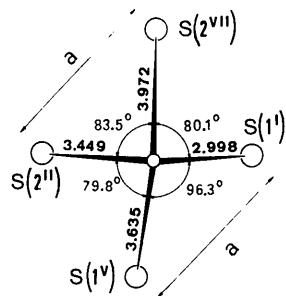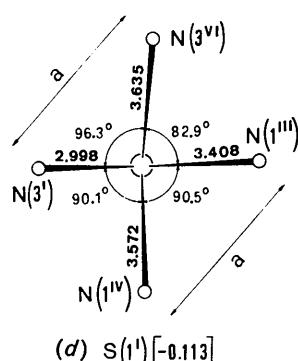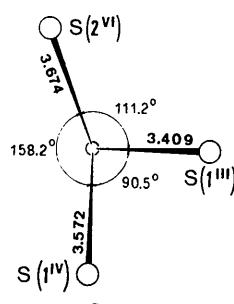
Fig. 5. Environments of the sulphur and nitrogen atoms. In (b) (d) (e) and (f) the signs of the distances from the plane of paper, reported in parentheses, are defined assuming as positive the distance of the carbon atom bonded to the central atom.

Table 6 (cont.)

$C(1^I) \cdots S(2^{VI})$	3·805
$C(2^I) \cdots S(2^{VI})$	3·887
$C(3^I) \cdots S(2^{VI})$	3·601
$N(1^I) \cdots N(2^{VI})$	3·727
$S(1^I) \cdots N(3^{VI})$	3·635
$C(3^I) \cdots N(3^{VI})$	3·979
$N(1^I) \cdots C(1^{VI})$	3·862
$S(1^I) \cdots C(4^{VI})$	3·868
$N(1^I) \cdots C(4^{VI})$	3·656
$C(3^I) \cdots C(4^{VI})$	3·659
$N(3^I) \cdots S(2^{VII})$	3·972
$N(3^I) \cdots N(3^{VII})$	3·391
$C(4^I) \cdots N(3^{VII})$	3·597

More important and much greater in number are the interactions between parallel chains, in the rows generated by the a-axis translation (Fig. 3). The perpendicular distance between the plane of a molecule and the next along the row is 3·506 Å, a value of the order of the normal van der Waals contacts between extended-resonance molecules (Pauling, 1948). Fig. 4 shows the projection of three consecutive chains on to the molecular plane: the hydrogen bridging of a chain is superimposed on the resonance system of the next, thus limitating the possible π–π interactions. Some atomic overlapping does occur, but none of the interatomic distances is less than 3·6 Å, except one, which is the shortest in the structure and is observed between $N(3^I)$ and $N(3^{VII})$ (3·391 Å). This distance is involved in the following overlapping of atoms in consecutive chains, which occur approximately along a line:

$$N(3^{VII}) \xrightarrow{\;3·391\;} \!\!\!\! \leftarrow N(3^I) \xrightarrow{\;3·635\;} S(1^V) \xrightarrow{\;3·572\;} N(1^{XII}) \rightarrow$$
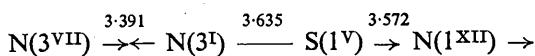
The arrows indicate the direction of the displacement of each atom from its own molecular plane; the last atom, $N(1^{XII})$, at $-1-x$, $1-y$, $1-z$, is displaced toward a free space, in between more distant atoms $S(2)$ and $N(2)$. The three contacts along the line are slightly larger than the corresponding van der Waals distances and almost by the same amount. The attaining of such an 'equilibrium' situation may be responsible for the opposite deviations of the $N(3)$ and $S(1)$ atoms from the molecular plane. These considerations and the observed contacts from $S(2^I)$ to molecule V may also account for the reported rotation (4·2°) of the two thiourea fragments from each other.

A more general survey of the atomic environments shows that each sulphur atom is mainly surrounded, in the crystal packing, by nitrogen atoms, and vice versa (Figs. 4 and 5). Both $S(1)$ and $N(3)$ are surrounded by four atoms in an exactly planar nearly square arrangement, originated by the a-axis repeat. Two of these four contacts are hydrogen bonds. The environments of $N(1)$ and $S(2)$ are less regular as shown in Fig. 5; the two bonds $C(3)$–$N(1)$ and $C(4)$–$S(2)$ are inclined to the plane of surrounding atoms by 48·7 and 45·7° respectively.

