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Structure–property relationships in phosphole oligomers: a theoretical insight

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Paper dedicated to Professor François Mathey, on the occasion of his 60th bithday, whose work on the phospholes chemistry remains a source of inspiration

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Abstract

The influence of cyclic π-conjugation and interannular rotation on the vertical ionization energies and energy gaps of phosphole oligomers has theoretically been investigated which provided some useful structure–property relationships. While vertical ionization energies were obtained from negative HOMO-energies using the Hartree–Fock method, energy gaps were calculated using a DFT/hybrid method (B3LYP). Combination of geometric (JULG and $d_{C\alpha}$) and magnetic (NICS) criteria gives a qualitative indication about the competition between the cyclic- and the carbon backbone π-conjugation. Results of this preliminary theoretical study suggest that phosphole oligomers have interesting tunable electronic properties.

Keywords: Phosphole oligomers; Ab initio calculations; π-Conjugation; Interannular rotation; Energy gaps; Vertical ionization energies

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1. Introduction

Organic heterocyclic polymers such as polythiophenes and polypyrroles have attracted much attention during the last decade owing to their interesting electrical and/or (non-linear) optical properties [1,2]. In contrast, the polymer chemistry of phospholes, the phosphorus analogs of thiophenes, is not well developed yet. Mathey and coworkers [3–6] have been attempting to design efficient routes to prepare a variety of phosphole oligomers that constitutes the first necessary steps toward phosphole polymers. Previous semi-empirical [7,8] and density functional [9] studies of heterocyclic oligomers have identified some polyphospholes as having remarkable conductive properties. Recently, we have reported a theoretical study of the properties of the phosphole monomer [10]. We now attempt to evaluate some potentially interesting properties of phosphole oligomers.

It is well known that oligomer properties are determined, on the one hand, by the building blocks used, and on the other hand, by the way those building blocks are connected to each other. The influence of cyclic delocalization and interannular rotations on the vertical ionization energy (IE) and the energy gap (E_g) is of particular interest [11]. Cyclic delocalization results in a competition between π-electron confinement within the rings and delocalization along the carbon backbone of the oligomer chain [12]. Strong interannular rotations usually contribute to an increase in the energy gaps. The most common way in synthetic chemistry to modify the HOMO and LUMO levels of a π-electron system involves the grafting of electron-donating and/or electron-accepting substituents that will, respectively, increase the HOMO level or lower the LUMO one. In this article, we will, however, concentrate on the properties of the phosphole backbones rather than on the substituent effect.

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2. Computational details

Geometries of phosphole oligomers, from monomers through hexamers, were optimized using density functional theory [13] employing the B3LYP hybrid functional. The split valence plus polarization SV(P) [14,15] and 6-31G* [16] basis sets were used. Both basis sets have comparable quality. The TURBOMOLE program [14] was employed for optimizing molecular geometries and calculating electronic properties such as vertical ionization energies and energy gaps. The GAUSSIAN 98 program [16] was used for computing NMR shielding tensors and torsional potential curves. Here we consider mainly the oligomers in which the phosphole units are connected to each other at the C_α-position of the ring. We have paid particular attention to their vertical ionization energies and energy gaps.

Vertical IEs were obtained from negative HOMO-energies using the Hartree–Fock method. The energy gaps (E_g) were determined by taking differences in frontier orbital HOMO and LUMO energy levels using a DFT/hybrid approach [9,17,18]. We are well aware that the present approaches provide rather crude estimates for the IEs and energy gaps; however, we think that the results are internally consistent pointing toward the trends of the properties considered. Therefore, we do not attach much importance to their absolute computed values, but rather on the relative evolutions.

As mentioned in Section 1, there is a competition between two types of π-conjugation, namely, the one over the ring versus the other along the oligomer backbone.

