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The Aromaticity of Polyphosphaphospholes Decreases with the Pyramidality of the Tricoordinate Phosphorus

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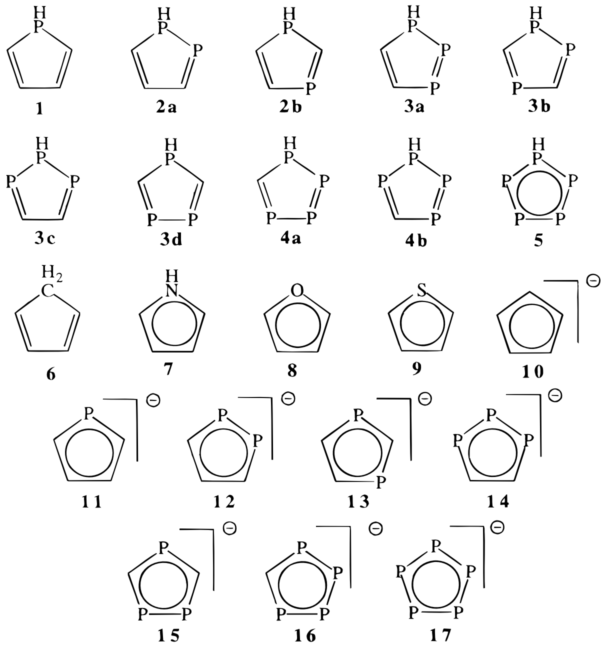
The aromaticity of phospholes, $P_n(CH)_{4-n}PH$ with $n = 0-4$, becomes larger as the number of dicoordinate atoms (n) in the ring increases. This is due to the decreasing pyramidality of the tricoordinate phosphorus. The aromaticity is shown by various criteria, e.g., the nucleus-independent chemical shifts (NICS), and the separated π contribution NICS(π), as well as the Bird aromaticity (BI) and the bond-shortening (BDSHRT) indexes. The change of the aromaticity is correlated with the bond angle sum (the degree of planarity) about the tricoordinate phosphorus (e.g., correlation coefficient = 0.968 with NICS). The aromaticities of the planar $P_n(CH)_{4-n}PH$ phospholes (first-order saddle points for $n = 0-3$, minimum for $n = 4$) (NICS values between −15.4 and −17.4 ppm) all are similar. The same is true for the NICS (−12.3 to −15.9) aromaticity of the phospholyl anions ($P_n(CH)_{4-n}P^-$), $n = 0-4$, which are close to those of the planar phospholes. According to NICS, BI and BDSHRT planar phospholes are more aromatic than pyrrol or thiophene. Isodesmic reaction energies do not correlate with the bond angle sum, since the energy cost of the increasing planarization of the tricoordinate phosphorus consumes the stabilization achieved by aromaticity.

Introduction

The aromaticity of phosphole, 1 (Chart 1), is one of the lowest among the 6 π electron heterocyclic five-membered rings.[1−5] This finding is a consequence not of the small overlap between the p atomic orbitals of the first- and second-row elements (this concept, once called the "double bond rule",[6] is known to be invalid)[7−9] but of the inherent pyramidal preference[10] of tricoordinate phosphorus in its compounds.[11] This idea was developed by Mislow,[11] who compared the phosphorus inversion barriers (measured by NMR spectroscopy) of alkyl-substituted phospholes with phospholanes (the saturated analogue of phosphole). Second-row elements, like S (which do not have the planarity problem), are not less efficient π donors than their first-row counterparts. Like the dicoordinate P^- anion,[12,13] planar tricoordinate phosphorus is an excellent p donor.[14] Indeed, geometric, energetic, and magnetic criteria show that planar phosphole is highly aromatic.[15,16]

Chart 1. Polyphosphaphospholes and Polyphosphaphospholides



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Tricoordinate phosphorus in the $P_n(CH)_{4-n}PH$, $n = 0-4$ (**1**−**5** Chart 1), rings can be planarized by replacing the −CH= units by −P=. The pyramidality of the tricoordinate phosphorus and the inversion barrier are reduced significantly in triphospholes (**3a**−**d**) with respect to phosphole.[17] The attempted isolation of pentaphosphole, **5**, was unsuccessful,[18] but it would clearly be planar according to high-level ab initio calculations.[19,20] Both ring strain effects and the different electronegativities of P and C are responsible for the planarization.[17,19,20] Electron-accepting substituents on the carbon atoms, like $P(Ph)_3^+$ [21,22] or BH_2,[15] also increase the planarity of phospholes. The use of bulky substituents (e.g., 2,4,6-tri-*tert*-butylphenyl group) on the tricoordinate phosphorus in 1,2,4-triphosphole results in full planarity.[23] Combination of all the above effects resulted in the synthesis of the first planar 1,2,4-triphosphole (1-(bis(trimethylsilyl)methyl)-3,5-bis(trimethylsilyl)-1,2,4-triphosphole), having structural characteristics similar to those predicted computationally.[24] The aromaticity of 1,2,4-triphosphole (**3b**) is comparable to that of other five-membered dienes (**6**−**9**), and the bond length equalization is similar[17] to that in furan (**8**). There is experimental evidence for the aromatic character of partially planarized phospholes. 1-(Bis(trimethylsilyl)methyl)-3,5-di-*tert*-butyl-1,2,4-triphosphole[25] (an alkylated derivative of **3b**) forms a η^5 complex as is characteristic of aromatic systems.[26] 1-(2,4,6-Tri-*tert*-butylphenyl)-3-methylphosphole undergoes electrophilic substitution.[27] The phosphorus lone pair ionization energy of 1-(4,6-di-*tert*-butyltolyl)-3-methylphosphole measured by photoelectron spectroscopy was larger than in the corresponding phospholane (the saturated analogue of phosphole).[28] This increase of the ionization energy, which is typical for other five-membered heterocycles (e.g., furan and tellurophene) indicates aromatic stabilization,[28] which has never been observed in the spectra of phospholes substituted by less bulky groups.

