

207. *An Accurate Determination of the Crystal Structure of Thioacetamide.*

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An X-ray crystal structure analysis has shown that thioacetamide is monoclinic, $a = 11.062$, $b = 10.005$, $c = 7.170$ Å, $\beta = 99.5^\circ$. The space group is $P2_1/a$ with two molecules in the asymmetric unit, both approximately parallel to (001). Three-dimensional anisotropic refinement was carried out and the bond lengths, corrected for rotational oscillations, are C-S 1.713 ± 0.006 , C-C 1.494 ± 0.008 , and C-N 1.324 ± 0.008 Å, and the angles are S-C-C $120.7^\circ \pm 0.4^\circ$, S-C-N $121.6^\circ \pm 0.4^\circ$, and C-C-N $117.7^\circ \pm 0.6^\circ$. The molecules excluding hydrogen atoms are planar.

DETERMINATION of the bond lengths of compounds which contain an apparent carbon-sulphur double bond, *e.g.*, dithio-oxamide,¹ ethylenethiourea (2-thioimidazolidine),² and thiourea³ suggested that the carbon-sulphur bond has only partial double-bond character.

¹ Long, Markey, and Wheatley, *Acta Cryst.*, 1954, **7**, 140.

² Wheatley, *ibid.*, 1953, **6**, 369.

³ Kunchur and Truter, *J.*, 1958, 2551.

Kohlrausch and Wagner⁴ and Spinner⁵ agree that the Raman and infrared spectra of thioacetamide indicate that the amide form, $\text{CH}_3\cdot\text{C}(\text{NH}_2)=\text{S}$, predominates, so that this molecule may contain a pure carbon-sulphur double bond.

An accurate crystal structure analysis of thioacetamide has been carried out to determine the bond lengths and angles as part of an investigation into the changes in bond lengths in a potential ligand in the free and the co-ordinated state.

Crystal Data.— $\text{C}_2\text{H}_5\text{NS}$, $M = 75.14$, m. p. 109° . Monoclinic, $a = 11.062$, $b = 10.005$, $c = 7.170$, all ± 0.005 Å, $\beta = 99.5^\circ \pm 0.2^\circ$, $U = 782.7$ Å³, $D_m = 1.269$ (by flotation), $Z = 8$, $D_c = 1.273$, $F(000) = 320$. Space group, $P2_1/a$ (C_{2h}^5 , No. 14). Cu- K_α radiation, single-crystal oscillation and Weissenberg photographs, absorption coefficient, $\mu = 84.35$ cm.⁻¹. Two molecules per asymmetric unit.

Three-dimensional Structure Determination.—Eight atoms other than hydrogen were to be located, four in each of the molecules (I) and (II) of the asymmetric unit; these were designated S(1), C(1), N(1), and C(2) for (I), and S(2), C(3), N(2), and C(4) for (II), C(1) and C(3) being the central carbon atoms. A Patterson projection along $[c]$ revealed the positions of the sulphur atoms; Fourier methods were used to find and refine the co-ordinates of the other atoms. In Fig. 1 the final atomic positions in this projection are shown. All the atoms are resolved, indicating that the molecules lie nearly parallel to (001). It was possible to locate the sulphur atoms from a Patterson projection along $[b]$, and the other atoms by trial and error followed by Fourier difference syntheses. An approximate allowance was made for the markedly anisotropic thermal motion of the molecules by multiplying the scattering factors by a temperature factor $\exp - \{1.42 \sin^2 \theta / \lambda^2 + 0.85l^2 / (4c^2 \sin^2 \theta)\}$, the average motion being greatest perpendicular to the planes of the molecules. Two-dimensional refinement was discontinued when the agreement indices were $R_{hk0} = 0.17$ and $R_{h0l} = 0.18$ ($R = \sum(|F_o| - |F_c|) / \sum|F_o|$). Hitherto, the light atoms had been treated as carbon atoms, but before three-dimensional refinement was started the methyl groups were distinguished from the amine groups on the assumption that the interatomic distances 1.45 Å (I) and 1.47 Å (II) corresponded to C-C bonds while 1.37 Å (I) and 1.38 Å (II) corresponded to C-N bonds; the C-S bond lengths were 1.68 Å (I) and 1.67 Å (II).

Three-dimensional anisotropic refinement was carried out in two stages. In the first stage, by using the method of differential synthesis, R was reduced in three cycles from 0.218 (for isotropic motion) to 0.124; no further significant shifts in the parameters were indicated (*i.e.*, the shifts were less than half the corresponding standard deviations). Attempts to locate the hydrogen atoms were unsuccessful.

