β-Sulphonylenamines. An *X*-Ray and ^{1}H Nuclear Magnetic Resonance Study of the Stereochemistry of the Isomeric β-Chloromethylsulphonyl-β-methyl-α-morpholinostyrenes

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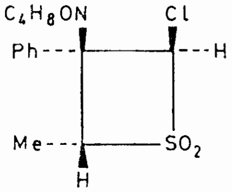
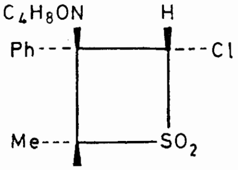
A study has been made, both in the solid state and in solution, of the stereochemistry of the components of the mixture of the isomeric β-chloromethylsulphonyl-β-methyl-α-morpholinostyrenes obtained among other products in the reaction between chloromethanesulphonyl chloride and (*E*)-β-methyl-α-morpholinostyrene in the presence of triethylamine. *X*-Ray analysis of two different kinds of manually separated crystals shows the presence of three conformational racemic rotamers of the same molecule with the *E*-configuration. Two of them coexist in the same crystal. The ^{1}H n.m.r. data give evidence for the presence in solution of an equilibrium mixture of the *E*- and *Z*-isomers. The position of equilibrium depends partially on the nature of the solvent.

DURING our studies on the stereochemistry and chemical behaviour of 2-substituted thietan 1,1-dioxide derivatives[1] we found that the reaction between chloromethanesulphonyl chloride and (*E*)-β-methyl-α-morpholinostyrene in the presence of triethylamine affords the epimeric 2-chlorothietan 1,1-dioxides (1) and (2) and a mixture of isomeric open chain β-sulphonylenamines of general formula (3).†,[2] We now report the details of the stereochemistry, both in the solid state and in solution, of these β-sulphonylenamines.



(1)



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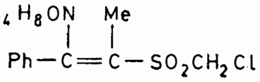
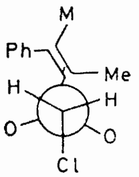


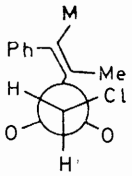
$$\mathrm{Ph{-}\overset{\overset{C_4H_8ON}{|}}{C}{=}\overset{\overset{Me}{|}}{C}{-}SO_2CH_2Cl}$$

(3)

Crystal Structure.—Two different crystal forms present in the product, obtained from slow crystallization of (3) from ethanol, were separated manually and submitted to *X*-ray analysis. Three conformational isomers were found in the crystals: all were racemic and had the *E*-configuration. The three isomers (4), (5), and (5′) were chosen for the present discussion from among the above racemic pairs because they contain the same spatial disposition with respect to the torsion angle C(7)–C(8)–S–C(10). Isomer (4) was the antiperiplanar conformer and (5) and (5′), which coexisted in the same crystal, proved to be slightly different synclinal rotamers.

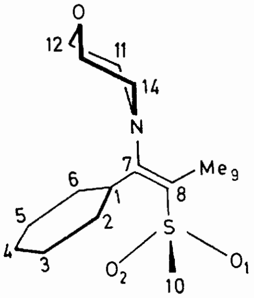


(4)



(5) and (5′)

M = morpholino



Molecular geometry. Table 1 lists bond distances and angles for the three rotamers and Figures 1 and 2 show projections of the molecules with the arbitrary numbering scheme used in the analysis. The diagrams, for the *E*-configurations, have been chosen to unify the results so

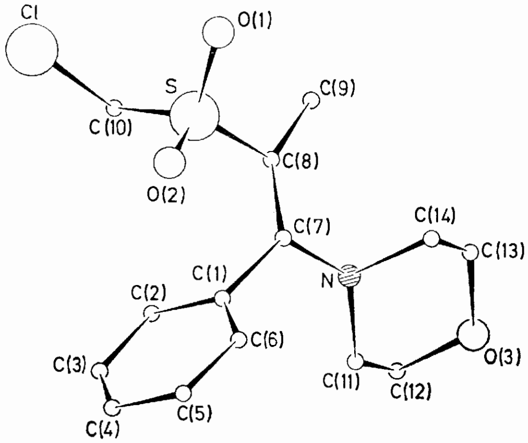


FIGURE 1 Antiperiplanar conformer: projection of the structure along (010)

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† Structure (3) indicates the compound in the solid state.

[1] S. Bradamante, P. Del Buttero, D. Landini, and S. Maiorana, *J.C.S. Perkin II*, 1974, 1676.

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

that the conformational rotations can be more clearly envisaged. In fact the three molecules found in these structures differ from these and each other by (a) rotations of groups around the single bonds C(7)-N, C(7)-C(1), and C(8)-S, (b) rotation around the S-C(10) bond, and (c) a twist deformation around the double bond.

TABLE 1

Bond lengths and angles for antiperiplanar and synclinal compounds (1) and (2) respectively

(*a*) Intramolecular distances (Å)

Cl–C(10)	1·784(11)	1·744(5)	1·750(5)
S–O(1)	1·438(8)	1·441(3)	1·445(4)
S–O(2)	1·411(7)	1·434(5)	1·431(5)
S–C(8)	1·769(10)	1·733(5)	1·737(6)
S–C(10)	1·843(10)	1·793(6)	1·798(5)
O(3)–C(12)	1·439(14)	1·425(7)	1·434(9)
O(3)–C(13)	1·400(16)	1·430(7)	1·415(7)
N–C(7)	1·408(12)	1·362(6)	1·369(6)
N–C(11)	1·467(15)	1·471(9)	1·460(6)
N–C(14)	1·496(13)	1·472(6)	1·464(7)
C(1)–C(2)	1·414(12)	1·386(6)	1·384(5)
C(1)–C(6)	1·352(11)	1·379(6)	1·384(7)
C(1)–C(7)	1·519(12)	1·494(5)	1·494(6)
C(2)–C(3)	1·403(11)	1·386(6)	1·400(10)
C(3)–C(4)	1·357(10)	1·403(7)	1·377(10)
C(4)–C(5)	1·412(13)	1·412(7)	1·378(7)
C(5)–C(6)	1·395(12)	1·382(7)	1·390(8)
C(7)–C(8)	1·317(13)	1·368(6)	1·354(6)
C(8)–C(9)	1·549(14)	1·515(6)	1·518(7)
C(11)–C(12)	1·500(17)	1·515(6)	1·496(8)
C(13)–C(14)	1·513(16)	1·506(6)	1·502(7)

(*b*) Bond angles (deg.)

