

Reactivity of *p*-Bromophenyl Vinyl Sulphone towards the Morpholine Enamine from 4a-Methyl-*trans*-decalin-2-one. Crystal and Molecular Structure of 1 α -(2-*p*-Bromophenylsulphonylethyl)-4a-methyl-2-morpholino- Δ^2 -*trans*-octalin

By Mirella Forchiassin, Amerigo Risaliti,* and Claudio Russo, Laboratorio di Chimica Organica, Università, 34127 Trieste, Italy

Nevina Bresciani Pahor and Mario Calligaris, Laboratorio di Strutturistica Chimica, Università, 34127 Trieste, Italy

The morpholine enamine from 4a-methyl-*trans*-decalin-2-one reacts with *p*-bromophenyl vinyl sulphone when heated under reflux in dioxan to give a mixture of 1 α - and 3-(2-*p*-bromophenylsulphonylethyl)-2-morpholino- Δ^2 -*trans*-octalin [(6) and (3) respectively]. The structure of (6) was determined by X-ray analysis, while that of (3) was assigned on the basis of spectroscopic properties and chemical behaviour. A possible pathway for the formation of the two enamine derivatives is discussed. The crystal structure was determined by the heavy-atom method from diffractometer data and refined by least squares to *R* 0.094 for 2 260 independent reflections.

PREVIOUSLY, we have reported¹ that the morpholine enamine from *trans*-decalin-2-one reacts with phenyl vinyl sulphone at 5 °C to give a cyclobutane adduct, whereas the corresponding enamine from 4a-methyl-*trans*-decalin-2-one fails to react unless heated under reflux in dioxan. Under these conditions 1 α -(2-phenylsulphonylethyl)-4a-methyl-2-morpholino- Δ^2 -*trans*-octalin was obtained in a yield (>32%) which did not correlate with the percentage of the Δ^1 -isomer (1b) (<10%) in the starting enamine mixture (1). The structure of the octalin derivative had been inferred exclusively on the basis of the resonance observed for the vinyl proton in its ¹H n.m.r. spectrum. On hydrolysis of the mother liquor, the expected 3 α -(2-phenylsulphonylethyl)-4a-methyl-*trans*-decalin-2-one was also isolated.

A product of this kind, *i.e.* with a substituent in the 1-position, seemed of interest in view of the possibility of obtaining 4-substituted steroids through enamine activation, since 4a-methyldecalin-2-one forms the A,B-moiety of 3-oxosteroids of the cholestane series. Before making further attempts with other electrophiles, we thought it of paramount importance

¹ M. Calligaris, M. Forchiassin, A. Risaliti, and C. Russo, *Gazzetta*, 1975, **105**, 689.

to establish unequivocally the correctness of the foregoing assignment, and we therefore repeated the reaction between the enamine (1) and *p*-bromophenyl vinyl sulphone under identical conditions, in order to obtain products suitable for X-ray analysis. In this case two isomeric enamines were isolated in approximately equal proportions. The structure of the product which showed spectral properties analogous to those of the non-brominated derivative, was determined by X-ray crystallography and proved to be 1 α -(2-*p*-bromophenylsulphonylethyl)-4a-methyl-2-morpholino- Δ^2 -*trans*-octalin (6), and therefore the structure postulated on the basis of the n.m.r. spectrum was confirmed. The geometry of the octalin system may be described in terms of the torsion angles reported in Table 1. As expected, the saturated ring has the usual chair conformation, whereas the unsaturated one is approximately in a half chair conformation. Distortions from the regular geometry of cyclohexene² are observed because of the steric hindrance between the substituents at C(9) and C(19) (see Figure). However all bond lengths and angles are in the expected

