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

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The bond character of sulfone (-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]

Ia Ib II III

On the other hand, several infrared spectral studies on sulfone[14~19] 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.

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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 SO_2 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 SO_2 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 SO_2, R_1 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 frequency[14] $(\nu_s+\nu_{as})/2$ of some phenylsulfonyl derivatives,[19] but the above result implies that β-substituent is still effective for the shift of SO_2 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 discussed[22] as to SO_2 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 SO_2 and much less mesomeric conjugative capacity

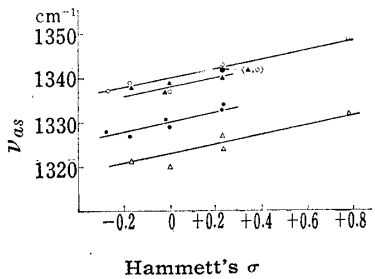

Fig. 1. Relationship between ν_{as} of SO_2 Group and Hammett's Constant of *p*-Substituent in Phenylsulfonyl Derivatives

R_2-C_6H_4-SO_2R_1

R_1: CH_2CH_2Cl ○
CH_2CH_2OMs ▲
$CH{=}CH_2$ •
CH_2CH_3 △

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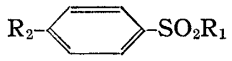
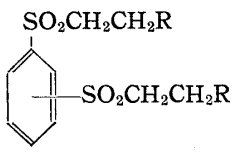
TABLE I. SO_2 Stretching Frequencies of Phenylsulfonyl Derivatives



No.	R_1	R_2	State	ν_{as} cm^{-1}			ν_s cm^{-1}
I	CH_2CH_2Cl	CH_3O	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_2CH_2OMs	CH_3	C	**1338**			1147
			N	1327	**1306**	1294	1142
			K	1331	**1308**		1144
X		CH_3CONH	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_3O	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_3CONH	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	ν_{as} cm^{-1}			ν_s cm^{-1}
XXII	CH_2CH_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_2CH_2P'	CH_3CONH	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_3CONH	N	**1327**			1141
			K	**1327**			1142
XXXI	CH_2CONH_2		N	1327	1317	**1304**	1146
			K	**1329**	1305		1146
XXXII	CH_2CN		N	1335	**1320**		1152
			K	**1336**	1321		1153
XXXIII	CH_2CH_2OH		N	1340	**1318**		1137
			K	**1338**	1319		1138
XXXIV	$CH_2CH_2SC_6H_5$		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	1149
			K	1329	1310	**1293**	1149
XXXVII	$Ts(CH_2)_4$		C	**1327**	1312	1297	1146
			K	1323	**1311**	1294	1148
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**	1145
XLI	*p*-$BrBs(CH_2)_3$	Br	C	**1333**			1153
			K	**1325**			1148
XLII	$(CH_2)_4Cl$	CH_3	K	1313*	1308	**1296**	1149
XLIII		H	K	1322	**1297**		1150
XLIV	$CH_2COOC_2H_5$		N	**1333**	1322		1163
			K	**1334**	1323		1165



	position	R					
XLV	*meta*	OCH_3	N	1319	**1299**		1133
			K	1322	**1301**		1135
XLVI	*para*		N	**1327**	1290		1152
			K	**1330**	1293		1153
XLVII	*meta*	SC_4H_9	N	1345	**1330**	1310	1144
			K	1346	**1330**	1307	1144
XLVIII	*para*	Cl	N	1338	**1320**		1157
			K	1340	**1322**	1298	1158

N : Nujol mull C : $CHCl_3$ solution K : KBr tablet *: Shoulder
Ms : CH_3SO_2– Bs : $C_6H_5SO_2$– Ts : *p*-$CH_3C_6H_4SO_2$– P′ : $(C_6H_5O)_2P(O)$–

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 phenylsulfonyl 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 4.7g. 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, $b.p_3$ 165~168°. 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, $b.p_3$ 175~180°. 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. 95~96°. Yield, 2.4 g. *Anal.* Calcd. for $C_9H_{11}O_5ClS_2$: 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 $C_9H_{11}O_5BrS_2$: 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. 219~220°. Yield, 1.0 g. *Anal.* Calcd. for $C_9H_9O_4ClS$: 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_2N_2 in the usual manner. Recrystallization from MeOH to give colorless needles, m.p. 105~105.5°. *Anal.* Calcd. for $C_{10}H_{11}O_4ClS$: 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. 98~99°.

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. 55~56°. Yield, 1.8 g. *Anal.* Calcd. for $C_9H_{11}O_3ClS$: 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. Et_2O, 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 $C_8H_7O_2BrS$: 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 $C_8H_7O_2ClS$: 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 $C_9H_{10}O_3S$: C, 54.52; H, 5.08. Found : C, 54.58; 5.32.

4-Chlorobutyl Phenyl Sulfone (XLIII)——Prepared from 3.2 g. of 4-chlorobutyl phenyl sulfide with 30% H_2O_2 and recrystallized from dil. EtOH to give colorless leaflets, m.p. 56～57°. Yield, 3.2 g. *Anal.* Calcd. for $C_{10}H_{13}O_2ClS$: 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% H_2O_2 and recrystallized from dil. EtOH to give colorless leaflets, m.p. 39～40°. Yield, 1.6 g. *Anal.* Calcd. for $C_{11}H_{15}O_2ClS$: 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 Et_2O. The crude product was treated with 30% H_2O_2 in AcOH and recrystallized from EtOH to give colorless needles, m.p. 122～123°. Yield, 0.4 g. *Anal.* Calcd. for $C_{16}H_{18}O_4S_2$: 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 $C_{18}H_{22}O_4S_2$: 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 $C_{15}H_{14}O_4Br_2S_2$: 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 SO_2 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 SO_2 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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