517. *A Detailed Refinement of the Crystal and Molecular Structure of Thiourea.*

By N. R. Kunchur and Mary R. Truter.

A three-dimensional *X*-ray crystal-structure analysis of thiourea has been made. The anisotropic thermal motion has been analysed and the bond lengths corrected for systematic errors arising from rotational oscillations of the molecule. The sulphur, carbon, and nitrogen atoms in each molecule are coplanar, with bond lengths C–N = 1·33 ± 0·01 Å and C–S = 1·71 ± 0·01 Å, and angles S–C–N = 122·2° ± 0·6° and N–C–N = 115·6° ± 1·1°.

Thiourea is conventionally written $S{=}C(NH_2)_2$ but its reactions show that the zwitterion $^{-}S{-}C({=}NH_2^{+})NH_2$ must also be considered. The Raman spectrum[1] of the solid has been interpreted as indicating that the ionic form is predominant; on the other hand the approximate bond lengths,[2] C–S = 1·64 and C–N = 1·35 ± 0·1 Å, are confusing because both seem to show a good deal of double-bond character. A refinement of the *X*-ray analysis of this simple molecule has therefore been undertaken in order to provide more accurate bond lengths for comparison with theory and also with the bond lengths in co-ordination compounds containing thiourea.[3]

Wyckoff and Corey[2] found that there were four molecules in the orthorhombic unit cell ($a = 7{\cdot}68$, $b = 8{\cdot}57$, $c = 5{\cdot}50$ Å) with space group $Pnma{-}D_{2h}^{16}$. (For convenience Wyckoff and Corey's *b* and *c* axes have been interchanged to conform with the space-group orientation in the International Tables.[4]) In each molecule the carbon and the sulphur atom lie on a mirror plane with the two equivalent nitrogen atoms on either side of it. The co-ordinates determined by two-dimensional analysis were C, 0·10, $\frac{1}{4}$, −0·14; S, −0·007, $\frac{1}{4}$, 0·12; N, 0·13, 0·125, $-0{\cdot}27_8$. The molecule was planar within the limits of experimental error.

Isotropic Refinement by Three-dimensional Methods.—The intensities of the 260 reflections observable with copper radiation were measured; few spots of high values of sin θ were observed so that very little additional information could have been obtained by the use of radiation of shorter wavelength at room temperature. Preliminary calculation showed good agreement between the observed structure amplitudes, $|F_{obs}|$, and those calculated from Wyckoff and Corey's co-ordinates which were therefore taken as a starting point for three-dimensional analysis. The atomic scattering factors used were those given by McWeeny[5] for carbon and nitrogen and by James and Brindley for sulphur,[6] multiplied by a temperature factor $\exp(-B \sin^2\theta/\lambda^2)$. This theoretical scattering factor for sulphur was chosen in preference to empirical values[7] determined more recently because the latter are not independent of the anisotropic thermal motion and bonding in the structures from which they were derived.

The co-ordinates were refined in three successive stages by calculation of differential syntheses[8] with a back-shift correction for finite-series effects, and at each stage the

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[1] Kohlrausch and Wagner, *Z. phys. Chem.*, 1940, *B*, **45**, 229.

[2] Wyckoff and Corey, *Z. Krist.*, 1932, **81**, 386.

[3] Truter, *Acta Cryst.*, 1957, **10**, 785.

[4] " International Tables for *X*-ray Crystallography," 1952, Kynoch Press, London.

[5] McWeeny, *Acta Cryst.*, 1951, **4**, 51.

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

[7] Cox, Gillot, and Jeffrey, *Acta Cryst.*, 1949, **2**, 356; Abrahams, *ibid.*, 1955, **8**, 661.

