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Does the Planar Aromatic Phosphorus Analogue of Pyridone Exist?

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Density functional calculations show that the minimum of *meta*-phosphanyl ketone on the potential energy surface is a planar conformation. The minima of *ortho*-phosphanyl ketone and *para*-phosphanyl ketone have nonplanar structures. However, according to the sum of the bonding angles about the tricoordinated phosphorus atom, the degree of planarity of the *ortho*- and *para*-phosphanyl ketones is higher than that of the known phosphole and PH_3. The nucleus-independent chemical shifts and other electronic properties show that the planar phosphorus analogues of pyridone are π aromatic. The position of the carbonyl group relative to the tricoordinate phosphorus atom affects the delocalization of the phosphorus lone pair of electrons and the aromaticity of the molecule. Introduction of a σ-donor, π-acceptor, and bulky substituents at the phosphorus atom can decrease the pyramidal character efficiently. We predict that planar aromatic phosphanyl ketones do exist.

Introduction

The structures and electronic properties of pyridone have been studied experimentally and theoretically for many years.[1] It is not surprising that some nitrogen-containing compounds, for example, pyrrole or pyridone, exist as planar species.[2] In these compounds, the driving force for planarity at the nitrogen center is believed to be the conservation of aromaticity.[3] Phosphorus analogues of pyridine, however, have not been reported so far. It is well known that phosphole is a nonplanar structure with an inversion barrier ranging from 17.19 to 26.46 kcal mol^{-1} at different levels of theory.[4,5] The planarity of the tricoordinated phosphorus atom in mono-, di-, and triphospholes has been discussed by Nyulászi who found that the proton inversion barrier decreases as the number of phosphorus atoms in phosphole increases.[5,6]

In a pentagon, the pyramidality of a tricoordinated phosphorus atom is mainly affected by two factors. One is the ring strain; the replacement of carbon atoms in the ring by bicoordinated phosphorus atoms with smaller bonding angles can release this strain and lead to a decrease in the inversion barrier about the phosphorus atom, as reported by Nyulászi.[5,6] The other factor is the presence of lone pairs of electrons on the tricoordinated phosphorus atom in the ring, which conflict with the planarity of a molecule owing to their repulsion by adjacent bonds. As the phosphorus lone pairs of electrons are more diffusive than the lone pair of electrons of the nitrogen atom, they repel the electrons in the adjacent bonds more strongly than the nitrogen lone pair. For example, in PH_3 and NH_3 at the B3LYP/6-31+G(2d,2p) level of theory, ∠HPH is 93.61°, whereas ∠HNH is 106.80°. Pyykkö et al.[7] systemically studied the inversion barriers of group-15 hydrides. The results calculated at various theoretical levels show that the inversion barrier of PH_3 is, on average, 0.4 kJ mol^{-1} more than that of NH_3. The delocalization of the lone pair of electrons also has an important effect on the planarity of the ring. The studies carried out by Nyulászi[6,8] have shown that the pyramidality of a tricoordinated phosphorus atom can be diminished by the introduction of a strong π-acceptor group.

In this work, we will study the structural and electronic properties of the phosphorus analogues of pyridone, the *ortho*-, *meta*-, and *para*-phosphanyl ketones. In a planar hexagon, the geometric strain can be considered to be a minimum. Boraphosphanes are familiar hexagonal aromatic systems containing a tricoordinated phosphorus atom.[9] The first known cyclic compounds with a planar tricoordinated phosphorus atom were the six-membered cyclic boraphosphanes. The planar hexagonal phosphinyl carbene ring has also been shown computationally to be a minimum on the potential energy surface (PES).[10] Moreover, as phosphorus and carbon lie in a diagonal line in the Periodic Table, according to the diagonal law, phosphorus has a comparable conjugative ability to carbon.[11] Recently,

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Moores et al.[12] successfully synthesized a 1-methylphosphininium gallium tetrachloride adduct and investigated its structural and electronic properties theoretically. On the basis of these results, a planar phosphabenzenone is expected to be more aromatic than pyridone. In addition, although pure planar phosphole parent molecules have so far not been reported experimentally, the first example of a fully delocalized 1,2,4-triphosphole containing a planar tricoordinated phosphorus atom has been synthesized and ascribed to the presence of substituent groups on the ring.[13] Thus, we believe that planar aromatic phosphanyl ketone compounds can also be synthesized.

