## Summary

A fluorescent compound produced in the reaction of 5-hydroxy-1-tetralone with glucose in sulfuric acid was separated in crystalline form and its probable structure was forwarded as benzonaphthenedione. The same compound was also isolated from the reaction mixture of glyceraldehyde with the same reagent. The mechanism of these reactions was discussed.

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## 80. **Tsutomu Momose, Yo Ueda, and Tatsuo Shōji**: Organic Analysis. XI.* Infrared Spectra of Phenylsulfonyl Derivatives. (1). The $SO_2$ Stretching Frequencies.

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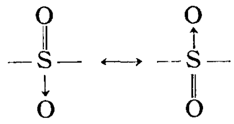
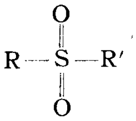
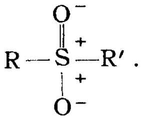
Several infrared spectral studies on phenylsulfonyl derivatives were reported by Schreiber,[1] Amstutz, *et al.*,[2] and by Barnard, *et al.*[3] concerning mainly with the hydrogen-bond formation of sulfonyl group. Bellamy,[4] quoting the data of Haszeldine,[5] Barnard,[3] and Baxter,[6] and their co-workers, concluded that the substituent effect of a sulfonyl group was much smaller than that of a carbonyl group, because sulfonyl group has a tetrahedral structure.

However, since sulfonyl group has decet electronic structure in its resonance state of  $\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\|}}{-S-}} \longleftrightarrow \underset{\underset{O}{\|}}{\overset{\overset{O}{\uparrow}}{-S-}}$, and has a double bond-like character, some substituent effect of this group may be expected. Thus, Amstutz, *et al.* already found a shift of 3 $cm^{-1}$ between 4-hydroxydiphenyl and 4-hydroxy-2-methoxydiphenyl sulfones, and Vogl-Högler[7] recognized some constitutive influence upon the SO frequencies. Szmant, *et al.*[8] assumed from the study of ultraviolet spectra that when a phenylsulfonyl compound had an electron-accepting radical it might take a structure of  $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-R'$, and when it had an electron-donating radical it might take a structure of  $R-\underset{\underset{O^-}{|^+}}{\overset{\overset{O^-}{\|^+}}{S}}-R'$.

In this paper, infrared spectra of 50 phenylsulfonyl derivatives that were measured and substituent effect on the sulfonyl group are discussed.

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* Part X : This Bulletin, **6**, 412(1958).

** Katakasu, Fukuoka (百瀬 勉, 上田 陽, 庄司達雄).

[1] K.C. Schreiber : Anal. Chem., **21**, 1168(1949).

[2] E.D. Amstutz, I.M. Hunsberger, J.J. Chessick : J. Am. Chem. Soc., **73**, 1220(1951).

[3] D. Barnard, J.M. Fabian, H.P. Koch : J. Chem. Soc., **1949**, 2442.

[4] L.J. Bellamy, R.L. Williams : *Ibid.*, **1957**, 863.

[5] R.N. Haszeldine, J.M. Kidd : *Ibid.*, **1955**, 2901.

[6] J.N. Baxter, J. Cymerman-Craig, J.B. Willis : *Ibid.*, **1955**, 669.

[7] R. Vogl-Högler : Acta Phys. Austriaca, **1**, 323(1948) (C.A., **42**, 6663(1948)).

[8] H.H. Szmant, G. Suld : J. Am. Chem. Soc., **78**, 3400(1956); H.H. Szmant, J. Dixon : *Ibid.*, **78**, 4384(1956).

## Results and Discussion

### Nature of the Spectra

Most of phenylsulfonyl derivatives were sparingly soluble in organic solvents except alcohols, and a Nujol mull method was used for all the samples. However, several typical compounds on which main discussion is based were measured in $CHCl_3$ solution to avoid any molecular aggregation effect. All compounds showed very strong bands of an asymmetric ($\nu_{as}$) and a symmetric ($\nu_s$) stretching mode of an S–O bond.

Fig. 1 shows typical spectra, and also the difference of vibration frequencies measured in Nujol mull (——) and in $CHCl_3$ solution (------). The $\nu_{as}$ frequencies in the solution spectra have $10\sim20\ cm^{-1}$ higher values than that of the solid spectra, but the $\nu_s$ frequencies do not show such large differences and conversely have rather diminishing tendencies. This result agrees with that of the studies of Barnard and Baxter. By the explanation of Barnard, the asymmetric vibration frequency is of a more purely bond-stretching type than the symmetric frequency, and the former may undergo a much greater shift.

