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Picture of Bonding in Protonated Phosphorus and Arsenic Clusters. Detection of 3-Center Bonds from the Generalized Population Analysis

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In this report we provide a theoretical support for the existence of nonclassical 3-center bonding recently invoked to explain the structure of protonated phosphorus and arsenic X_4H^+ clusters.For this purpose the electron structure of these clusters was analysed using the formalism of the generalized population analysis, in terms of which the eventual presence of multicenter bonds in a molecule can be directly detected and localized. Our results confirm the presence of 3-center bonding involving X–H–X fragments in these clusters.

Key words: phosphorus clusters, arsenic clusters, 3-center bonding.

INTRODUCTION

Despite its classical nature, the Lewis idea of chemical bond formed by a shared electron pair[1] has proved to be extremely fruitful and the Lewis mo-

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del of localized 2-center 2-electron bonds has become the basis of classical structural theory. Because of tremendous impact of Lewis electron pair model on chemistry, it is not surprising, that after the advent of quantum theory, which is the only tool allowing a quantitative description of the bonding phenomena, a lot of studies have been devoted to the reconciliation of both alternative pictures of bonding.[2–13]

Among several different approaches, the formalism of pair population analysis[14,15] and its subsequent generalizations[16,17] have clearly shown that in many cases Lewis electron pair model does indeed represent a simple and precise enough picture of the molecular structure.[18] However, in addition to these simple cases of molecules with well localized 2-center 2-electron bonds, there is a wealth of evidence suggesting that the molecules also exist with more complex bonding patterns. This is, for example, the case of electron deficient molecules like boranes, transition metal complexes or metal clusters for which the concept of multicenter bonding has been invoked[19,20] in order to get an appropriate explanation of their structure. With this in mind we[21–24] and others[25–31] have recently generalized the pair population analysis so it becomes applicable to the analysis of bonding in these complicated cases. Based on this generalized approach, the applicability of the corresponding analysis for the detection and localization of multicenter bonding has been demonstrated.[23,24]

One of the advantages of the techniques of population analysis is that they can be applied to any kind of systems, ranging from simple molecules or clusters to layers and solid state crystals. In this study we report the application of the generalized nonlinear population analysis[17] to the visualization of bonding in protonated phosphorus and arsenic X_4H^+ clusters for which previous theoretical treatments have suggested the existence of 3-center 2-electron bonds.[32,33] As will be shown below, this approach clearly supports the conclusions of previous qualitative studies, namely that these clusters do indeed represent a new class of molecular systems with 3-center X–H–X bonds.

THEORETICAL

The formalism of generalized population analysis, which underlies all existing approaches to the analysis of multicenter bonding is based on the idempotency property of SCF density matrix which can be expressed in the form

$$tr(\boldsymbol{PS})^p = 2^{p-1}N, \tag{1}$$

where $\boldsymbol{P}$ is the spin-free charge and bond order matrix and $\boldsymbol{S}$ the overlap one. This equation allows us to partition the total number of electrons N in a molecule into contributions associated with the products of p elements of the ($\boldsymbol{PS}$) matrix, where (α, β, γ.....ω) are the atomic orbitals (AO basis functions)

$$N = \frac{1}{2^{p-1}} \sum_{\alpha}\sum_{\beta} \cdots\cdots \sum_{\omega} (\boldsymbol{PS})_{\alpha\beta} (\boldsymbol{PS})_{\beta\gamma} \cdots\cdots (\boldsymbol{PS})_{\omega\alpha} \,. \tag{2}$$

Since each of the AO basis functions is usually localized on a certain atom, it is possible to distinguish in Eq. (2) contributions according to on which center the AO basis functions are localized. For the particular case of $p = 1$ this leads to the well known Mulliken population analysis,[34] while for $p = 2$, the resulting mono-and biatomic populations are identical with well known Wiberg[35] or Wiberg-Mayer indices,[36] which are generally accepted as a measure of the classical bond order.

