414. *Infrared Absorption of Heteroaromatic and Benzenoid Six-membered Monocyclic Nuclei. Part VIII.*[1] meta-*Disubstituted Benzenes.*

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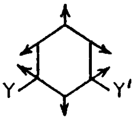
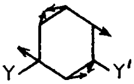
Absorption due to the *meta*-disubstituted benzene ring is recorded and discussed for 43 compounds.

FOLLOWING work on *para*-disubstituted benzenes,[1] we now report on 43 *meta*-disubstituted compounds (Table 1). The object of the work, the conditions of measurement, the regions of the spectrum investigated, and the arrangement of the tables are discussed in the preceding paper,[1] and the notes therein on substituent bands and experimental details also apply to this work.

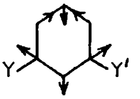
Ring Stretching Frequencies at ca. 1600—1400 cm.$^{-1}$ (Table 1, cols. 1—4).—The first band occurs at 1622—1610 [1616 ± 4] cm.$^{-1}$ for compounds containing a strongly electron-attracting group (Nos. 22—43 †), at 1580—1572 cm.$^{-1}$ when two halogens are present (Nos. 9, 10), and at 1611—1597 [1603 ± 4] cm.$^{-1}$ for the other compounds. A second band occurs at 1595—1575 [1586 ± 5] cm.$^{-1}$ except for the dinitro-compound (No. 43). The third band is at 1460 cm.$^{-1}$ when two halogens are present (Nos. 9, 10); the position is 1495—1471 cm.$^{-1}$ for the other compounds, but tends to lower frequencies as the electron-attracting ability of the substituents increases:



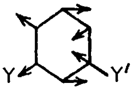
(I) A_1



(II) B_1



(III) A_1



(IV) B_1

Nos.	1—8, 11—19	20—35	36—43
Range	1495—1479	1483—1475	1478—1471 cm.$^{-1}$
Mean and deviation	1489 ± 5	1480 ± 3	1475 ± 3 cm.$^{-1}$

The intensities of these bands depend on the substituents present (Table 2).

The fourth band in this region occurs at 1467—1447 [1458 ± 7] cm.$^{-1}$ for compounds containing a donor group, a halogen atom, or two weak groups (Nos. 1—8 and 11—27), and at 1443—1430 [1437 ± 6] cm.$^{-1}$ for other compounds (Nos. 28—43), except that the dihalides (Nos. 9, 10) absorb at 1413—1410 cm.$^{-1}$. This band is frequently obscured, and the intensities are irregular (5—65) [(35 ± 20)].

Randle and Whiffen [2] reported these bands at [1611 ± 9 (s), 1590 ± 7 (s), 1499 ± 7 (vs), and 1447 ± 15 (m)] cm.$^{-1}$; these positions are in reasonable agreement with our results except for the third band. Our assignment of the bands to vibrations (I)—(IV), respectively, although slightly different from the previous one,[2] appears to explain the intensity variations better (see below).

Alterations in the charge density of a ring by the mesomeric effect of a substituent are

† Except No. 33 where the low frequency is probably partly due to overlap with a heterocyclic nuclear band.

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[1] Katritzky and Simmons, preceding paper.

[2] Randle and Whiffen, Paper No. 12, Report on Conference of Molecular Spectroscopy, 1954, Institute of Petroleum.

greatest in the *ortho-* and *para*-positions. Thus, *meta*-substituents of the same and opposite type respectively reinforce and lessen charge disturbance. Vibrations (I) and (II) (Table 1, cols. 1 and 2) should show intensities proportional to the amount of charge disturbance in the ring,[3] and this is so (Table 2) (donor groups appear to disturb the charge symmetry more than acceptor groups,[3] and weak groups are weak electron donors). For monosubstituted compounds the vibration analogous to (III) is intensified by electron-donor substituents,[3] and this is also true in the present series (Table 1, col. 3; Table 2). The intensity of the fourth band (Table 1, col. 4) shows little dependence on the substituent type, as expected.[3]

In-plane Hydrogen Deformation Modes (Table 1, cols. 5—8).—A band which occurs at 1297—1262 cm.$^{-1}$ (5—50) [1278 ± 12 cm.$^{-1}$ (30 ± 15)] for 13 compounds is absent for four others, and the region is obscured by substituent absorption for the remainder.