O(1)–S–O(2)	118·9(10)	117·2(6)	117·8(6)
O(1)–S–C(8)	108·6(10)	111·1(6)	109·3(8)
O(1)–S–C(10)	106·0(10)	102·8(5)	102·7(5)
O(2)–S–C(8)	113·2(10)	112·7(7)	113·1(6)
O(2)–S–C(10)	108·4(10)	107·5(6)	107·7(5)
C(8)–S–C(10)	99·8(9)	104·2(6)	105·1(6)
C(12)–O(3)–C(13)	111·7(12)	109·9(8)	110·3(9)
C(7)–N–C(11)	124·8(20)	124·2(11)	124·0(11)
C(7)–N–C(14)	121·7(16)	123·4(11)	123·3(10)
C(11)–N–C(14)	111·0(16)	111·6(9)	112·7(8)
C(2)–C(1)–C(6)	120·8(15)	119·8(8)	120·0(9)
C(2)–C(1)–C(7)	118·0(14)	121·0(8)	118·4(8)
C(6)–C(1)–C(7)	121·2(15)	119·0(9)	121·5(9)
C(1)–C(2)–C(3)	117·7(15)	120·5(9)	119·4(10)
C(2)–C(3)–C(4)	121·0(14)	119·2(10)	120·6(13)
C(3)–C(4)–C(5)	121·1(16)	120·4(8)	119·6(11)
C(4)–C(5)–C(6)	117·6(15)	118·4(9)	120·5(10)
C(1)–C(6)–C(5)	121·7(16)	121·6(10)	119·9(10)
N–C(7)–C(1)	111·8(12)	115·1(9)	113·1(7)
N–C(7)–C(8)	123·1(17)	122·8(9)	120·9(11)
C(1)–C(7)–C(8)	124·9(17)	122·1(8)	126·0(10)
S–C(8)–C(7)	121·0(13)	121·6(7)	122·3(10)
S–C(8)–C(9)	111·6(11)	113·1(7)	112·5(6)
C(7)–C(8)–C(9)	127·1(20)	125·3(9)	124·9(10)
Cl–C(10)–S	109·4(7)	112·5(5)	112·5(4)
N–C(11)–C(12)	107·9(16)	109·5(8)	111·5(10)
O(3)–C(12)–C(11)	111·2(11)	110·7(8)	111·6(9)
O(3)–C(13)–C(14)	111·0(17)	111·7(7)	112·7(9)
N–C(14)–C(13)	107·3(14)	109·3(8)	108·0(8)

(*c*) Carbon–hydrogen bonds (Å)

C(2)–H(1)	1·13(8)	1·02(4)	1·10(6)
C(3)–H(2)	1·08(9)	1·10(5)	1·08(6)
C(4)–H(3)	1·05(9)	1·03(4)	1·01(7)
C(5)–H(4)	1·04(8)	1·13(4)	1·01(6)
C(6)–H(5)	0·94(9)	0·97(4)	0·94(4)
C(9)–H(6)	1·09(10)	0·95(5)	1·02(4)
C(9)–H(7)	0·91(10)	0·94(4)	0·93(3)
C(9)–H(8)	1·08(10)	0·95(5)	0·97(7)
C(10)–H(9)	1·05(11)	1·00(4)	1·05(3)
C(10)–H(10)	1·04(9)	0·97(5)	0·95(6)
C(11)–H(11)	1·03(10)	1·01(4)	1·04(4)
C(11)–H(12)	1·14(10)	0·98(4)	1·04(6)
C(12)–H(13)	1·07(9)	0·95(7)	1·13(4)
C(12)–H(14)	1·03(9)	1·13(5)	1·03(6)
C(13)–H(15)	1·03(10)	1·10(4)	1·13(4)
C(13)–H(16)	1·09(8)	0·97(4)	0·98(7)
C(14)–H(17)	1·14(10)	0·87(4)	0·97(4)
C(14)–H(18)	1·05(10)	1·01(6)	0·99(3)

TABLE 1 (*Continued*)

(*d*) Torsion angles (deg.) involving the morpholino-group

C(11)–N–C(14)–C(13)	58·8	54·4	53·6
C(14)–C(13)–O(3)–C(12)	59·5	60·4	60·5
O(3)–C(12)–C(11)–N	57·5	57·8	52·7
N–C(14)–C(13)–O(3)	58·2	56·8	58·2
C(13)–O(3)–C(12)–C(11)	59·1	60·5	56·5
C(12)–C(11)–N–C(14)	58·7	55·0	52·4

TABLE 2

Parameters (deg.) defining the conformation of the molecule of the antiperiplanar and synclinal forms (1) and (2) respectively

Angles between planes			
C(11)–N–C(14); C(1)–C(7)–C(8)	−25·8	+31·7	+39·7
C(2)–C(1)–C(6); N–C(7)–C(8)	+74·1	+56·2	+58·8
S–C(8)–C(9); N–C(1)–C(7)	−19·5	+26·4	+20·3
C(7)–C(8)–S–O(1)	+152·9	+127·6	+151·4
C(7)–C(8)–S–O(2)	+18·6	−6·2	+18·1
C(7)–C(8)–S–C(10)	−96·4	−122·4	−99·1
C(8)–S–C(10)–Cl	−170·4	+60·6	+64·0
C(1)–C(7)–C(8)–C(9)	−156·0	+153·3	+163·2

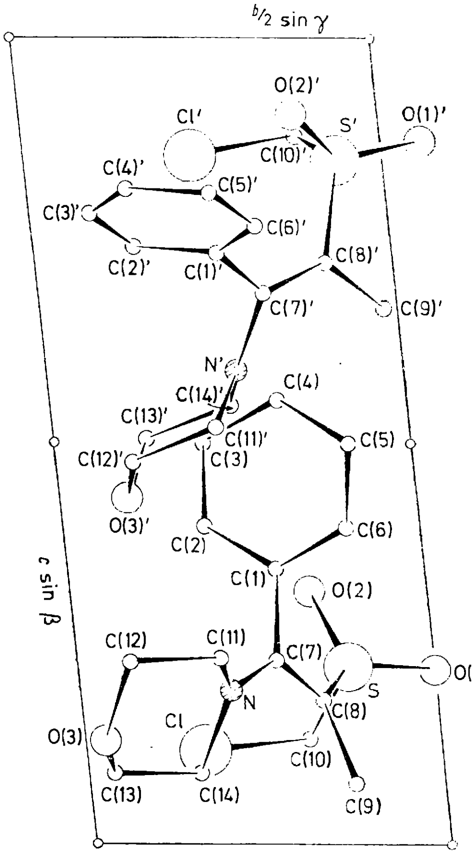

FIGURE 2 Synclinal conformers: projection of the structure along [100]

The corresponding bond distances and angles for the phenyl and morpholino-groups are comparable in the three molecules, while the orientation of these groups with respect to the sulphonylenamine system, which is mainly determined by packing interactions, can be described by the torsional and dihedral angles reported in Table 2 (see also Figure 3).

