The Reaction of 2,2′-Thiodiethanol with Chloramine-T (Sodium *N*-Chlorotoluene-*p*-sulphonamide): Crystal and Molecular Structures of 2,2′-(*p*-Tolylsulphonylimino-λ^4-sulphanyl)diethanol Monohydrate and 2,2′-Sulphinyldiethanol

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Chloramine-T, sodium *N*-chlorotoluene-*p*-sulphonamide reacts with 2,2′-thiodiethanol in weakly acidic methanol to yield 2,2′-(*p*-tolylsulphonylimino-λ^4-sulphanyl)diethanol monohydrate, $MeC_6H_4SO_2NS(CH_2CH_2OH)_2\cdot H_2O$ (**1**) and 2,2′-sulphinyldiethanol, $OS(CH_2CH_2OH)_2$ (**2**), in yields of 23 and 36%, respectively. Crystals of (**1**) are monoclinic, space group $P2_1/c$, with a = 7.497(1), b = 16.291(2), c = 11.843(2) Å, β = 92.52(1)°, and Z = 4. The structure was refined from diffractometer data to an R value of 0.033. The structure consists of a hydrogen-bonded array of $MeC_6H_4SO_2NS(CH_2CH_2OH)_2$ molecules and of water molecules, in which each molecule participates in three hydrogen bonds. Within the $MeC_6H_4SO_2NS(CH_2CH_2OH)_2$ molecules the S(VI)–N and N–S(IV) bond lengths are 1.602(2) and 1.629(2) Å, and there is a short intramolecular O···S contact distance of 2.931 Å. The structural data indicate a highly polarised, ylidic, molecule. Crystals of (**2**) are monoclinic, space group $P2_1/n$ with a = 11.057(4), b = 4.837(2), c = 12.332(4) Å, β = 103.61(3)°, and Z = 4. The crystals are always twinned, but by careful photographic and diffractometer studies a complete structural analysis was possible; R = 0.044 from 1 056 diffractometer data. The structure contains $OS(CH_2CH_2OH)_2$ molecules which are not maximally extended but which are linked by O–H···O hydrogen bonds to form centrosymmetric dimers, further linked into infinite spirals. The sulphur atom in (**2**) is pyramidal [O–$\hat{S}$–C, 105.8(1) and 105.9(1)°, C–$\hat{S}$–C, 96.7(1)°] with an S–O distance of 1.514(3) Å and S–C distances of 1.789(3) and 1.791(3) Å.

The sodium salt of chloramine-T reacts with a wide range of sulphides R_2S to provide sulphilimines, $MeC_6H_4SO_2N{=}SR_2$.[1,2] However, many years ago Mann reported[3] that the dihydroxy derivative 2,2′-thiodiethanol, $S(CH_2CH_2OH)_2$ gave, on treatment with chloramine-T, a compound (**1**) the analytical data of which supported the composition $MeC_6H_4SO_2NS(CH_2CH_2OH)_2\cdot H_2O$ rather than the expected $MeC_6H_4SO_2NS(CH_2CH_2OH)_2$. Since compound (**1**) could not be dehydrated by chemical or physical means,[3] a plausible formulation for (**1**) is a hydrogen-bonded adduct of $MeC_6H_4SO_2NH_2$ and the sulphoxide $OS(CH_2CH_2OH)_2$, rather analogous to the adducts formed between $MeC_6H_4SO_2NH_2$ and phosphine oxides:[4,5] against this must be set the fact that (**1**) could not be obtained by combination of $MeC_6H_4SO_2NH_2$ and $OS(CH_2CH_2OH)_2$, either in solution or in a melt.[3] In contrast to its reaction with chloramine-T, the sulphide $S(CH_2CH_2OH)_2$ was reported[3] to react with chloramine-B, $C_6H_5SO_2NCl^-Na^+$ to yield only the sulphoxide $OS(CH_2CH_2OH)_2$, (**2**) rather than a sulphilimine.

We have re-investigated the reaction of $S(CH_2CH_2OH)_2$ with chloramine-T, from which practical yields of both (**1**) and (**2**) can, in fact, be obtained: we have further characterised (**1**) and (**2**), both in solution by n.m.r. spectroscopy and in the solid state by *X*-ray crystallography.

