References

ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195.

AMMON, H. (1968). *FIRST: A Program for the Evaluation of a Fourier Synthesis in a General Plane for the IBM* 1130. Unpublished work.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.

CHU, S., JEFFREY, G. A. & SAKURAI, T. (1962). *Acta Cryst.* **15**, 661.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.

DAMIANI, A., GIGLIO, E. & RIPAMONTI, A. (1967). *Acta Cryst.* **22**, 692.

DEWAR, M. J. S. & SCHMEISING, H N. (1959). *Tetrahedron*, **5**, 166.

GAULTIER, J. & HAUW, C. (1965*a*). *Acta Cryst.* **18**, 179.

GAULTIER, J. & HAUW, C. (1965*b*). *Acta Cryst.* **18**, 604.

GAULTIER, J. & HAUW, C. (1965*c*). *Acta Cryst.* **19**, 919.

GAULTIER, J. & HAUW, C. (1966). *Acta Cryst.* **21**, 694, and references therein.

HAND, E. S. & COHEN, T. (1967). *Tetrahedron*, **23**, 2911.

HIRSHFELD, F. L. & RABINOVICH, D. (1967). *Acta Cryst.* **23**, 989.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

KARLE, I. L. & BRITTS, K. (1966). *Acta Cryst.* **21**, 532.

KLUG, H. P. (1965). *Acta Cryst.* **19**, 983.

PATTERSON, A. L. (1952). *Acta Cryst.* **5**, 829.

PROUT, C. K. & WALLWORK, S. C. (1966). *Acta Cryst.* **21**, 449.

PUMMERER, R., PFAFF, A., TIEGELBAUER, G. & ROSENHAUER, E. (1939). *Ber. dtsch chem. Ges.* **72**, 1623.

ROSENHAUER, E., BRAUN, F. & PUMMERER, R. (1937). *Ber. dtsch chem. Ges.* **70**, 2281.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

STEWART, R. F. (1966). *DIAGUS: Principal Directions of Thermal Ellipsoids and Rigid Body Analysis.* Unpublished work.

STEWART, R., DAVIDSON, E. & SIMPSON, W. (1965). *J. Chem. Phys.* **42**, 3175.

SUNDARALINGAM, M. (1961). *Acta Cryst.* **14**, 894.

TROTTER, J. (1960). *Acta Cryst.* **13**, 86.

X-ray 63 Crystal Structure Calculations System, TR-64-6 (NSG-398), Computer Science Center, University of Maryland, and Research Computer Center, University of Washington.

The Crystal and Molecular Structure of Thiosemicarbazide

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The crystal structure of thiosemicarbazide, $SC(NH_2)NHNH_2$, has been determined by a three-dimensional X-ray analysis and refined both by differential and least-squares methods, using anisotropic thermal parameters: final $R = 9.9\%$. The crystals are triclinic ($P\bar{1}$): $a = 4.911(5)$, $b = 7.127(7)$, $c = 8.340(7)$ Å, $\alpha = 45°28'(3')$, $\beta = 83°50'(3')$, $\gamma = 77°34'(3')$, $Z = 2$. The arrangement of the non-hydrogen atoms is nearly planar, with the S and the hydrazinic NH_2 group in a *trans* position with respect to the C–NH bond. Bond distances and angles are: C–S = 1.685(5), C–N(1) = 1.313(6), C–N(2) = 1.337 (6), N(2)–N(3) = 1.399(6) Å, SCN(1) = 119.7°(3), SCN(2) = 121.5°(3), N(1)CN(2) = 118.8°(4), CN(2)–N(3) = 122.5°(4). The nitrogen atom, N(3), of the hydrazinic NH_2 group is 0.04 Å out the plane through the thiourea part of the molecule.

Introduction

Thiosemicarbazide behaves as a bidentate ligand with conformation (I) in monomeric metal complexes: *e.g.* dichloromonothiosemicarbazidezinc (Cavalca, Nardelli & Branchi, 1960), bisthiosemicarbazidatonickel(II) (Cavalca, Nardelli & Fava, 1962), *trans*-bisthiosemicarbazidenickel(II) sulphate trihydrate (Grønbaek & Rasmussen, 1962), α and β forms of bisthiosemicarbazidenickel(II) sulphate (Grønbaek, 1963), tristhiosemicarbazidenickel(II) dinitrate and bisthiosemicarbazidenickel(II) dinitrate dihydrate (Grønbaek Hazell,

1966). In the polymeric monochloromonothiosemicarbazidesilver (Nardelli, Fava Gasparri, Giraldi Battistini & Musatti, 1965) its conformation is (II) with a monodentate behaviour.

(I)   (II)
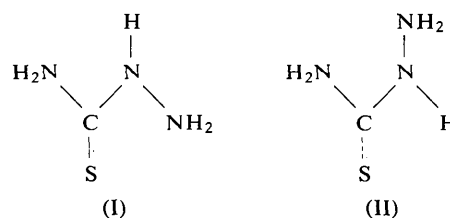
The dipole moment of thiosemicarbazide in dioxane [5·36 D at 30 °C (Mautner & Kumler, 1956)], compared with that of semicarbazide [3·77 D at 30 °C (Mautner & Kumler, 1956)], of thiourea [4·89 D at 25 °C (Kumler & Fohlen, 1942)] and of urea [4·56 D at 25 °C (Kumler & Fohlen, 1942)], suggests that conformation (II) must occur also in free thiosemicarbazide at 30 °C.

It would be interesting, therefore, to have direct information on the molecular structure of thiosemicarbazide in the solid state. A three-dimensional X-ray analysis, carried out on crystals obtained at room temperature from alcoholic solution, has confirmed that the conformation (II) is present. A preliminary account of this structure has been already given (Domiano, Gasparri & Nardelli, 1966).

Experimental

Crystal data

Thiosemicarbazide, $SC(NH_2)NHNH_2$, $M = 91\cdot13$.
$a = 4\cdot911$ (5), $b = 7\cdot127$ (7), $c = 8\cdot340$ (7) Å,
$\alpha = 45°28'$ (3'), $\beta = 83°50'$ (3'), $\gamma = 77°34'$ (3').
Space group: $P\bar{1}$ (from structure determination)
$Z = 2$, $F(000) = 96$, $V = 202\cdot8$ Å³.
$D_x = 1\cdot49$ g.cm⁻³; $\mu = 4\cdot9$ cm⁻¹ (Cu $K\alpha$).

The colourless crystals of thiosemicarbazide are thin plates elongated along [001] and optically biaxial. Preliminary crystal data were determined from rotation and Weissenberg photographs of crystals mounted about [100] and [001]; the unit-cell* dimensions and the angles were refined by a least-squares method from powder diffractometer data.

