837. *Infrared Absorption of Heteroaromatic and Benzenoid Six-membered, Monocyclic Nuclei. Part IV.*[1] *Monosubstituted Benzenes.*

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The infrared absorption due to the phenyl group in eighty-five compounds is recorded. The variations of the positions and the intensities of the characteristic bands with the nature of the substituent are discussed.

In monosubstituted pyridines,[1,2,3] pyridine 1-oxides,[4,5,6] pyridine–boron trichlorides,[7] and furans [8] all the bands, with few exceptions, are characteristic of either the nucleus or the substituent. Further, the position and intensity of each nuclear band are either

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[1] Part III, Katritzky, Hands, and R. A. Jones, *J.*, 1958, 3165. Parts I—III were published under the series title " Infrared studies of heterocyclic compounds."

[2] Katritzky and Gardner, *J.*, 1958, 2198.

[3] Katritzky and Hands, *J.*, 1958, 2202.

[4] Katritzky and Gardner, *J.*, 1958, 2192.

[5] Katritzky and Hands, *J.*, 1958, 2195.

[6] Katritzky, Beard, and Coates, unpublished work.

[7] Katritzky, unpublished work.

[8] Katritzky and Lagowski, *J.*, in the press.

reasonably constant or vary regularly with the type of substituent to which the nucleus is attached. We examined monosubstituted benzenes (i) to check the bands due to the phenyl groups in the pyridines and pyridine 1-oxides, (ii) to investigate the variations in the positions and intensities of the benzenoid nuclear bands with the nature of the substituent, and (iii) to compare the bands due to substituents in these compounds with those due to the same substituents in the heterocyclic compounds. We needed the information under (ii) to explain the intensity variation of nuclear bands in the heterocyclic compounds in terms of the variation of the dipole-moment during the vibration (see following paper).

The spectra were measured in chloroform, and apparent extinction coefficients were recorded.[9] Solvent absorption obscured the out-of-plane C–H deformation modes [10a, 11a] below 800 cm.$^{-1}$; the concentration used was not sufficient to distinguish the combination frequencies [10b, 11b] between 2000 and 1650 cm.$^{-1}$, and the sodium chloride prism gave poor resolution of the C–H stretching modes [10c, 11c] in the 3000 cm.$^{-1}$ region. Thus, this work is concerned with modes of predominantly C–C stretching at 1600—1400 cm.$^{-1}$ and CH in-plane deformation character at 1200—1000 cm.$^{-1}$; six bands were characteristic (Table 1), and four others appeared only in certain types of compound (Table 2 and text).

Randle and Whiffen [12] treated statistically the spectra of many monosubstituted benzenes and listed arithmetical means and standard deviations for twenty characteristic bands. They obtained data from many sources measured under varying conditions and were unable to give precise intensities or to correlate the intensity or position of a band with the type of substituent. Of the twenty bands, ten correspond to those given in Tables 1 and 2 (cf. last row). Three bands below 800 cm.$^{-1}$ and one at *ca.* 1240 cm.$^{-1}$ would be obscured by solvent in our work; the remaining six, near 837(w), 962(w), 982(vw), 1324(w), 1387(w), and 1663(w) cm.$^{-1}$, are evidently too weak to be distinguished under our conditions. Early work has been summarised.[13] Bellamy [11d] indicates that monosubstituted benzenes absorb at 1600 ± 5 cm.$^{-1}$, near 1580 and 1500 cm.$^{-1}$, and in each of the regions 1175—1125 (weak), 1110—1070, and 1070—1000 cm.$^{-1}$. The only indication of the position depending on the substituent was that bromo-, chloro-, and mercaptobenzene absorb near 1595 cm.$^{-1}$ but nitrobenzene near 1605 cm.$^{-1}$. The intensities were stated to be " notorious for very wide fluctuations "; the 1580 cm.$^{-1}$ band was very weak except when conjugated with a nitro-, carbonyl, or unsaturated group. Such conjugation was stated to enhance markedly, in most cases, the intensity of the 1600 and 1500 cm.$^{-1}$ bands also, but occasionally the 1500 cm.$^{-1}$ band became less intense. Jones and Sandorfy [10b] state that the simpler aromatic compounds absorb between 1610—1590 and 1500—1480 cm.$^{-1}$; their intensity data compare reasonably well with ours. Twenty monosubstituted benzenes showed [14] four characteristic bands in the 1600—1400 cm.$^{-1}$ region; the frequencies of the eleven compounds which we too have measured agree well; our peaks are [0·7 ± 2·4] cm.$^{-1}$ higher. Four bands found by McMurry and Thornton [15] at 1200—800 cm.$^{-1}$ are discussed below.

