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ABSTRACT

Using *ab initio* electronic structure methods with flexible atomic orbital basis sets, we investigated the electronic structure and stability of reduction products of selected representative cations (C^+) constituting ionic liquids. We found that an electron attachment to such cations leads to the neutral radicals, whereas a subsequent attachment of another (i.e., excess) electron leads to adiabatically stable anions only in two cases {$[P(CH_3)_4]^-$ and $[MeMePyr]^-$}. The possibility of the formation of various dimers (such as CC^+, CC, and CC^-) was also considered, and the resulting systems were characterized by predicting their lowest energy structures, ionization potentials, electron affinities, and susceptibilities to the fragmentation process. Among the cations studied, only the $[MeMePyr]^+$ was found to form a typical Rydberg radical (MeMePyr) and double-Rydberg anion ($[MeMePyr]^-$), whereas the remaining cations were predicted to form neutral radicals of a primarily valence (MeMeIm and MePy) or mixed Rydberg-valence $[P(CH_3)_4]$ character. Our calculations confirmed the stability of all CC^+ and CC dimers against fragmentation yielding the corresponding monomers (the binding energies of 12.2–20.5 kcal/mol and 11.3–72.3 kcal/mol were estimated for CC^+ and CC dimers, respectively). $[(MeMePyr)_2]^-$ was identified as the only adiabatically stable CC^- dimeric anion having its vertical electron detachment energy of 0.417 eV. We also found that in the $[(MeMePyr)_2]^-$ anionic state, three outermost electrons are described by Rydberg orbitals, which results in the $(\sigma)^2(\sigma^*)^1$ configuration.

I. INTRODUCTION

Ionic liquids (IL) are purely ionic compounds that are liquid at unusually low temperatures (below 100 °C) and consist of structurally large asymmetric organic cations and inorganic (e.g., PF_6^-, BF_4^-, NTf_2^-, and Cl^-) or organic (e.g., CH_3COO^-, $CH_3SO_3^-$, and the *p*-toluenosulfonate) anions. As far as the cationic part is concerned, ionic liquids comprise a wide range of imidazolium, pyridinium, ammonium, pyrrolidinium, phosphonium, and sulfonium derivatives.[1–3] Ionic liquids are considered to be "designer solvents" since their physical and chemical properties might be fine-tuned by the proper choice of either cation or anion or by the substitution pattern thereof. The commercially available ILs offer a very interesting combination of properties, such as the thermal stability, low vapor pressure, electric conductivity, diverse viscosity, high heat capacity, or non-flammability. Due to those superior and unique physicochemical properties, ILs have been used for many applications, e.g., as highly energetic materials,[4] active pharmaceutical ingredients,[4–6] thermal or magnetic fluids,[7–9] solvents,[10,11] electrolytes,[12] propellants,[13] and lubricants.[14–16] Moreover, potential and innovative applications (e.g., in artificial muscles[17] or in robotics[18]) of ILs continue to be a subject of many current research efforts.

Over the last two decades, ionic liquids are frequently reported for their diverse electrochemical application as electrolyte in batteries,[19] fuel cells,[20] solar cells,[21] metal depositions,[22] and gas sensors.[23] The use of ILs as electrolytes has a number of advantages (when compared to conventional aqueous solutions of inorganic

electrolytes), such as non-volatility, non-flammability, but most of all fair conductivity, and a wide electrochemical window within the low temperature range (<100 °C). Most ILs exhibit conductivity spanning the 1.0–10.0 mS/cm range; however, there are also some ILs characterized by remarkably higher (exceeding 20 mS/cm) electric conductivities {e.g., the 1-ethyl-3-methyl imidazolium cation combined with the thiocyanate (SCN^-) or dicyanamide [$N(CN)_2^-$] anion}.[24] As mentioned above, another crucial (for electrochemical applications) physicochemical property of ILs is their wide electrochemical window, which is a measure of their electrochemical stability against oxidation (anion$^-$ → neutral molecule + e^-) and reduction (cation$^+$ + e^- → neutral molecule) processes. Among various ionic liquids, those containing the sulphonium, phosphonium, ammonium, and pyrrolidinium cations have a particularly wide window (>5 V), while imidazolium and pyridinium based ILs are usually characterized by the lower electrochemical stability (of 2.3–4.3 V).[25] As a result, the ILs can be designed for a particular electrochemical application requiring certain conductivity and the electrochemical stability by a proper choice or modification of the cation and anion building blocks. However, taking into account all possible combinations of a broad variety of cations and anions, performing the experimental measurements before selecting the most appropriate IL's composition seems unrealistic. Therefore, several theoretical models have been proposed in the literature to allow the correlation and prediction of electrical conductivity and the electrochemical window. Most of the approaches proposed are structure-based models and relate the conductivity or electrochemical window of ILs to molar volumes of their constituent ions[26–28] or to the HOMO/LUMO gap of the ionic pair,[29,30] respectively. Regardless of the model and its accuracy, it was found that both cation and anion affect the conductivity and electrochemical stability. The most commonly used IL anions vary not only in their size but also in the electronic stability (being usually in the 3.6–9.5 eV range).[31] There is no doubt, however, that all of the anions used in ILs are valence bound anions and their stability against oxidation is strictly related to their electronic stability. On the other hand, the IL cations are prone to the attachment of an electron due to their excess positive charge. Since the IL cations differ in their size and chemical constitution, such a charge neutralization (effectuated by an electron attachment) may lead to corresponding radicals of various stabilities and reactivities. For instance, the NH_4^+ and its derivatives {such as $[NH_n(CH_3)_{4-n}]^+$; n = 1–4} that are the components of the ammonium-based ILs have been proven to form Rydberg neutral radicals (i.e., the radicals having one unpaired electron described by a diffuse Rydberg orbital) upon attachment of an electron.[32] It was found that adiabatic ionization potentials for all studied $NH_n(CH_3)_{4-n}$ (n = 1–4) radicals are very low (in the range of 2.3–4.5 eV) and decrease with the increasing number of methyl groups in the system.[33] Furthermore, it was predicted that such Rydberg radicals may likely dimerize to form Rydberg-bound $(NH_4)_2$ systems.[34,35] It is noteworthy that the ammonium cations are considered to be convenient IL's building blocks due to their high stability against reduction processes and very wide electrochemical window (>5 V) of the resulting ionic liquids formed by combining with proper anions.[25] Although various other cations utilized as ionic liquids components are structurally very different than ammonium-based cations, they may also attach an electron to form the corresponding neutral radicals of diverse stability and reactivity.