The observed arrangement around the sulphur and nitrogen atoms agrees with their different electronegativities (and formal charges) and is likely to be very important in defining the stacking of the chains along the a axis.

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* 6, 385.

ANDREETTI, G. D., CAVALCA, L., MANFREDOTTI, A. & MUSATTI, A. (1969). *Acta Cryst.* B25, 288.

BELLAMY, L. J. (1968). In *Advances in Infrared Group Frequencies*, p. 283. London: Methuen.

BRAIBANTI, A., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & LOGIUDICE, F. (1969). *Acta Cryst.* B25, 93.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *A Fortran Crystallographic Least-Squares Program* ORNL-TM-305, Oak Ridge, Tennessee.

D'ANGELI, F. & BANDEL, A. (1961). *Tetrahedron Letters*, 1, 5.

D'ANGELI, F., BANDEL, A. & GIORMANI, V. (1963). *J. Org. Chem.* 28, 1596.

DARLOW, S. F. (1960). *Acta Cryst.* 13, 683.

DIAS, H. W. & TRUTER, M. R. (1964). *Acta Cryst.* 17, 937.

DOMIANO, P., FAVA GASPARRI, G., NARDELLI, M. & SGARABOTTO, P. (1969). *Acta Cryst.* B25, 343.

DONOHUE, G. (1950). *J. Amer. Chem. Soc.* 72, 2701.

GIORMANI, V. & DI BELLO, C. (1969a). *Ric. Sci.* In the press.

GIORMANI, V. & DI BELLO, C. (1969b). Private communication.

HAHN, T. (1957). *Z. Kristallogr.* 109, 438.

HELM, D. VAN DER, LESSOR, A. E. JR & MERRITT, L. L. JR (1962). *Acta Cryst.* 15, 1227.

HUGHES, E. W., YAKEL, H. L. & FREEMAN, H. C. (1961). *Acta Cryst.* 14, 345.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

JEFFREY, G. A. & SAX, M. (1963). *Acta Cryst.* 16, 430.

KITAIGORODSKII, A. (1961a). In *Organic Chemical Crystallography*, pp. 155, 169. New York: Consultants Bureau.

KITAIGORODSKII, A. (1961b). In *Organic Chemical Crystallography*, p. 141. New York: Consultants Bureau.

KOGON, I. C. (1957). *J. Amer. Chem. Soc.* 79, 2253.

KUMLER, W. D. & LEE, C. M. (1960). *J. Amer. Chem. Soc.* 82, 6305.

KUNCHUR, N. R. & TRUTER, M. R. (1958). *J. Chem. Soc.* p. 2551.

MAMMI, M., D'ANGELI, F. & BEZZI, S. (1965). *J. Chem. Soc.* p. 1521.

MAMMI, M., DEL PRA, A. & DI BELLO, C. (1967). *Ric. Sci.* 37, 766.

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

MECKE, R. JR & MECKE, R. SEN (1956). *Chem. Ber.* 89, 343.

MILLS, O. S. & ROLLETT, J. S. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 117. Oxford: Pergamon Press.

PAULING, L. (1948). *The Nature of the Chemical Bond*, 2nd ed. Ithaca: Cornell Univ. Press.

PIMENTEL, G. C. & McCLELLAN, A. L. (1960). In *The Hydrogen Bond*, pp. 255–295. London: Freeman.

RAO, C. N. R. (1963). In *Chemical Applications of Infrared Spectroscopy*, p. 300. New York: Academic Press.

ROBERTSON, J. H. (1964). *Acta Cryst.* 17, 316.

STREITWIESER, A. (1961). *Molecular Orbital Theory for Organic Chemistry*, p. 26. New York: John Wiley.

THORN, G. D. & LUDWIG, R. A. (1954). *Canad. J. Chem.* 32, 872.

