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De-aromatizing Phosphole

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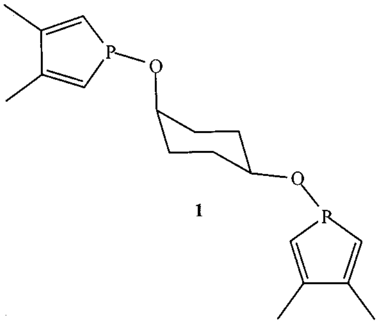
Quantum-chemical DFT calculations using the B3LYP functionals have been carried out for 1-R-substitued phospholes and some 1-R-substitued 3,4-dimethylphospholes where R = H, Me, Ph, CN, OH, OMe, F, Cl, and Br. The aromaticity of the phospholyl rings is interpreted as a function of geometric, magnetic, and energetic indexes. It is shown, in agreement with previous experimental results, that phosphole aromaticity does not correlate with pyramidality at phosphorus. Variation of hyperconjugative and, to a lesser extent, conjugative effects is responsible for the change in cyclic delocalization for the phospholes studied here.

Introduction

Phosphole aromaticity[1] has been debated for a long time.[2,3] It is now accepted that parent phosphole is poorly aromatic[4−6] and the least aromatic of the simple five-membered heterocyclic compounds (pyrrole, thiophene, and furan), being only slightly more aromatic than cyclopentadiene.[6] This reflects the nonplanar conformation of phosphorus in phosphole: the overlap of the lone pair with the diene π system is relatively small.

This situation has led several groups to look for ways to increase the aromaticity of phosphole. It has been shown theoretically that a planar phosphole has greatly enhanced aromaticity with respect to its nonplanar analogue.[7,8] Introduction of bulky substituents at P, which yielded phospholes having reduced pyramidal character,[9−12] provided experimental confirmation of this hypothesis. It has also been proposed that this electronic modification may be introduced by substituting intracyclic CR groups by P atoms.[13−15] Recently, a combination of these two effects has provided the first synthesis of a planar delocalized phosphole.[16] Conceptually very instructive, this work also led to phospholes showing aromatic reactivity.[11,17]

Very recently, two of us used a new approach to enhance the reactivity of phospholes.[18] By introducing substituents on P that reduce the conjugation between P lone pair and the diene, we were able to perform [4 + 2] cycloadditions between trivalent phospholes and dienophiles that do not occur with the corresponding 1-phenyl derivative. It was quite clear that the reactivity of 1-cyano and 1-alkoxyphospholes did not correlate to the degree of pyramidality at phosphorus (Σ(CPC angles) = 290° and 309°, respectively) because no [4 + 2] cycloaddition reactivity has been reported for 1-benzylphosphole (Σ(CPC angles) = 302°).[19] Thus, this work clearly showed that cyclic delocalization within the phosphole ring does



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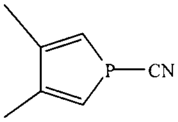
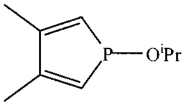


