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LETTER TO THE EDITOR

Thermal hysteresis in 4,4' dichlorobenzophenone studied by ^{35}Cl NQR

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Abstract. A pulsed NQR study of 4,4' dichlorobenzophenone has been performed to get information about dynamic features in its three crystalline phases. We found in phases I ($T > 190$ K) and III ($T < 180$ K) a normal thermal behaviour of the NQR frequency and spin-lattice relaxation time. In the intermediate phase II ($180 \text{ K} < T < 190 \text{ K}$) the behaviour of the NQR parameters could not be explained with a simple Bayer's model of molecular torsional oscillations. This phase has been previously studied and is a nearly incommensurate one. Furthermore, a thermal hysteresis has been observed in both phase transition temperatures. This thermal hysteresis and the temperature range of the intermediate phase II showed a strong impurity concentration dependence.

Some biphenyl compounds have been studied by different experimental techniques, and found to exhibit some interesting molecular structural and dynamic features. In fact incommensurate phases have been found in a biphenyl and also in a chlorinated biphenyl as 4,4' dichlorobiphenylsulphone (4,4' DCBS) (Corbero *et al* 1985, 1986, Pusiol *et al* 1989, Kasano *et al* 1990). Raman spectroscopy (Peretti and Ranson 1979, Kirin and Pawley 1982), calorimetric and Brillouin scattering (Ecolivet *et al* 1987) studies of 4,4' DCBP report two first-order structural phase transitions around 185 K and 190 K, which involve intramolecular changes without great variation of the primitive unit cell. Furthermore, hysteresis effects in the phase transition temperatures attributed to defect migration have been reported. Nuclear quadrupole resonance (NQR) is a very sensitive technique for detecting intramolecular changes; we used this especially suitable tool in the study of this kind of compound.

Previous work on 4,4' DCBP using ^{35}Cl NQR (Wolfenson *et al* 1990) verified the existence of three crystalline phases in the range $80 \text{ K} < T < 300 \text{ K}$. The high-temperature phase (phase I: $T > 185 \text{ K}$) and low-temperature phase (phase III: $T < 175 \text{ K}$) showed normal thermal dependence of the NQR parameters; similar behaviour has been observed in other molecular crystals (Chihara and Nakamura 1981). In the intermediate-temperature phase (phase II: $175 \text{ K} < T < 185 \text{ K}$) a high dispersion of the electric field gradient (EFG) values at the resonant nucleus site was observed; so the NQR spectra showed features and linewidth very different from those observed for the other phases. In the earlier work, to explain these spectra, a normal-incommensurate structural phase transition between phase I and phase II and a lock-in transition between phase II and phase III were assumed. However, the strong thermal hysteresis observed in the phase transition temperatures is incompatible with

the usual soft-mode second-order transition model for incommensurate phases (Blinic 1981); so that behaviour was assigned tentatively to impurities present in the sample.

In this work we have performed a more detailed analysis of the possible effects of impurities on the hysteresis. NQR measurements of ν_Q (NQR resonant frequency) and T_1 (spin-lattice relaxation time) have been performed on some crystalline samples of different purity. The number of impurities in each sample was impossible to evaluate quantitatively, so we adopted the number of recrystallizations performed on each sample as a comparative criterion of degree of purity. We used the zone-melting recrystallization method: each sample (initially powder, provided by Aldrich Chemical Incorporated), sealed in a glass tube (diameter = 1 cm, length = 3 cm), passes slowly through a circular heater filament (diameter = 1.2 cm, thickness \approx 0.1 cm), which melts a slice of sample at a few degrees centigrade above the melting point. Each passage took no less than 48 hours. We prepared three samples identified as 1, 2 and 3 (4, 6 and 12 passages respectively) in the order of increase of the degree of purity.

The measurements were performed using a conventional home-made high-power pulsed spectrometer (Brunetti and Pusiol 1983). The NQR spectra were obtained by fast Fourier transform (FFT) from the digitized free induction decay (FID) signal. The measurements of T_1 were performed by using the two-pulse standard sequence ($90^\circ - \tau - 90^\circ$). The temperature fluctuations of the sample were less than 0.1 K and the cooling and heating rates were both about 0.4 K h^{-1} .

