The frontier molecular orbital analysis of the phosphorus analogues of cyclopentadienyl anion

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Quantum chemical calculations at the semiempirical level reveal that in the phosphorus analogues of cyclopentadienyl anion having three or more in-ring phosphorus atoms, there is a marked lowering of the π* levels as compared to the lowering of the highest occupied π levels. This leads to the possibility of having significant interactions between the vacant π* orbitals of these species with the occupied orbitals of other substrates.

The past decade has seen a tremendous growth of organophosphorus compounds containing multiply bonded carbonphosphorus bonds. It emerges that these compounds exhibit chemical properties parallel to their organic counterparts although they are inherently less stable in view of the weaker bonding involved. Recently, we have investigated the phosphorus analogues of cyclopentadienyl anion and shown that they exhibit moderately aromatic or highly aromatic character. In this communication we analyze the frontier molecular orbitals (FMO) of these anionic species in order to account for the reactivity of these species.

Results and discussion

Figure 1 depicts the FMO energies of the phosphorus analogues of cyclopentadienyl anion obtained at the optimized geometries using the all-valence electron SCF method SINDO1. Our earlier work shows that SINDO1 predicts reliable geometries in these species and also accounts for their aromatic properties.

The degeneracy of the highest occupied π MOs e′′ in cyclopentadienyl anion is lifted in the phosphorus analogues resulting in the MOs of symmetries b_{1} and a_{2} (denoted by 1b_{1} and 1a_{2} in Fig. 1). These MOs are lower in energy than the e′′ orbitals of cyclopentadienyl anion as expected from the electronegative nature of the phosphorus atoms. Exception is noticed in the case of phosphoryl anion C_{3}H_{3}P− in which the 1b_{1} orbital is slightly higher than the e′′ of C_{3}H_{3}− which is in agreement with the findings from the photoelectron spectrum. The decrease in the energy of e′′ orbitals of P_{5}− as compared to that in C_{3}H_{3}− amounts to 0.88 eV.

The degenerate pair of lowest π* orbitals in C_{3}H_{3}− and the corresponding 2b_{1} and 2a_{2} orbitals in C_{4}H_{4}P− are quite high in energy. This is in agreement with the results of Mathey and coworkers who observed that the interaction of the vacant MOs of these ligand species with the occupied metal orbitals in the complexes [(η^{5}-C_{4}H_{4}P)Fe(η^{5}-C_{4}H_{4}P)] and [(η^{5}-C_{4}H_{4}P)Mn(CO_{3})] is weak. However, the interactions between the occupied orbitals of the ligand and the vacant metal orbitals are reported to be strong. The present comparative study shows that there is drastic lowering of the π* orbitals in the phosphorus analogues of cyclopentadienyl anion as the number of in-ring phosphorus atoms increases. In the penta-phosphorus analogue, the e′′ orbitals are lowered by 4.62 eV. Calculations using the
MNDO\textsuperscript{6} method showed an energy lowering of 5.29 eV for the \( \pi^* \) orbitals \( \varepsilon_{2''} \) in \( \text{P}_{5} \) as compared to that in \( \text{C}_5\text{H}_5 \). Although both the highest occupied \( \pi \) MO and the lowest vacant \( \pi^* \) MO are lower in energy in the phosphorus heterocycles than in the unperturbed system, the decrease in the former is less pronounced.

It is well-known that the substitution of a carbon atom in a chain or a ring by an electronegative hetero atom leads to lowering of both the HOMO and LUMO energies\textsuperscript{7-8}. The energy lowering in the HOMO as well as the LUMO is comparable when the hetero atom belongs to the same row of the Periodic Table, e.g. nitrogen and oxygen, due to comparable valence orbital overlaps. Computations reveal slightly more lowering of HOMO than the LUMO in the case of aza- substitution\textsuperscript{7-8}. The significant lowering of the LUMO than that of the HOMO when one or more carbon(s) is(are) replaced by a phosphorus atom(s), may be explained by the considerably weak valence-orbital overlaps \( 3p_x(P)-2p_n(C) \) and \( 3p_n(P)-3p_x(C) \). When the orbital overlaps between bonded atoms are weak, the interatomic interactions will be small and so the energy gap between the HOMO and LUMO is expected to be small. In other words, the HOMO will be raised and the LUMO lowered as compared to the situation involving strong orbital overlaps. This accounts for the drastic lowering of the LUMO with increased number of phosphorus atoms in the ring in Fig. 1. However, the HOMO does not increase in energy with phosphorus substitution due to the predominant effect of electronegativity of phosphorus towards lowering of the energy of HOMO. A similar trend in the HOMO and LUMO energies is observed with phosphorus substitution in 1,3-cis-butaadienes\textsuperscript{9}.

The pairs of molecular orbitals \( 1a_2, 1b_1 \) and \( 2a_2, 2b_1 \) do not show any uniform variation in energy with the number of substituted phosphorus atoms. In order to know the overall effect of phosphorus substitution on the energetics of \( \pi \) and \( \pi^* \) orbitals we have correlated the average energy of the pair of MOs with that of the degenerate pair by dotted lines in Fig. 1. The average energy of \( 2a_2 \) and \( 2b_1 \), corresponding to the energy \( \varepsilon_{2''} \), decreases with increase in the number of substituted phosphorus atoms. The decrease in the average energy of \( 1a_2 \) and \( 1b_1 \) with the number of phosphorus atoms is found to be less significant.

The marked lowering of the lowest unoccupied \( \pi^* \) levels in the tetra- and penta-phosphorus analogues of cyclopentadienyl anion indicates that there can be significant interactions between these MOs and the occupied orbitals of other substrate species. The present analysis reveals that the interactions between the \( \pi^* \) levels of these ligand species with the occupied metal orbitals will play a significant role in forming complexes, although earlier studies\textsuperscript{4-5} showed that these interactions are weak with the ligand species, cyclopentadienyl anion and the phospholyl anion.

References