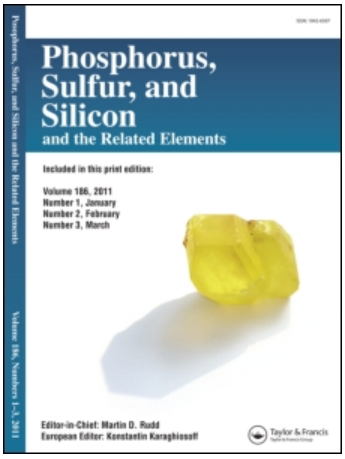

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Can Four Membered Heterophosphete Structures Exist? "Heterogen" Hetero Antiaromaticity as a Destabilizing Effect

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Can Four Membered Heterophosphete Structures Exist? "Heterogen" Hetero Antiaromaticity as a Destabilizing Effect

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Keywords ASntiaromaticity; heterophosphetes; p-heterocycles; ring opening

Four-membered heterophosphetes (Figure 1), existing as two conformers (**1A** and **1B**), are thermodynamically unstable and they readily undergo ring-opening reactions to form oxo-, imino-, or thiaphosphoranes **3**.[1] This may be one of the reasons that earlier synthetic attempts to produce heterophosphetes have mostly failed. Their saturated counterparts heterophosphetanes (**2A** and **2B**), which are well-known intermediates of the Wittig reaction are, however, stable and cannot undergo ring-opening reaction. The question arises: What is the reason for this sharp difference between the stability of **1** and **2**?

Our results based on quantum chemical calculations revealed that the instability of **1A** and **1B** should be attributed to their antiaromatic character, originated from the conjugation of the empty d-orbitals of the P atom and the occupied p_z orbital of the Y moiety. This type of antiaromaticity is defined as a "heterogenic" antiaromaticity. Compounds **1A** with equatorial Y possess a more considerable extent of antiaromatic character than species **1B** with axial Y, which practically can be considered as non-aromatic compounds. It has been shown that strong electron withdrawing substituents (F, Cl, CN) bound to the phosphorus atom are able to stabilize the ring system. The thermodynamic

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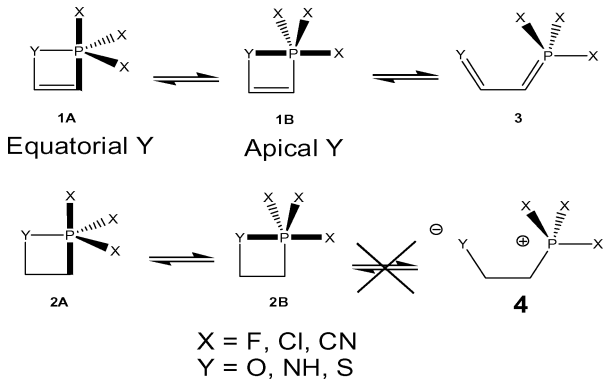

FIGURE 1 Transformations of heterophosphetes (**1A** and **1B**) and heterophosphetanes (**2A** and **2B**).

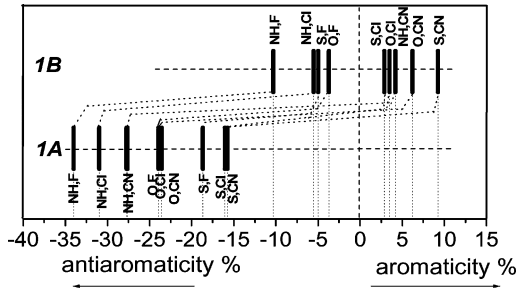

FIGURE 2 Computed aromaticity and antiaromaticity scale for **1A** and **1B**.

stability of **1A** and **1B** has been studied systematically and the extent of antiaromaticity of these species was quantified by a linear aromatic and antiaromatic scale (Figure 2). An overall 3-D potential surface, as well as an antiaromaticity % surface of **1** have been discovered.

REFERENCE

[1] G. Keglevich, H. Forintos, and T. Körtvélyesi, *Current Org. Chem.*, **8,** 1245 (2004).