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The Crystal and Molecular Structure of Thiourea Dioxide

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The crystal structure of thiourea dioxide has been determined using three-dimensional X-ray data. The crystals are orthorhombic, with space group *Pmnb*, and there are 4 molecules lying across mirror planes in a unit cell of dimensions $a=10{\cdot}13_3$, $b=10{\cdot}65_5$, $c=3{\cdot}92_4$ Å. The group $SC(NH_2)_2$ is approximately planar and the carbon and oxygen atoms form a pyramidal arrangement about the sulphur atom. The unusually great length of the carbon–sulphur bond (1·85 Å) accounts for the ease with which this bond is broken. Observed lengths of other bonds include 1·31 Å for carbon–nitrogen and 1·49 Å for sulphur–oxygen. Each molecule is joined to 4 neighbouring molecules by 8 hydrogen bonds and the hydrogen bonds form a continuous network which links together all the molecules in the crystal.

1. Introduction

Thiourea dioxide, $(H_2N)_2CSO_2$,—known in industry as Manofast—has unusual chemical properties; it is used as a reducing agent in the dyeing industry and in photographic processes. The examination of its crystal structure has been undertaken to determine the precise constitution of the molecule and in the expectation that accurate molecular dimensions will be of use in interpreting the chemical behaviour of the material.

2. Experimental

The material used in the present investigation was grown from water as colourless crystals in which the predominant habit is an elongated right prism with a rhombic cross-section. Optical and X-ray examinations show that the crystal system is orthorhombic and the axes have been chosen so that *a* is parallel to the length of the needle and *b* and *c* are respectively parallel to the longer and shorter diagonals of the rhomb. Occasionally (010) and (001) faces are developed. (100) is a plane of easy cleavage.

The unit-cell dimensions, deduced with limits of error less than 0·1% using Weissenberg photographs and the method of Farquar & Lipson (1946), are

$$a=10{\cdot}13_3,\ b=10{\cdot}65_5,\ c=3{\cdot}92_4\ \text{Å}\,.$$

With four molecules in the unit cell the calculated density (1·707 g.cm.$^{-3}$) agrees with the density measured by displacement of paraffin (1·706 g.cm.$^{-3}$).

Systematic absences in the X-ray reflexions (*hk*0 with *k* odd and *h*0*l* with $(h+l)$ odd) show that the space group is either *Pmnb* or $P2_1nb$. In an earlier attempt to determine the structure of thiourea dioxide (Hanson, Taylor & Lipson, 1952) it was reported that the space group is probably $P2_1nb$. However, a statistical examination of the intensities of the X-ray reflexions (§ 4) indicates strongly that there is a mirror plane perpendicular to *a* and that the space group is therefore *Pmnb*. This observation is confirmed by the low discrepancy factor ($R_{hkl}=9\%$) for the structure based on *Pmnb* which is described here.

An approximate structure was deduced using *h*0*l*, *hk*0 and 0*kl* reflexions recorded with Cu *K*-radiation in zero-layer multiple-film Weissenberg photographs. The intensities of the reflexions were measured by visual comparison with calibration spots of known relative exposure. Fairly small crystal specimens were used in recording the X-ray reflexions but the cross-sections were not uniform and the linear absorption coefficient ($\mu=60$ cm.$^{-1}$) is high; since the intensities were uncorrected for absorption it is possible, therefore, that the *F*-values deduced from them are subject to substantial errors.

The structure was refined using three-dimensional data recorded by a Nonius integrating Weissenberg camera with filtered Cu $K\alpha$ radiation and a crystal ground roughly to the shape of a rectangular parallelepiped. The crystal was gently rubbed on smooth paper in an alcoholic solution of fine oil containing diamond dust until an approximately rectangular parallelepiped was obtained with dimensions $0{\cdot}29_2$ mm. in the *a* direction, $0{\cdot}27_0$ mm. in the *b* direction and $0{\cdot}12_6$ mm. in the *c* direction. The layer-lines surveyed by multiple-film equi-inclination photographs were *hk*0 to *hk*3 and 0*kl* to 4*kl*: of the 506 possible reflexions which lie within the limiting sphere for Cu $K\alpha$ radiation 164 were observed twice, 163 once, 161 were too weak to be observed and 18 were not recorded. The intensities of the integrated reflexions were measured on a Joyce–Loebl double-beam photometer and corrected for absorption and Lorentz-polarization factors by a programme written for the Ferranti Mercury Computer by Dr M. M. Woolfson, in which three-dimensional Gauss-type quadratures are used for crystals in the shape of rectangular parallelepipeds.

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Initially, intersecting layers were correlated using common reflexions, each layer being treated in an exactly similar way. Later, when the layers were correlated by comparison of observed and calculated structure factors, it was found that the scale of no layer had been in error by more than 2·3%.

3. Determination of the structure

In determining the structure it has been assumed that the space group is *Pmnb* (§ 4). Since there are 8 equivalent general positions in *Pmnb* it follows that the 4 molecules in the unit cell must lie across the mirror planes at $y=\frac{1}{4}, \frac{3}{4}$.

The positions of the atoms in the [001] projection are easily obtained because of the shortness of the *c*-axis. They were determined independently by packing considerations, by optical methods (Hanson, Lipson & Taylor, 1953) and by the method of sign relationships (Woolfson, 1957, 1958). In the latter method 90 sign relationships were almost completely satisfied using 24 out of 83 (i.e. 29%) observed reflexions. The atoms could be clearly recognized in an electron-density projection calculated using these 24 reflexions although it was subsequently found that one sign was incorrect.

The [001] projection was refined by ϱ_o and $(\varrho_o-\varrho_c)$ maps until a discrepancy factor

$$(R=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$$

of 18% was obtained with a single temperature constant $B=2{\cdot}16$ Å^2 for all atoms. Clover-leaf patterns, observed in the difference syntheses (Fig. 1), could be ascribed to any of the following causes: (i) incorrect choice of space group, (ii) anisotropic thermal vibrations, (iii) absorption errors in the experimental data.

