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The stability of biradicaloid *versus* closed-shell $[E(\mu\text{-}XR)]_2$ (E = P, As; X = N, P, As) rings. Does aromaticity play a role?†

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High-level multiconfigurational self-consistent field calculations, supplemented with multiconfigurational quasi-degenerate perturbation theory *ab initio* calculations with the aug-cc-pVTZ basis set, demonstrate that the $[E(\mu\text{-}XH)]_2$ (E = P, As; X = N, P, As) compounds possess one planar and one butterfly-like isomer. The calculations predict that for X = N, planar isomers, which bear substantial biradicaloid character, are more stable than their butterfly-like counterpart isomers, which feature closed-shell electronic structures. This has been ascribed to the fact that the increased bond angle strain at E–N–E is not compensated by the E–E σ (deformed) bond formation in the butterfly-like isomers, yielding the planar structures, which hold wider E–N–E bond angles, as the most stable isomers. As N is substituted by heavier atoms, either P or As, the E–P(As)–E bond angle strain is released and, additionally, as the formed E–E σ-bond is less deformed, the butterfly isomer becomes the most stable isomer. Subsequent evaluation of the normalized Giambiagi multicenter electron delocalization indices revealed no sign of electron delocalization in the four-membered rings and consequently, it is concluded that aromaticity does not play any role in the stabilization of the planar isomers.

1 Introduction

Recently, Schulz *et al.*[1,2] reported on the synthesis, characterization and reactivity of 2,4-diterphenyl-*cyclo*-1,3-dipnictogen-2,4-diazane, $[E(\mu\text{-NTer})]_2$, (E = P, As), four-membered ring compounds that possess biradicaloid character, and are stable in inert atmospheres, in solutions of THF, diethyl ether or toluene, and in the solid state. These compounds, synthesized from the reaction of aniline hydrochloride with an excess of ECl_3, are envisaged to be good starting materials for polycyclic inorganic and organometallic compounds.

Schulz *et al.* describe the resulting 1,3-dichloro-2,4-diphenyl-*cyclo*-1,3-dipnictogen-2,4-diazane (**1**) as an eight electron four-membered ring, which could undergo further reactions to yield species with electronic structures that they claim to be related to Hückel-like $(4n + 2)$ aromatic π-electron species (**2–4**) and that their delocalization stabilizes the biradicaloid.[1]

The formal reaction scheme is shown in Fig. 1, and in accordance with their reports, the neutral compound (**3**) is pinpointed as the most promising candidate for synthesis through the two electron reduction along with the removal of the chlorine substituents, which can be efficiently carried out as indicated in Fig. 2. The resulting dipnictogen species form a planar ring with no transannular E–E bond which is indicative of the biradical character of both E centers.

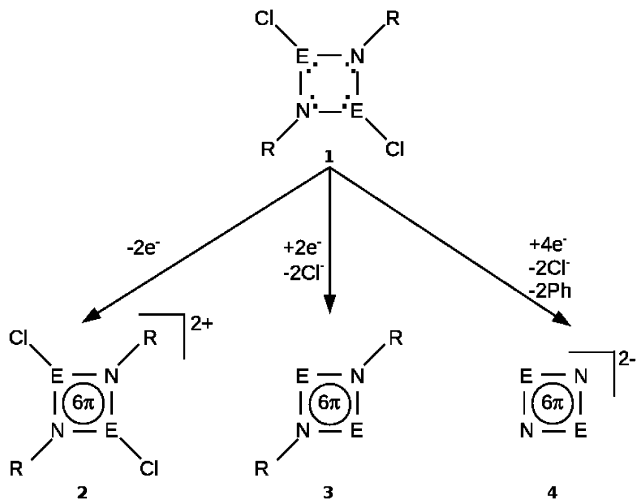

Fig. 1 Four-membered all pnictogen rings bearing 6π electrons derived from 1,3-dichloro-2,4-di(R)-*cyclo*-1,3-dipnictogen-2,4-diazane.

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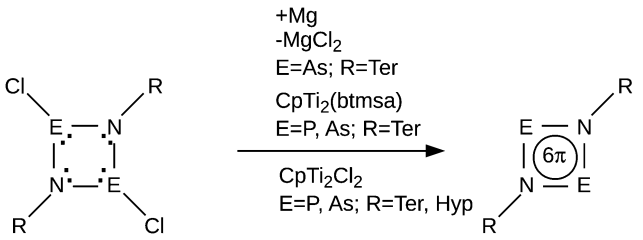

Fig. 2 Reduction of 1,3-dichloro-2,4-di(R)-*cyclo*-1,3-dipnictogen-2,4-diazane.

