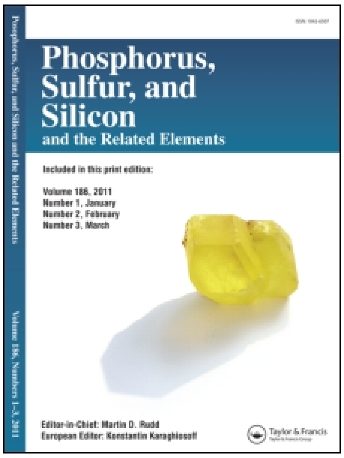

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X-RAY CRYSTALLOGRAPHIC AND ^{35}Cl N.Q.R. SPECTROSCOPIC STUDIES ON CHLOROCYCLOPHOSPHAZENES

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X-ray crystallographic structure determinations on a number of chlorocyclophosphazenes are compared with ^{35}Cl N.Q.R. spectroscopic studies of these compounds. Phase changes have been observed.

X-ray crystallography and nuclear quadrupole resonance (N.Q.R.) spectroscopy both deal with crystalline materials in their ground state. The results obtained by these two techniques are therefore comparable and the interaction of their findings synergic.

^{35}Cl is a particularly convenient nucleus for N.Q.R. spectroscopy and as P—Cl bond distances can be determined with a considerable degree of accuracy a study of compounds containing P—Cl bonds has proved particularly useful.

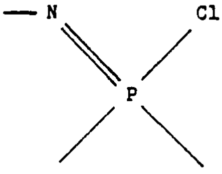
We have shown earlier[1,2] that a straight line relationship exists between P—Cl bond lengths, d(Å), and ^{35}Cl N.Q.R. frequencies, ν (MHz), (Figure 1a) which can be expressed by the equation

$$d = -0.0152\nu + 2.4166.$$

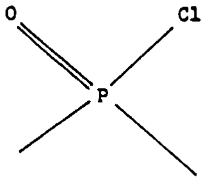
This equation pertains to the structural fragment (**A**).

We have shown that the phosphoryl fragment (**B**) gives a different slope (Figure 1b), which can be expressed[3] by $d = -0.0264\nu + 2.701$.

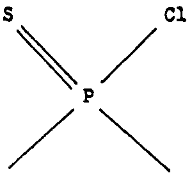
There seems little doubt that were adequate data available, fragments (**C**) and (**D**) would give lines with yet again different slopes.



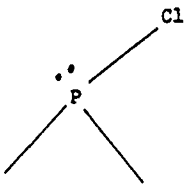
(**A**)



(**B**)



(**C**)



(**D**)

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*Author to whom all correspondence should be addressed.

