

### Crystal and Molecular Structure of (4*R*,6*R*)-3-Methoxycarbonyl-9,9-dimethyl-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene 4-Oxide

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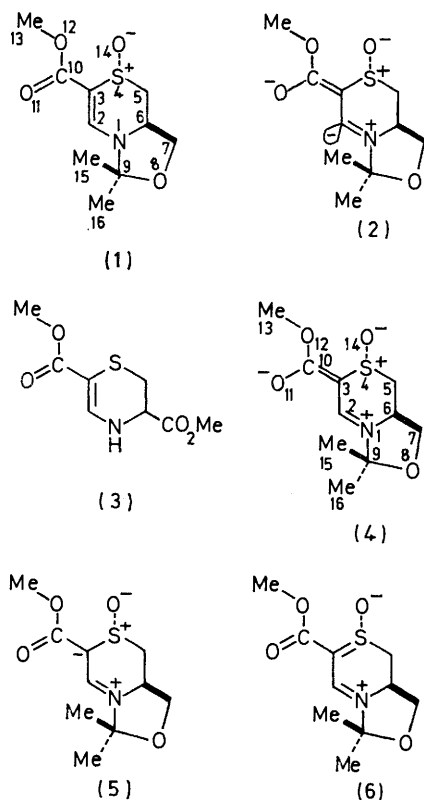
X-Ray crystallographic analysis of the title compound has established that there is substantial electron delocalisation involving the nitrogen atom and the ester group, with the bonds from the nitrogen atom nearly coplanar. The sulphur atom does not appear to be involved in the conjugation. The crystals are orthorhombic, space group  $P2_12_12_1$ , with  $Z = 4$  in a cell of dimensions  $a = 8.881 \pm 0.005$ ,  $b = 19.14 \pm 0.01$ ,  $c = 7.042 \pm 0.005$  Å. The structure was determined by Patterson and Fourier methods, by use of three-dimensional counter data, and refined by least-squares to  $R$  6.7% for 1011 structure amplitudes.

THE title compound (1) was prepared<sup>1</sup> by sodium periodate oxidation of the corresponding sulphide, and the sulphoxide group assigned the axial orientation on the basis of n.m.r. spectroscopic evidence.<sup>1</sup> An

unusual chemical property of (1), and also of the diastereoisomeric equatorial sulphoxide, is the ease with which they undergo vinylic hydrogen exchange. To

<sup>1</sup> J. Kitchin and R. J. Stoodley, *Tetrahedron*, 1973, **29**, 3023.

account for this, Stoodley and his co-workers<sup>2</sup> have suggested that structure (2) contributes to the stabilisation of the intermediate vinyl anion. A similar ground



state conjugative stabilisation of the 6-methoxycarbonyl-2,3-dihydro-1,4-thiazine derivative (3) is indicated from i.r. studies.<sup>3</sup>

We now report the results of an X-ray crystal structure analysis, based on three-dimensional counter data, of compound (1). Its stereochemistry is illustrated in Figure 1, which shows a view of the molecule as seen

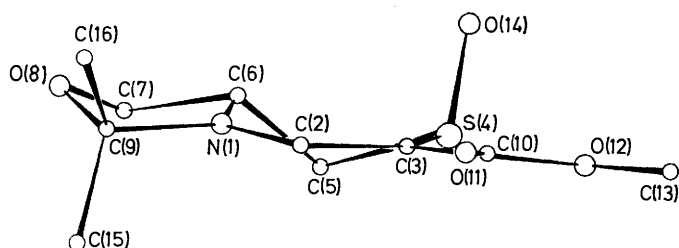


FIGURE 1 The molecule as viewed in a direction parallel to the mean plane of the ester group

in a direction parallel to the plane of the ester group, and also the atomic numbering scheme used. The final atomic co-ordinates are in Table I and the thermal parameters in Table 2. Molecular dimensions are listed in Tables 3 and 4. Bond length standard deviations range from 0.007 Å for bonds involving the sulphur atom, to 0.013 Å for C-C bonds. Bond angle standard deviations are 0.3–0.8°.

<sup>2</sup> A. J. Anderson, J. Kitchin, and R. J. Stoodley, *Tetrahedron Letters*, 1973, 3379.