[8] Booth, *Trans. Faraday Soc.*, 1946, **42**, 444.

scale and temperature factors were altered to make the observed and calculated mean curvatures and peak values of the electron-density distributions more nearly equal. (Because of the uncertainty in their structure amplitudes, planes which gave reflections too weak to be observed were omitted from the refinement.) These refinement operations and their results are summarised below {R is the agreement index,

	B (Å^2)				
Cycle	sulphur	nitrogen	carbon	R	Max. co-ordinate shift (Å)
1	4·0	4·0	4·0	0·20	0·18
2	3·5	4·5	4·5	0·16$_3$	0·04
3	3·5	4·5	4·24	0·15$_8$	0·01

$\sum|(|F_{obs}| - |F_{calc}|)|/\sum|F_{obs}|$}. The smallness of the co-ordinate shifts in the last cycle showed that no further improvement was possible by isotropic refinement, even though (as the figures below show) the mean B factor for carbon had not yet been adjusted to its best value. However, the need for anisotropic adjustment of the parameters was shown by the variation with direction of the observed curvature of the electron density in each atom; in the Table below r_x, r_y, and r_z are respectively the ratios of the observed curvatures, $\partial^2\rho/\partial x^2$, $\partial^2\rho/\partial y^2$, and $\partial^2\rho/\partial z^2$, to the corresponding calculated curvatures; ρ is the peak electron density:

	ρ_{obs}/ρ_{calc}	r_x	r_y	r_z
C	1·01	1·06	1·10	1·14
S	0·98	0·92	0·99	1·09
N	0·94	0·85	1·03	1·01

It can be seen that for all atoms r_x is smaller than the other two ratios, which indicates that the thermal motion is greatest in the direction of the a axis, *i.e.*, the axis which is most nearly normal to the planes of the molecules.

Determination of the Anisotropic Thermal Parameters.—A method of successive refinement for determining anisotropic thermal-motion parameters has been described by Cruickshank,[9] who also gives the refinement equations.

After three cycles of anisotropic refinement the agreement index was reduced to 0·112, the following parameters, which resulted from the third cycle, being used to calculate the structure factors:

	x/a	y/b	z/c	b_{33} ($\times 10^5$)	b_{23} ($\times 10^5$)	b_{22} ($\times 10^5$)	b_{13} ($\times 10^5$)	b_{12} ($\times 10^5$)	b_{11} ($\times 10^5$)
C	0·09151	0·25000	$\bar{0}\cdot\overline{16278}$	1161	0	1331	2115	0	1140
S	$\bar{0}\cdot\overline{00726}$	0·25000	0·11400	1770	0	1069	266	0	1789
N	0·13160	0·12011	0·27742	3885	819	1011	3026	$\overline{173}$	2941

The figures given are those actually used, although, as shown below, they are not all significant. The parameters b_{ij} for each atom were used in the expression exp $(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)$ to give the temperature factor for each *hkl*. A list of observed and calculated structure factors is given in Table 1; the scale factor, obtained by the criterion given above, also made $\sum|F_{obs}|$equal to $\sum|F_{calc}|$ where the summations are over all planes allowing for multiplicity. The poor agreement for the planes (020), (200), and (101) may be due to extinction; if these planes are omitted the scale factor is altered by 0·3% and the agreement index R is reduced to 0·109.

A fourth differential synthesis was carried out and the maximum change required in the atomic co-ordinates was 0·005 Å (in x_N). The final co-ordinates and their standard deviations (calculated from Cruickshank's formula [10]) are:

	x/a	y/b	z/c	x (Å)	$\sigma(x)$ (10^3 Å)	y (Å)	$\sigma(y)$ (10^3 Å)	z (Å)	$\sigma(z)$ (10^3 Å)
C	0·0916	0·2500	$\bar{0}\cdot\overline{1632}$	0·701	8	2·134	0	$\bar{0}\cdot\overline{901}$	13
S	$\bar{0}\cdot\overline{0073}$	0·2500	0·1138	$\bar{0}\cdot\overline{056}$	2	2·134	0	0·628	2
N	0·1322	0·1201	$\bar{0}\cdot\overline{2767}$	1·012	11	1·025	10	$\bar{1}\cdot\overline{527}$	11

The standard deviation of the electron density is 0·2e/Å^3.

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[9] Cruickshank, *Acta Cryst.*, 1956, **9**, 747.

[10] *Idem, ibid.*, 1949, **2**, 65.