Experimental

Preparation of Compounds (**1**) *and* (**2**).—Solutions of $S(CH_2CH_2OH)_2$ (3.05 g, 0.025 mol) in methanol (50 cm^3) and of $MeC_6H_4SO_2NCl^-Na^+\cdot 3H_2O$ (7.1 g, 0.025 mol), also in methanol (100 cm^3) were mixed at room temperature. A solution of glacial acetic acid (2.5 cm^3) in methanol (15 cm^3) was added dropwise with vigorous stirring. Stirring was continued for 4 h, after which the mixture was filtered, and the filtrate evaporated to dryness. Recrystallisation of the solid from acetone (300 cm^3) yielded compound (**2**) (1.25 g, 36%), m.p. 107–108 °C (Found: C, 34.6; H, 7.2. $C_4H_{10}O_3S$ requires: C, 34.8; H, 7.3%). $\delta_H(D_2O)$ 3.8–3.9 (m, 4 H, CH_2) and 4.75 (m, 4 H, CH_2); $\delta_C(D_2O)$: 56.9(t) and 57.6(t). The mother liquor, when reduced to half its original volume, provided crystals of compound (**1**) (1.80 g, 23%) m.p. 78–80 °C (Found: C, 42.8; H, 6.1; N, 4.5. $C_{11}H_{19}NO_5S_2$ requires: C, 42.7; H, 6.2; N, 4.5%). δ_H([$^2H_6$]-acetone) 2.38 (s, 3 H, CH_3), 2.96 (s, 3 H, H_2O), 3.1–3.3 (m, 4 H, 2 × CH_2), 3.9 (m, 4 H, 2 × CH_2), 4.18 (t, J 5.1 Hz, 1 H, OHO), and 7.3 and 7.7 (A_2B_2, 4 H, C_6H_4); δ_H([$^2H_6$]DMSO) 2.32 (s, 3 H, CH_3), 3.0–3.2 (m, 4 H, 2 × CH_2), 3.30 (s, 3 H, H_2O), 3.5–3.8 (m, 4 H, 2 × CH_2), 4.97 (t, J 5.0 Hz, 2 H, 2 × OH), and 7.3 and 7.6 (A_2B_2, 4 H, C_6H_4); δ_C([$^2H_6$]acetone) 2.13 (q, CH_3), 52.3 (t, 2 × CH_2), 55.7 (t, 2 × CH_2), 127.0(d), 129.9(d), and 142.1(s), 143.3(s) (aromatic); δ_C([$^2H_6$]DMSO) 20.8(q), 51.0(t), 54.1(t), 125.6(d), 129.0(d), 140.8(s), and 142.0(s).

X-*Ray Crystallography*.—Crystals of compounds (**1**) and (**2**) suitable for *X*-ray analysis were grown from acetone solution.

Crystal data. Compound (**1**) $C_{11}H_{19}NO_5S_2$, M = 309.4, monoclinic, a = 7.497(1), b = 16.291(2), c = 11.843(2) Å, β = 92.52 (1)°, U = 1 445.0(7) Å^3, space group $P2_1/c$ (No. 14), Z = 4, D_c = 1.42 g cm^{-3}, μ(Mo-K_α) = 3.7 cm^{-1}, λ = 0.710 73 Å, F(000) = 656.

Table 1. Positional parameters and e.s.d.s for (**1**).

Atom	x	y	z
S(1)	0.147 49(6)	0.140 35(3)	0.132 4(4)
S(2)	0.488 67(7)	0.183 08(4)	0.085 32(5)
O(1)	0.120 8(2)	0.215 0(1)	−0.232 2(1)
O(2)	0.151 7(2)	−0.023 5(1)	0.130 5(1)
O(3)	0.532 3(2)	0.146 6(1)	−0.020 1(1)
O(4)	0.566 6(2)	0.261 3(1)	0.112 2(2)
N	0.278 2(2)	0.195 6(1)	0.096 3(1)
C(1)	0.005 2(3)	0.218 7(1)	−0.049 5(2)
C(2)	0.100 6(3)	0.266 0(1)	−0.137 8(2)
C(3)	−0.008 4(3)	0.099 7(1)	0.109 3(2)
C(4)	0.081 3(3)	0.042 0(1)	0.191 6(2)
C(11)	0.558 6(2)	0.115 3(1)	0.195 4(2)
C(12)	0.605 2(3)	0.145 7(1)	0.301 9(2)
C(13)	0.662 9(3)	0.091 7(2)	0.385 2(2)
C(14)	0.674 3(3)	0.008 1(2)	0.365 8(2)
C(15)	0.624 3(3)	−0.020 4(1)	0.258 7(2)
C(16)	0.567 5(3)	0.032 1(1)	0.174 8(2)
C(17)	0.742 5(4)	−0.049 8(2)	0.455 8(2)
OW	0.179 8(3)	−0.127 2(1)	0.313 8(2)
H(O1)	0.177(3)	0.237(1)	−0.270(2)
H(O2)	0.177(3)	−0.047(1)	0.174(2)
HWA	0.095(3)	−0.157(2)	0.293(3)
HWB	0.282(4)	−0.166(2)	0.329(3)

Table 2. Positional parameters and their e.s.d.s for (**2**).

Atom	x	y	z
S(1)	0.265 92(6)	0.134 7(2)	0.036 43(5)
O(1)	0.383 1(2)	−0.068 4(5)	−0.143 7(2)
O(2)	0.073 4(2)	−0.052 1(5)	0.167 0(2)
O(3)	0.377 2(2)	0.248 4(5)	0.120 6(2)
C(1)	0.267 1(3)	0.300 8(7)	−0.093 2(2)
C(2)	0.380 6(3)	0.223 6(7)	−0.132 2(2)
C(3)	0.133 6(3)	0.313 6(6)	0.061 7(2)
C(4)	0.106 5(3)	0.230 8(7)	0.171 5(2)
H(O1)	0.456(3)	−0.105(7)	−0.133(3)
H(O2)	0.085(3)	−0.111(9)	0.234(3)

Data collection. Compound (**1**). A crystal of dimension 0.26 × 0.33 × 0.51 mm was used. Cell dimensions were determined by least-squares refinement using the setting angles of 25 reflections in the range of $14° \leq \theta \leq 18°$. Data were collected at 21 °C using a CAD4 diffractometer with graphite monochromated Mo-K_α radiation in the $\omega/2\theta$ scan mode; the ω scan rate was 1–3° min^{-1}, the ω scan width = 0.6 + 0.35 tan θ and the maximum value of 2 θ was 54°: 3 513 reflections were measured, of which 3 154 were unique and 2 288 had $I \geq 3\sigma(I)$. Lorentz and polarization corrections were applied, but no absorption correction was necessary.