The intensity data, obtained from integrated Weissenberg photographs using the multiple film technique and Ni-filtered Cu radiation, were collected up to the 4th layer around [100] and up to the 7th layer around [001]. The number of observed independent reflexions was 791 out of the 914 in the Cu $K\alpha$ limiting sphere.

For both sets of photographs, the samples used were prismatic fragments cut to nearly equal cross section

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* The unit cell given above does not agree with the usual conventions, but it was the most suitable for the experimental handling in connection with the elongated shape of the crystals. The Buerger all-acute 'reduced cell' has the parameters: $a = 4\cdot91$, $b = 6\cdot08$, $c = 7\cdot13$ Å, $\alpha = 77\cdot9°$, $\beta = 77\cdot6°$, $\gamma = 84\cdot0°$; the transformation matrix from our cell to the reduced cell is $\bar{1}00/001/0\bar{1}\bar{1}$.

(0·08 cm × 0·03 cm); to a first approximation, the absorption correction was assumed to be that of a cylinder. The blackening of the reflexions was measured photometrically and the intensity values obtained in this way were corrected by the appropriate Lorentz and polarization factors; allowance was made for the extension of the spots on upper layer Weissenberg photographs following Phillips (1956). After applying the cross-correlation method of Rollett & Sparks (1960) to put all the data on a common scale, the absolute scale was obtained by Wilson's method giving an overall temperature factor $B = 3\cdot17$ Å².

Structure analysis and refinement

The distribution of the vectors in the three-dimensional Patterson space was interpreted on the basis of the $P\bar{1}$ space group, in agreement with the absence of piezoelectric effects. The heavy atom technique was successfully applied; the residual error index $R = 46\cdot8\%$, obtained using only the contribution of the sulphur atom to the structure factors, dropped to $R = 24\cdot6\%$ at the first introduction of the contributions of all the other non-hydrogen atoms.

The refinement was carried out with several cycles of Booth's differential synthesis using anisotropic thermal parameters. The final values of residual error indices were: $R(hkl) = 9\cdot9\%$ and $R'(hkl) = 10\cdot1\%$ (R for observed reflexions only, R' including $F_o = \frac{1}{2}F_{min}$ when $F_c \geq F_{min}$ for unobserved reflexions; multiplicities not considered).

At this stage all attempts to locate the hydrogen atoms from $(F_o - F_c)$ syntheses were unsuccessful. With the aim of improving the refinement of the structure and to locate directly the hydrogen atoms, the full-matrix least-squares program by Busing & Levy (1962) was applied, starting with the coordinates and thermal parameters obtained at the end of the isotropic cycles of Booth's differential synthesis ($R = 19\cdot6\%$). The weighting scheme used was that of Hughes (1941) and only one scale factor was applied; unobserved reflexions were excluded from this refinement. After two isotropic and four anisotropic least-squares cycles, the R value came down to $10\cdot2\%$ and then remained practically constant. Atomic coordinates and thermal parameters did not differ significantly from those obtained by differential synthesis; all the quoted data thereafter are those obtained by this last method. No further attempt to locate the hydrogen atoms was made; their

Table 1. *Final atomic fractional coordinates* ($\times 10^4$), *thermal parameters* ($\times 10$ Å²) *with e.s.d.'s and ratios* (*e.s.d.*)/(*coordinate shift*)

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}	$|r(x)|$	$|r(y)|$	$|r(z)|$
S	−13 (3)	−1260 (1)	8212 (1)	46 (0)	40 (0)	25 (0)	−23 (0)	9 (0)	−23 (0)	30	14	10
N(1)	2607 (10)	2119 (2)	7391 (4)	49 (1)	47 (0)	33 (1)	−24 (0)	10 (1)	−33 (0)	40	7	26
N(2)	2646 (10)	2203 (2)	4604 (5)	41 (1)	33 (0)	24 (0)	−17 (0)	6 (1)	−19 (0)	18	4	15
N(3)	4259 (11)	4193 (3)	3283 (4)	42 (1)	32 (0)	25 (0)	−15 (0)	5 (1)	−19 (0)	23	6	8
C	1836 (10)	1211 (3)	6616 (4)	30 (1)	28 (0)	25 (0)	−8 (0)	1 (1)	−19 (0)	45	10	30

thermal motion is probably responsible for this failure and a low temperature analysis is required.

The final coordinates and anisotropic thermal parameters are listed in Table 1 together with their standard deviations, calculated following Cruickshank (1956), and the ratios between the estimated standard deviations and the shifts of the coordinates. In Table 2 the observed atomic peak shapes are compared with the calculated ones. The set of structure factors calculated with the final parameters listed in Table 1 is given in Table 3 together with the observed structure amplitudes. The atomic scattering factors used throughout the calculations were those of Dawson (1960) for S and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for N and C.

Discussion

In the following discussion, atoms belonging to different asymmetric units are labelled as follows:

Superscript	Coordinates
none	x, y, z
i	$\bar{x}, \bar{y}, 1-z$
ii	$1-x, \bar{y}, 1-z$
iii	$\bar{x}, \bar{y}, 2-z$
iv	$x, 1+y, z-1$
v	$1-x, 1-y, 1-z$

The thiosemicarbazide molecule has conformation (II) as shown in Fig. 1. Bond distances and angles in the molecule are:

S–C	1·685 (5) Å	S–C–N(1)	119·7 (3)°
C–N(1)	1·313 (6)	S–C–N(2)	121·5 (3)
C–N(2)	1·337 (6)	N(1)–C–N(2)	118·8 (4)
N(2)–N(3)	1·399 (6)	C–N(2)–N(3)	122·5 (4)

The S–C distance is intermediate between the usual values for a S(?)–C(sp^2) single (1·75–1·78 Å) and a double (1·59 Å) bond; the same is true for C–N(1) and

Table 2. *Atomic peak heights* (e.Å^{-3}), *curvatures* (e.Å^{-5}) *and e.s.d.'s*

