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The Crystal and Molecular Structure of 4-Trichloromethyl-1,2-dithia-3,5-diazolium Chloride, $C_2N_2S_2Cl_4$

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$C_2N_2S_2Cl_4$ was found to contain a novel five-membered ring. It is monoclinic with $a = 12.58$ (2), $b = 6.76$ (1), $c = 10.09$ (2) Å, $\beta = 81.75$ (10)°, space group $P2_1/c$, $Z = 4$. The structure was solved by a combination of Patterson and direct methods; least-squares refinement gave $R = 0.069$ for 100 parameters and 747 reflexions with $I > 3\sigma(I)$. The distances in the ring [S–S = 2.009 (6), S–N = 1.58 (1), C–N = 1.32 (1) Å] indicate considerable double-bond character. The ring is planar within experimental error; the Cl^- ion is almost in the plane of the ring and is about 2.86 Å from both S atoms suggesting that the S–Cl bonds are partially covalent.

Introduction

Crystalline compounds with the composition $C_2N_2S_2Cl_4$ can be prepared by reacting thiazyl chloride, $(NSCl)_3$, either with trichloroacetonitrile, Cl_3CCN, or with tetrachloroethylene, C_2Cl_4 (Banister, 1976). The crystal habit was different for the two products, but their IR spectra were practically identical. Their mass spectra showed strong peaks corresponding to $S_2N_2C_2Cl_3^+$. The present investigation shows the two products to be identical

The crystals are very sensitive to moisture, light and X-rays, which presents experimental difficulties. Irradiation of a single crystal of $S_2N_2C_2Cl_4$ yields a twinned crystal of an unidentified product; we hope to study this solid state reaction in more detail.

Experimental

Crystals from each of the two preparations were kindly provided by A. J. Banister. The crystals from the nitrile route were flat lozenges which showed extinction along the face diagonals while those from the olefin route were 'Christmas tree' shaped. All handling of crystals was done in a glove box filled with carefully dried nitrogen. The crystals were mounted in Lindemann glass capillaries. Oscillation, Weissenberg, and precession photographs showed the two types of crystal to be identical, the 'stem' of the 'trees' corresponding to the short diagonals of the lozenges.

All reflexions with $\sin\theta/\lambda < 0.6$ were measured on a linear diffractometer of the Arndt & Phillips (1961) design with Mo $K\alpha$ radiation monochromatized by a graphite crystal (Rasmussen & Henriksen, 1970) and a scintillation counter with pulse-height discrimination. After all the layers had been measured the zero layer was remeasured and comparison of the intensities showed that some reflexions had become stronger, others weaker; Patterson projections calculated with the two sets of equator data were, however, very similar.

A second crystal was then used to collect intensities for layers 6 to 10. Intensities were scaled by means of a standard reflexion measured before and after each layer. The poor quality of the crystals, the rapid fall-off of intensity with $\sin\theta$, and the radiation damage all contributed towards a data set of poor quality.

The crystals were approximately 0.4 × 0.4 × 0.15 mm; the data were collected with the crystal mounted along **c** (the long axis of the lozenges). No absorption correction was applied ($\mu r < 0.8$).

Crystal data

$C_2N_2S_2Cl_4$, $M_r = 258.0$. Monoclinic, $a = 12.58$ (2), $b = 6.76$ (1), $c = 10.09$ (2) Å, $\beta = 81.75$ (7)°, space group $P2_1/c$, $U = 857$ Å^3, $Z = 4$, $D_c = 2.00$ g cm^{-3} μ(Mo $K\alpha$) = 18 cm^{-1}.

Structure determination

The solution of the structure was not straightforward and since the problems encountered are more common than might be expected, we describe the procedure in more detail than is normal.

The Harker section of the Patterson synthesis contained many high peaks which were so large as to be from non-Harker vectors or overlapping vectors. It was not possible to find more than one atom which fitted the Patterson map. By direct methods (*SYMBAD*, Danielsen, 1969) it was possible to find signs for nearly all $E > 1.0$ with relatively few inconsistencies. The E

map which is shown schematically in Fig. 1 showed one exceptionally high peak, **a**, and many medium-sized peaks. The structure could not easily be recognized, and a comparison with the Patterson function showed that only peak **a** corresponded to possible Harker peaks whereas many interatomic vectors were confirmed. It was found that a shift of origin by a vector **S** would make several previously independent peaks symmetry related. The new positions fitted the Patterson function. Four atoms were located and the structure solution proceeded smoothly.

