The ^{35}Cl NQR Temperature Dependence of Hexa- and Octachlorocyclophosphazene *

Alexander A. Koukoulas
Pulp and Paper Research Institute of Canada, 570 St. John's Rd., Pointe Claire, PQ, Canada H9R 3J9

M. A. Whitehead
Department of Chemistry, McGill University, Montréal, PQ, Canada, H3A 2K6

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The ^{35}Cl NQR temperature dependence in $(PNCl_2)_3$ and $(PNCl_2)_4$ was measured between 77 K and 293 K. The dependence in both compounds was smoothly varying. A sudden decrease in T_2^* near 112 K indicated the presence of a strong broadening mechanism in $(PNCl_2)_3$. The nature of this mechanism is interpreted in terms of the ^{35}Cl spin-lattice relaxation.

Introduction

The nature of phosphorous-nitrogen bonding in the phosphazenes has generated a great deal of interest. In particular, the cyclophosphazenes are studied because of their unique and somewhat controversial π bonding and molecular geometry [1]. The chlorosubstituted cyclophosphazenes $(PNCl_2)_x$, where $x = 3$ or 4, or phosphonitrillic trimer and tetramer, as they are also known, exhibit a degree of aromaticity. The aromatic behaviour is partly responsible for the elevated ^{35}Cl NQR frequencies observed in these compounds.

This paper examines the temperature dependence of $(PNCl_2)_3$ and $(PNCl_2)_4$. Measurement of the inverse linewidth parameter (T_2^*) temperature dependence led to the identification of a previously undetected phase transition in $(PNCl_2)_3$.

Experimental

NQR frequencies (ν_Q) were measured on a super-regenerative oscillator (SRO). Both Colpitts and Dean oscillators were constructed for this purpose. Overall, the Colpitts oscillator was preferred because of its increased stability and linearity. The Voltage Difference Method (VDM) was used to obtain T_2^* from the SRO data [2].

Spin-lattice relaxation times (T_1) were measured with a Nicolet-Matec high-power, pulsed spectrometer [3]. 90° pulses of 10 μs were typical for the coil geometries used in the sample probe. Only the inversion recovery pulse sequence was used to measure T_1 [3]. Solvent baths were used to obtain temperatures between 77 K and 293 K. $(PNCl_2)_3$ and $(PNCl_2)_4$ (99%) were purchased from Aldrich. Since both compounds are highly hygroscopic, they were carefully ampouled under vacuum in glass vials (15 mm o.d.).

Results

The ^{35}Cl NQR temperature dependence of both $(PNCl_2)_3$ and $(PNCl_2)_4$ exhibited a smooth monotonic decrease in frequency as a function of increasing temperature (Figs. 1 and 2). The Bayer-like temperature dependence was true for all 4 resonance lines. They was no indication of a phase transition from the ν_Q vs. T data. The resonance lines did not coalesce at elevated temperatures and actually diverged for the ν_3 and ν_4 lines in $(PNCl_2)_3$. Least-squares analysis of the *average* $\log \nu_Q$ vs. T^2 gave α values of $-3.179 \times 10^{-7}\ K^{-2}$ for $(PNCl_2)_3$ and $-2.306 \times 10^{-7}\ K^{-2}$ for $(PNCl_2)_4$ [4]. The correlation coefficient for both fits was 0.99.

The T_2^* temperature dependence in the tetramer decreased with increasing temperature, 85 μs at 77 K to 25 μs at 293 K. Between 112 K and 250 K, T_2^* decreased 0.65 μs K^{-1}, from 198 μs to 75 μs.

In the trimer, T_2^* exhibited a sharp change between 112 K and 142 K, where it decreased from 214 μs to

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Reprint requests to Prof. M. A. Whitehead, Department of Chemistry, McGill University, Montreal, PQ, Canada, H3A 2K6

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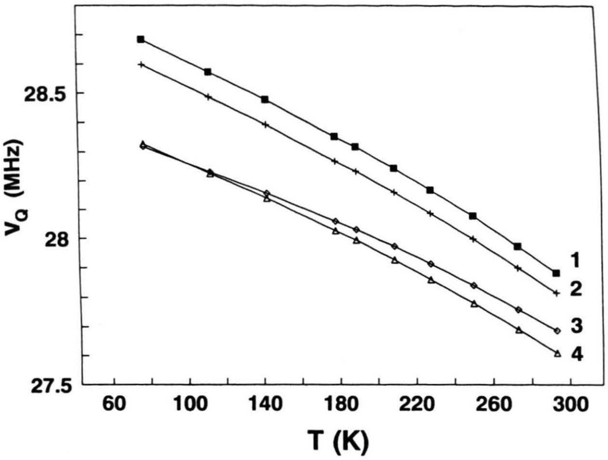

Fig. 1. The ^{35}Cl NQR temperature dependence in $(PNCl_2)_3$.

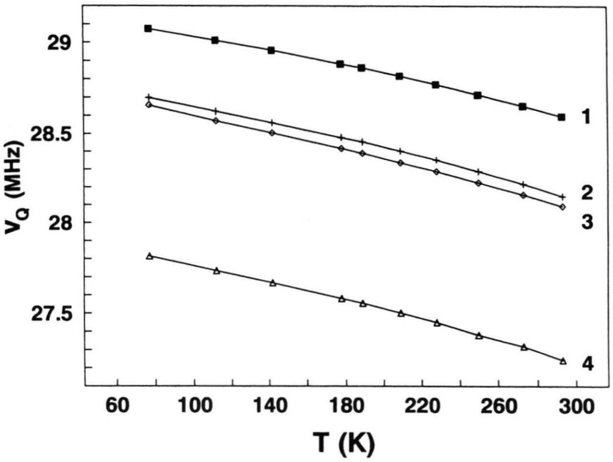

Fig. 2. The ^{35}Cl NQR temperature dependence in $(PNCl_2)_4$.

