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6-Chloro-4,5-diethyl-1,2,3-oxathiazine 2,2-Dioxide

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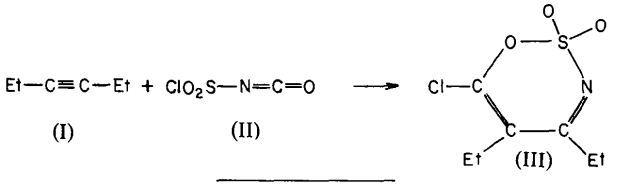
Abstract. $C_7H_{10}ClNO_3S$, monoclinic, $P2_1/c$, a = 7·970 (4), b = 14·55 (1), c = 17·77 (1) Å, β = 92·2 (1)°, V = 2059 Å^3, Z = 8, D_x = 1·44 g cm^{-3}. The structure has been determined by Patterson and trial methods. Block-diagonal least-squares refinement led to R = 0·070, R_w = 0·075 for the 1393 observed reflections. The compound contains a novel six-membered ring in which three hetero-atoms, O, S and N, are adjacent to each other. Analysis of the relationship between the two crystallographically independent molecules in the asymmetric unit has shown that the structure found is a superstructure of a simpler structure which would have a unit cell with b halved and contain four molecules in the space group $P2/c$.

Introduction. Reaction of 3-hexyne (I) with chlorosulfonyl isocyanate (II) yielded a novel adduct (III).



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Initially structure (III) was postulated as the only one which could account for the UV, IR and NMR spectra of the compound together with those obtained after reduction with $LiAlH_4$. Since the ring structure containing three adjacent hetero-atoms was most unusual an X-ray analysis was undertaken which confirmed this structure completely (Moriconi *et al.*, 1970). The mechanisms of this and related reactions have since been discussed in detail (Moriconi & Shimakawa, 1972). In the present paper we present the detailed results of the X-ray analysis after further refinement.

The compound was crystallized from pentane and formed transparent, needle-shaped crystals which were very unstable in air, and had to be sealed in capillaries for X-ray work. Density determination could not be made. Two crystals were used for data collection. The first, for rotation about the c (needle) axis, measured 0·16 × 0·14 mm in cross-section and 1·0 mm in length. The second, for rotation about the b axis, was 0·40 × 0·40 mm in cross-section and 0·36 mm in length. The reciprocal-lattice levels $hk0$–$hk11$, and $h0l$–$h10l$ were recorded using Ni-filtered Cu $K\alpha$ radiation and the equi-inclination Weissenberg technique. Intensities were estimated visually against a time-based standard scale from multiple-film packs and corrected for Lorentz–polarization effects. Cylindrical absorption corrections

were applied for the c-axis crystal and spherical absorption corrections for the b-axis crystal. The separate Weissenberg levels were brought to a common scale by a weighted least-squares fit of reflections common to the two sets. While the photographs taken covered 95% of the Cu sphere, and a few reflections were observed close to this limit, a severe general fall off in intensity occurred at $d \sim 1{\cdot}1$ Å, and only 1393 reflections, or 35% of those observable, were above background.

The structure was solved by Patterson and trial methods. After all the non-hydrogen atoms were located their atomic parameters were refined by block-diagonal least squares and the H atoms then located from a difference electron density map. Since the electron density was rather extended, particularly in the methyl groups, regularized H positions were adopted with all C—H bonds 1·08 Å and H—C—H angles tetrahedral. The estimated H positional standard deviations are 0·04 Å in the methylene groups and ~0·1 Å in the methyl groups. Final refinement of the non-hydrogen atomic parameters was carried out with isotropic H thermal parameters equal to those of the C atoms to which the H atoms were bonded. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/|\Delta F|^2$ and $|\Delta F| = 2{\cdot}3 + 0{\cdot}024F_o$, as obtained from a plot of $|\Delta F|$ *vs* F_o. In the final cycle $R = 0{\cdot}070$, $R_w = 0{\cdot}075$ for observed reflections only, and the average shift/e.s.d. was 0·070 and 0·053 for positional and thermal parameters. Inclusion of the very large number of unobserved reflections, weighted zero in refinement, at their most probable values, gave an R of 0·172. The atomic coordinates are given in Table 1.* The scattering factors used are those given in *International Tables for X-ray Crystallography* (1962). All major calculations were performed using the NRC system (Ahmed, Pippy & Hall, 1968).

