Spectrochimica Acta, Vol. 29A, pp. 1177 to 1189. Pergamon Press 1973. Printed in Northern Ireland

Vibrational spectra of some halogenopyridines

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(Received 23 August 1972)

Abstract—The infrared and Raman spectra are reported and completely interpreted for the following substituted pyridines—2,6-dichloro-; 2,6-dibromo-; 3,5-dichloro-; 3,5-dibromo-; 2,5-dichloro-; 2,5-dibromo-; 2,3-dichloro-; 2,4,6-trifluoro-; 2,4,6-trifluoro-pyridine. Some changes are made in previous assignments of the spectra of the corresponding dimethyl pyridines, of 2,6-difluoropyridine and of 2,4,6-trifluoropyrimidine.

PUBLISHED information on the vibrational spectra of halogenopyridines is confined to several mono-substituted derivatives [1], two penta-substituted pyridines [2] and to 2,6-difluoropyridine [3]. The infrared spectrum of the latter compound has now been re-examined, and i.r. and Raman spectral data measured for an additional seven dihalogeno- and two trihalogeno-derivatives. Although in some of the previous work use was made of vibrational calculations using force constants transferred from pyridine [4] or from hexafluorobenzene and benzene [3] the results were of no greater guidance to the interpretations of observed spectra than a straightforward intercomparison of the data for relevant compounds. For the assignments in the present work the data for the corresponding halogenobenzenes have been particularly relevant. The resulting values for the dihalogenopyridines suggested some changes in those previously given for the dimethylcompounds [5]; and those for 2,4,6trifluoropyridine suggest in their turn some changes in those for 2,4,6-trifluoropyrimidine [6].

1. 2,6- AND 3,5-DIHALOGENOPYRIDINES

For these compounds, the fundamentals will comprise, with the recommended [7] choice of axes $-10a_1 + 3a_2 + 5b_1 + 9b_2$. The values now proposed are numbered

- J. H. S. GREEN, W. KYNASTON and H. M. PAISLEY, Spectrochim. Acta 19, 549 (1963);
 R. ISAAC, F. F. BENTLEY, H. STERNGLANZ, W. C. COBURN, C. V. STEFHENSON and W. S. WILCOX, Appl. Spectry 17, 90 (1963); G. VARSANYI, T. FARAGO and S. HOLLY, Acta Chim. Hungary 43, 205 (1965).
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- [3] R. T. BAILEY and D. STEELE, Spectrochim. Acta 23A, 2997 (1967).
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- [5] J. H. S. GREEN, D. J. HARRISON, W. KYNASTON and H. M. PAISLEY, Spectrochim. Acta 26A, 2139 (1970).
- [6] R. T. BAILEY and D. STEELE, Spectrochim. Acta 23A, 2989 (1967).
- [7] R. S. MULLIKEN, J. Chem. Phys. 23, 1997 (1955).

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accordingly and presented in Tables 1 and 2 together with those for relevant 1,3dihalogenobenzenes [8]. Compared with the latter the dihalogenopyridines have one vibration less in each of the a_1 , b_1 and b_2 classes.

	2,6-difluoropyridine		1,3-difluoro- benzene [8]		2,6-dich	2,6-dichloropyridine		omopyridine
	i.r.	R[3]	i. r .	R	i.r.	R	i. r.	R
a ₁ y ₁	3105 s	3108 в, р	{	3095 3084	3085 w	3083 vs, p	3070 sh	30 73 m
V2		3052 s	(3086		3060 w	3060 m, р	3045 w	3046 m
ν_{3}	1614 vs, B	1612 s	1605	1600	1567 s	1570 s, p	1555 s,	1565 sh
<i>v</i> 4	1448 vs	1446 m	1449		$1390 \mathrm{sh}$	1387 m, p	1387 w	1386 s, p
νs	1310 vs	1307 s, p	1277	1277	1140 s	1141 vs, p	1133 s	1124 m, p
ν _s	1074 m	1071 s, p	1066	1067	1076 m	1077 s, p	1077 w	1073 s, p
¥7	998 vs	998 vs, p		1007	986 s	985 vs, p	982 s	978 vs, p
ν_8	740 s	736 vs, p	734	736	660 m	662 s, p	642 m	644 s, p
¥9	548 w	546 s, p	522	524	409 w	408 s, p	291 w	288 vs, p
¥10	346 m	348 w	329	329	183 m	184 s, dp	160 w	
a, v,11	(88	30)	879			887 vw		(888)
¥12	(880) [569] 219			591	(530)		(484)	
V13		219		250		210 s, dp		176 m
b2 V14	880 vw		(978 850		865 m		865 sh	
¥ 1.5	796 vs, C	795 w	771		784 s		780 s	
¥1.	721 s, C		674		719 m		716 m	
¥17	461 w	458 w	458		435 w		428 w	
V ₁₈	247 m	247 s	230	235	183 m		4	(130)
b. V19	<u> </u>	3090 sh	3086	900-0-00	3060 w	3060 в	3090 w	3085 w
P 20	1592 vs	1590 m	1613	1612	1558 s	1562 s, dp	1555 s	1555 s, dp
Pal	1448 vs, A		1490	1488	1415 s	1412 m, dp	1409 s	1408 w
¥	1284 m	1281 m	1337		$1245 \mathrm{m}$	1245 vw	1239 m	
V 23	1234 s	1228 w	1260	1254	1220 w		1202 m	
ν ₂₄	1145 s, A	1142 w	${1157 \\ 1120}$	1154 1118	1162 s		1162 s	
Var	998 s		952	952	795 s		746 s	
Vae	568 s. A	566 s	514	511	452 s	452 m, dp	371 m	376 m, dp
* 26 Van	500 m. A	498 w	478		378 s	378 w. dp	312 m	316 m. dp
* 27						,		, <u>F</u>

Table 1. Wavenumbers (cm⁻¹) of the fundamental vibrations of 2,6-disubstituted pyridines

s, strong; m, medium; w, weak; v, very; sh, shoulder. p, polarized; dp, depolarized. () inferred value, [] calculated value.

