489. *Infrared Absorption of Substituents in Aromatic Systems. Part V.*[1] *Halogeno-compounds.*

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Correlations are established between the orientation of substitution of disubstituted benzenes containing a halogen atom directly attached to the ring and absorption in the 1100 cm.$^{-1}$ region of the spectrum. This region of the spectra of some analogous heterocyclic compounds is discussed briefly.

DURING extensive investigation of the infrared spectra of heterocyclic and benzenoid compounds[2] it was found that many compounds which contained halogen atoms directly attached to an aromatic nucleus showed characteristic absorption bands in the 1100 cm.$^{-1}$ region. To determine whether such bands would be useful in diagnostic work, additional compounds were measured, our standard conditions of measurement being used: the results for the disubstituted benzenes are collected in Table 1.

TABLE 1.

		p-Cl		*m*-Cl		*o*-Cl		*p*-Br		*m*-Br		*o*-Br		*p*-I	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	$C_6H_4{\cdot}NH_2$	1092	130	1076	70	1080 1047	35 25	1070	95	1066	70	1042	45		
2	$C_6H_4{\cdot}OMe$	1093	140			1041	105	1073	85			1033	150		
3	$C_6H_4{\cdot}OH$	1093	145			1056	45	1070	105			1041	55	1057	40
4	$C_6H_4{\cdot}Me$	1092	165	1078	65	1054	135	1069	100	1073	85	1028	185	1061	60
5	$C_6H_4{\cdot}X$ [a]	1089	*350*	1123 1078	70 90	1087 1034	60 130	1068	*245*	1069	*80*	1086 1023	25 15		
6	$C_6H_4{\cdot}I$					1034	40	1073	190			1034	30		
7	$C_6H_4{\cdot}CO_2Me$	1093	280			1054	145	1072	160	1069	80	1030	125	1058	45
8	$C_6H_4{\cdot}CHO$	1094	200	1074	50	1052	120			1065	65	1028	70		
9	$C_6H_4{\cdot}NO_2$	1096	180	1128	110	1057	85	1069	180	1112	65	1040	50		
Arithmetic means (see text)		1093	175	1076	75	1050	95	1071	130	1068	75	1035	80	1059	50

TABLE 2.

	4-Substituted [b]		3-Substituted [b]		2-Substituted [b]	
	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
Chloropyridines	1129 1106	20 50	1120 * 1108	35 125	1121	190
Chloropyridine 1-oxides	1120 1090	15 15	1097	150	(—)	
Bromopyridines			1086	50	1108	215
Bromopyridine 1-oxides	1089	60	1087	80		

Footnotes to Tables 1 and 2.

Absence of an entry indicates that compound was not investigated.

* Shoulder.

ε_A *in italics* denotes compounds containing two halogen atoms.

a The dichloro- and dibromo-compounds.

b Some of these bands have been discussed in publications dealing with bands characteristic of the nucleus: Katritzky *et al.*, *J.*, 1958, 2192, 2195, 2198, 2202, 3165; 1959, 3680.

para-Substituted chloro-, bromo-, and iodo-benzenes are characterised by bands at 1096—1089 cm.$^{-1}$ (130—350) [1093 ± 2 cm.$^{-1}$ (175 ± 45)],* 1073—1068 cm.$^{-1}$ (85—190) [1071 ± 2 cm.$^{-1}$ (130 ± 40)], and 1061—1057 cm.$^{-1}$ (40—60), respectively. The frequency range of these bands is very narrow; the intensities vary more, and in general, electron-donating substituents are associated with weaker bands than electron-accepting or carbon–carbon multiple bond substituents. Thus, the bromo-compounds Nos. 1—4 absorb with ε_A 85—105

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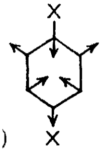
* Apparent extinction coefficients are enclosed in parentheses, and arithmetical means and standard deviations in brackets (see ref. 1 and refs. therein).

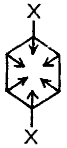
[1] Part IV, Katritzky and R. A. Jones, *J.*, 1960, 676.

