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Search for aromatic anions in the $P_2E_3^-$ ($E = N, P, As, Sb, Bi$) series†

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We report a systematic computational study focused on the global minimum and low-lying isomer search for the $P_2E_3^-$ ($E = N, P, As, Sb, Bi$) series of anions. We found nine planar five-membered rings and proved their aromatic character by various quantum chemical techniques. The possible use of two different $P_2N_3^-$ aromatic anions as ligands in a number of sandwich complexes was also studied.

Aromatic species with delocalized $(4n + 2)\pi$ electrons have increased stability compared to their non-aromatic analogues.^{1,2} Along with the well-known aromatic carbocyclic compounds (benzene ($n = 1$), naphthalene ($n = 2$), etc.), aromaticity was also detected in a number of species containing metals and main group elements.^{3,4} Special attention to this field leads to the novel aromatic compounds being intensively sought both experimentally and theoretically.^{5–8} Planar five-membered all-pnictogen cycles with 6π electrons are of particular interest among the main group aromatics because they are isovalent with the cyclopentadienyl anion ($C_5H_5^-$) and can be used as inorganic building blocks.^{9–11} Specifically, P_5^- and As_5^- fragments were stabilized in several sandwich complexes,¹² including a carbon-free metallocene $[(\eta^5-P_5)_2Ti]^{2-}$.¹³

Recently, Velian and Cummins reported the synthesis of $P_2N_3^-$ anion by an original “click” reaction between an anthracene-based source of P_2 , $P_2(C_{14}H_{10})_2$,¹⁴ and the azide anion N_3^- in tetrahydrofuran solution and computationally confirmed the aromatic properties of $P_2N_3^-$.¹⁵ The proposed P_2 transfer reaction opens new opportunities for synthetic realization of unusual phosphorus-containing compounds. After that, Mandal *et al.* have predicted a number of all-pnictogen aromatic species with $X_2Y_3^-$ and $X_3Y_2^-$ formulae and explored the possibility of using a $P_3N_2^-$ anion as

an η^5 -ligand in metallocenes by density functional theory calculations.¹⁶ Inspired by these two studies, here we report a systematic *ab initio* search for possible isomers with $P_2E_3^-$ ($E = N, P, As, Sb, Bi$) stoichiometry in order to characterize expected aromatic anions.

An unbiased quantum-chemical search¹⁷ for $P_2E_3^-$ species performed at the B3LYP-D3(BJ)/def2-SVP level of theory revealed that the global minimum for each E is a planar five-membered ring with a C_{2v} -symmetrical ($E = N, As, Sb, Bi$) or D_{5h} -symmetrical ($E = P$) structure (Fig. 1).¹⁸ It is important to note that two different kinds of such rings were found for $P_2E_3^-$ ($E = N, As, Sb, Bi$), both of them having increased stability over the rest of the corresponding isomers (Fig. 1 and Fig. S1–S5, ESI†). One structural motif has a pnictogen atom between two phosphorus centers (I.A-like), whereas another has no atoms between them (I.B-like). Bond lengths optimized at B3LYP-D3(BJ)/def2-QZVPD and CCSD/aug-cc-pVTZ(-PP) levels of theory (results obtained agree with each other within 0.06 Å) as well as natural population analysis (NPA)¹⁹ partial charges are presented in Fig. 1. Rather short P–P, E–P, and E–E interatomic distances suggest the presence of multiple bonding.

It should be stressed that, in contrast to the recently reported anion I.B,¹⁵ anionic heterocycle I.A has been unknown to date. Moreover, I.A is a global minimum structure, which lies 16.1 kcal mol^{−1} below I.B in energy (here and elsewhere results on the total energy differences for $P_2E_3^-$ are given at the CCSD(T)/aug-cc-pVTZ(-PP)//B3LYP-D3(BJ)/def2-QZVPD + ΔSR ($E = N, P, As$) + ΔSO + ΔZPE theoretical level; ΔSR , ΔSO , and ΔZPE denote scalar relativistic, spin-orbit, and zero-point energy corrections, respectively).¹⁸ However, isomers with I.B-like structures are the most preferred ones in the $P_2E_3^-$ ($E = As, Sb, Bi$) series so that the relative energy of the second lowest-lying isomer (I.A-like structures) changes from 1.1 kcal mol^{−1} ($P_2As_3^-$) and 3.6 kcal mol^{−1} ($P_2Sb_3^-$) to 10.5 kcal mol^{−1} ($P_2Bi_3^-$), as our calculations predict (Fig. 1). The energy difference between the first two lowest-lying isomers was calculated to be 7.0 kcal mol^{−1} and 32.6 kcal mol^{−1} in the case of $P_2N_3^-$ and P_5^- , respectively (Fig. S1 and S2, ESI†).