In this contribution, we present our theoretical investigation on the electronic structure and stability of reduction products (i.e., neutral molecules and their anions) of selected representative cations constituting ionic liquids. In addition, we discuss the reactivity of such species toward dimerization processes. Since radicals are highly reactive systems, the formation of variously charged dimers (upon the interaction of a given neutral radical with its cationic, neutral, or anionic counterpart) might occur in such fluids as ionic liquids where these species are in close proximity. We present the results for tetramethyl phosphonium cation {$[P(CH_3)_4]^+$}; 1,1-dimethylpyrrolidinium cation ($[MeMePyr]^+$); 1,3-dimethylimidazolium cation ($[MeMeIm]^+$); and 1-methylpyridinium cation ($[MePy]^+$), as these systems are known to serve as positively charged building blocks of many ionic liquids. In order to characterize the reactivity of the selected cations (and the reduction products thereof) toward dimerization processes, we describe the lowest energy isomeric structures of the $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ complexes as well as their corresponding neutral and anionic systems. We believe that our investigation may provide some new insight into the knowledge of the electrochemical stability of the ILs containing those cations and thus might be found useful for theoretical and experimental chemists who design novel electrolytes for electrochemical devices.

II. METHODS

The equilibrium structures and corresponding harmonic vibrational frequencies of the $[P(CH_3)_4]^+$, $[MeMePyr]^+$, $[MeMeIm]^+$, and $[MePy]^+$ as well as the $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ positively charged compounds and their corresponding neutral and anionic systems were determined by applying the second-order Møller–Plesset (MP2) perturbational method[36–38] with the aug-cc-pVDZ[39] basis set supplemented with a 3s3p set of additional diffuse functions (in order to properly describe also non-valence bound radicals and anions) centered on the phosphorus or nitrogen atom. The extra diffuse functions do not share exponent values, and we used even-tempered[40] three-term s and three-term p basis sets with the geometric progression ratio of 3.2.[41] For each symmetry, we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in the aug-cc-pVDZ basis set designed for either the P or N atom. As a consequence, we achieved the lowest exponents of 1.272×10^{-3} and 1.047×10^{-3} (for the functions centered on the P atom) and 1.869×10^{-3} and 1.712×10^{-3} (for the functions centered on the N atom) for the s and p symmetries, respectively. The electronic energies of the systems studied were refined by employing the coupled-cluster method with the single, double, and noniterative triple excitations [CCSD(T)][42–45] and the same basis sets. Since we determined that the electron binding energy (BE) predicted by applying the CCSD(T) method for the most weakly bound anion (i.e., $[MeMePyr]^-$) increases by less than 0.001 eV when the aug-cc-pVDZ+3s3p basis set is replaced with the aug-cc-pVTZ+3s3p, we are confident that our final basis set (i.e., aug-cc-pVDZ+3s3p) is appropriate for optimization of geometries, calculating harmonic frequencies, and evaluating the electron binding energies.

The adiabatic electron affinities (not including zero-point vibrational corrections) of the neutral and cationic species were calculated by employing the supermolecular approach (i.e., by subtracting the energy of the anion from that of the neutral) using the CCSD(T)/aug-cc-pVDZ+3s3p electronic energies, whereas the vertical ionization energies and vertical electron detachment energies of the radicals and anions, respectively, were obtained by applying the outer valence Green function (OVGF) method (*B* approximation)[46–54] and the same basis sets (all orbitals in the core and valence shells have been correlated during the OVGF calculations). Due to the fact that the OVGF approximation remains valid only for outer valence ionization for which the pole strengths (PS) are greater than 0.80–0.85,[55] we used only those results for which the PS values obtained were sufficiently large to justify the use of the OVGF method [in two cases indicated in the table, we used the values obtained by employing the CCSD(T) method instead].

All calculations were performed using the GAUSSIAN16 (Rev. C.01) package.[56]

III. RESULTS

A. $[P(CH_3)_4]^+$, [MeMePyr]$^+$, [MeMeIm]$^+$, and [MePy]$^+$ parent cations and their corresponding neutral and anionic systems

The most stable structures of $[P(CH_3)_4]^+$ and [MeMePyr]$^+$ represent typical quaternary phosphonium and ammonium cations, respectively, in which four alkyl substituents are attached to either the P or N atom in a tetrahedral manner. This results in the T_d-symmetry of the lowest energy structure of the tetramethyl phosphonium cation and the C_s-symmetry of the most stable structure of the 1,1-dimethylpyrrolidinium cation (the lower symmetry of the latter system is caused by the presence of a pyrrolidinium ring). The equilibrium structures of the next two closed-shell cations considered ([MePy]$^+$ and [MeMeIm]$^+$) contain planar six- or five-membered heteroaromatic rings substituted with one or two methyl groups bound to nitrogen atoms and correspond to the C_s and C_{2v} symmetry, respectively (see Fig. 1).

The attachment of an electron to phosphonium $[P(CH_3)_4]^+$ and ammonium [MeMePyr]$^+$ closed-shell cations leads to the corresponding open-shell T_d-symmetry $P(CH_3)_4$ and C_s-symmetry MeMePyr neutral species whose energies are lower than those of their parent cations by ~2.8 to 2.9 eV. This process causes only small changes in the bond lengths (<0.004 Å); however, in the case of $P(CH_3)_4$, the additional isomeric structure of the C_{2v} symmetry appears upon an electron attachment to $[P(CH_3)_4]^+$ (see Fig. 1). According to our predictions, this C_{2v}-symmetry isomer of $P(CH_3)_4$ is more stable by 13.7 kcal/mol than the T_d-symmetry isomer and has its adiabatic ionization potential (AIP) of 3.52 eV (see Table I). The relaxation of the [MeMeIm]$^+$ and [MePy]$^+$ molecular frameworks upon attachment of an electron leads to the non-planar C_s-symmetry structures of their corresponding neutral MeMeIm and MePy radicals whose energies are lower than those of their parent cations by ~3.8 and 4.7 eV, respectively (see Table I and Fig. 1). The structural changes are found to be larger in the case of MeMeIm than in the MePy radical (when compared to their corresponding cations), which might be related to the fact that the deviations from planarity in either imidazolium or pyridinium rings arise mainly from the deformations occurring in the vicinity of the N atoms caused by the changes in nitrogen hybridization [$N(sp^2) \rightarrow N(sp^3)$]. Thus, the puckering of the imidazolium ring (containing two nitrogen atoms) implies more profound geometry changes in MeMeIm in comparison to MePy as the latter system involves only one N atom. Such substantial relaxation upon an electron attachment causes large differences between adiabatic (AIP) and vertical (VIP) ionization potentials of MeMeIm and MePy. Indeed, the VIPs of these systems exceed 5 eV, and these values are larger than the corresponding AIPs by 1.278 and 0.445 eV for MeMeIm and MePy, respectively (see Table I). It is worth to emphasize that all studied neutral radicals are characterized by very low AIPs (2.790–4.732 eV), which makes

