

Folded Conformations. Part V.¹ Crystal and Molecular Structure of Ethyl *N*-Methyl-*N*-(*p*-tolylsulphonylmethyl)carbamate at -160°C

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The crystal and molecular structure at -160°C of the title compound (monoclinic, $a = 9.160 \pm 0.001$, $b = 7.970 \pm 0.002$, $c = 19.257 \pm 0.004$ Å, $\beta = 106.01 \pm 0.02^\circ$, space group $P2_1/c$, $Z = 4$) has been determined by direct methods and refined by anisotropic least-squares techniques to R 0.047 for 6805 independent reflections (diffractometer data). The molecule has a folded conformation; this corroborates evidence, from earlier n.m.r. and u.v. spectral studies for this and closely related compounds in solution. A number of bond lengths differ significantly from expected values: C-S (phenyl-sulphonyl) 1.751, C-S (methylene-sulphonyl) 1.806, and N-C (carbamate) 1.371 Å.

In previous studies^{2,3} it was established that alkyl (I) and aryl (II) *N*-methyl-*N*-(arylsulphonylmethyl)carbamates in solution adopt favoured folded conformations



(I) a; Ar = *p*-MeC₆H₄, X = Et

b; Ar = *p*-MeC₆H₄, X = Me

(II) Ar = *p*-NO₂-C₆H₄, X = *p*-Me₂NC₆H₄

in which the ester alkyl or aryl moiety is positioned above (or below) the plane of the aromatic ring (Ar) attached to the sulphonyl group. The major evidence is based on the following observations: (i) intramolecular shielding effects in the n.m.r. spectra of (Ia) and (Ib) indicating that the ester alkyl group is preferentially situated in the region of enhanced diamagnetic susceptibility perpendicular to the aromatic ring.³ For (Ib) the thermodynamic parameters⁴ of stabilization of the folded form were found to be $\Delta G^\circ = -1.0$ kcal mol⁻¹, $\Delta H^\circ = -3.4$ kcal mol⁻¹ and $\Delta S^\circ = -8$ cal mol⁻¹ K⁻¹ (25 °C); (ii) in the aryl carbamate (II) intramolecular shielding of the 2,6-protons of the ester aromatic ring is observed, depending on the magnitude of the ring current of the other aromatic ring in the molecule;² (iii) the u.v. spectrum of (II) exhibits a long wavelength absorption maximum (at 440 nm, ϵ 30 l mol⁻¹ cm⁻¹) which obeys

Beer's Law and is attributable to intramolecular charge-transfer interaction between the aromatic π -systems.² It has been inferred that an explanation for these conformational preferences is to be found in (i) the minimized intramolecular dipolar interactions involving the polarized S-O bonds and (ii) in the favoured position of the aryl ring (Ar) with the C-1 $2p$ orbital staggered between the sulphonyl oxygen atoms.³

N.m.r. spectral evidence has also indicated a folded conformation in solution for the cyclic dipeptide *cyclo*-glycyl-L-tyrosyl⁵ and the folding of the molecule was confirmed by X-ray crystallography.⁶ In contrast, 2-methyl-3-(*N*-methylanilinomethyl)-1,4-naphthoquinone, which is folded in solution,⁷ adopts a completely different conformation in the solid state.⁸

In view of these results it appeared worthwhile to determine the molecular geometry of (Ia) by X-ray diffraction and to ascertain whether the folding tendency is retained in the solid state.

EXPERIMENTAL

The compound was prepared by the method described in ref. 3. Suitable crystals were obtained from aqueous methanol by slow cooling. For the determination of the cell dimensions, zero-layer Weissenberg photographs calibrated with NaCl reflection spots were taken. During the

¹ Part IV, R. van Est-Stammer and J. B. F. N. Engberts, *Canad. J. Chem.*, 1973, **5**, 1187.

² R. van Est-Stammer and J. B. F. N. Engberts, *Rec. Trav. chim.*, 1972, **91**, 1298.

³ S. van der Werf and J. B. F. N. Engberts, *Rev. Trav. chim.*, 1970, **89**, 423.

⁴ R. van Est-Stammer and J. B. F. N. Engberts, Dissertation, University of Groningen, 1973.

⁵ K. D. Kopple and D. H. Marr, *J. Amer. Chem. Soc.*, 1967, **89**, 6193.

