Rearrangements in 2-Halogeno-3-Morpholinothietan 1,1-Dioxides. Formation and Structure of a Cyclic β-Sulphonylenamine

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Refluxing an ethanolic solution of *r*-2-chloro-*t*-4-methyl-*c*-3-morpholino-3-phenyl- (1) and *r*-2-chloro-*c*-4-methyl-*t*-3-morpholino-3-phenyl-thietan 1,1-dioxide (3) ultimately leads to the formation of 3-[2-(2-chloroethoxy)ethyl]-5-methyl-4-phenyl-Δ^4-thiazoline 1,1-dioxide *via* some isomeric intermediates. An *X*-ray crystallographic analysis of the structure of the Δ^4-thiazoline dioxide (8) is reported.

As part of our continuing interest in the chemistry and stereochemistry of 2-functionalized thietan 1,1-dioxides, we have recently described [1,2] the stereochemistry of a series of 2-halogeno-3-morpholinothietan 1,1-dioxides and their behaviour in base-promoted hydrogen halide elimination and ring cleavage. We now report further on the chemistry of some of these halogenothietan dioxides.

On refluxing in absolute ethanol, the pure *cis*- and *trans*-isomers † of 2-chloro-4-methyl-3-morpholinothietan 1,1-dioxide (1) and (3), or a mixture of the two, are rearranged ‡ to give isomeric products, *viz.* the open chain β-sulphonylenamine § (5), the quaternary salt (6), and the Δ^4-thiazoline (8). ¶

^{1}H N.m.r. monitoring of the reaction mixtures shows that the sequence of the reaction is: (i) ring cleavage of the cyclic sulphones (1) and (3) to give the open chain β-sulphonylenamines (5); (ii) formation of the quaternary salt (6); and (iii) cleavage of the morpholinium C–N bond of (6) affording the Δ^4-thiazoline (8). Although after a short time all the isomeric products are present in the reaction mixture, the intensity of the ^{1}H n.m.r. peaks of the open chain sulphones (5) decreases as the reaction proceeds while the amounts of the salt and of the thiazoline increase. The final product is the thiazoline (8) which is isolated in high yield. An analogous reaction is observed with the independently synthesized [1] open-chain sulphone (5). The quaternary

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† Where *cis* and *trans* refer to the relationship between the chloro- and morpholino-substituents.

‡ At present we do not have enough evidence to determine whether the reaction in absolute ethanol is a thermal or a base promoted rearrangement, since the starting morpholinothietan derivatives are themselves basic.

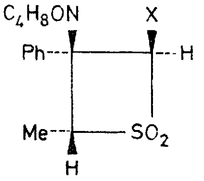
§ Full stereochemical data concerning the open chain β-sulphonylenamine (5) will be reported elsewhere.

¶ The thiazoline (8) is identical with the previously unidentified product [2] $C_{14}H_{18}ClNO_2S$ which was isolated on heating (1) and (3) with triethylamine in dioxan–water.

[1] P. Del Buttero and S. Maiorana, *J.C.S. Perkin I*, 1973, 2540.

[2] P. Del Buttero, S. Maiorana, and M. Trautluft, *J.C.S. Perkin I*, 1974, 1411.

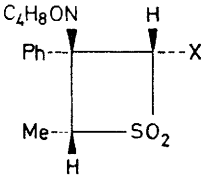
salt (6), which is slightly soluble in chloroform, can be isolated on stopping the reaction after 2 h (see the Experimental section). The isolated salt (6) quantitatively yields the thiazoline (8) on further heating in ethanol.



cis

(1) X = Cl

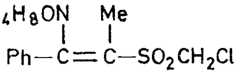
(2) X = Br



trans

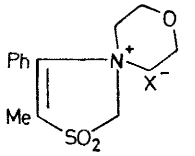
(3) X = Cl

(4) X = Br



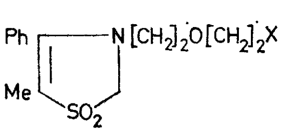
$$\mathrm{Ph{-}\overset{\displaystyle C_4H_8ON}{\overset{|}{C}}{=}\overset{\displaystyle Me}{\overset{|}{C}}{-}SO_2CH_2Cl}$$