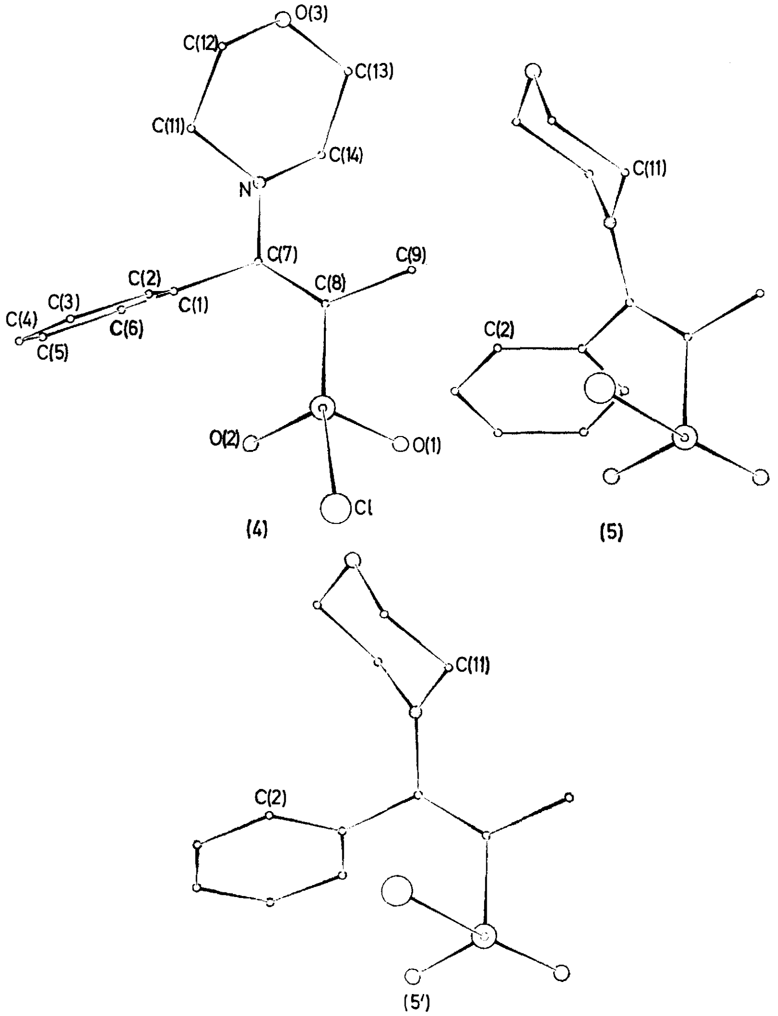

FIGURE 3 Projections of the molecules on a plane perpendicular to the S–C(10) bond

The mutual orientation of the chloromethyl and sulphonyl groups strongly affects the bond lengths of the sulphonylenamine system as shown in Table 3. On the other hand bond angles involving sulphur as a central atom are comparable in the three molecules. Carbon–chlorine distances agree with the values reported in the literature for C_{sp^3}–Cl bonds α to a sulphonyl group [1·749(5) in *trans*-2-chloro-3-morpholino-2,4,4-trimethylthietan 1,1-dioxide,[3] and 1·754(8) Å in *cis*-2-chloro-3-morpholino-4,4-dimethylthietan 1,1-dioxide [4]]. The C_{sp^3}–S distances in the synclinal conformers (5) and (5′) are near to the values found in alkyl sulphones [1·777(4) in the case of $(CH_3)_2SO_2$] [5] or in the alkylsulphonyl halides [1·763 (5) in CH_3SO_2Cl,[6] 1·759(6) Å in CH_3SO_2F [7]]. On the contrary the S–C(10) bond [1·843(10) Å] in the antiperiplanar conformer (4) is longer than the expected value for a single C–S bond [1·82 Å].[8]

TABLE 3

Effect of mutual orientation of the chloromethyl and sulphonyl groups on bond lengths

	Cl–C(10)	C(10)–S	S–C(8)	C(8)–C(7)	C(7)–N
anti (4)	1·784(11)	1·843(10)	1·769(10)	1·317(13)	1·408(12)
Average *syn* (5) + (5′)	1·747(5)	1·796(6)	1·735(6)	1·361(6)	1·365(6)

The steric effects, due to O · · · Cl repulsion, also cause some differences in the Cl–C–S and C–S–C bond angles in the three rotamers (see Table 1). They are generally less strained in (4). The S–C(vinyl) bond lengths can be compared with the values observed in propenyl *p*-tolyl sulphone [1·748(3) Å] [9] and in *N*-methyl-2-methylsulphonyl-2-phenylsulphonylvinylideneamine [1·735(10)

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[3] G. D. Andreetti, L. Cavalca, and P. Sgarabotto, *Gazzetta*, 1971, **101**, 440.

[4] G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *Gazzetta*, 1974, **104**, 1207.

[5] S. Saito and F. Makino, *Bull. Soc. Chem. Japan*, 1972, **45**, 92.

[6] M. Hargittai and I. Hargittai, *J. Chem. Phys.*, 1973, **59**, 2513.

