Table 10. *Angle results*

Combination[a]		χ^2 obtained	Slope	Intercept	Correlation coefficient
1	2	10·9	1·22 (11)	−0·17 (10)	0·97
1	3	13·1	1·48 (15)	−0·39 (15)	0·96
1	4	5·9	0·87 (8)	−0·10 (7)	0·97
2	3	8·3	0·92 (8)	−0·02 (8)	0·97
2	4	34·0	1·85 (7)	0·08 (7)	0·99
3	4	15·1	1·39 (11)	−0·14 (11)	0·97

$\chi^2_{10,0\cdot05} = 18\cdot3$ $\chi^2_{10,0\cdot01} = 23\cdot2$

(*a*) For numbering see Table 8.

Conclusions

Derived bond distances and angles are unaffected by TDS correction. The influence of the TDS correction on the r.m.s.d.'s is rather small. The phenyl ring of benzalazine is planar while the atoms C(1) and N are significantly out of this plane. The structure determined in this work (165 K) is significantly different from the structure determined at room temperature.

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A Simple Refinement of Density Distributions of Bonding Electrons.
IX. Bond Electron Density Distribution in Thiourea, $CS(NH_2)_2$, at 123 K

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(*Received* 11 *March* 1978; *accepted* 13 *April* 1978)

A model for thiourea is described in which valence electrons are included separately in the refinement. A significantly better R value is obtained for this model (0·017) compared with the usual spherical atom refinement (0·025). Core parameters agree within 2·5σ with those from the neutron diffraction study [Elcombe & Taylor (1968). *Acta Cryst.* A**24**, 410–420]. Bond population parameters are given, and a dynamic valence density based on the refined model is presented. This density is compared with the valence density of urea [Mullen & Hellner (1978). *Acta Cryst.* B**34**, 1624–1627].

Introduction

This study of thiourea represents a continuation of the work in which a model describing valence density distributions is refined (Hellner, 1977; Mullen & Hellner, 1977).

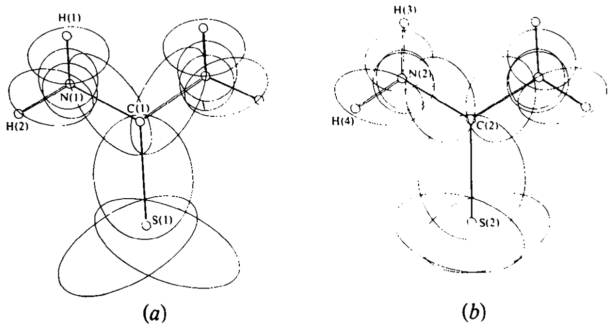
In a previous paper (Mullen & Hellner, 1978), the same valence density model was applied to urea, and a comparison of the two molecules is given below.

Thiourea has been studied by X-ray diffraction (Truter, 1967), by neutron diffraction (Elcombe & Taylor, 1968, hereafter ET) and by electron diffraction (Dvoryankina & Vainshtein, 1960). Thiourea undergoes a series of phase changes on cooling below room temperature (Goldsmith & White, 1959). While at room temperature there is only one molecule in the asymmetric unit, at 123 K there are two independent molecules.

Experimental

A crystal of thiourea was ground to a sphere of 0·50 mm diameter. Three-dimensional X-ray data at 123 ± 2 K were collected on a Philips (PW 1100) four-circle diffractometer equipped with a Heraeus–Leybold liquid nitrogen cryostat. Four symmetry-equivalent octants were measured to sin $\theta/\lambda = 0{\cdot}90$ Å^{-1} using graphite monochromated Mo $K\alpha$ radiation. Agreement between symmetry-equivalent reflections was 2·8%. A total of 1142 independent reflections were obtained, of which 21 had $F \leq 2\sigma(F)$ and were designated as unobserved. The averaged data were corrected for Lorentz and polarization effects and for absorption ($\mu = 6{\cdot}29$ cm^{-1}). An isotropic extinction correction was applied using Finger's (1972) program. The highest extinction correction factor (applied to F^2) was 0·63.

Cell dimensions at 123 K were measured as $a = 7{\cdot}487$ (3), $b = 8{\cdot}536$ (3) and $c = 5{\cdot}474$ (3) Å. At this temperature thiourea crystallizes in the orthorhombic space group $P2_1ma$ [$Pmc2_1$, *International Tables for X-ray Crystallography* (1952)].