The six-membered ring has atoms N(1), C(2), C(3), S(4), and C(6) approximately co-planar [plane (f), Table 4] with C(5) displaced by 0.80 Å from the mean plane. The ester group is planar to within 0.02 Å [plane (a), Table 4], and the angle between these planes is 11.1°. The ester group, the five atoms constituting the planar portion of the six-membered ring, and C(9)

TABLE 1  
Fractional atomic co-ordinates ( $\times 10^4$ ) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	-1780(6)	1851(3)	3340(9)
C(2)	-1330(8)	2384(4)	4373(10)
C(3)	-1557(8)	3082(4)	3899(11)
S(4)	-2264(2)	3351(1)	1665(3)
C(5)	-1909(10)	2528(4)	423(10)
C(6)	-2601(8)	1943(3)	1556(10)
C(7)	-2423(11)	1207(4)	707(11)
O(8)	-2349(8)	763(3)	2342(8)
C(9)	-1460(9)	1103(4)	3735(12)
C(10)	-1215(9)	3603(4)	5327(12)
O(11)	-842(7)	3470(3)	6952(9)
O(12)	-1324(7)	4258(2)	4636(10)
C(13)	-1032(13)	4814(4)	6027(18)
O(14)	-3921(7)	3425(3)	1767(10)
C(15)	191(12)	968(5)	3413(20)
C(16)	-2032(12)	901(4)	5663(12)
H <sup>1</sup> [C(2)]	-713	2291	5698
H <sup>1</sup> [C(5)]	-693	2437	303
H <sup>2</sup> [C(5)]	-2413	2545	-1008
H <sup>1</sup> [C(6)]	-3822	2060	1787
H <sup>1</sup> [C(7)]	-1406	1162	-190
H <sup>2</sup> [C(7)]	-3416	1059	-225

TABLE 2  
Anisotropic thermal parameters ( $\times 10^4$ ) for the heavier atoms

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
N(1)	199	203	323	-1	49	0
C(2)	120	340	326	68	13	69
C(3)	104	276	403	-44	50	20
S(4)	354	270	368	-28	7	96
C(5)	394	389	286	6	-146	86
C(6)	195	297	289	-7	-5	6
C(7)	585	375	330	-3	78	-40
O(8)	676	284	486	91	247	-38
C(9)	338	206	453	-120	161	-43
C(10)	203	310	487	54	21	5
O(11)	566	340	544	-22	165	-53
O(12)	462	214	577	38	12	9
C(13)	723	335	789	84	35	-179
O(14)	417	520	639	-175	110	6
C(15)	498	566	896	-171	102	-117
C(16)	651	302	422	61	43	104

Temperature factors are in the form:  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ .

are co-planar to within 0.22 Å. If C(6) is omitted from the mean plane calculation, the remaining nine atoms deviate from coplanarity by only 0.09 Å. The five-membered ring can best be described as a half-chair with C(7) and O(8) displaced by 0.32 and 0.25 Å on opposite sides of the plane defined by N(1), C(6), and C(9). Its description in terms of an envelope-type conformation is not satisfactory [*cf.* planes (i), (j), and (k)].

The three bonds from nitrogen, N(1)-C(2), N(1)-C(6),

<sup>3</sup> A. R. Dunn, I. McMillan, and R. J. Stoodley, *Tetrahedron*, 1968, 24, 2985.

and N(1)-C(9) are almost coplanar, the nitrogen atom being displaced by only 0.026 Å from the plane of C(2), C(6), and C(9). The nitrogen atom therefore appears to be essentially  $sp^2$  hybridised. The geometrical constraints imposed by the five-membered ring, however, cause the bond angles to deviate considerably from 120°.

TABLE 3

## Molecular dimensions

(a) Bond distances (Å) with standard deviations in parentheses			
N(1)-C(2)	1.316(9)	N(1)-C(9)	1.486(8)
C(2)-C(3)	1.390(10)	C(9)-C(15)	1.506(13)
C(3)-S(4)	1.770(8)	C(9)-C(16)	1.500(12)
S(4)-C(5)	1.830(8)	C(3)-C(10)	1.449(11)
C(5)-C(6)	1.506(10)	C(10)-O(11)	1.218(10)
N(1)-C(6)	1.463(9)	C(10)-O(12)	1.349(9)
C(6)-C(7)	1.538(10)	O(12)-C(13)	1.470(11)
C(7)-O(8)	1.433(10)	S(4)-O(14)	1.480(7)
O(8)-C(9)	1.417(9)		

