Solid State Effects in 4,6-Dichloropyrimidine Studied by ^{35}Cl-NQR Spectroscopy and ab initio Calculations

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Quantum chemistry methods – ab initio – have been used for the assignment of the ^{35}Cl-NQR resonance frequencies to particular chlorine atoms substituted in positions 4 and 6 of pyrimidine. The so-called solid state effect, that is the influence of intermolecular interactions, in particular hydrogen bond formation, on the NQR parameters has also been studied.

Key words: ^{35}Cl-NQR; 4,6-Dichloropyrimidine; Electronic Structure; B3LYP/6-31G*.

Introduction

Pyrimidine and its derivatives belong to the compounds of key importance in organic chemistry. Many of the derivatives which show biological activity have been synthesised, with applications including antibiotics and antihypertensive agents. One of the well known pyrimidine derivatives, 4,6-dichloropirymidine (Fig. 1), was investigated using ^{35}Cl-NQR spectroscopy by Bray et al. [1, 2] and Sastry et al. [3], where its bond analysis was performed according to the Townes-Dailey approximation. An assignment of individual resonance lines to particular chlorine atoms was not investigated in the above-mentioned papers. In this paper an attempt is made at assigning the resonance frequencies to particular chlorine positions and determining the influence of interactions (in particular the presence of hydrogen bonds) on the NQR parameters by ab initio methods.

The structure of 4,6-dichloropirymidine in the gas phase and solid phase at 150 K was recently investigated by Morrison et al. [4]. The crystals are monoclinic (a = 9.702 Å, b = 3.780 Å, c = 31.420 Å and β = 97.99) with 8 molecules in the elementary cell (Figure 2).

Significant molecular distortions were found and interpreted in terms of intermolecular bonding. In the crystal the 4,6-dichloropyrimidine molecules are packed as chains linked by C(H)...N hydrogen bonds and Cl...Cl contacts [4], cf. Figure 3. If the two chlorine atoms were chemically equivalent, only one resonance line would be recorded. The presence of four lines is a consequence of the presence of two inequivalent molecules in an elementary cell, and what is more, the neighbourhood of each of the chlorine atoms in the two inequivalent molecules is different, which leads to shifts in the resonance lines.

Material and Methods

Polycrystalline 4,6-dichloropyrimidine synthesised at the Department of Chemistry, Adam Mickiewicz University and used without further purification. The measurements were carried out on an NQR pulse spectrometer built in the Institute of Physics of the Adam Mickiewicz University at Poznań. From 77 to 300 K the spectra of the compound show four lines, confirming inequivalent positions of the Cl atoms in the elementary cell. The NQR signals assigned to Cl nuclei were strong (S/N = 3 after 1000 accumulations), and the resonant lines were broad (5 - 7 kHz). Therefore the classical Hahn sequence was applied. The optimised pulse length was about 10 μs.

Calculations

Since the use of a single basis set is always a source of uncertainties in the EFG components, the calcu-

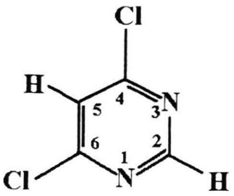

Fig. 1. Structural formula of 4,6-dichloropyrimidine.