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† Electronic supplementary information (ESI) available: Computational details, complete results of calculations performed, including IR and Raman spectra and

³¹P chemical shifts for aromatic $P_2E_3^-$ anions, and Cartesian coordinates of the most relevant species. See DOI: 10.1039/c6cp02241c



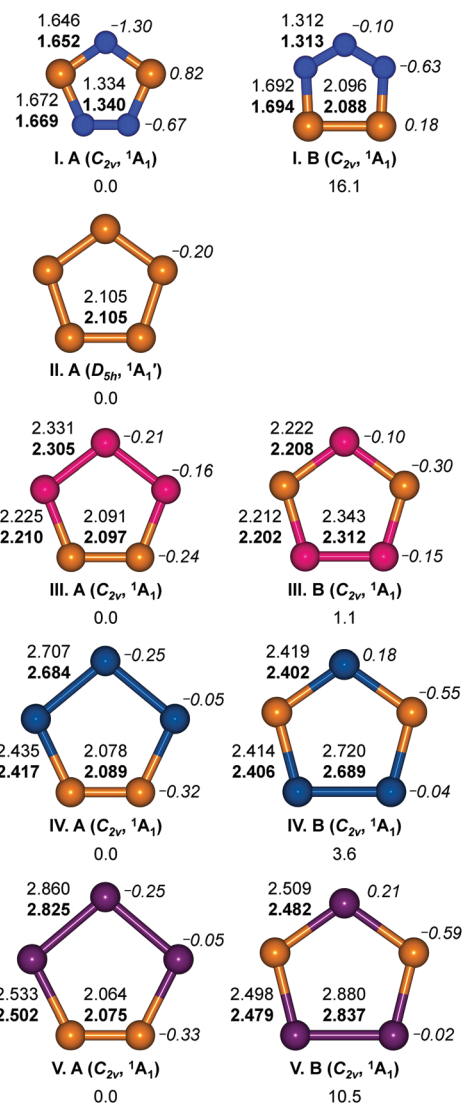


Fig. 1 Representative isomers of (II) $P_2N_3^-$, (III) P_5^- , (III) $P_2As_3^-$, (IV) $P_2Sb_3^-$, and (V) $P_2Bi_3^-$, their point group symmetries, spectroscopic states, bond lengths (Å), NPA partial charges ($|e|$, in italics), and relative energies (kcal mol⁻¹). The energies are given at the CCSD(T)/aug-cc-pVTZ(-PP)//B3LYP-D3(BJ)/def2-QZVPD + Δ SR ($E = N, P, As$) + Δ SO + Δ ZPE level of theory. Bond lengths are given at B3LYP-D3(BJ)/def2-QZVPD and CCSD/aug-cc-pVTZ(-PP) (in bold) theoretical levels.

Thus, our computational findings suggest that $P_2E_3^-$ ($E = N, As, Sb, Bi$) anions with I.A-like and I.B-like structures, most of which were characterized for the first time (see Tables S1 and S2, ESI[†] for predicted IR and Raman spectra and ³¹P chemical shifts), possess increased thermodynamic stability and can be considered as potential targets for chemical synthesis.

To check whether these $P_2E_3^-$ anions exhibit aromatic properties, we performed nucleus-independent chemical shift (NICS),²⁰ natural resonance theory (NRT),²¹ and adaptive natural density partitioning (AdNDP)²² calculations.¹⁸

All NICS_{zz} profiles calculated for both the planar $P_2E_3^-$ and $C_5H_5^-$ anions consist of negative NICS values and show a minimum (Fig. 2, Fig. S6, S7 and Table S3, ESI[†]), which is typical for aromatic compounds.²³ A decrease of the maximum absolute NICS_{zz} value