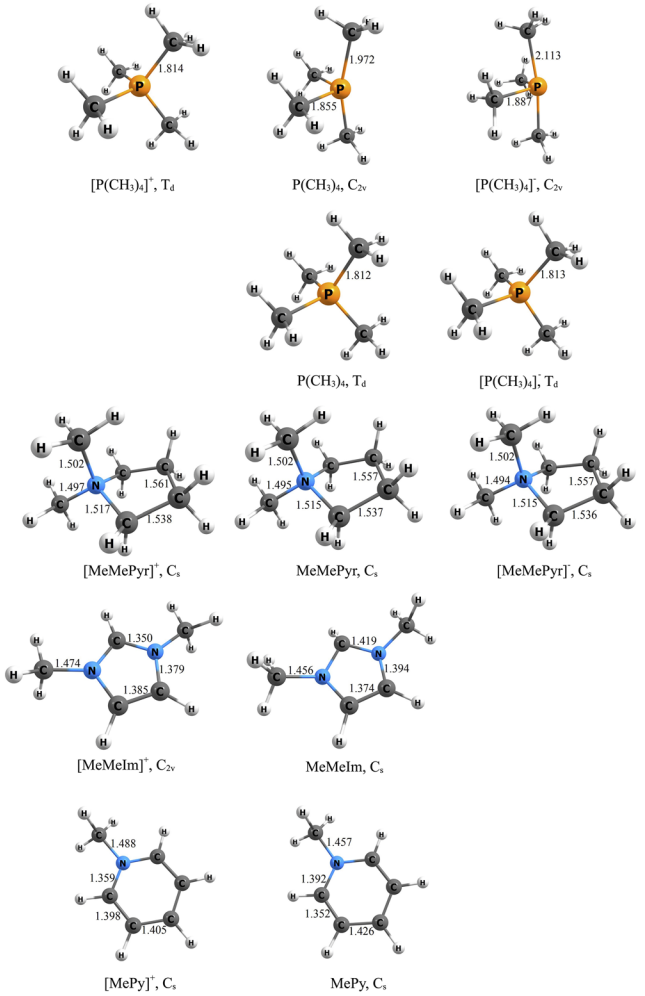


FIG. 1. The equilibrium structures of the cationic {$[P(CH_3)_4]^+$, [MeMePyr]$^+$, [MeMeIm]$^+$, and [MePy]$^+$}, neutral [$P(CH_3)_4$, MeMePyr, MeMeIm, and MePy], and anionic {$[P(CH_3)_4]^-$ and [MeMePyr]$^-$} systems. Selected bond lengths are provided in Å.

TABLE I. Adiabatic ionization potentials (AIP in eV) and adiabatic electron affinities (EA in eV) of the cationic and neutral systems, vertical ionization potentials (VIP in eV), and vertical electron detachment energies (VDE in eV) of their corresponding neutral and anionic systems calculated at the CCSD(T)/aug-cc-pVDZ+3s3p level (AIP and EA) and the OVGF/aug-cc-pVDZ+3s3p level (VIP and VDE) for the equilibrium structures obtained by employing the MP2/aug-cc-pVDZ+3s3p theoretical approach. The calculated values do not include zero-point energy corrections. For $P(CH_3)_4$ and $[P(CH_3)_4]^-$ species, only the results for the lowest energy C_{2v}-symmetry isomers are presented.

Species	AIP/VIP	Species	EA/VDE
$[P(CH_3)_4]^+/P(CH_3)_4$	3.517/5.573	$P(CH_3)_4/[P(CH_3)_4]^-$	0.486/1.159
$[MeMePyr]^+$/MeMePyr	2.790/2.792[a]	MeMePyr/$[MeMePyr]^-$	0.371/0.372[a]
$[MeMeIm]^+$/MeMeIm	3.793/5.071	MeMeIm/$[MeMeIm]^-$	Unstable
$[MePy]^+$/MePy	4.732/5.177	MePy/$[MePy]^-$	Unstable

[a]CCSD(T)/aug-cc-pVDZ+3s3p result.

them a possible source of cations in ILs. In addition, it seems important to stress that the adiabatic ionization potentials of these systems are indeed very small yet larger than the lowest AIP reported in the literature thus far {i.e., 1.52 eV predicted for potassium–cryptand complex [K([2.2.2]crypt)]}.[57]

The singly occupied molecular orbitals (SOMO) of MeMePyr and the T_d-symmetry isomer of $P(CH_3)_4$ neutral compounds depicted in Fig. 2 reveal the diffuse Rydberg-like character, and hence, both these systems might be viewed as Rydberg radicals.[58,59] This conclusion is also supported by the thermodynamic stability of their parent cations and 2.8 and 2.9 eV electron binding energy determined for MeMePyr and T_d-$P(CH_3)_4$, respectively. On the other hand, the SOMOs describing the unpaired electron in MeMeIm and MePy radicals are more compact and resemble typical valence-bound states with a significant π^*-character rather than Rydberg states (see Fig. 2). As far as the C_{2v}-symmetry $P(CH_3)_4$ isomer is concerned, we suggest to consider its outermost electron as occupying the orbital exhibiting a mixed Rydberg-valence character due to the fact that the straightforward interpretation cannot be provided in that case.

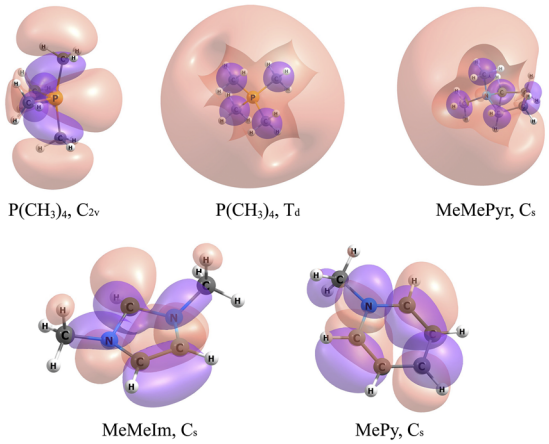


FIG. 2. Singly occupied molecular orbitals (SOMOs) of the neutral $P(CH_3)_4$, MeMePyr, MeMeIm, and MePy molecules {the HOMO orbitals of the corresponding electronically stable $[P(CH_3)_4]^-$ and $[MeMePyr]^-$ anions are qualitatively identical}.

Since all the neutral systems considered contain a half-filled orbital, we decided to verify the possibility of attaching one more electron, which would lead to the formation of the corresponding closed-shell anions. As revealed by our calculations, an excess electron attachment to $P(CH_3)_4$ and MeMePyr radicals leads to the formation of adiabatically stable anions, whereas MeMeIm and MePy radicals do not form stable anionic states. However, one may anticipate that the presence of neighboring cations (e.g., in an ionic liquid) or polar solvent molecules could likely render the $[MeMeIm]^-$ and $[MePy]^-$ anions adiabatically stable, which is additionally supported by the positive values of their vertical electronic stabilities estimated at the Koopmans theorem level in the gas phase.