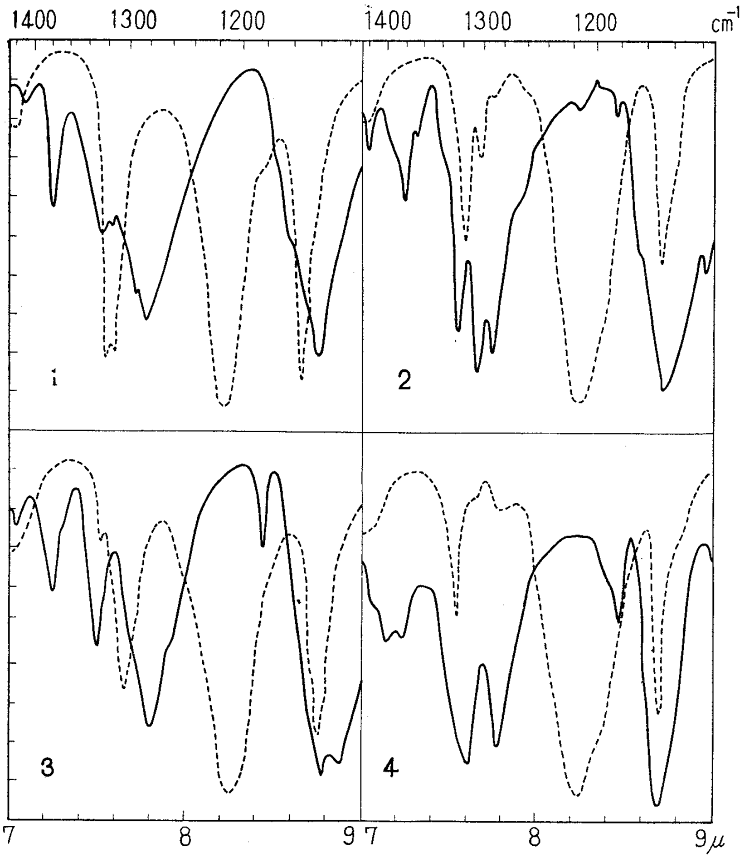


Fig. 1.

Infrared Spectra of Phenylsulfonyl Derivatives

—— Nujol mull
------ $CHCl_3$ solution

1. Phenylsulfonylmethane
2. 4-Methylphenylsulfonylmethane
3. 4-Aminophenylsulfonylmethane
4. 4-Cyanophenylsulfonylmethane

Fig. 1 also shows that the solid spectra has a characteristic feature; namely, their absorption bands are more broad and complex than that of the solution spectra. Therefore, when these bands overlap other bands, some difficulties may occur in the assignment of the group, and then a solution method will be recommended.

The $SO_2$ frequencies measured are listed in Tables I and II. The $\nu_s$ appears as one maximum absorption band or accompanied with one shoulder, and the $\nu_{as}$ appears as two absorption bands or accompanied with one shoulder. In the solid spectra, most of the $\nu_{as}$ consist of a few frequencies, but they have, in general, one maximum frequency which corresponds to the main band of the solution spectra. Then this maximum frequency becomes important in the discussion, and is listed in bold-face type in

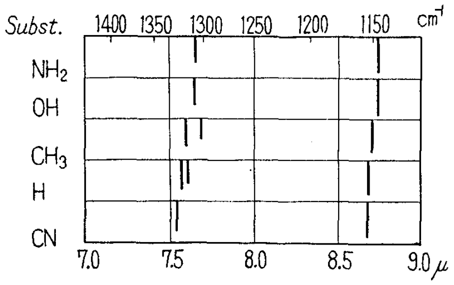


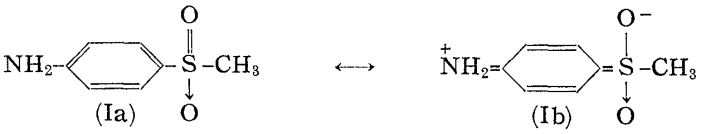
Fig. 2. Frequency Shifts of *para*-Substituted Phenylsulfonylmethanes

the table. The $\nu_{as}$ has a range of 1339~1279 cm$^{-1}$ (7.47~7.82 μ) in the solid state and of 1326~1305 cm$^{-1}$ (7.54~7.66 μ) in the solution. The $\nu_s$ has a range of 1172~1136 cm$^{-1}$ (8.53~8.80 μ) in the solid state, and of 1157~1144 cm$^{-1}$ (8.64~8.74 μ) in the solution.