(5)



(6) X = Cl

(7) X = Br



(8) X = Cl

(9) X = Br

The salt (6) is formed from (5) *via* intramolecular nucleophilic displacement of the chlorine by the morpholine nitrogen.* Clearly, this reaction can occur only if the sulphonylenamine attains the (*Z*)-configuration.† The formation of (8) can be explained as proceeding *via* cleavage of the morpholinium ring by nucleophilic attack of the chlorine ion. A similar attack has been reported.[5]

In accord with its enaminic structure (see also the discussion of *X*-ray data below) the thiazoline (8) readily undergoes hydrolysis in dilute hydrochloric or acetic acid. The resulting cleavage of the C(4)–N bond leads to an α-amino-β-oxo-sulphonyl compound which decomposes to propiophenone, sulphur dioxide, and formaldehyde as isolable products.

The thermal isomerization of the azoniaspiro-structure to a Δ^4-thiazoline has also been observed with the bromide (7). This compound was obtained as well as the expected 2-bromothietan dioxides (2) and (4) ‡ by treating bromomethanesulphonyl chloride with (*E*)-β-methyl-α-morpholinostyrene in the presence of triethylamine at 0°. The ready formation of (7) is in accord with the better leaving group character of bromine with respect to chlorine. In fact, the chloro-compound (6) can only be obtained by heating its precursors (1), (3), or (5) at reflux. Treatment of (7) successively with silver sulphate and barium chloride gives (6).

Molecular Geometry of the Thiazoline (8).—In Table 1 the least-squares analysis of some molecular planes is reported. The Δ^4-thiazoline 1,1-dioxide ring is not planar, the greatest deviation concerning the sp^3 atom C(10).§ The atoms of the enaminosulphonyl system of

TABLE 1

Distances (Å) of relevant atoms from least-squares planes * through the molecule

Plane (1): S, N, C(7), C(8), C(10)

S −0·003, N −0·070, C(7) 0·039, C(8) 0·046, C(9) −0·066, C(10) 0·053, C(11) 0·256, C(1) 0·091

Plane (2): S, N, C(7), C(8), C(11), C(1)

S 0·001, N −0·008, C(7) 0·021, C(8) −0·015, C(9) −0·215, C(10) 0·144, C(11) 0·375, C(1) 0·035

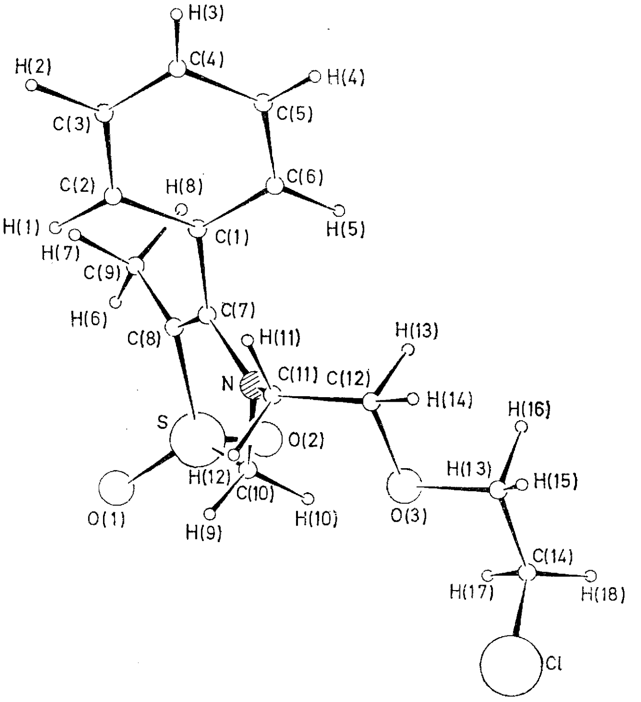
Plane (3): C(1)—C(6)

