

The Crystal and Molecular Structure of Thiuret Hydrobromide

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The crystal and molecular structure of thiuret hydrobromide has been solved by Patterson projections, and refined by least squares methods using anisotropic temperature parameters. The refinement comprises the $h0l$, $0kl$, and $1kl$ reflections.

Average length of C-N bonds in the thiuret ion is 1.34 Å and no C-N bond length deviates significantly from this value. The C-S bond lengths are 1.722 ± 0.025 Å and 1.742 ± 0.024 Å, and the S-S bond length is 2.081 ± 0.008 Å.

The thiuret ion is planar within experimental error, and the bond lengths show that the ion is stabilized through π -orbital delocalization. The conjugation is most pronounced in the carbon-nitrogen part of the ion.

In the crystal, the sulphur atoms of the disulphide group form four close contacts with three neighbouring bromide ions. Two of these contacts (3.391 and 3.453 ± 0.006 Å) occur in an approximately linear Br...S-S...Br arrangement, and two (3.382 and 3.399 ± 0.006 Å) between a third bromide ion and both sulphur atoms of the disulphide group.

X-Ray crystallographic structure investigations of the analogous five-membered cyclic disulphides, thiuret hydroiodide¹ and 3,5-diamino-1,2-dithiolium iodide,² give the lengths, 2.088 ± 0.012 Å and 2.08 ± 0.02 Å, respectively, for the sulphur-sulphur bonds in these compounds. The bonds are thus apparently pure single bonds.

The two compounds are isomorphous, and the disulphide groups lie across crystallographic mirror planes. The disulphide group is thus exactly planar in both compounds.

Disulphide groups are normally non-planar, with a dihedral angle of about 90° between the planes of the valencies of the two sulphur atoms.³ The normal dihedral angle of 90° cannot, for strain reasons, be maintained when the disulphide group is incorporated in a five-membered ring. In the saturated five-membered disulphide, 1,2-dithiolane-4-carboxylic acid,⁴ a dihedral angle of $27 \pm 1^\circ$ has been found, and the dithiolane ring is rather unstable.

The stability of the planar disulphide group in unsaturated cyclic disulphides is probably due to ring-conjugation in which sulphur π -orbitals participate.¹ Support for sulphur-carbon π -bonding derives from structure investigations of a series of unsaturated five-membered disulphides.⁵⁻⁹ Sulphur-sulphur π -bonding seems to be rather weak in 4-methyl-trithione,⁵ xanthan hydride,⁶ and rhodan-hydrate,⁷ for which the sulphur-sulphur bonds are found to be 2.047 ± 0.007 Å, 2.063 ± 0.005 Å, and 2.061 ± 0.007 Å, respectively. A sulphur-sulphur bond (2.00 ± 0.01 Å) with considerable π -bond character has been found in 3-phenyl-1,2-dithiolium iodide.⁸ The last-mentioned bond length agrees, if a linear relationship bond-length/bond-order is assumed, with the bond-order calculated by Bergson¹⁰ for the sulphur-sulphur bond in the 1,2-dithiolium ion.

A reason why the sulphur-sulphur bond is longer in thiuret hydroiodide (2.088 ± 0.012 Å) and 3,5-diamino-1,2-dithiolium iodide (2.08 ± 0.02 Å) than in the unsubstituted 1,2-dithiolium ion, may be the effect of the amino groups on the ring-conjugation.² Attention should, however, also be paid to the environment of the disulphide group.

In crystals of thiuret hydroiodide¹ and 3,5-diamino-1,2-dithiolium iodide² there are close contacts between the sulphur atoms of the disulphide group and the neighbouring iodide ions. Two of these close contacts occur in an approximately linear I...S-S...I arrangement and may influence the length of the sulphur-sulphur bond, through transfer of charge from the iodide ions to those *p*-orbitals on the sulphur atoms already engaged in the sulphur-sulphur σ -bond.⁸ One may expect the strength of this partial bonding to decrease with increasing electronegativity of the halide ion, and whether it affects the length of the sulphur-sulphur bond in thiuret hydroiodide might therefore be found through structure investigations of thiuret hydrobromide and hydrochloride. The present structure investigation of thiuret hydrobromide has been undertaken with this view.

EXPERIMENTAL

Crystal data on thiuret hydrobromide have been reported by Foss.¹¹ The compound crystallizes from water as large plates {010} or as prisms extended along the *a* axis with, also here, {010} predominant. The crystals are monoclinic prismatic, *a* = 5.11 Å, *b* = 12.76 Å, *c* = 10.47 Å, and $\beta = 110^\circ$. There are four formula units per unit cell, density, calc. 2.22, found 2.22 g/cm³. The space group, from systematic absences, is $P2_1/c$. Experimental error is estimated to be within 0.5 %.

