

NQR Investigation of the Influence of Intramolecular Interaction Geometry on CCl_3 Group Dynamics

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The CCl_3 group mobility in crystals of $(\text{CCl}_3)_m\text{PR}_{5-m}$ and $(\text{CCl}_3)_m\text{Cl}_{3-m}\text{P}=\text{NR}'$, $m = 1, 2$, is studied by NQR methods, using temperature dependence measurements of both the resonance frequencies and the spin-lattice relaxation times for ^{35}Cl nuclei. There are differences between the CCl_3 group motions in these crystals due to differences in steric interactions. In the first case the reorientation motions of the axial trichloromethyl groups are strongly hindered. In the second, reorientations take place, with the motions of the two CCl_3 groups which are bonded to the same phosphorus atom different as a result of differences in the potential barriers associated with the nonequivalent CCl_3 groups in the molecule.

CCl_3 group mobility in different compounds is essentially dependent on the character of the CCl_3 group interaction with the nearest molecular fragments which are bonded to the same atom of the molecule in question, and it may be studied by means of NQR spectroscopy. It is known that the reorientation motions of the CCl_3 group when bonded to a tetrahedral carbon atom are strongly hindered. For example, in the case of hexachloroethane crystals the potential barrier values corresponding to the motions of molecules as a whole are less than those corresponding to the CCl_3 group reorientations (1); this is also true in $\text{Cl}_3\text{CCCl}_2\text{N}=\text{PCl}_3$ crystals (2). On the other hand, the CCl_3 groups are much more free when bonded to tricoordinated carbon atoms in compounds containing double bonds or in trichloromethyl benzenes (for example, see (3, 4)).

In this paper, the CCl_3 group mobility with respect to the P-C bond in some crystals in which the phosphorus atom is penta- or tetraordinated (5) is studied by means of experimental investigations of the temperature dependence of NQR parameters on ^{35}Cl nuclei.

The following two types of crystals have been investigated: phosphoranes $(\text{CCl}_3)_m\text{PR}_{5-m}$, and phosphazo compounds $(\text{CCl}_3)_m\text{Cl}_{3-m}\text{P}=\text{NR}'$ with $m = 1, 2$. The NQR pulse method described in (6) has been used. The chlorine signals have been examined in the CCl_3 , R, and R' groups. The temperature-dependence measurements of both the NQR frequencies and the spin-lattice relaxation times have been performed to improve the measurement accuracy and the experimental data interpretation (see (7)). Some results which have been obtained previously (6, 8), are utilized in this report.

Table 1 gives data for the first class of compound investigated, namely, for phosphoranes and for cyclodiphosphazane (compound VI), which can be considered as a "double phosphorane." In these molecules the phosphorus atom is trigonal bipyramidal and the CCl_3 groups occupy the axial positions (8). The CCl_3 group chlorine atoms are staggered with respect to the equatorial bonds, and hence it is natural to expect the mobility of these groups to be hindered, and in fact, the character of the temperature dependence of the ^{35}Cl NQR frequencies ν and spin-lattice relaxation times T_1 shows this to be the case. For example, let us consider Figs. 1 and 2, which show the results of the $\nu(T)$ and $T_1(T)$ measurements, respectively,

TABLE 1
THE ^{35}Cl NQR SPECTRAL AND RELAXATION PARAMETERS FOR
PENTACOORDINATED PHOSPHORUS COMPOUNDS

No.	Compounds	Melting point temperature (K)	Molecular fragments	Resonance frequencies ^a at 77 K (MHz)	T_1 at 77 K (msec)
I	CCl_3PCl_4	398 ^b	CCl_3	39.689 (3)	216
			PCl_3 (equator.)	31.952 (3)	307
			PCl (axial)	28.250 (1)	575
II	$(\text{CCl}_3)_2\text{PCl}_3$	443 ^c	CCl_3 (A) ^d	39.609 (3)	719
			CCl_3 (B)	39.749 (3)	430
			PCl_3 (equator.)	29.458 (3)	1040
III	$(\text{CCl}_3)_2\text{Cl}_2\text{PNCO}$	360	CCl_3 (A and B) ^d	39.473 (4)	261
				38.948 (2)	260
			PCl_2 (equator.)	29.430 (2)	274
IV	$(\text{CCl}_3)_2\text{Cl}_2\text{PNH}_2$	418 ^b	CCl_3 (A and B) ^d	39.134 (4)	
				39.081 (2)	
			PCl_2 (equator.)	28.290 (2)	
V	$(\text{CCl}_3)_2\text{Cl}_2\text{PN}=\text{PCl}_3$	442	CCl_3 (A and B) ^d	39.258	240
				39.042	263
				38.955	276
				38.528	193
				38.439	284
				38.220	203
			PCl_2 (equator.)	28.918	422
				28.640	396
			PCl_3	30.243	202
	30.144				
		30.113			
VI	$(\text{CCl}_3\text{Cl}_2\text{PNCH}_3)_2$	448	CCl_3	40.018	290
				39.249	163
				39.112	156
			PCl_2 (equator.)	28.430	185
				27.950	329

