

## The Crystal and Molecular Structure of 5-Amino-2-thiol-1,3,4-thiadiazole

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The crystal structure of 5-amino-2-thiol-1,3,4-thiadiazole ( $C_2H_3N_3S_2$ ) has been determined by three-dimensional Patterson and Fourier methods and refined by block-matrix least-squares calculations. The crystals are monoclinic, space group  $P2_1/c$  with four molecules in a unit cell of dimensions  $a=6.167$ ,  $b=10.048$ ,  $c=9.007$  Å,  $\beta=116.8^\circ$ . The final  $R$  index is 0.106 for 796 observed reflexions, collected with  $Cu K\alpha$  radiation. The molecule may be regarded as being planar since the deviations of the atoms from the mean plane of the molecule are all less than 0.02 Å. Bond lengths indicate that the compound exists in the thione rather than the thiol form. The 1,3,4-thiadiazole ring possesses a fair degree of aromaticity with a localized  $C(1)=N(1)$  double bond of length 1.305 (6) Å. Other C–N bond lengths are 1.334 and 1.339 Å with a mean estimated standard deviation of 0.009 Å. The N–N bond length is 1.382 (8) Å. The cyclic C–S distances are 1.746 and 1.748 Å and the exocyclic C–S bond length is 1.678 Å, the mean e.s.d. of these three bonds is 0.006 Å. Of particular interest is the short S–S intramolecular contact of 3.008 Å which is approximately 0.5 Å shorter than the sum of the Pauling van der Waals radii. There is a reasonable probability that hydrogen bonds of type  $N-H \cdots S$  and length 3.32 Å exist, joining pairs of molecules across centres of symmetry.

### Introduction

Interest in the structure of this compound has arisen because of its use as an inhibitor of the corrosion of carbon steels in dilute sulphuric acid (Aronson & Belen'kii, 1965). These workers investigated the corrosion inhibitive properties of a large number of substances containing sulphur. They found that compounds containing two-valent sulphur in the  $NH-CS-NH$ -groups were active inhibitors and that 5-amino-2-thiol-1,3,4-thiadiazole (ATDZOLE), reduced the corrosion rate of steel by some 90%. The compound is one of a group of corrosion inhibitors being investigated in this laboratory in a study of the factors affecting corrosion inhibition.

The compound is also of interest chemically, largely because of the possible existence of several tautomeric forms. Katritzky & Lagowski (1963) collated the chemical data and considered the most likely possibilities to be either a thione (I) or a thiol (II) form (Fig. 1).

### Experimental

#### Crystal data

The compound ATDZOLE was obtained from the Aldrich Chemical Company.

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Suitable crystals for an X-ray investigation were obtained by recrystallization from acetone. The crystals grew as thin transparent plates slightly elongated along the [100] direction.

Unit-cell dimensions were obtained from precession photographs of the  $h0l$ ,  $hk0$ , and  $0kl$  reciprocal lattice nets using  $Mo K$  radiation ( $\lambda=0.7107$  Å) (Table 1). The density of the crystals was determined by flotation in a mixture of 1-bromonaphthalene and 1,2-dibromoethane.

Table 1. Crystal and experimental data for 5-amino-2-thiol-1,3,4-thiadiazole

Formula weight	133.19( $C_2H_3N_3S_2$ )
Unit-cell dimensions	
$a$	$6.167 \pm 0.020$ Å
$b$	$10.048 \pm 0.041$
$c$	$9.007 \pm 0.042$
$\beta$	$116.8 \pm 0.2^\circ$
$V$	$500.98$ Å <sup>3</sup>
Crystal density	
measured ( $D_m$ )	$1.75$ g.cm <sup>-3</sup>
calculated ( $D_c$ )	1.77
Systematic absences	$h0l$ when $l=2n+1$ $0k0$ when $k=2n+1$ $P2_1/c$ ( $C_2^2h$ )
Space group	$P2_1/c$ ( $C_2^2h$ )
Number of molecules per unit cell ( $Z$ )	4
$\mu$ ( $Cu K\alpha$ , $\lambda=1.5418$ Å)	$81.22$ cm <sup>-1</sup>
Total number of electrons per unit cell ( $F_{000}$ )	272
Number of observed reflexions	796

