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^{13}C-N.M.R. SPECTRA OF POLYCHLOROPYRIDINES; STRUCTURAL ASSIGNMENTS

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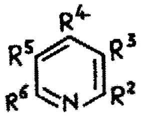
Summary ^{13}C-N.M.R. spectroscopy is used to distinguish between the structures of 2- and 4-substituted tetrachloropyridines.

A major difficulty in studies of polychloroaromatic compounds[1] has been the lack of a reliable spectroscopic technique for structure determination. In the polychloropyridine series, for example, U.V.,[2] I.R.,[3] ^{35}Cl NQR,[4] and photo-electron spectroscopy[5] (as well as X-ray crystallography[6]) have been used with limited success. Indeed, as late as 1967 it was necessary for us to resort to a classical chemical method to distinguish between 2- and 4-substituted tetrachloropyridines.[7] Although ^{13}C-N.M.R. spectroscopy is an obvious technique for application in this field, there are some difficulties. The low sensitivity caused by unfavourable relaxation parameters for chlorine[8] and the lack of nuclear Overhauser enhancement are compounded by poor solubility and high molecular weight of many of the compounds. Nevertheless, modern instruments have made it possible to record good spectra of many polychloroaromatic compounds. At present we are compiling a catalogue of these spectra in order to establish correlations which can be applied to an examination of more complex systems. To illustrate the usefulness of this technique we record in the Table results for several polychloropyridines.

The assignments of chemical shifts for pentachloropyridine (2), which are based on a comparison with those reported[8] for pyridine (see Table) are supported by the assignments made for the tetrachloropyridines (3)-(5). In these compounds the proton-bearing C-atoms are readily identified by a large nuclear Overhauser effect and the off-resonance proton decoupled spectrum. Where two resonances occur close together complete assignment is not possible.

In some cases predictions based on empirical increments can be made. For example, a comparison of the spectrum of 4-bromotetrachloropyridine (6) with that of pentachloropyridine (2) indicates that the Br-atom has a shielding effect of 7.6 ppm on the C-atom to which it is

^{13}C-N.M.R. Chemical Shifts (ppm) of Polychloropyridines in Chloroform

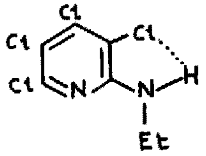


Compound	R^2	R^3	R^4	R^5	R^6	C-2	C-3	C-4	C-5	C-6
(1)[a]	H	H	H	H	H	150.6	124.5	136.4	124.5	150.6
(2)	Cl	Cl	Cl	Cl	Cl	146.2	129.7	144.7	129.7	146.2
(3)[b]	Cl	Cl	H	Cl	Cl	145.9	129.6	140.0	129.6	145.9
(4)[b]	Cl	H	Cl	Cl	Cl	147-8 or 149.5	124.4	145.7	128.7	147.8 or 149.5
(5)[b]	H	Cl	Cl	Cl	Cl	145.9	129.5 or 130.4	142.3	129.5 or 130.4	148.4
(6)	Cl	Cl	Br	Cl	Cl	146.5	129.7	137.1	129.7	146.5
(7)	Br	Cl	Cl	Cl	Cl	138.0	130.0 or 132.4	144.0	130.0 or 132.4	146.7
(8)[c]	Cl	Cl	OMe	Cl	Cl	146.8	124.8	162.1	124.8	146.8
(9)[d]	OMe	Cl	Cl	Cl	Cl	157.15	116.9	143.6 or 144.1	121.8	143.6 or 144.1
(10)[e]	Cl	Cl	NMe_2	Cl	Cl	146.8	125.8	156.4	125.8	146.8
(11)[f]	NMe_2	Cl	Cl	Cl	Cl	156.1	117.0	143.5 or 144.4	119.0	143.5 or 144.4
(12)[g]	Cl	Cl	NC_5H_{10}	Cl	Cl	146.9	126.0	156.1	126.0	146.9
(13)[h]	NC_5H_{10}	Cl	Cl	Cl	Cl	156.6	119.4 or 120.25	143.4 or 144.7	119.4 or 120.25	143.4 or 144.7
(14)[i]	Cl	Cl	NHEt	Cl	Cl	146.2	114.1	149.9	114.1	146.2
(15)[j]	NHEt	Cl	Cl	Cl	Cl	151.7	112.5	141.0	115.2	145.7
(16)	1-oxide of compound (2)					142.6	129.6	142.6	129.6	142.6
(17)	F	Cl	F	Cl	F	156.2	104.7	164.1	104.7	156.2

