

THE NUCLEAR MAGNETIC RESONANCE SPECTRUM OF N-METHYL SULFINAMIDES-
A MODEL FOR THE SULFINYL CARBANION-

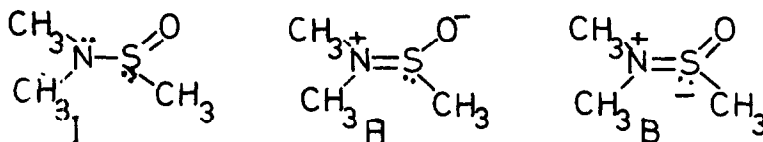
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While convincing evidence exists for the fact that the conjugative ability of the sulfinyl group is very close to that of the sulfonyl group,¹ the conformational requirements for $p\pi-d\pi$ delocalization of anionic species in the sulfinyl series have not been clearly defined. A related fact is the marked difference in optical stability of the sulfonyl carbanion^{2,3,4} relative to the sulfinyl carbanion.⁵ The sulfonyl carbanion is best described as intrinsically asymmetric possessing^{2,3} Case II geometry;⁶ no comparable model has been suggested for the sulfinyl carbanion.

The nuclear magnetic resonance method has proven useful for the detection and estimation of the barrier to internal rotation about the $\ddot{N}-CO$ bond of the amido group.⁷ This barrier arises from $p\pi-p\pi$ delocalization resulting in interconverting, planar rotamers.⁸ Applied to the sulfinamido group, analogous delocalization would involve $p\pi-d\pi$ overlap. The possible conformational consequences of such overlap, similarly, could be probed by means of temperature vs. signal measurements in the n.m.r. Further interest in such a study stems from the isoelectronic relationship of the sulfinamido, $\ddot{N}SO$, and the sulfinyl carbanion, $\bar{C}-SO$. Delocalization of the lone pair of electrons on nitrogen into the available d-orbitals of sulfur in N,N-dimethylmethanesulfinamide (I) may be represented by resonance structures A and B:



The shortened sulfur nitrogen bond of sulfur nitride, S_4N_4 , 1.62\AA observed compared to 1.7\AA , has been attributed to N=S contribution. Similar delocalization has been suggested for $S_4N_4H_4$.^{9,10} The electron accepting ability of the diffused 3d orbitals of sulfur in the $-\text{NSO}-$ group would be enhanced relative to $-\text{S}-\ddot{\text{N}}-$ due to the electro-negative oxygen atom attached to the sulfur atom.

NUCLEAR MAGNETIC RESONANCE SPECTRA OF N,N-DIMETHYLMETHANE-SULFINAMIDE (I), N,N-METHYLCYCLOHEXYLMETHANESULFINAMIDE (II), AND N,N-DIMETHYL-p-TOLUENESULFINAMIDE (III)^a AT 25° AND -60° .

Compound	Solvent	S-CH ₃ (δ)	N(CH ₃) ₂ (δ)
I	Neat	2.50	2.68
	Deuteriochloroform ^b	2.50	2.68
	Pyridine	2.08	2.28
	Benzene	1.75	2.02
II	Deuteriochloroform ^b	2.59	2.70
III	Carbon tetrachloride		2.60
	Deuteriochloroform ^b		2.69

- a) Spectra were recorded at $\nu=60.0$ Mc. on Varian A-60 spectrophotometer. Band positions are given in relation to tetramethylsilane and expressed in δ units.
- b) No change in band position or multiplicity was observed for I, II or III upon progressive cooling to -60° .

The n.m.r. spectra of N,N-dimethylmethanesulfonamide (I),¹¹ N-methylcyclohexylmethanesulfonamide (II)¹¹ and N,N-dimethyl-p-toluenesulfonamide (III)¹¹ are presented in Table I. Both the N-methyl groups and S-methyl group of I appear as sharp singlet peaks at room temperature and when cooled to -60° in deuteriochloroform.

Pyridine and benzene were used as solvent in order to check the possibility of accidental identity of the N-methyl rotamer peaks.¹³ No change in the multiplicity of the methyl peaks was observed in these aromatic solvents. The more highly hindered N,N-methylcyclohexyl-methanesulfonamide (II) also showed singlet methyl absorption even at -60° . Similarly, N,N-dimethyl-p-toluenesulfonamide (III) displayed singlet N-methyl resonance which broadened only slightly at -50° .

The magnetic equivalence of the N-methyl groups in I and II at temperatures as low as -60° is in agreement with the belief that $p\pi-d\pi$ overlap does not have any strict conformational requirements. This is due to the multiple degeneracy of the sulfur d orbitals. One orientation for N-S $p\pi-d\pi$ overlap may be converted to a second by rotation of the p -orbital on nitrogen through about 90° with respect to the XZ plane of the sulfur d orbitals. In contrast to the planar structure required for $2p\pi-2p\pi$ or $2p\pi-\rightarrow p\pi$ delocalization, only little overlap is lost by rotation about the N-S bond. With appropriate $p-d$ hybridization of the sulfur orbitals, positions of maximum overlap for $p\pi-d\pi$ delocalization are separated by only small angular increments with considerable overlap at all intermediary conformations. An apparently significant conclusion which may be drawn is that essentially free rotation may exist in this system with continuous and effective overlap.

Application of this picture to the sulfinyl carbanion may help to account for its symmetry properties. One would be led to emphasize environmental effects such as asymmetric solvation rather than intrinsic asymmetry in discussing differences in the ratio of deuterium exchange and racemization. Of course, any comparison between the sulfonamido group and the sulfinyl carbanion must be qualified due to the vastly different chemical environments of the two species. Undoubtedly, hydrogen bonding (in hydroxylic solvents) and the presence of full charges effect the nature of the anion relative to the amide; however, we feel that the above results may indicate a close geometric similarity between the two.

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- N,N-Dimethylmethanesulfonamide (I) b.p. 31-32° / 0.20 mm n²⁵_D 1.4633 and N,N-methylcyclohexylmethanesulfonamide (II) 85° / 0.20 mm., mp. ca 32° were prepared by treatment of the amine with methanesulfonyl chloride¹² in ether at -30°. N,N-Dimethyl-p-toluenesulfonamide (III)¹³ was prepared from dimethylamine and p-toluenesulfonyl chloride.¹⁴ Acceptable analyses for the new compounds (I, II) were obtained.
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