(b) Bond angles (deg.) with standard deviations in parentheses			
C(2)-N(1)-C(6)	122.2(5)	C(7)-C(6)-N(1)	99.9(5)
C(6)-N(1)-C(9)	111.8(5)	O(8)-C(7)-C(6)	103.6(6)
C(9)-N(1)-C(2)	125.9(6)	C(9)-O(8)-C(7)	108.0(6)
C(3)-C(2)-N(1)	124.6(6)	N(1)-C(9)-O(8)	101.9(5)
S(4)-C(3)-C(2)	123.0(6)	N(1)-C(9)-C(15)	108.8(7)
C(2)-C(3)-C(10)	117.6(7)	N(1)-C(9)-C(16)	110.6(7)
C(10)-C(3)-S(4)	119.4(5)	O(8)-C(9)-C(15)	111.1(8)
C(5)-S(4)-C(3)	96.5(3)	O(8)-C(9)-C(16)	108.6(7)
C(3)-S(4)-O(14)	109.7(4)	C(15)-C(9)-C(16)	115.0(8)
O(14)-S(4)-C(5)	106.1(4)	C(3)-C(10)-O(11)	124.5(7)
C(6)-C(5)-S(4)	108.4(5)	O(11)-C(10)-O(12)	123.4(7)
N(1)-C(6)-C(5)	109.9(6)	O(12)-C(10)-C(3)	112.1(7)
C(5)-C(6)-C(7)	115.6(6)	C(10)-O(12)-C(13)	114.9(7)

(c) Selected torsion angles (deg.); mean standard deviation 0.9°			
C(6)-N(1)-C(2)-C(3)	-0.7	C(15)-C(9)-N(1)-C(6)	107.0
N(1)-C(2)-C(3)-S(4)	-9.0	C(16)-C(9)-O(8)-C(7)	148.2
C(2)-C(3)-S(4)-C(5)	-16.7	C(16)-C(9)-N(1)-C(6)	-125.8
C(3)-S(4)-C(5)-C(6)	52.2	C(10)-C(3)-C(2)-N(1)	170.1
S(4)-C(5)-C(6)-N(1)	-68.4	C(10)-C(3)-S(4)-C(5)	164.3
C(5)-C(6)-N(1)-C(2)	42.2	O(12)-C(10)-C(3)-C(2)	173.3
C(9)-N(1)-C(6)-C(7)	-12.3	O(12)-C(10)-C(3)-S(4)	-7.7
N(1)-C(6)-C(7)-O(8)	30.5	C(13)-O(12)-C(10)-C(3)	178.3
C(6)-C(7)-O(8)-C(9)	-40.3	O(11)-C(10)-C(3)-C(2)	-5.3
C(7)-O(8)-C(9)-N(1)	31.4	O(11)-C(10)-C(3)-S(4)	173.8
O(8)-C(9)-N(1)-C(6)	-10.5	O(14)-S(4)-C(3)-C(2)	93.0
C(15)-C(9)-O(8)-C(7)	-84.4	O(14)-S(4)-C(5)-C(6)	-60.5

The stereochemistry of the molecule is thus consistent with a significant contribution from structure (4) to the ground-state electronic configuration. Consideration of bond lengths leads to the same conclusion.

Bonds N(1)-C(6) and N(1)-C(9) have lengths in good agreement with the accepted<sup>4</sup> value for a  $C(sp^3)$ -N single bond. The N(1)-C(2) bond, 1.316 Å, is, however, much shorter than a  $C(sp^2)$ -N single bond, and is intermediate in length between a double bond (*ca.* 1.27 Å),<sup>5</sup> and the C-N bond in aromatic systems (1.34 Å).<sup>4</sup> C(2)-C(3) is 0.055 Å longer than a C-C double bond and is close to the standard aromatic value (1.394 Å).<sup>4</sup> The ester group has C(3)-C(10) *ca.* 0.03 Å shorter than a normal  $C(sp^2)$ - $C(sp^2)$  single bond,<sup>6</sup> while the C(10)-O(11) length (1.218 Å) is slightly greater than the value for this bond generally found in esters (1.18-1.21 Å).<sup>7</sup>

<sup>4</sup> *Chem. Soc. Special Publ.*, No. 18, 1965.