3-CN



3-O^{i}Pr

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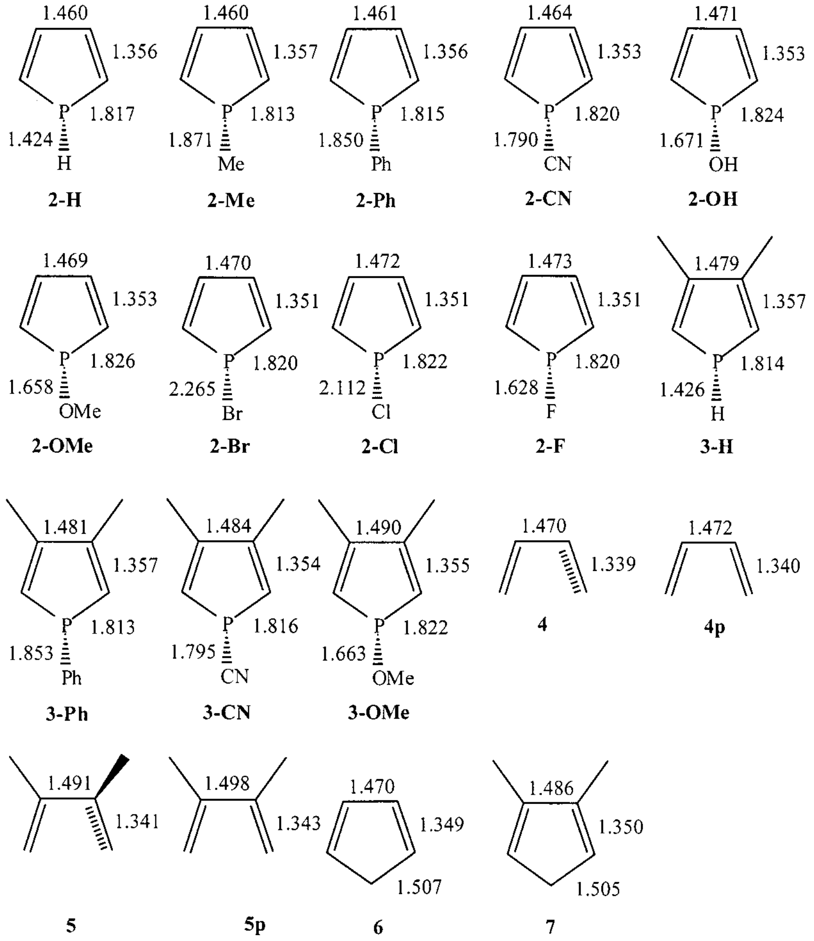
Chart 1. Important Bond Lengths for Compounds 2-R, 3-R, and 4−7 Calculated at the B3LYP/6-31G* Level



not uniquely reflect the pyramidality at phosphorus. However, it is not possible to deduce the precise influence of the P substituent on the electronic delocalization of phospholes **1**, **3-CN**, and **3-O^{i}Pr** purely on the basis of the study of reactivity and the X-ray analysis presented previously.[18]

Substituent effects on the aromaticity of phosphole have been investigated in two previous theoretical publications. It has been demonstrated that a BH_2 π-acceptor group increases delocalization within the ring by increasing planarity at phosphorus.[8,20] However, being more aromatic than pyramidal (fully optimized) parent phosphole, 1-BH_2 phosphole is less aromatic than planar (transition state) parent phosphole: competition for phosphorus lone pair between the BH_2 group and the phosphole ring lessens in this case the aromaticity of the ring by increasing the importance of the phosphaborafulvene resonance form.

Other substituents such as CH_3, NH_2, $C(CH_3)_3$, C_6H_5, or F, which were also introduced computationally, have been studied in less detail because they do not increase aromaticity within the phosphole. In view of the great synthetic potential of **1**, **3-CN**, and **3-O^{i}Pr** toward cycloaddition, it appeared useful to examine the effects of substituents on the electronic distribution in phosphole in depth. This is the aim of this study.

Methodology

All calculations were carried out with the Gaussian 98[21] suite of programs. Geometry optimizations of all compounds studied were performed, with no symmetry constraints, using Becke's hybrid three-parameter exchange functional and Lee, Yang, and Parr's nonlocal correlation functional (B3LYP)[22,23] using a 6-31G* basis set[24] containing six Cartesian d functions. To assess the reliability of our computation, **3-CN** was also optimized at the MP2/6-31G* and B3LYP/6-311G* level of theory.

Compounds **2-R, 3-R** (R = H, Me, Ph, CN, OH, OMe, Br, Cl, F, Chart 1) and **8-R** (Chart 2) show C_s symmetry in the optimized structures. Steric repulsion induces a nonplanar C_4 unit for **4** and **5**. For comparison, **4** and **5** were also optimized with a constraint of planar C_s geometry. The resulting structures are labeled **4p** and **5p**, respectively.

