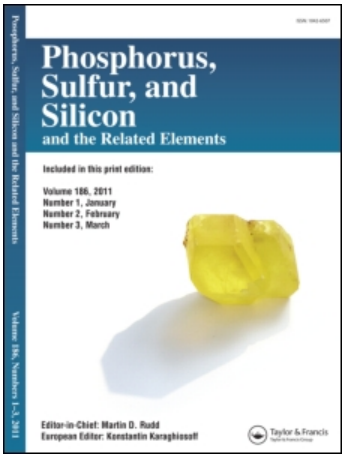

Phosphorus, Sulfur, and Silicon and the Related Elements

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On the Electronic Structure of Phosphorus- (III)-p-π-Bonded Systems: UV- and PE- Spectroscopic Investigations of Phosphaalkenes

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On the Electronic Structure of Phosphorus- (III)-p-π-Bonded Systems: UV- and PE- Spectroscopic Investigations of Phosphaalkenes

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UV- and He-I-p.e. spectra of phosphaalkenes 1 are discussed.

$$\underline{1} \quad R - P = C(SiMe_3)_2$$

$$R = Cl,\ F,\ OBu^t,\ SBu^t,\ NHBu^t,\ NHSiMe_3,\ NEt_2,\ NPr^i_2,$$
$$2,2,6,6\text{-}Me_4C_5H_6,\ N(Bu^t)SiMe_3,\ N(SiMe_3)_2,\ Me,\ Bu^t$$

Assignment of π(P=C)- and n(P)- ionization potentials agrees with u.v. data as well as semiempirical MNDO - calculations. The alkyl-substituted species exhibit a sequence of π(P=C) and n(P)-i.p.'s which is unusual for phosphaalkenes (i.p. (n) < i.p. (π)). Introduction of RO- and RS-substituents results in formation of a mesomeric 3-center-4-electron π-system. Two different conformers of amino-phosphaalkenes can be distinguished which depend on the steric demand of the substituent, and differ in the orientation of the amine-ligand in relation to the plane of molecular symmetry. Coexistence of both isomers is proved in the case of $R = NPr^i_2$ by temperature dependant u.v. studies.

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