Band Near 1600 *cm.*$^{-1}$ (*Table* 1, *col.* 1).—A band occurs at 1611—1599 [1604 ± 3] ‡ cm.$^{-1}$ for all the compounds except that the frequency is lowered to 1588—1581 cm.$^{-1}$ if a heavy atom (Cl, Br, or SH; Nos. 67—69) is attached directly to the nucleus (similar behaviour is found in other series [1-6]); in the only other exception, No. 49, the band is due mainly to

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

[10] Jones and Sandorfy in Weissberger, " Technique of Organic Chemistry, Vol. IX. Chemical Applications of Spectroscopy," Interscience Publ. Inc., New York, 1956: (*a*) p. 388, (*b*) p. 397, (*c*) p. 392, (*d*) p. 343.

[11] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1956: (*a*) p. 64, (*b*) p. 57, (*c*) p. 55, (*d*) pp. 59—63.

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

[13] Depaigne-Delay and Lecomte, *J. Phys. Radium*, 1946, **7**, 38.

[14] Josien and Lebas, *Bull. Soc. chim. France*, 1956, 53, 57.

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

substituent absorption. The intensity is high (125—290) [(200 ± 55)] ‡ for compounds with strong electron-donating substituents (Nos. 1—15), intermediate (25—45) for the sulphonamido-compounds (Nos. 16—17), and low (5—35) [(20 ± 7)] for compounds with a saturated carbon atom or a carbon–carbon multiple bond attached directly to the nucleus (Nos. 18—66). Higher intensities are shown again for halogeno- and thio-compounds (Nos. 67—69) (40—60) and for compounds carrying other electron-withdrawing substituents (Nos. 71—85) (30—80) [(50 ± 20)] except cyanobenzene (No. 70).

Band Near 1580 *cm.*$^{-1}$ (*Table* 1, *col.* 2).—Compounds with a saturated carbon atom adjacent to the ring (Nos. 18—46) show only a weak shoulder or do not absorb in this region, but an olefinic group next to the ring (Nos. 47—55) consistently causes absorption at 1581—1579 cm.$^{-1}$ (10—30). Shoulders sometimes occur for the ethynyl- and aryl-substituted compounds (Nos. 56—66), but the region is obscured too often by substituent absorption to permit generalisation. The halogeno-compounds show weak shoulders at *ca.* 1562 cm.$^{-1}$. The band is stronger for compounds with electron-withdrawing substituents (Nos. 71—85), 1588—1580 cm.$^{-1}$ (20—70) [1585 ± 3 cm.$^{-1}$ (35 ± 10)], except for the cyano-compound (No. 70). Compounds with electron-donating substituents show a strong band at *ca.* 1600 cm.$^{-1}$ which often masks this region; however, the ethers (Nos. 6—8) exhibit a well resolved band at *ca.* 1590 cm.$^{-1}$ (*ca.* 85). Thus, for benzyloxybenzene (No. 8) the band is due to the phenolic ring. The absorption bands shown by benzanilide and *N*-methylbenzanilide (Nos. 12, 14) are associated with the benzoyl rings, because acetanilide and *N*-methylacetanilide (Nos. 13, 15) do not show resolved bands.

Band Near 1500 *cm.*$^{-1}$ (*Table* 1, *col.* 3).—Nearly all the compounds show a band at 1511—1477 cm.$^{-1}$. Electron-donating groups (Nos. 1—17) cause absorption at 1511—1493 [1498 ± 5] cm.$^{-1}$, which is somewhat higher than for compounds with a saturated, olefinic, or acetylenic carbon atom adjacent to the ring (Nos. 18—59) absorbing at 1500—1490 [1494 ± 2] cm.$^{-1}$ (except Nos. 23, 31, and 42 where most of the absorption arises from the substituent). An aromatic ring directly attached to the nucleus (Nos. 60—66) lowers the frequency to 1483—1470 cm.$^{-1}$ and a heavy atom (Nos. 67—69) to 1483—1477 cm.$^{-1}$. Intensities are high (100—220) [(145 ± 40)] for compounds with electron-donating (including sulphonamido-, halogeno-, and thio-)substituents (Nos. 1—17, 66—69), intermediate (15—65) [(40 ± 10)] for saturated or olefinic substituents (Nos. 18—55), but variable (55—230) for the ethynyl-substituents (Nos. 56—59). The band is weak or absent for compounds carrying electron-withdrawing substituents (Nos. 71—86) except cyanobenzene.

