746. *Infrared Absorption of Heteroaromatic and Benzenoid Six-membered, Monocyclic Nuclei. Part IX.*[1] ortho-*Disubstituted Benzenes.*

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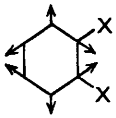
Absorption due to the *ortho*-disubstituted benzene ring for 45 compounds is recorded and discussed.

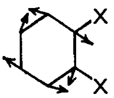
FOLLOWING our work on *para*-[2] and *meta*-disubstituted benzenes,[1] we now report on 45 *ortho*-compounds. The object of the work, the conditions of measurement, the regions of the spectrum investigated, and the arrangement of the Table have been discussed,[2] as has the classification of substituents, into donor (*d*), acceptor (*a*), halogen (*x*), and weak (*w*), on the basis of their electronic effects.[2]

Randle and Whiffen[3] treated statistically the spectra of many *ortho*-disubstituted benzenes and listed arithmetic means and standard deviations for eleven bands in the 1600—800 cm.$^{-1}$ region (see below), which they assigned on the basis of earlier work on both Raman and infrared spectra (the assignments in this paper are as in ref. 3). However, they obtained data from many sources, measured under varying conditions, and were unable to give any indication of quantitative intensities or to relate the intensity or position of bands to the nature of the substituents.

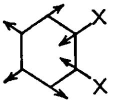
Ring-stretching Frequencies at ca. 1600—1400 *cm.*$^{-1}$.—Four bands occur in this region corresponding to the vibration modes (I—IV). The first band (I) (col. 1) occurs at 1576—1570 cm.$^{-1}$ when the substituents are two halogen atoms, at 1602—1591 [1595 ± 5] cm.$^{-1}$ where one of the substituents is a halogen atom, and at 1624—1591 [1607 ± 9] cm.$^{-1}$ otherwise.*



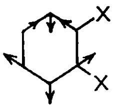
(I)



(II)



(III)



(IV)

da	*dd, dx, xa*	*dw, wa, aa*	*xx, xw, ww*
(140—330)	(60—150)	(15—65)	(10—25)
[210 ± 60]	[90 ± 25]	[40 ± 15]	[20 ± 7]

The intensity varies with the substituents in a manner intermediate between that shown by *para*-substituted benzenes (where the intensity varies as the difference in the electronic effects of the substituents) and that shown by *meta*-substituted benzenes (where the intensity varies as the sum of the electronic effects of the substituents).[1,2]

Many of the compounds show a second band (II) (col. 2) at 1593—1578 [1587 ± 5] cm.$^{-1}$ for *da* compounds (except No. 21) and at 1584—1571 [1577 ± 4] cm.$^{-1}$ otherwise. The intensity is (90—300) [(140 ± 65)] for *da* compounds, (20—85) [(40 ± 20)] for *aa, xw, xa,* and *wa* compounds; for other compounds the band is found only as a shoulder or not at all.

A third band (III) (col. 3) occurs at 1514—1452 cm.$^{-1}$ (20—460); both position and

dd		*dw*		*dx, ww, da, wa, aa*		*xa, xw*		*xx*
1514—1505	>	1503—1495	>	1498—1458	>	1478—1466	>	1460—1452
[1508 ± 4]		[1500 ± 4]		[1487 ± 5]		[1470 ± 5]		[1455 ± 4]

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* Parentheses indicate apparent molecular extinction coefficients, and square brackets arithmetic means and standard deviations. The intensities of shoulders and superimposed bands and the position of shoulders are not treated statistically.

[1] Katritzky and Simmons, *J.*, 1959, 2058.

[2] *Idem, J.*, 1959, 2051.

