Chlorinated Pyridine Compounds: Quantum Chemical Calculations and Chlorine-35 Nuclear Quadrupole Resonance Frequencies

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The ^{35}Cl n.q.r. frequencies were measured for some chlorinated pyridine compounds. The frequencies were assigned to chlorine atoms substituted in various positions in the pyridine ring. Quantum chemical calculations confirm the assignments given.

FINE structure may occur in an n.q.r. spectrum from the crystal field effect [1] and may be used to give some idea of the site symmetry of the nuclei considered, or the possible arrangement of the resonant atoms.[2] It is, therefore, interesting to consider a series of molecules in which multiple ^{35}Cl n.q.r. frequencies arise and use the INDO-SCF-MO approach to verify the assignment suggested for each resonance. Quantum chemical calculations have proved valuable[3] previously, using a modified computer program[4] in such a frequency assignment problem. The calculations were further extended to give values of the asymmetry parameter and coupling constants and the principal components of the electric field gradient associated with each ^{35}Cl n.q.r. frequency so that any trends in these values and the Cl substitution position in the pyridine ring may be shown.

EXPERIMENTAL

N.q.r. spectra of chlorinated pyridines were obtained at 77 K using a Decca Radar spectrometer. The sample of tetragonal crystals of pentachloropyridine was a specimen of the same material which featured in an X-ray analysis.[5]

Therefore quantum chemical calculations were performed using data from the crystal structure of the molecule.

3,4,5,6-Tetrachloropyridine was a liquid at room temperature and 3,4,5-tri- and 2,6-di-chloropyridine were crystalline solids. Since the crystal structures of these compounds were unknown, for comparison purposes, the C–H bond lengths and pyridine ring–$\overset{\frown}{C}$–H angle in the appropriate substitution positions were transferred, as is usual practice,[6] from parameters of pyridine obtained from ref. 7 to the pentachloropyridine crystal structure as obtained from ref. 5 and calculations were carried out on the structures so constructed.

Other n.q.r. frequencies were abstracted from the literature.[4,8]

RESULTS

The ^{35}Cl n.q.r. frequencies are given in Table 1.

Using the semi-empirical all-valence-electron INDO-SCF-MO method[9] and adopting the parameterisation[10] used previously[8] the density matrix was obtained. Since the validity of any comparison of calculated and experimental coupling constants depends upon the selection of the correct axes for MO calculations, the population submatrix for chlorine must be diagonalised.[11,12] The p orbital

[1] A. Weiss, *Topics Current Chem.*, 1972, **30**, 18,33.
[2] K. Shimomura, *J. Phys. Soc. Japan*, 1957, **12**, 652.
[3] M. Redshaw, *Org. Magnetic Resonance*, 1975, **7**, 358.
[4] QCPE 141, Quantum Chemistry Program Exchange, Indiana University.
[5] H. J. Rossell and H. G. Scott, *J. Cryst. Mol. Structure*, 1973, **3**, 259.
[6] Z. Latajka, H. Ratajczak, W. J. Orville-Thomas, and E. Ratajczak, *J. Mol. Structure*, 1974, **21**, 299.

[7] G. O. Sørensen, L. Mahler, and N. Rastrup-Andersen, *J. Mol. Structure*, 1974, **20**, 119.
[8] V. Galasso, *Theor. Chim. Acta*, 1974, **34**, 137.
[9] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, 1969, *J. Chem. Phys.*, **47**, 2026.
[10] B. M. Deb and C. A. Coulson, *J. Chem. Soc. (A)*, 1971, 958.
[11] M. Kaplansky and M. A. Whitehead, *Trans. Faraday Soc.*, 1969, **65**, 641.
[12] C. T. Yim, M. A. Whitehead, and D. H. Lo, 1968, *Canad. J. Chem.*, 1968, **22**, 3595.

populations thus obtained were used in further computations to yield the principal components of the quadrupole coupling tensor which were then used to obtain [13a] the asymmetry parameter and the expected ^{35}Cl n.q.r. frequency, taking the quadrupole coupling constant for valence shell p electrons of Cl as 109.746, as usual.[13b]

The values obtained from these computations are given in Table 2.