(*a*) (*b*)

Fig. 1. Thiourea molecules at 123 K, showing the nature of the electron density distributions in the planes of the molecules as 50% probability ellipsoids. (*a*) Molecule (1); (*b*) molecule (2).

Refinement of a model including valence electrons

For the starting model in the refinement, core parameters were taken from the neutron diffraction investigation of ET at 115 K. Bond charges were placed at the mid-points of bonds. The lone pairs on S and N were placed at the respective core positions, but allowed to move from these positions on refinement.

For the cores, form factors were taken from *International Tables for X-ray Crystallography* (1974). Bond charges were given Gaussian form factors described by β_{ij} tensors. The C=S bonds were given populations of 4 electrons, the C–N bonds 2 e and the N–H bonds 1·5 e in the starting model. The H atoms were allocated 0·5 e.

In the first stages of the refinement the population parameters and β_{ij} of the bond charges were allowed to vary. In later stages the positional parameters of the bond charges were refined. Finally all parameters, including positional and thermal parameters of the cores, were refined. The occupancy parameters for the cores were kept fixed throughout to the two 1*s* electrons (for C and N) which can be regarded as non-valence electrons. For S, the core consists of 10 electrons. This type of refinement has been described in detail in earlier papers in this series (Hellner, 1977; Mullen & Hellner, 1977, 1978).

Refinement of the structure of thiourea at 123 K by the method outlined above (162 parameters) led to an R of 0·017 ($R_w = 0{\cdot}021$) compared to 0·025 ($R_w = 0{\cdot}033$) for the usual spherical-atom refinement (58 parameters) using the same data set. This is a significant improvement (Hamilton, 1965) at the 0·005 level.

Discussion of results

Bond charge distributions (β_{ij}) are represented as 50% ellipsoids (Fig. 1) and are drawn using *ORTEP* (Johnson, 1965). Core and bond charge parameters are given in Table 1 and their populations in Table 2.* Mulliken populations appear in Table 3.

From Table 1 it can be seen that the agreement between the core parameters from this refinement and those from the neutron diffraction study (ET) at 115 K show some discrepancies which are quite large in absolute terms. However, all parameters for non-hydrogen atoms agree to within 2·5σ. The standard deviations of the β_{ij} of ET are rather large, reaching about 75% of the β_{ij} value in the worst case.

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33563 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Core and bond charge parameters*

(*a*) Comparison of core positional parameters for thiourea at 123 K. (*a*) Spherical atom, X-ray; (*b*) molecular model, X-ray; (*c*) high angle, X-ray, sin $\theta/\lambda > 0{\cdot}60$ Å^{-1}; (*d*) neutron diffraction (Elcombe & Taylor, 1968).

		x	y	z			x	y	z
Molecule (1)					Molecule (2)				
S(1)	*a*	0·0056 (3)	0	0·3457 (1)	S(2)	*a*	0·0256 (3)	0·5	0·1229 (1)
	b	0·0062 (7)	0	0·34562 (6)		*b*	0·0259 (7)	0·5	0·12296 (6)
	c	0·0057 (2)	0	0·34566 (5)		*c*	0·0254 (2)	0·5	0·12297 (6)
	d	0·0062 (16)	0	0·3454 (19)		*d*	0·0272 (16)	0·5	0·1215 (17)
C(1)	*a*	0·0737 (4)	0	0·0470 (4)	C(2)	*a*	−0·0978 (4)	0·5	0·3865 (4)
	b	0·0734 (7)	0	0·0460 (3)		*b*	−0·0974 (7)	0·5	0·3864 (3)
	c	0·0731 (3)	0	0·0466 (2)		*c*	−0·0981 (3)	0·5	0·3869 (2)
	d	0·0733 (10)	0	0·0455 (7)		*d*	−0·0985 (9)	0·5	0·3860 (6)
N(1)	*a*	0·1000†	0·1335 (2)	−0·0738 (3)	N(2)	*a*	−0·1472 (4)	0·3661 (2)	0·4919 (4)
	b	0·1000	0·1334 (1)	−0·0748 (2)		*b*	−0·1474 (7)	0·3660 (1)	0·4917 (2)
	c	0·1000	0·1338 (1)	−0·0738 (2)		*c*	−0·1475 (2)	0·3658 (1)	0·4923 (2)
	d	0·1000	0·1337 (3)	−0·0756 (4)		*d*	−0·1475 (5)	0·3656 (3)	0·4912 (6)
H(1)*	*a*	0·112 (7)	0·162 (5)	−0·262 (8)	H(3)	*a*	−0·223 (5)	0·366 (4)	0·632 (6)
	b,d	0·1365 (12)	0·1305 (10)	−0·2506 (13)		*b,d*	−0·2169 (13)	0·3698 (9)	0·6506 (14)
H(2)	*a*	0·071 (5)	0·240 (3)	−0·010 (6)	H(4)	*a*	−0·105 (5)	0·255 (4)	0·428 (6)
	b,d	0·0772 (18)	0·2378 (8)	0·0052 (14)		*b,d*	−0·1028 (16)	0·2614 (10)	0·4271 (13)