The adiabatic electron affinities of C_{2v}-$P(CH_3)_4$ and MeMePyr radicals were found to be 0.486 and 0.371 eV, respectively, whereas the vertical electron detachment energies of their corresponding $[P(CH_3)_4]^-$ and $[MeMePyr]^-$ anions were predicted to be equal to 1.159 and 0.372 eV, respectively. As far as the geometry relaxation effects upon an excess electron attachment are concerned, we found that the equilibrium structure of the $[MeMePyr]^-$ anion is very similar to those of its corresponding neutral and cation systems (the bond lengths differ by less than 0.004 Å). On the other hand, the attachment of an extra electron to the C_{2v}-symmetry isomer of $P(CH_3)_4$ causes the increase of the P–C distances and ∠CPC valence angles by ~0.032 to 0.141 Å and 2°–9°, respectively. Such relatively insignificant geometry changes upon an excess electron attachment to either $P(CH_3)_4$ or the MeMePyr neutral compound are likely caused by the fact that an outermost pair of electrons in the $[P(CH_3)_4]^-$ and $[MeMePyr]^-$ anions occupies the same molecular orbital as does an unpaired electron in $P(CH_3)_4$ and MeMePyr neutral radicals. Clearly, the $[MeMePyr]^-$ species might be considered a double-Rydberg (DR) anion,[41,60] whereas the nature of the mixed Rydberg-valence anionic state of $[P(CH_3)_4]^-$ remains disputable. It is worth to mention that the T_d-symmetry isomer of $[P(CH_3)_4]^-$ {near the equilibrium geometry of the $[P(CH_3)_4]^+$ cation} was also found to be geometrically and electronically (by ~0.4 eV with respect to the T_d-symmetry neutral isomer) stable but higher in energy than the C_{2v}-symmetry structure of $[P(CH_3)_4]^-$ by about 16 kcal/mol (0.69 eV). Since two outermost electrons in this

higher energy tetrahedral isomer of $[P(CH_3)_4]^-$ occupy a Rydberg orbital, the T_d-symmetry $[P(CH_3)_4]^-$ species should be considered a double-Rydberg anion. However, the T_d-$[P(CH_3)_4]^-$ DR anion is expected to easily evolve to the more stable C_{2v}-symmetry isomer as the isomerization process requires only moderate changes in the ∠CPC valence angles in this case. Taking also into account that the T_d-symmetry $[P(CH_3)_4]^-$ DR anion is electronically stable only near its equilibrium tetrahedral geometry but slightly unstable with respect to the C_{2v}-$P(CH_3)_4$ neutral, we conclude that the T_d-$[P(CH_3)_4]^-$ anion, although interesting due to its double-Rydberg nature, seems to be rather unimportant as its lifetime is expected to be relatively short.

B. $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ dimeric cations

As explained in Sec. III A, each of the parent cations considered may attach an electron to form a geometrically stable radical neutral system. Each of such radicals may then interact with a neighboring cation to form a singly positively charged dimer in which the unpaired electron occupies a bonding molecular orbital. In order to determine the most stable structures of the resulting $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ cationic dimers, various possibilities of mutual arrangement of monomers were used as the starting structures during the independent geometry optimizations. The lowest energy structures of the $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ systems are depicted in Fig. 3, whereas other representative higher energy isomers are shown in Fig. 4 along with their corresponding SOMO orbitals. Each cationic dimer is characterized by the binding energy (BE) calculated as the difference between the electronic energy of a dimer and the sum of the electronic energies of its components (i.e., cationic and neutral monomers).

According to our findings, the lowest energy isomer of $[(P(CH_3)_4)_2]^+$ might be viewed as a complex of two $P(CH_3)_4$ subunits separated by a distance of ~4.26 Å (measured as the distance between the phosphorus atoms) in which one monomer retains the tetrahedral configuration {as in the isolated $[P(CH_3)_4]^+$ cation}, whereas the other one adopts a quasi-sphenoidal structure [similar to that of the isolated neutral $P(CH_3)_4$ radical] (see Fig. 3). The SOMO orbital holding the unpaired electron is localized mostly on the sphenoidal $P(CH_3)_4$ subunit and resembles the SOMO obtained for the isolated neutral C_{2v}-symmetry $P(CH_3)_4$ radical. The binding energy (BE) predicted for $[(P(CH_3)_4)_2]^+$ is positive and relatively large (12 kcal/mol), which confirms the stability of this cationic dimer. As far as the electronic stability is concerned, the $[(P(CH_3)_4)_2]^+$ is predicted to have a larger (by ~3 eV) VIP value than the neutral $P(CH_3)_4$ monomer. Clearly, this VIP increase is caused mostly by the fact that the VIP of $P(CH_3)_4$ is related to the neutral compound, whereas that of $[(P(CH_3)_4)_2]^+$ refers to the cation. We also found another isomer of $[(P(CH_3)_4)_2]^+$ whose C_2-symmetry structure is qualitatively different than that of the lowest energy isomer as it consists of two tetrahedral $P(CH_3)_4$ subunits with the unpaired electron occupying the bonding Rydberg orbital (see Fig. 4). Since each of the cationic dimers studied might be viewed as composed of two closed-shell monomeric cations with an electron attached, the systems retaining their monomeric structures seem to be of particular interest. Despite the fact that the C_2-$[(P(CH_3)_4)_2]^+$ isomer is higher in energy by almost 10 kcal/mol than the corresponding most stable C_1-symmetry structure, we believe it is important to include this species in our description because the electron capture and electron transfer processes (which might occur in ionic liquids) are likely faster than the geometry relaxation of the $P(CH_3)_4$ moieties.