While this Wiberg-like partitioning gives a completely satisfactory picture of bonding for »normal« molecules with localized 2-center 2-electron bonds, the analysis of more complex bonding patterns like the multicenter bonding requires us to scrutinize higher powers of the ($\boldsymbol{PS}$) product. The simplest such situation, which covers most of the known cases of multicenter bonding is for $p = 3$, where the partitioning can be performed into mono-, bi- and triatomic contributions.

$$N = \frac{1}{2^2} \sum_{\alpha}\sum_{\beta}\sum_{\gamma} (\boldsymbol{PS})_{\alpha\beta} (\boldsymbol{PS})_{\beta\gamma} (\boldsymbol{PS})_{\gamma\alpha} = \sum_{A} \Delta_A^{(3)} + \sum_{A<B} \Delta_{AB}^{(3)} + \sum_{A<B<C} \Delta_{ABC}^{(3)} \,. \tag{3}$$

While mono- and biatomic contributions ($\Delta_A^{(3)}$ and $\Delta_{AB}^{(3)}$ respecively) are directly related to mono- and biatomic terms derived from the partitionings for $p = 1$ and $p = 2$, (for the exact relation see Ref. 22), the specific feature of the partitioning (3) is the presence of 3-center terms $\Delta_{ABC}^{(3)}$, which have been shown to serve as indicators of the eventual presence of 3-center bonding in a molecule. In this connection it is worth mentioning that another closely related definition of multicenter indices has also been reported in which the partitioning is normalized to $N/2$ rather than to N.[16,23,24] This change of normalization affects, of course, the numerical values of the indices, but their physical meaning is the same.

Having summarized the necessary theoretical background, we will discuss, in the next section, the results of the above presented third-power analysis for the protonated phosphorus and arsenic clusters X_4H^+.

COMPUTATIONS

Two types of calculations were performed in this study. In the first, the geometry of the most stable forms of protonated X_4H^+ clusters were completely optimized using *ab-initio* GAMESS-US program[37] in 3-21G** basis. The calculated geometries agreed closely with those reported earlier using better basis sets.[32,33] The density matrices generated in these calculations were then, in the second step, subjected to the formalism of the non-linear population analysis described by Eq. (3) through our own programs, which can be obtained upon request. The population analysis itself requires very little time as it takes only a few seconds for the studied systems. The selected values of calculated populations are summarized in Table I.

TABLE I

Calculated values of mono-, bi- and triatomic populations in X_4H^+ clusters[a]

fragment	$\Delta_A^{(3)}$	W_{AB}	$\Delta_{AB}^{(3)}$	$\Delta_{ABC}^{(3)}$
X_1	12.682 30.665			
X_2	12.750 30.708			
X_4	12.683 30.666			
H	0.243 0.227			
X_1X_2		0.905 0.949	1.291 1.337	
X_1X_4		0.561 0.490	0.642 0.509	
X_2X_3		0.929 0.946	1.347 1.349	
X_2X_4		0.905 0.949	1.292 1.337	
X_1H		0.430 0.457	0.567 0.584	
X_4H		0.427 0.456	0.562 0.581	
X–H–X				0.185 0.221

[a] Upper value corresponds to phosphorus and lower to arsenic cluster.

RESULTS AND DISCUSSION

Let us start by considering the case of the phosphorus cluster P_4H^+, the structure of which is visualized in Figure 1. As it is possible to see, this structure resembles that of the parent tetrahedral P_4 molecule but with one P–P bond replaced by two fractional P–H bonds. This situation is reminiscent of the bonding in diborane, and on the basis of this analogy, the existence of 3-center 2-electron bond localized in P–H–P fragment was proposed.[32,33] Let us now check this intuitive expectation against the results of our analysis. As it is possible to see from Table I, the values of W_{PP} or $\Delta^{(3)}_{PP}$ indices clearly show that while five of the six P–P bonding interactions correspond to normal 2-center 2-electron P–P bonds, the bond index of the remaining one localized between P_1 and P_4 is substantially reduced. This reduction is, however, offset by the appearance of two new P–H bonds. Hence, the picture of bonding provided by our analysis does indeed reproduce the basic structural features of the cluster suggested by Figure 1. In view of this qualitative match, the question can be raised whether the population analysis is also able to reveal the presumed existence of the 3-center P–H–P bond. For this purpose, the value of 3-center bond index $\Delta^{(3)}_{PHP}$ is to be inspected. As it is possible to see from Table I, this index is indeed substantially non-zero-, in fact it is the only significant 3-center bond index in the system- and even if its value is roughly half of that expected on the basis of Mayer's analytical model of 3-center bonding,[21,38] the existence of 3-center P–H–P bond in this cluster is unquestionable. Although the basic structural features of this cluster seem to be well described by the above analysis, there is yet another interesting aspect worth mentioning. This aspect con-

