Zeeman effect of NQR in 4,6-dichloropyrimidine and 6-chloro 2,4-dimethoxypyrimidine

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Abstract. Zeeman (^{35}Cl) NQR studies in polycrystalline samples of 4,6-dichloro-pyrimidine and 6 chloro 2,4 dimethoxypyrimidine show that the asymmetry at the four chemically inequivalent chlorine sites in the former is about 10%, while in the latter (one line) the asymmetry is almost zero. Using a valence-bond picture, C−Cl bonds in 4,6-dichloropyrimidine have been characterised, and the results are also compared with those in a corresponding benzene compound using a simple molecular orbital calculation. The axial symmetry of C—Cl bond in the second compound has been attributed to mesomeric effects.

Keywords. Zeeman effect; 4,6-dichloropyrimidine; 6-chloro 2,4 dimethoxypyrimidine; nuclear quadrupole resonance.

1. Introduction

Azabenzenes form an interesting class of compounds both chemically and biologically and have been a subject of studies employing the nuclear quadrupole resonance (NQR) technique (Schempp and Bray 1970). Either the nitrogen present in the ring is used as an NQR probe to study the charge distribution around the site, or a quadrupolar nucleus like chlorine is attached to the carbon to study the effect of nitrogen substitution. Pyrimidines, in this context, are of special significance since they form one of the two nucleic acid bases. Whereas the actual NQR frequency of the nucleus outside the ring in a particular bonding scheme is perturbed by substitutions in the ring through various effects like induction, conjugation, etc., the asymmetry parameter η of the electric field gradient (EFG) is entirely dependent on the π-electron charge distribution at the corresponding nucleus, as is well known in conjugated systems (Bersohn 1954). Bersohn related η to the π-electron loss by a very simple formula and the π-electron loss defines the double-bond character. The π-electron loss can also be evaluated using a molecular orbital (m.o.) approach in terms of λ, the coupling between the π-electron system of the atom under consideration and the ring (Bersohn 1954). An experimental determination of the π-electron loss, through a measurement of η, is helpful in understanding this coupling, if m.o. calculations on the ring, under some simplifying assumptions like the Huckel approximation are done. A comparison of the experimental results with calculations may throw some light on the validity of the assumptions made in the theory.

In this paper the results of Zeeman NQR experiments for ^{35}Cl in polycrystalline samples of 4,6-dichloropyrimidine and 6-chloro 2,4-dimethoxypyrimidine at room temperature are reported.   The ^{35}Cl NQR frequencies for these compounds are known (Bray 1958).   In 4,6-dichloropyrimidine four lines have been observed while 6-chloro 2,4-methoxypyrimidine gave only one line (all at room temperature).   Unfortunately, due to the symmetry of the molecule, and in the absence of crystal structure data, it was not possible to assign the frequencies to the different chlorines in 4,6-dichloropyrimidine.

2. Experimental details

These pyrimidines were obtained from Sigma Chemicals, USA and were better than 99% pure.   The signals were visible on the oscilloscope at 77°K while they could be comfortably recorded at room temperatures with a signal-to-noise (S/N) ratio varying from 40 to 70.   The samples are expected to be stored below 5°C and one is advised not to subject these substances to repeated heating and cooling cycles.   Thus, attempts were made at growing single crystals only by evaporation technique which yielded needle-like structures.   These are not suitable for single crystal study and only powder sample could be used.

A self-quenched super-regenerative oscillator was used to detect the signals.   A home-made solid state lock-in-amplifier and a Honeywell stripchart recorder were used to record the signals.   The frequency sweep was achieved by an HC7001 varicap diode which was frequency-calibrated in terms of the applied voltage.   The chart paper in turn was calibrated in terms of the voltage on the varicap diode.   The time constant used was about 10 sec and the sweep rate was 1 kHz/min.   The external static magnetic field was obtained using a Helmholtz coil system.   It was fed by a stabilised solid state d.c. power supply.   The magnetic field was calibrated with a BELL 620 Gaussmeter and the field was found to vary linearly at a rate of 42·6 G/amp.

3. Results and discussion

In the case of spin 3/2 systems, the value of η can be measured by the application of a small Zeeman perturbation on single crystals, and such a study yields the value of η, as well as the orientation of the EFG axes with respect to the crystal axes.   There are, however, some difficulties in such a measurement, the major one being the size of the single crystal required.   Morino and Toyama (1961) suggested a method wherein η can be estimated by studying polycrystalline samples.

