

SPECTROSCOPIC INVESTIGATIONS OF PHASE TRANSITION IN 5-CHLORO-2-PYRIDONE

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ABSTRACT

Spectroscopic investigation of 5-chloro-2-pyridone has been carried out in the temperature range 77–300 K. At room temperature the ^{35}Cl NQR spectrum shows a single line at 35.618 MHz, but at 250.7 K two lines appear at 35.850 MHz and 35.840 MHz respectively indicating the presence of a phase transition. IR, far-IR, laser Raman and dielectric measurements have been carried out to investigate the phase transition further. Low temperature IR studies show splitting of $\nu(\text{C}-\text{Cl})$, $\beta(\text{N}-\text{H})$ and $\nu(\text{C}=\text{O})$ bands at T_c . Dielectric measurements show a small, but finite, change in the value of the dielectric constant around T_c . Raman spectra at different temperatures support the existence of a new phase, as shown by the appearance of a new band at 81 cm^{-1} , the frequency of which changes slowly as T_c is approached and which disappears at T_c . The temperature dependence of the NQR frequencies has been analysed using Bayer Kushida and Brown equations to evaluate the torsional frequencies.

INTRODUCTION

Pyridinols have a tendency to exist in tautomeric forms both in solution and in the solid [1]. Infrared studies on the tautomerism of chloropyridinols isolated in an argon matrix indicated that the enol/keto ratio increases according to the position of the chlorine atom in the pyridine ring [2]. For example, 5-chloro-2-pyridinol exists in the keto form whereas 6-chloro-2-pyridinol exists in the enol form. In 5-chloro-2-pyridinol, the molecules form dimers consisting of two pyridine rings joined by hydrogen bonds [3]. The two chlorine atoms in the dimers are connected by a centre of symmetry. Since NQR spectroscopy has been extensively used for studying hydrogen bonding in the chlorosubstituted compounds [4, 5], it is of interest to investigate 5-chloro-2-pyridinol, especially at low temperatures because of the possibility of the change in the nature of the hydrogen bond at different temperatures.

EXPERIMENTAL DETAILS

5-Chloro-2-pyridone was prepared by diazotization of the corresponding chloroamino pyridine followed by hydrolysis using NaOH. About 10 g of 5-chloro-2-amino pyridine was dissolved in 70 ml of 6N HCl to which 10 g of NaNO₂ was added. After a careful neutralization of the resulting cold suspension to pH 5 with aqueous NaOH, the pyridone was filtered off, washed with ice water, and crystallized from alcohol (melting point 168.8°C, lit. 169°C, yield 80%).

The compound was characterized by IR and NMR. The IR spectrum of the compound taken in KCl showed two close bands at 1650 cm⁻¹ and 1645 cm⁻¹ which were absent in the parent compound. Two other bands, one around 2820 cm⁻¹ and another sharp band at 660 cm⁻¹ were attributed to $\nu(\text{OH})$ and $\nu(\text{C}-\text{Cl})$ respectively [6]. Bands at 1650 cm⁻¹ and 1645 cm⁻¹ were assigned to the stretching mode of the (C=O) group, suggesting that the compound exists in the keto form. A broad band around 1605 cm⁻¹ was assigned to $\beta(\text{N}-\text{H})$ in-plane bending. A ¹H NMR spectrum of the compound in deuterated acetone showed a broad signal at 11.06 δ which was absent in 5-chloro-2-amino pyridine. The signal at 7.2 δ assigned to the NH proton in the parent compound was also absent in the derivative indicating that the amino group had been converted to the hydroxyl group.

RESULTS

About 2 g of the substance was packed into the sample tube. Frequency sweep rate was of the order of 300 kHz h⁻¹. The quench frequency was varied from 35 kHz to 60 kHz under different conditions. A high quench frequency was required to separate the two signals at low temperatures. The time constant of the lock-in amplifier was 10 s.

Nuclear quadrupole resonance

The first observation of the ³⁵Cl NQR signal in 5-chloro-2-pyridone has been reported [7]. The frequency of the NQR signal was found to be 35.618 MHz compared with 35.126 MHz in 5-chloro-2-amino pyridine from which the present compound was synthesised. As the temperature of the sample was lowered, the frequency of the NQR signal increased until 250.7 K was reached. At this temperature, there was a slight broadening of the NQR signal and a new line appeared. Below 250.7 K, the single resonance line split into a pair of lines of unequal intensity and the magnitude of the splitting became progressively larger at lower temperatures. The temperature variation of the NQR signals in the temperature range 77–300 K is shown in Fig. 1. Splitting of the lines at 250.7 K indicates that there are two inequivalent chlorine atoms. This may be due to a phase transition. The NQR spectrum at 77 K is shown in Fig. 2.