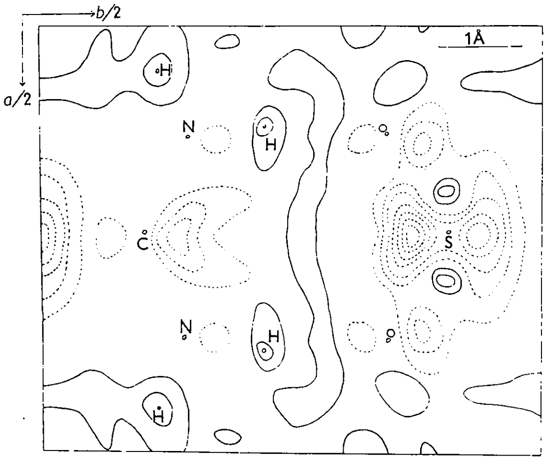


Fig. 1. Projection of $(\varrho_o-\varrho_c)$ along [001] showing clover-leaf pattern obtained using $h0l$ data uncorrected for absorption. Contours are at intervals of 0·6 e.Å^{-2}; negative contours are broken and the zero contour is omitted.

Only 28 $h0l$ reflexions were observed with Cu K radiation and since considerable overlap of atomic peaks was expected in the [010] projection the second projection to be examined was the [100]. In the latter the two oxygen atoms and, similarly, the two nitrogen atoms in the molecule superimpose exactly on the mirror plane, giving electron densities comparable in magnitude with that of the sulphur atom and much greater than that of the carbon atom. By chance all four peaks are close to one another and in consequence only one extremely large peak is visible in the [100] electron density map at low resolution. The solution of the [100] projection by sign relationships was achieved only after using 25 out of 49 (i.e. 51%) observed $0kl$ reflexions, making 66% of these relationships hold. Of the 25 derived signs 5 proved to be incorrect but it was possible, nevertheless, to refine the structure by ϱ_o and $(\varrho_o-\varrho_c)$ maps until a discrepancy factor of 19% was obtained with a single temperature constant $B=1{\cdot}79$ Å^2.

Both of the non-equivalent hydrogen atoms in the molecule can be observed in the $(\varrho_o-\varrho_c)$ maps for the [001] projection but neither was detected in the corresponding maps for the [100] projection.

At this stage three-dimensional X-ray data corrected for absorption were obtained in the hope that it would be possible to find and remove the cause of the clover-leaf patterns in Fig. 1, to find the z-coordinates of the hydrogen atoms and, generally, to obtain more accurate atomic parameters.

4. An examination of the space group by statistical methods

It was suggested in § 3 that one possible cause of the clover-leaf patterns in Fig. 1 is incorrect choice of the space group. Systematic absences in the X-ray reflexions (§ 2) do not allow a choice to be made between *Pmnb* and *P*2₁*nb*. But with three-dimensional X-ray data available it is possible to make a statistical survey of the X-ray intensities which should distinguish between the two space groups. Two statistical tests have been carried out.

(i) *The average multiple test*

The presence or absence of a mirror plane parallel to (100) was tested by comparing the average intensity of the $0kl$ reflexions, $\langle I_{0kl}\rangle$, with the average intensity of hkl reflexions $\langle I_{hkl}\rangle$ (Wilson, 1950). The 46 $0kl$ reflexions were grouped into 8 ranges of $\sin\theta$ and the ratio $\langle I_{0kl}\rangle/\langle I_{hkl}\rangle$ determined for each range. The weighted average ratios obtained thus (1·26 experimental, 1·00 calculated for $P2_1nb$ and 1·30 calculated for *Pmnb*) suggest that the space group is *Pmnb* but the result is not wholly convincing because of the considerable variations observed in the experimental ratios for the individual ranges of $\sin\theta$. It should be noted that the presence of the heavy sulphur atom on the mirror plane considerably reduces the effectiveness of the test.

(ii) *Moment tests*

A more satisfactory test (Foster, 1958), permitting full use of the three-dimensional experimental data, is provided by a comparison of theoretical and calculated moments of the quantity Z defined by $Z=I/\langle I\rangle$, where I is the intensity of a particular reflexion and $\langle I\rangle$ is the local average intensity. The 318 reflexions with $\sin\theta>0{\cdot}5$ were grouped into 5 ranges of $\sin\theta$ and the second and third moments of Z ($\langle Z^2\rangle$ and $\langle Z^3\rangle$) calculated for each range. Fuller details of the calculations will be given elsewhere (Hargreaves & Foster, in preparation). The weighted average values, obtained by combining the 5 ranges of $\sin\theta$, are given in Table 1: they indicate strongly that the true space group is *Pmnb*.

Table 1. *Comparison of experimental and theoretical moments of Z*

Moment	Experimental	Theoretical: $P2_1nb$	Theoretical: $Pmnb$
$\langle Z^2\rangle$	3·0	2·1	2·6
$\langle Z^3\rangle$	13·2	6·4	10·4

5. Refinement of the structure using three-dimensional data

In the earlier stages of the three-dimensional refinement the hydrogen atoms and reflexions with $\sin\theta<0{\cdot}55$ were omitted from the calculations (Jellinek, 1958) and isotropic temperature factors were assumed. The atomic scattering factors used were those given in analytical form by Forsyth & Wells (1959).

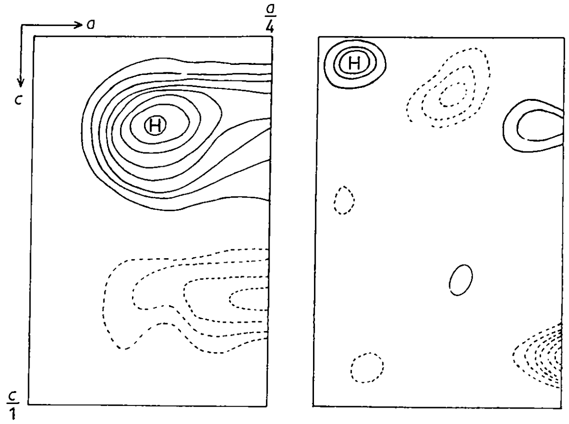
For refinement by the method of least squares the weighting factor for each reflexion was taken as

$$w=(1+F_o^2/8F_{\text{min.}}^2)^{-1} \quad \text{when } |F_o| \geq |F_{\text{min.}}|$$

$$\text{and } w=0 \quad \text{when } |F_o|<|F_{\text{min.}}|\,,$$

where $|F_{\text{min.}}|$, the 'minimum observable' $|F_o|$, was taken to be 3·0 electrons per unit cell for all reflexions. The quantity $\Sigma(|F_o|-|F_c|)^2$ was minimized by shifts in the parameters using the complete matrix of the coefficients. In three cycles the discrepancy factor fell from 24·4% to 18·7%.