At this time, the only theoretical scattering factor for sulphur was that of James and Brindley.⁶ Publication of new values by Tomiie and Stam⁷ enabled a more accurate structure analysis to be undertaken. The second stage of refinement was carried out by the method of least squares. Structure factors were calculated from the last set of parameters with the new scattering factor for sulphur; R rose to 0.128; one cycle of refinement reduced it to 0.125 and gave no more significant shifts. Location of the hydrogen atoms in the amine groups was achieved by computing an electron-density difference projection along $[c]$ using only planes with $\sin \theta < 0.5$; the result is shown in Fig. 1 where the positions marked for the hydrogen atoms are those calculated for a planar molecule in which N-H = 1.0 Å and H-N-H = 120° . The nitrogen-sulphur distances are also shown; those expected to be N-H...S bonds are significantly shorter than the other van der Waals contacts. Inclusion of these four hydrogen atoms reduced R to 0.122 without producing significant changes in the co-ordinates of the heavy atoms; one cycle of refinement reduced R to 0.121.

⁴ Kohlrausch and Wagner, *Z. phys. Chem.*, 1940, B, **45**, 229.

⁵ Spinner, *Spectrochim. Acta*, 1959, **95**.

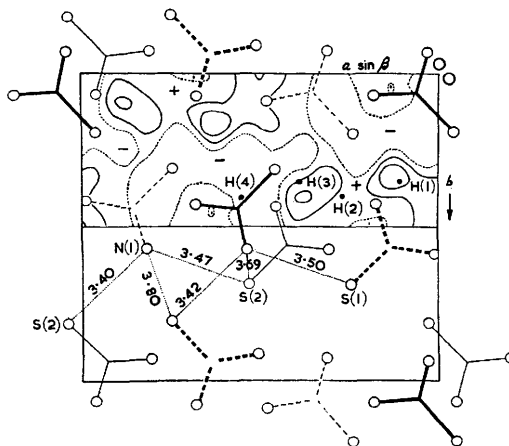
⁶ "International Tables for the Determination of Crystal Structures," Borntraeger, Berlin, 1935.

⁷ Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

The hydrogen atoms of the methyl groups were located approximately by calculating the electron-density difference in the sections at $x/a = 0.525$ and $x/a = 0.218$ in which the atoms attached to C(2) and C(4) respectively would be expected (see Fig. 1). Refinement of all ten hydrogen positions was carried out by using only planes with $\sin \theta < 0.5$; the shifts indicated were applied only to the hydrogen atoms, and refinement was complete in two cycles ($R = 0.133$ and 0.128).

A final set of structure factors was calculated by using the relevant anisotropic thermal parameters for the carbon, nitrogen, and sulphur atoms and the same isotropic temperature factor for all the hydrogen atoms. R was reduced to 0.117 ; a list of observed and calculated structure factors is given in Table 1. Application of the least squares procedure showed

FIG. 1. Projection of the structure along [001]. Molecules (I) are shown by broken lines, (II) by full lines; those shown by heavy lines lie approximately in planes at $z/c = 3/4$, and those shown by thin lines in planes at $z/c = 1/4$. The figures are distances in Å from the nitrogen atoms to neighbouring sulphur atoms. Hypothetical positions for hydrogen atoms, on the assumption that the nitrogen bond angles are trigonal, are marked by black dots. On half the unit cell is imposed the difference map, $(\rho_o - \rho_c)$ calculated from the final structure factors excluding hydrogen atoms; the positive contours are at $0.4\epsilon/\text{Å}^2$ intervals with the zero contour shown by a broken line.



that no significant changes were required in the parameters of the heavy atoms as a result of including the hydrogen atoms.

A rather high proportion of the reflections were too weak to be observed. The effect of including them among the observations and assuming their structure amplitudes to be half the minimum observable was to give significant shifts in some of the parameters. After two cycles, refinement was complete; R was 0.156 for all planes.

Results.—Comparison of the effects of various procedures is most interestingly seen in the values of R and the bond lengths as set out in Table 2. Columns (a) and (b) show the results for complete refinement for the heavy atoms alone with (a) the James and Brindley⁶ and (b) the Tomiie and Stam⁷ scattering factors for sulphur (they have also been derived by different computational methods). Although the agreement indices are the same, use of the new scattering factor gave better agreement between the independent C-N bond lengths and enabled the hydrogen atoms to be located. The larger standard deviation given by the least squares procedure (b) has been found in other examples⁸ and is probably due to omission of the unobserved planes; this view is supported by (d) the results including all planes. Comparison of columns (c) and (b) shows the effect of including the ten hydrogen atoms, and of columns (d) and (c) of using more but doubtful data.