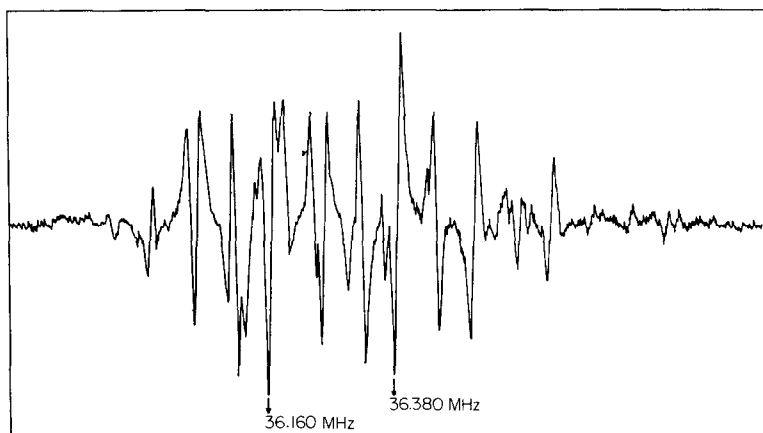


Fig. 1. ^{35}Cl NQR spectrum of 5-chloro-2-pyridone at 77 K.

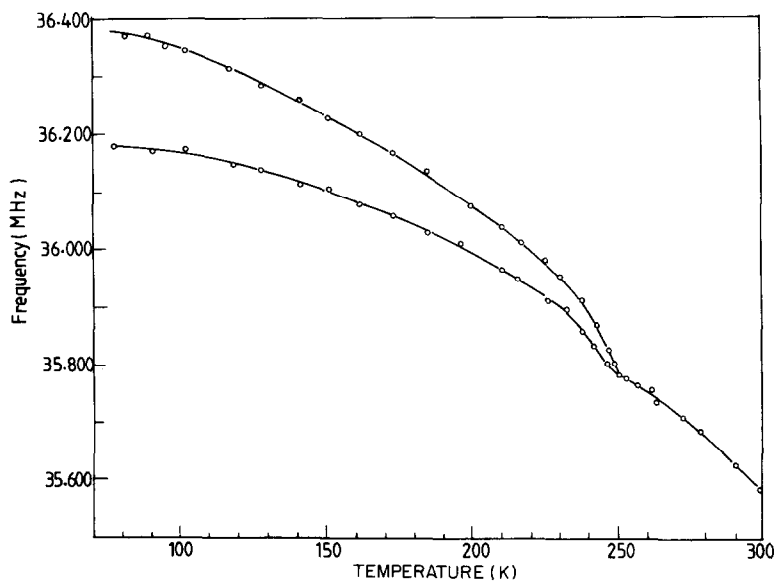


Fig. 2. Temperature variation of ^{35}Cl NQR signals in the range 77–300 K.

When the temperature of the sample was quenched to 77 K by directly immersing it into liquid nitrogen, the NQR line pattern appeared to be different from that obtained by slow cooling. Monitoring the temperature dependence of the NQR signals from 77 K upwards showed that they disappeared into the noise above 112 K. Around the same temperature, two lines were detected at higher frequencies which coincided with the lines from the sample subjected to slow cooling. The temperature at which the lines disappear seems to be dependent on the rate of quenching. It appears that there

could be more than two lines in the NQR spectrum at 77 K when the sample is subjected to fast cooling. An explanation for this behaviour is given below.