<sup>5</sup> A. Lofthus, *Mol. Phys.*, 1959, **2**, 367.

<sup>6</sup> D. W. J. Cruickshank, *Tetrahedron*, 1962, **17**, 155.

<sup>7</sup> (a) A. McL. Mathieson and H. K. Welsh, *Acta Cryst.*, 1965, **18**, 953; (b) J. J. Guy and T. A. Hamor, *J.C.S. Perkin II*, 1974, 101, and references therein.

TABLE 4

(a) Deviations (Å) of atoms from least squares planes

Plane (a): C(3), C(10), O(11), O(12), C(13)  
C(3) -0.008, C(10) -0.004, O(11) 0.006, O(12) 0.019, C(13) -0.013

Plane (b): N(1), C(2), C(3), S(4)

N(1) -0.019, C(2) 0.039, C(3) -0.034, S(4) 0.014, C(10) -0.176

Plane (c): N(1), C(2), C(3), C(6)

N(1) 0.003, C(2) -0.003, C(3) 0.001, C(6) -0.001, C(10) -0.227

Plane (d): N(1), C(2), C(6), C(9)

N(1) -0.019, C(2) 0.007, C(6) 0.006, C(9) 0.006

Plane (e): C(2), C(6), C(9)

N(1) -0.026

Plane (f): N(1), C(2), C(3), S(4), C(6)

N(1) 0.044, C(2) 0.025, C(3) -0.070, S(4) 0.051, C(6) -0.051, C(5) 0.802, C(7) 0.427, C(9) 0.242, C(10) -0.299

Plane (g): Atoms 1-4, 6, 9-13

N(1) -0.019, C(2) 0.096, C(3) 0.056, S(4) 0.071, C(6) -0.222, C(9) 0.117, C(10) -0.023, O(11) -0.148, O(12) 0.091, C(13) -0.019

Plane (h): Atoms 1-4, 9-13

N(1) -0.087, C(2) 0.068, C(3) 0.013, S(4) -0.049, C(9) 0.063, C(10) -0.016, O(11) -0.087, O(12) 0.078, C(13) 0.017

Plane (i): N(1), C(6), O(8), C(9)

N(1) -0.057, C(6) 0.036, O(8) -0.036, C(9) 0.056, C(7) 0.534

Plane (j): N(1), C(6), C(7), C(9)

N(1) 0.072, C(6) -0.068, C(7) 0.042, C(9) -0.046, O(8) -0.503

Plane (k): N(1), C(6), C(9)

C(7) 0.324, O(8) -0.252

(b) Equations of planes

$$\begin{aligned}
 \text{(a)} & -8.543x + 0.257y + 1.921z = 2.150 \\
 \text{(b)} & -8.134x + 0.313y + 2.825z = 2.430 \\
 \text{(c)} & -7.699x - 0.185y + 3.510z = 2.511 \\
 \text{(d)} & -7.622x - 1.024y + 3.595z = 2.349 \\
 \text{(e)} & -7.619x - 1.015y + 3.599z = 2.345 \\
 \text{(f)} & -7.924x + 0.928y + 3.162z = 2.683 \\
 \text{(g)} & -8.234x - 0.313y + 2.636z = 2.269 \\
 \text{(h)} & -8.378x - 0.351y + 2.334z = 2.119 \\
 \text{(i)} & -7.363x + 0.441y + 3.934z = 2.649 \\
 \text{(j)} & -8.022x - 3.587y + 2.718z = 1.745 \\
 \text{(k)} & -7.700x - 1.465y + 3.467z = 2.258
 \end{aligned}$$

$x$ ,  $y$ , and  $z$  are fractional co-ordinates relative to the cell axes.

(c) Dihedral angles (deg.)

(a) - (b)	7.8	(a) - (f)	11.1
(a) - (c)	14.1	(b) - (c)	6.4
(a) - (d)	15.4	(f) - (k)	7.7

The C(3)-S(4) bond length (1.770 Å) is only very slightly shorter than the values measured for the  $C(sp^2)$ -S bond in the sulfoxides *cis*-9-methylthioxanthan 10-oxide (1.782 Å)<sup>8</sup> and  $\beta$ -thianthren dioxide (mean of four lengths, 1.785 Å).<sup>9</sup> The sulphur atom, therefore, does not seem to be involved in the conjugation to any appreciable extent. The S(4)-C(5) and S(4)-O(14) lengths agree closely with previous

<sup>8</sup> J. Jackobs and M. Sundaralingam, *Acta Cryst.*, 1969, **B25**, 2487.

