31. Nariko Shinriki*² and Toshio Nambara*³: The Sulfone Stretching Frequencies of Some Phenylsulfonyl Derivatives.

(Faculty of Pharmaceutical Sciences, School of Medicine, Hokkaido University*¹)

The bond character of sulfone ($-\text{SO}_2-$) has been studied from the various points of view as to the important configuration among the three possible structures, I, II, and III. The conception that the sulfonyl group has a structure represented as the resultant of resonance between Ia and Ib, has been demonstrated by means of dipole moment measurement,¹⁻³⁾ ultraviolet absorption spectroscopy,⁴⁻⁹⁾ kinetic study with regard to the electronic effect on the neighboring group,^{10,11)} and some other methods.^{12,13)}

On the other hand, several infrared spectral studies on sulfone¹⁴⁻¹⁹⁾ were reported in connection with the frequency shift comparing with that of carbonyl group. Almost all reports concluded that the substituent effect on the frequency shift of sulfonyl group was far smaller than that of carbonyl because the substituents attached to sulfur can not occupy the same plane. However, Momose, *et al.*¹⁹⁾ reported that the order of the shift in wave number accorded with the sequential order of Hammett's constant of substituent on benzene ring by measuring infrared spectra of some *p*-substituted phenyl methyl sulfone derivatives. Furthermore, Rogers, *et al.*³⁾ recognized the intensity enhancement of symmetric stretching mode of SO_2 in the presence of adjacent group capable of conjugation in a few instances. Authors have been much interested in the polarization of sulfonyl group and attempted to examine the substituent effects systematically, which could presumably provide the further evidences on this question. In the present paper, infrared spectra of 48 phenylsulfonyl derivatives, most of which have been synthesized by one of the authors, are reported and substituent effects on the SO_2 stretching frequency are mainly discussed.

*¹ Kita-12-jo, Nishi-5-chome, Sapporo, Hokkaido (神力就子, 南原利夫).

*² Present Address: Government Industrial Development Laboratory, Hokkaido.

*³ Present Address: Faculty of Pharmaceutical Sciences, University of Tokyo.

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Results and Discussion

The assignment for sulfonyl group is not open to doubt since two characteristic bands of asymmetric (ν_{as}) and symmetric (ν_s) stretching mode of S-O bond are the strongest. In some cases the linear relationship between ν_{as} and ν_s ¹⁶⁾ can be helpful for assignment. As shown in Table I, ν_s appears as a maximum absorption band in the range 1133~1165 cm⁻¹, while ν_{as} appears as a few bands in the range 1287~1367 cm⁻¹. In Table I, the main band of the latter was distinguished with use of bold-faced type. The frequency of ν_{as} in the solution spectra shows approximately 20~30 cm⁻¹ higher value than that in solid spectra, whereas ν_s does not show such large difference. In the solid state such as nujol or KBr, the spectrum is generally complicated and a correlation of stretching frequency of SO₂ with the kind of substituent cannot be recognized clearly owing to the molecular aggregation as pointed out by Soloway, *et al.* on that of carbonyl in substituted acetophenone derivatives.²⁰⁾ Therefore, the effects of *p*-substituents such as methoxy-, methyl-, acetamido-, chloro-, bromo-, carboxy-, methoxycarbonyl-, and nitro group on the shift of SO₂ frequency were examined in the liquid state with series of 2-chloroethyl phenyl sulfone (I~VIII), 2-mesyloxyethyl phenyl sulfone (IX~XV), phenyl vinyl sulfone (XVI~XXI), and ethyl phenyl sulfone (XXII~XXVI). Since most of these compounds are sparingly soluble in non-polar solvent, the measurement of spectrum was carried out in the chloroform solution. Fig. 1 shows that in each series of homolog, there can be seen a linear relationship between ν_{as} and Hammett's constant σ ²¹⁾ of the *p*-substituent. The result seems to confirm the observations on some *p*-substituted phenyl methyl sulfone derivatives,¹⁹⁾ and suggest that in sulfonyl group the linkage between sulfur and oxygen has considerably double bond character and the bond-order will be increased or decreased depending on the electronic effect of substituent on benzene ring. Moreover, the result indicates that the group attached directly to SO₂, R₁ could also affect the bond-order to result in frequency shift. The influence of β -substituent such as chloro, and mesyloxy which have remarkable inductive effect, can be recognized distinctly by the comparison with those of ethyl sulfone series taken as standard. The similar observation was reported in terms of mean frequency¹⁴⁾ ($\nu_s + \nu_{as}$)/2 of some phenylsulfonyl derivatives,¹⁹⁾ but the above result implies that β -substituent is still effective for the shift of SO₂ stretching frequency to a certain degree of contribution. However, it seems very unnatural that the frequencies of vinyl sulfone series are generally higher rather than those of ethyl sulfone series despite of possessing α,β -unsaturated double bond. It coincides with the case of aromatic sulfone and quite different from that of carbonyl. The similar result was discussed²²⁾ as to SO₂ stretching frequency of thiolsulfonate. In this instance, the upward frequency shift of sulfonyl group was explained by ascribing to the inductive effect of sulfur attached directly to SO₂ and much less mesomeric conjugative capacity