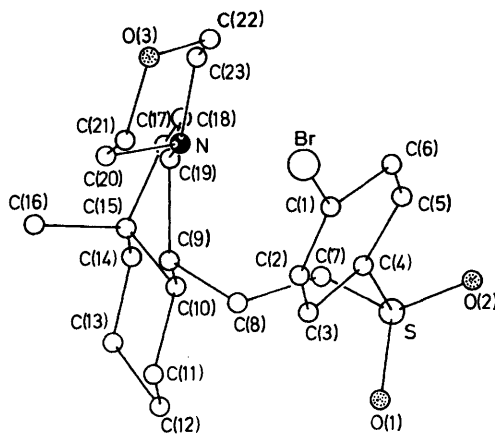
² 'Molecular Structure by Diffraction Methods,' ed. G. A. Sinn and L. E. Sutton, Chem. Soc. Specialist Periodical Reports, 1973, vol. 1, Part 1.

ranges (Table 2). The morpholine ring, in a chair conformation, is twisted around the N-C(19) bond [C(9)-C(19)-N-C(20) torsion angle 63.1°] to reduce the large A^{1,2}-strain,³ the lone pair of the nitrogen atom pointing towards the ethylsulphonyl group, which occupies an equatorial position. [C(8)-C(9)-C(10)-C(15)

TABLE 1

Some significant torsion angles (°)

(a) Octalin system	
C(10)-C(11)-C(12)-C(13)	53.8
C(11)-C(12)-C(13)-C(14)	-52.6
C(12)-C(13)-C(14)-C(15)	55.3
C(13)-C(14)-C(15)-C(10)	-53.3
C(14)-C(15)-C(10)-C(11)	54.6
C(15)-C(10)-C(11)-C(12)	-56.4
C(9)-C(10)-C(15)-C(17)	-54.6
C(10)-C(15)-C(17)-C(18)	51.5
C(15)-C(17)-C(18)-C(19)	-19.4
C(17)-C(18)-C(19)-C(9)	3.7
C(18)-C(19)-C(9)-C(10)	-5.6
C(19)-C(9)-C(10)-C(15)	40.3
(b) Morpholine base	
N-C(20)-C(21)-O(3)	-58.8
C(20)-C(21)-O(3)-C(22)	59.3
C(21)-O(3)-C(22)-C(23)	-56.7
O(3)-C(22)-C(23)-N	58.2
C(22)-C(23)-N-C(20)	-56.0
C(23)-N-C(20)-C(21)	56.5

A sketch of the molecule of (6) as viewed along the crystallographic *b* axis

165.9°] with the C·[CH₂]₂·S chain in the *anti*-conformation [S-C(7)-C(8)-C(9) 174.4°]. The bromine and sulphur atoms are coplanar with the aromatic ring (± 0.02 Å) which is symmetrically placed with respect to the morpholine [C(2) ··· C(21) 3.94(3), C(6) ··· C(22) 4.00(3) Å] and twisted 68.7° around the S-C(7) bond. No contact below the sum of the van der Waals radii is observed.

For the other product of the reaction structure (3) was assigned on the basis of spectroscopic properties and chemical behaviour. In its ¹H n.m.r. spectrum there was no resonance in the τ 4.5-6 region, characteristic of vinyl protons, while its i.r. spectrum showed a C=C-N stretching band at 1 670 cm⁻¹, typical for double bonds of tetrasubstituted enamines, where the base ring is rather twisted out of conjugation. On hydrolysis it furnished a ketone (4) which did not epimerise either in

acidic or in basic media. This ketone was isomeric with the decalone (7) generated from (6) under the same hydrolysis conditions. The reaction sequence is given in the Scheme.