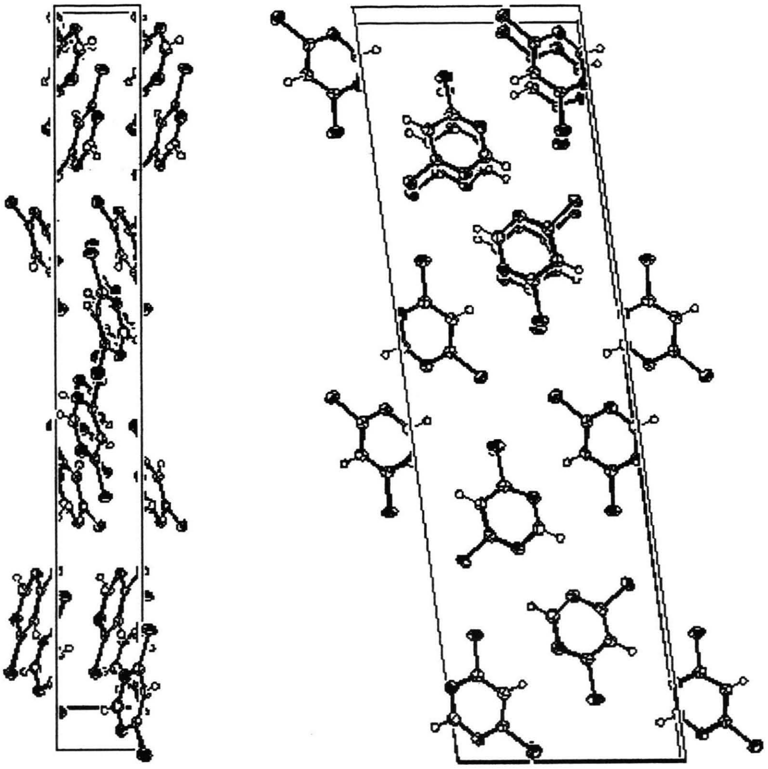

Fig. 2. The packing of 4,6-dichloropirymidine molecules in the elementary cell.

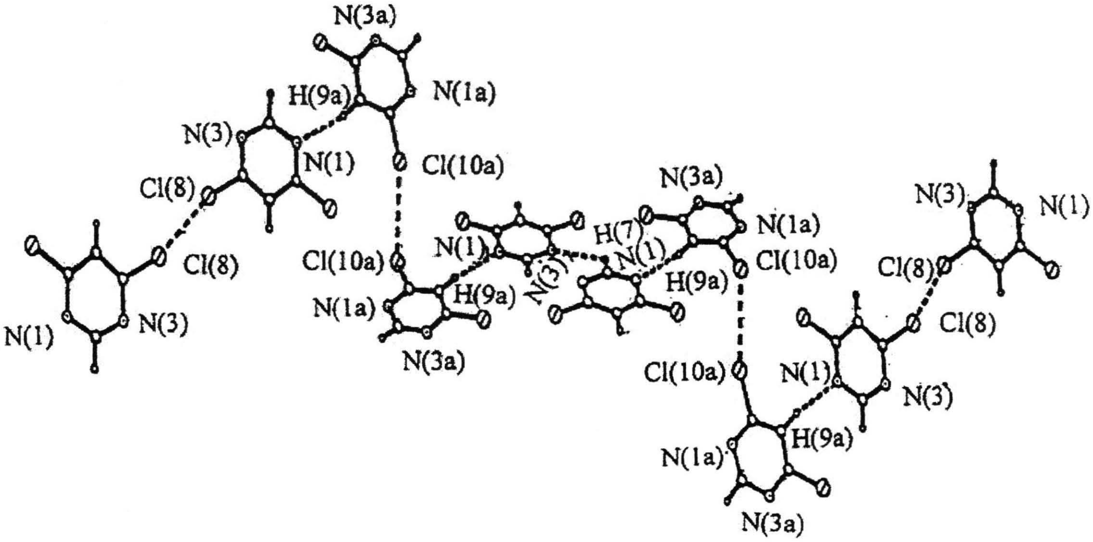

Fig. 3. Crystal packing arrangement of 4,6-dichloropyrimidine. Atoms labelled 'a' after their number are in molecule 2.

lations were performed with several basis sets, and regarding the effect of the functional – also at different levels of the theory. The ab initio calculations were performed in the middle 6-31G* basis set at the HF, MP2 and B3LYP levels of the theory, assuming the experimental geometry [4], at the supercomputer-network centre PCSS in Poznań, using the packet Gaussian 98$^{\text{TM}}$ [5, 6] at a Cray supercomputer.

