140. *Infrared Absorption of Substituents in Heteroaromatic Systems. Part IV.*[1] *Ethyl* N-*Arylurethanes.*

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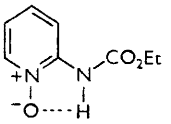
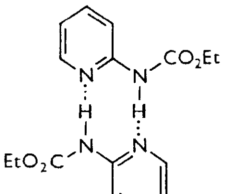
The absorption caused by the group $\cdot NH\cdot CO_2Et$ for 15 compounds is recorded. Tentative assignments are suggested for most of the characteristic bands and the variations of the intensity and position of these bands are discussed.

EARLIER papers have discussed the absorption characteristic of simple esters [2] and amides; [3] it was thought of interest to extend this work to urethanes, which combine the structural features of esters and amides, and to determine whether the regularities previously found [2,3] held for the more complicated class of compound. The infrared spectra of fifteen ethyl *N*-arylurethanes ($Ar\cdot NH\cdot CO_2Et$) were therefore measured in 0·189M-solutions in purified chloroform in a 0·106 mm. cell. Almost all the bands were characteristic either of the ring or of the $\cdot NH\cdot CO_2Et$ group; the positions of the latter are recorded in Table 1 together with apparent extinction coefficients (for the errors and approximations involved therein see ref. 2).

The 3500—3100 *cm.*$^{-1}$ *Region.*—All the compounds show the non-bonded NH stretching frequency at 3430—3390 [3410 ± 10] * cm.$^{-1}$ (Table 1, col. 1); the intensity is (50—100) [(75 ± 15)] * except for compounds in which the $\cdot NH\cdot CO_2Et$ is attached to the 2-position of a pyridine or pyridine 1-oxide ring (Nos. 10—13). The last two classes of compound show quite strong (50—70) bands respectively at 3180—3170 and 3290—3270 cm.$^{-1}$ (col. 2) which are assigned to H-bonded NH stretching modes; the 2-substituted oxides are probably intramolecularly bonded (I) and the 2-substituted pyridines may exist as dimers †


(I)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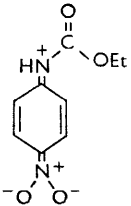
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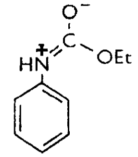
(IV)

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* Parentheses signify apparent molecular extinction coefficients, and square brackets indicate arithmetical means and standard deviations.

† For 2-substituted pyridines, the ϵ_A of the band assigned to the non-bonded NH group decreased (70→50→40) and the ϵ_A of the band assigned to the hydrogen-bonded NH group increased (30→45→60) as the solution concentration increased (0·05→0·1→0·2M). Molecular weight determinations indicated some association.

[1] Part III, Katritzky and R. A. Jones, *J.*, 1959, 3674.

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

[3] Katritzky and R. A. Jones, *J.*, 1959, 2067.

TABLE 1.

		1		2		3		4	
		νNH							
		Free		H-bonded		νC=O		Amide II	
No.	Radical †	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	$C_6H_4 \cdot NMe_2$	3430	85	3320 *	10	1719	420	1525	500
2	$C_6H_4 \cdot OMe$	3420	65	3330 *	15	1723	420	1516	500
3	C_6H_4Me	3410	65	3330 *	10	1725	400	1524	380
4	C_6H_4Cl	3420	85	3330 *	15	1726	420	1517	480
5	Ph	3410	75	3315	15	1730	430	1525	420
6	$C_6H_4 \cdot CO_2Me$	3400	80	3300	20	1730	440	1524	420
7	$C_6H_4 \cdot NO_2$	3400	100	3330 *	25	1736	410	1512	500
8	4Py	3410	50	—		1733	360	1512	340
9	3Py	3410	70	—		1728	390	1545 * 1525	130 380
10	2Py	3400	40	3180	50	1724	420	1533 * 1517	230 290
11	2Py(5Me)	3390	35	3170	50	1722	460	1540 * 1517	280 360
12	2PyO	3410	15	3290	70	1737	390	1518	420
13	2PyO(5Me)	3380 *	10	3270	65	1730	380	1531	480
14	1-$C_{10}H_7$	3410	85	—		1724	390	1533	300
15	2-$C_{10}H_7$	3390	60	3320 *	15	1728	380	1533	370

