

Comparison of Photographic and Counter Observations for the X-ray Crystal Structure Analysis of Thiourea

BY MARY R. TRUTER*

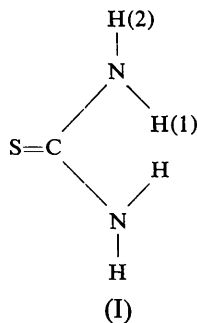
School of Chemistry, The University, Leeds 2, England

(Received 13 August 1966)

Complete three-dimensional observations at 20–25°C have been collected for thiourea, $S=C(NH_2)_2$, with an Arndt–Phillips linear diffractometer and $Mo\ K\alpha$ radiation. The results of refinement from these are compared with those from photographic observations and $Cu\ K\alpha$ radiation. There are no significant differences in the positions or anisotropic vibration parameters of the heavy atoms, S, C and N. Only one of the two crystallographically independent hydrogen atoms is unequivocally located, even with the counter observations. Molecular dimensions derived from counter observations are: S–C 1.720 ± 0.009 , N–C 1.34 ± 0.006 Å, S–C–N 120.5 ± 0.5 , N–C–N $119.0 \pm 0.5^\circ$. The hydrogen atoms are approximately coplanar with the heavy atoms.

Introduction

Thiourea (I) has been the subject of several structural investigations. The crystals are orthorhombic, $a=7.655$, $b=8.537$, $c=5.520$ Å, space group $Pnma$. The molecules lie with the C and S atoms in the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$, and the NH_2 groups are related by these planes.



In their X-ray investigation Kunchur & Truter (1958) used visually estimated intensities from photographs taken at room temperature about the three principal axes. Failure to locate the hydrogen atoms was attributed to large vibrations for these atoms. Subsequently Emsley & Smith (1961) deduced from a nuclear magnetic resonance study that the hydrogen atoms were coplanar with the rest of the molecule, as shown in (I), but that the molecules were undergoing hindered rotation about the C=S bond.

Investigation by electron diffraction (Dvoryankin & Vainshtein, 1960) on the solid at room temperature showed the hydrogen atoms to be nearly coplanar with the heavy atoms and indicated an r.m.s. amplitude of oscillation of these atoms about the C–N bond of 20–25°. It seemed possible that the hydrogen atoms could be located by X-ray methods with better obser-

vations. At low temperatures there is a ferroelectric structure in which the hydrogen atoms were located even by two-dimensional X-ray crystal structure analysis (Goldsmith & White, 1959).

In the present work, observations have been made with an Arndt & Phillips (1961) linear diffractometer, and the project incidentally provided information on the precision attainable with this instrument. Identical refinement procedures have been used for the counter and the photographic observations.

Measurements with the diffractometer

Molybdenum radiation from a stabilized source was used; the $K\alpha$ diffraction pattern was obtained by means of balanced zirconium and yttrium filters; measurements for each layer were made first with the zirconium filter then (on the following day) with the yttrium filter. Equality of the two readings for systematically absent reflexions served as a check that the balancing was satisfactory.

Crystals approximately cylindrical about any of the principal axes can be obtained. The absorption coefficient for $Mo\ K\alpha$ is 6 cm^{-1} and no absorption correction was applied. The diameter of each crystal was 0.7 mm, being limited by the need for the specimen to be bathed in the beam. Room temperature ranged from 20 to 25°C.

Different crystals were set about each of the three principal axes and all the available layers (*i.e.* 25 altogether) measured. All the quadrants were measured for each layer. With an oscillation angle of $2\frac{1}{2}^\circ$ and a scanning time of $\frac{1}{2}$ min, two measurements were made at each reciprocal lattice point.

The output tapes from the diffractometer were processed on the Leeds University Ferranti Pegasus computer with a program adapted by Smith (1962) from that devised by North (1964); the main adaptation was to adjust the standard deviations to allow for the number of successful readings. Another program written

* Present address: A.R.C. Unit of Structural Chemistry, Inveresk House, 346 Strand, London W.C.2, England.

by Smith was used to apply the usual factors to the intensities. The average values for the equivalent reflexions on each layer were calculated; the independent values did not differ from the mean by more than one standard deviation. The square roots of these average values were used for layer correlation by the Rollett & Sparks (1960) method with a computer program written by J. G. F. Smith. The independent values from the different crystals agreed within the standard deviation. The layer scaling factors lay in the range 0.65 to 1.0. An important feature was that about each axis they varied somewhat irregularly; the 'best' curve for the scaling factor as a function of the inclination angle was different for different crystals. Of the 440 possible independent structure amplitudes, 399 had intensities larger than the corresponding standard deviation; these were put approximately on the absolute scale by comparison with the 177 published values (Kunchur & Truter, 1958). The factor required was 0.5, and R for the common reflexions was 0.12.

