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Chemistry of the Sulfur–Nitrogen Bond. IX.[1] Transmission of Electronic Effects in *N*-Alkylidenearenesulfenamides, -sulfinamides, -sulfonamides, and Arenesulfenanilides

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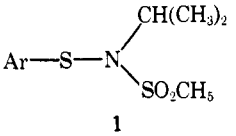
Abstract: Transmission of electronic effects through the sulfur–nitrogen bond has been investigated by observing the ^{1}H NMR chemical shifts of the imidoyl and hydroxyl protons in sulfenamide derivatives **3–6** and the amino proton in arenesulfenanilides, **7**. The measure of transmission of electronic effects is the Hammett ρ value. Substituent effects on the imidoyl protons were observed only in **3** and **6**, suggesting that there is conjugation between the two aryl groups mediated by the S–N bond. A mechanism for transmission involving both the p and d orbitals on sulfur was suggested. In **4** and **5**, transmission of electronic effects to the imidoyl protons and conjugation between the two aryl groups are destroyed. The ρ value obtained for the hydroxyl protons, which is a measure of transmission of substituent effects to the nitrogen lone pair of electrons, suggests that the nitrogen lone pair is not directly conjugated with the *N*-phenyl group. These results suggest that sulfur is a better transmitter of electronic effect when attached to a nitrogen which is sp^2 rather than sp^3 hybridized. The large solvent-induced modifications observed in the uv spectra of **4** and **5** were explained in terms of a shift in the phenolimine–quinoneamine equilibrium toward the quinoneamine form (**16**). The stability of **16** was in the order $SO_2 > SO \gg S$ and was attributed not to the presence of a strong intramolecular hydrogen bond, but rather to conjugation between the two aryl groups which stabilize the phenolimine form (**16**).

The ability of sulfur to utilize its d orbitals has been the subject of considerable controversy and discussion.[4] Studies aimed at elucidating the mechanism of transmission of electronic effects through sulfur have been used to investigate d orbital participation. Techniques used to measure transmission through sulfur include Hammett studies using NMR[5] and pK_a measurements,[6] ultraviolet spectroscopic techniques,[7] and polaragraphic methods.[8]

Studies of transmission using NMR[5b-e] and pK_a measurements[6b,e,f] all found evidence for transmission of electronic effects through sulfur with the order of transmission being $S > SO_2 > SO$. Enhanced transmission through sulfur, as measured by proton chemical shifts, was observed when sulfur was part of a conjugated system, i.e., phenyl vinyl sulfides.[5g] Investigation of the ultraviolet spectra of substituted diphenyl sulfides found evidence for[7b] and against[7a] transmission through sulfur. For the most part, the mechanism of transmission was ascribed to sulfur d orbital participation. However, Pasto et al. preferred to explain their results in terms of inductive effects.[6f]

A variety of studies have been aimed at elucidating the mechanism of transmission of electronic effects through the sulfur–nitrogen bond.[9] Raban and coworkers observed large barriers to rotation or stereomutation about the S–N bond in sulfenamides of type **1**.[10] The barriers in these compounds were attributed either to p-d π bonding in which one sulfur d orbital overlaps with both the aromatic π system and the nitrogen lone pair in the ground state but not the transition state for stereomutation or to σ–π conjugation (negative hyperconjugation) in which the nitrogen lone pair overlaps with the orbital that sulfur utilizes to bond to the aromatic π system. Both these effects are expected to increase the stability of the ground state as electronegative groups are attached to sulfur, and this is observed experimentally.[10]



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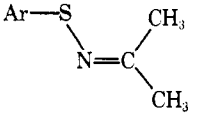

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The ^{15}N–H coupling constants[11] and an X-ray structure[12] of sulfenamides suggested that nitrogen in these compounds was sp^2 hybridized. The hybridization of nitrogen in the former case was attributed to electronegativity effects and not to p-d π bonding.[11]

Rotational barriers have been observed only for sulfinamides with very electronegative groups attached to sulfur.[13-15] Directionally dependent p-d π bonds are believed to be responsible for rotational barriers in sulfonamides when electronegative groups are attached to sulfur.[16]

Although electronegative groups attached to sulfur have measurable effects on S–N torsional barriers, they have little or no effect on inversion barriers. Barriers to stereomutation in *N*-sulfenyl,[17,18] sulfinyl, and sulfonyl[18] aziridines are insensitive to the substituent electronic effects of groups attached to sulfur. The lower barriers in trichloromethane and trifluoromethanesulfenyl aziridines were ascribed to σ–π conjugation.[19]