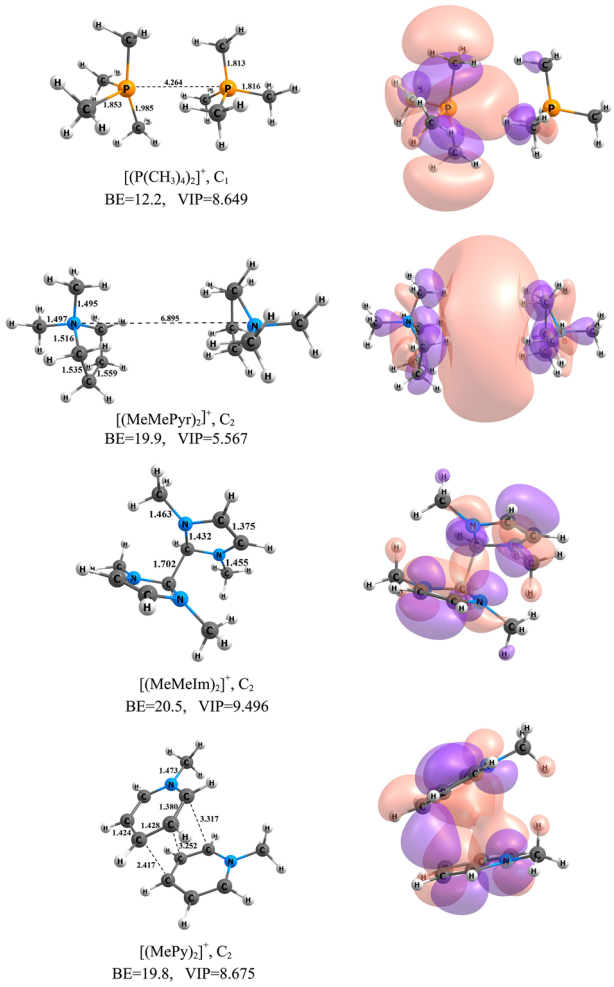


FIG. 3. The most stable structures of the $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ cationic dimers and their corresponding singly occupied molecular orbitals. Selected bond lengths and intermolecular distances are provided in Å, the binding energies (BE) are provided in kcal/mol, and vertical ionization potentials (VIP) are provided in eV.

Interestingly, the cationic dimer consisting of two MeMePyr fragments forms only Rydberg-bonded $[(MeMePyr)_2]^+$ complexes. Namely, we found four geometrically stable $[(MeMePyr)_2]^+$ isomers having their relative energies within ~7 kcal/mol and differing from one another by mutual arrangement of pyrrolidinium rings. Regardless of the isomeric structure considered, the MeMePyr monomer fragments in $[(MeMePyr)_2]^+$ adopt the configurations similar to that of the isolated $[MeMePyr]^+$ cation, while the unpaired

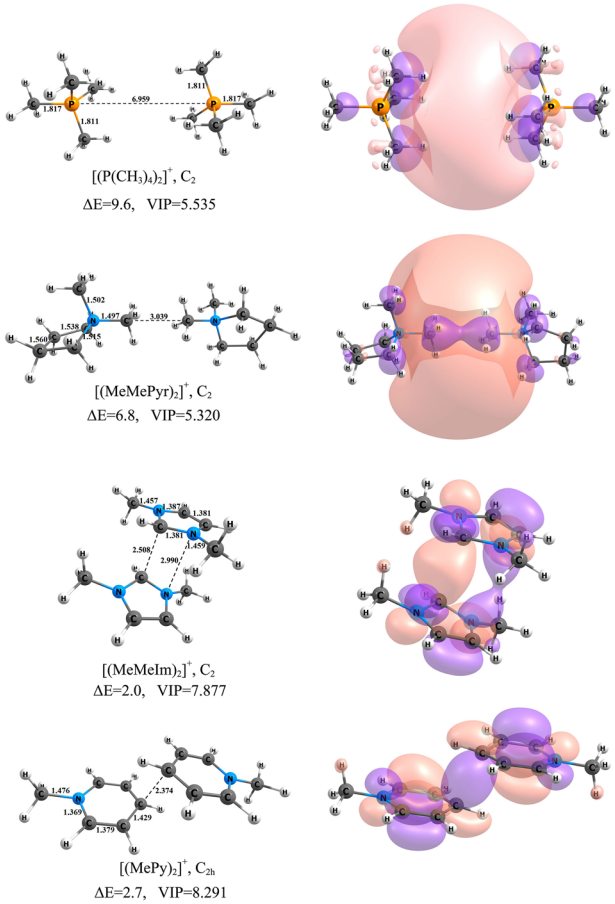


FIG. 4. The representative higher energy isomers of the $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ cationic dimers and their corresponding singly occupied molecular orbitals. Selected bond lengths and intermolecular distances are given in Å, the relative energies (ΔE) are given in kcal/mol, and vertical ionization potentials (VIP) are given in eV.

electron occupies the Rydberg bonding orbital. The structures of the most stable isomer and the representative higher energy isomer of $[(MeMePyr)_2]^+$ along with their SOMOs are presented in Figs. 3 and 4, respectively. The BE value for the most stable $[(MeMePyr)_2]^+$ was found to be relatively large (20 kcal/mol), which confirms the stability of this structure against fragmentation leading to MeMePyr and $[MeMePyr]^+$. The VIP characterizing the most stable $[(MeMePyr)_2]^+$ was calculated to be 5.567 eV and this value is significantly larger than the VIP predicted for the isolated neutral MeMePyr system. As mentioned earlier, the stability of the $[(MeMePyr)_2]^+$ dimeric cation is related to the monomer–monomer bonding interaction that manifests itself by the singly occupied Rydberg orbital localized mostly in between the MeMePyr moieties {alike the bonding orbital in the $[(NH_4)_2]^+$ system described elsewhere (Refs. 34, 61, and 62)}.

In the case of two remaining systems {i.e., $[(MeMeIm)_2]^+$ and $[(MePy)_2]^+$}, we found that three qualitatively different types of cationic dimers could be formed: (i) σ-dimer (in which two monomers are connected via the C–C σ-bond), (ii) π-dimer (in which the stability of a dimer results from the π-stacking interactions), and (iii) other complexes stabilized mostly by the cation-π interactions. Among these dimeric systems, the π-dimers seem of particular importance in designing organic conductors based on conjugated molecules as they are believed to play a key role in transferring electrons between molecules.[63,64] Since the σ- and π-dimers involving either MeMeIm or MePy monomers turned out to be significantly more stable than other isomers, we limit our discussion to such structures.

Due to several possible packing motifs of heteroaromatic rings (i.e., sandwich arrangement, displaced parallel structure, and perpendicular arrangement), the $[(MeMeIm)_2]^+$ and $[(MePy)_2]^+$ dimers might adopt various geometrically stable structures. We found that the relative energies of such isomers are similar and differ by less than 4 kcal/mol. Therefore, we present the results only for two low energy isomers of $[(MeMeIm)_2]^+$ and two most stable isomers of $[(MePy)_2]^+$.

The lowest energy structure of $[(MeMeIm)_2]^+$ corresponds to the C_2-symmetry σ-dimer involving a relatively long (r = 1.7 Å) intermolecular σ(C–C) bond connecting the imidazolium rings (see Fig. 3). According to our calculations, this σ-dimer is stable against the fragmentation leading to MeMeIm and $[MeMeIm]^+$, as indicated by the positive BE value of ~20 kcal/mol. The VIP of the C_2-symmetry $[(MeMeIm)_2]^+$ system was found to be very large (9.5 eV), while the analysis of SOMO (depicted on Fig. 3) reveals that the unpaired electron is delocalized over the entire molecular framework (see Fig. 3). The second low energy isomer of $[(MeMeIm)_2]^+$ is close in energy to the most stable one as its relative energy equals to 2 kcal/mol. However, the sandwich arrangement of the imidazolium rings indicates that this isomeric structure is stabilized mostly by the π-stacking interactions, and thus, we classify this system as a π-dimer (see Fig. 4). Similar to the most stable σ-dimer, the SOMO in the π-dimer isomer is delocalized over the entire structure and reveals the bonding interactions between the imidazolium rings. The VIP for the $[(MeMeIm)_2]^+$ π-dimer was predicted to be considerably lower (by ~1.6 eV) than that for the corresponding σ-dimer.