1.1 2,6-Difluoropyridine

The i.r. spectrum of the present sample was in good agreement with that reported [3], but some changes of assignment are now made. As a trace in the previous report [3] shows, the band at 501 cm⁻¹ has a type A contour and it is therefore assigned to a b_2 fundamental, rather than to $r_{17}(b_1)$ [3]. For the latter the value 461 cm⁻¹ is now preferred.

No assignment was made previously for $v_4(a_1)$, but it is evident it must be taken as coincident with $v_{21}(b_2)$ in the intense absorption at 1448 cm⁻¹. Location of the two highest out of plane CH bending vibrations, γ (CH), is not obvious. For the highest b_1 mode, sum bands were utilised [3] to derive the value 924 cm⁻¹ but neither this, nor that reported [3] at 941 cm⁻¹ were confirmed in the present infrared spectra even for a path length of 0.1 mm of the liquid substance. However, very weak

^[8] J. H. S. GREEN, Spectrochim. Acta 26A, 1523 (1970).

	3,5-dichl	3,5-dichloropyridine		1,3-dichloro- benzene [8]		3,5-dibromopyridine		obenzene [8]
	i.r.	R	i. r.	R	i.r.	\mathbf{R}	i. r .	R
a1 v1	3075 m	3066 m, p	3071	3072	3061 m	30 60 sh	3078	
ν_2	3055 m	3049 m, p			$3050 \mathrm{m}$	3047 m	3058	3056
v_{a}	$1550 \mathrm{sh}$	1550 sh, p	1577	1576	1550 s	$1550 \mathrm{m}$	1567	1560
V A	$1379 \mathrm{m}$	1379 w, p	1412	1411	1370 m	1372 vw	1412	
v 5	1111 s	1108 vs, p	1124	1123	1098 s		1096	1088
V.	1098 s		1073	1068	1086 s	1083 в	1059	1055
¥ 7	1016 s	1011 vs, p	997	997	1015 s	1010 vs	992	990
v	655 s	651 w, p	663	663	638 s	635 m	646	645
va	392 s	390 w, p	398	397	279 s	279 s, p	308	308
v_{10}	195 s	190 m, dp	198	198		156 vw	159	159
$a_{2} v_{11}$	905 w		892	891	910 w		894	888
P12		512 vw, dp	532	531	(4	190)	518	
ν_{13}		204 m, dp		212		193 m		199
b ₁ v ₁₄	878 s		(964		875 s		(868	
			867				{ 868	
v_{15}	814 s		(773	776	781 w		(769	
ν_{16}	691 s		672		689 s		669	
v_{17}	418 w	_	433		(415)	433	
v ₁₈	173 в	168 w, dp	175	176		134 w	132	132
b ₂ v ₁₉	3075 m	3084 sh	3095		3061 m		3078	
v_{20}	1565 s	1559 m, dp	1577		1550 s	1550 m	1567	1560
v_{21}	1418 s	1422 w, dp	1462		1413 s	1415 w	1460	
v_{22}	1298 m		1289		1297 s		1292	
v_{23}	1208 m	1211 w, dp	1258		1210 m	1207 w	1256	1246
			(1161	1160			(1161	1163
v_{24}	1134 s		{		1136 w	1133 w	{	
			(1080				(1078	
ν_{25}	788 m		784		762 w		726	727
v_{26}	447 s	446 w, dp		429	372 m	369 w, dp	357	351
v_{27}	356 m	356 w, dp	365	364		301 w, dp	285	287

Table 2. Wavenumbers (cm^{-1}) of the fundamental vibrations of 3,5 dihalogenopyridines

absorption at 880 cm⁻¹ was thus confirmed and this value is suggested for both the a_2 and $b_1 \gamma$ (CH) vibrations. The consistency of the present assignment with that for 1,3-diffuorobenzene [8] is shown in Table 1.

The confirmed sum-bands are interpreted as follows—

1.2 2,6-Dimethylpyridine

Relationships between the assignments for 2,6-diffuoro- and 2,6-dimethylpyridine have been discussed [3, 5]. Some changes in the assignment for the latter in Ref. [5] are now made. With additional evidence [9] for the $a_2 \gamma$ (CH) mode of 1,3-dimethylbenzene being at 888 cm⁻¹, for 2,6-dimethylpyridine is v_{11} (a_2) now put at 905 cm⁻¹,

 ^[9] Y. KAKIUTI, H. SAITO and T. YOROYAMA, J. Mol. Spectry 32, 247 (1969); C. L. LAU and R. G. SNYDER, Spectrochim. Acta 27A, 2073 (1971).

with $v_{14}(b_2)$ coincident with $v_{25}(b_1)$ at 888 cm⁻¹. Another choice now preferred is that of 1278 cm⁻¹ for $v_{22}(b_2)$ rather than 1326 cm⁻¹; the latter being interpreted as $430 + 894(A_1)$. The complete assignment is not now presented again, but the relationship between the fundamentals for dimethyl compounds now parallels that between the diffuoro compounds; all four form a well-behaved, consistent, set of values.

1.3 2,6-Dichloropyridine

The a_1 fundamentals (see Table 1) are identified at values close to those for 1,3 dichlorobenzene (see Table 2), by prominent Raman lines, all but the lowest of which are strongly polarised. A doublet at 1396, 1387 cm⁻¹ in the Raman spectrum is ascribed to $408 + 985(A_1)$ in resonance with r_4 . However, there is an additional polarised line at 1168 cm⁻¹ which cannot arise from another a_1 fundamental, even though it appears to have a counterpart of strong i.r. absorption at 1162 cm⁻¹. This absorption is assigned to $r_{24}(b_2)$ and the Raman line attributed to $378 + 795(A_1)$ which has gained intensity from the proximate $r_5(a_1)$. In support of such an interpretation, the absorption persists for 2,6-dibromopyridine at 1162 cm⁻¹ as $r_{24}(b_2)$, whilst the A_1 level has shifted to 312 + 746, which is indeed observed as weak absorption at 1059 cm⁻¹. (Similar contributions of sum bands to the spectra are found for 1,3-dihalogenobenzenes [8].)