While it has been suggested[15,17,20−22] that the planar (or partially planarized) tricoordinate phosphorus in phospholes has some pentavalent character (see resonance form **Ib** in Scheme 1), the ab initio calculated wave functions do not show valence shell expansion. Resonance forms **Ic** and **Id** instead of **Ib** provide an adequate description of the bonding situation in planar phospholes, too.[19] Phospholide anions, which have no pyramidality problem at phosphorus, also are known to be aromatic with equalized bond lengths[12,16] and form η^5 complexes[13] characteristic of aromatic compounds.

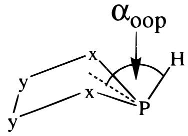
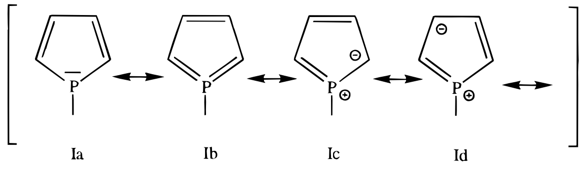


Figure 1. Definition of the out-of-plane angle of the tricoordinate phosphorus, oop, in $P_n(CH)_{4-n}PH$ molecules.

Scheme 1. Possible Resonance Structures Describing the Bonding in Planar Phosphole



The very recent interest[12−24] in compounds with planar tricoordinate phosphorus prompts us to examine the relationship between aromaticity and pyramidality. The recently introduced NICS (nucleus-independent chemical shift)[5] aromaticity criterion (the negative of the shieldings computed in the center of aromatic systems) provides an excellent measure of the aromaticity (e.g., NICS parallels the energetic geometric and magnetic susceptibility criteria for $(CH)_4X$ molecules with X = CH_2, NH, O, S, and CH^-, Chart 1).[5] We compare here the aromatic character of phospholide anions (**11**−**17**, Chart 1), and polyphosphaphospholes both with pyramidal (**1**−**4b**) and with imposed planar (distinguished by primed numbers **1′**−**4b′**) geometries, by employing magnetic as well as geometric and energetic aromaticity criteria. The relationship between aromaticity and the degree of pyramidalization of tricoordinate phosphorus is analyzed by comparing minima and (planar) transition structures for inversion at the tricoordinate phosphorus. The nature of the valency of the tricoordinate phosphorus also is discussed.

Computational Methods

Quantum chemical calculations were carried out with the Gaussian 94 program package.[29] Geometries were fully optimized at the B3LYP/6-311+G** level of density functional theory. For **1**−**4b**, geometries also were optimized with planarity constraints, resulting in structures **1′**−**4b′**. The fully optimized structures were all minima, whereas **1′**−**4b′** were first-order saddle points. In order to evaluate the relationship of planarity with aromaticity criteria, further optimizations of **1** and **3d** were carried out by constraining the out-of-plane angle (oop, the angle between the P−H bond and the bisector of the bonds from the tricoordinate phosphorus to its neighbors in the ring; defined in Figure 1) to various values.

Magnetic properties were calculated at GIAO[30,31]/6-311+G** [32] (NICS) and at IGAIM[31]/6-311+G** [32] (magnetic susceptibility, χ) on the optimized geometries. The NICS center is defined as the geometric

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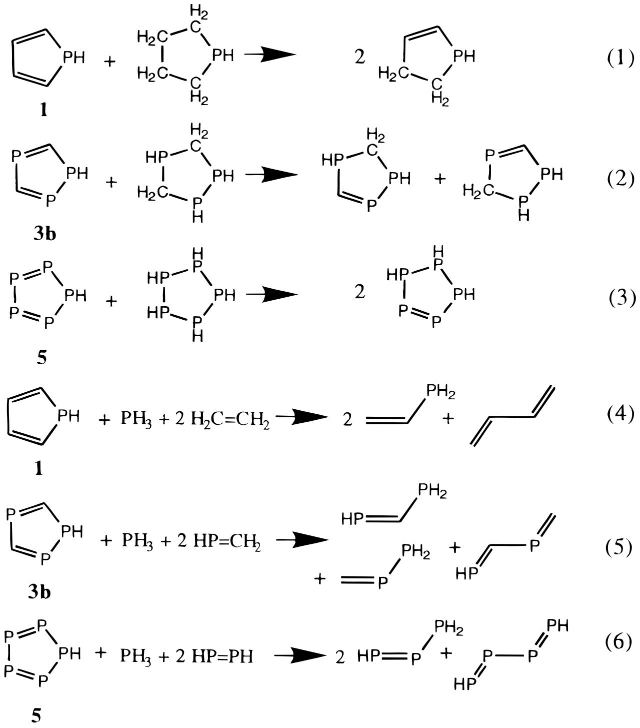
mean of the atoms in the aromatic system.[33] SOS-DFT routines[34] of the DeMon program package[35] were used with the BIII basis set[36] to compute the individual localized molecular orbital contributions to the NICS value by employing the Pipek−Mezey localization,[37] which separates σ and π components of the double bonds.

The Bird geometric aromaticity index[38] (BI) and the bond-shortening index[39] (BDSHRT) were based on bond orders (BOG) derived from the Gordy equation[40] (BOG $= r^{-2}A - B$; r is the bond length, and A and B are parameters for a bonded atom pair). The A and B parameters of the Gordy equation were derived using bond lengths from optimized B3LYP/6-311+G** geometries of the simplest single- and double-bonded reference compounds containing CC, CP, and PP bonds[41] ($A_{\mathrm{CC}} = 7.162$, $B_{\mathrm{CC}} = 2.055$, $A_{\mathrm{CP}} = 13.670$, $B_{\mathrm{CP}} = 2.901$, $A_{\mathrm{PP}} = 20.681$, $B_{\mathrm{PP}} = 2.916$).