The concept of aromaticity was defined a long time ago to explain the exceptional stability and special chemical behavior of a series of compounds and to distinguish these compounds from conventional aliphatic compounds.[14] Despite extensive research in the literature, aromaticity has eluded rigorous quantification. The main reason for this is that aromaticity is a differential property that often refers to the difference between the properties of an "aromatic" molecule and those of an artificial "nonaromatic" reference system. A rigorous definition of such a reference system does not exist, which constitutes the main obstacle for the satisfactory quantification of the aromaticity of a compound. Following this reasoning, v. R. Schleyer and coworkers proposed using the opposite of the computed magnetic shielding at the ring centers, referred to as the "nucleus-independent chemical shift" (NICS),[15] as an effective criterion for aromaticity and antiaromaticity. The reason for using the NICS as an aromatic measurement is the "abnormal" chemical shielding of hydrogen in some aromatic and antiaromatic ring compounds.[15] Also, it is independent of reference systems and is not affected by the size of a ring. Satisfactory results[16] have been obtained in the study of aromatic compounds, for example, heterocyclic 2π electron aromatic systems, pyridone derivatives, N-heterocyclic carbenes, and silylene complexes. In this work, we will analyze electron delocalization in the planar conformations of phosphanyl ketone compounds using the dissected NICS technique,[17] canonical molecular orbital NICS (CMO-NICS).

Computational Methods

All quantum chemical calculations were carried out with the Gaussian 03 program package.[18] Constrained (to planar geometry) and full geometry optimizations were performed on each of the three investigated molecules with the use of the B3LYP method at the 6-31+G(2d,2p) level of theory. To check the nature of the stationary points on PES, second-order derivatives of energy with respect to the nuclear coordinates were calculated at the same level of theory for all the optimized structures. In order to test the reliability of the DFT results, the QCISD/6-31+G(2d,2p) level of theory was employed to optimize geometries and calculate the vibrational frequencies of the three planar conformations.

In the natural bond orbital (NBO)[19,20] analysis, the density matrix was partitioned into localized one-center (core and lone pair) and two-center orbitals to describe a Lewis-type structure. CMO analysis serves as a bridge between valence bond theory and molecular orbital theory. By summing the contribution of the NBO within each type, one obtains a convenient measure of the total bonding, nonbonding, or antibonding character of each MO. These NBOs in turn can be decomposed into the contributions from individual atomic centers leading to a detailed description of the "atom–atom" bonding character of each MO.

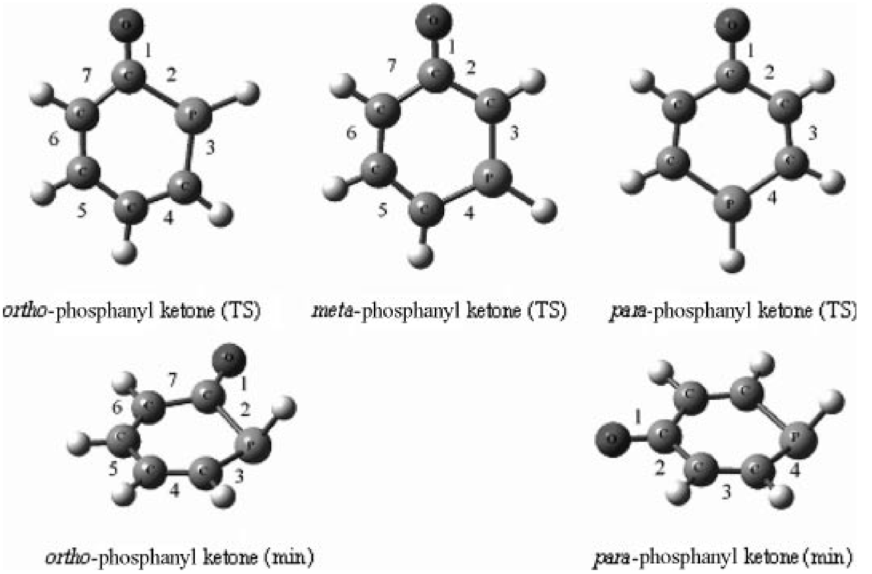
Magnetic properties (NICS) were predicted at the B3LYP/GIAO/6-31+G(2d,2p) level of theory for the planar conformations. The NBO model was used to analyze the electronic properties of these molecules and to calculate the dissected NICS.[17] NICS corresponds to the negative value of the magnetic shielding computed at chosen points in a molecule. In an uncoupled density functional treatment, that is, where the perturbation of the magnetic field B to the wave function is not calculated in a self-consistent way, the chemical shielding tensors (and the NICS tensors) can be described as the sum of the chemical shifts arising from the occupied molecular orbitals (OMOs).[20] We can thus obtain details about every MO's contribution to the total NICS.