^a The signal relative intensities are given in parentheses.

^b The substance decomposes when it melts.

^c The temperature at the beginning of decomposition.

^d A and B denote different CCl_3 groups in the molecule.

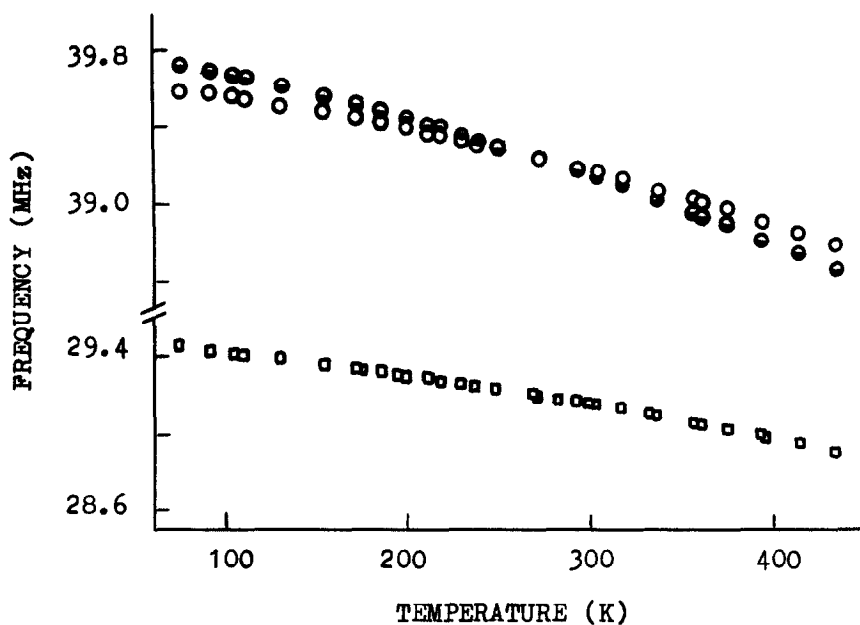


FIG. 1. Temperature dependence of the ^{35}Cl NQR frequencies in $(\text{CCl}_3)_2\text{PCl}_3$ (6): \circ , CCl_3 (A); \bullet , CCl_3 (B); \square , PCl_3 (equatorial).

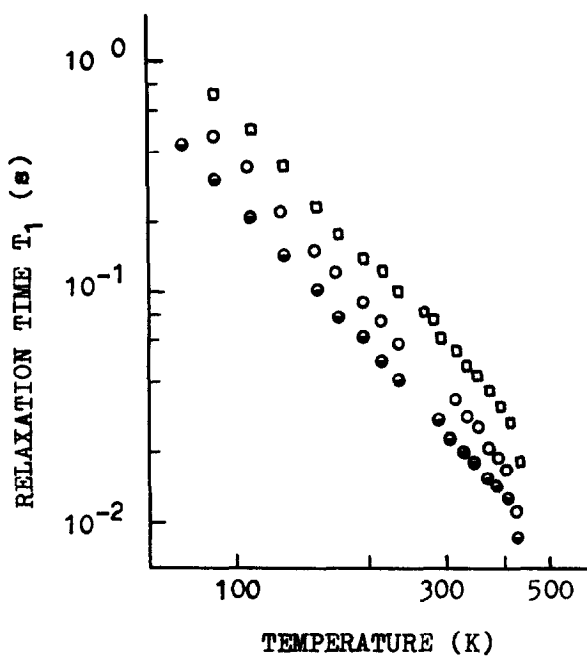


FIG. 2. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time in $(\text{CCl}_3)_2\text{PCl}_3$ (6) (the same marking as in Fig. 1).