Stereomutation barriers in *N*-isopropylidenearenesulfen-

Table I. Hammett Relationships for Sulfenamides, Sulfinamides, and Sulfonamides

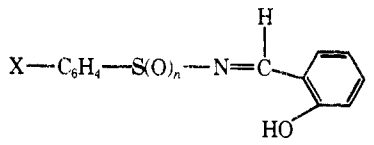
Entry	Compd		R^a	Solvent	Proton
1	X-$C_6H_4CH_3$[b]	−0.214	0.884	CCl_4	CH_3
2	X-$C_6H_4OCH_3$[b]	−0.270	0.937	CCl_4	CH_3
3	X-$C_6H_4SCH_3$	−0.115	0.891	CCl_4	CH_3
4	X-C_6H_4N=CHC_6H_5 (8)[c]	−0.04	0.834	$CDCl_3$	CH=
5	X-C_6H_4N=CHC_6H_4(OH) (9)[d]	0.885	0.981	$CDCl_3$	OH
6			No chemical shift change		CH=
7	X-C_6H_4SCH=CH_2[e]	−0.448	0.987	CCl_4	β-trans
8	X-C_6H_4S—N=CHC_6H_4(OH) (3)	0.315	0.977	$CDCl_3$	OH
9		0.220	0.944	CCl_4	OH
10		−0.326[f]	0.992	$CDCl_3$	CH=
11		−0.357[f]	0.990	CCl_4	CH=
12	X-$C_6H_4S(O)N$=CHC_6H_4(OH) (4)	0.398	0.999	$CDCl_3$	OH
13		0.433	0.996	CCl_4	OH
14	X-$C_6H_4S(O_2)N$=CHC_6H_4(OH) (5)	0.219	0.996	$CDCl_3$	OH
15		0.331	0.994	CCl_4	OH
16	X-C_6H_4S—N=CHC_6H_5 (6)	−0.334[f]	0.987	$CDCl_3$	CH=
17		−0.350[f]	0.991	CCl_4	CH=
18	X-$C_6H_4SNHC_6H_5$ (7)	−0.085	0.947	$CDCl_3$	NH
19		−0.185	0.999	CCl_4	NH
20	X-C_6H_4—S(=O)—NHC_6H_5[g]	−0.470	0.992	$CDCl_3$	NH

[a] Correlation coefficients. [b] Reference 5b. [c] Reference 27. [d] Calculated from the data of Brown and Nonhebel, see reference 33. [e] Reference 5g. [f] Correlation with σ^+. [g] Calculated from the values given in reference 2.

amides (**2**),[20a] sulfinamides,[20b] and *N*-(4,4′-dimethylbenzophenylidene)arenesulfenamides[21] were also insensitive to substituent electronic effects. The lower barriers in these compounds as compared with the corresponding oximes were interpreted in terms of both d orbital participation[20] and electronegativity effects.[20a]

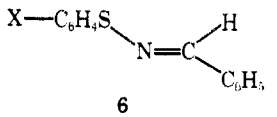
A recent study of transmission of electronic effects through the S-N bond in arenesulfinamides, using ^1H NMR chemical shifts, concludes that there is little through-conjugation involving p-d π bonding between sulfur and nitrogen.[21] Dipole moment and infrared studies of sulfonamides indicated transmission through the S-N bond,[22] while an NMR study of sulfonamides failed to detect any transmission.[23]

In an effort to better understand the mechanism of transmission of electronic effects through the sulfur-nitrogen bond, we initiated a proton NMR and ultraviolet spectroscopic study of the compounds in series **3–7**. Such a study



3, $n = 0$ **4**, $n = 1$ **5**, $n = 2$

a, X = 4-$N(Me)_2$; b, X = 4-OMe; c, X = 4-CH_3; d, X = H; e, X = 4-; f, X = 4-Cl; g, X = 3-NO_2; h, X = 4-NO_2; i, X = 2-NO_2



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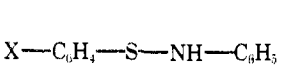

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may also contribute to a better understanding of the phenol-imine-quinoneamine equilibrium in *o*-hydroxyarylidene Schiff bases.

Results

Synthesis. *N*-Salicylidene and benzylidenesulfenamides (**3** and **6**) were prepared as previously described[24] from the corresponding disulfide, silver nitrate, ammonia, and appropriate aldehyde. Series **4** was prepared from series **3** by oxidation with *m*-chloroperbenzoic acid.[1] Series **5** was prepared either by oxidation of the corresponding sulfenamide (**3**) with 2 equiv of MCPBA or by treatment of salicylaldehyde diethyl acetal with the corresponding arenesulfonamide at 180°. Arenesulfenanilides (series **7**) were prepared from the sulfenyl chloride and an excess of aniline at −78°.

Structural proof of **3–7** was based upon elemental analysis, infrared, NMR, and method of synthesis. In cases where satisfactory elemental analysis could not be obtained due to compound instability, mass spectra were obtained. These results are summarized in Table III.[25]

NMR Spectra. Hammet ρ values[26] were used as the measures of transmission of substituent electronic effects through the S-N bond in **3–7**. Chemical shifts of the hydroxyl proton (OH) and imidoyl protons (N=CH) in **3–6** and the amino protons (NH) in **7** were plotted vs. Hammett σ values to give ρ (δ/σ). Chemical shifts were measured relative to Me_4Si in $CDCl_3$ and CCl_4 and extrapolated to infinite dilution. These results are summarized in Table I.

The imidoyl protons in **3** and **6** gave the best correlation when σ^+ values were used for electron-donating groups. Electron-withdrawing groups shifted the imidoyl proton chemical shift down field ($-\rho$). The hydroxyl protons in **3–5** correlated best with normal σ values and were shifted upfield by electron-withdrawing groups ($+\rho$).