TABLE 1.

hkl	F (calc.)	F (obs.)
000	(160)	—
020	−66	44
040	17	17
060	−31	27
080	28	20
0, 10, 0	−9	7
200	51	43
210	−38	37
220	−46	42
230	−14	20
240	35	37
250	—	—
260	−22	20
270	10	10
280	14	10
290	−4	3
2, 10, 0	−9	7
400	—	—
410	—	—
420	−21	20
430	—	—
440	29	27
450	—	—
460	−11	10
470	—	—
480	4	3
490	—	—
4, 10, 0	−6	3
600	13	10
610	10	10
620	−10	10
630	—	—
640	7	7
650	—	—
660	−7	7
670	−5	3
680	5	3
800	10	7
810	6	3
820	−7	7
830	−6	7
840	—	—
850	5	3
101	41	34
111	—	—
121	−40	37
131	5	7
141	31	30
151	—	—
161	−18	17
171	—	—
181	11	10
191	—	—
1, 10, 1	−7	7
301	26	27
311	—	—
321	−22	25
331	4	7
341	16	18
351	—	—
361	−13	14
371	—	—
381	9	10
501	15	14
511	—	—
521	−11	10
531	—	—
541	8	8
551	—	—
561	−7	8
701	7	7
711	4	5
721	−7	8
731	—	—
741	6	6
002	−33	30
022	−1	7
042	18	17
202	5	7
212	21	24
222	—	—
232	10	10
242	—	—
252	—	—
262	—	—
272	−9	9
402	17	17
103	−18	17
113	—	—
123	24	24
133	−7	7
143	−22	24
153	—	—
163	11	14
173	—	—
183	−6	7
303	−16	17
313	—	—
323	11	10
333	−9	10
343	− 8	10
353	5	7
363	8	10
503	−8	10
004	−19	17
024	26	27
044	−28	27
064	15	14
084	−7	7
204	−24	20
214	—	—
224	21	20
234	—	—
244	−15	15
254	—	—
264	13	7
404	−18	17
414	—	—
424	12	14
434	—	—
444	−7	7
454	—	—
464	8	3
604	−6	7
614	—	—
624	—	—
634	—	—
644	−8	8
105	−20	17
115	—	—
125	13	14
135	—	—
145	−9	10
305	−10	12
315	—	—
325	12	12
335	—	—
345	−11	14
505	−8	7
515	—	—
525	10	7
535	—	—
545	−10	10
011	14	14
031	39	38
051	−23	20
201	50	47
211	−23	25
221	−11	7
231	16	18
241	−12	12
251	−13	11
261	−7	7
271	10	9
281	10	10
291	−6	7
401	6	8
411	−33	30
421	−9	10
431	9	10
441	8	10
451	−9	10
461	−4	3
471	14	14
601	−4	3
611	−13	14
621	—	—
631	14	15
641	7	7
651	−10	8
661	—	—
671	—	—
681	−2	3
102	2	3
112	−34	41
122	−9	7
132	19	17
142	9	10
152	−17	17
162	—	—
172	16	15
182	—	—
192	−8	10
302	6	7
312	−29	30
322	−12	10
332	28	27
342	12	14
352	−20	20
362	—	—
372	12	14
382	—	—
392	−9	8
502	6	7
512	−21	20
522	—	—
532	23	20
542	—	—
552	−17	15
562	—	—
572	10	10
702	—	—
712	−12	10
722	—	—
732	10	10
013	−37	41
033	12	14
053	−11	14
073	16	17
093	−9	8
203	−11	14
213	−22	25
223	—	—
233	22	20
243	12	14
253	−17	17
263	—	—
273	10	14
283	—	—
293	−7	7
403	6	7
413	−13	14
423	—	—
433	21	20
443	—	—
453	−16	17
603	6	10
613	−11	14
623	—	—
633	7	7
104	—	—
114	−8	7
124	—	—
134	13	10
144	—	—
154	−9	9
304	—	—
314	—	—
324	—	—
334	—	—
344	−7	8
015	7	7
106	—	—
116	10	11
126	—	—
136	−12	10
146	—	—
156	9	7
306	—	—
316	13	13
506	—	—
516	9	8

The peak value of the electron density for each atom is given below together with the ratios of the observed and calculated values of the electron densities and curvatures.

