Polyhalogenoaromatic Compounds. Part 42.[1] ^{13}C N.m.r. Spectra of Polyhalogeno-pyridines[2] and -pyrimidines

By **Brian Iddon,* Arthur G. Mack, Hans Suschitzky, Jack A. Taylor,** and **Basil J. Wakefield,*** The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

^{13}C N.m.r. spectra are reported for a number of polyhalogeno-pyridines and -pyrimidines. Substituent effects have been calculated and the results used to assign structures.

In a preliminary communication[2] we explained the difficulties of determining the structures of polychloroaromatic compounds and showed that ^{13}C n.m.r. spectroscopy was useful for this purpose. We have extended this study and now report our results in detail.

Our recorded ^{13}C n.m.r. spectra of 2- (2) and 3-chloropyridine (3) were in good agreement with those reported in the literature † (see Table 1). Assignments of the various chemical shifts for the monochloropyridines (2)—(4) were made by reference to the substituent effects produced by chlorine in chlorobenzene.[6] The substituent effects produced by chlorine in the three monochloropyridines (2)—(4) relative to pyridine (1) are shown in Table 2.‡ Using these values it is possible to predict the chemical shifts in various polychloropyridines by summation. For 2,6-dichloropyridine (5), for example, the substituent effects for the 2-Cl atom are assumed to be the same as those calculated for 2-chloropyridine (2) (Table 2) and the substituent effects for the 6-Cl atom are in the reverse order. Summation gives the total substituent effects for 2,6-dichloropyridine (5) relative to pyridine (1): +0.3 (at C-2), −1.8 (C-3), +5.2 (C-4), −1.8 (C-5), and +0.3 p.p.m. (C-6).‡ Addition of these effects to the observed chemical shifts for pyridine (1) gives predicted chemical shifts in very close agreement with the experimentally observed values (Table 3). Good agreement is found also (see Table 3) between the calculated and experimental values for other polychloropyridines [compounds (6), (7), and (10)] in which C-4 is unsubstituted. The few compounds [(8), (9), and (11)] studied which carry a chlorine substituent at the 4-position appear to give calculated results for C-4 which are *ca.* 3 p.p.m. higher than the experimental values, an observation for which we have no explanation at the present time. In compounds [(17)—(19)] containing other halogen substituents agreement is not as close, but the results enable structural assignments to be made (see later).

In Table 1 we record also the ^{13}C n.m.r. spectra of some 2(or 4)-substituted tetrachloropyridines. From these results the effects of several substituents have been calculated using pentachloropyridine (11) as the reference compound. The assignments of chemical shifts for pentachloropyridine (11), which are based on those reported[7] for pyridine (1) (Table 1), are supported by the assignments made for the tetrachloropyridines (8)—(10). In these compounds the proton-bearing C-atoms are readily identified by a large nuclear Overhauser effect and by an examination of the off-resonance proton-decoupled spectrum. Where two signals occur close together unambiguous assignments are not always possible.

A comparison of the spectrum of 4-bromotetrachloropyridine (14) with that of pentachloropyridine (11) (see Table 4) indicates that the bromine atom has a shielding effect of −7.6 p.p.m. on C-4, with a negligible effect on the other C-atoms. This enables the following chemical shifts, which are close to the experimental values (Table 1), to be calculated for 2-bromotetrachloropyridine (16): 138.6 (C-2), 129.7 (C-3), 145.0 (C-4), 128.1 (C-5),§ and 146.5 (C-6). Similar agreement is found between the calculated and experimental values for 3-bromotetrachloropyridine (18) (Table 3).§ Substituent effects for an iodine atom can be obtained similarly by comparison of the chemical shifts of tetrachloro-4-iodopyridine (15) with those of pentachloropyridine (11) (Table 1) and used to predict the ^{13}C n.m.r. chemical shifts for tetrachloro-6-iodo- (17) and tetrachloro-5-iodo-pyridine (19) (Table 3).§ The chemical shift values calculated for the iodine-carrying C-atoms in the α- and β-iodo-substituted compounds (17) and (19) are some 7.5—7.9 p.p.m. too high (Table 3). Greater accuracy in predicting chemical shifts can be obtained by using substituent effects for bromine and iodine (relative to pentachloropyridine) in the three isomers of bromo (or iodo) tetrachloropyridines derived from the observed spectra. These are given in Table 4. The anomalous effect of a 4-substituent is reflected again in these values. By summation of the substituent effects at each C-atom of the ring for a 4-bromine atom (Table 4) with those for the β-H atom in 2,3,4,6-tetrachloropyridine (9) (calculated from Table 1), and by addition of these values to the chemical-shift

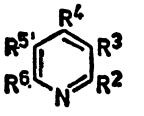
† The literature measurements were made with neat liquids[3] or (for solids) with solutions in benzene,[4] using carbon disulphide[3] or benzene[4] as internal standards, respectively. For convenience we have adjusted the recorded chemical shifts to the $SiMe_4$ convention by application of the factors 192.8 (for carbon disulphide) and 128.6 p.p.m. (for benzene), respectively.[5]

‡ Throughout this paper a + sign indicates a down-field shift and a − sign an up-field shift.

§ Substituent effects of −1.6 p.p.m. for bromine and zero p.p.m. for iodine have been applied, which correspond to the substituent effects on C-4 in bromobenzene[6] and iodobenzene,[8] respectively.