**Data collection**

The two crystals used to collect the intensity data had dimensions  $0.13 \times 0.33 \times 0.40$  mm for  $nk\ell$  ( $n=0$  to 3) and  $0.12 \times 0.25 \times 0.35$  mm for  $hmk$  ( $n=0$  to 5). Three-dimensional data were recorded photographically by the equi-inclination Weissenberg technique using nickel-filtered copper radiation. The multiple-film technique was used. Integrated intensities were measured on a Joyce-Loebl 'Flying Spot' integrating microdensitometer.

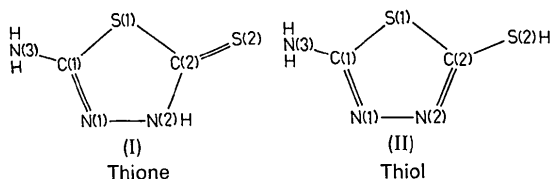


Fig. 1. Tautomeric forms of 5-amino-2-thiol-1,3,4-thiadiazole.

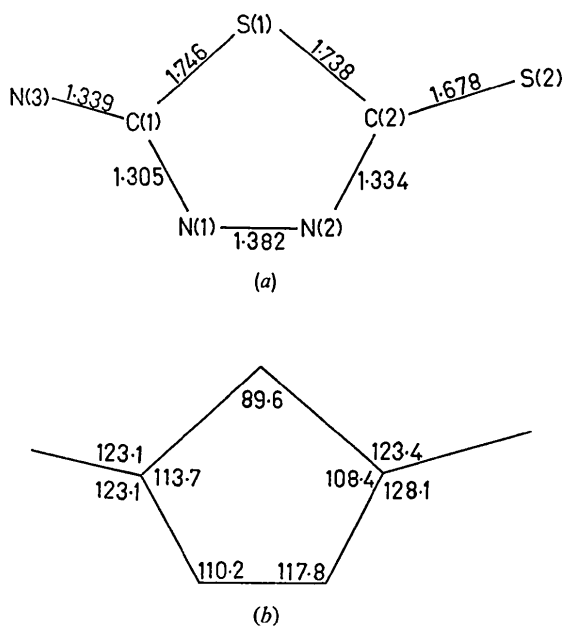


Fig. 2.(a) Bond lengths and (b) bond angles in 5-amino-2-thiol-1,3,4-thiadiazole.

Lorentz and polarization corrections were made in the usual way. Interlayer scaling factors were determined by comparing common reciprocal lattice rows, utilising the method of Monahan, Schiffer & Schiffer (1967). No corrections were made for absorption or extinction effects.

**Structure determination and refinement**

The coordinates of the two sulphur atoms S(1) and S(2) were determined from a three-dimensional, sharpened Patterson synthesis.

A structure factor calculation based on the S(1) and S(2) coordinates gave an  $R = \sum |kF_o| - |F_c| / \sum |kF_o|$  value of 0.44. The light atoms, excluding hydrogen atoms, were determined from a subsequent Fourier synthesis using the phases obtained from the sulphur atom contributions. A second structure factor calculation based on all atoms, excluding hydrogen atoms, reduced  $R$  to 0.32.

At this stage refinement proceeded by the method of least squares using the block-diagonal approximation. After four cycles using isotropic temperature factors,  $R$  had reduced to 0.16. Anisotropic temperature factors were then introduced and after three further cycles  $R$  was 0.116. Two further cycles reduced  $R$  to 0.109 using the weighting scheme.

$$\sqrt{W} = \left[ 1 / \left( 1 + \frac{(k|F_o| - b)^2}{a} \right) \right]^{1/2}$$

with  $a = 8.80$  and  $b = 5.50$ .