<sup>9</sup> H. L. Ammon, P. H. Watts, jun., and J. M. Stewart, *Acta Cryst.*, 1970, **B26**, 451.

results for bonds of this type, and the C(5)-S(4)-C(3) angle of  $96.5^\circ$  falls within the range of values generally observed for this angle in sulfoxides ( $95-98^\circ$ ).<sup>8-10</sup>

The deviations of the bond lengths from the values which might be expected on the basis of structure (1), and no contribution from (4), appear to decrease with increasing distance from the nitrogen atom. This might be rationalised in terms of a contribution from structure (5) to the  $\pi$ -electron delocalisation, although a small contribution from (6) cannot be excluded.

Intermolecular contact distances are listed in Table 5. These correspond to normal van der Waals interactions.

#### EXPERIMENTAL

*Crystal Data.*— $C_{10}H_{15}NO_4S$ ,  $M = 245.3$ . Orthorhombic,  $a = 8.881 \pm 0.005$ ,  $b = 19.14 \pm 0.01$ ,  $c = 7.042 \pm 0.005$  Å,  $U = 1197$  Å<sup>3</sup>,  $Z = 4$ ,  $D_o = 1.361$ ,  $F(000) = 520$ . Systematic absences:  $h00$  when  $h$  is odd,  $0k0$  when  $k$  is odd,  $00l$  when  $l$  is odd; space group  $P 2_1 2_1 2_1 (D_2^4)$ . Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å;  $\mu(\text{Mo-}K_\alpha) = 2.7$  cm<sup>-1</sup>.

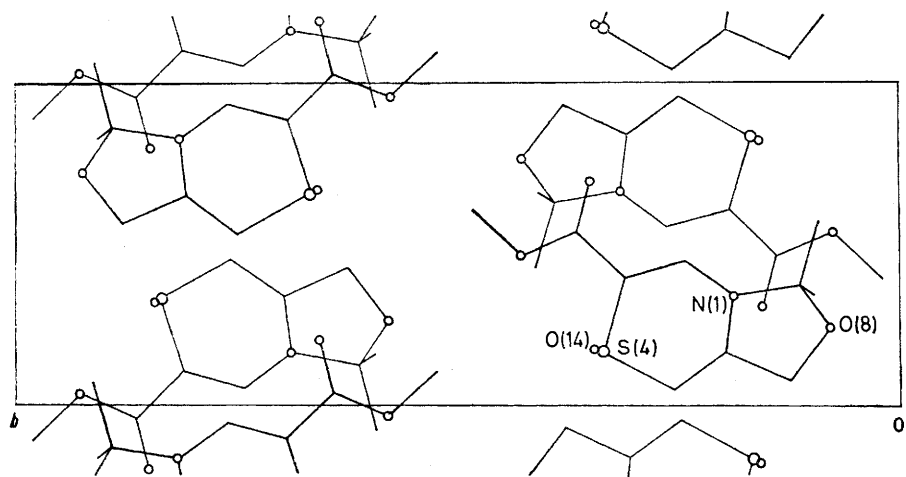


FIGURE 2 The crystal structure as seen along the  $a$  axis

There is a close intramolecular non-bonded contact between the ester oxygen atom O(12), and the sulphur atom of  $2.845$  Å. This is *ca.*  $0.4$  Å shorter than the sum of the van der Waals radii<sup>11</sup> of O and S, but is