for $(\text{CCl}_3)_2\text{PCl}_3$. The NQR signals from all the chlorine nuclei in this molecule are observable right up to the decomposition temperature with no singularities, and $T_1(T)$ to a good approximation has the form T^{-n} with n equal to 2.2 for CCl_3 (A), 2.1 for CCl_3 (B), and 2.1 for PCl_3 (equatorial). These facts are proof of the absence of separate reorientations of the CCl_3 groups in this compound. For the chlorine nuclei of the other compounds listed in Table 1 and with two CCl_3 groups, the T^{-n} law with n close to 2 also holds; the only exception is the PCl_3 group in compound V which gives no observable NQR signal at room temperature, thereby revealing the existence of separate reorientations of this group (compare (7)).

Table 2 contains data for the second class of compound investigated, that is, for trichloromethyl derivatives of phosphazo compounds in which one or two CCl_3 groups are bonded to a tetracoordinated phosphorus atom. The C-P-X bond angle in these is greater than the angle between the axial and equatorial bonds for the pentacoordinated phosphorus derivatives, so the CCl_3 groups may be expected to be more free. At the same time, additional hindrances are possible in compounds in which there are two CCl_3 groups. It may be concluded, from the character of

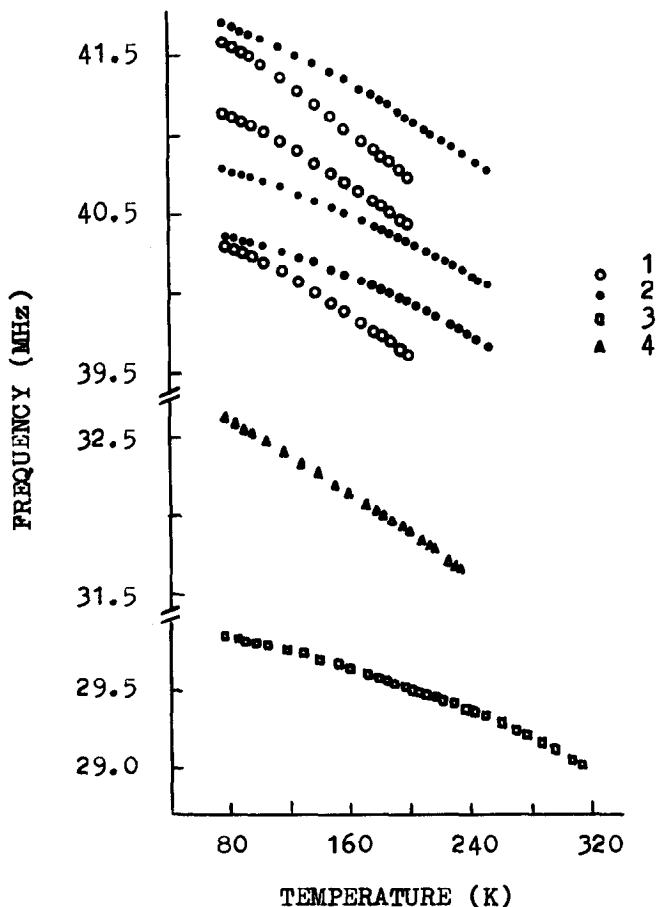


FIG. 3. Temperature dependence of the ^{35}Cl NQR frequencies in $(\text{CCl}_3)_2\text{CIP}=\text{NSO}_2\text{Cl}$: 1, CCl_3 (A); 2, CCl_3 (B); 3, PCl_3 ; 4, SO_2Cl .

