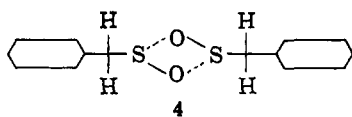


Figure 1. Methylene p.m.r. signals (60 Mc.) from 2-thiaindane 2-oxide (**1**) at various temperatures. Curve at 200° from melt of **1**, others from CDCl_3 solutions; c.p.s. measured downfield from TMS.

we have now found that sulfoxide **1** in cyclohexane causes a molal freezing point depression of just one-half the normal value (20°) for that solvent.⁴

As temperature decreases the intimacy of this bimolecular association of **1** must increase, apparently in such a manner as to decrease the chemical shift between H_c and H_t . Since these protons are symmetrically related to the aromatic ring, the chemical shift between them is a consequence of the distinction between the spatial orientations of sulfoxide oxygen relative to them,⁵ and hence Figure 1 shows that at a sufficiently low temperature H_c and H_t must be in an environment of essentially equivalently oriented oxygen atoms.



Our interpretation of these observations is the assignment to **1** of a dimeric structure tentatively depicted by **4**. The bonding of the dimer represented by dotted lines in **4** may be simply electrostatic, *i.e.*, dipole-dipole interaction of the two S-O groups, but these dotted lines could also represent some covalency, *i.e.*, $(3d\sigma)_S-(2p\sigma)_O$ overlap. We do not propose that the dotted and solid lines in the four-membered ring of **4** are equivalent.⁶ Thus it seems likely that with decrease in the temperature of the dimer the consequent decrease in torsional oscillations of the sulfoxide group may contribute to the elimination of a chemical

Nuclear Magnetic Resonance Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 99.

(4) Other workers have also recently noted the dimeric association of other sulfoxides in hydrocarbon medium [K. Mislow, M. M. Green, P. Lauer, and D. R. Chisholm, *J. Am. Chem. Soc.*, **87**, 665 (1965)] and in carbon tetrachloride (C. D. Ritchie, unpublished observations).

(5) Reference 3, p. 165 ff.

(6) The equivalency or equilibration of these four bonds would result in inversion of the sulfoxide geometry, which does not occur.

shift difference between H_c and H_t . Even so, the structural environment of each methylenic proton in the dimer must be essentially identical; the singlet methylene signal shown in Figure 1 is quite narrow (as narrow as that signal from the symmetrical sulfone **3**) and, at -37° , the singlet does not broaden even when the sulfoxide is in quite dilute CDCl_3 solution.⁷

Acknowledgment. This work was generously supported by a grant from the Research Corporation of America.

(7) Decrease in the chemical shift (δ) between H_c and H_t still occurs with decreasing temperature, ultimately to coalesce, even when only enough CDCl_3 is added to prevent its solidification (*ca.* an equimolar amount of chloroform). In carbon tetrachloride **1** shows the same decrease in δ with temperature, but the solution freezes just before coalescence. However, in D_2O and in dimethyl sulfoxide δ remains constant with temperature change, as would be expected if solvation by these very polar solvents prevented **1** from dimerizing.

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Optical Rotatory Dispersion and Absolute Configuration of Dialkyl Sulfoxides¹

Sir:

Our interest in the relation between structure and optical rotatory power of sulfoxides² has prompted a

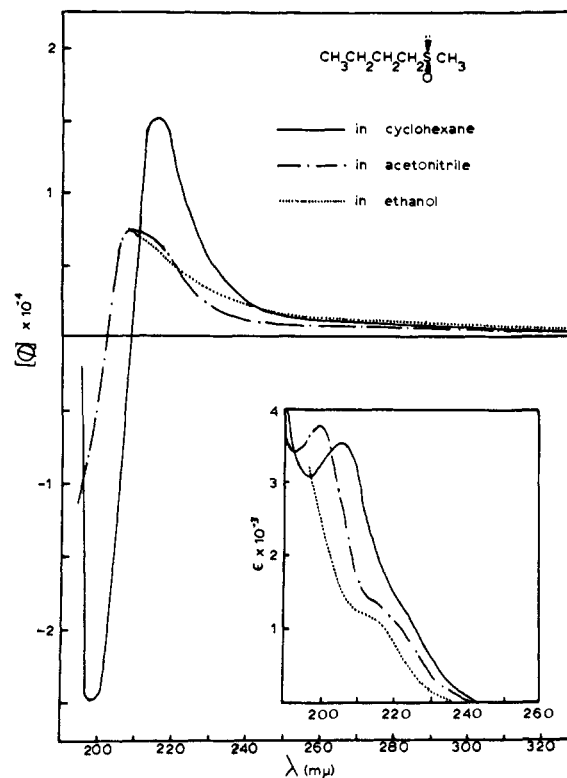


Figure 1. Spectra and o.r.d. curves (corrected to optical purity) of methyl *n*-butyl sulfoxide. Values of $[\phi]$ and ϵ are calculated on the basis of monomeric species.

