413. *Infrared Absorption of Heteroaromatic and Benzenoid Six-membered Monocyclic Nuclei. Part VII.** para-*Disubstituted Benzenes.*

By A. R. Katritzky and P. Simmons.

Absorption due to the *para*-disubstituted benzene ring in 69 compounds is recorded. The variations of the positions and intensities of nine characteristic bands with the nature of the substituents are discussed. The intensities of the ring-stretching frequencies at 1600—1400 cm.$^{-1}$ depend on the charge disturbance of the ring in a manner similar to that in monosubstituted compounds.

Previously we showed that for monosubstituted benzenes,[1a] pyridines,[1b] pyridine 1-oxides,[1c] and pyridine–boron trichloride adducts,* the intensities of the characteristic bands depend on the nature of the substituent. Variations in the intensities of the ring stretching bands at 1600—1400 cm.$^{-1}$ have been correlated [1d] with the charge disturbance created in the ring by the substituents and/or hetero-groups. We now extend this work to polysubstituted compounds; this and the following paper deal respectively with the absorption of the *para*- and the *meta*-disubstituted benzene ring.

---

* Part VI, preceding paper.

[1] Katritzky and his co-workers, *J.*, 1598, (*a*) 4155, (*b*) 2198, 2202, 3165, (*c*) 2192, 2195, (*d*) 4162, (*e*) 2182.

Problems in presenting the data arise because there are two substituents (*i.e.*, two variable parameters). Various measures of the effect of a substituent on a benzene ring are available; some examples are given in Table 1. There is no order in which substituents can be uniquely arranged; substituents can interact by inductive and mesomeric effects and have different polarisabilities, which can be invoked to a varying degree. However, on the basis of qualitatively similar effects, substituents can be divided into: (i) amino, hydroxy, and alkoxy groups; (ii) chlorine, bromine, and iodine atoms; (iii) groups with a saturated carbon atom adjacent to the ring; (iv) those attached to the ring by an unsaturated carbon atom; (v) cyano, alkoxycarbonyl, acyl, and nitro groups. For brevity, these substituent types are denoted as follows; donor (d), halogen (x), saturated carbon (s), unsaturated carbon (u), and acceptor (a). The effect on the infrared spectrum of an unsaturated carbon substituent is similar to that of a saturated carbon substituent except when it is *para* to a (strong) donor or acceptor group (*i.e.*, conditions of high polarisation); therefore, in other environments, these types of substituents are considered together and denoted as "weak (w)." The *para*-disubstituted benzenes are arranged in Table 2 in the order: dd, dx, xx, ds, xw, ww, du, da, ua, xa, sa, aa. The order for the *meta*-disubstituted benzenes (following paper) is identical except that categories du and ua disappear, and ds and sa become dw and wa.

TABLE 1. *Mesomeric moments and sigma constants for substituent groups*

Substituent	μ_M	σ_p	σ_m	σ'	σ_R
NMe_2 ...	1·66	−0·83	—	—	—
NH_2......	1·02	−0·66	−0·16	—	—
OH	—	−0·37	+0·12	+0·25	−0·61
OMe ...	0·96	−0·27	+0·11	+0·23	−0·50
OEt	—	−0·24	+0·1	—	—
Cl	0·41	+0·23	+0·37	+0·47	−0·24
Br	0·43	+0·23	+0·39	+0·45	−0·22
Me	0·35	−0·17	−0·07	−0·05	−0·13
Et	—	−0·15	−0·07	—	—
Ph	0·0	−0·01	+0·06	+0·10	−0·09
CN	0·45	+0·66	+0·56	+0·59	+0·07
CO_2Et ...	0·5	+0·45	+0·37	+0·32	+0·20
COMe ...	0·56	+0·50	+0·38	+0·27	+0·25
NO_2	0·76	+0·78	+0·71	+0·63	+0·15

μ_M represents mesomeric moments of benzenes (cf. Everard and Sutton, *J.*, 1951, 2818, and references therein).