TABLE 1

^{35}Cl N.q.r. frequencies (MHz) of some chloropyridines

	Pyridine	N.q.r. frequency (MHz)
(1)	2,3,4,5,6-Cl$_5$	38.117, 38.506, 38.379, 36.914, 36.623, 38 107, 38.501, 38.361, 36.895, 36.616
(2)	3,4,5,6 Cl$_4$	38.117, 37.797, 37.517, 36.461
(3)	3,4,5-Cl$_3$	37.516, 37.136, 36.948
(4)	2,6-Cl$_2$	34.654 (^{37}Cl 27.313)

	Pyridine	N.q.r. frequency (Hz)	Ref.
(5)	3,5-Cl$_2$	35.60	8
(6)	2-Cl	34.17	a,b
(7)	3-Cl	35.24	a
(8)	4-Cl	34.89	a

^{a} P. J. Bray, S. Moscowitz, H. O. Hooper, R. G. Barnes, and S. L. Segal, *J. Chem. Phys.*, 1958, **28**, 99. ^{b} M. J. S. Dewar and E. A. C. Lucken, *J. Chem. Soc.*, 1958, 2653.

TABLE 2

Experimental and calculated ^{35}Cl n.q.r. frequencies (MHz), asymmetry parameters, η, principal components of the electric field gradient along the η axis, q_z, and coupling constants of the compounds considered

Pyridine	Cl at position	Frequency exp. (MHz)	Calc.	q_z	η	Coupling constant
(1)	2	36.914, 36.895	33.046	0.060	0.042	66.072
	3	38.379, 38.361	38.622	0.070	0.028	77.234
	4	38.117, 38.107	37.800	0.068	0.039	75.582
	5	38.506, 38.501	38.622	0.070	0.028	77.234
	6	36.623, 36.616	33.046	0.060	0.042	66.072
(2)	3	37.517	36.206	0.066	0.028	72.402
	4	37.797	36.410	0.066 3	0.039	72.802
	5	38.117	37.650	0.068 6	0.027	75.292
	6	36.461	31.851	0.058	0.042	63.683
(3)	3	37.136	35.099	0.063 9	0.027	70.189
	4	36.948	34.946	0.063 6	0.039	69.875
	5	37.516	35.099	0.063 9	0.027	70.189
(4)	2	34.654	28.247	0.051	0.041	56.478
	6	34.654	28.247	0.051	0.041	56.478
(5)	3	35.60	32.110	0.058 5	0.028	64.212
	5	35.60	32.110	0.058 5	0.028	64.212
(6)	2	34.17	26.687	0.048 6	0.042	53.358
(7)	3	35.24	30.756	0.056 0	0.029	61.504
(8)	4	34.89	28.926	0.052 7	0.041	57.836

DISCUSSION

Five pairs of resonances are unexpected if the pentachloropyridine molecule only is considered, since 2- and 6-Cl are presumed equivalent, as are 3- and 5-Cl. In the free molecule these pairs of atoms are chemically equivalent. Quantum chemical calculations also show by their electronic charge density values that they are

[13] E. A. C. Lucken, ' Nuclear Quadrupole Coupling Constants,' Academic Press, London–New York, 1969, (a) p. 39; (b) p. 139.
[14] R. Bersohn, *J. Appl. Phys.*, 1962, **33**, suppl. to No. 1, 286.

equivalent, since only three different electronic charge densities are obtained for the five chlorine substitution positions.

The three chlorine atoms in the asymmetric unit of tetragonal pentachloropyridine are crystallographically non-equivalent, due to crystal field effects.[14] The electric field gradient differs from site to site within the asymmetric unit (Table 2). However, the frequency distribution of ' chemically equivalent ' chlorine atoms is

TABLE 3

Allocation of experimental n.q.r. frequencies (MHz) to ^{35}Cl positions in pentachloropyridine