⁶ L. E. Webb and Chi-Fan Lin, *J. Amer. Chem. Soc.*, 1971, **93**, 3818.

⁷ R. Carruthers, F. M. Dean, L. E. Houghton, and A. Ledwith, *Chem. Comm.*, 1967, 1206.

⁸ C. K. Prout and E. E. Castellano, *J. Chem. Soc. (A)*, 1970, 2775.

exposure the crystal was cooled to -160°C by a stream of cold nitrogen gas obtained by evaporation of liquid nitrogen. Cell dimensions were calculated by a least-squares program from the $\sin^2 \theta/\lambda^2$ values of 100 $h\bar{k}0$ and 103 $0kl$ reflections [$\lambda(\text{Cu}\alpha_1K) = 1.54050$, $\lambda(\text{Cu}\alpha_2K) = 1.54434$, $a(\text{NaCl}) = 5.64006 \text{ \AA}$ at 21°C].

Crystal Data (at -160°C).— $\text{C}_{12}\text{H}_{15}\text{NO}_4\text{S}$, $M = 269.3$. Monoclinic prismatic, $a = 9.160 \pm 0.002$, $b = 7.970 \pm 0.001$, $c = 19.257 \pm 0.004 \text{ \AA}$, $\beta = 106.01 \pm 0.02^\circ$, $U = 1351.3 \text{ \AA}^3$, $D_m = 1.26$ (20°C), $Z = 4$, $D_c = 1.32$. Space group $P2_1/c$ (C_2^h , No. 14). Mo- K_α radiation, $\lambda = 0.71069 \text{ \AA}$, μ (Mo- K_α) = 2.45 cm^{-1} .

Intensities were collected on a three-circle automatic Nonius diffractometer with zirconium-filtered molybdenum radiation by the θ - 2θ integrating scan technique. The crystal was again cooled to -160°C by a stream of cold nitrogen gas by use of the cooling system described in ref. 9. Owing to difficulties with the cooling system, it was necessary to use two crystals, of dimensions $0.5 \times 0.4 \times 0.3 \text{ mm}$ and $0.5 \times 0.5 \times 0.4 \text{ mm}$. All independent reflections with $\theta < 38^\circ$ were measured. The intensities of the strongest reflections were reduced by attenuation filters in order to keep the count rate within the linear range of the scintillation equipment. Every 2 h a reference reflection was measured accurately so that corrections for intensity variations in the primary beam and for possible deterioration of the specimen could be made; there were, however, no persistent changes in the reference intensities, the maximum fluctuation being ca. 8%.

Corrections for the Lorentz and polarization effects were applied. No correction for absorption was made; owing to the small value of the absorption coefficient and the small variation in the path length through the crystal, the correction was not expected to be significant. Reflections with net negative intensity were rejected; for the other reflections the weight w_c was obtained as $w_c = [\sigma_c(F)]^2$, where $\sigma_c(F)$ is the standard deviation in F from counting statistics, taking filter-factor errors into account. The data sets from the two crystals were merged; the mean ratio was calculated from the F values of 106 common reflections, weighted by w_c (merging $R' 0.031$). 6805 independent reflections were available for the structure determination.

The overall isotropic temperature factor ($B = 1.334 \text{ \AA}^2$) and F_o scale factors were calculated by minimizing $\sum_h (E_h^2 - 1)^2$. From the available E_h values, the structure was solved straightforwardly by a fully automatic symbolic addition program.¹⁰ All significant maxima in a Fourier synthesis computed from the signed E values were located by means of a peak-search program.¹⁰ On the assumption of anisotropic thermal motion, the atomic parameters of the non-hydrogen atoms were refined by a least-squares program,¹⁰ working with a full normal matrix. The quantity minimized was $\sum w(F_o - K^{-1}F_c)^2$, where K is the F_o scale factor. Scattering factors for nitrogen and sulphur (with the real part of the anomalous dispersion correction applied) were taken from ref. 11, and those for carbon, hydrogen, and oxygen from ref. 12. 1546 Reflections with intensity $< 3\sigma(I)$ were assigned 'less than' status, *i.e.* were not included in least-squares procedures for current $|F_c| < K|F_o|$. The weight $w = [w_c^{-1} + p_1 \cdot K \cdot |F_o| +$

$p_2 \cdot K^2 \cdot F_o^2]^{-1}$ was used in the refinement procedure. Values of p_1 and p_2 were varied as refinement progressed, final values being $p_1 = 0.0302$, $p_2 = 0.0053$, chosen to minimize the variation of $\langle w \cdot (K \cdot F_o - F_c)^2 \rangle$ with F_o .

