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176. Yukiko Tanaka, Tsugiharu Sugimura, and Yoshimasa Tanaka : Infrared Absorption Spectra of Organic Sulfur Compounds. III.[*1] Studies on Characteristic Bands of Aromatic Sulfinamide Derivatives.

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In the previous paper of this series,[1,2] it was reported that the S–N band always appeared near 900 cm^{-1} region in a variety of aromatic- and methane-sulfonamide derivatives. The band near 1090 cm^{-1} was found not only in aromatic sulfonamide derivatives but also in the aromatic sulfonic acid derivatives whicn have no S–N linkage, while, in methanesulfonamide derivatives no such characteristic absorption was detected at the same place. Moreover, deuteration resulted in shift of S–N band towards lower wave number region in several compounds having -S-NH- grouping.

In the present investigation the bands near 900, 1090 cm^{-1} and other characteristic bands also, were examined in 25 kinds of aromatic sulfinamides. Moreover the optical shifts of S–N band were examined on deuteration in 12 kinds of compounds having -S-NH- grouping.

Experimental

Preparation of Substances——Benzene- and *p*-toluenesulfinamide derivatives were prepared by the reaction of benzene- and *p*-toluenesulfinyl chloride and amines in dry ether under cooling with ice water. Sulfinyl chlorides were prepared by the general method.[3] Esters were prepared by the reaction of sulfinyl chloride and sodium alcoxide. Deuterated compounds were prepared by recrystallization from D_2O.

Measurements——The Koken DS-301 IR Spectrophotometer was used with NaCl prism (4000~650 cm^{-1}). The measurements of IR spectra were carried out as KBr tablets for solid substances or liquid film for liquid samples.

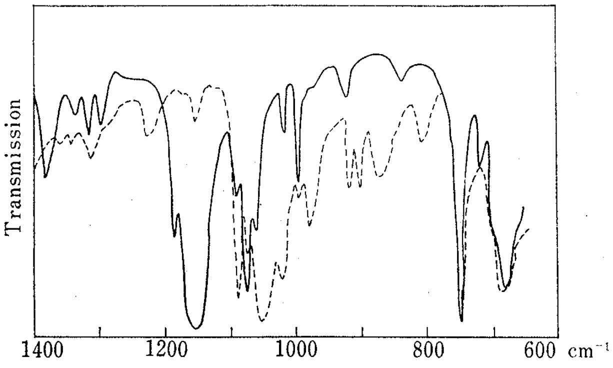


Fig. 1(a). Infrared Spectra of ⌬-SOCl (solid line) and ⌬-SONHCH$_2$-⌬ (broken line)

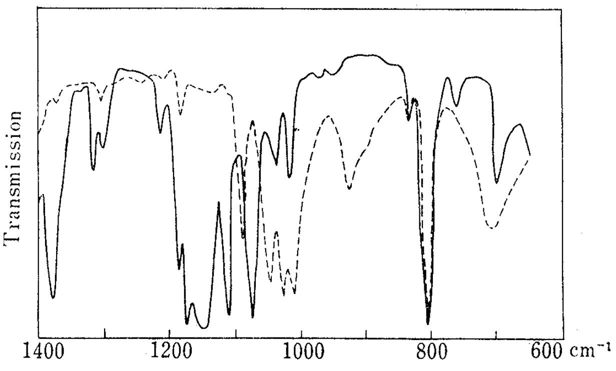


Fig. 1(b). Infrared Spectra of CH$_3$-⌬-SOCl (soild line) and CH$_3$-⌬-SONH$_2$ (broken line)

[*1] Part II. Y. Tanaka, Y. Tanaka : This Bulletin, **13**, 858 (1965).

[*2] Oe-machi, Kumamoto (田中由紀子, 杉村継治, 田中善正).

1) Y. Tanaka, Y. Tanaka : This Bulletin, **13**, 399 (1965).

2) *Idem* : *Ibid.*, **13**, 858 (1965).

3) Frederick Kurzer : Org. Syntheses, **34**, 93 (1954).

Results and Discussion

In preceding paper of this series[1,2] mention was made of the presence of S–N stretching vibration of some aromatic and methanesulfonamide derivatives in the region of 900 cm^{-1}, and the present report deals with the same absorption of aromatic sulfinamide derivatives.

S–N absorption of benzene- and *p*-toluenesulfinamides appeared as expected in 870 cm^{-1} and 925 cm^{-1} respectively, whilst no absorption occured in the above regions in benzene- and *p*-toluenesulfinyl chlorides (Fig. 1 (a) and (b)). The absorption near 900 cm^{-1} is also lacking in benzene- and *p*-toluenesulfinates (Fig. 2).

In 25 kinds of sulfinamides S–N absorption band of medium intensity invariably appeared in 928~865 cm^{-1} region and absorption near 1090 cm^{-1} could be detected not only in sulfinamide derivatives but also sulfinic acid derivatives lacking S–N linkage (Table I).