**Substituent Effect**

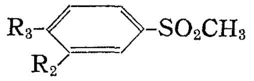
At first, phenylsulfonylmethane and *p*-amino-, *p*-hydroxy-, *p*-methyl-, and *p*-cyanophenylsulfonylmethane were compared with each other. Fig. 2 shows that when phenylsulfonylmethane is taken as a standard *p*-$NH_2$ has the greatest shift of the $\nu_{as}$ to a longer wave-length region, and *p*-CN shows a shift to a shorter wave-length region, whereas there is no such great shift of the $\nu_s$ in any of the compound.

The order of the shift of $\nu_{as}$ coincides with the order of Hammett's $\sigma$[9] (*p*-$NH_2$ : −0.660, *p*-OH : −0.357, *p*-$CH_3$ : −0.170, *p*-CN : +0.628) and with that of the chemical shift of benzene derivatives[10] (*p*-$NH_2$ : −0.40, *p*-OH : −0.37, *p*-$CH_3$ : −0.10, *p*-CN : +0.30). It may be supposed that if the electron density of S atom diminishes, a double bond character of S–O will increase, and then the force constant of the bond will become larger, absorbing in a shorter wave length region, and vice versa. *p*-Aminophenylsulfonylmethane can be written in resonance forms (Ia⟷Ib).



(Ia) (Ib)

Table I. Infrared Absorption Bands of $SO_2$ Group in Phenylsulfonylmethane Derivatives



| Compd. No. | $R_3$ | $R_2$ | State | $\nu_{as}$[a] | | | $\varepsilon_{max}$ | $\nu_s$[a] | $\varepsilon_{max}$ | Mean freq. |
|---|---|---|---|---|---|---|---|---|---|---|
| (I) | H | | N | 1297[b] | **1285** | | | **1143** | | 1214 |
| (I) | H | | C | **1321** | 1314 | | 556 | **1152** | 932 | 1237 |
| (II) | $CH_3$ | | N | **1304** | 1287 | | | **1149** | | 1227 |
| (II) | $CH_3$ | | C | **1318** | 1302 | | 774 | **1149** | 1187 | 1234 |
| (III) | $NH_2$ | | N | **1282** | | | | **1140** | | 1211 |
| (III) | $NH_2$ | | C | **1305** | | | 674 | **1144** | 1319 | 1225 |
| (IV) | OH | | N | **1282**[c] | | | | **1144**[c] | | 1213 |
| (IV) | OH | | C | **1307** | | | 481 | **1144** | 1094 | 1226 |
| (V) | CN | | N | **1319** | 1290 | | | **1156** | | 1238 |
| (V) | CN | | C | **1326** | | | | **1152** | | 1239 |
| (VI) | $CH_3CONH$ | | N | **1284** | 1263 | | | **1138** | | 1211 |
| (VII) | $(CH_3CO)_2N$ | | N | **1300** | 1282 | | | **1148** | | 1224 |
| (VIII) | $HCl \cdot H_2NCH_2$ | | N | **1314** | 1304[b] | 1292 | | **1155** | | 1235 |
| (IX) | $HCl \cdot H_2NCH_2$ | Cl | N | **1311** | | | | **1149** | | 1230 |
| (X) | $HCl \cdot H_2N(CH_3)CH$ | | N | **1309** | 1289 | | | **1151** | | 1230 |
| (XI) | $HCONHCH_2$[11] | | N | 1314 | **1297** | | | **1144** | | 1221 |
| (XII) | $CH_3CONHCH_2$[12] | | N | 1316 | **1297** | 1285 | | **1152** | | 1225 |
| (XIII) | $(CH_3CO)_2NCH_2$ | | N | **1304** | 1287 | 1267 | | **1147** | | 1226 |
| (XIV) | P[11] | | N | **1307** | 1292[b] | | | **1142** | | 1225 |
| (XV) | CHO | Cl | N | **1311** | 1290 | | | **1157** | | 1234 |

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9) H. H. Jaffé : Chem. Revs., **53**, 191(1953).
10) B. P. Dailey, *et al.* : J. Am. Chem. Soc., **78**, 3043(1956).
11) T. Momose, T. Shōji : Yakugaku Zasshi, **70**, 616(1950).
12) K. A. Jensen, *et al.* : Z. Physiol. Chem., **280**, 35(1944).