Structure solution and refinement for (**1**). The structure was solved by direct methods, followed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon were included in the refinement as riding atoms with d(C–H) 0.95 Å and B_{iso} 5.0 Å^2. The methyl hydrogens appeared as a torus of electron density: they were allowed for by including six half-hydrogen atoms at 60° intervals around the torus. Hydrogen atoms bound to oxygen were refined with individual isotropic thermal parameters. A secondary extinction coefficient[6] refined to a value of 6×10^{-7}. The final R and R_w values were 0.033 and 0.048 respectively, with 189 parameters. A final difference map was featureless.

Crystal data. Compound (**2**), $C_4H_{10}O_3S$, M = 138.2, monoclinic, a = 11.057(4), b = 4.837(2), c = 12.332(4) Å, β = 103.61(3), U = 641.0(7) Å^3, space group $P2_1/n$ uniquely from the systematic absences ($h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$), Z = 4, D_c = 1.43 g cm^{-1}, μ(Mo-K_α) = 4.1 cm^{-1}; λ = 0.710 73 Å, F(000) = 296.

Table 3. Molecular dimensions for (**1**).

(*a*) Bond lengths/Å

S(1)–N	1.629(2)
S(1)–C(1)	1.802(2)
S(1)–C(3)	1.793(2)
S(2)–O(3)	1.433(2)
S(2)–O(4)	1.431(2)
S(2)–N	1.602(2)
S(2)–C(11)	1.770(2)
O(1)–C(2)	1.407(3)
O(2)–C(4)	1.406(3)
C(1)–C(2)	1.505(3)
C(3)–C(4)	1.492(3)
C(11)–C(12)	1.386(3)
C(11)–C(16)	1.379(3)
C(12)–C(13)	1.378(3)
C(13)–C(14)	1.384(4)
C(14)–C(15)	1.386(3)
C(14)–C(17)	1.497(4)
C(15)–C(16)	1.365(3)

(*b*) Bond angles

N–S(1)–C(1)	100.78(9)
N–S(1)–C(3)	102.29(9)
C(1)–S(1)–C(3)	97.62(9)
O(3)–S(2)–O(4)	117.1(1)
O(3)–S(2)–N	112.76(9)
O(3)–S(2)–C(11)	108.1(1)
O(4)–S(2)–N	105.2(1)
O(4)–S(2)–C(11)	106.7(1)
N–S(2)–C(11)	106.30(9)
S(1)–N–S(2)	116.7(1)
S(1)–C(1)–C(2)	111.0(2)
O(1)–C(2)–C(1)	108.7(2)
S(1)–C(3)–C(4)	111.0(1)
O(2)–C(4)–C(3)	108.1(2)
S(2)–C(11)–C(12)	120.1(2)
S(2)–C(11)–C(16)	119.9(2)
C(12)–C(11)–C(16)	120.0(2)
C(11)–C(12)–C(13)	118.8(2)
C(12)–C(13)–C(14)	122.0(2)
C(13)–C(14)–C(15)	117.8(2)
C(13)–C(14)–C(17)	121.5(2)
C(15)–C(14)–C(17)	120.7(2)
C(14)–C(15)–C(16)	121.3(2)
C(11)–C(16)–C(15)	120.2(2)

(*c*) Hydrogen-bond dimensions

OW ··· O(1) (I)	2.805(3)	OW–HWA ··· O(1) (I)	172(3)
OW ··· O(2)	2.751(2)	OW–HWB ··· O(4) (II)	165(3)
OW ··· O(4) (II)	2.746(3)	O(1)–H(O1) ··· N (III)	166(3)
O(1) ··· N (III)	2.802(2)	O(2)–H(O2) ··· OW	164(3)
HWA–OW	0.83(3)	C(2)–O(1)–H(O1)	107(2)
HWA ··· O(1) (I)	1.98(3)	C(4)–O(2)–H(O2)	99(2)
HWB–OW	1.00(3)	HWA–OW–HWB	104(3)
HWB ··· O(4) (II)	1.77(3)		
H(O1)–O(1)	0.72(3)		
H(O1) ··· N (III)	2.10(3)		
H(O2) ··· OW	2.11(2)		
H(O2)–O(2)	0.66(2)		

The roman numerals refer to the following equivalent positions: (I) $-x, -y, -z$; (II) $1 - x, -1/2 + y, 1/2 - z$; (III) $x, 1/2 - y, -1/2 + z$.

