Theoretical Comparison of the Electronic Structures of $[PhN_2]^+$ and $[PhP_2]^+$ – Can the Benzenediphosphonium Cation Exist in the Gas Phase?

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Ab initio quantum-chemical investigations are used to outline the main differences between the phenyldiazonium cation $[PhN_2]^+$ (**1a**,**b**) and its P analogue $[PhP_2]^+$ (**2a**,**b**). Our results show that in contrast to **1**, **2b** exists preferentially as a bridged structure. The phenyl ion affinity toward P_2 has been determined and suggests that the phenyldiphosphonium cation should be stable in the gas phase and that it is probably accessible by reaction between P_2 and Ph^+.

Introduction

The theoretical, structural and synthetic aspects of diazonium ions, $[RN_2]^+$, have been comprehensively studied and discussed in numerous monographs and reviews.[1] In contrast, data on the chemistry of their phosphorus analogues is much more limited. Thus, the sterically crowded salts $[Ar^*NP]^+$ X^- (Ar^* = 2,4,6-$t$$Bu_3C_6H_2$) are the only compounds isolated to date containing the phosphoazonium (phosphanetriylammonium) cation.[2] The area of the respective diphosphonium (phosphanetriylphosphonium) cations, $[RP_2]^+$, is even less well explored. Mass-spectrometric evidence has been presented for the formation of the $[iPr_2NP_2]^+$ cation,[3] but the characterization of this species by other physicochemical methods has yet to be accomplished. The closest approach to $[RP_2]^+$ cations has been our work on protonated *P*-aminodiphosphenes, Ar*−P=P−NR_2.[4] We succeeded in the synthesis of the donor-stabilized arenediphosphonium cation, $[Ar^*PP(PPh_3)]^+$, but the free cation was found to be unstable and could not be directly observed in solution. It is evident that further synthetic design of diphosphonium ions requires a detailed theoretical examination of the electronic structure of these species and of the electronic influence of the substituent R on the stability and structure of the molecule. Earlier theoretical investigations on phosphorus analogues of diazonium ions based on ab initio calculations focused on the protonated $[HP_2]^+$[5a] and methyl-substituted $[MeNP]^+$, $[MePN]^+$ and $[MeP_2]^+$ species.[5b][5c][5d][5e] For the latter, the end-on structure appeared to be favoured. This fact could be rationalized in terms of a preference for a carbon coordination number of four. However, this hypothesis does not explain the end-on geometry adopted in the case of $[PhN_2]^+$. The purpose of this article is to compare the structures deduced from theory for $[PhN_2]^+$ and $[PhP_2]^+$ cations, so as to permit more considered interpretation of these geometrical preferences.

Computational Methods

Ab initio calculations were performed using Gaussian 94/DFT.[6][7] The optimization and the vibrational analysis were carried out at the RHF/6-31 G (d,p) level of theory with the inclusion of dynamic electron correlation at the MP2 (full)/6-31 G (d,p) level, as well as with density functional theory[8] using the hybrid Becke 3LYP[9] method in conjunction with the 6-31 G (d,p) basis set. The vibrational zero-point energies determined at the MP2 level and with the DFT method[10] are known to be accurate and were used unscaled. Graphical representations of the nature of the molecular orbitals were obtained using the Molden program.[11]

Results and Discussion

Phosphorus analogues of alkyldiazonium ions have recently been investigated theoretically by Glaser.[5c][5d][5e] In these reports, different geometric structures are advanced for ${RP_2}^+$, based on energetic considerations of a protonation process on the one hand, and a clear polarization of the P_2 fragment upon electrophilic attack on the other. However, no information is provided concerning the phenyldiphosphonium ion. In this work, we present the first theoretical investigation concerning the phenyl-substituted ion and its electronic characteristics.

