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Theoretical Study of the Structure−Property Relationship in Phosphole Monomers

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Use of the DFT method with the B3LYP functional offers an efficient way for determining geometries of phosphole structures. It also provides inversion barriers in good agreement with experiment. The molecular orbital MP2 method is better suited to calculate the relative stability of the considered isomers. Combination of geometric (Julg index) and magnetic (NICS) criteria leads to an interesting approach to analyze the π−electron delocalization and/or aromaticity in conjugated heterocyclic systems and can be used for investigation of much larger oligomers. It thus allows us to confirm that planarizing the phosphorus atom in phosphole monomers leads to a greater conjugation over the butadienic π-system and that substituents, characterized by a strongly pronounced π-system, exhibit a large extent of conjugation with the π-diene moiety of the heterocyclic system. In push−pull systems such as 2-BH_2-5-NH_2-1H-phosphole, the electron delocalization along the π-diene system is even more pronounced than in phospholes with strongly pronounced π-systems. The employed approach is also used to analyze the relationship between electron conjugation and the phosphorus inversion barrier. More relevant for chemical applications is the result that the computational study provides a method of fine-tuning of phosphole building blocks, which may enable us to obtain higher π-conjugation along the polymer backbone.

Introduction

One of the most promising aspects of low coordinated phosphorus compounds for synthetic and/or industrial applications is their possibility to form polymers. In fact, polyphospholes are an attractive target for synthetic chemists, as their polypyrroles analogues are intensively investigated for their electrical properties, whereas polythiophenes offer very interesting perspectives for their nonlinear optical properties.[1,2] Previous semiempirical[3,4] and DFT[5] studies of heterocyclic oligomers predicted some polyphospholes to have remarkable conductive properties.

Experimental groups have been attempting to design efficient routes[6−9] to prepare phosphole oligomers, which are the first necessary steps toward phosphole polymers. In this perspective, our purpose is to contribute to these investigations by deriving computationally some useful structure−property relationships of phosphole monomers using high level ab initio and density functional theory calculations. These methods are expected to support in an efficient way the fine-tuning of building blocks, which could advance the construction of polymers with interesting electronic properties.

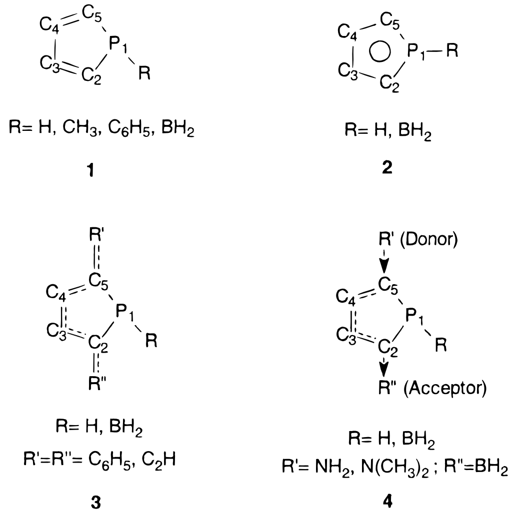

Figure 1. Structures of phospholes considered in this work.

An essential feature for electrical conduction and nonlinear optical response is efficient π−conjugation.[10] In phosphole monomers this property can be increased in three different ways (Figure 1). The first possibility is the generation of an aromatic ring structure by planarizing the phosphorus atom (**2** in Figure 1). This aromaticity could in oligomers result in a competition between π-electron confinement within the rings and delocaliza-

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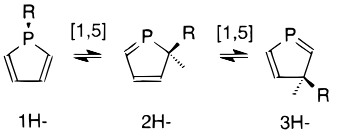

Figure 2. Possible interconversion between three distinct forms of phospholes.

