

Chemistry of the S=O Bond. Part IV.¹ Conformational Analysis of Ethylene Sulphites

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The conformational analysis of ethylene sulphites is discussed and for two sulphites an attempt is made to calculate the twist-envelope proportions.

RECENT i.r. and ¹H n.m.r. studies of methyl- and phenyl-ethylene sulphites^{1,2} suggest that they possess conformations in solution similar to those of ethylene sulphite. Although an electron diffraction study³ has indicated an essentially planar structure for the ring, solution studies have invariably suggested the possibility of ring mobility about the C-C bond with a rapid interconversion between the two envelope conformations (IA and B) (Figure 1). Also, the observation of rotational effects for the neat liquid⁴⁻⁶ and for solutions in hydrogen-bonded solvents indicates a more mobile structure in solution. In the conclusions of Havinga *et al.*,⁷ conformers (IA and B) should represent the average of a range of conformers of practically equal energy (pseudo-libration.⁸).

Routes for rapid interconversion between the two twist-envelopes are restricted to that involving rotation about the C-C bond, as a complete pseudorotatory circuit around the ring is prevented by a relatively high potential energy barrier imposed by the sulphite group. Indeed, the type of spin systems found for these sulphites^{1,2,9} suggests that inversion at sulphur does not occur or is infinitely slow.¹⁰ Twist-envelope conformations for a number of mono-, di-, and tri-substituted ethylene sulphites are shown in Figure 1.

The possibility of calculation of torsion angles from coupling constants is restricted to those sulphites which exhibit both *cis*- and *trans*-couplings, namely ethylene sulphite and monosubstituted ethylene sulphites. By using in the Karplus equation¹¹ the values of $J_{vic}(cis)$ and $J_{vic}(trans)$ given in the Table, one would expect it to be possible to calculate values for the torsion angle, ψ . Unfortunately, Abraham¹² and other workers^{13,14} have shown that values of J_{vic} in five-membered rings cannot be accounted for by the basic Karplus equation. The uncertainty in calculation by this method is the determination of the constants involved. The R parameter introduced by Lambert,¹⁵ modified by Buys¹⁶ to the relationship $\cos \psi = [3/(2 + 4R)]^{1/2}$ where $R =$

$J_{vic}(trans)/J_{vic}(cis)$, gives an expression for the torsion angle in which the Karplus constants are no longer present. R Values can only be obtained for sulphites interconverting between two equal conformers, as in ethylene sulphite. The R value of 0.95 for ethylene

Vicinal coupling constants for ethylene sulphite and monosubstituted ethylene sulphites

Compound	$J_{vic}^*(trans)$ / Hz	$J_{vic}^*(cis)$ / Hz
Ethylene sulphite (I) ² †	6.6	6.9
1-Methylethylene sulphite, isomer 1 (II) ²	6.9	6.1
1-Methylethylene sulphite, isomer 2 (III) ²	9.1	6.1
1-Phenylethylene sulphite, isomer 1 (X) ¹	7.2	6.5
1-Phenylethylene sulphite, isomer 2 (XI) ¹	10.3	6.7
1-Bromomethylethylene sulphite, isomer 1 (XII)	4.3	6.4
1-Bromomethylethylene sulphite, isomer 2 (XIII)	7.8	6.6
1-Chloromethylethylene sulphite, isomer 1 (XIV)	4.2	6.4
1-Chloromethylethylene sulphite, isomer 2 (XV)	7.8	6.7
1-Fluoromethylethylene sulphite, isomer 1 (XVI)	5.0	6.9
1-Phenoxymethylethylene sulphite, isomer 1 (XVII)	4.7	6.5
1-Phenoxymethylethylene sulphite, isomer 2 (XVIII)	7.8	6.9

* Coupling constants (averaged over four solvents^{1,2}) were obtained either by first-order analysis or as r.m.s. values by use of a modified version of LAOCOON III,¹ and are considered accurate to ± 0.15 Hz. † $R = 0.95$; $\psi = 44^\circ$.

