415. *Infrared Absorption of Substituents in Aromatic Systems. Part I. Methoxy- and Ethoxy-compounds.*

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The absorption bands caused by the methoxyl group in twenty-three compounds, and the ethoxyl group in fifteen compounds, are recorded and discussed.

KATRITZKY and his co-workers [1-3] have shown that a heteroaromatic or benzenoid ring substituted in the same position(s) possesses characteristic bands, the frequencies and intensities of which are either reasonably constant or vary in a regular manner with the electronic nature of the substituent. The remaining bands of $\varepsilon_A \geqslant 15$ are (with few exceptions) characteristic of the substituent and are also reasonably constant or show variations of intensity and/or position which can be correlated with the nature of the ring.

Details of these bands have been published for some carbonyl compounds; [1] this series will deal with other substituents. In this paper the absorption caused by methoxyl and ethoxyl groups is reported. For conditions of measurement, the justification for recording apparent extinction coefficients, and the errors and approximations involved therein, see ref. 1. The results are given in Tables 1 and 2.

Although dimethyl ether has been studied in detail,[4] relatively little has been reported for aromatic ethers.[5-9] In the most extensive investigation before the present work, Briggs *et al.*[9] measured eleven methoxy- and three ethoxy-compounds (as mulls, films, or in potassium bromide or carbon tetrachloride) and proposed several characteristic bands for each group. The results of the previous workers are compared below with our conclusions.

The 3000 *cm.*$^{-1}$ *Region.*—The symmetric methyl CH stretching frequency of methyl ethers was previously [8] reported at 2832—2815 cm.$^{-1}$ (calcium fluoride prism), and even with the poor resolution of the sodium chloride prism a band or shoulder is shown for the benzenoid methoxy-compounds at *ca.* 2850 cm.$^{-1}$; for the heterocyclic derivatives, this region is usually obscured by the CH stretching of the hydrogen-bonded solvent [2a] (Table 1, col. 1).

The 1500—1350 *cm.*$^{-1}$ *Region.*—Bands are found at 1468—1458 cm.$^{-1}$ (50—80) [1463 ± 3 cm.$^{-1}$ (60 ± 10)] * and 1445—1432 cm.$^{-1}$ [1440 ± 4 cm.$^{-1}$] for the methoxy-compounds (Table 1, cols. 2 and 3). The intensity of the latter band is (30—60) [(40 ± 10)]

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* Apparent extinction coefficients are enclosed in parentheses and standard deviations in brackets (cf. ref. 1). The intensities of shoulders and superimposed bands and the positions of shoulders are not treated statistically.

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

[2] (*a*) Katritzky and Gardner, *J.*, 1958, 2198; Katritzky and Hands, *ibid.*, pp. 2195, 2202; Katritzky, Hands, and Jones, *ibid.*, p. 3165; Katritzky and Gardner, *ibid.*, p. 2192; Katritzky, *J.*, 1959, 2049; Katritzky, Beard, and Coats, unpublished work. (*b*) Katritzky and Lagowski, *J.*, 1958, 4155.

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

[4] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, 1945, p. 353.

[5] Lecomte in " Traité de Chimie Organique," edited by Grignard, Masson et Cie, Paris, 1936, Vol. II, p. 238; Jones and Sandorfy in Weissburger, " Technique of Organic Chemistry," Interscience Publ. Ltd., London, 1956, Vol. IX, p. 435.

[6] Colthup, *J. Opt. Soc. America*, 1950, **40**, 397.

[7] Tschamler and Leutner, *Monatsh.*, 1952, **83**, 1502.

[8] Henbest, Meakins, Nicholls, and Wagland, *J.*, 1957, 1462.

[9] Briggs, Colebrook, Fales, and Wildman, *Analyt. Chem.*, 1957, **29**, 904.

for the benzenoid compounds (Nos. 1—16) but appreciably higher (70—110) for the heterocyclic compounds. Absorption occurs at 1480—1471 cm.$^{-1}$ (35—115) [1476 ± 3 cm.$^{-1}$ (80 ± 20)], 1448—1442 cm.$^{-1}$ (20—35) [1444 ± 2 cm.$^{-1}$ (25 ± 5)], and 1398—1385 cm.$^{-1}$ (35—110) [1392 ± 3 cm.$^{-1}$ (60 ± 20)] for the ethoxy-compounds (Table 2, cols. 1, 2, and 3). These bands have been assigned (see Tables) by comparison with the corresponding esters.