tion along the chain. The second idea is the addition of strongly pronounced $\pi-$systems such as ethynyl or phenyl groups at the end of the butadienic unit (**3** in Figure 1). The last presented approach is the construction of a push−pull system by putting at one end of the butadienic $\pi-$system a donor and at the other end an acceptor group (**4** in Figure 1). In the phosphole structures considered, the phosphorus atom is bound only to ring carbon atoms and possesses either a coordination state of two in the 2H- and 3H-isomers or of three in the 1H-isomers (Figure 2). A question of interest thus concerns the relative stability of these isomers, which could interconvert by [1,5]-sigmatropic shifts.[11,12] In the present paper we have focused on 1H-phospholes in which two important building blocks are distinguished: a pyramidal phosphorus atom and a butadienic π-system. Because both can be influenced by substituents, it is important to know how and to which extent the molecular properties are influenced by the structural and electronic changes induced by these substituents. To study the substituent effect on the phosphole molecular and electronic structure, a whole range of molecules was scanned in a systematic way. The number, location, and chemical nature of the substituents were varied. Only the interesting phosphole structures are mentioned in this paper, including the calculated conformational stability, π-electron conjugation, aromaticity, and phosphorus inversion barriers (IBs).

Methods

All quantum chemical calculations were performed using the Gaussian 94[13]/98[14] suite of programs. To evaluate the molecular structure and properties of the phosphole monomers we used, on one hand, ab initio molecular orbital (MO) calculations and, on the other hand, density functional theory (DFT) with the hybrid B3LYP functional for exchange and correlation. A MO and DFT approach does explicitly take into account the whole chemical structure, in such a way that the calculations are able to depict the strong interdependence of geometric structure and electronic properties on chemical substitution.

Aromaticity was investigated by using a geometric (Julg index[15−17]) and a magnetic criterion (nucleus-independent chemical shift method[18]). The Julg index (referred to hereafter as JI), which has proved to be useful for 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 is a measure for the bond length alternation (π-electron conjugation) in the diene unit and gives an idea about the aromaticity in the considered heterocyclic structure. In the nucleus-independent chemical shift method (referred to hereafter as NICS method), the absolute magnetic shieldings are computed at the ring center (nonweighted mean of the heavy atom coordinates). With correspondence to the familiar NMR chemical shift convention, the sign of the computed values are reversed: negative NICSs denote the existence of aromaticity. The NMR shielding tensors are calculated with the gauge-independent atomic orbital (GIAO) method.

The split-valence basis sets[12,13] of the 6-31G*, 6-31+G*, 6-311G*, and 6-311++G** types were used. Analytic harmonic vibrational frequency calculations were done to characterize the nature of stationary points on the potential energy surface and to estimate the zero-point vibrational energies (ZPEs). Note that throughout this paper, relative energies are given in kJ/mol, bond lengths are in Å, and bond angles are in degrees.

Results and Discussion

Calculated geometrical parameters are recorded in Tables 1−3. First, the approaches used to increase π-conjugation in phosphole monomers are described, including those evaluated by a geometric and magnetic criterion. The results are given in Table 4. Subsequently, the relationship between the molecular structure and the phosphorus inversion barrier is analyzed; the corresponding data are found in Tables 5 and 6. Finally, calculated relative energies of phosphole isomers are presented in Tables 7 and 8, and the obtained stability ordering is discussed.

1. Conjugated Phosphole Structures. As mentioned in the Introduction, three ways of increasing π-conjugation are investigated. At first, reduced pyramidality of σ^3-P in the phosphole monomer is achieved by bulky and by π-acceptor groups on the phosphorus atom (**1** in Figure 1). Complete cyclic delocalization of 1-R-1H-phospholes (**2** in Figure 1) is known as an *aromatic border* case. The two other ways tend to increase conjugation over the butadienic π-system and involve 2,5-R′,R″-1H-phospholes. The effect of planarizing σ^3-P in these structures was studied for a set of 1-BH_2-2,5-R′,R″-1H-phospholes with $R' = R'' = C_6H_5$, C_2H or $R' = NH_2$, $N(CH_3)_2$ and $R'' = BH_2$ (**3** and **4** in Figure 1).