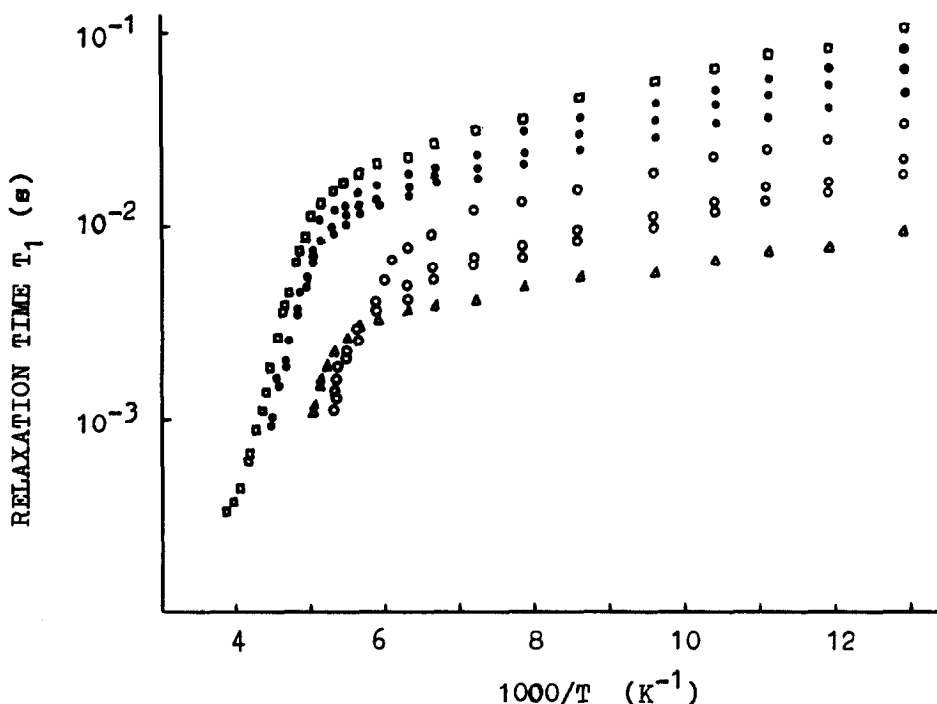


FIG. 4. Temperature dependence of the ³⁵Cl NQR spin-lattice relaxation time in (CCl₃)₂CIP=NSO₂Cl (the same line marking as in Fig. 3).

the experimental curves for $\nu(T)$ and $T_1(T)$, that in the molecules considered containing two CCl₃ groups the dynamics of these groups is of the same type. Consider, for example, compound I in Table 2. The experimental curves mentioned are shown in Figs. 3 and 4, respectively. The NQR signals from the chlorine nuclei of the two CCl₃ groups in question fade out at different temperatures, and in each case much earlier than the temperature at which melting begins. To a good approximation, $T_1^{-1}(T)$ has the form $a \cdot T^n + b \cdot \exp(-V_0/RT)$, in which the potential barrier V_0 has the values listed in Table 2 and the parameters a , n , b (T_1 is measured in seconds) have the values

$$\begin{aligned} \text{PCl: } & a = 1.12 \times 10^{-3}, \quad n = 2.07, \quad b = 2.38 \times 10^{13}; \\ \text{CCl}_3(\text{A}): & a' = 1.51 \times 10^{-2}, \quad a'' = 7.08 \times 10^{-3}, \quad a''' = 4.26 \times 10^{-3}, \\ & n' = 1.88, \quad n'' = 2.02, \quad n''' = 2.02, \\ & b = 1.21 \times 10^{12}; \\ \text{CCl}_3(\text{B}): & a' = 1.26 \times 10^{-2}, \quad a'' = 2.89 \times 10^{-3}, \quad a''' = 1.60 \times 10^{-3}; \\ & n' = 1.70, \quad n'' = 1.97, \quad n''' = 2.05, \\ & b = 4.84 \times 10^{13} \end{aligned}$$

($T_1' < T_1'' < T_1'''$ at 77 K).

For different chlorine nuclei of each of the atomic groups considered, the $T_1(T)$ curves coalesce at high temperatures. All these facts show that the CCl₃ groups undergo autonomous reorientations with different potential barrier values V_0 . This