TABLE 1. *Methoxy-compounds.*

		1		2		3		4		5		6	
		CH_3		CH_3 bending								COC sym. stretch	
		νCH		asym.		sym.		COC asym. stretch					
No.	Ring	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	Ph	2835	20	1466	50	1441 *	40	1301 1290 *	55 45	1244	250	1039	130
2	$C_6H_4{\cdot}NH_2$-*m*	2850 *	15	1460	70	1440	40	1300 *	55	1288	100	1038	120
3	$C_6H_4{\cdot}OMe$-*m*	2830	*45*	1459 †	*135*	1437	*100*	(—)		1282 1262	*150* *140*	1048 1032	*160* *110*
4	$C_6H_4{\cdot}OH$-*m*	2860	15	1464 †	85	1442	60	1329	65	1286	135	1040	105
5	$C_6H_4{\cdot}Me$-*m*	2850	20	1467 †	75	1436	35	1290	90	1260	150	1054 1042	70 80
6	$C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Me$-*m*	2840	20	1460 †	90	1438 †	145	1273 *	215	1260 *	235	1041	135
7	$C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Et$-*m*	2850 *	20	1465 †	110	1432 ‡	80	(—)		1257 *	250	1040 †	180
8	$C_6H_4{\cdot}NO_2$-*m*	2840 *	15	1458	55	1440 *	40	1283	155	1246	240	1040 * 1035	100 110
9	$C_6H_4{\cdot}NH_2$-*p*	2850	15	1468	50	1443	35	1327 1293	15 30	(1236	230)	1035	115
10	$C_6H_4{\cdot}OMe$-*p*	2850	*40*	1464	*100*	1442	*80*	1291	*35*	(1225	*270*)	1042	*220*
11	$C_6H_4{\cdot}OH$-*p*	2840	25	1467	80	1436 †	90	1294	45	($CHCl_3$)		1034	170
12	$C_6H_4{\cdot}Me$-*p*	2840 *	25	1465	55	1442 *	40	1293	75	1242	210	1033	105
13	$C_6H_4(CH{:}CH{\cdot}4P)$-*p*	2850 *	20	1465	55	1445	30	1325 * 1280	15 130	1252	290	1034	125
14	$C_6H_4(CH{:}CH{\cdot}4PO)$-*p*	2855 *	25	1465 *	120	1450 *	75	1330 * 1275 *	20 145	1247 †	450	1028 †	230
15	$C_6H_4(C{\vdots}C{\cdot}4P)$-*p*	2850 *	30	1463	50	1442	35	1315 * 1286	25 145	1247	310	1029	130
16	$C_6H_4{\cdot}NO_2$-*p*	2850	25	1459	80	1442	50	1295	105	1262	490	1028	190
17	4P	(—)		1466	75	1445	90	—		1288	260	1033	205
18	2P	(—)		1470 *	45	1445	110	1312	145	1292 1248	260 105	1045 † 1020	110 115
19	4PO	(—)		1464	60	1440 †	135	—		1292	210	1027 †	290
20	4PO(3Me)	(—)		1460 *	105	1442 *	115	1300	50	1283	310	1028	280
21	3PO	(—)		1460	70	1438 †	160	—		1308	165	1043	115
22	2PO	(—)		1459 *	70	1440 *	85	—		1311 1273	290 170	1023	175
23	$4PBCl_3$	—		1466 †	75	1440	70	1331 *	55	1313	220	1013	100

* Shoulder. † Absorption considered to be the superimposition of two peaks. — Absence of absorption. (—) Band masked by stronger absorption. ($CHCl_3$) Band masked by solvent. ‡ Band the intensity of which is markedly raised by overlap.

Ph phenyl, P substituted pyridine, PO substituted pyridine 1-oxide, PO(3Me) substituted 3-methylpyridine 1-oxide; the position of the substituent is indicated by a numeral.

ε_A values in italics indicate absorption by two alkoxyl groups in similar environments.

Unexplained bands ($\varepsilon_A \geqslant 15$) were shown for compound No. 19 at 2470 (25) and 1567 (25) cm.$^{-1}$; for No. 17 at 1633 (30) and 837 (55) cm.$^{-1}$; for No. 21 at 1080 (15) cm.$^{-1}$; and for No. 22 at 3300 (25) cm.$^{-1}$.

