

101. *The Vibrational Frequencies of the Ethylpyridines.*

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The infrared and Raman spectra of 2-, 3-, and 4-ethylpyridine have been measured in the liquid state. All the frequencies and all the vibrational fundamentals are assigned for each isomer.

ALTHOUGH the infrared spectra (2—15 μ) of the ethylpyridines have been recorded,¹ the Raman displacements have not previously been measured. In the present work the infrared measurements have been extended to 25 μ and the Raman spectra recorded. The results, together with those of similar studies of the methylpyridines² and ethylbenzene,³ lead to assignments of all the vibrational frequencies of the molecules.

¹ Sadtler Standard Spectra, Philadelphia, Nos. 1249—51.

² Green, Kynaston, and Paisley, *Spectrochim. Acta*, in the press.

³ Green, *Spectrochim. Acta*, 1962, **18**, 39.

TABLE I.
 Vibrational frequencies and assignment of the ethylpyridines.

4-Ethyl		2-Ethyl		3-Ethyl		Assignment
Raman	Infrared	Raman	Infrared	Raman	Infrared	
2935s	3072s	3064w	3072s	3046s	3087m	} $\nu_2, \nu_{7b}, \nu_{20a}, \nu_{20b}$
3029m	3035s	3013w	3006s	3031s	3035m	
2935s	2977s	2971m	2970s	2971m	2977vs	} CH_3 and CH_2 antisym. str. CH_3 antisym. str.
2914s	2942s	2938s	2936s	2935s	2900w	
	2900s	2907m		3903w	2900w	} $2 \times 1450 = 2900$ CH_3 and CH_2 sym. str.
	2881s		2873s	2871m	2872s	
	1983w		1983w			} $2\nu_1$ $\nu_{17a} + \nu_1$
			1952w		1974w	
	1937m		1921w			} $\nu_{12} + \nu_{17a}$ $2\nu_{17a}$ $2\nu_5$
			1868w		1922w	
	1848m		1842w		1909m	} $\nu_{17a} + \nu_5$ $\nu_{17a} + \nu_{10a}$ $\nu_{17a} + \nu_{10b}$
	1783w				1863vw	
					1745vw	} $\nu_{10a} + \nu_5$ $\nu_{10a} + \nu_{10b}$ $2\nu_{10a}$
	1731w		1773m		1649w	
1600s	1603s	1589s	1595s	1586s	1590sh	} $\nu_4 + \nu_5$ ν_{8a}
1553w	1561s	1568m	1573s	1573m	1578s	
		1534vw		1532vw		} $\nu_{12} + \nu_4$ $\nu_{10b} + \nu_{12}$
1495w	1499s		1479s		1481s	
1452m	1461s	1457m	1460s	1452m	1463vs	} ν_{19a} CH_3 antisym. def. and CH_2 bend $2\nu_4$
	1436w				1429vw	
1418vw	1415s	1440m	1438s	1429vw	1425vs	} ν_{10b} CH_3 sym. def.
				1381vw	1379m	
	1376m	1378vw	1372m		1367sh	} ν_{14} $762 \div 571 = 1333$
		1330w	1332vw		1319w	
1319w	1315m	1296vw	1300m	1319vw	1317m	} ν_3
				1278vw	1272m	
	1261vw	1248vw	1251w		1233w	} CH_2 twist and wag; $2\nu_{6b}$
	1219s		1221s		1224w	
1209s		1147w	1147s	1219m	1188s	} ν_{13} ν_{9a}
	1097w	1105w	1106m	1131w	1127s	
1112vw			1060sh	1106w	1108s	} ν_{18b} CH_3 rock $\nu_{8a} + \nu_{11}$ CH_3 rock
					1063m	
1066m	1066s	1049s	1050s	1041vs	1044m	} ν_{18a} CH_3 rock
1026vw	1031sh				1024vs	
997vs	995s	995s	995s	1026(5)		} ν_1 ν_{17a} $\nu(\text{C}-\text{C})$
974m	971m	975m	971m		966s	
	962sh		959sh		948m	} ν_5 ν_{10a} ν_{10b}
874vs	874w	890w	885m	933vw	924w	
822vw	822vs				809vs	} ν_{12} CH_2 rock
779s	777s	784s	796s	802m	779s	
	750m		762s	778m		} ν_{10b} ν_4
			749vs		714vs	
720vw	722w		719sh	718w		} ν_4 ν_{6b}
671m	665w	629m	626m	630m	629s	
569w	562s	572w	571m	567vw	567w	} ν_{11} ν_{8a}
493m	490s	500m	497s	488m	481w	
400w		405w	406w	402w	405vw	} ν_{16a} $\delta(\text{CCC})$
378vw				354vw		
292vw		290w		279vw		} ν_{15} ν_{16b}
144m		152s		153s		