Fig. 1. Relationship between ν_{as} of SO₂ Group and Hammett's Constant of *p*-Substituent in Phenylsulfonyl Derivatives

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TABLE I. SO₂ Stretching Frequencies of Phenylsulfonyl Derivatives

<div><div>R₂- -SO₂R₁</div></div>							
No.	R ₁	R ₂	State	$\nu_{as} \text{ cm}^{-1}$			$\nu_s \text{ cm}^{-1}$
I	CH ₂ CH ₂ Cl	CH ₃ O	C	1337	1308		1148
			N	1330	1312	1302	1144
			K	1335	1314	1306	1147
II		CH ₃	C	1339	1314		1152
			N	1319	1304	1297*	1148
			K	1322	1308		1149
III		H	C	1337	1315*		1154
			N	1333	1314*	1302	1155
			K	1334	1316*	1304	1155
IV		Cl	C	1342	1315*		1156
			N	1328	1313	1299*	1155
			K	1332	1316	1304*	1150
V		Br	C	1343	1318		1154
			N	1322	1311	1295*	1154
			K	1328	1316	1299*	1149
VI		COOH	N	1335	1315		1157
			K	1337	1316		1158
VII		COOCH ₃	C	1341			1156
VIII		NO ₂	C	1349	1318		1156
			N	1338	1323	1308	1160
			K	1339	1322*	1307	1159
IX	CH ₂ CH ₂ OMs	CH ₃	C	1338			1147
			N	1327	1306	1294	1142
			K	1331	1308		1144
X		CH ₃ CONH	C	1337			1145
			N	1321	1309		1142
			K	1322	1309		1144
XI		H	C	1339			1147
			N	1320	1298		1147
			K	1321	1300		1147
XII		Cl	C	1342			1150
			N	1319	1306		1143
			K	1321	1309		1143
XIII		Br	C	1340			1149
			N	1318	1303		1146
			K	1323	1307		1147
XIV		COOH	N	1334	1303		1147
			K	1336	1306		1149
XV		NO ₂	C	1367			1151
			N	1349	1330	1313	1153
			K	1349	1329	1311	1154
XVI	CH=CH ₂	CH ₃ O	C	1328	1317	1307	1146
			K	1321	1312*	1302	1141
XVII		CH ₃	C	1327	1316	1304	1149
			K	1320	1311	1299	1146
XVIII		CH ₃ CONH	C	1331	1315*		1147
			K	1332	1314		1147
XIX		H	C	1329	1319	1306	1151
			K	1328	1317	1306	1149
XX		Cl	C	1333			1152
			K	1330	1305*		1149
XXI		Br	C	1334			1153
			K	1329	1307*		1148