The intensities of the *h*0*l*, 0*kl*, and 1*kl* reflections were estimated visually from Weissenberg photographs taken with CuK α radiation ($\mu = 140$ cm⁻¹). Small crystals of cross-section 0.03×0.03 mm for the *h*0*l* reflections and 0.2×0.03 mm for the 0*kl* and 1*kl* reflections, were used in order to minimize absorption effects. 451 reflections were observed and measured, with a range of intensities of 3 to 10.000. The intensities were corrected for Lorentz and polarization factors but not for absorption. Common reflections in *h*0*l*, 0*kl* and 1*kl* were used to put all the reflections on the same scale.

The calculated structure factors in Table 6 are based on the atomic scattering curves for bromide, sulphur, nitrogen, carbon and hydrogen which are given in the *International Tables*,¹² the first set of the listed scattering factors for carbon being used.

DETERMINATION OF THE STRUCTURE

Coordinates for the bromide and sulphur atoms were found from Patterson maps, and the positions of the nitrogen and carbon atoms revealed themselves during subsequent Fourier refinement of the a and b -axis projections. The structure was thereafter refined by least squares methods on an IBM 1620¹¹ computer, using a program designed by Mair.¹³ Weighting scheme No. 3, recommended by Mair, was used with $a = 24$ and $b = 15$. The refinement comprised the $h0l$, $0kl$, and $1kl$ reflections, and was carried out with anisotropic temperature factors for all atoms except the hydrogens, which were given isotropic temperature factors. The hydrogen atoms were included in the structure factor calculations after the shifts in nitrogen positions had become small. The hydrogen position parameters were calculated on the basis of sp^2 -hybridized nitrogen and a nitrogen-hydrogen distance of 1.0 Å. They were not refined. Final value of the agreement factor $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ is 0.09.

Table 1. Final atomic coordinates, in fractions of corresponding cell edges.

	x	y	z
Br	0.7724	0.1954	-0.0628
S ₁	0.8607	-0.0109	0.1614
S ₂	0.9702	-0.1268	0.3103
N ₁	0.5011	0.1338	0.1687
N ₂	0.6000	0.0129	0.3426
N ₃	0.7406	-0.1211	0.5041
C ₁	0.6379	0.0499	0.2297
C ₂	0.7492	-0.0736	0.3883
H ₁	0.530	0.167	0.087
H ₂	0.383	0.173	0.210
H ₃	0.850	-0.183	0.536
H ₄	0.606	-0.088	0.554

Table 2. Final temperature parameters β_{ij} . The expression used is $\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + kl\beta_{23} + hl\beta_{13} + hk\beta_{12})$.

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Br	0.0341	0.0046	0.0083	-0.0004	0.0162	-0.0006
S ₁	0.0250	0.0043	0.0060	0.0005	0.0138	0.0028
S ₂	0.0247	0.0039	0.0066	0.0003	0.0155	0.0028
N ₁	0.0468	0.0042	0.0095	0.0028	0.0160	0.0049
N ₂	0.0283	0.0039	0.0054	-0.0007	0.0166	0.0030
N ₃	0.0427	0.0049	0.0052	0.0009	0.0197	-0.0049
C ₁	0.0183	0.0046	0.0063	-0.0007	0.0140	0.0128
C ₂	0.0159	0.0046	0.0070	-0.0010	0.0105	0.0014

For the hydrogen atoms a temperature factor $\exp [-3(\sin^2\theta/\lambda^2)]$ was used.

The final coordinates and temperature parameters are given in Tables 1 and 2, respectively. The observed and calculated structure factors are listed in Table 6. An electron density map of the a -axis projection, corresponding to the final state of refinement is shown in Fig. 1.

Table 3. Bond lengths l and standard deviation in bond length $\sigma(l)$ in the thiuret ion.

Bond	l (Å)	$\sigma(l)$ (Å)
S_1-S_2	2.081	0.008
S_1-C_1	1.72	0.025
S_2-C_2	1.74	0.025
C_1-N_1	1.32	0.04
C_1-N_2	1.35	0.03
C_2-N_2	1.33	0.03
C_2-N_3	1.37	0.03

Table 4. Bond angles and standard deviation in bond angles in the thiuret ion.

	Angle (°)	Standard deviation (°)
$C_1-S_1-S_2$	93.2	0.8
$S_1-C_1-N_1$	118.8	1.6
$S_1-C_1-N_2$	121.4	2.0
$N_2-C_1-N_1$	119.9	2.2
$C_1-N_2-C_2$	111.6	2.0
$N_2-C_2-N_3$	119.8	2.1
$N_2-C_2-S_2$	122.4	1.6
$N_3-C_2-S_2$	117.8	2.0
$C_2-S_2-S_1$	91.4	0.9