Electron localization function (ELF) topological analysis was carried out with TopMoD[21] and the molecular orbitals were plotted with the MOLDEN program.[22] ELF is considered as a useful tool to explore the electronic structure of a molecule, especially in a delocalized system.[23] It can be employed as a measure of electron localization. The average population of a region rich in electrons may be obtained by integrating the electron density over them. Such a population is not expected to have an integral value and the bond populations are about twice as large as the topologically defined Lewis bond orders. The related variance (labeled as σ^2), as defined by atomic overlap and electron population, has been predicted. The value of σ^2 can be interpreted as a consequence of electron delocalization.[24]

Results and Discussions

Structural and Electronic Properties

Figure 1 shows the optimized structures of the investigated molecules. Various structural parameters and the total energies are listed in Table 1. The results reveal that the planar *meta*-phosphanyl ketone is a minimum on the PES. Its lowest frequency, 135.3 cm^{-1}, corresponds to a bent vibration of the ring. We also tested the stability of the wave function of the *meta*-phosphanyl ketone at the same level of theory and discovered that the closed-shell singlet is stable under open-shell and triplet perturbation. The dimerization of the *meta*-phosphanyl ketone is quite difficult. However, the planar conformations of the other two molecules are transition states. The lowest frequency is –416.2 and –650.0 cm^{-1}, respectively, which indicates out-of-plane



ortho-phosphanyl ketone (TS) *meta*-phosphanyl ketone (TS) *para*-phosphanyl ketone (TS)

ortho-phosphanyl ketone (min) *para*-phosphanyl ketone (min)

Figure 1. The optimized structures of the *ortho*-, *meta*-, and *para*-phosphanyl ketones. Min denotes minimum on the potential energy surface. TS denotes a transition state.

Table 1. Total energies, bond lengths, bond angles summed about the tricoordinate phosphorus atoms, and the lowest frequency for the planar and stable conformations of the *ortho*-, *meta*-, and *para*-phosphanyl ketones. The bold numbers represent the Wiberg bond indices.

	Bond length [Å]							Σa	E_{tot}	Freq.$_{\text{min}}$
	B1	B2	B3	B4	B5	B6	B7	[°]	[kcal mol^{-1}]	[cm^{-1}]
ortho$_{\text{(TS)}}$	1.22	1.82	1.72	1.38	1.42	1.38	1.45	360.0	–610.0871	–416.2
	1.62	**1.05**	**1.25**	**1.56**	**1.29**	**1.60**	**1.18**			
ortho$_{\text{(min)}}$	1.21	1.87	1.80	1.35	1.45	1.36	1.47	304.1	–610.1047	107.8
	1.72	**0.96**	**1.03**	**1.76**	**1.17**	**1.71**	**1.12**			
meta$_{\text{(min)}}$	1.24	1.47	1.67	1.68	1.42	1.38	1.47	360.0	–610.0709	135.3
	1.59	**1.15**	**1.43**	**1.36**	**1.31**	**1.61**	**1.13**			
para$_{\text{(TS)}}$	1.24	1.47	1.37	1.73	1.47	1.37	1.73	360.0	–610.0754	–650.0
	1.62	**1.12**	**1.67**	**1.19**	**1.12**	**1.67**	**1.19**			
para$_{\text{(min)}}$	1.23	1.48	1.35	1.80	1.48	1.35	1.80	301.1	–610.1069	108.2
	1.70	**1.07**	**1.82**	**1.02**	**1.07**	**1.82**	**1.02**			

bending about the tricoordinated phosphorus atom. The higher level QCISD/6-31+G(d,p) calculations corroborate the DFT predictions (see the Supporting Information). The following discussion will be based on the DFT-optimized predictions.

The *ortho*- and *para*-phosphanyl ketones have inversion barriers of 11.04 and 19.77 kcal mol^{-1}, respectively. Although the planar conformation of *meta*-phosphanyl ketone is on the PES, the planar isomers of *ortho*- and *para*-phosphanyl ketone are 10.17 and 2.82 kcal mol^{-1} more stable than the *meta*-phosphanyl ketone, respectively. The energy difference between the *ortho* and *meta* compounds is so large that it is comparable to the inversion barrier of the *ortho*-phosphanyl ketone.