From the standard deviations an experimental 'reliability index' was calculated as Σ (standard deviation)/ $\Sigma |F_o|$ and was 0.08.

Method of refinement

Refinement was carried out by the method of least squares on the computer with a program written by

Cruickshank & Pilling (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). The scattering factors used were those in *International Tables for X-ray Crystallography* (1962). The function minimized was $R' = \Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2$ where the weighting factor w was chosen by the criterion that the average value of $\Sigma w(\Delta F)^2$ should be approximately the same for different ranges of $|F_o|$. The scale factor was one of the parameters of the refinement.

Results of refinement with observations obtained photographically

Structure factors calculated with the published (Kunchur & Truter, 1958) parameters for S, C and N gave an R of 0.12. The hydrogen atoms were added in the positions found by electron diffraction (Dvoryankin & Vainshtein, 1960) with an isotropic temperature factor $\bar{U} = 0.06 \text{ \AA}^2$; R fell to 0.115. For (020) the value of $|F_o|$ was 45.5 and of $|F_c|$ 61.6; the discrepancy was attributed to extinction and the plane omitted from the next cycle for which R was 0.112. The weighting factor $1/|F_o|$ was found to be satisfactory. In the final cycle R was 0.111 and the parameters are shown in Tables 1 and 2.

Hamilton's (1965) test was applied to discover whether the improvement in R on addition of hydrogen atoms was statistically significant. There are 30 par-

Table 1. Atomic coordinates (\AA), with their standard deviations in the last digits shown in parentheses

	Uncorrected Photographic observations			Corrected for libration		
	x	y	z	x	y	z
S	-0.062 (6)	2.1342 (0)	0.623 (16)			
C	0.683 (20)	2.1343 (0)	-0.900 (20)			
N	1.009 (16)	1.021 (12)	-1.524 (14)		1.000 (14)	
H(1)	1.61 (34)	1.27 (23)	-2.63 (18)		1.26	
H(2)	0.94 (19)	0.19 (22)	-1.21 (16)		0.17	
	Counter observations					
S	-0.059 (3)	2.1343 (0)	0.631 (2)	-0.062		0.636
C	0.706 (8)	2.1343 (0)	-0.901 (9)	0.706		-0.903
N	1.001 (7)	0.999 (5)	-1.512 (6)	1.002	0.980	-1.515
H(1)	1.50 (9)	0.81 (9)	-2.10 (9)	1.50	0.79	-2.10
H(2)	0.58 (6)	0.20 (6)	-1.18 (6)	0.59	0.18	-1.18

Table 2. Vibration parameters (\AA^2), with the standard deviations in the last digits shown in parentheses

	Photographic observations					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S	0.055 (3)	0.046 (2)	0.029 (2)	—	—	0.005 (4)
C	0.040 (9)	0.042 (9)	0.038 (13)	—	—	0.028 (11)
N	0.097 (10)	0.039 (6)	0.065 (19)	-0.005 (7)	0.012 (8)	0.048 (8)
H(1)	$U(\text{iso}) = 0.14$ (12)					
H(2)	$U(\text{iso}) = 0.08$ (7)					
	Counter observations					
S	0.063 (1)	0.046 (1)	0.027 (1)	—	—	0.001 (1)
C	0.035 (4)	0.056 (5)	0.044 (5)	—	—	0.005 (3)
N	0.093 (4)	0.045 (3)	0.064 (4)	-0.003 (3)	-0.003 (3)	0.040 (3)
H(1)	$U(\text{iso}) = 0.08$ (4)					
H(2)	$U(\text{iso}) = 0.02$ (2)					

ameters with, and 22 parameters without, the hydrogen atoms, and the corresponding values of $R'' (= R'^{\pm})$ are 0.150 and 0.175. The ratio of the R'' values is 1.168 while a value of only 1.076 is required for a probability of 0.005, *i.e.* the chance that the extra parameters are meaningless is less than 0.5% and they may be taken as significant.

A molecular vibration analysis was carried out by hand, the equations solved being those of Cruickshank (1956). The translational tensors with respect to the crystallographic axes are, in \AA^2 , $T_{aa}=0.047$, $T_{bb}=0.045$, $T_{cc}=0.041$, $T_{ac}=0.015$, $T_{ab}=T_{bc}=0$; the translational motions are nearly isotropic. For the rotational oscillations the principal directions were also calculated. The maximum value of ω was 0.055 radian² about an axis 2° from the C-S bond, *i.e.* close to the axis with the minimum moment of inertia; the minimum value was -0.004 radian² along the normal to the molecular plane and the other value was 0.000 about the *b* axis. As the minimum value cannot be less than zero an uncertainty of at least ± 0.004 radian² is suggested and this seems reasonable in view of the standard deviations shown in Table 2.