An examination of the weighting analysis indicated that planes with  $|F_o| < 4.0$  were unsatisfactorily weighted. The batch average of  $\sum W \Delta^2 / n$  for planes with  $|F_o| < 4.0$  was improved by two further cycles with  $F^*$  set equal to 4.0 in the weighting scheme  $\sqrt{W} = |F_o| / F^*$  if  $|F_o| \leq F^*$  or  $\sqrt{W} = F^* / |F_o|$  if  $|F_o| \geq F^*$ . The  $R$  value at this stage had fallen to 0.106. The largest indicated shift in a positional parameter was 0.0018 Å and in a thermal parameter, 0.0009 Å<sup>2</sup>. Further attempts to reduce  $R$  were unsuccessful. The refinement was then terminated.

A difference map was computed in order to determine the three hydrogen atom positions. Possible sites for two hydrogen atoms close to N(3) and for one hy-

Table 2. Positional and thermal parameters

The values of  $b_{ij}$  are defined by the expression  $\exp[-\frac{1}{2}(h^2 a^{*2} b_{11} + 2hka^* b^* b_{12} + \dots)]$  used in the structure-amplitude calculation.

All values are multiplied by a factor of  $10^5$ .

	$x/a$	$y/b$	$z/c$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{13}$	$b_{12}$
S(1)	31768	12046	21866	1708	675	417	-103	907	-485
S(2)	-9940	-2936	22667	2092	970	669	-251	1167	-1278
N(1)	46389	18234	52435	1707	694	606	-256	1285	-346
N(2)	25861	10496	47601	1645	718	608	-41	1192	-377
N(3)	70710	27103	41199	2330	949	1072	-390	1952	-1428
C(1)	51511	20114	39992	1674	555	461	-126	921	60
C(2)	15067	6387	31905	125.8	616	656	228	975	151



drogen atom close to N(2) were observed. However, the situation was complicated by a region of positive electron density, extending up to  $1.3 \text{ e.}\text{\AA}^{-3}$ , surrounding both the sulphur atoms. It was thought that this could possibly be due to absorption effects ( $\mu = 81.22 \text{ cm}^{-1}$  for Cu  $K\alpha$  radiation) since no correction for absorption was made. Because of the possibility that a hydrogen atom could be attached to either S(2) or N(2) (see Fig. 1) it was not possible to fix this hydrogen position with any certainty. Consequently, it was decided not to include any hydrogen positions in the calculations.

The final positional and thermal parameters, excluding hydrogen atoms, are shown in Table 2 and the observed and calculated structure factors in Table 3.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

### Description and discussion of the structure

Bond lengths and angles together with their e.s.d.'s are listed in Table 4. Fig. 2(a) and (b) illustrates bond lengths and angles in the molecule.

Table 4. Bond lengths and bond angles

E.s.d.'s are given in brackets and refer to the last decimal place.

*S(1)–S(2)	3.008 (3) Å	C(1)–S(1)–C(2)	89.7 (3)°
S(1)–C(1)	1.746 (7)	S(1)–C(1)–N(1)	113.7 (5)
S(1)–C(2)	1.738 (5)	S(1)–C(2)–N(2)	108.5 (4)
S(2)–C(2)	1.678 (7)	S(1)–C(2)–S(2)	123.4 (4)
C(1)–N(1)	1.305 (6)	S(1)–C(1)–N(3)	123.1 (4)
C(2)–N(2)	1.334 (9)	S(2)–C(2)–N(2)	128.1 (4)
C(1)–N(3)	1.339 (9)	C(1)–N(1)–N(2)	110.2 (5)
N(1)–N(2)	1.382 (8)	C(2)–N(2)–N(1)	117.8 (4)
		N(1)–C(1)–N(3)	123.1 (6)

