The authors thank Assist. Prof. E. Takabatake and Miss H. Ota for their technical assistances, Assist. Prof. Y. Ueda for the measurement of infrared absorption spectra, Miss S. Tada for elementary analyses, and also the Dainippon Pharmaceutical Co., Ltd. and Shionogi & Co. Ltd. for their supply of materials. This work was aided by a Grant-in-Aid for Scientific Research from the Ministry of Education, to which the authors' thanks are due.

Summary

3-OH-EHB was isolated from the urine of rabbits receiving EHB besides 3-keto-EHB and identified with the reduction product of 3-keto-EHB. After the administration of nor-MHB to rabbits, 3-OH-nor-MHB was also detected from the urine, using buffered paper chromatography. Both 3-OH-EHB and 3-OH-nor-MHB have no hypnotic action.

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133. **Tsutomu Momose, Yo Ueda, and Tatsuo Shoji**: Organic Analysis. XIV.[*1] Infrared Spectra of Phenylsulfonyl Derivatives. (3). The C-H Deformation Vibrations of Benzene Ring, the CH_3 Rocking Frequencies of SO_2CH_3 Group, and the Characteristic Absorption Bands of SO_2NH_2 Group.

(*Pharmaceutical Institute, Medical Faculty, University of Kyushu*[*2])

In the previous papers[1,2] of this series, the substituent effect on the SO_2-stretching frequencies and the CO-stretching frequency of the N-acetylsulfonamide group were described. In this work, the other absorption bands of phenylsulfonyl derivatives in the regions of 9～13 and 6～7 μ are discussed, dealing with 50 kinds of phenylsulfonyl, 52 kinds of benzenesulfonamide, and 6 kinds of aliphatic sulfonamide derivatives.

Experimental

Most of the spectra measured and reported in the previous papers were utilized in this work. Several new spectra were measured as liquid or Nujol mull by Koken DS-201 or DS-301 Infrared Spectrophotometer using NaCl prism.

Results and Discussion

C-H In-plane Deformation Vibration

All phenylsulfonyl compounds measured generally exhibited strong absorption bands in the region of 1106～1078 cm^{-1} (9.04～9.28 μ). Their frequencies are tabulated in the first column of Tables I and II, and typical curves are shown in Fig. 1. Two *ortho*-substituted derivatives showed the same bands at 1129 and 1120 cm^{-1}.

Baxter, *et al.*[3] already found these bands in several phenylsulfonyl derivatives and assigned them to S-N stretching vibration. In N-methyltoluene-*p*-sulfonamide, Hadži[4]

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*1 Part XVIII: This Bulletin, **7**, 31(1959).

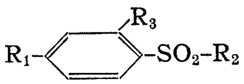
*2 Katakasu, Fukuoka (百瀬勉, 上田 陽, 庄司達雄).

1) T. Momose, Y. Ueda, T. Shoji: This Bulletin, **6**, 415(1958).

2) T. Momose, Y. Ueda, T. Shoji, H. Yano: *Ibid.*, **6**, 669(1958).

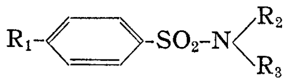
3) J.N. Baxter, J. Cymerman-Craig, J.B. Willis: J. Chem. Soc., **1955**, 669.

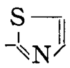
4) D.H. Hadži: *Ibid.*, **1957**, 847; S. Detoni, D.H. Hadži: Spectrochim. Acta, **9**, 601(1957).

Table I. 