A careful examination of the structures computed using different MO and DFT methods points out that the B3LYP method, in conjunction with the 6-31G* basis set, is an efficient level for performing geometry optimization.

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[15] $JI = 1 - (225/n)\Sigma(1 - r_i/r)^2$, $n = 3$ and represents the number of C−C bonds. JI = 1 for benzene (D_{6h}) and the cyclopentadienyl ion (D_{5h}), that is, for the fully delocalized, highest symmetric systems. The empirical factor 225 provides an aromaticity scale in which JI = 0 for the Kekulé form of benzene (assuming 1.33 and 1.52 Å C−C lengths).

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Table 1. Optimized Structural Parameters for Puckered 1-R-1H-Phospholes (B3LYP/6-31G*)

	R = H	R = CH_3	R = $C(CH_3)_3$	R = C_6H_5	R = BH_2	expt[a] R = CH_2Ph
P_1-R	1.424	1.871	1.904	1.850	1.840	1.858
P_1-C_2	1.816	1.813	1.813	1.815	1.782	1.783
$C_2=C_3$	1.355	1.357	1.358	1.356	1.364	1.343
C_3-C_4	1.459	1.460	1.458	1.461	1.452	1.438
$\angle C_2PC_5$	90.3	90.4	90.4	90.3	93.7	90.7
$\angle C_3C_2P_1$	109.9	110.0	110.1	110.0	108.1	110.0
$\angle C_4C_3C_2$	114.4	114.2	114.2	114.2	114.9	114.1
ΣCPX (X = C, R)	293.3	300.7	302.8	302.5	337.7	302.7

[a] Reference 30.

Table 2. Optimized Structural Parameters for 2,5-R′,R″-1H-Phospholes (B3LYP/6-31G*)

	2,5-C_6H_5-	2,5-C_2H-	puckered 2-BH_2-5-NH_2-	2-BH_2-5-$N(CH_3)_2$-	planar 2-BH_2-5-NH_2-
P_1-C_2	1.833	1.814	1.832	1.826	1.764
P_1-C_5			1.848	1.853	1.734
$C_2=C_3$	1.367	1.376	1.387	1.388	1.413
C_3-C_4	1.444	1.440	1.424	1.420	1.401
$C_4=C_5$			1.380	1.389	1.412
$\angle C_2PC_5$	91.3	90.2	90.8	91.2	99.6
$\angle C_3C_2P_1$	108.4	110.2	107.4	107.3	102.3
$\angle C_4C_3C_2$	115.5	114.2	118.1	118.3	118.1
$\angle C_5C_4C_3$			113.1	113.3	115.4
$\angle P_1C_5C_4$			109.9	109.2	104.6
ΣCPX (X = C, H)	292.1	291.8	289.5	291.2	360

Table 3. Optimized Structural Parameters for 1-BH_2-2,5-R′,R″-1H-Phospholes (B3LYP/6-31G*)

	1,2-BH_2-5NH_2	1,2-BH_2-5$N(CH_3)_2$
P_1-C_2	1.806	1.803
P_1-C_5	1.809	1.823
$C_2=C_3$	1.393	1.392
C_3-C_4	1.420	1.416
$C_4=C_5$	1.387	1.397
$\angle C_2PC_5$	94.0	94.2
$\angle C_3C_2P_1$	105.3	105.6
$\angle C_4C_3C_2$	118.5	118.5
$\angle C_5C_4C_3$	113.7	114.4
$\angle P_1C_5C_4$	108.0	107.1
ΣCPX (X = C, B)	330.6	332.4