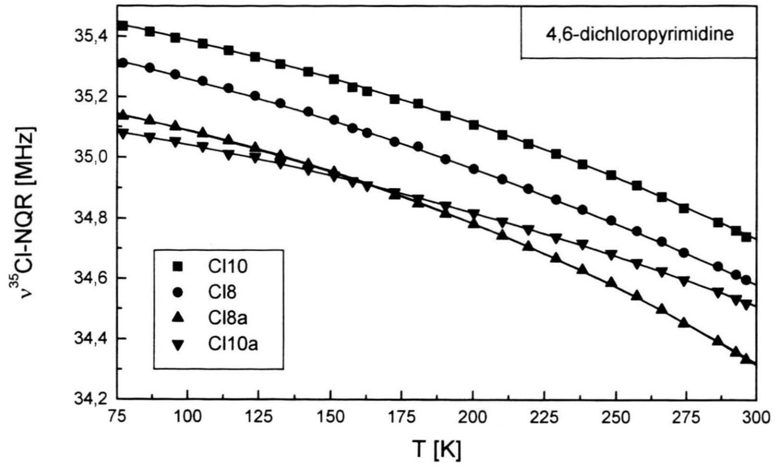

Fig. 4. The temperature depenedence of the ^{35}Cl-NQR frequencies.

Table 1. The experimental and calculated by ab initio ^{35}Cl-NQR frequencies (ν_Q) asymmetry parameters (η) and quadrupole coupling constants (e^2Qqh^{-1})

	— Experimental ^{35}Cl-NQR —											
Temp.	— 77 K [1] —				— 152 K —				— 293 K [2] —			
Position	Cl8	Cl10	Cl8a	Cl10a	Cl8	Cl10	Cl8a	Cl10a	Cl8	Cl10	Cl8a	Cl10a
ν_Q [MHz]	35.308	35.462	35.132	35.102	35.124	35.258	34.951	34.941	34.600	34.738	34.347	34.525
η	—	—	—	—	—	—	—	—	0.09	0.09	0.09	0.11
	— Calculations, solid phase (150 K) —											
Method	— HF/6-31G* —				— MP2/6-31G* —				— B3LYP/6-31G** —			
	- molecule 1 -		- molecule 2 -		- molecule 1 -		- molecule 2 -		- molecule 1 -		- molecule 2 -	
Position	Cl8	Cl10	Cl8a	Cl10a	Cl8	Cl10	Cl8a	Cl10a	Cl8	Cl10	Cl8a	Cl10a
ν_Q [MHz]	35.06	35.16	34.88	34.72	35.08	35.14	35.76	35.59	34.84	34.96	34.69	34.56
η	0.11	0.12	0.11	0.14	0.11	0.11	0.11	0.14	0.15	0.17	0.15	0.19
e^2Qqh^{-1} [MHz]	69.83	69.97	69.47	69.01	69.87	70.00	71.22	70.73	69.16	68.26	68.85	68.33

Result and Discussion

Using the crystallographic data from [4], the basic parameters characteris the hydrogen bonds and the so-called chlorine-chlorine contacts. The distance between the chlorine atoms Cl(8)..Cl(8) is 3.314 Å, while that between the atoms Cl(10a)...Cl(10a) is 3.440 Å, Figure 3. The hydrogen bond C(9a)(H9a)...N(1) stabilising the structure is short, of only 2.503 Å. However, the angle of the hydrogen bond ⟨C(9a)(H9a)N(1) is only 168°, so this bond is not very strong. The packing of the 4,6-dichloropirymidine molecules in the elementary cell is shown in Figure 2.

The occurrence of four resonance lines in the ^{35}Cl-NQR spectrum confirms the presence of two inequivalent molecules in the elementary cell, with the inequivalence due to differences in hydrogen bonds [4]. Measurements of the ^{35}Cl NQR frequency as a function of temperature at 77 to 300 K showed that the two resonance lines of the lowest frequencies intersect at a temperature of about 175 K (Figure 4). Because of the different behaviour of 4,6-dichloropirymidine compared to that of earlier studied compounds, we have undertaken a detailed study of the bondings in the former.