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Chart 2. P−R Bond Lengths and Sum of Bond Angles at Phosphorus (ΣP) in Phosphines 8-R Calculated at the B3LYP/6-31G* Level

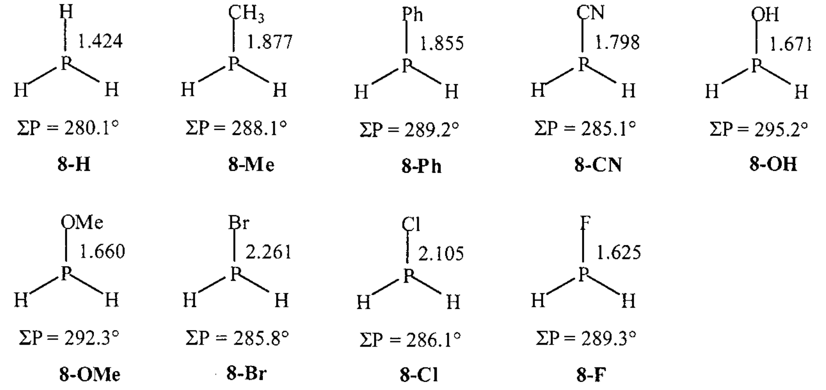


Table 1. Experimental and Calculated Bond Lengths (Å) and Bond Angles (deg) at B3LYP/6-31G*, B3LYP/6-311G*, and MP2/6-31G* Levels for 3-CN

method	P−CN	PC≡N	PC$_\alpha$	C$_\alpha$C$_\beta$	C$_\beta$C$_\beta$	C$_\alpha$−P−C$_\alpha$	P−C−N	ΣP^a
B3LYP/6-31G*	1.795	1.165	1.816	1.354	1.484	90.3	173.6	295.6
B3LYP/6-311G*	1.794	1.157	1.814	1.351	1.484	90.1	173.8	294.3
MP2/6-31G*	1.788	1.186	1.804	1.362	1.473	90.6	173.8	293.9
exptl^b	1.801(2)	1.151(3)	1.794(1)	1.347(2)	1.484(3)	90.9(1)	177.1(2)	290.3(2)

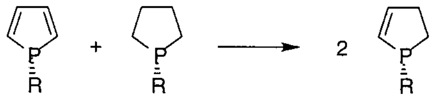
^{a} Sum of bond angles around P. ^{b} Reference 18.

For **2-OH**, **2-OMe**, and **3-OMe**, two minima were obtained, one with the H or Me group of the OR substituent endo and the other with the exo structure. As expected from the crystal structure of **1**, the endo isomer is the more stable in all three cases (by 0.7, 2.4, and 2.3 kcal mol^{-1} respectively). Accordingly, only results obtained for endo isomers are presented, unless otherwise noted. **8-OH** and **8-OMe** have been optimized with the endo structure.

A vibrational analysis was performed after optimization of each stationary point, to reveal its identity. All structures were energy minima, except for **4p** and **5p**, which were transition states. Absolute energies of localized orbitals in the molecules were analyzed using the natural bond orbital (NBO) partitioning scheme.[25−27]

As discrepancies between the various theoretical methods used to evaluate aromaticity have been known for some time,[28] we chose to use magnetic, energetic, and geometric criteria[29] in the present study. By comparing them, we were able to detect where (and sometimes why) a given result could be biased.

The nucleus-independent chemical shift (NICS, GIAO-SCF/6-31+G*//B3LYP/6-31G*) has been computed, as a magnetic criterion, at the center of the five-membered ring.[30,31] The homodesmic reaction (eq 1), with R = H, Me, Ph, CN, OH, OMe, Br, Cl, F, associated with cyclic delocalization, was used to evaluate the aromatic stabilization energies (ASE).[6]



(1)

For geometric criteria, we chose to compute both the Bird index (BI)[32] and the Julg parameter (JP).[33] The first, based on bond order, can be used to evaluate electronic delocalization in the entire five-membered ring, whereas the second, based on CC bond length, has been shown to give an indication of delocalization within the diene part of the ring.[20] A precision should be mentioned on the calculation of BI. It is based on the bond order *n* given by Gordy's formula:[34] $n = a/r + b$, where r is the bond length and a and b are coefficients that depend on the two atoms constituting the bond. a_{XY} and b_{XY} are found, for a X−Y bond, by means of a linear correlation with the lengths of X−Y, X=Y, and X≡Y. These coefficients were evaluated by Gordy[34] and Bird,[32] partly from experimental bond lengths but also from estimates. For the self-consistency of our computation, we decided to reevaluate these coefficients at the B3LYP/6-31G* level for CC and PC bonds, as done by others authors at a different level of computation.[15,35] In our case, B3LYP/6-31G* calculation give bonds length of 1.5301, 1.3311, 1.2048, 1.8765, 1.6746, and 1.5430, Å, respectively, for $H_3C{-}CH_3$, $H_2C{=}CH_2$, $HC{\equiv}CH$, $H_3C{-}PH_2$, $H_2C{=}PH$ and $HC{\equiv}P$. These values give rise to the coefficients: $a_{CC} = 7.6418$, $b_{CC} = 2.2804$, $a_{PC} = 14.6630$, and $b_{PC} = 3.1819$, used here.

