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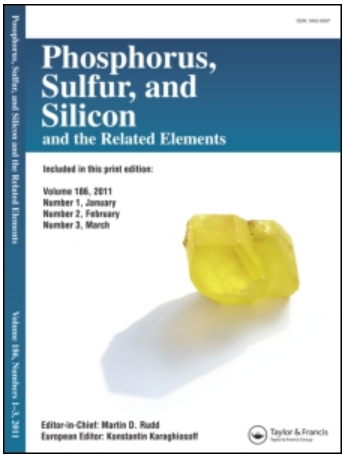

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Potential Energy Surface and Electron Density Analysis of Phosphorus Analogues of Aromatic and Aliphatic Diazonium Ions

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POTENTIAL ENERGY SURFACE AND ELECTRON DENSITY ANALYSIS OF PHOSPHORUS ANALOGUES OF *AROMATIC* AND *ALIPHATIC* DIAZONIUM IONS.

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Abstract. Potential energy surface analyses at *ab initio* levels including electron correlation are reported for the phosphorus analogues of diazonium ions, RXY^+ with X,Y=N,P. Protonated, methylated, and phenylated systems are compared with focus on the question regarding end-on versus edge-on coordination. Diphosphonium and phosphoazonium ions are predicted to be more stable toward dissociation than the diazonium ions. The calculated spectroscopic data may assist in their detection. Electronic density distributions of RXY^+ were analyzed in a variety of ways and with a new energy decomposition method. Charge distributions are contrasted with Lewis notations. CN- and CP-bonded ions show clearly distinct bonding patterns.

INTRODUCTION

Formal replacement of nitrogen by phosphorus in diazonium ions **I** leads to the P-analogues, **II** - **IV**. In contrast to the aromatic systems **I**, aliphatic ions **I** are highly reactive intermediates that have been fully characterized only in very few cases.[1] Representa

$$R\text{-}N^+{\equiv}N,\ \mathbf{I} \qquad R\text{-}P^+{\equiv}P,\ \mathbf{II} \qquad R\text{-}N^+{\equiv}P,\ \mathbf{III} \qquad R\text{-}P^+{\equiv}N,\ \mathbf{IV}$$

tives of **II** and **IV** are still elusive[2] and only two aromatic derivatives[3] of **III** are known.

Here, we report on the results of our studies of the smallest *aliphatic* and *aromatic* systems **I** - **IV**, the methyl and the phenyl

derivatives. Their potential energy surfaces were examined at *ab initio* levels including perturbationally and/or variationally determined effects of electron correlation

RESULTS AND DISCUSSION

Protonation of N_2, P_2, and PN

Stationary structures on the potential energy surfaces of the protonated systems were optimized and characterized by vibrational frequency analysis at the RHF, MP2(full), and CISD(full) levels with the 6-31G* basis set and the most stable structures also were examined at the level CISD(full)/6-311G(df,p) and including ΔVZPE values determined at that level. Results are shown in Figure 1.

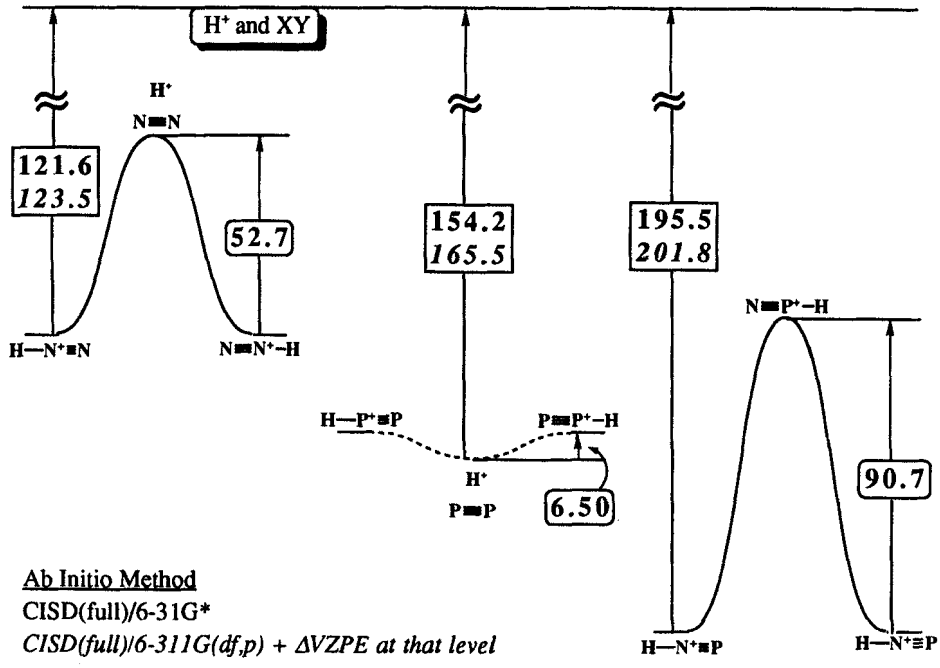

FIGURE 1 CISD(full) potential energy surfaces of HXY^+.