R_1	R_2	R_3	State	C–H in-plane (cm^{-1})	CH_3-rocking (cm^{-1})		
H	CH_3	H	N	1083	964	957*	787
〃	〃	〃	C	1086	957		
CH_3	〃	〃	N	1089	964	956	763
〃	〃	〃	C	1086	956		
NH_2	〃	〃	N	1087	959	953*	774
〃	〃	〃	C	1088	956		
OH	〃	〃	N	1085	962	948	773
〃	〃	〃	C	1087	957		
CN	〃	〃	N	1088	966	957	756
〃	〃	〃	C	1086	954		
CH_3CONH	〃	〃	N	1085	971	965	778
$(CH_3CO)_2N$	〃	〃	〃	1087	964	955	775
$HCl \cdot H_2NCH_2$	〃	〃	〃	1092	961		774
〃	〃	Cl	〃	1103	968		768
$HCl \cdot H_2N(CH_3)CH$	〃	H	〃	1088	968		787
$HCONHCN_2$	〃	〃	〃	1086	{978, 971	952	769
$CH_3CONHCH_2$	〃	〃	〃	1088	977	961	773
$(CH_3CO)_2NCH_2$	〃	〃	〃	1087	980	956	757
P	〃	〃	〃	1086	959		775
CHO	〃	Cl	〃	1094	968	956	771
$(CH_3COO)_2CH$	〃	H	〃	1088	961		774
〃	〃	Cl	〃	1099	969		786
HON=CH	〃	H	〃	1088	957		{778, 769
〃	〃	Cl	〃	1091	961		786
$HCl \cdot H_2NCH_2$	C_2H_5	H	〃	1091			
$HCl \cdot H_2NCH_2CH_2$	〃	〃	〃	1088			
$HCl \cdot H_2N(CH_3)CH$	〃	〃	〃	1087			
$(CH_3COO)_2CH$	〃	〃	〃	1087			
〃	〃	〃	C	1085			
CH_3	CH_2CO_2H	〃	N	1088			
CN	〃	〃	〃	1083			
H_2NCH_2	〃	〃	〃	1091			
P	〃	〃	〃	1083			
CHO	〃	〃	〃	1081			
HON=CH	〃	〃	〃	1087			
CN	$CH_2CO_2C_2H_5$	〃	〃	1080			
$HCONHCH_2$	〃	〃	〃	1085			
P	〃	〃	〃	1080			
CN	CH_2COCH_3	〃	〃	1084			
$HCl \cdot H_2NCH_2$	〃	〃	〃	1086			
$HCONHCH_2$	〃	〃	〃	1085			
P	〃	〃	〃	1087			
$HCl \cdot H_2NCH_2$	$CH_2COC_6H_5$	〃	〃	1086			
$HCONHCH_2$	〃	〃	〃	1085			
$HCl \cdot H_2NCH_2$	C_2H_4OH	〃	〃	1085			
P	〃	〃	〃	1082			
H_2NCH_2	CH_2I	〃	〃	1081			
$HCONHCH_2$	〃	〃	〃	1082			
P	〃	〃	〃	1079			
H	C_6H_5	〃	〃	1104			
CH_3	〃	〃	〃	1106			
$HCl \cdot H_2NCH_2$	〃	〃	〃	1104			
P	〃	〃	〃	1105			
$(CH_3COO)_2CH$	〃	〃	〃	1105			
〃	〃	〃	C	1100			
HON=CH	〃	〃	N	1104			
NH_2	$C_6H_4NH_2(p)$	〃	〃	1104			
〃	$C_6H_5SC_6H_5$	〃	L	1080			

*: shoulder; N: Nujol; C: $CHCl_3$ Solution; L: Liquid; P: Phthalimidomethyl

Table II. 