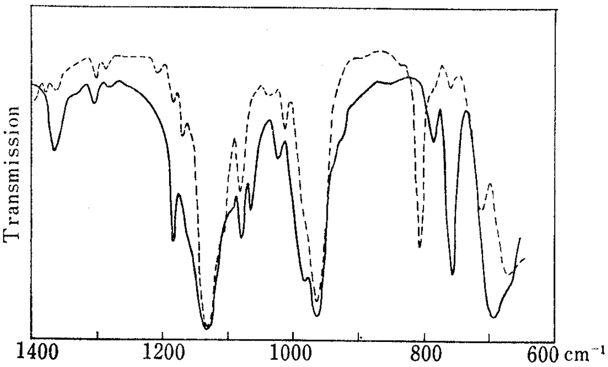


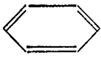
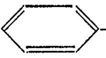
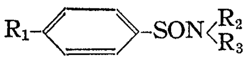
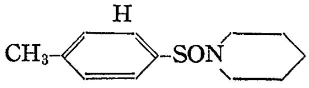
Fig. 2. Infrared Spectra of -SOOCH$_3$ (solid line) and CH$_3$--SOOCH$_3$ (broken line)

Table I. Infrared Spectra of Sulfinamide Derivatives

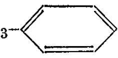
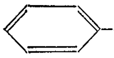


R$_1$	R$_2$	R$_3$	Near 1090 cm^{-1} (cm^{-1})	$\nu_{S=O}$ (cm^{-1})	ν_{S-N} (cm^{-1})
H	C$_2$H$_5$	C$_2$H$_5$	1090	1060	895
〃	H	C$_3$H$_7$ (iso)	1087	1051	872
〃	〃	〃 (*n*)	1088	1051	921
〃	〃	C$_4$H$_9$ (iso)	1087	1050	920
〃	〃	〃 (*n*)	1087	1053	880
〃	C$_3$H$_7$	C H (*n*)	1090	1035	920
〃	H	CH$_2$C$_6$H$_5$	1089	1053	870
〃	CH$_2$C$_6$H$_5$	〃	1090	1060	889
CH$_3$	H	H	1088	1048	925
〃	〃	CH$_3$	1085	1042	885
〃	CH$_3$	〃	1088	1068	922
〃	H	C$_2$H$_5$	1088	1060	928
〃	C$_2$H$_5$	〃	1090	1072	927
〃	H	C$_3$H$_7$ (*n*)	1090	1060	885
〃	C$_3$H$_7$ (*n*)	〃	1088	1068	883
〃	H	C$_3$H$_7$ (iso)	1088	1075	883
〃	〃	C$_4$H$_9$ (*n*)	1088	1055	878
〃	C$_4$H$_9$ (*n*)	〃	1090	1072	915
〃	H	C$_4$H$_9$ (iso)	1089	1055	920
〃	〃	C$_6$H$_5$	1090	1053	895
〃	C$_6$H$_5$	〃	1088	1035	880
〃	H	CH$_2$C$_6$H$_5$	1088	1055	865
〃	CH$_2$C$_6$H$_5$	〃	1090	1068	890
〃	H	β-C$_{10}$H$_7$,	1090	1058	868
			1088	1067	928

From these observations it appears extremely probable that all aromatic sulfinamides will show absorption in this range.

Moreover, in deuteration studies of 12 kinds of SO–NH type compounds a frequency fall of 18~110 cm^{-1} of S–N band near 900 cm^{-1} was observed, whereas no shift occurred in two bands near 1090 cm^{-1} and 1075~1035 cm^{-1} range (Table II, Fig. 3).

Table II. The Shifts of S–N Bands on Deuteration

	H (cm^{-1})	D (cm^{-1})
CH_3--$SONH_2$	925	815
-$SONHC_2H_5$	928	885
-$SONHC_3H_7$(*n*)	885	840
-$SONHC_3H_7$(iso)	883	853
-$SONHC_6H_5$	895	835
-$SONHC_{10}H_7$(β)	868	850
-$SONHCH_2C_6H_5$	865	833
-$SONHC_3H_7$(iso)	872	852
-$SONHC_3H_7$(*n*)	921	885
-$SONHCH_2C_6H_5$	870	828
-$SONHC_4H_9$(iso)	920	883
-$SONHC_4H_9$(*n*)	880	855

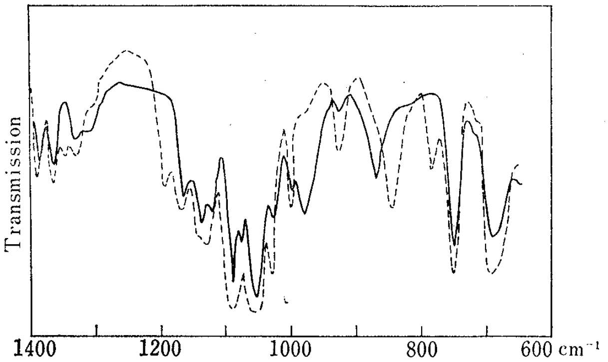
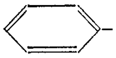
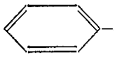


Fig. 3. Infrared Spectra of -SONH-C_3H_7(iso) (solid line) and -SONDC$_3$-H_7(broken line)

Momose, *et al.*[4] assigned the strong absorption around 1090 cm^{-1} of aromatic sulfonamide derivatives to C–H vibration and stated that a marked enhancement of the intensity of this band was due to the presence of highly polarized SO_2 group, whereas according to Nerdel, *et al.*[5] this was shown to be due to the φ–S band. More extensive work on this problem will be needed in order to recognize this absorption at 1090 cm^{-1} with reasonable certainty.