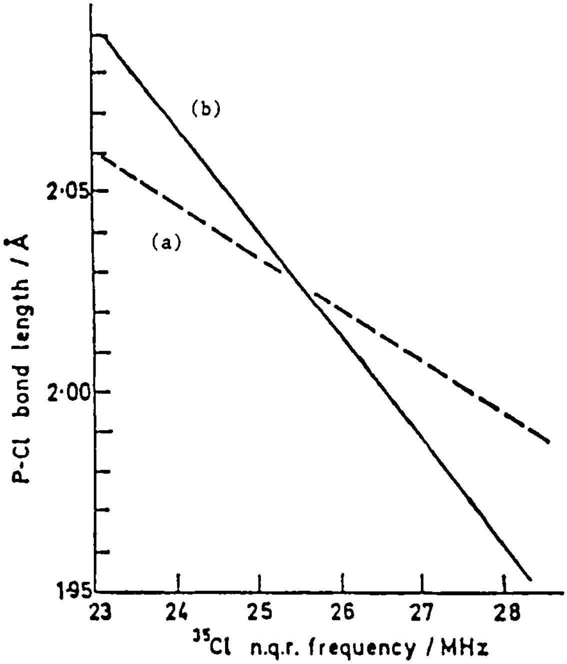
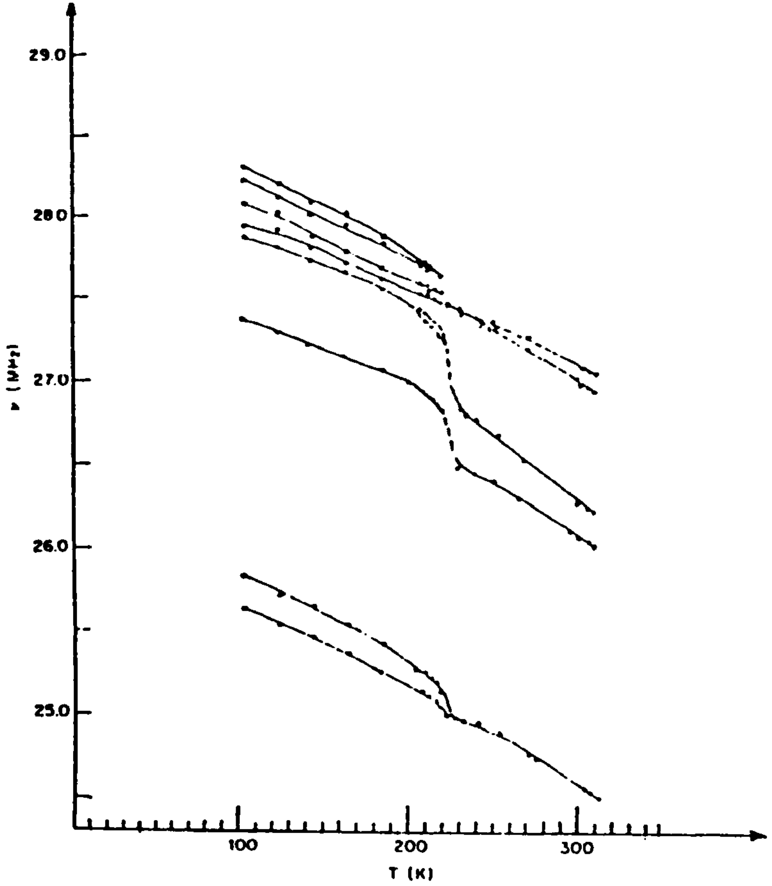


FIGURE 1. Plots of P—Cl bond length (not corrected for librational motions) against ^{35}Cl N.Q.R. frequency for (a) —N=PR$_2$—Cl and (b) O=PR$_2$Cl.

Attempts to fit the data from all these fragments to one line gave rise to a lot of scatter.[4]

Following the ^{35}Cl N.Q.R. signals over a temperature range is an excellent and sensitive method to observe phase transitions. In a number of compounds we have observed cusps,[5] usually near 150 K, indicating minor changes in the solid state in this temperature region. In two cases, we have, however, observed fairly drastic phase changes. In $N_3P_3Cl_5(NHPr^i)$ (**1**) a sharp phase change occurs between 220 and 235 K.[6] Above the transition temperature we observed five signals, below it eight signals. A crystal structure determination at room temperature by Bullen[7] shows centrosymmetric hydrogen-bonded dimers (Figure 2). Thus the five N.Q.R. signals at room temperature are accounted for. It may well be that this centre of symmetry is lost below the phase transition and thus we observe eight out of a possible ten signals. A low temperature crystal structure is required to answer this question.

A somewhat less drastic phase change has been observed for $(NPCl_2)_2(NSClO)$ (**2**) near 160 K.[2] The reverse of the effect observed above is noted here. Four signals below the phase transition increasing to five above it (Figure 3). A crystal structure determination by van Bolhuis and van de Grampel, at 133 K, i.e. below the phase transition, 165 K, shows the six-membered ring to have a slight boat conformation with four independent P—Cl bonds, satisfactorily accounting for the four ^{35}Cl N.Q.R. signals arising from these bonds observed below the phase transition. We have observed only one of these four signals to split into two above the phase



