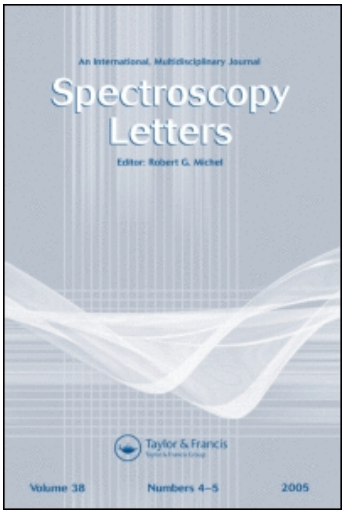

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Threefold Phosphorus-Nitrogen Reorientation Barrier in Trichlorophosphazocompounds from ^{35}Cl NQR Data

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THREEFOLD PHOSPHORUS-NITROGEN REORIENTATION BARRIER IN TRICHLOROPHOSPHAZOCOMPOUNDS FROM ^{35}Cl NQR DATA

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In the present paper we describe the ^{35}Cl NQR investigation of PCl_3-reorientations in the molecules of three trichlorophosphazocompounds, $Cl_3P{=}NCCl(CCl_3)_2$ (I), $Cl_3P{=}NP(O)(CCl_3)_2$ (II), $Cl_3P{=}NCOCF_3$ (III). In order to elucidate the quantitative parameters of the reorientational motion we have used (unlike[1]) the temperature dependence of the quadrupole spin-lattice relaxation time T_1 which is very sensitive to a molecular dynamics[2,3].

In the temperature range 77 ÷ 180°K an exponential decrease of T_1, an equalization of its values for the different chlorine nuclei of the PCl_3 group and fading out of the ^{35}Cl NQR signals of this group are observed. Typical experimental data for III are shown in the Figure. They confirm the participation of the chlorine atoms from the PCl_3 group in a reorientational motion between equilibrium position about their symmetry axis. The evidence in favour of autonomous reorientations of the PCl_3 group (in contrast to reorientations of

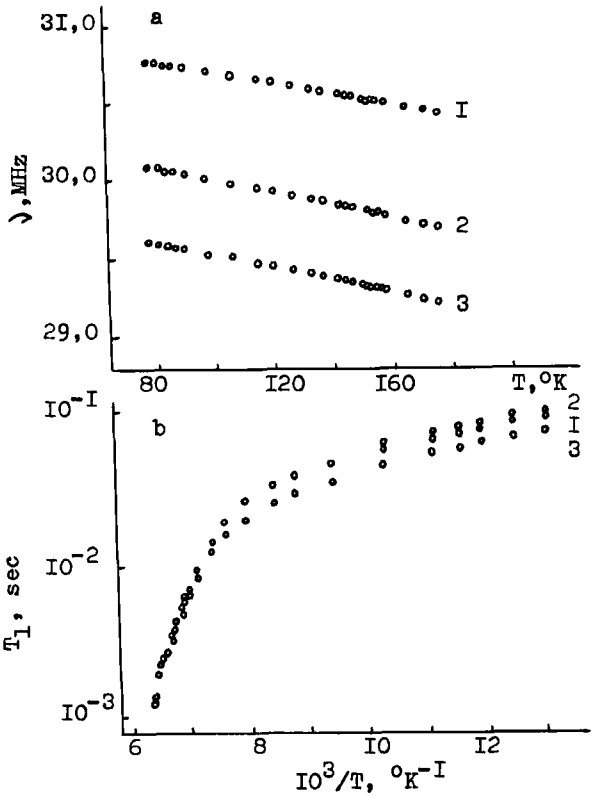

FIG. 1

The temperature dependence of the resonance frequencies (a) and of the quadruple spin-lattice relaxation time (b) of the ^{35}Cl nuclei in $Cl_3P{=}NCOCF_3$

the entire molecule) was obtained by studying temperature dependences of the ^{35}Cl NQR parameters for the C-Cl and CCl_3 groups in the compounds I and II, and those of the ^{19}F NMR parameters for the CF_3 group in III.

As seen from the Figure the equalization of the exponentially decreasing time T_1 for all three chlorine nuclei of

the PCl_3 group proceeds without an influence on the splittings in the resonance spectrum. It is connected with the fact that the reorientation rate which causes the signal fading out remains much lower than the NQR frequencies.

The relaxation process is determined by two relaxation mechanisms that combine additively. The former one represents librations and dominates at the low temperatures and the latter one is produced by reorientations which are effective at the high temperatures. Temperature dependence of the relaxation rates may therefore by described by a combined equation[2,3]:

$$(T_1^{-I})_{observ}=(T_1^{-I})_{libr}+(T_1^{-I})_{reor}=aT^n+b\exp(-\frac{V_o}{RT})$$

Here V_o is reorientational potential barrier which may be determined by a mathematical fitting of the experimental data together with a,b,and n parameters[4] (Table I,2).

TABLE I

The Parameters of Eq. for $Cl_3P{=}NCOCF_3$

^{35}Cl NQR line	n	-log a	log b	V_o, kcal/mol
lower	2.24±0.II	3.08±0.22	II.I6±0.40	6.07±0.28
middle	2.37±0.I3	3.47±0.26	II.39±0.39	6.23±0.27
upper	2.I0±0.04	2.9I±0.08	II.23±0.43	6.II±0.30
fitting of all the lines in common[4]	-	-	II.30±0.22	6.I6±0.I5

TABLE 2

The ^{35}Cl NQR Frequencies and the Reorientation Barriers of the PCl_3 Group in Trichlorophosphazocompounds

Substance	Tm.p., °K	ν_{P-Cl}, MHz, 77°K	Tf, °K	V_o, kcal/mol
$Cl_3P{=}NCCl(CCl_3)_2$	326	29.442 29.481 29.764	180	6.8±0.2
$Cl_3P{=}NP(O)(CCl_3)_2$	395	29.718 30.070 30.320	145	5.1±0.1
$Cl_3P{=}NCOCF_3$	245	29.600 30.085 30.762	175	6.2±0.2

The results of the present paper together with the data of[1] show that the potential barrier for the PCl_3 group reorientation about the P=N bond in several trichlorophosphazocompounds does not exceed 5 ÷ 7 kcal/mol. Since in a crystal the hindering potential is caused by intra- and intermolecular factors on may conclude that the threefold reorientational barrier about P=N bond have an even smaller value(cf.[5]). Thus, electronic distribution along the P=N bond does not produce an essential hindrance for the reorientational motion about this bond.

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