Assignment of the weak Raman feature at 887 cm⁻¹ to $r_{11}(a_2)$ finds support from sum bands given below, as does the choice, which is not obvious, between 795, 784 cm⁻¹ as $r_{25}(b_2)$ and $r_{15}(b_1)$. For the b_2 fundamentals r_{22} , r_{23} , use of the respective values 1368, 1245 cm⁻¹ rather than of 1245, 1220 cm⁻¹ as in Table 1, would appear from the infrared spectrum to be alternatives that better explain the observed intensities in the region of the higher of these wavenumbers. However, the resulting value for r_{22} seems too high by comparison with those for both the 2,6-dimethyl- and 2,6-dibromo- compounds where the assignment is clearer. With the choice in Table 1, absorption at 1368 cm⁻¹ is attributed to 378 + 986(B_2).

Other combination bands are-

1120: $452 + 660(B_2)$; 1200: $409 + 795(B_2)$; 1323: $183 + 1140(A_1)$; 1434: $452 + 986(B_2)$; 1455: $650 + 795(B_2)$; 1628: $719 + 887(B_2)$; 1645: 784 + 865 (A_1) ; 1673: $784 + 887(B_2)$; 1777: $2 \times 887(A_1)$; 1802: $378 + 1415(A_1)$; 1824: $409 + 1415(B_2)$; 1870: $795 + 1076(B_2)$; 1964: $2 \times 986(A_1)$; 3129: $2 \times 1558(A_1)$.

1.4 2,6-Dibromopyridine

Again prominent sum-bands confuse the identification of the a_1 fundamentals but the strong Raman lines at 1124, 1073 and 978 cm⁻¹ are taken as v_5 , v_6 and v_7 , successively. However, there remain two further polarised lines at 1098, 1112 cm⁻¹ and absorption at 1100 cm⁻¹ which must arise from appreciable interactions of sum levels with v_5 and v_6 . The only appropriate A_1 levels are 371 + 746; 160 + 982; and 428 + 716. The strong absorption at 1162 cm⁻¹ had no observed Raman counterpart and is satisfactorily taken as v_{24} .

Assuming the combination bands at 1776, 1670 cm⁻¹ to have the same origins as in 2,6-dichloropyridine, then they are $2 \times (888)(A_1)$ and $780 + (888)(B_2)$, and indicate that $v_{11}(a_2)$ is at 888 cm⁻¹. Less satisfactorily, there is a weak polarised

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Raman line at 968 cm⁻¹ which, if attributed to the overtone of v_{12} , places the latter ~484 cm⁻¹, a value which is probably too low.

Other sum-bands are-

660: $288 + 371(B_2)$; 1059: $312 + 746(A_1)$; 1104: $371 + 746(A_1)$; 1322: $160 + 1162(B_2)$; 1338: $371 + 978(B_2)$; 1872: $746 + 1133(B_2)$; 1962: $2 \times 982(A_1)$; 3112: $2 \times 1555(A_1)$; 3129: $2 \times 1565(A_1)$.

1.5 3,5-Dichloropyridine

Some of the assignments in Table 2 were made taking into account the values for 3,5-dibromopyridine. The Raman line at 1559 cm⁻¹ is depolarised, so it and the absorption at 1565 cm⁻¹ are assigned to $v_{20}(b_2)$. The a_1 mode v_3 is almost coincident with it (as in the dibromo compound), but may be the shoulder at 1550 cm⁻¹ which appears slightly polarised in the Raman. Other weak features in the Raman spectrum in this region are—

1539: 447 + 1098(B_2); 1572: 195 + 1379(A_1), 691 + 878(A_1).

The Raman spectrum also identifies $v_4(a_1)$ and $v_{21}(b_2)$ as weak lines at 1379(p) and 1422 cm⁻¹ (dp), respectively. But the corresponding infrared bands are at 1379, 1391 and 1418, 1425 cm⁻¹, so there are certainly sum-levels such as $2 \times 691(A_1)$; 390 + 1011(A_1); and 195 + 1208(B_2), interacting with the appropriate fundamentals.

Strong absorptions at 1111, 1098 and 1016 cm⁻¹ are assigned successively to v_5 , v_6 , v_7 although there are observed polarised Raman lines corresponding only to the first and last of these. Additional absorption at 1038 cm⁻¹ has a polarised Raman analogue at 1032 cm⁻¹, but cannot arise from another a_1 fundamental and is interpreted as $2 \times 512(A_1)$ or $390 + 651(A_1)$.

Another rather prominent infrared band at 1134 cm⁻¹ is assigned to $v_{24}(b_2)$ in obvious preference to an alternative weak Raman line at 1172 cm⁻¹. However, the Raman line at 1127 cm⁻¹ is polarised and must then have some origin such as $356 + 788(A_1)$ or $691 + 418(A_1)$ interacting with $v_5(a_1)$; that at 1172 is attributable to $392 + 788(B_2)$. Strong absorption at 1298 cm⁻¹ is certainly v_{22} even in the absence of a Raman counterpart, but the weaker absorption at 1218, 1208 cm⁻¹ finds a similar Raman pair at 1211, 1200 and $512 + 691(B_2)$ or $195 + 1016(A_1)$ are probably involved here, the former with $v_{23}(b_2)$.

The remaining assignments in Table 2 are straightforward with the guidance of the values for 1,3 dichlorobenzene. Additional sum-bands are-

1468: 356 + 1111(B_2); 1750: 2 × 878(A_1); 1776: 878 + 905(B_2); 1810: 2 × 905 (A_1); 1839: 450 + 1379(B_2); 1871: 655 + 1208(B_2); 3084(R): 2 × 1550(A_1); 3115 (3122 R, p): 2 × 1559(A_1).