sulphite giving $\psi = 44^\circ$ is similar to those for 1,3-dioxolans (42°),¹⁷ 1,3,2-dioxaphospholans (42°),¹⁸ 1,3,2-oxathiarisols (51°),¹⁹ 1,3,2-dithiaphospholans (48°),²⁰ and 1,3-dithiolans (49°).²¹

Although it is not possible to calculate R values (and hence the torsion angles) for monosubstituted ethylene sulphites it is interesting to compare $J_{vic}(cis)$ and $J_{vic}(trans)$ between isomers. The value of $J_{vic}(cis)$ is virtually the same for all the sulphites, but higher values of $J_{vic}(trans)$ are obtained for the second isomer. In each case the *trans*-coupling is greater than that for

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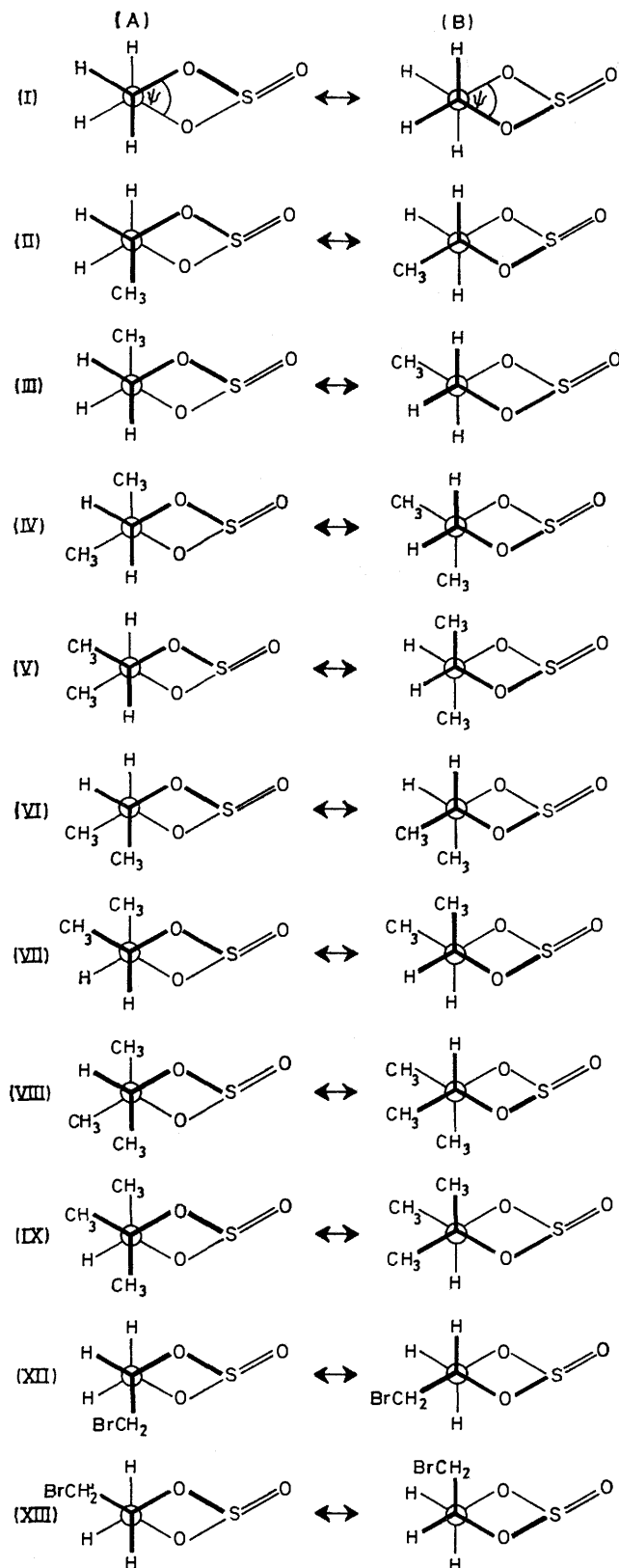