On account of the reversibility of the first step in the reaction between enamines and electrophiles,⁴ the formation of (6) in a yield higher than the percentage of the parent enamine (1b) in the starting mixture can be accounted for only by assuming that under the reaction

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(a) Distances			
Br-C(1)	1.92(2)	C(7)-C(8)	1.54(2)
S-O(1)	1.42(1)	C(8)-C(9)	1.58(2)
S-O(2)	1.45(1)	C(9)-C(10)	1.55(2)
S-C(4)	1.77(1)	C(9)-C(19)	1.54(2)
S-C(7)	1.78(1)	C(10)-C(11)	1.61(2)
O(3)-C(21)	1.48(2)	C(10)-C(15)	1.57(2)
O(3)-C(22)	1.41(2)	C(11)-C(12)	1.57(3)
N-C(19)	1.42(2)	C(12)-C(13)	1.55(3)
N-C(20)	1.49(2)	C(13)-C(14)	1.68(3)
N-C(23)	1.52(2)	C(14)-C(15)	1.55(2)
C(1)-C(2)	1.39(2)	C(15)-C(16)	1.54(3)
C(1)-C(6)	1.43(2)	C(15)-C(17)	1.51(2)
C(2)-C(3)	1.36(2)	C(17)-C(18)	1.50(2)
C(3)-C(4)	1.39(2)	C(18)-C(19)	1.35(2)
C(4)-C(5)	1.39(2)	C(20)-C(21)	1.52(3)
C(5)-C(6)	1.39(2)	C(22)-C(23)	1.54(3)
(b) Angles			
O(1)-S-O(2)	118.0(8)	C(8)-C(9)-C(19)	111.4(11)
O(1)-S-C(4)	106.0(7)	C(10)-C(9)-C(19)	111.4(12)
O(1)-S-C(7)	110.5(7)	C(9)-C(10)-C(11)	110.2(12)
O(2)-S-C(4)	108.4(7)	C(9)-C(10)-C(15)	110.7(13)
O(2)-S-C(7)	107.9(7)	C(11)-C(10)-C(15)	113.5(12)
C(4)-S-C(7)	105.2(7)	C(10)-C(11)-C(12)	113.2(13)
C(21)-O(3)-C(22)	110.6(15)	C(11)-C(12)-C(13)	109.2(17)
C(19)-N-C(20)	113.2(11)	C(12)-C(13)-C(14)	112.7(15)
C(19)-N-C(23)	117.0(12)	C(13)-C(14)-C(15)	112.6(14)
C(20)-N-C(23)	108.3(13)	C(10)-C(15)-C(14)	108.6(14)
Br-C(1)-C(2)	121.2(11)	C(10)-C(15)-C(17)	109.2(13)
Br-C(1)-C(6)	115.4(11)	C(14)-C(15)-C(16)	110.6(14)
C(2)-C(1)-C(6)	123.4(15)	C(16)-C(15)-C(17)	109.0(15)
C(1)-C(2)-C(3)	117.5(14)	C(15)-C(17)-C(18)	110.8(14)
C(2)-C(3)-C(4)	121.4(13)	C(17)-C(18)-C(19)	124.6(15)
S-C(4)-C(3)	120.5(10)	N-C(19)-C(9)	113.7(13)
S-C(4)-C(5)	118.5(11)	N-C(19)-C(18)	123.7(14)
C(3)-C(4)-C(5)	121.0(14)	C(9)-C(19)-C(18)	122.5(14)
C(4)-C(5)-C(6)	120.4(14)	N-C(20)-C(21)	108.3(13)
C(1)-C(6)-C(5)	116.3(14)	O(3)-C(21)-C(20)	112.7(15)
S-C(7)-C(8)	111.3(10)	O(3)-C(22)-C(23)	110.0(15)
C(7)-C(8)-C(9)	112.3(12)	N-C(23)-C(22)	111.7(14)
C(8)-C(9)-C(10)	112.1(13)		

conditions there is an equilibrium between (1a) and (1b). It has been reported⁵ that such equilibrations always require the presence of minute traces of acid, and are of course accelerated by increase in temperature. Since particular care was taken to purify the solvent, a possible explanation is that the methylenes α to sulphonyl groups act as a source of protons. Since both inter-

³ F. Johnson, *Chem. Revs.*, 1968, **68**, 375.

⁴ G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkowicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, **85**, 207; A. Risaliti, E. Valentin, and M. Forchiassin, *Chem. Comm.*, 1969, 233; F. P. Colonna, S. Fatutta, A. Risaliti, and C. Russo, *J. Chem. Soc. (C)*, 1970, 2377; S. Fatutta and A. Risaliti, *J.C.S. Perkin I*, 1974, 2387.