Table 4. Calculated Julg Indices (JI) and NICS Values (ppm) on B3LYP/6-31G* Optimized Geometries; NICS Calculations Are Performed Using the GIAO Method at the B3LYP/6-311G* Level

structure	point group	JI	NICS
1-R-1H-Phospholes			
1-H-1*H*- (parent phosphole)	C_s	0.720	−5.7
planar 1-H-1*H*- (ts)	C_{2v}	0.974	−16.9
1-CH_3-1*H*-	C_s	0.726	−5.6
1-C_6H_5-1*H*-	C_s	0.715	−4.9
1-BH_2-1*H*-	C_s	0.801	−9.1
2,5-R′,R″-1H-Phospholes			
2,5-C_6H_5-1*H*-	C_s	0.847	−3.1
2,5-C_2H-1*H*-	C_s	0.895	−5.2
2-BH_2-5-NH_2-1*H*-	C_1	0.957	−3.0
planar 2-BH_2-5-NH_2-1*H*- (ts)	C_1	0.997	−14.2
2-BH_2-5-$N(CH_3)_2$-1*H*-	C_1	0.975	−3.6
1-BH_2-2,5-R′,R″-1H-Phospholes			
1-BH_2-2,5-C_2H-1*H*-	C_s	0.922	−8.8
1,2-BH_2-5-NH_2-1*H*-	C_1	0.976	−6.3
1,2-BH_2-5-$N(CH_3)_2$-1*H*-	C_1	0.988	−6.7
Heterocyclic Analogues			
C_5H_6 (cyclopentadiene)	C_{2v}	0.621	−3.4
C_4H_5N (pyrrole)	C_{2v}	0.943	−14.7
C_4H_4O (furan)	C_{2v}	0.850	−12.6
C_4H_4S (thiophene)	C_{2v}	0.897	−13.8
Reference JI			
C_6H_6 (benzene)	D_{6h}	1.00	−8.8

a. 1-R-1H-Phospholes. The geometry of 1-CH_3-1H- or 1-C_6H_5-1H-phosphole does not differ in a significant way from that of the parent 1-H-1H-structure, which is known to be weakly aromatic.[19] A pyramidal phosphorus atom and a diene unit are observed as the phosphole building blocks (Table 1). Considerable effort has been made to planarize phospholes. To achieve some flattening of the phosphorus pyramid, bulky substituents[20,21] or π-acceptor groups can be used.[22] Earlier computational investigations[23,24] have shown that the aromaticity in phospholes increases if the pyramidality of the tricoordinate phosphorus atom decreases and predicted the planar phosphole to be highly aromatic. These observations are confirmed in this work. In structures such as 1-CH_3-1H-, 1-C_6H_5-1H-phosphole where the pyramidality, given by the sum of the CPX angles, does not change significantly toward the parent phosphole (Table 1), the NICS values and JI are nearly the same as in 1-H-1H-phosphole and are in the range of the nonaromatic cyclopentadiene values (Table 4). These observations are in agreement with a low aromaticity within these phosphole rings. Nevertheless in 1-BH_2-1H-phosphole, the substituted π-acceptor group strongly reduces the pyramidality at the phosphorus atom. The sum of the CPX angles increases to 337.7° (Table 1), in accord with the result reported earlier by Nyulászi.[24] An increase in the double bond length from 1.355 to 1.364 Å and a decrease in the single bond length from 1.459 to 1.452 Å are calculated (Table 1). This means a reduction in the bond length alternation over the diene unit; this is reflected in the JI, which increases from 0.720 to 0.801, in the parent and 1-BH_2-1H-phosphole, respectively. This is a consequence of the decrease in pyramidality at the phosphorus atom and an indication for a greater conjuga-

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Table 5. Inversion Barriers (kJ/mol) Calculated at the B3LYP/6-311++G//B3LYP/6-311++G** Level**

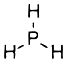
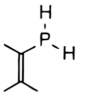
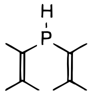
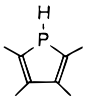
Molecule		I.B. (kJ/mol)
	min. (C_{3v}) ts (D_{3h}) - 1084i cm^{-1} (A_2'')	139
	min. (C_1) ts (C_s) - 900i cm^{-1} (A'')	120
	min. (C_s) ts (C_s) - 676i cm^{-1} (A'')	103
	min. (C_s) ts (C_{2v}) - 611i cm^{-1} (B_1)	72

