vent methanol was redistilled, b.p. 64.7°. Inorganic chemicals including cupric nitrate were used without further purification of the commercial chemicals of guaranteed grade.

Stoichiometry.—The same procedure previously reported[1] was employed for the examination of the stoichiometry of the reaction in the presence of cupric salts. Phenylhydroxylamine (1.2200 g., 0.01118 mole) with 0.001028 *M* cupric nitrate (20 ml.) gave azoxybenzene (1.0514 g., 0.00531 mole, m.p. 35.8°) on exposure to air for 29 hr. at room temperature. Hence, 0.475 mole of azoxybenzene was obtained from 1 mole of phenylhydroxylamine. The result was confirmed by spectrophotometric estimation of azoxybenzene using λ_{max} at 322 mμ (0.475 mole of azoxybenzene from 1 mole of phenylhydroxylamine).

A methanolic solution (10 ml.) of *ca.* 0.2 *M* phenylhydroxylamine and 1.028×10^{-4} *M* cupric nitrate consumed 4.32×10^{-4} mole of oxygen at 35°, giving in average 8.68×10^{-4} mole of azoxybenzene after 30 min.; hence, *ca.* 0.5 mole of oxygen/mole of azoxybenzene was absorbed.

Kinetics.—The same apparatus and procedure[1] were used for the rate measurements. The reaction temperature was 35 ±0.1°.

Acknowledgment.—The authors are grateful to the Japanese Ministry of Education for their grant-in-aid and to Mr. Y. Sawaki for his aid in performing these experiments.

The Stereochemistry of Sulfinamides. Magnetic Nonequivalence of Protons in the Vicinity of the Asymmetric Sulfinamido Group

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Received July 8, 1964

The n.m.r. spectra of several N,N′-dialkylsulfinamides have been determined. Geminal protons adjacent the sulfinamido group are magnetically nonequivalent and display an AB rather than A_2 behavior. For example, the methylene protons of N,N′-diethylmethanesulfinamide(IV) in 50% benzene solution give rise to a 16-line spectrum rather than a simple four-line pattern. The observed spectrum has been compared with computed spectra. The methyl protons of the isopropyl group in N,N′-dimethylisopropanesulfinamide (III) appear as a quartet owing to their magnetic nonequivalence. This nonequivalence is a consequence of asymmetry at sulfur which causes adjacent nuclei to assume a mutually diastereomeric relationship. Additional conclusions are presented and discussed concerning rotation about the N–S bond and the configuration at nitrogen in the sulfinamido group. Relative comparisons are also drawn between the sulfinamido group and the sulfonamido group.

Magnetic nonequivalence of geminal protons in substituted ethanes of the general formula RCH_2-$CR_1R_2R_3$ is frequently observed and fairly well understood.[1] Waugh and Cotton[2a] have interpreted such nonequivalence in terms of symmetry arguments alone. Roberts, *et. al.*,[2b] recently have emphasized the importance of conformational preference among rotamers with respect to the asymmetric center as making the major contribution to the magnetic nonequivalence. Geminal nuclei such as protons of a methylene group adjacent an asymmetric center are diastereomeric.[3] Similarly, the methyl groups of an isopropyl group in a dissymmetric molecule are also diastereomeric. Furthermore, an asymmetric center need not be involved. For example, nondissymmetric molecules such as cyclopropylcarbinyl ethyl ether[4] and acetaldehyde diethyl acetal[4] display nonequivalence of the methylene protons. If the equilibrium populations of rotamers are temperature independent, variations in temperature cause no change in the appearance of the AB quartet. Such temperature independence serves as a useful means for distinguishing between slow exchange among nonequivalent sites and nonequivalence due to diastereomeric protons.

Somewhat less familiar is the related phenomenon due to low symmetry at atoms other than carbon. Complex methylene multiplets for ethyl groups, *i.e.*, splitting beyond a quartet, involving asymmetry at sulfur have been reported for diethyl sulfite,[5] for ethyl phenylsulfinate,[2] and for the methylene and methyl protons in ethylene sulfite,[5] *p*-tolyl isopropyl sulfoxide,[6] and diethyl sulfide–borane,[7] respectively. For phosphorus, nonequivalent methylene protons have been reported for O,O-diethyl methylphosphonothioate.[8] Recently a similar effect was demonstrated for nitrogen in dibenzylmethylammonium chloride[9] and diethylmethylammonium iodide[7] and also for silicon in tetramethyldisilane.[10]

Since the sulfinamido group appeared to possess the requisite elements of low symmetry, we decided to study the n.m.r. spectra of suitably substituted derivatives in order to gain further knowledge about the stereochemical details of these compounds and also about possible conformational consequences of N–S $p\pi$–$d\pi$ delocalization.[11] Comparison of the sulfinamido group with the related but symmetrical sulfonamido group seemed potentially instructive.