After refinement of the heavy atoms, all hydrogen atoms, including those in the three methyl groups were located in a difference-Fourier synthesis. Some rotational disorder of the C(7) methyl group was apparent in the Fourier synthesis; this was simulated by a group of six hydrogen atoms with alternate occupancies of 0.6 and 0.4. Initially the isotropic temperature factors of all the hydrogen atoms together with the space parameters of all but the C(7) methyl hydrogens

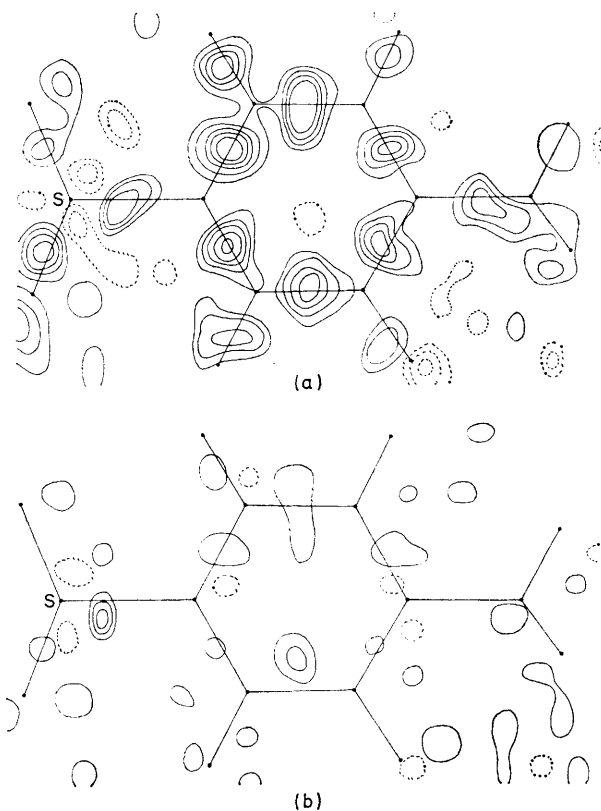


FIGURE 1 (a) Difference-Fourier synthesis in the plane of the phenyl ring after refinement with the full data. Contour spacing is 0.1 e\AA^{-3} ; positive contours (full lines) start at 0.1 e\AA^{-3} , negative contours (dashed) at -0.2 e\AA^{-3} . (b) The same synthesis but with contributions only from reflections with $\sin\theta/\lambda > 0.55$

were included in the refinement. Owing to limitations on computer core storage, it was necessary to refine the space and thermal parameters in alternate cycles. The scale factor and the isotropic extinction factor,¹³ were refined in the same block as the thermal parameters. It was found that all the refined C-H bond lengths (0.9 – 1.0 \AA) were significantly shorter than the accepted value (1.08 \AA); this effect has been frequently commented upon.¹⁴ All C-H bond lengths were therefore fixed at 1.08 \AA while maintaining the angular relationships between the bonds. Refinement was considered complete when the maximum ratio of

⁹ F. van Bolhuis, *J. Appl. Cryst.*, 1971, **4**, 263.

¹⁰ J. M. Stewart, F. A. Kundell, and J. C. Baldwin, *X-Ray System of Crystallographic Programs*, 1970.

¹¹ 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

¹² S. Harkema, Dissertation, Technische Hogeschool, Twente, 1971.

¹³ A. C. Larson, *Acta Cryst.*, 1967, **23**, 644.

¹⁴ G. M. Brown, *Acta Cryst.*, 1969, **B 25**, 1338.

shift to σ was <0.1 . At this stage the conventional R was 0.047 and R' 0.054.