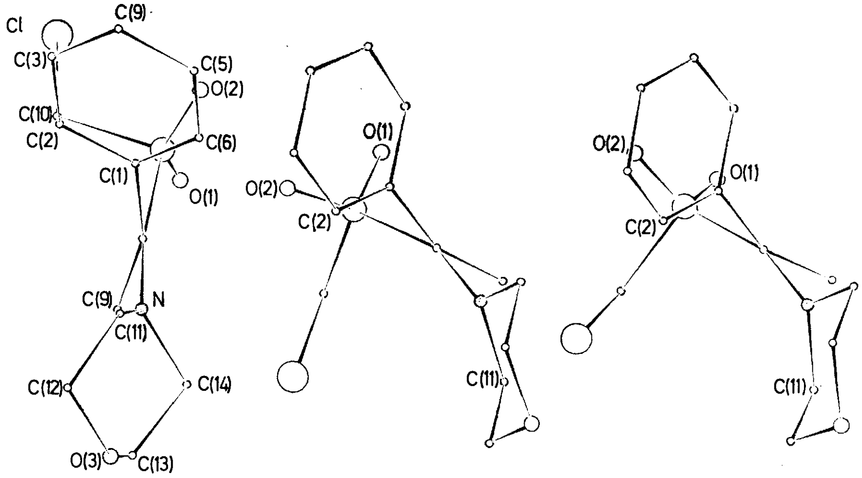
[7] I. Hargittai and M. Hargittai, *J. Mol. Struct.*, 1973, **15**, 399.

[8] S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 407.

[9] A. M. Klazing and A. Vos, *Rec. Trav. chim.*, 1973, **92**, 360.

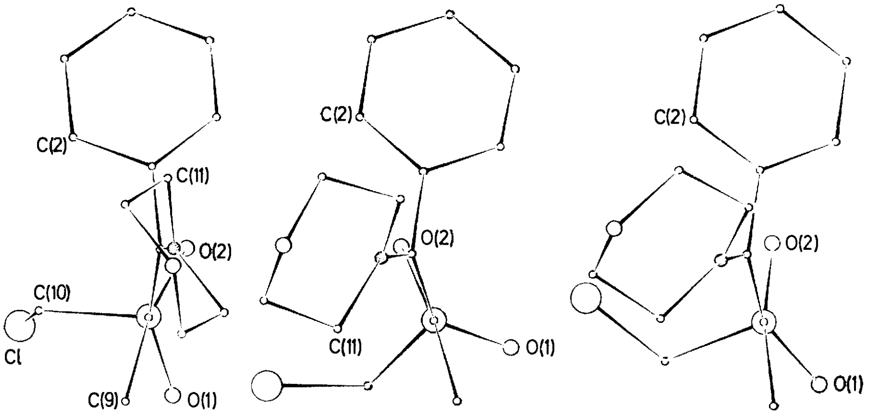
and 1·723(10) Å] [10] which to our knowledge are the only non-cyclic vinyl sulphones of known structure.

Finally, though comparison of the C=C and C–N bond lengths suggests less extended conjugation in the antiperiplanar conformer, the distortions from coplanarity of the six atoms S, C(8), C(9), N, C(1), and C(7) are comparable in the three molecules. In fact, the dihedral angles are +19·6, −26·4, and −20·4° for rotamers (4), (5), and (5′) respectively, as shown in Figure 4.



(4) (5) (5′)

FIGURE 4 Projections of the molecules on a plane perpendicular to the C(7)–C(8) bond



(4) (5) (5′)

FIGURE 5 Projections of the molecules on a plane perpendicular to the S–C(8) bond

Projections of the molecules along the S–C(vinyl) bond are shown in Figure 5 and allow consideration of the relative orientation of the sulphonyl group with respect to the C(8) vinyl π-orbital. The conformational requirements for conjugative interactions involving the sulphonyl group have been considered theoretically by Kock and Moffitt [11] and more recently by other authors.[12] In our molecules a double bond only flanks the SO_2 group, and in rotamers (4) and (5′) the torsion angle between the $C_\alpha(8)$ π-orbital and the $\widehat{\text{OSO}}$ bisector are 4·5 and 5·0° whereas the same angle is 23·0° in (5). Moreover $C_\alpha(8)$ of (4) and (5′) exhibits a slight but significant pyramidal distortion [0·050(5) and 0·046(5) Å respectively] out of the C(7)–C(9)–S plane, whereas in (5) $C_\alpha(8)$ has a strictly planar configuration. An analogous effect is observed in 3-[2-(2-chloroethoxy)ethyl]-4-phenyl-5-methyl-Δ^4-thiazoline [13] where the torsion angle between the $C_\alpha(8)$ π-orbital and the bisector of the $\widehat{\text{OSO}}$ angle is constrained to be *ca.* 90°. In this case $C_\alpha(8)$ is 0·056(4) Å out of the plane of S, C(7), and C(9).

Finally in our molecules the six S–O distances all lie in the range 1·41—1·45 Å usually found for sulphones.

Packing is consistent with van der Waals interactions; contacts <3·55 Å are listed in Table 4.

^{1}H *N.m.r. Studies on Isomers* (3).—A parallel study of the ^{1}H n.m.r. data for $CDCl_3$ solutions and of molecular

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[10] R. K. Bullough and P. J. Wheatley, *Acta Cryst.*, 1956, **10**, 233.

[11] H. P. Kock and W. E. Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.

[12] For leading references see B. S. Thyagarajan, *Mechanisms Reactions Sulfur Compounds*, 1969, **4**, 115.

[13] G. D. Andreetti, S. Maiorana, *et al.*, *J.C.S. Perkin II*, 1974, 1483.

TABLE 4

Contacts < 3·55 Å

Antiperiplanar conformer

$O(1)\cdots C(4)^{I}$	3·44(1)	$O(2)\cdots C(8)^{II}$	3·47(1)
$O(2)\cdots C(2)^{II}$	3·37(1)	$O(2)\cdots C(9)^{II}$	3·51(2)
$O(2)\cdots C(7)^{II}$	3·42(1)	$O(3)\cdots C(6)^{III}$	3·46(1)
$O(1)\cdots H(3)^{I}$	2·67(9)	$O(2)\cdots H(1)^{II}$	2·36(8)
$O(3)\cdots H(5)^{III}$	2·55(9)		