A three-dimensional difference synthesis, evaluated at this stage, showed peaks and troughs of electron density in regions near to the atoms. In the [001] projection these peaks and troughs can largely be interpreted in terms of clover-leaf patterns with the magnitude of the electron density reduced to about half the value observed when the two-dimensional data uncorrected for absorption were used. It is not clear whether the clover-leaf patterns are still caused by incomplete correction of the experimental data for absorption or whether they are now caused mainly by anisotropic thermal vibrations. But their elimination or further reduction is desirable because of the interest in the positions of the hydrogen atoms. Since the clover leaves seem to have axes parallel to the crystallographic axes, individual correction factors of the form $\exp(-\alpha_i h^2-\beta_i k^2-\gamma_i l^2)$ were applied to each atom i. In four cycles of least squares refinement the discrepancy factor was reduced to 12·2%.



(a) (b)

Fig. 2. Sections of $(\varrho_o-\varrho_c)$ parallel to (010) showing hydrogen atoms: (a) section $y=60/240$, (b) section $y=24/240$. Contours are at intervals of 0·1 e.Å^{-3} commencing at ±0·3 e.Å^{-3}; negative contours are broken.

A three-dimensional difference synthesis using all the observed reflexions was then evaluated in the regions where the hydrogen atoms were expected. The two non-equivalent hydrogen atoms were located as peaks of electron density (Fig. 2) which rise to heights of 1·01 and 0·55 e.Å^{-3} respectively, as compared with a highest background peak of 0·60 e.Å^{-3}. When the hydrogen atoms were included in two cycles of least-squares refinement, using all the observed reflexions but 200 and 011, which are markedly affected by extinction, the discrepancy factor fell to 9·8%: for the hydrogen atoms temperature factors $B=4{\cdot}0$ Å^2 were assumed and only the positional parameters refined. On correcting nine reflexions for secondary

Table 2. *Final parameters*

Atom	x	y	z	$10^5.\sigma(x)$	$10^5.\sigma(y)$	$10^5.\sigma(z)$	$10^4.\alpha$	$10^4.\beta$	$10^4.\gamma$
S	0·25000	0·46027	0·63527	0	18	66	88	44	778
O	0·12825	0·40178	0·49324	49	35	141	75	55	1236
N	0·13553	0·16379	0·16020	53	44	154	86	58	1041
C	0·25000	0·11140	0·09759	0	71	251	79	44	847
H_1	0·1284	0·2603	0·2504	900	620	288		$B=4{\cdot}0$ Å^2	
H_2	0·0253	0·1142	0·0831	700	660	247		$B=4{\cdot}0$ Å^2	

