869. *Infrared Absorption of Substituents in Aromatic Systems. Part VI.*[1] *Methanesulphonamides.*

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Absorption caused by the substituents in some compounds of type $ArNH{\cdot}SO_2Me$ and $ArNMe{\cdot}SO_2Me$ is recorded and discussed. Tentative assignments are suggested for most of the bands.

BAXTER, CYMERMAN-CRAIG, and WILLIS[2] (who summarise earlier work) measured the spectra of several sulphonamides and studied the N–H and SO_2 stretching vibrations. The SO_2 modes have also been investigated by Momose, Ueda, Shoji, and Yamo.[3] The present work aimed at the identification of other characteristic absorption bands; *N*-aryl-*N*-methyl- and *N*-aryl-methanesulphonamides were measured as 0·189M-solutions in purified chloroform in a 0·106 mm. cell with a sodium chloride prism. Nearly all the bands were found to be characteristic either of the aromatic ring[4] or of the substituent group; the latter are recorded in Tables 1 and 2 together with apparent extinction coefficients (for the errors and approximations involved therein see ref. 5). Methanesulphonamide (as a Nujol mull) and its mono- and di-*N*-methyl derivatives were included for comparison.

NH *Stretching Vibration.*—We found the band of the non-bonded NH mode at 3370—3350 cm.$^{-1}$ (45—50) * and the hydrogen-bonded NH mode at 3250 cm.$^{-1}$ (60—80) for the $ArNH{\cdot}SO_2Me$ compounds, and at 3410 (45) and 3330 cm.$^{-1}$ (30) for $MeNH{\cdot}SO_2Me$. These are in good agreement with the positions 3406—3380 and 3300—3245 cm.$^{-1}$ found previously for carbon tetrachloride solutions measured with a calcium fluoride prism.[2]

Methyl Deformation Modes.—The compounds $ArNH{\cdot}SO_2Me$ show a band at 1479—1445 (80—85) which is probably one of the methyl deformation modes of the SO_2Me group. The compounds $ArNMe{\cdot}SO_2Me$ show a shoulder near 1460 cm.$^{-1}$ and a band or shoulder at *ca.* 1415 cm.$^{-1}$ (*ca.* 25); the exact assignment of these bands to the S–Me and N–Me deformation modes is not clear. In this region *N*-methylmethanesulphonamide shows bands at 1474 (25) and 1466 cm.$^{-1}$ (25), and the *NN*-dimethyl analogue bands at 1480 (40), 1465 (65), and 1415 (25) cm.$^{-1}$.

NH *In-plane Deformation Mode.*—A strong band at 1400—1385 cm.$^{-1}$ (170—230) for the compound $ArNH{\cdot}SO_2Me$ is probably essentially the NH in-plane deformation mode. This assignment is supported by the spectrum of $PhND{\cdot}SO_2Me$, in which the band at 1400 cm.$^{-1}$ has disappeared and a new band has appeared at 1045 cm.$^{-1}$. This band is analogous to the " Amide II " band of compounds $R{\cdot}CO{\cdot}NHR$, and was not identified by the earlier workers.[2]

The SO_2 *Frequencies.*—The asymmetrical and symmetrical $-SO_2-$ stretching modes cause absorption as follows:

$ArNH{\cdot}SO_2Me$	1349—1332	(240—300)	1158—1154	(500—700)
$ArNMe{\cdot}SO_2Me$	1361—1347 1334—1325	(360—600) (150—190)	1156—1146	(260—400)
$Me_2N{\cdot}SO_2Me$	1340	(500)	1151	(380)
$MeNH{\cdot}SO_2Me$	1328	(480)	1152	(380)

It is of interest that the symmetrical vibration is the stronger for one class of aromatic compounds and the antisymmetrical for the other. The positions are in reasonable agreement with previous work. Precise intensities have not previously been recorded

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* Parentheses enclose apparent extinction coefficients.

[1] Part V, Katritzky and Lagowski, *J.*, 1960, 2421.