No.	R ₁	R ₂	State	$\nu_{as} \text{ cm}^{-1}$		$\nu_s \text{ cm}^{-1}$
				1321	1308	
XXII	CH ₂ CH ₃	CH ₃	C	1321	1308	1145
XXIII		H	C	1320		1148
XXIV		Cl	C	1327		1149
XXV		Br	C	1324		1150
XXVI		NO ₂	C	1332	1315	1151
XXVII	CH ₂ CH ₂ P'	CH ₃ CONH	N	1333		1154
			K	1330		1158
XXVIII		COOH	N	1305	1285	1145
			K	1304	1287	1146
XXIX		NO ₂	N	1318	1302	1152
			K	1319	1303	1154
XXX	CH ₃	CH ₃ CONH	N	1327		1141
			K	1327		1142
XXXI	CH ₂ CONH ₂		N	1327	1317	1146
			K	1329	1305	1146
XXXII	CH ₂ CN		N	1335	1320	1152
			K	1336	1321	1153
XXXIII	CH ₂ CH ₂ OH		N	1340	1318	1137
			K	1338	1319	1138
XXXIV	CH ₂ CH ₂ SC ₆ H ₅		N	1333	1311	1150
			K	1334	1312	1149
XXXV	Ts(CH ₂) ₂	CH ₃	C	1329	1309	1150
XXXVI	Ts(CH ₂) ₃		C	1326	1310	1298
			K	1329	1310	1293
XXXVII	Ts(CH ₂) ₄		C	1327	1312	1297
			K	1323	1311	1294
XXXVIII	Bs(CH ₂) ₂	H	C	1331	1318	1152
XXXIX	Bs(CH ₂) ₃		C	1328	1317	1152
			K	1312	1298	1154
XL	Bs(CH ₂) ₄		C	1329	1317	1149
			K	1325	1316*	1287
XLI	<i>p</i> -BrBs(CH ₂) ₃	Br	C	1333		1153
			K	1325		1148
XLII	(CH ₂) ₄ Cl	CH ₃	K	1313*	1308	1296
XLIII		H	K	1322	1297	1150
XLIV	CH ₂ COOC ₂ H ₅		N	1333	1322	1163
			K	1334	1323	1165

	position	R				
XLV	<i>meta</i>	OCH ₃	N	1319	1299	1133
			K	1322	1301	1135
XLVI	<i>para</i>		N	1327	1290	1152
			K	1330	1293	1153
XLVII	<i>meta</i>	SC ₄ H ₉	N	1345	1330	1310
			K	1346	1330	1307
XLVIII	<i>para</i>	Cl	N	1338	1320	1157
			K	1340	1322	1298

N : Nujol mull
Ms : CH₃SO₂-

C : CHCl₃ solution
Bs : C₆H₅SO₂-

K : KBr tablet
Ts : *p*-CH₃C₆H₄SO₂-

* : Shoulder
P' : (C₆H₅O)₂P(O)-

of sulfonyl group. In the same manner, it might be considered that sulfonyl group cannot participate in the normal conjugation with vinyl group, whereas it can be influenced by the inductive effect of that group to result in an increase of the bond-order. As well-known, Hammett's constant, an index of the electron density of benzene ring involves the magnitude of both inductive and mesomeric effect, the former of which might exert the dominant influence on the frequency shift of SO_2 group in phenyl-sulfonyl derivatives.

Concerning the other compounds, infrared spectra were measured in the state of nujol and/or KBr as listed in Table I. The result cannot be discussed in precision with respects to the electronic effect of substituent owing to the molecular aggregation. However, considering the mean frequency, the magnitude of shift can be recognized in accordance with the inductive effect approximately in each series of homolog such as *p*-acetamidophenylsulfonyl derivatives (XXX~XXXIV), α,ω -bis(arylsulfonyl)-alkane (XXXV~XLI).

It is noteworthy that unlike the case of carbonyl, groups capable of conjugation slightly offset a small increase in SO_2 stretching frequency as if they were acting in accordance with their inductive effect rather than conjugation capacity. The discrepancy between these results and the other observations described above might be explained by the following speculation. As to the bond between SO_2 and unsaturated group attached directly, the typical π_p conjugation could not take place, but a certain degree of overlapping between $3d$ orbitals of sulfur and $2p$ electrons of carbon, that is, π_d hybridization might occur.

Experimental

Synthesis of the Samples

***p*-Chlorophenyl 2-Hydroxyethyl Sulfone**—To a solution of 4.7 g. of *p*-chlorophenyl 2-hydroxyethyl sulfide in 8 cc. of glacial AcOH, 8 cc. of 30% H_2O_2 was added slowly. The reaction mixture was heated on a water bath for 1 hr. Upon concentration, the obtained oily residue was diluted with Me_2CO and dried over anhyd. Na_2SO_4 . After an evaporation of the solvent, distillation gave colorless viscous oil, b.p. $165\sim 168^\circ$. Yield, 3.5 g.

