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212. Motohiro Nishio*¹: Nuclear Magnetic Resonance Studies of
Sulfur Compounds. II.*² The Substituent Effect on
Geminal Coupling Constants and on Magnetic
Nonequivalence of the Methylene
Protons of Sulfoxides.*³

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Nuclear magnetic resonance spectra were obtained for a number of sulfoxides, whose methylene protons are magnetically nonequivalent. The coupling constants between these protons depend on the electronic properties of the substituent adjacent to the coupling protons. The substituent effect on magnetic nonequivalence was also studied and it is demonstrated that the electronic properties of the substituent constitute an important factor responsible for the magnitude of magnetic nonequivalence.

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It was shown in a previous paper*² that the methylene protons of sulfoxides of the type X-SOCH₂-Y give AB-type nuclear magnetic resonance (NMR) spectra when Y contains no other nuclei to interact with the methylene protons. Since an AB-type spectrum can be analysed unambiguously, this type of molecule is suitable for the investigation of effects caused by X and Y. The purpose of the work reported herein was to study the effects of substituent on geminal coupling constants and on the magnitude of the magnetic nonequivalence of methylene protons in sulfoxides.

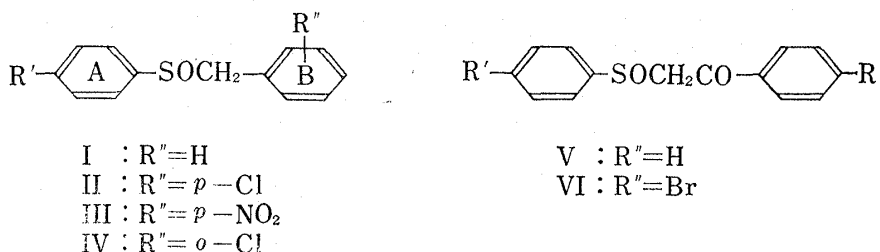
The compounds chosen were *p*-substituted phenyl sulfoxides of the type A.

In this molecule, R is phenyl (I), *p*-chlorophenyl (II), *p*-nitrophenyl (III), *o*-chlorophenyl (IV), benzoyl (V), *p*-bromobenzoyl (VI), acetyl (VII) or substituted and non-substituted carbo-anilide (VIII, R = CONHC₆H₄-R') groups; and R', CH₃, H, Cl and NO₂, in the increasing order of electron withdrawing power.

The chemical shifts and geminal coupling constants for methylene protons of these compounds are summarized in Tables I, II and III.

The effect of the substituent R

a) J_{AB}



R' = CH₃, H, Cl, NO₂

Fig. 2.

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*² Part I: M. Nishio, T. Ito: This Bulletin, 13, 1392 (1965).

*³ This work was presented at "The 4th Symposium on Nuclear Magnetic Resonance (Japan)" in Tokyo, November (1964).

TABLE I. Coupling Constants and Chemical Shifts of Methylene Protons in
 p -R'-C₆H₄SOCH₂-R