(*b*) Comparison of core thermal parameters for thiourea at 123 K ($\beta_{ij} \times 10^4$). Anisotropic temperature factors have the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

		β_{11} (or B)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule (1)							
S(1)	*a*	81 (1)	37 (1)	56 (1)	0	3 (1)	0
	b	80 (1)	35 (1)	50 (1)	0	2 (1)	0
	c	83 (1)	37 (1)	57 (1)	0	3 (1)	0
	d	99 (21)	26 (12)	52 (30)	0	−20 (19)	0
C(1)	*a*	58 (3)	40 (2)	79 (6)	0	9 (3)	0
	b	61 (2)	30 (1)	83 (4)	0	12 (2)	0
	c	63 (2)	34 (1)	79 (3)	0	14 (2)	0
	d	73 (10)	19 (5)	54 (13)	0	6 (8)	0
N(1)	*a*	115 (3)	37 (2)	102 (4)	−3 (2)	39 (3)	6 (2)
	b	117 (2)	37 (1)	97 (2)	−2 (1)	35 (2)	3 (1)
	c	122 (2)	35 (1)	101 (2)	−2 (1)	42 (2)	6 (1)
	d	113 (4)	36 (4)	94 (8)	1 (5)	33 (7)	5 (5)
H(1)*	*a*	4·48 (1·12)					
	b,d	242 (25)	70 (10)	151 (26)	−3 (11)	94 (17)	14 (11)
H(2)	*a*	0·78 (0·58)					
	b,d	183 (17)	50 (9)	198 (20)	14 (13)	34 (18)	−7 (12)
Molecule (2)							
S(2)	*a*	66 (1)	33 (1)	72 (1)	0	4 (1)	0
	b	64 (1)	31 (1)	67 (1)	0	2 (1)	0
	c	67 (1)	33 (1)	73 (1)	0	5 (1)	0
	d	86 (17)	35 (12)	34 (27)	0	−14 (18)	0
C(2)	*a*	48 (3)	44 (3)	87 (6)	0	1 (3)	0
	b	49 (2)	36 (2)	92 (4)	0	4 (2)	0
	c	49 (2)	40 (1)	88 (3)	0	4 (2)	0
	d	51 (7)	49 (7)	61 (13)	0	9 (9)	0
N(2)	*a*	82 (3)	37 (1)	143 (4)	−1 (2)	40 (3)	7 (2)
	b	84 (2)	39 (1)	132 (3)	−1 (1)	40 (2)	6 (2)
	c	89 (2)	35 (1)	144 (2)	−1 (1)	45 (1)	6 (1)
	d	84 (4)	40 (4)	117 (8)	−9 (5)	37 (5)	3 (5)
H(3)	*a*	1·79 (0·79)					
	b,d	174 (14)	85 (10)	189 (25)	−9 (11)	118 (20)	15 (13)
H(4)	*a*	1·51 (0·75)					
	b,d	133 (13)	66 (12)	217 (23)	−5 (11)	40 (14)	21 (12)

Table 1 (*cont.*)

(*c*) Positional parameters and β_{ij} ($\times 10^3$) for bond charges in thiourea at 123 K

