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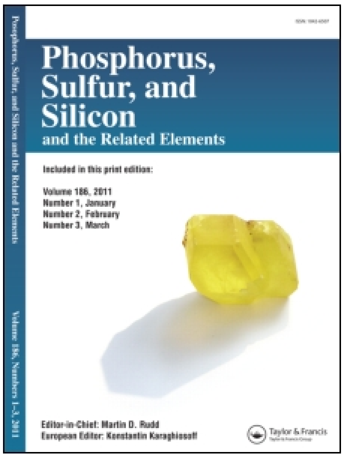

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

X-Ray Structural Study of the Novel Tautomeric Orgaijophosphorus Compounds

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To cite this Article Antipin, N. Yu. , Struchkov, Yu. T. and Nesmeyanov, A. d.(1990) 'X-Ray Structural Study of the Novel Tautomeric Orgaijophosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 224
To link to this Article: DOI: 10.1080/10426509008040758
URL: http://dx.doi.org/10.1080/10426509008040758

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Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 224
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Printed in the United Kingdom

X-RAY STRUCTURAL STUDY OF THE NOVEL TAUTOMERIC ORGANOPHOSPHORUS COMPOUNDS

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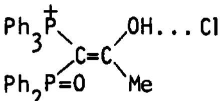
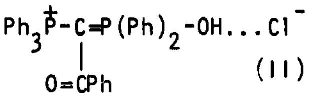
A number of acylsubstituted (diphenylphosphoryl)methyl-triphenylphosphonium salts I-IV, which are keto-enolic organophosphorus compounds with the new type of the phosphoryl-hydroxyylide tautomerism, were studied by X-ray diffraction method.


(I)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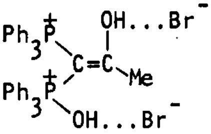
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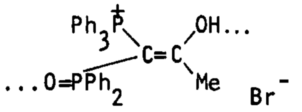
(III)

A vast variety of tautomeric forms, occurring in crystals and stabilized by the strong H-bonds of different types, was found. Analysis of main geometric features of the studied compounds allowed to elucidate the character of electronic delocalization in the observed tautomeric forms. It was found that in I Ph_2PO-group does not essentially participate in the resonance stabilization of the cation. On the contrary, in crystal III, wherein the strong C-OH..O=P H-bonds link the cations into infinite chains, the electronic system of the Ph_2PO group takes part in the stabilization of the enolic from of the cation. The geometric parameters of hydroxyylide cation also indicate the significant electronic delocalization in its central fragment. The unusual dication IV is stabilized due to the strong H-bonds of the P-OH and C-OH groups with the Br^--anions.

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