The Wiberg bond index is the sum of the charge between neighboring atoms over the occupied orbitals. It is an important descriptive measure of bond order. The value of the WBI of a double bond is equal to 2. The WBI of a single bond is 1. Because of the variation of bond lengths in different situations, it is difficult to tell how much bond alternation there is. However, bond order does not suffer from this deficiency. In the three planar conformations, the Wiberg bond indices (WBIs) of all the bonds in the hexagon are larger than 1.0 and smaller than 2.0 (as shown in Table 1), and all the C–C and C–P bond lengths are between the standard single and double bond lengths determined at the same level of theory. The C–C single bond length in ethane (C_2H_6) is 1.50 Å and the double bond length in ethylene (C_2H_4) is 1.33 Å, the C–P single bond length in PH_2CH_3 is 1.87 Å and the C–P double bond length in $PH_2CH_2^+$ is 1.63 Å at the B3LYP/6-31+G(2d,2p) level of theory. These data reveal that there is electronic delocalization in the planar conformations. Note that the WBIs of the bonds between the carbonyl carbon atom and its adjacent ring atoms, relative to those of the other bonds in the ring, are very small. One reason for this is as follows: In a planar hexagon, when all the atoms adopt sp^2 hybridization, maximal overlap between hybrid orbitals occurs, like that in benzene. The optimized ∠HCH of formaldehyde is 116.5° at the B3LYP/6-31+G(2d,2p) level of theory.

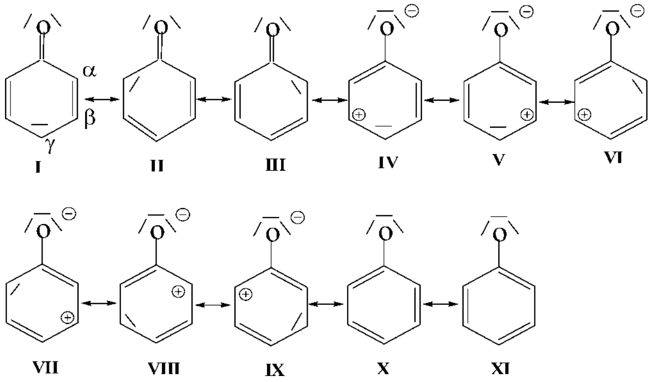
If we consider this value as the free bond angle of formaldehyde, then comparison of the bond angles of the carbonyl group of the three planar compounds (see Figure 1) shows there is angle strain between the carbonyl carbon atom and its adjacent sp^2 hybrid atoms. This weakens the overlap between the hybrid orbitals within the plane thus resulting in a small WBI value.

In addition, as an important group in a molecule, the structural parameters of the carbonyl group also reveal some important information about the electronic structure of the ring. The calculated WBIs of the carbonyl C–O bonds are 1.62, 1.59, and 1.62 for the three planar *ortho*, *meta*, and *para* tautomers, respectively. These values are smaller than that of a standard carbonyl, for example, the WBI of formaldehyde is 1.92. Moreover, the C–O bond lengths (1.22, 1.24, and 1.23 Å) are longer than that of formaldehyde (1.20 Å). Such structural features definitely provide evidence for the delocalization of electrons over the hexagon, which in turn means, to some extent, enhanced π conjugation in the three planar tautomers.

For the *ortho*- and *para*-phosphino ketones, there are some structural differences between the planar and nonplanar conformations, as outlined below. First, in the minima of the *ortho*- and *para*-phosphanyl ketones, the tricoordinated phosphorus atom adopts a pyramidal conformation. The sums of the bond angles about the tricoordinated phosphorus atoms are 304.1 and 301.0°, respectively, and they are much larger than that of the well-known phosphole (293.2°). In other words, they are more planar than phosphole. This can be explained by the fact that the strain in a hexagon is less than that in a pentagon. Secondly, the C–C bond alternation in nonplanar conformations is more drastic than that in the corresponding planar ones. The largest differences in the C–C bond lengths (0.11 and 0.13 Å) in the nonplanar *ortho*- and *para*-phosphino ketones are larger than those in their planar counterparts (0.08 and 0.10 Å). The differences in the WBIs of the C–C bonds increase by 0.31 and 0.20 from the planar to the nonplanar conformations for the *ortho*- and *para*-phosphino ketones, respectively. The C–P bonds in the nonplanar tautomers evidently have single bond character. For example, in the *ortho*-phosphanyl ketone, the C–P bond lengths (1.87 and 1.80 Å) are close to the classic C–P single bond length (1.87 Å). Their WBIs are reduced from 1.05 and 1.25 to 0.96 and 1.03, respectively. For the *para*-phosphanyl ketone, the C–P bond length is 0.07 Å longer and the WBI is 0.18 less than those in the planar counterpart. Thirdly, relative to the planar tautomers, the C–O bond lengths are reduced (1.21 versus 1.23 for *ortho*-phosphanyl ketone and 1.22 versus 1.24 for *para*-phosphanyl ketone) and the WBIs of the C–O bond increase (1.72 versus 1.62 for *ortho*-phosphanyl ketone and 1.70 versus 1.62 for *para*-phosphanyl ketone). The trends in the changes of the geometries reveal that the nonplanar tautomers have less delocalization.