Table 3. *Calculated and observed structure factors*

h	k	ℓ	F_c	F_o	
0	2	0	19.86	20.12	E
0	4	0	-21.55	21.42	E
0	6	0	- 3.19	2.83	
0	8	0	- 2.25	1.87	
0	10	0	- 2.83	3.19	
0	12	0	- 2.84	3.32	
1	2	0	5.48	5.81	
1	4	0	32.01	32.14	E
1	6	0	13.97	14.05	
1	8	0	1.59	1.18	U
1	10	0	5.96	5.36	
1	12	0	2.30	2.55	
2	0	0	-36.15	36.92	E
2	2	0	-19.60	20.17	E
2	4	0	- 3.47	3.77	
2	6	0	- 0.15	1.41	U
2	8	0	2.89	3.00	
2	10	0	5.44	5.53	
2	12	0	6.52	6.74	
3	2	0	1.81	1.79	U
3	4	0	0.91	1.79	U
3	6	0	-18.80	17.96	
3	8	0	-18.79	17.99	
3	10	0	- 2.20	2.68	
3	12	0	2.66	3.16	
4	0	0	-11.16	11.29	
4	2	0	17.12	17.77	
4	4	0	18.42	18.43	
4	6	0	0.71	1.18	U
4	8	0	- 1.75	2.05	
4	10	0	- 6.52	6.82	
4	12	0	- 9.87	10.20	
5	2	0	- 0.20	1.41	U
5	4	0	- 2.87	3.76	
5	6	0	15.76	15.57	
5	8	0	17.50	16.83	
5	10	0	0.39	1.00	U
5	12	0	- 2.77	2.26	
6	0	0	-10.18	10.94	
6	2	0	-11.90	13.02	
6	4	0	- 5.58	5.85	
6	6	0	1.70	1.10	U
6	8	0	1.29	1.00	U
6	10	0	3.26	2.83	
6	12	0	5.75	4.72	
7	2	0	- 5.58	5.81	
7	4	0	-10.99	10.64	
7	6	0	- 7.78	7.69	
7	8	0	- 3.34	3.35	
7	10	0	- 2.60	2.70	
8	0	0	22.75	22.27	
8	2	0	7.50	7.39	
8	4	0	- 4.27	4.29	
8	6	0	- 1.38	1.00	U
8	8	0	- 1.12	1.00	U
8	10	0	- 1.11	0.90	U
9	2	0	1.97	1.00	U
9	4	0	9.79	10.25	
9	6	0	5.39	4.86	
9	8	0	0.30	1.00	U
9	10	0	2.55	0.90	U
10	0	0	- 9.91	10.86	
10	2	0	- 4.34	3.89	
10	4	0	0.13	1.00	U
10	6	0	- 0.62	1.00	U
10	8	0	1.00	0.90	U
11	2	0	0.59	1.00	U
11	4	0	- 1.84	1.00	U
11	6	0	- 4.86	4.93	
12	0	0	0.35	0.90	U
12	2	0	2.84	3.08	
12	4	0	3.16	3.29	
13	2	0	0.08	0.90	U
0	1	1	44.18	43.91	E
0	2	1	-24.61	25.58	E
0	3	1	- 8.27	7.59	
0	4	1	- 2.01	2.17	
0	5	1	-12.00	10.95	
0	6	1	- 6.73	6.75	
0	7	1	- 1.87	1.90	
0	8	1	-10.98	11.02	
0	9	1	0.12	1.18	U
0	10	1	- 1.90	2.24	
0	11	1	- 0.13	0.78	U
0	12	1	- 0.36	0.78	U
0	13	1	- 3.95	3.91	
1	0	1	- 3.33	2.30	
1	1	1	1.80	1.95	
1	2	1	18.43	18.86	E
1	3	1	15.62	16.65	
1	4	1	13.33	13.85	
1	5	1	14.43	14.58	
1	6	1	- 2.90	2.49	
1	7	1	1.98	1.18	U
1	8	1	- 3.32	3.98	
1	9	1	1.62	1.10	U
1	10	1	- 4.13	3.35	
1	11	1	2.88	2.72	
1	12	1	- 5.62	5.39	
1	13	1	0.49	0.90	U
2	1	1	-16.61	17.33	
2	2	1	10.75	11.55	
2	3	1	- 5.06	4.67	
2	4	1	9.05	9.53	
2	5	1	- 0.16	1.41	U
2	6	1	7.64	7.40	
2	7	1	0.81	1.18	U
2	8	1	6.53	6.60	
2	9	1	2.17	2.21	
2	10	1	3.83	3.62	
2	11	1	3.64	4.00	
2	12	1	1.24	0.95	
2	13	1	3.98	3.52	
3	0	1	-18.21	19.01	
3	1	1	3.04	2.93	
3	2	1	- 6.29	7.18	
3	3	1	5.65	5.20	
3	4	1	- 5.20	4.84	
3	5	1	- 6.03	6.37	
3	6	1	- 4.25	4.36	
3	7	1	-14.77	14.56	
3	8	1	4.55	4.54	
3	9	1	- 6.70	6.75	
3	10	1	6.12	6.15	
3	11	1	1.56	1.00	U
3	12	1	2.42	2.24	
3	13	1	1.70	0.90	U
4	1	1	- 2.40	2.51	
4	2	1	- 0.60	1.79	
4	3	1	13.01	12.98	
4	4	1	-14.55	14.50	
4	5	1	7.50	7.31	
4	6	1	- 6.88	6.88	
4	7	1	0.24	1.10	U
4	8	1	- 1.33	1.10	U
4	9	1	- 3.02	3.38	
4	10	1	- 5.72	5.62	
4	11	1	- 6.57	6.68	
4	12	1	- 1.64	1.84	
5	0	1	15.28	14.45	
5	1	1	- 1.80	1.95	
5	2	1	4.01	3.76	
5	3	1	- 4.99	5.01	
5	4	1	3.37	3.39	
5	5	1	4.22	3.85	
5	6	1	4.89	5.03	
5	7	1	13.46	14.32	
5	8	1	- 4.28	4.22	
5	9	1	5.91	5.74	
5	10	1	- 5.65	6.71	
5	11	1	- 1.99	2.53	
5	12	1	- 1.40	0.90	U
6	1	1	- 6.81	6.74	
6	2	1	3.31	3.11	
6	3	1	- 5.48	6.25	
6	4	1	8.09	7.64	
6	5	1	- 0.60	1.10	U
6	6	1	5.36	4.99	
6	7	1	0.87	1.00	U
6	8	1	2.97	3.08	
6	9	1	1.00	1.00	U
6	10	1	3.53	3.87	
6	11	1	3.06	2.97	
6	12	1	1.07	0.90	U
7	0	1	- 3.67	3.49	
7	1	1	- 2.15	1.18	U
7	2	1	- 6.51	6.51	
7	3	1	- 6.28	5.89	
7	4	1	- 5.05	5.14	
7	5	1	- 6.14	6.16	
7	6	1	- 0.07	1.00	U
7	7	1	- 2.66	2.81	
7	8	1	2.24	3.18	
7	9	1	- 1.34	1.00	U
7	10	1	2.91	2.70	
7	11	1	- 1.13	0.90	U
8	1	1	11.99	11.33	
8	2	1	- 6.37	6.61	
8	3	1	- 0.68	1.10	U
8	4	1	- 2.30	2.05	
8	5	1	- 3.72	3.36	
8	6	1	- 3.45	3.39	
8	7	1	- 0.96	1.00	U
8	8	1	- 4.72	4.90	
8	9	1	0.15	0.90	U
8	10	1	- 1.08	0.90	U
9	0	1	0.40	2.21	
9	1	1	0.66	1.00	U
9	2	1	5.26	5.10	
9	3	1	4.71	4.46	
9	4	1	4.59	4.46	
9	5	1	5.26	4.70	
9	6	1	- 1.31	1.87	
9	7	1	0.73	1.00	U
9	8	1	- 1.19	0.90	U
9	9	1	0.44	0.90	U
10	1	1	- 5.11	5.25	
10	2	1	3.73	4.15	
10	3	1	- 0.70	1.00	U
10	4	1	2.01	2.05	
10	5	1	0.29	1.00	U
10	6	1	2.28	2.05	
10	7	1	0.07	0.90	U
10	8	1	2.71	2.57	
11	0	1	- 2.55	2.86	
11	1	1	0.73	1.00	U
11	2	1	- 2.36	2.63	
11	3	1	0.39	1.00	U
11	4	1	- 1.88	1.61	
11	5	1	- 2.21	2.37	
11	6	1	- 0.43	0.90	U
11	7	1	- 3.44	0.90	U
12	1	1	0.36	0.90	U
12	2	1	- 0.75	0.90	U
12	3	1	2.19	1.95	
12	4	1	- 2.64	2.78	
0	0	2	6.16	6.20	
0	1	2	-12.61	11.49	E
0	2	2	4.72	4.22	
0	3	2	-10.75	11.51	
0	4	2	- 7.22	6.72	
0	5	2	- 3.70	3.99	
0	6	2	- 7.49	7.38	
0	7	2	- 9.77	10.11	
0	8	2	2.35	1.55	
0	9	2	- 6.03	6.48	
0	10	2	4.76	4.90	
0	11	2	- 1.24	0.78	U
0	12	2	0.43	0.70	U
1	1	2	5.53	5.59	
1	2	2	7.11	7.31	
1	3	2	15.40	15.43	
1	4	2	0.36	1.41	
1	5	2	4.31	3.46	
1	6	2	- 3.02	3.00	
1	7	2	- 3.49	3.66	
1	8	2	- 2.29	1.95	
1	9	2	- 3.89	3.98	
1	10	2	- 1.70	1.00	U
1	11	2	- 5.51	5.89	
1	12	2	0.79	0.90	U
2	0	2	0.80	1.41	U
2	1	2	5.52	5.68	
2	2	2	0.80	1.41	U
2	3	2	9.63	10.18	
2	4	2	1.46	1.73	
2	5	2	7.91	7.76	
2	6	2	0.85	1.10	U
2	7	2	6.75	6.41	
2	8	2	- 0.90	1.00	U
2	9	2	5.16	5.35	
2	10	2	- 1.14	1.00	U
2	11	2	2.77	2.74	
2	12	2	- 0.30	0.90	U
3	1	2	-10.93	11.62	
3	2	2	8.19	8.32	
3	3	2	- 5.43	5.59	
3	4	2	3.10	2.66	
3	5	2	- 5.56	5.30	
3	6	2	- 1.48	2.05	
3	7	2	0.60	1.10	U
3	8	2	- 1.19	1.00	U
3	9	2	6.48	6.80	
3	10	2	0.05	1.00	U
3	11	2	4.04	4.06	
3	12	2	1.40	1.30	
4	0	2	- 4.73	4.82	
4	1	2	0.02	1.18	U
4	2	2	- 4.94	4.99	
4	3	2	- 8.96	8.93	
4	4	2	2.37	2.17	
4	5	2	-10.77	10.95	
4	6	2	4.93	4.90	
4	7	2	- 2.53	2.43	
4	8	2	- 0.32	1.00	U
4	9	2	- 3.92	4.25	
4	10	2	- 2.23	2.57	