Low temperature IR studies

Low temperature infrared studies carried out on this compound revealed interesting features. The IR spectrum was obtained with KCl in the form of a thin pellet, using a Perkin-Elmer 580 spectrometer with a built-in cryostat. The infrared spectra at 300 K, and 248 K are shown in Figs. 3 and 4, respectively. The two broad bands around 2820 cm^{-1} , 1605 cm^{-1} and the sharp band at 660 cm^{-1} have been attributed to $\nu(\text{OH})$ involved in hydrogen bonding, $\beta(\text{NH})$ in-plane bending and to the stretching mode of C—Cl respectively [6]. Two close bands at 1650 cm^{-1} and 1645 cm^{-1} are attributed to the stretching mode of the carbonyl (C=O) group. In addition bands at 985 cm^{-1} , 905 cm^{-1} and 840 cm^{-1} were observed, the assignment of which

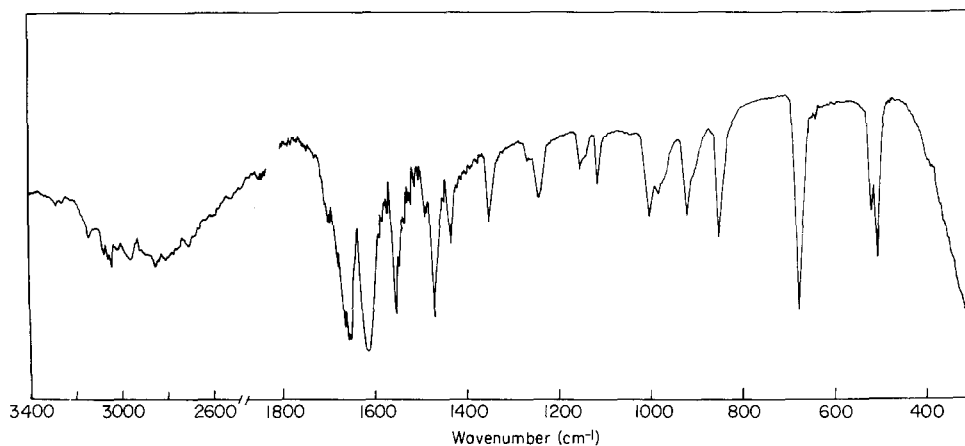


Fig. 3. IR spectrum of 5-chloro-2-pyridone at 300 K.

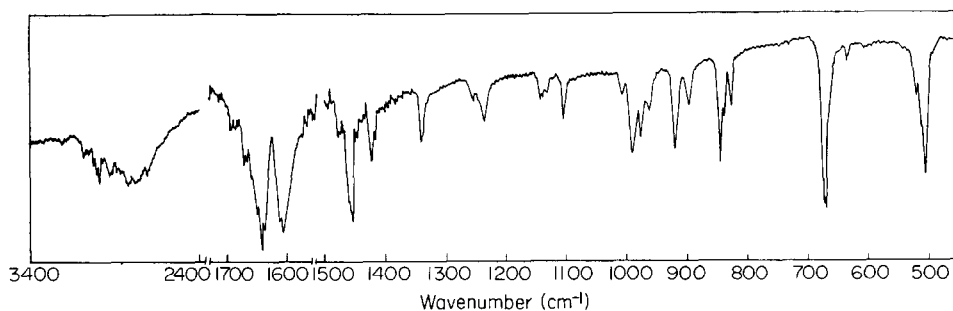


Fig. 4. IR spectrum of 5-chloro-2-pyridone at 248 K.

was not made. A shoulder on the 1605 cm^{-1} band appeared in the IR spectrum at 248 K. The band at 660 cm^{-1} was split into two lines, though the splitting was small. The bands at 985 , 905 and 840 cm^{-1} were also split. As the temperature was lowered further, there was no further splitting but the intensity of the bands increased. Details of the IR data at different temperatures are shown in Table 1.

Dielectric measurements

The dielectric constant of the sample at various temperatures from 300 to 245 K was measured at 1 kHz using a Marconi universal impedance bridge TF 1313 A. The sample was powdered and compressed into a pellet. Air drying silver paint was employed on the surface of the pellet for electrical contact.

TABLE 1

Temperature variation of infrared frequencies of 5-chloro-2-pyridone

Sl. no.	300 K (cm^{-1})	253 K (cm^{-1})	248 K (cm^{-1})	123 K (cm^{-1})	Remarks
1	1650	1655	1650	1675	Assigned to $\nu(\text{C=O})^a$ Stretching frequency
	1645	1652	1643	1667	
2	1605	1607	1607	1639	Assigned to $\beta(\text{N-H})$ [6]
			1640	1663	
			1615	1631	
3	985	985	990	990	
			972	972	
			962	962	
			895	895	
4	905	905	912	917	
			840	842	
5	840	840	835	835	
			825	823	
			660	668	
6	660	660	668	668	C-Cl bond ^a
			660	660	

^aA. R. Katritzky, and R. A. Jones, *J. Chem. Soc.*, (1960) 2947.