In the case of 4,6-dichloropyrimidine all the four lines are of almost equal intensity with a recorded S/N ratio of about 50.   Although the four lines were somewhat closely spaced, no serious problems were encountered and it was possible to avoid interference between unperturbed lines by suitably adjusting the quench frequency. In the presence of higher magnetic fields, however, some interference could not be avoided, but the measurements could be made without much difficulty after proper identification of the signal.   In the case of 6-chloro 2,4-dimethoxypyrimidine the

unperturbed line is quite intense (S/N~50). On the application of the magnetic field, the spectrum showed only two humps, one on either side of the unperturbed line, without any kinks between them. This corresponds to a line shape function consisting of only 'shoulders' and no 'divergences' and is characteristic of very low $\eta(\sim 0)$. This feature persisted with the increase of the magnetic field, the only difference being that the two humps moved apart, separated by $4\,\nu_H$, and there was a decrease in their intensity. The experiment was carried out till a field value of 40 G, and it was concluded that the value of η in this compound should be very close to zero.

The results show that the values of η for the four lines of 4,6-dichloropyrimidine are almost the same and of the order of 10%. Thus, the double bond character being the same, the presence of different frequencies can be attributed mainly to solid state effects (intermolecular interactions).

Bersohn's (1954) calculation of η assuming a hole with charge ρ corresponding to the π-electron loss shows that $(I = 3/2)$

$$\eta = \tfrac{3}{4}\,(e^2\,Q\,q_0/\nu_0)\rho \tag{1}$$

which for chlorine is given by

$$\eta = \tfrac{3}{4}\,(109{\cdot}74/\nu_0)\,\rho,$$

Here ν_0 is the experimentally determined NQR frequency (extrapolated to $0°K$). The value of ρ is a direct measure of the double bond character, provided the assumption that one of the lone pairs of chlorine is not participating in the bonding, is valid. The values of ρ for the four inequivalent sites are given in table 1.

The π-electron loss ρ, can also be expressed in terms of the coupling between the chlorine and the ring π-electron system, using a simple m.o. picture of the conjugate system. It is assumed that the resonance integral between C and Cl can be expressed as a constant (λ) times the Coulomb integral on C and, for weak coupling, λ is expected to be small. Calculation of the π-electron losses expected in the pyrimidine molecule for chlorine substitutions at the sites 2, 4, and 6 shows

$$\rho_2 = 0{\cdot}490\,\lambda^2; \quad \rho_4 = 0{\cdot}505\,\lambda^2; \quad \text{and } \rho_6 = 0{\cdot}505\,\lambda^2. \tag{2}$$

The two assumptions implicit in this calculation are that the Coulomb integral of nitrogen is $\beta/2$ (Coulson 1969), where β is the C-C resonance integral, and the carbon-nitrogen resonance integral is equal to the carbon-carbon resonance integral. It is

Table 1. Characterisation of C-Cl bond in 4,6-dichloropyrimidine

Line	Frequency (MHz)	η	π-electron loss (%) (in units of electron charge)	Relative importance of resonant structures		
				C-Cl	C^+Cl^-	$C^-=Cl^+$
I	34·738	0·09 ± 0·01	3·9	78·0	18·9	3·1
II	34·600	0·09 ± 0·01	3·9	78·0	18·9	3·1
III	34·525	0·11 ± 0·01	4·7	77·1	19·1	3·8
IV	34·347	0·09 ± 0·01	3·9	77·3	19·6	3·1

interesting to compare these values of ρ with that for a dichlorobenzene (Bersohn 1954), which is 0·350 λ^2. Assuming similar coupling in both the cases, it is expected that the value of η in 4,6-dichloropyrimidine could be more than that of p-dichlorobenzene, which is 0·08 (Dean 1952). It is found that the value of η in the present case is about 10% and thus the calculation and experiment are in qualitative agreement. However, the calculated values cannot be taken too seriously for a quantitative comparison because of the assumptions mentioned above (Adrian 1958).

The results can also be interpreted in terms of a valence-bond picture, following the assumptions of Meal (1956) regarding the percentage of p-character, the absence of contribution from d-orbitals, etc. The percentage importance of different resonant structures for the C-Cl bond have been indicated in table 1.

The case of 6-chloro 2,4-dimethoxypyrimidine is slightly different in the sense that the charge distribution is perturbed by the two electronegative methoxy groups at the 2nd and 4th positions. There is a possibility that the oxygen and nitrogen lone pairs interact appreciably in this compound and the resulting effect cannot be readily taken into account. The observed value of η, which is very close to zero, can be explained either as a case in which there are no unoccupied states in the totality of molecular orbitals, or as one in which the interaction between chlorine and the ring is for some reason very weak and λ is negligible (Bersohn 1954). The first possibility cannot be true and it is expected that λ is very small. This is supported by the possibility that the two oxygen atoms could be active conjugatively with the ring electrons, thereby decreasing the interaction of ring π-electrons with chlorine π-electrons.

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