Data collection. Compound (**2**). The crystals grown from acetone or dimethyl sulphoxide (DMSO) were always twinned, and initial diffractometer studies could not determine a unique cell. Careful photographic work (rotation and Weissenberg films, Cu-K_α radiation) showed clearly the nature of the twinning, which resulted in the 101 plane being an effective mirror plane. It was also clear from the photographs that (serendipitously) it would be possible to measure almost all the unique (untwinned) reflections, as only a few of the twinned reflections overlapped in reciprocal space. Using the RAMCEL option with an Enraf-Nonius CAD4 diffractometer, it was possible to identify and index the low-order strong reflections, determine precise cell parameters and orientation matrix using 25 reflections with $8 < \theta < 22°$, and collect and process an essentially 'untwinned' data set to a maximum (Mo-K_α) of 27° in a manner similar to that described above for (**1**). Reflections (1 663) were measured of which 1 367 were unique and 1 088 had $I > 3\sigma(I)$. By constructing reciprocal lattice plots we were able to identify 32 reflections which would not be precisely measured because of the twinning; removal of these reflections yielded a data set with 1 056 observed reflections.

Table 4. Molecular dimensions for (**2**).

(*a*) Bond lengths/Å		(*b*) Bond angles/°	
S(1)–O(3)	1.514(2)	O(3)–S(1)–C(1)	105.9(1)
S(1)–C(1)	1.791(3)	O(3)–S(1)–C(3)	105.8(1)
S(1)–C(3)	1.789(3)	C(1)–S(1)–C(3)	96.7(1)
O(1)–C(2)	1.418(4)	C(2)–O(1)–H(O1)	104(3)
O(2)–C(4)	1.412(4)	C(4)–O(2)–H(O2)	108.0(3)
C(1)–C(2)	1.493(5)	S(1)–C(1)–C(2)	111.0(2)
C(3)–C(4)	1.507(4)	O(1)–C(2)–C(1)	108.5(3)
O(1) ··· O(3) (I)	2.741(3)	S(1)–C(3)–C(4)	111.8(2)
O(2) ··· O(3) (II)	2.722(3)	O(2)–C(4)–C(3)	109.0(2)
H(O1)–O(1)	0.81(3)	O(1)–H(O1) ··· O(3) (I)	171(4)
H(O1) ··· O(3) (I)	1.94(3)	O(2)–H(O2) ··· O(3) (II)	175(4)
H(O2)–O(2)	0.86(4)		
H(O2) ··· O(3) (II)	1.87(4)		

The romal numerals in parentheses refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*: (I) 1 − *x*, −*y*, −*z*; (II) 0.5 − *x*, −0.5 + *y*, 0.5 − *z*.

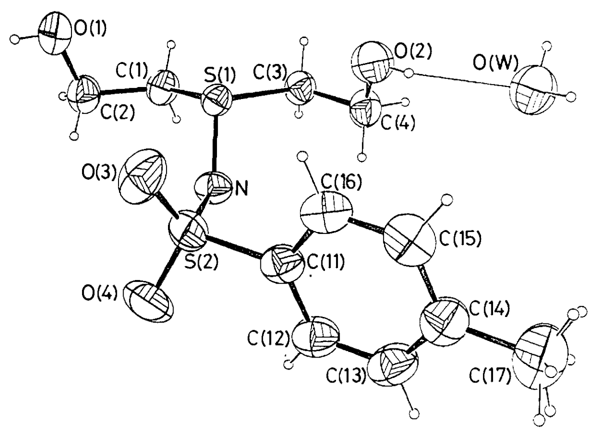


Figure 1. Perspective view of the asymmetric unit of (**1**) showing the atom numbering scheme. Ellipsoids are at the 50% level; the hydrogen atoms on the methyl carbon C(17) are disordered.

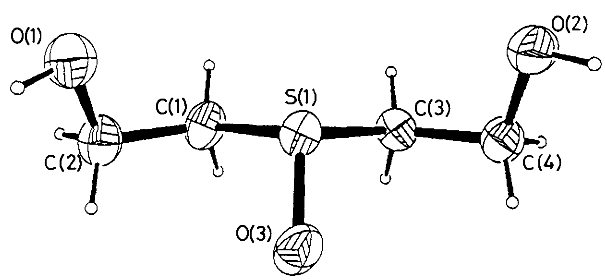


Figure 2. Perspective view of the asymmetric unit of (**2**) which shows the atom numbering scheme. Ellipsoids are at the 50% level.