FIGURE 1 Twist envelopes for ethylene sulphite (I), 1-methylethylene sulphite isomer 1 (II) and isomer 2 (III), 1,1-dimethylethylene sulphite (IV), (\pm)-1,2-dimethylethylene sulphite (V), 1,2-dimethylethylene sulphite isomer 1 (VI) and isomer 2 (VII), 1,1,2-trimethylethylene sulphite isomer 1 (VIII) and isomer 2 (IX), and 1-bromomethylethylene sulphite isomer 1 (XII) and isomer 2 (XIII)

ethylene sulphite, suggesting that these isomers possess larger torsion angles. The origins of the magnitude of the torsion angles for the sulphites (I)—(XVIII) may be discussed in terms of a rapid interconversion of conformers. For ethylene sulphite (I), rapid interconversion of the two equally populated sets of conformers (IA and B) results in mean values of $J_{vic}(cis)$ and $J_{vic}(trans)$, giving equations (1) and (2).

$$J_{vic}(cis) = [J_A(cis) + J_B(cis)]/2 = 6.9 \text{ Hz} \quad (1)$$

$$J_{vic}(trans) = [J_A(trans) + J_B(trans)]/2 = 6.6 \text{ Hz} \quad (2)$$

The introduction of a methyl group into the ring [(II) and (III)] will cause several changes relative to the unsubstituted ring and the pairs of conformers [(IIA and B) and (IIIA and B)] will no longer be equivalent. For example, in (IIIA) the methyl group occupies the pseudoaxial position and in (IIIB) the pseudoequatorial position. For both (II) and (III), consideration of steric interactions between non-bonded atoms shows that there will be a preference for the methyl group to occupy a pseudoequatorial position. This is particularly so for (III) where the methyl group is *cis* to the S=O bond, so the preferred conformer is expected to be (IIIB). The increase in $J_{vic}(trans)$ for (III) in comparison with (II) confirms this assumption. From the interconversion (IIIA) \leftrightarrow (IIIB), the relationship (3) is apparent. Further, for (II) and (III), respectively,

$$J_{(IIIB)}(trans) \geq 9.15 \text{ Hz} > J_{(IIIA)}(trans) \quad (3)$$

$$x_A J_A(trans) + x_B J_B(trans) = 6.9 \quad (4)$$

$$x'_A J'_A(trans) + x'_B J'_B(trans) = 9.2 \quad (5)$$

equations (4) and (5) apply, where x is a mole fraction ($x_A + x_B = x'_A + x'_B = 1$). If we assume similar torsional angles for (II) and (III), then $J_A(trans) \simeq J'_A(trans)$ and $J_B(trans) \simeq J'_B(trans)$, giving equations (6) and (7).

$$x_A J_A + x_B J_B = 6.9 \quad (6)$$

$$x'_A J_A + x'_B J_B = 9.2 \quad (7)$$

Subtraction of (6) from (7) gives equation (8), leading to (9) or (10). From (3), $J_B > J_A$; therefore $(x'_B - x_B)$

$$J_A(x'_A - x_A) + J_B(x'_B - x_B) = 2.3 \quad (8)$$

$$J_A(1 - x'_B - 1 + x_B) + J_B(x'_B - x_B) = 2.3 \quad (9)$$

$$(x'_B - x_B)(J_B - J_A) = 2.3 \quad (10)$$

is positive, that is, the relative amount of the conformer with the methyl group in the pseudoequatorial position is greater for (III) than for (II). In order to calculate x'_B and x_B some further speculative arguments must be considered.