By contrast, the most stable isomeric structure of $[(MePy)_2]^+$ corresponds to the π-dimer adopting the sandwich arrangement of the imidazolium rings (see Fig. 3). The BE = 20 kcal/mol predicted for this system confirms its stability with respect to the fragmentation leading to MePy and $[MePy]^+$ products, whereas its VIP of 8.675 eV was found larger than that of the neutral MePy monomer. Such a large thermodynamic stability of the $[(MePy)_2]^+$ π-dimer clearly results from strong stabilizing π-stacking interactions between the heterocyclic rings (see Fig. 3). Interestingly, the next stable $[(MePy)_2]^+$ isomer revealing the π-dimer nature resembles similar parallel arrangement of its cyclic fragments and owes its stability to the formation of a so-called pancake bond.[65] Another low energy isomer of $[(MePy)_2]^+$ was recognized as the structure stabilized by the elongated (2.37 Å) σ(C–C) bond and thus classified as a σ-dimer (see Fig. 4). The relative energy of that isomer is only 2.7 kcal/mol larger than that of the lowest energy isomer of $[(MePy)_2]^+$, and its structure involves two pyridinium rings aligned in a displaced-parallel manner, which results in the C_{2h} symmetry. The VIP of the $[(MePy)_2]^+$ σ-dimer (8.291 eV) was to be comparable to that of the most stable $[(MePy)_2]^+$ π-dimer.

C. $(P(CH_3)_4)_2$, $(MeMePyr)_2$, $(MeMeIm)_2$, and $(MePy)_2$ neutral dimers

Since each of the cationic dimers described in Sec. III B may attach an electron to form the corresponding neutral closed-shell molecule, we explored the potential energy surface of the $(P(CH_3)_4)_2$, $(MeMePyr)_2$, $(MeMeIm)_2$, and $(MePy)_2$ neutral systems. In the course of a thorough search for the global minima, we used various geometries, including those corresponding to the isomeric structures of cationic dimers, as the initial structures in the independent optimizations of geometric parameters. Hence, several starting structures containing monomers in various mutual orientations have been considered in each case. The resulting most stable structures together with their corresponding highest energy doubly occupied molecular orbitals are presented in Fig. 5.

The lowest energy isomer of $(P(CH_3)_4)_2$ contains two $P(CH_3)_4$ subunits connected via the relatively short P–P bond (2.605 Å). Clearly, the formation of this bond is enabled by the presence of two (instead of one) electrons occupying the bonding orbital depicted in Fig. 5. We consider this most stable isomer of $(P(CH_3)_4)_2$ as likely resulting from an electron attachment to the lowest energy structure of $[(P(CH_3)_4)_2]^+$ depicted in Fig. 3, and thus we interpret its binding energy of 25.0 kcal/mol as much larger than the BE predicted for $[(P(CH_3)_4)_2]^+$ (12.2 kcal/mol). As a result of such a stronger monomer–monomer stabilization, the separation between the $P(CH_3)_4$ fragments in the neutral $(P(CH_3)_4)_2$ (2.605 Å) is considerably smaller than that in the $[(P(CH_3)_4)_2]^+$ cation (4.264 Å). The adiabatic ionization potential of the $(P(CH_3)_4)_2$ dimer (4.072 eV) was predicted to be larger by ~0.56 eV than the AIP value estimated for the $[P(CH_3)_4]$ neutral monomer, whereas the value of the vertical ionization potential of $(P(CH_3)_4)_2$ (5.679 eV) was found to be similar to that of the $P(CH_3)_4$ (5.573 eV, see Table I). In addition, we verified the relative stability of another isomer of $(P(CH_3)_4)_2$ formed by an electron attachment to the higher energy C_2-symmetry $[(P(CH_3)_4)_2]^+$ cationic dimer having its unpaired electron described by the Rydberg orbital (see Fig. 4). As it turned out, the energy of the $(P(CH_3)_4)_2$ neutral dimer in which two outermost electrons occupy a bonding Rydberg orbital is much higher (by 44.05 kcal/mol) than the energy of the most stable $(P(CH_3)_4)_2$ isomer, and thus, its formation should not be considered as likely.

The lowest energy isomer of the $(MeMePyr)_2$ neutral dimer can be regarded as resulting from an electron attachment to the most stable isomer of $[(MeMePyr)_2]^+$ (see Figs. 3 and 5 for comparison). Indeed, the structure of the C_2-symmetry $(MeMePyr)_2$ is qualitatively similar to that of the C_2-symmetry $[(MeMePyr)_2]^+$, the intermonomer separation is smaller by only 0.36 Å, and the geometries of both MeMePyr subunits remain nearly unchanged upon attachment of an electron. The HOMO in the neutral $(MeMePyr)_2$ dimer (see Fig. 5) reveals the Rydberg character as it was the case for the SOMO in the lowest energy $[(MeMePyr)_2]^+$ cation (see Fig. 3); however, it seems considerably more diffuse when occupied by two electrons [in $(MeMePyr)_2$] instead of one electron {in $[(MeMePyr)_2]^+$}. The BE value calculated for the $(MeMePyr)_2$ neutral dimer (11.3 kcal/mol) is smaller than the BE predicted for the $[(MeMePyr)_2]^+$ cation (19.9 kcal/mol) despite the fact that two electrons occupy the bonding Rydberg orbital in the former system. Although this finding may seem surprising, a similar situation was reported by Barrios *et al.* who estimated the BEs of the neutral $(NH_4)_2$ and cationic $[(NH_4)_2]^+$ Rydberg-bonded systems as equal to 9 kcal/mol and 20 kcal/mol, respectively.[62] The adiabatic and vertical ionization potential values for the neutral $(MeMePyr)_2$ were estimated to be 2.416 eV and 2.432 eV, respectively, and these values are similar (although slightly smaller) to those predicted for the neutral MeMePyr monomer (see Table I). It is also worth noting that all other higher energy isomers of $(MeMePyr)_2$ were found to exhibit an analogous (i.e., Rydberg) nature with the outermost electron pair described by the bonding Rydberg orbital and various mutual arrangements of the MeMePyr monomers.