σ_p, σ_m, σ', and σ_R represent, respectively, Hammett's sigma *para* and *meta* constants, polar substituent constants, and resonance substituent constants (see Taft, in Newman's "Steric Effects in Organic Chemistry," Wiley, New York, 1956, p. 556 *et seq.*, and McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420).

The spectra were measured in chloroform, and apparent extinction coefficients were recorded.[1] Solvent absorption obscured CH deformation modes below 800 cm.$^{-1}$; the concentration used was not sufficient to distinguish the combination modes at 2000—1650 cm.$^{-1}$, and the sodium chloride prism gave poor resolution in the 3000 cm.$^{-1}$ region. Thus, this work is concerned with four ring-stretching modes at 1600—1400 cm.$^{-1}$, four CH in-plane deformation modes at 1300—1000 cm.$^{-1}$, and one of the CH out-of-plane deformation modes. The bands observed are recorded in Table 2.

Randle and Whiffen[2] treated statistically the spectra of many *para*-disubstituted benzenes and listed arithmetical means and standard deviations for eight characteristic bands in the 1600—800 cm.$^{-1}$ region. They obtained data from many sources, measured under various conditions, and were unable to give precise intensities or to correlate between intensity and position of a band. McMurry and Thornton[3] give data for *para*-dialkylbenzenes, and *para*-dihalogenobenzenes have been studied in detail.[4]

Ring-stretching Frequencies (Table 2, cols. 1—4).—The first band occurs at 1616—1592 [1606 ± 6]* cm.$^{-1}$ and for certain types of compounds the range is smaller: du, da, and ua at 1608—1597 [1602 ± 3] cm.$^{-1}$; xa, sa, and aa at 1616—1604 [1610 ± 3] cm.$^{-1}$. The

---

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

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

[4] Stojiljković and Whiffen, *Spectrochim. Acta*, 1958, **12**, 47, 57.

second band occurs at 1590—1570 [1579 ± 6] cm.$^{-1}$ but is frequently obscured and sometimes absent. The next band is at 1522—1469 cm.$^{-1}$; the position is lowered by halogen atoms and acceptor substituents:

dd, ds, du, ww, da	1522—1504 [1511 ± 4] cm.$^{-1}$
dx, xw, ua, sa, aa	1502—1479 [1491 ± 7] cm.$^{-1}$
xx, xa	1479—1469 [1475 ± 4] cm.$^{-1}$

A last band in this region occurs frequently at 1422—1396 [1409 ± 8] cm.$^{-1}$ (but at 1392—1382 cm.$^{-1}$ for dihalogeno-compounds). These bands were previously[2] reported at [1620 ± 8 (m), 1571 ± 11 (w), 1512 ± 12 (vs), and 1450 ± 10 (m)] cm.$^{-1}$; the most serious discrepancy in position is that of the last band. Bands at 1656—1633 cm.$^{-1}$ (5) and 1521—1510 cm.$^{-1}$ (100) were reported[3] for dialkyl compounds.

para-Disubstituted benzenes with identical substituents are of V_h symmetry;† those with different substituents are of C_{2v} symmetry. The predictions[1d] concerning the intensities of the four ring-stretching frequencies of monosubstituted benzenes, pyridines, etc., of C_{2v} symmetry should therefore apply. In agreement with this, the intensity* of the A_1 vibration near 1606 cm.$^{-1}$ (I) is low when the substituents are of the same type and increases with increasing difference between the substituents. The unsaturated carbon atoms can evidently be polarised by both strong donor and strong acceptor substituents. A nitro-group *para* to another electron-accepting substituent still causes an appreciable charge disturbance in the molecule; a similar effect has been noted for ultraviolet spectra.[5]

dd, xx, xw, ww, aa ‡	(0—30) [(5)]
dx, ds	(30—55) [(45 ± 10)]
xa, sa, aa′ ‡	(40—125) [(100 ± 20)]
du, ua	(85—240) [(175 ± 55)] §
da	(200—530) [(340 ± 100)]