Our theoretical approximation is more than adequate considering the large size of the molecule. Glaser[12] noted that regarding isomer stability of the phenyldiazonium ions, the MP2 results agree qualitatively with the CISD predic-

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tions, but tend to underestimate the stability of the bridged structure. Furthermore, many studies have shown the quality of the results obtained using B3LYP to describe geometries, as well as in estimating heats of formation.[13]

Considering the phenyldiazonium ion, we found at both the MP2 and DFT levels, two local minima **1a** and **1b**, which are associated with the linear and the out-of-plane edge-on approaches of N−N to the singlet phenyl cation, respectively. These results are consistent with earlier theoretical research[12], and suggest that the dative bond description with an overall neutral N_2 moiety is clearly preferable. However, the latter less stable structure **1b** is isoenergetic with the dissociated phenyl cation and N_2, and is not accessible by reaction between these components.

For the benzenediphosphonium ion, two local minima are found at the same level of calculation, but linear end-on coordinated **2a** is less favoured than the symmetrically bridged local minimum **2b** by 16.29 kcal/mol [6-31 G (d,p)/MP2], 16.84 kcal/mol [6-31 G (d,p)/B3LYP]. Furthermore, regarding the affinity of P_2 towards the phenyl cation, our results suggest that **2b** should be stable in the gas phase. Affinities are calculated to be 52.83 kcal/mol by HF/MP2 (45.50 kcal/mol by B3LYP) for the end-on coordination, and 69.67 kcal/mol by HF/MP2 (61.79 kcal/mol by B3LYP) for the bridged local minimum. It should be pointed out that, in contrast to **1b**, the generation of the phenyldiphosphonium ion **2b** by reaction between P_2 and the phenyl cation is not excluded in the gas phase.

Energies and geometries of **1a**,**b** and **2a**,**b** are summarized in Figure 1. For **2a**, differences are apparent between the optimal geometries computed with MP2 and DFT. A linear structure is found at the DFT/6-31 G (d,p) and RHF/6-31 G (d,p) levels, but a bent geometry appears as a minimum at the MP2 (full)/6-31 G (d,p) level. The potential energy surface characteristics for the edge-on coordinated structure are greatly affected by electron correlation. Structure **2b** is calculated to be the only minimum (MP2 and DFT levels) corresponding to the out-of-plane edge-on approach. The distance C−P is proportionally shorter than the C−N distance in **1b**. This fact explains the widening of the P−C−P angle (60°) compared to the N−C−N angle (41°). It is noteworthy that theoretical models do not affect the P−C−P and C−P−P angles, which are quasi-similar. In addition, the bond length alternation suggests that the π electrons are not fully delocalized into the phenyl ring. A significant lengthening is observed for the C−C bond in the α position of C_{spiro} compared to that in the phenyldiazonium ion.

Figure 1. Energies and geometrical parameters of **1**(**a**,**b**) and **2**(**a**,**b**) calculated at the MP2/6-31 G** and B3LYP/6-31G** levels of theory. Total energies, E_{tot}, in atomic units; zero-point vibrational energies, ZPVE, in kcal/mol; angles in°, and bond lengths in Å