⁵ H. Mazarguil and A. Lattes, *Tetrahedron Letters*, 1971, 975; F. Johnson, L. G. Duquette, A. Whitehead, and I. C. Dorman, *Tetrahedron*, 1974, **30**, 3241.

mediates (2) and (5) lead to alkylated decalin-2-one enamines with the double bond always in the Δ^2 -position, it must be concluded that at relatively high temperatures the driving force of the reaction is the formation of the double bond in the most stable position of the octalin system.⁶

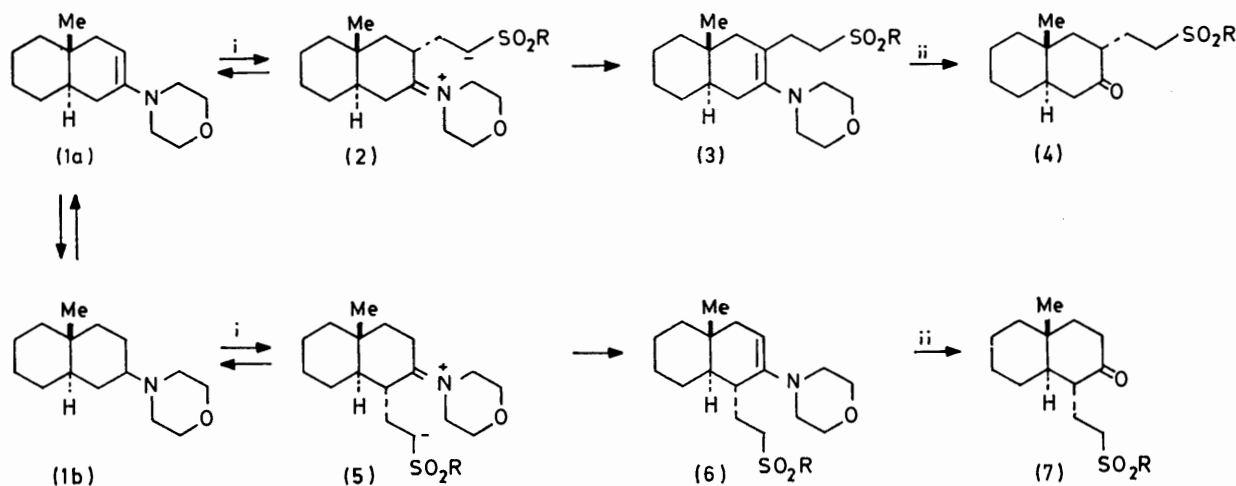
The distribution of (3) and (6) should therefore depend on their relative stabilities. In fact, the steric interactions between the base ring and the substituent are nearly the same both in tetra- and tri-substituted morpholine enamines having the substituent equatorially oriented.⁷ If we assume, however, that the equilibrium (1a) \rightleftharpoons (1b) is very fast, the ratio of the products would be dependent only on the difference in the free-energy levels of the transition states leading to (2) and (5). Since these intermediates are of comparable stability for steric reasons, it follows that (3) and (6) are formed in almost equal proportions. The remote possibility that under

furnish first the Δ^1 -isomer which in turn would equilibrate into the more stable Δ^2 -isomer on acidic catalysis at high temperature. Although no trace of the Δ^1 -isomeric enamine could be detected among the products, we think that this possible pathway to (3) cannot be rejected.

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls with a Perkin-Elmer 257 spectrophotometer. ¹H n.m.r. spectra were recorded with a JEOL JNM 60 HL spectrometer, with tetramethylsilane as internal standard, for CDCl₃ solutions. Analytical t.l.c. plates were spread with silica gel G (Merck-Stahl).

