

along the C(9)–C(10) and C(5)···C(8) lines, both in the same sense, and to a very slight buckling of the cyclobutene ring.

Table 4. *Deviations from the least-squares plane*

The normal to the mean plane of the carbon atoms, all weighted equally, has direction cosines of -0.4860 , 0.4272 , and 0.8691 relative to **a**, **b**, and **c**; the origin-to-plane distance is 1.781 Å.

C(1)	0.006 Å	H(1)	0.01 Å
C(2)	-0.004	H(2)	0.01
C(3)	-0.002	H(3)	0.01
C(4)	0.005	H(4)	-0.03
C(5)	0.005	H(5)	-0.05
C(6)	-0.018	H(6)	0.03
C(7)	-0.018	H(7)	-0.81
C(8)	0.011	H(8)	0.79
C(9)	0.016	H(9)	-0.81
C(10)	0.015	H(10)	0.80
C(11)	-0.014		
C(12)	-0.002		

A packing drawing of the molecule is shown in Fig. 2. The shortest intermolecular distances include

H···H, 2.52 Å, and C···H, 2.95 Å; there are no C···C distances below 3.5 Å. Despite this rather loose packing, the temperature factors are relatively small and isotropic. While a rigid-body treatment is not entirely satisfactory, the largest thermal motions are consistent with an in-plane libration of r.m.s. amplitude about 2° , with the axis of libration passing near the center of mass of the molecule. The effects of this motion on the bond distances would be no larger than 0.002 Å or so.

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The Crystal and Molecular Structure of *S,S*-Dimethyl-*N*-trichloroacetyl Sulphilimine, $C_4H_6ONSCl_3$

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S,S-Dimethyl-*N*-trichloroacetyl sulphilimine (DMTAS) crystallizes in the orthorhombic space group $P2_12_12_1$, with $a=8.934$ (5), $b=9.317$ (5), $c=10.952$ (6) Å, $Z=4$. The structure was solved by direct methods and refined by least-squares calculations to an R value of 0.060 with 939 diffractometric intensities. All hydrogen atoms were located in a difference Fourier synthesis. The S(IV)–N(sp^2) bond length (1.667 Å) is similar to that of 1.673 Å observed in *S,S*-diethyl-*N*-dichloroacetyl sulphilimine, but considerably longer than those found in several *N*-sulphonyl sulphilimines. It can, however, be regarded as a partial π bond involved in the mesomerism of the SNCO group. The electronic structure and conformation of the molecule are discussed.

Introduction

An X-ray study of *S,S*-dimethyl-*N*-trichloroacetyl sulphilimine (DMTAS; $Me_2S:N.CO.CCl_3$) has been carried out in order to gain support for the conclusions drawn from the structure determination (Kálmán, Sasvári & Kucsman, 1971) of *S,S*-diethyl-*N*-dichloroacetyl sulphilimine (DEDAS; $Et_2S:N.CO.CHCl_2$),

namely (i) there is an $>S=N-C=O \leftrightarrow >S^+-N=C-\bar{O}$ resonance in the fairly planar S, N, C(2), O, C(1) moiety; (ii) the S(IV)–N(sp^2) bond of intermediate bond order

is significantly (Cruickshank & Robertson, 1953) longer and therefore weaker than in *N*-sulphonyl sulphilimines (Kálmán, 1967; Kucsman, Kálmán & Kapovits, 1967; Kálmán, Duffin & Kucsman, 1971; Cameron, Hair & Morris, 1971; Kálmán & Sasvári, 1972) [1.673 vs. 1.620 – 1.636 Å,]; (iii) sulphur and oxygen atoms are in a *cis* arrangement.

Experimental

DMTAS was prepared and kindly provided by Dr I. Kapovits. Infrared and melting point data showed that

Table 1. *Fractional coordinates and anisotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms*

