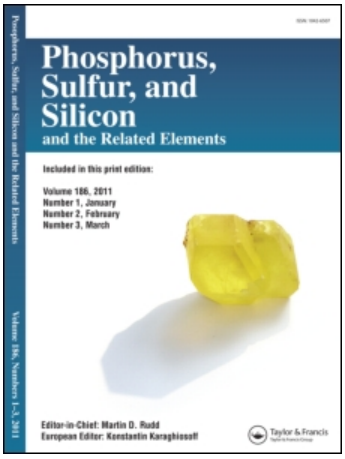

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[a] A.E. Arbuzov Institute of Organic and Physcial Chemistry, Kazan, Russia [b] Institut fur Anorganische und Analytiche Chemie der Technischen Universitat, Braunschweig, Germany

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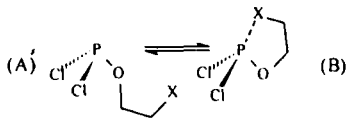
Studies of Hypervalency at Phosphorus (III) by Conformational "Sonde" Method

SERGEY KATSYUBA[a], VLADIMIR ALFONSOV[a], REINHARD SCHMUTZLER[b], RUSTEM KAMALOV[a], ALEXANDER VANDYUKOV[a], LYUDMILA AVVAKUMOVA[a], ALLA CHERNOVA[a], CARSTEN MELNICKY[b] and SVETLANA TERENT'EVA[a]

[a]*A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, 420088, Russia and* [b]*Institut fur Anorganische und Analytische Chemie der Technischen Universitat, Postfach 3329, D-38023 Braunschweig, Germany*

The compounds exhibiting hypervalent interactions of nonbonded atoms may be used as models of prereaction and transition states of nucleophilic substitution reactions. Our studies of the molecules $X(CH_2)_2$-O-PCl_2 (X = H (**1**); SCN (**2**); C_2H_5 (**3**); CH_3O (**4**); Cl (**5**)) revealed the possibility of subtle intramolecular 1-5 attractions between the sulfur (**2**) [1] or the oxygen (**4**) or the chlorine (**5**) and the phosphorus atoms. The attractions influenced perceptibly only the energy of the conformers with intramolecular contacts between the heteroatoms. A substantial energetical preference of the convoluted conformers (B) in the liquid state was observed in the case of **2**, **4** and **5**. In contrast, the molecules **1** and **3** preferred to exist in liquid in extended conformations (A). These dramatic changes cannot be explained by steric reasons or Coulomb attractions, and thus were attributed to hypervalent attractions between the heteroatoms. The relative energies of (A) and (B) conformers were used in quantitative assessing of the hypervalent interactions. The energetical effect of the interactions was evaluated to be ~2 - 4.5 kcal/mole in the liquid state.



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