3-(2-*p*-Bromophenylsulphonyl-ethyl)-4a-methyl-2-morpholino- Δ^2 -trans-octalin (3) and 1 α -(2-*p*-Bromophenylsulphonyl-ethyl)-4a-methyl-2-morpholino- Δ^2 -trans-octalin (6).—A solution of morpholine enamine from 4a-methyl-*trans*-decalin-2-one (1)¹² (5.7 g, 24 mmol) and *p*-bromophenyl vinyl



SCHEME Reagents: i, *p*-BrC₆H₄-SO₂-CH=CH₂, 100 °C; ii, H₃O⁺, 25 °C. R = *p*-BrC₆H₄

the reaction conditions the two products could have formed as an equilibrium mixture would imply their reversion to the reactants, and hence the reversibility of the second step also. The thermal reversion could be visualised on trapping the starting enamine⁸ or the electrophilic olefin⁹ by suitable reagents, as in the case of the cyclobutane adducts. This possibility was rejected since on heating (3) and (6) for several hours under reflux in dioxan in the presence of morpholine to trap *p*-bromophenyl vinyl sulphone, the products were recovered unchanged and no trace of *p*-bromophenyl 2-morpholinoethyl sulphone could be detected (t.l.c.).

For the formation of (3) from (2), an indirect route could be envisaged, *i.e.* by analogy with the results at low temperature,^{10,11} the dipolar intermediate would

sulphone¹³ (5.9 g, 24 mmol) in anhydrous dioxan (35 ml) was heated under reflux for 72 h and then evaporated at reduced pressure. The oily residue was washed with light petroleum, treated with ether, and kept overnight at -18 °C, giving a crude product (m.p. 98–105 °C) (7 g, 60%), with i.r. absorptions at 1 640 and 1 670 cm⁻¹, characteristic of enamine double bonds. T.l.c. data (ligroin-ethyl acetate, 1:1) indicated a *ca.* 1:1 mixture of two compounds (Found: C, 57.4; H, 6.55; N, 2.9. C₂₃H₃₂BrNO₃S requires C, 57.25; H, 6.68; N, 2.9%). Recrystallisation from anhydrous ethanol gave a mixture of colourless needles and prisms which were separated by hand.

The needles (m.p. 124–126 °C) corresponded to enamine

⁸ A. Risaliti, S. Fatutta, M. Forchiassin, and C. Russo, *Ricerca Sci.*, 1968, **38**, 827.

⁹ I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1965, 2165.

¹⁰ M. Forchiassin, A. Risaliti, C. Russo, M. Calligaris, and G. Pitacco, *J.C.S. Perkin I*, 1974, 660.

¹¹ M. Forchiassin, C. Russo, and A. Risaliti, *Gazzetta*, 1972, **102**, 607.

¹² M. E. Kuehne and T. J. Giacobbe, *J. Org. Chem.*, 1968, **33**, 3359.

¹³ N. Shinriki and T. Nambara, *Chem. Pharm. Bull.*, 1963, **11**, 178.

⁶ E. J. Corey and R. A. Sneed, *J. Amer. Chem. Soc.*, 1955, **77**, 2505; R. B. Turner, W. R. Meador, and R. E. Winkler, *ibid.*, 1957, **79**, 4122; S. K. Malhotra, D. F. Moakley, and F. Johnson, *Chem. Comm.*, 1967, 448.

⁷ W. D. Gurowitz and M. A. Joseph, *J. Org. Chem.*, 1967, **32**, 3289.

(3) (Found: C, 57.0; H, 6.27; N, 2.95%); ν_{\max} . 1 145 and 1 305 (SO_2), 1 670 cm^{-1} (C=C-N); τ 9.26 (3 H, s, CH_3).

The prisms (m.p. 119–120 °C) corresponded to enamine (6) (Found: C, 56.8; H, 6.32; N, 2.9%); ν_{\max} . 1 145 and 1 305 (SO_2), 1 640 cm^{-1} (C=C-N); τ 5.17 (1 H, m, $\text{CH}=\text{C}-\text{N}$), 9.19 (3 H, s, CH_3).