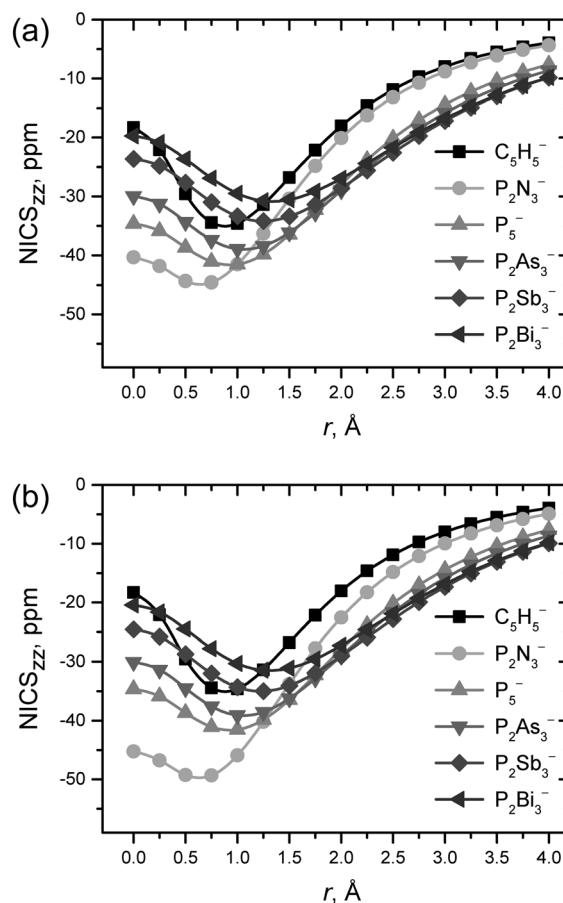


Fig. 2 NICS_{zz} profiles for $P_2E_3^-$ anions with (a) I.A-like and (b) I.B-like structures computed at the B3LYP/def2-QZVPD level of theory. Results for $C_5H_5^-$ anions are also presented for comparison.

is accompanied by the displacement of the profile's minimum to higher distances above the ring critical point at the electron density gradient field as the atomic weight of E is increased, indicating weakening of the π -aromaticity. It is worth noting that absolute NICS_{zz} values of I.B-like structures are higher than those of I.A-like ones.

NRT analysis reveals five canonical resonance structures with the contribution ranging from 11% to 17% for each system (Fig. S8 and S9, ESI[†]), reflecting electron delocalization.

In contrast to NRT analysis, the AdNDP method allows one to describe electron delocalization, being an important feature of aromatic compounds, *via* multicenter bonds without invoking the concept of resonance. As the picture of chemical bonding in $P_2E_3^-$ species of similar structure slightly depends on the pnictogen E , here we discuss in detail the results of AdNDP calculations only for the I.A and I.B anions with $E = N$ (Fig. 3). The complete AdNDP results are given in Fig. S10 and S11 (ESI[†]).

The chemical bonding pattern in the global minimum of $P_2N_3^-$ (I.A, Fig. 3a) represents five s-type lone pairs (two P lone pairs with occupation numbers (ON) equal to 2.0 $|e|$ and three N lone pairs with ON = 1.9 $|e|$), five covalent two-center two-electron (2c-2e) σ -bonds with ON = 2.0 $|e|$ (four P-N and one N-N bonds), and three 5c-2e π -bonds (ON = 2.0 $|e|$) between

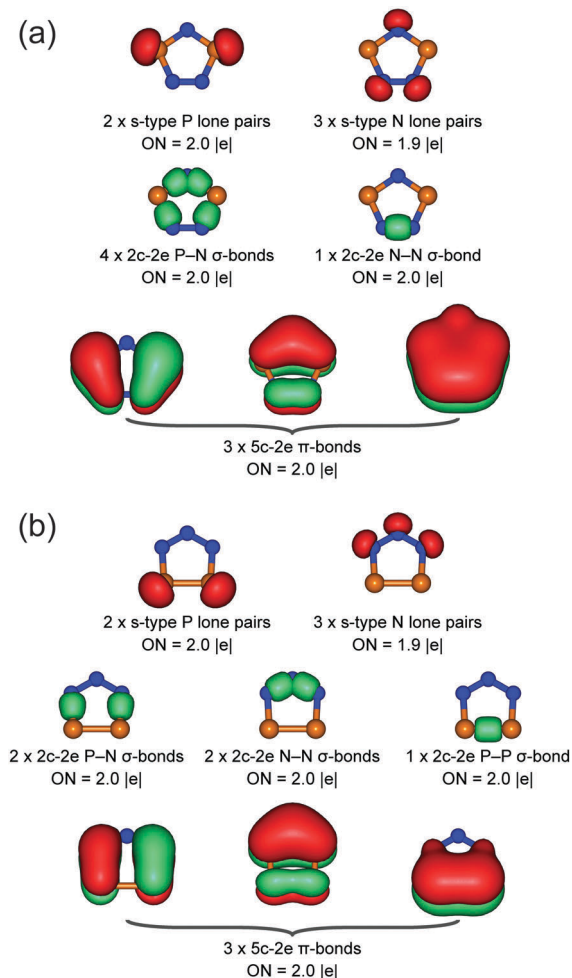


Fig. 3 Results of AdNDP analysis for the (a) I.A and (b) I.B structures.

all atoms of the ring. The same picture of chemical bonding is observed in structure I.B (Fig. 3b), except for the presence of three different types of 2c-2e σ -bonds (two P-N, two N-N, and one P-P bonds with ON = 2.0 |e|).²⁴ It is important to note that the set of three 5c-2e π -bonds found in $P_2E_3^-$ species is also the key element of the chemical bonding pattern for $C_5H_5^-$ (Fig. S12, ESI[†]), which is a well-known 6 π -electron aromatic system.

