Cationic P⋯N interaction in XH$_3$P$^+$⋯NCY complexes (X = H, F, CN, NH$_2$, OH; Y = H, Li, F, Cl) and its cooperativity with hydrogen/lithium/halogen bond

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ABSTRACT

The geometries, interaction energies and bonding properties of cationic pnicogen bond (CPB) interactions are studied in binary XH$_3$P$^+$⋯NCY (X = H, F, CN, NH$_2$, OH; Y = H, Li, F, Cl) complexes by means of MP2/aug-cc-pVTZ calculations. Interaction energies of these binary complexes span a large range, from −16.36 kcal/mol in (NH$_2$)H$_3$P$^+$⋯NCF to −71.36 kcal/mol in FH$_3$P$^+$⋯NCLi complex. The spin–spin coupling constant across P⋯N interaction depends considerably on the nature of X and Y substituents. The characteristic of CPB interactions is analyzed in terms of parameters derived from quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) analyses. The charge transfer from the nitrogen base to the cationic acid stabilizes these pnicogen–bonded complexes. For a given XH$_3$P$^+$, the net charge transfer value increases as the interaction energy of the complex becomes more negative, i.e., NCLi > NCCl > NCH > NCF. Moreover, mutual influence between the CPB and hydrogen/halogen/lithium bond is studied in the ternary XH$_3$P$^+$⋯NCY⋯NCH complexes. The results indicate that the formation of a Y⋯N interaction tends to strengthen CPB in the ternary systems.

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1. Introduction

The hydrogen bond is one of the most important weak interactions in nature and plays an essential role in chemical and biochemical processes [1]. The formation of hydrogen bond is responsible for the stability and biological activity of many macromolecules in living systems. It is also important for many guest-host interactions, crystal packing and drug design [2–5]. However, in recent years, considerable attention has been paid into other weak interactions such as halogen bond, due to their potential applications in material science, crystal engineering and biological systems [6–9]. A halogen bond is generally defined as a attractive Lewis acid–Lewis base R—X⋯B interaction, where X is a halogen (mostly Cl, Br or I) and B is an electron donor. In the literature, the formation of halogen bonding is generally described with an electron-deficient region or "σ-hole" [10–17] developed on the outermost portion of the halogen's surface, opposite to the R—X bond. When a half-filled *p* orbital on the halogen contributes in forming a covalent bond, the electron density around the halogen atom deviates from an ideal spherical distribution and therefore

an electron-deficient region is created in the outer lobe of that *p* orbital. The magnitude of the σ-hole potential on the halogen atom depends upon different factors, including the polarizability and electronegativity of the atom as well as the electron-withdrawing ability of the reminder of the molecule. Thus, according to the electrostatic model of halogen bond, it is expected that the heavier halogen atoms (less negative and more polarizable) such as Br and I would form a strong halogen bond. It should be noted that analogous interactions of covalently-bonded Groups VI, V and IV atoms have been also reported. Therefore, the noncovalent interactions of these atoms with potential electron donors can be mainly explained in terms of positive σ-holes developed along the extension of one or more of the covalent bonds to the atom [18–20]. The σ-hole interaction is called chalcogen [9,21–23], pnicogen [24–28] and tetrel bond [29–32] for Groups VI, V and IV atoms, respectively.

Subsequent to the landmark paper of Zahn et al. [33], the pnicogen bond interactions have been subjected to many theoretical studies [34–40]. Most of these studies involves sp, sp^2 or sp^3 hybridized P atoms. However, there are also some recent studies on the possibility of formation of charged [41–45] or uncharged complexes involving higher valence states of phosphorus [46]. Like other σ-hole interactions, the strength of the pnicogen bond can be enhanced by the substituents and cooperative effects in conjunction with other types of interactions [47–52]. For example, Del

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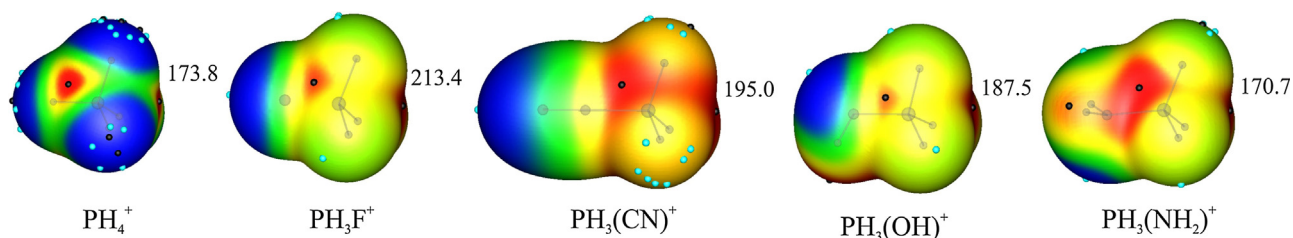 *E-mail address:* esrafili@maragheh.ac.ir (M.D. Esrafili).