The aromatic stabilization energies (ASE) of **1**, **3b**, and **5** are defined by eqs 1−3 using the B3LYP/6-311+G**//B3LYP/6-311+G** energies for the global minima of reference molecules. In eqs 1−3 the ring strain differences compensate approximately.[4,42] Energies in semihomodesmotic (SH) reactions of types 4−6 were shown[39] to give values close to those from superhomodesmotic reactions.[1]



To calculate the exaltation of the magnetic susceptibility (χ) two increment schemes have been constructed ($\Delta\chi_{=\mathrm{CH}-}$ $\Delta\chi_{=\mathrm{P}-}$, and $\Delta\chi_{>\mathrm{PH}}$ represent the increments for $=$CH$-$, $=$P$-$, and $>$PH groups in the ring) as follows:

I.

$$\Delta\chi_{=\mathrm{CH}-} = {}^{1}\!/_{2}(\chi_{\mathrm{CH_3CH{=}CHCH_3}} - \chi_{\mathrm{C_2H_6}}) = -6.8 \tag{7}$$

$$\Delta\chi_{=\mathrm{P}-} = {}^{1}\!/_{2}(\chi_{\mathrm{CH_3P{=}PCH_3}} - \chi_{\mathrm{C_2H_6}}) = -7.1 \tag{8}$$

$$\Delta\chi_{>\mathrm{PH}} = \chi_{\mathrm{CH_3PHCH_3}} - \chi_{\mathrm{C_2H_6}} = -16.5 \tag{9}$$

$$\chi_{\mathrm{C_2H_6}} = -24.7,\quad \chi_{\mathrm{CH_3CH{=}CHCH_3}} = -38.4,\quad \chi_{\mathrm{CH_3PHCH_3}} = -41.3,\quad \text{and}\quad \chi_{\mathrm{CH_3P{=}PCH_3}} = -38.9$$

II.

$$\Delta\chi_{=\mathrm{CH}-} = {}^{1}\!/_{2}(\chi_{\mathrm{PH_2CH{=}CHPH_2}} - \chi_{\mathrm{P_2H_4}}) = -6.1 \tag{10}$$

$$\Delta\chi_{=\mathrm{P}-} = {}^{1}\!/_{2}(\chi_{\mathrm{PH_2P{=}PPH_2}} - \chi_{\mathrm{P_2H_4}}) = -3.4 \tag{11}$$

$$\chi_{>\mathrm{PH}} = \chi_{\mathrm{PH_2PHPH_2}} - \chi_{\mathrm{P_2H_4}} = -14.0 \tag{12}$$

$$\chi_{\mathrm{PH_2PHPH_2}} = -47.4 \quad \text{and} \quad \chi_{\mathrm{PH_2P{=}PPH_2}} = -40.2$$

The magnetic susceptibility of the nonaromatic reference system can be obtained by the summation of the proper increments. The exaltation of the magnetic susceptibility has also been evaluated by using the semihomodesmotic (SH) reactions (cf. eqs 4−6). Calculated structures for **1**−**17** are presented in Figure 2. NICS values[43] of the anions **10**−**17** are shown in Table 1. Calculated magnetic and energetic data together with aromaticity indexes based on geometric parameters (Bird and bond-shortening index) for minima (**1**−**5**) and constrained planar structures (**1′**−**4b′**) together with the corresponding data of other five membered rings (**6**−**9**) are shown in Table 2.

Results and Discussion

Phospholide Anions (11−17). The calculated structures of the phospholide anions (**11**−**17**, Figure 2) show significant bond length equalization (the C−C bonds are between 1.387 and 1.418 Å, the C−P bonds are between 1.743 and 1.773 Å, and the PP bonds are between 2.128 and 2.149 Å).[44] The NICS value in the center of these anions (−12.3 to −15.9) is similar to that of cyclopentadienyl anion (**10**) (−13.9, Table 1). The π contribution gradually decreases from −20.6 to −17.9 ppm (13%) by the increasing number of phosphorus atoms. It is 90−120% of the total NICS value. The small change of the NICS values with different numbers of dicoordinate phosphorus atoms in the ring indicates that the conjugative ability of the P═C and C═C bonds (known to be similar)[45] holds for anionic systems as well. A previous analysis[12] based on Jug's semiempirically calculated (SINDO1) index[43] for **11**−**17** concluded that these rings have at least 86% of the aromaticity of the cyclopentadienyl cation.

Planar Phospholes (1′−4b′ and 5). The NICS values of the planar polyphosphaphospholes (**1′**−**4b′** and **5**) are all in the range −15.4 to −17.6 ppm. The Bird indexes (BI) are between 79 and 87, while the BDSHRT values are between 64 and 69 for the planar structures. These values are clearly different from those of the nonaromatic cyclopentadiene (NICS = −3.1, BI = 29, BDSHRT = 45). Benzene, as "aromatic reference" (NICS = −9.7, BI = 100, BDSHRT = 67), has values similar to those of the planar phospholes. These three different

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(41) Bond lengths in angstroms from optimized B3LYP/6-311+G** geometries: $R(\mathrm{CH_3CH_3}) = 1.531$, $R(\mathrm{H_2C{=}CH_2}) = 1.329$, $R(\mathrm{H_2PCH_3}) = 1.872$, $R(\mathrm{HP{=}CH_2}) = 1.670$, $R(\mathrm{H_2PPH_2}) = 2.297$, and $R(\mathrm{HP{=}PH}) = 2.051$.