1.6 3,5-Dibromopyridine

The spectra were rather simpler than the preceding and the assignment in Table 2 requires little further comment. For $v_{24}(b_2)$ there is again available an alternative to 1136 cm⁻¹ of 1171 cm⁻¹ also observed weakly in both spectra, and the former could be explained as $372 + 762(A_1)$. However, the lower value is clearly preferable if both dihalogeno-compounds are considered together; 1172 is

again taken as a combination band, even though the level $156 + 1010(A_1)$ involves different levels from those for 3,5-dichloropyridine.

Interpretation of weak features at 980 cm⁻¹ as $2v_{12}$ gives a reasonable value of $\sim 490 \text{ cm}^{-1}$ for the latter. Absorption arising from $v_{17}(b_2)$ was not observed, but a value $\sim 415 \text{ cm}^{-1}$ can be taken for it.

The remaining bands were—

1061: 301 + 762(A_1); 1112: 415 + 689(A_1); (490) + 689(B_2); 1375: 2 × 689(A_1); 1452: 372 + 1086(B_2); 1735: 2 × 875(A_1); 1782: 875 + 910(B_2); 1815: 2 × 910 (A_1); 1850: 638 + 1210(B_2); 1880: 762 + 1133(A_1); 3106: 2 × 1550(A_1).

1.7 3,5-Dimethylpyridine

Although $v_{11}(a_2)$ and $v_{14}(b_1)$ are now both appreciably higher for 3,5-dimethylpyridine [5] than for the 3,5-dihalogeno compounds in Table 2, no observed alternatives exist and the previous values are retained. Interaction of these γ (CH) modes with a''CH₃ rocking modes can, in principle, account for the shifted values.

2. 2,5-DIHALOGENOPYRIDINES

The 2,5 dihalogenopyridines possess only the molecular plane of symmetry and the fundamentals comprise 19a' + 8a''. A relationship is obviously to be expected to the spectra of the 1,4 dihalogenobenzenes [10] and the values in Table 3 show this; the fundamentals of the latter have been written under C_s symmetry but the D_{2h} labels retained. This makes explicable several of the observed intensity features; for example, in the Raman spectrum, the intensity of the lines arising from v_{14} and v_{18} which are of a_g origin; and the absence of v_{16} , which is of b_{1u} origin. On the other hand, v_{23} and v_{25} become active in the infrared spectrum, because compared with their D_{2h} progenitors the motions now involve displacement of the nitrogen atom out-of-the-plane, with consequent resultant change of dipole moment. The disubstituted pyridines have 2a' + a'' modes less than the corresponding disubstituted benzenes.

2.1 2,5 Dichloropyridine

The values for 1,4-dichlorobenzene show that v_4 and v_5 are reasonably taken as coincident at 1564 cm⁻¹ but, by contrast, a pair of strong bands at 1443, 1456 cm⁻¹ cannot arise from two separate fundamentals. Rather are they attributed to A' levels such as 362 + 1088; 335 + 1114; 335 + 1133 in resonance with $v_6(a')$. All the remaining a' fundamentals are prominent in the Raman spectrum with the exception of v_{13} and v_{16} which give strong infrared absorptions at wavenumber values very close to b_{14} modes for 1,4 dichlorobenzene.

All the $\gamma(CH)$ modes are observed in the i.r. spectrum as are all their possible binary (A') sum bands—

1652: 2×825 ; 1742: 825 + 919; 1785: 825 + 960; 1835: 2×919 ; 1882: 919 + 960; 1920: 2×960 .

Other (A') sum-bands are—

795: 303 + 491; 979: 2 × 491; 1101(R): 2 × 550; 1216: 491 + 727; 1240: 225 + 1013: 1313: 491 + 825; 1372: 362 + 1013; 1409: 628 + 771; 3122: 2 × 1564.

^[10] J. H. S. GREEN, Spectrochim. Acta 26A, 1503 (1970).

		2,5-dichloropyridine		1,4-dichlorobenzene [10]		2,5-dibrom	opyridine	1,4-dibromobenzene [10]	
		i.r.	R	i. r .	R	i. r.	R	i.r.	R
a'	<i>v</i> ₁	((3087(b2u)		1		3078(b2u)	
		3084 w	3084 w, p			3080 w			
		{		$3078(b_{1u})$		{		3068(b ₁₁)	
	v_2	3055 m	3057 m, p	($3072(a_{g})$	3050 m			$3068(a_g)$
	¥3	($3065(b_{3g})$	C.			3068(b ₃₀)
	v ₄	{1564 s	1562 s		$1574(b_{3g})$	1552 m			1570(b ₃₀)
	v_5	C			$1574(a_g)$	$1545 \mathrm{sh}$			$1570(a_g)$
	v ₆	1443 s	1447 w	$1477(b_{1u})$		1446 в		$1468(b_{1u})$	
	v_7	1360 s	1357 w	1394(b _{2u})		1352 s		1381(b _{2u})	
	v _s	1280 m	1274 w		$1290(b_{3g})$	1278 w			1289(b _{3g})
	v ₉	1230 w	1225 w, p	$1220(b_{2u})$		1220 w		$1212(b_{2u})$	
				($1169(a_g)$			($1170(a_{g})$
	v_{10}	1133 s	1128 m, p			1100 s		1	-
				$1107(b_{2u})$				$1100(b_{2u})$	
	v_{11}	1114 s	1110 s, p	{	$1096(a_g)$	1091 s		{	
								$1078(b_{1u})$	$1067(a_g)$
	v12	1088 m	1082 m, p	$1090(b_{1u})$		1085 s	1080 m		
	V13	1013 s		$(1015(b_{1u}))$		1005 s		$(1003(b_{1u}))$	
	V14	771 s	768 s, p	•	$747(a_{g})$	740 m	733 s	•	$708(a_{a})$
	V15	628 s	628 m		626(b3a)	619 s			623(ba)
	V16	546 s		$550(b_{1u})$		425 s		$424(b_{1,u})$	
	V17	362 w	363 m, p		$350(b_{3g})$	313 m	315 w		$307(b_{3a})$
	v18	335 w	332 s, p		$328(a_g)$	217 w	222 s		$218(a_a)$
	v19	225 m	224 w	$226(b_{2u})$		166 w†		171(b _{1u})	
a″	¥20	960 w		$(951(a_u))$		960 w		950(a _u)	
				$934(b_{3g})$				935(b3a)	
	v_{21}	919 m		{		918 m			
				$819(b_{3u})$				815(b _{1g})	
	v_{22}	825 s		\815(b _{1g})		821 s		807(b _{3u})	
	v_{23}	727 s	728 w	(68	7, b _{2g})	720 m		(68	9, b ₂₀)
	v_{24}	491 m		$485(b_{3u})$		475 s		473(b ₃₄)	
	v_{25}	417 m		$405(a_u)$		407 m		$402(a_{u})$	
	v_{26}	303 w	303 w, dp	$298(b_{2g})$		276 w	280 m	$282(b_{2g})$	
	v_{27}	106 w		122(b _{3u})		87 w*		$103(b_{3u})$	