	ρ_{obs} ($e/\text{Å}^3$)	ρ_{obs}/ρ_{calc}	r_x	r_y	r_z
C	7·0	0·95	1·00	1·00	0·97
S	28·0	1·00	1·00	0·99	1·02
N	7·2	1·01	1·00	0·99	0·98

The ratios still differ slightly from unity, and the final thermal parameters (all $\times 10^3$) quoted below have been obtained by calculating the changes corresponding to the differences between the observed and calculated curvatures.

	b_{33}	b_{23}	b_{22}	b_{13}	b_{12}	b_{11}	$\sigma(b_{33})$	$\sigma(b_{22})$	$\sigma(b_{11})$
C	14	0	13	28	0	11	8	2	3
S	18	0	11	3	0	18	2	0·4	0·6
N	40	8	10	32	$\bar{1}$	29	8	2	3

The standard deviations, $\sigma(b_{ii})$, are derived from the expression:

$$\sigma^2(b_{ii}) = \{\tfrac{6}{5}\textstyle\sum h_i^4\ \sigma^2(\mathrm{F})\}/(\textstyle\sum h_i^4 \mathrm{f})^2$$

given by Cruickshank,[9] in which f is the scattering factor and $\sigma^2(\mathrm{F})$ is taken as $(|\mathrm{F}_{\text{obs}}| - |\mathrm{F}_{\text{calc}}|)^2$.

Analysis of the Anisotropic Thermal Motion.—Cox, Cruickshank, and Smith [11] have

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[11] Cox, Cruickshank, and Smith, *Nature*, 1955, **175**, 766.

shown that rotational oscillations of molecules can give rise to systematic errors in bond lengths determined by *X*-ray methods, so that an analysis of the thermal motion of the molecule is necessary before the final corrected bond lengths can be given.

The mean square amplitudes of vibration of an atom in any direction can be represented by the radius of an ellipsoid; the magnitudes and orientation of the axes of this ellipsoid can be calculated from the six numbers b_{ij}. In the direction of the unit cell edge of length a_i the mean square amplitude of vibration, μ_{ii}^2, is given by $\mu_{ii}^2 = b_{ii}a_i^2/2\pi^2$. The cross terms, μ_{ij}^2 ($\mu_{ij}^2 = b_{ij}a_ia_j/4\pi^2$, where $i \neq j$), are required with the three values of μ_{ii}^2 to determine the dimensions and orientation of the ellipsoid; only if the values of b_{ij} are zero will the axes of the ellipsoid be parallel to the crystallographic axes. From the six values of μ^2 for all atoms we can derive (*a*) the r.m.s. amplitudes and directions of maximum and minimum thermal vibration of each atom with respect to the crystallographic axes, (*b*) the same quantities with respect to a set of molecular axes, and (*c*) the r.m.s. amplitudes of angular oscillation and translational vibration of the molecule as a whole assuming it to be a rigid body.

(*a*) The maximum and minimum r.m.s. amplitudes of vibration, $\mu_{\text{max.}}$ and $\mu_{\text{min.}}$, derived from the lengths of the major and minor axes of the ellipsoids, and their direction cosines are given in Table 2 with, for comparison, the direction cosines of the normal to the molecular plane and of the bonds.

TABLE 2.

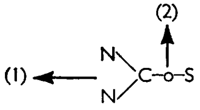
	μ_{max} (Å)	Direction	μ_{min} (Å)	Direction
C	0·232	(0·785, 0, 0·620)	0·040	(0·620, 0, $\bar{0}\cdot\bar{7}\bar{8}\bar{5}$
S	0·231	(0·992, 0, 0·129)	0·163	(0·129, 0, $\bar{0}\cdot\bar{9}\bar{9}\bar{2}$)
N	0·333	(0·812, ±0·057, 0·581)	0·169	(0·383, ±0·699, $\bar{0}\cdot\bar{6}\bar{0}\bar{4}$)
	Normal	(0·896, 0, 0·444)	C–S	(0·444, 0, $\bar{0}\cdot\bar{8}\bar{9}\bar{6}$)
			C–N	(0·237, 0·846, $\bar{0}\cdot\bar{4}\bar{7}\bar{8}$)
			C–N′	(0·237, $\bar{0}\cdot\bar{8}\bar{4}\bar{6}$, $\bar{0}\cdot\bar{4}\bar{7}\bar{8}$)