***p*-Bromophenyl 2-hydroxyethyl Sulfone**—A solution of 4.5 g. of *p*-bromophenyl 2-hydroxyethyl sulfide in glacial AcOH was treated with 30% H_2O_2 in the similar manner to the above. Distillation gave colorless viscous oil, b.p. $175\sim 180^\circ$. Yield, 3.4 g.

***p*-Chlorophenyl 2-(Methylsulfonyloxy)ethyl Sulfone (XII)**—To a solution of 3.5 g. of *p*-chlorophenyl 2-hydroxyethyl sulfone in 4 cc. of pyridine was added 2.5 g. of methanesulfonyl chloride. Treatment of the reaction mixture in the usual manner and recrystallization from EtOH gave colorless needles, m.p. $95\sim 96^\circ$. Yield, 2.4 g. *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{O}_5\text{ClS}_2$: C, 36.26; H, 3.74. Found: C, 36.18; H, 3.71.

***p*-Bromophenyl 2-(Methylsulfonyloxy)ethyl Sulfone (XIII)**—A solution of 2.8 g. of *p*-bromophenyl 2-hydroxyethyl sulfone in pyridine was treated with methanesulfonyl chloride in the same manner as XII. Recrystallization from EtOH gave colorless leaflets, m.p. 96° . Yield, 1.8 g. *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{O}_5\text{BrS}_2$: C, 31.49; H, 3.23. Found: C, 31.54; H, 3.15.

***p*-Carboxyphenyl 2-Chloroethyl Sulfone (VI)**—To a solution of 1.2 g. of *p*-tolyl 2-chloroethyl sulfone in 18 cc. of AcOH, were added 2.2 g. of CrO_3 and 1.5 cc. of conc. H_2SO_4 . The reaction mixture was heated on a water bath for 6 hr. and poured into ice-water. The white precipitate produced was filtered, washed and recrystallized from H_2O to give colorless needles, m.p. $219\sim 220^\circ$. Yield, 1.0 g. *Anal.* Calcd. for $\text{C}_9\text{H}_9\text{O}_4\text{ClS}$: C, 43.46; H, 3.65. Found: C, 43.66; H, 3.75.

2-Chloroethyl *p*-(Methoxycarbonyl)phenyl Sulfone (VII)—Prepared from VI with CH_3N_2 in the usual manner. Recrystallization from MeOH to give colorless needles, m.p. $105\sim 105.5^\circ$. *Anal.* Calcd. for $\text{C}_{10}\text{H}_{11}\text{O}_4\text{ClS}$: C, 45.72; H, 4.22. Found: C, 46.01; H, 4.17.

***p*-Bromophenyl 2-Chloroethyl Sulfone (V)**—Prepared from *p*-bromophenyl 2-chloroethyl sulfide and recrystallized from EtOH to give colorless needles, m.p. 113° .

2-Chloroethyl *p*-Chlorophenyl Sulfone (IV)—Prepared from *p*-chlorophenyl 2-chloroethyl sulfide and recrystallized from EtOH to give colorless needles, m.p. $98\sim 99^\circ$.

2-Chloroethyl *p*-Methoxyphenyl Sulfone (I)—Treatment of 2.0 g. of *p*-methoxyphenyl 2-chloroethyl sulfide with 30% H_2O_2 in AcOH and recrystallization from EtOH gave colorless needles, m.p. $55\sim 56^\circ$. Yield, 1.8 g. *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{O}_3\text{ClS}$: C, 46.06; H, 4.72. Found: C, 46.12; H, 4.61.

***p*-Bromophenyl Vinyl Sulfone (XXI)**—To a solution of 3 g. of V in anhyd. Et₂O, was added 5 cc. of triethylamine slowly under vigorous stirring. The reaction mixture was stirred for several hr. and then allowed to stand overnight. After a removal of the precipitated crystals by filtration, evaporation of the solvent and distillation under reduced pressure gave colorless viscous oil, b.p.₄ 153~154°. Yield, 1.9 g. *Anal.* Calcd. for C₈H₇O₂BrS : C, 38.88; H, 2.86. Found : C, 38.65; H, 3.00.