Band Near 1450 *cm.*$^{-1}$ (*Table* 1, *col.* 4).—Strong absorption (210—340) is shown by non-*N*-substituted-carbonamido-compounds (Nos. 10, 13, 15) at 1447—1440 cm.$^{-1}$; other electron-donating substituents (Nos. 1—9, 16—7) cause absorption at 1465—1445 cm.$^{-1}$ (25—45) [1456 ± 7 cm.$^{-1}$ (30 ± 10)]. Nuclei with a saturated substituent (Nos. 18—46) absorb at 1458—1450 [1454 ± 2] cm.$^{-1}$; the intensities are intermediate (25—65) [(45 ± 15)] except for the methyl esters Nos. 26 and 52 where the band is strongly overlapped by methoxyl absorption and, inexplicably, the 2-pyridylthiomethyl compound, No. 38. Compounds with an olefinic carbon atom adjacent to the ring (Nos. 47—55) absorb at 1452—1450 cm.$^{-1}$ (30—80) [1451 ± 1 cm.$^{-1}$ (50 ± 20)] with an acetylenic carbon atom (Nos. 56—59) at 1445—1443 cm.$^{-1}$ (20—25), with an aromatic ring (Nos. 61—66) at 1455—1451 cm.$^{-1}$ (except in diphenyl where the band is split) (10—110), and with a heavy atom (Nos. 66—69) at 1447—1446 cm.$^{-1}$ (30—60). Electron-accepting substituents (Nos. 70—85) cause absorption at 1455—1448 cm.$^{-1}$ (25—75, except for No. 79 where the band is overlapped by substituent absorption), but the nitro-compound shows only a weak

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‡ Throughout this paper values in parentheses are apparent molecular extinction coefficients. Values in brackets are arithmetical means and standard deviations of the positions and intensities, calculated by omitting those compounds where the band is present as a shoulder, and, in the case of ε_A, those in which it is superimposed on another band or the result of absorption by more than one benzene ring in different environments. When the molecule contains two benzene rings in the same environment, ε_A values are halved in the statistical treatment.

TABLE 1.