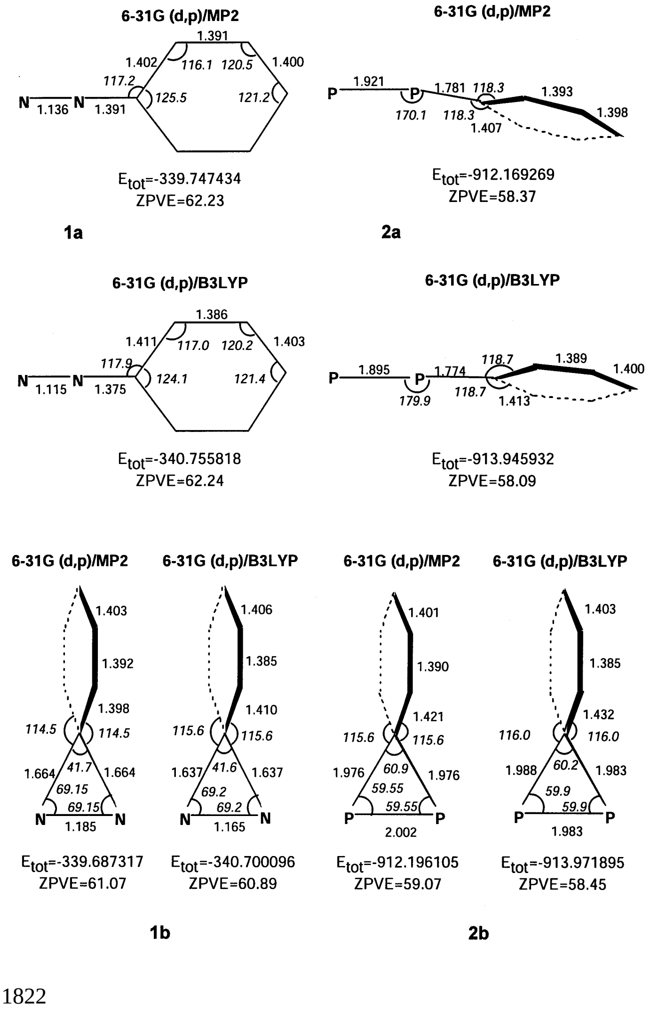
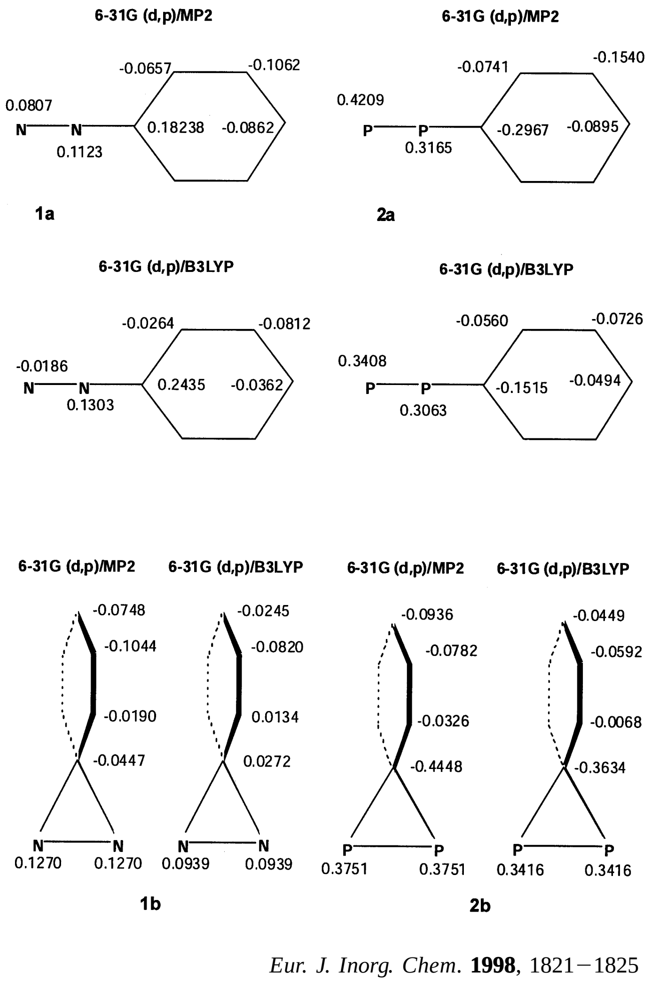


Figure 2. Charges of **1**(**a**,**b**) and **2**(**a**,**b**) calculated at the MP2/6-31 G** and B3LYP/6-31G** levels of theory



A key difference to the diazonium cation is seen in the polarization of these systems. Considering the charges displayed in Figure 2, it is clear that the positive charge (for **2a** and **2b**) is distinctly localized on the P−P moiety, while the stable structure of diazonium analogous **1a** can be viewed as a phenyl cation with a closely associated nitrogen molecule.