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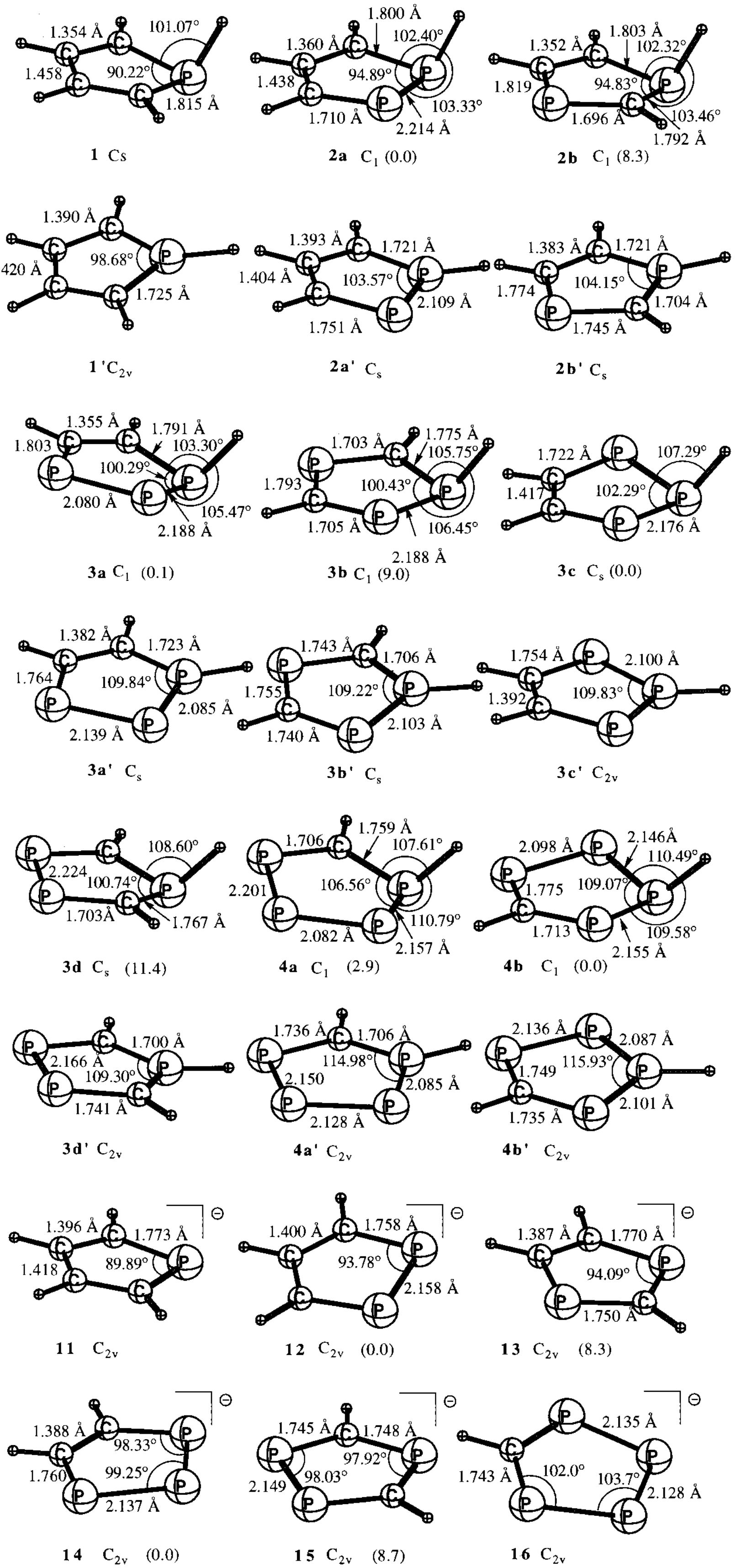

Figure 2. Structures of $P_n(CH)_{4-n}PH$ molecules, **1**−**5**, and $P_n(CH)_{4-n}P^-$ anions **11**−**17**. The PP bond length in P_5H (**5**, C_{2v}) are P1(tricoordinate)−P2 = P5−P1 = 2.091 Å, P2−P3 = P4−P5 = 2.121 Å, and P3−P4 = 2.140 Å. The PP bond length in $P5^-$ (**17**, D_{5h}) is 2.126 Å.

aromaticity criteria for all of the planar polyphosphaphospholes are larger than those for other five-membered heterocycles (pyrrole, **7**; furan, **8**; and thiophene, **9**; Table 2). This is in agreement with the conclusion drawn from the investigation of the substituent effects on carbocations[14] that planar tricoordinated phosphorus is a better p electron pair donor than >O,

Table 1. NICS^{a}Aromaticity for Reference Molecule *cyclo*$(CH)_5^-$ (**10**) and Anions $P_n(CH)_{4-n}P^-$ with $n = 0-4$ (**11**−**17**)

	formula	point group	NICS$_{\text{tot}}$a	NICS(π)^a
10	$(CH)_5^-$	D_{5h}	−13.9	−22.5
11	$C_4H_4P^-$	C_{2v}	−13.2	−22.6
12	1,2-$C_3H_3P_2^-$	C_{2v}	−13.9	−19.4
13	1,3-$C_3H_3P_2^-$	C_{2v}	−12.3	−19.3
14	1,2,3-$C_2H_2P_3^-$	C_{2v}	−14.2	−18.4
15	1,2,4-$C_2H_2P_3^-$	C_{2v}	−13.0	−18.3
16	CHP_4^-	C_{2v}	−14.5	−17.9
17	P_5^-	D_{5h}	−15.9	−18.0

[a] NICS, nucleus-independent chemical shift (ref 5) obtained at the ring center. Total (NICS$_{\text{tot}}$) values (GIAO/6-311+G**//B3LYP/6-311+G**) and the contribution of the localized π MOs (NICS(π)) are given separately.

>S, or >NH. Likewise, the electronegativity of phosphorus is smaller than that of N, S, and O, and this facilitates electron donation.

The NICS values of **1′**−**4b′** and **5** differ from each other by less than 2 ppm (cf. the changes of the NICS values among **11**−**17** (see above)). The contributions of the π bonds to the NICS values are between −21.1 and −18.6 ppm. As in the anions, these π contributions make up most of the nuclear shielding at the ring center, and the paramagnetic σ effects are smaller and depend inversely on the ring size[46] (i.e., the distance of the NICS center from the σ bonds).