No.	Substituent	A_1 νCC		B_1 νCC		A_1 νCC		B_1 νCC		B_1 βCH		A_1 βCH	
		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	$\mathrm{NMe_2}$	1605	250	1577*	40	1500	140	(—)		(—)		1030	35
2	NHMe[a]	1610	290	—		1511	220	1453	30	1072	25	1022	5
3	NH·Ph[a]	1598	*480*	(—)		1514* 1498	*340* *380*	1464	*55*	1081 1073	*20* *20*	1026	*40*
4	NH·4Py	1610*	130	(—)		1499*	150	1445	45	1074	15	1029	15
5	$\mathrm{NH_2}$	1605	125	—		1495	110	1465	25	—		1026	10
6	OMe	1601	140	1591*	85	1494	135	1453	40	1077	45	1018*	35
7	OEt	1602	135	1589	80	1494	120	1458	25	1076	40	(—)	
8	$\mathrm{OCH_2{\cdot}Ph}$	1602	*150*	1590	*90*	1493	*170*	1453	*60*	1075	*35*	1027	*85*
9	OH[a]	1603	170	—		1503	170	(—)		1069	40	1023	15
10	$\mathrm{NH{\cdot}CO_2Et}$[a]	1601	200	(—)		1505*	145	1447	340	(—)		1024†	95
11	NMe·COMe	1601	240	(—)		1497	190	(—)		1073	20	1023	25
12	NMe·COPh	1600	*260*	1583	*140*	1496	*250*	1460* 1448	60 80	1075	*45*	1031	*45*
13	NH·COMe[a]	1604	210	—		1502 1488*	220 70	1442	270	1077	15	1030	30
14	NH·COPh[d]	1604	*225*	1581	85	$\mathrm{(CHCl_3)}$		$\mathrm{(CHCl_3)}$		1072	*80*	1026	*55*
15	$\mathrm{NH{\cdot}COCH_2{\cdot}4Py}$	1602†	260	—		1500*	160	1440	210	1078	10	—	
16	$\mathrm{NMe{\cdot}SO_2Me}$	1603	25	—		1494	100	1455	25	1075*	55	1025	25
17	$\mathrm{NH{\cdot}SO_2Me}$	1605	45	—		1495	100	1460*	20	1077	20	1029	25
18	Me	1603	20	—		1496	45	1455	25	1081	20	1028	20
19	Et	1609	15	—		1495	35	1454	50	—		1028	20
20	$\mathrm{CH_2{\cdot}CH_2{\cdot}Ph}$	1605	*40*	—		1494	*90*	1454	*80*	1066	*20*	1028	*35*
21	$\mathrm{CH_2{\cdot}CH_2{\cdot}4Py}$	(—)		(—)		1496	50	1455	45	1070†	20	1030	15
22	$\mathrm{CH_2{\cdot}CH_2{\cdot}2Py}$	(—)		(—)		1495	45	1454	40	1071	15	1030	10
23	$\mathrm{CH_2{\cdot}CH_2{\cdot}4PyO}$	1606	15	—		1487†	280	1451†	90	1072	15	1030*	15
24	$\mathrm{CH_2{\cdot}CH_2{\cdot}2PyO}$	1606	20	—		1491†	105	1453*	65	1071	15	1030	10
25	$\mathrm{CH_2{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}CH_2{\cdot}4Py}$	(—)		(—)		1480*	45	1453*	65	1079*	25	1028	15
26	$\mathrm{CH_2{\cdot}CH_2{\cdot}CO_2Me}$	1609	15	—		1497	40	1455	80	1079	35	1028†	35
27	$\mathrm{CH_2{\cdot}CH_2{\cdot}CO_2Et}$	1609	15	—		1495	40	1454	65	1078	55	(—)	
28	$\mathrm{CH_2{\cdot}Ph}$	1601	*30*	1587*	*15*	1491	*75*	1450	*50*	1075	*30*	1029	*35*
29	$\mathrm{CH_2{\cdot}4Py}$	(—)		(—)		1493	40	1452	25	1069†	30	1029	15
30	$\mathrm{CH_2{\cdot}2Py}$	(—)		(—)		1493	40	1451	30	1072	10	1029	15
31	$\mathrm{CH_2{\cdot}4PyO}$	1603	20	—		1485†	280	1450†	80	1071	10	1030	30
32	$\mathrm{CH_2{\cdot}2PyO}$	1607	30	—		1490†	105	1454*	40	1074	15	1030	10
33	$\mathrm{CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}4Py}$	(—)		(—)		1495*	155	1454	60	(—)		1028	20
34	$\mathrm{CH_2{\cdot}CO_2Me}$	1609	15	1590*	10	1497	50	1457	55	1075	15	1030*	20
35	$\mathrm{CH_2{\cdot}CO_2Et}$	1607	15	1587*	10	1497	40	1454	45	1074	25	1028†	130
36	$\mathrm{CH_2{\cdot}NH{\cdot}COCH_2{\cdot}4Py}$	(—)		(—)		1500*	210	1452	55	1078	20	1027	15
37	$\mathrm{CH_2{\cdot}S{\cdot}4Py}$	1608*	20	(—)		1494	50	1453	50	(—)		1028	20
38	$\mathrm{CH_2{\cdot}S{\cdot}2Py}$	1609*	20	(—)		1495	60	1456	195	1069	25	1028	20
39	$\mathrm{CH_2{\cdot}S{\cdot}4PyO}$	1605	20	—		1496	50	1458*	170	1070	25	(—)	
40	$\mathrm{CH_2{\cdot}S{\cdot}2PyO}$	1608*	10	(—)		1496	55	1454	65	1070	20	1028	20
41	$\mathrm{CH_2{\cdot}O{\cdot}2Py}$	(—)		(—)		1495	35	1454	65	—		1026*	50
42	$\mathrm{CH_2{\cdot}O{\cdot}4PyO}$	(—)		(—)		1485†	360	1456†	105	1079	10	1026*	110
43	$\mathrm{CH_2{\cdot}OH}$	1600	5	—		1492	15	1454	40	1075*	15	1035*	50
44	CHPh·OH[a]	1604	*20*	(—)		1497	*80*	1456	*90*	1081	*15*	1030*	*70*
45	CH(4Py)OH	(—)		(—)		1492	40	1453	45	1077	20	1025	70
46	CH(2Py)OH	(—)		(—)		1494	40	1457	60	1080	35	1027	90
47	CH:CH·Ph	1602	*50*	1582	*15*	1495	*65*	1451	*60*	1070	*30*	1028	*20*
48	CH:CH·4Py	(—)		(—)		1495	25	1450	30	1073	10	1027	5
49	CH:CH·2Py	1592†	180	(—)		1494	65	1451	45	1073	10	1029	5
50	CH:CH·4PyO[c]	1600	15	1580	10	1493*	150	1452†	75	1073	15	1032†	110
51	CH:CH·2PyO	1610†	50	1579	15	1493*	75	1450	60	1071	15	1027	15
52	$\mathrm{CH{:}CH{\cdot}CO_2Me}$	1610*	20	1581	30	1493	35	1451	115	1070	25	1026*	30
53	$\mathrm{CH{:}CH{\cdot}CO_2Et}$	(—)		1580	20	1495	30	1450	80	1069	40	1028*	95
54	 $\mathrm{CH{:}C}{<}\genfrac{}{}{0pt}{}{\mathrm{4Py}}{\mathrm{COMorph}}$[e]	(—)		(—)		1493	55	(—)		1070†	65	1027	20
55	$\mathrm{CH{:}CH{\cdot}4Py{\cdot}BCl_3}$[d]	(—)		1580*	50	(1493	30)	$\mathrm{(CHCl_3)}$		(—)		1026*	10
56	C⋮C·Ph	1608	*55*	1573	*5*	1500	*125*	1445	*55*	1070	*30*	1026	*30*
57	C⋮C·4Py	1608*	165	(—)		1500	55	1445	25	1062*	10	1025	15
58	C⋮C·2Py	1601	35	(—)		1490	105	1443	20	1065	10	1025	10
59	C⋮C·4PyO	1600	30	—		1495	235	1445†	55	1065	15	1032†	130
60	Ph	1600	*40*	1568	*15*	1483	*135*	1460* 1431	*15* *40*	1073	*30*	1042	*15*
61	4Py	1610*	80	(—)		1480	55	1446*	10	1076*	15	1040	10
62	3Py	(—)		(—)		(—)		1450	55	1072	10	1023†	30