Results

Geometry. A crystal structure of **3-CN** has been reported,[18] so direct comparisons with our calculated structure can be made. Table 1 shows optimized structural parameters for **3-CN** at various high ab initio and DFT levels of calculation along with its crystal structure. All optimized structures of **3-CN** are very similar and close to the experimental structure. However, higher computational levels did not give clear-cut improvements, so we chose to use the less computationally expensive method for the rest of this study.

Chart 1 shows the calculated bond length for compounds **2-R**, **3-R** (R = H, Me, Ph, CN, OH, OMe, Br, Cl, F), and **4**−**7**. We will first examine unsubstituted phospholes **2-R** and then analyze the effect of introducing methyl groups at position C$_\beta$.

The C$_\alpha$C$_\beta$ and C$_\beta$C$_\beta$ phosphole bond length alternation in compounds **2-R** tends to increase along the series, thus

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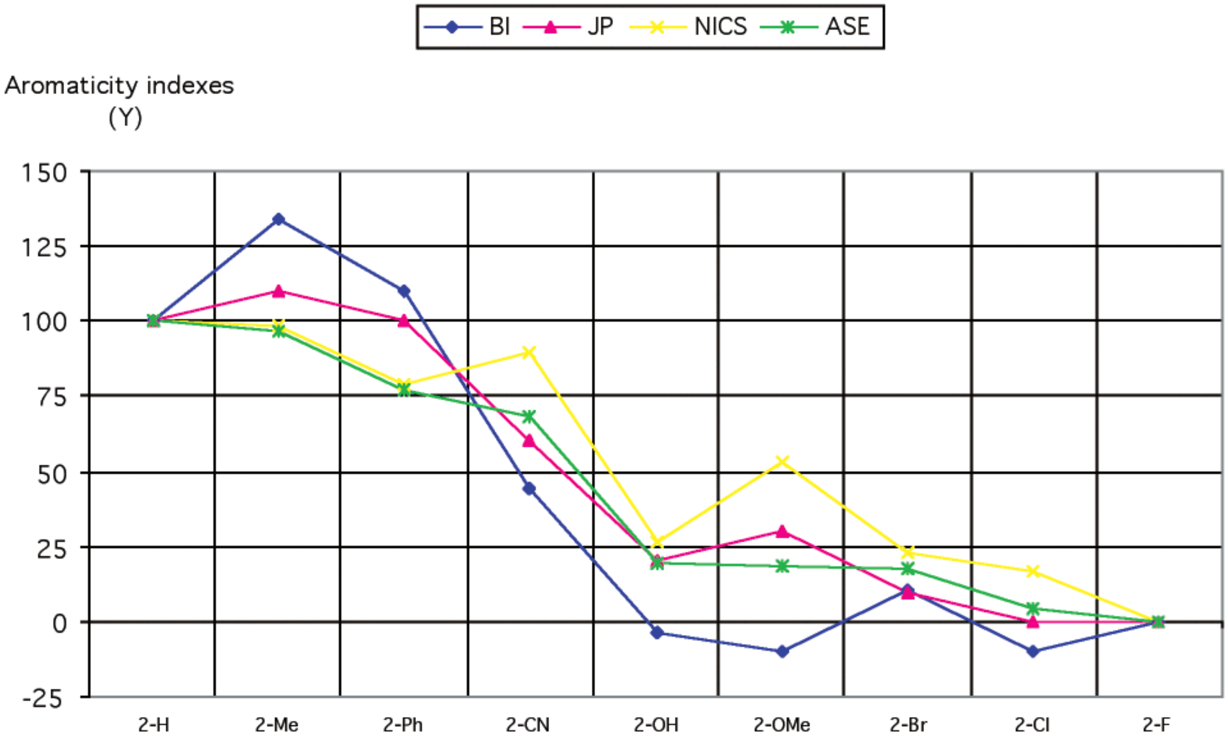