Table 6. Values of Inversion Barriers (kJ/mol) for 1H-phospholes Calculated with Different Methods on B3LYP/6-31G* Geometries

	1-H-	1-CH_3-	1-C_6H_5-	1-BH_2-	2-BH_2-5-NH_2-
HF/6-31+G*	103	98	96	11	115
MP2/6-31+G*	65	62	63	5	75
B3LYP/6-31+G*	74	67	65	1	89

Table 7. Energies Relative to the 1-R-1H-Phosphole Isomer, Taking ZPEs[a] into Account

		isomer	
method	R	2-R-2H-	3-R-3H-
HF/6-311++G**//B3LYP/6-31G*	H	7	18
	CH_3	25	29
	$C(CH_3)_3$	20	27
	C_6H_5	17	25
	BH_2	21	
MP2/6-311++G**//B3LYP/6-31G*	H	−16	−1
	CH_3	0	8
	$C(CH_3)_3$	−3	8
	C_6H_5	−9	4
	BH_2	−27	
B3LYP/6-311++G**//B3LYP/6-31G*	H	−9	9
	CH_3	13	25
	$C(CH_3)_3$	11	25
	C_6H_5	3	20
	BH_2	1	

[a] Zero-point energy corrections scaled by a factor 0.963 at the B3LYP/6-31G* level of theory.

Table 8. Energies Relative to the 1H-Phosphole Isomer Taking ZPEs[a] into Account

	parent phosphole			methyl phosphole		
method	planar 1H (ts)	2H	3H	planar 1H (ts)	2H'	3H
CCSD(T)/6-31G*// MP2/6-31G*	89	−26	−12	85	−7	2
CCSD(T)/6-31G*// B3LYP/6-31G*	89	−25	−11	85	−6	2
HF/6-31+G*// B3LYP/6-31G*	104	4	16	98	24	30
MP2/6-31+G*// B3LYP/6-31G*	66	−23	−8	62	−2	8
B3LYP/6-31+G*// B3LYP/6-31G*	75	−11	6	67	11	24
CCSD(T)/6-31+G*// B3LYP/6-31G*	85	−21	−8	81	−3	5
MP2/6-311++G**// B3LYP/6-31G*	64	−16	−1			
B3LYP/6-311++G**// B3LYP/6-31G*	73	−9	8			
CCSD(T)/6-311++G**// B3LYP/6-31G*	83	−15	−2			

[a] Zero-point energy corrections scaled by a factor 0.9 at the HF/6-31G* level of theory.

tion over the ring. The increase in NICS value from −5.7 to −9.1 further supports this view. The calculated value (−9.1) approaches the range of values for the planar aromatic heterocycles (−12.6 to −14.7) and becomes quite different from the corresponding value (−3.4) for the nonaromatic cyclopentadiene (Table 4).

b. 2,5-R′,R″-1H-Phospholes. Puckered Ring Structures. The phosphorus atom in 2,5-C_6H_5- and 2,5-C_2H-1H-phosphole shows a normal[25] pyramidality (Table 2). Phenyl or ethynyl groups are placed, respectively, in positions 2 and 5, at the ends of the butadienic unit (**3** in Figure 1, R = H). The substituents, characterized by a strongly pronounced π-system, show a large extent of conjugation with the heterocyclic π-diene units. An increase of the JI with respect to the parent phosphole (Table 4) is calculated. This indicates an increase in conjugation over the diene unit. The value changes from 0.720 to 0.847 and 0.895 in parent 1-H-1H-, 2,5-C_6H_5-1H-, and 2,5-C_2H-1H-phosphole, respectively. At the same time, an increase in the NICS value from −5.7 in the parent phosphole to −3.1 in 2,5-C_6H_5-1H-phosphole suggests a reduction in aromaticity. A decrease in π-electron delocalization toward the phosphorus atom is a likely explanation.