A previous study on phosphole monomers [10] has shown that combination of geometric (Julg index) and magnetic (NICS) criteria leads to an interesting approach to analyze the π-electron delocalization in conjugated heterocyclic systems. Since we are considering oligomers, the interring bond distances $d_{C\alpha}$ are also taken into account in order to reflect the strength of π-electron conjugation between neighboring repeat units. The Julg index [19], referred to hereafter as JI, which has proved to be useful for a quantitative comparison within five-membered heterocycles, is defined in terms of the deviations of the individual C–C bond lengths (r_i) from the mean carbon–carbon bond length (r). It constitutes a measure of the bond length alternation (π-electron conjugation) in the diene unit and thereby the aromaticity in the considered heterocyclic structure. In the nucleus-independent chemical shift-approach [20], the absolute magnetic shieldings are computed at the ring center (non-weighted mean of the heavy atom coordinates). With correspondence to the familiar NMR chemical shift convention, the sign of the computed values are reversed: negative NICS values denote the existence of aromaticity. The NMR shielding tensors are calculated with the gauge-independent atomic orbital (GIAO) method implemented in GAUSSIAN 98 [16].

Conformational energies were evaluated at the HF, MP2 and B3LYP levels. Previous work on 2,2′-bipyrrole [21], 2,2′-bifuran [22], 2,2′-bithiophene [23] and bithiophene analogs [24,25] revealed the MP2 method to be the best in evaluating conformational energies and pointed out that DFT methods in general overestimate the stability of planar π-systems.

3. Results and discussion

First, some comments will be made on the geometries and conformations of the phosphole oligomers considered. Subsequently, the influence of cyclic π-conjugation, chain length and interannular rotation on the ionization energies and energy gaps will be discussed. The vertical ionization energies and energy gaps for different conformers of phosphole oligomers are given in Table 1. JIs interring bond distances ($d_{C\alpha}$) and NICS values are listed in Table 2. The other energetics relative to the conformations are grouped in Tables 3 and 4. Fig. 1 represents the orbital correlation diagram for HOMO-1, HOMO and LUMO between phosphole (PH) and planar phosphole (Pl PH) monomers. The

Table 1
Calculated vertical ionization energies [a] (IE) and energy gaps [b] (E_g) for phosphole oligomers (both are given in eV)

$PH_{non\text{-}alt}$ (*anti–gauche*)				PH_{alt} (*anti*)			Pl PH (planar *anti*)		
n_C	Symmetry	IE	E_g	sym.	IE	E_g	Symmetry	IE	E_g
4	C_s	8.9	5.2				C_{2v}	7.8	5.7
8	C_2	7.6	3.6	C_1	7.6	3.5	C_{2h}	7.2	4.3
12	C_s	7.0	2.8	C_1	7.0	2.9	C_{2v}	6.6	3.6
16	C_2	6.7	2.4	C_1	6.7	2.4	C_{2h}	6.4	3.2
20	C_s	6.5	2.2	C_1	6.5	2.1	C_{2v}	6.2	3.0
24	C_2	6.4	2.0	C_1	6.4	1.9	C_{2h}	6.1	2.9

[a] IEs at HF/SV(P) level.

[b] E_g values at B3LYP/SV(P) level.

Table 2
Julg indices, *interring bond distances* $d_{C\alpha}$ (Å) and NICS [a] values (ppm, between brackets) for phosphole oligomers optimized at the B3LYP/SV(P) level

Conformation		Mono	Di	Tri	Tetra	Penta	Hexa
PH$_{non\text{-}alt}$ (*anti–gauche*)	Outer	0.737 (−5.5)	0.820 (−4.4)	0.831 (−4.3)	0.835	0.835	0.835
			1.447	*1.443*	*1.441*	*1.441*	*1.441*
	↓			0.908 (−3.4)	0.918	0.920	0.923
					1.438	*1.436*	*1.436*
	Inner					0.931	0.934
							1.435
PH$_{alt}$ (*anti*)	Outer	0.737 (−5.5)	0.816 (−3.8)	0.826 (−3.9)	0.826	0.832	0.832
			1.449	*1.444*	*1.443*	*1.443*	*1.443*
	↓			0.898 (−2.4)	0.915	0.920	0.920
					1.438	*1.437*	*1.436*
	Inner					0.931	0.935
							1.435
Pl PH (planar *anti*)	Outer	0.980 (−18.4)	0.989 (−16.6)	0.991 (−16.7)	0.991	0.991	0.991
			1.452	*1.450*	*1.449*	*1.450*	*1.450*
	↓			0.999 (−15.1)	0.999	0.999	0.999
					1.447	*1.447*	*1.446*
	Inner					0.999	0.999
							1.446

[a] The NICS calculations are performed using the GIAO-method at the HF/6-311G* level.