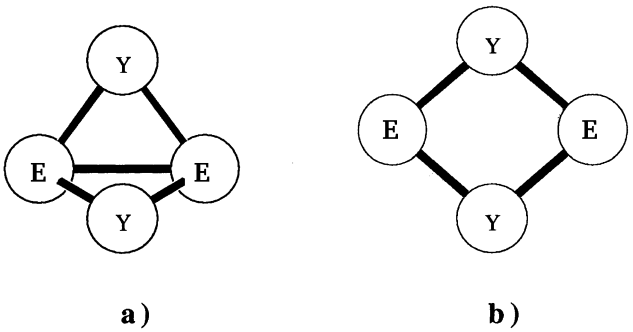

Fig. 3 Butterfly (a) and planar (b) E_2Y_2 structures.

However, the stability of these remarkable four-membered ring molecules is ascribed to the aromaticity of 6π electrons within the ring. Support for this claim is given on the basis of single-reference B3LYP/6-31G(d,p) type calculations for the geometry optimization and complemented with NICS(0) calculations at the same level of theory. The estimated value of NICS(0) is −6 ppm for the $[E(\mu\text{-NTer})]_2$, (E = P, As), species.

In this context one immediately raises the question as whether the level of theory used is sufficient for the investigation of the electronic structure and the associated properties, NICS aromatic indices included, for these inorganic species,[3] given that they possess biradicaloid character. Single-reference methods, like B3LYP, are ill-posed for biradicaloids, which require multi-configurational methods to appropriately account for the energetic near-degeneracy of spatially separated orbitals bearing a fraction of the electron. Single-reference methods cannot deal with either of them, namely, near-degenerate orbitals and fractional occupation of orbitals. In this vein, it is worth mentioning that Niecke and Schoeller *et al.*[4–6] have extensively studied the biradical character of the related 1,3-diphosphacyclobutane-2,4-diyl and its substituted compounds with multi-configurational self-consistent methods. They concluded that these species are best described as biradicaloids, rather than as biradicals, possessing a not too large singlet–triplet energy gap. Notice that Schulz *et al.* also reported the (U)B3LYP/6-31G(d,p) singlet–triplet energy gap for their $[E(\mu\text{-XR}^*)]_2$ species. In view of the above comments such an estimate must be taken with caution.

Interestingly, in ref. 1, Schulz *et al.* commented upon the fact that the $[P(\mu\text{-PMes}^*)]_2$, which is the isovalent electronic analog of $[P(\mu\text{-NTer}^*)]_2$, has a butterfly-like geometrical structure with a transannular P–P bond.[7] The reason given is that P prefers a trigonal-pyramidal environment and N prefers the trigonal-planar one when delocalization of the lone pair (occupying a p orbital) is possible. Hence, it is concluded that the delocalization of the 6π electrons stabilizes the biradical and prevents transannular bonding. Remarkably, the reason behind such a switch in the preferred environment is not resolved.

In 1997 we published an extensive study[8] of the molecular electronic structure of the E_2Y_2 (E = N, P, As, Sb; Y = O, S, Se, Te) rings, which might provide a clue to understand the above alluded to switch in the above-mentioned "preferred environment" on going from N to P and also shed light on the aromaticity of these species in terms of the number of delocalized and localized electrons in the four-membered ring. We focused ourselves on two isomers of the E_2Y_2 species referred to as butterfly-like and planar ones, see Fig. 3. The latter presents a biradicaloid character in its lowest energy lying singlet spin state and the former has no biradical character, *i.e.*, its electronic structure can be represented by a single determinant state.

At first glance, it can be expected that isomers in which all electrons are paired would be less reactive than their biradicaloid counterparts. However, formation of the E–E σ-bond forces the structure to pyramidalize and, consequently, to decrease the E–Y–E angle. While the formation of the E–E σ-bond stabilizes the structure the concomitant shrinking of the E–Y–E angle generates destabilizing bond-angle strain. In the end, it will be the interplay between these two opposite factors which determine which of the two isomers is more stable.