Methyl esters under the same conditions of measurement [1] show only the CH_3 symmetrical deformation at [1439 ± 3 cm.$^{-1}$ (110 ± 15)]; however, a weak shoulder on this band is shown [10] for methyl acetate at 1456 cm.$^{-1}$ due to the asymmetrical vibration. The changed environment of the methoxyl group in the ethers thus weakens the intensity of the symmetrical deformation and strengthens that of the asymmetrical deformation; the intensity of the symmetrical CH_3 bending frequency for the methyl ethers is highest for the heterocyclic compounds in which the heterocyclic rings have some of the electron-accepting ability of the carbonyl group.

Ethyl esters show CH_2 scissor [1465 ± 3 cm.$^{-1}$ (35 ± 10)] and wagging modes

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[10] Nolin and Jones, *Canad. J. Chem.*, 1956, **34**, 1382.

TABLE 2. *Ethoxy-compounds.*

		1		2		3		4		5	
		CH_2 scissor		CH_3 bending asym.		CH_3 bending sym.		COC asym. stretch			
No.	Ring	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	Ph	1478	95	1445	25	1389	35	1300 1289	45 45	1239	220
2	C_6H_4·NH_2-*m*	1476	75	1444 *	25	1390	40	(—)		1282	70
3	C_6H_4·OEt-*m*	1472	*130*	1447	*70*	1390	*105*	1330	*50*	1282 1260	*120* *120*
4	C_6H_4·Me-*m*	1476	60	1443	35	1390	85	1286	70	1253	120
5	C_6H_4·NO_2-*m*	1471	100	1442	35	1395	80	1282	140	1242	140
6	C_6H_4·NH_2-*p*	1480	85	1443	20	1393	45	1324 1292	15 35	(1230	260)
7	C_6H_4·Me-*p*	1480	35	1442	20	1390	45	1287	40	($CHCl_3$)	
8	C_6H_4·NO_2-*p*	1476	75	1444	25	1395	55	1298	155	1259	390
9	4P	1475	80	1445	20	1395	40	1360 *	25	1285 1255	250 110
10	3P	1472	70	(—)		1390	35	1278 *	105	1258	110
11	2P	1480 ‡	140	(—)		1385	70	1311	160	1286 1247	310 125
12	4PO	1476 ‡	220	1448 †	50	1398	70	—		1292	210
13	4PO(3Me)	(—)		1445 *	90	1393	110	1300 *	80	1281	320
14	3PO	1473	115	(—)		1397	65	—		1308	210
15	2PO	1475 ‡	125	(—)		1398	65	—		1313 1274	310 190

		6		7		8		9	
		CH_3 rock out-of-plane?		CH_3 rock in-plane?		COC sym stretch		C_2H_5 CC stretch	
No.	Ring	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	Ph	1114	55	1089 *	25	1045	135	919	30
2	C_6H_4·NH_2-*m*	1112	50	1090	20	1043	110	972	30
3	C_6H_4·OEt-*m*	1112	*120*	1086	*40*	1044	*175*	984	*25*
4	C_6H_4·Me-*m*	1113	50	1090	20	1045	85	947 * 919	30 70
5	C_6H_4·NO_2-*m*	1111	60	1094 †	75	1042	145	956	40
6	C_6H_4·NH_2-*p*	1114	60	1087	25	1046	115	920	30
7	C_6H_4·Me-*p*	1115	60	1090	20	1045	95	918	50
8	C_6H_4·NO_2-*p*	(—)		1088 *	30	1039	175	920	50
9	4P	1110	45	1088	25	1039 1010 *	190 35	922	50
10	3P	1112	60	1090 *	25	1050 1032	90 50	915	20
11	2P	1115	30	1091	35	1045 † 1030	180 95	921 903	45 15
12	4PO	1114	70	1088	20	1039	230	925	105
13	4PO(3Me)	1108	55	1086	30	1039	240	916	150
14	3PO	1113	60	1092	40	1043	135	915	25
15	2PO	1120 †	195	1090	35	1034	135	928 909	50 35

For symbols, etc., see footnotes to Table 1. Unexplained bands ($\varepsilon_A \geqslant 15$) were shown for compound No. 9 at 1700 (30) and 828 ● (40) cm.$^{-1}$; for No. 12 at 1555 (15) cm.$^{-1}$; and for No. 15 at 3370 (135) cm.$^{-1}$.

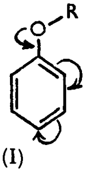
A band for No. 11 at 1266 ‡ (140) cm.$^{-1}$ is probably a nuclear band (cf. Katritzky and Hands, *J.*, 1958, 2202).