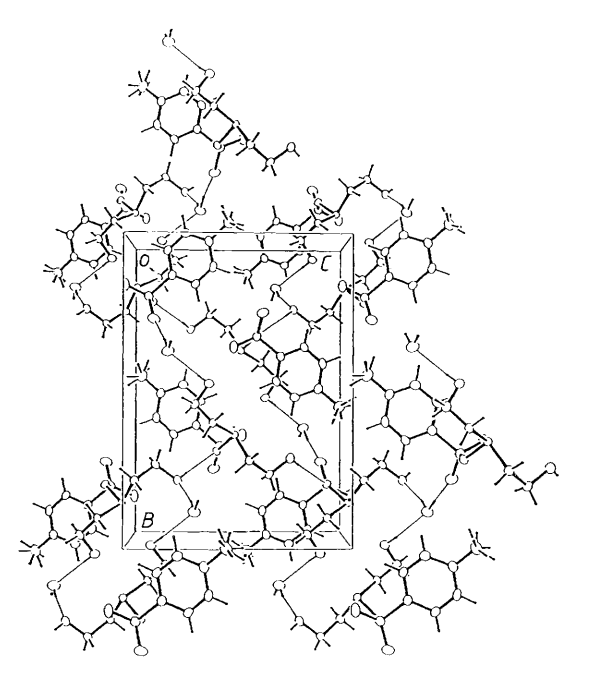


Figure 3. Perspective view of the crystal structure of (**1**) viewed down the *a* axis, showing the packing and the hydrogen bonding (thin lines).

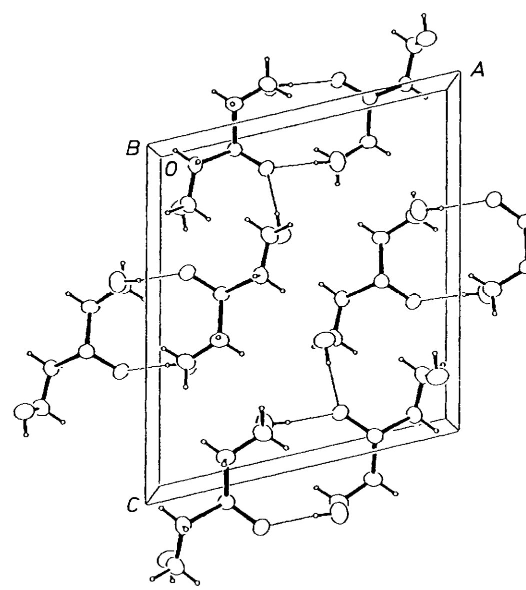


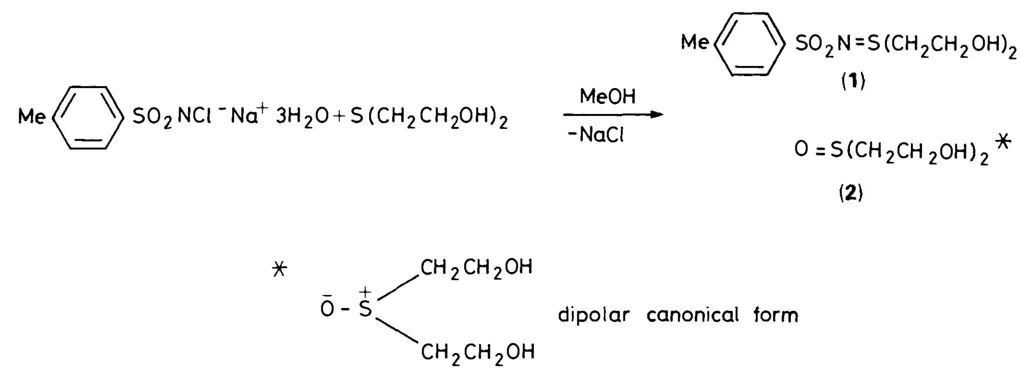
Figure 4. Perspective view of the crystal structure of (**2**) viewed down the *b* axis, showing the packing and hydrogen bonding (thin lines).

Structure solution and refinement for (**2**). The structure was solved using the SHELXS-86[7] program on a PC-XT computer. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations. All hydrogen atoms were well defined in difference maps. The methylene hydrogen atoms were included in the final rounds of refinement as riding atoms (C–H 0.95 Å, B_{iso} 4 Å^2); the hydroxy H atoms were allowed to refine isotropically. A secondary extinction coefficient refined to 1×10^{-6}. The final cycles of refinement included 82 variables and converged (largest shift/error ratio 0.03) with $R = 0.044$ and $R_w = 0.062$. There were no chemically significant features in the final difference map.

For both (**1**) and (**2**) scattering factor data were taken from refs. 8–10. The weighting scheme used in the refinements was of the form $w = 1/[\sigma^2 F_0 + 0.05(F_0{}^2)]$. All calculations except where noted were performed on an enhanced PDP-11/73 computer using SDP-PLUS.[11]

Final refined atom co-ordinates for (**1**) and (**2**) are given in Tables 1 and 2; bond lengths and angles are given in Tables 3 and 4. Perspective views of the asymmetric units showing our crystallographic numbering schemes are in Figures 1 and 2, and views of the unit-cell contents showing hydrogen bonding are in Figures 3 and 4.

For both (**1**) and (**2**), tables of calculated hydrogen atom co-ordinates, anisotropic thermal parameters, torisonal angles, and



Scheme 1.

observed and calculated structure factors are included in the Deposition Data.*

Results and Discussion

The reaction between the hydrated sodium salt of chloramine-T and 2,2′-thiodiethanol, in slightly acidic methanol solution provides both (**1**) and (**2**) (Scheme 1), readily separable in analytically pure form by fractional crystallisation from acetone solution, in yields of 23 and 36% respectively.