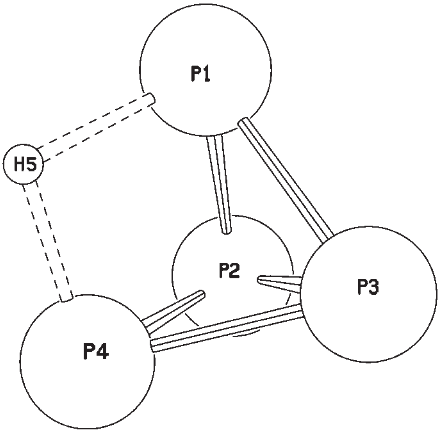

Figure 1.

cerns the comparison of calculated values of two- and three-center bond indices with those derived from Mayer's analytical model.[21,38] Thus, *e.g.,* according to this model, the idealized values of W_{PH} should be equal to 0.5, which is not very different from actual values. Greater discrepancies are, however, observed for 2-center index $W_{\mathrm{P_1P_4}}$, where the actual value is roughly twice the idealized value 0.25. This increase of P_1P_4 bond index, which might suggest the existence of some direct P_1P_4 bonding, is then compensated by the decrease of the value of 3-center index $\Delta^{3}_{\mathrm{PHP}}$ whose value is roughly half of that expected for Mayer's model. The origin of these interesting deviations can qualitatively be understood by taking into account the specificity of the studied cluster compared to analytical model. This specificity concerns the fact that while the idealized values were derived for essentially neutral situation, the studied cluster carries positive charge which, however, is not distributed uniformly over the individual atoms. As a consequence, an inherent polarity appears predominantly in the PHP fragment and the observed deviations thus only reflect the effect of this polarity of the cluster.

In a similar way it is possible to analyse also the bonding in the closely related arsenic cluster As_4H^+. The structure of this cluster is similar to that of P_4H^+, the only difference being the bond lengths of As–As and As–H bonds. The calculated optimized structure again closely resembles the structure determined in previous *ab-initio* calculations.[33] The similarity in geometrical structure of both clusters is mirrored also in the similarity of calculated populations (Table I). As we can see, there are again five substantial 2-center indices W_{AsAs} or $\Delta^{(3)}_{\mathrm{AsAs}}$ describing five essentially single As–As bonds, while the value of the remaining As_1– As_4 population is again reduced. Parallel to what was observed above, this missing As–As bond is replaced by the 3-center 2-electron bond involving the As–H–As fragment. We can thus see that the picture of bonding in both clusters is essentially the same. This concerns not only of the presence of presumed 3-center As–H–As bonding, but also the effect of inherent polarity of the cluster is again very similar.

In connection with this our conclusion a question may arise to what extent our conclusions are reliable because it is well known that in all types of Mulliken-like population analysis schemes the numerical values of calculated populations generally depend on the quality of the basis set used. For this reason, the basis set dependence of the pair population analyses was discussed in two recent studies.[39,40] Their conclusion is, that in even if the dependence is in the case of nonlinear population analysis slightly higher than for »normal«, (linear), population analysis, it is not in any case so important to question the reliability of calculated picture of bonding.

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SAŽETAK

Elektronsko vezivanje u protoniranim klusterima fosfora i arsena. Određivanje trocentričnih veza poopćenom analizom napučenosti elektronskih parova

Roberto Bochicchio, Luis Lain, Alicia Torre i Robert Ponec

Teorijski je dokazano postojanje neklasične trocentrične veze, nedavno pretpostavljene u strukturi protoniranih klustera fosfora i arsena (X_4H^+). Analiza elektronske strukture tih klustera temelji se na formalizmu poopćene analize napučenosti elektronskih parova kojim se direktno može utvrditi i lokalizirati prisustvo višecentričnih veza u molekuli. Rezultati potvrđuju prisutnost trocentričnog vezivanja u X–H–X fragmentima tih klustera.