Table 3. Wavenumbers (cm^{-1}) of the fundamental vibrations of 2,5 dihalogenopyridines and 1,4 dihalogenobenzenes

* Values for solid compound.

2.2 2,5-Dibromopyridine

The Raman data for this compound are incomplete owing to excessive fluoescence from solutions, only the strongest lines from the solid substance were observed but the infrared spectrum establishes values for all the fundamentals. No absorptions below 200 cm⁻¹ could be detected even for 6 mm path length of a saturated solution in cyclohexane. Those at 87 and 166 cm⁻¹ were observed for mulls of the solid substance dispersed in vaseline.

It is likely that v_5 is just resolved from v_4 as a shoulder, another band at 1510 cm⁻¹ is probably too low a value for v_5 and is attributed to 428 + 1085(A'). Again a doublet at 1432, 1446 cm⁻¹ is not taken as two a' fundamentals, but as 425 + 1005, or 313 + 1100 interacting with v_6 . Between 1000 and 1150 cm⁻¹ are to be expected four a' fundamentals and they are taken as the four strongest infrared bands: 1005, 1085, 1091, 1100 cm⁻¹. This leaves the following which are taken as A' sum-bands—

1050: 428 + 621; 1122: 276 + 821; 1131: 407 + 720; 1169: 425 + 740; 1199: 475 + 720.

Again the γ (CH) assignments are confirmed by—

1645: 2×821 ; 1775: 821 + 960; 1828: 2×918 ; 1872: 918 + 960; 1912: 2×960 .

Other combination bands are—

528: 217 + 313; 590: 166 + 428; 645: 217 + 425; 752: 313 + 425; 790: 166 + 619; 892: 275 + 619; 1300: 217 + 1085; 1394: 313 + 1085; 1690: 960 + 720; 1718: 619 + 1100; 3120: 2×1552 .

2.3 2,5-Dimethylpyridine

The data in Table 3 show that the value of 695 cm⁻¹ inferred [5] for v_{23} of 2,5dimethylpyridine is too low. This ring twisting mode is evidently uniformly at a higher wavenumber for the pyridines than the benzenes. For 2,5-dimethylpyridine it is most likely at 727 cm⁻¹ coincident with $v_{15}(a')$.

3. 2,3-DICHLOROPYRIDINE

The fundamentals comprise 19a' + 8a'', and complete interpretation of the infrared spectrum could be made even without the Raman spectrum. The values are given in Table 4 together with those [11] for 1,2-dichlorobenzene written under C_s symmetry when there arise three coincidences of true a_1 and b_2 vibrations. The corresponding fundamentals for 2,3-dichloropyridine comprise 2a' + a'' less than for the substituted benzene, and are readily located. However, absorptions at 1217, 1195 cm⁻¹ cannot arise from two separate fundamentals and are attributed to interaction of the A' sum level 429 + 765 with $\nu_7(a')$. All the γ (CH) modes are observed, as are five of their six possible binary sums (A'), thus confirming the assignments—

1728: 794 + 935; 1760: 794 + 972; 1867: 2×935 ; 1902: 935 + 972; 1941: 2×972 .

Other absorptions are accounted for as-

388: 137 + 252; 1039: 2×522 ; 1080: 429 + 653; 1258: 480 + 765; 1455: 2×728 ; 1640: 202 + 1436; 1811: 653 × 1161.

Two consequences for the assignment for 2,3-dimethylpyridine [5] follow from the values in Table 4. It is more likely that $v_{20}(a'')$ is at 971 cm⁻¹ rather than at 947 cm⁻¹; and the alternative choice of 413 cm⁻¹ for $v_{18}(a')$ and 439 cm⁻¹ for $v_{25}(a'')$ (rather than the reverse) is now made to establish consistency with the value of the latter fundamental for 2,3-dichloropyridine.

4. 2,4,6-TRIHALOGENOPYRIDINES

The 2,4,6-trihalogenopyridines have C_{2v} symmetry and the fundamentals comprise $10a_1 + 3a_2 + 5b_1 + 9b_2$. They are numbered accordingly with the assigned values, in Table 5. There is an obvious relationship to the modes of the trigonally symmetric (D_{3h}) 1,3,5-trihalogenobenzenes [12] which written under C_{2v} symmetry become—

 $11a_1(4a_1' + 7e') + 3a_2(3e'') + 6b_1(3a_2'' + 3e'') + 10b_2(3a_2' + 7e').$

The values, so written, are also given in Table 5. The pyridine derivatives again

1184

^[11] J. H. S. GREEN, Spectrochim. Acta 26A, 1913 (1970).

^[12] J. H. S. GREEN, D. J. HARRISON and W. KYNASTON, Spectrochim. Acta 27A, 793 (1971).

