^{35}Cl NQR study of bis(4-chlorophenyl)sulphoxide

LETTER TO THE EDITOR

^{35}Cl NQR study of bis(4-chlorophenyl)sulphoxide

T Osán, C Schürrer, J Schneider and A Brunetti

FaMAF, Universidad Nacional de Córdoba, Medina Allende y Haya de la Torre, Ciudad Universitaria, 5000 Córdoba, Argentina

Abstract. A pulsed ^{35}Cl nuclear quadrupolar resonance (NQR) study was performed on bis(4-chlorophenyl)sulphoxide. In order to characterize the structural thermal behaviour, the NQR spectra were recorded from 80 to 350 K. The results suggest the coexistence of two crystalline phases over the whole scanned temperature range. In spite of the very close molecular structure of the compound with the bis(4-chlorophenyl)sulphone, there is no evidence of any incommensurate phase transition. This fact demonstrates the fundamental role of the molecular group linking phenyl rings in the appearance of a normal–incommensurate phase transition in biphenyl-type compounds.

Normal–incommensurate phase transitions (NIPT) in molecular crystals are triggered by the competition among inter- and intramolecular forces. These mechanisms have been experimentally and theoretically studied in biphenyl, a compound in which the dihedral angle between phenyl rings is incommensurately modulated below 40 K [1, 2]. In biphenyl, the intramolecular forces involved in NIPT are the conjugation of the π electrons and the steric repulsion among *ortho*-hydrogens [3, 4]. The 4-4'bis(chlorophenyl)sulphone ($(C_6H_4Cl)_2$ SO_2, abbreviated as BCPS) is the other biphenyl compound with an NIPT affecting the dihedral angle of the molecule [5, 6]. To explain the features of this NIPT, the nature of the molecular group joining the phenyl rings must be taken into account, in addition to the intramolecular forces present in biphenyl. Until now, there have been neither experimental nor theoretical studies showing how the features of this molecular group can enable the NIPT in BCPS.

In this work, we report a nuclear quadrupolar resonance (NQR) spectroscopy study of the 4-4'bis(chlorophenyl) sulphoxide ($(C_6H_4Cl)_2$ SO, abbreviated as BCPSX). In this compound the sulphur atom is acting with valence four instead of six as in BCPS. To detect a possible NIPT, the temperature behaviour of the ^{35}Cl NQR spectrum of powder samples of BCPSX was studied in the temperature range 80–350 K.

The BCPSX sample (purity 97%) was provided by Aldrich Chemical Co. and was recrystallized and purified by slow sublimation from the melt. Two powder samples, with and without recrystallization, were packed into glass cylinders of 1 cm diameter and 2.5 cm length. We have not found in the literature any information about the crystalline structure of the compound.