An examination of the molecular orbital interactions that occur in these two systems is clearly relevant, since these directly affect the nature of the preferentially adopted structure and thus will be a source of information with regard to the synthesis and detection of such species.

Localization and energetic positions of MOs allow us to visualize these interactions as in Figures 3 and 4[14]. If we analyse them for the end-on coordination structures **1a** and **2a**, they are very well described as an interaction between the σ_{XX} orbital and the LUMO of the phenyl cation [$\sigma_{XX}\rightarrow\sigma^*_{Ph}$ −17.29 eV (X = N), −13.32 eV (X = P)] and a back-donation from π_2 (phenyl cation) to the π^*_{XX} orbital of the same symmetry [$\pi_{2Ph}\rightarrow\pi^*_{XX}$ −12.78 eV (X = N), −11.75 eV (X = P)]. Furthermore, the formation of σ_{PC} becomes easier than that of σ_{NC} as a consequence of the σ_{PP} energetic position in comparison with that of σ_{NN}. In fact, experimentally determined ionic state energies for N_2 and P_2 [$^2\Sigma^+{}_g$ and $^2\Pi^+{}_u$ associated with the ejection of an electron from $^1\pi_u$ (π bond) and $^3\sigma_g$ (σ_{XX}) orbitals] are observed at 15.60, 16.98 and 10.81, 10.62 eV, respectively. The electron transfer should be more important in the case of P_2 than in the case of N_2, and the π back-donation is not expected to compensate this transfer. In agreement with this hypothesis, the charges are found to be negative at C_{ipso} and positive on the two phosphorus atoms. It is noteworthy that a slightly less pronounced polarization is obtained by using B3LYP than at the MP2 level.

Figure 3. Selected molecular orbitals (MO) of the linear compound **1a** calculated at the B3LYP/6-31 G** level

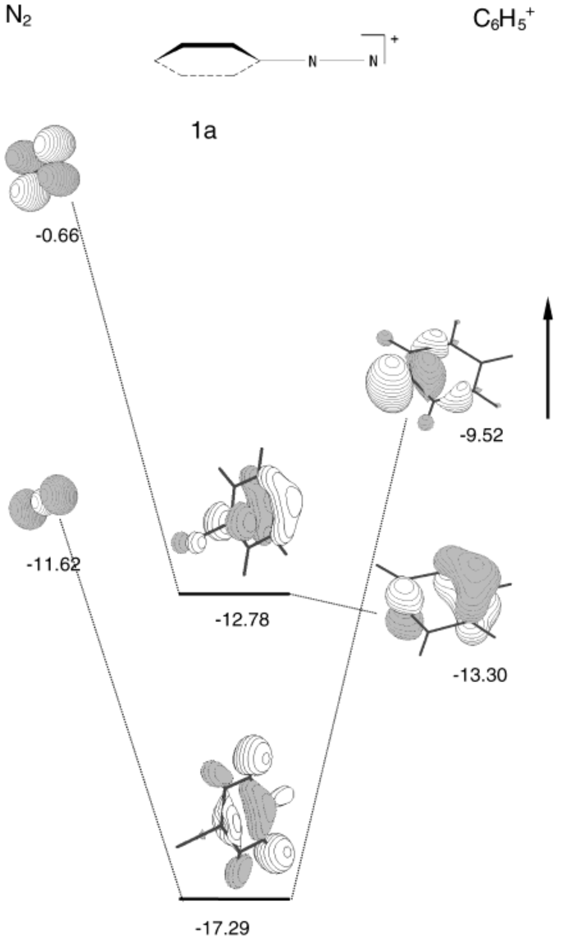
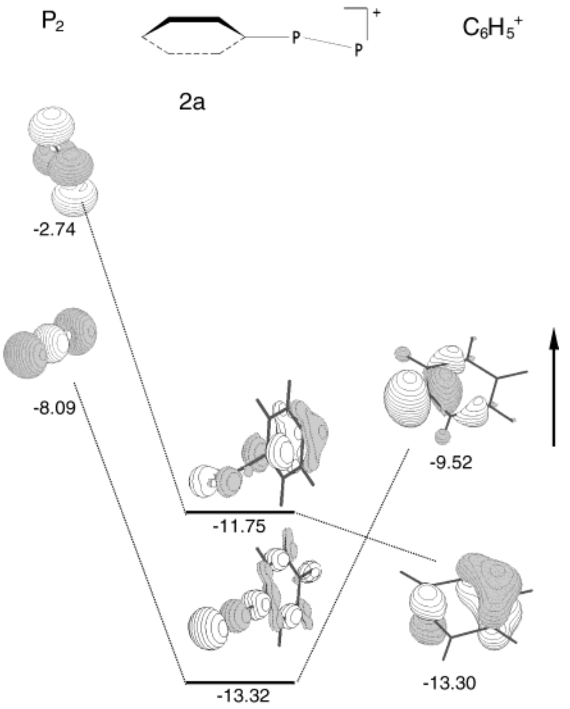