Thus, there are a number of E_2Y_2 structures for which the more reactive biradicaloid structure is the lowest in energy. In particular, it is observed[8] that for Y = O, planar biradicaloid structures are favored over the closed-shell butterfly-like ones. Furthermore, for E = N, the planar structures are also found to be more stable, but larger Y atoms lead to a preference for the butterfly-like N_2Y_2 isomers.

In view of the conclusions listed above, it seems fair to propose that the stability of the planar biradicaloid $[E(\mu\text{-NTer})]_2$, (E = P, As), species might result from the relaxation of the bond-angle strain at the nitrogen atoms of the four-membered ring in the planar conformer which overcompensates the breaking of the transannular E–E σ-bond of the butterfly-like structures.

Recall that Schulz *et al.* claim[1,2] that the stability of the planar biradicaloid structures stems from the aromaticity of their six delocalized π-electrons, along with the sterical protection provided by the bulky Ter substituents at positions 2 and 4 of the four-membered ring.

This reseach aims at elucidating which of the two above-mentioned mechanims accounts better for the stability of the title species.

2 Methods

Using the GAMESS[9] program, we have optimized without symmetry constraints and characterized as stationary points of the potential energy surface with the frequency analysis the butterfly and planar isomers of the $[E(\mu\text{-XH})]_2$ (E = P, As; X = N, P, As) species at the

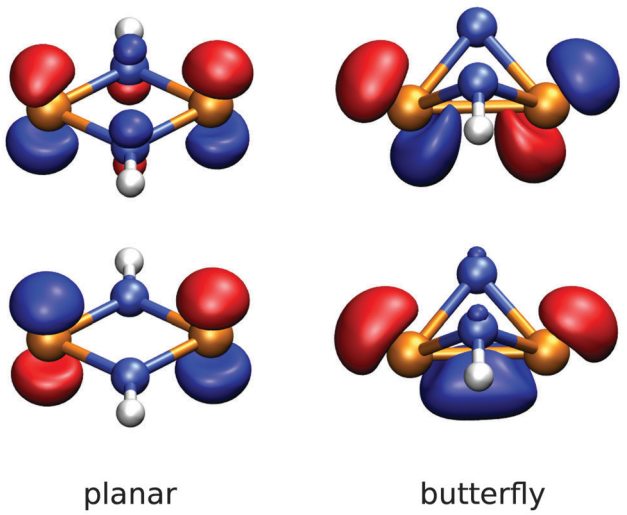

Fig. 4 The two molecular orbitals included in the active space of the MCSCF(2,2)/aug-cc-PVTZ wave function.

multiconfigurational self-consistent field (MCSCF) level of theory[10] using the augmented correlation-consistent polarized valence triple-ζ basis set,[11] hereafter denoted MCSCF(2,2)/aug-cc-pVTZ.

The active space of the MCSCF wave function was carefully chosen and consists of two electrons in the E–E bonding and antibonding orbitals (see Fig. 4).

In the case of butterfly structures, these two molecular natural orbitals were of a_1 and b_1 symmetry, while in the planar isomers the b_{1g} and b_{2g} orbitals of the ring's π-system were included. Augmentation of this active space to the six electrons and four orbitals of the ring's π-system yielded no appreciable changes either in the optimized structures or in their relative energies.

Subsequently, multiconfigurational quasi-degenerate perturbation (MCQDPT) theory[12] was used to include the dynamic correlation. All valence and virtual orbitals have been correlated in the MCQDPT calculations. Inconsistencies caused by the so-called intrude states which appear when the perturbation expansion of the reference MCSCF wave function has vanishingly small energy denominators were remedied by shifting them by 0.02 a.u., as recommended earlier.[13]

The aromaticity of the isomers characterized has been assessed by means of the so-called delocalization-based indices, which have been found to perform well in describing the aromaticity of highly correlated electronic structures in general,[14] and of the electronic states with a large degree of multiconfigurational character in particular.[15] We will focus on the normalized Giambiagi multicenter electron delocalization index I_{NG},[16]

$$I_{NG} = \frac{\pi^2}{4}\frac{[I_G(\mathcal{A})]^{1/N}}{N\delta(\mathcal{A})} \quad (1)$$

where $\mathcal{A}$ is an ordered set $\{A_k\}_{k=1}^{N}$ of the N atoms of the ring, and