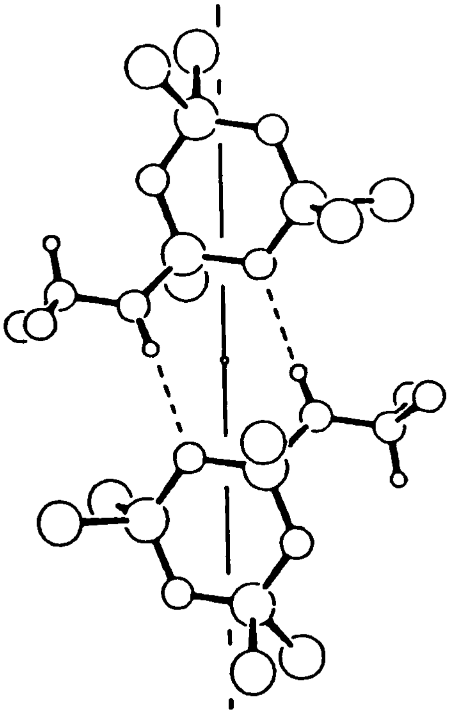


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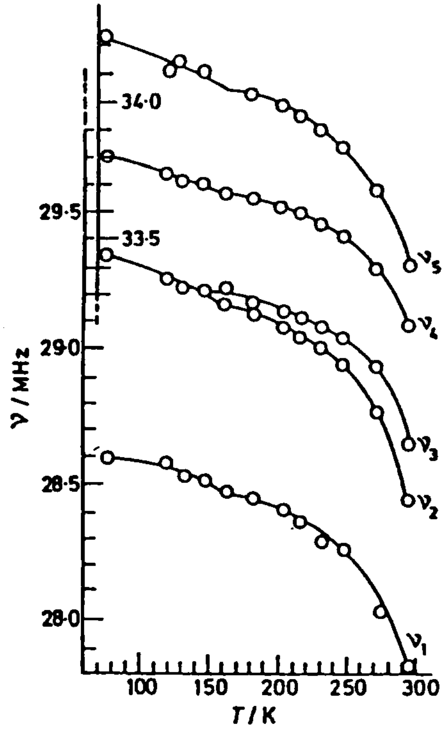
FIGURE 2. Plots of ^{35}Cl N.Q.R. frequencies versus temperature for $N_3P_3Cl_5NHPr^i$.



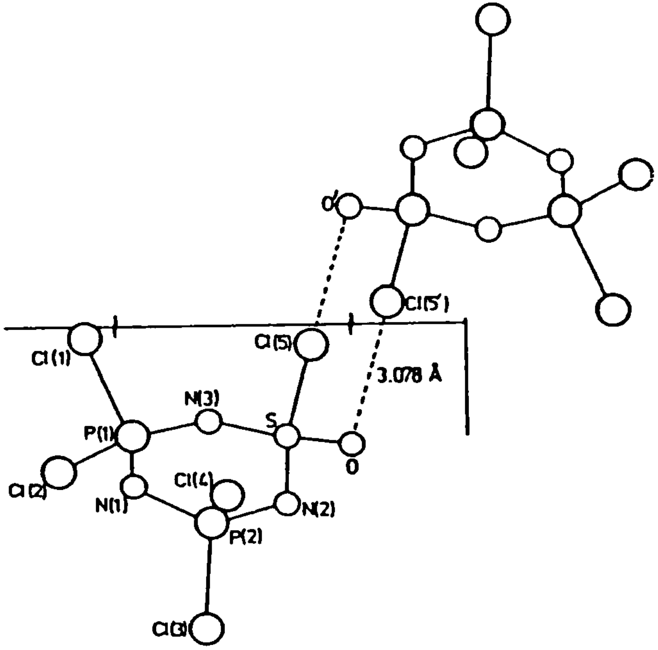


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FIGURE 3. Plots of ^{35}Cl N.Q.R. frequencies versus temperature for $(NSClO)(NPCl_2)_2$. Upper scale applies to ν_5 values only.