The B_1 vibration near 1579 cm.$^{-1}$ (II) should show intensities that are lower than the previous band but vary with the nature of the substituents in much the same way.[1d] Although the band is often not resolved or is only partly resolved (shoulder), the band is usually more intense for compounds with substituents of different types and less intense than the preceding mode (except for the halogenonitro-compounds Nos. 50, 51).

dd, dx, xx, xw, ww, aa	(0—15) [(5 ± 5)]
ds, du, da, ua, sa	(0—95) [(30 ± 25)]

The intensity of the A_1 vibration near 1500 cm.$^{-1}$ (III) should be approximately the same as for benzene (40) for compounds with substituents that interact weakly with the ring. For other substituents it should show variations which cannot be predicted from first principles;[1d] for the monosubstituted compounds, donor substituents were found to

---

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

† The designation of the symmetry species of the vibration is not unambiguous for V_h molecules. In our work, as in ref. 4, yz is taken as the plane of the molecule, with the z axis passing through the substituents; in ref. 2 (published before the recommendations of *J. Chem. Phys.*, 1955, **23**, 1997) another convention has been used.

‡ Here aa indicates identical acceptor groups (Nos. 61, 62, 69), and aa′ different acceptor groups (Nos. 63—68).

§ Except No. 25 for which the intensity is (500).

[5] Schubert, Craven, Steadly, and Robins, *J. Org. Chem.*, 1957, **22**, 1285.

TABLE 2.

			1 A_1–A_g νCC		2 B_1–B_{3g} νCC		3 A_1–B_{1u} νCC		4 B_1–B_{2u} νCC		5 B_1–B_{3g} βCH		6 A_1–A_g βCH		7 B_1–B_{2u} βCH		8 A_1–B_{1u} βCH		9 B_2–B_{3u} 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
Donor–donor																				
1	NMe_2	NH_2	(—)		(—)		1513	300	—		(—)		(—)		(—)		—		816	110
2	NH_2	OMe	(—)		(—)		1510	230	—		(—)		1176	50	1122	25	(—)		822	135
3	NH_2	OEt	(—)		(—)		1510	360	(—)		(—)		1170	25	(—)		—		821	105
													1150 *	20						
4	OMe	OMe	1600	15	—		1508	270	—		(—)		1178	115	1106	45	(—)		826	150
5	OMe	OH	1607	15	—		1508	380	—		(—)		1172 ‡	230	1100	80	—		828	220
Donor–halogen																				
6	NH_2	Cl	1604 *	45	1578	10	1491	190	—		(—)		1170	45	1119	20	1004	20	819	130
7	NH_2	Br	1597	55	—		1487	185	1420	10	(—)		1171	40	1119	15	1005	30	816	100
8	OH	Cl	1592	45	(—)		1490	320	—		(—)		1170 ‡	170	(—)		1008	25	824	170
Halogen–halogen																				
9[a]	Cl	Cl	—		—		1476	185	1392	35	—		—		1115 *	20	1012	190	819	195
10[b]	Br	Br	—		—		1469	230	1383	55	—		—		1102	20	1005	330	810	170
Donor–saturated carbon																				
11	NH_2	Me	(—)		(—)		1512	140	—		(—)		1177	15	1122	20	—		812	110
12	OEt	Me	1615	30	1590	15	1510	145	(—)		(—)		1173	60	(—)		1005	25	818	60
13	OMe	Me	1616	55	1588	25	1510	200	—		(—)		1175	70	1110	30	(—)		818	80
Halogen–weak																				
14	Cl	Me	—		—		1491	170	(—)		—		—		1111	25	1017	55	808	115
15	Br	Me	—		—		1485	120	(—)		—		—		1110	20	1011	125	($CHCl_3$)	
16	I	Me	—		—		1482	135	(—)		1300	10	—		1110	25	1008	160	($CHCl_3$)	
17	Cl	CH:CHPy	(—)		(—)		1492	140	1408 *	40	1288	15	—		1112	25	1013	95	823	215
18	Cl	C⋮CPy	1603 *	165	(—)		1493	140	(—)		—		—		(—)		1013	115	828	235
19	Cl	C⋮CPyO	1613	5	—		1493 ‡	310	1400	20	(—)		(—)		(—)		1014	95	828 ‡	175
Weak–weak																				
20	Me	Me	—		—		1510	50	—		—		—		1119	20	1022 *	25	($CHCl_3$)	
															1102	15				
21	Me	Pr^{i}	—		—		1510	90	(—)		1298	10	—		1102	15	1019	15	818	100
22	Me	CH:CHPy	(—)		(—)		1510	50	(—)		1296	10	1179	25	1119	15	1016	15	818	195
23	Me	CH:CHPyO	1611	30	1573	10	1510	50	—		(—)		(—)		1113	15	1017	20	($CHCl_3$)	
24	Me	C⋮CPy	(—)		—		1505	15	(—)		—		1177	10	1103	15	1017	20	818 ‡	280
Donor–unsaturated carbon																				
25	NMe_2	CH:CHPyO	1601	500	(—)		1521	280	—		(—)		1182	180	1123 *	60	—		826 ‡	170
26	NH_2	3-Py	(—)		(—)		1519	85	(—)		(—)		1181	130	1127 ‡	25	(—)		832	80
27[c]	NH_2	2-Py	(—)		(—)		1522	45	1425 *	40	(—)		1181	140	1127	15	1009	5	837	70
28	OMe	CH:CHPy	1610 *	175	1585 *	85	1512	210	(—)		(—)		1174	240	1109	20	(—)		828	190
29	OMe	CH:CHPyO	1605	230	1577	45	1508	165	1423 *	25	(—)		1168 ‡	350	1108	20	(—)		833 ‡	260
30	OMe	C⋮CPy	1610 *	85	1576 *	50	1509	115	(—)		(—)		1173	130	1105	30	—		831	190