The angles between the various directions are

between μ_{max}(C) and normal, 12°
between μ_{max}(S) and normal, 19°
between μ_{max}(N) and normal, 10°

between μ_{min}(S) and C–S bond, 19°
between μ_{min}(N) and C–N bond, 14°

(*b*) Molecular axes were chosen thus:



with axis (3) as the normal to the molecular plane through the mass centre, o. Tensor transformations (Cruickshank [12]) gave the following mean square amplitudes U_{ij} (all in Å^2) referred to these axes:

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
C	0·004	0	$\bar{0}\cdot\bar{0}\bar{1}\bar{3}$	0·049	0	0·051
S	0·030	0	0·008	0·041	0	0·051
N	0·039	$\bar{0}\cdot\bar{0}\bar{1}\bar{0}$	$\bar{0}\cdot\bar{0}\bar{1}\bar{4}$	0·038	0·003	0·109
N′	0·039	0·010	$\bar{0}\cdot\bar{0}\bar{1}\bar{4}$	0·038	$\bar{0}\cdot\bar{0}\bar{0}\bar{3}$	0·109

From these we obtain the following r.m.s. amplitudes (in Å) of vibration:

along the normal, C, 0·227; S, 0·225; N, 0·330
along the C–S bond, C, 0·061; S, 0·172
along the C–N bond, C, 0·190; N, 0·173
perpendicular to the C–S bond in the molecular plane, C, 0·221; S, 0·202
perpendicular to the C–N bond in the molecular plane, C, 0·129: N, 0·211

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[12] Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

(*c*) For the molecule as a whole the tensors T (in Å^2) and ω (in radians^2) for the mean square amplitudes of the translational and rotational motions can be obtained by suitable transformations.[12] The values are:

T_{11}	T_{12}	T_{13}	T_{22}	T_{23}	T_{33}
0·0234	0	$\overline{0{\cdot}0098}$	0·0332	0	0·0515
ω_{11}	ω_{12}	ω_{13}	ω_{22}	ω_{23}	ω_{33}
0·0470	0	0·0020	0·000	0	0·0077

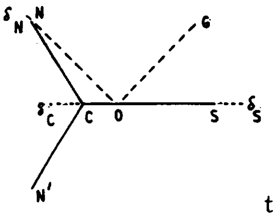
giving a r.m.s. angular oscillation of 5·0° about axis (3), 0° about (2), and 12·5° about (1), *i.e.*, the main oscillation is about an axis through the C–S bond. The r.m.s. amplitudes of translation are 0·153 Å along axis (1), 0·182 Å along (2), and 0·227 Å along (3).

The effect of rotational oscillation is to make an atom, P, appear closer to the centre of oscillation, O (taken as the mass centre), by a small distance δ which can be determined from the relation:[13]

$$\delta = \frac{1}{2r}\left\{\frac{s^2}{1 + s^2/q^2} + \frac{t^2}{1 + t^2/q^2}\right\}$$

where r is the uncorrected distance from O to P, $q^2 = \rho/(\delta^2\rho/\delta x_{ti}^2)$, and s^2 and t^2 are the mean square amplitudes of oscillation about two axes through O orthogonal to OP.

For carbon and sulphur $t^2 = \omega_{22}r^2$ and $s^2 = \omega_{33}r^2$, whence $\delta_C = 0{\cdot}0016$ Å and $\delta_S = 0{\cdot}0045$ Å and the correction to the C–S bond length is $+0{\cdot}006$ Å. For nitrogen $s^2 = \omega_{33}r^2$ and $t^2 = r^2\omega_{OG}$, where OG is perpendicular to ON in the plane of the molecule. ω_{OG}, calculated from ω_{11}, ω_{12}, ω_{22}, and the direction cosines of OG, has the value 0·0231 radians^2, whence $\delta_N = 0{\cdot}0189$ Å. The correction to the C–N bond is the component of δ_N along the bond minus the component of δ_C along the bond and is 0·018 Å.