A second difference Fourier synthesis, based on all the atoms, was computed; the estimated standard deviations of the electron density was $\sigma(\rho) = 0.1 \text{ e}\text{\AA}^{-3}$. Significant maxima (up to $0.6 \text{ e}\text{\AA}^{-3}$) appeared at the midpoints of all the bonds. Figure 1(a) shows a section of the synthesis in the plane of the aromatic ring (the sulphonyl and methyl groups in the section do not lie exactly on it; see later Discussion). Figure 1(b) shows the same section [$\sigma(\rho) = 0.07 \text{ e}\text{\AA}^{-3}$] when reflections with $\sin \theta/\lambda$ less than an arbitrary limit of 0.55 \AA^{-1} ($\theta \approx 23^\circ$) are excluded. In the absence of programming facilities to handle 'bond scattering factors' it was decided to continue the refinement with only those

($\leq 4\sigma$) were rather greater than the differences in the thermal parameters ($<1\sigma$), the reverse of what might have been expected. The difference-Fourier syntheses were re-computed from the new parameters. Except for a trough of $-0.5 \text{ e}\text{\AA}^{-3}$ which appeared at the location of the sulphur atom in a synthesis to which all reflections contributed, the differences between these and the earlier syntheses were only slight. Nevertheless, it is concluded that the refinement based only on the high-angle reflections produces a significantly better fit of the parameters to the data; the parameters so derived are shown in Table 1.

A rigid-body analysis^{15,16} of the thermal motion of the molecule was performed: it was clear, however, that a rigid-body model for the whole molecule is inadequate, although

TABLE 1

Fractional atomic co-ordinates and thermal parameters* with standard deviations in parentheses. Hydrogen atoms are numbered according to the carbon atoms to which they are attached

	x/a	y/b	z/c	$10^4 U_{11}$	$10^4 U_{22}$	$10^4 U_{33}$	$10^4 U_{12}$	$10^4 U_{13}$	$10^4 U_{23}$
S	0.48209(3)	0.07641(4)	0.34042(2)	1399(9)†	1710(9)†	1684(9)†	361(9)†	682(7)†	370(9)†
O(1)	0.56323(15)	-0.04040(18)	0.39478(7)	236(5)	264(5)	231(5)	131(4)	69(4)	91(4)
O(2)	0.55927(13)	0.14619(16)	0.29065(6)	178(4)	258(5)	223(4)	-10(3)	121(3)	26(4)
O(3)	-0.00385(15)	0.23374(21)	0.20824(9)	199(5)	344(6)	281(5)	74(4)	36(4)	99(5)
O(4)	0.08121(12)	0.10852(13)	0.31782(6)	155(3)	202(4)	200(4)	34(3)	76(3)	12(3)
N	0.21350(13)	0.07734(16)	0.23685(6)	170(4)	201(4)	163(4)	14(3)	64(3)	10(4)
C(1)	0.41268(13)	0.24227(15)	0.38177(6)	157(4)	157(4)	145(4)	21(3)	46(3)	26(3)
C(2)	0.37456(16)	0.39331(16)	0.34458(7)	230(5)	157(5)	193(5)	7(4)	69(4)	34(4)
C(3)	0.30925(21)	0.51992(18)	0.37559(9)	307(7)	146(5)	251(6)	37(5)	64(5)	9(4)
C(4)	0.28329(18)	0.49892(19)	0.44326(9)	238(6)	211(6)	211(5)	47(4)	26(4)	-47(4)
C(5)	0.32408(19)	0.34693(22)	0.47983(7)	264(6)	271(6)	164(5)	73(5)	59(4)	-7(4)
C(6)	0.38724(18)	0.21768(19)	0.44912(7)	245(5)	225(5)	151(4)	68(4)	72(4)	33(4)
C(7)	0.21156(27)	0.63678(28)	0.47585(12)	375(9)	307(8)	331(8)	120(7)	52(7)	-124(7)
C(8)	0.31461(15)	-0.03071(16)	0.28729(7)	173(4)	131(4)	225(5)	17(3)	97(4)	8(3)
C(9)	0.24168(19)	0.11213(26)	0.16726(9)	252(6)	382(8)	183(5)	-19(5)	86(5)	16(5)
C(10)	0.08803(15)	0.14697(16)	0.25115(7)	145(4)	171(5)	188(5)	4(3)	41(3)	7(4)
C(11)	-0.05676(19)	0.15457(26)	0.33516(11)	197(5)	340(7)	309(7)	106(5)	136(5)	50(6)
C(12)	-0.04788(19)	0.08079(28)	0.40787(9)	229(5)	373(8)	267(6)	26(6)	133(5)	-15(6)

* The temperature factor has the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.
† Thermal parameters for S $\times 10^5$.