C(1) 0·000, C(2) 0·001, C(3) −0·001, C(4) −0·002, C(5) 0·003, C(6) −0·002

* Equations of least-squares of planes in the form $lX + mY + nZ = p$, where X, Y, and Z are orthogonal co-ordinates in Å. The transformation matrix from crystallographic to orthogonal axes is:

$$\begin{bmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\cos\beta^* \end{bmatrix}$$

Plane	*l*	*m*	*n*	*p*
(1)	0·8830	−0·3830	0·2714	−2·1825
(2)	0·8550	−0·4126	0·3142	−1·7220
(3)	0·0519	−0·8740	0·4832	3·5256



Molecular structure of the thiazoline (8)

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* Another example of a reaction of this type has been recently reported.[3]

† Although the stereochemistry of the enamine (5) is under investigation, the ready interconversion of *cis*- and *trans*-sulphonylenamines is well established.[4]

‡ The structures of (2) and (4) were assigned by comparison of their ^{1}H n.m.r. spectra with those [1] of the corresponding chloro-derivatives (1) and (3).

§ For the atomic numbering system, see the Figure.

[3] C. T. Goralski and T. E. Evans, *J. Org. Chem.*, 1972, **37**, 2080.

[4] W. E. Truce and D. G. Brady, *J. Org. Chem.*, 1966, **31**, 3543, and references therein.

[5] H. J. Veith and M. Hesse, *Helv. Chim. Acta*, 1969, **52**, 2004.

the ring are coplanar and the two S–C bond lengths are significantly different. While the S–C(10) bond length [1·796(6) Å] is comparable with the value accepted for a simple S^{IV}–C_{sp^3} bond (1·81 Å), the S–C(8) bond [1·721(5) Å] is appreciably short, taking as the standard S–C_{sp^2} bond length that of 4,5-dihydrothiepin dioxide † (1·753 Å).[8] The two S–O bonds of (8) have almost the same length [1·448(4) Å] and are slightly longer than the ordinary values (1·42—1·44 Å), being comparable with those of the thiopyran-pyridine 1,1-dioxide derivatives mentioned in refs. 6 and 7.

TABLE 2

Bond distances (Å) and bond and torsion angles (deg.) with estimated standard deviations in parentheses

(*a*) Bond distances (Å)

Cl–C(14)	1·778(7)	C(1)–C(6)	1·396(7)
S–O(1)	1·450(5)	C(1)–C(7)	1·493(7)
S–O(2)	1·446(4)	C(2)–C(3)	1·402(8)
S–C(8)	1·721(5)	C(3)–C(4)	1·384(8)
S–C(10)	1·796(6)	C(4)–C(5)	1·364(6)
O(3)–C(12)	1·431(6)	C(5)–C(6)	1·396(7)
O(3)–C(13)	1·410(6)	C(7)–C(8)	1·354(7)
N–C(7)	1·376(6)	C(8)–C(9)	1·510(7)
N–C(10)	1·456(6)	C(11)–C(12)	1·502(7)
N–C(11)	1·469(6)	C(13)–C(14)	1·482(9)
C(1)–C(2)	1·377(6)		

(*b*) Bond angles

O(1)–S–O(2)	115·4(7)	C(4)–C(5)–C(6)	119·3(10)
O(1)–S–C(8)	112·4(6)	C(1)–C(6)–C(5)	119·7(9)
O(1)–S–C(10)	111·6(7)	N–C(7)–C(1)	119·2(9)
O(2)–S–C(8)	111·7(6)	N–C(7)–C(8)	117·5(9)
O(2)–S–C(10)	109·1(6)	C(1)–C(7)–C(8)	123·3(9)
C(8)–S–C(10)	94·8(6)	S–C(8)–C(7)	108·9(6)
C(12)–O(3)–C(13)	112·8(8)	S–C(8)–C(9)	119·3(9)
C(7)–N–C(10)	113·3(8)	C(7)–C(8)–C(9)	131·3(12)
C(7)–N–C(11)	125·5(10)	N–C(10)–S	104·5(5)
C(11)–N–C(10)	116·0(8)	N–C(11)–C(12)	111·4(8)
C(2)–C(1)–C(6)	119·4(8)	O(3)–C(11)–C(12)	108·8(7)
C(1)–C(2)–C(3)	121·1(10)	O(3)–C(13)–C(14)	110·0(8)
C(2)–C(3)–C(4)	118·4(11)	Cl–C(14)–C(13)	111·6(8)
C(3)–C(4)–C(5)	121·4(10)		