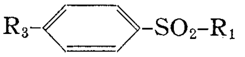
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (XVI) | $(CH_3CO_2)_2CH$ | | N | **1309** | 1292 | **1160** | 1235 |
| (XVI) | $(CH_3CO_2)_2CH$ | | C | **1323** | | **1153** | 1238 |
| (XVII) | $(CH_3CO_2)_2CH$ | Cl | N | **1321** | | **1153** | 1237 |
| (XVIII) | HON=CH 11) | | N | **1307** | 1289 | **1153** | 1230 |
| (XIX) | HON=CH | Cl | N | **1302** | 1294 | **1147** | 1225 |

*a*) Maximum absorption in bold-face type. *b*) Shoulder. *c*) Broad.
N : Nujol. C : $CHCl_3$ solution. P : Phthaliminomethyl.

The structure (Ib) may be possible by the +M effect of $NH_2$, and the S–O bond may have greater single-bond character than phenylsulfonylmethane, absorbing at a fairly longer wave-length region. The +M effect of *p*-OH is next to that of *p*-$NH_2$ and the shift is also in the following step. *p*-$CH_3$ has a +I effect, and absorbs at a somewhat longer wave-length region. The effect of *p*-OH cannot be directly compared with that of *p*-$CH_3$, but in general it is known that *p*-OH has a greater influence than *p*-$CH_3$, and the results shown in Fig. 2 agree with this order. *p*-CN has −I effect and will give a greater double-bond character to the S–O bond, which will absorb at a shorter wave-length region.

Substituents other than those just discussed all have effect on the $SO_2$ group, but they cannot be discussed in detail since the spectra were measured in Nujol mull and the estimation of electronic shifts is rather complex. However, as the first approximation, a mean frequency $(\nu_{as}+\nu_{s})/2$ which was proposed by Barnard[3] in the calculation of force constants may be used to compare with each other. This is also shown in Tables I and II, and it will be clear that the compounds which have similar substituents will have similar frequencies.

TABLE II. Infrared Absorption Bands of $SO_2$ Group in Phenylsulfonyl Derivatives