The phosphorus atom in 2-BH_2-5-NH_2- and 2-BH_2-5-$N(CH_3)_2$-1H-phosphole is also characterized by a normal pyramidality (Table 2) in which, at the one end of the conjugated diene sytem, a π-donor group (NH_2 or $N(CH_3)_2$) and, at the other end, a π-acceptor (BH_2) group are placed (**4** in Figure 1). Intuitively, due to a push−pull effect, a greater π-electron delocalization over the diene unit is expected, as compared to the parent phosphole. The JI indeed increases from 0.720 in the parent phosphole to 0.957 and 0.975 in the 2-BH_2-5-NH_2-1H- and 2-BH_2-5-$N(CH_3)_2$-1H-phosphole, respectively. Such an increase is more pronounced than in the case of the conjugated substituents. This implies that, in the push−pull systems, the electron delocalization along the π-diene system is somewhat greater. The NICS value for the push−pull boryl-substituted phosphole structures (−3.0 and −3.6) indicates an aromaticity that is similar to the one calculated in cyclopentadiene (−3.4).

Planar Ring Structures. Calculations for the planar 2-BH_2-5-NH_2-1H-transition state pointed out that planarization further increases the conjugation in the push−pull system. The JI reaches a value of 0.997 compared to 0.957 in the puckered minima. The NICS value (−14.2) indicates a strong aromatic system situated between thiophene (−13.8) and pyrrole (−14.7).

c. 1-BH_2-2,5-R′,R″-1H-Phospholes. By substitution of a BH_2 group on phosphorus the pyramidality of this atom in the ring system strongly decreases, and a greater π-electron delocalization toward this group is expected. As a consequence the conjugation in the π-diene system also increases. The phosphole structure becomes thus

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(25) Normal pyramidality means similar to the pyramidality observed in the parent 1-H-1H-phosphole structure with ΣCPX = 293.3°.

more aromatic. This is illustrated by comparing the calculated JI and NICS values for the 2,5-R′,R″-1H-phospholes and 1-BH_2-2,5-R′,R″-1H-phospholes, respectively. For an example, look at the 2-BH_2-5-NH_2-1H- and 1,2-BH_2-5-NH_2-1H-phospholes. The ΣCPX angles (Tables 2 and 3) increases from 289.5° to 330.6°. This induces an increase in the JI (0.957 → 0.976) and NICS value (−3.0 → −6.3). This is in agreement with the above statement that planarizing the phosphorus atom in 2,5-R′,R″-1H-phospholes creates a stronger conjugated diene and a more aromatic ring system.

2. Inversion Barriers. Experimentally, inversion barriers of about 67 kJ/mol were measured in phospholes, as compared with 151 kJ/mol in the saturated phospholanes.[26] Table 5 shows the evolution of the inversion barriers in going from phosphine to phosphole. It is clear that the low inversion barrier in phosphole is due to the high ring conjugation (aromaticity) in the planar transition structure (NICS −16.9, Table 4). The inversion barrier is virtually unchanged upon methyl or phenyl substitution (Table 6). As earlier concluded from the ΣCPX angles, these substituents are not sterically crowded enough for a pronounced flattening of the phosphorus pyramid. Therefore no meaningful increase in p-character of the lone-pair orbital is obtained, which implies that there is no significant change in overlap with the butadienic π-system. As a result the lack of aromaticity stays, and the inversion barrier remains almost unchanged.

In contrast, in 1-BH_2-1H-phosphole, there is a strong reduction of the pyramidality (Table 1). A larger stabilization is obtained by a better overlap of the lone-pair orbital with the π-diene system. Calculations point out that the inversion barrier becomes negligible (Table 6), namely, 5 kJ/mol at the MP2/6-31+G* and 1 kJ/mol at the B3LYP/6-31+G* levels of theory, suggesting a practically planar phosphole. In push−pull sytems, like 2-BH_2-5-NH_2, the inversion barrier is calculated to be about 10−15 kJ/mol higher than that in the parent phosphole (Table 6). The fact the π-electron conjugation is localized between the π−donor (NH_2) and π-acceptor (BH_2) over the butadienic π-system and not toward the phosphorus atom lowers the ring delocalization (aromaticity). This observation appears to be a reasonable explanation for the enhanced inversion barrier.