S=O band of methyl benzene- and *p*-toluenesulfinates appears at 1135 and 1130cm^{-1} respectively in agreement with the Detoni's suggestion[6] that S=O band of esters of sulfinic acid appears in higher frequency region than that of acid 1090 cm^{-1}.

In view of the fact that C=O absorption of amides is at an appreciably lower wave number about 60 cm^{-1} than that of ester the strong band at 1075~1035 cm^{-1} common to Ar–SON-type compounds can be reasonably assigned to S=O stretching vibration. Barnard, *et al.*[7] reported that the sulfoxide linkage is associated with a strong infrared band at 1060~1045 cm^{-1}.

The authors wish to thank Prof. T. Uno of Kyoto University for many helpful discussions and suggestions during this work. Thanks are due to Miss T. Nagata for her assistance in this experimental work.

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4) T. Momose, Y. Ueda, T. Shoji : This Bulletin, **7**, 734 (1959).
5) F. Nerdel, H. Goelz, E. Fabienke : Ann., **643**, 6 (1961).
6) S. Detoni, D. Hadzi : J. Chem. Soc., **1955**, 3136.
7) D. Barnard, J. M. Fabian, H. D. Koch : *Ibid.*, **1949**, 2442.

Summary

The infrared spectra of 25 kinds of benzenesulfinamide and *p*-toluenesulfinamide derivatives were measured. The S-N bands were observed between 928 cm^{-1} and 872 cm^{-1} as in benzenesulfonamide and methanesulfonamide derivatives. Moreover, the bands near 1090 cm^{-1} were found in all of the sulfinamide derivatives. The spectral change on deuteration were examined. In the compounds having -S-NH- and $-S-NH_2$ form, the bands near 900 cm^{-1} region shifted to the lower wave number (about 110~18 cm^{-1}). But no such shift has been observed in the bands near 1090 cm^{-1} and in the range 1075~1035 cm^{-1}.

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177. Hisashi Nogami, Tsuneji Nagai, and Akira Suzuki[*1]: Studies on Powdered Preparations. XIII.[*2] Reaction between Dried Aluminum Hydroxide Gel and Organic Acid.[*3]

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It was described in previous papers,[1~3] that the rate of reaction between dried aluminum hydroxide gel (DAHG) and such an inorganic acid as hydrochloric, nitric, and/or sulfuric acid was not in accordance with the Noyes-Whitney equation,[4] but was expressed by

$$-\frac{dH}{dt}=K_1WH^n \qquad (1)$$

where H is the hydrogen ion concentration in bulk liquid at the time t, K_1 the apparent rate constant, W the amount of test sample, and n the apparent order of the reaction. In the cases of hydrochloric acid and nitric acid, n was nearly zero, while it was around 0.5 in the case of sulfuric acid. K_1 was dependent not only on the acid used, but also on the total amount of electrolyte and/or test sample, even if the same kind of samples were used. Based upon this point, a method was established for the quantitative evaluation of the antacidic reactivity of DAHG.

Generally organic acids are weak. Therefore, the rate of dissolution of DAHG into organic acid is considered to be not always in accordance with equation (1) and, paying an attention on the pH change in bulk liquid, the apparent order of the reaction with respect to the hydrogen ion may be influenced by the dissociation constant of acid.

[*1] Present adress: Pharmaceutical Research Laboratory, Tanabe Seiyaku Co., Ltd., Kashima-cho, Higashi-yodogawa-ku, Osaka.

[*2] Part XII. H. Nogami, Y. Nakai: Presented at the 82nd Annual Meeting of Pharmaceutical Society of Japan, Yokohama, April 1962; cf., This Bulletin, **11**, 1389 (1963).

[*3] Presented at the 83rd Annual Meeting of Pharmaceutical Society of Japan, Kanazawa, April 1963.

[*4] Hongo, Tokyo (野上 寿, 永井恒司, 鈴木 章).

1) Part VII. H. Nogami, T. Nagai: This Bulletin, **10**, 728 (1962).

2) Part VIII. H. Nogami, T. Nagai: *Ibid.*, **10**, 741 (1962).

3) Part IX. H. Nogami, J. Hasegawa, T. Nagai, M. Miyamoto: *Ibid.*, **10**, 747 (1962).

4) A. A. Noyes, W. R. Whitney: J. Am. Chem. Soc., **19**, 930 (1897).