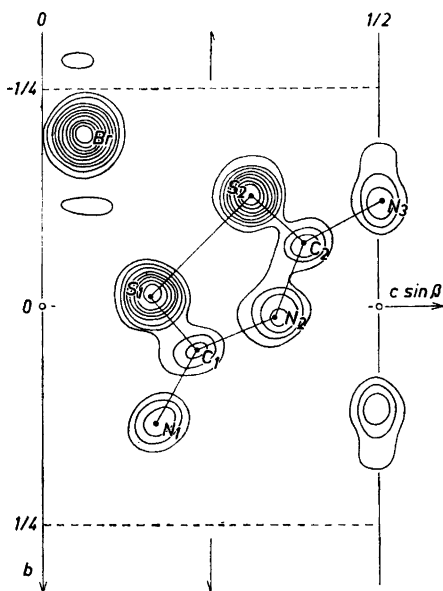


Fig. 1. Electron density projection of thiuret hydrobromide along the a axis, showing one asymmetric unit. Plane group pgg and origin in center of symmetry. Contour intervals for carbon and nitrogen $2e \cdot \text{Å}^{-2}$, for sulphur $3e \cdot \text{Å}^{-2}$ and for the bromide ion $6e \cdot \text{Å}^{-2}$. Lowest contour at $4e \cdot \text{Å}^{-2}$.

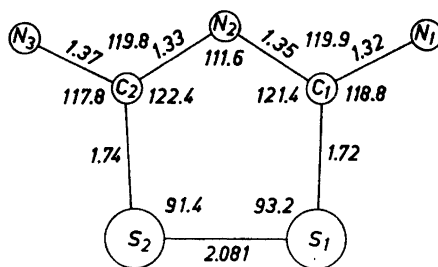


Fig. 2. Bond lengths (Å) and bond angles (°) in the thiuret ion.

DISCUSSION OF RESULT

The thiuret ion. Bond lengths and angles in the thiuret ion, corresponding to the coordinates in Table 1 are listed in Tables 3 and 4 and shown in Fig. 2.

The thiuret ion is planar within the error. The equation for the least squares plane of the ring atoms, with sulphur given three times the weight of carbon and nitrogen, and $a \sin \beta$ chosen as the third orthogonal axis is

$$0.7512X + 0.5717Y + 0.3297Z = 3.0890$$

where X , Y and Z are in Å units. S_1 and S_2 are -0.002 Å and 0.003 Å, respectively, out of this plane, and the deviation from the plane for the carbon and nitrogen atoms are: C_1 0.002 Å, C_2 -0.013 Å, N_1 -0.012 Å, N_2 0.008 Å, and N_3 0.014 Å. All deviations are less than the corresponding standard deviations in atomic positions.

The average value of carbon-nitrogen bond lengths in thiuret hydrobromide is 1.34 Å and thus the same as in thiuret hydroiodide.¹ No C—N bond length in thiuret hydrobromide deviates significantly from the mentioned average value, and the bond lengths are in good agreement with the length of the aromatic carbon-nitrogen bond, which in pyridine¹⁴ has been found to be 1.340 Å.

The S—C bonds in thiuret hydrobromide are found to be 1.722 ± 0.025 Å and 1.742 ± 0.024 Å and the S—S bond is found to be 2.081 ± 0.008 Å. If the lengths of the sulphur-carbon and sulphur-sulphur single bond are taken as 1.81 Å and 2.08 Å, respectively,¹⁵ the S—C bonds in thiuret hydrobromide are significantly shorter than the single bond, and the S—S bond apparently equal to a single bond. For thiuret hydroiodide¹ the S—C and S—S bond lengths are reported to be 1.73 ± 0.03 Å and 2.088 ± 0.012 Å, respectively.

There is thus good agreement between the dimensions of the thiuret ion as found in thiuret hydroiodide¹ and in thiuret hydrobromide. The thiuret ion is stabilized through π -orbital delocalization, which is most pronounced in the carbon-nitrogen part of the ion. It is still a question, however, whether the conjugation extends over the sulphur-sulphur bond, and it is hoped that an accurate structure determination of thiuret hydrochloride hemihydrate,¹⁶ see below, may provide additional information on this point.

The bond angle $C_1-N_2-C_2$ in thiuret hydrobromide is found to be $111.6 \pm 2.0^\circ$ and is apparently significantly smaller than the 120° valency angle of an sp^2 -hybridized atom. N_2 , regarded as sp^2 -hybridized, contributes one π -electron to the π -bonding system of the thiuret ion, and has one of its sp^2 -orbitals occupied by a lone pair.

Coppens and Hirshfeld¹⁷ have discussed how the asymmetry in the electron cloud about an atomic nucleus, due to lone pair electrons, may constitute an appreciable "atomic" dipole moment. This implies that the centroid of the electron cloud is displaced from the nucleus in direction of the lone-pair orbital. For such an atom in a crystal, coordinates as determined by X-ray methods should deviate from the real coordinates of the atomic nucleus, and the deviation should be in direction of the lone-pair orbital. Support for this idea derives from structure investigations, carried out for the same compounds both by X-ray diffraction and neutron diffraction.¹⁷

According to the above, the $C_1-N_2-C_2$ angle of $111.6 \pm 2.0^\circ$ seems to indicate that the centroid of the electron cloud of the cyclic nitrogen atom N_2 in thiuret hydrobromide is displaced from the nucleus. A displacement of the centroid in direction of the lone-pair orbital corresponding to apparent atomic coordinates (X-ray) about 0.03 \AA from the nucleus, is not improbable,¹⁷ and would correspond to a corrected value for the $C_1-N_2-C_2$ angle of about 115° . This value agrees with the value, 116.25° , found for the C-N-C angle in pyridine¹⁵ by microwave methods.