TABLE 1. (*Continued.*)

		A_1		B_1		A_1		B_1		B_1		A_1	
		νCC		νCC		νCC		νCC		βCH		βCH	
No.	Substituent	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
63	2Py	1607 *	20	(—)		1470 †	130	1451	110	1072	15	1019	20
64	4PyO [b]	1605	25	1585 *	10	1500 *	25	(—)		1076	10	(—)	
65	3PyO	(—)		1582 *	25	1472 †	120	1455	65	1078	10	1028 *	10
66	2PyO	1611	10	1580	10	1478 †	130	1451	35	1075	10	1016	65
67	SH [a]	1588	45	(—)		1483	110	1446	55	1091 1068	30 10	1023	45
68	Cl	1587	40	1562 *	10	1479	110	1447	30	1084 1066 *	80 20	1023	65
69	Br [a]	1581	60	1563 *	10	1477	145	1446	60	1067	120	1018	95
70	·C≡N [a]	1604	15	1585 *	5	1495	45	1452	40	1068	10	1025	20
71	CO·NH·4Py [d]	(—)		(—)		($CHCl_3$)		($CHCl_3$)		1072 †	45	1027	40
72	CO·NH·3Py	1603 *	90	(—)		(—)		1448	25	1073	25	1026 †	45
73	CO·NH·2Py	(—)		(—)		(—)		1447 *	95	1072	30	1027	35
74	CO·NH·2PyO	(—)		(—)		(—)		1449 *	80	1069	50	1027	30
75	CO·NMe·3Py	1613 *	60	(—)		(—)		1450 *	75	1075	15	1023 †	80
76	CO·NMe·2Py	(—)		(—)		1472 †	260	(—)		1075	20	1029 *	15
77	CO·NMe·4PyO	1610 *	70	1582	45	1487 †	510	1451 †	100	1074	20	1030	80
78	CO·NMe·2PyO	(—)		1580	40	(—)		1450 *	100	1075	30	1028	20
79	CO_2Me	1605	40	1582	20	1490	10	1453	95	1071	60	1026	60
80	CO_2Et	1606	30	1588	25	1490 *	5	1451	75	1070	90	1028 †	140
81	$CO_2CMe(CN)$·4Py	(—)		(—)		1490	15	1451	75	(—)		(—)	
82	CHO	1601	80	1588	70	—		1455	25	1070	10	1021	10
83	COMe	1601	55	1585	30	—		1448	55	1075	20	1022	30
84	$CO·CH_2$·4Py	(—)		1588	50	1499	10	1452	75	1071 †	30	1020 *	20
85	NO_2	1621 * 1609	25 30	1590 *	20	1478	30	1458 *	15	1068	25	1021	30
	(*f*)	[1606 ± 7] m		[1588 ± 9] w		[1499 ± 7] vs		[1451 ± 12] s		[1072 ± 7] m		[1029 ± 5] s	

Assignments of symmetry and type of vibration (from ref. 12) are given at tops of columns.