Discussion. The bond distances in both molecules are given in Fig. 1, and the bond angles in Table 2. The standard deviations of the bond distances, rounded off in Fig. 1, vary from 0·009 Å for the S—O bonds to 0·015–0·019 Å in the ethyl groups. Comparison of the two independent molecules shows that there are no individual differences, in either distances or angles between bonded atoms, which can be regarded as significant. The average difference in the bond distances is 1·3 times the average σ, while in the angles it is 1·2 times the average σ. The limited accuracy of the analysis does not justify any serious discussion of the bond distances. However, there do not appear to be any

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33484 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for the non-hydrogen atoms and* $\times 10^3$ *for the hydrogen atoms*)

	x	y	z
S(1)	−952 (3)	2761 (2)	3175 (2)
Cl(1)	153 (4)	49 (2)	3003 (2)
N(1)	954 (10)	3135 (6)	3236 (5)
O(1)	−816 (9)	1658 (5)	3338 (5)
O(2)	−1859 (10)	3090 (6)	3804 (5)
O(3)	−1628 (10)	2903 (6)	2439 (4)
C(1)	580 (13)	1217 (7)	3061 (5)
C(2)	2067 (12)	1620 (8)	2919 (6)
C(3)	2204 (14)	2584 (7)	3103 (6)
C(4)	3560 (16)	1046 (9)	2620 (7)
C(5)	4654 (16)	632 (10)	3248 (8)
C(6)	3958 (13)	3040 (9)	3091 (7)
C(7)	3989 (16)	4005 (10)	3375 (9)
S(2)	2157 (3)	2822 (2)	471 (2)
Cl(2)	374 (4)	292 (2)	968 (2)
N(2)	371 (9)	3318 (6)	306 (2)
O(4)	1736 (9)	1721 (6)	430 (5)
O(5)	3202 (9)	2945 (7)	−146 (5)
O(6)	2783 (10)	3030 (7)	1201 (5)
C(8)	238 (13)	1431 (8)	730 (5)
C(9)	−1138 (12)	1942 (7)	746 (5)
C(10)	−1015 (12)	2895 (8)	455 (6)
C(11)	−2831 (14)	1549 (9)	1054 (7)
C(12)	−3841 (15)	1078 (9)	435 (7)
C(13)	−2666 (13)	3461 (9)	383 (7)
C(14)	−2412 (14)	4406 (9)	13 (7)
H(4,1)	430	148	225
H(4,2)	304	49	225
H(5,1)	496	115	368
H(5,2)	582	37	303
H(5,3)	401	7	351
H(6,1)	437	305	251
H(6,2)	485	264	342
H(7,1)	361	403	394
H(7,2)	524	429	333
H(7,3)	312	442	302
H(11,1)	−358	209	130
H(11,2)	−255	105	151
H(12,1)	−506	88	61
H(12,2)	−319	47	24
H(12,3)	−401	154	−5
H(13,1)	−315	356	94
H(13,2)	−359	307	4
H(14,1)	−263	436	−60
H(14,2)	−326	490	23
H(14,3)	−112	464	12

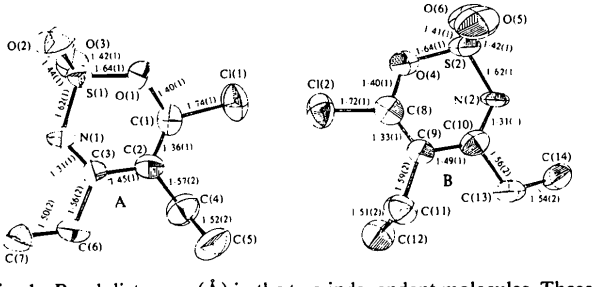

Fig. 1. Bond distances (Å) in the two independent molecules. These have been corrected for molecular libration. The thermal-vibration ellipsoids are drawn at 50% probability.