***p*-Chlorophenyl Vinyl Sulfone (XX)**—Treatment of 2.5 g. of IV in the same manner as XXI and distillation gave colorless viscous oil, b.p.₅ 145~147°. Yield, 1.5 g. *Anal.* Calcd. for C₈H₇O₂ClS : C, 47.41; H, 3.48. Found : C, 47.18; H, 3.47.

***p*-Methoxyphenyl Vinyl Sulfone (XVI)**—Treatment of 2.0 g. of I in the same manner as XXI and recrystallization from dil. EtOH gave colorless leaflets, m.p. 73.5°. Yield, 1.3 g. *Anal.* Calcd. for C₉H₁₀O₃S : C, 54.52; H, 5.08. Found : C, 54.58; H, 5.32.

4-Chlorobutyl Phenyl Sulfone (XLIII)—Prepared from 3.2 g. of 4-chlorobutyl phenyl sulfide with 30% H₂O₂ and recrystallized from dil. EtOH to give colorless leaflets, m.p. 56~57°. Yield, 3.2 g. *Anal.* Calcd. for C₁₀H₁₃O₂ClS : C, 52.03; H, 5.63. Found : C, 51.71; H, 5.63.

4-Chlorobutyl *p*-Tolyl Sulfone (XLII)—Prepared from 1.8 g. of 4-chlorobutyl *p*-tolyl sulfide with 30% H₂O₂ and recrystallized from dil. EtOH to give colorless leaflets, m.p. 39~40°. Yield, 1.6 g. *Anal.* Calcd. for C₁₁H₁₅O₂ClS : C, 53.29; H, 6.13. Found : C, 53.11; H, 5.84.

1,4-Bis(phenylsulfonyl)butane (XL)—To a solution of 0.5 g. of 4-chlorobutyl phenyl sulfone in 50% EtOH containing 0.13 g. of NaOH was added 0.25 g. of thiophenol and the reaction mixture was refluxed on a water bath for 1 hr. After an evaporation of the solvent, the oily product was extracted with Et₂O. The crude product was treated with 30% H₂O₂ in AcOH and recrystallized from EtOH to give colorless needles, m.p. 122~123°. Yield, 0.4 g. *Anal.* Calcd. for C₁₆H₁₈O₄S₂ : C, 56.78; H, 5.36. Found : C, 56.58; H, 5.64.

1,4-Bis(*p*-tolylsulfonyl)butane (XXXVII)—Prepared from 0.5 g. of 4-chlorobutyl *p*-tolyl sulfone and *p*-thiocresol in the same manner as XL. Recrystallization from EtOH gave colorless needles, m.p. 148.5~149.5°. Yield, 0.5g. *Anal.* Calcd. for C₁₈H₂₂O₄S₂ : C, 58.98; H, 6.05. Found : C, 58.47; H, 6.04.

1,3-Bis(*p*-bromophenylsulfonyl)propane (XLI)—To a solution of 1.9 g. of *p*-bromobenzenesulfonic acid in EtOH containing 0.4 g. of KOH was added 1 g. of trimethylene dibromide slowly and the reaction mixture was refluxed for 1 hr. The precipitates produced were recrystallized from AcOH to give colorless needles, m.p. 188~189°. Yield, 0.95 g. *Anal.* Calcd. for C₁₅H₁₄O₄Br₂S₂ : C, 37.36; H, 2.92. Found : C, 36.96; H, 2.92.

Synthesis of the samples which were not mentioned above, have been already reported in the previous papers.²³⁾

Infrared spectra—Measurement of infrared spectra was carried out with a Koken Model DS-301 recording infrared spectrophotometer using NaCl prism.

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Summary

Infrared spectra of 48 kinds of phenylsulfonyl derivatives were measured and the substituent influence on the SO₂ stretching frequency was discussed in terms of electronic effects. In each series of homolog of phenyl 2-chloroethyl sulfone, 2-mesyloxyethyl sulfone, vinyl sulfone, and ethyl sulfone, the linear correlation of ν_{as} with Hammett's σ of *p*-substituent was recognized. It was also observed that β -substituents such as chloro- and mesyloxy- exert a certain degree of effect on the frequency shift, respectively. The SO₂ stretching vibration of phenyl vinyl sulfone derivatives appeared in somewhat upward wave number compared with that of phenyl ethyl sulfone series.

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