3. Relative Stabilities. Experimentally,[9,18] tervalent 1-H-1H-phospholes are observed to readily rearrange to their 2H-isomers, even at low temperatures. The 2H-isomers are rather unstable and, in most cases, readily undergo [4 + 2] Diels−Alder cycloadditions or, alternatively, can be trapped by alkynes. In contrast, 1-CH_3-1H- and 1-C_6H_5-1H-phosphole are more stable at room temperature, even though, upon heating, 1-C_6H_5-1H-phospholes also rearrange to their 2H-isomers.[27] Calculated relative energies between different isomeric forms are summarized in Table 7. It shows that the predicted stability ordering strongly depends on the method used. An evaluation of the methods was performed for parent phosphole toward the high level CCSD(T) calculations using the 6-311++G** basis set (Table 8). Conclusions are that the MP2 method is reasonable good in predicting the relative stability of the different isomers, while the inversion barrier is better described by the B3LYP method.

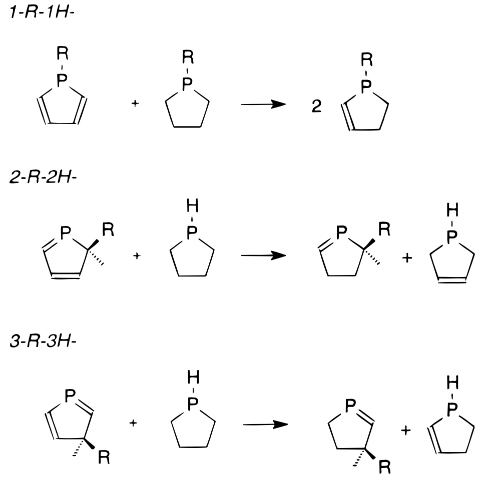

Figure 3. Homodesmotic reactions used to evaluate ASEs.

From Table 7 it is clear that while HF results favor the 1-R-1H-form in which even the 1-H-1H-phosphole is calculated to be more stable than the 2-H-2H-phosphole, the MP2 results suggest that in parent (R = H), C_6H_5- and BH_2-phosphole, the 2R-isomer is the most stable form. For CH_3- and $C(CH_3)_3$-phospholes, both isomers are calculated equally stable. This is not in agreement with the conclusion of Bachrach,[28] who suggested that substituents with highly steric hindrance would preferentially select phosphorus over carbon. The relative stability of the 3R-isomer with respect to the 1R-isomer evolves from equally stable in the parent phosphole to unstable in CH_3- and $C(CH_3)_3$-phosphole; C_6H_5-phosphole lies in between. The 3-BH_2-3H-phosphole is calculated to be unstable. In better agreement with experimental results, the B3LYP method predicts that for the parent phosphole the 2-H-2H-isomer is more stable (9 kJ/mol) than the 1-H-1H-isomer. Concerning the CH_3- and $C(CH_3)_3$-phospholes, the 1H-form is calculated to be around 10 kJ/mol more stable than the 2H-form. For C_6H_5-phosphole and BH_2-phosphole, the 1H- and 2H-isomers are calculated evenly stable. From all phosphole structures mentioned so far, the 3H-isomers are the least stable forms.