Table 3
Energetics (kJ mol^{-1}) of stationary points in 2,2′-biphosphole on B3LYP/6-31G* optimized geometries

Structure	Method	Conformation					
		syn–gauche	*perp*	*anti–gauche*	*perp*	*syn–gauche*	*syn*
PEC PH$_{alt}$	HF/6-31G*	7.4	10.7	-	10.7	7.4	12.2
	B3LYP/6-31G*	7.3 (−26.4)	20.4 (−92)	-	20.4 (92)	7.3 (26.4)	8.4
	MP2/6-31G*	5.5	14.4	-	14.4	5.5	9.0
PEC PH$_{non\text{-}alt}$	HF/6-31G*	-	13.9	0	13.3	5.6	-
	B3LYP/6-31G*	-	24.6 (−81.3)	0 (−159.8)	23.7 (101.7)	4.6 (29.8)	-
	MP2/6-31G*	19.8	0	18.7	3.6	-	

The torsional angle (°) is given between brackets. Energies in PEC PH$_{alt}$ are taken relative to the *anti*-conformer. In PEC PH$_{non\text{-}alt}$ the *anti–gauche* structure is taken as reference.

Table 4
Influence of interannular rotation ϕ (°) on JI, $d_{C\alpha}$ (Å) and NICS [a] (ppm), IE [b] (eV) and E_g [c] (eV) values of conformations [d] lying on PEC PH$_{alt}$ and PEC PH$_{non\text{-}alt}$

PEC	ϕ	JI	$d_{C\alpha}$	NICS	ε_{HOMO}	ε_{LUMO}	IE	E_g
PH$_{alt}$	0	0.815	1.452	−4.4	−5.5	−2.0	7.4	3.5
	26	0.800	1.452	−4.6	−5.6	−1.9	7.5	3.7
	92	0.754	1.468	−4.8	−6.2	−1.2	8.5	5.0
	180	0.802	1.446	−3.8	−5.5	−1.9	7.4	3.6
PH$_{non\text{-}alt}$	−160	0.809	1.444	−4.4	−5.5	−1.9	7.4	3.6
	−81	0.754	1.469	−4.8	−6.2	−1.2	8.5	5.0
	30	0.812	1.448	−4.9	−5.5	−1.8	7.4	3.7
	102	0.754	1.470	−4.7	−6.2	−1.2	8.5	5.0

[a] The NICS calculations are performed using the GIAO-method at the HF/6-311G* level.

[b] The IEs are computed at HF/SV(P) level.

[c] The E_g values are calculated at B3LYP/SV(P) level.

[d] The conformations are optimized at B3LYP/6-31G* level.

trend of HOMO and LUMO orbitals with increasing chain-length for PH- and Pl PH oligomers is given in Fig. 2. The shapes of the HOMO's of puckered and planar phosphole monomers and dimers are shown in Fig. 3. Figs. 4 and 5 represent the potential energy curves for PH_{alt} and $PH_{non\text{-}alt}$ conformers of 2,2′-biphosphole, respectively. The HOMO and LUMO orbitals for coplanar and perpendicular conformations of 2,2′-biphosphole are plotted in Fig. 6.

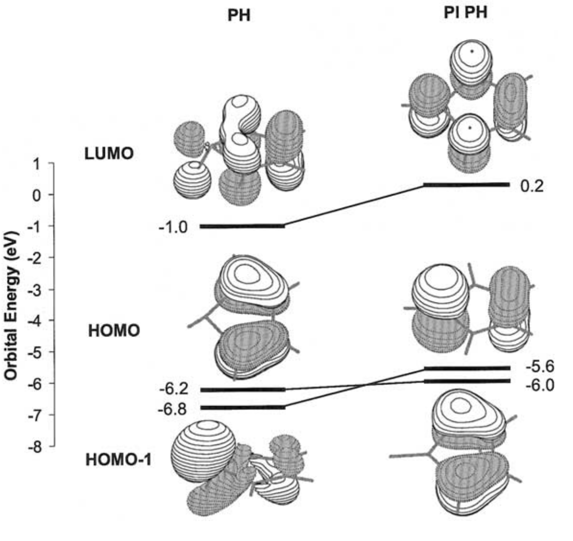

Fig. 1. Orbital correlation diagram for HOMO-1, HOMO and LUMO of phosphole (PH) and planar phosphole (Pl PH) monomers at B3LYP/6-31G* level.