Hydrogen Atoms.—When the anisotropic thermal motion for the other atoms had been determined, attempts were made to locate the hydrogen atoms. First the intermolecular N–S distances were calculated; the shortest N–S distance (see Figure) is 3·42 Å which, being longer than the sum of the van der Waals radii (3·35 Å), indicates that there is no hydrogen bonding, so that no deductions could be made in this way about the positions of the hydrogen atoms.

By analogy with urea[14] the hydrogen atoms would be expected to lie in the plane of the heavy atoms forming, with the carbon atom, a trigonal arrangement about the nitrogen atom; these positions have been designated H_1 and H_2. Another position consistent with trigonally hybridised nitrogen would be with the H–N–H plane perpendicular to the S–C–N–N′ plane; these positions are designated H_3 and H_4. However, three-dimensional values for $\rho_{obs} - \rho_{calc}$ at all four postulated hydrogen positions did not differ significantly from the standard deviation in the electron density (0·2e/Å^3) and calculation of structure factors with hydrogen atoms at either H_1 and H_2 or H_3 and H_4 with an isotropic $B = 5{\cdot}0$ Å^2 gave no change in the agreement index.

Hydrogen atoms in any position should be shown by a $\rho_{obs} - \rho_{calc}$ projection, the most favourable one being along the [010] axis on to the mirror plane. This projection was calculated and is shown in the Figure where the positions of the heavy atoms and the previously postulated hydrogen atoms are marked. In fact the only appreciable electron density, 1·7e/Å^2, is at $x/a = 0{\cdot}183$, $z/c = 0{\cdot}400$ and a line difference synthesis along y through this point showed peaks of 0·4 and 0·5e/Å^3 at $y/b = 3/4$ and 1/4 respectively, and some additional peaks of 0·2e/Å^3. The individual peaks are not of significant height and are 2 Å from the nearest atom (S).

These results suggest that the thermal motion of the hydrogen atoms is so large that

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[13] Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

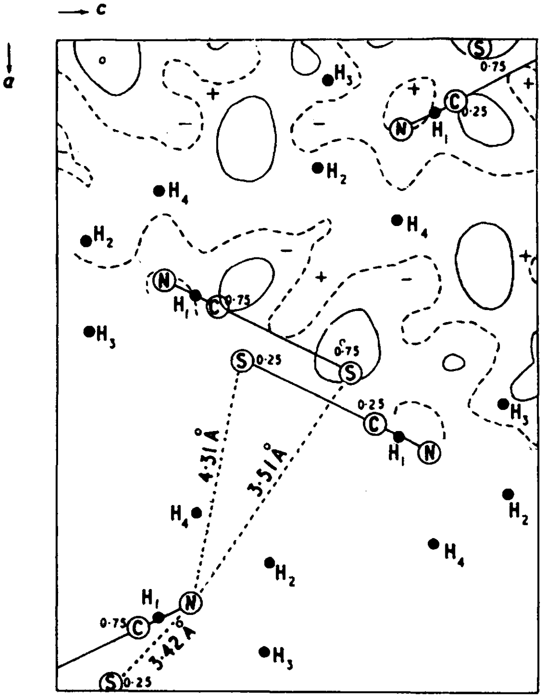
[14] Worsham, Levy, and Peterson, *ibid.*, 1957, **10**, 319; Vaughan and Donohue, *ibid.*, 1952, **5**, 530.

the peak electron density has been reduced to an insignificant level; completely free rotation, however, is not consistent with some preliminary nuclear magnetic resonance observations.[15]

Dimensions of the Molecule.—For comparison the bond lengths and angles and their standard deviations are given below after (*a*) isotropic refinement, (*b*) anisotropic refinement, and (*c*) correction for rotational oscillation:

	C–S (Å)	σ (Å)	C–N (Å)	σ (Å)	S–$\hat{\mathrm{C}}$–N	σ	N–$\hat{\mathrm{C}}$–N	σ
(*a*)	1·710	0·016	1·319	0·015	123·0°	0·8°	114·0°	1·6°
(*b*)	1·707	0·012	1·311	0·012	122·2	0·6	115·6	1·1
(*c*)	1·713	0·012	1·329	0·012	122·2	0·6	115·6	1·1

The molecule is accurately planar, the deviation from the plane being less than 0·0003 Å for all atoms other than hydrogen. The values of σ are derived from the estimated standard deviations in the atomic co-ordinates and do not allow for possible uncertainties in the corrections for rotational oscillation. Final values for the bond lengths are S–C = 1·71 ± 0·01 Å and C–N = 1·33 ± 0·01 Å, and for the angles S–C–N = 122·2° ± 0·6° and N–C–N = 116° ± 1°.