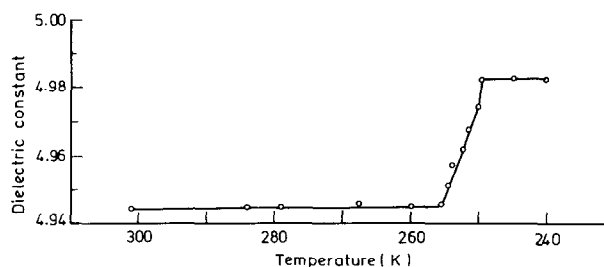


Fig. 5. The temperature variation of the dielectric constant of 5-chloro-2-pyridone.

The variation of the dielectric constant with temperature is shown in Fig. 5. The value of the dielectric constant does not change over the temperature range 302–255 K. Between 255 and 249 K, there is a small change in the value of the dielectric constant from 4.91 to 4.98 after which it again remains constant. During the heating cycle also, the same variation in the value of the dielectric constant was observed over the temperature range 248–254 K.

Far-IR and low temperature laser Raman studies

The sample was subjected to laser Raman studies in the temperature range 290 to 240 K to observe any changes in the low frequency lattice modes. Raman spectra were recorded on a spex Ramalag 4 spectrometer using spectra/physics argon ion laser exciting line (4080 nm). A conventional cryostat was employed for temperature variation. The sample was compressed into a pellet of approximate thickness 0.3 mm for measurements. The far-IR spectrum was recorded on a polytec FIR 30 spectrophotometer at room temperature. The far-IR spectrum showed absorptions at 33, 66.6, 90.5 and 152 cm^{-1} . The Raman spectrum of the solid at 293 K showed a sharp band at 63 cm^{-1} and a broad band at 140 cm^{-1} when swept from 30 to 200 cm^{-1} while in the high frequency range (200–3000 cm^{-1}) a weak band at 1260 cm^{-1} was also observed.

As the temperature was lowered, there was no change either in the intensity or in the line width of the bands observed in the Raman spectrum. However, below T_c (around 240 K) a small shoulder appeared at 81 cm^{-1} , which as the sample was warmed, shifted towards the main band at 63 cm^{-1} and disappeared at T_c (250.7 K). The weak band could be recognised just below T_c in the warming cycle, but in the cooling cycle, it appeared only when the sample was cooled below T_c by about 10°. This weak band was almost invisible as soon as the transition temperature was reached while good correspondence was observed for the other bands in both phases. The variable temperature Raman spectrum is shown in Fig. 6.

DISCUSSION

The x-ray structure [3] of 5-chloro-2-pyridone (Fig. 7) shows that it exists in the pyridone form (C=O). The crystal belongs to the monoclinic system and to the space group $C2/c$ with $Z = 8$. The two pyridine rings are joined by two hydrogen bonds to form a dimer and four such dimers are present in the unit cell. The chlorine atoms of the dimers are connected by a centre of symmetry.

At laboratory temperature the NQR spectrum shows a single sharp line indicating that all the chlorine atoms in the unit cell of the crystal are crystallographically equivalent. However, below 250.7 K, the single line splits into a pair of lines of unequal intensity and the two signals have different