	R	Solvent \ R'	CH ₃ (a)	H (b)	Cl (c)	NO ₂ (d)
I	C ₆ H ₅	CDCl ₃ J _{AB} (c.p.s.) ($\tau \frac{A+B}{2}$)	12.7 (5.98)	— (5.97)	12.7 (5.96)	— (5.88)
		C ₆ H ₅ N	— (5.83)	— (5.82)	— (5.81)	12.9 (5.69)
		Me ₂ CO		12.9 (5.93)		
II	C ₆ H ₄ Cl- p	CDCl ₃	— (6.04)	— (6.01)	— (6.01)	
		C ₆ H ₅ N	12.9 (5.85)	12.9 (5.86)	13.0 (5.82)	13.0 (5.69)
		Me ₂ CO			12.9 (5.85)	
III	C ₆ H ₄ NO ₂ - p	CDCl ₃	12.8 (5.91)	12.8 (5.89)	12.9 (5.89)	13.0 (5.80)
		C ₆ H ₅ N	12.6 (5.69)	12.8 (5.68)	13.0 (5.59)	13.0 (5.51)
		Me ₂ CO	13.1 (5.61)	13.4 (5.58)	13.2 (5.53)	13.4 (5.40)
IV	C ₆ H ₄ Cl- o	CDCl ₃			13.0 (5.73)	— (5.70)
		C ₆ H ₅ N			— (5.63)	— (5.53)
		Me ₂ CO			— (5.60)	— (5.48)
V	COC ₆ H ₅	CDCl ₃	14.1 (5.59)	14.1 (5.57)	14.3 (5.56)	14.7 (5.46)
		C ₆ H ₅ N		14.0 (5.07)	14.8 (5.10)	— (4.91)
		CCl ₄	13.7 (5.67)	13.9 (5.64)	14.3 (5.62)	
VI	COC ₆ H ₄ Br- p	CDCl ₃	14.4 (5.59)	14.4 (5.57)	14.8 (5.57)	
		C ₆ H ₅ N	14.2 (5.16)	14.7 (5.14)	— (5.09)	
VII	COCH ₃	CDCl ₃			— (6.11)	— (6.06)

The sign "—" indicates that the chemical shift difference between two protons is too small (assumed to be less than 3 c.p.s.) for the coupling constant to be obtained.

 TABLE II. Chemical Shifts and Coupling Constants of Methylene Protons in
 C₆H₅SOCH₂CONHC₆H₄-R'' (VIII) (in CDCl₃) (R=CONHC₆H₄-R'')

R''	Chemical shift ($\tau \frac{A+B}{2}$)	Coupling constant J _{AB} (c.p.s.)	$\nu_A - \nu_B$ (c.p.s.)
H	6.22	14.1	13.6
o -CH ₃	6.31	14.2	18.6
m -CH ₃	6.30	13.8	13.9
p -CH ₃	6.33	13.9	15.2
p -OCH ₃	6.32	13.8	11.4
o -Cl	6.29	14.1	21.1
m -Cl	6.30	14.1	17.9
p -Cl	6.30	13.8	13.5
o -Br	6.28	14.2	19.5
m -Br		insoluble	
p -Br	6.31	14.1	16.8
o,m,p -NO ₂		insoluble	

TABLE III. Magnetic Nonequivalence of Methylene Protons in p -R'C₆H₄SOCH₂-R (c.p.s.)

R	R' Solvent	CH ₃ (a)	H (b)	Cl (c)	NO ₂ (d)
C ₆ H ₅ I	CDCl ₃	6.3	<3	5.7	<3
	C ₆ H ₅ N	<3	<3	<3	7.0
	Me ₂ CO		5.4		
p -ClC ₆ H ₄ II	CDCl ₃	<3	<3	<3	
	C ₆ H ₅ N	7.9	8.9	9.8	12.6
	Me ₂ CO			10.8	
p -NO ₂ C ₆ H ₄ III	CDCl ₃	9.4	12.0	11.2	15.2
	C ₆ H ₅ N	12.8	14.4	14.7	16.0
	Me ₂ CO	13.5	14.7	14.6	16.6
o -ClC ₆ H ₄ IV	CDCl ₃			5.2	<3
COC ₆ H ₅ V	CCl ₄	16.2	15.3	13.6	insoluble
	CDCl ₃	16.7	14.7	13.9	8.3
	C ₆ H ₅ N	10.8	9.1	7.9	<3
COC ₆ H ₄ Br- p VI	CDCl ₃	12.1	12.1	9.9	
	C ₆ H ₅ N	7.2	4.9	<3	

Since the substituents R are in the nearer position to the methylene group than R', one would expect that the effect of R is more important. In fact, a difference in the magnitude of the coupling constant is observed between I~IV (12.6~13.4 c.p.s.) and V, VI (14.0~14.8 c.p.s.). The only structural difference common to all members of these two series of compounds is the presence of an adjacent carbonyl group in the latter series. Geminal coupling constants in the former series (I~IV), where the methylene group is directly bonded to a phenyl group, are smaller than in the latter series (V and VI), in which the methylene is bonded to a carbonyl group conjugated with a phenyl group. Coupling constants of amide derivatives (VIII) were found to be between these values (13.8~14.2 c.p.s.). The coupling constants of the geminal protons are given in Table IV.