Donor–acceptor																				
31	NH_2	N:NPh	1605	290	(—)		1504	115	(—)		(—)		1152 *	115	1123 *	40	—		834	150
32	NH_2	CN	1606	200	(—)		1510	120	—		(—)		1169	135	1128	15	—		827	165
33	NH_2	CO_2Et	1608	275	1582 *	40	1513	60	(—)		(—)		1170	320	(—)		(—)		841	95
34	NH_2	Ac	1600	450	1574	95	1510	20	(—)		(—)		1173	225	1128	20	—		828	125
35[d]	NH_2	NO_2	1606	320	1580 *	50	($CHCl_3$)		($CHCl_3$)		($CHCl_3$)		($CHCl_3$)		1112	155	—		($CHCl_3$)	
36	NMe_2	NO_2	1598	530	(—)		(—)		1414 *	40	(—)		1190	130	1111	440	998	40	824	195
37	OMe	NO_2	1612 *	160	(—)		1499 *	310	1420	15	(—)		1180	70	1112	250	(—)		844	230
			1598	370									1170	160						
38	OEt	NO_2	1613 *	170	(—)		1500 *	245	(—)		(—)		1170	160	1111	260	—		845	170
			1603	340																
39	OH	NO_2	1620	100	(—)		1500 *	210	—		(—)		1177	150	1112	270	—		848	180
			1603	280									1164	165						
Unsaturated carbon–acceptor																				
40	C⋮CPy	NO_2	1601 ‡	400	(—)		1495	80	(—)		1282	50	1174	15	1108	100	1014	25	855	230
41	C⋮CPyO	NO_2	1601	240	(—)		1482	200	—		(—)		(—)		1106	85	1015	35	843	240
42	CH:CHPy	NO_2	1601 ‡	380	1577 *	45	1490 *	50	(—)		1290	15	1179	20	1110	115	1008	10	839	165
43[d]	CH:CHPyO	NO_2	1600	230	(—)		(—)		($CHCl_3$)		($CHCl_3$)		($CHCl_3$)		1109	135	1011 *	20	($CHCl_3$)	
44	CH:CH·CO_2Et	NO_2	1602	135	(—)		1491 *	50	1413	55	(—)		1183 *	240	1108	90	1012	45	845	200
45	Py	NO_2	1597	210	(—)		1481	50	1400	55	1282	20	1182	15	1105	25	1011	15	853	115
46	3-Py	NO_2	1605	170	1574 ‡	25	(—)		1396	50	1283	20	1188 ‡	25	1110 ‡	50	1018 *	15	856 ‡	220
47	2-Py	NO_2	1605	85	(—)		(—)		1405 *	10	1293	20	—		1109	50	1013	40	855	155
48	PyO	NO_2	1602	180	—		1502 *	110	1400	40	1300	40	1182 *	140	1111	100	1022	100	835 ‡	450