TABLE 1

^{13}C N.m.r. spectra of polychloropyridines



Compound no.	R^2	R^3	R^4	R^5	R^6	Chemical shifts (δ/p.p.m.) C-2	C-3	C-4	C-5	C-6	Others
(1) [a]	H	H	H	H	H	150.6	124.5	136.4	124.5	150.6	
(2) [b]	Cl	H	H	H	H	151.1	123.9	138.5	122.4	149.7	
c						152.0	125.0	139.6	123.1	150.3	
d						151.5	124.5	139.0	122.7	149.9	
(3) [b]	H	Cl	H	H	H	148.0	131.8	136.7	124.5	148.0	
c						149.4	132.5	136.1	125.0	148.3	
d						149.0	132.2	135.7	124.6	147.8	
(4)	H	H	Cl	H	H	150.9	124.2	144.0	124.2	150.9	
(5)	Cl	H	H	H	Cl	150.5	123.0	141.0	123.0	150.5	
(6)	Cl	Cl	H	H	H	149.0	130.5	138.8	123.4	147.3	
(7)	Cl	H	H	Cl	H	149.4	125.1	138.4	130.9	148.3	
(8) [d]	H	Cl	Cl	Cl	Cl	145.9	129.5	142.3	130.4	148.4	
(9)	Cl	H	Cl	Cl	Cl	147.8	124.4	145.7	128.7	149.5	
(10)	Cl	Cl	H	Cl	Cl	145.9	129.6	140.0	129.6	145.9	
(11)	Cl	Cl	Cl	Cl	Cl	146.2	129.7	144.7	129.7	146.2	
(12)	1-oxide of (11)					142.6	129.6	129.6	129.6	142.6	
(13) [e]	HCl salt of (4)					143.9	127.4	151.3	127.4	143.9	
(14)	Cl	Cl	Br	Cl	Cl	146.5	129.7	137.1	129.7	146.5	
(15) [f]	Cl	Cl	I	Cl	Cl	143.2	135.0	121.9	135.0	143.2	
(16) [f]	Br	Cl	Cl	Cl	Cl	138.0	132.4 [g]	144.0	130.0 [g]	146.7	
(17) [f]	I	Cl	Cl	Cl	Cl	115.5	136.9	141.6	130.6	146.7	
(18) [f,h]	Cl	Br	Cl	Cl	Cl	148.2	120.6	147.0	128.7	147.1	
(19) [f]	Cl	I	Cl	Cl	Cl	152.5	99.4	148.7	127.8	150.8	
(20) [e]	Cl	Cl	OH	Cl	Cl	145.0	117.9	160.0	117.9	145.0	
(21)	Cl	Cl	OMe	Cl	Cl	146.8	124.8	162.1	124.8	146.8	61.3 (q, Me)
(22)	Cl	Cl	$OCH_2CH{:}CH_2$	Cl	Cl	146.7	125.0	161.0	125.0	146.7	75.1 (t, CH_2), 120.2 (t, olefinic CH_2), 131.6 (d, CH)
(23)	Cl	Cl	$OCH_2C{:}{:}CH$	Cl	Cl	146.9	125.5	159.9	125.5	146.9	61.1 (t, CH_2), 76.3 (s, C), 78.1 (d, CH)
(24)	Cl	Cl	OPh	Cl	Cl	147.5	125.8	156.2	125.8	147.5	121.1 (d, C′-2,6), 131.0 (d, C′-4), 132.4 (d, C′-3,5), 147.0 (s, C′-1)
(25)	Cl	Cl	OC_6H_4Cl-*o*	Cl	Cl	147.3	125.0	157.2	125.0	147.3	115.4 (d, C′-6), 123.5 (s, C′-2), 125.0 (d, C′-4), 127.8 (d, C′-5), 131.2 (d, C′-3), 150.8 (s, C′-1)
(26)	Cl	Cl	OC_6H_4Br-*o*	Cl	Cl	147.2	125.1	157.2	125.1	147.2	112.2 (s, C′-2), 115.0 (d, C′-6), 125.3 (d, C′-4), 128.6 (d, C′-5), 134.3 (d, C′-3), 151.7 (s, C′-1)
(27)	OH	Cl	Cl	Cl	Cl	158.2	115.6	142.7 [g]	118.6	143.2 [g]	
(28)	OMe	Cl	Cl	Cl	Cl	157.15	116.9	143.6 [g]	121.8	144.1 [g]	55.6 (q, Me)
(29)	$OCH_2CH{:}CH_2$	Cl	Cl	Cl	Cl	156.4	117.0	143.6 [g]	121.8	144.0 [g]	68.8 (t, CH_2), 118.6 (t, olefinic CH_2), 131.7 (d, CH)
(30)	$OCH_2{:}{:}CH$	Cl	Cl	Cl	Cl	155.7	117.0	144.1 [g]	122.9	144.1 [g]	55.8 (t, CH_2), 75.7 (d, CH), 77.3 (s, C)
(31)	$OCH_2CH{:}CHMe$	Cl	Cl	Cl	Cl	156.6	117.0	143.4 [g]	121.5	143.9 [g]	17.9 (q, *trans*-Me), 69.0 (t, CH_2), 124.8 (d, CH), 131.8 (d, *C*HMe)

TABLE 1 (*Continued*)

Compound no.	R^2	R^3	R^4	R^5	R^6	Chemical shifts (δ/p.p.m.) C-2	C-3	C-4	C-5	C-6	Others
(32)	$OCH_2CH{:}CMe_2$	Cl	Cl	Cl	Cl	156.9	117.1	143.4 [g]	121.4	143.9 [g]	18.3 (q, *cis*-Me), 25.8 (q, *trans*-Me), 65.4 (t, CH_2), 118.4 (d, CH), 139.8 (s, C)
(33)	OC_6H_4Cl-*o*	Cl	Cl	Cl	Cl	155.8	117.6	144.6	124.1	146.5	123.8 (d, C′-6), 127.1 (d, C′-4), 129.6 (s, C′-2), 127.9 (d, C′-5), 130.6 (d, C′-3), 148.7 (s, C′-1)
(34)	OC_6H_4Br-*o*	Cl	Cl	Cl	Cl	156.9	117.5	144.3	124.0	146.3	123.8 (d, C′-6), 127.3 (d, C′-4), 128.6 (d, C′-5), 129.6 (s, C′-2), 133.7 (d, C′-3), 151.6 (s, C′-1)
(35) [e]	OH	H	H	Cl	H	161.7	119.8	135.5	112.6	141.2	
(36) [e]	Cl	OH	H	H	H	138.8	150.3	124.5 [g]	124.2 [g]	139.8	
(37)	Cl	Cl	NHMe	Cl	Cl	146.4	114.1	151.0	114.1	14.64	33.8 (q, Me)
(38)	Cl	Cl	NHEt	Cl	Cl	146.2	114.1	149.9	114.1	146.2	16.5 (q, Me), 41.3 (t, CH_2)
(39)	Cl	Cl	$NHCH_2CH{:}CH_2$	Cl	Cl	146.3	114.7	150.0	114.7	146.3	48.3 (t, CH_2), 117.6 (t, olefinic CH_2), 134.2 (d, CH)
(40)	Cl	Cl	NHPh	Cl	Cl	146.5	118.6	147.3	118.6	146.5	122.2 (d, C′-2,6), 125.1 (d, C′-4), 128.8 (d, C′-3,5), 138.9 (s, C′-1)
(41)	Cl	Cl	NHC_6H_4Cl-*o*	Cl	Cl	146.8	119.7	146.8	119.7	146.8	122.5 (d, C′-6), 125.7 (d, C′-4), 126.7 (s, C′-2), 127.0 (d, C′-5), 129.8 (d, C′-3), 135.9 (s, C′-1)
(42)	Cl	Cl	NHC_6H_4Br-*o*	Cl	Cl	146.8	119.8	147.7	119.8	146.8	116.9 (s, C′-2), 122.5 (d, C′-6), 126.0 (d, C′-4), 127.7 (d, C′-5), 133.1 (d, C′-3), 137.3 (s, C′-1)
(43)	Cl	Cl	NHC_6H_4Br-*p*	Cl	Cl	147.0	119.1	147.0	119.1	147.0	117.9 (s, C′-4), 123.5 (d, C′-2,6), 132.0 (d, C′-3,5), 138.3 (s, C′-1)
(44)	Cl	Cl	$NHC_6H_4Br_3$-2′,4′,6′	Cl	Cl	146.6	121.4	146.6	121.4	146.6	116.4 (s, C′-4), 124.1 (s, C′-2,6), 134.4 (d, C′-3,5), 135.6 (s, C′-1)
(45)	Cl	Cl	NMe_2	Cl	Cl	146.8	125.8	156.4	125.8	146.8	42.75 (q, Me)
(46)	Cl	Cl	piperidin-1-yl	Cl	Cl	146.9	126.0	156.1	126.0	146.9	24.0 (γ-CH_2), 26.4 (β-CH_2), 51.9 (α-CH_2)
(47)	NH_2	Cl	Cl	Cl	Cl	153.9	112.3	141.6	115.3	145.3	
(48)	NHMe	Cl	Cl	Cl	Cl	152.7	113.1	140.8	115.9	146.1	28.8 (q, Me)
(49)	NHEt	Cl	Cl	Cl	Cl	151.7	112.5	141.0	115.3	145.7	14.6 (q, Me), 36.9 (t, CH_2)
(50)	$NHCH_2CH{:}CH_2$	Cl	Cl	Cl	Cl	151.3	112.6	141.2	115.8	145.6	44.2 (t, CH_2), 116.8 (t, olefinic CH_2), 133.8 (d, CH)
(51) [f]	NHC_6H_4Br-*o*	Cl	Cl	Cl	Cl	148.4	114.3	141.8	119.3	145.4	116.9 (s, C′-2), 121.0 (d, C′-6), 124.1 (d, C′-4), 128.5 (d, C′-5), 132.5 (d, C′-3), 136.6 (s, C′-1)
(52)	NHC_6H_4Br-*p*	Cl	Cl	Cl	Cl	148.4	114.0	142.4	119.0	145.5	116.5 (s, C′-4), 121.7 (d, C′-2,6) 132.1 (d, C′-3,5), 137.6 (s, C′-1)