If, in (II) and (III), the inductive effect of the methyl group on $J_{vic}(trans)$ is small, and if we assume comparable torsion angles for (I)—(III) such that $J_A + J_B$ is constant for these three sulphites, that is, 13.2 Hz [equation (2)], with the relationship (3), equation (8) becomes $x'_B - x_B > ca. 0.4$. Similarly the increase in the B conformer for (II) (x_B) relative to (I) (x_{ES}) in terms of J_B can be deduced as $x_B - x_{ES} \simeq$

$0.30/(2J_B - 13.2)$, and, from equation (2), then $(x_B - x_{BS}) \geq 0.07$. By symmetry, $x_{BS} = 0.5$; thus $x_B \approx 0.57$ and $x_B' \approx 0.97$. This suggests that the conformer with the methyl group occupying the pseudoequatorial position is present to the extent of 50–60% for (II) and ca. 95% for (III).

Although the above represent very crude speculations on the magnitude of coupling constants it is interesting that the difference in free energy between the two conformers would be ca. 0.2 kcal mol⁻¹ for (II) [in favour of (IIB)] and ca. 1.3 kcal mol⁻¹ for (III) [(IIB)]. The difference between these figures should, by symmetry, be solely a measure of the interaction of the methyl group with the S=O bond, *i.e.* ca. 1.1 kcal mol⁻¹. In fact ΔG between (II) and (III) obtained by equilibration experiments is ca. 0.9 kcal mol⁻¹.²¹

The repulsive interactions between non-bonded atoms along the C–C axis are the same in both sets of conformers in the *gem*-dimethyl derivative (IV), so this factor will not directly affect the preferential population of one conformer relative to another. Geminal methyl groups will increase the energy barrier to rotation relative to structures (I)–(III), and will be important in determining the torsion angle within each conformer. From the discussion above this would correspond to a preference for (IVB). Also, the observed 4J (0.4 Hz) arises from an *M* path across the ring, and this is only possible for conformer (IVB).

The interplay of interatomic interactions in the *vic*-dimethyl derivative (V) is not resolved as straightforwardly as those of the previous compounds. Conformer (VA) has both methyl groups occupying the preferred pseudoequatorial position but it would be expected for this conformer that the *gauche* vicinal interactions between methyl groups would be greater than any corresponding interaction observed with (II), (III), or (IV). This interaction would be expected to decrease with a smaller torsion angle relative to the previous compounds. Although $J_{vic}(trans)$ is greater than in (I) or (II) it is smaller than that for (III), in agreement with this postulate.

For the other *vic*-dimethyl isomers, (VI) and (VII), the substitution of two methyl groups *cis* (VII) and *trans* (VI) to the S=O bond produces in each case conformers that are equivalent by symmetry. A lower value of $J_{vic}(cis)$ than for (I), (II), or (III) suggests a relative increase in torsion angle. This is expected in order for the systems to accommodate the repulsive interactions between the non-bonded atoms along the C–C bond. Opposing this increase will be the interaction of the protons of the *cis*-methyl groups with the exocyclic S=O bond, and hence (VII) will show less tendency to 'relax' than (VI).

As in the case of 1,1-dimethylethylene sulphite (IV), the presence of geminal methyl groups in the trimethyl derivatives (VIII) and (IX) cannot allow the existence of a preferred conformer with methyl groups

only in pseudoequatorial positions. The absence of distinct long-range couplings in either isomer suggests the presence of reasonable amounts of conformers (VIII) and (IXA); a predominance of the other extreme conformers would result in 4J couplings (*M* path). Although the methyl groups occupy the usually favoured pseudoequatorial position in (VIII) and (IXB), the repulsive interactions between the non-bonded atoms are greatest for these conformers. These interactions must be greater than or of the same order as that experienced by the methyl group in the pseudoaxial positions for (III) (that is, ca. 1 kcal mol⁻¹); this order of energy is certainly not disproportionate.²²