| Compd. No. | $R_3$ | $R_1$ | State | $\nu_{as}$ a) | | | $\nu_s$ a) | | Mean freq. |
|---|---|---|---|---|---|---|---|---|---|
| (XX) | $HCl\cdot H_2NCH_2$ 11) | $C_2H_5$ | N | **1316** | 1294 | 1279 | **1148** | | 1232 |
| (XXI) | $HCl\cdot H_2NCH_2CH_2$ | $C_2H_5$ | N | 1307 | **1279** | 1258 | **1136** | | 1222 |
| (XXII) | $HCl\cdot H_2N(CH_3)CH$ | $C_2H_5$ | N | **1314** | 1294 | 1274 | **1147** | | 1231 |
| (XXIII) | $(CH_3CO_2)_2CH$ 11) | $C_2H_5$ | N | **1319** | 1292 | | **1151** | | 1235 |
| (XXIII) | $(CH_3CO_2)_2CH$ 11) | $C_2H_5$ | C | **1323** | | | **1148** | | 1236 |
| (XXIV) | $CH_3$ | $C_6H_5$ | N | 1323 | **1311** | 1294 | **1157** | | 1234 |
| (XXV) | $HCl\cdot H_2NCH_2$ | $C_6H_5$ | N | 1314 b) | **1305** | 1285 | **1156** | | 1231 |
| (XXVI) | P | $C_6H_5$ | N | **1318** | 1309 | | **1159** | | 1238 |
| (XXVII) | $(CH_3CO_2)_2CH$ 13) | $C_6H_5$ | N | **1333** | 1318 | 1300 | **1166** | | 1250 |
| (XXVII) | $(CH_3CO_2)_2CH$ 13) | $C_6H_5$ | C | **1325** | | | **1157** | | 1241 |
| (XXVIII) | HON=CH | $C_6H_5$ | N | 1304 | **1287** | | **1149** | | 1218 |
| (XXIX) | $NH_2$ | $C_6H_4NH_2(p)$ | N | 1295 | **1282** | | **1143** | | 1213 |
| (XXX) | $CH_3$ | $CH_2COOH$ | N | **1326** | | | **1163** | | 1245 |
| (XXXI) | CN | $CH_2COOH$ | N | 1316 b) | **1295** | | **1156** | | 1226 |
| (XXXII) | $H_2NCH_2$ 14) | $CH_2COOH$ | N | **1309** | 1299 | | **1168** | | 1239 |
| (XXXIII) | P 14) | $CH_2COOH$ | N | **1321** | 1312 b) | | 1148 b) | **1138** | 1230 |
| (XXXIV) | CHO | $CH_2COOH$ | N | **1307** | 1300 b) | 1276 | **1166** | | 1237 |
| (XXXV) | HON=CH | $CH_2COOH$ | N | **1316** | 1284 | | **1149** | | 1233 |
| (XXXVI) | CN | $CH_2COOC_2H_5$ | N | **1339** | | | **1156** | | 1248 |
| (XXXVII) | $HCONHCH_2$ 14) | $CH_2COOC_2H_5$ | N | **1328** | | | **1167** | | 1248 |
| (XXXVIII) | P 14) | $CH_2COOC_2H_5$ | N | **1332** | | | **1147** | | 1240 |
| (XXXIX) | CN | $CH_2COCH_3$ | N | **1332** | | | 1159 | **1148** | 1240 |
| (XL) | $H_2NCH_2$ 14) | $CH_2COCH_3$ | N | **1326** | 1314 b) | 1294 | **1155** | | 1241 |
| (XLI) | $HCONHCH_2$ 14) | $CH_2COCH_3$ | N | **1319** | 1300 | | 1168 | **1149** | 1234 |
| (XLII) | P 14) | $CH_2COCH_3$ | N | **1330** | 1316 b) | | **1164** | | 1247 |
| (XLIII) | $HCl\cdot H_2NCH_2$ 14) | $CH_2COC_6H_5$ | N | 1335 b) | **1321** | 1304 | **1172** | | 1247 |
| (XLIV) | $HCONHCH_2$ 14) | $CH_2COC_6H_5$ | N | 1330 b) | **1312** | 1290 b) | 1161 | **1145** | 1229 |
| (XLV) | $HCl\cdot H_2NCH_2$ 14) | $C_2H_4OH$ | N | 1311 b) | **1295** | 1274 b) | 1152 | **1142** | 1219 |

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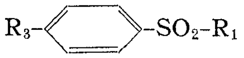
13) H. Burton, P. F. Hu : J. Chem. Soc., **1948**, 601.
14) T. Momose, T. Shōji : Yakugaku Zasshi, **71**, 681(1951).

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (XLVI) | P14) | $C_2H_4OH$ | N | **1295** | 1277 | | **1138** | | 1217 |
| (XLVII) | $H_2NCH_2$14) | $CH_2J$ | N | **1314** | 1297b) | | **1152** | | 1233 |
| (XLVIII) | $HCONHCH_2$14) | $CH_2J$ | N | **1318** | 1292b) | | 1170 | **1148** | 1233 |
| (XLIX) | P14) | $CH_2J$ | N | 1325 | **1312** | 1302 | **1160** | 1143 | 1236 |
| (L) | H | $C_6H_5$ | N | 1324 | **1316** | 1300 | **1156** | | 1236 |

*a*) Maximum absorption in bold-face type. *b*) Shoulder.
N : Nujol. C : $CHCl_3$ solution. P : Phthaliminomethyl.

TABLE III. Shift of Mean Wave-number by the Subsituent ($R_1$)