Measurements of $\nu_Q(T)$ and $T_1(T)$ were performed on sample 3 (the purest) in the temperature range $80 \text{ K} < T < 300 \text{ K}$ in order to characterize all the phases dynamically. Thermal cycle involving passing through the transition temperatures, represented in table 1, were performed on the other samples in order to study the hysteresis effects.

Table 1. Thermal cycles performed with the different samples of 4, 4' DCBF

| Sample | Cycle No | Cooling | Heating |
|--------|----------|----------|----------|
| 1 | 1 | I→II→III | III→II→I |
| 2 | 2 | I→II→III | III→II→I |
| 2 | 3 | I→II | II→I |

We can see in figure 1 that the thermal dependence of ν_Q of sample 3 shows a similar behaviour to that of other molecular crystals which present good agreement with Bayer's model of torsional oscillations. Following this model, we can write (Chihara and Nakamura 1981)

$$\nu_Q(T) = \nu_0 \left(1 - \frac{3}{2} \langle \theta^2 \rangle \right) \quad (1)$$

where ν_0 is the resonance frequency corresponding to a static lattice and $\langle \theta^2 \rangle$ is the angular displacement due to the libration, which can be expressed as a function of all the internal bending modes of the C-Cl bond, the lattice torsional modes and the moment of inertia I_i associated with each normal mode of frequency ω_{ei} .

Following Brown (Brown 1960), we can consider the thermal expansion effects on the lattice frequencies assuming a linear dependence on the temperature:

$$\omega_{ei} = \omega_{ei}^0 (1 - gT_i). \quad (2)$$

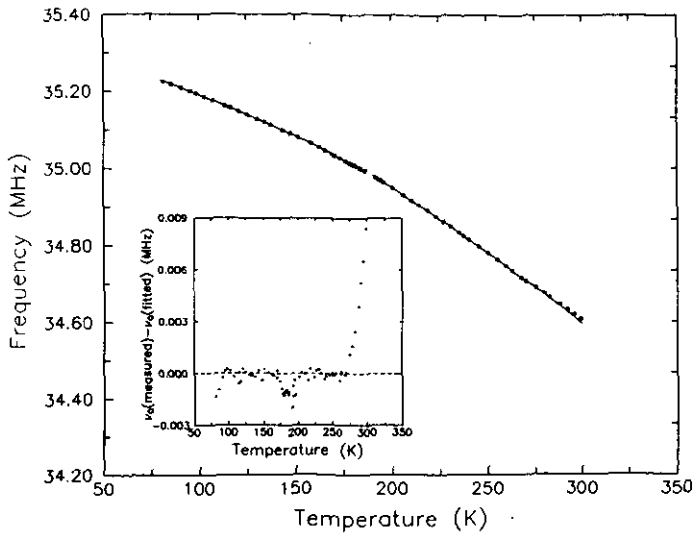


Figure 1. The temperature behaviour of the NOR frequency in 4, 4' DCBP. The solid line represents Bayer's fit in phases I and III. Inset: dispersion of the experimental data from the fitting.

We assume that there is one mode dominant on the averaging effect of the EFG, since we have not found vibrational frequency values in the literature. So we can express $\langle \theta^2 \rangle$ in (1) as a function of a mean torsional frequency ω^0 and a moment of inertia I in this way:

$$\langle \theta^2 \rangle = \frac{3}{2} (h / I \omega_e) \coth(h \omega_e / k_B T). \quad (3)$$

Table 2 shows the experimental values of the fitting parameters of $\nu_Q(T)$ in phases I and III. The dispersion of the data from the fitting function is represented in figure 1 (inset); it shows that the thermal dependence of ν_Q , in a wide temperature range, corresponds to that observed in normal molecular crystals, except around the transition temperatures and above 270 K. A thermally activated process (i.e. neighbour modulation), or the precursor effects of the phase transition at 330 K reported recently (Nakayama and Eguchi 1991), may produce the departure of the experimental data from Bayer's model for $T > 270$ K.