[1370 ± 2 cm.$^{-1}$ (100 ± 10)] and CH_3 asymmetric [1446 ± 1 (30 ± 5)] and symmetric bending modes [1391·5 ± 2 cm.$^{-1}$ (30 ± 5)].[1] The CH_2 modes should, because of proximity, show the biggest difference between ester and ether; the wagging mode apparently disappears,* and the scissor mode is shifted and enhanced in intensity. The CH_3 asymmetrical deformation mode is little altered; the symmetrical CH_3 deformation mode is somewhat intensified.

* Possibly the wagging frequency is shifted upwards and contributes to the apparent intensification of the CH_3 symmetrical bending modes.

We are thus able to make a more complete assignment of the bands in this region than previous workers who found [9] absorption at 1471—1453 cm.$^{-1}$ (s) and 1361—1328 cm.$^{-1}$ (s) for methoxy-compounds (assigned respectively to the asymmetrical and symmetrical CH bending modes) and at 1473—1462 and 1389—1387 cm.$^{-1}$ (intensity not indicated) for the ethoxy-compounds (assigned to the asymmetrical and symmetrical methyl and methylene modes [9]). It has also been reported by Jones *et al.*[5] that methoxyl and methyleneoxy (·O·CH$_2$·) groups do not show characteristic CH deformation frequencies in the 1500—1350 cm.$^{-1}$ region.

The 1350—1240 *cm.*$^{-1}$ *Region.*—For ROR′, when R = R′ the OR and the OR′ stretching modes are coupled, forming an asymmetric and a symmetric mode. If R and R′ are appreciably different (*e.g.*, aromatic and aliphatic), coupling is less important, and one mode is principally the OR and the other the OR′ stretching frequency. The strong band for the methyl and ethyl ethers (Tables 1 and 2, col. 5) at 1313 to < 1240 cm.$^{-1}$ is principally the ring-oxygen stretching frequency because this has some double-bond character and will therefore absorb at higher frequencies than the alkyl-oxygen mode; the regularities discussed below confirm this assignment. Absorption is similar for corresponding methoxy- and ethoxy-compounds; for the latter the position is −2 to +7 [3 ± 3] cm.$^{-1}$ lower than, and the intensity is 0·6 to 1·3 [0·9 ± 0·2] times greater than, that of the former. The following discussion includes both the methoxy- and ethoxy-compounds.



(I)

The frequency should be higher the greater the electron-withdrawing power of the ring, for this increases mesomerism of type (I) and thus the double-bond character of the oxygen-ring linkage. As expected, all the heterocyclic ethers absorb at higher frequencies than anisole and phenetole and in the order (series 1) of the electron-withdrawing ability of

Ph < 3P < 4P ~ 2P < 4PO < 3PO ~ 2PO ~ 4PBCl$_3$....Series 1 *
0 19 44—48 48—52 64—74 cm.$^{-1}$

the ring in various positions, an order which is in agreement with chemical [11] and dipole-moment [12] evidence, with the positions of the ring-nitrogen stretching band for amines,[13] and with the intensity variation of ring nuclear bands.[3] The effect of *para*-substituents in the benzene ring is also as expected (series 2). However, *meta*-substituted benzenes are

NH$_2$, OMe, OH < Me < H < CH:CHX, C:CX < NO$_2$....Series 2
? (obscured by CHCl$_3$) −2 0 3—8 18—20 cm.$^{-1}$

anomalous; the position is higher than expected (series 3) for compounds with electron-

H < NO$_2$ < Me < OMe,† OEt,† OH, NH$_2$....Series 3
0 2—3 14—16 28—44 cm.$^{-1}$

donor substituents, possibly because of coupling with a nuclear band.

The intensity is (70—150) [(115 ± 30)] for the anisoles and phenetoles with a *meta*-substituent other than a nitro-group; in these phenetoles and in all the other compounds, the intensity is (110—490) [(260 ± 65)]. Frequently a subsidiary to the main aryl-oxygen bond-stretching band is shown at somewhat higher frequencies (Tables 1 and 2, col. 4).

Absorption at 1271—1242 cm.$^{-1}$,[9] at 1270—1230 and up to 1300 cm.$^{-1}$ for *meta*-substituted compounds,[6] and at 1270—1150 cm.$^{-1}$ had previously [7] been assigned to the aryl-oxygen stretching mode.

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* In this and the following paper, substituted pyridine, pyridine 1-oxide, and pyridine–boron trichloride nuclei are represented by P, PO, and PBCl$_3$, respectively, together with a numeral to indicate the position of the substituent.