TABLE 1 (*Continued*)

Compound no.	R^2	R^3	R^4	R^5	R^6	Chemical shifts (δ/p.p.m.) C-2	C-3	C-4	C-5	C-6	Others
(53)	NMe_2	Cl	Cl	Cl	Cl	156.1	117.0	143.5	119.0	144.4	41.4 (q, Me)
(54)	piperidin-1-yl	Cl	Cl	Cl	Cl	156.6	119.4 [g]	143.4 [g]	120.25 [g]	144.7 [g]	24.4 (γ-CH_2), 25.75 (β-CH_2), 50.3 (α-CH_2)
(55)	Cl	SH	Cl	Cl	Cl	143.9	131.8	141.4	129.0	145.5	
(56) [j]	Cl	Cl	SH	Cl	Cl	145.6	126.1	149.8	126.1	145.6	
(57)	Cl	Cl	SMe	Cl	Cl	146.0	132.9	150.2	132.9	146.0	18.5 (q, Me)
(58)	Cl	Cl	$SCH_2CH{:}CH_2$	Cl	Cl	145.8	134.2	147.6	134.2	145.8	38.0 (t, CH_2), 118.9 (t, olefinic CH_2), 131.8 (d, CH)
(59)	Cl	Cl	$SCH_2C{:}CH$	Cl	Cl	146.2 [g]	134.5	146.5 [g]	134.5	146.2 [g]	22.85 (t, CH_2), 73.5 (d, CH), 77.3 (s, C)
(60)	Cl	Cl	SPh	Cl	Cl	146.4	133.7	147.5	133.7	146.4	128.0 (d), 129.4 (d), 130.0 (d, C′-2,3,4,5,6), 131.8 (s, C′-1)
(61)	Cl	Cl	SC_6H_4Cl-*o*	Cl	Cl	146.7	134.9 [k]	146.7	134.9 [k]	146.7	127.7 (d, C′-6), 128.5 (s, C′-2), 129.3 (d, C′-5), 130.4 (d, C′-4), 131.2 (d, C′-3), 133.5 (s, C′-1) [k]
(62)	Cl	Cl	SC_6H_4Br-*o*	Cl	Cl	146.8	133.6 [k]	147.1	133.6 [k]	146.8	124.5 (s, C′-2), 129.2 (m, C′-4, C′-5), 130.75 (d, C′-6), 133.7 (d, C′-3)
(63)	Cl	Cl	2-thienylthio	Cl	Cl	146.5	133.7	147.4	133.7	146.5	127.5 (s, thienyl 2-C), 127.5 (d), 131.5 (d), 136.3 (d, thiophen ring C-atoms)
(64) [e]	Cl	Cl	SCN	Cl	Cl	145.9	133.5	139.6	133.5	145.9	107.5 (s, SCN)
(65)	Cl	Cl	SOMe	Cl	Cl	147.6	128.1	152.0	128.1	147.6	37.8 (q, SMe)
(66) [e]	Cl	Cl	SO_2Me	Cl	Cl	143.4	129.6	132.6	129.6	143.4	44.2 (q, SO_2Me)
(67) [e]	Cl	Cl	SO_2NH_2	Cl	Cl	147.8	127.5	150.2	127.5	147.8	
(68)	Cl	Cl	SO_2NHMe	Cl	Cl	147.9	128.1	147.9	128.1	147.9	28.5 (q, Me)
(69) [e]	Cl	Cl	SO_3H	Cl	Cl	147.2	121.35	140.7	121.35	147.2	
(70)	Cl	Cl	Ph	Cl	Cl	146.4	129.9	151.8	129.9	146.4	128.1, 128.8, 129.5 (aromatic), 135.1 (s, C′-1)
(71)	Cl	Ph	Cl	Cl	Cl	147.6	136.2	145.7	129.9	146.0	127.0, 128.9, 129.1 (aromatic), 130.9 (s, C′-1)
(72)	Ph	Cl	Cl	Cl	Cl	155.2	130.5	145.1	128.9	145.7	128.3, 129.6, 129.8 (aromatic), 136.7 (s, C′-1)
(73)	Cl	CN	Cl	Cl	Cl	148.9	111.7	148.1	129.2	151.6	111.7 (s, CN)
(74)	CN	Cl	Cl	Cl	Cl	129.3	133.8	144.0	135.5	148.5	112.3 (s, CN)
(75)	Cl	Cl	COPh	Cl	Cl	146.8	126.4	149.3	126.4	146.8	129.5 (d, C′-3,5), 133.4 (s, C′-1), 135.4 (d, C′-2,4,6), 188.5 (CO)

[a] From G. C. Levy and G. L. Nelson, in ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972, p. 99. [b] From H. L. Retcofsky and R. A. Friedel, *U.S. Bur. Mines Bull.*, 1969, No. 649 (*Chem. Abs.*, 1969, **71**, 65812) (adjusted). [c] From C. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. Pharm. Bull.* (*Japan*), 1972, **20**, 429 (adjusted). [d] Neat liquid. [e] In Me_2SO. [f] From A. G. Mack, H. Suschitzky, and B. J. Wakefield, *J.C.S. Perkin I*, 1979, 1472. [g] Assignments could not be made unambiguously (see Discussion). [h] In tetrachlorothiophen, δ 121.2 and 122.8 p.p.m. [i] $CDCl_3$–Me_2SO. [j] $CDCl_3$–dioxan. [k] C-3,C-5 and C′-1 indistinguishable.

values of pentachloropyridine (11) (Table 1) it is possible to make the following assignments for 4-bromo-2,3,6-trichloropyridine (76): 148.1 (147.8) (C-2), 121.4 (127.5) (C-3), 138.1 (135.9) (C-4), 128.7 (d) (130.6) (C-5), and 149.8 (149.0) (C-6) (the experimental values are in parentheses).

4-Substituted tetrachloropyridines show only three resonance signals, whereas their 2 (or 3)-substituted isomers display five signals, as expected.

The ^{13}C n.m.r. spectrum of pentachloropyridine 1-oxide exhibits only two signals at δ 129.6 and 142.6 p.p.m. By analogy with the results reported recently in the literature for pyridine 1-oxides [9] we suggest that the β- and γ-C-atom signals are accidentally equivalent at δ 129.6 p.p.m. (and not as suggested in our preliminary communication [2]).

TABLE 2

Chlorine substituent effects on ^{13}C n.m.r. spectra of monochloropyridines

Compound no.	Substituent effects (δ/p.p.m.) C-2	C-3	C-4	C-5	C-6
(2) (α-Cl)	+0.9	0	+2.6	−1.8	−0.6
(3) (β-Cl)	−1.6	+7.7	−0.7	+0.1	−2.8
(4) (γ-Cl)	+0.3	−0.3	+7.6	−0.3	+0.3

Similar effects are observed with their 2-isomers [compounds (27)—(34) in Table 1] and similar comparisons can be made (Table 1) for other 2- (and 4)-substituted tetrachloropyridines. These are summarised in Table 5. For 2-substituted tetrachloropyridines the signals for C-4 and C-6 often appear close together and it has not been possible to assign these unambiguously in these cases. By an examination of Table 5 it can be seen that a 4-alkoxy- (or aryloxy)-group exerts a strong inductive effect (−*I*) on the C-atoms to which it is attached but little mesomeric effect on the adjacent C-atoms, presumably because of steric inhibition of resonance. By contrast, however, a 2-alkoxy(or aryloxy)-group strongly shields the adjacent C-atom *via* a mesomeric effect and deshields the C-atom to which it is attached by an inductive effect. Similar comparisons can be made (see Table 5) between 4-alkyl (and aryl)amino-groups and 2-alkyl (and aryl)amino-groups. In the case of 4-(secondary amino)-substituents, however, the steric inhibition of resonance is apparently less than in the case of an oxygen substituent at this position. A comparison of a 4-(tertiary amino)-substituent with a 2-(tertiary amino)-substituent is more marked in terms of steric inhibition of resonance at the 4-position. In the case of