A band or shoulder at 1192—1181 cm.$^{-1}$ for nine compounds {for Nos. 1—6 and 12—14, respectively: 1181 (35) 1192 (35), 1183 (190), 1190 (70), 1180 (285), 1185* (85), 1186 (55), 1190* (25), 1182 (65)} appears to be a subsidiary of the band at 1157 ± 5 cm.$^{-1}$. The intensity of the band at 1166—1149 [1157 ± 5] cm.$^{-1}$ (col. 6) is enhanced by the presence of strong electron-donor groups, particularly alkoxyl and hydroxyl:

Nos.	4, 5, 6	2, 3	12, 13, 14	1	7, 8, 11	9, 10, 15—43
Subst.	OR, OR	OR, NH$_2$	OR, Me	NH$_2$, NH$_2$	NH$_2$ with Me, Cl, or Br	others
ε_A	310—440	165—280	150—155	110	25—50	$\leqslant$25

Compounds with a strong electron-attracting group, two weak groups, or two halogen atoms (Nos. 9, 10, 20—43) show a band (col. 7) at 1109—1082 cm.$^{-1}$ (10—75) [1096 ± 7 cm.$^{-1}$ (30 ± 15)]. Another band (col. 8) is found at 1091—1061 [1076 ± 7] cm.$^{-1}$. The intensity is high (60—135) for compounds containing two nitro-, ethoxycarbonyl-, or methoxycarbonyl-groups (Nos. 34, 35, 37, 38, 43) and moderate (20—50) [(30 ± 10)] for compounds containing one of these groups (Nos. 22—33, 36, 39—42); the band appears ($\leqslant$45) for five of the ten other compounds in which the region is not obscured by substituent absorption.

Randle and Whiffen [2] expected, but did not find, the first βCH frequency (Table 1, col. 5) at >1200 cm.$^{-1}$; they reported other bands at [1165 ± 6 (var.), 1081 ± 10 (m), and 1045 ± 7 (m) cm.$^{-1}$]. Agreement with the present work is good for the first and the second band, but instead of the band near 1045 cm.$^{-1}$, we find absorption near 1096 cm.$^{-1}$. McMurry and Thornton report [4] bands at 1200—1155 cm.$^{-1}$ (10), 1185—1150 cm.$^{-1}$ (10), 1120—1085 cm.$^{-1}$ (10), and 1060—1030 cm.$^{-1}$ (10) for *meta*-dialkylbenzenes.

Ring-breathing Frequency (Table 1, col. 9).—Twenty-five of the compounds absorb at 1002—990 cm.$^{-1}$ (5—70) [995 ± 3 cm.$^{-1}$ (20 ± 15)], and the band is absent for nine compounds; it was previously reported [2] at [999 ± 5] cm.$^{-1}$ (var).

Out-of-plane Hydrogen Deformations (Table 1, cols. 10—12).—Compounds with two strong donor groups absorb in the 950 cm.$^{-1}$ region {for Nos. 1—6 respectively 952 (25), 940 (25), 960* (10), 920* (15), 977* cm.$^{-1}$ (20), (—)}. A band at 930—903 [914 ± 8] cm.$^{-1}$ is shown by most compounds with an electron-attracting group and some others. The intensity is (5—45) [(20 ± 10)], except for the dinitro-compound (No. 43). Another band occurs at 841—828 [836 ± 5] cm.$^{-1}$ for donor-donor compounds (Nos. 1—6) and at 903—862 [880 ± 11] cm.$^{-1}$ otherwise; the intensity is (10—95) [(40 ± 25)]. Absorption is sometimes shown just above the solvent cut-off at 805 cm.$^{-1}$.

These bands were previously reported [2] at [964 ± 10 (w), 904 ± 13 (var), 876 ± 10 (vs), and 782 ± 9 (vs)] cm.$^{-1}$, respectively. The second and the third band were found [4] for *meta*-dialkylbenzenes at 930—880 cm.$^{-1}$ (10) and 895—860 cm.$^{-1}$ (20). An attempt has

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[3] Katritzky, *J.*, 1958, 4162.

[4] McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318.

TABLE 1.