The final results were taken as those derived from the observed planes only and are shown in Tables 3 and 4. In addition to the fractional co-ordinates, Table 3 also shows the co-ordinates X' , Y' and Z' in Å in a system of orthogonal axes parallel to $[a]$, $[b]$, and $[c^*]$; the corresponding standard deviations are also shown. Table 4 shows the thermal parameters and standard deviations found for sulphur, carbon, and nitrogen; U_{11} , U_{22} , and U_{33} are the mean square amplitudes of oscillation parallel to the $[a^*]$, $[b^*]$,

⁸ Sparks, Ph.D. Thesis, University of California, Los Angeles, August, 1955.

TABLE 1. (Continued.)

| <i>hkl</i> | $ F_o $ | F_e | <i>hkl</i> | $ F_o $ | F_e | <i>hkl</i> | $ F_o $ | F_e | <i>hkl</i> | $ F_o $ | F_e | <i>hkl</i> | $ F_o $ | F_e |
|------------------|---------|-------|------------|---------|-------|------------|---------|-------|--------------------|---------|-------|--------------------|---------|-------|
| 183 | 9.1 | 7.1 | 493 | 4.5 | -4.6 | 10,9,0 | 11.0 | -13.4 | 5,10, ₃ | 8.7 | -9.2 | 4,11, ₃ | 3.7 | 3.7 |
| 38- ₃ | 8.1 | -7.9 | -3 | 7.9 | -7.1 | -2 | 14.3 | 19.3 | -3 | 12.5 | -14.1 | -2 | 8.8 | 7.8 |
| -4 | 6.3 | -6.0 | 4 | 18.7 | -17.8 | 4 | 1.0,0 | 14.3 | 11.7 | 4 | 6.8 | -2 | 12.2 | 8.6 |
| 092 | 18.1 | -18.9 | -4 | 8.0 | 6.6 | -1 | 22.2 | 18.2 | 7,10,0 | 22.5 | -19.8 | -3 | 5.4 | 4.4 |
| 4 | 16.0 | 19.0 | 690 | 15.5 | -14.9 | -2 | 10.3 | -1.12 | 2 | 11.9 | 12.1 | -2 | 9.6 | -9.1 |
| 6 | 6.4 | -8.4 | -1 | 15.8 | 15.5 | -3 | 18.6 | -17.5 | -2 | 16.9 | 15.6 | 1,12,0 | 10.9 | -18.0 |
| 291 | 24.6 | -23.7 | -2 | 22.7 | 20.4 | 4 | 10.3 | -10.5 | -3 | 7.9 | 7.7 | -1 | 2.0 | 3.1 |
| -1 | 24.4 | 23.9 | -3 | 5.9 | -6.1 | -1 | 19.0 | -18.5 | -4 | 6.6 | -5.6 | 3 | 14.0 | 18.7 |
| -2 | 10.5 | 12.1 | -4 | 17.7 | -15.3 | 3,10,0 | 8.9 | -11.2 | 2,11,0 | 7.1 | 5.1 | -3 | 19.2 | 20.5 |
| -3 | 10.6 | 10.6 | 890 | 11.6 | -10.9 | 2 | 12.7 | 13.6 | 1 | 9.8 | 9.9 | 3,12,0 | 11.5 | 12.3 |
| -3 | 11.6 | -11.4 | 1 | 20.6 | 19.1 | -2 | 7.4 | 8.9 | -1 | 11.0 | -12.5 | 1 | 13.9 | -16.0 |
| -4 | 9.7 | -8.4 | -1 | 20.4 | -17.2 | 3 | 12.6 | 12.5 | -1 | 3.7 | -3.7 | 2 | 13.3 | -12.6 |
| 490 | 19.6 | -16.9 | 2 | 15.2 | 14.0 | -4 | 6.2 | 4.6 | 2,11, ₃ | -3 | 10.2 | 9.6 | 10.1 | -16.2 |
| 2 | 28.0 | 25.0 | 3 | 6.6 | -9.9 | -1 | 11.4 | 10.9 | -4 | 6.4 | 5.2 | 5,12,-1 | | |

Reflections which were too weak to be observed have been omitted.