Table 3 (*cont.*)

h	k	ℓ	F_o	F_o	
4	11	2	- 4.33	4.34	
4	12	2	0.20	0.90	U
5	1	2	9.40	8.72	
5	2	2	- 7.64	7.96	
5	3	2	3.36	3.29	
5	4	2	- 2.32	2.17	
5	5	2	5.21	5.38	
5	6	2	1.56	2.00	
5	7	2	- 0.00	1.00	U
5	8	2	0.98	1.00	U
5	9	2	- 6.18	6.85	
5	10	2	0.18	0.90	U
5	11	2	- 3.17	2.95	
6	0	2	0.30	1.10	U
6	1	2	1.79	1.58	
6	2	2	1.34	1.10	U
6	3	2	6.46	6.37	
6	4	2	0.91	1.10	U
6	5	2	6.83	6.32	
6	6	2	- 0.55	1.00	U
6	7	2	3.47	3.44	U
6	8	2	- 0.38	1.00	U
6	9	2	3.38	4.09	
6	10	2	- 0.23	0.90	U
6	11	2	2.65	0.90	U
7	1	2	- 4.67	4.21	
7	2	2	- 1.90	2.00	
7	3	2	- 6.37	6.55	
7	4	2	- 0.23	1.00	U
7	5	2	- 2.83	3.27	
7	6	2	1.35	1.00	U
7	7	2	1.39	1.00	U
7	8	2	1.38	1.38	
7	9	2	2.91	3.35	
7	10	2	0.74	0.90	U
8	0	2	2.09	2.00	
8	1	2	- 4.10	3.91	
8	2	2	1.20	1.00	U
8	3	2	- 4.63	3.94	
8	4	2	- 2.71	2.34	
8	5	2	- 2.40	2.61	
8	6	2	- 3.09	3.08	
8	7	2	- 4.36	4.75	
8	8	2	1.09	0.90	U
8	9	2	- 2.84	2.53	
9	1	2	2.28	2.28	
9	2	2	2.31	2.32	
9	3	2	5.82	6.35	
9	4	2	- 0.02	1.00	U
9	5	2	1.64	1.87	
9	6	2	- 1.18	1.82	
9	7	2	- 1.57	1.79	
9	8	2	- 0.94	0.90	U
10	0	2	0.19	1.00	U
10	1	2	2.42	2.55	
10	2	2	- 0.04	1.00	U
10	3	2	3.18	3.49	
10	4	2	0.61	0.90	U
10	5	2	1.89	1.58	
10	6	2	0.83	0.90	U
10	7	2	2.54	0.90	U
11	1	2	- 2.35	2.49	
11	2	2	1.36	1.67	
11	3	2	- 2.27	2.65	
11	4	2	0.88	0.90	U
11	5	2	- 1.34	0.90	U
12	0	2	- 1.11	0.90	U
12	1	2	- 0.36	0.90	U
0	1	3	- 5.08	4.47	
0	2	3	- 3.77	3.54	
0	3	3	- 1.73	1.70	
0	4	3	- 3.08	3.03	
0	5	3	- 5.28	5.20	
0	6	3	- 2.17	2.45	
0	7	3	- 1.46	1.76	
0	8	3	- 2.13	2.24	
0	9	3	4.81	4.78	
0	10	3	- 1.75	1.61	
0	11	3	3.10	2.41	

h	k	ℓ	F_c	F_o	
1	0	3	1.85	2.19	
1	1	3	2.67	2.55	
1	2	3	3.12	3.27	
1	3	3	- 1.05	2.78	
1	4	3	3.93	3.74	
1	5	3	- 6.75	7.00	
1	6	3	0.78	1.00	U
1	7	3	- 4.77	5.16	
1	8	3	- 1.87	1.90	
1	9	3	- 3.30	3.08	
1	10	3	- 2.35	2.63	
1	11	3	- 1.26	0.90	U
2	1	3	6.16	5.78	
2	2	3	3.28	3.61	
2	3	3	3.49	3.44	
2	4	3	3.39	3.55	
2	5	3	1.48	1.52	
2	6	3	2.08	2.14	
2	7	3	- 0.48	1.00	U
2	8	3	1.72	1.76	
2	9	3	- 2.10	2.28	
2	10	3	1.70	1.84	
3	0	3	- 2.66	2.79	
3	1	3	3.86	3.80	
3	2	3	- 3.06	3.08	
3	3	3	5.23	5.44	
3	4	3	- 2.67	2.68	
3	5	3	3.43	3.38	
3	6	3	- 0.82	1.00	U
3	7	3	3.84	3.95	
3	8	3	1.78	1.73	
3	9	3	1.94	2.00	
3	10	3	2.02	1.61	
4	1	3	- 6.27	6.20	
4	2	3	- 3.13	3.22	
4	3	3	- 5.10	5.25	
4	4	3	- 3.51	3.82	
4	5	3	2.14	2.34	
4	6	3	- 1.51	1.00	U
4	7	3	2.34	2.24	
4	8	3	- 1.06	1.00	U
4	9	3	- 0.77	0.90	U
4	10	3	- 1.62	1.26	
5	0	3	2.18	1.98	
5	1	3	- 4.02	4.12	
5	2	3	2.47	2.24	
5	3	3	- 4.59	4.75	
5	4	3	2.27	2.17	
5	5	3	- 2.24	2.41	
5	6	3	0.78	1.00	U
5	7	3	- 3.46	3.46	
5	8	3	- 1.55	1.70	
5	9	3	- 1.58	1.61	
6	1	3	3.94	4.06	
6	2	3	2.26	1.98	
6	3	3	3.35	3.46	
6	4	3	2.48	2.41	
6	5	3	0.32	1.00	U
6	6	3	1.35	1.00	U
6	7	3	- 0.87	0.90	U
6	8	3	1.05	0.90	U
6	9	3	- 0.73	0.90	U
7	0	3	- 1.22	1.00	U
7	1	3	- 0.50	1.00	U
7	2	3	- 1.79	1.00	U
7	3	3	0.93	1.00	U
7	4	3	- 2.11	2.10	
7	5	3	3.25	3.46	
7	6	3	- 0.53	0.90	U
7	7	3	3.04	2.81	
7	8	3	1.12	0.90	U
8	1	3	- 2.37	2.28	
8	2	3	- 1.71	1.00	U
8	3	3	- 1.06	1.00	U
8	4	3	- 1.50	1.00	U
8	5	3	- 2.37	2.17	
8	6	3	- 1.01	0.90	U
8	7	3	- 0.64	0.90	U