49[d]	2-PyO	NO_2	1601	95	(—)		($CHCl_3$)		($CHCl_3$)		($CHCl_3$)		($CHCl_3$)		1103 ‡	10	1008	35	($CHCl_3$)	
Halogen–acceptor																				
50	Cl	NO_2	1609	110	1582	135	1479	135	1422	15	1278	20	1170	15	1109	115	1012	80	847	220
51	Br	NO_2	1609	110	1580	80	1475	100	1412	10	1271	10	1171	30	1103	55	1012	145	844	200
Saturated carbon–acceptor																				
52	Me	CN	1610	40	—		1498	10	—		—		1175	30	1117	10	1020	15	816	165
53	Me	CO_2Et	1616	115	1580	20	1501	10	1408	35	(—)		(—)		(—)		(—)		840	35
54	Me	CO_2Me	1612	90	1585	15	1502	5	1406	25	(—)		(—)		(—)		1020	70	839	40
55	Me	NO_2	1607	125	1572	20	1498 *	45	1419	10	1297	20	1177	35	1109	90	1016	20	835	130
56	CH_2Py	NO_2	(—)		(—)		1493 *	35	—		—		1180	15	1111	40	1106	20	(—)	
57	CH_2Py-2	NO_2	1603 *	100	(—)		1489	45	(—)		—		1177	20	1108	70	1014	30	827	30
58	CH_2PyO	NO_2	1608	115	(—)		(—)		(—)		(—)		(—)		1110	70	1017	30	(—)	
59	CH_2PyO-2	NO_2	1609	120	(—)		(—)		1419 *	85	(—)		(—)		1112 ‡	80	1018	40	(—)	
60	CH_2Cl	NO_2	1609	85	1570	15	1492	35	1410	15	1264	85	1176	15	1109	70	1015	25	(—)	
Acceptor–acceptor																				
61	CO_2Me	CO_2Me	—		1580	15	1501	15	1410	100	(—)		1150 *	30	1106 ‡	275	1020	165	838	10
62	CO_2Et	CO_2Et	1613	15	1585	15	1500	15	1408	120	(—)		(—)		(—)		(—)		842	25
63	CN	NO_2	1610	90	—		1490 *	30	—		1290	65	—		1106	35	1017	35	857 ‡	310
64	CO_2Me	NO_2	1612	75	—		(—)		1410	20	(—)		1167 *	15	1103 *	180	1015	85	857	90
65	CO_2Et	NO_2	1608	80	1578 *	15	(—)		1410	40	(—)		1168	30	1109 *	165	(—)		839	120
66	CHO	NO_2	1610	115	1585 *	10	(—)		—		1293	75	1162	15	1106	35	1012	35	(—)	
67	COMe	NO_2	1604	115	(—)		(—)		1408 *	35	(—)		—		1105	25	1011	50	853 ‡	250
68	COPy-2	NO_2	1609	105	(—)		—		1406	35	(—)		1156	45	1106	25	1015	25	851	190
69	NO_2	NO_2	—		(—)		1479	30	1402 *	20	(—)		—		1102	60	1011	60	836	400