TABLE 2. Comparison of the results of refinement procedures.

| <i>R</i> | (a) 0.124 | (b) 0.125 | (c) 0.117 | (d) 0.156 |
|-----------|-----------------|-----------------|-----------------|-----------------|
| C(1)-S(2) | 1.701 ± 0.007 Å | 1.702 ± 0.010 Å | 1.692 ± 0.008 Å | 1.683 ± 0.007 Å |
| C(3)-S(2) | 1.690 ± 0.007 | 1.690 ± 0.010 | 1.694 ± 0.008 | 1.703 ± 0.007 |
| C(1)-C(2) | 1.497 ± 0.012 | 1.490 ± 0.013 | 1.479 ± 0.011 | 1.486 ± 0.010 |
| C(3)-C(4) | 1.486 ± 0.012 | 1.481 ± 0.013 | 1.480 ± 0.011 | 1.481 ± 0.010 |
| C(1)-N(1) | 1.286 ± 0.009 | 1.303 ± 0.014 | 1.308 ± 0.011 | 1.311 ± 0.009 |
| C(3)-N(2) | 1.331 ± 0.009 | 1.332 ± 0.014 | 1.313 ± 0.012 | 1.306 ± 0.009 |

TABLE 3. Atomic co-ordinates.

| (I) | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>X'</i> | $\sigma(X)$ | <i>Y'</i> | $\sigma(Y)$ | <i>Z'</i> | $\sigma(Z)$ |
|-------|------------|------------|------------|-----------|-------------|-----------|-------------|-----------|-------------|
| S(1) | 0.2531 | 0.1850 | 0.1804 | 2.587 Å | 0.002 Å | 1.850 Å | 0.002 Å | 1.276 Å | 0.003 Å |
| C(1) | 0.3565 | 0.0590 | 0.2163 | 3.688 | 0.007 | 0.590 | 0.008 | 1.529 | 0.008 |
| C(2) | 0.4889 | 0.0896 | 0.2386 | 5.126 | 0.008 | 0.896 | 0.011 | 1.687 | 0.013 |
| N(1) | 0.3224 | -0.0659 | 0.2228 | 3.303 | 0.008 | -0.659 | 0.008 | 1.575 | 0.010 |
| H(1) | 0.3836 | -0.1342 | 0.2000 | 4.00 | 0.1 | -1.34 | 0.1 | 1.41 | 0.1 |
| H(2) | 0.1893 | -0.0914 | 0.2091 | 1.85 | 0.1 | -0.91 | 0.1 | 1.48 | 0.1 |
| H(5) | 0.5147 | -0.0122 | 0.2538 | 5.39 | 0.1 | -0.12 | 0.1 | 1.79 | 0.1 |
| H(6) | 0.5147 | 0.1466 | 0.3454 | 5.29 | 0.1 | 1.47 | 0.1 | 2.44 | 0.1 |
| H(7) | 0.5196 | 0.1276 | 0.1018 | 5.63 | 0.1 | 1.28 | 0.1 | 0.72 | 0.1 |
| (II) | | | | | | | | | |
| S(2) | -0.0365 | 0.1878 | -0.2756 | -0.077 | 0.002 | 1.878 | 0.002 | -1.949 | 0.003 |
| C(3) | 0.0644 | 0.0597 | -0.2678 | 1.030 | 0.007 | 0.597 | 0.008 | -1.894 | 0.008 |
| C(4) | 0.1851 | 0.0766 | -0.3284 | 2.436 | 0.009 | 0.766 | 0.010 | -2.322 | 0.011 |
| N(2) | 0.0393 | -0.0596 | -0.2080 | 0.680 | 0.007 | -0.596 | 0.008 | -1.471 | 0.008 |
| H(3) | 0.1224 | -0.1370 | -0.1610 | 1.545 | 0.1 | -1.37 | 0.1 | -1.13 | 0.1 |
| H(4) | -0.0809 | -0.0711 | -0.1389 | -0.73 | 0.1 | -0.71 | 0.1 | -0.98 | 0.1 |
| H(8) | 0.2068 | 0.1382 | -0.4460 | 2.82 | 0.1 | 1.38 | 0.1 | -3.15 | 0.1 |
| H(9) | 0.2362 | 0.1384 | -0.2188 | 2.87 | 0.1 | 1.38 | 0.1 | -1.55 | 0.1 |
| H(10) | 0.2106 | 0.0020 | -0.3692 | 2.77 | 0.1 | 0.02 | 0.1 | -2.61 | 0.1 |

TABLE 4. Thermal parameter (all units are 10^{-4} Å²).