TABLE IV.

		Solvent	J _{AB} (c.p.s.)	Number of compounds examined	Refer- ences
I~IV	ArSOCH ₂ Ar	CDCl ₃	12.7~13.0	7	a)
		C ₆ H ₅ N	12.6~13.0	9	a)
		Me ₂ CO	12.9~13.4	6	a)
V~VI	ArSOCH ₂ COAr	CDCl ₃	14.1~14.8	7	a)
		C ₆ H ₅ N	14.0~14.8	4	a)
VIII	ArSOCH ₂ CONHAr	CDCl ₃	13.8~14.2	10	a)
X	C ₆ H ₅ SOOCH ₂ C ₆ H ₅	CCl ₄	11.4	1	1)
X	(RC ₆ H ₄ CH ₂ O) ₂ SO R= p -Cl, -OCH ₃ , -CH ₃ , H R= p -NO ₂	CCl ₄	11.2~12.0	4	1)
		CHCl ₃	12.8	1	1)

a) This work

Compared with the values obtained for sulfoxides I~IV (12.6~13.4 c.p.s.), those of the sulfites¹⁾ (X and X; 11.2~12.0 c.p.s.) are appreciably smaller.

1) M. Ōki, H. Iwamura : Bull. Chem. Soc. Japan, 35, 1428 (1962).



Fig. 3.

This may be explained qualitatively by considering the contribution of π -electron on sulfur atom for sulfoxides. It has been well established that a S-O bond has some π -character.^{2,3)} Therefore, it is expected that π -electrons of this group contribute to the magnitude of coupling constant to some extent. Barfield and Grant⁴⁾ estimated the π -electron contribution for a coupling constant of methylene group adjacent to a π -bond to be -1.5 c.p.s. In sulfites, however, contribution by the sulfur π -electrons is structurally impossible because of the extra oxygen atom.

In Table II, chemical shifts and coupling constants of anilides $C_6H_5SOCH_2CONH-C_6H_4-R''$ (VIII) are summarized. Efforts have been made to correlate J_{AB} with the Hammett's sigma-parameters. Although there seems to be a relationship between them, it was not possible to demonstrate a clear dependence because the differences are very small among these derivatives.

b) $\nu_A - \nu_B$

An interesting feature seen in Table III is that the magnitude of magnetic non-equivalence is markedly dependent on the substituent R. For example, phenyl benzyl (I), phenyl *p*-chlorobenzyl (II), phenyl *o*-chlorobenzyl sulfoxides (IV) exhibited very small chemical shift differences between two protons in $CDCl_3$. On the other hand, phenyl *p*-nitrobenzyl sulfoxides (III), which contain a *p*-nitro group on B-phenyl ring (see Fig. 2), exhibited large chemical shift differences ($9.4 \sim 15.2$ c.p.s.) in the same solvent. In contrast, the compounds which contain a *p*-nitro group on the A-phenyl ring (Id and IVd) give a singlet which may be due to the small chemical shift difference between the methylene protons (assumed to be less than 3 c.p.s.). Phenyl phenacyl (V) and phenyl *p*-bromophenacyl sulfoxides (VI) exhibited a large chemical shift difference in the same solvent ($8.3 \sim 16.7$ c.p.s.). It should be noted that the *p*-chloro (IVc) and *p*-nitro-phenyl *o*-chlorobenzyl sulfoxides (IVd), which possess a bulky chlorine atom in the *o*-position of the B-phenyl ring, give rise to signals with small chemical shift differences, as in the case of compounds I, which possess no substituent on the *o*-position of the B-ring. Whitesides, *et al.*⁵⁾ studied the effect of structure on

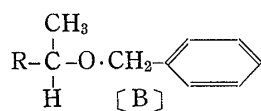


Fig. 4.

the magnitude of the magnetic nonequivalence of the methylene protons in benzyl ethers of the structure B, and observed a correlation between methylene protons and the size of R where R is an alkyl group. In the present case of sulfoxides, however,

the electronic properties of the substituent are more important in determining the magnitude of magnetic nonequivalence.

