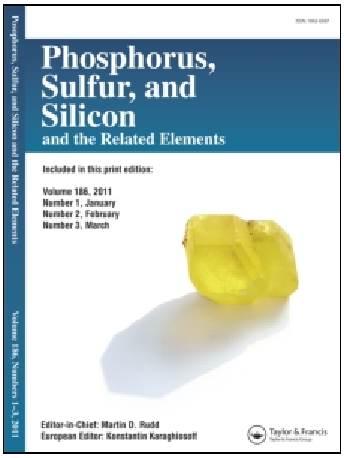


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Substitution Effects on Multiple Phosphoru-Carbon Bond

Alexander N. Chernega[a]; Anatolii A. Korkin[a]
[a] Institute of Organic Chemistry Acad. Sci. of the Ukraine, Ukraine

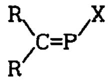
To cite this Article Chernega, Alexander N. and Korkin, Anatolii A.(1993) 'Substitution Effects on Multiple Phosphoru-Carbon Bond', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 65
To link to this Article: DOI: 10.1080/10426509308032359
URL: http://dx.doi.org/10.1080/10426509308032359

Phosphorus, Sulfur, and Silicon, 1993, Vol. 76 p. 65
Reprints available directly from the publisher
Photocopying permitted by license only

SUBSTITUTION EFFECTS ON MULTIPLE PHOSPHORUS-CARBON BOND

Alexander N.Chernega, Anatolii A.Korkin
Institute of Organic Chemistry Acad. Sci. of the
Ukraine, Murmanskaya St.5, Kiev-94, 253660, Ukraine

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 phosphaalkenes I and phosphaalkynes 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 π-donating (acceptor) substituents is a more complex one. Thus, in P-aminosubstituted phosphaalkenes n_N-$\pi_{P=C}$ conjugations causes, on one side, a weakening of the double bond π-component, and on the other side, an increase of bond polarization. As a result of mutual compansation of these two effects, the P=C bond length does not change. On the contrary, in C-aminosubstituted phosphaalkenes the direction of these two effects coincides, which causes a very large elongation of the P=C bond. The LP(P) in phosphaalkenes, 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 π-system of the triple bond in phosphaalkynes $P\equiv C-NR_2$ and nitriles $N\equiv C-R$ are essentially different; this fact is caused by a different character of polarization of these triple bonds.



$X-C\equiv P$

I: R,X = H, Hlg, $SiMe_3$, NR'_2, OR' et al.

II: X = Bu^t, NR_2