(*c*) Carbon–hydrogen bond distances

C(2) *	1·02(6)	C(10)	1·06(5)
C(3)	1·06(4)	C(11)	1·01(5)
C(4)	1·02(5)	C(11)	1·04(4)
C(5)	0·99(6)	C(12)	1·04(4)
C(6)	1·03(4)	C(12)	1·02(5)
C(9)	0·96(6)	C(13)	0·98(5)
C(9)	1·02(5)	C(13)	1·06(4)
C(9)	1·15(5)	C(14)	1·00(7)
C(10)	1·04(5)	C(14)	1·07(6)

(*d*) Torsion angles

N–C(11)–C(12)–O(3)	66·9	C(12)–O(3)–C(13)–C(14)	177·0
C(11)–C(12)–O(3)–C(13)	167·0	O(3)–C(13)–C(14)–Cl	73·2

* Bond from H to carbon atom indicated.

The appreciably long S–O bonds accompanied by the short C_{sp^2}–S bonds have been taken as evidence in support of the possibility of conjugation involving the SO_2 group.[7,9]

The N–C(7) bond length 1·376(6) Å {shorter than the value expected for a C–N single bond [0·74 + 0·772 (C) − 0·045 (electronegativity correction) = 1·467 Å [10]], the C(7)–C(8) bond length [1·354(7) Å] (longer than the expected value for a C=C bond 1·33 Å), and the fact that the nitrogen is less pyramidal than expected, being 0·227(4) Å out of the plane defined by C(11), C(10), and C(7), provide evidence for the expected contributions of a delocalized structure in this cyclic β-sulphonylenamine.

Finally, in the thiazoline (8) the orientation of the phenyl group (torsion angle with the Δ^4-thiazoline ring, 56·2°) and of the 2-(2-chloroethoxy)ethyl chain, are mainly determined by inter- and intra-molecular interactions. The conformation of the 2-(2-chloroethoxy)ethyl chain is described by the torsion angles reported in Table 2.

The packing is consistent with van der Waals interactions. Contacts less than 3·5 Å are given in Table 3.

TABLE 3

Intermolecular contacts (<3·5 Å)

$O(1) \cdots C(4^{I})$	3·37	$O(2) \cdots C(12^{II})$	3·28
$O(1) \cdots C(5^{I})$	3·25	$C(14) \cdots O(1^{III})$	3·49
$O(2) \cdots C(11^{I})$	3·12	$C(10) \cdots O(2^{III})$	3·17

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x, y, z - 1$ II $x, y - 1, z$ III $\bar{x} - 1, \bar{y} - 1, 1 - z$

EXPERIMENTAL

Reaction of α-Morpholino-β-methylstyrene with α-Bromomethanesulphonyl Chloride.—α-Bromomethanesulphonyl chloride [1] (13·5 g, 0·07 mol) in anhydrous ether (70 ml) was added dropwise to a stirred and cooled (0—2°) solution of α-morpholino-β-methylstyrene [1] (14·2 g, 0·07 mol) and triethylamine (9·1 g, 0·09 mol) in anhydrous ether (300 ml). After 2 h at room temperature the solid was collected, washed with water (6—7 ml), and crystallized from ethanol to give r-2-*bromo*-c-4-*methyl*-t-3-*morpholino*-3-*phenylthietan* 1,1-*dioxide* (4), m.p. 138° (9·5 g, 38%) (Found: C, 46·6; H, 4·95; N, 3·6. $C_{14}H_{18}BrNO_3S$ requires C, 46·65; H, 5·05; N, 3·9%), τ ($CDCl_3$) 2·4 (5H, m, Ph), 3·9 (1H, d, $^4J_{H,H}$ 1·63 Hz, CHBr), 5·1 (1H, dq, $^4J_{H,H}$ 1·63, $J_{Me,H}$ 7·11 Hz, MeC*H*), 6·22—7·18 (8H, m, morpholine), and 8·99 (3H, d, $J_{Me,H}$ 7·11 Hz, *Me*CH).