| $R_1$ | $R_3$ | Mean wave number | Mean wave number of $R_1=CH_3$ | Shift |
|---|---|---|---|---|
| $C_2H_5$ | $HCl\cdot H_2NCH_2$ | 1232 | 1235 | − 3 |
| | $HCl\cdot H_2N(CH_3)CH$ | 1231 | 1230 | + 1 |
| | $(CH_3CO_2)_2CH$ | 1235 | 1235 | 0 |
| | $(CH_3CO_2)_2CH$ | 1236 | 1238 | − 2a) |
| $C_6H_5$ | $CH_3$ | 1234 | 1227 | + 7 |
| | $HCl\cdot H_2NCH_2$ | 1231 | 1235 | − 4 |
| | P | 1238 | 1225 | +13 |
| | $(CH_3CO_2)_2CH$ | 1250 | 1235 | +15 |
| | $(CH_3CO_2)_2CH$ | 1241 | 1238 | + 3a) |
| | HON=CH | 1218 | 1230 | −12 |
| | H | 1236 | 1214 | +22 |
| $CH_2CO_2H$ | $CH_3$ | 1245 | 1227 | +18 |
| | P | 1230 | 1225 | + 5 |
| | HON=CH | 1233 | 1230 | + 3 |
| $CH_2CO_2C_2H_5$ | CN | 1248 | 1238 | +10 |
| | $HCONHCH_2$ | 1248 | 1225 | +23 |
| | P | 1240 | 1225 | +15 |
| $CH_2COCH_3$ | CN | 1240 | 1238 | + 2 |
| | $HCl\cdot H_2NCH_2$ | 1241 | 1235 | + 6 |
| | $HCONHCH_2$ | 1234 | 1225 | + 9 |
| | P | 1247 | 1225 | +22 |
| $CH_2COC_6H_5$ | $HCl\cdot H_2NCH_2$ | 1247 | 1235 | +12 |
| | $HCONHCH_2$ | 1229 | 1225 | + 4 |
| $C_2H_4OH$ | $HCl\cdot H_2NCH_2$ | 1219 | 1235 | −16 |
| | P | 1217 | 1225 | − 8 |
| $CH_2I$ | $HCONHCH_2$ | 1233 | 1225 | + 8 |
| | P | 1236 | 1225 | +11 |

*a*) In $CHCl_3$ solution; others in Nujol. P : Phthaliminomethyl.

Using this mean frequency the substitution effect of some substituents attached directly to the sulfonyl group was examined. This is shown in Table III. It is clear from the table that electron-accepting groups like $C_6H_5$, $CH_2COOH$, $CH_2COOC_2H_5$, $CH_2COCH_3$, $CH_2COC_6H_5$, and $CH_2I$ give a stronger double-bond character to the S-O bond than $CH_3$ group, forcing it to absorb in a rather shorter wave-length region. Inversely electron-donating groups such as $C_2H_5$ and $C_2H_4OH$ give a stronger single-bond character to the S-O bond which absorbs at a longer wave-length region. These results again confirm the fact that the inductive effect can affect the character of S-O bond and its absorption frequency. and therefore, the substituents attached to the phenyl ring or directly to the sulfonyl group take an important part in the S-O stretching vibration frequency.

Lastly, the apparent molecular extinction coefficients of four typical phenylsulfonylmethane derivatives were measured in $CHCl_3$ solution. Though only the integrated intensities have theoretical significance, these apparent coefficients will be useful in

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15) R. N. Jones, C. Sandorfy : "Chemical Applications of Spectroscopy," Technique of Oragnic Chemistry, Interscience Publ. Inc., U. S. A., **IX**, 271, 476(1956).

distinguishing some of the groups. Results show that the values are in a range of 481~774 ($\varepsilon$) for $\nu_{as}$ and of 932~1319 ($\varepsilon$) for $\nu_s$. Barnard also reported that $\varepsilon_{max}^{CCl_4}$ of $\nu_{as}$ and $\nu_s$ of sulfonyl group were in a range of 250~600 ($\varepsilon$) and of 500~900 ($\varepsilon$), respectively. Therefore, the maximum absorbancy of $\nu_s$ is roughly twice as strong as that of $\nu_{as}$. Jones[15] stated that the maximum absorbancy of organic compounds were between 1 and 1500 ($\varepsilon$), and the maximum molecular extinction coefficients of carbonyl bands lay in a range of 290~1335 ($\varepsilon$). The absorption band of sulfonyl group has strength comparable to that of carbonyl group, and the $\nu_s$ is more valuable for the identification of sulfonyl group, since the $\nu_{as}$ may have a larger chance of overlapping other frequencies and a smaller extinction coefficient.

