The $^{35}\text{Cl}$ nuclear quadrupole resonances (77 K) and ab initio calculations of trichloromethyl-dichlorophosphine (I) show that it exists in the chess conformation form. The barrier to internal rotation about the P-C bond in I at the RHF/6-31++G(d,p) level equals to 38.1 kJ mol$^{-1}$. In chloromethyldichlorophosphine (II) the extension of the basis set up to the RHF/6-311++G(df, pd) level does not improve the description of the most preferable gauche-conformation; only if electron correlation (at the MP2 level) is taken into account the results are in a good agreement with experimental data.

**Key words:** Chloromethyl- and Trichloromethyldichlorophosphine; Conformations; $^{35}\text{Cl}$ NQR Frequencies; *ab initio* and MNDO-PM3 Calculations.