The ethereal mother liquors were evaporated to give an oil which was dissolved in chloroform (125 ml) and washed with water (3 × 70 ml). The solvent was evaporated off and the residue taken up in a little methanol and left for 2 days. A *ca.* 80 : 20 mixture (3·5 g, 14%) of the *cis*- and *trans*-cyclic sulphones (2) and (4) respectively, was obtained, m.p. 113—115° (from ethanol) (Found: C, 46·65; H, 5·0; N, 3·6%). No attempts to obtain the pure *cis*-isomer (2) were made and its ^1H n.m.r. peaks were inferred from the ^1H n.m.r. of the mixture, τ ($CDCl_3$) 2·63 (5H, m, Ph), 3·68 (1H, d, $^4J_{H,H}$ 0·697 Hz, CHBr), 5·18 (1H, dq, $^4J_{H,H}$ 0·697, $J_{Me,H}$ 7·21 Hz, MeC*H*), 6·28—7·28 (8H, m, morpholine), and 8·7 (3H, d, $J_{Me,H}$ 7·21 Hz, *Me*CH).

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† Values ranging between 1·693(5) and 1·737 Å have been reported for 3-phenyl-2*H*-thiopyrano[3,2-*b*]quinoline 1,1-dioxide,[6] 1,2-dihydro-1-methyl-2-(5-phenylthiopyran-2-ylidene)-pyridine 1,1-dioxide, and 1,4-dihydro-1-methyl-4-(2-methyl-5-phenylthiopyran-4-ylidene)pyridine 1,1-dioxide,[7] which are structurally analogous with (8).

[6] G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *Cryst. Struct. Comm.*, in the press.

[7] G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *J.C.S. Perkin II*, 1973, 1189.

[8] H. L. Ammon, M. R. Smith, and E. Kelso, *Acta Cryst.*, 1972, **B28**, 246.

[9] G. Pagani, personal communication.

[10] V. Shomaker and P. D. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

The methanolic mother liquors and the water used before to wash the chloroform layer were mixed and evaporated to dryness under reduced pressure. The solid residue was taken up in a little chloroform and the slightly soluble 3-*methyl*-2,2-*dioxo*-4-*phenyl*-8-*oxa*-2-*thia*-5-*azoniaspiro*[4.5]-*dec*-3-*ene bromide* (7) was filtered off (1·9 g, 7·6%), m.p. 154—155° (from ethanol–ether) (Found: C, 46·8; H, 4·7; N, 3·5. $C_{14}H_{18}BrNO_3S$ requires C, 46·65; H, 5·05; N, 3·9%), τ [$(CD_3)_2SO$] 2·25 (5H, s, Ph), 3·90 (2H, s, $SO_2CH_2\overset{+}{N}$), 6·13 (8H, m, morpholine), and 8·1 (3H, s, Me).

3-[2-(2-*Chloroethoxy*)*ethyl*]-5-*methyl*-4-*phenyl*-Δ^4-*thiazoline* 1,1-*Dioxide* (8).—The pure single isomers (1) and (3)[2] or their mixture (3 g, 9·5 mmol), were refluxed in ethanol (80 ml) for 24 h, heating with an oil-bath at 95°. The ethanol was evaporated off and the *thiazoline* (8) crystallized from ethanol, m.p. 101° (2·84 g, 95%) (Found: C, 52·65; H, 5·65; N, 4·5. $C_{14}H_{18}ClNO_3S$ requires C, 53·25; H, 5·75; N, 4·45%), τ ($CDCl_3$) 2·6 (5H, m, Ph), 5·48 (2H, s, SO_2CH_2N), 6·44—6·88 (8H, m, $[CH_2]_2O[CH_2]_2$), and 8·12 (3H, s, Me). Compound (8) is also obtained in quantitative yield on refluxing the independently isolated salt (6) for 6 h in ethanol (see below).