			1 A_1 νCC cm.$^{-1}$	ε_A	2 B_1 νCC cm.$^{-1}$	ε_A	3 A_1 νCC cm.$^{-1}$	ε_A	4 B_1 νCC cm.$^{-1}$	ε_A	5 B_1 βCH cm.$^{-1}$	ε_A	6 B_1 βCH cm.$^{-1}$	ε_A	7 A_1 βCH cm.$^{-1}$	ε_A	8 B_1 βCH cm.$^{-1}$	ε_A	9 A_1 ring cm.$^{-1}$	ε_A	10 A_2 γCH cm.$^{-1}$	ε_A	11 B_2 γCH cm.$^{-1}$	ε_A	12 B_2 γCH cm.$^{-1}$	ε_A
Donor–donor																										
1	NH$_2$	NH$_2$	1600 *	205	(—)		1495	110	(—)		—		1159	110	—		—		—		—		834	85	—	
2	NH$_2$	OMe	1607	220	(—)		1493	210	(—)		(—)		1170	90	—		1072 *	25	992	5	—		841	50	—	
													1156	280									828	55		
2	NH$_2$	OEt	1602	220	1590 *	160	1492	150	1460 *	60	(—)		1158	165	(—)		(—)		992	5	—		839	40	—	
													1152 *	160									817 *	20		
4	OMe	OMe	1597	270	(—)		1490	250	1459 †	135	(—)		1161 *	110	—		1079	45	990	10	905	45	850 *	20	—	
													1150	440									835	70		
																							822	25		
5	OEt	OEt	1602	220	1592 *	200	1489	155	(—)		(—)		1151	310	(—)		(—)		992 *	20	905	10	859 *	20	—	
																							841	30		
																							820	20		
6	OMe	OH	1605	250	(—)		1495	200	1464 †	85	(—)		1169	95	(—)		1078	30	996	10	922	20	850 *	15	—	
													1149	360									837	50		
																							820 *	15		
Donor–halogen																										
7	NH$_2$	Cl	1603	210	(—)		1484	150	1450	40	1297	30	1161	25	—		(—)		993	55	—		888	95	—	
																							848	65		
8	NH$_2$	Br	1597	180	1586	110	1480	210	1447	50	1295	25	1160	35	—		(—)		990	70	—		872 *	35	—	
																							862	85		
																							848 *	65		
Halogen–halogen																										
9	Cl	Cl	1580	185	(—)		1460	165	1413	40	1285	5	1155	10	1109	25	1071 *	70	997	15	—		867	60	—	
									1400 *	30																
10	Br	Br	1572	175	(—)		1460	90	1410	30	—		1150	5	1098	15	(—)		992	25	—		869	25	—	
									1398 *	25																
Donor–weak																										
11	NH$_2$	Me	(—)		1594 *	85	1491	85	1467	30	(—)		1166	50	—		—		993	10	919	5	868 *	15	—	
12	OEt	Me	1602	90	1585	95	1487	90	(—)		(—)		1168	90	(—)		(—)		1000	50	(—)		875	15	—	
													1155	155												
13	OMe	Me	1608	120	1590	90	1490	130	1467 †	70	1300 *	30	1163	100	—		1083	10	994	20	910	20	895	10	—	
													1152	150									874	10	—	
14	OH	Me	1616 *	65	1595	110	1488	70	1460	35	1263 *	45	1150	150	—		1080	15	999	15	925	40	876	10	—	
15	OMe	CH:CH·CO$_2$Me	1603	110	1586	140	1488	90	1460 †	90	(—)		(—)		—		1081	15	(—)		913	15	872 *	20	—	
16	OMe	CH:CH·CO$_2$Et	1600 *	110	1585	140	1487	105	(—)		(—)		(—)		(—)		1081 *	30	(—)		—		880 *	10	—	
17	NH$_2$	4Py	1601 †	360	(—)		1479	60	1451	30	(—)		1165	15	—		—		997 †	50	—		863	30	—	
18[a]	NH$_2$	2-Py	(—)		(—)		1498 *	20	1450 *	45	(—)		(—)		(—)		(—)		992 †	40	—		883	25	—	
							1478 *	70															865	25		
19	NH$_2$	2-PyO	(—)		1590 *	110	(—)		1452 *	20	1296	40	—		(—)		—		993	20	—		893	60	—	
																							868	30		
Halogen–weak																										
20[b]	Cl	Me	1600	50	1578	40	1476	80	(—)		—		1160	5	1098	20	(—)		995	10	—		868	20	—	
Weak–weak																										
21	Me	Me	1611	40	1596 †	20	1483	35	(—)		—		1165	10	1094	15	—		—		903	10	880	10	—	