The effect of substituent R'

a) J_{AB}

The results are summarized in Table I. No appreciable relationship was found between the substituent R' and geminal coupling constants.

2) N. Kharasch: "Organic Sulfur Compounds," Vol. I, p. 35 (1961), Pergamon press.

3) G. Leandri, A. Mangini, R. Passerini: J. Chem. Soc., 1957, 1386.

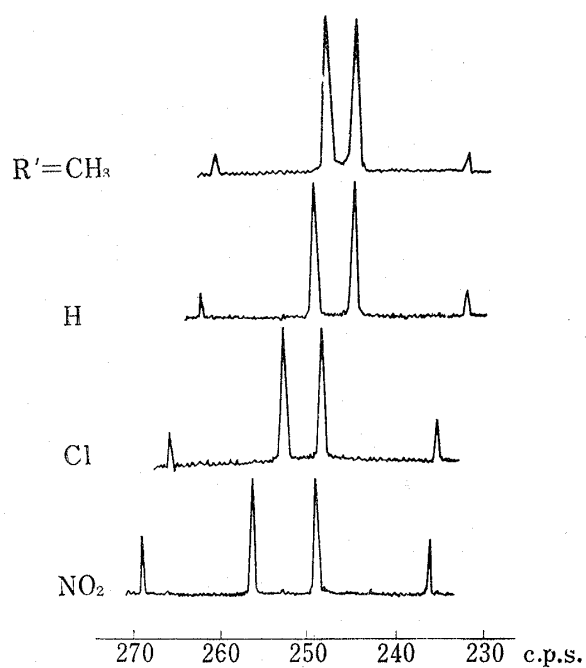
4) M. Barfield, D.M. Grant: J. Am. Chem. Soc., 85, 1899 (1963).

5) G.M. Whitesides, D. Holtz, J.D. Roberts: J. Am. Chem. Soc., 86, 2628 (1964).

b) $\nu_A - \nu_B$

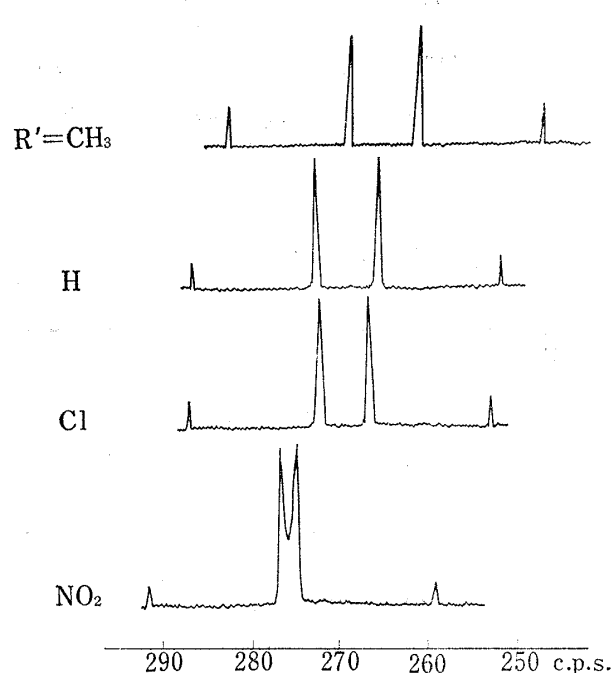
In substituted phenyl benzyl (I) and phenyl *o*-chlorobenzyl sulfoxides (IV), no relationship was found between $\nu_A - \nu_B$ and the substituent R'. In these compounds, it seems that it is the interaction of solute and solvent molecules which plays an important rôle in determining the magnitude of the magnetic nonequivalence.