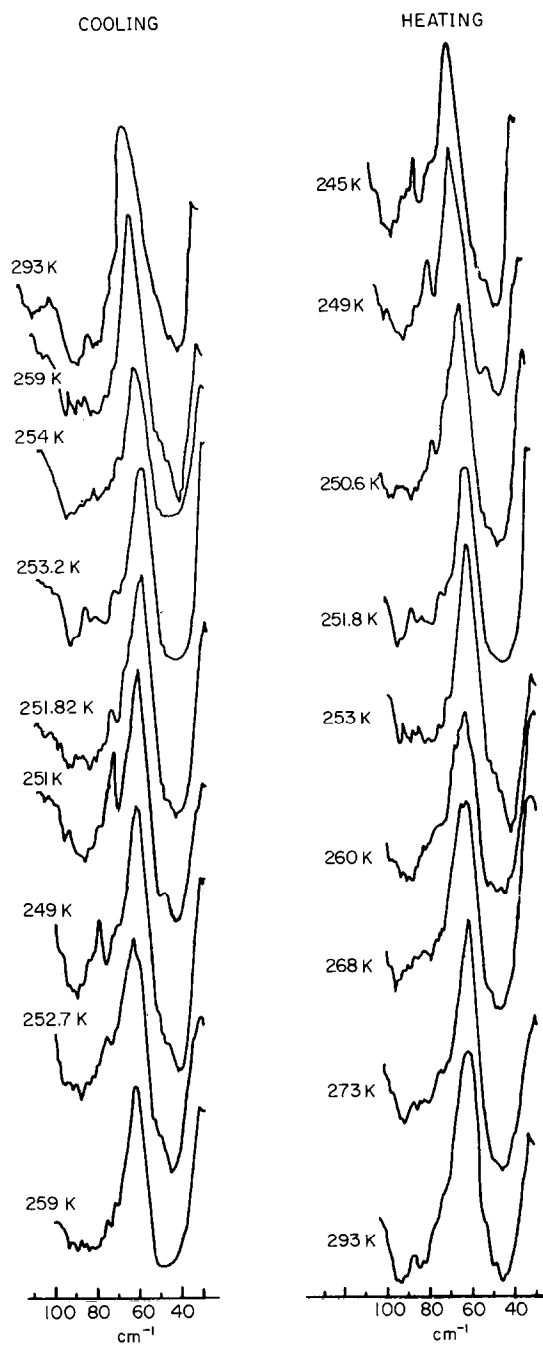


Fig. 6. Raman spectra of 5-chloro-2-pyridone at different temperatures.

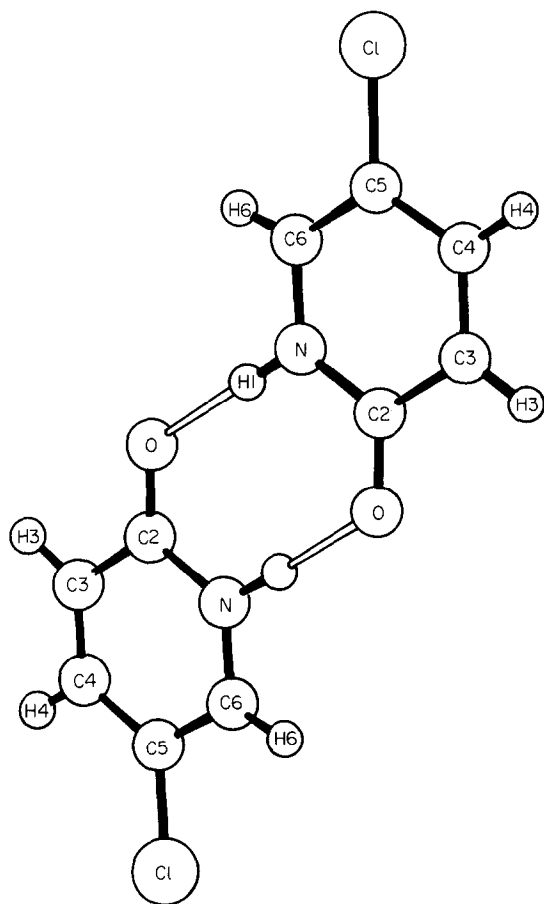


Fig. 7. X-ray structure of 5-chloro-2-pyridone.

temperature coefficients ($\partial\nu/\partial T$). From NQR and X-ray data [3] it is reasonable to assume that the centre of symmetry of the crystal is lost, making the two chlorine atoms inequivalent and giving rise to the NQR signals.

Low temperature infrared studies show a small splitting (shoulder peak) at 1605 cm^{-1} attributed to the $\beta(\text{N-H})$ in-plane bending frequency and the band at 660 cm^{-1} , assigned to the C-Cl stretching frequency, also splits below T_c indicating the presence of two different chlorines. The small magnitude of the splitting both in the NQR and IR spectra shows that there is only a slight difference between the low temperature phase (LTP) and the high temperature phase (HTP) structures. The IR band around 2820 cm^{-1} is broad both at low and room temperatures. This broad band is attributed to the presence of intermolecular hydrogen bonding. Often, but not always, the $\nu(\text{OH})$ stretching frequency band at 2820 cm^{-1} is accompanied by a band at 1605 cm^{-1} attributed to $\beta(\text{N-H})$ in-plane bending [6]. The small but finite

splitting of the 1605 cm^{-1} band in the low temperature phase shows that the two hydrogen bonds in the dimer are no longer equivalent and the strength of one differs slightly from the other. The broad band at 2820 cm^{-1} does not change across T_c , because it is the low frequency lattice modes which are generally more affected rather than the high frequency stretching modes during structural phase transitions [8, 9]. The splitting of the bands at 985 cm^{-1} and 840 cm^{-1} , however, could not be explained because the assignment of the bands is not known.