	$10^3 x/a$	$10^3 y/b$	$10^3 z/c$	$10^3 U_{100}$		$10^3 x/a$	$10^3 y/b$	$10^3 z/c$	$10^3 U_{100}$
H(20)	392(2)	411(2)	292(1)	32(6)	H(81)	261(2)	-84(2)	326(1)	20(5)
H(30)	288(2)	639(2)	348(1)	48(8)	H(82)	361(2)	-127(2)	260(1)	34(6)
H(50)	298(2)	337(3)	531(1)	34(6)	H(91)	135(3)	108(2)	125(1)	48(7)
H(60)	407(2)	99(2)	477(1)	32(6)	H(92)	286(3)	237(3)	165(1)	52(7)
H(71)	150	732	439	76	H(93)	306(3)	11(3)	153(1)	65(6)
H(72)	90	650	456	76	H(111)	-161(3)	116(3)	297(1)	50(8)
H(73)	128	599	503	76	H(112)	-67(2)	289(3)	336(1)	59(9)
H(74)	227	631	533	76	H(121)	46(3)	134(3)	449(1)	51(9)
H(75)	287	713	517	76	H(122)	-151(3)	102(2)	423(1)	51(9)
H(76)	249	763	470	76	H(123)	-28(3)	-52(3)	404(1)	51(9)

reflections for which $\sin \theta/\lambda > 0.55 \text{ \AA}^{-1}$ since it is for the high-angle reflections that the scattering power of the bond electrons is proportionately less. The scale and isotropic extinction factors were held invariant, the procedure for the weighting scheme and the treatment of hydrogen atoms were the same as those previously adopted. There were 4140 reflections with non-zero weight and at convergence R was 0.047 and R' 0.040. The statistically significant guide to the goodness-of-fit of the parameters to the data is the standard error of fit, $\{[\sum_w(\Delta^2(F))]/(N_o - N_p)\}^{1/2}$. The values obtained in the refinement calculations with the full- and high-angle data were 0.44 and 0.32 respectively; the standard deviations of the atomic parameters obtained in the two calculations, however, did not differ significantly ($<10\%$). Comparison of the two sets of atomic parameters revealed that the relative differences in the space parameters

it was possible to analyse the motion of the aromatic ring alone in this way. The libration corrections¹⁷ for the ring atoms varied from 0 to 2σ ; the corrections were not applied.

The estimated standard deviations in the atomic parameters calculated from the diagonal elements of the inverse normal matrix were multiplied by 1.5 to allow for the effect of varying the weighting scheme parameters.

Observed structure amplitudes and structure factors calculated from the atomic parameters in Table 1 are listed in Supplementary Publication No. SUP 20792 (24 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Interatomic distances and interbond angles with standard deviations are listed in Table 2. The standard

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

¹⁵ D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

¹⁶ G. S. Pawley, *Acta Cryst.*, 1963, **16**, 1204.

¹⁷ D. W. J. Cruickshank, *Acta Cryst.*, 1961, **14**, 896.

deviations were calculated assuming an isotropic variance for each atomic position; covariances were ignored. Figure 2 shows a projection of the molecule on the plane

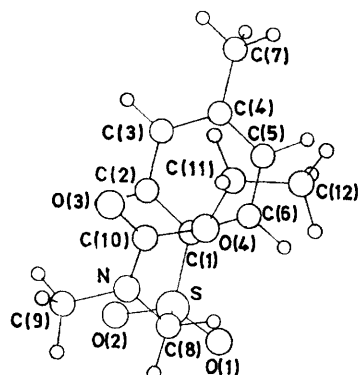


FIGURE 2 Projections of the molecule on the plane of the phenyl ring showing the atom numbering system used

of the aromatic ring and Figure 3 a stereoscopic projection of the contents of the unit cell on the *ac* plane.