3-*Methyl*-2,2-*dioxo*-4-*phenyl*-8-*oxa*-2-*thia*-5-*azoniaspiro*-[4.5]*dec*-3-*ene Chloride* (6).—The cyclic sulphones (1) or (3) were heated at reflux in ethanol solution for 2 h. The ethanol was evaporated off under reduced pressure and the residue was taken up in a little chloroform. After some hours the solid *salt* (6) was collected (25% yield), m.p. 162° (from ethanol–petroleum) (Found: C, 53·2; H, 5·8; N, 4·3. $C_{14}H_{18}ClNO_3S$ requires C, 53·25; H, 5·75; N, 4·45%), τ [$(CD_3)_2SO$] 2·28 (5H, m, Ph), 3·72 (2H, s, $SO_2CH_2\overset{+}{N}$), 6·08 (8H, m, morpholine), and 8·12 (3H, s, Me).

3-[2-(2-*Bromoethoxy*)*ethyl*]-5-*methyl*-4-*phenyl*-Δ^4-*thiazoline* 1,1-*Dioxide* (9).—The salt (7) (0·156 g, 0·39 mmol) was refluxed in ethanol (8 ml) for 24 h. The ethanol was evaporated off under reduced pressure to leave the solid *thiazoline* (9), m.p. 105° (from ethanol), 95% yield (Found: C, 47·0; H, 5·1; N, 3·85. $C_{14}H_{18}BrNO_3S$ requires C, 46·65; H, 5·05; N, 3·9%), τ ($CDCl_3$) 2·51 (5H, m, Ph), 5·45 (2H, s, SO_2CH_2N), 6·52 (8H, m, $[CH_2]_2O[CH_2]_2$), and 8·1 (3H, s, Me).

Transformation of the Bromide (7) *into the Chloride* (6).—A solution of Ag_2SO_4 (0·178 g, 5·71 mmol) in the minimum amount of distilled water was added dropwise to an aqueous solution of the bromide (7) (0·410 g, 1·14 mmol). The mixture was heated for 30 min and the precipitated silver bromide was filtered off. A solution in the minimum of water of $BaCl_2,2H_2O$ was then added to the filtrate. After 2 h at room temperature, the water was evaporated off under reduced pressure to leave the salt (6), m.p. 162° (from ethanol–petroleum), i.r. and ^1H n.m.r. spectra identical with those of an authentic sample.

Acidic Hydrolysis of the Δ^4-*Thiazoline Dioxide* (8).—The thiazoline (0·25 g, 0·795 mmol) was dissolved in 10% HCl or H_2SO_4 (5 ml) (eventually adding a little methanol) and stirred for 3—5 h at room temperature. Extraction with ether and distillation gave an 80% yield of propiophenone identified by comparison of the i.r. and ^1H n.m.r. spectra with those of an authentic sample. Basification and extraction of the acidic mother liquors gave an unidentified mixture.

Sulphur dioxide was identified by heating the acidic reaction mixture and collecting the gas in H_2O_2 solution. Treatment with barium chloride resulted in precipitation of insoluble barium sulphate. Formaldehyde was identified by distilling a few ml of the starting hydrolysis solution and preparing the dimedone derivative, which was identical (m.p. and i.r. spectrum) with an authentic sample.

