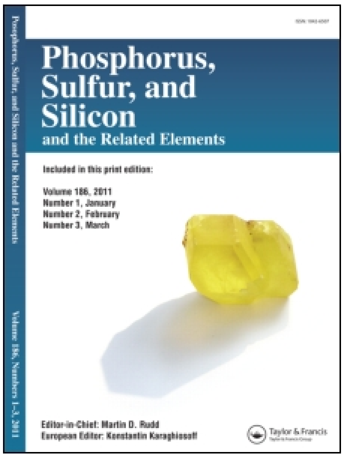

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AN NMR STUDY OF THE PROTONS IN α-ALKYLTHIOSULFOXIDES, $RS(O)CH_2SR$

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AN NMR STUDY OF THE PROTONS IN α-ALKYLTHIOSULFOXIDES, RS(O)CH$_2$SR

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By means of nmr studies, including lanthanide shift experiments, the two "R's" in Structure (I) (**a**, R = Methyl; **b**, R = *tert*-Butyl) have been assigned. The alkyl group at lower field in each case is attributed to the one adjacent to the sulfoxide. The diastereotopic protons in (**Ia**) are less well resolved than those in (**Ib**), and their separation is concentration-dependent, an observation suggesting the importance of association in (**Ia**). On the basis of a simple conformational analysis, the diastereotopic protons in (**Ib**) can be assigned in relationship to the chiral sulfoxide center.

INTRODUCTION

Compounds of the general structure (**I**) have become of interest since they were first reported by Ogura and Tsuchihashi,[1] who showed they could be monoalkylated at the methylene position. Because these alkylated derivatives can be hydrolyzed under mild conditions to the corresponding aldehydes, this synthetic method is advantageous over the Corey–Seebach route.[2] Now a variety of compounds of the structure (**I**) have been prepared,[3] and in a few special cases they can serve as synthons for ketones[4] as well as aldehydes.

$R\overset{O}{\overset{\|}{S}}CH_2SR$

(**Ia**) (R = Methyl)
(**b**) (R = *tert*-Butyl)

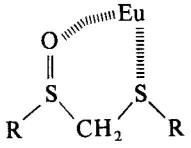
Ogura and Tsuchihashi first reported the nmr spectrum of (**Ia**) as one consisting of three singlets: two attributed to the two "R" methyl groups (but unassigned) and the third to the methylene protons.[1] It would be expected, however, that the diastereotopic methylene protons would appear as an AB quartet rather than a singlet. It was thus the purpose of the present investigation to carry out experiments to assign the chemical shifts to "R" and to explore the nmr behavior of the diastereotopic protons in (**I**).

RESULTS AND DISCUSSION

Assignment of Chemical Shifts to R

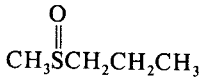
Chosen for study were two examples of structure (**I**): (**Ia**) (R = Methyl); and (**Ib**) (R = *tert*-Butyl).

Chemical shifts for the R groups, with and without Europium shift reagent, were measured as described in the Experimental Section. Of particular significance is the marked difference in shift of the two R's, especially in (**Ia**), as depicted in Figures 1 and 2. Because sulfoxides are known to be strong coordinating ligands, whereas sulfides are weak,[5] it is reasonable to conclude that the lower field singlet in each compound is adjacent to the sulfoxide, inasmuch as it is the peak which shifts downfield more sharply. The alternative chelating arrangement (**II**) seems less likely.



(**II**)

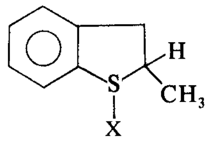
As a basis for comparison, we examined the magnitude of lanthanide induced shift (LIS) in methyl *n*-propyl sulfoxide(**III**). In accord with the assignments in (**Ia**) and (**Ib**), the lower field, singlet methyl in (**III**) underwent a larger shift, approaching a value of 6 ppm at a rho value of 1. The methyl protons from the *n*-propyl group in (**III**) (a triplet), underwent a shift of only 2 ppm at the same rho value. These shifts are comparable to those of (**Ia**), 5.4 ppm and 2.5 ppm, respectively, and thus argue against any significant contribution from structure (**II**).