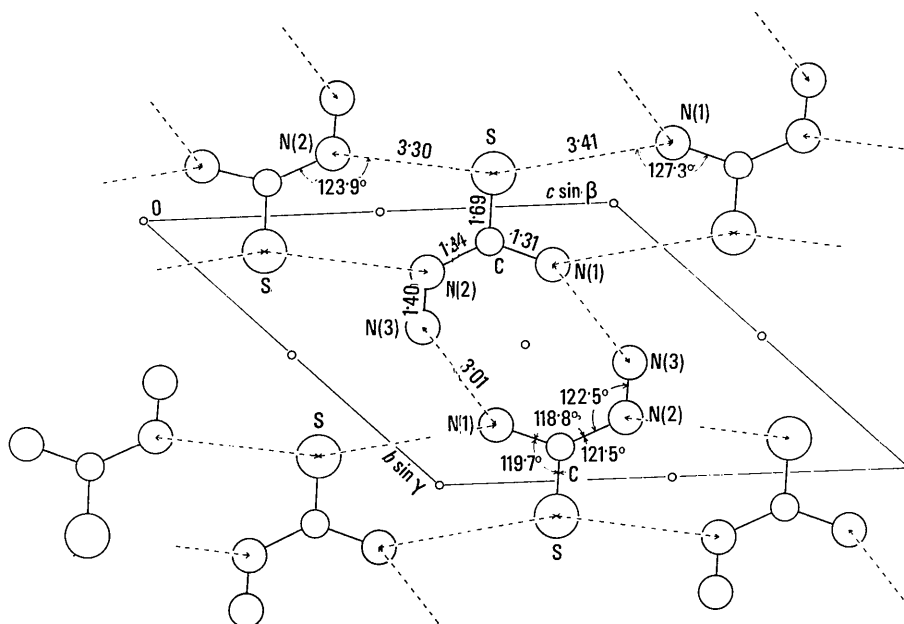|		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
S	obs	32·5	297	323	355	242	53	107
	calc	32·7	302	328	361	246	53	108
N(1)	obs	10·3	87	95	103	73	12	29
	calc	10·4	88	95	104	73	13	29
N(2)	obs	10·9	89	98	97	67	11	26
	calc	11·0	91	100	99	68	11	27
N(3)	obs	10·4	87	89	98	66	13	23
	calc	10·5	87	89	98	66	13	23
C	obs	9·6	86	91	98	68	16	22
	calc	9·9	87	92	99	69	15	22
	e.s.d.	0·2	2	2	2	2	1	1

Fig. 1. Diagrammatic projection of the structure along [100].

Table 3. *Observed and calculated structure factors*

A minus sign with F_o means 'less than'.

h	k	l	$10F_o$	$10F_c$
1	0	0	156	187
2	0	0	23	37
3	0	0	82	88
4	0	0	91	99
5	0	0	54	51
6	0	0	8	10
0	1	0	159	211
1	1	0	20	-6
1	1̄	0	421	498
2	1	0	43	51
2	1̄	0	12	8
3	1	0	137	141
3	1̄	0	10-	2
4	1	0	84	80
4	1̄	0	34	35
5	1	0	6	8
5	1̄	0	38	34
6	1	0	24	29
0	2	0	87	-99
1	2	0	123	-121
1	2̄	0	58	51
2	2	0	57	55
2	2̄	0	114	124
3	2	0	60	49
3	2̄	0	53	-54
4	2	0	56	-53
4	2̄	0	25	-22
5	2	0	18	19
5	2̄	0	12-	2
6	2	0	9-	3
0	3	0	160	-169
1	3	0	78	-75
1	3̄	0	92	-88
2	3	0	26	-25
2	3̄	0	13	-14
3	3	0	141	-146
3	3̄	0	12	8
4	3	0	45	-36
4	3̄	0	46	-43
5	3	0	29	-26
0	4	0	88	-85
1	4	0	41	-43
1	4̄	0	98	-96
2	4	0	147	-153
2	4̄	0	37	-35
3	4	0	76	-69
3	4̄	0	6	-8
4	4	0	55	-49
4	4̄	0	6-	-5
5	4	0	41	-44
0	5	0	7	-9
1	5	0	68	-76
1	5̄	0	35	-35
2	5	0	38	-37
2	5̄	0	28	-28
3	5	0	29	-24
3	5̄	0	4-	-1
4	5	0	20	-19
0	6	0	12	-15
1	6	0	11-	4
1	6̄	0	9	9
2	6	0	12	12
3	6	0	18	22
0	0	1	109	-118
1	0	1	245	238
1	0	1̄	48	41
2	0	1	197	212
2	0	1̄	81	72
3	0	1	15	-15
3	0	1̄	132	132
4	0	1	8-	10
4	0	1̄	14	12
5	0	1	8-	1
5	0	1̄	19	21
6	0	1̄	8	10
0	1	1	96	132
1	1	1	198	189
1	1̄	1	52	61
1	1	1̄	135	151
1	1̄	1̄	291	-317
2	1	1	159	-147
2	1̄	1	174	194
2	1	1̄	289	289
2	1̄	1̄	66	-63
3	1	1	80	-68
3	1̄	1	110	122
3	1	1̄	78	79
3	1̄	1̄	11	-20
4	1	1	53	-54
4	1̄	1	10	13
4	1	1̄	70	77
4	1̄	1̄	22	19
5	1	1	9-	2
5	1̄	1	11	14
5	1	1̄	46	52
5	1̄	1̄	17	-19
6	1	1	10	-10
6	1̄	1	11	14
6	1̄	1̄	2-	-4
0	2	1	37	38

h	k	l	$10F_o$	$10F_c$
0	3̄	1	55	70
1	2	1	235	-258
1	2	1	65	71
1	2	1̄	230	252
1	2	1̄	146	-166
2	2	1	159	-195
2	2	1	49	47
2	2	1̄	81	89
2	2	1̄	186	-220
3	2	1	155	-167
3	2	1	99	87
3	2	1̄	92	98
3	2̄	1̄	51	-55
4	2	1	45	-44
4	2̄	1	42	42
4	2	1̄	80	85
4	2	1̄	23	-28
5	2	1	53	-56
5	2	1	4-	0
5	2	1̄	26	30
5	2	1̄	7-	-5
6	2	1	25	-28
6	2	1̄	21	22
0	3	1	116	-142
0	3	1̄	88	88
1	3	1	150	-167
1	3	1	15	-17
1	3	1̄	16	13
1	3	1̄	9-	-4
2	3	1	206	-210
2	3	1	10-	6
2	3	1̄	35	32
2	3	1̄	91	-102
3	3	1	55	-59
3	3	1	8	8
3	3	1̄	43	51
3	3	1̄	87	-92
4	3	1	90	-93
4	3	1	27	23
4	3	1̄	11	7
4	3	1̄	13	-16
5	3	1	57	-62
5	3	1	7	5
5	3	1̄	4-	-7
0	4	1	33	-32
0	4	1̄	43	-40
1	4	1	109	-108
1	4	1	12-	-1
1	4	1̄	42	-32
1	4	1̄	14	-15
2	4	1	9-	1
2	4	1	42	-36
2	4	1̄	18	-13
2	4	1̄	14	12
3	4	1	51	-50
3	4	1	9	-9
3	4	1̄	40	-42
3	4	1̄	34	-35
4	4	1	53	-52
4	4	1	29	-35
4	4	1̄	21	-22
5	4	1	7-	3
5	4	1̄	32	-38
0	5	1	11	-13
0	5	1̄	40	-34
1	5	1	51	52
1	5	1	35	-33
1	5	1̄	33	-28
1	5	1̄	35	31
2	5	1	25	24
2	5	1	10	-12
2	5	1̄	63	-53
2	5	1̄	23	21
3	5	1	10-	0
3	5	1	57	-52
3	5	1̄	14	13
4	5	1	42	46
5	5	1	24	29
0	6	1	41	43
1	6	1	42	43
1	6	1̄	9	9
2	6	1	25	27
2	6	1̄	27	27
3	6	1	57	62
4	6	1	49	57
0	7	1	21	18
1	7	1	10	13
2	7	1	32	34
0	0	2	220	-237
1	0	2	88	-90
1	0	2	102	-106
2	0	2	182	-155
2	0	2	28	-21
3	0	2	24	-17
3	0	2	75	-73
4	0	2	25	-24
4	0	2	43	-43
5	0	2	16-	-16
5	0	2	52	-52
6	0	2	6-	-5