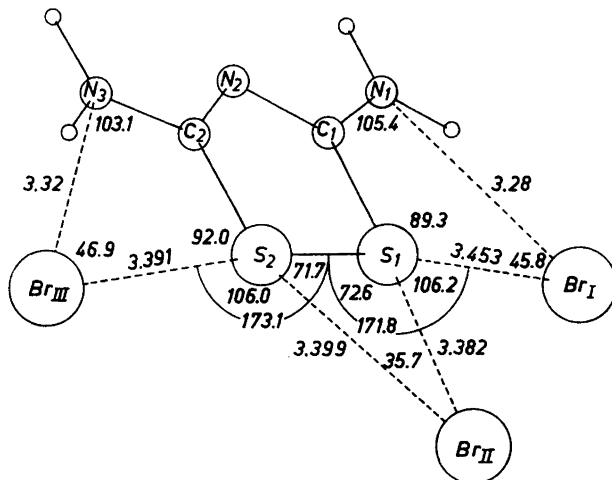


Fig. 3. Atomic distances (\AA) and angles ($^\circ$) in the environment of the disulphide group.

Table 5. Atomic distances and angles with reference to the environment of the disulphide group, together with the respective standard deviations in atomic distances and angles.

	Distance (\AA)	Standard deviation (\AA)
$S_1 \cdots Br_I$	3.453	0.006
$S_1 \cdots Br_{II}$	3.382	0.006
$S_2 \cdots Br_{II}$	3.399	0.006
$S_2 \cdots Br_{III}$	3.391	0.006
$N_1 \cdots Br_I$	3.28	0.02
$N_3 \cdots Br_{III}$	3.32	0.02
	Angle ($^\circ$)	Standard deviation ($^\circ$)
$Br_I \cdots N_1 - C_1$	105.4	1.6
$Br_I \cdots S_1 - C_1$	89.3	0.8
$Br_I \cdots S_1 - S_2$	171.8	0.5
$Br_I \cdots S_1 \cdots Br_{II}$	106.2	0.2
$S_1 \cdots Br_I \cdots N_1$	45.8	0.5
$Br_{II} \cdots S_1 - S_2$	72.6	0.5
$Br_{II} \cdots S_2 - S_1$	71.7	0.5
$Br_{II} \cdots S_2 \cdots Br_{III}$	106.0	0.2
$S_1 \cdots Br_{II} \cdots S_2$	35.7	0.3
$Br_{III} \cdots S_2 - S_1$	173.1	0.5
$Br_{III} \cdots S_2 - C_2$	92.0	0.8
$Br_{III} \cdots N_3 - C_2$	103.1	1.6
$S_2 \cdots Br_{III} \cdots N_3$	46.9	0.5