[2] Baxter, Cymerman-Craig, and Willis, *J.*, 1955, 669.

[3] Momose, Ueda, Shoji, and Yamo, *Chem. and Pharm. Bull.* (*Japan*), 1958, **6**, 669.

[4] Katritzky, *Quart. Rev.*, 1959, **13**, 353.

[5] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.

(cf. ref. 2 which records 1370—1333 and 1170—1155 cm.$^{-1}$; ref. 3 records 1345—1330 and 1170—1150 cm.$^{-1}$).

The N-*Aryl Stretching Frequency.*—A band found at 1316—1261 cm.$^{-1}$ (55—80) is assigned to this mode by analogy with the *N*-Aryl stretching mode [6] in compounds of the type ArNR·COR′ (R = H, Me, R′ = Me, Ph) which show bands near 1300 cm.$^{-1}$. Usually, the frequency of the band increases as the ring becomes more electron-accepting, which is in accordance with a greater contribution for the structure $\overset{-}{\text{Ring}}{=}\overset{+}{\text{N}}\text{Me}\cdot\text{SO}_2\text{Me}$.

TABLE 1. N-*Arylmethanesulphonamides*, Me·SO_2·NHAr.

		νNH				Me defn.				νSO_2	
		free		bonded		$MeSO_2^-$		NH defn.		antisym.	
No.	Aryl group	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	Ph	3350	45	3250	65	1479	85	1400 1395 *	170 145	1349 1329	240 225
2	p-ClC_6H_4	3370	50	3250	60	1445	85	1387	230	1334	280
3	p-BrC_6H_4	3350	45	3250	80	1446	80	1385	220	1332	300
4	3-Py [a]	3340	m	3250	w	1457	s	1391	s	1347	s

					Skeletal					
	νN–Ar		νSO_2 sym.		νCS		νNS		M. p.		
No.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	Found	Lit.	Ref.
1	1301 * 1282 *	80 65	1156	500	970	190	912	80	99—100°	100·5°	*b*
2	1293 1272	65 40	1155	640	968	230	902	80	148—149°	148°	*c*
3	1294 1270	60 45	1154	700	969	240	910 902	60 60	137—138°	136°	*c*
4	1316	s	1158	s	967	s	900	m	140—141°	140—141°	*d*

TABLE 2. N-*Aryl*-N-*methylmethanesulphonamides* (Me·SO_2·NMeAr).

		Me defn.				νSO_2 antisym.		νN–C NAr		Me rock N–Me	
No.	Aryl group	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
5	C_6H_5	1470 *	30	1415	25	1347 1326	360 160	1266	55	1174	145
6	p-ClC_6H_4	1460 *	35	1413	25	1348 1325	500 150	1264	75	1171	200
7	p-BrC_6H_4	1460 *	40	1415	25	1348 1324	600 155	1261	80	1171	200
8	2-Py	(—)		1418 *	60	1350 1326 *	600 130	1295	75	1180	150
9	3-Py	1459 *	40	1412 *	50	1353 1327 *	500 150	1277	75	1174	220
10	4-Py	1465	35	1415	45	1361 1334	480 190	1282	100	1174	210

					Skeletal						
	νSO_2 sym.		νN–C NMe		νCS		νNS				
No.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	M. p.	Lit. m. p.	Ref.
5	1149	260	1068	100	960	215	866	110	77°	76·5°	*c*
6	1147	320	1065	150	957	300	870	140	67—68°	—	*e*
7	1146	380	1062	120	956	350	869	135	82—83°	—	*e*
8	1147	400	1070	105	958	280	889 873	130 160	130—135° †/ 0·1 mm.	130—135° †/ 0·1 mm.	*d*
9	1152	300	1076	130	961	280	873	125	62°	62°	*d*
10	1156	310	1066	120	960	260	874	230	53°	53°	*d*

* Shoulder. (—) Band masked by stronger absorption.

a Satd. soln. (<0·2M) in $CHCl_3$. *b* McGowan, *J. prakt. Chem.*, 1884, **30**, 282. *c* Marvel, Helfrick, and Belsley, *J. Amer. Chem. Soc.*, 1929, **51**, 1273. *d* See ref. 7. *e* This work. † B. p.