The n.m.r. absorption bands of interest for N,N′-dimethylmethanesulfonamide (II), N,N′-dimethyliso-

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TABLE I

PROTON SHIFTS (δ) FOR N,N′-DIALKYLSULFINAMIDES AND SULFONAMIDES[a,b]

Compound	Solvent	CH_3N	CH_3CH_2N	CH_3CH_2N	CH_3S	$(CH_3)_2CH$ or CH_3CH_2	p-$CH_3C_6H_4$
$(CH_3)_2NSOCH_3$ (I)	$CDCl_3$	2.68			2.50		
	Neat	2.67			2.54		
$(CH_3)_2NSO_2CH_3$ (II)	$CDCl_3$	2.87			2.79		
$(CH_3)_2NSOCH(CH_3)_2$ (III)	$CDCl_3$	2.77				1.07, 1.19, 1.25, 1.37 J = 7.2 c.p.s. J = 7.2 c.p.s. AB = 0.175 p.p.m.	
$(CH_3CH_2)_2NSOCH_3$ (IV)	$CDCl_3$		Complex multiplet (see text)	1.08, 1.20, 1.32 J = 7.2 c.p.s.			
	50% C_6H_6	2.14		0.803, 0.920, 1.04 J = 7.0 c.p.s.			
$(CH_3)_2NSOCH_2CH_3$ (V)	Neat	2.65				0.96, 1.08, 1.20 J = 7.5 c.p.s.	
	50% C_6H_6	2.54				0.86, 0.98, 1.10 J = 7.5 c.p.s.	
$(CH_3)_2NSOCH_2CH_2CH_3$ (VI)	$CDCl_3$	2.76				0.93, 1.05, 1.17 J = 7.0 c.p.s.	
$(CH_3)_2NSOC_6H_4$-p-CH_3 (VII)	$CDCl_3$	2.60					2.42
$(CH_3)_2NSO_2C_6H_4$-p-CH_3 (VIII)	$CDCl_3$	2.70					2.42
$(CH_3CH_2)_2NSO_2C_6H_4$-p-CH_3 (IX)	$CDCl_3$		3.06, 3.18, 3.30, 3.42 J = 7.0 c.p.s.	1.20, 1.14, 1.26 J = 7.0 c.p.s.			2.42

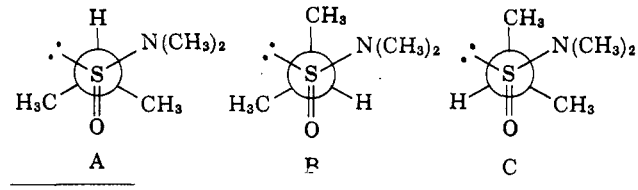
[a] Chemical shifts in p.p.m. = $10^6(H - H_{ref})/H_{ref}$ are relative to tetramethylsilane as internal standard at ν_0 = 60.0 Mc./sec. [b] The experimental error in the chemical shifts is no greater than ±0.5 c.p.s.

propanesulfinamide (III), N,N′-diethylmethanesulfinamide (IV), N,N′-dimethylethanesulfinamide (V), N,N′-dimethyl-p-toluenesulfonamide (VIII), and N,N′-diethyl-p-toluenesulfonamide (IX) are collected in Table I. The spectrum of III in deuteriochloroform shows a quartet (J = 7.0 c.p.s., δ_{AB} = 0.175 p.p.m.) methyl pattern for the isopropyl group rather than the doublet which would be predicted on the basis of a simple A_6X system. The methine proton multiplet lies partially beneath the N-methyl peak. No change in the appearance of the spectrum occurred upon warming to 60°. The spectrum of N,N′-diethylmethanesulfinamide (IV) in deuteriochloroform is also complex. The methyl part of the ethyl group has the expected triplet structure; however, the methylene part showed eight principal lines with a suggestion of further splitting. In order to improve matters, the spectrum was determined in 50% benzene solution. Better resolution of the component spin–spin multiplets was achieved and 16 lines could be discerned.