$$I_G(\mathcal{A}) = \int d\mathbf{r}_1 \hat{A}(\mathbf{r}_1)\Gamma(\mathbf{r}_1,\mathbf{r}_1)\int\cdots\int\prod_{k=2}^{N}\hat{A}_k(\mathbf{r}_k)\Gamma(\mathbf{r}_k,\mathbf{r}_{k+1})d\mathbf{r}_k \quad (2)$$

is the non-normalized Giambiagi electron delocalization multicenter index.[17] It is worth mentioning that in eqn (1), the numerical factor accounting for the straight linear correlation between I_{NG} and the topological resonance energy per π-electron, has not been included for convenience. $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is the spinless one-electron density matrix, and the projector operator

$$\hat{A}_k(\mathbf{r}_1) = \int_{\Omega(A_k)}\delta(\mathbf{r}_1 - \mathbf{r}')d\mathbf{r}' \quad (3)$$

restricts the integrals in eqn (2) to the atomic basins, $\Omega(A_k)$, of atoms A_k, which are defined by using the fuzzy-atom partition method of Mayer and Salvador.[18,19] Finally, in eqn (1), $\delta\mathcal{A}$ stands for the total delocalization index,[20] which is the sum of all the atom-pair delocalization indices, of the ring. $D(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2)$ is the diagonal element of the spinless two-electron density matrix.

$$\delta(A_j,A_k) = 2\int d\mathbf{r}_1\hat{A}_j(\mathbf{r}_1)\Gamma(\mathbf{r}_1,\mathbf{r}_1)\times\int d\mathbf{r}_1\hat{A}_k(\mathbf{r}_1)\Gamma(\mathbf{r}_1,\mathbf{r}_1) - 2\int d\mathbf{r}_1\hat{A}_j(\mathbf{r}_1)\int d\mathbf{r}_2\hat{A}_k(\mathbf{r}_2)D(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2) \quad (4)$$

The I_{NG} index is known to capture the extent of delocalization of the electron density, which is considered to be one salient signature of aromaticity.[21] Additionally, it produces the appropriate quantitative ordering of aromaticities of both mono- and heterocyclic compounds.[16] Table 3 shows the normalized Giambiagi multicenter electron delocalization indices, I_{NG}, computed with the ESI-3D[22] program for all the isomers calculated using their corresponding MCSCF(2,2) multiconfigurational wavefunctions.

3 Results

The relative energies at the MCQDPT level and the geometrical data for the optimized structures calculated at the MCSCF(2,2)/aug-cc-pVTZ level of theory can be found in Table 1.

We can observe that the P–P distance decreases by 0.496 Å upon formation of the transannular P–P bond in $[P(\mu\text{-NH})]_2$. But it decreases substantially more upon formation of the transannular P–P bond in $[P(\mu\text{-PH})]_2$, with a reduction of 1.102 Å, and 1.223 Å for $[P(\mu\text{-AsH})]_2$. Concomitantly, the optimum E–X–E bond angles decrease as well upon P–P transannular bond formation, namely, from 100.0 degress to 72.6 degress in $[P(\mu\text{-NH})]_2$, and from 107.2 degrees to 58.8 degrees in $[P(\mu\text{-PH})]_2$, and from 93.3 degrees to 55.4 degress for $[P(\mu\text{-AsH})]_2$. The larger acuteness of the latter structure reflects the fact that the P and As atoms can bear more bond angle strain as compared to the smaller N atom.

A similar conclusion is reached by inspecting the geometrical data corresponding to the $[As(\mu\text{-NH})]_2$, $[As(\mu\text{-PH})]_2$ and $[As(\mu\text{-AsH})]_2$ structures. Thus, the decrease of the As–As distance upon As–As transannular bond formation is 0.477 Å for $[As(\mu\text{-NH})]_2$, but it is 1.049 Å for $[As(\mu\text{-PH})]_2$, and 1.068 Å for $[As(\mu\text{-AsH})]_2$. The E–X–E bond angles decrease from 101.8 degrees to 76.2 degrees in combination with N, and from 100.5 degress to 63.0 degress with P, and from 92.1 degrees to 60.3 degrees with As.