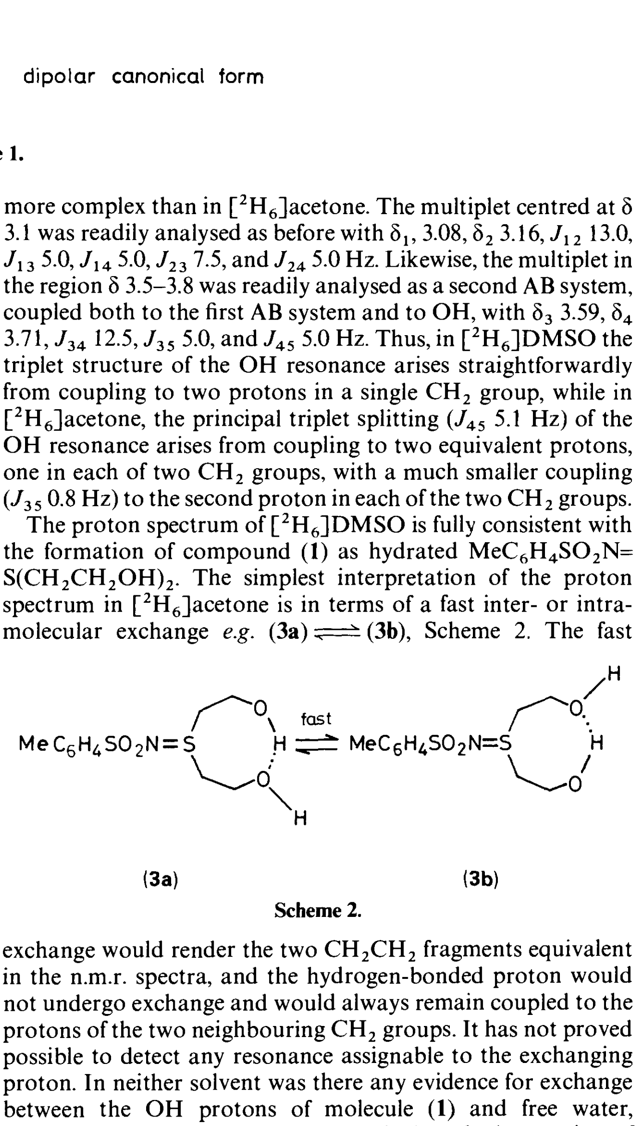
Microanalysis of (**1**) was repeatedly consistent with the formulation $C_{11}H_{19}NO_5S_2$ originally reported by Mann,[3] rather than with the anhydrous formulation $C_{11}H_{17}NO_4S_2$. However, the solution n.m.r. spectra clearly ruled out any formulation based upon a hydrogen-bonded adduct[5] of $MeC_6H_4SO_2NH_2$ and $OS(CH_2CH_2OH)_2$. In particular, there was no resonance assignable to NH_2, while the ^1H and ^{13}C n.m.r. spectra of (**1**) in general were quite different from a summation of the spectra of $MeC_6H_4SO_2NH_2$ and of $OS(CH_2CH_2OH)_2$.

In solution in each of [$^2H_6$]acetone and [$^2H_6$]DMSO, the ^{13}C n.m.r. spectra of (**1**) were extremely simple, with just two resonances aside from those of the *p*-tolyl group, showing that the two CH_2CH_2O fragments are equivalent in solution.

The proton n.m.r. spectrum in [$^2H_6$]acetone solution contained, in addition to the readily assigned signals from the *p*-tolyl group, three multiplets centred at δ 3.2, 3.9, and 4.2. These correspond to 4, 4, and 1 proton respectively for each *p*-tolyl group present, and were thus assigned as 2 × CH_2, 2 × CH_2, and OH, respectively, indicating that only one of the original OH protons of the original $S(CH_2CH_2OH)_2$ fragment is detected at δ 4.2, but that nevertheless the two CH_2CH_2 fragments are equivalent, as deduced from the ^{13}C spectrum. The multiplet at δ 3.2 was readily assigned as an AB system coupled to a second distant AB system with δ_1 3.14, δ_2 3.26, J_{12} 13.1, J_{13} 4.4, J_{14} 1.4, J_{23} 8.1, and J_{24} 4.9 Hz. The triplet centred at δ_5 4.18 was assigned to OH coupled to two protons with J 5.1, and to two further protons with J 0.8 Hz. The multiplet centred at δ 3.9 was complex, and not readily assigned: however, irradiation at δ 4.18 simplified the δ 3.9 multiplet to an AB system coupled to the first AB system with δ_3 3.82, δ_4 3.90, J_{34} 12.0 Hz. Comparison of the normal and the spin-decoupled spectra allowed the final assignment of J_{35} 0.8, J_{45} 5.1 Hz.