The small change in the π contributions to the NICS value when a C=C bond is replaced by −P=C is not surprising. The π ionization energies of corresponding C=C and −P=C bonded compounds were shown[45] to correlate with each other with a near unit (0.974) slope (correlation coefficient (cc) = 0.987). This correlation indicates that there is little change when a C=C unit is replaced by P=C in a conjugated system. The π contributions to the NICS values change less than 1 ppm between the planar phosphole structures and the corresponding anions (**1′**−**11**, **3b′**−**15** and **5**−**17**). Thus the in-plane complexation of the phosphorus lone pair has little effect on the π system.[47]

Fully Optimized Structures (1−5). NICS, BI, and BDSHRT Aromaticity Indexes. The fully optimized $P_n(CH)_{4-n}PH$ structures display decreasing pyramidality at the tricoordinate phosphorus atom with increasing n (Table 2) as measured by the sum of the bond angles (Σα). However, there is no Σα value between 330° and 360° in **1**−**5**. A systematic study can be carried out on the C_s "symmetric" molecules **1**, **3c,** and **3d** where the oop (see Figure 1) can be fixed at various values while all other geometrical parameters are allowed to relax. This gives data for the entire range of bond angle sums between 290° (**1**) and 360° (**1′**−**4b′** and **5**). Aromaticity characteristics of these deformed **1** and **3d** structures are compiled in Table 3.

Structures **1**−**4** have significantly smaller NICS values and Bird and BDSHRT indexes than their planar counterparts (**1′**−**4b′**) as shown in Table 2. The difference in the NICS values is mainly due to the increase in the magnitude of the π contributions. When more dicoordinate phosphorus atoms are present, all of these aromaticity indexes approach the values of the corresponding planar systems. Since the change of a =CH− to a =P− building block is known[45] only to have a slight effect on the conjugation (see above), it is reasonable to relate the changes in aromaticity of **1**−**5** quantitatively to the flattening of the tricoordinated phosphorus.

A linear correlation is obtained (cc = 0.968) by plotting the NICS values for all polyphosphaphospholes (**1**−**5**) against the bond angle sums (Figure 3). The Bird index, BI, and the BDSHRT values also correlate with Σα, but the correlations are less satisfactory (cc = 0.926 for BI and 0.933 for BDSHRT). This supports the empirically derived idea[11a] that the low aromaticity of phosphole is due mainly to the nonplanarity of the tricoordinated phosphorus. Significant effects are already apparent when bond angle sum is 335° (corresponding to an oop angle about 40°). Planarized phospholes with sums in this range should have aromatic characteristics similar to those of furan (cf. data in Table 2). The participation of the phosphorus lone pair orbital in the π system is already considerable in triphospholes.[17] The bond angle sums (X-ray data) at the tricoordinate phosphorus in 1-(bis(trimethylsilyl)methyl)-3,5-di-*tert*-butyl-1,2,4-triphosphole (Σα = 342°),[25] which showed aromatic complexing behavior (η^5 coordination),[26] and the supermesityl substituted phosphole derivative (Σα = 332°)[27] that undergoes electrophilic substitution are near 335°.

Magnetic Susceptibility Exaltations. While the NICS values and the geometry aromaticity indexes correlate with the bond angle sum, there is no satisfactory relationship between the exaltation of the magnetic susceptibility (Λ) (using the increments from increment scheme I) and the bond angle sum (cc = 0.684). However, the exaltations are larger when there are more phosphorus atoms in the ring (Table 2). To check the consistency of the increment scheme II (see Computational Methods), we investigated a second increment scheme, where instead of carbon, phosphorus substituents were used throughout (increment scheme II in Computational Methods). While the =CH− and the >PH increments do not change significantly, a 4.4 ppm difference is found between the two =P− increments (derived by I or II). Hence, the magnetic susceptibility of dicoordinate phosphorus depends on the atom's environment. To overcome this problem, we investigated the exaltation of the magnetic susceptibility by using the semihomodesmotic (SH) equations (examples given by eqs 4−6; data are given in Table 2). The susceptibility exaltations in these reactions increase with the number of dicoordinate phosphorus atoms in the ring. Furthermore, a reasonable linear correlation (cc = 0.968) was obtained with the bond angle sum. However, the exaltations are extremely large when two or more dicoordinate phosphorus atoms are present in a ring. In thiophene or pyrrole, the exaltations of the magnetic susceptibilities in the SH reactions are 5.1 and 11.3 ppm, respectively (see Table 2). This contrasts sharply with the 57.8 ppm value obtained for pentaphosphole. Such a large difference is unlikely to be due only to differences in aromaticity (see below).

We also investigated the variation in magnetic susceptibility (Δχ) between the planar and the nonplanar structures. Since the aromaticities of **1′**−**4b′** and **5** differ only slightly (see above), Δχ might be related to the bond angle sum. However, the correlation of Δχ with Σα (cc = 0.610) is poor. Correlations between Δχ and the bond angle sum at tricoordinate phosphorus (Σα) were examined for the series of deformed structures of phosphole, **1**, and of 1*H*-1,3,4-triphosphaphosphole, **3d**. For both systems with various out-of-plane angles, oop (see Figure 1), linear Δχ−Σα correlations (cc = 0.958 for **1** and cc = 0.996 for **3d**) are obtained. However, the Δχ−Σα slopes (−0.24 and −0.15 per degree, for **1** for **3d**, respectively) are distinctly different, explaining the lack of Δχ−Σα correlation for different

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(46) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. v. E.; Malkin, V. G.; Malkina, O. J. *J. Am. Chem. Soc.* **1997**, *118*, 12669.

(47) It is known that the in-plane complex formation of dicoordinate phosphorus with d elements results in slight shortening of either bond at the phosphorus atom. Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; p 157.