Compounds containing an *o*-nitro group failed to give satisfactory correlations when included in the Hammett treatment (Figure 1) and consequently were omitted from the correlation. These compounds will be discussed in a separate section.

Ultraviolet Spectra. The ultraviolet spectra of series **3–7** were measured in both polar and nonpolar solvents. In 95% alcohol, **5** was rapidly hydrolyzed to the sulfonamide and salicylaldehyde. In absolute alcohol, these compounds were stable with half-lives on the order of 55 hr. Table II summarized the ultraviolet spectra of series **3–7** in cyclohexane, ethanol, and acetonitrile.[25]

Discussion

Chemical shifts of protons are believed to be dependent largely on the total electron density of the atom to which they bonded. Although the chemical shifts are dependent upon the diamagnetic, paramagnetic, and magnetic anisotropic contributions to the screening constant, in a closely related series of compounds these factors may be considered

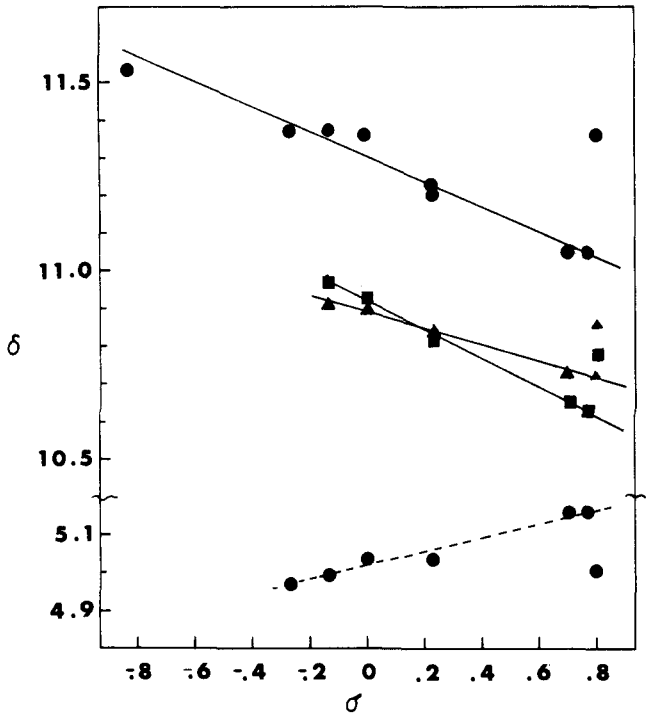


Figure 1. Proton chemical shifts of OH protons in 3 (—●—●—), 4 (—■—■—), and 5 (—▲—▲—) vs. Hammett σ constants ($CDCl_3$ solvent). Proton chemical shifts for NH protons in 7 (--●--●--) vs. Hammett σ constants (CCl_4 solvent).

"systematic" such that the chemical shift is dependent on the substituent.[5g] The fact that the chemical shift of the β-trans protons in aryl vinyl sulfides correlates with Hammett σ values,[5g,27a,b] ^{13}C NMR chemical shifts,[27b,c] and pK_a measurements[27a] supports these assumptions. ^{13}C NMR chemical shifts are known to correlate with the electron density on carbon.[28]

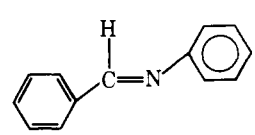
The transmission of electron effects from the substituent X to the site being monitered in series **3–7** may take place through the bonds (inductive and resonance effects) and/or through space (field effect). Transmission involving field effects is believed to be small compared with transmission by resonance and inductive effects.[29]

A solvent effect on ρ was observed in $CDCl_3$ and CCl_4 (Table I). The size of ρ in CCl_4 was SO > SO_2 > S and in $CDCl_3$ was SO > S > SO_2. The more reliable solvent is expected to be CCl_4 rather than $CDCl_3$ since both the polarity and hydrogen bonding of $CDCl_3$ could affect the chemical shifts.[5b]

We believe that ρ is a measure of the transmission of electronic effects through the sulfur–nitrogen bond primarily conducted through the π and σ electrons. The ^1H NMR chemical shift of the hydroxyl (OH) proton, which is hydrogen bonded to the nitrogen, is a measure of the electron density on nitrogen. The greater the electron density on nitrogen, the stronger the hydrogen bond and the further downfield is the hydroxyl proton chemical shift (ρ positive for electron-donating groups).

The anisotropy of the C–N double bond is responsible for the low-field position of the imidoyl (=CH) proton. The greater the C–N bond order, the further downfield is the imidoyl proton chemical shift (ρ negative for electron-withdrawing groups).

The preferred conformation for *N*-benzylideneaniline (**8**) is with the two phenyl rings trans coplanar resulting in conjugation between the two aryl groups. There is substantial evidence, however, suggesting that the *N*-phenyl ring is actually twisted out of the plane of the C–N double bond as a result of nonbonded interactions between the ortho hydrogens of the *N*-phenyl ring and the imidoyl proton.[30-32] Additional evidence in support of this theory is the lack of correlation of the imidoyl proton chemical shifts in **8**[27] and **9**[33] with σ and the large ρ (0.885, entries 5 and 6, Table I) obtained for the hydroxyl proton in **9**.