h	k	ℓ	F_c	F_o	
9	0	3	0.58	0.90	U
9	1	3	1.27	0.90	U
9	2	3	1.25	0.90	U
9	3	3	- 0.30	0.90	U
9	4	3	1.62	0.90	U
9	5	3	- 2.88	2.34	
10	1	3	2.13	1.79	
10	2	3	1.22	1.55	
10	3	3	0.70	0.90	U
0	0	4	- 3.97	4.07	
0	1	4	0.90	1.10	U
0	2	4	- 2.50	2.32	
0	3	4	0.38	0.78	U
0	4	4	- 1.53	2.02	
0	5	4	0.16	0.78	U
0	6	4	- 1.36	1.18	
0	7	4	1.54	1.05	
0	8	4	0.99	1.00	
1	1	4	- 1.04	1.00	U
1	2	4	0.29	2.83	
1	3	4	- 1.11	1.00	U
1	4	4	- 2.54	2.32	
1	5	4	0.57	1.00	U
1	6	4	- 3.64	3.77	
1	7	4	0.41	3.16	
1	8	4	- 2.51	0.90	U
2	0	4	4.16	4.20	
2	1	4	- 0.04	1.00	U
2	2	4	3.02	2.98	
2	3	4	- 0.21	1.00	U
2	4	4	1.15	1.00	U
2	5	4	- 0.78	1.00	U
2	6	4	0.07	0.90	U
2	7	4	- 1.07	0.90	U
2	8	4	- 0.64	0.90	U
3	1	4	1.37	1.00	U
3	2	4	2.00	1.87	
3	3	4	- 0.10	1.00	U
3	4	4	2.36	2.32	
3	5	4	0.13	1.00	U
3	6	4	2.66	2.49	
3	7	4	0.21	0.90	U
4	0	4	- 3.92	4.28	
4	1	4	- 0.95	1.00	U
4	2	4	- 3.29	2.63	
4	3	4	- 0.07	1.00	U
4	4	4	- 0.69	1.00	U
4	5	4	1.42	1.41	
4	6	4	1.21	1.22	
4	7	4	0.54	0.90	U
5	1	4	- 1.30	NR	
5	2	4	- 1.93	NR	
5	3	4	0.36	NR	
5	4	4	- 1.84	NR	
5	5	4	- 0.20	NR	
5	6	4	- 2.17	NR	
6	0	4	2.72	NR	
6	1	4	0.32	NR	
6	2	4	2.26	NR	
6	3	4	- 0.08	NR	
6	4	4	0.83	NR	
6	5	4	- 0.82	NR	
7	1	4	0.72	NR	
7	2	4	0.06	NR	
7	3	4	0.39	NR	
7	4	4	1.33	NR	
8	0	4	- 1.86	NR	
8	1	4	0.38	NR	
0	1	5	- 0.62	0.71	U
0	2	5	1.08	0.71	U
1	0	5	- 1.15	0.90	U
1	1	5	0.09	0.90	U
1	2	5	- 1.37	0.90	U
2	1	5	0.88	0.90	U

E = Corrected for extinction. U = Unobserved. NR = Not recorded. SCALE = 0·4758 × absolute.

extinction (Darwin, 1922), the discrepancy factor fell further to 9·0%.

The final fractional coordinates (x, y, z) with their estimated standard deviations ($\sigma(x)$, $\sigma(y)$, $\sigma(z)$) and the final values of α, β, γ are given in Table 2; the e.s.d.'s (estimated standard deviations) were calculated using the least-squares programme. Structure factors calculated using these parameters are compared with the observed structure factors in Table 3.

6. Discussion

The bond lengths and bond angles with their e.s.d.'s, calculated from the data in Table 2, are listed in

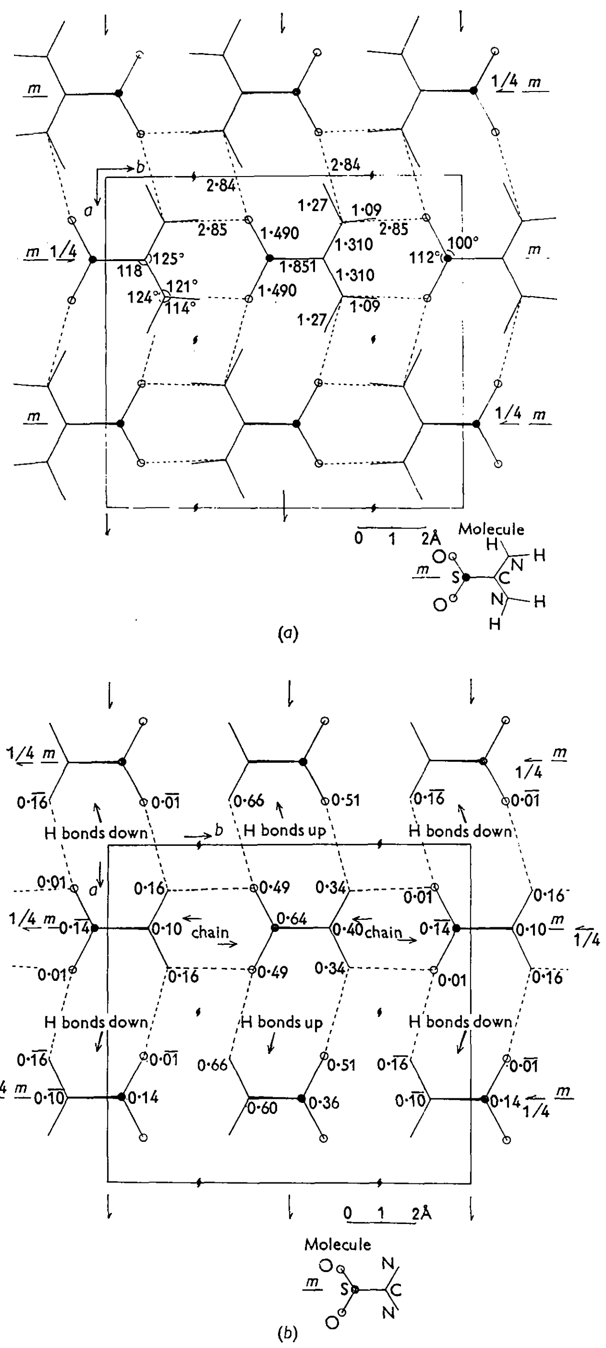


Fig. 3. The structure of thiourea dioxide viewed along [001] showing the molecule and its environment and the nature of the hydrogen bonding: (a) bond lengths (Å) and valency angles (degrees), (b) fractional z-coordinates.