Table 2. Fitting parameters of $\nu_Q(T)$ in phases I and II.

| | Phase I | Phase II |
|--------------------------------|----------------------|----------------------|
| ν_0 (MHz) | 35.518 | 35.369 |
| ω^0 (cm ⁻¹) | 25 | 25 |
| I (amu Å ²) | 925 | 1380 |
| g (K ⁻¹) | 3.7×10^{-4} | 6.6×10^{-4} |

Phase II is characterized by a more complex spectrum than that observed for other phases (figure 2). The spectra show two well defined regions with different

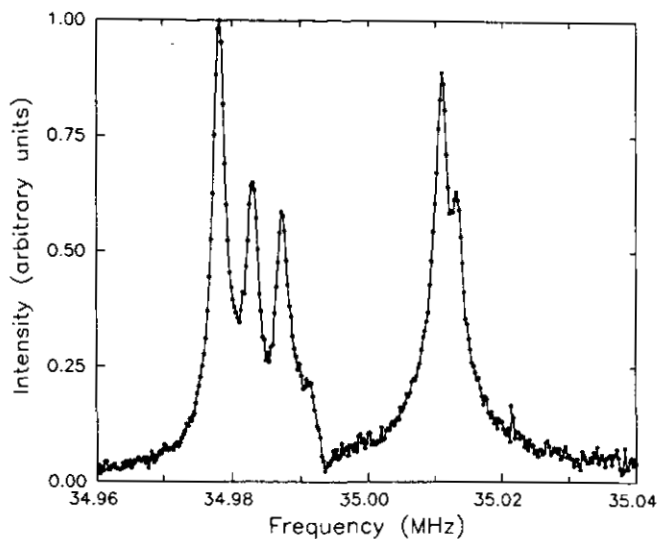


Figure 2. A typical NQR spectrum on heating 4, 4' DCBP in the intermediate phase (phase II) ($T = 188.5$ K). There are two well defined regions in the EFG distribution.

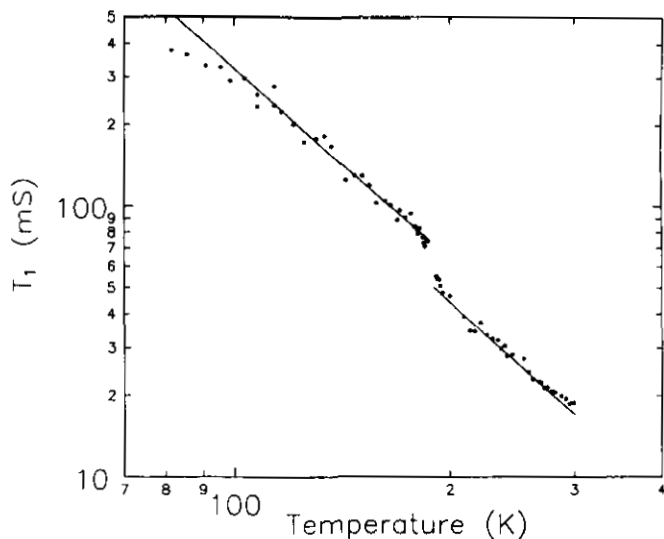


Figure 3. The temperature behaviour of the spin-lattice relaxation time T_1 in phases I and III. Solid lines represent the fitting of $T_1 = aT^{-\lambda}$ in each phase.

structures. Each region presents a linewidth broader than the resonance lines of phases I and III.

Measurements of $T_1(T)$ (figure 3) are in good agreement with the observed behaviour of $\nu_Q(T)$. These measurements for phases I and III correspond to the model of torsional oscillations (Chihara and Nakamura 1981), which gives a thermal dependence for $T_1(T)$:

$$T_1(T) = AT^{-\lambda}. \quad (4)$$

Table 3 shows the fitting parameters for each phase. There is a deviation from the behaviour predicted by equation (4) near the transition temperatures. At these temperatures T_1 -values show a dramatic drop correlated with the deviation of $\nu_Q(T)$ from Bayer's model. There is another possible deviation from the fit below 90 K, but there are few experimental data to support this (these data were excluded from the fitting).