Assignments for symmetry (both C_{2v} and V_h) and vibration type are given immediately below the column number (cf. ref. 2).

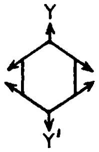
* Shoulder. ‡ Absorption considered to be the superimposition of two peaks, — absence of absorption, (—) bands masked by stronger absorption, ($CHCl_3$) band masked by solvent, Py pyridyl radical (number indicates position of linkage, unless this is 4), PyO substituted pyridine oxide.

(*a*) Combination bands at 1632 (10) and 1420 cm.$^{-1}$ (10) (cf. ref. 4). (*b*) Combination bands at 1628 (10), 1495 (20), 1408 (10), and 1136 cm.$^{-1}$ (10) (cf. ref. 4). (*c*) A band at 1448 cm.$^{-1}$ (150) is probably due to the 2-pyridyl nucleus rather than the shoulder at 1425 cm.$^{-1}$ as previously reported.[1] (*d*) Measured in a 1-mm. cell.

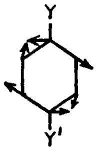
increase and attractor substituents to decrease the intensity. This is the case here also:

dd, dx, xx	(185—380) [(265 ± 75)]
ds, xw, xa	(100—200) [(140 ± 25)]
ww	(15—90) [(50 ± 25)]
sa, aa	(0—45) [(20 ± 15)]

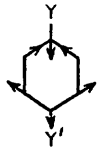
except that the intensity is very irregular for those compounds in which the substituents interact strongly: du, da, ua (20—280) [(120 ± 75)].



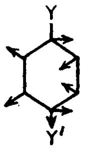
(I) A_1 (A_g)



(II) B_1 (B_{1g})



(III) A_1 (B_{2u})



(IV) B_1 (B_{3u})

The intensity of the B_1 vibration near 1409 cm.$^{-1}$ (IV) should be approximately (40) and not vary regularly with the electron-donor or -acceptor ability of the substituents.[1d] Agreement is least satisfactory in this case. This region of the spectrum is obscured by substituent absorption for 31 compounds, and for 8 of these this band appears as a shoulder. Of the remaining compounds, 18 showed no band, and 20 absorb with intensity (10—55) [(30 ± 15)] except that it is higher (100—120) for alkoxycarbonyl compounds. Compounds with electron-accepting substituents tended to show more intense absorption; this was also noticed with monosubstituted compounds.[1d]

In-plane CH *Bending Vibrations* (Table 2, cols. 5—8).—Absorption at 1300—1264 cm.$^{-1}$ (15—85) [1285 ± 11 cm.$^{-1}$ (35 ± 25)] for most of the ua, xa, sa, and aa compounds is presumably the B_1–B_{3g} mode, previously expected, but not found,[2] near 1290 cm.$^{-1}$.

The A_1–A_g mode occurs at 1190—1164 [1175 ± 6] cm.$^{-1}$ except that for aa compounds the frequency is depressed to 1168 1156 [1162 ± 6] cm.$^{-1}$. The intensity depends on the substituents present:

du, da	(130—320) [(175 ± 60)]
dd, dx, ds	(15—115) [(50 ± 30)]
xx, xw	band absent
all others	(0—45) [(15 ± 10)]

The B_1–B_{2u} vibration absorbs at 1128—1100 [1111 ± 7] cm.$^{-1}$. The intensity varies with the type of substituents present:

dd, dx, xx, ds, xw, ww, du	(15—80) [(25 ± 15)]
da	(155—440) [(275 ± 85)], when a is the nitro-group; otherwise (15—20)
ua, xa, sa, aa	(10—135) [(65 ± 35)]

The A_1–B_{1u} mode occurs at 1022—1004 [1013 ± 5] cm.$^{-1}$; the intensity depends on the substituents:

xx	(190—330)
xw, xa	(55—160) [(110 ± 35)]
ua, sa, aa	(10—165) [(45 ± 35)]
dx, ds, ww	(0—30) [(15 ± 10)]
dd, du, da	absent