\* Non-bonded intramolecular distance

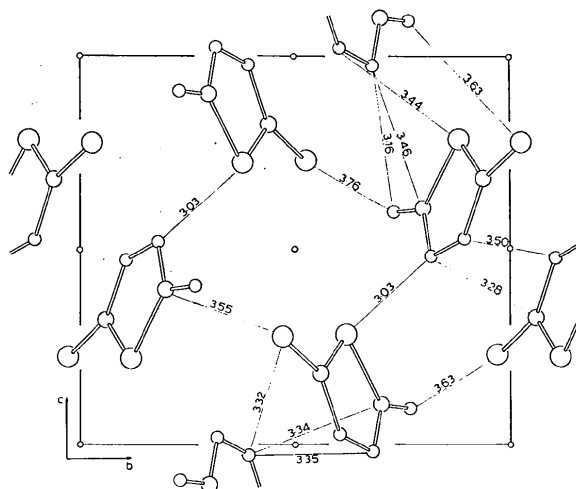


Fig. 3. Molecular packing diagram ( $a^*$  projection) in 5-amino-2-thiol-1,3,4-thiadiazole.

### Ring planarity

Each plane is represented by an equation of the form  $IX+kY+nZ-P=0$  and the equation of the mean plane passing through the molecule, referred to an orthogonal system of axes which has  $X$  along the  $a$  axis,  $Y$  in the  $(a,b)$  plane and  $Z$  along the  $c^*$  axis, is:

$$-0.4970X + 0.8264Y - 0.2645Z = 0.0104.$$

The deviations of atoms from this mean plane are S(1)  $-0.019$  Å; S(2)  $0.012$  Å; N(1)  $-0.001$  Å; N(2)  $-0.012$  Å; N(3)  $0.009$  Å; C(1)  $0.008$  Å and C(2)  $0.004$  Å. The most significant deviations are those for S(1), S(2) and N(2). However, since these are all less than  $0.02$  Å the molecule is most likely to be planar. The equation of the mean plane through the 1,3,4-thiadiazole ring is:

$$-0.4984X + 0.8246Y - 0.2677Z = -0.0074.$$

The deviations of the ring atoms from this mean plane are S(1)  $-0.011$  Å; N(1)  $-0.002$  Å; N(2)  $-0.009$  Å; C(1)  $0.009$  Å and C(2)  $0.013$  Å. The largest deviations in this case are those for S(1) and C(2) but again they are probably not significant and the ring is most likely to be planar. The two exocyclic atoms, not included in the ring calculation, have deviations S(2)  $0.026$  Å and N(3)  $0.007$  Å.

### Ring dimensions

Table 5 contains a selected comparison of bond lengths found in this investigation with relevant values from other investigations.

The cyclic C–N and N–N bond lengths found in ATDZOLE are significantly shorter than those found for single bonds and suggest multiplicity in these bonds and aromaticity in the ring. The cyclic C(1)–N(1) bond length is significantly shorter than the other cyclic C(2)–N(2) or the exocyclic C(1)–N(3) bond lengths. Reference to Wheatley's (1955) order/length curve for C–N bonds indicates 60% double-bond character in C(1)–N(1) and 30% in both C(2)–N(2) and C(1)–N(3). This suggests that in addition to general bond shortening, there is a fairly well localized double bond between C(1) and N(1); in addition, the cyclic C(2)–N(2) bond and the exocyclic C(1)–N(3) bond must be regarded as being essentially the same in character. Reference to Table 5 indicates the general agreement between these bond lengths and related values. There is one instance where a major disparity exists. The N–N bond length in diphenylthiadiazole is similar to an N–N partial triple bond distance (*International Tables for X-ray Crystallography*, 1962), and is considerably shorter than the corresponding value for ATDZOLE. Zvonkova & Khvatkina however have pointed out that this N–N bond length is likely to be inaccurate.

The cyclic C(1)–S(1) and C(2)–S(1) bond lengths show good agreement with each other but the exocyclic C(2)–S(2) bond length is significantly shorter than the two cyclic bonds. Valle, Buseti, Mammi & Carazzolo

(1969) reported a mean value of 1.814 Å for the C–S bonds in 1,3,5-trithiane, a saturated cyclic compound. This value is in good agreement with that reported by Kitaigorodski (1961) for a single C–S bond (1.81 Å). Consequently the cyclic C–S bonds in this compound appear to contain some multiple character. On Abraham's (1956) scale the cyclic C–S bonds have about 50% double-bond character and the exocyclic C–S bond has approximately 75% double-bond character. Reference to Table 5 again shows the extent of the agreement between these and related C–S bond lengths.