The correct assignment of the NQR resonance frequencies requires ab initio calculations for the solid and gas phase (Table 1). The NQR frequency calculations for the solid were based on its crystallographic structure, and those for the gas on the optimised geometry of the molecule. Since the crystal structure has been determined by X-ray diffraction at 150 K, i. e. at a lower temperature lower than that at which the lines intersect, the assignment of frequencies was unambiguous. Results closest to the experimental ones

Table 2. The parameters of the fit (a_0, a_1, a_2, a_{-1}, a, b, c) with different theoretical dependences.

Theory	$a_0(a)$ [MHz]	a_1 10^{-3} [MHzK^{-1}]	a_2 10^{-6} [MHzK^{-2}]	a_{-1} [MHzK]	b [MHz]	c [K]	s [kHz]
Bayer	35.44	—	—	—	1.36	322.87	3.63
	35.34				1.16	281.09	5.05
	35.14				2.08	383.28	9.29
	35.09				1.12	324.64	5.37
Brown[a]	35.56	–1.18	–5.26	—	—	—	3.59
	35.47	–1.67	–4.33				3.65
	35.24	–0.73	–7.77				3.54
	35.18	–0.95	–4.29				2.88
KBB[b]	35.99	–3.93	—	–20.82	—	—	8.76
	35.84	–3.96		–17.75			5.94
	35.89	–4.80		–30.84			13.05
	35.54	–3.21		–17.17			6.71

[a] Extended for low-temperature region;
[b] Kushida, Benedek, Bloembergen.

were obtained for the basis set 6-31G* at the B3LYP level of the theory (correlation coefficient $r = 0.9505$ and curve standard error $s = 0.0043$). Adding a double polarisation function to 6-31G** did not cause a significant improvement of the results ($r = 0.9582$; $s = 0.0037$, Table 1).

A comparison of the ab initio with the experimental results leads to the conclusion that the two lines of higher frequencies belong to the chlorine atoms of molecule 1, while the two of lower frequencies belong to the chlorine atoms of molecule 2 (Fig. 3, Table 1). The line corresponding to the highest frequency should be assigned to Cl(10), while that of a bit lower frequency to Cl(8), Figure 3. From the two lines of lower frequencies, that of the lowest frequency should be assigned to Cl(10a), while that of a bit higher frequency to Cl(8a), Figure 3. This means that in molecule 1 the C-Cl bonds are somewhat more covalent than in molecule 2. The differences amounts to merely 1%. In the gas phase the chlorine atoms are equivalent, as expected. Intermolecular interactions change the molecular geometry (bond length, bond angles), which leads to changes in the electron density distribution, manifested by shifts of the resonance frequencies by 0.07 MHz and 0.18 MHz on the chlorine atoms at the positions Cl(8a) and Cl(10a) in molecule 2 and 0.11 MHz and 0.27 MHz at Cl(8) and Cl(10) in molecule 1.

The temperature dependencies of the ^{35}Cl-NQR frequencies of the four resonance lines indicated much greater dynamics of molecule 2 than of molecule 1, the latter seeming rather rigid due to stronger intermolecular bondings, Table 2.

Table 3. The physical parameters calculated from the parameters of the fit: frequencies at 0 K ($\nu(0)$), moments of inertia (I) and anharmonicity (g).

Theory	$\nu(0)$ [cm^{-1}]	I [10^{-47}kgm^2]	ΔE [kJ/mol]	g [10^{-6}K]
		— NQR —		
Bayer	79.93	17.04	2.68	—
	64.36	22.80	2.34	
	87.76	9.40	3.19	
	74.34	10.15	2.69	
Brown	35.56	—	—	28.43
	35.47			2.59
	35.24			10.64
	35.18			4.52
		— Other methods —		
Measured or calculated	410[a]	27.38[c]	—	—
	443[a]	26.94[c]		
	411[b]	27.18[c]		
	422[b]	26.33[c]		
	449[b]			
	160[b]			
	212[b]			

[a] IR data taken from [8]; [b] Raman data taken from [8]; [c] calculated from the crystallographic data.