The molecule has a folded conformation in which the oxygen atom O(4) lies over the carbon atom C(1) of the aromatic ring at a distance of 3.132(2) Å, whereas the ester methylene group lies directly over the centre of the

be expected, as are indeed observed.³ The conformation of the tolylsulphonyl group is such that the C(1) p_π orbital

TABLE 2

Distances (Å) and angles (deg.) within the molecule

(a) Distances			
S-O(1)	1.444(1)	C(5)-C(6)	1.391(2)
S-O(2)	1.450(1)	C(6)-C(1)	1.393(2)
S-C(8)	1.806(1)	C(8)-N	1.431(2)
S-C(1)	1.751(1)	C(9)-N	1.460(2)
C(1)-C(2)	1.395(2)	C(10)-N	1.371(2)
C(2)-C(3)	1.389(2)	C(10)-O(3)	1.219(2)
C(3)-C(4)	1.398(3)	C(10)-O(4)	1.338(2)
C(4)-C(5)	1.399(2)	O(4)-C(11)	1.441(2)
C(4)-C(7)	1.503(3)	C(11)-C(12)	1.500(3)
(b) Angles			
O(1)-S-O(2)	118.63(8)	C(10)-O(4)-C(11)	116.11(13)
O(1)-S-C(1)	109.63(7)	O(4)-C(11)-C(12)	106.93(16)
O(1)-S-C(8)	107.02(8)	S-C(1)-C(6)	119.27(10)
C(1)-S-C(8)	104.85(6)	S-C(1)-C(2)	119.48(10)
C(1)-S-O(2)	108.39(7)	C(1)-C(2)-C(3)	118.86(14)
C(8)-S-O(2)	107.44(7)	C(2)-C(3)-C(4)	121.20(17)
S-C(8)-N	112.94(10)	C(3)-C(4)-C(7)	120.53(17)
C(8)-N-C(9)	119.50(13)	C(5)-C(4)-C(7)	120.62(17)
C(8)-N-C(10)	121.93(13)	C(3)-C(4)-C(5)	118.84(16)
C(10)-N-C(9)	118.55(14)	C(4)-C(5)-C(6)	120.79(16)
N-C(10)-O(3)	123.63(15)	C(5)-C(6)-C(1)	119.18(15)
O(3)-C(10)-O(4)	125.04(15)	C(2)-C(1)-C(6)	121.12(13)

lies approximately in the plane through C(1)-S and bisecting O-S-O. Significant overlap of the filled p_π

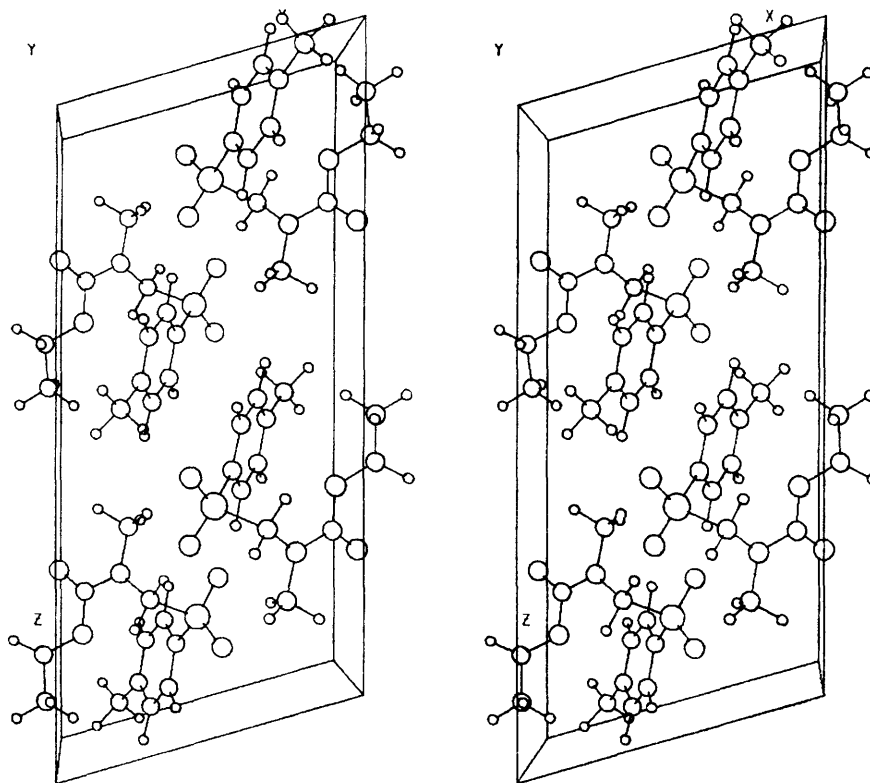


FIGURE 3 Stereoscopic projection of the unit cell contents on to (010)