sh = Shoulder

The frequencies are assembled in Table I, all relating to the liquid state. The assignments are given in the notation for pyridine⁴ and other monosubstituted pyridines, and a comparison with the values for the methylpyridines is made in Table 2 which also lists the corresponding frequencies for ethylbenzene with some minor changes of notation.

⁴ Wilmshurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 1183.

TABLE 2.

Fundamental vibrational frequencies of the methyl- and ethyl-pyridines and of ethylbenzene.

Mode	4-Me ²	4-Et	2-Me ²	2-Et	3-Me ²	3-Et	PhEt ³
<i>a'</i> <i>a</i> ₁ 2	3050	3072	3080	3072	3085	3087	3080
20 <i>a</i>	3040	3035	3046	3006	3054	3035	3064
8 <i>a</i>	1604	1603	1590	1595	1594	1590	1613
19 <i>a</i>	1495	1499	1475	1479	1477	1480	1499
13* <i>a</i>	1212	1219	1236	1220	1227	1219	1179
9 <i>a</i>	1220	1219	1143	1147	1190	1187	1201
18 <i>a</i>	1070	1066	1047	1050	1041	1041	1031
1	994	995	994	995	1025	1026	1003
12* <i>a</i>	801	779	800	784	800	802	771
6 <i>a</i> *	514	493	548	500	538	488	487
<i>a''</i> <i>b</i> ₂ 20 <i>b</i>	3040	3072	3080	3072	3085	3087	3080
7 <i>b</i>	310	3035	3046	3006	3030	3035	3040
8 <i>b</i>	1566	1561	1565	1573	1575	1578	1585
19 <i>b</i>	1417	1415	1440	1438	1414	1425	1441
14	1365	1376	1376	1372	1340	1367	1330
3	1289	1315	1291	1300	1286	1317	1330
18 <i>b</i>	1090	1097	1099	1106	1106	1127	1156
6 <i>b</i>	669	671	629	626	628	629	624
15* <i>a</i>	341	292	259	290	338	299	314
<i>a'</i> <i>b</i> ₂ 17 <i>a</i>	972	962	972	971	987	966	964
10 <i>a</i>	872	874	886	886	923	924	840
16 <i>a</i>	384	400	403	405	399	402	404
<i>a''</i> <i>b</i> ₁ 5	872	874	940	959	941	948	985
10 <i>b</i>	799	822	751	749	788	809	745
4	728	707	729	719	708	714	696
11* <i>a</i>	490	562	470	572	457	567	556
16 <i>b</i> *	211	144	203	152	217	153	158
CH ₃ sym. str.	2934	2881	2925	2873	2923	2872	2890
antisym. str.	2959	2940	2960	2938	2980	2935	2950
sym. bend	1383	1376	1376	1372	1385	1379	1374
antisym. bend	1445	1461	1440	1460	1452	1463	1456
rock	1042	1031	1040	1050	1043	1063	1031
	1042	1097	1040	1106	1043	1108	1091
CH ₂ sym. str.		2881		1873		2872	2890
antisym. str.		2977		2970		2977	2974
bend		1461		1460		1463	1456
twist and wag		1252		1251		1261	1246
rock		750		762		779	787
$\nu(\text{C-C})$		971		971		966	964
$\delta(\text{CCC})$		378		—		354	365

* *X*-Sensitive vibration.

4-Ethylpyridine has, at most, a plane of symmetry perpendicular to the ring if the equilibrium configuration of the ethyl group is assumed to be as in ethylbenzene; the point group is C_s , so that the vibrations comprise only a' (planar) and a'' (non-planar) modes. 2- and 3-Ethylpyridine are entirely without symmetry. In all the molecules all frequencies are permitted in both the Raman and the infrared spectra and the selection rules are of little value. Nevertheless, the modes associated with the ring behave, to a good approximation, as if the plane of the ring is preserved and it is reasonable to make a classification of the vibrations on that basis.