On the other hand, an interesting relationship between $\nu_A - \nu_B$ and substituent R' is observed for II (in pyridine), III (in CDCl_3 , pyridine and Me_2CO), V (in CCl_4 , CDCl_3 and pyridine) and VI (in CDCl_3 and pyridine). It is noteworthy that $\nu_A - \nu_B$ of II and III increases with the increasing electronegativity of the substituent R'. In contrast, in V and VI, $\nu_A - \nu_B$ decreases as the electron withdrawing power of R' increases. In Fig.



$p\text{-R}'\text{C}_6\text{H}_4\text{SOCH}_2\text{C}_6\text{H}_4\text{-NO}_2\text{-}p$ (III) in CDCl_3

Fig. 5a.



$p\text{-R}'\text{C}_6\text{H}_4\text{SOCH}_2\text{COC}_6\text{H}_5$ (V) in CDCl_3

Fig. 5b.

TABLE V.

R'	$\nu_A + \nu_B/2$	ν_A	ν_B	$\nu_A - \nu_B$	$\nu_A + \nu_B/2$	ν_A	ν_B	$\nu_A - \nu_B$ (c.p.s.)
III in CDCl_3					II in $\text{C}_5\text{H}_5\text{N}$			
CH_3	245.8	250.5	241.1	9.4	249.1	253.1	245.1	7.9
H	246.4	252.4	240.4	12.0	248.5	253.0	244.0	8.9
Cl	250.1	255.7	244.5	11.2	250.5	255.4	245.6	9.8
NO_2	252.1	259.7	244.5	15.2	258.3	264.6	252.0	12.6
III in Me_2CO					V in CDCl_3			
CH_3	263.0	269.8	256.2	13.5	264.6	272.8	256.0	16.7
H	265.0	272.4	257.6	14.7	265.9	273.3	258.5	14.7
Cl	268.0	275.3	260.7	14.6	266.6	273.6	259.6	13.9
NO_2	276.0	284.3	267.7	16.6	272.3	276.5	268.1	8.3
III in $\text{C}_5\text{H}_5\text{N}$					V in CCl_4			
CH_3	258.5	264.9	252.1	12.8	259.9	268.0	251.7	16.2
H	259.4	266.6	252.2	14.4	261.8	269.5	254.1	15.3
Cl	264.6	272.0	257.2	14.7	262.5	269.3	225.7	13.6
NO_2	269.7	277.7	261.7	16.0			insoluble	

5a and 5b are shown a part of their NMR spectra. An independent inspection of chemical shifts ν_A and ν_B summarized in Table V may give a solution to this apparent paradox. In the case of compounds II and III, the chemical shift of the proton which gives rise to a peak in a lower field (ν_A) is more sensitive to the substituent. On the contrary, for V and VI, the proton in a higher field (ν_B) is more sensitive to the substituent

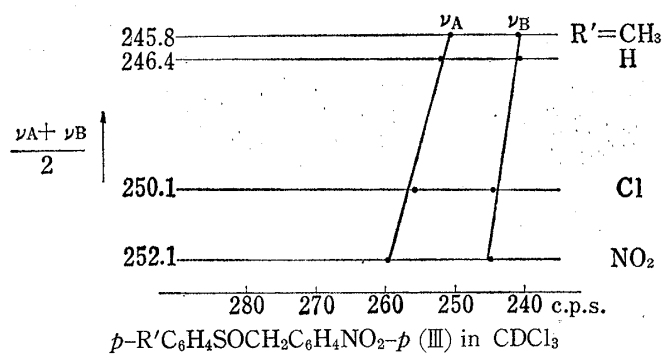


Fig. 6a.