Measurements of the ^{35}Cl NQR lineshape were performed from liquid nitrogen temperature to 350 K. The NQR spectrometer has been described elsewhere [7]. The NQR lineshape was obtained from the fast Fourier transform (FFT) of the $\pi/2$–π echo signal by the reconstruction method [8]. The $\pi/2$ pulse was 23 μs in width and 150 W in power. The spectrometer temperature control provides a sample temperature stability better than
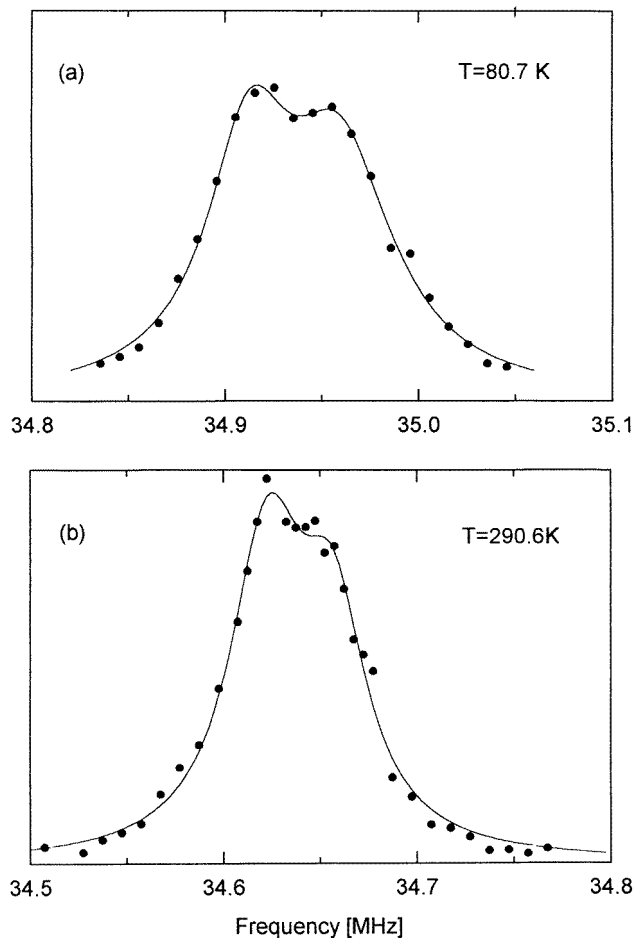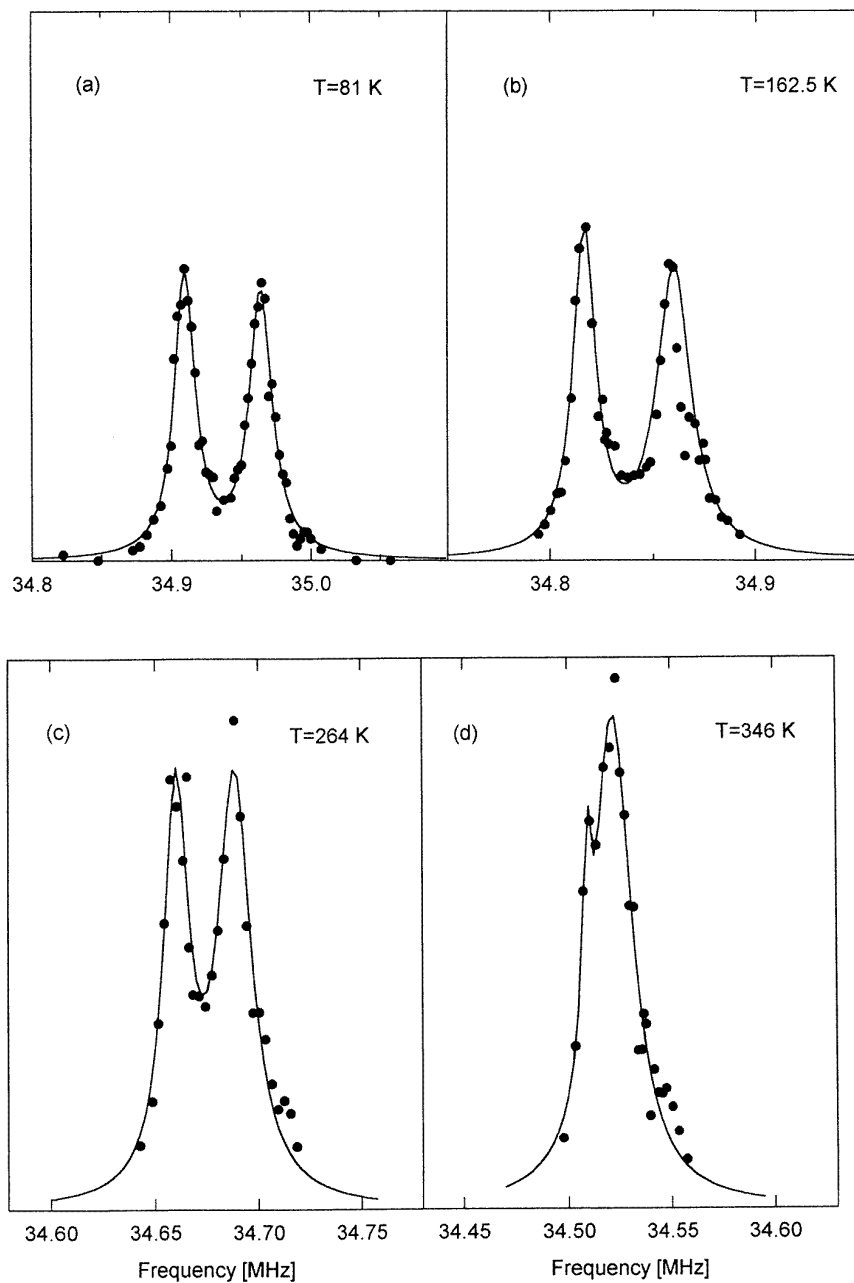
Figure 1. ^{35}Cl NQR spectra of a non-purified sample of bis(4-chlorophenyl)sulphoxide at (a) 80.7 K and (b) 290.6 K.