$CH_3\overset{O}{\overset{\|}{S}}CH_2CH_2CH_3$

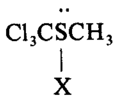
(δ2.32) (δ0.94)

(**III**)

The assignment of the lower field singlet to the R adjacent to sulfoxide in (**Ia**) and (**Ib**) is also supported by examination of some model compounds. Andersen, Caret, and Karup-Nielsen[6] have already noted that conversion of the sulfide (**IVa**) to sulfoxide (**IVb**) causes a downfield shift in both the α-methinyl and 2-methyl protons. A similar situation prevails in the case of Compounds (**Va**) and (**Vb**). We prepared (**Va**) as previously described[7] and found its chemical shift to be 1.96 ppm; the corresponding sulfoxide (**Vb**) has already been reported at 2.84 ppm.[8]



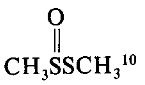
(**IVa**) (X = :)
(**b**) (X = 0)

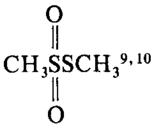

$Cl_3C\overset{..}{S}CH_3$, with X on S

(**Va**) (X = :)
(**b**) (X = 0)

It is interesting to note that this general downfield shift with increasing oxidation state of sulfur[9] seems to hold for compounds containing the S–S bond, as well. Representative examples in the methyl series, together with their chemical shifts (all singlets), are as follows.

CH_3SSCH_3[9]


$CH_3\overset{O}{\overset{\|}{S}}SCH_3$[10]


$CH_3\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}SCH_3$[9,10]

(δ2.30) (δ2.92) (δ2.52) (δ3.20) (δ2.60)

The Diastereotopic Protons in (*I*)

We have found that the splitting of the diastereotopic protons in (**Ia**) is concentration-dependent. They appear essentially unresolved as a broad singlet when measured in 10–20% CCl_4 solution; presumably the spectrum reported by Ogura and Tsuchihashi was taken under similar conditions. As the concentration of (**Ia**) increases, however, the peak becomes separated into an AB pattern. The first-order J value for a 70% (about 2.5 molar) solution is 12 Hz, and this is the case for the neat sample as well. In striking contrast, the diastereotopic protons in (**Ib**) appear as a well resolved AB quartet ($J = 15$ Hz) at concentrations ranging from 10–70% in CCl_4.

These results suggest the importance of association in the methyl compound (**Ia**). The associated structure must be such that the diastereotopic protons are situated in relatively different positions and are thus distinguishable. If one assumes that the dimerization results from a head-to-tail arrangement between the two sulfoxide bonds, as is the case for dimethyl sulfoxide,[11] then the sulfoxide–sulfur atoms take on a distorted trigonal bipyramidal geometry. In a molecular model of this dimer, with O and lone pair in axial positions, there appears to be substantial preference for some rotamers about the S(O)—CH_2 bonds. In the favorable rotamers, one of the two diastereotopic protons is eclipsed with the dimeric bridge, whereas the other is removed from it.

Lanthanide shift studies on the diastereotopic protons in (**Ia**) and (**Ib**) were most revealing. Results are represented in Figures 1 and 2. In the case of (**Ia**), where the two protons are less distinct, $Eu(fod)_3$ affects both about equally, the difference in shift for the two protons ($\Delta\delta$) being virtually constant. On the other hand, the two diastereotopic protons in (**Ib**) are shifted to different extents and diverge as the molar ratio $[Eu(fod)_3]/[S]$ increases. Furthermore, the two protons in (**Ib**) cross over at $\rho = 0.3$. Thus,

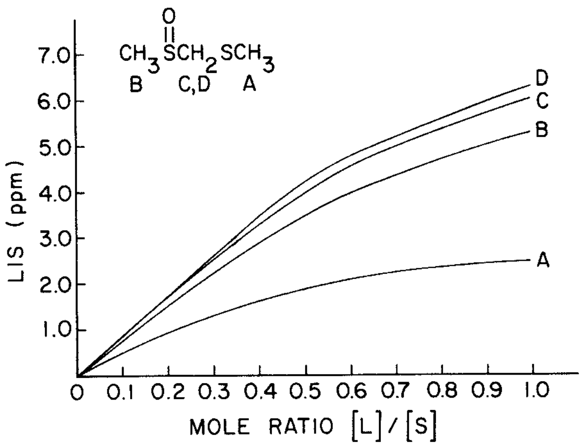


FIGURE 1 Lanthanide-induced Shifts in (**Ia**) with $Eu(fod)_3(CCl_4)$.

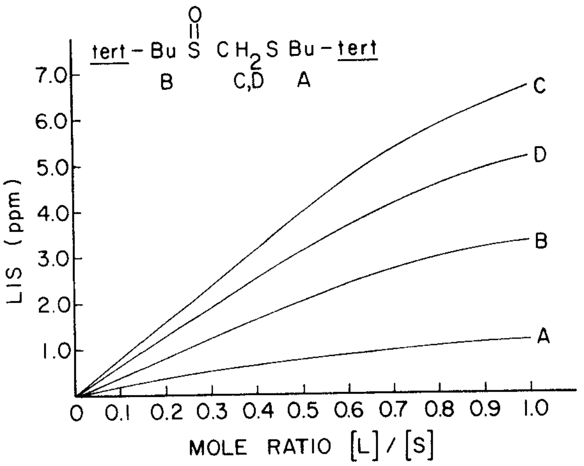
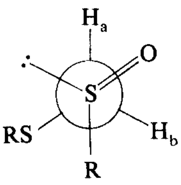
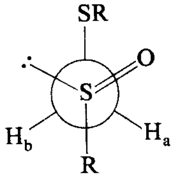


FIGURE 2 Lanthanide-induced Shifts in (**Ib**) with Eu(fod)$_3$(CCl$_4$).