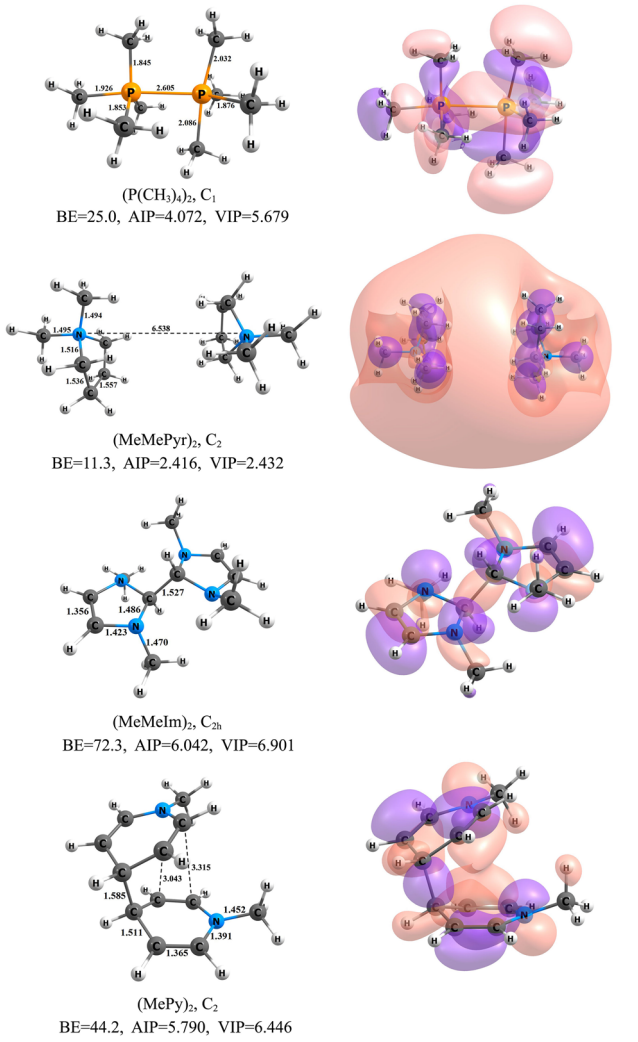


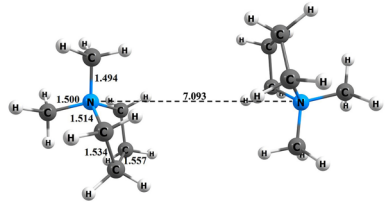
FIG. 5. The lowest energy structures of the neutral $(P(CH_3)_4)_2$, $(MeMePyr)_2$, $(MeMeIm)_2$, and $(MePy)_2$ systems and their corresponding doubly occupied highest energy molecular orbitals. Selected bond lengths and intermolecular distances are provided in Å, binding energies (BE) are provided in kcal/mol, and adiabatic and vertical ionization potentials (AIP and VIP) are provided in eV.

The attachment of an electron to the remaining $[(MeMeIm)_2]^+$ and $[(MePy)_2]^+$ cations leads to the formation of strongly bound neutral molecules. In particular, the binding energies of the most stable $(MeMeIm)_2$ and $(MePy)_2$ are large and equal to 72.3 and 44.2 kcal/mol, respectively. Clearly, the presence of the inter-monomer two-electron C–C bond is responsible for such large binding energy in each of these two compounds (see Fig. 5). The most stable isomer of $(MeMeIm)_2$ corresponds to the C_{2h}-symmetry structure that resembles the lowest energy isomer of $[(MeMeIm)_2]^+$ (characterized as the σ-dimer in Sec. III B) whose BE was also found substantial (20.5 kcal/mol) yet considerably smaller. Indeed, these two structures exhibit similar mutual arrangement of the imidazolium rings, whereas the length of the C–C bond connecting the rings is only ~0.2 Å smaller in the neutral dimer. The AIP and VIP values estimated for the $(MeMeIm)_2$ system (6.042 and 6.901 eV, respectively) are significantly larger than the corresponding values predicted for the neutral MeMeIm monomer (3.793 and 5.071 eV, respectively). On the other hand, the lowest energy isomer of the $(MePy)_2$ neutral compound (see Fig. 5) resembles the most stable isomer of the $[(MePy)_2]^+$ cation (characterized as the π-dimer in Sec. III B) with the pyridinium rings nearly parallelly stacked. However, in contrast to the $[(MePy)_2]^+$ cation, the heterocyclic rings in the $(MePy)_2$ system are connected via the C–C σ-bond whose length was estimated as equal to 1.585 Å. Clearly, the presence of this σ-bond causes a substantial increase (by 24.4 kcal/mol) of the BE value predicted for $(MePy)_2$ in comparison to that estimated for the lowest energy $[(MePy)_2]^+$ cation. As far as the AIP and VIP of the $(MePy)_2$ dimer are concerned, they were found larger than the corresponding ionization potentials of the MePy monomer and equal to 5.790 and 6.446 eV, respectively.

D. Stability of the $[(P(CH_3)_4)_2]^-$, $[(MeMePyr)_2]^-$, $[(MeMeIm)_2]^-$, and $[(MePy)_2]^-$ dimeric anions

Since it has been reported in the earlier studies that certain neutral Rydberg-bonded dimers may attach an excess electron to form adiabatically stable anions,[62] we decided to investigate the electronic and adiabatic stability of $[(P(CH_3)_4)_2]^-$, $[(MeMePyr)_2]^-$, $[(MeMeIm)_2]^-$, and $[(MePy)_2]^-$ systems. In such negatively charged dimers, three electrons are expected to occupy Rydberg orbitals, which would lead to the $(\sigma)^2(\sigma^*)^1$ configuration. Therefore, one should anticipate the e–e repulsion among these three electrons to reduce the stability of the resulting system.

According to our calculations, the only adiabatically stable dimeric anion can be formed upon an electron attachment to $(MeMePyr)_2$, whereas the remaining neutral dimers are not capable of an excess electron binding. In particular, the attachment of an extra electron to $(P(CH_3)_4)_2$ leads to a vertically stable (VDE = 1.213 eV) but adiabatically unstable (with respect to the ground state neutral dimer) $[(P(CH_3)_4)_2]^-$ anion. As far as the $(MeMeIm)_2$ and $(MePy)_2$ neutral dimers are concerned, none of them was found to bind an excess electron (even vertically). By contrast, we confirmed that the neutral $(MeMePyr)_2$ system having its outermost electron pair occupying the bonding σ Rydberg orbital (depicted in Fig. 5) may attach the additional electron to its virtual antibonding σ* Rydberg orbital and form an adiabatically stable $[(MeMePyr)_2]^-$ anionic state. The equilibrium structure of the $[(MeMePyr)_2]^-$ anion (Fig. 6) reveals a different mutual orientation of the MeMePyr monomers in comparison to the either neutral or cationic dimer (see also Figs. 3 and 5). In addition, the attachment of an extra electron to the σ* antibonding orbital of $(MeMePyr)_2$ increases the monomer–monomer separation as the distance between the nitrogen atoms in the $[(MeMePyr)_2]^-$ anion is larger by ~0.5 Å than the N–N separation in the neutral $(MeMePyr)_2$. The $[(MeMePyr)_2]^-$ anion was found to be adiabatically stable by almost 0.4 eV with respect to the ground electronic state of the corresponding neutral dimer [i.e., EA of 0.368 eV was predicted for the $(MeMePyr)_2$ system]. The positive BE value of 6.2 kcal/mol calculated for the $[(MeMePyr)_2]^-$ anionic dimer confirms its stability against fragmentation leading to MeMePyr and $[MeMePyr]^-$; however, this binding energy is substantially smaller than that predicted for the neutral $(MeMePyr)_2$ system (11.3 eV). Clearly, it is the presence of the excess electron occupying the antibonding σ* Rydberg orbital (see Fig. 6) that causes such a decrease in the binding energy of $[(MeMePyr)_2]^-$ in



