

## PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/142130>

Please be advised that this information was generated on 2019-06-26 and may be subject to change.

ASSIGNMENT OF CONFIGURATION TO SULFINES BY MEANS OF SHIFT REAGENT AND ASIS<sup>1)</sup>

A. Tangerman and B. Zwanenburg  
Department of Organic Chemistry, University of Nijmegen,  
Toernooiveld, Nijmegen, The Netherlands

(Received in UK 27 November 1972; accepted for publication 6 December 1972)

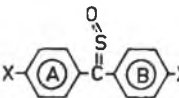
Sulfines represent a bent heterocumulenic system, as was recognized first by King and Durst<sup>2)</sup> for chloro-phenyl-sulfine (thiobenzoylchloride-S-oxide), and later also by us<sup>3)</sup> for sulfines derived from dithiocarboxylic esters and by an Italian group<sup>4)</sup> for aromatic sulfines.

The geometrical isomers of chloro-phenyl-sulfine were distinguished by means of their dipole moments<sup>2)</sup>. The Z- and E-geometry of phenyl-phenylthio-sulfines (formula III in Table II) was assigned on the basis of their NMR spectra<sup>3c)</sup>. In the E-isomer two aromatic protons (ortho-hydrogens) are shifted downfield as a consequence of their exposure to the magnetic anisotropic deshielding effect<sup>5)</sup> of the SO-part of the CSO-system, whereas the spatial position of the SO-group in the Z-isomer is such that this effect on the aromatic protons is negligible<sup>3c)</sup>. However, difficulties arise when this deshielding effect of the sulfine moiety is used to differentiate between isomeric sulfines in which hydrogens which are expected to be shifted are either obscured by other aromatic signals (e.g. as in sulfine I, Table II), or substituted by other groups, e.g. methyl groups (see Table III). Differentiation between the isomeric forms of mesityl-phenylthio-sulfine (formula III in Table II), which represents an example of the latter case, could be accomplished by comparison of dipole moments<sup>3c)</sup>.

However, determinations of dipole moments are quite laborious and require considerable amounts of material. Moreover, the method is only applicable when the groups attached to the sulfine system differ sufficiently in group dipole moment. To circumvent these problems we have been searching for a simple and reliable spectroscopic method.

As is well documented<sup>6)</sup> lanthanide complexes,  $\text{Eu}(\text{DPM})_3$  for instance, when coordinated with certain functional groups induce remarkable changes in the chemical shifts of protons. It is assumed that in sulfines  $\text{Eu}(\text{DPM})_3$  complexes at the oxygen atom of the CSO-system, just as it does in ordinary sulfoxides<sup>7)</sup>. Because the CSO-system is bent, complexation at oxygen will result in a larger shift for protons in a syn position than for those in an anti position. This statement only holds for protons which are situated in the direct environment of the CSO moiety. The effect of  $\text{Eu}(\text{DPM})_3$  on the spectra of symmetrically di-para-sub-

stituted diphenylsulfines (see Table I) demonstrates that the ortho-protons of ring A (syn protons) are shifted considerably more downfield than the ortho-protons of the B-ring (anti protons). The data also clearly reveal that for the syn and anti meta-protons the differences in  $\Delta\delta$  are negligible (presumably because of balancing of the influence of  $r_i$  and  $\theta$  in the McConnell-Robertson equation<sup>8</sup>),  $\Delta\delta = k(3\cos^2\theta - 1)/r_i^3$

Table I<sup>9</sup>) Eu(DPM)<sub>3</sub> induced shifts ( $\Delta\delta$ ) for X--X

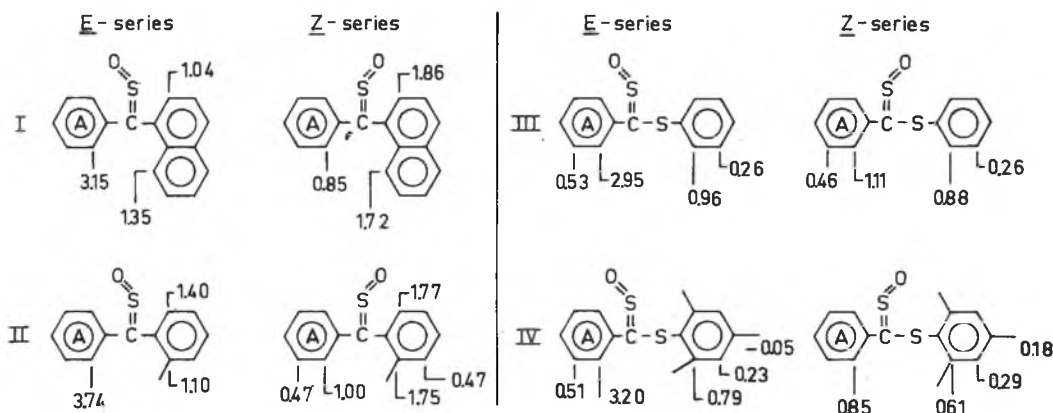
X:	<u>o</u> -H(A)	<u>o</u> -H(B)	<u>m</u> -H(A)	<u>m</u> -H(B)
H	2.77	1.00	0.40	0.40
CH <sub>3</sub>	2.95	1.11	0.42	0.38
OCH <sub>3</sub>	3.11	1.18	0.50	0.48
Cl	2.82	1.11	0.42	0.43

$$\Delta\delta = \delta[\text{CDCl}_3 + 0.3 \text{ equiv. Eu(DPM)}_3] - \delta(\text{CDCl}_3)$$

Conc. substrate: 0.12 mmole/0.5 ml CDCl<sub>3</sub>, spectra recorded with a Varian T-60.