† The band is split in these compounds; average intensities and frequencies are taken.

[11] Katritzky, *Quart. Rev.*, 1956, **10**, 395.

[12] Katritzky, Randall, and Sutton, *J.*, 1957, 1769; Bax, Katritzky, and Sutton, *J.*, 1958, 1254.

[13] Katritzky and R. A. Jones, following paper.

The 1200—1050 *cm.*$^{-1}$ *Region* (Table 2, cols. 6 and 7).—The ethoxy-compounds show bands at 1115—1108 cm.$^{-1}$ (30—70) [1113 ± 2 cm.$^{-1}$ (55 ± 10)] (except in No. 15 where the band is displaced to 1120 cm.$^{-1}$ by overlap) and at 1092—1086 cm.$^{-1}$ (20—40) [1089 ± 2 cm.$^{-1}$ (25 ± 5)] which are probably due to a mode of the ethyl group since no corresponding absorption was found for the methoxy-compounds. Possible assignments are methyl in- and out-of-plane rocking modes.[14] Ethyl esters show a band corresponding to the second but not to the first mode.[1] Briggs *et al.*[9] reported absorption bands at 1122—1117 and 1156 cm.$^{-1}$ for ethoxy-compounds and at 1192—1175 and 1148—1079 cm.$^{-1}$ for methoxy-compounds; in the last three cases this was probably due to aromatic CH in-plane vibrations which are sometimes greatly intensified by alkoxyl groups.[2*b*,15]

The 1050—1000 *cm.*$^{-1}$ *Region* (Table 1, col. 6; Table 2, col. 8).—Bands shown for the ethoxy-compounds at 1050—1034 [1043 ± 4] cm.$^{-1}$ and by the methoxy-compounds at 1048—1013 [1034 ± 8] cm.$^{-1}$ are assigned to a mode involving mainly alkyl–oxygen bond stretching, in agreement with Briggs *et al.*[9] who found these bands at 1048—1024 and 1042—1000 cm.$^{-1}$ for ethoxy- and methoxy-compounds, respectively, and others [6,7] who quote ranges of 1070—1000 cm.$^{-1}$ and 1120—1030 cm.$^{-1}$. The band is split for *m*-dimethoxybenzene, and average values of position and intensity have been used in the following treatment; when splitting occurs for other compounds, the position and intensity of the strongest component have been taken.

Absorption for corresponding pairs is 0—12 [7 ± 4] cm.$^{-1}$ higher and 0·8—1·3 [1·0 ± 0·15] times as intense for the ethoxy- as for the methoxy-compounds. Intensities

3P < 4PBCl$_3$ < 3PO ~ Ph < 4P < 4PO,4PO(3Me)....Series 4
90 100 115—135 130—135 190—205 230—285

are (80—170) [(115 ± 20)] for all the benzenoid compounds except those with a *p*-nitro-substituent, for which they are (175—190). The relative intensities for the heterocyclic compounds, anisole, and phenetole (series 4) do not bear any obvious relation to the nature of the ring.

The 1000—900 *cm.*$^{-1}$ *Region* (Table 2, col. 9).—A band occurs at 928—915 [920 ± 4] cm.$^{-1}$ for all the ethoxy-compounds except *m*-amino-, *m*-ethoxy-, and *m*-nitro-phenetole, for which the position is 984—956 cm.$^{-1}$. The intensity is (20—70) [(40 ± 15)] except for the 4PO and the 4PO(3Me) compound, where it is (105—150). This band is tentatively assigned to the CC stretching mode of the ethyl group.[14]

Nuclear Bands.—The compounds also show bands due to vibrations of the nuclei; these have been published [2] for 2-, 3-, and 4-monosubstituted pyridines, for 2-, 3-, and 4-monosubstituted pyridine 1-oxides, and for monosubstituted benzenes. Very few bands ($\varepsilon_A \geqslant 15$) were found which could not be assigned to the alkoxyl group, nucleus, or other substituent; the exceptions are shown in footnotes to Tables 1 and 2.

Experimental.—References to the methods for the preparation of the compounds are given elsewhere.[1–3] The spectra were measured on the Oxford Perkin-Elmer 21 spectrophotometer with a sodium chloride prism, slit programme 4, and the settings previously given.[1] ε_A values were calculated as in ref. 2(*b*).

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[14] Cf. Sheppard and Simpson *Quart. Rev.*, 1953, **7**, 19.