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

Synclinal conformers

$O(1)\cdots C(5)'^{I}$	3·34(1)	$O(2)\cdots C(14)^{VI}$	3·26(1)
$O(1)\cdots C(6)'^{I}$	3·32(1)	$O(2)'\cdots C(10)^{VII}$	3·21(1)
$O(1)\cdots C(10)'^{II}$	3·26(1)	$O(3)\cdots O(3)^{VIII}$	3·42(1)
$O(1)'\cdots C(11)^{III}$	3·49(1)	$O(3)\cdots C(13)^{VIII}$	3·33(1)
$O(1)'\cdots C(10)^{IV}$	3·41(1)	$O(3)'\cdots C(12)^{IX}$	3·22(1)
$O(1)'\cdots C(10)'^{V}$	3·36(1)		
$O(1)\cdots H(4)'^{I}$	2·66(4)	$O(1)'\cdots H(10)^{IV}$	2·57(5)
$O(1)\cdots H(5)'^{I}$	2·73(5)	$O(1)'\cdots H(9)'^{V}$	2·34(4)
$O(1)\cdots H(10)'^{I}$	2·34(5)	$O(2)\cdots H(17)^{VI}$	2·32(4)
$O(1)'\cdots H(11)^{III}$	2·70(4)	$O(2)'\cdots H(9)^{VII}$	2·24(4)
$O(3)\cdots H(15)^{VIII}$	2·43(3)	$O(3)'\cdots H(13)^{IX}$	2·53(7)

I, $x, y - 1, z$
II, $1 + x, y - 1, z$
III, $x, 1 + y, z$
IV, $x - 1, 1 + y, z$
V, $-1 - x, 1 - y, -z$
VI, $1 - x, -y, 1 - z$
VII, $-x, -y, -z$
VIII, $-1 - x, -y, -z$
IX, $-x, -y, 1 - z$

models made on the basis of the *X*-ray data shows that the signals at τ 2·54 and 2·56 (m, ArH), 5·86 and 5·23 (s, SO_2CH_2Cl), 6·29—6·82 (m, morpholine H), and 7·79 and 8·22 (s, $MeCSO_2$) can be attributed respectively to the (*E*)- and (*Z*)-isomers present in *ca.* 70 : 30 ratio. In fact, the methyl group of the (*Z*)-isomer is more likely at higher fields because of phenyl group shielding while the higher field absorption of the CH_2SO_2 group of the (*E*)-isomer can be explained analogously.

Hand picked pure crystals of the racemic rotamers gave the ^1H n.m.r. spectrum described above and evaporation of the solvent and slow crystallization from ethanol again gave the mixture (3).

The easy equilibration in solution * of the (*E*)- and (*Z*)-stereoisomers confirms earlier reports.[14] The electron-withdrawing sulphonyl group and the electron-donating morpholine nitrogen are linked to opposite ends of the carbon–carbon double bond and in general, in comparable structures, the barrier to isomerization of the C=C bond is particularly low.[14,15]

The *E* : *Z* ratio in solution is partially solvent dependent being *ca.* 73 : 27 in [$^2H_6$]acetone and 60 : 40 after 4 days in [$^2H_6$]benzene. Irradiation of the benzene solution using a HPK 125 W lamp gives the 60 : 40 mixture after 13 h.

Finally, the ^1H n.m.r. spectrum at high temperature (60—140°) showed only that the thermally promoted rearrangements previously described[15] occur easily in [$^2H_6$]benzene or [$^2H_6$]dimethyl sulphoxide.

At temperatures down to −100° ([$^2H_6$]acetone–algofrene 12) no appreciable variation of the multiplicity of the methyl or methylene signals occurs. However, a downfield shift of the methylene protons [more pronounced in the (*E*)-isomer] can be observed and is probably due to a variation in the conformer populations.

EXPERIMENTAL

β-Chloromethylsulphonyl-β-methyl-α-morpholinostyrene (3).—The mixture of isomeric β-sulphonylenamines (3) was obtained as previously reported.[2]

Irradiation of (E)- *and* (Z)-*β-Chloromethylsulphonyl-β-methyl-α-morpholinostyrenes.*—A benzene solution of the (*E*)- and (*Z*)-isomers in the equilibrium ratio 60 : 40 was irradiated in an n.m.r. tube using a 125 W lamp. The ^1H n.m.r. spectrum of the mixture at different time showed the presence of an increasing amount of the (*Z*)-isomer. After 13 h, the mixture of the (*E*)- and (*Z*)-isomers in 60 : 40 ratio was present.

Antiperiplanar β-Chloromethylsulphonyl-β-methyl-α-morpholinostyrene (4).—Slow crystallization of an ethanol solution of the compound gave crystals of form (4) as tabular prisms elongated along [010], together with crystals of the synclinal conformers. Preliminary cell dimensions and space group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were then refined by least-squares by use of 15 $(\theta,\chi,\phi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal Data.—$C_{14}H_{18}ClNO_3S$, $M = 315{\cdot}8$. Monoclinic, $a = 16{\cdot}29(1)$, $b = 8{\cdot}87(1)$, $c = 10{\cdot}47(1)$ Å, $\beta = 101{\cdot}2(2)°$, $Z = 4$, $D_c = 1{\cdot}41$ g cm^{-3}, $U = 1484{\cdot}0$ Å^3, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\text{Cu-}K_\alpha) = 35{\cdot}0$ cm^{-1}. Space group *Cc* from structure determination.

Intensity data were collected up to $\theta = 70°$ by use of the ω–2θ scan method and the ' five-values ' technique[16] with nickel-filtered Cu-K_α radiation on a Siemens single-crystal diffractometer. Throughout data collection a standard reflection was checked every twenty measurements and indicated practically no decomposition of the specimen. 1418 Independent reflections were measured of which 18 were not used in the crystal analysis, having intensities less than $2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$, where *I* is the relative intensity and $\sigma^2(I)$ its variance. The dimensions of the crystal roughly in the *x*, *y*, *z* directions were 0·2, 0·4, and 0·6 mm; absorption was ignored.

Structure Analysis and Refinement.—The data were put on an absolute scale by Wilson statistics[17] and normalized structure factor magnitudes $|E_{hkl}|$ were derived. The structure was solved using 322 reflections with $|E| \geqslant 1{\cdot}26$ by multisolution and phase permutation technique, with the reflections in the basic set (Table 5) chosen by the program MULTAN.[18] 32 Combinations of phases *a*, *b*, and *c* (Table 6) were used as input to a routine[19] called ' weighted numerical addition,' which has been useful for centrosymmetrical structure and has been used for the first time for

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* The C–C bond is considerably distorted in the solid state also (Figure 4).