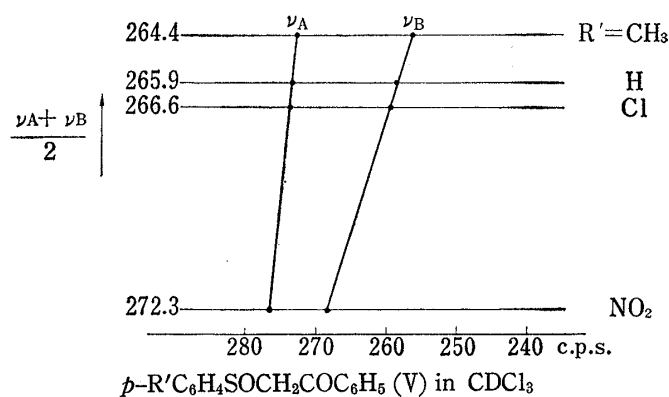


Fig. 6b.

R' . By plotting the chemical shift of each proton independently as a function of the mean value of chemical shift, linear relationships are shown to exist between ν_A , ν_B and $\nu_A + \nu_B/2$. A comparison of the two slopes is illustrated in Fig. 6a (III in CDCl_3). These linearities suggest that there is a relationship between the chemical shift (ν_A and ν_B) and the electronegativity of the substituent R' , since it is well known that the electronegativity of a substituent is proportional to the chemical shift of methyl or methylene protons adjacent to the substituent.⁶⁾ In this case it is shown that the lower proton is more sensitive to the electronegativity of substituent R' . Two different slopes demonstrate that the electronegativity of substituent $\text{E}_{\text{R}'}$ does contribute in a different degree to each proton. Two linear slopes were obtained also for V (in CDCl_3). In this case, however, it is the higher

proton which is more sensitive to the electronegativity of substituent R' (Fig. 6b).

Since the nonequivalence of the methylene protons in an asymmetric acyclic compound is considered to be mainly due to conformational preference,⁶⁾ the conformations (a), (b) and (c) are unequally populated under the conditions of this experiment, and it is very likely that a conformation which possesses two bulky groups in a *trans* relation

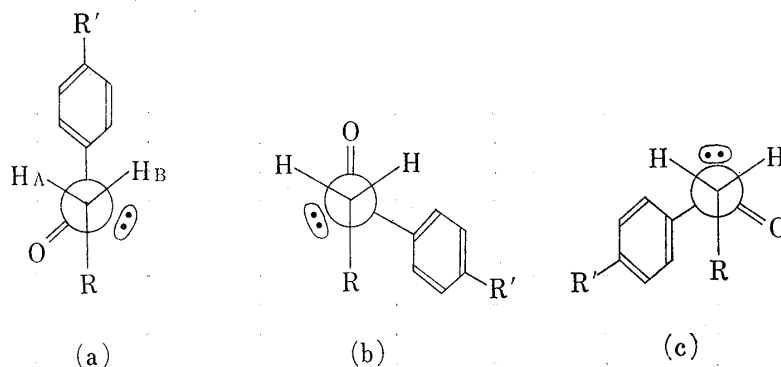


Fig. 7.

6) B.P. Dailey, J.N. Shoolery : J. Am. Chem. Soc., **77**, 3977 (1955).

7) M. Ōki, H. Iwamura, K. Sakaguchi : Preliminary reports of International Symposium on NMR, Tokyo, (1965), N-3-8; from a NMR study of *t*-butyl neopentyl sulfoxide in CDCl_3 at various temperatures, they concluded that this compound is fixed to a conformation having two bulky groups in a *trans* relation.

such as (a) exists in predominance⁷⁾ (see Fig. 7; $R = C_6H_4Cl-p$, $C_6H_4NO_2-p$, COC_6H_5 or COC_6H_4Br-p). The data presently available do not permit an interpretation of the mechanism by which the substituent R' influences the chemical shifts of two protons in a different degree. Assuming that the conformation having two bulky groups is a *trans* relation, however, a speculation based on an anisotropic deshielding effect of the A-phenyl ring on these protons leads us to some such explanation as a preferred conformation having a twisted structure.