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

		1		2		3		4		5		6		7		8		9		10	
		A_1		B_1		A_1		B_1		B_1		A_1		B_1		A_1		?		?	
		νCC		νCC		νCC		νCC		βCH		βCH		βCH		βCH		γCH		γCH	
		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	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
Donor–donor																					
1 NH_2	NH_2	1596	95	—		1505	200	1463	35	(—)		1150	20	—		1033	5	913	25	862	35
2 NH_2	OMe	(—)		1590 *	40	1507	300	1470 †	95	(—)		1181	80	—		1023	65	906	25	839	15
3 OMe	OMe	1594	105	—		1506	255	(—)		(—)		1176	145	—		1050	45	905	10	—	
4 OMe	OH	1619 * 1601	40 70	—		1506	440	(—)		(—)		1174 1156	50 25	(—)		1039	130	913	20	830	15
5 OH	OH	1613	60	—		1514	175	1472	40	(—)		1186 * 1173 *	60 60	(—)		1028	35	916	15	861 845	20 30
Donor–halogen																					
6 NH_2	Cl	(—)		1590 *	25	1492	220	1457	75	1316 *	50	1158	30	1142	15	1023	45	—		832	10
7 NH_2	Br	(—)		1575 *	20	1486	220	1451	65	(—)		1158	30	1142	15	1015	85	—		839	5
8 OMe	Cl	1594	90	1580 *	45	1491	320	1454	80	(—)		1184 1162	10 10	1132	40	1026	105	—		—	
9 OMe	Br	1591	70	1580 *	40	1486	320	1452	70	(—)		1183 1163	10 10	1124	30	1025 *	105	—		—	
10 OH	Cl	1599	90	1590 *	60	1484	320	1465 *	35	—		1154	25	1125	25	1027	65	927	5	830	35
11 OH	Br	1602	85	1590 * 1580 *	60 40	1479	300	1454 *	20	1323 *	20	1156	40	1115	15	1023	170	932	5	826	45
Halogen–halogen																					
12 Cl	Cl	1576	20	—		1460	110	1438	50	1252	10	—		1126	80	1012	35	937	10	816	25
13 Cl	I	1570	25	—		1453	170	1432	65	1255	10	—		1116 1103	30 40	1012	110	940	5	—	
14 Br	Br	1571	25	—		1452	155	1434	50	1254	10	—		1106	90	1011	125	940	5	—	
Donor–weak																					
15 NH_2	Me	1591	40	—		1501	90	1473	70	1319 *	20	1155 *	10	—		1034	10	985	15	840	15
16 NH_2	Ph	1584 *	35	—		1503	65	1459	30	1313 *	20	1156	25	—		1045	10	990	10	850	10
17 OH	Me	1593	65	—		1495	90	1466	60	(—)		1150 *	40	(—)		1037	25	980	10	840	45
Halogen–weak																					
18 Cl	Me	1596	10	1575	20	1489 * 1476	40 85	1442	30	—		—		1127	15	1040	50	—		—	
19 Br	Me	1600	15	1572	25	1478 * 1467	50 90	1435	25	—		—		1120	5	1044	25	996	10	830	10
Weak–weak																					
20 Me	Me	1607	10	—		1498	55	1460 *	45	—		—		1118	15	1020	20	984	15	—	