	5		6		7		8		9		10		11	
	Ethyl								C–N–C–O					
	CH_2 scissor		CH_3 Asym. bend.		CH_3 Sym. bend.		CH_2 Wag.							
No.	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
1	1482 §	135	(—)		1388 *	50	1369	55	1331 *	115	1319	220	($CHCl_3$)	
2	(—)		(—)		1390	60	1380 *	55	1331 *	75	1297	165	1242 ‡	300
3	(—)		1448 *	65	1391 *	70	1383 *	55	1330 *	70	1314	190	1247	105
4	1467 *	50	1447	40	1391 *	95	1380 *	60	1325 *	120	1304	240	1250	160
5	1484	65	(—)		1393	45	1383 * 1371 *	40 25	1324 *	75	1312	200	1253	105
6	1480	60	(—)		1390 *	55	1369 *	45	—		1310	280	1263 *	160
7	(—)		1447	45	1392	65	1374	85	(—)		1305	370	1266	100
8	1475 *	50	1448	35	1392	45	1368	50	—		1334 1302	230 75	1242	420
9	(—)		1447	35	1392	40	1380 1368	30 25	1345	25	1330 1300	115 75	1245	310
10	(—)		(—)		1390	45	1367	50	1326	45	1308	320	1257	230
11	1486 *	105	1449 *	75	(—)		1369 *	70	1327 *	60	1307	360	1253	350
12	(—)		(—)		1394	75	(—)		—		1307	100	1255 ‡	550
13	(—)		1450 *	140	(—)		(—)		1325 *	50	1304	105	1254 ‡	500
14	—		1446	65	1395 *	55	1378	60	1347	130	1328	85	1256	85
15	(—)		(—)		1389	70	1367	125	1357	140	1318	65	1257	105

	12		13		14	
	CO·O					
No.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	1192 *	150	1095	90	1066	260
2	(—)		1094	85	1065	240
3	1198	135	1093	75	1063	260
4	1199	140	1092 ‡	270	1061	260
5	(—)		1095 1087	95 110	1063	280
6	1191	210	1096 *	145	1060	240
7	1196	185	1095	110	1060	280
8	1198	370	1095	85	1060	180
9	1190 *	110	1094	70	1069	230
10	($CHCl_3$)		1104	130	1069	240
11	1196	190	1093 *	95	1069	320
12	1165	210	1096	75	1064	200
13	(—)		1094	65	1061	240
14	1180	80	1108	135	1072	115
15	1184 *	75	1093	75	1060	260

* Shoulder. § Intensity increased owing to overlap of absorption bands. ‡ Absorption considered to be the superimposition of two peaks. — Absence of absorption. (—) Band masked by stronger absorption. ($CHCl_3$) Band masked by solvent.

† Py substituted pyridine, Py(5Me) 5-methyl disubstituted pyridine, PyO substituted pyridine 1-oxide, PyO(5Me) 5-methyl disubstituted pyridine 1-oxide; the position of the substituent is indicated by a numeral.

(II). The other compounds often show a shoulder or weak band at 3330—3300 cm.$^{-1}$ presumably due to intermolecular hydrogen bonds.

Under similar conditions acylamino-compounds showed the NH stretching band at [3420 ± 10 cm.$^{-1}$ (40 ± 5)].[3] In a Nujol mull, the band for Ph·NH·CO$_2$Et was reported[4] at 3290 cm.$^{-1}$.