[14] For a discussion of the mechanism and barrier of *Z–E*-isomerization see H. O. Kalinowski and H. Kessler, ' Topics in Stereochemistry,' Wiley, New York, 1973, vol. 7, p. 295; W. E. Truce and D. G. Brady, *J. Org. Chem.*, 1966, **31**, 3543, and references therein.

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[16] W. Hoppe, *Acta Cryst.*, 1969, **25A**, 67.

[17] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

[18] P. Main, M. M. Woolfson, and G. Germain, ' MULTAN,' A Computer Programme for the Automatic Solution of Crystal Structures, University of York, 1971.

[19] G. D. Andreetti, VII Meeting of Italian Crystallographic Association, Trieste, 1973.

this non-centrosymmetric structure. This calculates a figure of merit G, defined by equation (1) where the weights

$$G = \sum_{\mathbf{h}} \left[\sum_{ij \neq lm} w(k_{ij}) w(k_{lm}) \cos \{(\phi_{\mathbf{h}i} + \phi_{\mathbf{h}j}) - (\phi_{\mathbf{h}l} + \phi_{\mathbf{h}m})\} / \sum \{w^2(k_{ij}) + w^2(k_{lm})\} \right] \quad (1)$$

$w(k_{ij})$ are the square root of the inverse of the variance of the cosine invariants, as a measure of the internal consistency, together with the Karle factor and AF, the absolute figure of merit introduced by Germain *et al.*[18] Set number 5 stood out from all others especially in terms of index G. Phases calculated by the weighted numerical addition are just a rough estimate of the true phases, for the recycling process typical of tangent formula refinement has been suppressed, so the E map calculated with these phases revealed several spurious peaks. On the other hand the E map calculated

TABLE 5

Basic sets of reflections

Antiperiplanar conformer					Synclinal conformers				
h			E(**h**)	ϕ(**h**)	**h**			E(**h**)	ϕ(**h**)
9	3	−6	1·99	0	6	1	7	3·03	0
1	5	5	2·64	0	2	10	1	2·98	0
12	0	4	2·37	*a*	7	10	−12	2·70	0
3	7	3	2·66	*b*	2	−2	−11	3·56	*a*
10	4	−3	2·15	*c*	7	0	−13	3·31	*b*
					5	−8	−5	3·12	*c*
					4	2	4	2·94	*d*
					3	8	−5	2·80	*e*
					1	9	−2	2·57	*f*

TABLE 6

Results for the 32 starting sets in the phase determination procedure for the antiperiplanar conformer

Set	*a*	*b*	*c*	*R*	*AF*	10^2G
1	45°	45°	45°	27·7	1·339	3·48
2	135	45	45	27·9	1·337	1·61
3	225	45	45	27·6	1·348	3·55
4	315	45	45	27·8	1·344	1·64
5	45	135	45	27·8	1·349	7·06
6	135	135	45	27·8	1·347	2·31
7	225	135	45	28·0	1·338	5·67
8	315	135	45	27·8	1·342	1·42
9	45	45	135	27·7	1·347	3·09
10	135	45	135	27·6	1·347	2·37
11	225	45	135	27·8	1·345	2·04
12	315	45	135	27·6	1·345	2·18
13	45	135	135	27·9	1·339	2·53
14	135	135	135	27·7	1·349	0·98
15	225	135	135	29·1	1·323	2·77
16	315	135	135	27·7	1·343	2·11
17	45	45	225	27·9	1·342	2·57
18	135	45	225	27·6	1·344	2·90
19	225	45	225	27·8	1·343	1·18
20	315	45	225	27·7	1·349	3·52
21	45	135	225	27·8	1·347	1·63
22	135	135	225	27·7	1·346	2·70
23	225	135	225	29·7	1·306	2·13
24	315	135	225	27·8	1·349	4·73
25	45	45	315	27·6	1·348	2·39
26	135	45	315	27·7	1·348	2·35
27	225	45	315	27·6	1·339	2·19
28	315	45	315	27·7	1·342	2·54
29	45	135	315	27·7	1·346	1·30
30	135	135	315	28·1	1·348	5·30
31	225	135	315	27·7	1·347	2·23
32	315	135	315	27·9	1·345	4·67

TABLE 7

Antiperiplanar rotamer

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

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	509(2)	2070(3)	3718(3)	479(10)	406(10)	671(14)	−35(10)	87(10)	−30(11)
S	1183(2)	5746(2)	4298(3)	313(7)	349(8)	356(7)	20(8)	92(6)	1(8)
O(1)	371(4)	5522(7)	4552(7)	462(30)	429(30)	684(37)	44(26)	301(28)	35(29)
O(2)	1817(4)	4693(8)	5346(6)	493(32)	513(34)	412(29)	−78(28)	−19(23)	136(26)
O(3)	2929(5)	10537(7)	1241(7)	839(45)	270(27)	589(37)	47(29)	257(33)	106(25)
N	2591(5)	8166(8)	2827(8)	479(37)	308(31)	579(41)	128(29)	212(32)	138(30)
C(1)	3013(5)	5801(9)	3921(7)	282(29)	275(31)	328(22)	52(25)	89(25)	44(26)
C(2)	3108(5)	4496(9)	3187(9)	347(34)	320(34)	386(37)	32(30)	106(29)	−8(30)
C(3)	3777(5)	3527(10)	3669(9)	362(37)	341(37)	410(39)	62(29)	96(31)	−2(31)
C(4)	4305(5)	3819(10)	4813(10)	330(35)	335(37)	444(40)	51(30)	91(30)	90(32)
C(5)	4215(6)	5132(11)	5535(9)	357(35)	387(39)	354(35)	−17(30)	4(28)	−14(30)
C(6)	3559(5)	6108(9)	5037(8)	389(37)	301(34)	366(36)	−25(29)	95(30)	−47(29)
C(7)	2303(6)	6875(9)	3388(9)	345(36)	301(33)	377(35)	106(30)	121(29)	51(29)
C(8)	1504(5)	6595(10)	3343(8)	386(38)	337(36)	377(37)	115(30)	109(30)	55(30)
C(9)	750(7)	7309(14)	2410(11)	519(51)	629(62)	608(58)	267(47)	105(44)	157(50)
C(10)	1010(7)	3613(11)	3088(10)	600(53)	404(43)	578(52)	−63(40)	307(43)	−116(39)
C(11)	3431(7)	8338(12)	2535(11)	540(51)	453(48)	621(56)	86(41)	226(43)	210(43)
C(12)	3344(8)	9105(13)	1239(12)	801(65)	406(47)	693(63)	130(44)	377(54)	207(45)
C(13)	2129(8)	10381(12)	1528(11)	734(61)	382(46)	581(54)	159(41)	162(47)	105(39)
C(14)	2172(8)	9664(11)	2851(11)	784(66)	293(38)	667(60)	186(42)	248(51)	85(40)

