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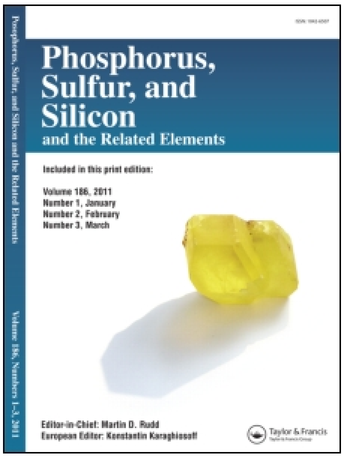

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CATION AND ANION STABILITIES OF LOW-COORDINATED Π-BONDED PHOSPHORUS SYSTEMS. AN AB INITIO QUANTUM CHEMICAL INVESTIGATION

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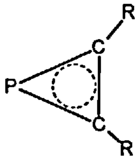
Abstract Quantum chemical calculations at RHF/6-31+g(d,p) with electron correlation (MP4SDTQ) corrections are reported on (a) a relative scale of model cations and anions derived from low-coordinated π-bonded phosphorus, (b) on band structure calculations (tight-binding approximation) of the P-iodine iminophosphane and (c) on lithiation to (unsolvated) corresponding structures derived from the anionic species.

There is a particular interest in the experimental and theoretical investigations of bonding in cationic and anionic low-coordinated π-bonded phosphorus compounds of the type 1



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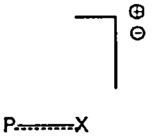

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(R=alkyl, aryl etc.), 2 (X = NR_2, PR_2, Hal, alkyl), 3 (X = O, NR, CR_2) either as cations (in solution)[1] or in the crystal environment (triflate structures[2], periodic band structures). We explore the following aspects, on the basis of quantum chemical ab initio calculations:

(1) A relative scale of cation and anion stabilities (within the gas phase). These are given by corresponding group transfer reactions of a hydrid (proton) from PH_3 to the cationic (anionic) fragmental species under question, according to the reaction $PH_3 + PX_2^{(+)}$ (or $PX_2^{(-)}$) ---> $PH_2^{(+)}$ [$PH_2^{(-)}$] + PX_2H - ΔE. The largest cation stability possesses the diaminophosphenium cation, X = NH_2 (ΔE = 92.1 kcal/mol, exothermic, at MP4 (SDTQ(fc))/6-31+g(d) level, all details are given elsewhere[3]. In comparison with, the relative stability of the corresponding (closed shell) anion is nihil (2.4 kcal/mol). Further species with strong cation stabilities are: $P(PH)_2^{(+)}$ 54.4, $PNH^{(+)}$ 94.7 $PS^{(+)}$ 67.2, phosphirenyl cation 73.1 kcal/mol. Hence a large variation in cation stability is revealed (see following scheme for cation stabilities, exothermic energy balance, in kcal/mol).

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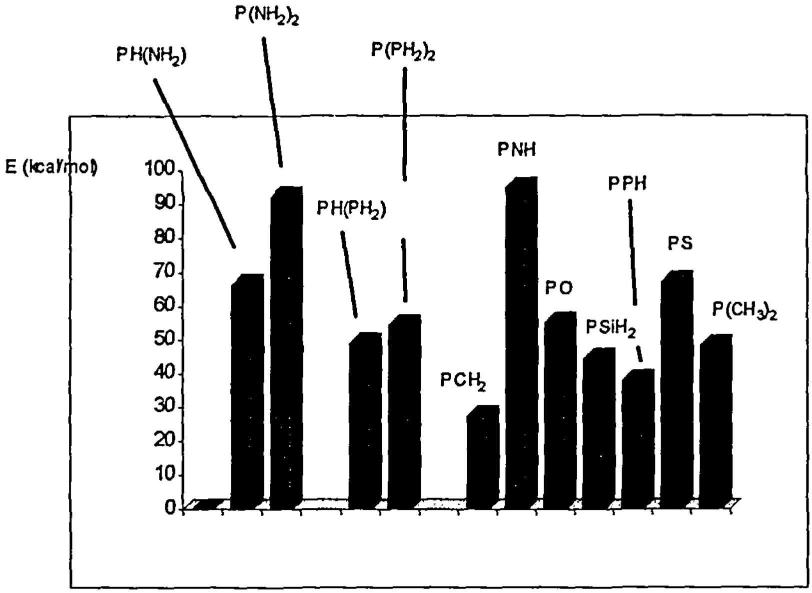
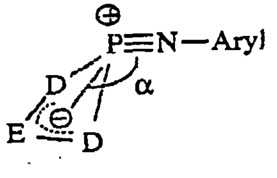