The observed spectrum in benzene solution was compared with various computed spectra.[12] An acceptable fit was obtained between the observed and calculated spectrum using J_{AB} = 10.0 c.p.s., δ_{AB} = 0.350 p.p.m., $J_{AC} = J_{BC}$ = 7.0 c.p.s. Of course it must be realized that using only a few iterations leads to a solution which may not be unique. Conceivably other completely different parameters could fit the observed spectrum within experimental error and so it is emphasized that the above analysis is a possible one and by no means the final solution.

Similarly, the methylene part of the spectrum of N,N′-dimethylethanesulfinamide (V) is split beyond a simple quartet; however, a portion of it was partially obscured by the N-methyl resonance. The methylene group adjacent to sulfur in N,N′-dimethyl-n-propanesulfinamide (VI) is complex, but poor resolution precluded further analysis. Comparison of the spectra for N,N′-dimethylmethanesulfinamide (I) and N,N′-dimethylmethanesulfonamide (II) reveals a shift to lower field of 0.190 for the N-methyl group and 0.290 p.p.m. for the S-methyl group of the sulfonamide relative to the sulfinamide. This effect is correlative with the expected increased deshielding by the extra oxygen attached to sulfur in the sulfonamide. A similar shift of 0.10 p.p.m. to lower field is observed for the N-methyl group in N,N′-dimethyl-p-toluenesulfonamide (VIII) relative to N,N′-dimethyl-p-toluenesulfinamide (VII). The position of the p-methyl group in this pair is unaffected by the oxidation level at sulfur. The ethyl groups in N,N′-diethyl-p-toluenesulfonamide appear as a simple A_2B_3 pattern in agreement with the symmetry at sulfur in the sulfonio group. Finally, the N-methyl resonance for all the compounds studied appears as a sharp singlet. Coupling constants for AB systems studied appear to be solvent independent within the accuracy of the measurements.

Interpretation of the spectra of the sulfinamides requires a stable pyramidal structure at sulfur. This is not unusual since it is well known that the sulfur atom in molecules of the type OSX_2 is pyramidal. For example, electron diffraction studies on thionyl chloride indicates a pyramidal structure with Cl–S–Cl and O–S–Cl bond angles of about 114 and 106°, respectively.[13] Also the sulfite ion is pyramidal with C_{3v} symmetry.[14] Thus the observed quartet for the protons of the two methyl groups of the isopropyl group in N,N′-dimethylisopropanesulfinamide (III) is a consequence of the two always residing in different



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magnetic environments when distributed among the three possible staggered rotamers.

Similar considerations may be applied to N,N′-diethylmethanesulfinamide (IV). Asymmetry at sulfur causes the adjacent methylene protons to be nonequivalent resulting in the observed 16-line pattern.

As far as assigning relative populations to conformations A, B, and C, the size of the lone pair on sulfur must be considered. Aroney and Le Fevre,[15a] as well as Barton and Cookson,[15b] state that the steric requirement of a lone pair on nitrogen is greater than hydrogen and approximately equal to a methyl group. Recent studies,[15c] however, assign a relatively smaller value: hydrogen-solvated electron pair > hydrogen–hydrogen > hydrogen-free electron pair. Assuming in the present system that the free electron pair is about equal to hydrogen, then conformation B would be the most highly populated. The chemical shifts of the stereochemically nonequivalent nuclei are affected by external effects (solvation) and internal effects such as the electrical fields of neighboring groups and the magnetic anisotropies of adjacent σ- and π-bonds. In the present investigation, solvent variation studies were not carried out, although such measurements would be of interest in so far as the lone-pair interaction might become more important in more polar solvents. Such an effect might change the relative populations of the possible conformations. The part of the chemical shift of the AB nuclei adjacent the SON group due to the electrical field is dependent upon the orientation and pole strength of nearby dipoles. This contribution, $\delta\Delta EI = \delta A - \delta B$, is given the equation due to Buckingham,[16] $\delta \times 10^6 = 9.6e \times \cos\theta/R^2 - 23e^2/R^4$, where e is the pole strength, R the distance and θ the angle between the C–X bond and the charge on the atom in question. Direct application of this equation to the sulfinamides is difficult owing to the existence of more than one possible conformation and also owing to the unknown magnitudes of the pole strengths for oxygen and nitrogen in the resonance hybrids $O{=}\overset{-}{S}{=}\overset{+}{N}$ and $-O-\overset{+}{S}{=}N$. The magnetic anisotropies of the S=N, S—O, or S=O and lone pair are also, at present, undetermined owing to unknown importance of the relative contributions of S=O and S=N in the sulfinamido group. Without some knowledge of the three principal magnetic susceptibilities for these bonds a meaningful estimate of $\Delta\delta AN = \delta A - \delta B$ is impossible. Estimates of these quantities in the case of a cyclic N-methylsulfinamide are possible and synthesis of such a compound is in progress.