Major theoretical model dependencies occur for H-II and a CISD-level PES-scan as a function of the H-P-P angle revealed a local minimum that corresponds to an asymmetrically bridged structure that is nearly isoenergetic with the linear structure. Our systematic studies show that at least third-order perturbational theory is required to reproduce the CISD potential energy surface

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characteristics and relative energies adequately. Available experimental data agree well with the calculated results at those levels.

Potential Energy Surface Analysis and Binding Energies

For **I** and all R, end-on coordination is preferred compared to bridged structures. For the N≡P systems, bridging never becomes an important issue because of the great N≡P-polarity. The N-bonded structures **III** are greatly preferred over the P-bonded structures **IV** for all R and structures **IV** either are transition state structures or *very* shallow minima. Interestingly, the nature of R affects the type of the most stable structures of **II**. Protonation and phenylation both result in symmetrically bridged C_{2v}-**II** minima, whereas end-on coordination is preferred for Me-**II** by about 5 kcal/mol over an asymetrically bridged local minimum.

Our best estimates for the R^+ affinities of N_2, P_2, and P≡N are listed in Table I. *These affinities predict that **II** and **III** are more stable toward dissociation than **I** even when the oligomerizations* $2 \cdot P_2$ --> P_4 *and* PN --> D_{3h}-$(PN)_3$ *are considered.* Our results suggest that methyldiphosphonium and methylazophosphonium ions as well as phenyldiphosphonium ion are stable molecules in the gas phase and possibly also in solution. The calculated structural, energetic and spectroscopic properties may assist in their detection.

TABLE I Cation affinities in kilocalories per mole.

R Group	I	II	III	Level
Hydrogen	123.5	165.5	201.8	CISD/6-311G(df,p)+VZPE
Methyl	43.0	71.3	100.4	MP4//MP2/6-311G(df,p)+VZPE
Phenyl	27.8	45.9	87.9	MP3//RHF/6-31G(d)+VZPE

Electron Density Difference Functions

The electronic and energetic relaxations upon bond formation consist of effects caused by the structural changes *within* the fragments (eqs 1 and 2) and of effects associated with the charge transfer between these "profragments" (eq 3). The notation XY[M] refers to the *free* molecule XY with the geometry XY assumes *in* M. The electronic changes associated with the combination of the profragments are illustrated in a compelling fashion by the electron

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R^+ ---> R+[RXY+]	$\Delta E(R^+)$	(1)
XY ---> XY[RXY+]	$\Delta E(XY)$	(2)
R+[RXY+] + XY[RXY+] ---> RXY+	ΔE_{pro}	(3)
R^+ + XY ---> RXY+	CA	(4)

density difference function $\Delta\rho = \rho(RXY^+) - \rho^M(R^+) - \rho^M(X{\equiv}Y)$. The superscript "M" indicates that the fragment densities were determined with their geometries in molecule M. The major differences in the cation affinities are found to be caused by the combination of the profragments (eq 3). The E_{pro} values have the quality of charge transfer energies and the charge transfer can be studied graphically *via* the electron density difference functions $\Delta\rho$.

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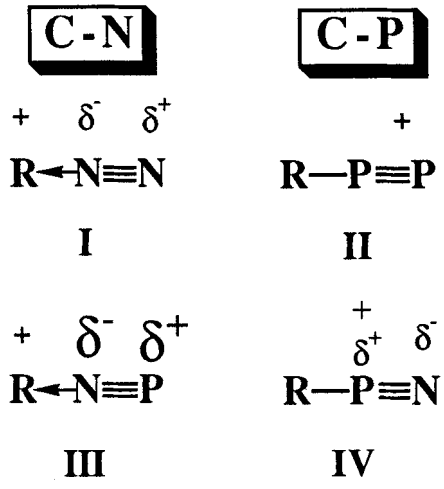
Topological Electron Density Analysis and Integrated Properties

Electron density distributions were analyzed within the framework of the theory of atoms in molecules with focus on integrated populations and atomic moments.

Charge distributions are contrasted with Lewis notations. CN- and CP-bonded ions show clearly distinct bonding patterns. Best representations of the charge distributions in **I** - **IV** are shown in Scheme 1.

SCHEME 1



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