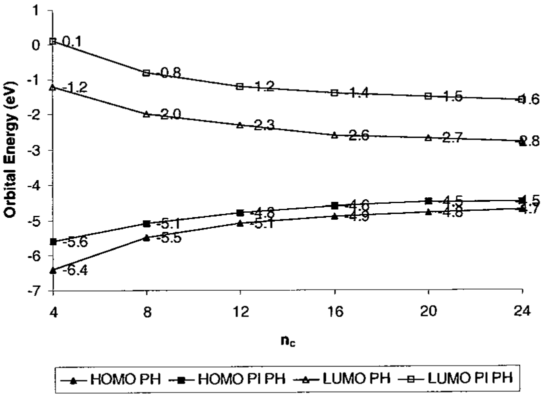

Fig. 2. Trend of HOMO and LUMO's with increasing chain length for non-aromatic PH- and aromatic Pl PH-phosphole oligomers at the B3LYP/SV(P) level.

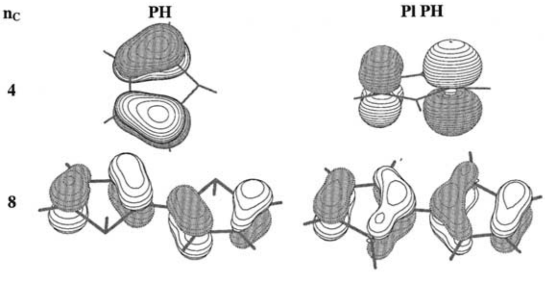

Fig. 3. Shape of the HOMO's of puckered and planar phosphole monomers and dimers.

3.1. Geometries and conformations

The parent phosphole (PH) monomer is non-planar. It contains a pyramidal phosphorus atom, which restricts cyclic electron delocalization [10,26]. The calculated NICS value of PH amounts to − 5.5 ppm (Table 2) [20]. On the other hand, the NICS value of − 18.4 ppm (Table 2) for planar phosphole [27] proves it to be an aromatic heterocycle such as pyrrole and thiophene. The planarity of the tricoordinate phosphorus and thus the aromaticity of phosphole can be influenced by substituents [28]. Here, only the parent phosphole oligomers and their planarized structures are considered. The puckered minima will further be mentioned as phosphole (PH) and the planar transition state structure for inversion as planar phosphole (Pl PH). For the oligomers, the number of possible conformations rapidly increases with increasing chain length. Therefore, calculations were restricted to structures fully optimized in the *anti*- and *anti–gauche* region since for all investigated dimers the minimum energy conformation was found in this region. Two isomers were considered for the phosphole oligomers, including the one with alternating hydrogens which is labeled as PH_{alt} and the other with hydrogens pointing in the same direction which is named $PH_{non\text{-}alt}$ (Figs. 4 and 5). The PH_{alt}-oligomers are found to be nearly coplanar ($\alpha =$ 0–2°, *anti* conformation), whereas $PH_{non\text{-}alt}$-oligomers are weakly distorted ($\alpha = 15$–20°, *anti–gauche* conformation, α denotes the deviation from coplanarity between the repeat units).

3.2. Influence of cyclic π-conjugation

The influence of cyclic π-conjugation in the monomer unit on the vertical ionization energy (IE) and energy gap (E_g) was approached by calculating IE and E_g values of oligomers based on puckered phosphole units (PH-oligomers) against oligomers based on planar phosphole units (Pl PH-oligomers).

Since properties such as IE and E_g are related to the frontier orbital energies, we thought them important to examine the behavior of HOMO and LUMO orbitals. Fig. 1 shows that the HOMO orbital for PH resembles the 1,3-butadiene HOMO and corresponds with the HOMO-1 orbital for Pl PH and both have similar energy. The HOMO-1 orbital for PH consists of the lowest π-bonding 1,3-butadiene orbital ($1b_1$) in antibonding interaction with the phosphorus lone-pair (n_P). Note that there is also some bonding interaction between the σ_{PH} orbital on phosphorus and the $\pi(b_1)$ 1,3-butadiene orbital. Increase of cyclic π-conjugation