Now the next question is: Why is the planar structure of the *meta*-phosphanyl ketone a minimum, whereas the planar structures of the *ortho* and *para* compounds are transition states?

In conventional resonance theory, this type of compound can be viewed as a hybrid resonance represented by the classic enol and ketone structures.[25] Competition between these two resonance structures leads to different structural and electronic properties. The natural resonance theory (NRT) module[26] in the NBO analyses provides an accurate quantitative analysis of the molecular bond and electron density in terms of resonance structures and their relative contributions. For a molecule more complex than benzene, too many radical resonance forms need to be considered. However, the weight of many resonance structures is very low. Here, we select 11 resonance forms, shown in Scheme 1, that make larger contributions (>1.2%) than other resonance forms. The sums of the weights of these resonance structures are 79.1, 82.7, and 85.4%, respectively, for the three planar molecules (see Table 2). In these resonance forms, the first three are classified as being ketone-type and the others as enol-type. Note that the resonance structures X and XI are similar to the Kekulé structures of benzene, which are regarded as the symbol of electron delocalization in hexagonal aromatic compounds.



Scheme 1. Resonance structures for the planar tautomers of *ortho*-, *meta*-, and *para*-phosphanyl ketones. The tricoordinated phosphorus atom lies at the α, β, and γ positions, respectively.

Table 2. The weight of resonance structures for the planar tautomers of *ortho*-, *meta*-, and *para*-phosphanyl ketones.[a]

Resonance structure	NRT% (*ortho*)	NRT% (*meta*)	NRT% (*para*)
I	4.23	20.42	47.81
II	6.95	19.29	10.16
III	34.65	11.54	10.11
IV	–	2.06	2.67
V	–	2.38	2.37
VI	1.47	4.51	1.95
VII	–	1.77	1.95
VIII	3.73	2.80	–
IX	4.50	2.68	–
X	–	9.04	4.01
XI	23.45	6.24	4.01

[a] Values are given as percentages.

The degree of pyramidality of the tricoordinated phosphorus atom is closely related to the magnitude of its lone pair of electrons. One might expect the percentage of the resonance structures containing the tricoordinated phosphorus atom with a lone pair of electrons to decrease for a stable planar tautomer. Here, the total weights of all such resonance structures in Scheme 1 are given as the "NRT% lone pair". The NRT results for the *ortho*-phosphanyl ketone show that the NRT% lone pair value is very high, **III** + **VI** = 36.12%, in agreement with a nonplanar minimum on the PES. The contribution of ketone-type structure **III** (34.65%) is larger than that of enol-type structure **VI** (1.47%). We know that this value is close to the lower limit of the actual weight of the NRT% lone pair because small contributions have been neglected. For the *meta*-phosphanyl ketone, the NRT% of the lone pair (about 4.51%) is very low, as anticipated from its geometric characteristics. The main reason for this is that the contribution of the ketone-type resonance structure with a phosphorus lone pair of electrons is too small as the octet rule is not obeyed for all atoms in the hexagon if the lone pair is in the *meta* position (such resonance structures are not shown in Figure 1). The lone-pair character in the *para*-phosphanyl ketone is the most prominent of the three compounds. The sum of the NRT% lone pairs is greater than 53.1%, of which the contribution from structure **I** is the most significant (47.8%). This suggests significant pyramidality of the tricoordinate phosphorus atom in the *para*-phosphanyl ketone. As is illustrated, the NRT results can be explained qualitatively on the basis of the MO pictures (Figure 2). We observe that for the *meta*-phosphanyl ketone, the tricoordinated phosphorus atom participates in all three π-bonding MOs, whereas for the other two tautomers, only two π-bonding MOs involve the tricoordinated phosphorus atom. Moreover, note that the HOMO-6 of the three planar molecules varies significantly. For the *meta*-phosphanyl ketone, the π-electrons are distributed evenly around the ring. In contrast, shape variation of the MOs of the *ortho*- and *para*-compounds is observed at 0.04 and 0.03 a.u., respectively. Because the phosphorus lone pair of electrons in the *meta*-phosphanyl ketone are well delocalized, they preserve a stable planar structure.