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule (1)									
S(1)–C(1)	−0·004 (9)	0	0·197 (7)	112 (14)	79 (9)	301 (38)	0	−6 (26)	0
C(1)–N(1)	0·083 (3)	0·058 (2)	−0·009 (5)	47 (3)	51 (4)	221 (25)	−8 (3)	6 (6)	−67 (9)
N(1)–H(1)	0·144 (4)	0·133 (5)	−0·149 (4)	65 (8)	54 (5)	65 (6)	−9 (6)	6 (6)	−1 (5)
N(1)–H(2)	0·081 (3)	0·172 (4)	−0·040 (3)	47 (4)	58 (6)	64 (5)	5 (5)	−1 (4)	−12 (4)
S(1)(l.p.)$^{(i)}$	0·022 (9)	−0·038 (7)	0·408 (4)	78 (10)	162 (25)	181 (17)	−35 (17)	22 (17)	−101 (20)
N(1)(l.p.)$^{(ii)}$	0·136 (1)	0·134 (1)	−0·043 (2)	20 (1)	25 (1)	60 (4)	−4 (1)	−2 (2)	−3 (2)
	0·069 (2)	0·137 (1)	−0·097 (2)	37 (3)	29 (2)	74 (5)	−3 (2)	4 (3)	−1 (3)
Molecule (2)									
S(2)–C(2)	−0·033 (7)	0·5	0·234 (7)	107 (21)	92 (14)	246 (41)	0	−55 (22)	0
C(2)–N(2)	−0·115 (4)	0·441 (1)	0·442 (5)	69 (5)	39 (3)	122 (10)	3 (3)	−13 (7)	−13 (4)
N(2)–H(3)	−0·160 (4)	0·360 (3)	0·545 (3)	51 (4)	37 (4)	51 (5)	−3 (4)	−8 (4)	3 (3)
N(2)–H(4)	−0·127 (4)	0·321 (3)	0·443 (4)	74 (8)	63 (8)	62 (6)	−13 (6)	18 (6)	−27 (6)
S(2)(l.p.)$^{(i)}$	0·041 (7)	0·475 (10)	0·098 (7)	74 (8)	135 (17)	168 (17)	51 (11)	34 (9)	−4 (21)
N(2)(l.p.)$^{(ii)}$	−0·108 (1)	0·368 (2)	0·506 (2)	31 (2)	30 (2)	73 (4)	4 (2)	−1 (3)	1 (4)
	−0·179 (1)	0·370 (2)	0·461 (2)	33 (2)	25 (1)	68 (5)	−1 (2)	−2 (3)	−4 (3)

(i) Lone pairs on S.
(ii) Lone pair on N.

* H fixed at neutron diffraction values.
† Parameter fixed to define origin.

Table 2. *Bond and core populations (electrons) in thiourea at* 123 K

Molecule (1)		Molecule (2)	
S(1)	10·0	S(2)	10·0
C(1)	2·0	C(2)	2·0
N(1)	2·0	N(2)	2·0
H(1)	0·64 (4)	H(3)	0·57 (4)
H(2)	0·72 (3)	H(4)	0·74 (3)
S(1)–C(1)	3·20 (8)	S(2)–C(2)	2·86 (8)
C(1)–N(1)	1·85 (3)	C(2)–N(2)	1·92 (3)
N(1)–H(1)	1·11 (3)	N(2)–H(3)	1·10 (3)
N(1)–H(2)	1·19 (3)	N(2)–H(4)	1·19 (3)
l.p. S(1)	2·86 (6)	l.p. S(2)	2·90 (6)
l.p. N(1)	1·64 (6)	l.p. N(2)	1·64 (6)

Table 3. *Mulliken populations (electrons) for thiourea at* 123 K

Molecule (1)			Molecule (2)		
	(*a*)	(*b*)		(*a*)	(*b*)
S(1)	14·46 (10)	14·46 (10)	S(2)	14·33 (10)	14·33 (10)
C(1)	5·45 (7)	5·45 (7)	C(2)	5·35 (7)	5·35 (7)
N(1)	5·72 (11)	6·40 (11)	N(2)	5·75 (11)	6·40 (11)
H(1)	1·20 (6)	0·88 (6)	H(3)	1·12 (6)	0·84 (6)
H(2)	1·32 (5)	0·96 (5)	H(4)	1·34 (5)	0·97 (5)

(*a*) Mulliken population calculated in the usual way.
(*b*) Mulliken populations considering H as having no core structure.