Table 1 Relative energies at the MCQDPT level, and the lowest frequency and geometry parameters of the MCSCF(2,2)/aug-cc-pVTZ optimizations. ΔE in kcal mol^{-1}, ν_{min} in cm^{-1}, bond lengths in Å, bond angles and dihedral angles in degrees

	[P(μ-XH)]$_2$			[As(μ-XH)]$_2$		
	N	P	As	N	P	As
Planar						
ΔE	0.0	0.0	0.0	0.0	0.0	0.0
ν_{min}	338.6	175.8	39.3	238.6	102.3	−19.8
E–X	1.684	2.055	2.333	1.814	2.268	2.453
E–E	2.580	3.308	3.393	2.814	3.494	3.531
X–H	0.990	1.396	1.508	0.992	1.400	1.510
E–X–E	100.0	107.2	93.3	101.8	100.5	92.1
X–E–X	80.0	77.9	86.7	78.2	100.8	87.6
X–E–E–X	180.0	176.5	179.9	180.0	180.0	167.8
Butterfly						
ΔE	21.5	−98.9	−176.3	17.2	−27.7	−180.7
ν_{min}	468.4	234.5	148.4	280.9	192.1	127.0
E–X	1.760	2.212	2.333	1.893	2.339	2.450
E–E	2.084	2.206	2.170	2.337	2.445	2.463
X–H	1.004	1.410	1.516	1.004	1.409	1.515
E–X–E	72.6	58.8	55.4	76.2	63.0	60.3
X–E–X	80.1	82.1	84.3	78.1	80.4	81.6
X–E–E–X	106.0	98.6	97.5	106.4	98.4	98.1

It is worth mentioning that the two symmetry distinct optimum P–P bond lengths of the butterfly isomer of [P(μ-PH)]$_2$ are indeed very similar, 2.212 Å and 2.206 Å, and resemble closely the experimental P–P bond length of T_d P_4, 2.210 Å.[23] Likewise, the butterfly isomer of [As(μ-As)]$_2$ also shows very similar As–As optimum bond lengths, 2.463 Å and 2.450 Å, which agree closely with the experimetal As–As bond length of T_d As_4, 2.435 Å.[24] In both cases, it seems that saturation of one of the bonds of the tetrahedral tetramers does not affect noticeably the remaining bonds.

The ability of the hydrogen saturated atom to hold bond angle strain has, nonetheless, a big effect on the relative stability of the two isomers studied, since in all cases the transannular bond is formed by the same atoms, either P or As, therefore the σ contribution to the bond would be almost the same in all cases.[25] Thus, when the hydrogen saturated atoms are nitrogen, the planar isomer with long transannular distances, results to be the most stable isomer. Namely, the planar isomer of [P(μ-NH)]$_2$ is more stable than its corresponding butterfly isomer by 21.5 kcal mol^{-1}, while for [As(μ-NH)]$_2$ it is by 17.2 kcal mol^{-1}. However, when N is substituted by heavier atoms, like P or As, the butterfly isomer turns out to be the most stable isomer, by 98.9 kcal mol^{-1} for [P(μ-PH)]$_2$ and 176.3 kcal mol^{-1} for [P(μ-AsH)]$_2$, and by 27.7 kcal mol^{-1} for [As(μ-PH)]$_2$ and 180.7 kcal mol^{-1} for [As(μ-AsH)]$_2$, in accordance with the experimetal result of Schulz *et al.*[1,2] who found only the planar isomer for [E(μ-NTer)]$_2$, (E = P, As), and of Riedel *et al.*[7] who found exclusively the butterfly isomer for [P(μ-PMes)]$_2$. The absolute and relative energies at both CASSCF and MCQDPT levels of theory are given in Table S1 of the ESI.†

The biradicaloid nature of the planar isomers is revealed by the calculated occupation number of the natural orbitals of their corresponding MCSCF(2,2)/aug-cc-pVTZ active spaces, shown in Table 2.

Table 2 Natural orbital occupancies of the MCSCF(2,2)/aug-cc-pVTZ active natural orbitals

	[P(μ-NH)]$_2$		[P(μ-PH)]$_2$		[P(μ-AsH)]$_2$	
	NO #23	NO #24	NO #31	NO #32	NO #49	NO #50
Planar	1.77	0.23	1.88	0.12	1.27	0.73
Butterfly	1.92	0.08	1.95	0.05	1.95	0.05
	[As(μ-NH)]$_2$		[As(μ-PH)]$_2$		[As(μ-AsH)]$_2$	
	NO #41	NO #42	NO #49	NO #50	NO #67	NO #68
Planar	1.73	0.27	1.71	0.29	1.16	0.84
Butterfly	1.87	0.13	1.93	0.07	1.94	0.06