R_1	R_2	R_3	C–H in-plane (cm^{-1})	S–N stretching (cm^{-1})
H	H	H	1091	904
CH_3	〃	〃	1091	908
NH_2	〃	〃	1094	900
CN	〃	〃	1094	903
COOH	〃	〃	1089	901
NH_2CH_2	〃	〃	1095	901
$HCl \cdot NH_2CH_2$	〃	〃	1083	902
$HCl \cdot NH_2(CH_3)CH$	〃	〃	1089	898
$HCl \cdot CH_3NHCH_2$	〃	〃	1094	908 w
$HCl \cdot NH_2CH_2CH_2$	〃	〃	1098	903 w
$HCl \cdot NH_2(C_3H_7)CH$	〃	〃	1099	909
$CH_3CONHCH_2$	〃	〃	1087	903
$CH_3CONH(CH_3)CH$	〃	〃	1088	898
$CH_3(CH_3CO)NCH_2$	〃	〃	1090	916
$CH_3CONHCH_2CH_2$	〃	〃	1094	909
$CH_3CONH(CH_3)CHCH_2CH_2$	〃	〃	1089	908 w
$NH_2CONHCH_2$	〃	〃	1092	{ 915 { 919
$(CH_3COO)_2CH$	〃	〃	1086	914
HON=CH	〃	〃	1089	908 w
H	CH_3	H(L)	1093	837
CH_3	〃	〃	1091	835
CHO	〃	〃	1086	
HON=CH	〃	〃	1093	
NH_2CH_2	〃	〃	1085	
$HCl \cdot NH_2CH_2$	〃	〃	1091	
H	〃	CH_3	1091	
CH_3	〃	〃	1091	
CN	$COCH_3$	H	1079	943
COOH	〃	〃	1081	943
$HCl \cdot NH_2CH_2$	〃	〃	1088	946
$CH_3CONH(CH_3)CH$	〃	〃	1089	946
$CH_3(CH_3CO)NCH_2$	〃	〃	1089	952
$CH_3CONHCH_2$	〃	〃	1089	952
$(CH_3CO)_2NCH_2$	〃	〃	1087	947
$CH_3CONHCH_2CH_2$	〃	〃	1093	948
$(CH_3CO)_2NCH_2CH_2$	〃	〃	1088	946
$CH_3CONHCH_2$*	〃	〃	1129	955
$(CH_3CO)_2NCH_2$*	〃	〃	1120	945
$CH_3CONHCH_2$	〃	CH_3	1087	
$(CH_3CO)_2NCH_2$	〃	〃	1087	
$(CH_3COO)_2CH$	〃	〃	1086	
NH_2CH_2		H	1078	
$HCl \cdot NH_2CH_2$	〃	〃	1085	
〃	C_6H_5	〃	1086	
NH_2CH_2	$C_6H_4CH_3(p)$	〃	1088	
$HCl \cdot NH_2CH_2$	〃	〃	1091	
〃	$C_6H_4OC_2H_5(p)$	〃	1083	
NH_2CH_2	$C_6H_4OH(p)$	〃	1089	
$HCl \cdot NH_2CH_2$	〃	〃	1091	
NH_2CH_2	$C_6H_4CO_2H(p)$	〃	1092	
$HCl \cdot NH_2CH_2$	〃	〃	1087	
〃	$C_6H_4NO_2(p)$	〃	1092	

w : weak; L : Liquid; * : *ortho* compound assigned the same band to the overtone of OSO angle deformation vibration, but both assignments might be questionable by the following two reasons. (1) The benzene sulfonyl halides,[5,7] benzenesulfonic esters,[6,7] and phenyl sulfone derivatives which had no S–N bond, also showed the same absorption bands, and (2) diphenyl sulfide also showed this band at 1080 cm^{-1} in spite of the fact that aliphatic sulfonamide derivatives shown in Table III had no absorption in this region of frequency.

TABLE III.

Compound	State	CH_3 Rocking (cm^{-1})			S–N Stretching (cm^{-1})
CH_3SCH_3	Liquid	1031	973	904	
$CH_3SO_2CH_3$	Nujol	934		762	
$CH_3SO_2NH_2$	〃	989		774	882
$CH_3SO_2NHCH_3$	Liquid	967		778	835
$CH_3SO_2N(CH_3)_2$	Nujol	945		780	
$C_2H_5SO_2NH_2$	〃				896
$C_2H_5SO_2NHCH_3$	Liquid				844
$C_2H_5SO_2N(CH_3)_2$	〃				

On the other hand, it is well known that benzene derivatives have absorption bands in this region; e.g. $(Ph)_nX$ molecules show strong absorption at 1045~1185 cm^{-1},[8] and mono-substituted and *para*-disubstituted benzene derivatives also have absorption bands of variable intensity which depends on the substituents.[9] Therefore, it is more probable that the bands mentioned above are associated with an aromatic ring and may be assigned to the C–H in-plane deformation vibration of benzene ring. The intensity of this vibration is generally rather weak, but it may be intensified by the polar and heavy SO_2 group in phenylsulfonyl compounds.

CH_3 Rocking Frequencies of SO_2CH_3 Group

Some detailed studies on the CH_3 deformation vibration were reported by Nakagawa[10] and others, but the rocking vibration of CH_3 group bound with heteroatoms other than halogen is hardly known.

