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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### Substitution Effects on Multiple Phosphoru-Carbon Bond

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**To cite this Article** Chernega, Alexander N. and Korkin, Anatolii A.(1993) 'Substitution Effects on Multiple Phosphoru-Carbon Bond', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 76: 1, 65

**To link to this Article:** DOI: 10.1080/10426509308032359

**URL:** <http://dx.doi.org/10.1080/10426509308032359>

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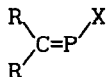
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## SUBSTITUTION EFFECTS ON MULTIPLE PHOSPHORUS-CARBON BOND

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To elucidate the character of an influence of the substituent nature and the substituent location at the phosphorus-carbon multiple bond on structural and electronic parameters of this bond, a cycle of X-ray investigations of phosphaaalkenes I and phosphaaalkynes II as well as *ab initio* HF/6-31G\* calculations were performed. In I, introduction of a halogen atom at phosphorus does not practically change the bond angle distribution, but causes essential shortening of the P=C bond (due to the increasing of its polarization) and increase of LP(P) s-character. Besides that, a peculiarity of structure of these compounds is a considerable elongation of the P-Hlg bond in comparison with the 3-coordinated phosphorus compounds. Introduction of a halogen atom at carbon has much weaker influence on the double bond and causes a reverse effect: its polarization decreases, and as a result, it is slightly elongated. The influence of  $\pi$ -donating (acceptor) substituents is a more complex one. Thus, in P-aminosubstituted phosphaaalkenes  $n_N-\pi_{P=C}$  conjugations causes, on one side, a weakening of the double bond  $\pi$ -component, and on the other side, an increase of bond polarization. As a result of mutual compensation of these two effects, the P=C bond length does not change. On the contrary, in C-aminosubstituted phosphaaalkenes the direction of these two effects coincides, which causes a very large elongation of the P=C bond. The LP(P) in phosphaaalkenes, independently of the bond angle at phosphorus atom and type of substituents, is found to be mainly of s-character (by 60-75 %). The structural consequences of the LP(N) conjugation with the  $\pi$ -system of the triple bond in phosphaaalkynes  $P\equiv C-NR_2$  and nitriles  $N\equiv C-R$  are essentially different; this fact is caused by a different character of polarization of these triple bonds.



I: R, X = H, Hlg, SiMe<sub>3</sub>, NR'<sub>2</sub>, OR' et al.

II: X = Bu<sup>t</sup>, NR<sub>2</sub>