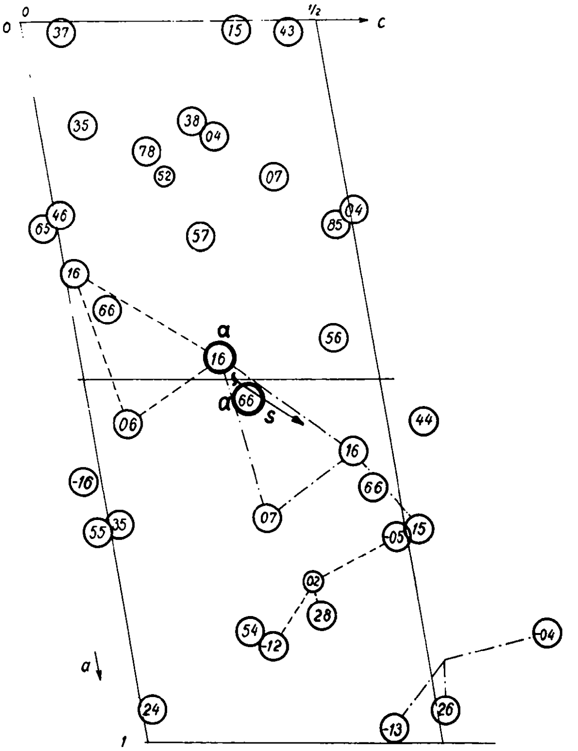

Fig. 1. Schematic drawing of E map showing the two partial structures (indicated by differently dotted lines) shifted by the vector **S** in opposite directions. The numbers are $100y$.

The peaks **a** and **a**′ which were symmetry related in the original E map, corresponded to two independent atoms after changing the origin. The highest peak in the Harker section is due to the vector **a** − **a**′.

The vector **S** is that of half an interatomic vector, Cl(1) to S(2), which is perpendicular to the 2_1 axis. The vector 2**S** corresponds to the highest peak in the Patterson map outside the Harker line and section.

Similar difficulties with E maps where a shift of origin was needed have been encountered by the authors and by others, *e.g.* Duffin (1968), Bürgi & Dunitz (1971), Huber (1975), Hazell & Hazell (1975).

The structure was refined by block-diagonal least squares. Layer-line scale factors were refined, and in the final stages anisotropic temperature factors were introduced for all atoms. The weights used were $w = \sigma(F)^{-2}$ where $\sigma(F)$ was derived from the standard deviation from counting statistics, $\sigma_C(F^2)$, and $|F_o|:\sigma(F) = [\sigma_C(F^2) + (1+k)F_o^2]^{1/2} - |F_o|$. The term kF_o^2 was expected to cover other errors, and k was adjusted to

Table 2. *Interatomic distances* (Å) *and angles* (°)

Standard deviations, calculated including cell errors and correlation matrix, are given in parentheses.

S(1)–S(2)	2·009 (5)	S(1)–S(2)–N(2)	95·4 (4)
S(1)–N(1)	1·587 (10)	S(2)–S(1)–N(1)	95·4 (5)
S(2)–N(2)	1·579 (10)	S(1)–N(1)–C(1)	113·5 (8)
N(1)–C(1)	1·308 (15)	S(2)–N(2)–C(1)	113·4 (10)
N(2)–C(1)	1·329 (13)	N(1)–C(1)–N(2)	122·2 (11)
C(1)–C(2)	1·517 (16)	N(1)–C(1)–C(2)	121·2 (11)
C(2)–Cl(2)	1·739 (15)	N(2)–C(1)–C(2)	116·6 (13)
C(2)–Cl(3)	1·780 (13)	C(1)–C(2)–Cl(2)	112·4 (8)
C(3)–Cl(4)	1·750 (12)	C(1)–C(2)–Cl(3)	106·1 (9)
S(1)–Cl(1)	2·837 (6)	C(1)–C(2)–Cl(4)	109·8 (10)
S(2)–Cl(1)	2·874 (6)	S(1)–Cl(1)–S(2)	41·2 (1)
S(2)–Cl(1$^{\text{i}}$)	3·394 (7)	N(2)–Cl(1$^{\text{iii}}$)	3·361 (11)
S(1)–Cl(1$^{\text{ii}}$)	3·440 (7)	C(1)–Cl(1$^{\text{iii}}$)	3·295 (11)
S(1)–Cl(1$^{\text{iii}}$)	3·516 (6)	S(2)–Cl(1$^{\text{iv}}$)	3·399 (7)
S(2)–Cl(1$^{\text{iii}}$)	3·519 (7)	N(2)–Cl(1$^{\text{iv}}$)	3·618 (11)
N(1)–Cl(1$^{\text{iii}}$)	3·384 (10)		