Table 2. *Bond angles* (°) *involving non-hydrogen atoms*

N(1)–S(1)–O(3)	109·7 (5)	N(2)–S(2)–O(6)	110·5 (5)
N(1)–S(1)–O(2)	109·7 (5)	N(2)–S(2)–O(5)	110·2 (5)
O(1)–S(1)–O(3)	109·2 (5)	O(4)–S(2)–O(6)	108·4 (5)
O(1)–S(1)–O(2)	102·8 (5)	O(4)–S(2)–O(5)	102·4 (5)
N(1)–S(1)–O(1)	105·3 (4)	N(2)–S(2)–O(4)	104·6 (4)
O(2)–S(1)–O(3)	119·2 (5)	O(5)–S(2)–O(6)	119·3 (5)
S(1)–O(1)–C(1)	116·1 (7)	S(2)–O(4)–C(8)	117·1 (7)
O(1)–C(1)–C(2)	125·6 (9)	O(4)–C(8)–C(9)	124·1 (9)
O(1)–C(1)–Cl(1)	108·4 (7)	O(4)–C(8)–Cl(2)	109·9 (7)
C(2)–C(1)–Cl(1)	125·7 (8)	C(9)–C(8)–Cl(2)	125·6 (8)
C(1)–C(2)–C(3)	116·0 (10)	C(8)–C(9)–C(10)	116·8 (9)
C(1)–C(2)–C(4)	121·0 (10)	C(8)–C(9)–C(11)	121·4 (9)
C(3)–C(2)–C(4)	123·0 (10)	C(10)–C(9)–C(11)	121·8 (9)
C(5)–C(4)–C(2)	112·7 (10)	C(12)–C(11)–C(9)	110·6 (9)
C(2)–C(3)–N(1)	125·9 (10)	C(9)–C(10)–N(2)	125·5 (9)
C(2)–C(3)–C(6)	118·3 (9)	C(9)–C(10)–C(13)	117·2 (9)
N(1)–C(3)–C(6)	115·7 (9)	N(2)–C(10)–C(13)	117·1 (9)
C(3)–C(6)–C(7)	113·7 (10)	C(10)–C(13)–C(14)	112·5 (9)
C(3)–N(1)–S(1)	120·2 (8)	C(10)–N(2)–S(2)	120·1 (7)

Table 3. *Torsion angles* (°) *in the six-membered rings*

S(1)–O(1)	−36·1	S(2)–O(4)	−38·5
O(1)–C(1)	24·8	O(4)–C(8)	30·1
C(1)–C(2)	2·5	C(8)–C(9)	−3·0
C(2)–C(3)	−15·5	C(9)–C(10)	−12·2
C(3)–N(1)	−2·0	C(10)–N(2)	−2·8
N(1)–S(1)	26·1	N(2)–S(2)	25·7

abnormalities. The six-membered rings are far from planar. In each molecule the S and O atoms are displaced by 0·2 Å in opposite directions from the least-squares mean plane of the ring. The ring conformations are best expressed in terms of the torsion angles given in Table 3. Here there are small but significant differences between the molecules.

The ellipsoids of thermal vibration, corresponding to the refined anisotropic thermal parameters, are shown in Fig. 1. Corrections to the bond lengths for librational motion (Schomaker & Trueblood, 1968) have been included in the values of Fig. 1. These are quite small (≤ 1 e.s.d.). The angular corrections are negligible and have not been applied. The major libration axis in each molecule is close to the direction N(1)–C(1) or N(2)–C(8).

All intermolecular contacts are at normal van der Waals distances. The two molecules whose coordinates are given in Table 1 are related by a pseudo twofold axis. However, standard molecule *B* and molecule *A* at $-x, \frac{1}{2}+y, \frac{1}{2}-z$ (the two molecules which are labelled *B* and *A'* in Fig. 2) are almost identically oriented and are related by a translation of approximately $b/2$. The crystal structure may therefore be regarded as a superstructure of a simpler one, which would be realized by atomic movements of less than 1·3 Å, and which would contain four molecules in a unit cell with b halved and space group $P2/c$. Presumably the superstructure exists because of a gain in energy by this mode of packing. One aspect of this is illustrated in Fig. 3 where

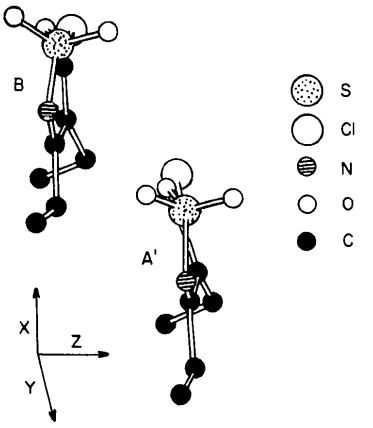

Fig. 2. A projection showing two crystallographically independent molecules. These are very similarly oriented and are related by a translation of approximately $b/2$.

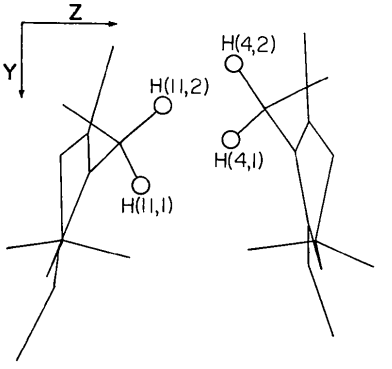

Fig. 3. A view of molecules *A* and *B* projected on (100). The staggered positions of the H atoms could not be achieved if a true twofold axis existed between the two molecules.

molecules *A* and *B* are viewed projected in the (100) plane. It can be seen that the staggering of the H-atom pairs H(4,1) and H(4,2) with respect to H(11,1) and H(11,2) is achieved by a small difference in tilt of the two molecules, thus allowing a closer approach than would be possible if the orientations were symmetry related.

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