Table 2. B3LYP/6-311+G** Relative Energies (E_{rel} in Kcal/Mol), Bond Angle Sums about Tricoordinate Phosphorus ($\Sigma\alpha$ in Degrees), and Geometric (BI, BDSHRT), Magnetic ($NICS_{tot}$, NICS(π), χ, Λ, $\Delta\chi_{SH}$), and Energetic (ΔE_{SH}) Aromaticity Criteria for **1**−**9**

	formula	point group	E_{rel}	$\Sigma\alpha$	BI	BDSHRT	$NICS_{tot}$	NICS(π)	χ	Λ	$\Delta\chi_{SH}$	ΔE_{SH}
1	C_4H_5P	C_s	-	292.4	46	50	−5.0	−13.2	−47.6	−5.3	−2.2	0.0[a]
1′	C_4H_5P	C_{2v}	18.0	360.0	87	64	−17.4	−21.1	−57.4	−15.1		26.0[b]
2a	$C_3H_4P_2$	C_1		300.6	58	52	−6.0	−13.3	−48.2	−5.7	−6.6	5.0
2a′	$C_3H_4P_2$	C_s	9.9	360.0	88	64	−16.7	−20.0	−65.2	−22.7		24.8[b]
2b	$C_3H_4P_2$	C_1		300.6	48	52	−5.0	−13.2	−44.5	−2.0	−6.0	6.7
2b′	$C_3H_4P_2$	C_s	12.1	360.0	79	65	−16.8	−19.8	−63.7	−21.2		25.7[b]
3a	$C_2H_3P_3$	C_1		309.1	55	56	−7.3	−12.9	−56.7	−13.9	−17.2	5.6
3a′	$C_2H_3P_3$	C_s	6.4	360.0	80	67	−17.3	−19.3	−71.3	−28.5		22.9[b]
3b	$C_2H_3P_3$	C_1		312.6	63	56	−6.8	−13.1	−59.5	−16.7	−16.3	10.0[a]
3b′	$C_2H_3P_3$	C_s	5.2	360.0	83	66	−15.9	−19.2	−70.9	−28.1		22.8[b]
3c	$C_2H_3P_3$	C_s		316.9	66	57	−7.9	−13.0	−60.6	−17.8	−18.7	8.7
3c′	$C_2H_3P_3$	C_{2v}	3.9	360.0	82	66	−15.4	−19.4	−71.5	−28.7		22.2[b]
3d	$C_2H_3P_3$	C_s		310.8	56	56	−5.5	−13.0	−56.9	−14.1	−15.7	10.7
3d′	$C_2H_3P_3$	C_{2v}	6.1	360.0	79	67	−16.8	18.9	−69.1	−26.3		22.7[b]
4a	CH_2P_4	C_1		325.0	67	61	−9.3	−15.4	−64.4	−21.4	−26.4	9.1
4a′	CH_2P_4	C_s	1.8	360.0	83	69	−17.3	−18.6	−77.0	−34.0		19.4[b]
4b	CH_2P_4	C_1		329.2	76	62	−10.1	−15.5	−65.7	−22.7	−23.4	9.2
4b′	CH_2P_4	C_s	1.5	360.0	83	69	−15.7	−18.8	−76.8	−33.8		20.8[b]
5	HP_5	C_{2v}		360.0	87	68	−17.2	−18.8	−83.6	−40.4	−57.8	8.8[a]
6	C_5H_6	C_{2v}			29	45	−3.1	−12.1	−42.3	−2.4	0.8	0.2
7	C_4H_5N	C_{2v}		360.0	73	55	−14.7	−20.4	−46.7	−12.1	−11.3	8.1
8	C_4H_4O	C_{2v}			49	51	−12.3	−20.3	−28.7	−9.1	0.1	3.3
9	C_4H_4S	C_{2v}			68	57	−13.2	−20.5	−54.5	−10.0	−5.1	11.9

[a] These semihomodesmotic reaction energies (ΔE_{SH}, eqs 4 and 5) can be compared to aromatic stabilization energies (ASE, B3LYP/6-311+G**, obtained with eqs 1−3) for **1** (5.8), **3b** (9.6), and **5** (10.6 kcal/mol). [b] Based on geometries with constrained planar phosphorus; 17.3 kcal/mol for planar P_5H, **5**.

Table 3. Bond Angle Sum at the Tricoordinate Phosphorus ($\Sigma\alpha$) in Degrees, NICS[a] in Parts per Million, Magnetic Susceptibility (χ),[b] and Geometric Aromaticity Criteria (BI[c,d] and BDSHRT[c,e]) of **1**, **1′**, **3d**, and **3d′** Together with Data for $(CH)_4PH$ and 3,4-(P)$(CH)_2PH$ Optimized (B3LYP/6-311+G**) with Various Constrained Out-of-Plane Angles (Figure 1) of the Tricoordinate Phosphorus

Molecule: *cyclo*-$(CH)_4PH$ (**1**, **1′**)

oop	74° (**1**)	60°	40°	20°	0° (**1′**)
$\Sigma\alpha$	292.35	312.62	337.28	354.08	360.0
NICS[a]	−5.0	−7.0	−11.4	−15.7	−17.4
χ[b]	−47.6	−48.9	−52.3	−55.9	−57.4
BI[c,d]	46	54	77	86	87
BDSHRT[d,e]	50	54	58	62	64

Molecule: cyclo-1-PH-3,4-P2(CH)2 3d, 3d′

oop	65.4° (**3d**)	60°	40°	20°	0° (**3d′**)
$\Sigma\alpha$	310.84	317.94	340.94	355.06	360.0
NICS[a]	−5.5	−6.6	−11.6	−15.4	−16.8
χ[b]	−56.9	−58.1	−63.4	−67.6	−69.1
BI[c,d]	56	61	77	78	79
BDSHRT[d,e]	55	57	62	66	67

[a] NICS: nucleus-independent chemical shift (GIAO/6-311+G**, ref 5). [b] Magnetic susceptibility (IGAIM /6-311+G**) in cgi units. [c] Indexes are calculated with Gordy[40] bond orders (GBO) based on B3LYP/6-311+G** geometries. [d] Bird index; see Computational Methods and ref 38. [e] BDSHRT: bond-shortening index; see Computational Methods and ref 39. [f] Remarkably, similarly deformed pyrrole with an oop as in phosphole has a NICS value of −9 (cf. NICS = −15 planar structure, ref 5).