Vibrational spectra of some halogenopyridines

	2,3-dichloro- pyridine i.r.	1,2-dichlorobenzene [11]			2,3-dichloro-	1,2-dichlorobenzene [11]	
		i. r .	R		i.r.	i. r.	R
a' v ₁	(3065 m	3072	3070	a' v15	653 s	660	660
v2	{ 3057 m			P18	480 s	480	480
¥3	l			¥17	429 m	427	428
VA	1562 s	1576	1571	V 18	352 m	336	334
vs	1552 s	1576	1571	V 19	202 w	202	203
Va	1436 m	1458	1452	••			
•				a" v **	972 m	(975	
ν_{2}	1400 vs	1438				{ 940	
V.	1305 w	1276	1273	V	935 w	850	
v	1217 m	1252		y.,	794 s	748	
V10	1161 s	(1)==	1158	P 23	728 s	695	
V11	1127 m	1100	1128	V 24	522 w		504
V19	1063 m	1130		Pas	442 w	435	
v13	1032 s	(1040	1038	V	252 m	239	
P14	765 m	740	749	P 27	137 m	152	154

Table 4. Wavenumbers (cm^{-1}) of the fundamental vibrations of 2,3 dichloropyridine and of 1,2 dichlorobenzenes

 Table 5. Wavenumbers (cm⁻¹) of the fundamental vibrations of 2,4,6 trihalogenopyridines and 1,3,5 trihalogenobenzenes

	2,4,6-trifluoropyridine		1,3,5-trifluoro benzene [12] 131		2,4,6 trichloropyridine		1,3,5-trichlorobenzene	
	i. r .	R	i.r.	R	i. r.	R R	i.r.	R
a ₁ v ₁	3116 m	3119 m, p	3108	3080	3084 w	3088 m, p	3089	3084
v 2	1601 vs	1601 m, p	1624		1558 s	1562 m, p	1570	
ν_{3}	1462 s	1466 vw	1475		1390	1391 m, p	1420	
¥4	1386 m	1388 m, p		1350	1180 w	1180 s, p		1149
v_5	1134 s	1134 m, p	1112		1087 s	1086 m, p	1098	
ν_{6}	1006 w	1005 vs, p		1010	984 m	982 vs, p		995
v7	985 s	987 s, p	993		825 s	823 w, p	816	
r _s	594 m	594 vs, p		578	432 m	431 m	429	
v,	510 m	506 m, p	500		376 w	385 s, p		379
¥ 10	348 m	344 w, p	326		193 s	198 s	190	
		882 vw	(86	0)		865 w, dp	869	
¥12	(!	590)		595	575 vw	583 w	530	
v 13		228 s(dp)		253		223 w, dp		215
b ₁ y ₁₄	844 vs		{ (86	80)	855 s		{ 869	
1 /	721	723 m dn	665		715	710	(803	
×15	634 a	630 w dp	000	505	710 m	710 w 559 m do	520	
- 16 V	267 m	268 m dn		253	220 s	000 w, up	030	01 <i>K</i>
v ₁₈	214 m	200 m, up	(21	4)	145 w	146 vw, dp	149	210
P19	•••••••••	3089 w	3108		3095 w		3089	
v_{z0}	1631 vs	1632 vw	1624		1545 s	1544 w. dp	1570	
V21	1428 s		1475		1359 s	1358 dp	1420	
ν_{22}	1282 m	1283 w, dp	(1294)		1235 m	1233 dp	(1333)	
v ₂₃	1167 в	1170 w, dp	(1165)		1156 s	1158 vw	{(1194) 1098	
-	1096 -		(1122					
v_{24}	1030 8		1 993		810 s	811 w	816	
v_{25}	610 s	606 m, dp	(565)		468 m	469 m	464	
V 26	521 m	516 m, dp	500		426 m		429	
V27	335 m	332 w, dp	326			184 sh	190	

have one less fundamental in each of the a_1 , b_1 and b_2 classes than the trisubstituted benzenes.

4.1 2,4,6-Trifluoropyridine

The intense infrared and Raman features at 3116, 3119 cm⁻¹, respectively, certainly identify $\nu_1(a_1)$, at a rather high value probably characteristic for highly fluorinated aromatic and related molecules. The other (b_2) CH stretching vibration is taken as the weaker Raman line at 3089 cm⁻¹ which is not resolved in the infrared spectrum [and could arise from 1462 + 1631(B_2)]; other weak features in the latter are—

3025: $1428 + 1601(A_1)$; **3051**: $1428 + 1631(A_1)$; **3195**: $2 \times 1601(A_1)$; **3227**: $1601 + 1631(B_2)$.

Of the pair of intense i.r. bands at 1631, 1601 cm⁻¹, only the latter has a Raman counterpart of any prominence and is therefore taken as $v_2(a_1)$; the other is then taken as $v_{20}(b_2)$. There is a similar pair of prominent i.r. bands at 1462, 1428 cm⁻¹, whilst the Raman lines are at 1466 and 1446 cm⁻¹, both being very weak. Taking the coincidence as identifying the a_1 mode, v_3 is taken at 1462 cm⁻¹ with, therefore $v_{21}(b_2)$ at 1428 cm⁻¹. The Raman feature at 1446 cm⁻¹ is attributed to $2 \times 721(A_1)$.

The strong, polarised Raman line at 1386 cm⁻¹ certainly arises from an a_1 fundamental (v_4) . But there is a shoulder at 1374 cm⁻¹ and in the infrared a resolved pair of bands at 1386, 1377 cm⁻¹. The second component is assigned to 335 + 1036 (A_1) in Fermi resonance with v_4 .

A pair of prominent i.r. bands at 1167, 1134 cm⁻¹ clearly corresponds to the e' pair at 1122 cm⁻¹ for 1,3,5-trifluorobenzene; the depolarisation ratios of the Raman lines being 0.80 and 0.64, the assignments to $v_{23}(b_2)$ and $v_5(a_1)$, respectively, are made accordingly. Similar experimental facts are the basis for assigning the pair at 510, 521 cm⁻¹ to $v_9(a_1)$ and $v_{26}(b_2)$, respectively, and that at 348, 335 cm⁻¹ to $v_{10}(a_1)$ and $v_{27}(b_2)$, respectively. The two remaining fundamentals of a_1' origin (v_6 and v_8) are identified by strong, polarised Raman lines.