For ethylpyridines, assignments for the pyridine ring substituted in the 2-, 3-, and 4-position were based on those for the corresponding methyl compound; assignments for the *X*-sensitive modes, and for those associated with the ethyl group, were made by using ethylbenzene as a guide. A few points deserve special mention.

Of the planar ring vibrations, all those derived from the a_1 class of monosubstituted pyridines with C_{2v} symmetry are readily located; the lowest *X*-sensitive mode, appearing throughout as a medium Raman line at 490 cm^{-1} , is surprisingly weak in the infrared spectrum of 3-ethylpyridine. Arguments have been given previously for placing the

b_2 -derived frequencies ν_3 and ν_{14} at *ca.* 1290 and 1370 cm^{-1} , respectively. Candidates for the former are available in 2-, 3-, and 4-ethylpyridine at 1300, 1317, and 1315 cm^{-1} , respectively. In 2-methylpyridine, ν_{14} was not resolved from the symmetrical methyl deformation, nor was it with 2- and 4-ethylpyridine; in 3-ethylpyridine, ν_{14} is probably the shoulder of medium intensity at 1367 cm^{-1} , almost completely resolved from the methyl mode at 1379 cm^{-1} .

The a_2 -derived frequencies are known to be almost independent of the substituent; for 2- and 3-ethylpyridine the highest is lost under the $\nu(\text{C}-\text{C})$ skeletal stretch of the ethyl group, whilst the lowest, usually slightly lower for 4- than for 2- or 3-substituted pyridines, is for 4-ethylpyridine just beyond the range of the present infrared measurements.

For ethylbenzene the out-of-plane ring bending mode (ν_{11} here) was placed at 567 cm^{-1} , raised above its expected position at about 470 cm^{-1} by interaction with the skeletal bending of the ethyl group. Similar candidates at *ca.* 565 cm^{-1} are available in all the ethylpyridines. The relative intensities of these bands, which are strong, medium and weak in 4-, 2-, and 3-ethylpyridine, respectively, parallel those for other monosubstituted pyridines.²

The pattern of combination bands in the 1600—1900 cm^{-1} region is in accord with that found previously.²

The methyl stretching and bending vibrations are obviously located, but the rocking modes are assigned with less certainty; alternatives for one or both of them are coincidences with the row assigned to ν_{18a} . Likewise only weak or very weak bands are available for the methylene wagging and twisting vibrations in the range 1230—1270 cm^{-1} , but the methylene rocking vibration is found in the range 750—780 cm^{-1} as a band of strong or medium intensity.

The bending vibration $\delta(\text{CCC})$ of the ethyl group in ethylbenzene was assigned to the weak band at 365 cm^{-1} on a basis of the calculated value⁵ of 380 cm^{-1} . (An alternative attribution,⁶ 557 cm^{-1} , is considered to be an unreasonably high value, and this frequency is otherwise assigned above.) In view of the close similarity of the values of the frequencies ν_{15} and ν_{16b} of the methylpyridines to those for toluene,⁷ it is clear that repetition of the calculation with a pyridine nucleus will yield nearly the same value for $\delta(\text{CCC})$ in the ethylpyridines as in ethylbenzene. Weak Raman shifts of 354 and 378 cm^{-1} observed for 3- and 4-ethylpyridine are accordingly assigned to $\delta(\text{CCC})$.

Experimental.—Distilled samples (Midland Tar Distillers Ltd.) of the ethylpyridines were dried and fractionated, and the course of removal of a few weak bands from the infrared spectrum followed. The materials used had b. p. 91°/20 mm. (2-), 165.5°/748 mm. (3-), and 167—168°/760 mm. (4-ethylpyridine). A second sample of 4-ethylpyridine, synthesised in this laboratory, gave an identical spectrum after redistillation (b. p. 166°/760 mm.).

Spectral measurements were made as previously described.⁷

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⁵ Taylor and Pitzer, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 1.

⁶ Bellanato and Schmid, *Anales real Soc. españ. Fís. Quím.*, 1960, **61**, 949.

⁷ Green, *J.*, 1961, 2236.