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form: $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
Cl(1)	4871 (3)	2735 (2)	1750 (2)	190 (4)	126 (2)	99 (2)	-55 (5)	-9 (5)	49 (4)
Cl(2)	3264 (4)	3463 (4)	-382 (2)	298 (5)	251 (4)	95 (2)	-213 (9)	-140 (5)	33 (6)
Cl(3)	2943 (4)	5184 (3)	1772 (4)	206 (5)	183 (3)	262 (4)	-3 (7)	201 (7)	-164 (7)
S	7784 (3)	6577 (2)	869 (2)	147 (3)	83 (2)	78 (1)	-2 (4)	10 (4)	31 (3)
O	5258 (9)	5921 (7)	-485 (5)	200 (11)	150 (7)	92 (5)	-1 (17)	-53 (13)	82 (11)
N	6599 (9)	5263 (7)	1235 (6)	91 (9)	129 (8)	94 (6)	-17 (16)	-25 (12)	41 (13)
C(1)	4195 (11)	4198 (8)	872 (8)	146 (14)	110 (8)	86 (7)	-14 (19)	-7 (18)	-19 (15)
C(2)	5466 (10)	5246 (7)	462 (7)	134 (12)	79 (7)	76 (6)	49 (15)	-12 (14)	-32 (12)
C(3)	8983 (14)	5808 (12)	-267 (11)	240 (19)	175 (13)	144 (10)	-138 (28)	176 (22)	-42 (21)
C(4)	8983 (12)	6467 (11)	2166 (8)	175 (15)	157 (11)	96 (7)	-99 (25)	-25 (18)	0 (19)

the product crystallized from ether was of analytical purity. The crystals were colourless transparent needles, the main axis of which was parallel to *c*. The lattice parameters were determined from Weissenberg and precession photographs and the density measured by flotation.

Crystal data

C₄H₆NOCl₃, *M* = 222.54. Orthorhombic;
a = 8.934(5), *b* = 9.317(5), *c* = 10.952(6) Å,
V = 911.62 Å³,
*D*_c = 1.621, *D*_x = 1.620 g cm⁻³, *Z* = 4.
F(000) = 448
μ for Cu *Kα* (*λ* = 1.5418 Å) 106.7 cm⁻¹.
 Space group *P*2₁2₁2₁ (No. 19).

Data were collected on a Stoe semi-automatic two-circle diffractometer. After setting the crystal and the counter in an equi-inclination arrangement, the intensities of each two-dimensional reciprocal layer (up to *μ*_{max} = 37.2°) were measured automatically, but independently in the *ω* region of crystal rotation between 0 and 150° at fixed counter positions of 2*θ*'. The reflexion peaks were counted at an interval of 2.5° with a scanning speed of 1° min⁻¹. Background measurements were made at both ends of the peaks for 60 sec. The positioning of the crystal and the scintillation counter (with a Ni filter and pulse height discriminator) and the reflexion and background measurements were controlled by a Güttinger electronic unit according to setting data computed previously and stored on punched tape. After recording a layer, some reflexions of medium intensity were re-measured to check the stability of the counting system. The mean deviations were comparable to the final residual. Error caused by decomposition of the crystal (usually considerable in sulphilimines) during the exposures were negligible. From a long needle, a small cylindrical sample was shaped (Kálmán & Argay, 1965) to a diameter of 0.06 mm. Absorption corrections were neglected. The standard deviations of the integrated intensities corrected for the background were calculated from the formula

$$\sigma(I) = \left[I_2 + \left(\frac{T_2}{T_1 + T_3} \right)^2 \cdot (I_1 + I_3) \right]^{1/2}$$

where *I*₂ and *T*₂ are the total counts and counting time for reflexion peaks, and the other quantities refer to the background measurements. 113 of the total 939 independent reflexions with *I* - 1.5*σ*(*I*) < 0 were taken as unobserved with a value of *I*₀ = ½*σ*(*I*). After data reduction an absolute scale factor and overall isotropic temperature factor *B* = 4.16 Å² were determined by Wilson's method.

Structure determination and refinement

The phase problem was solved by direct methods using *E* values computed from the observed structure factors in the conventional way. To accomplish the phase determination the program *MULTAN* of Main, Woolfson & Germain (1970) was used with local modification

Table 2. *Fractional coordinates ($\times 10^3$) and bond distances (Å) for the hydrogen atoms*

Estimated standard deviations are given in parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	C-H distance
H(31)	993 (11)	651 (10)	-54 (7)	1.11 (9) Å
H(32)	815 (13)	593 (10)	-119 (10)	1.26 (10)
H(33)	872 (12)	491 (11)	-43 (8)	0.89 (10)
H(41)	989 (8)	730 (7)	193 (6)	1.15 (7)
H(42)	835 (8)	675 (6)	291 (6)	1.03 (7)
H(43)	943 (10)	564 (10)	235 (10)	0.89 (10)