h	k	l	$10F_o$	$10F_c$
0	1	2	193	-220
0	1̄	2	12	12
1	1	2	423	-378
1	1̄	2	37	-35
1	1	2	59	92
1	1̄	2	222	-297
2	1	2	135	-135
2	1̄	2	20	21
2	1	2	31	23
2	1̄	2	127	-115
3	1	2	121	-100
3	1̄	2	20	-22
3	1̄	2	34	27
3	1̄	2	59	-55
4	1	2	64	-52
4	1̄	2	29	26
4	1	2	39	-40
4	1̄	2	74	-69
5	1	2	56	-49
5	1̄	2	10-	7
5	1	2	19	15
5	1̄	2	39	-38
6	1	2	32	-35
0	2	2	303	-343
0	2	2	110	126
1	2	2	139	-111
1	2	2	58	59
1	2	2	107	110
1	2	2	104	-106
2	2	2	183	-133
2	2	2	32	26
2	2	2	123	123
2	2	2	127	-124
3	2	2	70	-54
3	2	2	41	36
3	2	2	18	13
3	2	2	45	-36
4	2	2	74	-62
4	2	2	8	10
4	2	2	65	61
4	2	2	20	-22
5	2	2	70	-65
5	2	2	48	45
5	2	2	32	-27
6	2	2	11	-16
0	3	2	13	14
0	3	2	94	86
1	3	2	49	-25
1	3	2	84	71
1	3	2	128	124
1	3	2	91	-104
2	3	2	60	46
2	3	2	32	31
2	3	2	38	33
2	3	2	14	17
3	3	2	14	11
3	3	2	12	13
3	3	2	80	71
3	3	2	12	-8
4	3	2	50	-46
4	3	2	69	66
4	3	2	10	10
5	3	2	16-	1
5	3	2	45	50
5	3	2	10-	1
6	3	2	9-	-6
0	4	2	54	62
0	4	2	69	61
1	4	2	128	133
1	4	2	27	26
1	4	2	15-	4
1	4	2	54	58
2	4	2	121	118
2	4	2	16	16
2	4	2	29	26
2	4	2	14-	-2
3	4	2	39	29
3	4	2	36	32
3	4	2	41	39
4	4	2	68	57
4	4	2	46	37
4	4	2	14	15
5	4	2	24	24
6	4	2	30	36
0	5	2	103	105
0	5	2	17	-14
1	5	2	126	126
1	5	2	17	-15
1	5	2	48	47
2	5	2	70	64
2	5	2	13	-12
2	5	2	31	30
3	5	2	93	90
3	5	2	12-	7
4	5	2	43	47
4	5	2	17	19
5	5	2	92	67
0	6	2	60	61
1	6	2	29	27
1	6	2	39	38

h	k	l	$10F_o$	$10F_c$
2	5	2	56	54
2	5	2	8'	8
3	5	2	22	22
3	6	2	3-	3
4	6	2	53	51
5	6	2	32	37
0	7	2	11-	-5
1	7	2	12-	6
1	7	2	12	14
2	7	2	17	-18
3	7	2	8-	5
0	0	3	74	-64
1	0	3	248	-245
1	0	3	101	-99
2	0	3	90	-74
2	0	3	111	-112
3	0	3	64	-65
4	0	3	62	-55
4	0	3	75	-69
5	0	3	15	-15
5	0	3	17-	-2
0	1	3	244	-271
0	1̄	3	56	-62
1	1	3	72	-52
1	1̄	3	58	-59
1	1	3	55	-60
1	1̄	3	32	23
2	1	3	40	-33
2	1̄	3	96	-114
2	1	3	183	-191
2	1̄	3	43	-35
3	1	3	115	-96
3	1̄	3	31	-31
3	1	3	107	-105
3	1̄	3	69	-62
4	1	3	26	-30
4	1̄	3	29	-29
4	1	3	14-	-2
4	1̄	3	88	-80
5	1	3	17-	-5
5	1̄	3	31	-30
5	1̄	3	12	-13
0	2	3	69	81
0	2	3	28	30
1	2	3	183	137
1	2	3	18-	5
1	2	3	86	-82
1	2	3	97	-81
2	2	3	42	-31
2	2	3	15-	-1
2	2	3	71	-67
2	2	3	136	118
3	2	3	12-	4
3	2	3	32	-27
3	2	3	37	38
3	2	3	27	23
4	2	3	42	29
4	2	3	7-	-1
4	2	3	12-	3
4	2	3	15-	-6
5	2	3	59	52
5	2	3	10	-10
5	2	3	14	-14
6	2	3	10-	-7
0	3	3	252	241
0	3	3	17-	3
1	3	3	114	101
1	3	3	65	56
1	3	3	17	-12
1	3	3	136	131
2	3	3	111	80
2	3	3	31	23
2	3	3	75	72
2	3	3	32	34
3	3	3	116	88
3	3	3	54	50
3	3	3	101	95
4	3	3	171	155
4	3	3	30	32
4	3	3	24	23
5	3	3	39	34
5	3	3	12-	7
6	3	3	11-	6
0	4	3	100	101
0	4	3	11-	2
1	4	3	87	83
1	4	3	17	-16
1	4	3	17	17
1	4	3	69	54
1	4	3	144	144
2	4	3	91	76
2	4	3	70	57
2	4	3	73	72
3	4	3	255	222
3	4	3	54	51
3	4	3	25	28
4	4	3	94	81
4	4	3	39	38
5	4	3	24	24
6	4	3	18	24