Figure 4. Selected molecular orbitals (MO) of the linear compound **2a** calculated at the B3LYP/6-31 G** level



If we consider the bridged structures **1b** and **2b**, the LUMO σ* of the phenyl cation is seen to interact with the π_{XX} orbital. Regarding the energetic gap between the LUMO Ph^+ and π_{XX}, this interaction will be easier in the case of P_2 (ΔE = 1.70 eV cf. 3.06 eV for N_2/Ph^+). This is well represented for the phosphonium ion by the MO at −14.38 eV.

We note that, in contrast to the aforementioned behaviour, in the case of N_2, a destabilizing interaction occurs between π_{NN} and the lower $\sigma_{Ph}{}^+$ orbitals. If we consider the charges, notable differences are evident in their distribution between the phenyldiphosphonium cation and the phenyldiazonium cation. The large positive charge localized on each phosphorus atom and the negative one on C_{ipso}, could be explained first of all by the high σ transfer, which is not sufficiently compensated by the π back-donation (vide infra).

Finally, π back-donation appears as for the linear molecule, involving the $\pi_{2Ph}{}^+$ and the π^*_{XX} orbitals, which can be visualized by the MO at −12.69 eV for the phosphorus compound, and at −13.29 eV for the nitrogen analogue.

Figure 5. Selected molecular orbitals (MO) of the bridged compound **1b** calculated at the B3LYP/6-31 G** level