| (I) | U_{11} | σ | U_{22} | σ | U_{33} | σ | U_{12} | σ | U_{23} | σ | U_{13} | σ |
|------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| S(1) | 278 | 9 | 257 | 11 | 665 | 15 | -6 | 10 | 39 | 11 | 84 | 9 |
| C(1) | 339 | 37 | 285 | 42 | 410 | 45 | -49 | 36 | -67 | 35 | 105 | 32 |
| C(2) | 215 | 35 | 416 | 61 | 1099 | 91 | -57 | 43 | -25 | 60 | 147 | 44 |
| N(1) | 353 | 35 | 235 | 40 | 1045 | 69 | -57 | 36 | -24 | 41 | 160 | 39 |
| (II) | | | | | | | | | | | | |
| S(2) | 259 | 9 | 252 | 11 | 751 | 17 | 6 | 9 | 77 | 11 | 99 | 10 |
| C(3) | 223 | 31 | 303 | 39 | 455 | 46 | -41 | 32 | -30 | 34 | 90 | 30 |
| C(4) | 343 | 39 | 517 | 58 | 707 | 62 | -18 | 47 | -85 | 50 | 232 | 41 |
| N(2) | 356 | 33 | 311 | 41 | 661 | 49 | 40 | 34 | 32 | 36 | 174 | 33 |

For all H atoms, isotropic U assumed 0.05 Å²; standard deviation found, 0.03 Å².

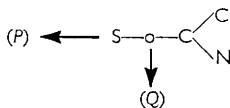
and $[c^*]$ axes respectively and with U_{12} , U_{23} , and U_{13} give the magnitude and orientation of the ellipsoid of vibration with respect to the crystallographic axes.

The co-ordinates in Table 3 give the bond lengths in Table 2 column (c); these are not the final bond lengths because they have not been corrected for systematic errors due to

rotational oscillation. The corrections are determined by analysis of the anisotropic thermal motion.

Analysis of the Anisotropic Thermal Motion.—A detailed description of the use of Cruickshank's⁹ methods for determining the correction for rotational oscillation has been given³ for the similar molecule, thiourea, so that only the results for thioacetamide will be quoted.

Molecular axes were chosen:



where *o* is the mass centre and (*R*) is the normal to the plane of the molecule.

For both molecules (I) and (II), the translational motion was the same (to 0.001 Å²), the mean square amplitudes of vibration being 0.032 Å² along (*P*), 0.025 Å² along (*Q*), and 0.039 Å² along (*R*), so that the main translational motion is along the normal to the plane.

The rotational motions of the two molecules are not significantly different (standard deviation 1°) about (*R*) for which the r.m.s. angular oscillations are 3.6° and 4.2° for (I) and (II) respectively, nor for those about (*Q*) which are 7.9° and 8.9°. However, for molecule (I) the largest rotational oscillation is about (*P*) with a r.m.s. value of 9.5° while

TABLE 5. *Molecular dimensions.*

| (I) | Å | | (II) | Å | | | |
|--------|---------------|-------------|---------------|---------|---------------|--------------|---------------|
| C-S | 1.710 ± 0.008 | S-C-C | 119.7° ± 0.6° | C-S | 1.716 ± 0.008 | S-C-C | 121.7° ± 0.6° |
| C-C | 1.497 ± 0.011 | S-C-N | 121.7 ± 0.6 | C-C | 1.490 ± 0.011 | S-C-N | 121.6 ± 0.6 |
| C-N | 1.324 ± 0.011 | C-C-N | 118.6 ± 0.7 | C-N | 1.323 ± 0.012 | C-CN | 116.7 ± 0.7 |
| N-H(1) | 1.0 ± 0.1 | C-N-H(1) | 116 ± 6 | N-H(3) | 1.2 ± 0.1 | C-N-H(3) | 119 ± 5 |
| N-H(2) | 1.5 ± 0.1 | C-N-H(2) | 117 ± 4 | N-H(4) | 1.5 ± 0.1 | C-N-H(4) | 115 ± 4 |
| | | H-N-H | 125 ± 7 | | | H-N-H | 122 ± 6 |
| C-H(5) | 1.1 ± 0.1 | C-C-H(5) | 93 ± 6 | C-H(8) | 1.1 ± 0.1 | C-C-H(8) | 128 ± 5 |
| C-H(6) | 1.0 ± 0.1 | C-C-H(6) | 112 ± 6 | C-H(9) | 1.1 ± 0.1 | C-C-H(9) | 104 ± 5 |
| C-H(7) | 1.2 ± 0.1 | C-C-H(7) | 114 ± 6 | C-H(10) | 0.9 ± 0.1 | C-C-H(10) | 111 ± 7 |
| | | H(5)-C-H(6) | 117 ± 8 | | | H(8)-C-H(9) | 95 ± 7 |
| | | H(5)-C-H(7) | 107 ± 7 | | | H(8)-C-H(10) | 96 ± 8 |
| | | H(6)-C-H(7) | 113 ± 8 | | | H(9)-C-H(10) | 125 ± 8 |

for molecule (II) there is no oscillation about this axis. The motion of molecule (I), with the principal oscillation about the C-S bond as axis is similar to that of thiourea; the behaviour of (II) is hard to understand, the only obvious difference between the environments of the two molecules being the proximity of (II) to the centrosymmetrically related one (see Fig. 1).