The parameters of the fit obtained for different theoretical models (the Bayer's theory, Kushida, Benedek, Bloembergen (KBB), modified Brown theory) and curve fit standard errors are given in Table 2, which shows that the experimental results are best described by the Brown dependence in the low-temperature range. In the hig-temperature range the Brown dependence yields unphysical parameter values. The fitted curves obtained assuming the Brown model are shown in Figure 4. The best fit is obtained assuming the Brown's theory which does not take the anharmonicity of the vibrations into account and neglects the effect of changes in the crystal volume on the resonance frequency. According to the available crystallographic data, the temperature changes of a 4,6-dichloropyrimidine crystal are relatively insignificant [4]. In view of the above, it is understandable that the fits following from the Bayer and KBB theories are rather poor. Their fundamental assumption of a constant frequency of the molecular vibrations fails.

The basic parameters characterising the compound's dynamics calculated from the parameters of the fit given in Table 2 are collected in Table 3. Interestingly the vibration-frequencies calculated from the parameters of the fit are much lower than those obtained from the IR or Raman spectra (Table 3). The differences follow mainly from the fact that the IR and Raman studies were carried out in the liquid phase (4,6-dichloropirymidine solution in $POCl_3$ [7]). In the solid state such studies were not made. Moreover, when in the molecule studied there are no rotating groups and the only probable relaxation mechanism involves librations, such deviations have been observed [8] and explained by the simplicity of the model.

The moments of inertia estimated from the parameters of the fit (the Bayer theory) are much lower than those calculated from the crystallographic data (Table 3); a similar conclusion was drawn in [8]. The differences follow from the poor quality of the fit (Bayer's model does not give a good description of the experimental data, especially for the Cl8a chlorine atom of molecule 2, as indicated by the high standard deviation).

A comparison of the temperature dependencies of the NQR frequencies and the parameters describing the vibrations, collected in Table 2, reveals that the relaxation processes are more effective in molecule 2 than in molecule 1. In Fig. 4 the slope of the curve corresponding to the chlorine atom Cl(8a) is much greater than that corresponding to Cl(10a) or chlorine atoms from molecule 1 (Cl(8) and Cl(10)). Moreover, the vibrations of Cl(8a) are much more effective than those of Cl(10a), which is indicated by e. g. higher values of *c* for Cl(8a) than for Cl(10a) (383.28 K and 324.64 K, respectively) and activation energies calculated only for the sake of comparison (3.19 and 2.69 kJ/mol, respectively). The differences between the chlorine atoms Cl(8a) and Cl(10a) are due to the intermolecular interaction of the chlorine atoms Cl(10a)-Cl(10a), which makes Cl(10a) more rigid than Cl(8a). On the other hand, Cl(8) is not much different from Cl(10) although there is intermolecular Cl(8)...Cl(8) contact which should be stronger than the Cl(10a)..Cl(10a) one, since the distance is shorter. The reason for this difference is the fact that the two C(10a)...Cl(10a) bonds are not collinear and the angle between them is much greater than that between the C(8)...Cl(8) bonds. Moreover, the hydrogen bond C(9a)(H9a)...N(1) certainly stabilises the structure and in particular the bonds involving the chlorine atoms Cl(10a) and Cl(10), Figure 3.

A study of the temperature dependencies of the relaxation times, aiming at elucidating of the effect of hydrogen bonds on the relaxation processes taking place in solid 4,6-dichloropirymidyne, is under way.

Conclusions

i) The most important conclusion following from our study is that the known temperature dependence of the NQR frequencies and the crystallographic data for the solid state allow a correct assignment of particular resonance frequencies to particular chlorine atoms. It should be emphasised that the analysis of NOR data of the spectra recorded at 77 K and 293 K only, could be misleading.

ii) Results closest to the experimental ones were obtained for the basis set 6-31G* at the B3LYP level of the theory.

iii) The temperature dependencies of ^{35}Cl-NQR frequencies were analysed for all four resonance lines. Moreover, the results ascribed to molecule 2 proved untypical, indicating much greater dynamics of molecule 2 than those to that of molecule 1, which seemed rather rigid.

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