Figure 1. Plot of the various aromaticity indexes, percentage relative to **2-H** and **2-F** ($Y = 100(\text{index} - \text{index}(\mathbf{2\text{-}F}))/(\text{index}(\mathbf{2\text{-}H}) - \text{index}(\mathbf{2\text{-}F}))$).

indicating decreasing delocalization. **2-Br**, **2-Cl**, and **2-F** show degrees of bond length alternation very close to that in cyclopentadiene **6**. The effect of substitution on the PC_α bond length is less even, but the slight increase from **2-H** to **2-F** fits well with a decrease in delocalization.

The introduction of methyl groups on C_β atoms provokes an increase in the $C_\beta C_\beta$ bond length of about 0.02 Å. This is also found for the cyclopentadienyl ring ($C_\beta C_\beta$ = 1.470 Å in **6**, 1.486 Å in **7**) and planar (1.472 Å in **4p**, 1.498 Å in **5p**) or fully optimized (1.470 Å in **4**, 1.491 Å in **5**) butadienes. Phospholyl rings show the same trend when compared **3-H**, **3-Ph**, **3-CN**, and **3-OMe**, respectively, with **2-H**, **2-Ph**, **2-CN**, and **2-OMe**. $C_\alpha C_\beta$, PC_α (or $C_{sp2}C_\alpha$), and PR (R = H, Ph, CN, OMe) bond lengths remain almost unchanged.

Aromaticity. The geometric indexes (Table 2, Figure 1) indicate a sizable decrease in aromaticity along the series **2-R** (R = H, Me, Ph, CN, OH, OMe, Br, Cl, F), with both the Bird index (BI) and the Julg parameter (JP). A parallel variation is found for the methylated phospholes.

BI, calculated for the five-membered ring, is systematically much higher for phospholes (BI between 36 and 46) than for cyclopentadienes (23−24), while JP, calculated for the diene part, shows neighboring values between cyclopentadienes and the less aromatic phospholes. These two indexes thus give very different results when compared cyclopentadienes to phospholes.

Table 2. B3LYP/6-31G* Geometric (Bird Index (BI) and Julg Parameter (JP)), Magnetic (NICS[a]) and Energetic (ASE in kcal/mol) Aromaticity Measures of the Ring Systems under Investigation

	BI	JP	NICS	ASE
phospholes				
2-H	44.4	0.72	−4.98	+5.87
2-Me	46.4	0.73	−4.91	+5.60
2-Ph	45.0	0.72	−4.13	+3.91
2-CN	41.1	0.68	−4.57	+3.20
2-OH[b]	38.3 (41.1)	0.64 (0.64)	−1.97 (−1.82)	−0.91
2-OMe[b]	37.9 (40.3)	0.65 (0.64)	−3.05 (−2.08)	−0.97
2-Br	39.1	0.63	−1.81	−1.10
2-Cl	37.9	0.62	−1.57	−2.20
2-F	38.5	0.62	−0.87	−2.56
3,4-dimethylphospholes				
3-H	42.4	0.62	−4.64	-
3-Ph	42.3	0.61	−3.69	-
3-CN	39.2	0.57	−3.69	-
3-OMe	36.3	0.54	−2.98	-
cyclopentadienes				
6	24.1	0.62	−3.21	-
7	22.8	0.53	−3.06	-
butadienes				
4	-	0.55	-	-
4p	-	0.55	-	-
5	-	0.42	-	-
5p	-	0.38	-	-

[a] Calculated at the GIAO-HF/6-31+G*//B3LYP/6-31G* level. [b] Values in parentheses are given for the exo conformation of the P substituent.