* Shoulder, † absorption considered to be the superimposition of two peaks, — absence of absorption, (—) band masked by stronger absorption, ($CHCl_3$) band masked by solvent, Ph phenyl, Py substituted pyridine(4Py = 4-pyridyl, etc.), PyO substituted pyridine 1-oxide.

ε_A *in italics* denotes absorption by two benzene rings.

[a] These substances were measured at Cambridge, the others at Oxford. [b] Extra band at 1301 (20). Extra band at 1145 (85). [d] Measured at 0·02M in 1 mm. cell because of poor solubility. [e] Morpholide. [f] Arithmetical means and standard deviations reported by Randle and Whiffen.[12]

TABLE 2.

		A_1		B_1		A_1		B_2	
		βCH		βCH		ring		γCH	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NMe_2	(—)		1160	45	991	50	860	10
2	NHMe	1181	65	(—)		990	20	868	25
3	NH·Ph	1175	*55*	1155	*20*	995	*15*	871	*30*
4	NH·4Py	1170 *	15	—		(—)		885	30
5	NH_2	1173	25	1150	10	994	10	878	25
6	OMe	1177 * 1171	45 60	1151	20	992	15	882	20
7	OEt	1170	60	1151	25	995 *	10	883	20
8	OCH_2·Ph	1170	*70*	1151	*20*	992	*25*	913 882	10 20
9	OH	1169 *	100	(—)		998	15	882	20
10	$NH·CO_2Et$	1178	70	1158	30	998 *	10	894	15
11	NMe·COMe	(—)		(—)		—		—	
12	NMe·COPh	1174	*25*	—		997	*20*	(—)	
13	NH·COMe	1176	15	—		1002	25	898	15
14	NH·COPh	($CHCl_3$)		($CHCl_3$)		—		883 899	20 15
	Randle and Whiffen [12]	[1177 ± 6] m		[1156 ± 5] m		[1001 ± 4] Var		[908 ± 10] mw	

shoulder at 1458 cm.$^{-1}$. This band is often overlapped by substituent C–H deformations, sometimes making interpretation of the intensities difficult.

Bands at 1200—1100 *cm.*$^{-1}$ (*Table* 2, *cols.* 1 *and* 2).—Randle and Whiffen [12] found two bands in practically all the spectra examined. We find that most of the compounds with electron-donating substituents absorb at 1181—1170 cm.$^{-1}$ (15—100) and 1160—1150 cm.$^{-1}$ (10—45). Of the remaining seventy-one compounds, forty-three absorb (ε_A >10) in this region; however, all bands could be assigned to substituents. In agreement, McMurry and Thornton[15] found these bands in hydrocarbons at 1184—1176 and 1160—1152 cm.$^{-1}$ with average ε_A of (5) and (4),¶ respectively.

Band Near 1070 *cm.*$^{-1}$ (*Table* 1, *col.* 5).—All the compounds except aniline and ethylbenzene absorb at 1082—1065 [1073 ± 4] cm.$^{-1}$; for certain groups the range is less, *e.g.*, olefins absorb at 1073—1069 cm.$^{-1}$, heteroaryl compounds at 1078—1072 cm.$^{-1}$. Split bands and abnormally high intensities occur if a heavy atom is attached directly to the ring. For halogenobenzenes, Randle and Whiffen[12,16] showed that this is because a vibration in which the substituent moves appreciably absorbs in that region for heavy substituents {their values in carbon disulphide are in reasonable agreement with ours: PhCl 1083 cm.$^{-1}$ (109),¶ PhBr 1070 cm.$^{-1}$ (119)}; similar behaviour in other series[1-6] can thus be explained. The intensity is low (10—25) [(15 ± 5)] for weakly conjugating substituents (Nos. 18—66) except for one alcohol (No. 46, strongly overlapped by substituent absorption) and some esters (Nos. 26, 27, 53). Electron-donating (Nos. 1—17) and electron-accepting (Nos. 70—85) substituents cause somewhat higher intensities (10—50) [(25 ± 10)]; esters Nos. 79 and 80 absorb more strongly.