There are a number of crystals where phase transitions are accompanied by the loss of one of their symmetry elements. For example, chloranil [10], phosphorus pentachloride [11] (P_4Cl_{10}), pentaerythryl chlorides [12] and many of the perovskites (barium titanate (BaTiO_3)) give rise to phase transitions by losing one of their symmetry elements. Such compounds generally exhibit a very weak heat anomaly seen over a wide range of temperatures. The broad curve of heat anomaly has been explained on the basis of a soft vibrational mode. The reorientation of the molecule, which is responsible for the loss of symmetry, often acts as an order parameter.

Based on such similarities, it is not unreasonable to consider the phase transition in 5-chloro-2-pyridone as due to a slight reorientation (tilt) of one of the molecules in the dimer. The temperature coefficients are different for the two NQR lines indicating that the torsional modes which are responsible for the averaging of the electric field gradients have different effects at the two chlorine sites. This could be explained on the basis of the reorientation of one half of the dimer in the plane of the dimer about an axis perpendicular to its plane. This would change the inter-dimer interaction in the crystal, which facilitates loss of the centre of symmetry of the crystal.

In the low temperature phase (LTP) the low frequency line (LTP 1) is almost an extension of the high temperature phase line (HTP line) whereas LTP line 2 follows a different path away from the HTP line (Fig. 1). The frequency of LTP line 2 increases faster than LTP line 1 as the temperature is lowered. This behaviour has already been observed in *p*-chloranil where Zeeman effect studies [13] have revealed that one of the C-Cl bond directions changes with respect to the laboratory coordinates below T_c . The extent of splitting of NQR signals increases progressively in the LTP but much of the contribution to the splitting comes from LTP line 2 rather than LTP line 1. Such an experimental observation could be explained on the basis of a slight tilt of one of the molecules of the dimer with respect to the other in such a way that it loses the centre of symmetry and hence produces different effects at the two inequivalent chlorine sites by torsional motion of the molecule.

Low frequency lattice modes play an important role in structural phase transitions [8]. It may be expected that the slight tilt of the molecule in the low temperature phase may either change the frequency of some of the vibrational modes or create new modes altogether. Far-IR and laser Raman spectra should show any such changes. The Raman spectrum of 5-chloro-2-

pyridinol shows a small shoulder at 81 cm^{-1} in the low temperature phase. This may be due to the fact that some of the lattice modes are not active in the high temperature (also high symmetry) phase, but become active as the symmetry is lowered. Since, 5-chloro-2-pyridone is centrosymmetric at room temperature, only three modes could be observed in the high temperature phase. Lattice modes at 63 and 81 cm^{-1} are probably librational modes because they are generally observed in the low frequency range (below 200 cm^{-1}). The potential barriers for these vibrations are determined by the coulomb, repulsive and van der Waals interactions. It can be considered that some of the potential functions are affected by the tilt of the molecule in the crystal, i.e. this tilt produces an anharmonic coupling between lattice modes causing one to shift its frequency, which is probably why the 83 cm^{-1} band shifts as the temperature is increased. At high temperature, the molecule regains its centre of symmetry and consequently the mode becomes Raman inactive. It is difficult to say whether softening of the mode is responsible for the phase transition because the mode disappears at T_c rather than changing its frequency to zero. Since the frequency of the new band does not shift to zero, even though it tends to decrease, it is unlikely to be a soft mode.

According to the crystal structure of the compound at room temperature (Fig. 7), the double bond character in the (C_3-C_4) bond (1.343 \AA) and (C_5-C_6) bond (1.342 \AA) is large whereas the (C_2-C_3) bond (1.427 \AA) and (C_4-C_5) bond (1.405 \AA) interactions have smaller contributions to π -bonding. The C=O distance of 1.250 \AA in 5-chloro-2-pyridone is somewhat shorter than that of 1.262 \AA found in pyridone. The carboxyl bond distance depends on the H-bond interaction with oxygen. In pyridone, a strong $O-H\cdots O$ hydrogen bond of length 2.570 \AA increases the C—O bond length. Hence, 5-chloro-2-pyridone which has an $O-H\cdots O$ length of 2.796 \AA has a weaker H-bond compared with pyridone. As the temperature is lowered, molecular motion changes the inter-molecular interactions which facilitate a change in the strength of the H-bond. Thus, it is quite likely that the polarizability of the molecule may change due to the change in the nature of the H-bond. The slight deformation of the dimer at low temperatures may result from the different π -bond characters of the C(4)—C(5) and C(3)—C(4) bonds in the pyridine ring making it more polarizable than that of the dimer in the high temperature phase. This change in the polarizability of the molecule in the LTP may make some of the librational modes active in Raman spectra, and is possibly the reason why the new band at 81 cm^{-1} appears in the low temperature Raman spectrum.