In the planar classes there remain the three modes (v_{22}, v_{23}, v_{25}) related to the inactive a_2' modes of 1,3,5-trifluorobenzene. All can be identified in the i.r. spectrum, and have depolarised Raman counterparts, at values entirely consistent with those deduced [12, 13] for the benzene derivative.

Assignment of the b_1 fundamentals is straightforward: the observation of infrared absorption at 214 cm⁻¹ establishes v_{18} , and incidentally is support for the inferred value for 1,3,5-trifluorobenzene.

In the a_2 class, v_{11} is an essentially CH out of plane bending mode and its assignment to a very weak Raman line at 882 cm⁻¹ finds support from the observed sumlevels (c.f. [12]) 1731: 844 + 882(B_2); 1764: 2 × 882(A_1). Similarly v_{13} can be confidently assigned to a strong depolarised Raman line with no corresponding i.r. absorption, at 228 cm⁻¹. However, the likely location (~590 cm⁻¹) of v_{12} is very close to that of other fundamentals (v_8 , v_{25}) giving prominent Raman features, and only this likely value for it can be given.

^[13] J. R. SCHERER, J. C. EVANS, W. W. MUELDER and J. OVEREND, Spectrochim. Acta 18, 57 (1962).

All the remaining observed features in the spectrum are accounted for as follows— 442: $2 \times 228(A_1)$; 946: 335 + 610 (A_1) ; 1105: 610 + 594 (A_1) ; 1206: 594 + 610 (B_2) ; 1220: $2 \times 610(A_1)$; 1250: 1601 - 348 (A_1) ; 1268: $2 \times 634(A_1)$; 1292: 1631 - 348 (B_2) ; 1324: 348 + 985 (A_1) ; 1355: 348 + 1006 (A_1) ; 1387 $(\mathbb{R}, 1374)$: 335 + 1036 (A_1) ; 1499: 510 + 985 (A_1) ; 335 + 1167 (A_1) ; 1515: 521 + 985 (B_2) ; 510 + 1006 (A_1) ; 1526: 521 + 1006 (B_2) ; 1547: 510 + 1036 (B_2) ; 1642: 610 + 1036 (A_1) ; 1731: 844 + 882 (B_2) ; 1810: 348 + 1462 (A_1) ; 1891: 510 + 1386 (A_1) ; 1935: 335 + 1601 (B_2) .

4.2 2,4,6-Trichloropyridine

Combination bands are less prominent in the spectrum of this compound, but some features of the observed spectra require explanation. A pair of prominent polarised Raman lines at 3088, 3125 cm⁻¹ cannot arise from two a_1 fundamentals. The relative intensities of the infrared counterparts, at 3084, 3120 cm⁻¹, are reversed, the latter being the stronger, and there is evidently substantial mixing of 2×1562 (A_1) with $\nu_1(a_1)$.

A pair of polarised Raman lines is observed at 1391, 1420 cm⁻¹ and again cannot arise from two a_1 modes. The former is the sharper band, has the lower depolarisation ratio, and has much the stronger corresponding infrared absorption, and is taken as $v_3(a_1)$. That at 1420 cm⁻¹ is taken to arise from an A_1 sum-level such as 2×710 , or 432 + 982, interacting with v_3 . Two further moderately intense, depolarised Raman lines at 1358, 1233 cm⁻¹ are considered to identify v_{21} and v_{22} , respectively. (This value for the latter points up the unexpectedly high value (1333 cm⁻¹) of the highest a_2' fundamental for 1,3,5-trichlorobenzene, and again calls it in question [12].) A shoulder in the i.r. at 1370 cm⁻¹ is attributed to 193 + 1180(A_1) or 376 + 984(A_1).

Polarised Raman lines establish v_4 , v_6 , v_9 at 1180, 982 and 385 cm⁻¹, successively, but neither v_7 nor v_8 are identified with such certainty—the choices made, of 823 and 421 cm⁻¹ having somewhat lower depolarisation ratios from the alternatives of 811, 469 cm⁻¹ which are placed in the b_2 class.

The 'umbrella' $\gamma(CH)$ mode certainly affords the intense absorption at 855 cm⁻¹, and that at 1710 cm⁻¹ is very likely its overtone; but the use of 865 cm⁻¹ for the $a_2 \gamma(CH)$ mode v_{11} seems rather a low value and there is no sum-level to substantiate it. Whilst the weak features observed ~ 580 cm⁻¹ are attributed to $v_{12}(a_2)$ in Table 5, they could arise from 198 + 385(A_1), and a very weak infrared band at 527 cm⁻¹ is a possible alternative for the fundamental.

Remaining observed features are—

900 (906, R, p): $426 + 468(A_1)$, 930: $2 \times 468(A_1)$; 1117(R, p): $2 \times 553(A_1)$; 1141: $553 + 583(B_2)$; 1295: $468 + 825(B_2)$; 1310: $583 + 715(B_2)$; 1452: $468 + 982(B_2)$; 1522(R): $432 + 1086(A_1)$.

5. 2,4,6-TRIFLUOROPYRIMIDINE

The vibrational spectra of 2,4,6-trifluoropyrimidine have been interpreted [6] with the guidance of the data for 1,3,5-trifluorobenzene, and the results of calculations using force constants transferred from benzene and hexafluorobenzene. However the corresponding fundamentals for 1,3,5-trifluorobenzene, 2,4,6-trifluoropyrimidine should additionally form a smooth progression

of values, and this is found to be so for the a_1 and b_2 classes where the assignments are well founded on the observed spectra.