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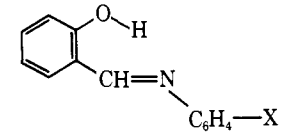

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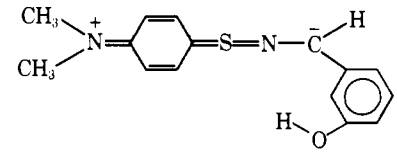
The insertion of a sulfur atom between the *N*-phenyl and imino group in **8** and **9** to give series **6** and **3** is expected to result in a longer distance for transmission of electronic effects and elimination of nonbonded interactions that would prevent coplanarity of the orbitals in **8** and **9** inhibiting through-conjugation (Drieding models).

In **3** it is noted that transmission to the hydroxyl proton is lower than in **9** (0.315 vs. 0.885) and that substantial transmission to the imidoyl proton is now observed. The imidoyl proton chemical shifts in **8**[27c] and **9**[33] were not affected by substituents. Similar transmission for the imidoyl proton in **6** was observed, suggesting that the mode of transmission of electronic effects in these compounds is not affected by the presence of an ortho hydroxyl group.

The substantial transmission of electronic effects to the imidoyl proton and the correlation with σ^+ values for electron-donating groups suggested that there is conjugation between the substituent X and the C–N double bond. This through-conjugation may be rationalized in terms of a mechanism which involves the lone pairs of electrons on sulfur and sulfur 3d orbitals (canonical form **10**). A mechanism of through-conjugation involving p-π, d-π, p-π conjugation has been suggested for phenyl vinyl sulfides[27a,b] and supported by CNDO/2 calculations.[34] The more stable configuration for sulfenamides **3** and **6** is one in which the orbitals are situated such that there is conjugation between the two aryl groups.



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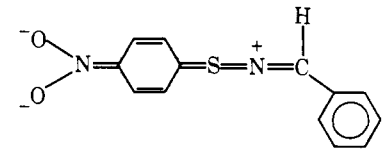

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The reduced transmission to the hydroxyl proton in **3** and the lack of correlation with σ^- values for electron-withdrawing groups indicate that the nitrogen lone pair of electrons is not in direct conjugation with the *N*-phenyl ring. Bonding involving overlap of one sulfur d orbital with both the aromatic π system and nitrogen lone pair is unimportant in these compounds (canonical form **11**). A mechanism of transmission of electronic effects to the nitrogen lone pair may be rationalized in terms of a combination of inductive effects, localized p-d π bonds between nitrogen and sulfur and/or σ-π conjugation (see below).

Conjugation between the two aryl groups in **3** is destroyed on oxidation to **4** and **5** as indicated by the lack of substituent electronic effects on the imidoyl proton chemi-

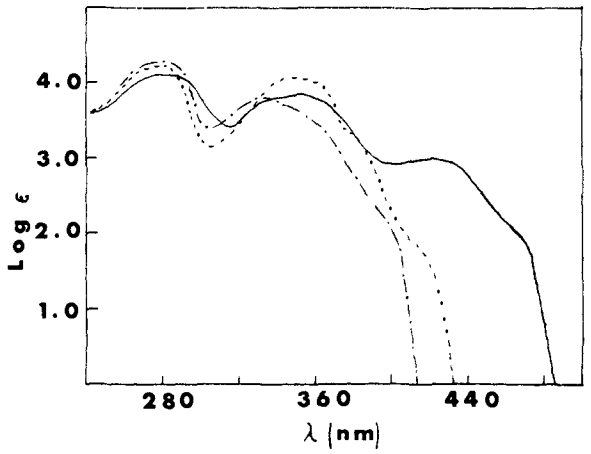


Figure 2. Ultraviolet spectra of **5d** in cyclohexane (- - -), acetonitrile (— • — •), and ethanol (—).

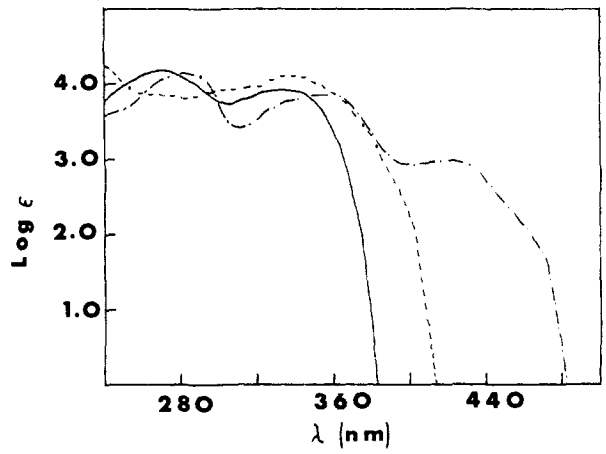


Figure 3. Ultraviolet spectra of **3d** (—), **4d** (- - -), and **5d** (— • — •) in ethanol.

cal shifts. This lack of transmission to the imidoyl proton in **4** and **5** is consistent with the mechanism postulated for through-conjugation in **3** and **6**.