h	k	l	$10F_o$	$10F_c$
0	5	3	17	13
1	5	3	15	-12
1	5	3	31	26
2	5	3	157	152
2	5	3	48	44
3	5	3	73	65
3	5	3	17	19
4	5	3	14-	3
4	5	3	8-	4
5	5	3	15-	8
0	6	3	63	-60
1	6	3	43	39
1	6	3	33	-25
2	6	3	16-	8
2	6	3	11	-8
3	6	3	43	-42
3	6	3	9-	6
4	6	3	42	-42
5	6	3	11	-14
0	7	3	15-	-7
1	7	3	18	-18
1	7	3	49	-46
2	7	3	53	-52
2	7	3	16	-18
3	7	3	66	-67
4	7	3	45	-47
1	8	3	18	-22
2	8	3	31	-42
0	0	4	12-	-2
1	0	4	34	25
1	0	4	82	-78
2	0	4	22	-19
2	0	4	103	-105
3	0	4	33	-33
3	0	4	55	55
4	0	4	10	12
4	0	4	10-	2
5	0	4	12	-14
5	0	4	21	-21
0	1	4	147	167
0	1̄	4	95	-105
1	1	4	93	79
1	1̄	4	52	-45
1	1	4	159	-173
1	1̄	4	92	85
2	1	4	8	5
2	1̄	4	20	-26
2	1	4	19	-16
2	1̄	4	17-	4
3	1	4	103	94
3	1̄	4	32	-31
3	1	4	33	-36
3	1̄	4	11-	3
4	1	4	10	11
4	1	4	28	-26
4	1̄	4	56	-59
4	1̄	4	90	87
5	1	4	9-	5
5	1̄	4	41	-47
5	1̄	4	19	20
0	2	4	188	190
0	2	4	137	-128
1	2	4	72	54
1	2	4	60	-56
1	2	4	38	-36
1	2	4	234	228
2	2	4	273	237
2	2	4	21	-22
2	2	4	39	-38
3	2	4	97	93
3	2	4	98	86
3	2	4	10	-11
3	2	4	59	-61
4	2	4	39	37
4	2	4	70	-68
4	2	4	37	37
5	2	4	29	27
5	2	4	56	58
0	3	4	24	12
0	3	4	10	-9
1	3	4	375	268
1	3	4	56	-51
1	3	4	10-	-4
1	3	4	159	142
2	3	4	168	137
2	3	4	17	-16
2	3	4	135	121
3	3	4	55	48
3	3	4	46	-40
3	3	4	25	30
4	3	4	31	25
4	3	4	16	16
5	3	4	64	63
5	3	4	19	19
6	3	4	34	43
0	4	4	116	111
1	4	4	81	70
1	4	4	58	-57
2	4	4	24	-12

h	k	l	$10F_o$	$10F_c$
2	4	4	42	37
3	4	4	67	-61
2	4	4	21	19
4	4	4	46	37
4	4	4	9	-10
5	4	4	55	56
5	4	4	2-	0
6	4	4	10	-11
0	5	4	17	-19
1	5	4	77	-72
1	5	4	27	-6
2	5	4	173	-159
2	5	4	58	-60
3	5	4	60	-53
3	5	4	11-	-6
4	5	4	32	29
5	5	4	9	-10
0	6	4	59	-58
1	6	4	149	-150
1	6	4	27	-29
2	6	4	105	-106
2	6	4	15	-16
3	6	4	12-	-2
3	6	4	30	-30
4	6	4	66	-69
5	6	4	58	-66
0	7	4	70	-71
1	7	4	71	-73
1	7	4	14	-13
2	7	4	12-	5
2	7	4	7-	-7
3	7	4	39	-39
4	7	4	49	-56
0	8	4	22	-25
1	8	4	21	20
1	8	4	7	-15
2	8	4	7-	7
3	8	4	9	-9
0	0	5	28	33
1	0	5	59	63
1	0	5	100	105
2	0	5	36	37
2	0	5	107	109
3	0	5	55	57
3	0	5	40	38
4	0	5	19	21
4	0	5	29	32
0	1	5	102	122
0	1̄	5	21	21
1	1	5	85	79
1	1̄	5	28	-25
1	1	5	45	44
1	1̄	5	68	71
2	1	5	140	122
2	1̄	5	11-	2
2	1	5	12-	-3
3	1	5	61	58
3	1̄	5	7-	0
3	1̄	5	10-	2
3	1̄	5	107	103
4	1	5	38	45
4	1	5	18	-14
4	1̄	5	31	32
5	1	5	21	24
5	1̄	5	19	25
0	2	5	43	37
0	2	5	11-	-5
1	2	5	138	128
1	2	5	23	-20
1	2	5	41	-36
1	2	5	73	80
2	2	5	58	49
2	2	5	35	-31
2	2	5	39	35
3	2	5	72	63
3	2	5	89	80
4	2	5	43	46
4	2	5	46	41
5	2	5	9-	2
5	2	5	7-	2
0	3	5	22	25
1	3	5	66	-56
1	3	5	70	-65
2	3	5	8-	-1
2	3	5	32	-9
3	3	5	24	23
3	3	5	14	-15
4	3	5	41	-34
4	3	5	22	20
5	3	5	16	-17
0	4	5	132	-140
1	4	5	115	-103
1	4	5	61	-56
2	4	5	49	-37
2	4	5	105	-92
3	4	5	134	-105
3	4	5	36	-34

Table 3 (cont.)