		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 A_1 βCH cm.$^{-1}$	ε_A	7 B_1 βCH cm.$^{-1}$	ε_A	8 A_1 βCH cm.$^{-1}$	ε_A	9 ? γCH cm.$^{-1}$	ε_A	10 ? γCH cm.$^{-1}$	ε_A
Donor–acceptor																					
21 NH_2	CO_2Me	1592	240	1564	130	1490	90	1458	75	(—)		1162	230	(—)		1027	15	(—)		—	
22 NH_2	NO_2	1587 *	125	1578	180	1483	40	1445	180	(—)		1168 1157 *	170 75	1105	65	1017	15	950	10	843	10
23 NH·COMe	NO_2	1613	230	1591	300	1458	150	1437	300	(—)		1164 1147	65 120	—		1040	25	956	15	831	20
24 OMe	CHO	1604	330	1589 *	60	1488	210	1443 ‡	90	(—)		1163	145	1104	50	1044	65	—		(—)	
25 OMe	NO_2	1613	200	1588	90	1493	85	1456 *	40	(—)		1184 1165	25 70	1147	25	1055 * 1045	20 35	943	10	(—)	
26 OH	CO_2Me	1618	190	1589	120	1490	300	1446 ‡	360	(—)		1160	310	(—)		1033	75	(—)		846	130
27 OH	CO_2Et	1616	195	1589	100	1489	260	(—)		(—)		1158	360	1113 *	30	1032	75	952	10	815	35
28 OH	CHO	1624	145	1584	100	1491	140	1464	165	(—)		1150	170	1114	25	1027	40	942	10	858	10
29 OH	COMe	1620	140	1584	90	1490	140	1452	165	(—)		1159	120	1129	10	1032 1022	30 25	944 *	15	834	45
30 OH	NO_2	1620	240	1593 1577 *	160 60	1479	260	1457	150	(—)		1161	60	1115 *	15	1027	60	950	10	815	25
Halogen-acceptor																					
31 Cl	CO_2Me	1596	65	1580 *	15	1478	50	1439 ‡	145	1273 *	140	1163	20	(—)		1040	50	(—)			
32 Br	CO_2Me	1594	80	1571	25	1474	60	1438 ‡	160	1270 *	150	1164	15	(—)		1044	85	(—)			
33 Cl	CHO	1595	150	1571	30	1466	40	1447	80	1291	15	1160	15	1115	15	1034	40	952	10	—	
34 Cl	NO_2	1593	105	1585 *	75	1474	60	1444	20	1260	20	—		1131	20	1035	10	949	10	—	
35 Br	NO_2	1590	110	(—)		1468	60	1438	10	1256	20	—		—		1035 †	50	945	10	—	
Weak-acceptor																					
36 CH:CH·CO_2Me	NO_2	1608	50	1576	85	1481	30	1446 *	95	1278 *	220	(—)		1142	25	1036	60	935	15	—	
37 CH:CH·CO_2Et	NO_2	1608	35	1576	50	1480	30	(—)		1275 *	130	(—)		1143 *	25	(—)		—		—	
38 CH_2Cl	CN	1606	15	—		1494	25	1458	45	1288	20	1165	5	—		—		955	10	—	
39 Me	CN	1606	30	—		1491	65	1446 *	20	1292	25	1163	15	1108	20	1043	15	947	10	—	
40 Me	CO_2Me	1604	40	1578	25	1490	35	(—)		1287 *	110	1164	25	1142 1135 *	70 65	1051	25	990	20	—	
41 Me	CO_2Et	1604	30	1578	20	1490	30	(—)		1280 *	110	1165 *	40	1142 1135 *	80 75	1051	35	999	40	—	
42 Me	NO_2	1616	55	1582	35	1486	40	1433	25	1278	20	1163	20	1148	20	1049	10	950	10	—	
Acceptor–acceptor																					
43 CO_2Me	CO_2Me	1602	45	1582	45	1491	35	1452 *	80	(—)		1165 *	20	(—)		1039	50	955 †	65	—	
44 CO_2Et	CO_2Et	1604	45	1584	45	1492	35	(—)		(—)		(—)		(—)		1040	115	958	15	—	
45 CO_2Me	NO_2	1608	35	1580	40	1485	30	1448 *	55	(—)		(—)		(—)		1036	15	(—)		(—)	
46 CHO	NO_2	1607	25	1576	55	1477 *	15	1449	40	(—)		1162 *	15	—		—		960	10	—	

* Shoulder. ‡ Peaks considered to be the superimposition of two bands. — Absence of absorption. (—) Region obscured by other absorption.
† Intensity of band increased owing to overlap of two bands.

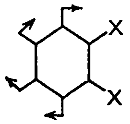
intensity can be correlated with the substituent type. The position is raised by donor substituents and lowered by halogen substituents. In general, the intensity is raised by donor or halogen substituents, as shown; but the intensity is irregular (40—300) [(170 ± 80)] in *da* compounds. In other series it has been found that donor substituents raise the intensity of the corresponding band.[1,2]

dd, dx		*xx*		*dw, xw*		*ww, xa, wa, aa*
(175—440)	>	(110—170)	>	(65—90)	>	(25—60)
[(280 ± 80)]		[(145 ± 30)]		[(80 ± 10)]		[(40 ± 15)]

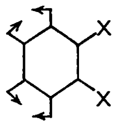
The fourth band (IV) (col. 4) is found at 1473—1460 [1467 ± 6] cm.$^{-1}$ for compounds of the *dd* and *dw* classes and otherwise at 1464—1432 [1447 ± 10] cm.$^{-1}$. The intensity is high (75—300) [(170 ± 90)] for *da* compounds, but otherwise shows only random variations (10—80) [(50 ± 20)].

Randle and Whiffen reported[3] these four bands at 1609 ± 10 (var), 1575 ± 9 (var), 1490 ± 11 (s), and 1445 ± 8 (s); these positions are in good overall agreement with our more precise data.