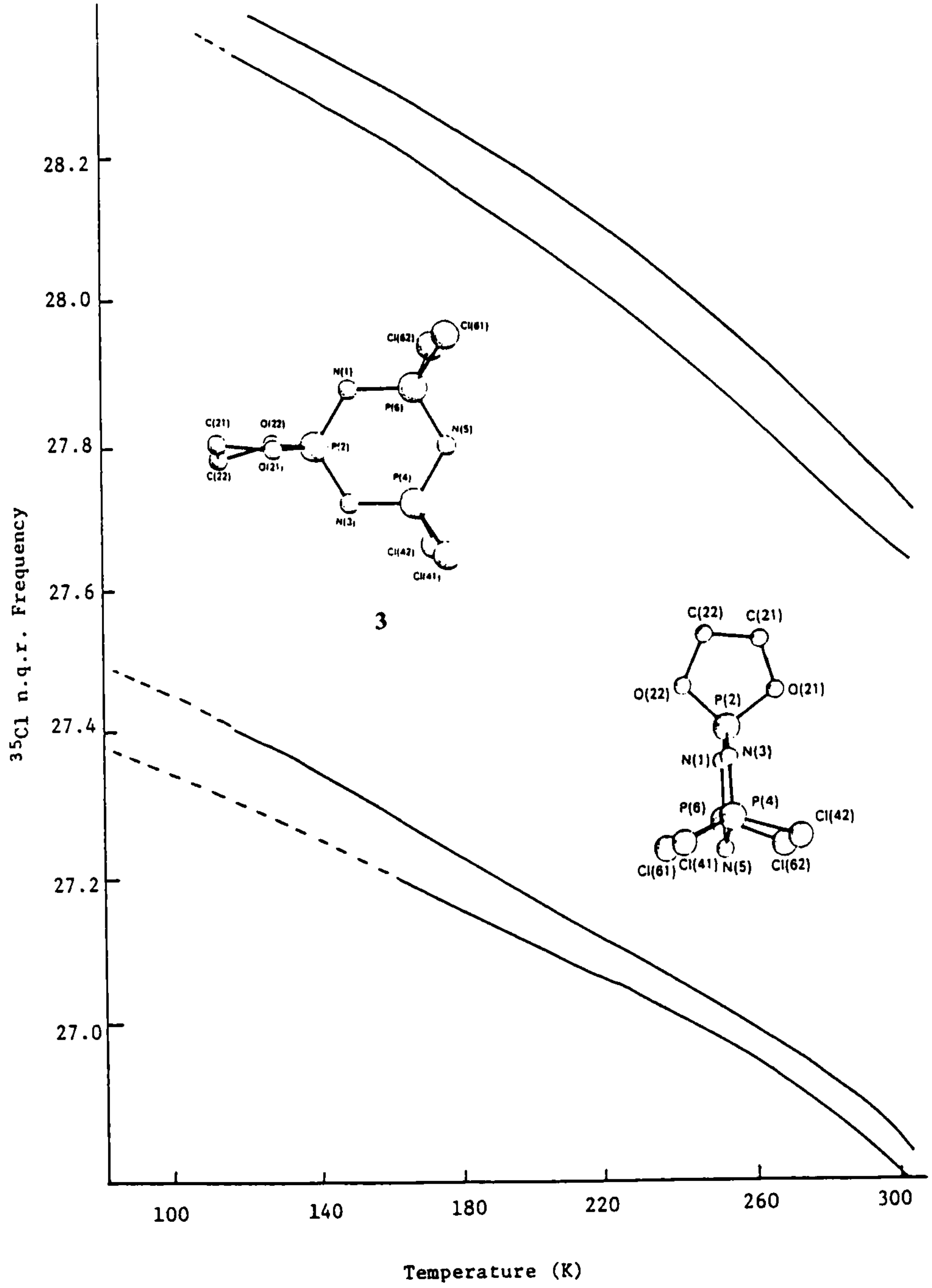

FIGURE 4. Plots of ^{35}Cl N.Q.R. frequencies versus temperature for $N_3P_3[O(CH_2)_2O]Cl_4$.

transition, indicating a less drastic structural change than that observed for $N_3P_3Cl_5(NHPr^i)$ (**1**).[6] A crystal structure determination above the phase transition is required to clarify this problem.