h	k	l	|10F$_o$|	10F$_c$	h	k	l	|10F$_o$|	10F$_c$	h	k	l	|10F$_o$|	10F$_c$	h	k	l	|10F$_o$|	10F$_c$	h	k	l	|10F$_o$|	10F$_c$	h	k	l	|10F$_o$|	10F$_c$
4	4	5	88	-80	2	1̄	6	28	30	2	6	6	45	38	4	3̄	7	10	-12	1	2̄	8	12-	4	1	3̄	9	70	68
4	4̄	5	16	-18	2	1	6	52	46	2	6̄	6	11-	-3	0	4	7	97	102	2	2	8	34	-15	2	3	9	48	52
5	4	5	54	-60	2	1̄	6	11-	-4	3	6	6	44	35	1	4	7	56	-51	2	2̄	8	40	-35	2	3̄	9	50	50
0	5	5	99	-105	3	1	6	42	-9	3	6̄	6	24	21	1	4̄	7	17	15	3	2	8	4-	9	0	4	9	23	27
1	5	5	47	-50	3	1̄	6	37	36	4	6	6	38	35	2	4	7	60	-51	0	3	8	16-	2	1	4	9	49	52
1	5̄	5	105	-100	4	1	6	27	27	5	6	6	9	10	2	4̄	7	25	-22	1	3	8	23	22	1	4̄	9	51	52
2	5	5	155	-118	4	1̄	6	6-	8	0	7	6	72	80	3	4	7	23	17	1	3̄	8	14-	6	2	4	9	32	38
2	5̄	5	46	-44	0	2	6	15	-4	1	7	6	68	65	3	4̄	7	20	-19	2	3	8	60	66	2	4̄	9	51	48
3	5	5	138	-116	1	2	6	81	-76	1	7̄	6	24	23	4	4	7	25	26	2	3	8	51	52	3	4	9	57	59
3	5̄	5	52	-51	1	2̄	6	46	-39	2	7	6	72	67	4	4̄	7	5-	7	3	3	8	26	31	0	5	9	15-	-1
4	5	5	123	-116	2	2	6	101	-96	2	7̄	6	17	16	5	4	7	7	8	3	3̄	8	7-	4	1	5	9	13	-10
4	5̄	5	10	-13	2	2̄	6	29	-27	3	7	6	71	71	0	5	7	44	41	0	4	8	58	56	1	5̄	9	15	-16
5	5	5	21	-27	3	2	6	11-	-6	3	7̄	6	2-	7	1	5	7	11-	10	1	4	8	134	131	2	5	9	35	33
0	6	5	15-	-3	3	2̄	6	53	-52	4	7	6	37	39	1	5̄	7	143	137	1	4̄	8	41	41	2	5̄	9	12	12
1	6	5	50	-45	4	2	6	8	-11	0	8	6	30	33	2	5	7	64	71	2	4	8	101	107	3	5	9	8-	6
1	6̄	5	35	-39	4	2̄	6	7-	-8	1	8	6	44	42	2	5̄	7	39	37	2	4̄	8	45	42	0	6	9	64	-61
2	6	5	60	-60	5	2	6	2-	-3	1	8̄	6	32	30	3	5	7	104	95	3	4	8	12	14	1	6	9	24	-19
2	6̄	5	32	-32	0	3	6	113	-126	2	8	6	52	50	3	5̄	7	8	8	3	4̄	8	57	57	1	6̄	9	41	-39
3	6	5	118	-105	1	3	6	190	-199	3	8	6	29	28	4	5	7	54	60	4	4	8	32	33	2	6	9	34	-39
3	6̄	5	9	-11	1	3̄	6	63	-46	4	8	6	37	39	4	5̄	7	3-	5	0	5	8	121	118	2	6̄	9	34	-32
4	6	5	13	-16	2	3	6	89	-80	1	9	6	10	13	5	5	7	10	12	1	5	8	146	137	3	6	9	41	-45
5	6	5	9-	-7	2	3̄	6	89	-78	2	9	6	3-	-3	0	6	7	28	27	1	5̄	8	35	32	0	7	9	29	-34
0	7	5	20	18	3	3	6	74	-65	0	0	7	9-	-5	1	6	7	77	68	2	5	8	27	27	1	7	9	45	-51
1	7	5	15	16	3	3̄	6	53	-51	1	0	7	16	-19	1	6̄	7	57	58	2	5̄	8	30	28	1	7̄	9	58	-57
1	7̄	5	25	22	4	3	6	34	-31	1	0̄	7	24	23	2	6	7	142	121	3	5	8	44	48	2	7	9	58	-63
2	7	5	44	-40	4	3̄	6	49	-49	2	0	7	30	-24	2	6̄	7	90	87	3	6	8	26	28	2	7̄	9	24	-29
2	7̄	5	8-	-2	5	3	6	37	-44	0	1	7	80	-88	3	6	7	108	102	4	5	8	40	48	3	7	9	51	-60
3	7	5	25	23	0	4	6	174	-185	1	1	7	32	-34	3	6̄	7	15	17	0	6	8	88	84	0	8	9	17	-20
4	7	5	31	33	1	4	6	143	-104	1	1̄	7	50	-51	4	6	7	31	32	1	6	8	11	-8	1	8	9	28	-31
5	7	5	4-	9	1	4̄	6	87	-104	2	1	7	14	-17	5	6	7	51	58	1	6̄	8	49	41	1	8̄	9	11	-14
0	8	5	33	35	2	4	6	120	-90	2	1̄	7	22	-21	0	7	7	19	15	2	6	8	12-	8	2	8	9	35	-37
1	8	5	10-	-2	2	4̄	6	30	-23	3	1	7	13	-14	1	7	7	64	63	2	6̄	8	11	-12	3	8	9	46	-50
1	8̄	5	22	23	3	4	6	45	-36	3	1̄	7	62	-60	1	7̄	7	11-	6	3	6	8	22	22	1	9	9	3-	1
2	8	5	35	25	3	4̄	6	49	-44	0	2	7	84	-93	2	7	7	71	75	3	6̄	8	5-	0	0	4	10	8-	-6
3	8	5	57	56	4	4	6	77	-73	1	2	7	55	-52	2	7̄	7	22	26	4	6	8	36	40	1	4	10	40	-37
4	8	5	34	40	4	4̄	6	25	-26	1	2̄	7	115	-128	3	7	7	12	11	0	7	8	34	-35	1	4̄	10	4-	0
0	0	6	82	89	5	4	6	35	-42	2	2	7	34	-32	4	7	7	45	51	1	7	8	49	-45	0	5	10	69	-74
1	0	6	63	65	0	5	6	39	-39	2	2̄	7	62	-63	0	8	7	10-	1	1	7̄	8	25	24	1	5	10	45	-47
1	0̄	6	44	39	1	5	6	45	-36	3	2	7	87	-96	1	8	7	18	19	2	7	8	36	-38	1	5̄	10	27	-28
2	0	6	43	46	1	5̄	6	81	-73	3	2̄	7	35	-36	1	8̄	7	16	-16	2	7̄	8	7-	-8	2	5	10	34	-41
2	0̄	6	79	80	2	5	6	25	30	4	2	7	27	-42	2	8	7	28	-29	3	7	8	9-	0	0	6	10	48	-52
3	0	6	9	10	2	5̄	6	11-	-2	4	2̄	7	48	-53	3	8	7	9	7	4	7	8	24	-29	1	6	10	47	-48
3	0̄	6	45	43	3	5	6	49	-39	0	3	7	40	-41	4	8	7	5-	6	0	8	8	41	-46	1	6̄	10	57	-59
4	0	6	22	26	3	5̄	6	15	12	1	3	7	11	10	0	9	7	2-	-4	1	8	8	53	-60	2	6	10	60	-71
0	1	6	35	42	4	5	6	26	-24	1	3̄	7	85	-82	1	9	7	29	-37	1	8̄	8	27	-24	0	7	10	14	-14
0	1̄	6	33	30	4	5̄	6	7	-9	2	3	7	118	-121	2	9	7	15	-19	2	8	8	22	-28	1	7	10	40	-39
1	1	6	56	51	5	5	6	12	-13	2	3̄	7	86	-85	0	1	8	31	-28	3	8	8	46	-56	1	7̄	10	15	-18
1	1̄	6	64	59	0	6	6	25	21	3	3	7	66	-73	1	1	8	64	-64	0	9	8	32	-36	2	7	10	22	-27
1	1	6	74	66	1	6̄	6	82	93	3	3̄	7	26	-25	0	2	8	48	-54	0	3	9	54	62	0	8	10	6-	0
1	1̄	6	47	49	1	6̄	6	19	16	4	3	7	17	-13	1	2	8	22	-39	1	3	9	35	38	1	8	10	7-	7
2	1	6	11	-9																									