Table 4. No corrections have been made for apparent atomic displacements caused by rotational oscillations of the molecule (Cruickshank, 1956). With small molecules the rotational oscillations may have considerable magnitude; they necessitate bond length corrections of up to 0·02 Å in similar molecules such as thiourea (Kunchur & Truter, 1958*a*), dichlorobisthioureazinc (Kunchur & Truter, 1958*b*) and thioacetamide (Truter, 1960). In thiourea dioxide these corrections may be smaller because of the extensive hydrogen bonding which links all molecules together (Fig. 3). Schematic diagrams of the molecule and its environment are given in Fig. 3.

Each molecule possesses a plane of mirror symmetry which passes through the carbon–sulphur linkages whilst the oxygen, nitrogen and hydrogen atoms are disposed about this plane in exactly equivalent pairs of mirror images.

The group $SC(NH_2)_2$, consisting of all atoms in the molecule except the oxygen atoms, is approximately planar. The best plane through the 8 atoms in this group misses the sulphur by 0·07 Å; this is the largest deviation from the best plane and it may be noted that the e.s.d.'s of the 4 hydrogen atoms from the plane are about 0·1 Å.

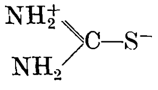
The oxygen atoms are situated at distances of 0·78 Å from the best plane through the $SC(NH_2)_2$ group: their linkages to the sulphur atom and the carbon–sulphur linkage form a pyramidal arrangement about the sulphur atom.

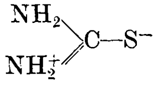
Table 4. *Bond lengths and valency angles with their estimated standard deviations*

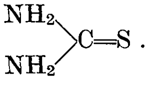
S–C	1·851 ± 0·016 Å	$N{-}\hat{C}{-}N$	124·5 ± 0·7°
C–N	1·310 ± 0·008	$N{-}\hat{C}{-}S$	117·6 ± 0·4
S–O	1·490 ± 0·008	$O{-}\hat{S}{-}O$	111·7 ± 0·3
		$O{-}\hat{S}{-}C$	100·3 ± 0·3
$N{-}H_1$	1·09 ± 0·08		
$H_1 \cdots O$	1·78 ± 0·13	$N{-}\hat{H}_1 \cdots O$	166 ± 7
$N \cdots O$	2·85 ± 0·02	$N{-}\hat{H}_2 \cdots O$	161 ± 6
$N{-}H_2$	1·27 ± 0·09	$H{-}\hat{N}{-}H$	144 ± 6
$H_2 \cdots O$	1·60 ± 0·12	$H_1{-}\hat{N}{-}C$	121 ± 5
$N \cdots O$	2·84 ± 0·02	$H_2{-}\hat{N}{-}C$	124 ± 3

From the following considerations of the structures of molecules containing bonds similar to those present in thiourea dioxide, Mr D. Hardcastle of Hardman and Holden Ltd. (1959, 1961) has suggested structure V for thiourea dioxide.

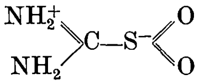
The crystal structure of thiourea has been determined by Kunchur & Truter (1958*a*) who suggest, after comparing the carbon–nitrogen and carbon–sulphur bond lengths with those in other molecules containing these bonds, that structures I and II make a large contribution to the bonding with some contribution from structure III


I

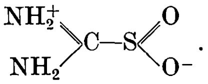

II


III

Also it seems likely from several papers on sulphur–oxygen bonds that the sulphur–oxygen bonds in thiourea dioxide will be double bonds, and that 3*d* orbitals will be involved in the valence state of the sulphur atom. Therefore, writing the valence state of sulphur in the thiourea structures I and II as $(3s)^2(3p)^5$, it may be assumed that two 3*p* electrons are promoted to 3*d* orbitals to give structure IV when thiourea is oxidized to thiourea dioxide



IV



V

Because of the greater electronegativity of the oxygen atoms, however, most of the negative charge will be associated with the oxygen atoms and so structure V (and the associated canonical structures) will probably best represent the valence bond structure of thiourea dioxide. It may be expected that the 3*d* character of the carbon–sulphur bond will increase the bond length since both IV and V involve 3*d* orbitals whose covalent radii are greater than those of 3*p* orbitals.

By means of molecular orbital methods Dunitz (1956*a*) has given a more elegant way of treating the –SO_2^- group, which is considered to be sulphur dioxide plus an extra electron. This electron is assumed to go into an orbital having d_π character and is anti-bonding, so that the π bond order is reduced on going from SO_2 to SO_2^- with consequent increase in the sulphur–oxygen bond length. In thiourea dioxide the SO_2^- group with the odd electron in the orbital having d_π character will combine with the p_σ orbital of the carbon atom to give a bond weaker than the p_σ–p_σ bond in the normal carbon–sulphur bond so that the bond length is increased. Although the extra electron in the anti-bonding orbital is concentrated largely on the sulphur atom, this does not imply that the negative charge is concentrated entirely on the sulphur atom. This orbital will decrease the electron affinity of the other sulphur orbitals and increase the polarity of the sulphur–oxygen bonds so that most of the charge is associated with the oxygen atoms.

The observed molecular dimensions of thiourea dioxide support these suggestions. In particular the carbon–sulphur bond length of 1·851 Å with an e.s.d. σ of 0·016 Å exceeds the value of about 1·81 Å usually accepted as the carbon–sulphur single bond distance by an amount which is probably significant. The discrepancy Δ is, in fact, significant (Cruickshank, 1949) if 1·81 Å is accepted as the single bond value since $\Delta/\sigma = 2{\cdot}6$, and any corrections for rotational oscillations of the molecule will tend to increase the bond length further. Also, the sulphur–oxygen bonds are longer than the accepted value of about 1·44 Å for a double bond.

Probably the three most important reducing agents in the textile industry are thiourea dioxide, sodium hydroxymethanesulphinate (sodium formaldehyde sulphoxylate) and sodium dithionite (sodium hydrosulphite). The crystal structure of sodium hydroxymethanesulphinate has been determined by Truter (1955) and that of sodium dithionite by Dunitz (1956*a*). Comparison of the three molecules shows that they all contain the –SO_2^- group and that the structures of these groups are very similar.