Energetic (ASE) and magnetic (NICS) measures of aromaticity are also collected in Table 2 and Figure 1. These data show almost the same changes in aromaticity as a function of the substituent as geometric indexes. This confirms that introducing alkoxy, halogen, and to a lesser extent, cyano substituents at phosphorus results in a decrease in delocalization. It is noteworthy that the position of 1-cyano- and 1-phenylphosphole within the series varies according to the index employed. NICS indicates a greater or equal aromaticity of **2-CN** (−4.57) with respect to **2-Ph** (−4.13) and **3-CN** (−3.69) with respect to **3-Ph** (−3.69), whereas the opposite trend is observed with geometrical and energetic indexes. This discrepancy between aromaticity indexes has been known for many years[36] and is still a subject of debate.[6,28] Experimentally, **3-CN** shows dienic reactivity, which is not observed for **3-Ph**. The geometrical and aromaticity

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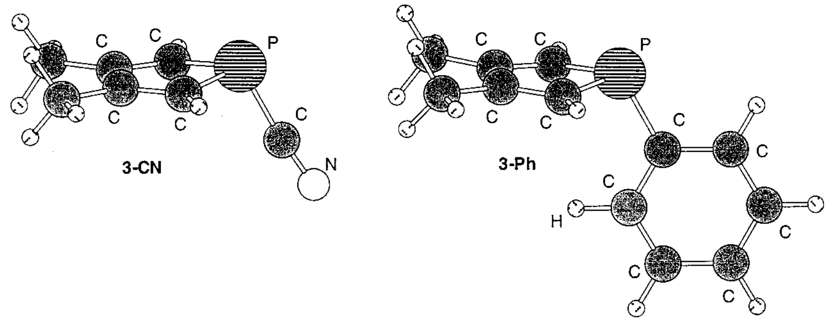
Chart 3. Optimized Structures of 3-CN and 3-Ph at B3LYP/6-31G*



3-CN **3-Ph**

Table 3. B3LYP/6-31G* Geometric (Sum of the Bond Angle at P (ΣP) in Phosphole, Difference between ΣP in 1-R-Substituted Phosphole and in Phosphine PH_2R (Δ(ΣP))), and Energetic (Absolute Energy Given by Kohn−Sham Orbitals (E_{KS}(LP) and E_{KS}(P−R)) and by Localized NBO Orbitals (E_{NBO}(LP) and E_{NBO}(P−R)) of Phosphorus Lone Pair and σ P−R Bond in Phosphines PH_2R) Effects of Substituents in the Investigated Phospholes (Values for 3,4-Dimethylphospholes Are Given in Parentheses) and Phosphines

R	phosphole ΣP	phosphole vs phosphine Δ(ΣP)	phosphine			
			E_{KS}(LP)	E_{NBO}(LP)	E_{KS}(P−R)	E_{NBO}(P−R)
H	293.3 (292.2)	13.2 (12.1)	−0.27571	−0.44546	−0.38793	−0.48289
Me	300.7	12.6	−0.25126	−0.42091	−0.35157	−0.52605
Ph	302.6 (300.8)	13.4 (12.7)	−0.25740	−0.42016	−0.33478/−0.40196	−0.54727
CN	297.2 (295.6)	12.1 (10.5)	−0.29908	−0.47402	−0.49605	−0.66109
OH	306.9	11.7	−0.26445	−0.43204	−0.51290	−0.75259
OMe	308.9 (307.1)	16.6 (14.8)	−0.26401	−0.43371	−0.47727	−0.74686
Br	298.9	13.1	−0.26466	−0.49336	−0.39536	−0.54686
Cl	299.8	13.7	−0.27660	−0.49059	−0.41799	−0.60082
F	304.0	14.7	−0.27240	−0.45879	−0.47823	−0.85017

indexes thus seem in our case more reliable than NICS value. This NICS result may reflect the position of the phosphorus substituent in space. The cyano group is located outside the area exerting a diamagnetic influence on the ring, whereas one hydrogen of the phenyl group is located inside this area (Chart 3) and thus should influence the ring current. Consequently, comparison between the NICS values for **3-CN** and **3-Ph** (or of **2-CN** and **2-Ph**) does not seem strictly valid. The same effect is observed in compound **2-OMe**, where a hydrogen atom of the methoxy group stays close to the five-membered heterocycle. This could account for the quite large difference in NICS values for **2-OH** and **2-OMe** (−1.97 against −3.05), despite very similar structures (OH against OMe). This effect is absent when comparing the exo conformers of **2-OH** and **2-OMe** (Table 2). In this conformation, the substituent effects are similar, leading to coherent BI, JP, and NICS values, all typical of low aromaticity.