TABLE 3

Comparison of calculated and observed ^{13}C n.m.r. chemical shifts for some polychloropyridines [a]

Compound no.	C-2	C-3	C-4	C-5	C-6
(5)	150.9 (150.5)	122.7 (123.0)	141.6 (141.0)	122.7 (123.0)	150.9 (150.5)
(6)	149.9 (149.0)	132.2 (130.5)	138.3 (138.8)	122.8 (123.4)	147.2 (147.3)
(7)	148.7 (149.4)	124.6 (125.1)	138.3 (138.4)	130.4 (130.9)	148.4 (148.3)
(8)	145.9 (145.9)	130.2 (129.5)	145.2 (142.3)	132.0 (130.4)	147.4 (148.4)
(9)	148.4 (147.8)	122.5 (124.4)	148.5 (145.7)	130.1 (128.7)	149.6 (149.5)
(10)	146.5 (145.9)	130.5 (129.6)	140.2 (140.0)	130.5 (129.6)	146.5 (145.9)
(11)	146.8 (146.2)	130.2 (129.7)	147.8 (144.7)	130.2 (129.7)	146.8 (146.2)
(17)	123.4 (115.5)	135.0 (136.9)	141.7 (141.6)	129.7 (130.6)	143.2 (146.5)
(18)	146.2 (148.2)	122.1 (120.6)	144.7 (147.0)	130.0 (128.7)	144.6 (147.1)
(19)	151.5 (152.2)	106.9 (99.4)	150.0 (148.7)	126.7 (127.8)	146.2 (150.8)

[a] The experimental values are in parentheses.

Tetrachloropyridines substituted also by a hydroxy-, alkoxy-, or aryloxy-group in position 4 [compounds (20)—(26) in Table 1] display a marked similarity for the chemical shifts of the different ring C-atoms, C-4 being

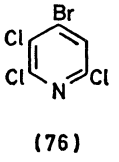
TABLE 4

Substituent effects of bromine and iodine in bromo- or iodo-tetrachloropyridines relative to pentachloropyridine

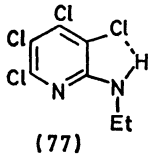
Substituent	Substituent effects (δ/p.p.m.) C-Br (or -I)	*'ortho'*	*'meta'*	*'para'*
4-Br	−7.6	0.0	+0.3	
3(5)-Br	−9.1	+2.15 [a]	−1.0	+0.9
2(6)-Br	−8.2	+2.7	−0.1 [a]	+0.3
4-I	−22.8	+5.3	−3.0	
3(5)-I	−30.3	+5.15 [a]	−1.9	+4.6
2(6)-I	−30.7	+7.2	−1.3 [a]	+0.9

[a] Average value.

deshielded relative to C-4 in pentachloropyridine by 12.5—17.4 p.p.m., C-3 and C-5 being shielded by 3.9—4.9 p.p.m. [excepting tetrachloro-4-hydroxypyridine (20) in this case], whilst C-2 and C-6 are little affected. tetrachloro-4-ethylaminopyridine (38) only the signal for C-3 shows coupling with the N-H proton (*J* 6.6 Hz) whereas for its 2-isomer (49) the signals for C-2, C-3, and C-6 are coupled with the N-H proton (*J* 3.5, 2.3, and 3.5



(76)



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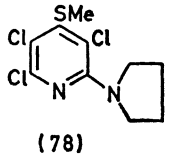


(78)

Hz, respectively). The magnitude of the long-range (4-bond) coupling between C-6 and the N-H proton in the 2-isomer indicates that this compound exists in solution predominantly in the conformation shown (77), in which the bonds have the favourable W-geometry. Hydrogen bonding, as shown in (77), probably slows down the rate of exchange of the N-H proton, thus allowing the coupling to be observed. In tetrachloro-4-ethylaminopyridine (38) the bulky β-chlorine atoms (enhanced by the butressing effect of the α-chlorine atoms) prevent the

TABLE 5

Substituent effects in 2(or 4)-substituted tetrachloropyridines relative to pentachloropyridine

Substituent	Substituent effects (δ/p.p.m.) [a] C-2	C-3	C-4	C-5	C-6
4-OR	+0.5 to +0.7 (0.6)	−4.2 to −4.9 (4.6)	+15.2 to +17.4 (16.3)	−4.2 to −4.9 (4.6)	+0.5 to +0.7 (0.6)
4-OAr	+1.0 to +1.3 (1.1)	−3.9 to −4.7 (4.4)	+11.5 to +12.5 (12.0)	−3.9 to −4.7 (4.4)	+1.0 to +1.3 (1.1)
2-OR	+9.5 to +10.95 (10.35)	−12.6 to −12.8 (12.3)	−0.6 to −1.3 (1.1)	−7.9 to −8.3 (7.8)	−2.1 to −2.3 (2.2)
2-OAr	+9.6 to +10.7 (10.15)	−12.1 to −12.2 (12.15)	−0.1 to −0.4 (0.25)	−5.6 to −5.7 (5.65)	+0.1 to +0.3 (0.2)
4-NHR	+0.1 to +0.2 (0.1)	−15.0 to −15.6 (15.4)	+5.2 to +6.3 (5.6)	−15.0 to −15.6 (15.4)	+0.1 to +0.2 (0.1)
4-NHAr	+0.3 to +0.8 (0.5)	−8.3 to −11.1 (10.0)	+1.9 to +3.0 (2.4)	−8.3 to −11.1 (10.0)	+0.3 to +0.8 (0.5)
2-NHR	+5.1 to +6.5 (5.7)	−16.6 to −17.2 (17.0)	−3.5 to −3.9 (3.7)	−13.8 to −14.4 (14.0)	−0.1 to −0.6 (0.4)
2-NHAr	−2.2	−15.4 to −15.7 (15.55)	−2.3 to −2.9 (2.6)	−10.4 to −10.7 (10.55)	−0.7 to −0.8 (0.75)
4-NR_2	+0.6 to +0.7 (0.65)	−3.7 to −3.9 (3.8)	+11.4 to +11.7 (11.55)	−3.7 to −3.9 (3.8)	+0.6 to +0.7 (0.65)
2-NR_2	+9.9 to +10.4 (10.15)	−10.3 to −12.7 (11.5)	−1.2 to −1.3 (1.25)	−9.45 to −10.7 (10.1)	−1.5 to −1.8 (1.65)
4-SR	0.0 to −0.4 (0.2)	+3.2 to +4.8 (4.2)	+1.8 to +5.5 (3.4)	+3.2 to +4.8 (4.2)	0.0 to −0.4 (0.2)
4-SAr	+0.2 to +0.6 (0.4)	+3.9 to +5.2 (4.3)	+2.0 to +2.8 (2.5)	+3.9 to +5.2 (4.3)	+0.2 to +0.6 (0.4)

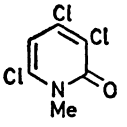
[a] Mean values in parentheses.

ethylamino-group from adopting the favourable W-conformation.

