H, 4.43. Found: C, 75.32; H, 4.40. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1679 (quinone), ν_{max}^{KBr} cm^{-1}: 1676. UV λ_{max}^{EtOH} mμ (log ε): 251 (4.85), 278—282infl. (4.53), 296 (4.51), 405 (4.08). Mass Spectrum *m/e* (%): 318 (M$^+$, 100), 289 (68).

The fourth fraction gave crystals which were recrystallized from EtOH–H_2O to give 62 mg (23%) of 6-methoxy-11-(4-methoxybutoxy)naphthacenequinone (IV) as yellow needles, mp 81—83°. *Anal.* Calcd. for $C_{24}H_{22}O_5$: C, 73.83; H, 5.68. Found: C, 73.83; H, 5.57. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1679 (quinone), ν_{max}^{KBr} cm^{-1}: 1682. UV λ_{max}^{EtOH} mμ (log ε): 251 (4.84), 279—283infl. (4.49), 294 (4.48), 405 (4.06). NMR δ: 8.60—8.10 (4H, m, arom.), 7.90—7.50 (4H, m, arom.), 4.20 (2H, t, J=6.5 cps, Ar–OC$\underline{H}_2$), 4.13 (3H, s, Ar–OC$\underline{H}_3$), 3.54 (2H, t, J=6.0 cps, –C$\underline{H}_2$OCH$_3$), 3.37 (3H, s, –CH$_2$OC$\underline{H}_3$), 2.50—1.70 (4H, m, C–C$\underline{H}_2$C$\underline{H}_2$–C). Mass Spectrum *m/e* (%): 390 (M$^+$, 5), 375 (1), 303 (5), 290 (5), 275 (16), 87 (100), 55 (11), 45 (45).

The fifth fraction gave crystals which were recrystallized from EtOH–H_2O to give 20 mg (6.3%) of 6,11-bis(4-methoxybutoxy)naphthacenequinone (V) as yellow needles, mp 84—86°. *Anal.* Calcd. for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54. Found: C, 72.90; H, 6.47. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1679 (quinone), ν_{max}^{KBr} cm^{-1}: 1683. UV λ_{max}^{EtOH} mμ (log ε): 252 (4.57), 279—284infl. (4.20), 296 (4.17), 405 (3.73). Mass Spectrum *m/e* (%): 462 (M$^+$, 5), 375 (2), 290 (11), 87 (100), 55 (17), 45 (53).

Methylation of 6,11-Dihydroxynaphthacenequinone (I) in Acetone——Compound I (200 mg) was refluxed with dimethyl sulfate (600 mg) in acetone (30 ml) in the presence of anhyd. K_2CO_3 (10 g) for 18 hr. The reaction mixture was treated as above to give the crude product (193 mg), which was chromatographed on silica gel with C_6H_6–$CHCl_3$ as eluent.

The first fraction gave 44 mg (22%) of the starting material.

The second fraction gave 14 mg (7%) of II and was identified with that obtained above by mp, mixed mp, TLC and IR spectrum comparison.

The third fraction gave 133 mg (60%) of III and was identified with that obtained above by mp, mixed mp, TLC and IR spectrum comparison.

Methylation of Phenol (VII) in Tetrahydrofuran——Phenol (VII, 1.0 g) was refluxed with dimethyl sulfate (2.8 g) in THF (50 ml) in the presence of anhyd. K_2CO_3 (20 g) for 18 hr. The reaction mixture was treated in the same manner as in the case of the naphthacenequinone (I). The crude product was distilled to give 470 mg (40%) of anisole (VIII) as a colorless oil, bp 55° (20 mmHg), which was identical with authentic sample in bp, TLC and IR spectrum.

Chromatography of the residue resulted from distillation on silica gel with $CHCl_3$ as eluent, followed by distillation gave 64 mg (3.3%) of 4-methoxybutyl phenyl ether (IX) as a pale yellow oil, bp 135° (7 mmHg) (bath temp.). *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.93; H, 8.90. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1600 (arom.). UV λ_{max}^{EtOH} mμ (log ε): 220.5 (4.00). NMR δ: 7.45—6.70 (5H, m, arom.), 3.98 (2H, t, J=6.0 cps, ArOC$\underline{H}_2$–), 3.44 (2H, t, J=6.0 cps, –C$\underline{H}_2$OCH$_3$), 3.34 (3H, s, –CH$_2$OC$\underline{H}_3$), 1.95—1.60 (4H, m, C–C$\underline{H}_2$C$\underline{H}_2$–C). Mass Spectrum *m/e* (%): 180 (M$^+$, 7), 94 (27), 87 (78), 55 (28), 45 (100).