Discussion

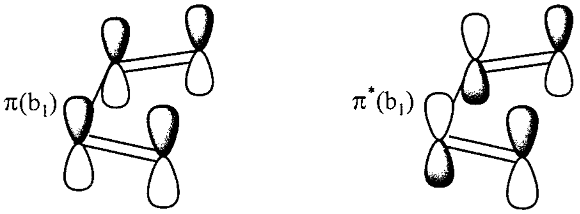
The preceding values agree well with the experimental results implying low aromaticity in 1-cyano- and 1-alkoxyphospholes relative to 1-alkyl- and 1-phenylphospholes. Furthermore, they show less cyclic delocalization in 1-alkoxyphosphole than 1-cyanophosphole, which nicely correlates with the greater reactivity of acrylonitrile toward **1** (rt, 30 min) than **3-CN** (80 °C, 8 h). They also indicate that 1-halogenophospholes are not aromatic. We now examine whether structural or electronic effects influence these variations.

Pyramidality at Phosphorus. The sum of the bond angles around phosphorus in phospholes **2-R** (ΣP) is collected in Table 3. ΣP decrease in the order OMe > OH > F > Ph > Me > Cl > Br > CN > H. This series clearly does not follow the trends observed for the aromaticity, and more closely reflects the steric influence of the substituent (vide infra). This confirms the conclusion drawn from experimental results:[18] aromaticity in 1-substituted phospholes does not correlate directly to pyramidality at phosphorus. A previous theoretical study[15] has indicated that, for a given phosphole, the aromaticity increases as the pyramidality of the tricoordinated phosphorus is made to fall from 290° (pyramidal phosphorus) to 360° (planar phosphorus): in planar phosphole, the overlap between phosphorus lone pair and the diene π system is maximal. In this perspective, the phospholes under investigation here are rather pyramidal: the sums of bond angles lay between 293° and 309°. Our results show that, in this range, the relationship between pyramidality and aromaticity does not hold any longer. Therefore, variation in the overlap between phosphorus lone pair and the π system of the diene does not govern the level of aromaticity of the phospholes we present in this paper: the electronic influence of the substituent must also play a role (vide infra). No conclusions about the respective aromaticity of various phospholes should thus be drawn solely from examination of pyramidality.

Table 3 also compares the pyramidality at phosphorus for 1-substituted phosphine PH_2R **8-R** (Chart 2) and 1-substituted phosphole in terms of the function Δ(ΣP). These data show that Δ(ΣP) in a phosphole is always about 13.5 ± 3 less than in PH_2R. The good correlation of these values implies that the variation in pyramidality at phosphorus in 1-substituted phospholes is predominantly governed by the factors influencing pyramidality in the corresponding 1-substituted phosphines.

The steric factors, which influence ΣP for phosphines **8-R,** also appear to dominate for phospholes. The case of the fluorine substituent, which induces a lower pyramidality at P (i.e., greater ΣP) than for Ph and other halogens, merits some attention. The P−F bond length (1.625 Å in **8-F**) is close to the P−H value (1.424 Å in **8-H**). For PFH_2 this induces a steric repulsion between

Chart 4. π Molecular Orbitals of b_1 Symmetry in Butadiene



the lone pairs of F and the hydrogen atoms also located at P. This effect is not seen for the other halogens, despite their more voluminous lone pairs, because of the much greater P−Cl and P−Br bond length. We think that this could explain the smaller pyramidality of **8-F**, although other influences could not be excluded.

An early study of phosphole aromaticity explored the relative importance of phosphorus lone pair conjugation and P−R bond hyperconjugation with the π molecular orbitals of the dienic functionality (Chart 4):[2] hyperconjugation was suggested to have a much greater influence. What is the importance of these two effects in the case of 1-substituted phospholes?

To provide an answer to this question, we looked at the phosphorus lone pair and σ P−R bond energies in phosphines PH_2R **8-R**. Table 3 gives values obtained using delocalized Kohn−Sham molecular orbitals and localized natural orbitals of the NBO partitioning scheme.[37] As the Kohn−Sham MOs are delocalized and not necessarily associated uniquely with any given atom or pair of atoms, we focused more closely on the NBO results.