$[(MeMePyr)_2]^-$, C_2

BE=6.2, EA=0.368, VDE=0.417

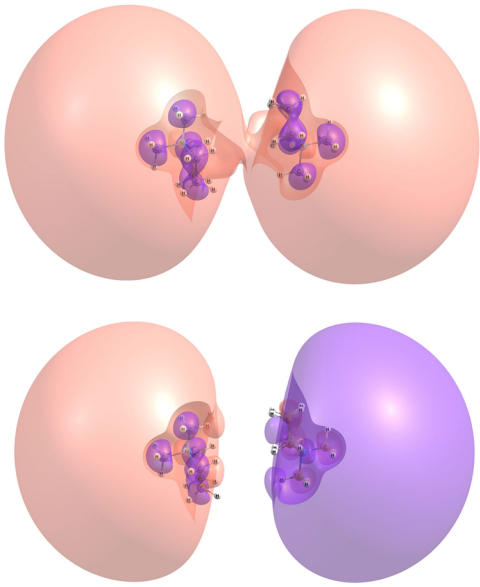


FIG. 6. The equilibrium structure of the $[(MeMePyr)_2]^-$ anion (top), its doubly occupied Rydberg σ bonding orbital (center), and its singly occupied Rydberg σ* antibonding orbital (bottom). Selected bond lengths and intermolecular distances are given in Å, the binding energy (BE) are given in kcal/mol, and the adiabatic electron affinity (EA) and vertical electron detachment energy are given in eV.

comparison to the $(MeMePyr)_2$ neutral parent. Nevertheless, the $[(MeMePyr)_2]^-$ anionic dimer remains a stable system despite destabilizing e–e repulsion among three Rydberg electrons (two σ′s and one σ*).

IV. CONCLUSIONS

On the basis of the CCSD(T)/aug-cc-pVDZ+3s3p//MP2/aug-cc-pVDZ+3s3p and OVGF/aug-cc-pVDZ+3s3p//MP2/aug-cc-pVDZ+3s3p calculations performed for the $[P(CH_3)_4]^+$, $[MeMePyr]^+$, $[MeMeIm]^+$, and $[MePy]^+$ cations and their corresponding neutral and anionic systems as well as for their cationic, neutral, and anionic dimers, we arrive at the following conclusions:

(i) The attachment of an electron to $[P(CH_3)_4]^+$, $[MeMePyr]^+$, $[MeMeIm]^+$, and $[MePy]^+$ cations leads to the corresponding neutral radicals whose adiabatic ionization potentials span the 2.790–4.732 eV range. The unpaired electron in the MeMePyr is described by the Rydberg orbital, whereas those in MeMeIm and MePy are described by the π* valence orbitals. The singly occupied orbital in the $P(CH_3)_4$ exhibits a mixed Rydberg-valence character.

(ii) The attachment of an excess electron to either $P(CH_3)_4$ or MeMePyr results in the formation of electronically stable $[P(CH_3)_4]^-$ and $[MeMePyr]^-$ anions whose vertical electron detachment energies are equal to 1.159 and 0.372 eV, respectively. The $[MeMePyr]^-$ anion can be classified as a double-Rydberg anionic state, while the lowest energy $[P(CH_3)_4]^-$ anion corresponds to the mixed Rydberg-valence state. By contrast, neither MeMeIm nor MePy forms an electronically stable anionic state.

(iii) Each of the monomeric cations considered may interact with its corresponding neutral system to form $[(P(CH_3)_4)_2]^+$, $[(MeMePyr)_2]^+$, $[(MeMeIm)_2]^+$, and $[(MePy)_2]^+$ cationic dimers whose binding energies (describing their stability against fragmentation) are predicted to be large (12.2–20.5 kcal/mol). The lowest energy $[(MeMePyr)_2]^+$ system resembles a Rydberg-bonded dimer stabilized by the one-electron σ-bond, whereas the most stable structures of the remaining dimers correspond to the systems stabilized by the presence of the σ(C–C) intermonomer bond $\{[(MeMeIm)_2]^+\}$ or π-stacking interactions $\{[(MePy)_2]^+\}$. The stability of the $[(P(CH_3)_4)_2]^+$ dimer is related to the presence of the one-electron σ-bond {similar to the $[(MeMePyr)_2]^+$ system}, although the singly occupied bonding orbital exhibits mixed a Rydberg-valence rather than a pure Rydberg character.

(iv) The lowest energy structures of $(P(CH_3)_4)_2$, $(MeMePyr)_2$, $(MeMeIm)_2$, and $(MePy)_2$ neutral dimers are similar to those of their corresponding cations, and their binding energies span the 11.3–72.3 kcal/mol range. The adiabatic IPs of $(P(CH_3)_4)_2$ (4.072 eV), $(MeMeIm)_2$ (6.042 eV), and $(MePy)_2$ (5.790 eV) are predicted to be much larger than the AIP calculated for the $(MeMePyr)_2$ (2.416 eV) due to the different bonding nature of the latter system whose stability results from the presence of the two-electron Rydberg σ-bond.

(v) The only adiabatically stable dimeric anion can be formed upon an electron attachment to $(MeMePyr)_2$, whereas the remaining neutral dimers are not capable of an excess electron binding. The vertical electron detachment energy predicted for the $[(MeMePyr)_2]^-$ anion is equal to 0.417 eV, while the binding energy calculated for this system is 6.2 kcal/mol. In the $[(MeMePyr)_2]^-$ anionic state, three outermost electrons are described by Rydberg orbitals, which result in the $(\sigma)^2(\sigma^*)^1$ configuration.

DEDICATION

This paper honors Dr. Kazimiera Smiataczowa, who was an outstanding teacher of physical chemistry. Dr. Smiataczowa has mentored and inspired many students, including one of the authors, to pursue careers in physical chemistry/chemical physics.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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