[a] Ref. 9. [b] The proton-bearing C-atom exhibits a strong nuclear Overhauser effect and, in the off-resonance proton decoupled spectrum, appears as a doublet. [c] Me 61.3 ppm. [d] Me 55.6 ppm. [e] Me 42.75 ppm. [f] Me 41.4 ppm. [g] NC_5H_{10} = piperidino; α-CH_2, 51.9; β-CH_2, 26.4; γ-CH_2, 24.0 ppm. [h] NC_5H_{10} = piperidino; α-CH_2, 50.3; β-CH_2, 25.75; γ-CH_2, 24.4 ppm. [i] CH_2, 41.3; Me, 16.5 ppm. [j] CH_2, 36.9; Me, 14.6 ppm.

attached, with a negligible effect on the other C-atoms. This enabled the following chemical shifts, which are close to the observed values (cf. Table), to be predicted for 2-bromotetrachloropyridine[9] (7): 138.6 (C-2), 129.6 (C-3), 144.7 (C-4), 129.6 (C-5), and 146.2 (C-6). A methoxyl {Compounds (8) and (9)} or secondary amino-group {Compounds (10)-(13)} deshields the C-atom to which it is linked and shields adjacent C-atoms. 4-Substituted tetrachloropyridines {Compounds (3), (6), (8), (10), (12) and (14)} show only three resonance signals, whereas 2- {Compounds (5), (7), (9), (11), (13) and (15)} or 3-substituted tetrachloropyridines {Compound (4)} display five signals. The accidental equivalence of the two α-C-atoms with the γ-C-atom in pentachloropyridine 1-oxide (16) is noteworthy.

In the case of tetrachloro-4-ethylaminopyridine (14) only the signal for C-3 shows coupling with the N-H proton (J 6.6 Hz), whereas for its 2-isomer (15) 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 Hz, respectively). The magnitude of the long-range (4-bond) coupling between C-6 and the N-H proton in compound (15) indicates that this compound exists in solution predominantly in the conformation shown, in which the bonds have the favourable W geometry. Hydrogen bonding, as shown, probably slows down the rate of exchange of the N-H proton, thus allowing the coupling to be seen. In tetrachloro-4-ethylaminopyridine (14) the bulky β-chlorine atoms (enhanced by the butressing effect of the α-chlorine atoms) prevent the ethylamino-group from adopting the favourable W conformation.


(15)

The ^{13}C-N.M.R. spectra of mixed chlorofluoropyridines are exemplified by 3,5-dichlorotrifluoropyridine (17) (Table). The $^{13}C-^{19}F$ coupling constants for this compound are as follows: C-2/F-2 (C-6/F-6) 246 Hz; C-2/F-4 (C-6/F-4) 7 Hz; C-2/F-6 (C-6/F-2) 17 Hz; C-3/F-2 (C-5/F-6) 42.5 Hz; C-3/F-4 (C-5/F-4) 21 Hz; C-4/F-4 264 Hz; C-4/F-2 (C-4/F-6) 7 Hz. Two remarkable features of this spectrum, viz. the large $J_{C-2/F-6}$ and the fact that it is the C-4 signal which occurs at lowest field, are consistent with the data recently reported for the three monofluoropyridines.[10]

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