Band Near 1030 *cm.*$^{-1}$ (*Table* 1, *col.* 6).—Compounds with a saturated or olefinic carbon atom next to the ring (Nos. 18—55) absorb at 1030—1025 [1028 ± 1] cm.$^{-1}$ (except No. 50 where the band at 1032 cm.$^{-1}$ is due mainly to substituent absorption); the intensity is low (5—20) [(15 ± 5)] (except Nos. 31, 45, 46 which are strongly overlapped by substituent absorption). Acetylenic substituents cause absorption at 1026—1025 cm.$^{-1}$ (except No. 59, cf. No. 50) (10—15). The position is variable, 1042—1016 cm.$^{-1}$ (10—65), for compounds with another aromatic ring directly attached to the nucleus; similar behaviour occurs in other series often making it difficult to assign bands in this region to a specific aromatic ring. Electron-donating (Nos. 1—17) and electron-accepting (Nos. 70—85) substituents cause absorption at slightly lower frequencies, 1031—1022 cm.$^{-1}$ (5—35) [1026 ± 3 cm.$^{-1}$ (20 ± 10)] and 1030—1021 cm.$^{-1}$ (10—80) [1026 ± 3 cm.$^{-1}$ (35 ± 20)], respectively. The positions and intensities for PhMe 1031 cm.$^{-1}$ (22) ¶; PhEt 1031 cm.$^{-1}$ (18); PhCl 1023 cm.$^{-1}$ (91); PhBr 1021 cm.$^{-1}$ (106) in carbon disulphide[16] solution and the values 1032—1027 cm.$^{-1}$ (20) ¶[15] for hydrocarbons are in reasonable agreement with our data.

Band Near 1000 *cm.*$^{-1}$.—Most electron-donating groups cause absorption at 1002—990 cm.$^{-1}$ (10—50) (Table 2, col. 3). Compounds with two aromatic rings directly attached to each other {substituent is given: Ph, 1007 cm.$^{-1}$ (*35*); 4-Pyridyl, 1000 (20); 3-Pyridyl, 992 (15); 4-Pyridyl oxide, 999 (10); 3-Pyridyl oxide, 998 † (30); 2-Pyridyl oxide, 999 (15)}, the halogenobenzenes {Cl, 1001 cm.$^{-1}$ (10); Br, 998 (45)}, and a few other compounds {$CH_2S\cdot4Py$, 996 cm.$^{-1}$ (15); CO_2Et, 999 (25)} also absorb in this region.

Band Near 900 *cm.*$^{-1}$.—Most electron-donating substituents cause absorption at 898—860 cm.$^{-1}$ (10—20) (Table 2, col. 4). In addition, absorption is shown in this region for those compounds in which a saturated carbon atom next to the ring carries an oxygen atom {$CH_2O\cdot2Py$, 905 cm.$^{-1}$ (15); $CH_2O\cdot4PyO$, 914 (20); $CH_2\cdot OH$, 905 (10); CH·Ph·OH, 915 (*20*); CH(4Py)OH, 918 (10); CH(2Py)OH, 918 (15)}, for ethynyl substituents {C⋮C·Ph, 914 (*25*); C⋮C·4PyO, 915 (15)}, for aminocarbonyl-compounds {CONH·4Py, 885 (15); CONH·3Py, 888 (15); CONH·2Py, 891 (20); CONH·2PyO, 895 (55); CONH·3Py, 874 (10); CONMe·Ph, 874 (15); CONMe·2Py, 883 (10); CONMe·2PyO, 885 † (80)}, and for a few other compounds {Ph, 905 (*15*); CN, 922 (15)}. For hydrocarbons, McMurry and Thornton[15] found a band at 909—897 cm.$^{-1}$ (9) ¶.

Substituent Bands.—Absorption bands due to ester, aldehyde, and ketone groups,[9]

¶ Values so marked are converted into ε_A from units used in the original papers.

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

2-,[3,17] 3-,[1] and 4-substituted pyridine,[2,17] and 2-,[5] 3-,[6] and 4-substituted pyridine 1-oxide [4] rings have been published. All the bands in the spectra of the methyl and ethyl esters (Nos. 26, 27, 34, 35, 52, 53, 79, and 80), benzaldehyde (No. 82), acetophenone (No. 83), and the phenylpyridines and their 1-oxides (Nos. 60—66) have been reported now; bands not correlated (four in the above seventeen compounds) are given in footnotes to the Tables.