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## Experimental

**Infrared Spectra**—Measured with a Kōken Model DS-201 recording infrared spectrophotometer, using NaCl prism.

**4-Phthalimidomethylphenylsulfonylbenzene** (**XXVI**)—To a solution of 5 g. of 4-phthalimidomethylphenylsulfonyl chloride[16] in 15 cc. of dry benzene, 5 g. of anhyd. $AlCl_3$ was slowly added under cooling. After the reaction ceased the solution was poured into ice water and precipitated crystals were recrystallized from AcOH to colorless prisms, m.p. 211~213°. *Anal.* Calcd. for $C_{21}H_{15}O_4NS$: N, 3.71. Found: N, 3.70.

**4-Aminomethylphenylsulfonylbenzene Hydrochloride** (**XXV**)—(XXVI) was heated for 15 hrs. in dehyd. EtOH with $NH_2NH_2 \cdot H_2O$. Separated phthalohydrazide was removed, EtOH was distilled off, and the residual solution was acidified with HCl. After removing insoluble substance while hot, crystals that appeared on cooling were recrystallized from EtOH to colorless plates, m.p. 250~252°. *Anal.* Calcd. for $C_{13}H_{14}O_2NClS$: N, 4.93. Found: N, 5.04.

**4-Hydroxyiminomethylphenylsulfonylbenzene** (**XXVIII**)—Prepared from 4-formylphenylsulfonylbenzene,[13] $NH_2OH \cdot HCl$, and AcONa. Recrystallization from EtOH yielded colorless prisms, m.p. 148~150°. *Anal.* Calcd. for $C_{13}H_{11}O_3NS$: N, 5.36. Found: N, 5.52.

The solution of (XXVIII) in 30% AcOH was reduced with Zn powder and treated as usual. Its hydrochloride formed colorless plates of m.p. 250~252° after recrystallization from EtOH, which showed no depression of mixed m.p. with (XXV).

**3-Chloro-4-methylphenylsulfonylmethane**—4-Methylphenylsulfonylmethane and calculated weight of $Cl_2$ gas gave colorless plates which crystallized from EtOH to crystals of m.p. 92°. *Anal.* Calcd. for $C_8H_9O_2ClS$: C, 46.93; H, 4.43. Found: C, 46.92; H, 4.45.

**3-Chloro-4-diacetoxymethylphenylsulfonylmethane** (**XVII**)—A solution of $CrO_3$ in 5 cc. of $Ac_2O$ was added slowly under cooling to a solution of 5 g. of 3-chloro-4-methylphenylsulfonylmethane in 20 cc. of $Ac_2O$ and maintained at 15~20°. After the reaction ceased it was poured into ice water and the separated oily substance was extracted with ether. The ether was evaporated and the residue was recrystallized from EtOH to colorless plates, m.p. 93~95°. *Anal.* Calcd. for $C_{12}H_{13}O_6ClS$: C, 44.93; H, 4.08. Found: C, 44.82; H, 3.83.

**3-Chloro-4-formylphenylsulfonylmethane** (**XV**)—(XVII) was saponified with ethanolic HCl. Recrystallization of its product from AcOEt yielded colorless needles, m.p. 137~138°. *Anal.* Calcd. for $C_8H_7O_3ClS$: C, 43.94; H, 3.22. Found: C, 44.02; H, 3.10.

**3-Chloro-4-hydroxyiminomethylphenylsulfonylmethane** (**XIX**)—Prepared from (XV), $NH_2OH \cdot HCl$, and $Na_2CO_3$. Recrystallization from EtOH yielded colorless needles, m.p. 155~156°. *Anal.* Calcd. for $C_8H_8O_3NClS$: N, 5.74. Found: N, 5.98.

**3-Chloro-4-aminomethylphenylsulfonylmethane Hydrochloride** (**IX**)—(XIX) was reduced with AcOH and Zn powder, and its hydrochloride was recrystallized from EtOH to colorless plates, m.p. 265°. *Anal.* Calcd. for $C_8H_{11}O_2NCl_2S$: N, 5.46. Found: N, 5.68.

**4-Cyanophenylsulfonylacetone** (**XXXIX**)—Two g. of chloroacetone was added to a solution of 4 g. of sodium 4-cyanophenylsulfinate[17] in 20 cc. of water, and the mixture was refluxed for 2 hrs. On cooling crystals separated which were recrystallized from EtOH to colorless needles of m.p. 112~113°. Yield, 4 g. *Anal.* Calcd. for $C_{10}H_9O_3NS$: N, 6.28. Found: N, 6.22.

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[16] M. Kusami, K. Yamaguchi, S. Yamaguchi: Yakugaku Zasshi, **64**, 240(1944).