The corrections to the bond lengths for (I) are C-S + 0.0175, C-N + 0.0163, C-C + 0.0179 Å, and for (II) C-S + 0.0220, C-N + 0.0096, C-C + 0.0107 Å.

Molecular Dimensions.—Table 5 shows the corrected values for the bond lengths between the heavy atoms, the uncorrected values for bonds to hydrogen atoms, and the corresponding standard deviations; the bond angles and their standard deviations, which are not significantly affected by the corrections, are also given. The independent values for the two molecules agree; the final mean values and their standard deviations in parentheses are in Fig. 2.

For clarity the hydrogen atoms of the methyl groups have been omitted; for these the mean C-H distance is 1.04 Å and the angles do not differ significantly from those of a regular tetrahedron. The standard deviations do not allow for uncertainties in the corrections for rotational oscillation.

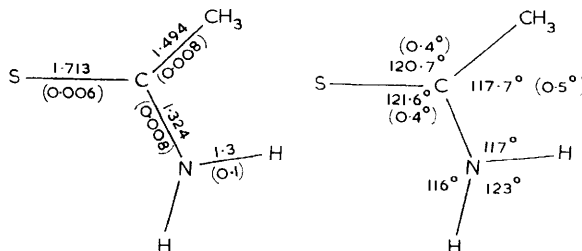
⁹ Cruickshank, *Acta Cryst.*, 1956, **9**, 754, 757.

Both molecules are planar, except for the hydrogen atoms of the methyl groups. For (I) the equation of the plane S-C-C-N (related to the orthogonal axes parallel to $[a]$, $[b]$, and $[c^*]$) is:

$$0.1304X' - 0.0783Y' - 0.9884Z' + 1.0720 = 0$$

the maximum deviation of any heavy atom from this plane being 0.005 \AA ; for the amine hydrogen atoms the departures from the plane are $+0.30 \text{ \AA}$ for H(1) and -0.07 \AA for H(2),

FIG. 2.



the former being just significant. One of the hydrogen atoms, H(5), of the methyl group also lies in this plane (deviation $+0.01 \text{ \AA}$).

For molecule (II) the plane is given by the equation:

$$0.2515X' + 0.2593Y' + 0.9325Z' + 1.3528 = 0$$

with a maximum deviation of 0.003 \AA for the heavy atoms, $+0.32 \text{ \AA}$ for H(3), and $+0.07 \text{ \AA}$ for H(4); these results are similar to those for (I) but the methyl groups are oriented differently: none of the hydrogen atoms lies in the plane, H(9) is at $+1.0 \text{ \AA}$, and the other two at -0.4 and -0.5 \AA .

The angle between the normals to the two molecular planes is 24.6° .

All the intermolecular contacts of less than 3.5 \AA were calculated: the shortest ones of various categories and those connected with $S \cdots H-N$ hydrogen-bonding are shown in Table 6.

TABLE 6. *Interatomic distances and angles in possible N...S hydrogen bonds.*

| | | | |
|--|--------------------------|-----------------------------|--------------------------|
| (Single primes refer to atoms in molecules at positions $-x/a$, $-y/b$, $-z/c$, and double primes to molecules at $\frac{1}{2} - x/a$, $\frac{1}{2} + y/b$, $-z/c$.) | | | |
| S(2)'-H(2) 2.07 Å | S(2)'-N(1)-S(2)'' 111.4° | S(1)'-H(4) 2.20 Å | S(1)'-N(2)-S(1)'' 110.3° |
| S(2)''-H(1) 2.46 | S(2)'-H(2)-N(1) 155° | S(1)''-H(3) 2.27 | S(1)'-H(4)-N(2) 142° |
| S(2)'-N(1) 3.469 | S(2)''-H(1)-N(1) 158° | S(1)'-N(2) 3.504 | S(1)''-N(3)-N(2) 137° |
| S(2)''-N(1) 3.396 | | S(1)''-N(2) 3.420 | |
| <i>Shortest intermolecular distances (Å)</i> | | | |
| S-S or C > 3.5 | S(2)-H(4) 3.26 | N-N | N(2)'-N(2) 3.454 |
| S-H on N, not H-bonded, | S(1)-H(8) 2.85 | N-H on N | N(2)'-H(4) 2.78 |
| S-H in CH ₃ group, | | N-H in CH ₃ | N(1)''-H(9) 3.03 |
| C-C or N > 3.5 Å | | H on N-H on N | H(2)'-H(4) 2.0 |
| C-H on N | C(3)'-H(4) 2.89 | H on N-H in CH ₃ | H(1)'-H(7) 2.6 |
| C-H in CH ₃ | C(2)'-H(7) 3.26 | H on C-H on C | H(5)'-H(7) 2.8 |