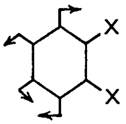
In-plane CH-*Bending Vibrations at* ca. 1300—1000 *cm.*$^{-1}$.—Four bands corresponding to the modes (V—VIII) occur in this region. The first band (V) (col. 5) is frequently obscured by substituent absorption, but occurs as a discrete band at 1292—1252 cm.$^{-1}$ (10—25) [1269 ± 17 cm.$^{-1}$ (15 ± 5)] in *xx, xa,* and *wa* compounds.



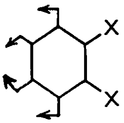
(V)



(VI)



(VII)

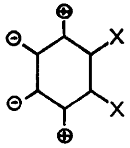


(VIII)

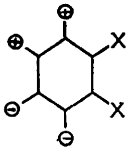
The position of the second band (VI) (col. 6) is 1168—1150 [1160 ± 4] cm.$^{-1}$ except for four compounds of the donor–donor class (Nos. 2—5) where it occurs at 1181—1174 cm.$^{-1}$. The band is absent for *xx, xw,* and *ww* compounds, and is of intensity (20—145) [(70 ± 45)] for *dd* compounds, (60—360) [175 ± 95] for *da* compounds, and (5—40) [(20 ± 10)] otherwise.

The third band (VII) (col. 7) is absent for compounds of the *dd, dw,* and *aa* classes but otherwise occurs at 1148—1103 cm.$^{-1}$ (5—65) [1125 ± 14 cm.$^{-1}$ (25 ± 15)] except that the intensity is higher (70—115) for the *xx* compounds and certain esters (Nos. 40, 41, 44).

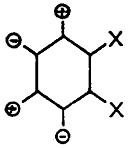
The fourth band (VIII) (col. 8) occurs at 1056—1011 cm.$^{-1}$ (5—170) [(50 ± 40)]. The position is 1051—1034 [1040 ± 6] cm.$^{-1}$ for *dw, xw, xa, wa,* and *aa* compounds, 1045—1017 [1033 ± 8] cm.$^{-1}$ for *dd* and *da* compounds, and 1027—1011 [1018 ± 7] cm.$^{-1}$ for *dx, xx,* and *ww* compounds.



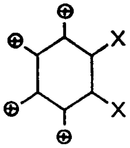
(IX)



(X)



(XI)



(XII)

Randle and Whiffen[3] found the last three of these bands at 1159 ± 7 (m), 1126 ± 12 (m), and 1031 ± 5 (s) cm.$^{-1}$, respectively, in reasonable agreement with our results.

Out-of-plane CH-*Bending Vibrations below* 1000 *cm.*$^{-1}$.—Four modes (IX—XII) are expected. Most of the compounds show weak absorption for the 1000—900 and the 900—800 cm.$^{-1}$ region (cols. 9 and 10) which are probably due to some of these modes. For the 1000—900 cm.$^{-1}$ region most types of compound show a band at 960—935 [948 ± 7] cm.$^{-1}$ (10—15), but *dd* type show instead a band at 916—906 cm.$^{-1}$ (10—25), and *dw*, *xw*, and *ww* types show only a band at 996—980 cm.$^{-1}$ (10—15). About half the compounds show a band in the 900—800 cm.$^{-1}$ region.

Randle and Whiffen found[3] that the "umbrella" mode (XII) caused a strong band at 751 ± 7 cm.$^{-1}$ which would be obscured by solvent absorption in our work. They tentatively assigned bands at 977 ± 9 (w), 934 ± 11 (w), and 865 ± 14 (w) cm.$^{-1}$ to the other modes (IX—XI).

Other Bands.—Nearly all the remaining bands, $\varepsilon_A > 10$, could be assigned to substituent absorption; the following were exceptions: 1140 (45), 1070 (35) in No. 2; 1479 (50) in No. 12; 1486 (25), 1472 (35) in No. 14; 1143 (15) in No. 15; 1140 (15) in No. 16; 1340 * (35) in No. 21; 1091 (35) in No. 25.

Experimental.—The compounds were commercial products or were prepared by standard methods; all were recrystallised or distilled immediately before measurement and had melting or boiling points in agreement with values in the literature.

The spectra were measured on a Perkin-Elmer 21 Spectrophotometer with a NaCl prism and the setting previously reported.[4] ε_A values were calculated as before.[5]

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THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, April 9th*, 1959.]

[4] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.
[5] Katritzky and Lagowski, *J.*, 1958, 4155.