From the positive value of ω the correction was applied by Cruickshank's (1961) method to the *y* coordinates of the nitrogen and hydrogen atoms. These corrected values are shown in Table 1 with an adjustment in the standard deviation to allow for the uncertainty in ω . The bond lengths and angles calculated from the corrected coordinates are shown in Table 3.

Table 3. Bond lengths and angles with their standard deviations

	Photographic observations	Counter observations
S-C	1.70 \pm 0.02 \AA	1.720 \pm 0.009 \AA
C-N	1.33 \pm 0.02	1.340 \pm 0.006
N-H(1)	1.29 \pm 0.18	0.80 \pm 0.09
N-H(2)	0.89 \pm 0.16	0.96 \pm 0.06
S-C-N	122 \pm 1°	120.5 \pm 0.5°
N-C-N	116 \pm 1	119.0 \pm 0.5
C-N-H(1)	111 \pm 10	114 \pm 5
C-N-H(2)	127 \pm 10	118 \pm 4
H(1)-N-H(2)	122 \pm 23	109 \pm 6

Results of refinement

with observations obtained by counter methods

Refinement started with the final parameters from the photographic data. For the first set of structure factors R was 0.15. The weighting factor was changed to $1/(5+|F_o|)$, 5 being the average standard deviation in the strong reflexions. Another cycle of refinement reduced R to 0.093 and three more cycles converged at $R=0.082$ to give the parameters shown in Tables 1 and 2.

The shortness of the N-H(1) bond, 0.8 \AA , and the large temperature factor for H(1) cast doubt upon the location of this atom. One cycle of refinement was

carried out with the hydrogen atoms omitted and the results used in Hamilton's (1965) test and in a Fourier difference synthesis. Comparison of R'' without hydrogen, 0.117, and with hydrogen, 0.093, indicated that the addition of these atoms was highly significant; the observed ratio is 1.245 while that calculated for a probability of 0.005 is 1.030. A three-dimensional Fourier difference synthesis was calculated on the KDF9 computer with a program written by Sime (1965). The most prominent feature was a peak of 0.7 $e.\text{\AA}^{-3}$ at the position of H(2). There were several peaks of 0.3 $e.\text{\AA}^{-3}$ one of which coincided with the position of H(1) but, as the troughs were -0.3 $e.\text{\AA}^{-3}$, H(1) is not unequivocally located in the difference map.

A molecular vibration analysis was carried out by hand. The translational tensors with respect to the crystallographic axes were, in \AA^2 , $T_{aa}=0.045$, $T_{bb}=0.048$, $T_{cc}=0.038$, $T_{ac}=0.03$, $T_{ab}=T_{bc}=0$. The principal axes of the rotational oscillation coincided with the axes of inertia; the values of the mean square oscillations were 0.052 radian² about the C-S bond, 0.010 radian² about an axis parallel to *b* and zero about the normal to the molecular plane. Corrections calculated by Cruickshank's (1961) method gave the coordinates in Table 1 from which are derived the bond lengths and angles in Table 3.

Discussion

The R value achieved with the counter data is consistent with the precision of the observations. It is comparatively high for counter data because the crystal used even at 0.7 mm was much less than the optimum size, giving low counts. For the plane (020) there is still some evidence for extinction; $|F_o|$ is 50.8 and $|F_c|$ is 58.1 while the average R value for planes with $|F_o| > 32$ is 0.05. The standard deviations obtained with counter data are less than those from the photographic observations partly because R is lower and partly because there are over twice as many observations, of which 100 are in the region available to Mo and not to Cu. Most of the extra observations have $|F_o| < 8$; for all planes with $|F_o| < 8$, $R=0.111$.

Although the two sets of observations have been obtained by different techniques with different radiations, there are no significant differences between the two sets of coordinate parameters for the heavy atoms, and only one possibly significant ($\Delta/\sigma=2.5$) difference in the vibration parameters, U_{11} for S. No absorption corrections were applied; μr was 0.2 for counter observations and 0.3-0.45 for photographic observations.