Fig. 1. Calculated MEPs on the 0.001 electrons/Bohr³ contour of PH_4^+, PH_3F^+, $PH_3(CN)^+$, $PH_3(OH)^+$ and $PH_3(NH_2)^+$ cations. The color code ranges from blue (more negative) to red (more positive). The locations of the σ-holes on the P atom, associated with the P—X bond are indicated with black circles, and their values are given in kcal/mol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
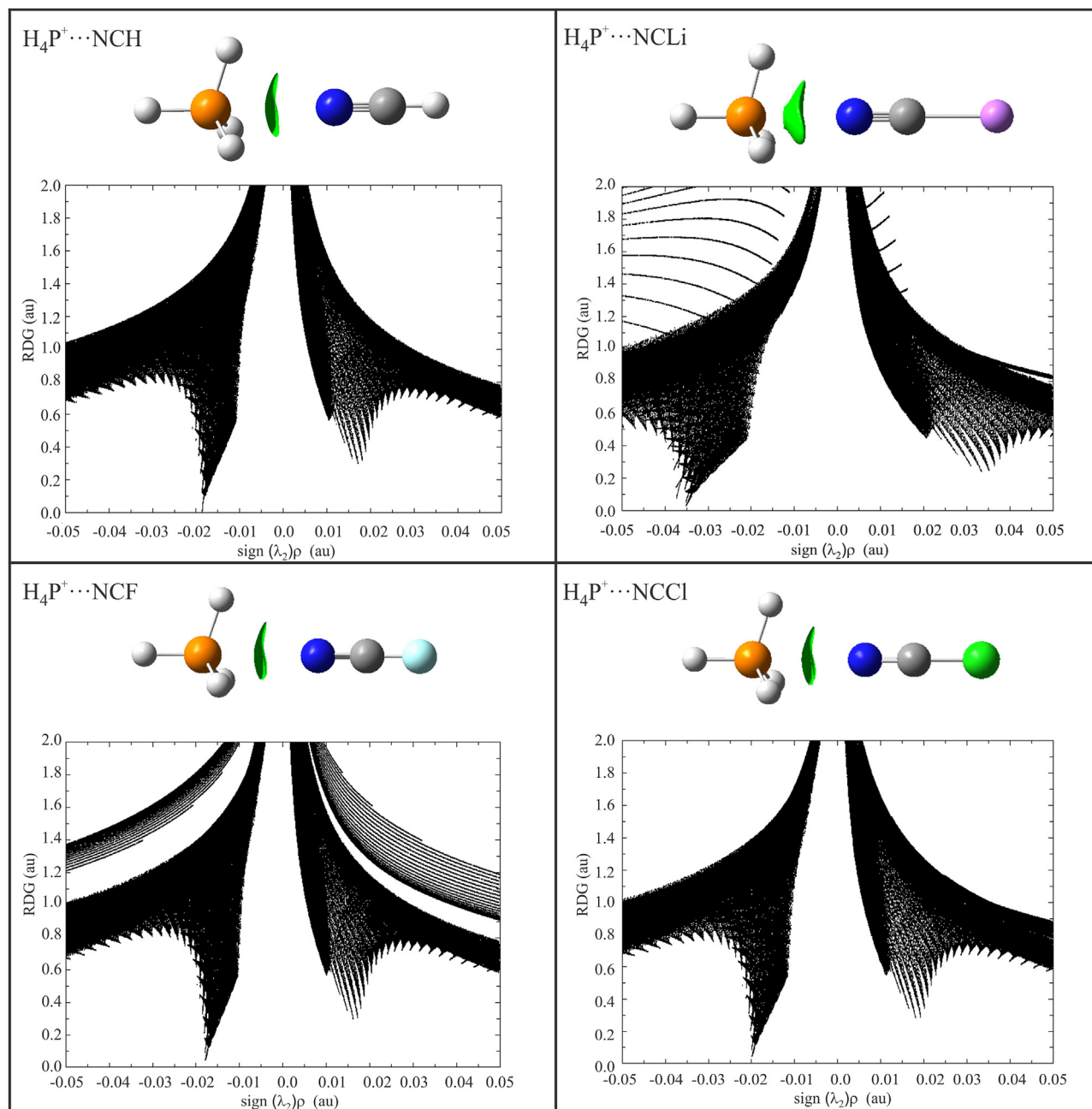

Fig. 2. Non-covalent interaction (NCI) isosurface (green disk) and plot of the reduced density gradient (RDG) versus sign $(\lambda_2)\rho$ of the $H_4P^+\cdots$NCY complexes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Bene et al. [48] indicated that the presence of F—H⋅⋅⋅F hydrogen bond interactions in complexes nFH:(H_2FP:NFH_2) for n = 1–3 leads to shorter P⋅⋅⋅N distances, increased strength of P⋅⋅⋅N bonds, and cooperative effects.