We have recently carried out the crystal structure determination of the five-, six-, and seven-membered monospiro derivatives $N_3P_3[O(CH_2)_2O]Cl_4$ (**3**), $N_3P_3[O(CH_2)_3O]Cl_4$ (**4**) and $N_3P_3pO(CH_2)_4O]Cl_4$ (**5**) (Figures 4–6)[9-10] and have investigated their ^{35}Cl N.Q.R. spectra over a temperature range.

The five-membered spiro ring (**3**) (Figure 4) has a twist boat conformation.[9,10] All the four chlorine atoms are structurally distinguishable and this is mirrored in the four signals observed in its ^{35}Cl N.Q.R. spectrum.

One P—Cl bond in each PCl_2 group is significantly longer than the other (the two longer bonds being in a *cis*-relationship) and these can be assigned to the two lower N.Q.R. frequencies.

The seven-membered spiro derivative (**6**) possesses a diad axis of symmetry along the P(2)N(5) line.[9,10] Only two N.Q.R. signals are observed over the whole temperature range in keeping with the above crystal structure. A slight cusp[5] (see above) was observed near 120 K (Figure 5).

The compound containing the six-membered spiro ring (**5**) is the most interesting of the three reported here. The crystal structure of this compound at room temperature shows the molecule to have a mirror plane, which passes through the

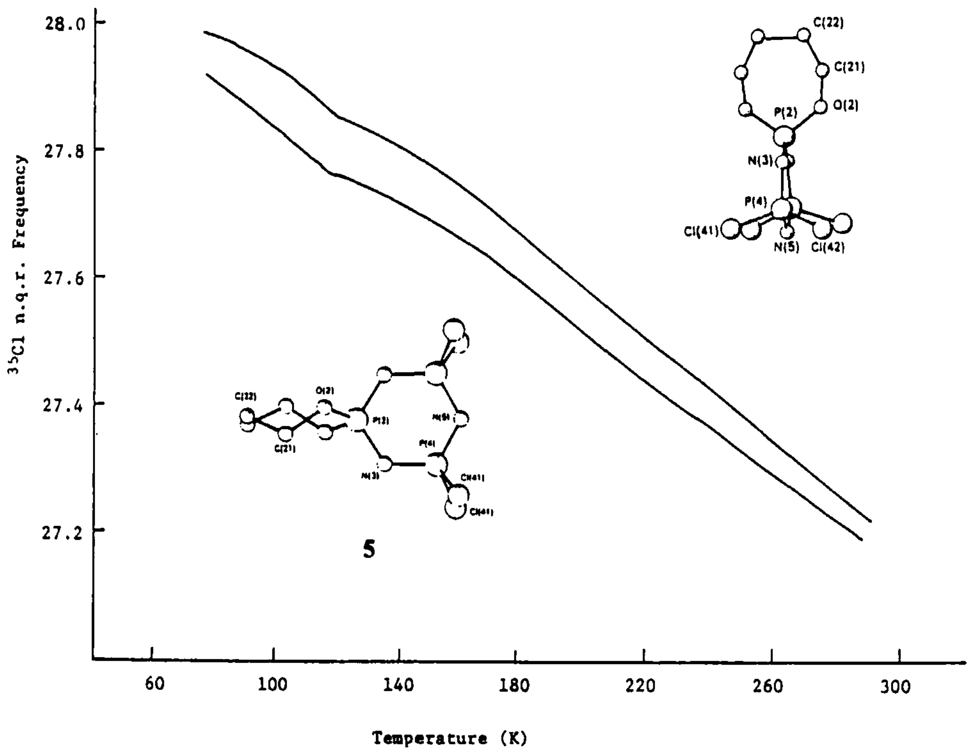

FIGURE 5. Plots of ^{35}Cl N.Q.R. frequencies versus temperature for $N_3P_3[O(CH_2)_4O]Cl_4$.

plane of the six-membered N_3P_3 ring (Figure 6).[9,10] In keeping with this the N.Q.R. spectrum exhibits two signals at room temperature.

At 280 K these signals fade out and at 260 K four signals appear. This suggests that the mirror plane is lost below the transition temperature.