To analyze the relative stability ordering of phosphole isomers, various properties such as bond energies, aromatic stabilization energies, and steric interactions[22] need to be taken into account. From a bond energy additivity viewpoint, the 2H- and 3H-isomers of the parent phosphole should be more stable than the 1H-isomer by up to about 38 ± 21 kJ/mol.[2929−30] The 1H- and 2H-methylphosphole isomers are predicted to be equally stable.[22] Aromatic stabilization energies (ASEs) have also been calculated to have an idea about the stabilization created by electron delocalization. In Figure 3 are given the homodesmotic reactions used here to evaluate the ASEs. In Table 9 are presented the deduced homodesmotic reaction energies in which a positive energy denotes stabilization for the cyclic conjugated systems. In BH_2-phosphole, the ASE is up to 20−30 kJ/mol higher

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Table 9. Aromatic Stabilization Energies (ASEs) and ΔASEs (kJ/mol)

isomers	ASE B3LYP/6-31G*// B3LYP/6-31G*	ASE B3LYP/6-311++G**// B3LYP/6-31G*
	1R-1H	
1H-1H	25	24
1-CH_3-1H	22	20
1-C_6H_5-1H	16	14
1-BH_2-1H	43	42
	2R-2H	
2H-2H	29	27
2-CH_3-2H	23	21
2-C_6H_5-2H	24	22
2-BH_2-2H	57	51
	3R-3H	
3H-3H	16	17
3-CH_3-3H	12	13
3-C_6H_5-3H	10	11

R	$\Delta ASE_{(2R\text{-}2H)-(1R\text{-}1H)}$: B3LYP/6-311++G**// B3LYP/6−31G*	$\Delta ASE_{(3R\text{-}3H)-(1R\text{-}1H)}$: B3LYP/6-311++G**// B3LYP/6−31G*
H	3	−7
CH_3	1	−7
C_6H_5	8	−3
BH_2	9	

than in the other structures, which are slightly aromatic. BH_2-phosphole is clearly characterized by a greater electron delocalization or aromaticity. The high JI (0.801) and NICS (−9.1) value have in fact earlier proved this in an alternative way. Table 9 also gives the difference in aromatic stabilization energies (ASE) between the isomers. In both parent and methyl phospholes, the $\Delta ASE_{(2R\text{-}2H)-(1R\text{-}1H)}$ is negligible, and the $\Delta ASE_{(3R\text{-}3H)-(1R\text{-}1H)}$ predicts a slightly higher aromatic stablization energy in the 1H-isomer. For C_6H_5- and BH_2-phospholes the ASE is slightly higher in the 2H-isomer, and the $\Delta ASE_{(3R\text{-}3H)-(1R\text{-}1H)}$ is negligible for phenyl phosphole. To check the influence of steric hindrance on the stability ordering of the isomers, we have optimized and calculated the relative stabilities of *tert*-butyl ($C(CH_3)_3$) structures. Supposing *tert*-butyl substituents to be more sterically crowded than methyl substituents, we expected that the stability of the 1H-isomer would be increased relative to the 2H-isomer. To our surprise, the stability of the 1-$C(CH_3)_3$-1H-structure toward the 2-$C(CH_3)_3$-2H-structure was found a bit less pronounced than that in the case of the methyl substituent. From all this, it can be concluded that for the slightly aromatic structures the relative stabilities calculated with the MP2 method are mainly determined by the bond energies. The influence of aromatic stabilization energy is rather weak but needs to be taken into account to explain the calculated stability differences between the 2H- and 3H-isomers. Nevertheless, while MP2 ASE calculations should give better quantitative results, the trends are expected to be the same. It appears that the effect of steric hindrance on the relative stability ordering is negligible.

Conclusion

Use of the DFT method with the B3LYP functional offers an efficient way for performing geometry optimizations of phosphole structures. It also provides inversion barriers in good agreement with experiment. The MP2 method is more suited to calculate the relative stability ordering between the isomers. Combination of structural (JI) and magnetic (NICS value) criteria show that by putting strongly pronounced π-systems or placing a donor and acceptor substituent at the ends of the butadienic π-system, the electron delocalization over the entire system is significantly augmented. It also proves that the employed approach is useful to analyze the π-electron delocalization or aromaticity in conjugated heterocyclic systems and could be used for investigation of much larger oligomers. More relevant for chemical applications is the result that the computational study provides a method of fine-tuning of phosphole building blocks, which may enable us to obtain higher π-conjugation along the polymer backbone.

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