[17] A.T. Fuller, I.M. Tonkin, J. Walker: J. Chem. Soc., **1945**, 633.

**Ethyl 4-Cyanophenylsulfonylacetate (XXXVI)**—Two g. of ethyl chloroacetate was added to a solution of 4 g. of sodium 4-cyanophenylsulfinate in 20 cc. of water and the mixture was refluxed for 3 hrs. Recrystallization of the separated crystals from EtOH yielded colorless needles of m.p. 70°. Yield, 4 g. *Anal.* Calcd. for $C_{11}H_{11}O_4NS$ : N, 5.53. Found : N, 5.39.

**4-Formylphenylsulfonylacetic Acid (XXXIV)**—To a solution of 5 g. of 4-methylphenylsulfonylacetic acid in a mixture of 20 cc. of $Ac_2O$ and 5 cc. of conc. $H_2SO_4$, 4 g. of $CrO_3$ dissolved in 8 cc. of $Ac_2O$ was dropped in under stirring at 10~15°. After the reaction ceased the mixture was poured into ice water, the separated oily substance was heated with 20 cc. of 10% HCl for a while, and crystals that separated after cooling were recrystallized from EtOH to colorless plates, m.p. 150~152°. Yield, 3.5 g. *Anal.* Calcd. for $C_9H_8O_5S$ : C, 47.38; H, 3.53. Found : C, 47.24; H, 3.83.

**4-Hydroxyiminomethylphenylsulfonylacetic Acid (XXXV)**—Prepared from (XXXIV), $NH_2OH \cdot HCl$, and NaOH. Recrystallization from water yielded colorless needles of m.p. 205°(decomp.). *Anal.* Calcd. for $C_9H_9O_5NS$ : N, 5.76. Found : N, 5.85.

**4-Diacetylaminophenylsulfonylmethane (VII)**—4-Acetamidophenylsulfonylmethane (VI) of m.p. 190° was converted to diacetyl derivative by refluxing with $Ac_2O$ for several hrs. After distillation of $Ac_2O$ in vacuum, MeOH and water were added and separated crystals were recrystallized from dil. MeOH to colorless needles of m.p. 152~153°. *Anal.* Calcd. for $C_{11}H_{13}O_4NS$ : C, 51.76; H, 5.13. Found: C, 51.87; H, 5.26.

When dil. NaOH was added to a solution of (VII) in EtOH and kept at room temperature, (VI) separated as crystals of m.p. 190°.

**4-Diacetylaminomethylphenylsulfonylmethane (XIII)**—Prepared from (XII) similarly as above. Recrystallization from dil. MeOH gave colorless needles of m.p. 140°. *Anal.* Calcd. for $C_{12}H_{15}O_4NS$: N, 5.49. Found : N, 500.

## Summary

Infrared spectra of 50 phenylsulfonyl derivatives were measured and substituent effect on the sulfonyl group was discussed. Inductive and mesomeric effects of substituents attached to the phenyl ring or directly to the sulfonyl group somewhat affected the frequencies of asymmetric and symmetric stretching vibrations of $SO_2$. The frequency shifts had some correlations with Hammett's $\sigma$-value of the chemical shifts of benzene derivatives. Synthesis of some phenylsulfonyl derivatives is also described.

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# 81. **Masaharu Yamagishi and Isao Nakamura** : Studies on Determination of Sapogenins in Plants belonging to Dioscorea growing in Japan. II.[1) Determination of Diosgenin, Tokorogenin, and a New Genin contained in the Roots.

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In Part I of this series,[1) the authors announced that a new color reaction of diosgenin and tokorogenin satisfies Beer's law and is available for colorimetric determination of these genins. In the present work a method for determining the sapogenins present in roots of *Dioscorea Tokoro* MAKINO and *D. nipponica* M. was established utilizing the above color reaction. As a new genin was found in the sapogenin extract of *D. Tokoro* M. (X-substance**), the present method was studied centering on the separatory determination of diosgenin, tokorogenin, and the X-substance. The main procedures of this method are as follows :

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1) Part I : Yakugaku Zasshi, **78**(1958) in press.

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** Morita in this Laboratories found that this substance is identical with yonogenin, m.p. 238~240°, $\alpha_D$ −63° (cf. K. Takeda, *et al.* : Yakugaku Zasshi, **77**, 822(1957)).