Symmetry code: (i) x, $1·5-y$, $z-0·5$; (ii) $1-x$, $1-y$, $1-z$; (iii) $1-x, y-0·5, 0·5-z$; (iv) $1-x, y+0·5, 0·5-z$.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters*, U_{ij} ($\times 10^3$)

The temperature factor is defined as: $\exp[-2\pi^2(h^2U_{11}a^{*2} + \cdots + 2hkU_{12}a^*b^* \cdots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	3746 (2)	5734 (4)	3332 (3)	53 (2)	52 (2)	39 (2)	2 (2)	−6 (2)	−3 (2)
S(2)	4594 (2)	6581 (4)	1584 (3)	50 (2)	50 (2)	50 (2)	−13 (1)	−14 (2)	8 (2)
Cl(1)	5904 (2)	6486 (4)	3693 (3)	47 (2)	49 (2)	55 (2)	−7 (1)	−9 (2)	9 (2)
Cl(2)	2166 (3)	4527 (6)	−918 (4)	69 (2)	88 (3)	79 (4)	−2 (2)	−24 (2)	−21 (2)
Cl(3)	1164 (3)	7726 (6)	657 (5)	65 (2)	122 (3)	90 (4)	41 (2)	−14 (2)	−7 (3)
Cl(4)	865 (3)	3747 (7)	1608 (5)	85 (3)	189 (5)	114 (5)	−84 (3)	−35 (3)	61 (4)
N(1)	2660 (7)	5354 (14)	2744 (13)	43 (6)	60 (7)	54 (9)	8 (5)	3 (5)	−6 (6)
N(2)	3645 (7)	6290 (13)	734 (10)	50 (5)	50 (6)	49 (7)	−16 (5)	−8 (5)	10 (6)
C(1)	2739 (8)	5668 (16)	1454 (15)	40 (6)	41 (6)	44 (9)	−1 (6)	−8 (6)	−9 (7)
C(2)	1786 (8)	5368 (18)	710 (15)	39 (6)	71 (9)	77 (13)	−11 (6)	2 (7)	12 (3)

make the average $w\Delta^2$ independent of $|F_o|$ ($k = 0{\cdot}02$). The final R was 0·103 for 927 reflexions with $F^2 > 2\sigma_C(F_o^2)$ and 0·069 for 747 reflexions with $F^2 > 3\sigma_C(F_o^2)$; there were 100 parameters. The parameters from the two refinements differed by less than a standard deviation; those corresponding to the 3σ criterion are used in the following. Scattering factors were from Cromer & Mann (1968).

Atomic coordinates and thermal parameters are listed in Table 1,* bond lengths and angles in Table 2.

Discussion

The structure contains a 1,2-dithia-3,5-diazolium ring (Figs. 2, 3), an aromatic ring which has not been previously described. The five-membered ring and the C atom attached to it are coplanar, and the distances in the ring indicate considerable double-bond character. The S—S distance is slightly shorter than that in the 3-phenyl-1,2-dithiolium ion, 2·00 Å, for which a π-bond order of 0·426 was calculated (Hordvik & Sletten, 1966). The S—N distances are among the longest of those found in planar, aromatic ring systems, *e.g.* $S_4N_3^+$ 1·527–1·581 (Weiss, 1964; Svenningsen & Hazell, 1977), $S_5N_5^+$ 1·465–1·590 (Hazell & Hazell, 1972; Roesky, Böwing, Raymond & Shearer, 1975), and $S_3N_2Cl_2$ 1·542–1·615 (Zalkin, Hopkins & Templeton, 1966), but still have considerable double-bond character, the π-bond order being 0·45 (Glemser, Müller, Böhler & Krebs, 1968). The C—N bonds are almost as short as double bonds.

A striking feature is the close approach of the Cl ion to both S atoms of the disulphide group. Similar triangular arrangements have been reported by Hordvik (1970) for several 1,2-dithiolium and for some thiuret salts. The S—Cl distances in the present structure are,