DISCUSSION

The structure as a whole consists of layers of planar molecules probably held by $N-H \cdots S$ hydrogen-bonds within the layers and by van der Waals forces between the layers. Because the standard deviations in the positions of the hydrogen atoms are large, the existence of hydrogen bonds is not proved conclusively but their presence would explain the comparatively poor packing and the interatomic distances observed. Pauling's

values¹⁰ for the van der Waals radii of hydrogen, nitrogen, and sulphur are 1.0—1.4, 1.5, and 1.85 Å respectively. The minimum H···H distance, 2.0 Å, and the S···H (CH₃), 2.85 Å, agree with these values whereas the average S···H which might be bonded is 2.2 Å. The hydrogen atoms do not lie on the line joining the sulphur and nitrogen atoms because they are displaced by 0.3—0.4 Å from the S'—N—S'' plane; a similar departure from linearity is common in hydrogen-bonded structures.

Apart from the statistical standard deviation, the agreement between the independent values for the bond lengths between the heavy atoms leads to the conclusion that they are reliable to at least 0.01 Å; it is not surprising that the agreement between the bond angles is less good because angles are more readily deformed by environmental factors. The crystal structures of four thioamides^{1,2,3} have now been determined, but only for thiourea and thioacetamide have the anisotropic thermal motions been determined and the consequent systematic errors corrected; experience has shown that these have such comparatively large effects on the molecular dimensions that, at present, we can only say that for the other thioamides the carbon–nitrogen and carbon–sulphur bond lengths do not differ significantly from those in thioacetamide.

The C–S and C–N bond lengths in thioacetamide are the same as those (1.713 and 1.329 Å respectively) found in thiourea at room temperature by Kunchur and Truter.³ Other values (1.61 and 1.28 Å) for thiourea have been reported by Zvonkova and Tashpulatov;¹¹ the large difference probably arises through omission by the Russian workers of corrections for finite series effects and through neglect of the anisotropic thermal motion and corrections for systematic errors. Although the agreement index is not an absolute guide to the accuracy of structure determinations, the difference between their value of *R* (0.23) and ours (0.11) suggests that our results, which are supported by White's¹² results for thiourea at 121° K, are more reliable.

As more accurate bond lengths become available it is apparent that bond order–bond length relations must be reappraised along the lines originally suggested by Coulson¹³ and elaborated by Dewar and Schmeising,¹⁴ Brown,¹⁵ and others. There are now sufficient results¹⁶ of high accuracy (reliable to at least 0.01 Å) for some carbon bond lengths to indicate that the apparent single-bond radius of a carbon atom in a bond C–X depends (*a*) upon its state of hybridisation, (*b*) upon the electronegativity of X, and (*c*) upon the other atoms bound to it. Although for carbon–carbon bonds a consistent scheme can be proposed¹⁵ on the basis that the single-bond radii are 0.773 Å for *sp*³, 0.733 Å for *sp*², and 0.687 Å for *sp*-hybridisation, the same values for the radii do not give the observed carbon–hydrogen and carbon–chlorine bond lengths. The useful concept of fixed radii may have to be replaced by a series of standard bond lengths between atoms in specified hybridisations.

Application of these new ideas to thioamides suggests that the structures of thioacetamide and thiourea correspond to the purely amide forms, S=C(CH₃)·NH₂ and S=C(NH₂)·NH₂. The trigonal arrangement of bonds about the central carbon atom indicates *sp*²-hybridisation. The carbon–carbon bond length (1.494 ± 0.008 Å) does not differ significantly from a single C(*sp*²)–C(*sp*³) bond length (1.505 Å). If we postulate that 1.325 Å (±0.005 Å) is the C(*sp*²)–N(*sp*²) single-bond length while 1.713 Å represents a double bond C(*sp*²)=S(?) in both compounds, the total bond order round the central carbon atom is four. This simple hypothesis has the advantage not only of agreeing with the latest interpretation⁵ of the infrared spectra of thiourea, thioacetamide, and the corresponding cations, but also of removing an anomaly in the bond lengths of amides.

¹⁰ Pauling, "The Nature of the Chemical Bond," Cornell University Press, 1945.

¹¹ Zvonkova and Tashpulatov, *Kristallografia*, 1958, **3**, 553.

