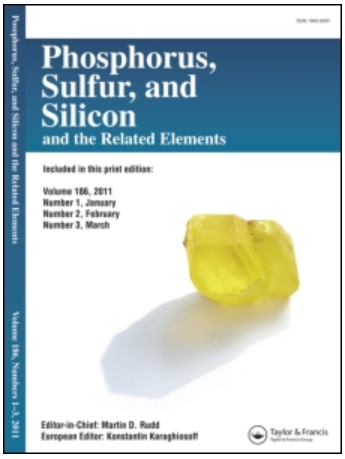

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SULFENAMIDES AND SULFINAMIDES III. CONJUGATIVE AFFINITY AND pKa VALUES OF ARYL SULFENAMIDES

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Relationships are discussed between the pKa values determined spectroscopically in aqueous media and the conjugative affinity of the sulfur atom in transmitting substituent effects in a series of aryl sulfenamides.

Key words: Sulfenamides; pKa values; conjugative affinity.

INTRODUCTION

Considerable attention has been given to the participation of sulfur at various oxidation levels in resonance and inductive (conjugative) interactions in organic compounds. However, much of this interest has concerned compounds in which the sulfur atom and interrelating atom or group are separated by an aromatic ring,[1] a vinyl group[2] or a methylene group as in the mercaptoacetic acids.[3] In the present context the question arises regarding conjugation involving a vacant *d*-orbital and non-bonding electrons of an adjacent nitrogen atom. This question has been discussed previously with conflicting conclusions. On the one hand the concept has been used to explain differences in the reactivities of sulfur and analogous carbon compounds,[4–6] but on the other it has been considered that the absence of substituent effects in torsional reactions negated involvement of the conjugative mechanism.[7–9] Transmission of electronic effects through sulfur has been reviewed.[10] Present concern by way of pKa values, which do not appear to have been determined previously, is with substituent effects on the proton acceptor properties of sulfenamides in aqueous media where only one functional group is concerned in the equilibrium

$$R{\cdot}S{\cdot}NH{\cdot}R' + H^+ \rightleftharpoons R{\cdot}S{\cdot}NH_2^+{\cdot}R' \qquad (1)$$

RESULTS AND DISCUSSION

Changes in absorption by the sulfenamides with change in pH of the medium are illustrated with N-(phenyl)-benzenesulfenamide, R=R′=C_6H_5, to show that

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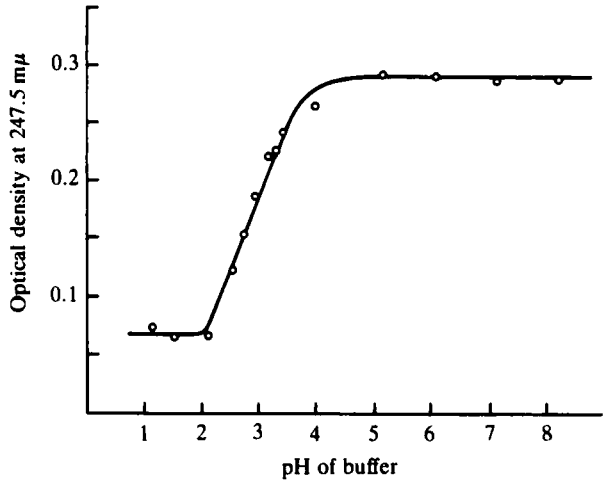


FIGURE 1 Relationship between optical density at 247.5 nm and pH of buffer for N-(phenyl)-benzenesulfenamide.

suitably distinguishing differences exist in the protonated and unprotonated species (Figure 1).

The type of change in the absorption curves of the sulfenamides with change in the pH is also illustrated with N-(phenyl)benzenesulfenamide (Figure 2).

The stability of the sulfenamides under the conditions of the determinations was examined at three wave lengths *viz.* 220, 247 and 270 nm, sites of the trough, peak and isosbestic points of Figure 2. No change was observed over more than two hours standing. Recordings of the decomposition of sulfenamides by acids refer to anhydrous medium, e.g. hydrogen chloride in ether[11] in contrast with the present aqueous media. The smoothness of the curves of Figure 2 with the