The agreement generally is better for the cyclic rather than the exocyclic bonds. The value reported by Valle, Cojazzi, Buseti & Mammi (1970) for a thione (C=S) bond however is in particularly good agreement with the exocyclic C(2)–S(2) bond in ATDZOLE. This observation indicates that the exocyclic C–S bond is also thione rather than thiol in nature and that configuration (I) in Fig. 1 is the dominant tautomeric form in the solid. Both configurations in Fig. 1 require all the atoms in the molecule with the possible exception of the sulphur atoms, to be  $sp^2$  hybridized and would therefore account for the planarity of the molecule. Furthermore, the introduction of a sulphur atom, S(2), an amino group, N(3), and a hydrogen atom attached to N(2) seems to have had little effect on the aromaticity of the 1,3,4-thia-

diazole ring. This is in sharp contrast to the situation in the substituted 1,3,4-thiadiazolidine ring investigated by Karle & Karle (1965), the existence of a saturated carbon atom [C(2)] being responsible for the puckering of the ring and the differences in the cyclic bond lengths between that compound and ATDZOLE (Table 5).

The large deviation of the bond angles in the ring from the 120° usually found in trigonal planar arrangements is common in five-membered rings. The small internal angle at C(2), *i.e.* 108.4°, is not inconsistent with substitution at such a position, for example, in thiophene-2-carboxylic acid (Sutton 1965) the angle is 107°. In a review of the internal valence angle at nitrogen atoms in six-membered rings, Singh (1965) pointed out the angle is significantly larger than 120° when the nitrogen atom is carrying an extra-annular hydrogen, and less than 120° when the nitrogen has no hydrogen attached to it. This treatment has been extended to cover nitrogen atoms in five-membered rings by Sletten, Sletten & Jensen (1969). Applying these empirical considerations to the angles at N(2), 117.8°, and N(1), 110.2°, in ATDZOLE the inference is that the hydrogen atom is most likely attached to N(2); giving further indication that the thione form is the predominant form in the solid. The bond angle at S(1) namely 89.6° is close to the corresponding angle in similar five-membered 1,3,4-thiadiazole ring sys-

Table 5. *A comparison of bond lengths (Å) obtained from relevant compounds*

Compound	C=N	C–N	N–N	C–S (cyclic)	C=S	Reference
5-Amino-2-thiol-1,3,4-thiadiazole (ATDZOLE)	1.305	1.334, 1.339	1.382	1.746, 1.738	1.678	This investigation
Diphenylthiadiazole	1.261	—	1.190	1.769	—	Zvonkova & Khvatkina, (1965)
2- <i>p</i> -Methoxyphenol-3,4-dibenzyl-1,3,4-thiadiazolidine-5-thione	—	1.355, 1.514	1.420	1.777, 1.842	1.650	Karle & Karle (1965)
1-Thiocarbamoylimidazolidine-2-thione	—	—	—	—	1.673	Valle, Cojazzi, Buseti & Mammi (1970)
5-Aminotetrazole monohydrate	—	1.329, 1.321, 1.377	1.381, 1.382	—	—	Britts & Karle (1967)
Tetrathylthiuram disulphide	—	1.334, 1.362	—	—	1.662, 1.634	Karle, Estlin & Britts (1967)
2-Mercaptopurine monohydrate	1.307, 1.326	1.362 (mean)	—	—	1.676	Sletten, Sletten & Jensen (1969)
2-Oxide of 4-methyl-3-( <i>p</i> -bromophenyl)-1,2,5-oxadiazole	1.309, 1.313	—	—	—	—	Calleri, Ferraris & Viterbo (1969)
6-Amido-3-pyrazone-7- <i>H</i> -tetrazolo[5,1- <i>i</i> ]-purine	1.305, 1.29	1.369, —	1.354, 1.38	—, —	—, —	Cucka (1963) Glusker, Van der Helm, Love, Minkin & Patterson (1968)
4-Methyl-1:2-dithiacyclopent-4-ene-3-thione	—	—	—	1.747, 1.713	1.627	Jeffrey & Shiono (1959)
Dithiouracil	—	1.36 (mean)	—	—	1.684, 1.645	Sheftner & Mautner (1967)
Imidazole and histidine complexes	—	1.33 (mean), 1.35 (mean), 1.37 (mean)	—	—	—	Freeman (1967)
1,3,5,-Trithiane	—	—	—	1.814 (mean)	—	Valle <i>et al.</i> (1969).
4,5-Dioxo-2-thioxo-1,3,dithio lan( $\beta$ -form)	—	—	—	—	1.603	Krebs & Koenig (1969)
Thioacetamide	—	—	—	—	1.713	Truter (1960)
Chlorpromazine	—	1.40, 1.40	—	1.75, 1.75	—	McDowell (1969)