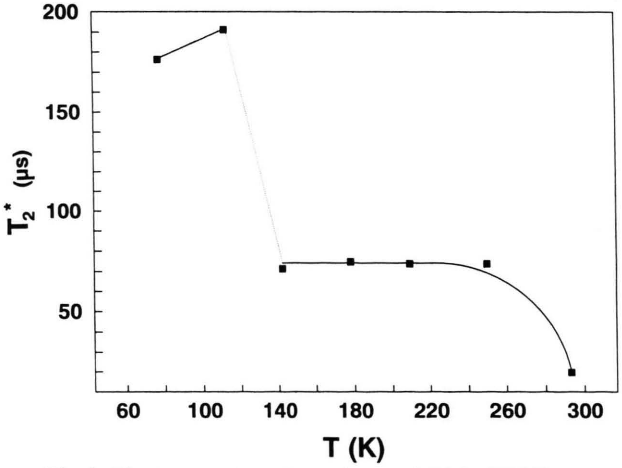

Fig. 3. The temperature dependence of T_2^* in $(PNCl_2)_3$.

62 μs (Figure 3). The plot of log T_1^{-1} vs. T^{-1} was smoothly decreasing over the entire temperature range (Figure 4). An activation energy of 25 kJ mol^{-1} was calculated from a least-squares fit of the high temperature values.

Discussion

The temperature dependence of the NQR frequency is often not very useful for examining higher-order phase transitions. Smooth monotonic behaviour of the ν_Q vs. T curve, as exhibited by the chlorocyclophosphazenes, is frequently observed in the study of NQR temperature dependence. However, the absence of an obvious (i.e. first-order) phase transition in ν_Q vs. T does not preclude the presence of higher-order phase transitions.

The abrupt increase in T_2^* at 112 K for $(PNCl_2)_3$ indicates the presence of a strong broadening mechanism. Since the resonance frequency is smoothly changing at this temperature, the mechanism must have its origin in the lattice; any intramolecular reorientations would most likely result in a discontinuity in ν_Q vs. T. It is for this reason that the temperature dependence of the T_1 relaxation was measured. Although the rate of change in T_1 does increase near 112 K and above, the contribution of T_1 to the resonance linewidth is expected to be small. Nonetheless, the T_1 temperature dependence does indicate the presence of increased molecular motions. Other factors, such as the concentration of lattice imperfections, may be responsible for the observed broadening in $(PNCl_2)_3$ [5].

The VDM is valid only if the resonance signal as a function of the applied radiofrequency voltage is measured near *threshold*. Unfortunately, the threshold condition does not allow the T_2^* measurement of closely spaced resonance lines. The T_2^* for closely spaced lines represents an *average* of the lines. However, linewidths calculated from T_2^* values agree well with those obtained from the pulsed spectrometer. For example, at 77 K $(PNCl_2)_3$ has 4 resonance lines: $\nu_1 =$ 28.6901 MHz, $\nu_2 = 28.6045$ MHz, $\nu_3 = 28.3305$ MHz, and $\nu_4 = 28.3196$ MHz. The linewidths for each of these lines, measured with the pulsed spectrometer, were 2405 Hz, 1923 Hz, 2208 Hz, and 2830 Hz. These linewidths, under a Gaussian assumption for the lineshape, correspond to T_2^* values of 220 μs, 270 μs, 240 μs, and 187 μs. In comparison, the VDM results in

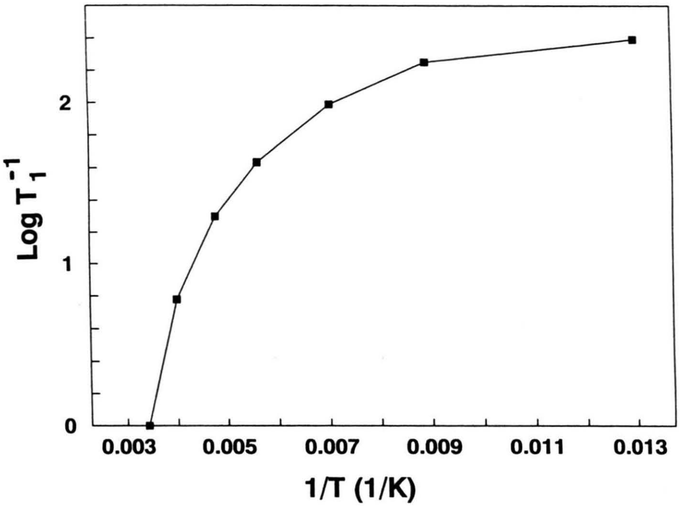

Fig. 4. The inverse temperature dependence of log T_1^{-1} in $(PNCl_2)_3$.

only 2 T_2^* values: a high frequency $T_2^* = 202$ μs, and a low frequency $T_2^* = 150$ μs. The correlation between the two methods is quite good and indicates that the VDM is sampling an average of the lines.

Conclusions

The ^{35}Cl NQR frequency in $(PNCl_2)_3$ and $(PNCl_2)_4$ smoothly decreased as a function of increasing temperature. The temperature dependence did not suggest the presence of a phase transition between 77 K and 293 K in either compound. However, the T_2^* temperature dependence in $(PNCl_2)_3$ showed an increased broadening of the resonance linewidth beginning at 112 K. In addition, the T_1 values are rapidly decreasing near this temperature. The data suggests the presence of a higher-order phase transition between 112 K and 142 K.

The validity of the VDM for obtaining T_2^* for closely spaced resonance lines was demonstrated.

Acknowledgements

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