It is noteworthy that compound (**5**), despite repeated attempts with different crystals, gave a structure with considerably higher e.s.d.'s than either compound (**4**) or (**6**). The probable explanation of this is the proximity of the temperature of the crystallographic determination to the transition temperature.

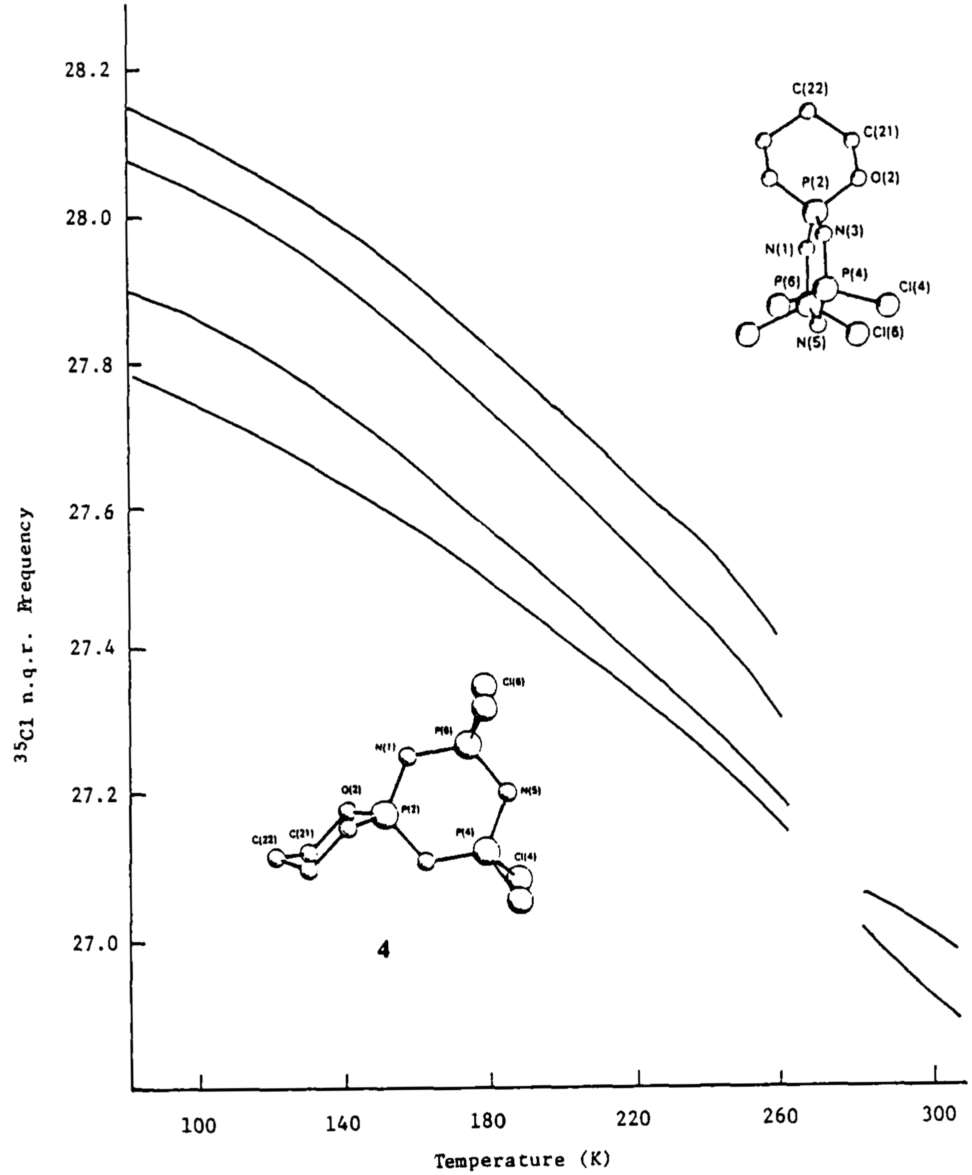

FIGURE 6. Plots of ^{35}Cl N.Q.R. frequencies versus temperature for $N_3P_3[O(CH_2)_3O]Cl_4$.

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