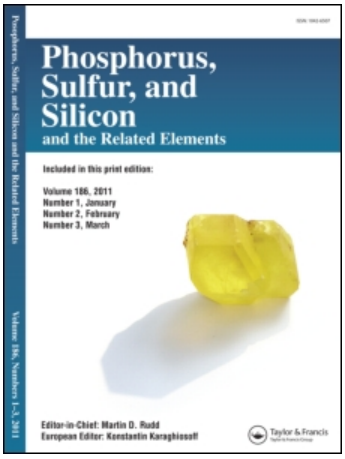

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Quantum-Chemical Study of Electronic Structure and Reactivity of Diphospha-1,3-Butadienes

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QUANTUM-CHEMICAL STUDY OF ELECTRONIC STRUCTURE AND REACTIVITY OF DIPHOSPHA-1,3-BUTADIENES

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Quantum-chemical calculations of the electronic structure of 1,3-, 1,4- and 2,3-diphospha-1,3-butadienes (DPB) and their derivatives with different substituents were performed. The MNDO method was used to describe the electronic structure of phosphaalkenes. The frontier orbitals of all unsubstituted DPB are of π-type. The highest occupied molecular orbital (HOMO) is delocalized through both double phosphorus-carbon bonds; the next occupied MO is a combination of two phosphorus lone pairs (n-MO). The HOMO of 2,3-DPB differs markedly from those of 1,3- and 1,4-isomers: the contributions of phosphorus and carbon p-orbitals are nearly equal, and the energy gap between HOMO and n-MO is very small (0.008 eV). The introduction of the electron-withdrawing substituents results in the reverse order of these MO's. In contrast with 1,3- and 1,4-isomers, the double bonds of 2,3-DPB are almost non-polar. Effect of substituents upon the electron density distribution are considered. The results indicate that orbitally controlled 1,4-additions should be characteristic for the derivatives of 1,3- and 1,4-DPB, similar to 1,3-butadiene. In case of 2,3-DPB, tendency to 1,4-addition should be lower; for its derivatives the reaction type depends greatly upon the electronic effects of substituents. In particular, reactions involving phosphorus lone pairs should be typical for the derivatives of 2,3-DPB with electron-withdrawing substituents.