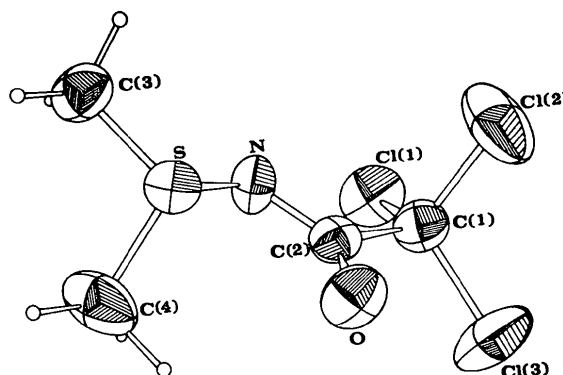


Fig. 1. Molecular conformation observed in the crystal structure of *S,S*-dimethyl-*N*-trichloroacetyl sulphilimine showing atomic labels and the anisotropic thermal ellipsoids.

anisotropic thermal parameters with their estimated standard deviations for the non-hydrogen atoms are given in Table 1. The coordinates of the hydrogen atoms and the C–H atomic distances are shown in Table 2. The structure factors calculated from the atomic parameters given in Tables 1 and 2 are listed in Table 3. The interatomic distances and bond angles with their estimated standard deviations are given in Table 4.

Discussion

The S(IV)–N(sp^2) bond length in DMTAS is almost the same as in DEDAS (1.667 and 1.673 Å, respectively) while the C–N, C–O and C–C bond lengths are somewhat different (by 0.02–0.04 Å), indicating a greater contribution of the polar structure in the resonance outlined above. The S(IV)–C bond lengths are identical within experimental error. The noticeable differences between the C–Cl bond lengths (*cf.* 1.795 and 1.760 Å, respectively in DEDAS) are due to the vigorous, but different, thermal motions of the chlorine atoms. The bond lengths were not corrected for these motions.

The S(IV) hybridization reflected in the bond angles of the S(C,C,N) pyramid (Fig. 1) is similar to that in the other *N*-acyl sulphilimines. The surprisingly low S(IV)–N(sp^2)–C(2) bond angle of 110.0° *vs.* those given in Table 5 and the characteristic *trans* arrangement of the carbonyl oxygen and the lone pair of the sp^2 nitrogen atom (*i.e.* the *cis* arrangement of the sulphur and oxygen atoms in the SNCO group) can also be explained here by the repulsion of the lone pair on the nitrogen atom. The remarkable deviation of the sulphur atom ($\Delta_s = 0.24$ Å *vs.* 0.13 Å in DEDAS) from the plane (Table 6) formed by the N, C(2), O, C(1) atoms may be attributed to the unfavourable proximity of the sulphur and oxygen atoms in the *cis* arrangement. The haloacetyl group is linked to the nitrogen atom of the $R_2S:N$ group more asymmetrically in DMTAS than in DEDAS (Fig. 2).

Table 6. Equation for the atomic plane formed by N, C(2), O, C(1) moiety and atomic deviations (Å) from the plane

$$-0.4358X + 0.7368Y + 0.5169Z = 1.7407$$

where X, Y and Z are orthogonal coordinates (Å).

O	0.0024*	Cl(1)	-0.7691	S	0.2356
N	0.0021*	Cl(2)	-0.8504	C(3)	-1.4022
C(1)	0.0015*	Cl(3)	1.6753	C(4)	0.4274
C(2)	-0.0060*				

* Identifies the atoms defining the planes.

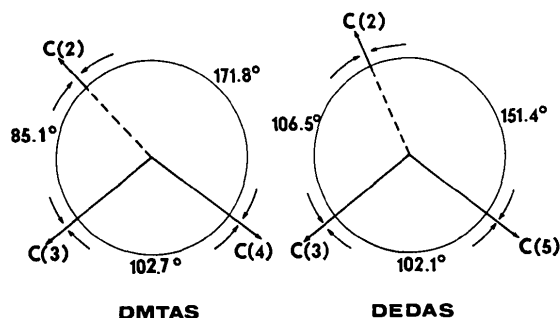


Fig. 2. Newman projection of the (C,C)S–N(C) group in DMTAS and DEDAS.

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