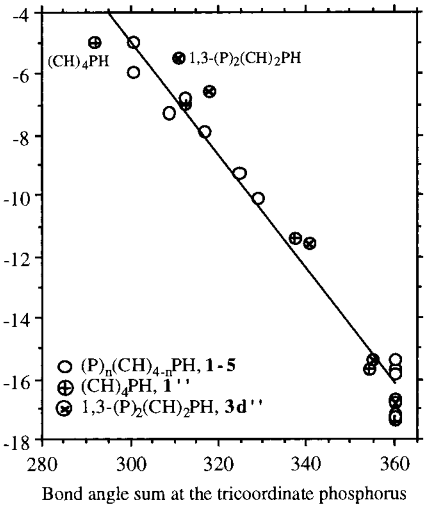


Figure 3. Plot of NICS values (GIAO/6-311+G**//B3LYP/6-311+G**) versus bond angle sum at the tricoordinate phosphorus for **1**−**5** (Figure 2) and geometries of $(CH)_4PH$ optimized with fixed oop (Figure 1; crossed circles). Correlation coefficient square, cc, for the minima is 0.941 (solid line, slope = −0.19 ppm/deg).

polyphosphaphospholes. The $\Delta\chi$−NICS correlations have cc = 0.999 both for **1** and for **3d**, while the slopes are 0.79 and 1.07, respectively. The difference between the slopes indicates that the magnetic susceptibility is influenced not only by aromaticity but also by the effects specific to the dicoordinate phosphorus atom (e.g., the lone pairs).

To understand the huge exaltations in the isodesmic reactions of types 4−6, as well as the differences in the slopes of the $\Delta\chi$−$\Sigma\alpha$ correlation, we investigated the magnetic susceptibilities of allyl- and phosphaallyl-substituted phosphines in their planar and nonplanar forms. While for allylphosphine the magnetic susceptibility of the nonplanar minimum was −31.7 ppm vs −32.3 ppm for the planar form, the planar form of $HP{=}PPH_2$ has a magnetic susceptibility of −39.2, which differs by as much as 10.1 ppm from the value for the nonplanar structure. For $HP{=}CHPH_2$ and $H_2C{=}PPH_2$ the differences between the planar and the nonplanar forms are 2.8 and 3.2 ppm, respectively. Hence, planarization decreases dramatically (larger negative value) the magnetic susceptibility of tricoordinate phosphorus atoms which have a dicoordinate phosphorus substituent, even in acyclic nonaromatic systems. Thus, the use of the magnetic susceptibility exaltation criterion to evaluate aromaticity in dicoordinate phosphorus systems requires care in the choice of the reference systems.

Stabilization Energies. While the geometric and magnetic aromaticity criteria correlate with the sum of the bond angles ($\Sigma\alpha$) about the tricoordinate phosphorus as discussed above, no significant stabilization can be expected in reactions 1−3. In each of these reactions, the tricoordinate phosphorus atoms in the reference structures (geometries are given in the Supporting Information) are more pyramidal than those in the corresponding phospholes. Thus, part of the stabilization achieved by the (partial) delocalization is consumed in making the tricoordinate phosphorus more planar than in the nonconjugated systems. Indeed, the ASE values calculated are small, 5.8 kcal/mol for phosphole (**1**, eq 1) and only increasing to 9.6 kcal/mol for **3b** (eq 2) and 10.6 kcal/mol for the planar pentaphosphole **5** (eq 3).[48]

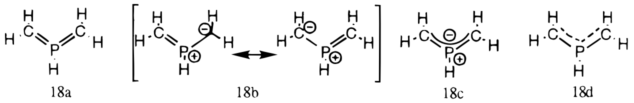
The computationally less demanding semihomodesmotic reactions[39] (illustrated for **1**, **3b**, and **5** by eqs 4−6) were evaluated (ΔE_{SH} values in Table 2) as alternative estimates of the stabilization energies for all of the systems (**1**−**5**). These reactions compensate for conjugative interactions in the fragments, giving results close to those of superhomodesmotic reactions, but ring strain is not included. The energies of eqs 2 and 3 are very close to those obtained from eqs 5 and 6, respectively. However, eq 4 gives a near zero value for **1**. Gordon's superhomodesmotic reaction[1] also gave a value near zero, indicating that the difference between eqs 1 and 4 can be attributed to ring strain. Indeed the strain in phosphole is estimated to be 5.2 kcal/mol on the basis of the energy difference of *all-trans*-$PH_2CH{=}CHC{=}CHPH_2$ optimized fully and with PCC and CCC angles constrained at the geometry of the ring. In any event, the ΔE_{SH} values of the polyphospholes are nearly unchanged throughout **1**−**5** and do not correlate with the bond angle sum.

When planar-constrained structures were used in the SH reactions (examples are given by eqs 4−6), the computed stabilization energies are much larger than those using the minimum energy structures (see Table 2). The stabilization energies of the planar phospholes decrease somewhat with the increasing number of dicoordinate phosphorus atoms in the ring.

Bonding at the Planar Tricoordinate Phosphorus. The bonding of tricoordinate planar phosphorus in the phospholes has been represented using both pentavalent[15,17,20−22] (**Ib**) and ylidic[19] (**Ic**, **Id**) depictions. The importance of the ylidic resonance contributions is best appraised with pentaphosphole **5** (the polarity of the PC bonds complicates the assessment of the other compounds). The NBO charge is +0.12 at the PH group in **5** (the hydrogen charge is summed with the tricoordinate phosphorus). The charges of the two dicoordinate phosphorus positions (α and β in **5**) are 0.00 and −0.06, respectively. Although there is some electron transfer from the tricoordinate phosphorus toward the other ring atoms, a much larger charge separation is expected from the delocalization implied by the ylidic resonance structures (**Ic** and **Id**).