Position	N.q.r. frequency (MHz)
2, 6	36.616, 36.623, 36.895, 36.914
3, 5	38.361, 38.379, 38.501, 38.560
4	38.117, 38.107

within the suggested range of 500 kHz for this crystal field effect[1] so, assigning higher electronic charge density to lower frequency values,[4] the tetragonal pentachloropyridine frequencies are attributed to the appropriate Cl substitution positions in Table 3.
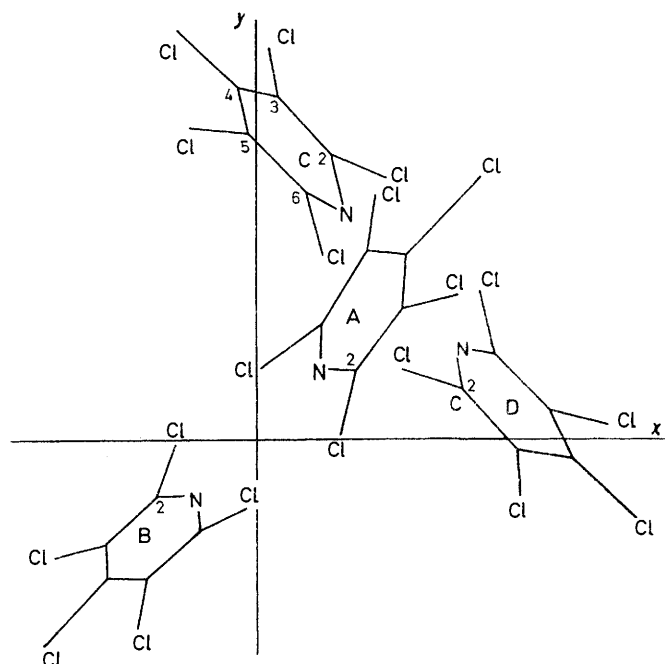
The four molecules in the unit cell of tetragonal pentachloropyridine. Value of Z axis through N–C(4)–Cl(4): molecule A, 0; B, 14; C, 7; D, 21

Since there are four molecules per unit cell for tetragonal pentachloropyridine[3] the orthogonal cartesian co-ordinates used in the quantum chemical calculations were derived from refs. 3 and 15 and the symmetry operations required to obtain the co-ordinates of the positions of all the atoms in the cell can be expressed as

$$x, y, z; \ \bar{x}, \bar{y}, \tfrac{1}{2} + z; \ \tfrac{1}{2} - y, \tfrac{1}{2} + x, \tfrac{1}{4} + z; \ \tfrac{1}{2} + y, \tfrac{1}{2} - x,$$

[15] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1965, vol. 1.

$\frac{3}{4} + z$. In the simplest terms, the four molecules are arranged in four layers related by 90° rotation about the C–N–C system. The Figure gives some idea of the arrangement of the molecules. The atoms C(2) and Cl(2) are marked on the Figure so that the effect of the symmetry operations carried out to obtain the cartesian co-ordinates can be clearly shown. The results given in Table 2 for tetragonal pentachloropyridine are the same for each molecule in the unit cell. The diagonalisation of the 3×3 population submatrix for each Cl in the four molecules, as well as giving the p population components $i.e.$ eigenvalues of the sub-matrix, gave the eigenvectors associated with these values. The 20 sets of eigenvectors obtained fell into 10 different pairs, those associated with position 2 on molecules (1) and (2), position 3 on molecules (1) and (2), and, similarly, positions 4—6 on molecules (1) and (2), and positions 2—6 on molecules (3) and (4).

The assignment of frequencies to appropriate Cl substitution positions in the series of compounds considered (Table 2), show that the experimental and calculated ^{35}Cl n.q.r. frequencies display the same trends in that the frequencies of Cl at various substitution positions in the pyridine ring decrease in the substitution order: $\beta > \gamma > \alpha$. A frequency shift, on increased chlorine substitution, is observed within the series at each position, $e.g.$ the frequency of Cl at position 3 on compounds (7), (5), (3), (2), and (1)increases as the number of chlorine atoms in the molecule increases.

Conclusions.—N.q.r. frequencies calculated by means of the Kaplansky–Whitehead theory with the INDO-MO approximation follow the trends of the experimentally obtained frequencies and have the correct order of magnitude; the asymmetry parameters and coupling constants are consistent within the limitations of the theory. The results show that higher electronic charge density is associated with longer C–Cl bond lengths and with lower ^{35}Cl n.q.r. frequencies. The frequency assignments shown are compatible with suggestions [16] that the higher frequency of 3-chloropyridine is due to inductive effects as compared with 2- or 4-chloropyridine. Combined use of accurate X-ray crystallographic data and quantum chemical calculations have proved useful in assigning n.q.r. frequency values to particular substitution positions in a molecule.

[16] E. A. C. Lucken, ' Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, London–New York, 1971, vol. IV, p. 35.