Donor–acceptor																										
22	NH_2	NO_2	(—)		1587	50	1482	60	1460 *	20	(—)		1159	10	1108	20	1091	30	994	20	927	10	888	10	813	120)
23	OEt	NO_2	1620	65	1581	55	1482	75	(—)		(—)		1152	10	1094 †	75	1078 *	30	996	10	—		870	55	(805	70
24	OMe	NO_2	1620	50	1582	50	1482	95	1448 *	50	(—)		1181 *	30	1092	45	1073	25	994	15	—		896	15	(795	50)
																							875	25		
25	OH	NO_2	1622	50	1592	35	1476	35	1452	35	(—)		1157 *	55	1087	20	1071	25	999	20	928	30	874	35	812	145
Halogen–acceptor																										
26	Cl	NO_2	1602 *	15	1582	20	(—)		1462	40	1265	20	—		1095	10	1065	50	—		917	10	888	65	—	
27	Br	NO_2	1598 *	10	1578 *	10	1500 *	35	1464	45	1267	25	—		1125 *	25	1061	50	998	15	918	5	888	45	—	
															1094	20										
Weak–acceptor																										
28	Me	CO_2Et	1610	25	1592	40	(—)		(—)		(—)		1165 *	25	(—)		1082 †	110	1003 *	20	910	10	862	10	—	
29	Me	CO_2Me	1610	30	1594	45	1481 *	15	(—)		(—)		—		(—)		1084 †	95	1000	35	—		870	10	—	
30	Me	NO_2	—		1587 *	15	1482	35	(—)		1289 *	20	—		1096	40	1080	25	—		906	25	880	15	(798	35)
31	CH_2Cl	NO_2	1615	10	1587	15	1480	30	1442	20	1262	50	—		1097	40	1074	25	—		910	10	—		(807	65)
32	4Py	NO_2	1617 *	50	1593 *	55	1475	20	1436	10	1288	25	—		1103	20	1083	20	1001 *	15	905	30	879 †	90	(802	65)
											1270	30														
33	2PyO	NO_2	1605	35	(—)		(—)		1442	65	(—)		(—)		1100	45	1085 *	15	—		906	25	886 †	90	(803	20)
Acceptor–acceptor																										
34	CO_2Me	CO_2Me	1612	30	1590	15	1482	15	(—)		(—)		(—)		(—)		1078	105	(—)		—		—		($CHCl_3$)	
35	CO_2Et	CO_2Et	1610	45	1588	45	1475 *	45	(—)		(—)		(—)		(—)		1076	135	1003 *	50	916	20	(—)		($CHCl_3$)	
36	CN	NO_2	1620	45	1580 *	15	1473	15	1430	5	1279	15	1160	5	1095	30	1075	20	—		905	45	902 *	45	806	50
37	CO_2Me	NO_2	1618	70	1587 *	15	1478	55	(—)		(—)		(—)		1082	35	1068	60	—		919	15	892	35	818	40
38	CO_2Et	NO_2	1620	65	1587 *	10	1478	60	1440 †	45	(—)		1170 *	30	1094 †	75	1068	60	1002 *	30	920	20	910 *	15	816	20
39	COCl	NO_2	1618	115	1584	20	1471	20	1431	20	1278	40	1162 *	15	1094 *	70	(—)		1000	10	916 *	60	—		809	40
40	CHO	NO_2	1618	120	1583	35	1478	40	1443	30	1283	50	1157	15	1083	60	1071 *	40	1002	10	930	40	903	50	817	70
41	COMe	NO_2	1613	105	1575	25	1473	60	1428 †	55	1275	50	1157	20	1109	75	1070	35	997	10	912	15	898	35	808	40
42	CO·Py-2	NO_2	1618	110	1575 *	60	1477	45	(—)		1274 *	5	(—)		1094 †	110	(—)		(—)		908	20	871	55	820	50
43	NO_2	NO_2	1618	110	1608	140	1470 *	15	—		1266	30	1158	25	1091	35	1065	120	—		913	85	903	70	808	60

Assignments for symmetry and vibration type are given immediately below the column number (cf. Ref. 2).

* Shoulder. † Absorption considered to be the superimposition of two peaks, — absence of absorption, (—) bands masked by stronger absorption, ($CHCl_3$) band masked by solvent, Py pyridyl radical (number indicates position of linkage), PyO substituted pyridine 1-oxide.

(*a*) Band at 1462 cm.$^{-1}$ (175) is now considered to be due to the 2-pyridyl nucleus in place of that at 1478 * (70), cf. Katritzky and Hands, *J.*, 1958, 2202.

(*b*) Extra band at 855 (85).

TABLE 2. ε_A *Values.*

Nos.		Band near 1600 cm.$^{-1}$		Band near 1580 cm.$^{-1}$		Band near 1480 cm.$^{-1}$	
		Range	M and α *	Range	M and α *	Range	M and α *
1—10	Donor–donor Donor–halogen Halogen–halogen	175—270	215 ± 30	90—140	115 ± 20	90—250	170 ± 50
11—19	Donor–weak	90—120	105 ± 15			60—130	90 ± 20
20—25	Halogen–weak Weak–weak Donor–acceptor	40—65	50 ± 10	35—55	45 ± 10	35—95	65 ± 25
26—33	Halogen–acceptor Weak–acceptor	0—35	20 ± 15	15—45[a]	30 ± 10	20—35	30 ± 5
34—43	Acceptor–acceptor	30—120	80 ± 35			15—60	40 ± 20

[a] Except No. 43, see text.

* M and α, Arithmetical mean and standard deviation.

been made [5] to correlate a band at 906—838 cm.$^{-1}$ with the sum of Hammett's *meta*-sigma constants for the substituents.

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[5] Bellamy, *J.*, 1955, 2818.