ture through reasonable variations of the torsional and van der Waals potentials failed to reduce appreciably the discrepancy noted above. The polar character of the polypeptide molecule suggested investigation of the influence on the chain configuration of dipolar interactions between peptide units. The charge distribution within the peptide groups has been expressed by associating with each such group a point dipole moment vector of magnitude 3.7 D. This vector, shown as μ in Figure 1, is located in the plane of the peptide unit at the midpoint of the peptide bond. It makes an angle of 56° with this bond and points in the N–H direction. The assigned magnitude is consistent with the observed dipole moments of a number of alkyl amides[10]; the orientation specified above is suggested by the sum of peptide group bond moments[11] and supported by the observed dipole moment vector in formamide.[12] If the dielectric constant is assigned the value 3.5, then differences in nearest neighbor interaction energies as large as 3 kcal./mole occur for sets of discrete rotation angles which are not excluded by steric repulsions. Energy differences of this magnitude make decisive contributions to the rotational potential function. Calculations of the characteristic ratio carried out using rotational potentials which include the dipole–dipole contributions to the energy are in satisfactory agreement with the experimental results quoted above.

The strong influence of dipole interactions on the unperturbed polypeptide coil dimensions suggests that similar effects may play an important role in ordered polypeptide configurations as well. We have accordingly calculated the total dipole interaction energy for a peptide unit within and at the ends of α-helical sequences. Interactions between helix and coil units are ignored while those between peptide dipoles in the helix separated by more than 20 units in the chain sequence are found to be negligible. If the effective dielectric constant is again chosen to be 3.5, a peptide unit buried in a long α-helical sequence experiences a favorable dipole interaction energy of about -1.2 kcal./mole. This value does not, however, represent the net dipole contribution to the Zimm and Bragg[13] helix stability parameter, s, which must be estimated with reference to the average dipole energy for the random coil. Preliminary calculations suggest that dipole interactions are particularly important with respect to the parameter σ characterizing helix–coil junctions. These results will be included in a paper in preparation.

(10) R. M. Meighan and R. H. Cole, *J. Phys. Chem.*, **68**, 503 (1964).
(11) A. Wada, "Polyamino Acids, Polypeptides and Proteins," M. A. Stahmann, Ed., University of Wisconsin Press, Madison, Wis., 1962, p. 131.
(12) R. J. Kurland and E. B. Wilson, Jr., *J. Chem. Phys.*, **27**, 585 (1957).
(13) B. H. Zimm and J. K. Bragg, *ibid.*, **31**, 526 (1959).

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Dimeric Structure of a Sulfoxide

Sir:

Extensive current interest in the stereochemistry of sulfoxides has concerned various configurational equilibrations of this group. Recent communications[1] which have reported the inversion of configuration of the sulfoxide group by acid catalysis[1a,b] and by thermal isomerization[1c,d] prompt us to report an interesting and related observation made with the sulfoxide **1**, 2-thiaindan 2-oxide.
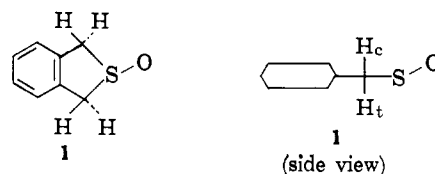
It had occurred to us that this compound might be well suited to nuclear magnetic resonance studies of the inversion of the sulfoxide group. This system (**1**) should possess two types of n.m.r.-distinguishable methylenic hydrogens, the pairs cis and trans (H_c and H_t) to the oxygen of the sulfoxide group, which should yield a proton resonance "quartet"—actually two doublets, 2(AB).[2] It was conceived that under the proper conditions of temperature and acidity, rapid inversion of the sulfur–oxygen bond might be obtained producing a symmetrical environment for the methylenic hydrogens and a singlet n.m.r. signal.

The spectrum (Figure 1) at room temperature of the methylenic hydrogens of 2-thiaindan 2-oxide does consist of a quartet, which may be contrasted with the singlet signals obtained from the analogous but symmetrical systems of 2-thiaindan (**2**) and 2-thiaindan 2,2-dioxide (**3**). The quarter was observed to coalesce
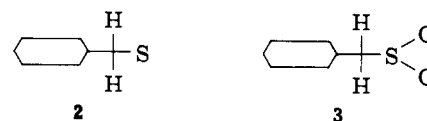
to a singlet at room temperature in the presence of a 50% solution of deuterated trifluoroacetic acid in deuterium oxide. However, the interesting observation we wish to discuss here concerns a purely thermal effect on the methylenic n.m.r. signal of **1**.