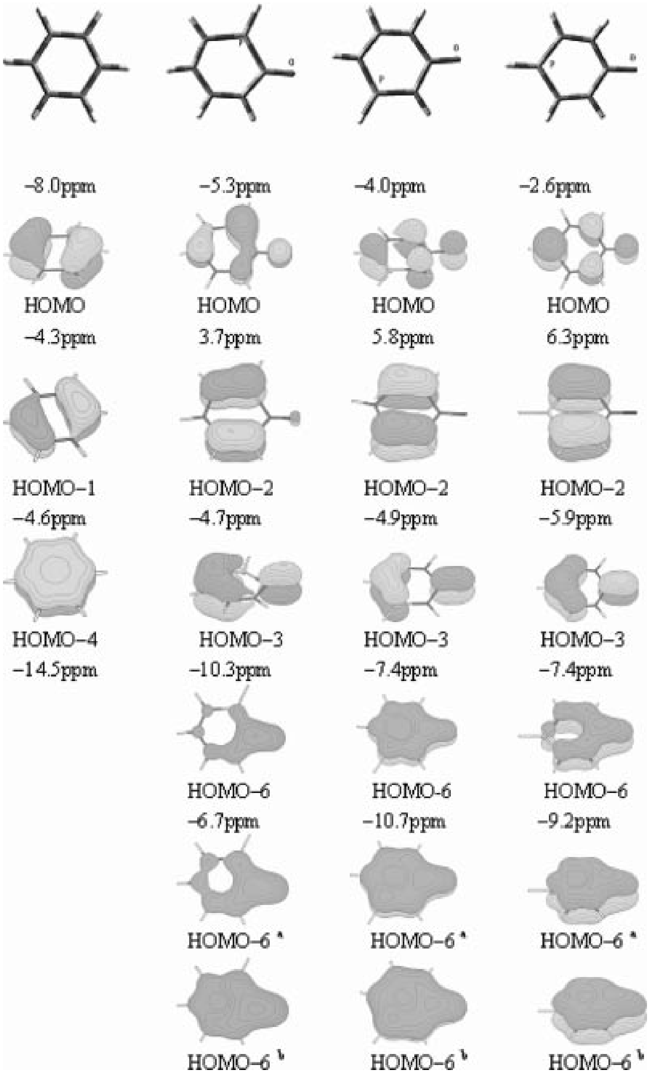


Figure 2. All the π molecular orbitals (MOs) of benzene and the three planar phosphanyl ketone conformations, their total NICSs and contributions of the π molecular orbitals to aromaticity [ppm]. All the MOs without marks are drawn with 0.05 contour line. [a] The value of contour line is 0.04 a.u. [b] The value of the contour line is 0.03 a.u.

In the ELF calculations, a localization domain is a region of space encompassed by an isoELF surface. Some selected localization domains are presented in Figure 3 for the three planar tautomers. We found that the C=O basins are easily distinguished at ELF = 0.635 for *ortho*-phosphanyl ketone, at ELF = 0.615 for *meta*-phosphanyl ketone, and at ELF = 0.600 for *para*-phosphanyl ketone in all the electronic density pictures, which implies that the carbonyl carbon atom has the weakest conjugation in the conjugative rings. On the one hand, this result can be explained as mentioned above by less a overlap between the carbonyl carbon and adjacent atoms in the ring. On the other hand, owing to the larger electronegativity of the oxygen atom relative to that of the carbon atom, the p_z electrons on the carbonyl carbon transfer to the oxygen atom to reduce the size of the p_z orbital of the carbonyl carbon atom thus resulting in poor p_z overlap in this position. In addition, in the *ortho*- and *para*-phosphanyl ketones, there are tricoordinate phosphorus lone pair basins with populations of 1.34 and 1.76, respectively (Figure 3). The absence of the corresponding basin in the *meta*-phosphanyl ketone suggests that the phosphorus lone pair of electrons participates well in ring π conjugation. Meanwhile, populations of 3.00 and 3.20 for two C=P basins in the *meta*-phosphanyl ketone, which are in agreement with a partial double bond similar to that of benzene, and the corresponding variances σ^2 of 1.28 and 1.23 for the C=P bonds, support the aromatic character of this molecule. These results, in agreement with previous reports,[8] indicate that in the planar phosphanyl ketones, delocalization of the lone pair of electrons of the tricoordinated phosphorus atom has a decisive effect on the planarity of this molecule.