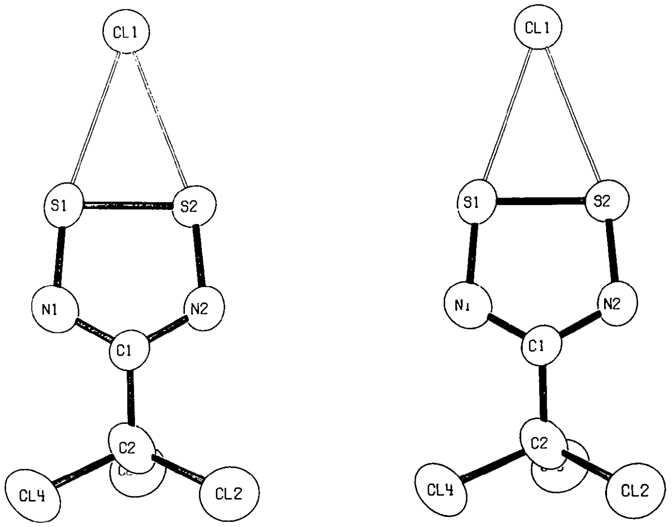

Fig. 2. One molecule of 4-trichloromethyl-1,2-dithia-3,5-diazolium chloride drawn by *ORTEP* (Johnson, 1965).

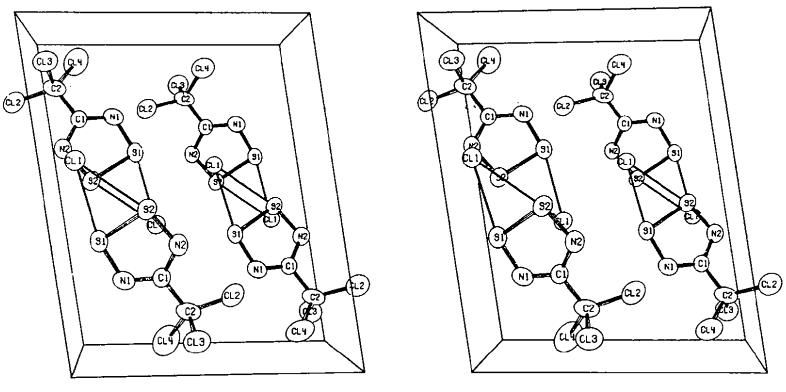

Fig. 3. Stereoscopic drawing of one unit cell of 4-trichloromethyl-1,2-dithia-3,5-diazolium chloride.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32214 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Distances* (Å) *in molecules with triangular*  *X arrangements*

D_X is the distance of X from the plane of the ring, X is a Cl atom or an O atom of a nitrate ion.

	S–X	S–X	D_X	S–S	Reference
$S_2N_2C_2Cl_4$	2·863	2·884	0·16	1·992	This work
S_4N_3Cl	2·807	2·921	0·41	2·076	Svenningsen & Hazell (1977)
	2·801	2·921	0·24	2·079	
	2·810	2·926	0·28	2·077	
$C_9H_7S_2Cl$	3·187	3·187	0·13	2·021	Grundtvig & Hordvik (1971)
$C_3H_4N_3S_2Cl$	3·272	3·315	0·22	2·071	Hordvik & Sletten (1966)
$S_3N_2Cl_2$	2·93	3·04	0·17	2·136	Zalkin, Hopkins & Templeton (1966)
$(S_4N_3)_2SbCl_6$	3·003*	3·022*	0·14	2·066	Kruss & Ziegler (1972*a*)
	3·004*	3·071*	0·43		
$S_4N_3BiCl_4$	3·105*	3·108*	0·31	2·105	Kruss & Ziegler (1972*b*)
$S_4N_3NO_3$	2·591*†	2·722*†	0·01	2·064	Cordes, Kruh & Gordon (1965)

* Calculated from the published atomic coordinates.
† Sulphur to oxygen.

however, 0·3 Å shorter than those described by Hordvik and are the shortest so far reported. If we use Pauling's (1960) formula for calculating atomic radii, assuming each S atom to have a charge of $+\frac{1}{2}$ and the Cl^- ion a charge of -1, we obtain a S—Cl distance of 3·6 Å; since the distance is 0·7 Å shorter than this there must be some covalent bonding.

Short disulphide-to-anion distances occur in several compounds; Table 3 shows the S—S and S—anion distances and the deviation of the anion from the plane of the ring. This triangular arrangement is only found when the disulphide group is part of a planar π-bonded system. No correlation is found between S—Cl and S—S distances or deviation from planarity, but there may be a connexion between π-bond order of the C—S or N—S bond and the S—Cl length, though within a molecule the shorter S—Cl approach seems to be next to the longer N—S bond.

Hordvik (1970) finds S—halogen contacts collinear with the S—S bond and of the same length as those in the triangles. In the present investigation we find such contacts at distances of 3·4 Å, but we also find a Cl^- ion placed over the centre of a five-membered ring with distances of 3·35 to 3·55 Å to the ring atoms and under a S(2)—N(2) bond at similar distances, which may mean that the ionic radii are overestimated.

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