The last three bands were previously reported[2] at [1179 ± 7 (s), 1125 ± 10 (var), and 1018 ± 10 (s)] cm.$^{-1}$. Bands were found[3] for *p*-dialkylbenzenes at 1230—1195 cm.$^{-1}$ (5), 1205—1175 cm.$^{-1}$ (5), 1130—1090 cm.$^{-1}$ (20), 1070—1035 cm.$^{-1}$ (20), and 1030—1010 cm.$^{-1}$ (10). The positions and intensities of the A_1–B_{1u} band near 1013 cm.$^{-1}$ given by Randle and Whiffen[6] for several compounds agree reasonably with the present results; for this band, it was shown[5] that for *p*-halogenomethyl- and *p*-dihalogeno-benzenes, the band intensity increased with the mass sum of the substituents.

Out-of-plane CH *Bending Mode* (Table 2, col. 9).—The B_2–B_{3u} mode is shown at 828—808 [819 ± 6] cm.$^{-1}$ for compounds in classes dd ⟶ ww (Nos. 1—24) (except for Nos. 15, 16, 20, and 23 where the band is apparently masked by solvent absorption below 805) and at 857—824 [841 ± 10] cm.$^{-1}$ for the other compounds (except for No. 52 with a frequency of 816 cm.$^{-1}$; the cyano-group often does not behave as a strong electron acceptor; cf. ref. 1). The intensity is (60—240) [(155 ± 50)] for compounds in classes dd ⟶ xa (Nos. 1—51), but for compounds of the sa class it is often much lower (30—165), and in the aa class the intensity is very high for the dinitro-compound (No. 69), very low for the dialkoxycarbonyl compounds (Nos. 61, 62), and intermediate for the others.

This band has been much studied previously. Ranges of [817 ± 13 (vs)],[2] 833—810 (200),[3,7] and 860—800 cm.$^{-1}$ [8] have been suggested. Many individual values for the band position have been quoted (see, *e.g.*, refs. 9—11) which generally agree well with our values. Attempts have been made to correlate the positions of the band with Hammett's σ values[10] and with shifts observed in monosubstituted benzenes.[11]

Substituent Bands.—With few exceptions, all other bands of $\varepsilon_A \geqslant 15$ for these compounds could be assigned to the substituents. Those for pyridine and pyridine 1-oxide rings have already been published.[1]

Experimental.—The preparations of the compounds containing a pyridine or pyridine 1-oxide ring have been given elsewhere.[1,12] The other compounds were commercial products or were prepared by standard methods. All compounds were recrystallised or redistilled immediately before measurement and had melting or boiling points in agreement with literature values.

The spectra were measured on the Oxford Perkin–Elmer 21 spectrophotometer with a sodium chloride prism, slit programme 4, and the settings previously reported.[1e] ε_A values were calculated as before (see ref. 1*a*).

THE DYSON PERRINS LABORATORY, OXFORD.
THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, November* 17*th*, 1958.]

---

[6] Randle and Whiffen, *Trans. Faraday Soc.*, 1956, **52**, 9.

[7] Jones and Sandorfy, in Weissburger, "Techniques of Organic Chemistry, Vol. IX. Chemical Applications of Spectroscopy," Interscience Publ. Inc., London 1956, p. 391.

[8] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958, 2nd Edn., p. 65; Colthup, *J. Opt. Soc. America*, 1950, **40**, 397.

[9] Whiffen and Thompson, *J.*, 1945, 268; Bell, Thompson, and Vago, *Proc. Roy. Soc.*, 1947, *A*, **192**, 498; Cole and Thompson, *Trans. Faraday Soc.*, 1950, **46**, 103.

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

[11] Margoshes and Fassell, *Spectrochim. Acta*, 1955, **7**, 14.

[12] Hands and Katritzky, *J.*, 1958, 1754.