The second column of Table I shows that all phenylsulfonylmethane derivatives have one or two strong absorption bands in the region of 980~950 cm^{-1} (10.20~10.53 μ) and one strong band in 790~760 cm^{-1} (12.66~13.16 μ). The typical curves are also shown in Fig. 1. These bands may be characteristic to SO_2CH_3 group, because other derivatives listed in the Table have no absorption in these regions. This conclusion will be confirmed by the fact that dimethyl sulfone, methanesulfonamide, N-methylmethanesulfonamide,[11] and N,N-dimethylmethanesulfonamide[12] exhibit strong absorption bands in the same region as shown in Table III.

Dimethyl sulfide is known to have three CH_3 rocking absorption bands at 1028, 972, and 906 cm^{-1}, and C–S–C skeletal vibrating absorption at 741 and 691 cm^{-1}. The characteristic absorption bands mentioned above will be assigned to the CH_3 rocking deformation vibrations, as the methanesulfonamide derivatives listed in the table have no C–S–C linkage. The CH_3 rocking vibrations in SO_2CH_3 group have smaller wave numbers than

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6) P. Hirsjarviand, E. Tommila: Ann. Acad. Sci. Fennicae Ser. A. II, **78**, 20(1957)(C.A., **51**, 16103).
7) D.E. Freeman, A.N. Hambly: Australian J. Chem., **10**, 239(1957)(C.A., **51**, 16103).
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9) R.R. Randle, D.H. Whiffen: Trans. Faraday Soc., **52**, 9(1956)(C.A., **50**, 12656).
10) I. Nakagawa: Nippon Kagaku Zasshi, **75**, 535, 1259(1954); *ibid.*, **76**, 540(1955); I. Nakagawa, S. Mizushima: Bull. Chem. Soc. Japan, **28**, 589(1955).
11) B. Helferich, H. Grünert: Ber., **73B**, 1131(1940).
12) O. Eisleb: Ger. Pat., 735,866 (1943)(to I.G. Farbenind. A.G.)

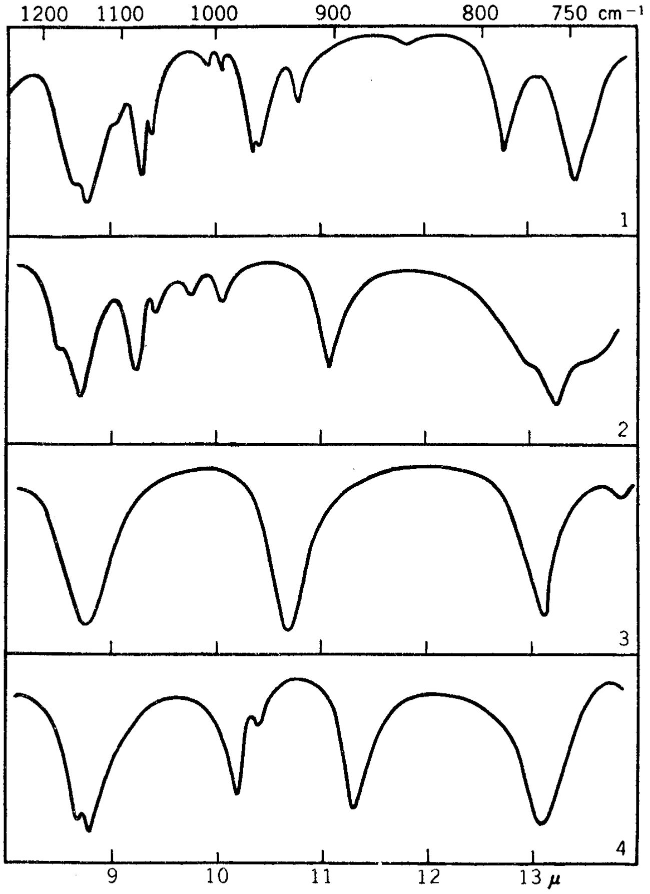


Fig. 1. Infrared Spectra of Sulfonyl Compounds

1 : Phenylsulfonylmethane
2 : Benzenesulfonamide
3 : Dimethyl sulfone
4 : Methanesulfonamide

that of dimethyl sulfide. This difference of absorption area may be caused by the change of –S– group for heavy and polar $-SO_2-$ group.