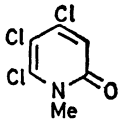
To illustrate further how the results discussed so far can be applied to the calculation of chemical shifts for more complex systems we refer to the ^{13}C n.m.r. spectrum of 2,3,5-trichloro-4-(methylthio)-6-pyrrolidin-1-ylpyridine (78) in which the signals for the pyridine ring C-atoms appear at δ 118.4, 120.3, 144.2, 147.9, and 153.1 p.p.m., the methyl group signal appears at δ 18.4 p.p.m., whilst the α- and β-C-atoms of the pyrrolidine ring appear at δ 50.5 and 25.7 p.p.m. respectively. By summation of the substituent effects for a 4-*S*-alkyl substituent (Table 5) with those for a 2-(tertiary amino)-substituent (Table 5) (using the mean values) and by addition of these additive substituent effects for each C-atom of the pyridine ring to the observed chemical shift values (Table 1) for pentachloropyridine, the following assignments can be made (the calculated values are in parentheses): 118.4 (122.4) (C-3), 120.3 (123.8) (C-5), 144.2 (144.35) (C-6), 147.9 (146.85) (C-4), and 153.1 p.p.m. (156.15) (C-2).

In Part 40 [10] we reported the preparations of some polychloro-2-pyridones. Their ^{13}C n.m.r. spectral data together with those of some related compounds synthesised previously [11,12] are given in Table 6. The structure of 5-chloro-1-methyl-2-pyridone (79) followed from its synthesis (see Experimental section) and from an examination of its ^1H n.m.r. spectrum. Assignments for the ^{13}C n.m.r. chemical shifts of this compound then followed from an examination of the off-resonance proton-decoupled spectrum and led to the assignments given in Table 6 for compounds (80)—(87). Assignment for 3,5,6-trichloro-1-methyl-2-pyridone (80) can be made unambiguously by reference to its off-resonance proton-decoupled spectrum.

Hydrolysis of 2,3,4,6-tetrachloro-1-methylpyridinium fluorosulphonate could give rise to two products, (81)



(81)

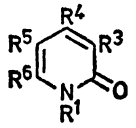


(88)

and (88), but in practice only one product was obtained. The ^{13}C n.m.r. spectrum of this compound (Table 6) suggests that it is 3,4,6-trichloro-1-methyl-2-pyridone

TABLE 6

^{13}C N.m.r. spectra of some polychloro-2-pyridones



Compound no.	R^1	Substituents R^3	R^4	R^5	R^6	Chemical shifts (δ/p.p.m.) C-2	C-3	C-4	C-5	C-6	Other
(79)	Me	H	H	Cl	H	161.3	140.3d	121.3d	111.8	136.2d	37.4 (q, Me)
(80)	Me	Cl	H	Cl	Cl	157.7	124.75	137.2d	110.2	134.5	35.6 (q, Me)
(81)	Me	Cl	Cl	H	Cl	158.3	122.6	142.7	107.5d	136.2	34.5 (q, Me)
(82)	Me	Cl	Cl	Cl	Cl	156.65	124.2	142.6	111.5	135.2	36.0 (q, Me)
(83)	$CH_2CH{:}CH_2$	Cl	Cl	Cl	Cl	156.3	124.6	142.9	111.8	134.7	51.1 (t, CH_2), 119.8 (t, olefinic CH_2), 129.8 (d, CH)
(84)	$CH_2CH{:}CMe_2$	Cl	Cl	Cl	Cl	156.3	124.5	142.5	111.5	134.6	18.4 (q, *cis*-Me), 25.8 (q, *trans*-Me), 47.9 (t, CH_2), 116.7 (d, CH), 139.1 (s, C)
(85)	OMe	Cl	Cl	Cl	Cl	153.1	125.5	142.35	110.5	134.6	65.0 (q, Me)
(86)	$OCH_2CH{:}CH_2$	Cl	Cl	Cl	Cl	153.4	125.3	142.3	110.4	135.0	78.4 (t, CH_2), 123.8 (t, olefinic CH_2), 129.5 (d, CH)
(87)	OCH_2Ph	Cl	Cl	Cl	Cl	153.2	125.2	142.1	111.3	134.8	79.2 (t, CH_2), 128.5 (d), 129.6 (d), 130.1 (d), 132.3 (s) (all aromatic)

(81) and this assignment of structure is supported by the absence of any long-range ^1H–^{13}C coupling between the proton and carbonyl C-atom in (81). The long-range ^1H–^{13}C coupling constants have been reported for pyridine.[13] From this information, the expected long-range ^1H–^{13}C coupling of the ring proton to the carbonyl C-atom (readily identified by its ^{13}C n.m.r. chemical shift) would be in the order of 4.6 Hz for compound (88) and less than 0.8 Hz for compound (81). In further support of the assignment of structure (81), the observed coupling constants $J_{C^6H^6}$ and $J_{C^3H^5}$, for pyridine are 4.6 and 6.7 Hz, respectively, whilst those for our product (81) are 3.4 and 7.5 Hz, respectively. The observed coupling constant, $J_{C^5H^5}$, for this compound was 181.7 Hz whilst the ^1H–^{13}C coupling for the methyl group was 143.5 Hz.

In Part 40 [10] we reported also that allyl 2,3,5,6-tetrachloro-4-pyridyl ether (22) undergoes a Claisen rearrangement to give the phenol (89) (major product) together with compounds (90) and (91). The phenol (89) displayed in its ^{13}C n.m.r. spectrum signals at δ 31.35 (t), 116.7 (s), 117.1 (t), 121.9 (s), 132.4 (d), 145.5 (s), 148.3 (s), and 159.9 (s) p.p.m. The signals at δ 31.35, 132.4, and 117.1 p.p.m. are readily attributed to the α-, β-, and γ-C-atoms of the allyl group. From the information given in Table 1 the signal at δ 159.9 p.p.m. can be assigned to C-4 whilst those at 145.5 and 148.3, and at 116.7 and 121.9 p.p.m. can be assigned to C-2, C-6 and C-3, C-5, respectively (unambiguous assignments for these C-atoms is not possible on the information available). The furopyridine (90) exhibits signals (in CCl_4) at 21.7 (q), 35.5 (t), 84.45 (d), 111.1 (s), 123.4 (s), 142.4(s), 146.9 (s), and 164.9 p.p.m. (s). The signals at 35.5, 84.45, and 21.7 p.p.m. can be assigned to C-a and C-b of the furan ring and C-c of the methyl group [see (90)]. By reference to Table 1, the signal at 164.9 p.p.m. can be assigned to C-4 whilst those at 142.4 and 146.9 and at 111.1 and 123.4 p.p.m. can be assigned to C-2, C-6 and C-3, C-5, respectively (unambiguous assignments not possible for these C-atoms). Similar assignments can be made for compound (91) as follows: δ 31.9 (t,C-a), 85.0 (d, C-b), 45.5 (t, C-c), 164.9 (s, C-4), 142.7 and 147.8 (both s, C-2, C-6), and 111.7 and 122.5 p.p.m. (both s, C-3, C-5).

