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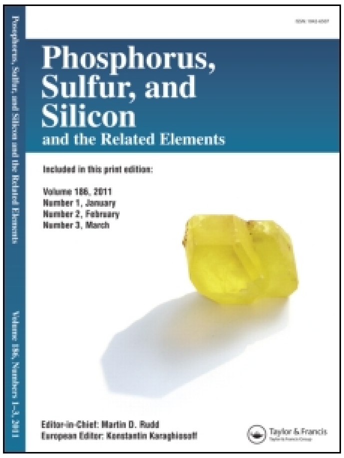

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphorus in Strained Ring Systems

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Phosphorus in Strained Ring Systems

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Abstract. The effect of phosphorus substitution on the properties of strained cyclic systems is evaluated by means of quantum chemical claculations at an *ab initio* calculations at SCF and MCSCF level. Main emphasizes is directed to an investigation of bonding in the series of phosphacyclobutadienes (in comparison to azacyclobutadienes), cyclophosphenes and phosphacylopropenes.

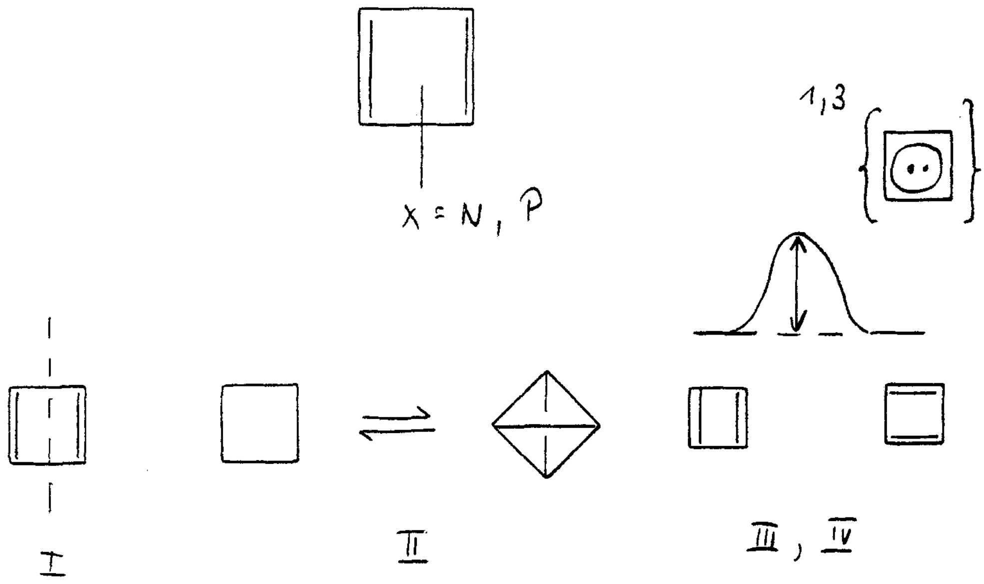
Multiple bonded phosphorus chemistry in low coordination states is now well established, as documented in a recent monograph on this subject [1]. While the synthetic aspects of this relatively new field of chemistry are well understood there is still a large lack in the evaluation of the bonding aspects of phosphorus multiple bonded compounds. Here we continue our lines and present quantum chemical investigations on phosphorus double-bonded systems within ring systems. The following topics will be dealt with:

1. Phospha- and Aza-cyclobutadienes.

While cyclobutadienes are well known[2] reports on heterocyclobutadienes are rare. Hitherto the monoazacyclobutadiene[3] has been reported. Of interest in this respect is the development of a complete theory of bonding of the whole series of aza- and phospha-cyclobutadienes. It includes all members from mono- to tetra-hetero substitution. The quantum chemical calculations were considered at MCSCF level, to account for the biradical character in these species, and include the following aspects: 1. The stabilities of the species towards fragmentation (route I). While the phospha-cyclobutadienes are stable towards fragmentation into HCP, HCCH and/or P_2, this is not the case for the corresponding aza-derivates. They tend to fragment with increasing nitrogen substitution in the four-membered ring moiety.

The borderline case is the diaza-cyclobutadiene which is thermodynamically less stable than N_2 and acetylene (or two HCN).

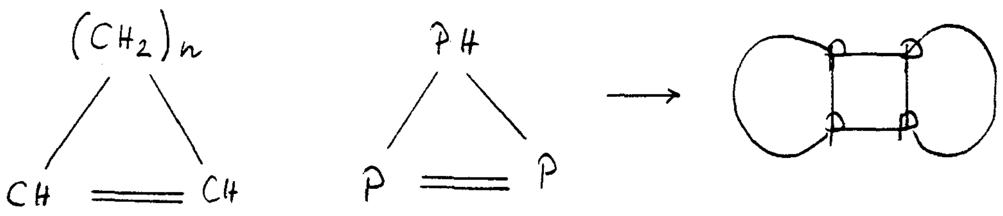
2. For the aza-cyclobutadienes the energy balance between the cyclic π-system and the corresponding tetrahedrane (route II) derivative is always in favour of the open congener and the energy difference between both structural isomers is approximately constant. For the phospha-derivatives the tetrahedrane derivative comes to the fore with increasing phosphorus substitution. Thus P_4 is exceedingly more stable in the tetrahedrane form than as cyclic π-system. To isolate and structurally elucidate a phosphacyclobutadiene point 3 (see vide infra) must be met. 3. For the structural stability of corresponding phosphorus congeners a large energy difference between the rectangular and quadratic structure (route III) is a necessary prerequisite for structural identification. In the aza-cyclobutadienes it is comparable in energy to cyclobutadiene itself. Hence aza-substitution tends to localize the double bonds in the ring system. On the contrary, the energy barrier for valence isomerization decreases in the phospha-derivatives, the more phosphorus atoms are in the ring system. Finally the energy barrier for valence isomerization is zero in the (hypothetical) planar P_4. On this basis phosphorus substitution in cyclobutadiene promotes the formation



of a singlet biradical rather than an isolable closed shell systems. The matter is in contrast to the aza-cyclobutadienes. 4. Finally, aza- as well as phospha-ring systems possess a definite singlet ground state (route IV), due to the operation of "dynamic spin polarization"[3] within the cyclic π-system. In other words for all cases the energy lowest triplet state is higher in energy than the energy lowest singlet state.

Cyclophosphenes, Ring Strain

The cyclophosphenes are a hitherto unknown class of endocyclic π-bond systems. Bonding in these systems is modelled and compared with the one in cycloalkenes. It will be shown that the cyclophosphenes possess low ring strain energies, as

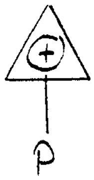


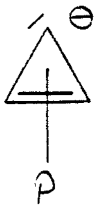
$n = 1 \ldots 4$

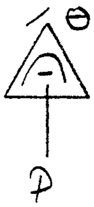
evaluated theoretically by isodesmic and homodesmic reactions. The strain energy in these ring systems decrease with increasing phosphorus substitution of the ring members. Furthermore we report on the possibility of [2+2] dimerization reaction of these π-systems towards corresponding four-membered ring systems. In addition the strain in the corresponding saturated derivatives, the cyclophosphanes is compared with. The calculations indicate singlet-triplet energy differences similar in magnitude to parent diphosphene, which reveals a similar stability of an endocyclic π-bond.

3. Phosphacyclopropene Systems

We furthermore analyze in detail the effect of phosphorus substitution on the bonding properties of cyclopropene systems[5]; the thermodynamic stabilities of corresponding cation and anionic systems. On this basis the effect of phosphorus substitution on carbon analogue systems is explored.







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