Another speculation, which seems to be more likely, is that the proton which is more sensitive to the change of electronegativity of substituent R' is that which exists in the *trans* position to the unshared pair on sulfur⁸⁾ (H_A ; see Fig. 7). As discussed by Hamlow, *et al.*, a partial participation of the lone pair in a σ^* C- H_A orbital is possible⁹⁾ and such a participation allows some overlap between σ^* and lone pair orbitals to generate some double bond character between C and S. Since such an interaction can be expected only in the direction of H_A (*trans* to the lone pair on sulfur atom), it is possible that the substituent R' affects these protons to a different degree. In view of this, efforts are now being made to answer this problem, especially by experiments on deuterium-exchange and on solvent effect, and the results will be published in a subsequent paper.

TABLE VI. $p-R'C_6H_4SOCH_2-R$

R'	R	m.p. (°C)	Analyses (%)						ν_{S-O} (cm ⁻¹)
			Calcd.			Found			
			C	H	S	C	H	S	
CH ₃	C ₆ H ₅	140	73.0	6.09	13.9	73.05	6.28	14.13	1034
H	C ₆ H ₅	127							1033
Cl	C ₆ H ₅	134	62.3	4.39		62.61	4.28		1034
NO ₂	C ₆ H ₅	159~166	59.8	4.22	12.25	60.07	4.17	12.60	1032
CH ₃	<i>p</i> -ClC ₆ H ₄	160	63.5	4.92		63.07	4.90		1032
H	<i>p</i> -ClC ₆ H ₄	171	62.3	4.39		61.55	4.43		1030
Cl	<i>p</i> -ClC ₆ H ₄	126	54.8	3.51		54.69	3.67		1039
NO ₂	<i>p</i> -ClC ₆ H ₄	139	52.8	3.39		53.11	3.49		1047
CH ₃	<i>p</i> -NO ₂ C ₆ H ₄	164	61.1	4.73	11.6	60.79	4.89	11.65	1040
H	<i>p</i> -NO ₂ C ₆ H ₄	161	59.8	4.22	12.25	59.30	4.73	12.50	1020
Cl	<i>p</i> -NO ₂ C ₆ H ₄	154	52.8	3.39		53.02	3.33		1040
NO ₂	<i>p</i> -NO ₂ C ₆ H ₄	176	51.0	3.26	10.8	51.08	3.07	10.87	1044
Cl	<i>o</i> -ClC ₆ H ₄	83	54.8	3.51		54.07	3.78		1033
NO ₂	<i>o</i> -ClC ₆ H ₄	137	52.8	3.39		53.54	3.36		1042
CH ₃	COC ₆ H ₅	109	69.8	5.43	12.4	68.75	5.01	12.57	1036
H	COC ₆ H ₅	81							1052
Cl	COC ₆ H ₅	85	60.3	3.96		60.26	4.34		1022
NO ₂	COC ₆ H ₅	126	60.2	3.97	11.5	57.39	4.07	11.50	1030
CH ₃	COC ₆ H ₄ Br- <i>p</i>	139(decomp.)	53.4	3.86		53.61	3.81		1035
H	COC ₆ H ₄ Br- <i>p</i>	134(decomp.)	52.1	3.41		52.23	3.43		1047
Cl	COC ₆ H ₄ Br- <i>p</i>	139(decomp.)	47.0	2.80		46.74	2.51		1046
Cl	COCH ₃	108	49.9	4.17		49.48	4.30		1026
NO ₂	COCH ₃	129	49.8	4.15	14.75	48.24	4.07	13.98	

8) cf. J. Am. Chem. Soc., **87**, 5498 (1965), A. Rauk, E. Buncel, R. Moir, S. Wolfe; they observed a difference in the rates of deuterium exchange of the two methylene protons of benzyl methyl sulfoxide and speculated that, for a proton to be exchanged, it must be *trans* to the unshared pair on sulfur.

9) H. Hamlow, S. Okuda, N. Nakagawa: Tetrahedron Letters, 2553 (1964). cf. F. Bohlmann, D. Schumann, H. Schulz: Tetrahedron Letters, 173 (1965) and F. Bohlmann: Ber. **91**, 2157 (1958).