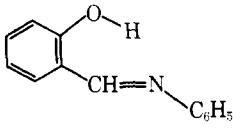
Transmission of electronic effects to the nitrogen lone pair of electrons (hydroxyl group) in series **4** is enhanced in both CCl_4 and $CDCl_3$ as compared with **3** and **5**. This trend is opposite to that observed in other studies[5,6] and may be rationalized in terms of the mechanism of transmission involving inductive effects and localized p-d π bonding between sulfur and nitrogen.

As the electronegativity of sulfur increases, the sulfur d orbitals contract, thus lowering their energy.[10,13-15] More effective p-d π bonding between sulfur and nitrogen would be the result, and transmission of electronic effects should be enhanced. However, increasing the electronegativity of sulfur also decreases the polarizability of the sulfur electrons and consequently would result in reduced transmission via inductive effects. More effective localized p-d π bonding in **4** may be responsible for the enhanced transmission in these compounds. In series **5** removal of the last pair of nonbonded electrons on sulfur and the increase in electronegativity of sulfur reduces transmission via the inductive route.

Ultraviolet Spectra. The ultraviolet spectra of **3** and **6** in cyclohexane and ethanol display longer λ_{max} and greater absorption than the corresponding *N*-isopropylidenearenesulfenamides (**2**),[20] suggesting a longer conjugated system in the former. The solvent shifts observed for **3** and **6** are small except for **3h** and **4h** (X = 4-NO_2) where bathochromic shifts of 13 and 7 nm were observed (Table II).

When the solvent is changed from cyclohexane to ethanol, a dramatic change in the uv spectra of **4** and **5** is observed (Figure 2). In ethanol, a new absorption at 400 nm (ϵ 300) for **4** and at 440 nm (ϵ 1300) for **5** is observed. These solvent shifts were not observed for **3, 6** (Table II).[25]

Similar solvent shifts have been reported for salicylaldehyde and 2-hydroxy-1-napththaldehyde Schiff bases. The bathochromic shifts, which are too large for a π-π^*[35] band, have been interpreted in terms of a phenolimine-quinoneamine equilibrium (**12–13**) and zwitterionic (**14**)[36] forms which are more stable in a polar medium. A large body of information, obtained from ultraviolet,[37a,b,38] NMR,[33,39] and infrared[35,38b] studies, suggests that the solvent-induced modifications in the ultraviolet spectra of these Schiff bases are due to the quinoneamine form (**13**).



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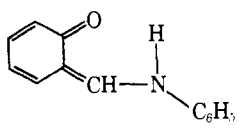

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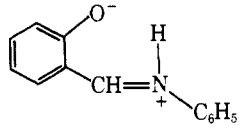

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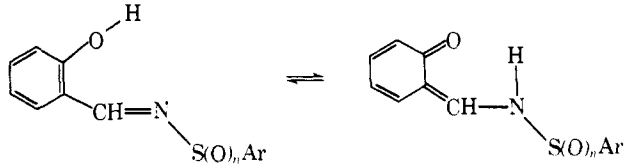
The quinoneamine form exists only in polar protic media,[37b,d] is not observed for *N*-salicylideneanilines, but is observed for *N*-salicylidenealkylamines.[33,37b] The factors which control the equilibrium (**12–13**) are not well understood. It is generally believed that the strength of the intramolecular hydrogen bond is responsible for the stability of the quinoneamine form and that an N-H···O hydrogen bond is stronger than an N···H-O hydrogen bond.[33,39]

We believe that the solvent-induced modifications observed in the uv spectra of **4** and **5** result from a shift in the equilibrium from the phenolimine form (**15**) to the quinioneamine form (**16**). The formation of **16** in series **3–5** is favored in the order SO_2 > SO > S (see Figure 3), as indicated by the magnitude of the ultraviolet extinction coefficients.[37b] The fact that the sulfonamide **5** yields more of the quinoneamine form than **4** or **3** makes it unlikely that a zwitterionic form (**14**, Ar = $ArSO_2$) is responsible for the solvent shift.



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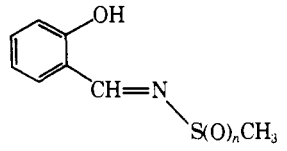
The hypothesis that the strength of the intramolecular hydrogen bond, as determined by the basicity of nitrogen, is responsible for the stability of the quinoneamine form (**13**) in salicylaldehyde Schiff bases is clearly inadequate in explaining the order of stability of the quinoneamine form in **3–5**. The basicity of nitrogen is in the order S > SO > SO_2, and the order of stability of **16** is just the reverse.

We believe that the major factor controlling the phenolimine-equinoneamine equilibrium (**15–16**) is not the presence of a strong intramolecular hydrogen bond, but rather conjugation between the two aryl groups which stabilizes the phenolimine form (**15**). The observed order for formation of the quinoneamine form (**16**), SO_2 > SO > S, is then readily understood. Conjugation between the two aryl groups, which is possible only in the phenolimine form, was

shown by the ^1H NMR studies (vide supra) to be present only in the sulfenamide series **3** and **6**. The lack of conjugation between the two aryl groups in **4** and **5** shifts the equilibrium toward quinoneamine form (**16**).