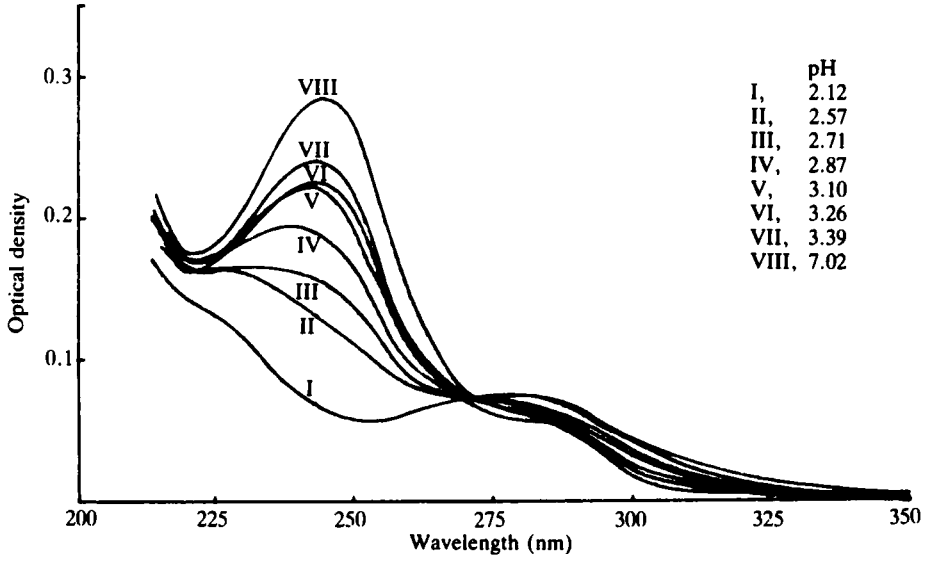


FIGURE 2 Change in the absorption curve of N-(phenyl)-benzenesulfenamide with change in pH of buffer.

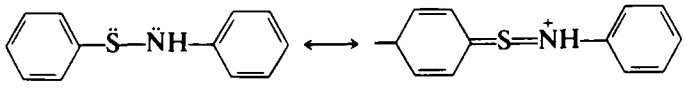
TABLE I

N-Phenylbenzenesulfenamide (R=R'=C_6H_5), pKa value

Curve	pH	Optical density at 270 nm	Optical density at 247.5 nm	pKa	Mean pKa
	1.12	0.080	0.072		
	1.48	0.074	0.066		
	2.12	0.073	0.076		
	2.57	0.075	0.127		
I	2.71	0.072	0.153	2.91	
II	2.87	0.072	0.188	2.79	
III	3.10	0.072	0.220	2.75	2.82
IV	3.27	0.067	0.226	2.85	
V	3.39	0.071	0.241	2.82	
VI	3.95	0.066	0.264		
VII	5.09	0.079	0.292		
	6.00	0.077	0.290		
VIII	7.02	0.076	0.288		
	8.13	0.081	0.288		
	11.98	0.078	0.283		

isosbestic point provides further evidence of the stability of the sulfenamides during the determinations. In more detail changes in absorption providing the basis for calculation of pKa values are shown in Table I for N-(phenyl)-benzenesulfenamide. A summary of results for methyl substituted derivatives is given in Table II.

Appearance of the isosbestic point in Figure 2 is taken as confirmation of the equilibrium (1). The pKa values of the aryl sulfenamides in the range 2.82–3.97 are below that of aniline (pKa 4.69)[12] but are above that of diphenylamine (pKa 0.77). Thus an electron withdrawing effect of the phenylthio- group is demonstrated indicating conjugation between the aromatic ring and the nitrogen atom through the sulfur atom which, however, introduces a moderating effect in leading to pKa values higher than that of diphenylamine.



p-Substitution with a methyl group in the aniline residue produces an inductive effect similar to that produced in *p*-toluidine, whose pKa value relative to aniline is +0.41. A much greater effect (pKa +0.71) produced by substitution in the phenylthio-group shows the greater inductive effect of the methyl substitution in counterpoise to the mesomeric effect, and also indicates interaction between the

TABLE II

Methyl substituted aryl sulfenamides, pKa values

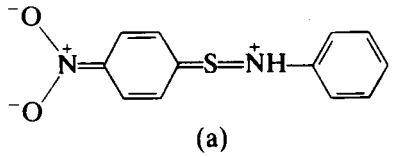
p-X·C_6H_4·S·$NH_2^+$$C_6H_4$·Y-*p*

X	Y	pKa	ΔpKa
H	H	2.82	—
H	CH_3	3.21	+0.39
CH_3	H	3.53	+0.71
CH_3	CH_3	3.97	+1.15

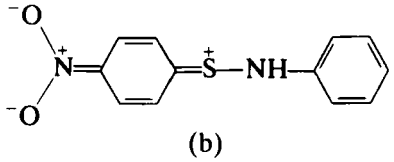
aromatic ring and the nitrogen atom probably involving (p–d) interaction between the ring and sulfur atom. The effect of substitution in both rings is additive giving a total pKa +1.15, which is close to the sum of the separately determined values. In fact the double substitution almost completely negates the influence of the phenylthio-group on the pKa value of aniline as shown in the parent sulfenamide.