TABLE 5

Intermolecular contacts ( $< 3.8$  Å), excluding hydrogen atoms

C(6) $\cdots$ O(11 <sup>II</sup> )	3.16	C(5) $\cdots$ O(14 <sup>V</sup> )	3.57
C(5) $\cdots$ O(11 <sup>III</sup> )	3.18	C(7) $\cdots$ C(16 <sup>III</sup> )	3.62
C(13) $\cdots$ O(14 <sup>III</sup> )	3.41	C(7) $\cdots$ O(14 <sup>V</sup> )	3.63
C(10) $\cdots$ C(15 <sup>I</sup> )	3.41	O(8) $\cdots$ C(13 <sup>I</sup> )	3.64
O(12) $\cdots$ C(15 <sup>I</sup> )	3.41	N(1) $\cdots$ O(11 <sup>I</sup> )	3.66
O(8) $\cdots$ C(16 <sup>IV</sup> )	3.44	O(14) $\cdots$ C(15 <sup>I</sup> )	3.67
O(8) $\cdots$ O(11 <sup>I</sup> )	3.47	O(11) $\cdots$ C(15 <sup>I</sup> )	3.69
C(7) $\cdots$ O(11 <sup>I</sup> )	3.51	C(13) $\cdots$ C(15 <sup>I</sup> )	3.69
O(14) $\cdots$ C(16 <sup>I</sup> )	3.55	C(2) $\cdots$ O(14 <sup>V</sup> )	3.79
S(4) $\cdots$ O(11 <sup>II</sup> )	3.56		

The superscripts refer to molecules in the following equivalent positions relative to the reference molecule at  $x, y, z$ :

I $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$	IV $-\frac{1}{2} - x, -y, -\frac{1}{2} + z$
II $x, y, -1 + z$	V $\frac{1}{2} + x, \frac{1}{2} - y, -z$
III $-\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$	VI $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$

comparable with S  $\cdots$  O contacts of  $2.81$  Å in penthienate bromide<sup>12</sup> and  $2.95$  Å in thiophen-2-carboxylic acid.<sup>13</sup>

The arrangement of the molecules in the unit cell as viewed in projection along the  $a$  axis is shown in Figure 2.

<sup>10</sup> D. J. Watkin and T. A. Hamor, *J. Chem. Soc. (B)*, 1971, 1692, and references therein.

<sup>11</sup> L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960; A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

*Crystallographic Measurements.*—A plate-like crystal, of dimensions  $0.3 \times 0.3 \times 0.05$  mm was mounted about one of the plate diagonals ( $a$ ) and unit cell dimensions measured from oscillation, Weissenberg, and precession photographs. Final cell dimensions and the intensity data were measured with a Stoe two-circle computer-controlled diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation and a scintillation counter. The  $\omega$ -scan mode with a variable scan width was employed as described elsewhere.<sup>7b</sup> Reflections were scanned within the range  $0.1 < \sin \theta/\lambda < 0.65$ , and of these, 1011, for which  $I > 2.5\sigma(I)$ , were considered observed and were used in the structure analysis. Intensities were converted into structure amplitudes in the usual way, but absorption corrections were not applied.

*Structure Analysis.*—The co-ordinates of the sulphur atom were obtained from a three-dimensional Patterson synthesis. Structure factors were calculated ( $R$  63%) and the phase angles used with the observed amplitudes to obtain a three-dimensional electron-density map. From this the positions of all atoms in the asymmetric unit (apart from hydrogen atoms) were determined. Least-squares refinement of positional and isotropic thermal parameters reduced  $R$  to 10.7%. The atoms were now allowed to vibrate anisotropically and the refinement continued until all shifts were  $< 0.1\sigma$ . The hydrogen atoms linked to atoms C(2), C(5), C(6), and C(7) were located from a Fourier difference synthesis and were included in the calculations in their theoretical positions, but their

<sup>12</sup> J. J. Guy and T. A. Hamor, preceding paper.

<sup>13</sup> M. Nardelli, G. Fava, and G. Giraldo, *Acta Cryst.*, 1962, **15**, 737.

parameters were not refined. The final value of  $R$  is 6.7% for the 1011 reflections used in the analysis.\*

The weighting scheme employed in the final cycles of least-squares refinement was  $w^{\frac{1}{2}} = 1.0$  if  $|F_0| < 14.5$  and  $w^{\frac{1}{2}} = 14.5/|F_0|$  if  $|F_0| > 14.5$ . Atomic scattering factors were taken from ref. 14, except for hydrogen atoms, for which those of ref. 15 were used.

Computations were carried out on the Birmingham University KDF 9 computer. Local versions of FORDAP,

\* Observed and calculated structure amplitudes and phase angles are published in Supplementary Publication SUP No. 21023 (8 pp.). See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue. Items less than 10 pp. are supplied as full-size copies.

the Zalkin Fourier program, and ORFLS and ORFFE, the Busing, Martin, and Levy full-matrix least-squares and function-and-error programs were used.

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<sup>14</sup> H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

<sup>15</sup> R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.