N.m.r. spectra of **1** were obtained at temperatures ranging from $-50°$ to $+200°$. It was expected that at sufficiently elevated temperatures a purely thermal inversion of sulfoxide might occur and be revealed by coalescence of the methylene quartet. This coalescence was not observed, but conversely the splitting appeared more pronounced at 200°. Most startling of all, *the signal was observed to coalesce at low temperatures*, yielding finally a single sharp peak at $-37°$. These results suggested to us the possibility of some type of association between sulfoxide molecules.[3] Indeed,

(1) *Cf.* (a) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **86**, 2935 (1964); (b) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, **86**, 1452 (1964); (c) H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1964); (d) K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 2957 (1964); (e) J. C. Martin and J. J. Vevel, *ibid.*, **86**, 2936 (1964); and numerous additional references cited in these.
(2) For recent leading references to factors influencing the AB pattern of a methylene group see G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964), and K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *ibid.*, **86**, 1710 (1964).
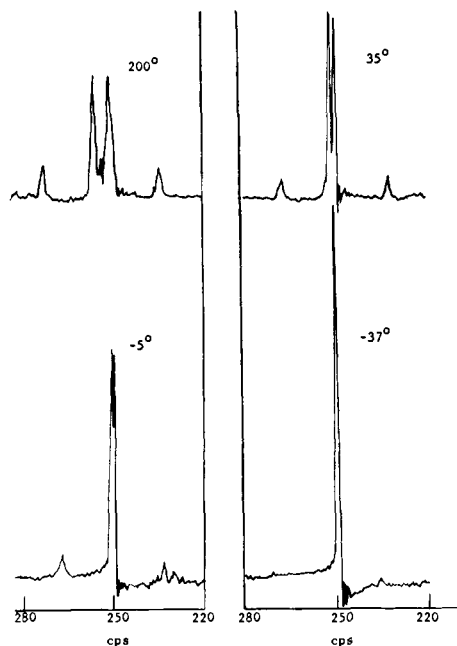(3) J. A. Pople, W. G. Schneider, and H. Bernstein, "High Resolution

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 CDCl₃ solutions; c.p.s. measured downfield from TMS.

we have now found that sulfoxide **1** in cyclohexan: 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.

4
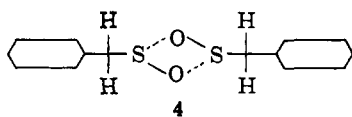
Our interpretation of these observations is the assignment to **1** of a dimeric structure tentatively depicted by **4**. The bonding of the dimer represented by dotted lines in **4** may be simply electrostatic, i.e., dipole-dipole interaction of the two S–O groups, but these dotted lines could also 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 CDCl₃ solution.[7]

(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 CDCl₃ is added to **1** 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 D₂O 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 Sulfoxides[1]

Sir:

Our interest in the relation between structure and optical rotatory power of sulfoxides[2] has prompted a
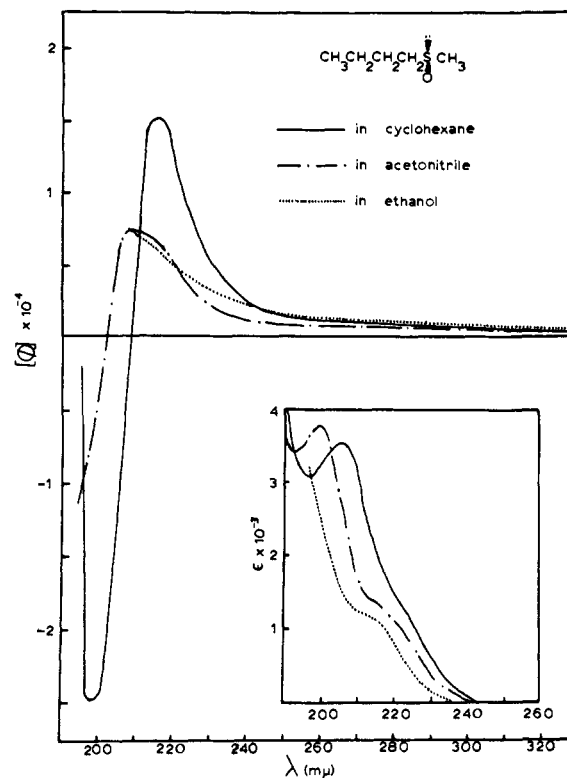

Figure 1. Spectra and o.r.d. curves (corrected to optical purity) of methyl *n*-butyl sulfoxide. Values of [φ] and ε are calculated on the basis of monomeric species.

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