0.1 K during the measurements. Measurements were performed by raising the temperature at a maximum rate of 0.1 K min^{-1}.

Figure 1 shows the NQR spectra of the non purified sample at 81 K and room temperature. Figure 2 shows some NQR spectra of the purified sample obtained at different temperatures. As can be qualitatively observed from figures 1(a) and 2(a), there is a strong impurity effect on the resonance lineshape of BCPSX. The NQR spectrum of the purified sample is composed of two Lorentzian lines, each with a half-width of about 9 kHz at 80 K, while in the non-purified sample the half-widths are 30 kHz. In both cases, broadening could be due to the effects of the impurity concentration and strains [9]. The subsequent studies of the NQR spectrum of BCPSX as a function of temperature were performed on the purest sample.

Figures 3 and 4 show the areas and half-widths of the fitted Lorentzian as functions of temperature. As can be seen, both areas are approximately the same up to 300 K. Above this temperature, the area of the high-frequency line begins to grow at the expense

Figure 2. ^{35}Cl NQR spectra of a purified sample of bis(4-chlorophenyl)sulphoxide at different temperatures.

of the area of the low-frequency line. Simultaneously, the low-frequency line becomes narrower for temperatures above 300 K. This behaviour suggests that observed lines could be associated with two coexisting phases, one of which is a metastable state. At temperatures
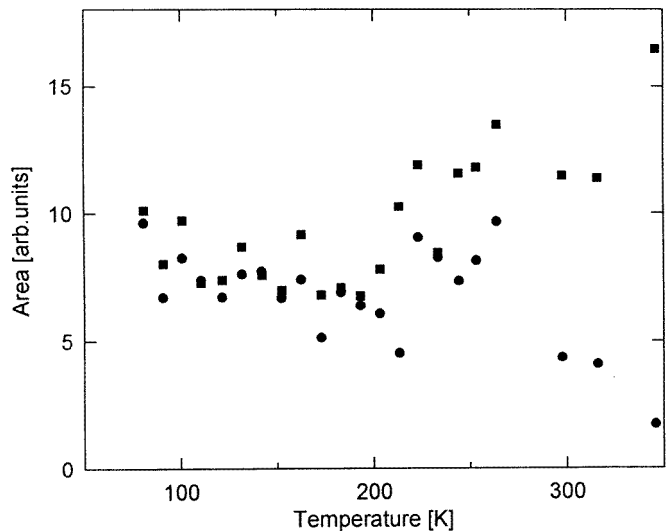
Figure 3. The areas of the two Lorentzian functions fitted to NQR spectra as a function of temperature. Circles: low-frequency peak. Squares: high-frequency peak.
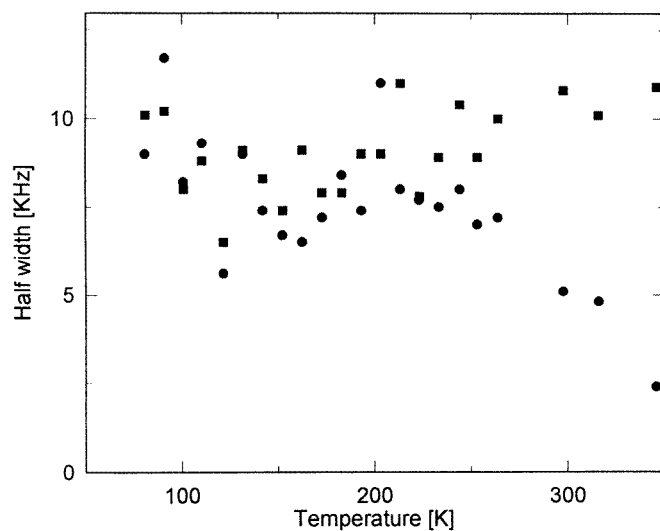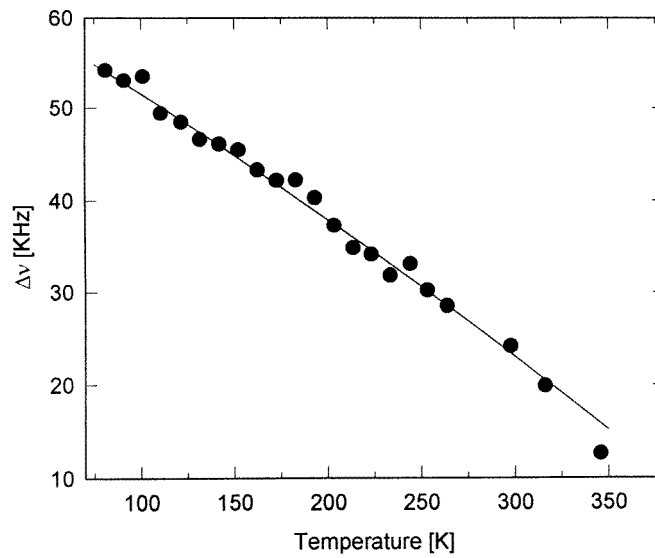