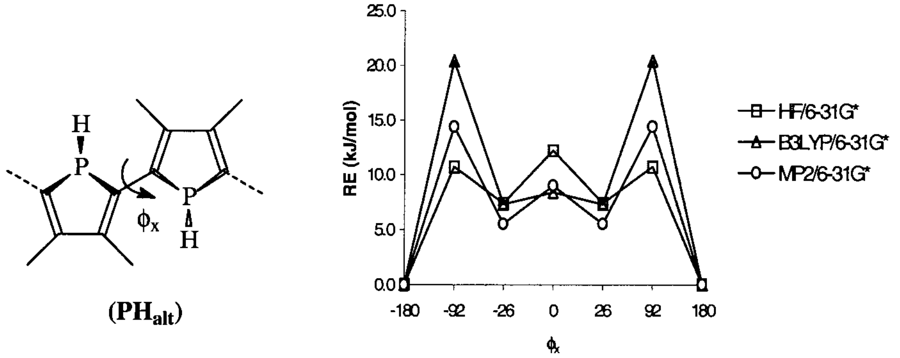

Fig. 4. Potential energy curve for PH_{alt} conformers of 2,2′-biphosphole (PEC PH_{alt}).

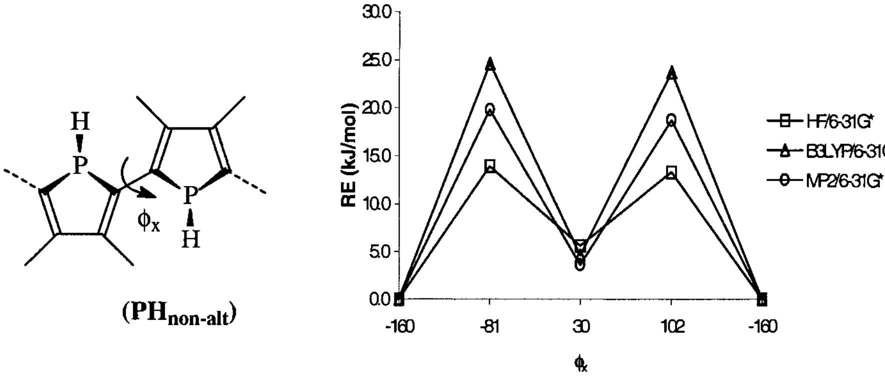

Fig. 5. Potential energy curve for $PH_{non\text{-}alt}$ conformers of 2,2′-biphosphole (PEC $PH_{non\text{-}alt}$).

by planarizing tricoordinate phosphorus allows stronger anti-bonding interaction between n_p and $\pi(b_1)$, which leads to the HOMO orbital for Pl PH which lies 1.2 eV higher in energy [29,30]. The LUMO orbital for PH, which is built up from the lowest π^* 1,3-butadiene orbital ($2b_1$) in anti-bonding interaction with n_P, undergoes the same rise in energy when planarizing phosphorus and correlates with the LUMO orbital for Pl PH. We conclude that an increase of cyclic π-conjugation by planarizing tricoordinate phosphorus enhances the interaction between n_P and the $\pi(b_1)$ 1,3-butadiene unit, which rises the HOMO and LUMO energies, for e.g. phosphole hexamers by 0.3 and 1.2 eV, respectively. This results in a small decrease in IE by 0.3 eV and a larger increase in E_g by 1.0 eV (Table 1).

An important difference between PH- and Pl PH-oligomers lies in the cyclic π-conjugation of the monomer unit. A JI and an NICS value can characterize each ring of a phosphole oligomer. The π-conjugation along the 1,3-butadiene unit of that ring will be more pronounced if the JI becomes closer to one and the phosphole ring will be more aromatic (stronger cyclic π-conjugation) if the NICS value becomes more negative. The shorter the interring bond distance $d_{C\alpha}$, the more pronounced is the linear π-conjugation between neighboring repeat units. In oligomers, the JI values for the inner rings are larger than those for the outer rings, and $d_{C\alpha}$ values between inner rings are smaller than those between outer rings (Table 2), which clearly indicates a more pronounced linear π-conjugation between inner rings than between outer rings. Cyclic π-conjugation becomes smaller in the inner rings as proven by their more positive NICS values. Since the interring bond distances $d_{C\alpha}$ are shorter in phosphole oligomers made from non-aromatic PH building blocks as compared to oligomers built up from aromatic Pl PH building blocks (Table 2), we conclude that the linear π-conjugation is more pronounced in non-aromatic PH-oligomers.