¹² White, 1959, personal communication.

¹³ Coulson, "Contribution a l'Étude de la Structure Moleculaire," Victor Henri, Desoer, Liège, 1948.

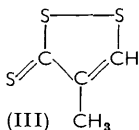
¹⁴ Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166.

¹⁵ Brown, *Trans. Faraday Soc.*, 1959, **55**, 694.

¹⁶ "Interatomic Distances," Chem. Soc. Special Publ. No. 12, 1958.

For these the average value¹⁶ of C-N is $1.322 \pm 0.003 \text{ \AA}$; if this represents a pure single bond then the carbon-oxygen bonds should be pure double bonds and it is no longer surprising that their average length, 1.23 \AA , is the same as the C=O distance in ketones and in carboxylic acids and esters.¹⁶

Because the new ideas do not postulate double-bond character for the carbon-nitrogen bonds it is not possible to explain the trigonal hybridisation of the nitrogen atoms in amides and thioamides by delocalisation of the lone-pair electrons to take part in the π -bond system; a similar difficulty arises in explaining the planarity of the oxalate ion, oxamide, and butadiene if their central bonds are regarded as single bonds and this problem



is still unresolved (but it is likely that there is interaction between the isolated π -bond systems or between the π -bonds and the lone pair electrons). There is only one experimental observation at variance with the proposed standard bond length for a C(sp^2)=S(?) double bond and that is a value of 1.627 \AA in 4-methyl-1,2-dithiacyclopent-4-ene-3-thione (III);¹⁷ in this compound, however, the carbon (sp^2) atom is not bonded to a nitrogen atom, so the difference may be another example of the change in one bond length when the substituents on one of the atoms is changed.¹⁸

More investigations of high accuracy are required to solve the problems raised by the new theories.

EXPERIMENTAL

Thioacetamide recrystallised from benzene as colourless acicular crystals. A film of Vaseline, so thin that it did not produce a diffraction halo, was effective in preventing decomposition of the crystal under the combined influence of air and X-rays.

The unit-cell dimensions were measured by the Straumanis method. The crystals were approximately spherical and 0.2 mm. in diameter; no absorption correction was applied.

Equi-inclination Weissenberg photographs were taken about the three principal axes for all the available layer lines (*i.e.*, up to $6kl$, $h6l$, and $hk4$); of the 1407 possible reflections 927 gave measurable intensities. A multiple-film technique was used and the intensities of the spots were estimated visually with the aid of a calibration strip. Lorentz and polarisation factors were applied by use of a Cochran chart. For the ($hk0$) reflections the approximate scale factor was obtained by Wilson's method.¹⁹ After two-dimensional refinement this scale was adjusted to make $\sum |F_o| = \sum |F_c|$, and the absolute values of F_o^2 were used to correlate and reduce to an approximately absolute scale the observed arbitrary values of F_{hk}^2 ; during three-dimensional refinement the scale factor was one of the parameters.

The first stage of the three-dimensional anisotropic refinement was carried out with McWeeny's scattering factors²⁰ for carbon and nitrogen, and James and Brindley's⁶ for sulphur; the co-ordinates were refined by differential Fourier syntheses with back-shift corrections for finite series errors and the thermal parameters by Cruickshank's method,²¹ the equations given in Section 3 of his paper being used. These computations were carried out on the Manchester University electronic computer with programmes devised by Dr. D. W. J. Cruickshank and Miss D. E. Pilling. In the second stage the scattering factors used were those of Tommie and Stam⁷ for sulphur and Berghuis *et al.*²² for the other atoms. Refinement was carried out by the method of least squares on the Leeds University Pegasus computer with programmes devised by Dr. D. W. J. Cruickshank and Miss D. E. Pilling. The function minimised was $R' = \sum w(|F_o| - |F_c|)^2$ where the weighting factor, w , was at first taken as $1/|F_o|$. It was modified by using the criterion that R'/n , where n is the number of planes within a given range of $|F_o|$, should be constant for different ranges; this criterion was satisfied by $w = 1/(8|F_o| + 0.3|F_o|^2)$ for the observed planes and $1/30$ for the unobserved planes.

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¹⁷ Jeffrey and Shiono, *Acta Cryst.*, 1959, **12**, 447.

¹⁸ Sutton, *Tetrahedron*, 1959, **5**, 118.

¹⁹ Wilson, *Nature*, 1942, **150**, 152.

²⁰ McWeeny, *Acta Cryst.*, 1951, **4**, 51.

²¹ Cruickshank, *ibid.*, 1956, **9**, 747.

²² Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *ibid.*, 1955, **8**, 478.

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