In the XCH₂-substituted series [(XII)–(XVIII)] $J_{vic}(cis)$ retains values similar to those of other ethylene sulphites. $J_{vic}(trans)$ values show a marked difference from those of the methyl and phenyl analogues in that all are significantly lower. The effect of the electronegativity of the group X is uncertain, although some lowering is predicted.²³ The values can be partly

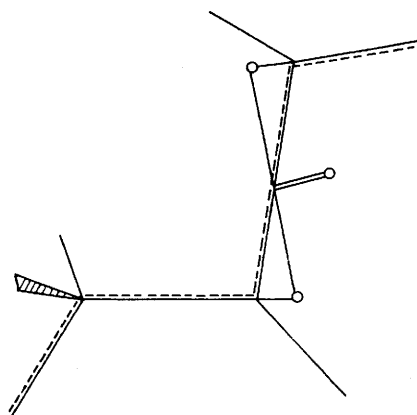


FIGURE 2 The *M* coupling path in isomers 1 [(XII), (XIV), (XVI), and (XVII)]

rationalised in terms of repulsive interactions between non-bonded atoms. The increased size of the group X (relative to H) in isomers 1 [(XII), (XIV), (XVI), and (XVII)] leads to a preference for staggering as in (XIIA). This is also suggested by 4J couplings between *one* of the protons of the XCH₂ group and the methylene proton *cis* to the S=O bond. The *M* path for this coupling (Figure 2) can only be resolved when the XCH₂ group lies in a pseudoaxial position; the comparatively large values for some compounds (4J ca. 0.7 Hz) indicate a highly favourable path.

For isomers 2 [(XIII), (XV), and (XVIII)] the interaction between the XCH₂ group and the S=O bond should result in a preference for conformer type (A), where the XCH₂ group occupies the pseudoequatorial position. Indeed, a larger $J_{vic}(trans)$ value is observed (relative to isomers 1) but this is smaller than the value for the methyl (X = H) derivative (III) since the interactions about the C–C bond are in an opposed direction; the differences in energy between the two

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²³ A. D. Cohen and T. Schaefer, *Mol. Phys.*, 1966, **10**, 209; H. Booth and P. D. Thornburrow, *Chem. and Ind.*, 1968, 65.

extreme conformers will be lower than for the methyl analogue. This should be reflected in a lower ΔG value between the *cis*- and *trans*-isomers, which has been confirmed in one example.*

EXPERIMENTAL

¹H N.m.r. spectra were recorded under the conditions previously described.¹

All sulphites were prepared by the method previously described.¹

1-Chloromethylethylene Sulphite, Isomers 1 and 2.—From 3-chloropropane-1,2-diol (Kodak) an 80% yield of crude sulphite was obtained. This was purified by distillation to give the isomeric mixture, b.p. 95° at 12 mmHg, n_D^{25} 1.4808; ratio of isomer 1 to isomer 2, 2:1. The isomers were separated by g.l.c. With a 7 ft column of tritolyol phosphate on Kieselguhr at 150 °C (gas flow 85 ml min⁻¹), retention times of 21.5 min for isomer 1 and 14.5 min for isomer 2 were observed. Each product had an isomeric purity of at least 99.5%. *Isomer 1* had n_D^{25} 1.4809; *isomer 2* had n_D^{25} 1.4798 [Found (isomeric mixture): C, 23.4; H, 3.6; Cl, 19.9; S, 22.5. Calc. for C₃H₅ClO₃S: C, 23.1; H, 3.2; Cl, 20.5; S, 22.7%].