Extra bands: No. 1: 1422 * (65), 895 * (60); No. 2: 830 * (80); No. 4: 1191 * (m); No. 5: 912 cm.$^{-1}$ (15).

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[6] Katritzky and R. Alan Jones, *J.*, 1959, 2067.

[7] R. Alan Jones and Katritzky, *J.*, in the press.

Methyl Rocking and N–Me *Stretching Modes.*—Bands found in the compounds $ArNMe{\cdot}SO_2Me$ at 1180—1171 cm.$^{-1}$ (145—220) and 1070—1062 cm.$^{-1}$ (100—150) are probably caused by these vibrational modes; a possible assignment is indicated in the table. Comparable bands were found [6] for ArNMe·COMe compounds at 1140 ± 2 cm.$^{-1}$ (75 ± 20) and near 1030 and 1000 cm.$^{-1}$. The compounds $Me_2N{\cdot}SO_2Me$ and $MeNH{\cdot}SO_2Me$ each show a single band, at 1054 cm.$^{-1}$ (30) and 1074 cm.$^{-1}$ (100) respectively. Possibly other bands are hidden by the strong asymmetric SO_2 vibration.

CS *and* NS *Skeletal Stretching Modes.*—Two strong bands are found below 1000 cm.$^{-1}$ as follows:

$ArNH{\cdot}SO_2Me$	970—967	(190—240)	912—900	(60—80)
$ArNMe{\cdot}SO_2Me$	961—956	(215—350)	874—866	(110—160)
$Me_2N{\cdot}SO_2Me$	963	(400)	—	
$MeNH{\cdot}SO_2Me$	966	(130)	829	(120)
$NH_2{\cdot}SO_2Me$	974	m	878	m

These are probably the CS and NS skeletal stretching modes; the position of that of higher frequency varies least, and it is tentatively assigned to the C–S mode. Previous workers have assigned a band near 1070 cm.$^{-1}$,[8] 1090 cm.$^{-1}$,[2] or 550 cm.$^{-1}$ [9] to the S–N stretching mode, but the evidence for these assignments is not compelling.

Other Bands.—The compounds showed the bands expected for the aromatic rings; their frequencies and positioning were in reasonable agreement with earlier work. Bands characteristic of *p*-substituted chloro- and bromo-benzenes have been reported recently; [1] such bands were found at:

	X = Cl	X = Br
p-$X{\cdot}C_6H_4{\cdot}NH{\cdot}SO_2Me$	1092 (120)	1073 (60)
p-$X{\cdot}C_6H_4{\cdot}NMe{\cdot}SO_2Me$	1095 (210)	1072 (210)

The positions of these bands agree excellently with the ranges of 1096—1089 and 1073—1068 cm.$^{-1}$ reported.

The few bands which could not be assigned to the ring or substituent are given as footnotes to the Tables.

Experimental.—The spectra were measured on a Perkin–Elmer model 21 spectrophotometer with the settings previously given.[5]

p-*Chloro*-N-*methylmethanesulphonanilide*, m. p. 67—68° (plates from ethanol) (Found: C, 43·6; H, 4·4; N, 6·2. $C_8H_{10}ClNO_2S$ requires C, 43·7; H, 4·6; N, 6·4%), and p-*bromo*-N-*methylmethanesulphonanilide*, m. p. 82—83° (plates from ethanol) (Found: C, 36·4; H, 4·1; N, 5·4. $C_8H_{10}BrNO_2S$ requires C, 36·4; H, 3·8; N, 5·3%), were prepared by the action of diazomethane on the corresponding methanesulphonanilides.

All other compounds were prepared by literature methods.[7]

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[8] Angus, Leckie, and Williams, *Trans. Faraday Soc.*, 1938, **34**, 793.

[9] Hoffmann and Andress, *Naturwiss.*, 1954, **4**, 94.