While the butterfly isomers have occupation numbers close to 2 and 0, respectively, the occupation numbers of the planar isomers largely deviate from these figures. In particular we would like to draw attention to the occupation numbers of planar [As(μ-AsH)]$_2$, 1.16 and 0.84, which pinpoint to this structure as an almost pure biradical. Recall that this planar structure is not the most stable one (*vide infra*). On the other hand, planar [P(μ-NH)]$_2$ and [As(μ-NH)]$_2$ are the most stable isomers and as shown in Table 2 bear substantial biradicaloid character, *i.e.*, their structure features two unpaired, singlet coupled, electrons each localized on each of the phosphorus or arsenic atoms. Indeed, the Lewis structure depicted in Fig. 5 can be ascribed to 6π-electrons of the four-membered ring. If these six electrons were delocalized along the ring it could, in principle, account for the 6π-electron Hückel like aromaticity.

The degree of electron delocalization has been examined with the normalized Giambiagi multicenter electron delocalization index I_{NG}, described in Section 2. The calculated indices for all the isomers are shown in Table 3. One remarkable feature observed in Table 3 is that for all the species considered in the present research the values of the normalized Giambiagi multicenter electron delocalization indices of the butterfly structures are larger than those of their corresponding planar ones. Since for the butterfly structures all the valence electrons are involved in chemical bonding, one must expect them to possess very little electron delocalization. Hence one can take the I_{NG} values of the butterfly isomers as reference small values for the electron delocalization index. Our calculations predict even less electron delocalization for the planar isomers. Furthermore, recall that the value of the MSCSF(8,8)/6-311G** normalized Giambiagi multicenter electron delocalization of the $^1A_{1g}$ ground state of Al_4^{2-}, which has 6 valence electrons as our title species do, is I_{NG} = 52.4.[26]

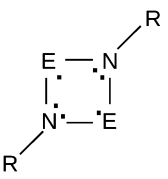

Fig. 5 The biradicaloid Lewis structure.

Table 3 Normalized Giambiagi multicenter electron delocalization index, I_{NG}, (multiplied by 10^3) calculated at the MCSCF/aug-cc-pVTZ level of theory

	Planar	Butterfly
$[P(\mu\text{-}NH)]_2$	6.6	35.5
$[P(\mu\text{-}PH)]_2$	19.7	28.0
$[P(\mu\text{-}AsH)]_2$	25.2	26.7
$[As(\mu\text{-}NH)]_2$	20.6	27.3
$[As(\mu\text{-}PH)]_2$	21.4	27.4
$[As(\mu\text{-}AsH)]_2$	22.8	26.0

Considering the above-mentioned facts, one can conclude that while butterfly isomers should be stabilized over planar ones due to bonding arguments, the strain on the E–X–E angle leads to destabilization of these structures. Additionally, for the species with small X, like nitrogen, the E–E transannular σ-bond is significantly strained (see Fig. 4) and therefore some of the stabilization gained by forming that bond is lost, giving in this way a chance to the more reactive planar biralicaloid isomers to became the most stable ones. Schulz *et al.*[1,2] have taken advantage of this fact in order to synthesize their stable biradicaloid $[E(\mu\text{-NTer})]_2$, (E = P, As), four-membered ring compounds.

4 Conclusions

We have performed high-level MCQDPT//MCSCF(2,2) *ab initio* calculations with the aug-cc-pVTZ basis set for the planar and butterfly isomers of the $[E(\mu\text{-}XH)]_2$ (E = P, As; X = N, P, As) compounds. All isomers correspond to stable species of the corresponding potential energy surface.

Our calculations predict that for X = N, planar, biradicaloid isomers should be more stable than their butterfly closed-shell counterparts. This is due to the fact that the increased bond angle strain at E–N–E (E = P, As) is not compensated by the E–E σ (deformed) bond formation in the butterfly like isomers, yielding the planar structure, which holds a wider E–N–E bond angle, as the most stable isomer. As N is substituted by large atoms, either P or As, the E–P(As)–E bond angle strain is released and, additionally, as the formed E–E σ-bond is less deformed, the butterfly isomer becames the most stable isomer.

We have found no signs of electron delocalization in the planar four-membered rings and consequently, we believe that aromaticity does not play any role in the stabilization of planar isomers.

Acknowledgements

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