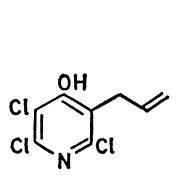
Irradiation of 4-benzyltetrachloropyridine in THF [1] gives a product for which structure (92) can be assigned from an examination of its ^{13}C n.m.r. spectrum. For the starting material the following signals are observed: 38.7 (t), 127.0 (d), 128.3 (d), 128.6 (d), 130.5 (s), 134.9 (s), 146.3 (s), and 150.4 p.p.m. (s). The signal at 38.7 p.p.m. can be assigned to the methylene C-atom and those at 127.0, 128.3, and 128.6 p.p.m. to those C-atoms bonded to hydrogen in the phenyl group. After reference to the ^{13}C n.m.r. spectrum of toluene [6] the remaining phenyl-group C-atom can be assigned to the signal at 134.9 p.p.m. The signals at 150.4 and 146.3 p.p.m. can be assigned (though not unambiguously) to

TABLE 7

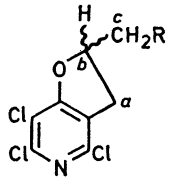
^{13}C N.m.r. chemical shifts of some chlorofluoropyridines

Compound no.	Solvent	Chemical shifts (δ/p.p.m.) C-2	C-3	C-4	C-5	C-6	Apparent coupling constants (J_{CF}/Hz) [a]
 (93)	$CHCl_3$	145.6d	127.8d	144.9d	116.9d	155.7d	$J_{C^2F^6}$ 15, $J_{C^3F^6}$ 6, $J_{C^4F^6}$ 14, $J_{C^5F^6}$ 35, $J_{C^6F^6}$ 244
 (94)	$CDCl_3$	143.4d	129.8d	134.3d	151.1d	135.2d	$J_{C^2F^5}$ 4, $J_{C^3F^5}$ very small, $J_{C^4F^5}$ 51, $J_{C^5F^5}$ 266, $J_{C^6F^5}$ 54
 (95)	Neat liq.	155.4dd	114.8t [b]	147.6s	114.8t *	155.4dd	$J_{C^2F^3}$ ($J_{C^6F^6}$) 247, $J_{C^2F^5}$ ($J_{C^6F^2}$) 15.6, $J_{C^3F^2}$ ($J_{C^5F^6}$),[b] $J_{C^4F^2}$ ($J_{C^4F^6}$) very small
 (96)	Neat liq.	156.2	104.7	164.1	104.7	156.2	$J_{C^2F^3}$ ($J_{C^6F^6}$) 246, $J_{C^2F^4}$ ($J_{C^6F^4}$) 7, $J_{C^2F^6}$ ($J_{C^6F^2}$) 17, $J_{C^3F^2}$ ($J_{C^5F^6}$) 42.5, $J_{C^3F^4}$ ($J_{C^5F^4}$) 21, $J_{C^4F^4}$ 264, $J_{C^4F^2}$ ($J_{C^4F^6}$) 7

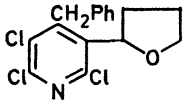
[a] These ' coupling constants ' are those derived from a first-order analysis of the spectra. See text for discussion. [b] Sum of $J_{C^3F^2}$ and $J_{C^3F^6}$ is 40 Hz. [b] ' Inverted triplet ' (see Discussion).



(89)



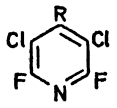
(90) R = H
(91) R = Cl



(92)

TABLE 8

^{13}C N.m.r. chemical shifts and multiplicities [a] of 4-substituted-3,5-dichloro-2,6-difluoropyridines



Compound no.	R	Chemical shifts (δ/p.p.m.; in $CHCl_3$ or $CDCl_3$ unless otherwise stated) C-2,C-6	C-3,C-5	C-4	Others	Coupling constants (Hz) [b] $J_{C^2F^2}$ ($J_{C^6F^6}$)	$J_{C^2F^6}$ ($J_{C^6F^2}$)	$J_{C^2F^2} + J_{C^2F^6}$
(97)	OCH_2Ph	155.7dd	108.9t *	163.8s	76.0 (t, CH_2Ph), 128.4, 128.9 (both d, aromatic), 134.8 (s, C′-1)	245	18	37
(98)	OC_6H_4Br-*o*	156.1dd	109.1t *	152.0s	112.5 (s, C′-2) 115.9 (d, C′-6), 125.7 (d, C′-4), 128.7 (d, C′-5), 134.3 (d, C′-3), 160.1 (s, C′-1)	245	17	42
(99)	OC_6H_4Cl-*o*	156.2dd	109.0t *	151.0s	116.4 (d, C′-6), 123.9 (s, C′-2), 125.5 (d, C′-4), 128.0 (d, C′-5), 131.3 (d, C′-3), 160.2 (s, C′-1)	245	17	42
(100)	OC_6Cl_5	155.6dd	105.4t *	158.5s	126.2 (s, C′-2,6), 131.4 (s, C′-4), 132.5 (s, C′-3/5), 146.9 (s, C′-1)	245	17	41
(101)	NH_2	155.6	97.0 *	152.3		238	18	41
(102)	$NH{\cdot}CO{\cdot}CH_2Cl$	155.7dd	97.0t *	152.3s	42.6 (t, CH_2), 163.9 (s, C:O)	237	19	41
(103)	$NH{\cdot}CO{\cdot}CH_2SC_6H_4Br$-*o* [c]	154.9dd	112.0t *	148.2s	36.1 (t, CH_2), 122.2 (s, C′-2), 127.1, 128.0, 128.3, 132.7 (all doublets, C′-3—C′-6), 136.8 (s, C′-1), 166.2 (s, C:O)	244	17	39
(104)	$NH{\cdot}CO{\cdot}CH_2SO_2C_6H_4Br$-*o* [c]	155.4dd	111.4t *	147.3s	41.1 (t, CH_2), 121.1 (s, C′-2), 128.0, 132.6, 135.2, 135.5 (all doublets, C′-3—C′-6), 138.3 (s, C′-1), 159 (s, C:O)	244	17	38
(105)	$NH{\cdot}C_5NCl_2F_2$-4 [d]	155.8	106.9 *	147.7		244	18	43
(106)	SO_2Cl	156.6dd	114.9t *	150.4s		248	14	36
(107)	SEt	155.3dd	118.1t *	152.4s	15.1 (q, Me), 29.9 (t, CH_2)	248	15	39
(108)	SPh	155.4dd	118.0t *	151.1s	128.5 (d, C′-4), 129.6 (d, C′-2,6), 131.1 (d, C′-3,5), 131.6 (s, C′-1)	248	15	39
(109)	SC_6H_4Br-*o*	155.8dd	118.2t *	150.4s	125.3 (s, C′-2), 128.3, 129.6, 131.6 (all doublets, C′-3—C′-6), 132.3 (s, C′-1)	232	14	*ca.* 40
(110)	SC_5H_4N-2 [e]	155.4dd	119.1t *	154.6s	121.7 (C′-5), 123.2 (C′-2, C′-3), 137.4 (C′-4), 150.4 (C′-6)	246	14	36

[a] Multiplicities for the pyridine ring signals are those observed in the proton-decoupled spectra; those for the other signals are observed in the ' off-resonance ' spectra. [b] $J_{C^4F^2}$ ($J_{C^4F^6}$) was small in every case. [c] In $CHCl_3$–Me_2SO. [d] $C_5NCl_2F_2$ is 3,5-dichloro-2,6-difluoro-4-pyridyl. [e] 2-Pyridyl.

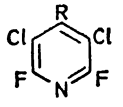
* ' Inverted triplet.' See text.

C-2, C-6 and C-4, respectively, whilst the remaining signal at 130.5 p.p.m. can be assigned to C-3, C-5. Based on these assignments the structure of the photolysis product (92) follows. The C-atoms of the phenyl group produce signals at δ 126.85 (d), 128.4 (d), 128.6 (d), and 135.7 p.p.m. (s, C-1) whilst those of the tetrahydro-2-furyl group appear at δ 26.1 (t, C-3, C-4), 30.8 (t, C-3, C-4) (unambiguous assignments not possible), 69.3 (t, C-5), and 77.3 p.p.m. (d, C-2), respectively. With the evidence available it is not possible to assign all the signals produced by the pyridine-ring C-atoms. However, signals at δ 147.45, 148.5, and 156.7 p.p.m. (all singlets) can be assigned to C-6, C-4, and C-2, respectively, whilst the remaining signals at δ 127.8 (s) and 130.3 p.p.m. (s) can be assigned to C-5 and C-3, respectively.