Figure 4. Temperature behaviour of the half-widths of the two Lorentzian functions fitted to NQR peaks. Circles: low-frequency peak. Squares: high-frequency peak.

above 300 K, the phase associated with the low-frequency line becomes unstable and the compound transforms progressively to the other phase.

The frequencies of the observed peaks were obtained from the least-squares fit of two Lorentzian functions to the experimental data. The temperature behaviour of these frequencies is plotted in figure 5. Qualitatively, the observed temperature dependence agrees with the expected behaviour in molecular crystals [10]. Figure 6 shows the difference
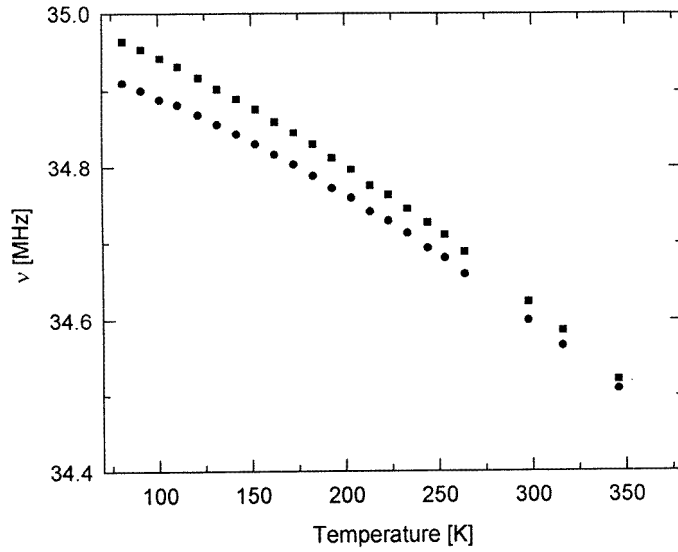
Figure 5. Temperature behaviour of the frequencies of the observed NQR lines. Circles: low-frequency peak. Squares: high-frequency peak.

Figure 6. Temperature behaviour of the difference between the NQR frequencies of the two lines. Solid line: fitting of the expression (1).

$\Delta \nu = \nu_H - \nu_L$ between the two observed NQR frequencies. To study the temperature behaviour of the NQR frequencies, a comparative study can be carried out [11]. The frequency difference $\Delta \nu$ can be expressed as

$$\Delta \nu_Q(T) = \Delta \nu_0 + aT + bT^2 \tag{1}$$

where

$$\Delta \nu_0 = \nu_0^H - \nu_0^L \tag{2a}$$

$$a = -\frac{3}{2} k_B \sum_i \left(\frac{\nu_{0i}^H A_i^H}{\omega_{iH}^2} - \frac{\nu_0^L A_i^L}{\omega_{iL}^2} \right) \tag{2b}$$

$$b = -3 k_B \sum_i \left(\frac{\nu_{i0}^H g_i^H A_i^H}{\omega_{iH}^2} - \frac{\nu_{i0}^L g_i^L A_i^L}{\omega_{iL}^2} \right). \tag{2c}$$