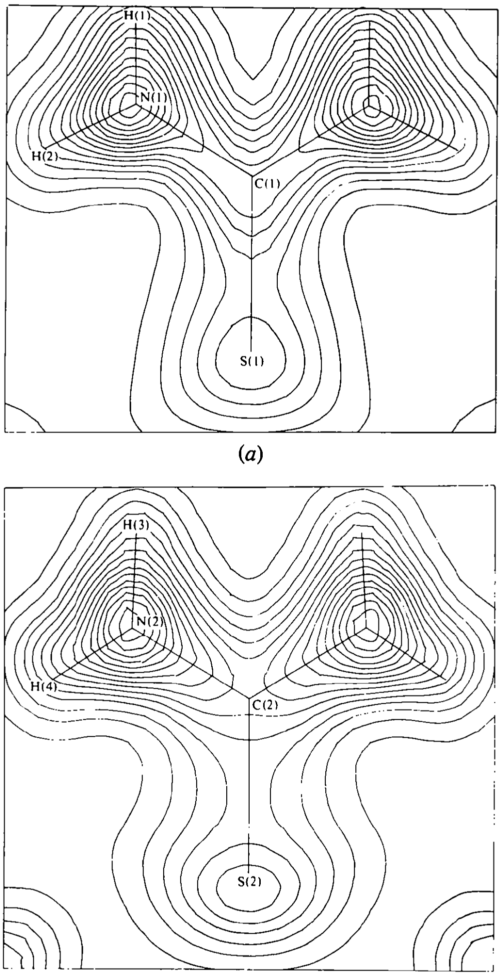
The absolute agreement with parameters from a high-order X-ray refinement ($\sin\theta/\lambda > 0{\cdot}60$) is much better, as can be seen from Table 1. However, since the standard deviations for both sets of parameters compared are quite small, the agreement ranges to as much as 7σ.

The refinement led to abnormally low temperature factors for the residual charges at the protons, and these parameters (x,y,z,β_{ij}) were therefore kept fixed at the neutron diffraction values of ET.

The electron populations for the bond charges in the two molecules are very similar (Table 2). The largest difference is for C–S ($\sim 5\sigma$). Attempts to constrain the two molecules to have the same bond charge parameters for this bond showed that these differences had no significant effect on the valence or deformation densities obtained from constrained and unconstrained models. In addition, when the constraints were removed towards the end of the refinement, these differences reappeared on further refinement with all parameters free.

The sum of the Mulliken populations (Table 3) is about 9% below the ideal value. If Mulliken populations are calculated in the usual way (*i.e.* by dividing the bond population between the atoms involved in the bond) a rather low value is obtained for the N atoms and somewhat high values for H atoms. Correlation between the excess charge at the protons and the N–H bonds is very high and probably leads to an underestimate of the N–H bond population and an overestimate of the populations at the proton. Since H has no real core structure (Stewart, 1976), if we sum the N–H bond and corresponding proton populations for each N–H bond (*i.e.* valence electrons only) more reasonable values for the Mulliken populations of N and H are obtained [Table 3, column (*b*)].

In Fig. 2 valence density maps for the two independent thiourea molecules are shown. These densities are calculated according to the expression:



(a)

(b)

Fig. 2. Valence electron density sections for thiourea at 123 K in the molecular planes. S, C, N cores are subtracted but not H. Contour intervals are 0·25 e Å^{-3}. Both zero and positive contours are solid lines; all negative contours are less than −0·25 e Å^{-3}. (a) Molecule (1); (b) molecule (2).

$\rho_{\text{valence}} = \rho_{\text{molecule}} - \rho_{\text{cores}}$, where the C and N cores comprise the $1s^2$ electrons, and S the $1s^2 2s^2 2p^6$ electrons. H atoms are considered to have no core structure and are not subtracted from the molecular density.

In the two molecules the densities at the N atoms are nearly equal (3·66 and 3·69 e Å^{-3}). The peaks at S differ slightly at 1·22 and 1·38 e Å^{-3} in molecules (1) and (2) respectively. Electron densities in Table 4 are quoted for approximate mid-points of bonds since valence peaks generally occur at atom positions.

An error map based on the coefficients ($F_o - F_c$) for the molecular model showed no peaks outside the range ±0·1 e Å^{-3}. This is less than 2σ, where σ for the electron density in the model is 0·059 e Å^{-3} (Rees, 1976).