Table 6. Observed and calculated $h0l$, $0kl$ and lkl structure factors for thiuret hydrobromide. The values given are fifty times the absolute values.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
1	0	0	2421	2279	0	10	1	797	674	0	7	7	1896	2045	-1	5	1	2594	2720
2	0	0	3469	-1514	0	11	1	1861	1647	0	8	7	220	144	-1	6	1	3359	-3469
3	0	0	1326	-1291	0	12	1	1151	967	0	9	7	402	432	-1	7	1	2230	-2105
4	0	0	2094	2001	0	13	1	1259	-1126	0	10	7	603	615	-1	8	1	2877	2629
5	0	0	1274	1287	0	14	1	585	-595	0	11	7	645	-611	-1	9	1	384	-243
6	0	0	374	-374	0	15	1	856	847	0	12	7	600	582	-1	10	1	2702	2475
0	0	2	597	717	0	16	1	580	604	0	13	7	900	944	-1	11	1	1281	1126
0	0	4	1450	-1278	0	1	2	1921	1815	0	1	8	233	207	-1	12	1	930	-820
0	0	6	1070	771	0	2	2	5281	-5271	0	2	8	2018	1826	-1	13	1	825	-734
0	0	8	3497	-3251	0	3	2	4023	-3807	0	3	8	754	623	-1	14	1	1197	1173
0	0	10	1054	-1054	0	4	2	222	287	0	4	8	259	90	-1	15	1	< 179	85
0	0	12	710	774	0	5	2	1327	1391	0	5	8	772	668	1	1	2	3229	2948
1	0	2	4118	-3944	0	6	2	< 138	237	0	6	8	1354	-1407	1	2	2	3364	2976
1	0	4	4876	-4804	0	7	2	3251	3518	0	7	8	582	588	1	3	2	3510	-3187
1	0	6	985	-1016	0	8	2	3237	-3298	0	8	8	412	516	1	4	2	1668	1475
1	0	8	620	-572	0	9	2	2020	-1940	0	9	8	393	420	1	5	2	< 148	282
1	0	10	1007	934	0	10	2	1980	1765	0	10	8	1164	-1247	1	6	2	238	-241
-1	0	2	3321	3464	0	11	2	1953	1779	0	11	8	307	348	1	7	2	2507	2869
-1	0	4	5306	5468	0	12	2	376	-373	0	12	8	797	813	1	8	2	1065	1184
-1	0	6	3361	3171	0	13	2	987	918	0	1	9	1542	-1380	1	9	2	2160	-2074
-1	0	8	2686	-2431	0	14	2	386	-385	0	2	9	1470	-1348	1	10	2	1438	-1262
-1	0	10	845	-790	0	15	2	283	324	0	3	9	1106	1084	1	11	2	1313	1214
-1	0	12	710	-717	0	1	3	757	-580	0	3	9	685	662	1	12	2	1183	1063
2	0	2	4084	-3925	0	2	3	3298	2893	0	4	9	1757	-1807	1	13	2	292	274
2	0	4	1892	-1672	0	3	3	3101	-2893	0	5	9	< 188	153	1	14	2	< 210	-42
2	0	6	1067	947	0	4	3	3228	-3174	0	6	9	248	376	1	15	2	< 136	66
2	0	8	1380	1395	0	5	3	179	184	0	7	9	267	259	1	16	2	3048	-2938
2	0	10	465	504	0	6	3	3965	4351	0	8	9	405	-493	-1	2	2	4247	-4416
-2	0	2	5838	-6878	0	7	3	1231	-1487	0	9	9	405	-493	-1	3	2	2204	2237
-2	0	4	2158	1938	0	8	3	1019	-1052	0	10	9	305	-376	-1	4	2	454	445
-2	0	6	5213	5381	0	9	3	277	-277	0	11	9	722	-795	-1	5	2	877	1048
-2	0	8	1196	-1058	0	10	3	1268	-1181	0	1	10	851	-749	-1	6	2	210	280
-2	0	10	2049	1902	0	11	3	< 197	-166	0	2	10	< 188	79	-1	7	2	1071	-1104
-2	0	12	< 445	-110	0	12	3	1312	1211	0	3	10	632	613	-1	8	2	4110	-4143
3	0	2	870	782	0	13	3	959	-969	0	4	10	1403	-1582	-1	9	2	1650	1479
3	0	4	3020	3076	0	14	3	1014	-967	0	5	10	561	-687	-1	10	2	1359	1178
3	0	6	605	571	0	15	3	435	397	0	6	10	851	-1049	-1	11	2	1528	-1326
3	0	8	< 405	207	0	1	4	6076	6418	0	7	10	922	-1194	-1	12	2	450	379
-3	0	2	4354	-4221	0	2	4	1046	-974	0	8	10	568	681	-1	14	2	223	-230
-3	0	4	2766	-2608	0	3	4	1913	-1627	0	9	10	740	781	-1	15	2	357	348
-3	0	6	1231	-1095	0	4	4	2787	-2577	0	1	11	591	-621	1	1	3	1313	-1171
-3	0	8	823	791	0	5	4	942	-913	0	2	11	282	-307	1	2	3	1135	961
-3	0	10	2673	2737	0	6	4	786	870	0	3	11	648	809	1	3	3	295	139
-3	0	12	903	891	0	7	4	786	870	0	4	11	886	1015	1	4	3	2066	-1937
4	0	2	1598	1607	0	8	4	453	-508	0	5	11	< 142	154	1	5	3	5406	-5545
4	0	4	1451	1493	0	9	4	1875	-1969	0	6	11	942	-1170	1	6	3	1956	2056
4	0	6	562	-559	0	10	4	688	-643	0	7	11	< 111	54	1	7	3	1549	1865
-4	0	2	1864	1759	0	11	4	1588	1538	0	8	11	1106	-1232	1	8	3	342	-127
-4	0	4	1898	-1913	0	12	4	777	-662	0	1	12	1106	-1232	1	9	3	< 256	-147
-4	0	6	2183	-2162	0	13	4	1436	-1491	0	2	12	< 424	533	1	10	3	< 264	62
-4	0	8	1958	-1941	0	14	4	431	-435	0	3	12	< 138	125	1	11	3	1999	-1909
-4	0	10	762	794	0	15	4	1026	-1109	0	4	12	< 310	427	1	12	3	1589	1482
-4	0	12	592	545	0	1	5	820	-771	0	5	12	< 310	427	1	13	3	775	654
5	0	2	1485	-1421	0	2	5	1881	1637	0	6	12	< 310	427	1	14	3	< 195	144
5	0	4	< 323	157	0	3	5	3553	3104	1	1	0	4214	4118	1	15	3	441	-460
-5	0	2	2742	2863	0	4	5	4221	-3940	1	2	0	345	-294	-1	1	3	2017	1768
-5	0	4	< 551	115	0	5	5	163	-72	1	3	0	398	-4279	-1	2	3	2978	-2533
-5	0	6	< 541	525	0	6	5	1891	2047	1	4	0	451	-498	-1	3	3	7232	-8438
-5	0	8	1122	-1163	0	7	5	240	-148	1	5	0	208	-205	-1	4	3	790	792
-5	0	10	1662	-1616	0	8	5	1028	-1185	1	6	0	806	763	-1	5	3	932	1113
-6	0	2	475	426	0	9	5	807	-838	1	7	0	3307	3166	-1	6	3	477	-553
-6	0	4	< 413	-90	0	10	5	1013	-892	1	8	0	1220	1036	-1	7	3	1761	-2000
-6	0	6	1823	1870	0	11	5	288	317	1	9	0	3630	-3260	-1	8	3	407	-423
-6	0	8	803	879	0	12	5	845	862	1	10	0	1048	854	1	9	3	< 247	31
0	2	0	352	152	0	13	5	1134	1110	1	11	0	1375	1239	-1	10	3	1101	-1003
0	4	0	227	-155	0	14	5	1054	-1027	1	12	0	477	-415	-1	11	3	599	-541
0	6	0	4068	4019	0	1	6	1723	-1586	1	13	0	660	-569	-1	12	3	988	-931
0	8	0	< 160	-171	0	2	6	3624	3348	1	14	0	< 223	165	1	13	3	2498	-2419
0	10	0	3601	3094	0	3	6	2045	-1762	1	15	0	719	-693	-1	14	3	256	233
0	12	0	1839	-1610	0	4	6	542	-476	1	1	1	3900	3311	-1	15	3	1121	1152
0	14	0	511	518	0	5	6	281	-223	1	2	1	7951	8743	1	1	4	1121	1026
0	16	0	1336	1546	0	6	6	743	674	1	3	1	5046	5276	1	2	4	1575	1474
0	1	1	934	945	0	7	6	1295	1387	1	4	1	3446	-3804	1	3	4	811	612
0	2	1	2862	2929	0	8	6	3029	3700	1	5	1	1261	1159	1	4	4	2576	-2233
0	3	1	2626	-3063	0	9	6	1959	-2226	1	6	1	1143	1423	1	5	4	< 217	-27
0	4	1	1393	-1783	0	10	6	447	-453	1	7	1	1532	1393	1	6	4	1821	-1850
0	5	1	4641	6320	0	11	6	328	356	1	8	1	635	-796	1	7	4	< 243	53
0	6	1	328	367	0	12	6	433	407	1	9	1	671	616	1	8	4	1880	2221
0	7	1	2048	-2116	0	13	6	< 140	77	1	10	1	742	703	1	9	4	< 262	-63
0	8	1	690	-588	0	14	6	318	386	1	11	1	706	597	1	10	4	2154	-2170
0	9	1	< 176	17	0	1	7	497	-497	1	12	1	1421	1255	1	11	4	322	281
					0	2	7	1542	-1272										