The principal differences between the ^1H n.m.r. spectrum in [$^2H_6$]DMSO and that in [$^2H_6$]acetone, aside from the detailed values of the chemical shifts, are that in [$^2H_6$]DMSO, the OH resonance at δ 4.97 represents two protons for each *p*-tolyl group, and that the higher frequency CH_2 multiplet is rather more complex than in [$^2H_6$]acetone. The multiplet centred at δ 3.1 was readily analysed as before with δ_1, 3.08, δ_2 3.16, J_{12} 13.0, J_{13} 5.0, J_{14} 5.0, J_{23} 7.5, and J_{24} 5.0 Hz. Likewise, the multiplet in the region δ 3.5–3.8 was readily analysed as a second AB system, coupled both to the first AB system and to OH, with δ_3 3.59, δ_4 3.71, J_{34} 12.5, J_{35} 5.0, and J_{45} 5.0 Hz. Thus, in [$^2H_6$]DMSO the triplet structure of the OH resonance arises straightforwardly from coupling to two protons in a single CH_2 group, while in [$^2H_6$]acetone, the principal triplet splitting (J_{45} 5.1 Hz) of the OH resonance arises from coupling to two equivalent protons, one in each of two CH_2 groups, with a much smaller coupling (J_{35} 0.8 Hz) to the second proton in each of the two CH_2 groups.

The proton spectrum of [$^2H_6$]DMSO is fully consistent with the formation of compound (**1**) as hydrated $MeC_6H_4SO_2N{=}S(CH_2CH_2OH)_2$. The simplest interpretation of the proton spectrum in [$^2H_6$]acetone is in terms of a fast inter- or intramolecular exchange *e.g.* (**3a**) $\rightleftharpoons$ (**3b**), Scheme 2. The fast



(**3a**) (**3b**)

Scheme 2.

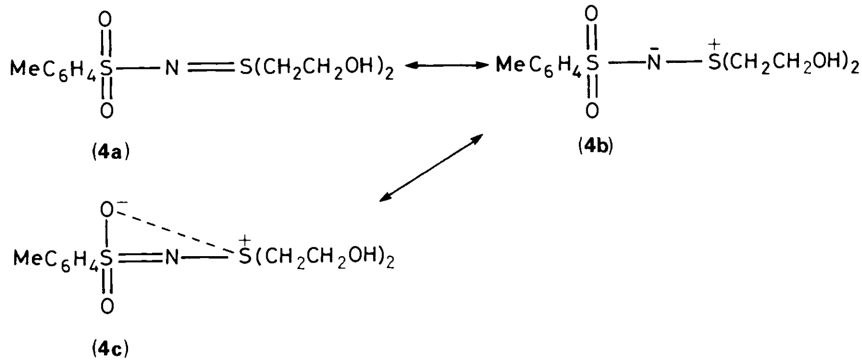
exchange would render the two CH_2CH_2 fragments equivalent in the n.m.r. spectra, and the hydrogen-bonded proton would not undergo exchange and would always remain coupled to the protons of the two neighbouring CH_2 groups. It has not proved possible to detect any resonance assignable to the exchanging proton. In neither solvent was there any evidence for exchange between the OH protons of molecule (**1**) and free water, although no significance can be attached to the integration of the free water resonance. In [$^2H_6$]DMSO, the spectrum is consistent, not with any intramolecular hydrogen bonding, but rather with hydrogen bonding of the OH protons in (**1**) to the solvent.

That the hydrogen bonding is intramolecular in acetone solution but involves the solvent in DMSO is fully consistent with the much higher donor properties of DMSO, compared with either acetone or water.[12]

The constitution of compounds (**1**) and (**2**) and the very extensive hydrogen bonding in the solid state, were established by *X*-ray crystallography.

Crystal and Molecular Structure of (**1**).—The crystal structure determination confirms the molecular constitution as $MeC_6H_4SO_2NS(CH_2CH_2OH)_2{\cdot}H_2O$: the asymmetric unit of the structure, which illustrates the molecular configuration, is shown in Figure 1.

* For information regarding deposition of supplementary data at the Cambridge Crystallographic Data Centre, see 'Instructions for Authors, (1989)' *J. Chem. Soc., Perkin Trans. 2*, 1989, p. xvii sect 5.0.



(4a) (4b) (4c)

Scheme 3.

Within the organic fragment, the N–S(1) and N–S(2) bond lengths are respectively 1.629(2) and 1.602(2) Å with an S(1)–$\hat{N}$–S(2) angle 116.7(1)°: the configuration of S(1) is sharply pyramidal, with the sum of bond angles about this atom of only 300.7°. The two N–S bond lengths are very close in magnitude, and lie almost mid-way between the values of 1.55 and 1.67 Å typically found for double and single nitrogen–sulphur bonds.[13–16] Moreover, there is a very short intramolecular contact distance between S(1) and O(3) of 2.931 Å, very significantly less than the sum of the van der Waals radii, 3.3 Å.[17] Such short contacts were also noted by us[18,19] in arsenic and antimony ylides.