TABLE 2
THE ^{35}Cl NQR SPECTRAL AND RELAXATION PARAMETERS FOR TETRACOORDINATED PHOSPHORUS COMPOUNDS

No. (1)	Compound (2)	Melting point temperature (K) (3)	Molecular fragments (4)	Resonance frequencies ^a at 77 K (MHz) (5)	T_1 at 77 K (msec) (6)	Fadeout temperature (K) (7)	Reorientation potential barrier (kcal/mole) (8)		
II	$(\text{CCl}_3)_2\text{CIP}=\text{NSO}_2\text{Cl}$	347	CCl_3 (A) ^b	41.594	19	205	8.1 ± 0.5		
				41.141	35				
			CCl_3 (B) ^b	40.324	22				
				41.706	84			255	11.1 ± 0.2
				40.800	50				
				40.376	67				
				29.835	105			325	11.1 ± 0.3
				32.620	10			235	—
			$(\text{CCl}_3)_2\text{CIP}=\text{NSOCl}$	353	PCl SO_2Cl CCl_3 (A) ^b	41.792	84	215	8 ± 1
						40.772	78		
40.430	64								
41.874	166	265				11 ± 1			
III	$(\text{CCl}_3)_2\text{CIP}=\text{NPOCl}_2$	331	PCl SOCl CCl_3 (A) ^b	40.672	121				
				40.554	134				
			CCl_3 (B) ^b	29.056	440			338	12 ± 1
				26.110	123			—	—
				41.410	—			225	7.9 ± 0.4
				40.448	23				
				40.299	21			250	9.2 ± 0.2
				41.410	—				
			PCl POCl_2		CCl_3 (B) ^b	41.160	112		
						40.712	98		
28.745	145								
27.432	176								
				27.282	166				

IV	$(\text{CCl}_3)_2\text{ClP}=\text{NSiCl}_3$	318	CCl_3 (A and B) ^e	40.847 (1)	89	<293
				40.758 (1)	93	
				40.554 (2)	59	
				40.323 (2)	49	
				28.385	232	
				19.511	165	
				19.395	195	
				19.172	195	
				40.686 (1)	44	
				40.578 (2)	54	
V	$\text{CCl}_3\text{Cl}_2\text{P}=\text{NC}_6\text{H}_4p\text{-Cl}$	311	CCl_3 (C and D) ^d	40.510 (2)	39	<293
				40.136 (1)	46	
				27.730	101	
				27.664	101	
				27.368	95	
				27.288	101	
				35.183	153	
				34.453	142	
				40.586 (1)	82	
				40.474 (2)	64	
VI	$\text{CCl}_3\text{Cl}_2\text{P}=\text{NC}(\text{CH}_3)_3$	~225	$\text{C}_6\text{H}_4p\text{-Cl}$ (C and D) ^d	27.265	222	
				26.745	180	
				40.334 (1)	24	
				40.061 (2)	49	
				27.075	63	
				26.630	45	
				CCl_3 (C) ^d		
				CCl_3 (D) ^d		
				PCl_2 (D) ^d		

^a The signal relative intensity is given in parentheses.

^b A and B denote nonequivalent CCl_3 groups in the molecule.

^c At 77 K in the CCl_3 spectrum range two additional less intensive lines are observable at the frequencies 40.698 and 40.470 MHz.

^d C and D denote nonequivalent positions of the molecules in the crystal unit cell.

difference (and the corresponding difference between the reorientations of two CCl_3 groups of the same molecule) is believed to be due to the different characters of interaction of the two CCl_3 groups with the chlorine atom in the P-Cl residue. The $T_1(T)$ curves for the P-Cl chlorine atom and for the more hindered of the two CCl_3 groups prove to be similar; in particular, the corresponding potential barrier values are essentially the same. This similarity leads us to believe that the more hindered CCl_3 group is situated closer to the P-Cl chlorine atom than the other group, and the relaxation mechanism for this chlorine atom is the modulation effect due to the motion of the CCl_3 group mentioned. If this is true than the $T_1(T)$ curve for the chlorine atom in question has to possess a minimum. It is plausible to assume that the sample melting made it impossible to observe this minimum.

As to the compounds in Table 2 which contain only one CCl_3 group, similar arguments lead to the conclusion that separate reorientations of these groups exist, but the corresponding potential barrier values could not be measured because of the complexity of the spectrum and low signal-to-noise ratio.

Summing up the results obtained, we can make the following statements. In the pentacoordinated phosphorus compounds that were investigated, intramolecular steric hindrances exist and prevent autonomous reorientations of axially bonded CCl_3 groups; the higher mobility of these groups usually observed (in comparison with the other molecular fragments) is due to the more active librational motions (6). In the tetracoordinated phosphorus compounds, CCl_3 group autonomous reorientations occur, even if two such groups are bonded to the same phosphorus atom; in the last case, the two CCl_3 groups are dynamically distinguishable.

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