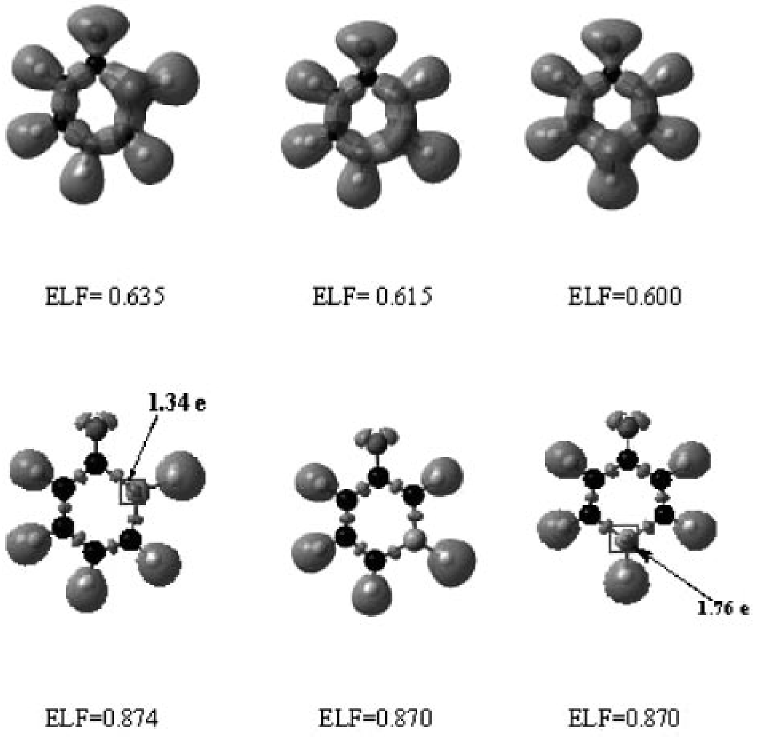


Figure 3. Some selected localization domains of the planar *ortho*-, *meta*-, and *para*-phosphanyl ketones.

Aromaticity

Aromatic molecules are characterized by planar conformations with delocalized π orbitals. The interaction between the lone pair of electrons of the heteroatom and the rest of the π-system in the heteroaromatic compounds is considered an important factor that affects the magnitude of aromaticity.[27] It is feasible for phosphanyl ketone compounds to be pyramidal as the tricoordinated phosphorus atom has lone pairs of electrons. The more the phosphorus lone pair participates in the cyclic electron conjugation, the less pyramidal the phosphorus atom becomes. When the balance between aromatic stabilization and the energy cost of planarization at the phosphorus atom lies in favor of aromatic stabilization, a stable planar molecule forms.

NICS is a simple and efficient tool for measuring aromaticity. Negative NICS values denote aromaticity, whereas small and positive NICS values indicate nonaromaticity and antiaromaticity, respectively. The NICS values calculated at the center of the rings are negative for the planar conformations of the three molecules. Thus, they are aromatic. But compared with benzene (NICS = –7.95 ppm at the same level of theory), the classic aromatic compound, these values are very small and the aromaticity percentages relative to benzene are 66.9, 50.8, and 32.8% for the planar *ortho*, *meta*, and *para* tautomers, respectively. In a previous report, on the basis of NMR ring-current measurements, it was estimated that 2-pyridone has about 35% of the aromaticity of benzene.[28] For comparison, we also calculated the NICS values of *ortho*-, *meta*- and *para*-pyridone at the same level of theory. Their NICS values are –2.08, –2.65, and –1.37 ppm and their aromaticity percentages relative to benzene are 26.2, 33.3, and 17.2%, respectively. Clearly they are less aromatic than the corresponding phosphorus analogues, as expected.