A similar argument may be used to explain the lack of quinoneamine form for the *N*-salicylidene Shiff bases (**12**, R = aryl). Conjugation between the two aryl groups shifts the equilibrium toward the more stable phenolimine form. Furthermore the recent reports of quinoneamine forms for *p*-hydroxy-*N*-benzylidene-2-aminopropane mean that the presence of an intramolecular hydrogen bond is not essential for formation of the quinoneamine.[37d]

The ultraviolet spectra of series **17**, in which the *S*-aryl group has been replaced by a nonconjugating methyl group, support this argument. The ultraviolet spectrum of **17a** did show absorption in the region expected for the quinoneamine form, 415 nm (ϵ 53), and **17b** and **17c** had larger λ_{max}

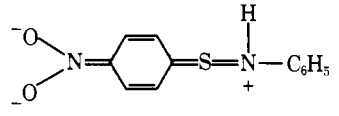


17a, $n = 0$
b, $n = 1$
c, $n = 2$

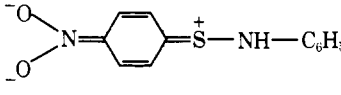
and greater extinction coefficients than **4** and **5** (Table II). The fact that more of the quinoneamine form was not observed for **17a** may suggest that some stabilization of the phenolimine form results from conjugation with the lone pairs of electrons on sulfur.

Arenesulfenanilides. The value (-0.085 in $CDCl_3$ and -0.185 in CCl_4) for arenesulfenanilides, series **7**, indicates a low degree of transmission through the S-N bond. Transmission ability is lower in **7** than in **3**, and the order of transmission in arenesulfenanilides, arenesulfinanilides, and arenesulfonanilides is SO > S > SO_2 (Table I).

The lack of correlation with σ^- rules out extensive conjugation with the nitrogen lone pair of electrons involving the p-d π bond and represented by canonical structure **18**. The



18



19

similar ρ for **7**, thioanisole, and toluene (Table I) suggests that the mechanism of transmission involves inductive effects σ-π conjugation and/or localized p-d π bonding between sulfur and nitrogen.

The ultraviolet spectra of series **7** agree with the NMR results, suggesting little or no transmission through the S-N bond (Table II).[25] In fact, the ultraviolet spectra of series **7** are similar to the ultraviolet spectra for similarly substituted diphenyl sulfides reported by Mangini and Passerini.[7a] These authors concluded that the major type of interaction is between the substituent and the sulfur, i.e., **19** for arenesulfenanilides.

Bathochromic solvent shifts on the order of 3-15 nm are observed for series **7** with electron-withdrawing substituents showing the largest shifts. These solvent shifts are what would be anticipated for a π-π^* transition.[35] If the nitrogen lone pair of electrons were involved in conjugation with the rest of the molecule (i.e., **18**), it would be expected that the intensity and λ_{max} would be diminished in ethanol relative to acetonitrile as a result of hydrogen bonding between the protic solvent and the nitrogen lone pair of electrons. The ultraviolet spectra of series **7** in ethanol and acetonitrile are nearly identical.[25]

***o*-Nitro Compounds.** The NMR and ultraviolet spectra of compounds containing an *o*-nitro group (**3i**, **4i**, **5i**, and **7i**) exhibit widely divergent behavior compared with the other members of their series. In series **3–5**, when the *o*-nitro derivatives were included in the Hammett treatment, their inclusion resulted in much poorer correlations (Figure 1). It would appear that transmission through the S-N bond is inhibited by the presence of an *o*-nitro group. Similar results were obtained for the arenesulfenanilides.

The ultraviolet spectra of the *o*-nitro compounds also failed to follow the pattern exhibited by the other members of their series. In general, longer λ_{max} and greater absorption were observed.

The unusual behavior displayed by the ^1H NMR spectra of the *o*-nitro compounds is explained in terms of a ground-state structure of *o*-nitrosulfenyl compounds first suggested by Kharasch et al. to explain the stabilization of the 2,4-dinitrobenzenesulfenium ion.[39] Essentially their argument was that one of the oxygens of the nitro group is in close proximity to the sulfur atom. An X-ray crystallographic study of methyl-2-nitrobenzenesulfenate supports this hypothesis.[40] This interaction between one of the oxygens of the nitro group and sulfur apparently inhibits transmission of electronic effects through the sulfur-nitrogen bond.

Alternatively the unusual behavior of the *o*-nitro groups may be due to steric factors. The bulky *o*-nitro groups may distort the molecular conformations which would result in deviations from ideality.

Conclusions

Evidence for transmission of electronic effects through the sulfur-nitrogen bond in *N*-salicylidenearenesulfenamides, sulfinamides, and sulfonamides (**3–7**) has been demonstrated by the effect of substituents on the ^1H NMR chemical shifts of the hydroxyl and imidoyl protons. In sulfenamides **3** and **6** there appears to be transmission through the sulfur-nitrogen bond resulting in conjugation between the two aryl groups. The mechanism of transmission is rationalized in terms of p-π, d-π, p-π bonding involving both the sulfur p and d orbitals. This through-conjugation is destroyed on oxidation to the sulfinamide and sulonamide series (**4** and **5**).