(1) We gratefully acknowledge support by the National Science Foundation (GP-3375).

(2) K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 2329 (1963).

study of the optical rotatory dispersion (o.r.d.) of (+)-methyl *n*-butyl sulfoxide (I). A Cotton effect is found to be centered at the absorption maximum below 210 $m\mu$ whose solvent dependence (Figure 1) characterizes it as an $n \rightarrow \pi^*$ transition³; in contrast, the shoulder near 215 $m\mu$ is relatively solvent insensitive.⁴ We have found by vapor pressure osmometry⁵ (v.p.o.) at 37° that, whereas I is monomeric in ethanol and acetonitrile, it is *dimeric* in cyclohexane; over the range from 0.018 to 0.055 *M* the dimerization appears to be essentially complete.⁶ It has previously been reported that sulfoxides associate in solution.^{7,8} We therefore cannot rule out at present the possibility that the absorption spectrum (and o.r.d.) of I in cyclohexane is that of the dimer or a composite of monomer and dimer.⁹

The previously proposed² classification of optically active dialkyl sulfoxide chromophores as "asymmetrically perturbed symmetric" was based on the presumption that this system could be usefully discussed from a viewpoint analogous to that employed in the treatment of saturated ketones.¹⁰ In light of the unexpectedly high amplitude of the Cotton effect of I, this approach, which is eminently successful for aromatic sulfoxides,¹¹ may have to be modified in the case of dialkyl sulfoxides.

Sulfoxide I, $[\alpha]_D +42^\circ$ (isooctane), was prepared by reaction of an excess of methylmagnesium bromide with a diastereomeric mixture of *l*-menthyl 1-butanesulfinates, $[\alpha]_D -50^\circ$ (acetone), which was obtained by asymmetric synthesis from racemic 1-butanesulfinyl chloride.¹² *p*-Tolyl *n*-butyl sulfoxide, $[\alpha]_D +88^\circ$ (acetone), was prepared by reaction of an excess of *p*-tolylmagnesium bromide with the same diastereomeric mixture. Since the ratio of diastereomers in the starting material equals the ratio of enantiomers in the product,¹² and since optically pure *p*-tolyl *n*-butyl sulfoxide has $[\alpha]_D +187^\circ$ (acetone),¹² the optical purity of (+)-I is 47%. Assuming inversion in the Grignard reaction¹³ and given the absolute configuration of

(3) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(4) Further studies of this problem are in progress. For previous work on the absorption spectra of dialkyl sulfoxides see H. P. Koch, *J. Chem. Soc.*, 2892 (1950), and ref. 18.

(5) C. Tomlinson, *Microchim. Acta*, 457 (1961).

(6) In contrast, we find that aryl alkyl and diaryl sulfoxides are essentially monomeric in cyclohexane in that concentration range. The effect of structure on the association of sulfoxides is being investigated further.

(7) DMSO forms association polymers in the neat state (H. L. Schläfer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960)) and in benzene solution (J. J. Lindberg, J. Kenttämaa, and A. Nissema, *Suomen Kemistilehti*, **B34**, 98, 156 (1961)), and it appears to dimerize in carbon tetrachloride solution (C. D. Ritchie, unpublished observations; we are grateful to Professor C. D. Ritchie for informing us of his results prior to publication).

(8) 2-Thiaindan 2-oxide exists as a dimer in cyclohexane (R. F. Watson and J. F. Eastham, *J. Am. Chem. Soc.*, **87**, 664 (1965)).

(9) We find adherence to Beer's and Biot's laws in the spectrometrically accessible region over the concentration range of ca. 10^{-2} *M* to ca. 10^{-4} *M*. However, since the spectroscopic properties of monomeric and dimeric species may be similar, this result is in the nature of negative evidence. It is noteworthy that I has λ_{max} 205 $m\mu$ and 193 $m\mu$ in the vapor phase, where it is presumably monomeric, whereas I in cyclohexane lacks the maximum at shorter wave lengths (as investigated down to 186 $m\mu$).