tems investigated by Karle & Karle (1965) and Zvonkova & Khvatkina (1965) namely  $89.3^\circ$  and  $89^\circ 33'$  respectively.

The combination of bond shortening and small dihedral angle involving the C-S-C ring atoms in ATD-ZOLE is characteristic of both 5 and 6-membered sulphur-containing ring systems. McDowell (1969) has explained the C-S bond lengths (1.75 (1) Å; 1.74 (1) Å, the C-S-C angle ( $97.33^\circ$ ) and the folding of the molecule in chlorpromazine by assuming the participation of the 3*d* orbitals of the sulphur atom in the bonding scheme. On the other hand Salmond (1968) in his review has commented on the availability of bonding schemes for sulphur containing heterocyclic compounds which either involve or reject the use of the 3*d* orbitals of sulphur.

### Molecular packing and non-bonded contacts

Fig. 3 illustrates the molecular packing and Fig. 4 shows a single, labelled, molecule; both are viewed in the  $a^*$  direction.

Table 6. Shortest, non-bonding intermolecular contacts

Equivalent position		Symmetry code		
$x, y, z$		1		
$\bar{x}, \bar{y}, \bar{z}$		2		
$x, \frac{1}{2}+y, \frac{1}{2}-z$		3		
$x, \frac{1}{2}-y, \frac{1}{2}+z$		4		

Atom A	Atom B	Symmetry code	Cell	Length
S(1)	N(1)	4	0, 0, -1	3.03 Å
N(3)	N(1)	4	0, 0, -1	3.16
N(1)	C(2)	2	1, 0, 1	3.28
N(2)	S(2)	2	0, 0, 1	3.32*
C(1)	N(2)	2	1, 0, 1	3.34
N(1)	N(2)	2	1, 0, 1	3.35
S(1)	N(2)	4	0, 0, -1	3.44
C(1)	N(1)	4	0, 0, -1	3.46
N(2)	N(2)	2	1, 0, 1	3.50
S(2)	C(1)	3	0, -1, 0	3.55
C(2)	C(1)	2	1, 0, 1	3.61
N(3)	S(2)	4	1, 0, 0	3.63
N(3)	S(2)	3	1, 0, 0	3.75

\* Possible hydrogen bond N(2)-H...S(2).

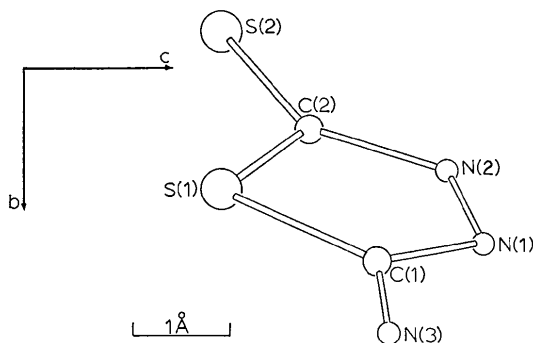


Fig. 4. A single molecule of 5-amino-2-thiol-1,3,4-thiadazole, viewed in the  $a^*$  direction.