Unhindered rotation about the N–S bond as a consequence of the lack of strict geometric requirements for $p\pi$–$d\pi$ overlap has already been demonstrated for N,N′-dimethylmethanesulfinamide (II).[10] This finding is supported and extended by the present results. Were reorientation about the N–S bond slow in N,N′-diethylmethanesulfonamide (IV), the methyl portion of the ethyl group would appear as two triplets and the methylene portion would show in the limit 32 lines instead of 16. The results also require either a planar arrangement about nitrogen or a pyramidal structure which is rapidly undergoing a configuration-inverting vibration. Were a locked pyramidal structure involved at nitrogen, the two methyl groups in the N,N′-dimethyl examples would be stereochemically nonequivalent for the same reason that the methyl groups of the isopropyl group in N,N′-dimethylisopropanesulfinamide (III) are nonequivalent.

The concept of structure for the sulfinamido group which emerges from these studies requires a pyramidal asymmetric configuration at sulfur and probably a planar sp^2 configuration at nitrogen. Since only a single N-methyl resonance is observed even at low temperature, rotations about the N–S must be extremely rapid. Residence at any one rotational site must be $\tau_A << \sqrt{2}/2\pi(\nu_A - \nu_B)$. A considerably less likely explanation is that only one rotamer exists and the methyl groups in this rotamer are accidentally equal.

Experimental

Spectra were recorded on a Varian Associates high-resolution A-60 n.m.r. spectrometer operating at 60.0 Mc. Band positions are considered accurate to 0.01 p.p.m. Temperatures are considered accurate to 1° and a temperature calibration was performed by using a plot of temperature *vs.* the two resonance signals for ethylene glycol.[17] All solvents were reagent grade quality. Infrared spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer.

Infrared Spectra.—The dilute carbon tetrachloride spectra of the alkyl sulfinamides and sulfonamides are similar. The sulfonamides display absorption at 7.50, 8.75, 9.50, and 10.40 μ. Absorption at 7.50 and 8.75 μ has previously been assigned to the antisymmetrical and symmetrical vibrations of the two sulfur–oxygen bonds in sulfonamides.[18] The sulfinamides examined in the present study show absorption at 7.20, 8.50, 9.25, and 10.80 μ. In addition to these bands, the sulfinamides display absorption around 6.10 μ which is not present in the sulfonamides. The sulfur–oxygen vibration in sulfoxides appears around 9.45–9.62 μ. Attachment of a nitrogen atom might shift this band to 9.25 μ. A similar shift is noted upon going from sulfone to sulfonamide.

N,N′-Dimethylmethanesulfinamide (I).—Methanesulfinyl chloride[19] (9.8 g., 0.10 mole) was dissolved in 50 ml. of ether and the solution was cooled to 0°. To this, a solution of dimethylamine (9.0 g., 0.20 mole) dissolved in 50 ml. of ether was added dropwise with constant stirring. After 2 hr. at room temperature, the mixture was filtered and the ether was removed by distillation. The product was distilled, b.p. 31–32° (0.20 mm.).

Anal. Calcd. for C_3H_9NOS: C, 33.61; H, 8.47. Found: C, 33.50; H, 8.41.

N,N′-Dimethylmethanesulfonamide (II).—To a solution of 5.7 g. (0.05 mole) of methanesulfonyl chloride in 50 ml. of ether at 5°, a solution of 4.5 g. (0.10 mole) of dimethylamine in 30 ml. of ether was added in 2-ml. portions. After standing at room temperature the dimethylamine hydrochloride was separated by filtration and the ether solution was concentrated *in vacuo* to dryness. Crystallization of the resulting oil from pentane yielded 4.3 g., m.p. 48–49°, lit.[20] m.p. 48–49°.

N,N′-Dimethylethanesulfinamide (V) was prepared by the method given for I using ethanesulfinyl chloride[21] and had b.p. 42° (4 mm.).

Anal. Calcd. for $C_4H_{11}NOS$: C, 39.64; H, 9.14. Found: C, 39.51; H, 9.00.

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N,N'-Dimethyl-*p*-toluenesulfinamide (VII) has already been reported.[11]

N,N'-Dimethyl-*p*-toluenesulfonamide (VIII) was prepared according to the method of Klamann[22] and had m.p. 87–88°, lit. m.p. 86–87°.