A detailed investigation of the electronic hypersurfaces of corresponding energy lowest singlets and triplets indicate that $PSiH_2^{(+)}$ possesses a triplet ground state[3,4] and reveals only a small tendency for adopting a bridged structure, as is known for the (isoelectronic) $P_2H^{(+)}$ cation. Continous medium effects were also explored within the Onsager model. They are in general much weaker than the Born effects. The strong cation stability of the $PNH^{(+)}$ cation is related to experimental work[5] on a variety of structures of donor-acceptor complexes of the following type (D = S, Se, t-BuN, O; E = R_2P, R = alkyl, aryl).



In the experiment[5] the PN-distances range from 1.53 (E = $(C_6H_{11})_2$, D = S) to 1.486 Å (D = S, E = t-Bu_2P), A detailed evaluation of the potential hypersurfaces are presented for the $N{=}CH_2^{(+)}$ and $P{=}CH_2^{(+)}$ cations. The former is lowest in energy in form of its acetylenic structural isomer $HNCH^{(+)}$ while for the latter the corresponding acetylenic isomer is unstable and rearranges to $P{=}CH_2^{(+)}$. This difference in structural stability is due to the stereochemically active lone pair in the corresponding phosphorus compound and is also apparant in the isoelectronic $Si{=}CH_2$.

A simplified plot of relative cation versus relative anion stabilities is given as follows,