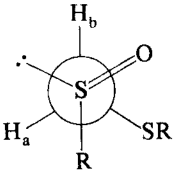
the higher-field proton at $\rho = 0$ becomes the lower-field proton as the Europium concentration increases. No such crossing over is observed in the methyl compound. This suggests a substantial conformational bias in the case of the *tert*-butyl compound.



A



B



C

It is reasonable to assume that B is the favored staggered conformer over A and C in (**Ib**) (R = *tert*-butyl). According to earlier studies,[12] the H_a proton in this conformation should be at higher field than H_b. Yet, placement of the Europium at any reasonable location[13] leads to the prediction that H_a should be shifted downfield preferentially over H_b. At sufficiently high Europium concentration its effect would predominate, H_a appearing at lower field. If we further make the reasonable assumption that there is less conformational preference among A, B, and C in (**Ia**) (R = methyl), then it follows that there would be less distinction between H_a and H_b. It would appear that effects of conformation and induced shifts tend to compensate one another, there being no crossover in (**Ia**).

The conformations A, B, C are represented for only the R enantiomer of (**I**). On the basis of the above reasoning for (**Ib**), the diastereotopic protons can be assigned from their lanthanide-induced shifts. In the R-sulfoxide, the pro-R hydrogen is the one shifted eventually to lower field; in the S-sulfoxide, the pro-S hydrogen shows similar behavior.

EXPERIMENTAL

Materials. Compound (**Ia**) was obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. (**Ib**) was prepared as previously described.[4] Methyl *n*-propyl sulfoxide was kindly supplied by K. K. Andersen. The lanthanide shift reagent was either Resolve-Al EuFOD™ (Aldrich) or Euroshift-F (Pierce Chemical Company, Rockford, Illinois).

NMR Experiments. Spectra were measured on a JEOL JMN-MH-100 spectrometer in carbon tetrachloride at ambient temperature, with TMS as internal standard. Lanthanide shift experiments were carried out by preparing initially a solution of Eu(fod)$_3$ and (**Ia**) or (**Ib**) with $\rho = 1$. Then aliquots of a stock solution of (**Ia**) or (**Ib**) were added.

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REFERENCES AND NOTES

1. K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.* 3151 (1971).
2. E. J. Corey and D. Seebach, *Angew. Chem.* **77**, 1134 (1965).
3. J. E. Richman, J. L. Hermann and R. H. Schlessinger, *Tetrahedron Lett.* 3267 (1973).
4. G. Schill and P. R. Jones, *Synthesis* 117 (1974).
5. (a) B. C. Mayo, *Chem. Soc. Rev.* **2**, 49 (1973); (b) O. Hofer in "Topics in Stereochemistry", N. L. Allinger and E. L. Eliel, Ed., Vol. 9, p. 111, Wiley Interscience, New York, 1976. (c) T. C. Morrill, R. J. Optiz and R. Mozzer, *Tetrahedron Lett.* 3715 (1973).
6. K. K. Andersen, R. L. Caret and I. Karup-Nielsen, *J. Amer. Chem. Soc.* **96**, 8026 (1974).
7. W. E. Truce, G. H. Birum and E. T. McBee, *J. Amer. Chem. Soc.* **74**, 3594 (1952).
8. V. D. Martin, A. Berger and R. Peschel, *J. Prakt. Chem.* **312**, 683 (1970).
9. G. R. Pettit, I. B. Douglass and R. A. Hill, *Can. J. Chem.* **42**, 2357 (1964).
10. T. L. Moore and D. E. O'Connor, *J. Org. Chem.* **31**, 3587 (1966).
11. R. Thomas, C. B. Shoemaker and K. Eriks, *Acta Crystallogr.* **21**, 12 (1966).
12. (a) J. B. Lambert and R. G. Keske, *J. Org. Chem.* **31**, 3429 (1966); (b) B. J. Hutchinson, K. K. Andersen and A. R. Katritzky, *J. Amer. Chem. Soc.* **91**, 3839 (1969).
13. R. M. Wing, J. J. Uebel and K. K. Andersen, *J. Amer. Chem. Soc.* **95**, 6046 (1973).