Table 4. *Valence density distribution in thiourea at* 123 K (e Å^{-3})

Molecule (1)		Molecule (2)	
S(1)	1·22	S(2)	1·38
C(1)	1·60	C(2)	1·40
N(1)	3·62	N(2)	3·69
H(1)	1·45	H(3)	1·15
H(2)	1·00	H(4)	1·25
S(1)–C(1)$^{(a)}$	0·94	S(2)–C(2)	0·83
C(1)–N(1)	1·80	C(2)–N(2)	2·15
N(1)–H(1)	2·60	N(2)–H(3)	2·00
N(1)–H(2)	2·20	N(2)–H(4)	2·50

(a) At mid-points of bonds.

Table 5. *Bond lengths in thiourea* (Å)

	This work (123 K)		Elcombe & Taylor (1968) (~115 K)
C(1)–S(1)	1·716 (8)		1·723 (11)
C(2)–S(2)	1·712 (8)		1·733 (11)
C(1)–N(1)	1·332 (6)		1·334 (3)
C(2)–N(2)	1·334 (8)		1·335 (4)
N(1)–H(1)	1·001$^{(a)}$	0·80 (6)$^{(b)}$	1·000 (8)
N(1)–H(2)	1·008	1·00 (6)	1·006 (8)
N(2)–H(3)	1·014	0·93 (6)	1·021 (8)
N(2)–H(4)	1·017	0·93 (5)	1·012 (10)

(a) H positions fixed at neutron diffraction values.
(b) H atom parameters included in refinement.

In Table 5 bond lengths from our model are compared with those of ET. The C–S bond lengths obtained by ET are longer than those from this work. This arises mainly from differences in the cell constants. It appears that ET have used the cell constants of Goldsmith & White (1959) which are based on film measurements. While no difference in the two C–S bond lengths appear from our results, the neutron diffraction results of ET (Table 5) show a difference of 0·01 Å (~1σ). In the case of deuterated thiourea, ET obtain very different C–S bond lengths for molecules (1) and (2), *i.e.* 1·707 (13) and 1·740 (12) Å respectively.

Summary

A comparison of the valence densities of the two independent molecules (Table 4) shows small differences only in the C–S bonds and at the S core positions. While the densities at N are closely similar in both molecules, the values for C–S (at bond mid-points) are about 0·9 and 0·8 e Å^{-3}, and for S 1·22 and 1·38 e Å^{-3}, in molecules (1) and (2) respectively.

The valence density of urea at 123 K has been reported in a previous paper by Mullen & Hellner (1978). A comparison with the thiourea molecules described here shows that the peak height at N in urea (3·75 e Å^{-3}) is very close to the values found for both thiourea molecules (3·62 and 3·69 e Å^{-3}). In contrast, the peak height at O in urea (7·0 e Å^{-3}) is considerably higher than those at S in thiourea. The mean C—S bond population (3·03 e) may be compared with a value of 3·27 e for C—O in urea.

The C—N bond populations (e) compare very closely: 1·89 in urea; 1·85 and 1·92 in thiourea (Table 2). The N—H bond populations are lower in thiourea (1·15 e) than in urea (1·33 e), mean values being quoted in both cases. The populations of the residual charge at the protons show the opposite trend with mean values of 0·67 and 0·39 e for thiourea and urea respectively.

Lone-pair populations at S in thiourea are much lower (mean = 2·88 e) than at O in urea (4·16 e). The N lone pair also has a lower population in thiourea (1·64 e) than in urea (2·36 e).

It is intended in future papers in this series to publish experimental deformation densities and to compare these with quantum chemically derived densities. Additionally, form factors for bond charges obtained from the experimental model (Scheringer, Kutoglu, Mullen & Hellner, 1978) will be compared with those of Fritchie (1966) and Cromer & Larson (1974).

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The Crystal and Molecular Structure of 2′,3′,5′-Tri-*O*-acetyl-6-*O*-(mesitylenesulphonyl)guanosine

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(*Received* 22 *March* 1978; *accepted* 21 *April* 1978)

The structure of a 6-*O*-mesitylenesulphonyl derivative of 2′,3′,5′-tri-*O*-acetylguanosine, $C_{24}H_{29}N_5O_{10}S$, has been determined by X-ray diffraction. Crystals are monoclinic, a = 26·370 (4), b = 8·200 (2), c = 17·991 (3) Å, β = 132·77 (4)°. The solution of the structure in space group $C2$ was not straightforward and is described in detail. Refinement converged at R = 0·110 for 1102 observed reflections. The guanine base displays some deviations from its usual geometry due to the loss of C(6)—O(6) double-bond character. The ribose sugar is C(2′)-*endo* puckered.