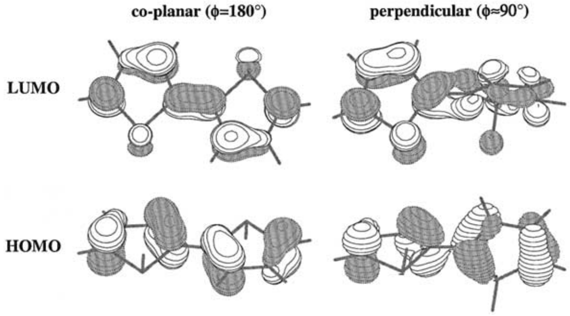

Fig. 6. HOMO and LUMO of coplanar and perpendicular conformations of 2,2′-biphosphole.

3.3. Influence of chain length

Fig. 2 confirms that the HOMO energy rises up and the LUMO energy lowers as the chain length increases. As a consequence, both IE and E_g decrease with increasing chain length. For longer oligomers, both ε_{HOMO} and ε_{LUMO} and the related properties IE and E_g appear to be leveled off, irrespective of whether the building blocks are aromatic or not. For the phosphole dimer the difference in HOMO orbital between puckered and planar phosphole is severely reduced, as compared to the monomer (Fig. 3). In fact, now they both have 1,3-butadiene HOMO in common. The HOMO orbital of the planar phosphole still has a little phosphorus n_P-contribution that explains the 0.4 eV lower IE (Table 1).

3.4. Interannular rotations

Comparison of the frontier orbital energies of *anti* PH_{alt}- with *anti–gauche* $PH_{non\text{-}alt}$- oligomers provides us with an idea about the influence of small rotational distortions on vertical IEs and energy gaps (E_g). The influence of large interannular disorders on the IE and E_g values was probed by investigating the torsional potential of 2,2′-biphosphole. Two possible starting structures have to be taken into account: while the PH_{alt}-dimer gives rise to the potential energy curve PEC PH_{alt} displayed in Fig. 4, the $PH_{non\text{-}alt}$-dimer generates the PEC $PH_{non\text{-}alt}$ shown in Fig. 5.

From results tabulated in Table 1, it is clear that a small torsional distortion ($\leq 20°$) does not influence the E_g in a significant way, and does not affect IE at all. Since JI and $d_{C\alpha}$ values recorded in Table 2 are not altered going from $PH_{non\text{-}alt}$ towards PH_{alt}, we conclude small distortions also do not affect the linear π-conjugation.

The potential energy curve PEC PH_{alt} illustrated in Fig. 4, is characterized by an *anti* conformation with an inversion center (minimum), two perpendicular transition structures, two *syn–gauche* minima separated by a *syn* transition structure. The relative energies with respect to the *anti* conformation are given in Table 3. Unless otherwise noted, the discussions hereafter are based on results obtained at the MP2-level. The torsional barrier between both *anti*- and *syn–gauche* conformers, formed by a perpendicular conformation, amounts to 14 kJ mol^{-1}. The *anti* conformer is calculated to be 6 kJ mol^{-1} more stable than the *syn–gauche* one. The torsional barrier between the *syn–gauche* conformers associated with the *syn* transition structure, amounts to merely 4 kJ mol^{-1}. PEC PH_{alt} of 2,2′-biphosphole resembles very much that of 2,2′-bifuran [22] which exhibits a similar curvature.

The potential energy curve PEC $PH_{non\text{-}alt}$ given in Fig. 5 shows that the relative stability is taken toward the *anti–gauche* structure which is 4 kJ mol^{-1} more stable than the *syn–gauche* conformer. Both minima are separated from each other by a perpendicular transition structure that is associated with a rotational barrier of 20 kJ mol^{-1}. There is no resemblance between PEC $PH_{non\text{-}alt}$ of 2,2′-biphosphole and the corresponding ones calculated for the other heterocyclic analogs.

Regarding the methods used, a comparison of the HF and B3LYP results with the MP2 results reveals that the perpendicular transition structures in PEC PH_{alt} and PEC $PH_{non\text{-}alt}$ are calculated about 5 kJ mol^{-1} too low or too high, respectively. The HF method tends to overestimate the *syn* transition state in PEC PH_{alt} by 3 kJ mol^{-1} and the *syn–gauche* minima (PEC PH_{alt}, PEC $PH_{non\text{-}alt}$) by 2 kJ mol^{-1}. For its part, the B3LYP method performs well in calculating the *syn* transition structure (PEC PH_{alt}, PEC $PH_{non\text{-}alt}$) and slightly overestimates the *syn* gauche minima (PEC PH_{alt}, PEC $PH_{non\text{-}alt}$) relative to the MP2 results.