Crystal Structure of the Thiazoline (8).—Crystals of the compound are pale yellow, triclinic prisms. A crystal of dimensions 0·2 × 0·3 × 0·4 mm was used for intensity measurements. The space group and initial unit cell parameters were obtained from oscillation and Weissenberg photographs. Accurate unit cell parameters were obtained by a least-squares treatment of $(\theta,\chi,\phi)_{hkl}$ values of 15 reflections measured on a Siemens single crystal diffractometer at room temperature.

Crystal Data.—$C_{14}H_{18}ClNO_3S$, $M = 315·5$. Triclinic, $a = 11·07(1)$, $b = 7·83(1)$, $c = 10·24(1)$ Å, $\alpha = 66·8(2)$, $\beta = 72·4(2)$, $\gamma = 89·2(2)°$, $U = 772·0$ Å^3, $Z = 2$, $D_x = 1·36$. Cu-K_α Radiation, $\lambda = 1·5418$ Å, μ(Cu-K_α) = 34·6 cm^{-1}. Space group $P\bar{1}$ (from structure determination).

The diffraction data were collected automatically using Cu-K_α radiation. The moving-counter moving-crystal scan and the so called ' five points '[11] technique were used for intensity and background measurements. Reflection data were collected in the octants $\pm h$, $\pm k$, $\pm l$. Of the 2945 independent reflections measured ($2\theta \leqslant 140°$ for Cu radiation), 72 had intensities $< 2[\sigma^2(I) + 0·01\ I)^2]^{1/2}$ [where I is the relative intensity and $\sigma^2(I)$ its variance] and were considered unobserved. No corrections for absorption were applied.

Structure Analysis and Refinement.—The structure amplitudes were put on an absolute scale by the method of Wilson[12] ($\bar{B} = 3·8$ Å^2), and normalized structure amplitudes $|E_{hkl}|$ were then obtained by using the overall temperature parameter. 450 Reflections with $|E| \geqslant 1·40$ were used for sign determination. The structure was solved by the multisolution and phase permutation technique, with the reflections in the basic set (Table 4) chosen by the program MULTAN.[13] Phases were determined by the weighted numerical addition technique.[14] An E map computed by use of the most consistent set of signs with $a = +$, $b = +$, $c = -$, $d = -$, $e = -$, $f = +$ revealed the whole structure. A structure factor calculation based on the co-ordinates derived from the E map for all atoms gave $R = 0·24$. Refinement was carried out by cycles of block-diagonal least-squares, first with isotropic and then with anisotropic thermal parameters, reducing R to 0·091. A difference synthesis revealed significant residual peaks

TABLE 4

Starting set of reflections

			$\lvert E(h)\rvert$	$\phi(h)$
7	−3	−3	3·41	0
2	−1	1	2·24	0
0	2	−1	2·23	0
8	−2	3	3·16	*a*
9	0	−3	3·09	*b*
5	5	8	2·84	*c*
10	0	3	2·72	*d*
8	2	4	2·68	*e*
4	−3	−6	2·54	*f*