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Studies on the Physical Properties of Aromatic Sulfinamides. II.[1] Infrared Absorption Spectrum[2]

KŌICHI MORI and YO UEDA

Faculty of Pharmaceutical Sciences, Kyushu University[3]

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Although the physical properties of sulfonamide derivatives have been investigated in detail,[4] those of sulfinamide derivatives have been left almost in ambiguity. This paper deals with the results obtained from the infrared spectra of 25 aromatic sulfinamide derivatives[5] measured in both $CHCl_3$ solution and KBr disks.

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[1] Part I: K. Mori and Y. Ueda, *Yakugaku Zasshi*, **91**, 940 (1971).

[2] A part of this paper was read at the 90th Annual Meeting of the Pharmaceutical Society of Japan (Sapporo) on July 29, 1970.

[3] Location: *Katakasu, Fukuoka.*

[4] A review by J.K. Seydel, *J. Pharm. Sci.*, **57**, 1455 (1968).

[5] We are expecting these spectra will be published by I.R.D.C. cards.

Result and Discussion

The strong absorption band at 1070 (in $CHCl_3$) or 1056 cm^{-1} (KBr disk) of the infrared spectrum of *p*-toluenesulfinanilide (XI) (Fig. 1) was commonly observed throughout the spectra of all compounds (Table I), therefore, this band should be very characteristic of aromatic sulfinamides.

An examination of the region of this band (about 1050—1090 cm^{-1}) of all spectra measured in $CHCl_3$ solution revealed that every one of *p*-toluenesulfinamide and *p*-methoxybenzenesulfinamide derivatives had only one strong absorption band at about 1070 cm^{-1}, but every one of benzenesulfinamide and *p*-chlorobenzensulfinamide derivatives had two strong bands at about 1064 and 1077 cm^{-1} and at 1070 and 1085 cm^{-1}, respectively. In order to assign these two bands we examined two possibilities: the existence of rotational isomers and the accidental coexistence of absorption bands of two different vibrational modes.

Ōki, *et al.*[6] reported that the hindrance of rotation about C–S bond permitted the existence of isomers of sulfoxides having different S–O stretching absorption frequencies, and Moriarty[7] reported that the same kind of hindrance brought about the magnetic nonequivalence of geminal protons adjacent to the sulfinamide group of N,N'-dialkylsulfinamide. However, sulfur atom of the compounds employed in this work is attached to *p*-substituted phenyl rings directly, therefore, the existence of rotational isomers can be safely neglected.[6]

On the other hand, mono-substituted benzene derivatives are known to show C–H in plane vibration of medium intensity at 1072±7 cm^{-1},[8] and *p*-substituted chlorobenzenes were reported to show a band of strong intensity at 1093±2 cm^{-1}.[9] Therefore, the appearance of two bands may be explained as an accidental coexistence of the characteristic absorption band of sulfinamide group and the band mentioned above.

As shown in Table I benzenesulfinamide derivatives showed their S–O absorption bands at exceptionally lower wavenumbers than those of other compounds. Although we have no experimental or theoretical proof, this shift may be understood when we assume a vibrational coupling between the S–O stretching vibration and the C–H in plane vibration of phenyl ring. In the cases of *p*-toluene- and *p*-methoxybenzenesulfinamide derivatives which have no band in the region of S–O band their original S–O frequencies are seemed to be retained.

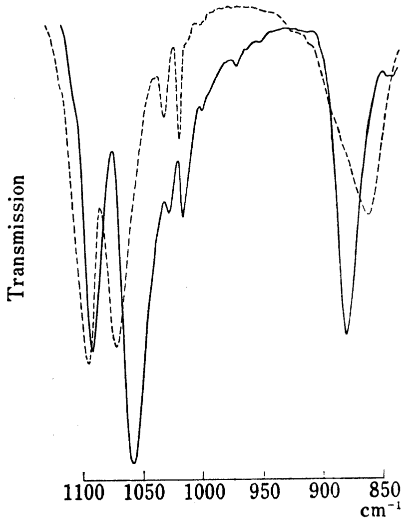

Fig. 1. Infrared spectra of *p*-toluenesulfinanilide in $CHCl_3$ (------) and KBr disk (——)