There was no sharp anomaly in the heat content of the sample across the phase transition when it is subjected to differential scanning calorimetry (DSC). However, there was a small change in the slope of the molar heat capacity versus temperature curve from which it was difficult to characterize T_c . Such behaviour could be expected, based on earlier observations on chloranil and others [10–12]. A phase transition of this kind hardly affects the macroscopic properties such as ΔH indicating the microscopic nature of

the phase transition. This unusually small heat content and entropy change of the transition has been found in many substances such as PCl_5 (P_2Cl_{10}) [11], *o*-chloranil [10], *p*-chloranil [14], 3,5-dichloropyridine [15], (phase II–III). This also suggests that the transition may be of a higher order.

When the sample was subjected to fast cooling, by quenching it with liquid nitrogen directly, the NQR pattern shown is different from that obtained from a sample which is cooled slowly.

Low temperature IR spectra indicated the splitting of bands only when the sample is cooled slowly and for a longer time well below T_c . The intensity of the bands increased after prolonged cooling for 1–1.5 h. Raman spectra show the appearance of a new band when it is cooled well below T_c . Thus the transition appears to be sluggish in nature. Quenching of the high temperature phase down to 77 K may result in a mixture of the two phases. When kept for a sufficient time, the metastable phase disappears giving rise to two well-resolved lines of the LTP phase.

Torsional mode analysis of the temperature dependence of resonance frequencies

It is well known that the librational (torsional) modes average the electric field gradient (EFG) accounting for the temperature dependence of NQR frequencies. Bayer's equation for the temperature dependence of NQR frequencies, as modified by Tatsuzaki [16] is given by

$$\nu_q(T) = \nu_0 \left[1 - (3h/8\pi^2c) \sum_i (\sin^2 \alpha_i / A_i f_i) \left(\frac{1}{2} + \frac{1}{[\exp(hcf_i/kT) - 1]} \right) \right]$$

where ν_0 is the NQR frequency for the stationary molecules, f_i the frequency (cm^{-1}) of the torsional mode, A_i the corresponding moment of inertia and α_i the angle between the axis of the i^{th} torsional mode and the principal Z -axis of the EFG tensor, and T is the absolute temperature.

The molecule is planar and a three mode analysis would be ideal but the numerical solution becomes complicated. Hence, a two-mode analysis has been carried out using a procedure similar to the one used by Vijaya and Ramakrishna [17]. Torsional frequencies have been calculated from both the Bayer and the Tatsuzaki model. The moment of inertia values for both Bayer and Tatsuzaki models and the angles α_1, α_2 were calculated using the centre of mass as the origin of the coordinate systems; it was found that $\alpha_1 = 90^\circ$ and $\alpha_2 = 154.5^\circ$, respectively. Since the molecule exists as a dimer even in the solid state [3], the dimer structure has been retained for the calculation of moment of inertia. The principal values of the moment of inertia tensor were calculated using the EIGEN subroutine. The two axes of moment of inertia are chosen in terms of the higher weightage factors ($\sin^2 \alpha_i / A_i$). To find the ν_0 NQR frequency at 0 K, and also to find which model fits the experimental data better the functional dependence of was least square-fitted to the following three equations

$$\nu_q(I) = A + BT + CT^2 + DT^3 + ET^4 \text{ (fourth order polynomial)}$$

$$\nu_q(I) = a + bT + C/T \text{ (Kurhida's high temperature expression)}$$

$$\nu_q(I) = A' + B'(T - T_0) + C'(T - T_0)^2 \text{ (Brown's parabolic equation)}$$

After about 125 iterations, convergence was more or less achieved and the constant A in the fourth order polynomial provided the expected NQR frequency at 0 K. It was found that the parabolic and fourth order equations were good fits to the experimental curves. The high temperature equation, however provided a poor fit.