The influence of strong rotational distortions on ε_{HOMO} and ε_{LUMO} and consequently on IE and E_g is illustrated in Table 4. In going from a coplanar ($\phi = 0$, 180°) towards a perpendicular structure ($\phi \approx 90°$), the overlap between the C_α atoms of neighboring repeat units decreases, or the interaction between the repeat units through the C_α atoms diminishes. This results in an increase in $d_{C\alpha}$ and a decrease in JI and NICS values (Table 4), indicating that the π-backbone conjugation weakens, whereas cyclic conjugation becomes more important. Fig. 6 shows that the anti-bonding interaction between the C_α values in the HOMO orbital becomes more bonding in the perpendicular conformation, which stabilizes the HOMO and results in a lowering of ε_{HOMO} by 0.7 eV compared to ε_{HOMO} in the coplanar conformation. On the other hand, the bonding interaction between the C_α values in the LUMO is weakened by torsion and ε_{LUMO} rises in energy by 0.8 eV. As a consequence, in going from the coplanar towards the perpendicular conformation there is an increase of 1.1 eV in the IE and of 1.5 eV in E_g. The same conclusion can be drawn for conformers on PEC $PH_{non\text{-}alt}$.

3.5. Tunable phosphole oligomers

In contrast to thiophene or pyrrole, phosphole is non-aromatic and possesses a heteroatom which retains a versatile reactivity [26b,c]. This offers the interesting possibility of tuning the electronic properties of phosphole oligomers by chemical modifications. For example, bulky substituents at the phosphorus atom can reduce the pyramidality of the tricoordinate phosphorus (σ^3-P) in the phosphole monomer [28]. Some alkylarylphospholes [29,30] even become aromatic, although they are not completely planar, due to the strong interaction between the phosphorus lone-pair (n_P) and the 1,3-butadiene system. Such regulation of the cyclic π-conjugation in the phosphole rings could allow fine-tuning of the energy gaps of corresponding oligomers to be realized.

4. Conclusions

Oligomer properties are determined, by the building blocks used, and the way those building blocks are connected one to another. The influence of cyclic π-conjugation in the monomer unit on the vertical ionization energy (IE) and energy gap (E_g) was approached by calculating the IE and E_g values of oligomers based on puckered phosphole units (PH) against oligomers based on planar phosphole units (Pl PH). The puckered building blocks are non-aromatic, whereas the planar ones are aromatic and characterized by strong cyclic π-electron delocalization. We have found that an increase of cyclic π-conjugation by planarizing tricoordinate phosphorus enhances the interaction between the phosphorus lone-pair (n_P) and the $\pi(b_1)$ 1,3-butadiene unit, which rises the HOMO and LUMO orbital energy and results in a small decrease in IE and a larger increase in E_g. Whereas, the $d_{C\alpha}$ values point out that any increase of cyclic π-conjugation restricts linear π-conjugation.

Comparison of the frontier orbital energies of *anti*- with *anti–gauche* PH-oligomers provides us with an idea about the influence of small rotational distortions on the IE and E_g values. The influence of large interannular disorders on the IE and E_g values was probed by investigating the torsional potential of 2,2′-biphosphole. Calculations have shown that small torsional distortions ($\leq 20°$) do not influence IE, E_g and the linear π-conjugation in a significant way, whereas large rotational disorders ($\approx 90°$) weaken linear π-conjugation and increase the IE and E_g values by more than 1 eV.

We have demonstrated that if cyclic π-conjugation could be regulated within the phosphole rings, it becomes possible to fine-tune the energy gaps of phosphole oligomers.

We hope that this information would stimulate further experimental searches for phosphole-based materials as well as theoretical studies on their potentially interesting properties. We note that the silicon analogs poly(2,5)siloles, which were proposed more than a decade ago by theoretical study [31], have been quite recently synthesized for the first time [32]. Future theoretical refinements should involve more accurate computations of the energy gaps and other energetic properties, as well as evaluations of various electric and optical properties of oligophospholes.

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