As mentioned in the previous paper[1] a fairly small inductive electron-withdrawing effect of amino group of sulfinalkylamide derivatives is considered to be practically cancelled by a small electron-donating effect due to a weak *dπ-pπ* double bond character of S–N bond. Accordingly, both S–O bonds of sulfoxide and sulfinalkylamide derivatives are expected to

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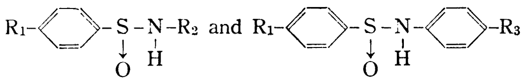
[6] M. Ōki, I. Oka, and K. Sakaguchi, *Bull. Chem. Soc. Japan*, **42**, 2944 (1969).

[7] R.M. Moriarty, *J. Org. Chem.*, **30**, 600 (1965).

[8] A.R. Katritzki and J.M. Lagowski, *J. Chem. Soc.*, **1958**, 4155.

[9] A.R. Katritzki and J.M. Lagowski, *J. Chem. Soc.*, **1960**, 2421.

TABLE I



No. of compound	R_1	R_2	R_3	KBr disk ν_{S-O}	KBr disk ν_{S-N}	$CHCl_3$ solution ν_{S-O}	$CHCl_3$ solution ν_{S-N}
I	H	H		1016	919	1051	
II	H	C_3H_7	(liquid film)	1054	922	1056	
III	CH_3	H		1047	925	1053	
IV	CH_3	C_3H_7	(liquid film)	1058	913	1058	
V	H		H	1056	877	1063	861
VI	H		CH_3	1053	894	1063	863
VII	H		OCH_3	1050	898	1063	865
VIII	H		Cl	1054	881	1064	863
IX	H		$CO_2C_2H_5$	1051	885	1065	867
X	H		$COCH_3$	1055	876	1065	865
XI	CH_3		H	1056	880	1070	861
XII	CH_3		CH_3	1058	892	1070	863
XIII	CH_3		OCH_3	1046	905	1069	863
XIV	CH_3		Cl	1059	877	1071	863
XV	CH_3		$CO_2C_2H_5$	1058	877	1074	868
XVI	CH_3		$COCH_3$	1059	874	1073	865
XVII	OCH_3		CH_3	1055	891	1069	865
XVIII	OCH_3		OCH_3	1051	924	1068	863
XIX	OCH_3		Cl	1063	897	1071	863
XX	Cl		H	1051	883	1071	860
XXI	Cl		CH_3	1057	885	1070	865
XXII	Cl		OCH_3	1051	923	1070	864
XXIII	Cl		Cl	1057	882	1071	863
XXIV	Cl		$CO_2C_2H_5$	1056	877	1073	865
XXV	Cl		$COCH_3$	1059	876	1073	865

have analogous electronic structures having similar infrared absorption frequencies. And actually, sulfinalkylamide derivatives show their absorption bands at very close wave numbers to those of sulfoxide group (1065—1030 cm^{-1}).[10] Moreover, it was shown that sulfinanilides absorb at slightly higher wavenumbers than sulfinalkylamides.[11] Therefore, this characteristic band may reasonably be assigned to the S–O stretching mode of vibration.

Kobayashi, *et al.*[12] stated that the frequencies of S–O stretching vibration of aromatic ethylsulfinates are closely related to the Hammett's σ values of the substituents on the aromatic ring. However, present results are not enough to examine the influence of substituents.

All compounds except liquid substances (II and IV) measured in solid dispersed in KBr disks showed considerably strong bands at around 880—930 cm^{-1}, and they may be assigned to S–N stretching absorption band. And in $CHCl_3$ solution of all sulfinanilides these bands were observed at almost constant wave number, 860—867 cm^{-1}. On the contrary, both II and IV measured as liquid film showed weak band to give assignments in $CHCl_3$ or $CHBr_3$ solution.

Experimental

All compounds employed in this work were synthesized and purified in our laboratory.[1]

Infrared spectra were recorded on a Nihon-Bunko DS-301 infrared spectrometer equipped with NaCl prism.

Acknowledgement Thanks are due to Miss Y. Soeda for the measurement of infrared spectra.

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[10] N.B. Colthup, L.H. Daly and S.E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, 1964, p. 307.

[11] Anilino group is considered to show larger electron-withdrawing effect than amino group.

[12] M. Kobayashi and N. Koga, *Bull. Chem. Soc. Japan*, **39**, 1788 (1966).