Difference projection along [010] *with contour intervals of* 1 e/Å². *The zero contour is dotted and contours are drawn over half the area only. For the carbon and sulphur atoms* y/b *is given. The shortest* N–S *separations are indicated.*

DISCUSSION

The carbon–sulphur (1·71 Å) and carbon–nitrogen (1·33 Å) bond lengths are significantly shorter than the generally accepted single-bond values, 1·82 and 1·475 Å, respectively. The double-bond lengths are not known accurately. For the carbon–nitrogen bond in *s*-triazine the order of which is at least 1·50, Lancaster and Stoicheff[16] obtained a very accurate value of 1·338 ± 0·001 Å, which is the same, within the limits of error, as in thiourea. This suggests that structures (I) and (II) must make a large contribution to the bonding, but the short carbon–sulphur bond with a bond order greater than 1·0

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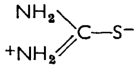
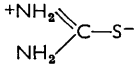
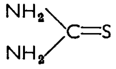
[15] Emsley and Smith, *Proc. Chem. Soc.*, 1958, 53.

[16] Lancaster and Stoicheff, *Canad. J. Physics*, 1956, **34**, 1016.

shows that there is also a contribution from the conventional form (III). Thus the apparent bonding capacity of the carbon atom is more than 4·0, a result which has been obtained for other π-bonded molecules and which indicates the need for a molecular-orbital treatment.


(I)


(II)


(III)

Davies and Hopkins[17] have recently carried out molecular-orbital calculations on urea, all the atoms of which, hydrogen included, have been shown experimentally[14] to be coplanar. They obtain the following results: (i) complete delocalisation of the two lone pairs of electrons on the nitrogen atoms being assumed, the bond order of both C–O and C–N is 1·50, and the agreement between the calculated delocalisation of resonance energy and Pauling's[18] empirical value is good; (ii) delocalisation of the lone pairs being assumed to be sufficient only to make the C–O bond order 1·60, which is the value found from force constants, the bond order calculated for C–N is 1·40 and the calculated resonance energy is smaller than Pauling's empirical value.

Since the carbon–nitrogen bond length in thiourea does not differ significantly from that in urea (1·35 Å) we may infer that the lone-pair electrons are delocalised to about the same extent in the two substances, but a detailed theoretical treatment of sulphur compounds is much more difficult than that of the corresponding oxygen compounds. Accordingly, and because few suitable data for comparison are available, further discussion will be deferred to a later paper in which accurate bond lengths for thioacetamide will be presented.

EXPERIMENTAL

Crystals of thiourea were grown from alcohol. The unit cell dimensions, determined by Straumanis's method from the reflections (501), (404), and (0, 10, 0), were found to be $a = 7{\cdot}655$, $b = 8{\cdot}537$, $c = 5{\cdot}520$ Å all $\pm$ 0·007 Å ($v = 360{\cdot}7$ Å^3). The density calculated for four molecules per unit cell is 1·399 g./c.c.; the observed value is 1·405 g./c.c. The absorption coefficient is 59·6 cm.$^{-1}$ and no absorption correction was made because very small crystals (diam. 0·1—0·15 mm.) were used.

Equi-inclination Weissenberg photographs were taken with Cu-K radiation about the three principal axes for all layer lines up to ($hk4$), ($4kl$), and ($h3l$). A multiple-film technique was used and the intensities were estimated visually by comparison with a calibration slip. After corrections for Lorentz and polarisation factors had been applied, the intensities from different layer lines were correlated and their square roots extracted to give structure factors on an arbitrary scale; the scale factor required to make these values absolute was one of the parameters refined. For structure factors determined by each of us independently R was 0·076.

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[17] Davies and Hopkins, *Trans. Faraday Soc.*, 1957, **53**, 1563.

[18] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1939, p. 197.