Additionally, vertical detachment energies (VDEs) from the highest occupied molecular orbital range from 3.1 eV (V.B) to 4.3 eV (I.B), as calculated by the OVGF/aug-cc-pVTZ(-PP) method (Table S4, ESI[†]). The VDEs are similar to those for E_5^- (E = P, As, Sb, Bi) aromatic cluster anions reported by Zhai and coworkers (2.9–4.1 eV),⁴ but they are higher than VDE for $C_5H_5^-$ (2.0 eV, Table S5, ESI[†]).

Thus, one can conclude that all $P_2E_3^-$ anions shown in Fig. 1 are aromatic.

Taking into account the resembling aromatic properties of $C_5H_5^-$ and $P_2N_3^-$ anions, we also studied hypothetical $M(\eta^5-P_2N_3)_2$, $M(\eta^5-C_5H_5)(\eta^5-P_2N_3)$, and $M(\eta^5-C_5Me_5)(\eta^5-P_2N_3)$ sandwich complexes (M = Fe, Ru, Os; Me = CH₃) to draw a parallel with classical metallocenes $M(\eta^5-C_5H_5)_2$. Compounds with one $P_2N_3^-$ (I.B) moiety were found to be ca. 20 kcal mol⁻¹

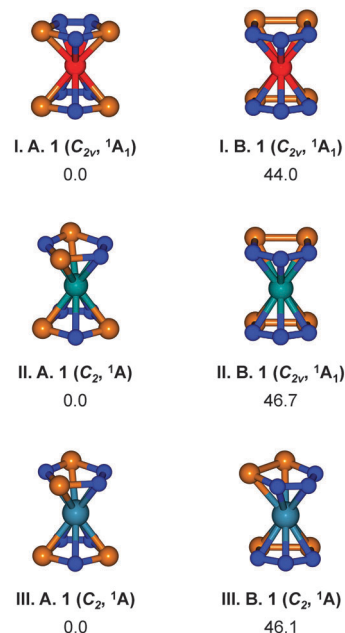


Fig. 4 Representative isomers of (I) $Fe(\eta^5-P_2N_3)_2$, (II) $Ru(\eta^5-P_2N_3)_2$, and (III) $Os(\eta^5-P_2N_3)_2$ complexes with $P_2N_3^-$ (I.A and I.B) ligands, their point group symmetries, spectroscopic states and relative energies (kcal mol⁻¹). The energies are given at the M06-L/def2-TZVP//M06-L/def2-TZVP + Δ ZPE level of theory.

higher in energy (M06-L/def2-TZVP level of theory) than their $P_2N_3^-$ (I.A)-substituted isomers (Fig. 4, Fig. S14 and S15, ESI[†]), which is in line with the results obtained for $P_2N_3^-$ anions (Fig. 1). Dissociation energies of the $P_2N_3^-$ -containing complexes into the M^{2+} and two negatively charged ligands ($\Delta G_{298}^\circ = 610$ –740 kcal mol⁻¹) are comparable with those of $M(\eta^5-C_5H_5)_2$ ($\Delta G_{298}^\circ = 720$ –780 kcal mol⁻¹), indicating their thermodynamic stability (Tables S6 and S7, ESI[†]).

According to an energy decomposition analysis (EDA; Tables S8 and S9, ESI[†]), the energy of electrostatic interactions (ΔE_{elstat} , 50–55%) between ML^+ and $P_2N_3^-$ fragments gives slightly higher contribution to the total attractive interactions compared to the orbital interaction energy (ΔE_{orb} , 45–50%). EDA results for $M(\eta^5-C_5H_5)_2$ compounds show that $M(\eta^5-C_5H_5)^+$ and $C_5H_5^-$ fragments interact more strongly than ML^+ and $P_2N_3^-$ ones ($\Delta \Delta E_{int} = 24$ –58 kcal mol⁻¹) because of the gain in electrostatics (ΔE_{elstat} , 57–58%).

In summary, exploring the potential energy surfaces of $P_2E_3^-$ (E = N, P, As, Sb, Bi) anions revealed planar five-membered cyclic structures for each E under study. An increased stability of the structures over the corresponding isomers can be explained by their aromatic properties. Two different structural motifs were found for aromatic anions (E = N, As, Sb, and Bi), one of them being theoretically characterized for the first time. Remarkably, the recently synthesized $P_2N_3^-$ aromatic anion turned out to lie ca. 16 kcal mol⁻¹ higher in energy than the global minimum, which is the aromatic anion predicted in this work. Substitution of the $C_5H_5^-$ or $C_5Me_5^-$ ligand by the $P_2N_3^-$ moiety can lead to sandwich complexes with bonding properties, similar to the classical metallocene ones. Recent progress in the synthesis of



aromatic pnictogen-containing heterocycles^{15,25–27} allows us to expect that the present contribution will stimulate further development of this research field.

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