Table 5. *Comparison of dimensions of* –SO_2^- *groups*

	Thiourea dioxide	Sodium hydroxymethane-sulphinate	Sodium dithionite
S–C	1·851 Å	1·838 Å	—
S–S	—	—	2·389 Å
S–O	1·490 Å	1·495; 1·511 Å	1·496; 1·515 Å
O–$\hat{S}$–O	111° 45′	108° 36′	108° 11′
O–$\hat{S}$–C	100° 19′	101° 25′; 100° 7′	—
O–$\hat{S}$–S	—	—	98° 01′; 99° 23′

One conclusion from this comparison is that the reducing properties of all three compounds originate from the –SO_2^- group which gives rise to the free radical anion SO_2^- after fission of the carbon–sulphur or sulphur–sulphur bond. In sodium dithionite the bond order of the sulphur–sulphur bond is 0·36 (Dunitz, 1956*b*), so that the material only needs very mild conditions to show its reducing properties. In thiourea dioxide and sodium hydroxymethanesulphinate the carbon–sulphur bonds have a bond order of about 0·85, and they need more violent conditions to show their reducing properties. However, these two compounds do have very different properties, so that the nature of the rest of the molecule attached to the –SO_2^- group is an important factor.

The lengths of the N–H · · · O hydrogen bonds (2·84 and 2·85 Å with e.s.d.'s of 0·02 Å) are shorter than accurate values for this bond observed in urea (2·99 and 3·04 Å) by Vaughan & Donohue (1952) and in succinamide (2·94 and 2·94 Å) by Davies & Pasternak (1956). The average nitrogen–hydrogen distance is 1·18 Å with e.s.d. 0·06 Å, the average oxygen–hydrogen distance is 1·69 Å with e.s.d. 0·09 Å and the average angle N–$\hat{H}$ · · · O is 164° with e.s.d. 5°. Each molecule is linked to four neighbouring molecules by eight hydrogen bonds as indicated in Fig. 3. In the [010] direction the molecules are bonded in step-like chains and, in addition, each molecule is bonded to nearest neighbours in approximately the [101] and [$\bar{1}$01] directions. Adjacent molecules in the chain, however, are not bonded to the same neighbouring chain. The net result is that each chain is linked to four others and the whole system of hydrogen bonds forms a network running throughout the crystal. The extensive hydrogen bonding, with fairly strong bonds, accounts for the high density (1·706 g.cm.$^{-3}$) of thiourea dioxide.

The shortest van der Waals distances are 3·54 Å between oxygen and nitrogen atoms in neighbouring cells in the [001] direction, and 3·84 Å between nitrogen atoms in approximately the [110] direction.

We wish to thank Hardman and Holden Ltd. for drawing our attention to this problem, for supplying the material examined and for financial assistence, Mr D. Hardcastle for helpful correspondence, Prof. H. Lipson for his continued interest and Prof. F. C. Williams for providing the facilities of the Manchester University computing laboratory. One of us (R. A. L. S.) acknowledges with thanks a maintenance grant from the Department of Scientific and Industrial Research.

References

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757.
Darwin, C. G. (1922). *Phil. Mag.* **43**, 800.
Davies, D. R. & Pasternak, R. A. (1956). *Acta Cryst.* **9**, 334.
Dunitz, J. D. (1956*a*). *Acta Cryst.* **9**, 579.
Dunitz, J. D. (1956*b*). *J. Amer. Chem. Soc.* **78**, 878.
Farquar, M. C. M. & Lipson, H. (1946). *Proc. Phys. Soc.* **58**, 200.
Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.
Foster, F. (1958). Thesis for the degree of Ph.D., University of Manchester.
Hanson, A. W., Lipson, H. & Taylor, C. A. (1953). *Proc. Roy. Soc.* A, **218**, 371.
Hanson, A. W., Taylor, C. A. & Lipson, H. (1952). *Nature, Lond.* **169**, 1086.
Hardcastle, D. (1959). Private communication.
Hardcastle, D. (1961). Private communication.
Jellinek, F. (1958). *Acta Cryst.* **11**, 677.
Kunchur, N. R. & Truter, M. R. (1958*a*). *J. Chem. Soc.*, p. 2551.
Kunchur, N. R. & Truter, M. R. (1958*b*). *J. Chem. Soc.*, p. 3478.
Truter, M. R. (1955). *J. Chem. Soc.*, p. 3064.
Truter, M. R. (1960). *J. Chem. Soc.*, p. 997.
Vaughan, P. & Donohue, J. (1952). *Acta Cryst.* **5**, 530.
Wilson, A. J. C. (1950). *Acta Cryst.* **3**, 258.
Woolfson, M. M. (1957). *Acta Cryst.* **10**, 116.
Woolfson, M. M. (1958). *Acta Cryst.* **11**, 4.

Acta Cryst. (1962). **15**, 682

Compton Incoherent Scattering Functions for Ions of the First Transition Series

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Compton incoherent scattering functions have been found for the transition elements Sc through Cu using the complete Waller–Hartree theory including the effects of the non-sphericity of the charge distributions. These calculations were based on analytic Hartree–Fock wave functions recently determined by Watson but restricted to $3d^n$ configurations. Results are given for three states of ionization ($+1$, $+2$, and $+3$) for each of the elements; the configurations $3d^n$ differ from the ground state only for the $+1$ ions other than Cr and Cu. These values are also compared with the few available earlier calculations for these ions and the role of the neglected 4*s* electrons is discussed.

Introduction

It is now generally accepted that in the absence of a theory for crystalline scattering the use of Hartree–Fock self-consistent field (SCF) wave functions in the Waller & Hartree (1929) free atom expression yields the best available incoherent scattering intensities. These have now been calculated for a large number of neutral atoms and ions (see Appendix I for a bibliography) and some of the general results may be summarized as follows:

(1) The exchange terms in the Waller–Hartree equation must be included as these may be as large as the total intensity itself; the earlier James & Brindley (1931) values, which were based on SCF wave functions without exchange, are in error by at least the magnitude of the exchange terms. This error increases with Z, the atomic number.

(2) The properly calculated incoherent scattering intensities are in good agreement (except at very small scattering angles) with the few experimental determinations that have been made to date (Keating & Vineyard, 1956; Freeman, 1959*a*, *b*, *c*, and 1960*a*). While this means that free atom calculations may be used without loss of accuracy (despite all the differences between an atom in free space and one in a solid), it is also a disappointing result since it means

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