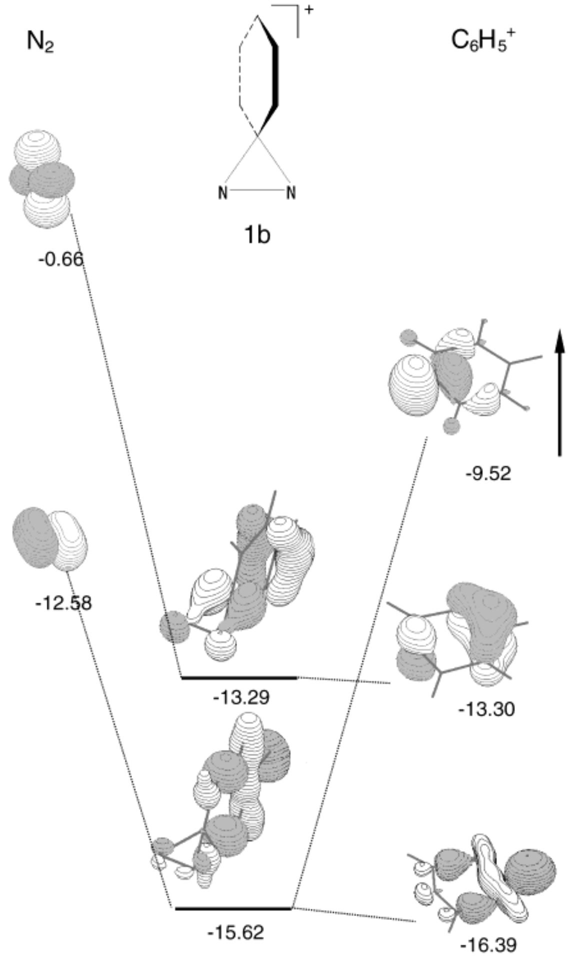
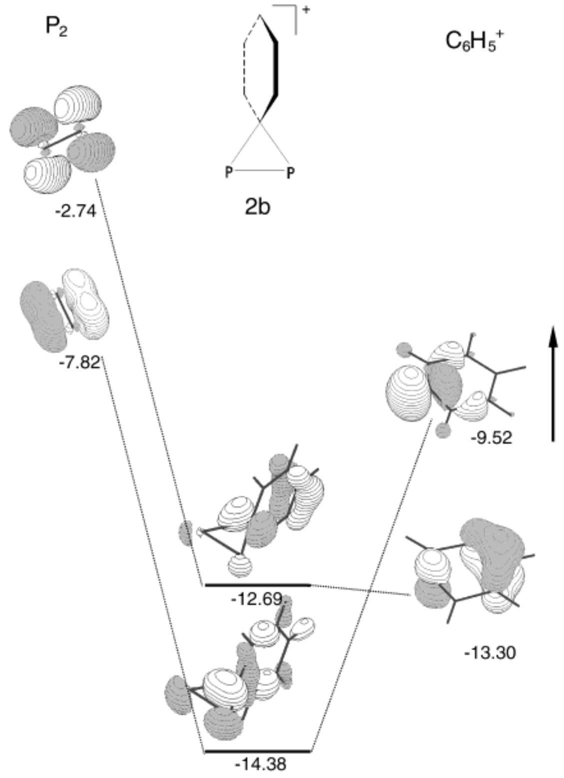


Figure 6. Selected molecular orbitals (MO) of the bridged compound **2b** calculated at the B3LYP/6-31 G** level



Why is the bridged form **2b** stabilized in comparison with the linear one? An explanation is found mainly in the stabilizing interactions and notably in the interaction $\pi^{\perp}{}_{PP}\rightarrow\sigma^{*}{}_{Ph}{}^{+}$, which is observed only in the bridged form. Naturally, other interactions play an important role in determining the stability of these systems, such as the interaction $\pi 2Ph^{+}\rightarrow\pi^{*}{}_{PP}$, but these are in fact found in both isomers. Nevertheless, the interaction $\pi^{\perp}{}_{PP}\rightarrow\sigma^{*}{}_{Ph}{}^{+}$ leads to a more effective overlap, compared with the $\sigma_{PP}\rightarrow\sigma^{*}{}_{Ph}{}^{+}$ interaction that exists in the linear form. In other words, the overlap is more effective with two phosphorus atoms (bridged form) than with only one (linear form). Finally, taking into account the energetic positions, the molecular orbitals π_{PP} and σ_{PP} remain localized on this moiety, while π_{NN} and σ_{NN} are mixed with the σ-MO from the phenyl ring (destabilizing interactions).

Conclusion

The new insight given by the present study shows that aromatic diphosphonium ions might be stable species. To date, all attempts to isolate these molecules have failed, mainly due to difficult kinetic control rather than because of thermodynamic factors. However, considering the $\sigma^{*}{}_{PP}$-MO energetic position (−7.69 eV) for the bridged structure, the availability of the diazonium ion complex, and the position of the corresponding σ* MO (−7.66 eV), we can reasonably expect that it should be possible to stabilize the system by means of nucleophilic assistance.

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[14] It is well known that ab initio orbitals do not derive from a purely one-electron Hamiltonian and therefore do not possess the property of associativity necessary to justify a construction from fragment orbitals. Thus, we preferred to present Kohn-Sham orbitals, which are more appropriate from this point of view.

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