In addition to the bands characteristic of the rings, benzylpyridines and their oxides (Nos. 28—32) show shoulders at *ca.* 1430 cm.$^{-1}$ where this region is not obscured {Ph·CH$_2$·Ph, 1434 * (20); Ph·CH$_2$·4Py, 1435 * (30); Ph·CH$_2$·4PyO, 1430 * (30); Ph·CH$_2$·2PyO 1420 * (50)}; this is possibly the scissor CH$_2$ vibration displaced from its normal position at *ca.* 1465 cm.$^{-1}$.[10d]

Benzylthio- (Nos. 37—40) and phenylethyl-pyridines and their oxides (Nos. 20—24) show no additional bands (with $\varepsilon_A \geqslant 15$) except those at 1106 cm.$^{-1}$ (50) in 4Py·SCH$_2$Ph which is probably an *X*-sensitive nuclear band of the pyridine nucleus (cf. halides above) and at 1420 * (55) in 2PyO·CH$_2$·CH$_2$·Ph which is probably due to the CH$_2$ group; others are evidently either hidden by the nuclear absorption or have $\varepsilon_A < 15$. The α-CH$_2$ group in 2-substituted pyridine 1-oxides could show abnormal absorption.

Reproducibility of Intensity with Different Machines.—Some spectra were measured at Cambridge, the others at Oxford (see footnote to Table 1). To establish the validity of comparing these spectra, the reproducibility of intensities measured on different instruments was investigated. The spectrum of 4-nitropyridine 1-oxide was measured in duplicate or triplicate using three Perkin-Elmer and two Unicam instruments; || statistical treatment of the intensities gave the results shown in Table 3. Later, a fourth Perkin-Elmer instrument gave intensities which in two runs were (*a*) 0 to 25% [11 ± 7]% and (*b*) −2 to 19 [7 ± 7]% higher than the arithmetical means in Table 4. Thus, apparent extinction coefficients measured under standard conditions, but without any elaborate precautions and with different instruments, are a valuable measure of intensity for diagnostic purposes.

TABLE 3. *Statistical treatment of apparent extinction coefficients.*

Position of band	Range	Arith. mean	Standard deviation	Deviation as % of mean	Position of band	Range	Arith. mean	Standard deviation	Deviation as % of mean
1605 cm.$^{-1}$	195—270	240	23	10	1297 cm.$^{-1}$	370—460	410	23	5
1585	135—160	145	8	6	1286	370—480	435	32	7
1527	210—360	—	—	—[a]	1240	40—45	—	—	—[b]
1517	210—260	240	14	6	1170	105—130	115	9	8
1470	210—300	265	25	9	1120	370—490	430	39	9
1444	25—35	30	4	13	1089	25—50	35	9	26[c]
1353	270—340	310	19	6	1023	65—95	85	8	10
1343	430—540	500	31	6	869	120—180	155	14	9
					852	190—280	230	28	12

[a] This peak not resolved properly on Oxford Perkin-Elmer machine, probably because of wave-length linearity and speed. [b] Peak resolved only on Unicam machines. [c] High standard deviation because one Unicam machine had much higher value.

EXPERIMENTAL

Preparation of Compounds.—The preparations for the pyridines and pyridine 1-oxides have been reported; other compounds were commercial products or were prepared by standard procedures. All compounds were recrystallised or redistilled immediately before measurement.

Measurement of Spectra.—At Oxford, a Perkin-Elmer model 21 instrument was used with an NaCl prism, slit programme 4, and the settings previously reported.[9]

The spectra measured at Cambridge were obtained with a Perkin-Elmer model 21 spectrometer with an NaCl prism and the following settings: gearing, 1 cm. per 100 cm.$^{-1}$ in the

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|| One instrument of another make appeared to give considerably higher results.

[17] R. A. Jones and Katritzky, *J.*, 1958, 3610.

4000—2000 cm.$^{-1}$ region and 4 cm. per 100 cm.$^{-1}$ between 2000 and 600 cm.$^{-1}$; gain 2; other settings as in ref. 9. 0·179M-Solutions in purified chloroform were measured in a 0·112 mm. compensated cell.

Apparent Extinction Coefficients.—In this as in all our previous work, intensities were calculated from $\varepsilon_A = (1/Cl) \log_{10} (I_0/I)$, where C is concentration in moles per litre, and l is cell length in cm.

As solutions were measured at the same concentration and in the same cell, a given percentage absorption always corresponded to the same ε_A, apart from the base-line correction. Measurement of the intensities was facilitated by the construction of a series of rulers for use with different base lines, which permitted ε_A values to be read directly from the graphs.

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