C–N(2) bonds, whereas the N(2)–N(3) distance corresponds to a single bond. Thus the most important canonical structures are:

$$H_2N\diagdown \quad \diagup NH_2 \qquad H_2N\diagdown \quad \overset{+}{\diagup} NH_2$$
$$\overset{\diagup\diagup}{S}C\text{—}N\diagdown H \longleftrightarrow \underset{-S}{C}=N\diagdown H \longleftrightarrow$$

$$\overset{+}{H_2N}\diagdown \quad \diagup NH_2$$
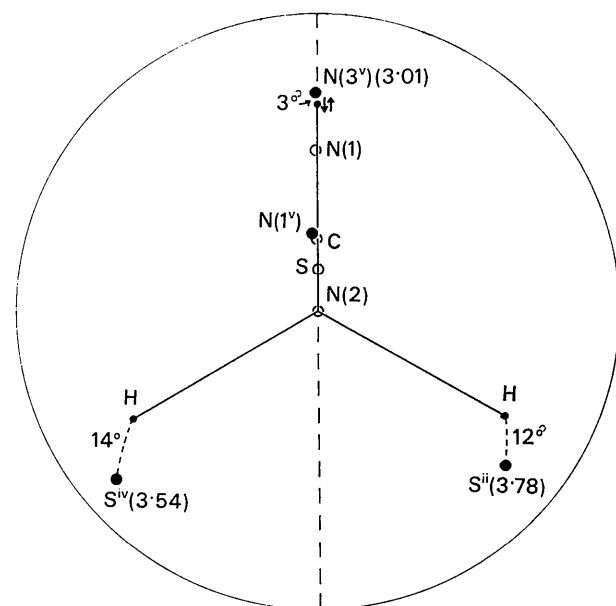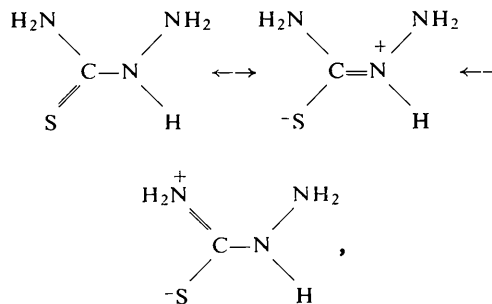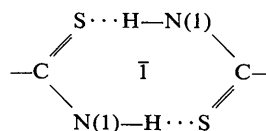$$\underset{-S}{\diagup}C\text{—}N\diagdown H \quad,$$

Fig. 2. Stereographic projection of the environment of N(3), viewed down N(3)–N(2).

which is in agreement with the observation that the N(3) atom is significantly out of the mean plane passing through the remaining heavy atoms (0·04 Å). The analysis of the planarity in the thiosemicarbazide molecule, shown in Table 4, indicates that the carbon atom also is a little out of the plane of the other non-hydrogen atoms, but it is doubtful that this distortion is significant. The most striking evidence for the single bond character of the N(2)–N(3) bond is that the hydrogen atoms, placed in the positions calculated on the assumption that N(3) is trigonally hybridized in the mean molecular plane, give rise to H···H contacts, with an adjacent molecule, which are much shorter (1·22 Å) than the sum of the van der Waals radii (2·4 Å, Pauling, 1960). This indicates a tetrahedral bond configuration for N(3), as could be expected for a hydrazinic hydro-

gen. This assumption explains the environment of N(3) (Fig.2), and it can be deduced that the most probable orientation of the hydrogen atoms attached to N(3) is symmetrical with respect to the molecular plane, with the H atoms pointing towards two sulphur atoms [N(3)H⋯S^{iv}=3·54 Å, N(3)H⋯S^{ii}=3·78 Å, N(2)–N(3)S^{iv}=97·9°, N(2)N(3)S^{ii}=101·9°], while the lone pair lies in the molecular plane. In this arrangement the lone pair interacts with one of the hydrogen atoms attached to N(1) and both together interact with the corresponding lone pair and hydrogen atom of the molecule centrosymmetrical with respect to Ī($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$), as shown in Fig.3.

Since this symmetry centre is displaced from the mean molecular plane by only 0·06 Å, the two molecules can be considered to be practically coplanar and to be joined together in a dimer by the lone pair–hydrogen interactions. Consequently, the other H atom

attached to N(1) is directed towards S^{iii}[N(1)H⋯S^{iii}= 3·41 Å, CN(1)S^{iii}=127·3°], and the ring

$$\begin{array}{ccc} & \text{S}\cdots\text{H—N(1)} & \\ \diagup & & \diagdown \\ \text{—C} & \overline{\text{I}} & \text{C—} \\ \diagdown & & \diagup \\ & \text{N(1)—H}\cdots\text{S} & \end{array}$$

is formed around the symmetry centre at (0,0,1). Assuming a trigonal configuration of bonds for N(2), its hydrogen is directed towards S^i [N(2)H⋯S^i=3·30 Å, CN(2)S^i=123·9°] and a ring is formed of the same kind as the previous one around the symmetry centre at (0,0,$\frac{1}{2}$). All the molecules connected by these three kinds of rings lie approximately in a plane [Ī(0,0,1) and Ī(0,0,$\frac{1}{2}$) lie 0·3 Å out of the molecular plane] running parallel to (1Ī0), which explains the particu-

Table 4. *Analysis of the planarity in the thiosemicarbazide molecule*

Equation of the plane referred to orthogonal axes: $m_1x' + m_2y' + m_3z' = d$.

Best plane through		SCN(1)N(2)N(3)		SCN(1)N(2)	
m_1		0·8183		0·8209	
m_2		−0·3814		−0·3832	
m_3		0·4301		0·4235	
d		0·3505		0·3118	
	$\sigma_\perp$ (Å)*	$\varDelta$ (Å)	$\varDelta/\sigma_\perp$	$\varDelta$ (Å)	$\varDelta/\sigma_\perp$
S	0·0015	0·0013	0·85	0·0004	0·27
C	0·0050	−0·0222	−4·39	−0·0162	−3·20
N(1)	0·0049	0·0037	0·76	0·0055	1·12
N(2)	0·0050	−0·0101	−2·03	0·0056	1·12
N(3)	0·0052	0·0147	2·85	(0·0362)	(7·38)
$\Sigma (\varDelta/\sigma_\perp)^2$			32·82		12·81
$\chi^2_{95\%}$			5·99		3·80

* $\sigma_\perp = \{m_1^2\sigma^2(x') + m_2^2\sigma^2(y') + m_3^2\sigma^2(z')\}^{\frac{1}{2}}$.