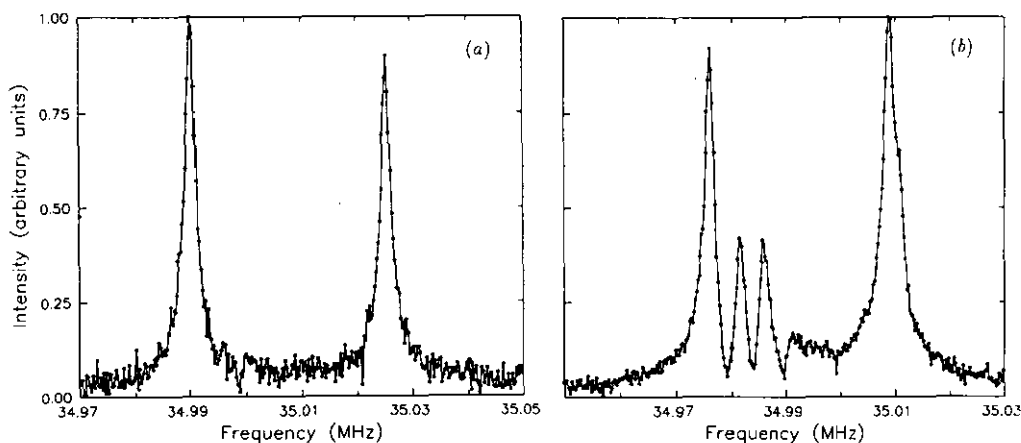


Figure 4. (a) A typical NQR spectrum on cooling 4, 4' DCBP in the intermediate phase (phase II) ($T = 183.4$ K). (b) A typical NQR spectrum on heating 4, 4' DCBP in the intermediate phase (phase II) ($T = 188.4$ K). The EFG distribution is clearly different from the cooling shown in (a).

Table 3. Fitting parameters of $T_1(T)$ in phases I and III.

| | Phase I | Phase III |
|-----------|-------------------|-------------------|
| λ | 2.32 | 2.36 |
| a | 1.4×10^7 | 1.2×10^7 |

Thermal cycles were performed in this way (table 1):

- (i) Cycle 1: sample 1 was slowly cooled from room temperature (phase I) to $T = 150$ K (phase III), and was then immediately heated to room temperature again;
- (ii) Cycle 2: sample 2 was cooled and heated in a similar way to the cycle 1 procedure, but keeping the sample for 8 h at $T = 150$ K;
- (iii) Cycle 3: sample 2 was cooled from room temperature to the transition temperature between phases II and III and was then heated immediately to room temperature again.

The aim of cycles 2 and 3 was to verify the effects of the stabilization of phase III on the transition temperature hysteresis.

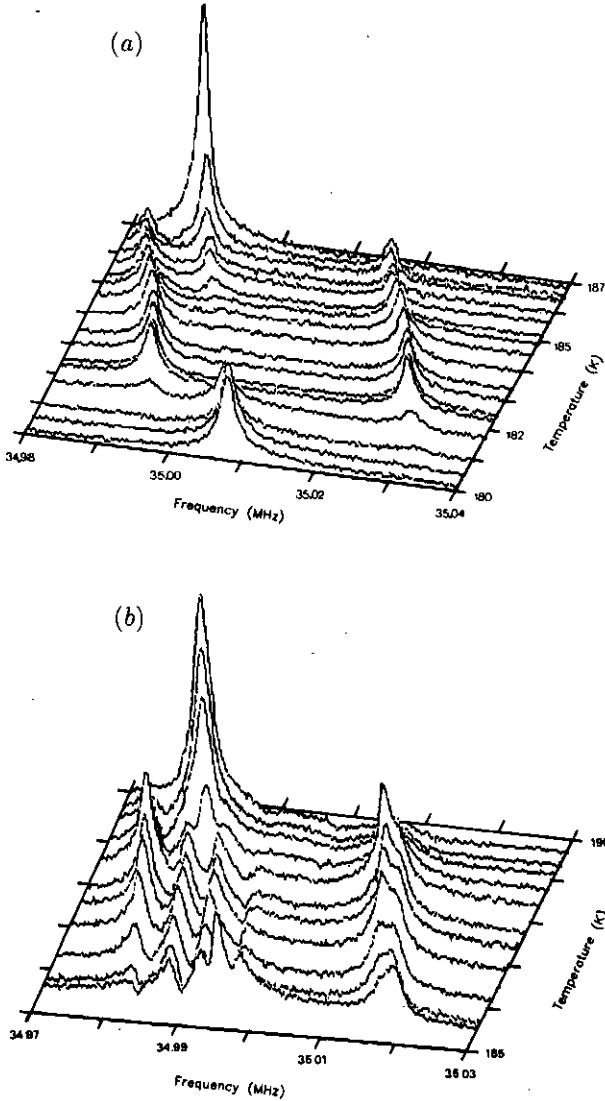


Figure 5. The temperature evolution of NQR spectra on phase II in cycle 2 cooling (a) and heating (b).