In order to obtain a single crystal for the X-ray analysis the product was further crystallised from ethanol.

In an attempt to cause the enamines (3) and (6) to revert to the starting reagents, each was heated under reflux in anhydrous dioxan with an excess of morpholine for 96 h. Solvent was removed under reduced pressure and t.l.c. analysis (benzene–acetone, 9 : 1) indicated the presence of the starting materials [(3) or (6)] only; no trace of *p*-bromophenyl 2-morpholinoethyl sulphone was detected.

3 α -(2-*p*-Bromophenylsulphonylethyl)-4 α -methyl-trans-decalin-2-one (4).—To a solution of (3) (0.6 g) in acetone (20 ml), AcOH (0.75 ml) and water (2 ml) were added and the solution kept at room temperature for 96 h. Removal of solvent *in vacuo* afforded a gum which, after treatment with ether, gave the ketone (4) (0.5 g) as a white solid, homogeneous on t.l.c. (ligroin–ethyl acetate, 1 : 1), m.p. 110–111 °C (from ethanol) (Found: C, 55.9; H, 5.95. $\text{C}_{19}\text{H}_{25}\text{BrO}_3\text{S}$ requires C, 55.2; H, 6.1%); ν_{\max} . 1 141 and 1 302 (SO_2) and 1 700 cm^{-1} (CO).

1 α -(2-*p*-Bromophenylsulphonylethyl)-4 α -methyl-trans-decalin-2-one (7).—Compound (6) was similarly worked up, to give quantitatively the ketone (7) as white crystals, homogeneous on t.l.c., m.p. 132–133 °C (from ethanol) (Found: C, 55.8; H, 6.0%); ν_{\max} . 1 140 and 1 312 (SO_2) and 1 703 cm^{-1} (CO). Ketones (4) and (7) were unaffected by treatment with either acids and bases.

***p*-Bromophenyl 2-Morpholinoethyl Sulphone.**—Equimolecular amounts of *p*-bromophenyl vinyl sulphone and morpholine in dioxan were gently boiled under reflux for 12 h. Removal of solvent gave a viscous oil which solidified when set aside at low temperature. It was recrystallised from ligroin as shining plates, m.p. 110–112 °C (Found: C, 43.2; H, 4.85; N, 4.3. $\text{C}_{12}\text{H}_{16}\text{BrNO}_3\text{S}$ requires C, 43.1; H, 4.8; N, 4.2%); ν_{\max} . 1 140 and 1 320 cm^{-1} (SO_2).

Crystal Data for (6).— $\text{C}_{23}\text{H}_{33}\text{BrNO}_3\text{S}$, $M = 483.5$. Monoclinic, $a = 8.774(7)$, $b = 22.83(3)$, $c = 11.92(4)$ Å, $\beta = 103.7(2)^\circ$, $U = 2 319.5$ Å³, $D_m = 1.39$, $Z = 4$, $D_o = 1.385$ g cm^{-3} . Mo- $K\alpha$ radiation, $\lambda = 0.710 7$ Å; $\mu(\text{Mo}-K\alpha) = 19.9$ cm^{-1} . Space group $P2_1/c$ (C_2^5).

Cell parameters were determined from Weissenberg photographs taken with Co- $K\alpha$ radiation ($\lambda = 1.790 2$ Å) and refined with an on-line automated single-crystal Siemens diffractometer with Mo- $K\alpha$ radiation.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ – 2θ scan technique by use of Mo- $K\alpha$ radiation for $2\theta_{\max}$. 50°. Reflections with $I_o < 3\sigma(I_o)$ were rejected, the remainder being corrected for Lorentz-polarisation factors. A total of 2 260 independent reflections was obtained. No correction for absorption (μR ca. 0.64), extinction, or anomalous dispersion of the sulphur and bromine atoms was applied.