1-Bromomethylethylene Sulphite, Isomers 1 and 2.—1-Bromo-2,3-epoxypropane (50 g), dissolved in aqueous methanol containing 4N-hydrochloric acid (6 drops), was gently refluxed for ca. 36 h. The hydrolysis was monitored by g.l.c. and when complete the excess of acid was neutralised (NaHCO₃) and most of the solvent was distilled off. The residue was extracted with diethyl ether and the extracts dried (MgSO₄). Removal of solvent left 3-bromopropane-1,2-diol (36 g, 64%). From this diol, with diethyl ether as solvent, a 55% yield of crude sulphite mixture was obtained (ratio of isomer 1 to isomer 2, 2:1). Purification and separation were effected by g.l.c. With a 5 ft column of 25% Montan Wax on Chromosorb P at 169 °C (gas flow 138 ml min⁻¹), retention times of 22 min for isomer 1 and 16.5 min for isomer 2 were observed. The mixture was 'topped and tailed' twice to give each isomer (>99% pure): *isomer 1*, n_D^{25} 1.5117; *isomer 2*, n_D^{25} 1.5183 [Found (isomeric mixture): C, 17.8; Br, 39.1; S, 15.8. Calc. for C₃H₅BrO₃S: C, 18.0; Br, 39.5; S, 16.0%].

1-Fluoromethylethylene Sulphite, Isomers 1 and 2.—1,2-Epoxy-3-fluoropropane (6 g) dissolved in water (60 ml)

together with ethanol (35 ml) and 4N-hydrochloric acid (5 drops) was stirred at 50 °C under reflux for 2 days. The reaction was monitored by g.l.c. and when complete the excess of acid was neutralised (CaCO₃), the solution was filtered, and most of the solvent was distilled off under reduced pressure. The residue was extracted with diethyl ether and the extracts were dried (MgSO₄). Removal of solvent left 3-fluoropropane-1,2-diol (38%).

From the diol, with diethyl ether as solvent, a 69% yield of crude sulphite was obtained; g.l.c. indicated >98% purity. With a 7 ft column of 25% Montan Wax on Chromosorb P at 156 °C (gas flow 87 ml min⁻¹), retention times of 28.5 min for isomer 1 and 21.5 min for isomer 2 were obtained with complete resolution, giving *isomer 1*, n_D^{25} 1.4368 and *isomer 2*, n_D^{25} 1.4372 [Found (isomeric mixture): C, 25.4; H, 3.2; S, 34.6. Calc. for C₃H₅FO₃S: C, 25.7; H, 3.0; S, 34.4%].

1-Phenoxymethylethylene Sulphite, Isomers 1 and 2.—1,2-Epoxy-3-phenoxypropane (25 g) dissolved in methanol-water with a few drops of 2N-hydrochloric acid as catalyst was gently refluxed for 5 h. Excess of acid was then neutralised (NaHCO₃) and the solvent evaporated off until crystals began to form. On cooling, crude 3-phenoxypropane-1,2-diol (20 g) was obtained. This was washed with water and recrystallised from methanol-water to give pure diol (16 g), m.p. 53–54° (Found: C, 64.2; H, 7.0. C₉H₁₂O₃ requires C, 64.3; H, 7.2%).

From the diol a 64% yield of crude sulphite was obtained. The crude product slowly deposited a solid which when recrystallised from carbon disulphide gave material which g.l.c. showed to contain isomers 1 and 2 in the ratio 9:1. Complete isomeric purification was effected by g.l.c. With a 1.5 ft column of Apiezon L (30%) on Chromosorb P at 181 °C (gas flow 273 ml min⁻¹), retention times of 38.5 min for isomer 1 and 28.3 min for isomer 2 were observed, giving *isomer 1*, m.p. 66–67°, and *isomer 2*, m.p. 57–58° [Found (isomeric mixture): C, 50.5; H, 4.7; S, 15.0. Calc. for C₉H₁₀O₃S: C, 50.5; H, 4.7; S, 15.0%].

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* H. F. van Woerden, University of Amsterdam (personal communication) reports $\Delta G_{313}^{\ddagger}$ (for X = OPh) values of 0.35 (CCl₄) and 0.32 (CHCl₃) kcal mol⁻¹ in favour of isomer 1 (XVII).