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
-1	5	4	2418	-2266	1	5	6	930	818	-1	10	7	764	805	-1	8	9	556	-692
-1	6	4	1826	1961	1	6	6	940	-878	-1	11	7	< 233	37	-1	9	9	235	-240
-1	7	4	1152	-1238	1	7	6	491	-471	-1	12	7	1388	1314	-1	10	9	950	-1035
-1	8	4	2318	-2486	1	8	6	1207	1516	-1	13	7	316	-324	-1	11	9	832	-866
-1	9	4	< 254	107	1	9	6	< 258	92	1	1	8	1731	-1732	1	1	10	825	-923
-1	10	4	2476	2313	1	10	6	921	-987	-1	2	8	473	-507	1	2	10	854	-960
-1	11	4	886	793	1	11	6	1420	-1379	1	3	8	991	915	1	3	10	350	430
-1	12	4	735	-686	1	12	6	399	419	1	4	8	866	812	1	4	10	608	-732
-1	13	4	656	-665	1	13	6	300	321	1	5	8	< 260	70	1	5	10	< 198	169
-1	14	4	< 201	72	-1	1	6	3010	2748	1	6	8	< 254	113	1	6	10	< 181	-21
-1	15	4	610	-627	-1	2	6	1435	-1293	1	6	8	< 254	113	1	6	10	< 181	-21
					-1	3	6	1715	-1480	1	7	8	-746	-918	1	7	10	405	-447
1	1	5	3470	-3169	-1	4	6	598	476	1	8	8	< 230	-74	-1	1	10	1614	1590
1	2	5	1058	-876	-1	5	6	398	348	1	9	8	1375	1493	-1	2	10	1340	1251
1	3	5	3395	3016	-1	6	6	1696	1620	1	10	8	192	155	-1	3	10	< 259	140
1	4	5	590	471	-1	7	6	2097	2277	1	11	8	455	-485	-1	4	10	735	-709
1	5	5	2546	-2470	-1	8	6	< 260	-205	-1	1	8	3156	2908	-1	5	10	475	-516
1	6	5	918	-892	-1	9	6	1427	-1562	-1	2	8	681	-507	-1	6	10	411	-430
1	7	5	< 256	178	-1	10	6	1380	1376	-1	3	8	1100	-951	-1	7	10	< 227	65
1	8	5	< 262	-154	-1	11	6	1223	1179	-1	4	8	210	207	-1	8	10	1180	1393
1	9	5	896	-984	-1	12	6	120	-655	-1	5	8	714	-657	-1	9	10	666	-579
1	10	5	310	-341	-1	13	6	< 159	75	-1	6	8	671	-658	-1	10	10	716	-700
1	11	5	636	-528	-1	14	6	< 155	-32	-1	7	8	1080	1088					
1	12	5	649	-628						-1	8	8	740	-998	1	1	11	239	-295
1	13	5	1142	1089	1	1	7	1178	1043	-1	9	8	1247	-1451	1	2	11	< 172	-27
1	14	5	260	-215	1	2	7	209	-129	-1	10	8	610	-670	1	3	11	535	-700
-1	1	5	2151	1990	1	3	7	1942	1815	-1	11	8	1172	1116	-1	4	11	157	206
-1	2	5	568	-338	1	4	7	1619	1565	-1	12	8	250	285	-1	1	11	284	-199
-1	3	5	237	-22	1	5	7	< 264	-11					-1	2	11	< 239	114	
-1	4	5	1848	-1704	1	6	7	2625	-2650	1	1	9	289	-172	-1	3	11	2195	2399
-1	5	5	5468	5424	1	7	7	1660	1894	1	2	9	1111	-1092	-1	4	11	406	-379
-1	6	5	2666	2740	1	8	7	340	456	1	3	9	859	-817	-1	5	11	< 216	-142
-1	7	5	1145	-1340	1	9	7	785	892	1	4	9	1743	1919	-1	6	11	< 202	157
-1	8	5	921	-1054	1	10	7	779	879	1	5	9	< 238	-41	-1	7	11	674	841
-1	9	5	614	648	1	11	7	225	-148	1	6	9	< 227	-134	-1	8	11	171	-215
-1	10	5	1708	-1561	1	12	7	676	-715	1	7	9	263	-361					
-1	11	5	2393	2382	-1	1	7	1323	1158	1	8	9	514	610	-1	1	12	807	-499
-1	12	5	361	406	1	2	7	3708	3318	1	9	9	< 163	-88	-1	2	12	1268	1363
-1	13	5	352	-294	-1	3	7	791	-676	-1	1	9	1368	-1269	-1	3	12	212	-231
-1	14	9	352	-312	-1	4	7	2635	-2414	-1	2	9	-379	-340	-1	4	12	216	263
					-1	5	7	202	232	-1	3	9	890	-794	-1	5	12	178	208
1	1	6	2814	-2584	-1	6	7	1736	1828	-1	4	9	2206	-2099	-1	6	12	288	-281
1	2	6	2753	2475	-1	7	7	559	-545	-1	5	9	2317	-2362					
1	3	6	242	-90	-1	8	7	< 265	51	-1	6	9	1808	1973					
1	4	6	347	-315	-1	9	7	275	-136	-1	7	9	307	350					