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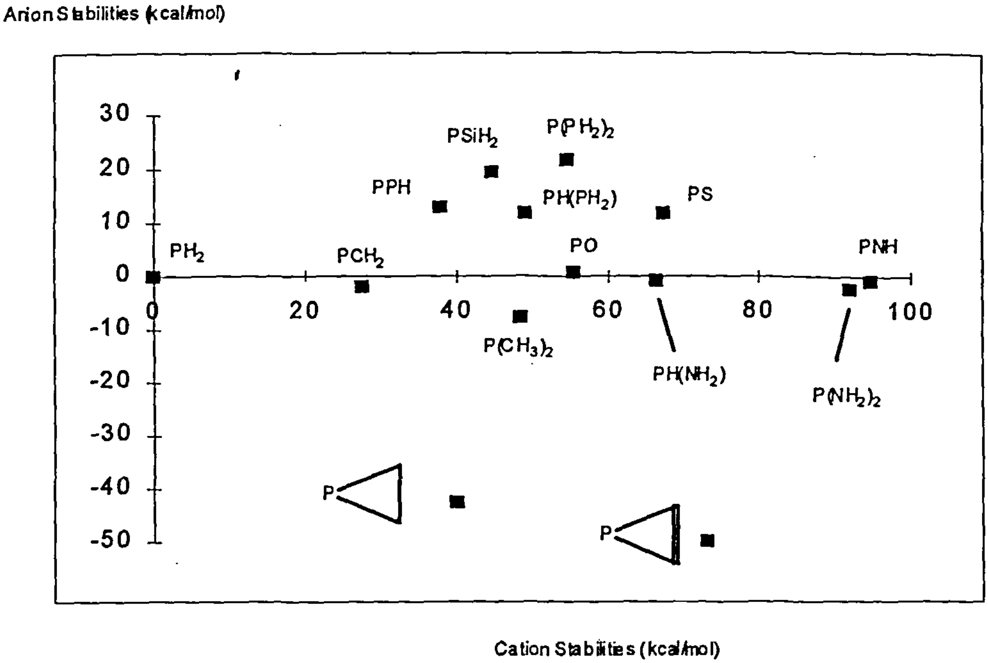
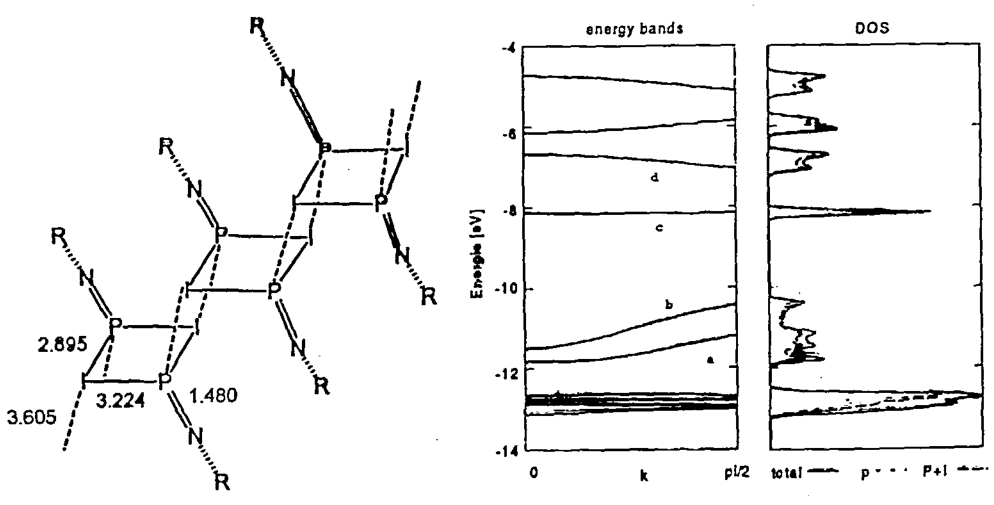


indicating only a relative small variation in anion versus cation stabilities (positive values on the plot refer to extra stabilization energies and are actually exothermic in the group transfer reactions). In addition to the relative stabilities of the charged species the frontier orbital properties are evaluated[3].

(2) Formation of periodic band structures. The P-halogen substituted compounds, $XPCH_2$, XPNH (X=F, Cl, Br, I) are experimentally well known and possess according to the quantum chemical calculations energetically low lying π-orbitals at X[6] which are suitable for the formation of periodic band structures; e.g. a ladder structure of the following type (following scheme, left, ladder structure, right, band structure within the tight-binding approximation) obtained for the iodine compound.



Bonding is here rationalized and related to another periodic iodine-containing phosphorus compound, qualitatively on the basis of extended Hückel considerations within the tight-binding approximation. Thus, the compound possesses a large energy gap between the Fermi level and the lowest conduction band (right of the scheme), although it can be formally derived from the planar periodic structure, suffering Peierls distortion and causing significant σ/π orbital set mixing by folding to the ladder structure.

(3) Lithium affinities of anions. The lithiated structures (unsolvated) of a selected variety of anions are reported[3,4]. Considerably differences between lithiation at N versus P are drawn. The latter posseses a stereochemically active lone pair as already witnessed in a number of metal complexed compounds. Detailed investigations are reported on lithiation on the model compounds $N{=}CH_2^{(-)}$ and $P{=}CH_2^{(-)}$. Lithiation is in general more effective at N than at P, due to the larger ionic contribution in bonding in the former compared with the latter type of bonds. For some of the anions the electron affinities were also evaluated by successive attachment of an electron to the cations, under formation of radicals and anionic species. Some of the anions also prefer a triplet rather than a singlet ground state as an entity in the gas phase[3,4]. The lithium affinities (of the unsolvated species) do not correlate with the gas phase stabilities obtained by the group transfer reactions, rather the linkage of the (electropositive) lithium atom to the (more electronegative) nitrogen than the phosphorus atom is determining the stabilities.

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