Hyperconjugation Effect. A recent theoretical study of the aromaticity of 5,5′-substituted cyclopentadienes has shown that cyclic delocalization is increased by electropositive substituents and reduced by electronegative substituents (Cl, F), which may give antiaromatic systems.[35] The same effect was also observed in 1*H*-substituted phosphirenium cations.[38] Our results show that this effect is also present in phosphole rings.

The effectiveness of hyperconjugation is directly related to the energy gap between the π(b1) and π^*(b1) orbitals of butadiene and the P−R σ bond.[1] The introduction of a σ electron-withdrawing substituent at P lowers the σ bond energy and, as a consequence, lessens its conjugation with the π^*(b1) orbital above. Given that the energy levels of the P−R σ bonds in **8-R** approximately follow the electronegativities of the substituents (Table 3),[39] so will the hyperconjugation. Thus, it is efficient in parent phosphole, built from **8-H**, and operates poorly in the phosphole built from **8-F**.

Since the electronegativity of the σ substituent is reflected in the energy of the σ bond, we note that the σ^* MO energy should follow the same trend as the corresponding σ orbital[40,41] and that a decrease in σ^* energy enhances its conjugation with the π(b1) MO of butadiene. This leads to a 4-electron cyclic delocalization and, again, a de-aromatizing effect.

However, in the case of halogens Cl and Br, the energy level ordering for the P−R σ bonds does not fit the trend previously calculated for phosphole aromaticity (vide infra).

Conjugation Effect. Table 3 gives the energies for the phosphorus lone pair in phosphines **8-R**, which were obtained using delocalized Kohn−Sham molecular orbitals or localized natural orbitals of the NBO partitioning scheme.[37] The most striking feature in these results is the low energy of chloro- and bromophosphines lone pairs, which weakens its conjugation with the π^*(b1) orbital of butadiene in the corresponding phospholes. This is probably the reason for their very low aromaticity, rather than hyperconjugation.

In the other phosphines listed here, the influence of the substituent on the lone pair energy is much smaller than upon the P−R bonds above. Furthermore, neither the KS nor the NBO values for E(LP) show any trend capable of explaining the reduction of aromaticity upon moving from **2-H** to **2-OMe**.

Conclusion

The calculations above nicely complement previous theoretical studies on phosphole aromaticity as well as recent experimental work, which demonstrates the possibility of fine-tuning the reactivity of phospholes by choosing the appropriate substituents at phosphorus.

1-Alkyl- and 1-arylphospholes show the same aromaticity as parent phosphole whereas 1-cyanophosphole is slightly less aromatic. 1-Alkoxy- and 1-halogenophospholes have lost, for their part, most of the cyclic delocalization.

It has been demonstrated that pyramidality at phosphorus does not explain these variations. This study does not contradict an earlier work, which draws conclusions concerning the influence of phosphorus pyramidality for different geometries of any given phosphole. However, it clearly demonstrates that the use of the pyramidality criterion above is not valid for a series of 1-substituted phospholes where only minute variations in pyramidality are observed. In this case, other parameters will predominantly influence cyclic delocalization.

Variations in conjugative (delocalization of phosphorus lone pair), and hyperconjugative effects have been shown to be responsible for the change in cyclic delocalization in the phospholes studied here. Hyperconjugation dominates, but cannot explain alone the overall variation in aromaticity observed: while conjugation is generally less important, it may become significant, especially in the case where a halogen substituent is present at phosphorus.

These subtle effects greatly alter the reactivity of phosphole as reflected in promoting [4 + 2] cycloaddition of the ring.

Supporting Information Available: Cartesian coordinates and absolute energies of compounds **2-R**, **3-R**, **4**−**7**, and **8-R**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[37] We would like to stress out that the absolute energy of these orbitals did not have physical signification. However, their relative energies could be used to give trend in a series of comparable compounds. See, for example: Stowasser, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1999**, *121*, 3414−3420.

[38] Goeller, A.; Heydt, H.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840−5846.

[39] Values of Pauling electronegativities and group electronegativities (Boyd R. J.; Boyd S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652−1655) for the substituents used here: H, 2.1; Me, 2.55; Ph, 2.58; CN, 2.69; OH, 3.55; OMe, 3.53; F, 4.0; Cl, 3.0; Br, 2.8.

[40] Xiao, S.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033−7.

[41] Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391−8.