The environment of the disulphide group. The environment of the disulphide group in crystals of thiuret hydrobromide is shown in Fig. 3, and the corresponding interatomic distances and angles are listed in Table 5.

The sum of the van der Waals radii for bromine and sulphur is 3.80 Å, according to Paulig's¹⁵ values, and thus Fig. 3 shows that the sulphur atoms of the disulphide group form four close contacts with three neighbouring bromide ions. Two of the close contacts occur in a very nearly linear Br...S—S...Br arrangement, with bromide-sulphur distances 3.391 and 3.453 ± 0.006 Å and corresponding Br...S—S angles 173.1 and 171.8 ± 0.5°, respectively. This partial covalent bonding between bromide and sulphur may be established through a transfer of charge from the bromine ions to those *p*-orbitals on the sulphur atoms already engaged in the sulphur-sulphur σ -bond, probably at the expense of this bond. Bromine-sulphur distances of 3.40–3.45 Å correspond to σ -bond orders of 0.26–0.23, if a linear relationship bond-order/bond-length is assumed, and if the sum of van der Waals radii and single bond radii for bromine and sulphur are taken to be 3.80 Å and 2.18 Å, respectively.

In crystals of thiuret hydroiodide there is a very nearly linear I...S—S...I arrangement analogous to that in thiuret hydrobromide. The iodine-sulphur close contacts are 3.62 Å and the I...S—S angles 171°. If the sum of van der Waals radii and single bond radii¹⁶ for sulphur and iodine are taken to be 4.00 Å and 2.37 Å, respectively, and if a linear relationship bond-order/bond-length is assumed, the iodide-sulphur distances of 3.62 Å correspond to a σ -bond order of 0.23. The σ -bond order of the partial halogen-sulphur bonding

in the linear $X\cdots S-S\cdots X$ arrangement is thus about the same in thiuret hydroiodide and hydrobromide.