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TABLE 5

(*a*) Fractional co-ordinates ($\times 10^4$) and thermal parameters * (in 10^{-2} Å^2), with standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	−1231(1)	1168(2)	3094(2)	488(7)	954(11)	632(8)	95(7)	118(6)	199(8)
S	−6510(1)	−5586(1)	6941(1)	228(3)	303(4)	294(4)	−11(3)	−21(3)	−170(3)
O(1)	−7363(3)	−5461(5)	6084(4)	381(14)	747(20)	410(15)	−58(13)	−164(12)	−262(14)
O(2)	−5593(3)	−6913(4)	6891(4)	423(14)	379(14)	583(17)	111(11)	−39(13)	−286(13)
O(3)	−3508(3)	−837(4)	6148(3)	252(11)	406(13)	378(13)	−25(9)	−38(10)	−126(11)
N	−5988(3)	−3091(4)	7809(3)	308(13)	228(12)	263(12)	−29(10)	20(10)	−132)10)
C(1)	−7454(3)	−4205(5)	10422(4)	237(14)	265(14)	248(14)	6(11)	−35(11)	−124(12)
C(2)	−8749(4)	−4206(7)	11013(5)	259(16)	534(22)	352(18)	31(15)	−59(13)	−249(17)
C(3)	−9276(4)	−4055(7)	12387(5)	272(17)	693(28)	414(21)	62(17)	−15(15)	−323(20)
C(4)	−8463(4)	−3902(7)	13140(5)	426(20)	480(21)	305(17)	43(17)	−42(15)	−211(16)
C(5)	−7177(4)	−3889(6)	12569(5)	385(18)	395(19)	324(17)	17(15)	−111(14)	−188(15)
C(6)	−6655(3)	−4050(5)	11205(4)	246(15)	329(16)	328(16)	23(12)	−62(12)	−149(14)
C(7)	−6935(3)	−4412(5)	8973(4)	195(13)	263(14)	247(14)	18(11)	10(11)	−107(12)
C(8)	−7316(3)	−5885(5)	8754(4)	276(15)	283(15)	242(14)	−36(12)	−12(12)	−110(12)
C(9)	−8155(4)	−7698(6)	9833(5)	414(20)	327(18)	374(19)	−126(15)	−19(15)	−112(15)
C(10)	−5681(4)	−3341(5)	6414(4)	362(17)	288(16)	264(15)	−40(13)	3(13)	−134(13)
C(11)	−5681(4)	−1189(5)	7657(4)	326(16)	205(14)	377(17)	−1(12)	−31(14)	−137(13)
C(12)	−4313(4)	−836(6)	7535(5)	336(17)	311(17)	436(20)	−43(14)	−33(15)	−183(15)
C(13)	−2218(4)	−924(7)	6077(6)	276(17)	437(21)	556(24)	−14(15)	−94(16)	−211(19)
C(14)	−1451(4)	−1021(7)	4651(6)	307(18)	437(21)	551(24)	18(15)	−40(16)	−158(19)

(*b*) Fractional co-ordinates ($\times 10^3$) and isotropic thermal parameters † (in 10^{-1} Å^2) for the hydrogen atoms

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
H[C(2)]	−935(4)	−435(6)	1047(5)	53	H[C(10)]	−471(6)	−345(8)	591(6)	93
H[C(3)]	−1028(4)	−409(6)	1284(5)	40	H[C(11)]	−629(4)	−101(6)	854(5)	43
H[C(4)]	−888(4)	−379(6)	1413(5)	54	H[C(11)]	−585(4)	−21(6)	671(5)	49
H[C(5)]	−661(4)	−381(6)	1313(5)	51	H[C(12)]	−409(4)	−185(6)	843(5)	45
H[C(6)]	−569(4)	−403(6)	1074(5)	38	H[C(12)]	−424(4)	48(6)	751(5)	49
H[C(9)]	−821(4)	−840(6)	926(5)	57	H[C(13)]	−192(4)	23(6)	611(5)	56
H[C(9)]	−903(5)	−737(7)	1031(5)	59	H[C(13)]	−208(4)	−206(6)	700(5)	48
H[C(9)]	−775(5)	−856(7)	1077(5)	58	H[C(14)]	−188(5)	−197(8)	446(6)	85
H[C(10)]	−594(5)	−212(7)	572(5)	61	H[C(14)]	−57(5)	−158(8)	471(6)	86

* Temperature factors are of the form $\exp[-\frac{1}{4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$, where $b_{11} = a^{*2}B_{11}$, $b_{12} = a^*b^*B_{12}$, *etc.* † Temperature factors are of the form $\exp(-\beta\sin^2\theta/\lambda^2)$.

near the positions where the hydrogen atoms were expected to occur. Further least-squares cycles were then computed, including the hydrogen atoms with isotropic thermal parameters, which gave a final R of 0·076. The atomic scattering factors used throughout the calculations are those of Cromer and Mann [15] for Cl, S, O, N, and C and those of Stewart, Davidson, and Simpson [16] for H atoms. The positional and thermal parameters are listed in Table 5, and bond lengths and angles are given in Table 2. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21096 (13 pp., 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

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