N,N'-Diethyl-*p*-toluenesulfonamide (IX).—Addition of 7.3 g. (0.10 mole) of diethylamine in 50 ml. of ether to a solution of 3.8 g. (0.02 mole) of *p*-toluenesulfonyl chloride in 25 ml. of ether resulted in a slow precipitation of diethylamine hydrochloride. After 16 hr. at room temperature, the precipitate was filtered and the solution was concentrated to dryness *in vacuo*. The resulting crystalline residue was recrystallized from pentane to yield 4.3 g. of IX, m.p. 59–60°, lit.[17] m.p. 60°.

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Acknowledgment.—We wish to thank Dr. R. J. Highet, National Institutes of Health, Bethesda, Maryland, for determining the spectra reported in this study and for many helpful suggestions. Theoretical spectra were computed using the facilities of the National Institutes of Health. Our thanks is given also to Dr. J. S. Luloff, Shulton Chemical Company, Clifton, New Jersey, for supplying samples of sulfinamides.

Cyanogenesis in *Sorghum vulgare*. II. Mechanism of the Alkaline Hydrolysis of Dhurrin (*p*-Hydroxymandelonitrile Glucoside)[1,2]

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Received July 21, 1964

Dhurrin, the cyanogenetic glucoside of *Sorghum vulgare*, is alkali labile although not structurally related to any of the known classes of alkali-labile glycosides. A mechanism for the alkaline hydrolysis is proposed, involving the successive ejection, from the dhurrin anion, of the two groups attached to the benzyl carbon. As predicted by this mechanism, the rate of the decomposition is proportional to the concentration of the anion. The reaction is first order, with $k = 0.032$ min.$^{-1}$ at 25°. The glucosyloxy group is ejected first, then the cyanide. *p*-Methoxymandelonitrile β-D-glucopyranoside and *o*- and *p*-hydroxybenzyl β-D-glucopyranosides were prepared in solution and characterized. The *p*-methoxy derivative is stable to alkali; the hydroxybenzyl glucosides are alkali labile, but less so than dhurrin.

In the course of work on the isolation of dhurrin (**1**, *p*-hydroxy-L-mandelonitrile β-D-glucopyranoside) from *Sorghum vulgare*, we found that this glucoside, while showing no unusual instability in acid, was extremely labile to alkali.[1] This property of dhurrin has also been observed by Conn and co-workers.[3] Alkali-labile glycosides are not common; however, a considerable number are known, and according to Ballou[4] they can be grouped into three structural types: (a) glycosides of phenols, (b) glycosides of enols, and (c) glycosides of alcohols substituted in the β-position by a negative group. Since dhurrin does not belong to any of these three types, a study of the mechanism of its alkaline hydrolysis seemed to be of interest.

The long-known mandelonitrile glucosides such as amygdalin (D-mandelonitrile β-gentiobioside)[5] and prunasin (D-mandelonitrile β-D-glucopyranoside),[5] which have no substituents in the aromatic ring, undergo certain changes in alkaline solutions, but their glycoside linkages are not cleaved.[6] It is therefore clear that the hydroxyl group on the benzene ring of dhurrin is responsible for its alkali sensitivity. A consideration of the ways in which alkali could act on the dhurrin molecule led us to postulate a reaction sequence (this is shown in Scheme I), which is an elaboration of the mechanism for the base-catalyzed decomposition of the *p*-hydroxybenzyl halides and related compounds.[7] This mechanism involves the formation of a quinone methene intermediate by the ejection of a leaving group from the benzyl carbon of the substrate anion. When dhurrin is the substrate a second elimination is possible, after addition of hydroxide ion to the quinone methene, and the reaction could follow either of two pathways: A, ejection of a glucosyloxy anion (**4**) in the first step, or B, ejection of a cyanide ion in the first step. There seemed to be no *a priori* basis for favoring one of these pathways over the other. However, the over-all mechanism has the following features: (a) the rate of alkaline hydrolysis should be proportional to the concentration of the anionic form of dhurrin (*i.e.*, a plot of the rate of decomposition against pH should be identical with the dissociation curve); (b) the decomposition rate at any given pH should obey the first-order rate law; (c) if the phenolic hydroxyl is converted into a nonionizing group, such as methoxyl, the resulting glucoside should be stable in alkaline solution; and (d) the bond cleaved should be the one between the glycosidic oxygen and the aglycone. The present paper describes experiments on the behavior of dhurrin and related compounds in which these predictions were tested, and the sequence of appearance of the hydrolysis products was determined.

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