With the counter measurements the location of one hydrogen atom, H(2), is clear; for H(1) there is more doubt but, as the hydrogen atoms are unlikely to vibrate less than the nitrogen atom, for which $\bar{U}=0.07 \text{\AA}^2$, the value of \bar{U}_{iso} for H(1) is more reasonable than that of H(2). The mean isotropic temperature factor of the hydrogen atoms is 0.05 \AA^2 , which is close to the value 0.06 \AA^2 found by electron diffraction (Dvoryankin &

Vainshtein, 1960). Both hydrogen atoms take part in hydrogen bonds, H(1) in a bond of 3.54 Å from N to the S at $\frac{1}{2}+x, y, \frac{1}{2}-z$ and H(2) in a bond of 3.24 Å from N to the S at $-x, -y, -z$; thus the hydrogen atom in the shorter hydrogen bond has the lower vibration parameter. In the electron diffraction study H(2) was found to be 0.2 Å from the plane of the heavy atoms, the displacement being towards the sulphur atom to which it was bonded. A similar effect is found in this study but the displacement, +0.23 Å, is only possibly significant statistically. For H(1) the displacement from the plane is -0.18 Å, again towards the sulphur atom, but it is not statistically significant.

I am grateful to the Science Research Council for the linear diffractometer, to colleagues in the University of Leeds and in the University of Glasgow for the use of their crystallographic programs, to the authors of the Pegasus simulator program for KDF9, and to the Director of the Leeds University Computing Laboratory for computing facilities.

References

- ARNDT, U. W. & PHILLIPS, D. C. (1961). *Acta Cryst.* **14**, 807.
 CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem*. Oxford: Pergamon Press.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.
 DVORYANKIN, V. F. & VAINSHTEIN, B. K. (1960). *Kristallografia*, **5**, 589.
 EMSLEY, J. W. & SMITH, J. A. S. (1961). *Trans. Faraday Soc.* **57**, 1233.
 GOLDSMITH, G. J. & WHITE, J. G. (1959). *J. Chem. Phys.* **31**, 1175.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KUNCHUR, N. R. & TRUTER, M. R. (1958). *J. Chem. Soc.* p. 2551.
 NORTH, A. C. T. (1964). *J. Sci. Instrum.* **41**, 42.
 ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
 SIME, J. G. (1965). Personal communication.
 SMITH, J. G. F. (1962). Personal communication.

Acta Cryst. (1967). **22**, 559

The Crystal and Molecular Structure of the Monorubidium Salt of Furantetracarboxylic Acid

BY IAIN C. PAUL AND LESLIE L. MARTIN*

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801, U.S.A.

(Received 22 November 1965 and in revised form 23 August 1966)

The crystal structure analysis of the rubidium salt of furantetracarboxylic acid has been carried out on three-dimensional counter data collected on an automatic diffractometer. The salt crystallizes in the monoclinic system with $a=9.70 \pm 0.01$, $b=6.38 \pm 0.01$, $c=17.70 \pm 0.02$ Å, and $\beta=115^\circ 40' \pm 10'$. The space group is $P2_1/c$. Considerable overcrowding exists in the anion, and the resulting strain is accommodated in three principal ways. The bond angles made by the carbon atoms of the carboxyl groups to the ring show large deviations from the expected values. The carbon atoms of the carboxyl groups lie at distances of up to 0.194 Å from the best plane through the five ring atoms and the planes of all of the carboxyl groups are twisted with respect to the plane of the ring. Despite the magnitude of the distortions due to intramolecular overcrowding, there is a very close approach of 2.386 Å between two oxygen atoms on adjacent carboxyl groups. This distance is effectively the same as that found in potassium hydrogen chloromaleate, in which a centered hydrogen bond has been established.

Introduction

There has been speculation (Cocker, Davis, McMurry & Start, 1959) as to the structure of furantetracarboxylic acid [Fig. 1(a)] and its monopotassium salt. The infrared spectrum was interpreted in terms of structure (b) for the anion (Cocker *et al.*, 1959). Examination of a model of this structure suggests that there will be considerable steric strain among the carboxyl groups in the ion, and some deformation from ideal molecular dimensions must be expected if the oxygen atoms are

not to approach each other very closely. After due allowance has been made for the effects of molecular deformation, there remains the possibility of some very short hydrogen bonds in the furantetracarboxylate anion. A recent determination of the crystal structure of 3,4-furandicarboxylic acid [Fig. 1(d)] (Williams & Rundle, 1964) revealed a distance of 2.555 Å between the atoms O(5) and O(5'), and the authors speculated as to whether the hydrogen atom was placed symmetrically between the oxygen atoms.

A crystal structure determination of the monorubidium salt of furantetracarboxylic acid was undertaken to investigate the geometry of the anion.

* Present address: Department of Chemistry, Iowa State University, Ames, Iowa.