ring. If molecules with a similar conformation are present in solution then diamagnetic shielding effects by the aromatic ring on the ester methylene group would

orbital, and also of the S-C(8) σ orbital, with the sulphur $d_{x^2-y^2}$ and d_{z^2} orbitals is thus possible (the *z* axis is defined as the bisector of O-S-O). This type of system has

been discussed,^{18,19} and it was concluded that in systems of the type $R^1R^2SO_2$ where R^1 has a filled p_π orbital parallel to the R^2-S σ orbital, the R^1-S π -bond-order increases with increasing electronegativity of R^2 . The C(1)-S C(8)-S length [1.806(1) Å], rather longer than expected. In *N*-methyl-2-methylsulphonyl-2-phenylsulphonyl-vinylideneamine²⁰ S-C(phenyl) is the same [1.772(9) Å], within the stated error, as S-C(methyl) [1.761(12) Å]. Other observed lengths are: S-C(phenyl) 1.766(3) in propenyl *p*-tolyl sulphone²¹ and 1.779(5) and 1.784(4) in [1]benzothieno[2,3-*b*][1]benzothiophen SSS'S'-tetroxide;²² and for S-C(methylene or methyl) 1.756(5) and 1.763(4) in 4-methylthiomorpholine 1,1-dioxide²³ and 1.765(5) Å in dimethyl sulphone.²⁴

The mean C-C(aromatic) bond length is 1.393 Å, but there are significant systematic variations of the bond lengths and angles in the ring which are compatible with the *mm*2 point-symmetry conferred by the immediate substituents; there is in fact a slight tendency towards quinonoid geometry which is consistent with the increased π -bond-order of S-C(1). The sulphur and the carbon atom C(7) lie 0.112 and 0.022 Å, respectively, out of the ring plane.

The enhanced electronegativity of C(8) can be attributed to the inductive effect of the carbamate group. This group [N, C(8)-(10), O(3), and O(4)] is essentially planar (Figure 4); the nitrogen atom lies 0.010 Å from the plane of the three carbons attached to it and this plane is inclined at 2.9° to the plane of N, C(10), O(3), and O(4). Nonplanar distortions of amide groups are usually rather greater than this.²⁵ The amide bond N-C(10) [1.371(2) Å] is longer than is usually observed in amides and carbamates, *e.g.* 1.342(4) in ethyl carbamate²⁵ (at -105 °C), 1.352(6) in ethyl *N*-phenylcarbamate,²⁶ and 1.343(4) in 6-diethylcarbamoylcyclohex-3-enecarboxylic acid;²⁷ otherwise the dimensions of the carbamate moiety agree fairly well with those in ethyl carbamate. The long N-C(10) bond, and also the rather short N-C(8) bond, can be attributed to the electron-withdrawing inductive effect of the sulphonyl group.

The high electronegativity of C(8) induced by both the sulphonyl and the carbamate group is also consistent with a rather close intermolecular approach (2.27 Å) of

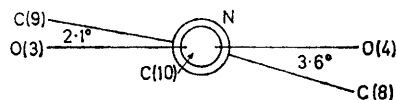


FIGURE 4 Out-of-plane distortions in the carbamate group

O(2) to H(82) in the molecule at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$. There is also a short intermolecular contact O(1) \cdots H(60) at $(1-x, -y, 1-z)$ of 2.45 Å. However, these values refer to the hydrogen atoms fixed in calculated positions 1.08 Å from their parent carbons. The corresponding values for the refined hydrogen atom co-ordinates were 2.42 and 2.48 Å respectively.

It is clearly of interest to ascertain whether inter- or intra-molecular interactions are principally responsible for the observed conformation in the crystal. The fact that a similar conformation is favoured in solution suggests the latter, since the occurrence of strongly folded conformations in solution with lifetimes sufficiently long to be observable by the n.m.r. method is not normally expected in the absence of intramolecular interactions. It is reasonable to suppose that in the sulphonylmethylcarbamate moiety, the barrier to rotation is lowest about the S-C(8) bond. Rotation about this bond would bring together the negatively charged carbonyl and sulphonyl regions in the molecule and thereby induce unfavourable interactions. It is, however, impossible in a system of this complexity, to pinpoint a specific interaction as the major cause of the observed structure.

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