As the compound undergoes phase transition at T_c , the torsional frequencies were calculated for the high temperature phase line (HTP line) and the low temperature phase lines (LTP 1 and LTP 2) separately.

As discussed earlier, there should be no major changes in the X-ray crystal structure except the centre of symmetry was lost. Hence values for the principal moment of inertia were retained as in the HTP. Since one of the molecules of the dimer in the crystal was tilted in the LTP phase, in the same plane, angles α_1 and α_2 would change. Hence α_2 i.e., the angle between EFG and the moment of inertia tensor in the plane of the molecule, was varied from 154.5° to 145° by 2° at a time to fit the experimental data. For values of α_2 in the range 145 – 147° , the experimental data could be matched, i.e. it may be reasonably assumed that there was a small angular tilt of about 5 – 7° by one of the pyridine rings which could have destroyed the centre of symmetry. The temperature variation of the calculated torsional frequencies in both phases is shown in Figs. 8 and 9. The torsional frequencies calculated from NQR data using the Brown model are in the range 31 – 45 cm^{-1} (f_x) and 18 – 20 cm^{-1} (f_y) in the temperature range 77 – 300 K . The lowest frequency mode of the far-IR spectrum (33 cm^{-1}) agrees well with results from the torsional frequency calculations using NQR data.

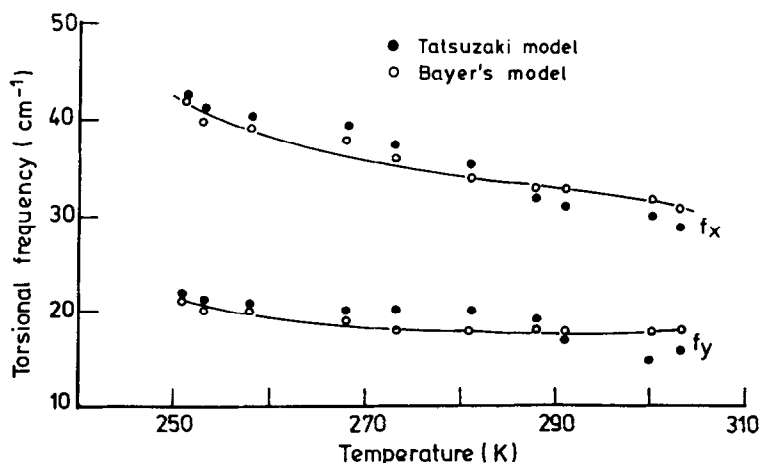


Fig. 8. Temperature variation of torsional frequencies for the HTP phase.

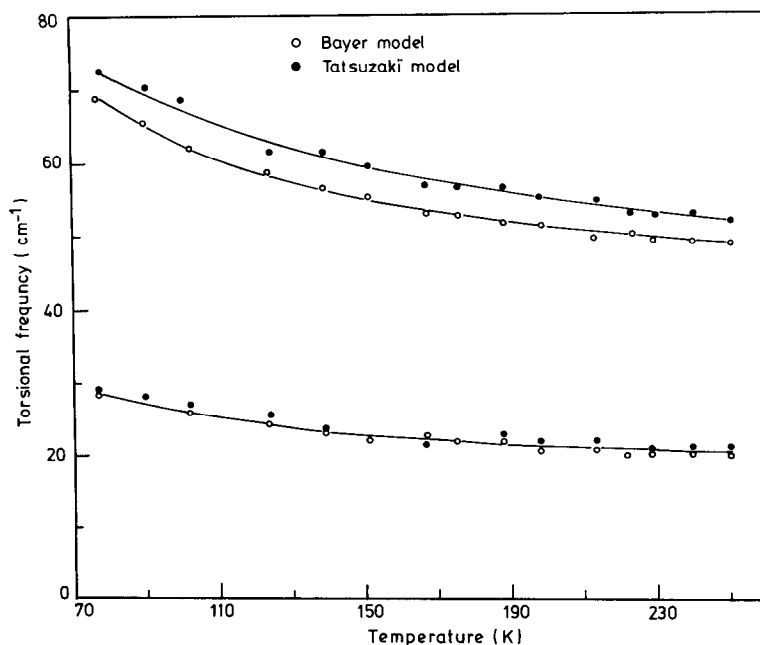


Fig. 9. Temperature variation of torsional frequencies for the LTP phase.

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