Transmission of electronic effects to the hydroxyl proton, which is a function of the basicity of nitrogen, was rationalized in terms of localized p-d π bonding between sulfur and nitrogen and inductive effects.

The solvent-induced modifications in the ultraviolet spectra of *N*-salicylidenearenesulfinamides and sulfonamides were attributed to a shift of the phenolimine-quinoneamine (**15–16**) equilibrium toward the quinoneamine form. This equilibrium is shifted toward the quinoneamine form in the order SO_2 > SO > S (5 > 4 > 3). The major factor determining the stability of the quinoneamine form is not the presence of a strong intramolecular hydrogen bond, but rather conjugation between the two aryl groups which stabilize the phenolimine form.

The effect of substituents on the ^1H NMR chemical shifts in **3–6** and **7** indicates that there is transmission of electronic effects through the sulfur-nitrogen bond when sulfur is attached to an sp^2 hybridized nitrogen, but little if any when attached to an sp^3 hybridized nitrogen. This would suggest the p-d π bonding between sulfur and nitro-

gen is dependent upon the hybridization of the nitrogen lone pair.

The large effect of electronegative substituents on the barriers to stereomutation in sulfenamides[10] and the absence of substituent effects on the barriers to planar inversion in *N*-alkylidenearenesulfenamides[20] and sulfinamides[20c] is difficult to explain and will require additional experiments to clarify these seemingly incongruous results.

Experimental Section

Melting points were measured on a Fisher-Johns apparatus and are uncorrected. Mass spectra were obtained at 70 eV on a Hitachi RMU-6 mass spectrometer. Proton NMR spectra were measured on a Varian A60-A spectrometer. Infrared and ultraviolet spectra were measured on Perkin-Elmer 457 and 402 spectrometers, respectively. Solvents were commercial spectrograde solvents or were purified by literature methods. *N*-Alkylidenearenesulfenamides (**3**, **6**, **17a**)[24] and arenesulfenanilides (**7**)[41] were prepared as previously described.

Sulfenamides (% yield, mp, in degrees): **3a**, 18, 135–136; **3b**, 54, 69–70; **3c**, 54, 97–98; **3d**, 52, 82–83; **3e**, 54, 114–115; **3f**, 48, 113–114; **3g**, 40, 104–105; **3h**, 38, 149–150; **3i**, 40, 134–135; **6b**, 45, 65–66; **6c**, 25, 42–43; **6d**, 25, 35–36; **6e**, 42, 73; **6f**, 28, 60–61; **6g**, 47, 93–94; **6h**, 63, 132–133; **7b**, 70, 77–78; **17a**, 30, 97 (0.03 mm).

^{1}H NMR Spectra. Proton chemical shifts were obtained in $CDCl_3$ and CCl_4 referenced against internal Me_4Si. Spectra were measured at at least three concentrations and extrapolated to infinite dilution.

***N*-Alkylidenearenesulfinamides.** In a 250-ml three-necked flask equipped with dropping funnel and overhead stirrer were placed 0.0182 mol of the appropriate *N*-alkylidenearenesulfenamide in 50 ml of $CHCl_3$ and 2.3 g of $NaHCO_3$ in 20 ml of water. The reaction mixture was cooled to 0° and stirred vigorously. To the reaction mixture was added 4.07 g (0.02 mol) of *m*-chloroperbenzoic acid (Aldrich) dropwise over 20 min and the reaction allowed to stir for an additional 0.5 hr at 0° and then for 1 hr at room temperature. After drying the $CHCl_3$ solution over anhydrous K_2CO_3, the solvent was removed under vacuum to yield the crude *N*-alkylidenearenesulfinamide which was crystallized from alcohol or ether.

Sulfinamides (% yield, mp, in degrees): **4c**, 70, 110–111; **4d**, 74, 92–93; **4f**, 80, 139–140; **4g**, 92, 128–129; **4h**, 68, 142–143; **4i**, 92, 124–125; **17b**, 60, 108–109.

***N*-Alkylidenearenesulfonamides. Method A.**[42] In a 100-ml round-bottomed flask equipped with magnetic stirring bar and condenser were placed equimolar amounts (usually 0.015 mol) of the appropriate sulfonamide and salicylaldehyde diethyl acetal,[43] and the reaction mixture was heated at 150–180° in an oil bath. Heating was continued until the sulfonamide had gone into solution, at which time the reaction mixture was cooled and placed under vacuum (water pump and oil pump). The crude *N*-salicylidenearenesulfonamide was crystallized from ether or chloroform.

Method B. In a 100-ml three-necked flask equipped with dropping funnel and overhead stirrer was placed 0.005 mol of the appropriate *N*-alkylidenearenesulfenamide in 20 ml of $CHCl_3$. The reaction mixture was cooled to 0° and stirred vigorously, and 2.3 g (0.0115 mol) of *m*-chloroperbenzoic acid in 60 ml of $CHCl_3$ was added dropwise to the reaction mixture over 0.5 hr. After stirring for an additional 0.5 hr at 0° and 1.5 hr at room temperature, the solution was reduced to about 20 ml under vacuum and cooled to −20°. After removal of the precipitated *m*-chlorobenzoic acid, the solvent was removed under vacuum to yield the crude sulfonamide which was crystallized from ether.