Table 4(a) shows the transition temperatures obtained in each cycle. From the observed results in the different cycles we can make the following conclusions:

(a) The transition temperatures (T_1 from phase I to phase II and T_c from phase II to phase III) obtained in cooling the sample are different to those observed in heating it; so there is a strong thermal hysteresis effect. We can see that this hysteresis is smaller for purer samples.

(b) The temperature range of the intermediate phase (phase II) decreases as the purity of the sample increases (see table 4(b)).

(c) We obtained different spectra of phase II when the sample was heated and

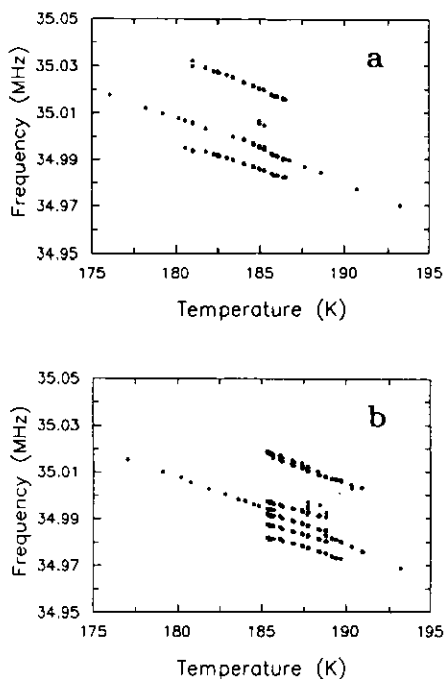


Figure 6. The temperature behaviour of the NQR main line peaks on cooling (*a*) and heating (*b*) the sample. There is a strong hysteresis effect in the transition temperatures.

Table 4. (*a*) Transition temperatures between phase I and II (T_i) and between phases II and III (T_c). (*b*) The thermal range of phase II and the transition temperature hysteresis: $\Delta T_i = T_{i, \text{heating}} - T_{i, \text{cooling}}$ and $\Delta T_c = T_{c, \text{heating}} - T_{c, \text{cooling}}$.

| (a) | Cooling | | Heating | | |
|-----|---------|-----------|-----------|-----------|-----------|
| | Sample | T_i (K) | T_c (K) | T_i (K) | T_c (K) |
| | Powder† | 185 | 175 | 197 | 189 |
| | 1 | 186 | 181 | 190 | 185 |
| | 2 | 186 | 181 | 190 | 185 |
| | 3 | — | — | 190 | 187 |

| (b) | Range of phase II | | Hysteresis | | |
|-----|-------------------|---------|------------|--------------|--------------|
| | Sample | Cooling | Heating | ΔT_i | ΔT_c |
| | Powder† | 10 K | 8 K | 12 K | 14 K |
| | 1 | 5 K | 5 K | 4 K | 4 K |
| | 2 | 5 K | 5 K | 4 K | 4 K |
| | 3 | — | 3 K | — | — |

† Extracted from Wolfenson *et al* (1990).

when it was cooled (figure 4). Figure 5 shows the evolution of the NQR spectra of phase II and figure 6 shows the position of the peaks as a function of temperature in cycle 2.

(d) Stabilization of phase III affected neither the thermal hysteresis nor the

temperature of phase II, nor the transition temperatures, nor the spectral features.

Structural changes involved in the phase transitions of 4, 4' DCBS cannot be determined from the experimental NQR results. However, the experimental values obtained for ν_0 , from the fitting of $\nu_Q(T)$ in phases I and III, show that such structural changes are small. These results are in good agreement with that obtained by means of Raman spectroscopy (Peretti and Ranson 1979). It was concluded that the phase transitions involve conformational changes in individual molecules without alteration of the molecular symmetry (C_2) or space group of the unit cell (C_{2h}). Therefore, it is reasonable to assume that the order parameter of these phase transitions is the variation of the dihedral angle between benzene rings.

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