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

and Nos. 6—9 with ε_A 160—190. *p*-Dibromo- and *p*-dichloro-benzene fit into the pattern best if the intensities are halved; the single band for *p*-bromoiodobenzene also has a high ε_A value; however, the position fits well for the bromo-compounds. Stojilković and Whiffen [3] have shown that this band is due to a mode involving considerable motion of both the ring atoms and the halogen atom (see also Randle and Whiffen [4]). For identical substituents (V_h symmetry) the mode is approximately (I) [3] which is allowed in the infrared spectrum unlike the analogous mode (II). For *para*-dihalogenobenzenes with two different halogens, modes corresponding to (I) and (II) are both allowed, and so two bands are to be expected in the infrared spectrum, although one of these may be weak.



(I)



(II)

From previous work [5,6] it is evident that unsymmetrical *p*-dihalogenobenzenes containing chlorine absorb at 1090 vs, 1087 vs, and 1090 vvs, those containing bromine at 1064 s, 1068 vs, and 1069 vvs, and those containing iodine at 1050 vs, 1054 s, and 1052 m * cm.$^{-1}$. These compounds thus fit reasonably well into the correlations established above, at least as far as the positions are concerned. It may be significant that unsymmetrical *p*-dihalogenobenzenes containing fluorine absorb at 1154 s, 1155 s, and 1158 s cm.$^{-1}$.[5,6]

It appears that *meta*-substituted chloro- and bromo-benzenes usually give rise to bands at 1078—1074 cm.$^{-1}$ (50—110) [1076 ± 2 cm.$^{-1}$ (75 ± 10)] and 1073—1065 cm.$^{-1}$ (65—85) [1068 ± 3 cm.$^{-1}$ (75 ± 10)], respectively. However, this does not hold for the *m*-nitrohalogeno-compounds where the band is found at considerably higher frequencies, 1128 and 1112 cm.$^{-1}$. For *m*-dichlorobenzene the mode appears to be split into two bands.

The *ortho*-disubstituted chloro- and bromo-benzenes measured absorb at 1057—1034 cm.$^{-1}$ (40—145) [1050 ± 9 cm.$^{-1}$ (95 ± 40)] and 1042—1028 cm.$^{-1}$ (30—185) [1035 ± 6 cm.$^{-1}$ (80 ± 55)], respectively, except that the mode appears to be split into two bands for the *o*-dihalogeno-compounds and for *o*-chloroaniline. There is no obvious correlation between the wide intensity variations and the nature of the second substituent.

Monohalogeno-pyridines and -pyridine 1-oxides show bands near 1100 cm.$^{-1}$ which are either additional to those of analogous compounds containing substituents other than halogen atoms or are much more intense than expected. These bands are listed in Table 2. The positions are considerably shifted from those of their benzenoid analogues. 2-Chloro- and 2-bromo-thiophen show bands at 1004 cm.$^{-1}$ (160) and 974 cm.$^{-1}$ (105), respectively, which are not characteristic of the nucleus.

The bands which are characteristic of these nuclei and those associated with many of the substituents other than halogen atoms have been published (see ref. 2 and refs. therein). For each compound, all bands with $\varepsilon_A > 10$, with few exceptions, could be assigned to the nucleus, halogen atom(s), or second substituent in accordance with previous work.[2]

Experimental.—Compounds were redistilled or recrystallised immediately before measurement and had m. p.s or b. p.s in agreement with literature values. For the methods used to measure the spectra, see ref. 1 and references therein; 0·2M-chloroform solutions were measured in 0·1 mm. cells.

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* Under the conditions used in the present work, this band appears only as a weak shoulder at 1054 cm.$^{-1}$.

[3] Stojilković and Whiffen, *Spectrochim. Acta*, 1958, **12**, 47.
[4] Randle and Whiffen, *Trans. Faraday Soc.*, 1956, **52**, 9.
[5] Stojilković and Whiffen, *Spectrochim. Acta*, 1958, **12**, 57.
[6] Narasimham, El-Sabban, and Nielsen, *J. Chem. Phys.*, 1956, **24**, 420.