Structure Determination and Refinement.—The structure was solved by the heavy-atom method, the approximate co-ordinates of the crystallographically independent sulphur and bromine atoms being determined from a three-dimen-

sional Patterson map. After isotropic block-diagonal least-squares refinement R was 0.12. A few further cycles, with anisotropic thermal parameters assigned to the heavy atoms, reduced R to 0.094. The function minimised

TABLE 3

Fractional co-ordinates ($\times 10^4$) and temperature factors, with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Br	9 601(2)	3 139(1)	3 554(2)	*
S	570(4)	631(2)	1 388(3)	*
O(1)	–12(14)	685(5)	171(10)	4.0(2)
O(2)	2 199(14)	472(5)	1 820(10)	4.2(2)
O(3)	6 963(15)	1 583(6)	4 960(11)	4.9(3)
N	7 259(14)	493(5)	3 771(11)	2.9(2)
C(1)	9 826(18)	2 392(7)	2 867(13)	3.2(3)
C(2)	8 841(19)	2 227(7)	1 819(14)	3.3(3)
C(3)	9 069(18)	1 687(7)	1 396(13)	2.9(3)
C(4)	256(16)	1 319(6)	1 978(12)	2.6(3)
C(5)	1 247(19)	1 487(7)	3 020(14)	3.3(3)
C(6)	1 057(20)	2 028(8)	3 507(15)	3.5(3)
C(7)	9 407(16)	126(6)	1 968(12)	2.6(3)
C(8)	7 647(17)	236(7)	1 479(13)	2.7(3)
C(9)	6 593(16)	–164(6)	2 068(12)	2.5(3)
C(10)	6 635(17)	–813(7)	1 707(13)	2.7(3)
C(11)	5 784(19)	–889(7)	359(14)	3.5(3)
C(12)	5 807(23)	–1 535(9)	–80(17)	4.8(4)
C(13)	5 113(24)	–1 945(9)	708(18)	5.0(4)
C(14)	5 980(21)	–1 861(8)	2 115(16)	4.1(3)
C(15)	5 935(19)	–1 219(7)	2 526(14)	3.3(3)
C(16)	4 247(22)	–1 041(9)	2 550(16)	4.3(4)
C(17)	6 963(19)	–1 183(8)	3 739(14)	3.7(3)
C(18)	7 234(19)	–559(7)	4 116(14)	3.5(3)
C(19)	7 037(17)	–96(7)	3 394(13)	2.8(3)
C(20)	5 814(19)	854(8)	3 421(14)	3.6(3)
C(21)	6 251(24)	1 492(9)	3 714(18)	4.8(4)
C(22)	8 337(24)	1 244(9)	5 317(18)	5.2(4)
C(23)	7 961(20)	593(8)	5 048(15)	3.9(3)

* Anisotropic temperature factors ($\times 10^4$) in the form $\exp[-(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)]$, with parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Br	159(2)	11(2)	83(3)	17(0)	–18(1)	89(1)
S	114(4)	–3(3)	88(5)	13(1)	–0(3)	63(2)

was $\Sigma(w|F_o| - |F_c|)^2 / \Sigma w|F_o|^2$, where the weighting factor $w = (A + B|F_o| + C|F_o|^2)^{-1}$ with $A = 6.0$, $B = 1.0$, and $C = 0.003 0$ chosen so that $w(|F_o| - |F_c|)^2$ was nearly independent of both $|F_o|$ and $(\sin \theta/\lambda)$. No attempt was made to locate hydrogen atoms. Final atomic parameters are listed in Table 3 together with their estimated standard deviations, calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. The numbering scheme for the atoms is shown in the Figure. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21928 (6 pp).^{*} Atomic scattering factors were calculated according to ref. 14.

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 15.

This work was supported by a grant from the C.N.R. Rome (Italy).

[6/1489 Received, 30th July, 1976]

¹⁴ F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1976, Index issue.

¹⁵ V. Albano, A. Domenicano, and A. Vaciano, *Gazzetta*, 1966, **96**, 922; A. Immirzi, *Ricerca Sci.*, 1967, **37**, 846.