The diagrams show that the planar molecules lie mainly in the ( $b, c$ ) plane, being slightly inclined to and also packed in the direction of the  $a$  axis. This is consistent with the unit-cell dimensions in which the  $a$  axis has the shortest translation. The four asymmetric molecules in the unit cell are grouped around symmetry centres forming two pairs of 'right-handed' and 'left-handed' molecules. The closest intermolecular contacts (up to 3.75 Å) are listed in Table 6.

The two sulphur atoms in this structure make some interesting non-bonded contacts. Within the molecule the two sulphur atoms S(1) and S(2) make a non-bonded contact of 3.003 (8) Å (Table 4). This value indicates a van der Waals radius in the region of 1.5 Å for these two sulphur atoms. Kitaigorodski has used sulphur radii of 2.0 Å for crystal packing considerations and S...S contacts in the region 3.4 to 3.5 Å observed in several structures suggest a value of 1.75 Å for that atom. Both of these values are far in excess of the 1.5 Å suggested for S(1) and S(2). The S(1) atom also forms an intermolecular contact of 3.03 Å with N(1) in a neighbouring molecule. Taking Pauling's (1960) 1.50 Å value for nitrogen, this contact also indicates an S(1) radius in the region of 1.50 Å.

The S(2)-N(2) contact of 3.32 Å is within the range of values usually observed for these elements (Downie, Harrison, Raper & Hepworth, 1972). The fact that this contact is across a centre of symmetry and the likelihood of a hydrogen atom attached to N(2) leads to the strong possibility that there is a hydrogen bond of the type S(2)...H-N(2) joining these two atoms.

Pimentel & McClellan (1960) have suggested a van der Waals radius for nitrogen in the range 1.6-1.7 Å from a detailed analysis of hydrogen-bonded distances. This would indicate a non-bonded radius for S(2) in the direction of N(2) of the order of 1.6-1.7 Å.

The very small van der Waals radius for S(1) and the variations in radii observed for S(2) certainly support the views of Sletten *et al.* (1969) that the element does not display a unique van der Waals radius. This is also in accord with Pauling's (1960) qualitative views on the directional dependence of van der Waals radii.

### Computing

All calculations were performed on an IBM 1620 computer in the Department of Mathematics, Statistics and Computing at the Newcastle-upon-Tyne Polytechnic.

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## The Crystal and Molecular Structure of Potassium Dinitrotrichlorocyclopentadienide

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Potassium dinitrotrichlorocyclopentadienide crystallizes in space group  $P2_1/c$  with  $a=13.684$ ,  $b=8.765$ ,  $c=8.065$  Å,  $\beta=93.2^\circ$  and with  $Z=4$ . The structure was determined from photographic data and refined by the least-squares method to  $R=0.10$  for 723 reflexions. The analysis established the structure of the anion as 1,2-dinitro-3,4,5-trichlorocyclopentadienide. The three chlorine atoms are in the plane of the five-membered ring but the two nitrogen atoms are displaced on the opposite sides of the plane by about 0.3 Å. The bond distance between the two carbon atoms to which nitro groups are attached (1.46 Å) is longer than the others owing to the repulsion between the two nitro groups. The potassium atom is surrounded irregularly by six oxygen atoms and the unit negative charge of the molecule seems to be distributed on the oxygen atoms.

### Introduction

Potassium dinitrotrichlorocyclopentadienide was originally synthesized by Haga (1969) by nitration of hexachlorocyclopentadiene with alkali nitrite in an aqueous or alcoholic solution. Potassium dihydroxycyclopenta-

trionide is obtained by hydrolysis of the former, in which the nitro groups and the chlorine atoms are replaced by hydroxyl groups and oxygen atoms respectively. Data from chemical and spectroscopic measurements do not allow an unambiguous distinction between possible molecular structures for these two sub-