In Table 7 we report the ^{13}C n.m.r spectra of some chlorofluoropyridines, in Table 8 the spectra of some 4-substituted-3,5-dichloro-2,6-difluoropyridines, and in Table 9 we give the substituent effects for the compounds

TABLE 9

Substituent effects produced in 4-substituted-3,5-dichloro-2,6-difluoropyridines relative to 3,5-dichloro-2,4,6-trifluoropyridine

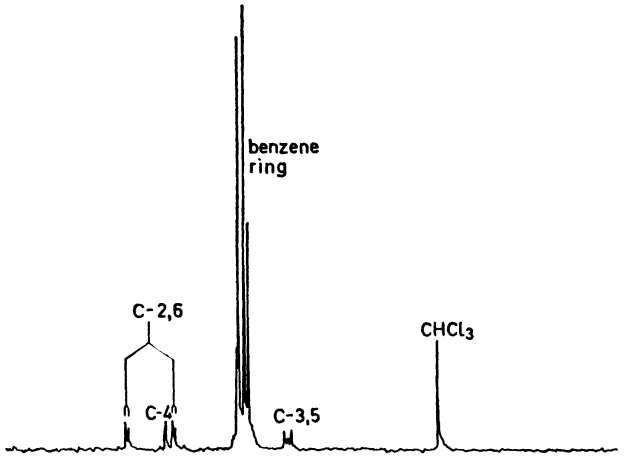


Substituent effects (δ/p.p.m. in $CHCl_3$) [a]

Substituent	C-2, C-6	C-3, C-5	C-4
OAr	−0.1 to	+0.7 to	−5.6 to
	−0.4 (0.2)	+4.4 (3.1)	−13.1 (10.3)
NH_2	−0.6	−7.7	−11.8
$NHCOCH_2R$	−0.5 to	−7.7 to	−7.7 to
	−1.3 (0.9)	+7.3 (2.1)	−14.8 (12.1)
NHAr [b]	−0.4	+2.2	−16.4
SEt	−0.9	+13.4	−11.7
SAr	−0.4 to	+13.3 to	−9.5 to
	−0.8 (0.7)	+14.4 (13.7)	−13.7 (12.0)
Cl	−0.8	+10.1	−16.5

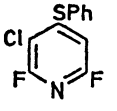
[a] Mean values in parentheses. [b] Ar = 3,5-dichloro-2,6-difluoro-4-pyridyl.

in Table 8, relative to 3,5-dichlorotrifluoropyridine. Assignments are made easy in this series of compounds, (93)—(110), by the presence of ^{13}C–^{19}F coupling. However, the spectra are in some respects deceptively simple, so that the coupling constants cannot be fully evaluated by simple inspection of the spectra. The spectrum of 3,5-dichloro-2,6-difluoro-4-phenylthiopyridine (108),[14] shown in the Figure, is taken as an example. The signal at δ 151.1 p.p.m. is a singlet and is assigned to C-4. The four signals centred on δ 155.4 p.p.m. are assigned to C-2 and C-6, and on a first-order analysis are grouped as a doublet of doublets, with $J_{C^2F^2} = J_{C^6F^6} = 248$ Hz and $J_{C^2F^6} = J_{C^6F^2} = 15$ Hz. The remaining pyridine-ring signals, for C-3 and C-5, are a triplet centred on δ 118.0 p.p.m. This is clearly not a case of a simple AXX′ system, since the outer members of the triplet are more intense than the central one, giving the 'inverted triplet' pattern observed for most of these compounds. Ladd and Lui [15] have observed a similar pattern in the proton-decoupled spectrum of 2,6-difluoropyridine, and have analysed it as an AXY system in which $\delta_X = \delta_Y$, with $J_{C^3F^3} = 35.4$ Hz and $J_{C^3F^5} = 4.3$ Hz. In Table 8 we have recorded the sum of $J_{C^3F^3}$ and $J_{C^3F^5}$, which corresponds to the separation of the outer members of the triplets. In our preliminary communication [2] we



Proton-decoupled ^{13}C n.m.r. spectrum of 3,5-dichloro-2,6-difluoro-4-phenylthiopyridine (108)

reported ^{13}C–^{19}F coupling constants for 3,5-dichlorotrifluoropyridine, derived from a first-order analysis of the spectrum, and we reproduce them in Table 7 for convenience. However, this spectrum must also be deceptively simple, and while the one-bond splittings correspond to those reported for the monofluoropyridines [16] and are probably a close approximation to the coupling constants, the others must be regarded merely as a record of the observed splittings rather than the true coupling constants. Spectra of substituted chlorofluoropyridines can usually be interpreted, and thus used for determining or confirming structures, by first-order analysis. For example, the signals for the pyridine-ring carbon atoms in the proton-decoupled spectrum of 3-chloro-2,6-difluoro-4-phenylthiopyridine (111) [17] comprise a singlet



(111)

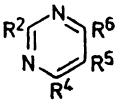
at δ 154.0 p.p.m. assigned to C-4, two overlapping doublets of doublets at δ 159.7 and δ 157.2 p.p.m., both with apparent coupling of 248 and 14 Hz, assigned to C-2 and C-6, a doublet of doublets at δ 108 p.p.m. (apparent coupling 41 and 6 Hz) assigned to C-3, and a more intense doublet of doublets at δ 102.8 p.p.m. (apparent coupling 41 and 6 Hz) assigned to C-5 on the evidence of nuclear Overhauser enhancement by the attached proton.

Finally, in Table 10, we give the ^{13}C n.m.r. chemical shifts for several polyhalogenopyrimidines. Assignments are based on a comparison with those obtained for pyrimidine (112) (Table 10). In most polychloroaromatic compounds there is little nuclear Overhauser enhance-

ment and relaxation times are all long on the n.m.r. time-scale, so that peak heights can give some indication of the number of carbon atoms in one environment. In the absence of other indications, we have used the relative peak heights to distinguish between the chemical shifts for the 2- and 4(6)-positions in the compounds studied. The chemical shifts for C-5 are distinct. In 5-bromo-2,4,6-trichloropyrimidine (115) the bromine atom shields C-5 by −8.9 p.p.m. relative to tetrachloropyrimidine [*cf.* 4-bromotetrachloropyridine (14), −7.6 p.p.m.]. Comparison with tetrachloropyrimidine was used to assign structures to its photolysis products in diethyl ether,[1] namely compounds (119) and (120) (Table 10). Each compound showed two signals at similar positions to those for the corresponding carbon atoms in the starting material and the one due to the alkyl-substituted carbon atom at lower field [the magnitude of the shift for C-5 in compound (120) was unexpectedly large].

TABLE 10

^{13}C N.m.r. chemical shifts of polyhalogenopyrimidines



	Compound				Chemical shifts (δ/p.p.m. in $CDCl_3$)		
No.	R^2	R^4	R^5	R^6	C-2	C-4, C-6	C-5
(112) [a]	H	H	H	H	159.1 (159.5)	157.0 (157.5)	121.7 (122.1)
(113)	Cl	Cl	Cl	Cl	156.4	160.9	127.9
(114) [b]	Cl	Cl	H	Cl	160.2	163.1	120.6d
(115)	Cl	Cl	Br	Cl	160.9	163.1	119.0
(116)	H	Cl	Br	Cl	155.4d	162.0	120.5
(117)	H	Cl	H	Cl	158.8d	162.1	122.0d
(118)	H	Cl	Ph [c]	Cl	156.5d	161.2	129.1
(119)	CHMeOEt [d]	Cl	Cl	Cl	171.6	160.0	127.1
(120)	Cl	Cl	CHMeOEt [d]	Cl	157.8	160.7	169.2

[a] Figures in parentheses from G. C. Levy and G. L. Nelson in 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972, p. 99. [b] Neat liquid. [c] 132.7 (C'-1), 128.6, 128.9 (other aromatic). [d] Run as a mixture.