This difference in  $\Delta\delta$  for syn and anti protons provides an excellent method of differentiating between Z- and E-isomers of sulfines. As illustrated in Table II the  $\Delta\delta$ -value for ortho-protons of the A-ring in the E-series (syn protons) is much larger than that for the ortho-protons of the A-ring in the Z-isomers (anti protons). Again, the data show that a considerable difference between syn and anti protons is only observed when they are situated in the immediate vicinity of the sulfine moiety.

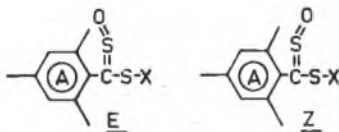
Table II<sup>10</sup>) Eu(DPM)<sub>3</sub> induced shift ( $\Delta\delta$ ) for E- and Z-sulfines



$\Delta\delta$  = see Table I; Conc 30mg/0.5 ml; Spectra were recorded with a Varian T-60

We now turn our attention to sulfoxines in which the ortho-protons are substituted by methyl groups. The results with  $\text{Eu}(\text{DPM})_3$  for mesityl substituted sulfoxines (see Table III) show that the differences in  $\Delta\delta$  for the ortho-methyl groups in the E- (syn methyls) and the Z-series (anti methyls) are much smaller than those found for the ortho-hydrogens in their unsubstituted analogs (Table II). However, these differences in  $\Delta\delta$  for the mesityl sulfoxines are still of such a magnitude that a Z or E geometry can be reliably assigned.

Table III<sup>11)</sup>  $\text{Eu}(\text{DPM})_3$  induced shifts ( $\Delta\delta$ ) for o-methyl groups.



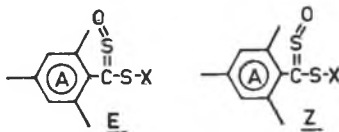
X:	phenyl	2-naphthyl	2-thienyl	ethyl
$\Delta\delta$ : <u>E</u>	1.46	1.17	0.96	1.17
.. : <u>Z</u>	0.96	0.67	0.78	0.90

$$\Delta\delta = \delta[\text{CDCl}_3 + 0.30 \text{ equiv. Eu}(\text{DPM})_3] - \delta(\text{CDCl}_3)$$

Conc. substrate: 30 mg/0.5 ml, spectra were run on a Varian A-60.

A further distinction between these isomeric mesityl-substituted sulfoxines was made by means of aromatic solvent induced shifts (ASIS). It is known<sup>12)</sup> that benzene associates with the positive end of a dipole in a molecule. Accordingly, in the E-series benzene will complex at the right-hand side of the molecule and in the Z-series at the left-hand side (formulas, see Table IV). As a consequence of this solvent molecule orientation the ortho-methyl signals in the Z-series will be shifted more to higher field than in the E-series. The results are listed in Table IV. The conclusions with respect to the geometry of the molecules are entirely consistent with those obtained with the  $\text{Eu}(\text{DPM})_3$  shift reagent.

Table IV<sup>11)</sup> ASIS for o-methyl groups.



X:	phenyl	2-naphthyl	2-thienyl	ethyl
$\Delta\delta$ : <u>E</u>	0.07	0.09	0.08	0.03
.. : <u>Z</u>	0.18	0.19	0.19	0.21

$$\Delta\delta = \delta(\text{CDCl}_3) - \delta(\text{C}_6\text{D}_6). \text{ Spectra were run on a Varian A-60.}$$

In conclusion, lanthanide induced shifts and ASIS may be useful in assigning the geometry to sulfines.

#### References and Notes

1. Part XIX in the series "Chemistry of Sulfines".  
Part XVIII, A. Tangerman and B. Zwanenburg, J.C.S. Perkin II. in press.
2. J.F. King and T. Durst, J.Amer.Chem.Soc. 85, 2676 (1963); Can.J.Chem. 44, 819 (1966).
3. B. Zwanenburg, L. Thijs and J. Strating, a: Tetrahedron Letters. 3453 (1967); b: 2871 (1968); c: Rec.Trav.Chim. 90, 614 (1971).
4. S. Ghersetti, L. Lunazzi, G. Maccagnani and A. Mangini, Chem.Comm. 834 (1969).
5. B. Zwanenburg, L. Thijs and A. Tangerman, Tetrahedron. 27, 1731 (1971).
6. R. von Ammon and R.D. Fischer, Angew.Chem. 84, 737 (1972).
7. R.R. Fraser and Y.Y. Wigfield, Chem.Comm. 1471 (1970); K.K. Andersen and J.J. Uebel, Tetrahedron Letters. 5253 (1970); M. Kishi, K. Tori and T. Komeno, ibid. 3525 (1971).
8. H. McConnell and R.E. Robertson, J.Chem.Phys. 29, 1361 (1958).
9. For the preparation of these sulfines, see ref.5.
10. The new sulfines I and IV were prepared from the corresponding thiones by oxidation with m-chloroperbenzoic acid (cf.ref.3c and 5); the sulfines II were kindly supplied by Professor Maccagnani.
11. For the preparation of these sulfines, see ref.1 (part XVIII of this series) and ref.3c.
12. J. Ronayne and D.M. Williams, J.Chem.Soc.(B), 540 (1967).