Sulfonamides (% yield, mp, in degrees): **5c**, 94, 122–123; **5d**, 79, 114–115; **5f**, 90, 143–145; **5g**, 83, 176–177; **5h**, 75, 169–170; **5i**, 77, 173–174; **17c**, 60, 108–109.

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Supplementary Material Available. Table II, Ultraviolet Spectra of Sulfenamides, and Table III, Analytical Data for Sulfenamides, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-7085.

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Chemistry of α-Nitro Sulfones. V.[1] An Electron Spin Resonance Spectroscopic Study of Arylsulfonylalkyl Alkoxy Nitroxides, the Spin Adducts of Arylsulfonylalkanenitronic Acid Esters

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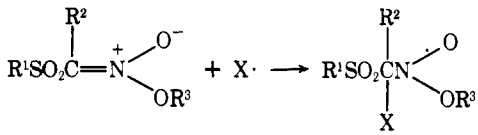
Abstract: Arylsulfonylalkanenitronic acid esters were obtained upon reaction of five α-nitro sulfones with diazomethane or diazoethane. Four of these products readily add a variety of radicals to produce arylsulfonylalkyl alkoxy nitroxides which were studied by ESR spectroscopy. If the trapped radical is bulky, two nitrogen hyperfine splitting constants are observed. We infer that these nitroxides occur in two favored conformations, both with the α-carbon to sulfonyl bond eclipsed with the half-filled orbital on nitrogen. The same types of nitroxides could also be generated by reaction of α-nitro sulfones with alkoxycarbinyl radicals. When the α-nitro sulfone contains a chiral center and the groups attached to the carbinyl radical site are different from each other, diastereomeric nitroxides are formed. The dependence of the nitrogen hyperfine splitting constant on the substitution pattern in the nitroxides is discussed. The reaction of several nitronic acid esters with lead tetraacetate led to the production of α-sulfonyl iminoxy radicals. This reaction most likely proceeds via thermal decomposition into α-oximino sulfones and subsequent oxidation.

The spin trapping technique[2,3] has proven to be extremely useful for the detection and identification in solution of paramagnetic species which are too short-lived to be studied directly by electron spin resonance (ESR) spectroscopy under the employed reaction conditions. Of the various spin traps, monomeric *C*-nitroso compounds and nitrones occupy a paramount position. Both types of compounds often scavenge rapidly and efficiently short-lived radicals to afford relatively stable nitroxide radicals that are conveniently studied by means of ESR. The relative merits of these and other spin trapping agents[4-8] as well as the applicability and pitfalls of the method have been discussed extensively.[2,3] Besides its usefulness in mechanistic and analytic investigations, the spin trapping technique has also a considerable potential for the production of radicals of intrinsic interest otherwise difficult to prepare.

We anticipated that possibilities of this kind could be explored when we prepared five arylsulfonylalkanenitronic acid esters in the course of our continuing investigations on α-nitro sulfones.[1] Should these species behave like nitrones, then addition of free radicals, X·, would lead to the previously unreported arylsulfonylalkyl alkoxy nitroxides[9] (eq 1). This expectation was borne out in practice and, more-

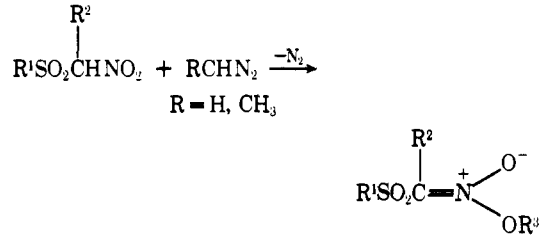


(1)

over, the generated nitroxides turned out to be versatile probes for the study of subtle conformational and electronic perturbations[10] induced by varying R^2 and R^3. Variation of R^3 was accomplished more easily by using a different method for the production of the nitroxides, i.e., the direct addition of free radicals to α-nitro sulfones.

Results and Discussion

Arylsulfonylalkanenitronic Acid Esters. The nitronic acid esters **1–5** were prepared by alkylation of the appropriate α-nitro sulfones with diazomethane or diazoethane (eq 2).



(2)

1, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = H$; $R^3 = CH_3$
2, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = R^3 = CH_3$
3, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = C_6H_5$; $R^3 = CH_3$
4, $R^1 = C_6H_5$; $R^2 = H$; $R^3 = CH_3$
5, $R^1 = p\text{-}CH_3C_6H_4$; $R^2 = H$; $R^3 = C_2H_5$

Previously, Arndt and Rose[11] have described **1** as a pungent, viscous, yellow oil which resisted crystallization. In our hands **1–3** crystallized readily and could be obtained analytically pure. The crude **4** and **5** were not purified further, but were used immediately in the ESR experiments. Although **1–5** in principle can exist as geometrical isomers, the above synthetic procedure afforded only one isomer for **1–3** and **5** as indicated by NMR analysis. Isomerization of **1** was observed during recrystallization leading to a 1:1