The valence of the tricoordinate phosphorus atoms depends on the different measures employed. The sum of the Gordy bond orders (based only on the bond lengths) in **5** gives 4.6 as the valence of the tricoordinated phosphorus (assuming a bond order of 1 for the PH bond). This value, larger than 4, implies the contribution of the resonance structure **Ib**. The sum of the Wiberg covalent bond indexes,[49] however, is 3.6 for the tricoordinate phosphorus in **5**; this value indicates that the pentavalent structure **Ib** has only a small weight. The NLMO/NPA bond order sum is an even smaller value, 2.7, which is below 3! The difference between 4.6 and 2.7 results from the various definitions of the bond order. But which of them provides the best description?

Scheme 2. bis-methylene-phosphorane and its resonance structures



For better understanding, we consider the bonding in bis(methylene)phosphorane ($H_2C{=}P(H){=}CH_2$ (**18**)), a simple compound with tricoordinate "pentavalent" phosphorus. The Gordy PC bond order in **18** is 2.096 (the B3LYP/6-311+G** bond length is 1.654 Å). The Wiberg bond index, however, is only 1.513 for the same bond. The sums of the Gordy bond orders and the Wiberg bond indexes for the P atom in **18** are 5.1 and 3.9, respectively. The Wiberg bond index[49] is the sum of the AO coefficient products of the neighboring atoms (multiplied by the overlap) over the occupied orbitals. **18** (and its relatives in C_{2v} symmetry, such as HPP(H)PH (**19**)) has an allylic (3-center−4-electron: 3c−4e) π system.[50] Due to symmetry, the central atom (tricoordinate phosphorus) has a zero MO coefficient in the HOMO. As a result, the HOMO does not contribute to the Wiberg index. (For unsymmetric cases, such as CH2P(H)PH, the contribution should still be small.) Due to the nature of the HOMO, the PC π bond is polarized. Indeed, the B3LYP/6-311+G** natural charges calculated for **18** are +1.11 on the PH group and −0.55 on the CH_2 groups (with the hydrogen charges included onto the heavy atom). This charge separation supports the ylide resonance formulation **18b**, which can be summarized by the single depiction **18c** (Scheme 2). However, the σ bond polarity contributes; this already is considerable for the PC single bond: the partial charges in PH_2CH_3 (**20**) are +0.23 and −0.23 on PH_2 and CH_3, respectively (at the same level of the theory). Hence a significant portion of the phosphorus charge is due to the polarization of the σ framework. The separation of the charges in **19** (+0.2 and −0.1 on the central and terminal groups, respectively) is significantly smaller than in **18**. Whatever the charge separation, the two electrons from the π AO of the tricoordinate phosphorus take part fully in the delocalized π bonding. Planar phosphorus, being an excellent π donor, should be especially effective in such delocalization. Thus, the delocalized **18d** type structure, with some polarity (**18c**), is much more accurate for describing the bonding than the commonly used pentavalent representation (**18a**).[51] There is no need to invoke expansion of the valence shell. Neither in the planar phospholes (**1′**−**4b′**, **5**) nor in **18** or **19** do the d orbitals on phosphorus have considerable occupancies, in agreement with earlier findings.[19,50] This conclusion even applies to pentacoordinate phosphorus and tetra- or hexavalent sulfur compounds.[52,53]

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(48) The MP2(fc)/6-31G* ASE energies of **1**, **3b**, and **5** are 8.7, 12.3, and 17.0 kcal/mol, respectively.

(49) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(50) Schoeller, W. W.; Lerch, C. *Inorg. Chem.* **1986**, *25*, 576.

(51) The description of the bonding about tricoordinate phosphorus with two double and one single bond appears even in the most recent literature (e.g. Lamande, L.; Dillon, K.; Wolf, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *103*, 1). Nevertheless, this representation does not account properly for the delocalization of the phosphorus lone pair.

(52) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

(53) Magnusson, E. *J. Am. Chem. Soc.* **1993**, *115*, 1051.

Conclusions

Magnetic and geometric criteria show that the sequential replacement of −CH═ units by −P═ in phospholes, **1**−**5** as minima, increases the aromatic character. This trend is due to the decreased pyramidality of the tricoordinate phosphorus, when more P atoms are present. The aromaticities of all planar polyphospholes are very similar (or even decrease slightly) along the same series according to NICS and NICS(π) as well as the BI and the BDSHRT geometry aromaticity indexes. Due to the intermediate electronegativity of phosphorus (2.06), planar tricoordinate phospholes are among the most delocalized 6 π electron five-membered rings, and they are even more aromatic than pyrrole.

The magnetic susceptibilities are influenced considerably not only by aromaticity but also by substituent effects (e.g., by in-plane lone pair interactions). Hence, evaluations of the aromaticity based on exaltation estimates should be carried out with care. However, correlations of the susceptibility vs phosphorus pyramidalization are excellent, when only one system with various degrees of pyramidalization is examined. The stabilization energies deduced from isodesmic reactions are also less informative for phospholes since the energy consumed to flatten pyramidal tricoordinate phosphorus arrangements compensates for the energy gained by aromaticity.

The different descriptions of the valence of the tricoordinate phosphorus (pentavalent versus trivalent) discussed controversially before[19,20] resulted from differences in the definition of bond orders. Wiberg bond indexes give low values for allyl-type 3c−4e systems, which are highly delocalized. Analysis of the wave function shows that there is no need to invoke d orbitals or valence shell expansion at the tricoordinate phosphorus in planar phospholes, or for phosphorus generally.[52] While all five valence electrons of such phosphorus atoms are involved, the bonding is described better by employing delocalized and aromatic resonance representations. Even the simple allyl anion like model, which describes delocalization, is more realistic than the pentavalency assumption. Differences in the spectroscopic and chemical behavior of molecules containing planar and nonplanar tricoordinate phosphorus are due to variation in the availability of the phosphorus lone pair for conjugation with the π system and not to changes in valency.

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Supporting Information Available: B3LYP/6-311+G** geometries of the dihydro and tetrahydro derivatives of phosphole, 1,2,4-triphosphole, and pentaphosphole (1 page). Ordering information is given on any current masthead page.

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