The controversy regarding conjugative interactions of the S—N bond raises the question about the extent to which correlation is possible between results from different procedures. Determinations of NMR and ultraviolet absorption properties of sulfenamides in non-aqueous solvents would be concerned with a state of the molecule subject to solvent interaction and association of a different type from those of a more dynamic character applying to determinations in aqueous media of changing pH values. Attempts to correlate NMR results with pKa of a series of substituted anilines, with the aim of determining the significance of the Hammett constants, found an excellent correlation in acetonitrile solution but a less precise correlation in carbon tetrachloride.[10] Efforts to reduce solvent interaction to a minimum have employed cyclohexane as solvent.[13] Solvent effects in passing from deuterochloroform to carbon tetrachloride were greater in the sulfenamides with respect to the labile N—H proton than with those of the methyl groups (Table III).

Although results indicate very little correlation between NMR and pKa values, the important feature emerges that whereas substitution in the aniline residue produces a marked shift, 6 Hz, for the N—H proton in both solvents, substitution in the phenylthio-group had practically no effect. This is in direct contrast with the effect on pKa values where the greater change followed substitution on the sulfur side. A versatility in behavior of the sulfur atom is thus shown, since the capacity to absorb the effect of an electron donating group may be compared with that reported for substitution by the electron withdrawing nitro group in which it was considered that extensive conjugation represented by structure (a) was ruled out in favor of the limited conjugation (b).[14]



(a)



(b)

TABLE III

^{1}H NMR frequencies, Hz, of sulfenamides

p-X·C_6H_4S·NH·C_6H_4·Y-p		N—H		CH_3	
X	Y	$CDCl_3$	CCl_4	$CDCl_3$	CCl_4
H	H	309	300.5	—	—
H	CH_3	304.5	294	136.0	134.8
CH_3	H	310	299	137.8	137.4
CH_3	CH_3	303	294	136.0(N)	134.7(N)
				137.8(S)	137.3(S)

^{1}H Frequencies ±0.2 Hz. Spectra recorded at 60 MHz (N) and (S) indicate position in the sulfenamide–amine or sulfur side of the molecule.

EXPERIMENTAL

Sulfenamides were prepared by a standard method-condensation of sulfenyl chloride with the required amine

$$R{\cdot}SCl + 2R'{\cdot}NH_2 \rightarrow R{\cdot}S{\cdot}NH{\cdot}R' + R'NH_3^+Cl^-$$

Products were recrystallized from light petroleum or ethanol to satisfactory elemental analysis and melting point. Because of the low solubility of the sulfenamides in aqueous media pKa values were determined spectrophotometrically. Solutions of acids, bases and buffers were prepared using doubly distilled water in all-glass apparatus and were free from carbon dioxide. The pH range 1–12 was covered starting from solutions shown in Table IV, adjusting the pH as required with acid or base 0.1 M strength to reduce volume changes.

TABLE IV

Master solutions for pKa determinations

pH Range	Solution*	pH Range	Solution*
1	0.1 M HCl	5.0–7.0	KH_2PO_4
2	HCl	8.0–10.0	NH_4OH
2–3.5	HCOOH	11	KOH
3.5–5.0	CH_3COOH	12	0.1 M KOH

* 0.01 M unless otherwise stated.

Determinations. In each instance a standard solution of the sulfenamide (0.25%) in 70% ethanol was prepared by first dissolving the derivative in ethanol (7 ml) then diluting to volume (10 ml) with water. Using a semi-micro pipette, 0.1 ml capacity graduated in 0.001 ml units, aliquots (0.1 ml) were added to the buffer solution (35–40 ml) and then made to volume (50 ml) with more buffer. Absorption curves (calibrated Beckmen spectrophotometer model DU) were then determined as quickly as possible over the range 215–375 nm, reading against a reference buffer containing ethanol (0.2%). Each determination required about 12–15 minutes, and because of the sensitivity of sulfenamides to light,[15] were made in a darkened room with the only light source a 15 W globe. pH values of the solutions were checked before and after addition of the sulfenamide. pKa values were calculated using the conventional procedure for spectrophotometric determinations.[16]

$$pKa = pH + \log \frac{d_m - d}{d - d_i}$$

where d_m and d_i are the optical densities due to the neutral molecule and cation, determined at pH 7.02 and pH 2.1 respectively, and d is the optical density of the mixture of cation and neutral molecule.

Approximate pKa values were first determined by plotting the optical density of the solution at 247.5 nm, the peak wave length, against pH from which the pH corresponding to the equivalence point of the contributing species could be determined. Accurate determinations were then made using buffer solutions covering the range ±0.5 pH unit on either side of the predetermined values progressing in steps of about 0.2 pH unit. As a check on the validity of results a full absorption curve was obtained for each buffer solution rather than a series of measurements at one particular wave length. The criterion of acceptability of results was taken as the closeness with which the curves fitted the isosbestic point at 270 nm (Figure 2). NMR spectra were recorded on a Varian A60 spectrometer using tetramethylsilane as internal standard.

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