The Carbonyl Stretching Frequency (*col.* 3).—This mode causes absorption at 1739—1719 cm.$^{-1}$ (360—460) [(405 ± 25)]. As in other *N*-arylamides,[3] electron-attracting rings should lead to increased importance of canonical forms of type (III) and thus to less contribution from forms (IV) and to higher C=O frequencies. *para*-Substituents in a phenyl group do raise (NO$_2$) or lower (Cl, Me, OMe, NH$_2$) the position according to their electron-donor ability. The naphthalene rings appear to have electron-acceptor ability in the order Ph > 2-C$_{10}$H$_7$ > 1-C$_{10}$H$_7$, in agreement with chemical evidence. Of the heterocyclic compounds, the 4-pyridyl ring raises the frequency whilst the position of the band for the 3-pyridyl compound varies little from that for the phenyl compound. The relatively low positions of the 2-substituted heterocycles are possibly connected with the hydrogen bonding (I, II). Previous workers have found the C=O stretching band near 1700 cm.$^{-1}$ in the solid state and 1735 cm.$^{-1}$ for chloroform solutions,[5] at 1722—1705 cm.$^{-1}$ (*N*-alkylcarbamates),[6] and at 1728—1690 cm.$^{-1}$ (various Ph·NH·CO$_2$R).[7]

The " Amide II " Band (*col.* 4).—This occurs at 1533—1512 cm.$^{-1}$ (290—500) [1521 ± 7 cm.$^{-1}$ (400 ± 70)]; it was found for ·NH·COMe and ·NH·COPh compounds at [1513 ± 7 cm.$^{-1}$ (310 ± 100)].[3] This band had been previously reported near 1530 cm.$^{-1}$ in various compounds of type R·NH·CO$_2$R′.[4,5,7]

The 1500—1350 cm.$^{-1}$ *Region.*—The four expected CH deformation modes of the ethyl group occur at:

CH$_2$ scissor	1484—1480 cm.$^{-1}$ (*ca.* 60)	frequently hidden
CH$_3$ asym bend	1448—1446 cm.$^{-1}$ (35—65)	
CH$_3$ sym bend	1393—1389 [1391 ± 2] cm.$^{-1}$ (40—70) [(55 ± 13)]	
CH$_2$ wag	1380—1367 [1372 ± 5] cm.$^{-1}$ (50—125) [(70 ± 30)]	

These positions are near those found for the corresponding modes in ethyl esters [2] and ethers; [8] the intensities of the first three bands are somewhat higher, and those of the CH$_2$ wagging somewhat lower than those found in other ethyl esters.[2]

The 1350—1240 *cm.*$^{-1}$ *Region.*—In general a band or shoulder is found at 1357—1324 cm.$^{-1}$. All the compounds absorb at 1334—1297 [1313 ± 10] and 1266—1242 [1253 ± 7] cm.$^{-1}$; these bands are of variable intensity (65—370) [(205 ± 95)] and (85—420) [(200 ± 115)] but there is no obvious relation between intensity and the nature of the ring. This absorption is assigned to C·N·C·O skeletal modes; corresponding modes of esters and amides also absorb in this region.

The 1200—1050 *cm.*$^{-1}$ *Region.*—Three bands are shown (cols. 12—14): 1198—1161 cm.$^{-1}$ (80—370) [1190 ± 18 cm.$^{-1}$ (190 ± 80)]; 1108—1092 cm.$^{-1}$ (65—135) [1096 ± 5 cm.$^{-1}$ (90 ± 25)]; and 1072—1060 cm.$^{-1}$ (200—320) [1064 ± 4 cm.$^{-1}$ (250 ± 35)] {except that the intensity of the third band is lower (115) in No. 15}. The bands probably correspond to skeletal modes of the ·CO·O· group.[2,9]

Other Bands.—Nearly all the other bands with $\varepsilon_A > 10$ could be assigned to the ring or second substituent.‡ Those for most of the heterocyclic compounds have been

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‡ Exceptions: Bands at 1468 (40), 1415 (30) and 824 cm.$^{-1}$ (25) for No. 5 and at 1785 (25) and 1008 cm.$^{-1}$ (25) for No. 12.

