Sulphine Isomerisation

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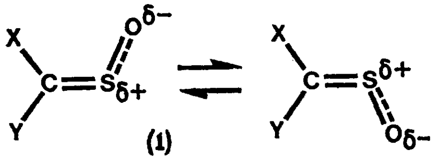
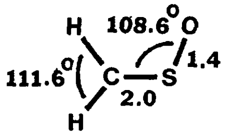
Summary An SCF–MO–CNDO investigation of the geometry, electron distribution, and *E/Z* isomerization for thioformaldehyde oxide (sulphine) and derivatives suggests that the rotation mechanism is favoured over inversion.

Sulphines (**1**), although reported as early as 1923,[1] have been investigated actively only recently.[2] The initial observation that compounds (**1**; X = Cl, Y = Ph) could be isolated as interconvertible geometric isomers[3] was confirmed by subsequent work[2,4] which supported a planar structure for the sulphine fragment. However, the mechanism by which *E* and *Z* forms are interchanged has not been determined. We report here an SCF–MO–CNDO investigation for the parent sulphine† (**1**; X = Y = H) and some of its derivatives in their ground and possible intervening transition states.

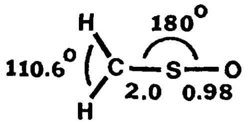


(1)

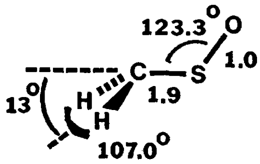
Computed values are illustrated by structure (**2**). The system prefers planarity, with ∠ C–S–O 108·6° in excellent agreement with a recent *X*-ray study for (**1**; X,Y = $-S{\cdot}CH_2{\cdot}CH_2{\cdot}S-$): ∠CSO 109·4°; *r*(S–O) 1·50, *r*(C–S) 1·64 Å.[4]



(2)



(3)



(4)

Calculated bond lengths [*r*(S–O) 1·59, *r*(C–S) 1·63 Å] also conform closely to experimental values. Bond orders‡ and charge densities[7] (ρ_C −0·032, ρ_S +0·51, ρ_O −0·61) suggest a full C–S double bond and a polar, partial S–O double bond.

Interconversion of *E*- and *Z*-isomers can be viewed either as an inversion at sulphur or as a rotation about the C–S bond. Bond-angle and bond-order parameters for the corresponding transition states are given by structures (**3**) and (**4**) respectively [ρ_C (inv,rot) +0·0091, +0·16, ρ_S +0·37, +0·26, ρ_O = −0·48, −0·49].

Barriers to *E–Z* conversion are 26·6 kcal mol^{-1} for inversion and 23·9 kcal mol^{-1} for rotation. The results compare favourably with experimental enthalpy values for sulphine isomerization of 18§ and 23[8] kcal mol^{-1}.

In spite of the agreement between the present calculations and experiment, computed activation energies are too similar [$\Delta\Delta E$(inv–rot) = 2·7 kcal mol^{-1}] to permit an unambiguous choice between the rotation–inversion mechanisms. Thus, we have also computed activation barriers for hypothetical sulphine derivatives (**1**; X = H; Y = CH_2^+, CN, NH_3^+, NH_2, and CH_2^-) (Table).

For all cases studied the rotation mechanism is favoured. Further, the barrier differential increases as Y becomes either strongly electron-donating or electron-attracting. Thus, rotation is suggested to become more ready and inversion more difficult as significant perturbations are introduced by the substituents. If the present work reflects the actual molecular situation, it provides an experimental test for distinguishing the interconversion pathways of thioketone oxide isomers.

TABLE

Calculated isomerisation barriers for substituted sulphines[a] (**1**; X = H)

ΔE kcal mol^{-1}	CH_2^+	CN	NH_3^+	H	NH_2	CH_2^-
Inversion	40·6	30·9	34·4	26·6	28·2	30·5
Rotation	21·6	>27·6	30·0	23·9	17·3	8·6

[a] Ground and transition state geometries were assumed to be identical to those calculated for (**2**), (**3**), and (**4**). ΔE is the difference between the energy of the lowest ground state isomer and that of the corresponding transition state.

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† The CNDO scheme of R. J. Boyd and M. A. Whitehead,[5] parameterised to give geometries and bonding energies in accord with experiments, has been used. The bonding energy for the different geometric forms (**2**), (**3**), and (**4**) has been minimised with respect to all internal atomic co-ordinates. Sulphur *d*-orbitals are neglected. Thus atomic charges on sulphur and oxygen as well as S–O bond lengths are probably overestimated.[6]

‡ The CNDO bond-order definition applied here is due to R. J. Boyd, Mathematical Institute, Oxford; personal communication.

§ Calculated from the estimated half-lives cited by King and Durst.[3]

[1] E. Wedekind, D. Schenck, and R. Stüsser, *Ber.*, 1923, **56**, 633.

[2] B. Zwanenburg and J. Strating, *Quart. Reports Sulfur Chem.*, 1970, **5**, 79; B. Zwanenburg, L. Thijs, J. B. Broens, and J. Strating, *Rec. Trav. chim.*, 1972, **91**, 433, and references cited.

[3] J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 1963, **85**, 2676; *Canad. J. Chem.*, 1966, **44**, 819.

[4] R. B. Bates and G. A. Wolfe, *J. Amer. Chem. Soc.*, 1968, **90**, 6854; the 10° out-of-plane deviation observed for (**1**; X,Y = $-S{\cdot}CH_2{\cdot}CH_2{\cdot}S-$) is absent in other *X*-ray evaluations of sulphines (O. H. Jarchow, *Acta Cryst.*, 1968, **25B**, 267; B. Zwanenburg, personal communication).

[5] R. J. Boyd and M. A. Whitehead, *J. Chem. Soc.*, 1971, 3579; *J.C.S. Dalton*, 1972, 73, 78, 80.

U. Gelius, B. Roos, and P. Siegbahn, *Theor. Chim. Acta*, 1971, **23**, 59; B. Roos and P. Siegbahn, *ibid.*, p. 368.

[7] *Cf.* B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 571, give a Hückel calculation predicting a similar charge distribution.

[8] B. F. Bonini, L. Lunazzi, C. Maccagnani, and C. Mazzanti, Abstracts, Symposium on Organic Sulfur Chemistry, Lund, Sweden, June 1972.