TRUTER, M. R. (1960). *J. Chem. Soc.* p. 997.

VALLE, G., BUSETTI, V., MAMMI, M. & CARAZZOLO, G. (1969). *Acta Cryst.* B25, 1432.

VALLE, G., COJAZZI, G. & BUSETTI, V. (1963). *Acta Cryst.* 16, A53, paper 5.24.

WALKER, L. A., FOLTING, K. & MERRITT, L. L., JR (1969). *Acta Cryst.* B25, 88.

WHEATLEY, P. J. (1953). *Acta Cryst.* 6, 369.

WOOLFSON, M. M. (1961). *Direct Methods in Crystallography.* Oxford: Clarendon Press.

X-ray 63 Program System for X-ray Crystallography (1965). Univ. of Washington, Seattle and Univ. of Maryland, College Park.

ZACHARIASEN, W. H. (1952). *Acta Cryst.* 5, 68.

Structure Cristalline du 'Méthylparathion'

PAR RENÉE BALLY

*Laboratoire de Rayons X de l'IrChA, 12, quai Henri-IV, Paris 4e, France*

The crystal structure of methylparathion, $(CH_3O)_2PSOC_6H_4NO_2$, has been determined by the symbolic addition method. There are four formula units in the monoclinic cell, $a = 6\cdot82$, $b = 21\cdot78$, $c = 8\cdot39$ Å, $\beta = 103°54'$, space group $P2_1/c$. The material crystallizes along a direction perpendicular to the stacking of the phenyl rings.

Introduction

La détermination de la structure cristalline du 'méthylparathion'
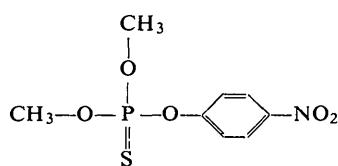
a été entreprise pour essayer d'apporter des renseignements sur son mode d'action dans l'organisme animal. Les propriétés sont à comparer à celles du 'sumithion'
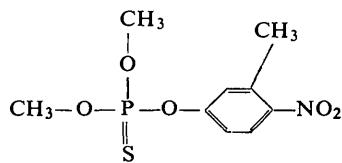
dont la cristallisation, très difficile, est en cours. Le 'méthylparathion' est biologiquement beaucoup plus actif. La dose léthale à 50 % pour la souris est de 20 à 30 mg. kg⁻¹ pour le 'méthylparathion' et de 700 à 900 mg. kg⁻¹ pour le 'sumithion'.

Partie expérimentale

Le 'méthylparathion' cristallise facilement dans le cyclohexane ou dans l'éther de pétrole, en plaquettes incolores et transparentes. La direction d'allongement ne coïncide pas avec un axe cristallographique (*cf*.Fig.6).

L'étude a été faite par diffraction des rayons X sur monocristaux. Les clichés ont été enregistrés sur chambre de Weissenberg en utilisant la technique des films multiples. L'ensemble des intensités utilisées au nombre de 2570 ont été relevées sur 7 strates selon l'axe *a*; elles ont été lues au moyen d'un densitomètre et d'une échelle étalonnée.

La maille appartient au système monoclinique; le groupe spatial est $P2_1/c$ avec les paramètres:

$$a = 6,82 \pm 0,02 \text{ Å}$$
$$b = 21,78 \pm 0,02$$
$$c = 8,39 \pm 0,02$$
$$\beta = 103°54' \pm 20'$$
$$V = 1210 \text{ Å}^3$$

La densité mesurée par flottaison $(1,448 \pm 0,010$ g.cm⁻³) dans une solution d'iodure de potassium impose 4 molécules par maille et est en accord avec la densité calculée (1,444).

Les corrections de Lorentz et de polarisation ont été effectuées sur calculateur CDC 3600. Le facteur d'échelle absolue et le facteur d'agitation thermique général $(B = 6,0 \text{ Å}^2)$ ont été obtenus graphiquement par la méthode statistique de Wilson (1942). Un second programme de calculs préliminaires a permis le calcul des modules des facteurs de structure $|F_H|$ et des modules des facteurs de structure normalisés $|E_H|$. Pour le groupe