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.*

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

	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*
H(1)	269(5)	430(10)	221(8)	44	H(10)	57(6)	395(11)	226(9)	57
H(2)	390(5)	262(11)	305(8)	50	H(11)	376(6)	735(11)	255(9)	56
H(3)	482(6)	317(10)	525(8)	47	H(12)	377(6)	934(12)	309(9)	70
H(4)	464(5)	539(10)	638(8)	48	H(13)	296(6)	841(11)	52(9)	59
H(5)	347(5)	697(10)	552(8)	50	H(14)	395(5)	923(10)	111(9)	48
H(6)	95(6)	807(11)	171(9)	56	H(15)	178(6)	1136(11)	141(9)	54
H(7)	53(6)	799(10)	290(8)	49	H(16)	169(5)	967(9)	87(8)	41
H(8)	29(6)	665(12)	177(10)	67	H(17)	250(6)	1039(12)	370(10)	73
H(9)	155(6)	333(11)	274(9)	64	H(18)	154(6)	955(11)	291(9)	58

Temperature factors are of the form $\exp(-B \sin^2 \theta/\lambda^2)$.

TABLE 8

Synclinal rotamers

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

Molecule 1

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	−2946(2)	1671(1)	8841(1)	1283(11)	413(5)	1188(10)	−186(6)	950(10)	−74(6)
S	−3425(1)	3774(1)	7753(1)	322(3)	427(4)	318(3)	−49(3)	200(3)	−57(3)
O(1)	−3911(3)	4961(2)	7795(2)	529(13)	405(11)	703(15)	22(10)	420(12)	17(10)
O(2)	−4469(3)	3332(3)	6835(2)	339(10)	931(18)	317(11)	−177(11)	165(9)	−209(11)
O(3)	3617(3)	259(2)	8735(2)	388(11)	537(13)	443(12)	85(9)	197(10)	86(10)
N	831(3)	2107(2)	8089(2)	317(11)	463(14)	272(11)	1(10)	163(10)	16(10)
C(1)	−1799(4)	2908(3)	6547(2)	287(12)	390(14)	269(13)	−29(10)	167(11)	−28(10)
C(2)	−2109(4)	1967(3)	6033(2)	333(14)	467(17)	335(14)	−86(12)	181(12)	−75(12)
C(3)	−3080(5)	2081(3)	5000(3)	404(16)	590(20)	350(15)	−121(14)	198(13)	−98(14)
C(4)	−3668(4)	3157(4)	4479(2)	520(15)	1487(29)	643(17)	−136(17)	318(14)	−28(18)
C(5)	−3309(5)	4114(3)	5001(3)	439(17)	561(20)	375(16)	−4(14)	233(14)	29(14)
C(6)	−2377(4)	3962(3)	6030(3)	411(15)	434(16)	349(15)	−12(12)	228(13)	−1(12)
C(7)	−738(4)	2795(3)	7660(2)	305(12)	337(13)	290(13)	−62(10)	162(11)	−32(10)
C(8)	−1290(4)	3373(3)	8201(2)	322(13)	419(15)	278(13)	−67(11)	164(11)	−73(11)
C(9)	−160(5)	3706(3)	9234(3)	421(17)	624(21)	347(16)	−161(15)	185(14)	−193(15)
C(10)	−3590(5)	3136(3)	8683(3)	513(18)	461(17)	450(18)	−142(14)	346(15)	−106(14)
C(11)	1862(4)	1995(3)	7662(5)	358(14)	455(16)	373(15)	2(12)	241(13)	26(12)
C(12)	2620(5)	760(3)	7728(3)	441(17)	499(18)	393(17)	23(14)	234(15)	15(14)
C(13)	2585(5)	340(3)	9128(3)	431(17)	548(20)	410(17)	−4(15)	192(14)	105(15)
C(14)	1814(4)	1548(3)	9114(2)	359(15)	613(20)	270(14)	−9(14)	133(12)	31(13)

Molecule 2

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl′	−3620(1)	2343(1)	1447(1)	541(5)	391(4)	926(8)	−136(4)	412(5)	−108(5)
S′	−2319(1)	4354(1)	1485(1)	334(3)	373(4)	323(3)	−54(3)	190(3)	−28(3)
O(1)′	−3005(3)	5556(2)	1258(2)	539(13)	381(11)	487(13)	−62(9)	251(11)	28(9)
O(2)′	−1684(3)	3812(2)	923(2)	396(11)	677(14)	330(10)	−62(10)	226(9)	−79(10)
O(3)′	2497(4)	960(3)	5696(2)	641(16)	817(18)	535(15)	30(14)	354(13)	221(13)
N′	1177(3)	2666(3)	4124(2)	334(12)	520(15)	323(12)	−78(10)	200(10)	−3(11)
C(1)′	1256(4)	2555(3)	2665(2)	308(13)	387(14)	293(13)	−61(11)	175(11)	−52(11)
C(2)′	1357(5)	1411(3)	2595(3)	678(22)	411(17)	514(20)	−92(16)	400(18)	−106(14)
C(3)′	2208(7)	841(4)	2179(4)	996(33)	489(21)	712(27)	6(21)	575(26)	−141(19)
C(4)′	2966(6)	1404(4)	1857(3)	609(22)	736(26)	521(21)	32(19)	376(19)	−94(19)
C(5)′	2858(5)	2543(4)	1929(3)	406(17)	751(24)	430(18)	−106(16)	286(15)	−110(16)
C(6)′	1996(4)	3124(3)	2327(3)	347(14)	514(17)	370(15)	−119(12)	223(12)	−89(13)
C(7)′	433(4)	3131(3)	3167(2)	315(13)	364(14)	299(13)	−125(11)	188(11)	−74(11)
C(8)′	−893(4)	4033(3)	2764(2)	378(14)	364(13)	314(13)	−94(11)	218(12)	−79(11)
C(9)′	−1418(5)	4789(3)	3352(3)	590(20)	440(17)	448(18)	−33(15)	339(17)	−107(14)
C(10)′	−4115(4)	3811(3)	1201(3)	339(14)	430(16)	485(18)	−60(12)	223(14)	−69(13)
C(11)′	3002(4)	2265(4)	4822(3)	350(15)	778(24)	326(16)	−159(15)	133(13)	−18(15)
C(12)′	3439(6)	1082(5)	5269(4)	474(20)	879(31)	596(24)	102(20)	280(19)	232(22)
C(13)′	738(6)	1308(4)	4971(3)	615(22)	625(23)	606(22)	−93(18)	437(20)	59(18)
C(14)′	219(5)	2521(3)	4558(3)	505(18)	578(20)	475(19)	−45(15)	374(16)	5(15)