Characteristic Absorptions of SO_2NH_2 Group

In N-methyl-toluene-*p*-sulfonamide Hadži assigned an absorption frequency of 839 cm^{-1} to S–N stretching vibration. According to the present results, some of $R-SO_2NHCH_3$ and $R-SO_2NHCOCH_3$ compounds showed absorptions in this region, but the others gave rather ambiguous absorption, which might overlap the absorption of C–H out-of-plane deformation vibrations of *para*-disubstituted benzene ring. RSO_2NHR' ($R'=C_6H_4R''(p)$ or thiazole) compounds sometimes showed absorptions at ca. 900 cm^{-1}, but there was no relation between chemical structure and absorption frequencies.

On the other hand, almost all of RSO_2NH_2 compounds had characteristic absorption bands in the region of 919~896 cm^{-1} (11.16~10.88 μ). Their frequencies are tabulated in the second column of Tables II and III, and might be assigned to S–N stretching vibration, though Hoffmann, *et al.*[13] stated that this vibration might occur in a more longer wave-length region.

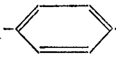
In Tables IV and V, other absorption bands of sulfonamide compounds are shown.

Table IV.

Compound	State	Absorption band (cm^{-1})	Compound	State	Absorption band (cm^{-1})
$CH_3SO_2NH_2$	N	1585 s	$C_2H_5SO_2NH_2$	N	{1572 m, 1562 sh}
$CH_3SO_2NHCH_3$	L	{1639 w, 1630}	$C_2H_5SO_2NHCH_3$	L	1643 w
$CH_3SO_2N(CH_3)_2$	N		$C_2H_5SO_2N(CH_3)_2$	〃	

s : strong; m : medium; w : weak; sh : shoulder; N : Nujol; L : Liquid

13) cf. H. J. Hoffmann, K. R. Andress : Naturwiss., **4**, 94(1954).

Table V. R_1--SO_2-NHR_2

R_1	R_2	State	Absorption band (cm^{-1})
H	H	Nujol	1559 m
〃	CH_3	Liquid	1621 vw
〃	$(CH_3)_2$	Nujol	
CH_3	H	〃	1580 m
〃	CH_3	〃	
〃	$(CH_3)_2$	〃	
NH_2	H	〃	1558 w
CN	〃	〃	1554 m
COOH	〃	〃	1559 m
NH_2CH_2	〃	〃	1550 sh
$HCl \cdot NH_2CH_2$	〃	〃	1550 sh
$HCl \cdot NH_2(CH_3)CH$	〃	〃	1547 w
$HCl \cdot CH_3NHCH_2$	〃	〃	1560 m
$HCl \cdot NH_2CH_2CH_2$	〃	〃	1558 m
$HCl \cdot NH_2(C_3H_7)CH$	〃	〃	1531 w
$(CH_3COO)_2CH$	〃	〃	
HON=CH	〃	〃	1558 m

m: medium; w: weak; sh: shoulder

They are medium to strong bands at 1549~1586 cm^{-1} (6.47~6.31 μ) in RSO_2NH_2 compounds, and weak bands at 1621~1643 cm^{-1} (6.17~6.09 μ) in RSO_2NHCH_3. In aliphatic sulfonamide they were obviously recognized in the spectra, but they were generally obscure in benzenesulfonamide derivatives, overlapping the absorption of aromatic ring. $RSO_2N(CH_3)_2$ compounds had a band in these regions.

Above results showed that these bands resembled the amide-II bands. Baxter, *et al.* reported briefly on these bands in some sulfonamides and stated that the absorption might be caused by SO_2NH_2 group which had more N-H bending character than $CONH_2$ group. However, previous works[1,2] proved that sulfonyl group received fairly large conjugative effects, and therefore, the assignment of the bands was still not ascertained.

The authors are indebted to Mr. H. Yano, and Misses Y. Mukai and M. Nagasaki for their technical cooperation in the preparation of samples.

Summary

The C-H in-plane deformation vibrations of benzene ring may be intensified by the polar and heavy SO_2 group in phenylsulfonyl compounds. The CH_3-rocking vibrations in SO_2CH_3 group have smaller wave numbers than that of dimethyl sulfide, and are in the region of 980~950 cm^{-1} and 790~760 cm^{-1}. RSO_2NH_2 compounds have characteristic frequencies in the region of 919~896 cm^{-1}, which may be assigned to S-N stretching vibration.

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