Transformation matrix from triclinic x,y,z to orthogonal x',y',z' coordinates:

$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^* \end{pmatrix}$$
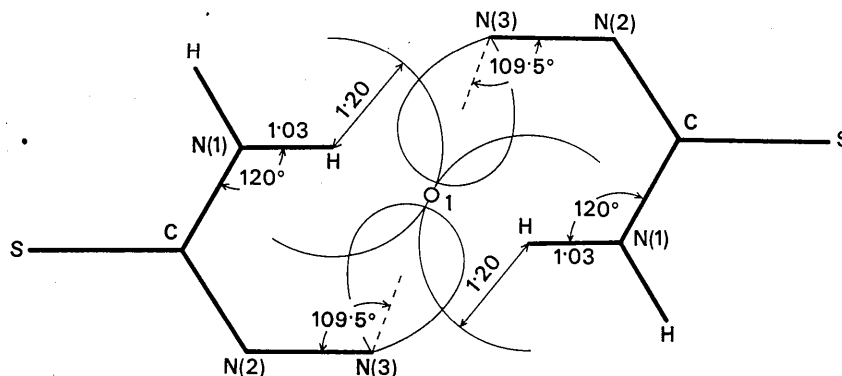

Fig.3. Planar arrangement of the two centrosymmetrical molecules with respect to Ī($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$).
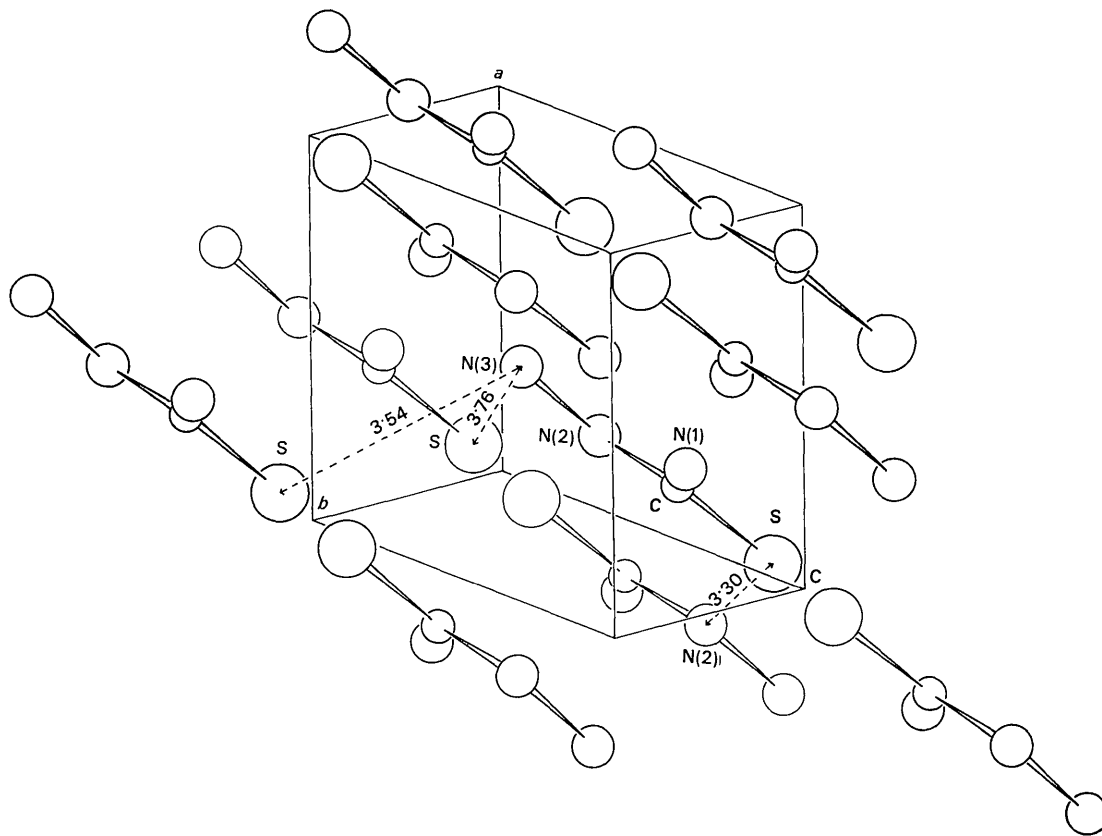
Fig. 4. Clinographic projection of the structure, showing the packing of the planes.

larly high intensity observed for the reflexion with these indices. In Fig. 4 a clinographic projection of the structure, showing the packing of these planes, is presented.

All the calculations were performed on the Olivetti Elea 6001/S computer of the Centro di Calcolo Elettronico dell'Università di Parma, using the programs of Nardelli, Musatti, Domiano & Andreetti (1964, 1965), with the exception of the least-squares refinement which was performed using the *ORFLS* program on the IBM 7090 of CNUCE of Pisa. The authors are indebted to the Consiglio Nazionale delle Ricerche for financial support.

References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BUSING, W. R. & LEVY, H. A. (1962). *ORFLS Least-squares Program*. I. U. Cr. *World List of Crystallographic Computer Programs*, No. 360.

CAVALCA, L., NARDELLI, M. & BRANCHI, G. (1960). *Acta Cryst.* **13**, 688.

CAVALCA, L., NARDELLI, M. & FAVA, G. (1962). *Acta Cryst.* **15**, 1139.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

DOMIANO, P., FAVA GASPARRI, G. & NARDELLI, M. (1966). *Ric. Sci.* **36**, 744.

GRØNBAEK, R. & RASMUSSEN, S. E. (1962). *Acta Chem. Scand.* **16**, 2325.

GRØNBAEK, R. (1963). *Acta Cryst.* **16A**, 65.

GRØNBAEK HAZELL, R. (1966). *Acta Cryst.* **21A**, 142.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

KUMLER, W. D. & FOHLEN, G. M. (1942). *J. Amer. Chem. Soc.* **64**, 1944.

MAUTNER, H. G. & KUMLER, W. D. (1956). *J. Amer. Chem. Soc.* **78**, 97.

NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. (1964). *Ric. Sci.* **34**, II–A, 711.

NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. (1965). *Ric. Sci.* **35**, II–A, 469, 477 and 807.

NARDELLI, M., FAVA GASPARRI, G., GIRALDI BATTISTINI, G. MUSATTI, A. (1965). *Chem. Comm.* 187.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.

ROLLET, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.