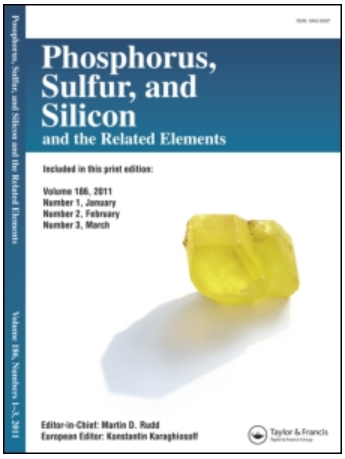

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Electric and Magnetic Anisotropy in Structural Organophosphorus Chemistry

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ELECTRIC AND MAGNETIC ANISOTROPY IN STRUCTURAL ORGANOPHOSPHORUS CHEMISTRY

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The principles of study of the electric polarizability and magnetic susceptibility anisotropy of phosphorus derivatives have been discussed. The molar constants of birefringence in the transverse magnetic field (Cotton-Mouton constants, 10^{18} e.m.u.) have been determined for 2-methoxy-4--methyl-1,3,2-dioxaphosphorinane (-1.3), its 2-oxoanalogue (1.5), 2-thioanalogue (-16.3), phosphorus chloride (-112), phosphorus oxychloride (-87), and thiophosphoryl chloride (-12). The principal semiaxes of molecular magnetic susceptibility ellipsoids (10^{29} cm^3) for the three latter compounds have been found equal: PCl_3 k_1 -9.90, $k_{2,3}$ -11.36; $POCl_3$ k_1 -8.83, $k_{2,3}$ -11.28; $PSCl_3$ k_1 -13.28, $k_{2,3}$ -13.17. The components of the magnetic susceptibility tensors of the phosphorus lone pair k_L -2.15, k_t -2.32 and of the bonds P-O k_L -4.35, k_T -2.23; P-Cl k_L -4.17, k_T -2.05; P→O k_L -1.11, k_T -0.44; P→S k_L -4.17, k_T -2.17 have been calculated using data on the magnetic anisotropy effects on chemical shifts in PMR spectra of dioxaphosphorinanes. The relationship between the mean values of the magnetic susceptibility and electric polarizability phosphorus derivatives has been established, $k = -0.060 - 1.046 \cdot 10^{-5} b$. The magnetic anisotropies of bonds have been shown to depend on their environment, for phosphoryl on the Kabachnik constants of substituents at the phosphorus atom.