The indices H and L refer to the high- and low-frequency lines, respectively. The summation ranges over all inter- and intramolecular oscillation modes involved in the average of the electric field gradient (EFG) [10], $\omega_i = \omega_{0i}(1 - g_i T)$ is the frequency of the mode at the temperature T, A_i is a quantity related to the inverse of the moment of inertia and ν_0 is the limiting static value of the NQR frequency. Assuming only one dominant oscillating mode involved in the EFG average, the coefficients (2b) and (2c) can be written as

$$a = -\frac{3}{2} k_B \left(\frac{\nu_0^H A^H}{\omega_H^2} - \frac{\nu_0^L A^L}{\omega_L^2} \right) \qquad b = -3 k_B \left(\frac{\nu_0^H g^H A^H}{\omega_H^2} - \frac{\nu_0^L g^L A^L}{\omega_L^2} \right).$$

Fitting of expression (1) to the experimental data yields the following parameters

$$\Delta \nu_0 = 64 \pm 1 \text{ kHz} \qquad a = (-1.2 \pm 0.2) \times 10^{-4} \text{ MHz K}^{-1} \qquad b = (-6 \pm 4) \times 10^{-8} \text{ MHz K}^{-2}.$$

The value of the quadratic coefficient b is very small and can be neglected within the experimental uncertainty. The sign of the coefficient $\Delta \nu_0$ indicates that $\nu_0^H > \nu_0^L$. This fact expresses only static differences between both phases. The sign of a and the negligible magnitude of b could be explained by assuming the same dynamical parameters of the oscillating modes affecting the EFG in both phases. In this case, the small value of b indicates negligible anharmonicities and the temperature dependence of $\Delta \nu$ is due only to the static differences

$$a = -\frac{3}{2} k_B \frac{A}{\omega_0^2} \left(\nu_0^H - \nu_0^L \right).$$

The order of magnitude of the dynamic quantity A/ω_0^2 can be estimated from the fitted coefficients as 10^{20} J^{-1}. This value is expected in biphenyl-type compounds with frequencies ω less than 100 cm^{-1}.

In conclusion, this first NQR study of the BCPSX shows no evidence of any incommensurate phase transition in the scanned temperature range. This indicates the fundamental role of the chemical bond between phenyl rings in the appearance of the NIPT. The stability of the periodic crystalline structure is extremely sensitive to the electronic state of the sulphoxide group, which is less electronegative than the sulphone group.

The obtained results suggest the existence of two coexisting crystalline phases in the temperature range 80–340 K. This broad temperature range could indicate that the free energies of both phases differ only by a small amount [12]. Each of these phases could have only one NQR line, as in the monoclinic ordered phases of BCPS [5] and 4-4'dichlorobezophenone [13]. This could suggest structural similarities of BCPSX with these closest substituted biphenyl compounds. Above 300 K the most stable crystalline phase is that associated with the high-frequency line.

References

[1] Cailleau H, Messanger J C, Moussa F, Bugaut F, Zeyen C and Vettier C 1986 *Ferroelectrics* **67** 3
[2] Cailleau H 1986 *Incommensurate Phases in Dielectrics Materials* vol 2 ed R Blinc and A P Levanyuk (Amsterdam: North-Holland)
[3] Benkert C and Heine V 1987 *J. Phys. C: Solid State Phys.* **20** 3355
[4] Heine V and Price S 1985 *J. Phys. C: Solid State Phys.* **18** 5259
[5] Schneider J, Wolfenson A and Brunetti A 1994 *J. Phys.: Condens. Matter* **6** 11 035
[6] Zúñiga F, Perez-Mato J and Breczewski T 1993 *Acta Crystallogr.* B **49** 1060
[7] Pusiol D and Brunetti H 1984 *J. Phys. C: Solid State Phys.* **17** 4487
[8] Jellison G, Petersen G and Taylor P 1980 *Phys. Rev.* B **22** 3903
[9] Stoneham A M 1969 *Rev. Mod. Phys.* **41** 82
[10] Chihara H and Nakamura N 1981 *Advances in Nuclear Quadrupole Resonance* vol IV ed J A S Smith (London: Heyden) p 1
[11] Schneider J, Schürrer C and Brunetti A, 1996 *Phys. Rev.* B **54** at press
[12] Bonadeo H, D'alessio E, Halac E and Burgos E 1978 *J. Chem. Phys.* **68** 4714
[13] Schneider J, Wolfenson A and Brunetti A 1992 *J. Phys.: Condens. Matter* **4** L571