If the partial bonding between halogen and sulphur, described above, influences the length of the sulphur-sulphur bond in thiuret hydroiodide and hydrobromide, it probably does so to a rather small degree. Preliminary results from an almost completed X-ray crystallographic investigation of thiuret hydrochloride hemihydrate,¹⁶ show that the sulphur-sulphur bond in this compound is 2.063 ± 0.004 Å. Also in crystals of thiuret hydrochloride hemihydrate a very nearly linear $X\cdots S-S\cdots X$ arrangement occurs, the corresponding sulphur-chlorine distances being 3.864 ± 0.004 Å and 3.527 ± 0.004 Å. Taking 3.65 Å as the sum of van der Waals radii for sulphur and chlorine,¹⁵ the sulphur-chlorine distance of 3.527 Å indicates a weak bond, which, however, probably is too weak (σ -bond order 0.10) to influence the sulphur-sulphur bond. Accordingly the sulphur-sulphur bond in thiuret hydrochloride should be unaffected by neighbouring chloride ions, and the bond length 2.063 ± 0.004 Å then indicates that there is some conjugation, albeit very weak, over the sulphur-sulphur bond in the thiuret ion; the sulphur-sulphur bonds, 2.081 ± 0.008 Å and 2.088 ± 0.012 Å, in thiuret hydrobromide and hydroiodide are slightly lengthened due to partial sulphur-halogen bonding.

In crystals of 3-phenyl-1,2-dithiolium iodide,⁸ a linear $I\cdots S-S$ arrangement occurs, with $S-S = 2.00 \pm 0.01$ Å and $I\cdots S = 3.374 \pm 0.007$ Å; the partial iodine-sulphur bonding of σ -bond order 0.39 does here not seem to have caused a lengthening of the sulphur-sulphur bond. However, aside from other effects, in thiuret hydroiodide and hydrobromide the sulphur-sulphur bond is "attacked" from both sides.

Beside the sulphur-bromine close contacts discussed above, the sulphur atoms of the disulphide group in crystals of thiuret hydrobromide form two close contacts with a third bromide ion. This bromide ion lies close to the nor-

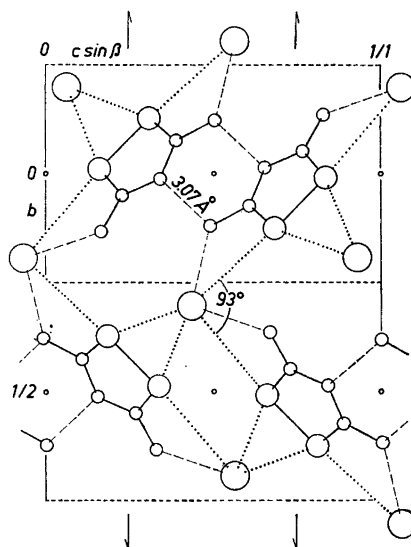


Fig. 4. The arrangement of ions in the unit cell as seen along the a axis. Broken lines indicate hydrogen bonds $N-H\cdots N$ and $N-H\cdots Br^-$, and dotted lines indicate the partial covalent bonding between bromine and sulphur.

mal to the sulphur-sulphur bond through its midpoint, 0.57 Å from the plane of the thiuret ion; the sulphur-bromide distances are 3.399 and 3.382 \pm 0.006 Å. The S...Br...S angle is rather small, 35.7°, and it appears likely that partial sulphur-bromine bonds are established through overlap of one filled orbital of the bromide ion with two orbitals of the sulphur atoms, one from each. The bonding thus seems to be of the same nature as the sulphur-iodine bonding in an equivalent triangular sulphur-iodine-sulphur configuration in 3-phenyl-1,2-dithiolium iodide. Because both sulphur atoms form weak bonds with bromide, one may assume that electrons are partially transferred from the bromide ion to the sulphur atoms, *e. g.* to those *p*-orbitals on the sulphur atoms already engaged in the sulphur-carbon σ -bonds, with weak three-center two-electron bonds as result.

The *a*-projection of the crystal structure of thiuret hydrobromide is shown in Fig. 4. The thiuret ions are arranged in pairs across a center of symmetry, through N—H...N hydrogen bonds of length 3.07 \pm 0.03 Å. The least squares plane of a thiuret ion passes 0.15 Å from this center. The exocyclic nitrogen atoms of each ion in a pair form hydrogen bonds to the bromide ions in their respective Br...S—S...Br arrangements. Br...S—S...Br...S—S...Br chains, with S...Br...S angles of 93°, zig-zag through the crystal in the direction of the *b* axis; the chains are interconnected through the partial bonding between the bromide ion and *both* sulphur atoms of the disulphide group.

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