(10) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(11) Aryl alkyl sulfoxides have been discussed from the viewpoint of inherently dissymmetric chromophores²; diaryl sulfoxides may be profitably discussed from either point of view, depending on the structure (unpublished results).

(12) E. B. Fleischer, M. Axelrod, M. Green, and K. Mislow, *J. Am. Chem. Soc.*, **86**, 3395 (1964).

(13) K. K. Andersen, *Tetrahedron Letters*, No. 3, 93 (1962); *J. Org. Chem.*, **29**, 1953 (1964).

starting material,¹² the absolute configuration of (+)-I is (*S*).

Absolute configurations may now be assigned to other methyl alkyl sulfoxides by comparison of o.r.d. curves with that of I. Thus, the methyl alkyl sulfoxides studied by Klyne, *et al.*,¹⁴ have negative plain curves which are tails of negative sulfoxide Cotton effects¹⁵ centered near 203 $m\mu$ (acetonitrile); these compounds therefore have the (*R*)-configuration.¹⁶ Similarly, since (–)-*L*-sulphoraphane^{17–19} ($\text{CH}_3\text{SO}(\text{CH}_2)_4\text{NCS}$) has a negative Cotton effect²⁰ and therefore has the (*R*)-configuration,¹⁶ the arbitrary *D* and *L* nomenclature adopted for derivatives of this compound¹⁷ may now be abandoned.

Our work on sulfoxides is continuing.

(14) W. Klyne, J. Day, and A. Kjaer, *Acta Chem. Scand.*, **14**, 215 (1960).

(15) As determined in these Laboratories on $\text{CH}_3\text{SO}(\text{CH}_2)_5\text{NHCSNH}_2$. We are indebted to Professor W. Klyne for a sample of this material.

(16) Professor A. Kjaer has kindly informed us that the same conclusion has been arrived at independently by X-ray analysis.

(17) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **31**, 1497 (1948).

(18) P. Karrer, N. J. Antia, and R. Schwyzer, *ibid.*, **34**, 1392 (1951).

(19) We are indebted to Dr. Ž. Procházka for a sample of this material.

(20) As judged by the o.r.d. above 225 $m\mu$ (J. T. Melillo, Ph.D. Dissertation, New York University, 1964).

(21) N.I.H. Predoctoral Fellow, 1964–1965.

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Diastereoisomerism in 9-Dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene

Sir:

In 1953 Wittig and Zimmermann reported¹ the isolation of two diastereomers of amine II upon reaction of azepinium bromide I with phenyllithium in ether and with potassium amide in liquid ammonia, respectively. However, the claimed¹ isolation of the separate diastereomers of amine II by distillation at elevated temperatures (116–119°) is not compatible with the demonstrated optical instability of the 9,10-dihydro-4,5-dimethylphenanthrene system.² We have reinvestigated the work of Wittig and Zimmermann¹ and have obtained results which are at variance with their report and which confirm our earlier views.²

Reaction of (+)-(*S*)-I³ with phenyllithium in ether gave II, a basic oil (74%, b.p. ca. 130° (0.07 mm)). The oil crystallized, neat or from methanol, to give a material (IIA, m.p. 82–85°; *Anal.* Found: C, 85.96; H, 8.48; N, 5.31) which mutarotated in toluene. The mutarotation followed strict first-order kinetics with $k^{32.8} = 3.3 \times 10^{-4} \text{ sec}^{-1}$. Extrapolation from three mutarotation experiments to zero time gave values for the initial rotation of $[\alpha]^{32.8}_{435} +566$ to $+607^\circ$. In repetitions of this experiment starting from (+)-(*S*)-I, another crystalline substance was fortuitously obtained (IIB, m.p. 85–90°; *Anal.* Found: C, 86.24; H, 8.69; N, 5.72), which mutarotated in toluene with $k^{32.8} = 3.4 \times 10^{-4} \text{ sec}^{-1}$. However, extrapolation to zero

(1) G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953).

(2) K. Mislow and H. B. Hopps, *J. Am. Chem. Soc.*, **84**, 3018 (1962).

(3) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *ibid.*, **86**, 1710 (1964).