The *trans*-geometry of the side-chain in compound (31) (Table 1) can be assigned by a comparison of its off-resonance proton-decoupled ^{13}C n.m.r. spectrum with those of *cis*- (Me group at δ 12.6 p.p.m.) and *trans*-1-chlorobut-2-ene (Me group at δ 17.5 p.p.m.) [18] [*cf.* δ 17.9 p.p.m. for (31)] and this assignment is in agreement with that proposed following a detailed ^{1}H n.m.r. spectroscopic analysis (at 220 MHz), reported earlier.[10] On the basis of similar comparisons with the ^{13}C n.m.r. spectrum of 1-chloro-3-methylbut-2-ene (*cis*- and *trans*-Me groups at δ 17.5 and 25.6 p.p.m., respectively) the geometries of the side-chain methyl groups in compounds (32) (Table 1) and (84) (Table 6) [δ 18.3 and 25.8 p.p.m. for (32) and δ 18.4 and 25.8 p.p.m. for (84)] have been assigned.

EXPERIMENTAL

^{13}C N.m.r. spectra were recorded in chloroform or deuteriochloroform, unless stated otherwise, with $SiMe_4$ as an internal standard using a Varian CFT20 spectrometer. The peak multiplicities recorded are for the off-resonance proton-decoupled spectra except where otherwise noted. Other instruments used are described in Parts 40 [10] and 41 [1] of this Series.

The preparations of most of the compounds whose spectra we have recorded are described in earlier parts of this Series: other compounds were available commercially, except benzyl 3,5-dichloro-2,6-difluoro-4-pyridyl ether (97) which was a gift from I.C.I. Plant Protection Limited, Jealott's Hill, and the halogenated pyrimidines which were gifts from Drs. J. Clark and R. Colman of this Department. Light petroleum had b.p. 60—80 °C unless stated otherwise.

2,5-*Dichloropyridine* (7).—A mixture of 5-chloro-2-hydroxypyridine (1.3 g, 10 mmol) and phosphoryl chloride (6 ml) was heated under reflux for 10 h, then poured into water (100 ml). The resulting solution was made alkaline with 4M-potassium hydroxide and extraction with chloroform gave the product (7) (0.8 g, 53%), m.p. 58—59 °C (from light petroleum) (lit.,[19] m.p. 60 °C); δ ($CDCl_3$) 8.40 (1 H, d, $J_{6,4}$ 2.5 Hz, H-6), 7.67 (1 H, dd, $J_{4,3}$ 8 Hz, $J_{4,6}$ 2.5 Hz, H-4), and 7.27 p.p.m. (1 H, d, $J_{3,4}$ 8 Hz, H-3).

5-*Chloro*-1-*methyl*-2-*pyridone* (79).—A mixture of 2,5-dichloropyridine (1.3 g, 8.8 mmol) and methyl fluorosulphonate (5.0 g, 44 mmol) was heated under reflux under nitrogen for 30 min. Water (15 ml) was added cautiously to the cooled reaction mixture and the mixture was made alkaline with 4M-potassium hydroxide. Extraction with dichloromethane gave 5-*chloro*-1-*methyl*-2-*pyridone* (79) (0.85 g, 67.5%), m.p. 39—40 °C (from hexane); $\nu_{max.}$ (Nujol) 1 662 cm^{-1} (C : O); δ ($CDCl_3$) 7.55 (1 H, d, $J_{6,4}$ 3 Hz, H-6), 7.30 (1 H, dd, $J_{4,6}$ 3.0 Hz, $J_{4,3}$ 9.0 Hz, H-4), 6.40 (1 H, d, $J_{3,4}$ 9.0 Hz, H-3), and 3.50 p.p.m. (3 H, s, Me) (Found C, 49.9; H, 4.3; N, 10.0%; M^+, 143. C_6H_6ClNO requires C, 50.2; H, 4.2; N, 9.8%; *M*, 143).

The following compounds are prepared similarly: 3,5,6-*trichloro*-1-*methyl*-2-*pyridone* (80) (89%), m.p. 133—134 °C (from ethanol); $\nu_{max.}$ (Nujol) 1 663 cm^{-1} (C:O); δ ($CDCl_3$) 7.63 (1 H, s, H-4) and 3.76 p.p.m. (3 H, s, Me) (Found: C, 33.5; H, 1.8; N, 6.6%; M^+, 211. $C_6H_4Cl_3NO$ requires C, 33.9; H, 1.9; N, 6.6%; *M*, 211): and 3,4,6-*trichloro*-1-*methyl*-2-*pyridone* (81) (47%), m.p. 151—152 °C (from ethanol); $\nu_{max.}$ (Nujol) 1 665 cm^{-1} (C:O); δ ($CDCl_3$) 6.56 (1 H, s, H-5) and 3.75 p.p.m. (3 H, s, Me)(Found: C, 34.0; H, 1.95; N, 6.5%; M^+, 211).

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REFERENCES

[1] Part 41, J. Bratt, B. Iddon, A. G. Mack, H. Suschitzky, J. A. Taylor, and B. J. Wakefield, 1980, 648.

[2] Preliminary communication, B. Iddon, O. Meth-Cohn, H. Suschitzky, J. A. Taylor, and B. J. Wakefield, *Tetrahedron Letters*, 1976, 627.

[3] H. L. Retcofsky and R. A. Friedel, *J. Phys. Chem.*, 1968, **72**, 290, 2619; H. L. Retcofsky and R. A. Friedel, *U.S. Bur. Mines Bull.*, 1969, No. 649 (*Chem. Abs.*, 1969, **71**, 65812).

[4] G. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. Pharm. Bull.* (*Japan*), 1972, **20**, 429.

[5] G. C. Levy and G. L. Nelson, in ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972, pp. 23 and 90.

[6] Ref. 5, p. 81.

[7] Ref. 5, p. 99.

[8] G. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. Pharm. Bull.* (*Japan*), 1971, **19**, 2301.

[9] F. A. L. Anet and I. Yavari, *J. Org. Chem.*, 1976, **41**, 3589; S. A. Sojka, F. J. Dinan, and R. Kolarczyk, *J. Org. Chem.*, 1979, **44**, 307.

[10] B. Iddon, H. Suschitzky, and J. A. Taylor, *J.C.S. Perkin I*, 1979, 2756.

[11] E. Ager and H. Suschitzky, *J.C.S. Perkin I*, 1973, 2839.

[12] E. Ager and H. Suschitzky, *J. Fluorine Chem.*, 1973, **3**, 230.

[13] G. Miyajima, K. Takahashi, and H. Sugiyama, *Org. Magnetic Resonance*, 1974, **6**, 181.

[14] J. Bratt and H. Suschitzky, *J.C.S. Perkin I*, 1973, 1689.

[15] J. A. Ladd, personal communication; S. S. Lui, Ph.D. Thesis, University of Salford, 1977.

[16] R. L. Lichter and R. E. Wasylishen, *J. Amer. Chem. Soc.*, 1975, **97**, 1808.

[17] A. G. Mack, H. Suschitzky, and B. J. Wakefield, unpublished work; A. G. Mack, Ph.D. Thesis, University of Salford, 1978.

[18] M. M. Coleman, D. L. Tabb, and E. G. Brame, *Rubber Chem. Technol.*, 1977, **50**, 49 (*Chem. Abs.*, 1977, **86**, 190551); see also examples of spectra in ' Carbon-13 N.M.R. Spectra; A Collection of Assigned, Coded, and Indexed Spectra,' Wiley-Interscience, New York, 1972.

[19] H. Meyer and R. Graf, *Ber.*, 1928, **61B**, 2202.