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.*

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

Molecule 1

	x	y	z	B
H(1)	−171(4)	118(3)	640(2)	48
H(2)	−331(6)	131(4)	463(3)	81
H(3)	−434(5)	328(4)	371(3)	91
H(4)	−394(5)	497(3)	456(3)	80
H(5)	−211(4)	461(3)	640(2)	48
H(6)	95(5)	369(3)	940(3)	61
H(7)	−57(5)	446(3)	928(3)	65
H(8)	6(5)	324(3)	978(3)	61
H(9)	−288(5)	342(3)	934(3)	66
H(10)	−476(5)	327(3)	848(3)	58
H(11)	279(5)	242(3)	802(3)	94
H(12)	113(4)	234(3)	697(3)	50
H(13)	333(6)	67(4)	748(4)	81
H(14)	163(6)	28(4)	723(3)	87
H(15)	345(4)	−8(3)	989(3)	55
H(16)	169(4)	−6(3)	876(3)	64
H(17)	265(5)	185(3)	954(3)	70
H(18)	96(5)	158(3)	930(3)	57

Molecule 2

	x	y	z	B
H(1)′	78(5)	99(4)	289(3)	78
H(2)′	229(7)	−3(5)	204(4)	98
H(3)′	360(6)	98(5)	157(4)	97
H(4)′	342(5)	299(3)	172(3)	67
H(5)′	195(4)	389(3)	242(3)	46
H(6)′	−182(5)	562(3)	309(3)	50
H(7)′	−45(5)	473(3)	399(3)	69
H(8)′	−222(6)	453(4)	344(4)	80
H(9)′	−511(5)	389(3)	45(3)	80
H(10)′	−450(5)	409(3)	161(3)	58
H(11)′	342(5)	282(3)	536(3)	71
H(12)′	356(4)	232(3)	443(3)	57
H(13)′	479(6)	76(4)	591(3)	90
H(14)′	325(6)	54(4)	474(4)	89
H(15)′	24(5)	79(3)	432(3)	66
H(16)′	15(6)	118(4)	529(3)	85
H(17)′	41(4)	306(3)	505(3)	61
H(18)′	−101(4)	278(3)	406(3)	55

Temperature factors are of the form exp $(-B \sin^2\theta/\lambda^2)$.

with the phases of the corresponding set refined *via* the tangent formula revealed the entire structure with no spurious peaks. As the numerical addition routine is *ca.* 50 times faster than the tangent formula, one can save computer time by using the tangent formula to refine only the sets with highest figure of merit G calculated with the numerical addition program. A structure factor calculation based on the co-ordinates derived from the E map, with $\bar{B} = 4{\cdot}3$ Å^2 for all atoms gave R 0·24. Several cycles of block-diagonal least-squares reduced R to 0·083. A difference synthesis was then computed which revealed peaks near the positions where the hydrogen atoms were expected to occur. All the atom parameters were then refined (the heavy atoms anisotropically and the hydrogen atoms isotropically). The final value of R was 0·062. The final positional and thermal parameters together with their standard deviations are given in Table 7.

Synclinal β-*Chloromethylsulphonyl*-β-*methyl*-α-*morpholinostyrenes* (5) *and* (5′).—Crystals are prisms elongated along [001]. Cell parameters and space group were determined as before and lattice parameters refined from 19 $(\theta,\chi,\phi)_{hkl}$ measurements.

Crystal Data.—$C_{14}H_{18}ClNO_3S$, $M = 315{\cdot}8$. Triclinic, $a = 9{\cdot}65(1)$, $b = 12{\cdot}18(1)$, $c = 16{\cdot}08(1)$ Å, $\alpha = 91{\cdot}0(2)$, $\beta = 122{\cdot}9(2)$, $\gamma = 78{\cdot}6(2)°$, $Z = 4$, $D_c = 1{\cdot}36$ g cm^{-3}, $U = 1546{\cdot}9$ Å^3, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 34·5 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Intensity data were collected similarly and of 5590 independent reflections 579 were not used in the crystal analysis. The dimensions of the crystal roughly in the x, y, z directions were 0·4, 0·4, and 0·5 mm. Absorption effects were neglected.

Structure Analysis and Refinement.—499 Reflections with $|E| \geqslant 1{\cdot}70$ were used to solve the structure by direct methods. The most consistent set of signs derived from the basic set reported in Table 5 gave $+,-,-,-,+,-$ for the signs of the six symbolic reflections and was used to compute an E map which revealed the whole structure. A structure-factor calculation based on the co-ordinates derived from the E map with $B = 4{\cdot}6$ Å^2 for all atoms gave R 0·273. Refinement was carried out by means of cycles of block-diagonal least-squares at first isotropically and then anisotropically until R was 0·072. A ΔF synthesis then revealed significant peaks, all interpreted as hydrogen atoms. All the atom parameters were then refined (heavy atoms anisotropically and hydrogen atoms isotropically). The final value of R was 0·057. The final positional and thermal parameters together with their standard deviations are reported in Table 8.

The atomic scattering factors used for both crystal analyses are those of Cromer and Mann [20] for Cl, S, O, N, and C and those of Stewart *et al.*[21] for H.

For both compounds the observed and calculated structure factors are listed in Supplementary Publication No. SUP 21296 (19 pp., 1 microfiche).*

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue, for details of Supplementary Publications.

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