[4] Barr and Haszeldine, *J.*, 1956, 3428.

[5] Thompson, Nicholson, and Short, *Discuss. Faraday Soc.*, 1950, **9**, 229.

[6] Pinchas and Ben-Ishai, *J. Amer. Chem. Soc.*, 1957, **79**, 4099.

[7] Hayes, Thomson, and Flett, *Experientia*, 1955, **11**, 61.

[8] Katritzky and Coats, *J.*, 1959, 2062.

[9] Katritzky and his co-workers, unpublished work.

published.[10] Nuclear bands for the *para*-disubstituted benzenes are given in Table 2; for each compound the positions and intensities agree reasonably with those of compounds carrying substituents of similar types ($\cdot NH\cdot CO_2Et$ behaving as an electron donor [11]). except that the bands at *ca.* 1590 and 1415 cm.$^{-1}$ (Table 2, cols. 2 and 4) are stronger than usual; this appears to be a specific effect of the $\cdot NH\cdot CO_2Et$ group. Bands corresponding to the substituents NMe_2 {2790 (50), 1447 (95), 1348 * (100), (—), 1164 ‡ (180), 1133 (85), (—), 944 (75)}, OMe {2840 (25), 1467 (105), 1445 (80), (—), 1242 ‡ (300), 1033 (190)}, and CO_2Me {1709 (500), 1437 (175), —, 1280 (600), ($CHCl_3$), 1112 (300), (—), 964 (30)} agree with previous work.[1,2,8]

TABLE 2. *Nuclear bands of* para-*disubstituted benzenes*, $X\cdot C_6H_4\cdot NH\cdot CO_2Et$.

Substit. X	1 νCC A_1–A_g cm.$^{-1}$	ε_A	2 νCC B_1–B_{3g} cm.$^{-1}$	ε_A	3 νCC A_1–B_{1u} cm.$^{-1}$	ε_A	4 νCC B_1–B_{2u} cm.$^{-1}$	ε_A	5 βCH B_1–B_{3g} cm.$^{-1}$	ε_A
NMe_2 ...	1617	60	1589	90	(—)		1423 1412	90 80	1305 *	140
OMe ...	1615 *	35	1597	80	(—)		1416	135	(—)	
Me	1615	60	1598	125	(—)		1409	115	1295 *	90
Cl	1615 *	35	1594	160	1496	270	1405	200	1284	75
CO_2Me ...	1607	270	1592	190	1507 *	230	1413	260	(—)	
NO_2	1612 *	240	1602	320	(—)		1415	210	(—)	

Substit. X	6 βCH A_1–A_g cm.$^{-1}$	ε_A	7 βCH B_1–B_{2u} cm.$^{-1}$	ε_A	8 βCH A_1-B_{1u} cm.$^{-1}$	ε_A	9 γCH B_2-B_{3u} cm.$^{-1}$	ε_A
NMe_2	1164 ‡	180	(—)		1007	15	816	135
OMe	1177	185	1110	30	1012 *	45	828	150
Me	1174 *	50	1120	40	1018	30	810	80
Cl	1175	90	1115	65	1010	95	824	160
CO_2Me	1174	400	(—)		1014	50	850	55
NO_2	1178	310	1113	190	1005	25	849	220

For significance of column headings see ref. 11.

Experimental.—Compounds were prepared by standard methods and recrystallised before measurement; m. p. agreed with values in the literature. The spectra were measured on a Perkin–Elmer 21 spectrophotometer with the settings previously given.[2]

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[10] Katritzky and his co-workers, *J.*, 1958, pp. 2192, 2195, 2198, 2202, 3165, 4155.
[11] Katritzky and Simmons, *J.*, 1959, 2051.