Experimental

The proton magnetic resonance spectra were obtained with a Varian Associates A-60 high-resolution NMR spectrometer. Samples were run as 5% or saturated solution with tetramethylsilane as an internal reference at the operating temperature (35°) of the instrument. Chemical shifts are reported in τ -values and are accurate to ± 1 c.p.s. and coupling constants are accurate to ± 0.3 c.p.s. The infrared spectra were obtained with Nippon Bunko DS-401 type spectrometer in solid state (nujol suspension).

Materials—Sulfoxides are easily distinguished from sulfides or sulfones by examining the infrared spectra in S-O stretching region. As summarized in Tables VI and VII, all sulfoxides exhibited strong S-O stretching absorption between 1012~1052 cm^{-1} . Sulfoxides examined in this experiment were prepared by general procedures illustrated below, and the properties of these compounds are listed in Tables VI and VII. Melting points are uncorrected.

General Procedures—Sulfides, except those corresponding to VIII, were prepared by condensation of thiophenol derivatives $\text{R}'\text{C}_6\text{H}_4\text{SH}$ with substituted or nonsubstituted benzyl halide $\text{R}''\text{C}_6\text{H}_4\text{CH}_2\text{X}$, ω -bromoacetophenone $\text{R}''\text{C}_6\text{H}_4\text{COCH}_2\text{Br}$ or chloroacetone in EtOH in the presence of equimolecular amount of KOH.

Oxidation of Sulfides to Sulfoxides—To a solution of 0.01 mole of sulfide in 10 ml. of AcOH, 1.2 g. (0.01 mole) of 30% aqueous H_2O_2 was added dropwise with stirring at room temperature. After the initial reaction was over, the mixture was kept at room temperature for 3 hr. On dilution with H_2O , a sulfoxide separated. After standing in refrigerator for a while, the precipitate was filtered, washed with H_2O and dried. Recrystallization from EtOH, MeOH or from AcOH gave pure crystals.

Derivatives of Benzenesulfinylacetic Acid Anilide (VIII)—Phenylthioacetic acid chloride, obtained by chlorination of phenylthioacetic acid with thionylchloride, was treated with aniline or substituted aniline in benzene solution to give corresponding anilides $\text{C}_6\text{H}_5\text{SCH}_2\text{CONHAr}$. Oxidation of these compounds with 30% aqueous H_2O_2 in AcOH at room temperature gave the corresponding sulfoxides.

TABLE VII. $\text{C}_6\text{H}_5\text{SOCH}_2\text{CONHC}_6\text{H}_4\text{-R}''$ (VIII)

R''	m.p. (°C)	Analyses (%)						$\nu_{\text{S-O}}^{a)}$ (cm ⁻¹)
		Calcd.			Found			
		C	H	S	C	H	S	
H	148	64.9	5.02	12.7	64.63	4.97	11.47	1013
<i>o</i> -CH ₃	134	66.0	5.50	11.7	65.09	5.43	11.82	1040
<i>m</i> -CH ₃	142				65.87	6.01	11.50	1027
<i>p</i> -CH ₃	122				66.25	5.25	11.91	1014
<i>p</i> -OCH ₃	130	62.3	5.19	11.1	61.62	5.46	11.22	1013, 1022 1029, 1038
<i>o</i> -Cl	123	57.3	4.09		57.14	3.91		1040
<i>m</i> -Cl	159				57.54	4.60		1030
<i>p</i> -Cl	168				58.07	4.54		1012
<i>o</i> -Br	129	49.7	3.56		49.24	4.19		1049
<i>m</i> -Br	161				50.01	3.75		1032
<i>p</i> -Br	177				49.83	4.12		1020
<i>o</i> -NO ₂	155	55.3	3.95	10.5	55.19	4.20	10.55	1035
<i>m</i> -NO ₂	171				54.95	4.21	10.60	1032
<i>p</i> -NO ₂	223 (decomp.)				55.66	4.20	10.70	1020, 1030

a) An interesting relationship between $\nu_{\text{S-O}}$ and the position of the substituent was observed. The S-O stretching vibration frequency decreased in the order: ortho>meta>para for all substituents except the nitro group.

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