For the a_2 class the values in Table 5 suggest that the highest fundamental for the pyrimidine should lie ~600 cm⁻¹ rather than at 511 cm⁻¹, as proposed [6]. Accordingly, the value 600 cm⁻¹ is now taken and the feature at 511 cm⁻¹ attributed to 2 × 260(A_1). Although this involves the appearance of an a_2 fundamental in absorption, this is considered a more likely interpretation than that of 258(b_1) + 358(a_1). A revision of the b_2 fundamentals for 2,4,6-trifluoropyrimidine, corresponding to v_{25} and v_{26} in Table 5, is also indicated by the values therein. Rather than 528 and 465 cm⁻¹, respectively are 643 and 528 cm⁻¹, respectively, now proposed thus establishing a smooth progression of values. Use of the features at 643 cm⁻¹ as a fundamental is again more satisfactory than the implausible $a_2 + b_2$ sum-level requiring cross terms in the potential energy for non-planar and planar vibrations. The weak feature at 465 cm⁻¹ is now accounted for as 2 × 233(A_1) or 210 + 260(B_2).

By contrast, location of the lowest b_2 fundamental of 2,4,6-trifluoropyrimidine at 369 cm⁻¹ is consistent with the values in Table 5. The value calculated with the transferred force constants is ~70 cm⁻¹ too low, as are those for the next two highest fundamentals, with the present assignment. This points the need for significant change(s) of force constant. Other trends must reflect a similar regular change of force constant. For example, the essentially ring twisting vibrations r_{15} , r_{16} of Table 5 increase smoothly on the insertions of nitrogen atoms into the ring (the values for 2,4,6-trifluoropyrimidine are 693 and 774 cm⁻¹, respectively). Obviously acceptable force fields for these molecules must reproduce such trends and values established by the observed spectra, and which are inadequately predicted by simple transference of force constants between the molecules.

EXPERIMENTAL

6.1 Materials

Commercial samples, from suppliers or Plant Protection Ltd, were purified and their purity checked by gas chromatography. Melting temperatures (°C) were as follows (literature values (14) in parentheses): 2,6-dichloro-, 86.7 (85-87); 2,6-dibromo-, 118.5 (118.5-119); 3,5-dichloro-, 65.0 (67-68); 2,5-dichloro-, 59.4 (59-60); 2,5-dibromo-, 93.1 (93-94); 2,3-dichloropyridine, 66.2 (66.5-67).

3,5-Dibromopyridine was prepared as follows (cf. [15]). To 20 ml of dry pyridine were added dropwise 29 ml of sulphuryl chloride, the mixture being cooled during the addition, after which the temperature was raised to 90°C and 32 ml of bromine added slowly during 2 hr. The mixture was stirred for 4 hr, whilst the temperature was raised to 130°C, and was then poured onto crushed ice, and neutralized with 40% aqueous sodium hydroxide. The crude product, extracted by steam distillation, was recrystallized from ethanol to constant melting temperature, 110.7°C (lit. [14] 111.5–112°C). Found: C, 25.2; H, 1.26; N, 5.97; Calc. for C₅H₃NBr₂: C, 25.3; H, 1.26; N, 5.91. The sample was pure by gas chromatography.

6.2 Vibrational spectroscopy

Infrared spectra were measured using Perkin-Elmer 457, 625 and 301 spectrophotometers. The tabulated data relate to solutions in carbon tetrachloride ($3650-1300 \text{ cm}^{-1}$), carbon disulphide ($1400-400 \text{ cm}^{-1}$) and cyclohexane ($500-50 \text{ cm}^{-1}$). Raman spectra excited with a

^[14] E. KLINGSBERG (Editor), Pyridine and its Derivatives, pp. 386-388, Interscience, New York (1961).

^[15] T. BATKOWSKI, D. TOMASIK and P. TOMASIK, Roczniki Chemii 41, 2101 (1967).

Spectraphysics Model 140 ionized argon laser (488 nm) were measured with a Spex 1401 double monochromator.

6.3 Nuclear magnetic resonance spectroscopy

NMR spectra of 10% solutions in carbon tetrachloride were determined as part of the characterisation of the materials. Chemical shifts (Table 6) were measured relative to tetramethylsilane for proton spectra and external trifluoroacetic acid for fluorine spectra. With two exceptions, the proton spectra were readily interpreted as first order systems, the structures given unambiguously assuming the following shifts— $H_{2.6}$, 1·4–1·8; $H_{3.5}$, 2·6–2·8; H_4 , 2·0–2·4; and coupling constants (Hz)— $J_{2.3}$ and $J_{3.4}$, 5–9; $J_{2.4}$, 1·5–2·5; $J_{2.5}$, <0·5. For the fluoropyridines, the resonances of protons adjacent to the fluorine atoms were shifted by ~ 0.5 ppm above the normal range.

Table 6. Chemical shifts (τ) and coupling constants J(Hz) for substituted pyridines

	$ au_2$	$ au_{3}$	$ au_4$	J_{23}	J_{24}	J_{34}
2,6-dichloro-	-	2.78	2.4	_	-	8
2,6-dibromo-	-	2.6	2.6	-		*
2,5-dichloro-	1.65	2.75	2.38	0†	2.5	8
2,5-dibromo-	1.60	2.68	2.35	0†	2.5	8
3,5-dichloro-	1.52	-	2.30	_	2	_
3,5-dibromo-	1.42	-	2.02	-	2	-
2,3-dichloro-	1.75	2.82	2.25	5	2	9
2,4,6-trifluoro-	15·5‡	3.46	14 <u>†</u>	18	8	8
2,6-difluoro-	10·3±	3.18	2.07	Ň	8¶	8
2,4,6-trichloro-	- 1	2.78	-	_"		
2,4,6-trimethyl-	_	3.42		-	-	_

* Not observed owing to coincidence of H₂ and H₄.

† H₃-H₆ coupling.

f ppm to low field of trifluoroacetic acid. § This is probably a deceptively simple system. The proton-fluorine coupling gives a triplet (J = 1 Hz); but the coupling of F_s with H_s , and of F_6 with H_s are not expected to be the same.

|| Unresolved. || H-F coupling.

The spectrum of 2,6-dichloropyridine was more complex than expected for a first order system and the tabulated values were obtained assuming an AB_2 system. The spectrum of 2,6-dibromopyridine contained only a single line at 2.6τ . Addition of benzene to the solution resolved the spectrum but interpretation was prevented by the benzene.