The dimensions of the S(1)–N–S(2) fragment in compound (**1**) together with the short S(1) $\cdots$ O(3) distance, therefore, point to the forms (**4a–c**) as important contributors to the overall structure of compound (**1**), Scheme 3. Such short intramolecular S $\cdots$ O interactions have in fact been observed previously in several related compounds (**5**)–(**10**), although their significance appears to have been largely overlooked.[20–25]

$MeC_6H_4SO_2N{=}SR^1R^2$	$RC(=O)N{=}SMe_2$	$MeSO_2N{=}SMe_2$
(**5**) $R^1 = R^2 = Ph$	(**8**) R=Ph	(**10**)
(**6**) $R^1 = Ph$, $R^2 = C_3H_7$	(**9**) $R{=}CCl_3$	
(**7**) $R^1 = R^2 = CH_3$		

In each of (**5**)–(**7**) and (**10**), the two N–S distances are intermediate between single- and double-bond values. On the other hand, in $O_2NC_6H_4NSMe_2$, the N–S distance is 1.651 Å, close to the value for a single bond.[26]

The crystal structure of (**1**) exhibits extensive hydrogen bonding, as shown in Figure 3: each organic fragment and each water molecule participate in three hydrogen bonds. In the organic fragment at (x, y, z), O(1) acts as a hydrogen acceptor from the water molecule at ($-x$, $-y$, $-z$), and its proton acts as a hydrogen donor to the nitrogen atom in the molecule at ($x, \frac{1}{2} - y, \frac{1}{2} + z$), while the proton on O(2) acts as a hydrogen donor to the water molecule in the same asymmetric unit. The water molecule at (x, y, z) additionally acts as a hydrogen donor to O(1) in the molecule at ($-x, -y, -z$) and to O(4) in the molecule at ($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$). In this manner a three-dimensional network of hydrogen bonds between the organic molecules and the water molecules is developed. None of the hydrogen bonds involves O(3), the oxygen atom which is involved in the short S $\cdots$ O interaction.

In all of the hydrogen bonds, the O–H $\cdots$ X (X=N, O) group is nearly linear (Table 3), with O $\cdots$ X distances of 2.80 Å (X=N) and 2.75–2.81 Å (X=O): the hydrogen bonds are, therefore, all weak.[27]

Crystal and Molecular Structure of (**2**).—Compound (**2**) comprises molecules $OS(CH_2CH_2OH)_2$ which adopt the non-maximally extended conformation shown in Figure 2, with gauche O–C–C–S torsion angles (58.3 and −64.3°); an essentially similar conformation is found for the corresponding fragment of compound (**1**) (with O–C–C–S torsion angles 71.0 and −61.2°). As in (**1**), the sulphur atom is markedly pyramidal, with a sum of bond angles about sulphur of 308.4°. For S=O bond distances in C–S(=O)–C systems, Allen *et al.* have reported[28] values [mean, 1.497(13); lower quartile, 1.489; upper quartile, 1.505 Å] derived from ninety structures: the S=O distance in (**2**), 1.514(2) Å, is above their upper quartile value.

The mean C–S distances in both (**1**), 1.798(2), and (**2**), 1.790(3) Å are less than the lower quartile value reported[28] for such bonds [mean C–S, 1.818(24), lower quartile, 1.802; upper quartile, 1.829 Å] derived from sixty-nine structures. The dimensions of (**2**) are thus consistent with a significant contribution to the ground state of the dipolar canonical form of (**2**).

The crystal structure of (**2**) shows extensive hydrogen bonding (Figure 4). Pairs of molecules are linked to form centrosymmetric hydrogen-bonded dimers. In the molecule at (x, y, z), O(1) acts as a hydrogen donor to O(3) in the molecule at ($1 - x, -y, -z$), with O $\cdots$ O, 2.741(3); O(1)–H, 0.81(3) Å, and O–H $\cdots$ O 171(4)°. These dimers are linked into infinite sheets by further hydrogen bonds in which O(2) in the molecule at (x, y, z) acts as a hydrogen donor to O(3) in the molecule at ($\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$), with O $\cdots$ O, 2.722(3); O(2)–H, 0.86(4) Å, and O–H $\cdots$ O 175(4)°. Thus the molecules of $OS(CH_2CH_2OH)_2$ are linked into spirals extending along the b direction about the 2_1 axes.

The isolation of both (**1**) and (**2**) from the reaction between chloramine-T and $S(CH_2CH_2OH)_2$ is consistent with a mechanism[29] in which the first steps involve protonation by water of the chloramine-T anion, and subsequent oxidation of $S(CH_2CH_2OH)_2$, equations (1) and (2):

$$MeC_6H_4SO_2NCl^- + H_2O \rightleftharpoons OH^- + MeC_6H_4SO_2NHCl \quad (1)$$

$$MeC_6H_4SO_2NHCl + S(CH_2CH_2OH)_2 \rightleftharpoons MeC_6H_4SO_2NH^- + [ClS(CH_2CH_2OH)_2]^+ \quad (2)$$

There are then two nucleophilic anions present, $MeC_6H_4SO_2NH^-$ and OH^- which can react with the intermediate $[ClS(CH_2CH_2OH)_2]^+$ to provide the products (**1**) and (**2**) respectively, equations (3) and (4):

$$MeC_6H_4SO_2NH^- + [ClS(CH_2CH_2OH)_2]^+ \xrightarrow[-HCl]{+H_2O} (\mathbf{1}) \quad (3)$$

$$OH^- + [ClS(CH_2CH_2OH)_2]^+ \xrightarrow[-HCl]{} (\mathbf{2}) \quad (4)$$

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