Why is the aromaticity of the investigated molecules different? We employed a refinement of the NICS method, the CMO-NICS analysis which can give the contribution of a single MO to the total NICS, to provide a more detailed insight into the role of MOs. Moreover, studies[29] on some compounds have proved that the dissected NICS approach can provide a more effective evaluation of aromaticity than the total NICS. The difference between the phosphanyl ketone compounds and benzene is that the former have eight π electrons; thus, four MOs with π character (three bonding MOs and one nonbonding MO). Canonical MOs with π character, which have been selected for the NICS calculation, are displayed in Figure 2, along with the corresponding NICS contributions to aromaticity. From the NICS values for the three planar conformations, the three benzene-like π orbitals (HOMO-2, HOMO-3, and HOMO-6) have large negative NICS values. Alternatively, the NICS values of the nonbonding π orbitals (HOMO) are positive. In benzene, the contribution of the multicenter π MO (HOMO-4), which is characteristic of an aromatic system, to aromaticity is most dominant; its NICS value is larger than the sum of the NICS values of the other two π MOs. In the phosphanyl ketones, the NICS values of the corresponding MOs (HOMO-6), relative to benzene, decrease markedly, especially for the *ortho*-phosphanyl ketone (the NICS value is only –6.43 ppm). This is in good agreement with the electron density change of this MO (in Figure 2) mentioned above. It implies that the quantitative description of delocalization of electrons with the use of the dissected NICS approach is reliable.

Our calculations show that the HOMO-4 of benzene has predominantly (>99%) bonding character from NBO analyses. In the phosphanyl ketone compounds, however, the weights of bonding of the corresponding MO (HOMO-6) (87.4% for *ortho*-phosphanyl ketone, 85.6% for *meta*-phosphanyl ketone, and 88.2% for *para*-phosphanyl ketone) are evidently lower than that of benzene from the CMO analyses. So, the NICS values of HOMO-6 in the phosphanyl ketones are smaller than that of the multicenter π orbital of benzene. Owing to the contribution of the C=O unit, which is an electron-withdrawing group and can reduce the electron density in the ring framework, the weight of C=O in the HOMO-6 of *ortho*-phosphanyl ketone is higher (60%) than that in either the *meta*- or *para*-phosphanyl ketone (33 and 42%, respectively), so the HOMO-6 of the *ortho*-phosphanyl ketone has a smaller NICS value than the other two compounds.

If all the π orbitals are included, *ortho*-phosphanyl ketone would be the most aromatic because it has a $\mathrm{NICS}_{\mathrm{c}\pi}$ value of –18.1 ppm (the sum of the NICS values of the canonical π orbitals). The $\mathrm{NICS}_{\mathrm{c}\pi}$ value of *meta*-phosphanyl ketone is –17.5 ppm, which is slightly lower than that of the *ortho*-phosphanyl ketone. The *para*-phosphanyl ketone is the least aromatic, with a $\mathrm{NICS}_{\mathrm{c}\pi}$ value of –16.4 ppm. The small difference between the NICS values reveals these three compounds to have similar aromatic character. This sequence is the same as that of the total NICS values. In contrast to the total NICS values, the percentage of $\mathrm{NICS}_{\mathrm{c}\pi}$ in these conformations increases relative to the $\mathrm{NICS}_{\mathrm{c}\pi}$ (–23.4 ppm) of benzene, which are 77.3, 74.7, and 69.7%, respectively. This indicates that they are good π aromatic molecules. If the contribution of the HOMO orbital (nonbonding π orbital) is not considered, the NICS values of the other three π orbitals can even increase to a value similar to that of benzene. Then, the magnitude of aromaticity changes to *meta*-phosphanyl ketone > *ortho*-phosphanyl ketone > *para*-phosphanyl ketone, which indicates that the effect of the HOMO on the aromaticity of phosphanyl ketone compounds is not only qualitative but also quantitative. The HOMO mainly consists of the p_z orbitals of the carbonyl oxygen atom and the α and γ atoms of the ring. The NICS contributions of the HOMO to the aromaticity are 4.5, 5.4, and 5.6 ppm, respectively, for the three planar conformations, thus suggesting that they reduce the aromaticity of these molecules. The CMO-NICS analyses show that the bonding weights of the HOMO in the three molecules do not exceed 40.0% of the sum of the bonding, nonbonding, and antibonding orbitals, which suggests distinct nonbonding character. For the *meta*- and *para*-phosphanyl ketones, the bonding weights of the HOMO and the contributions of the C=O NBO to the HOMOs are 39.0, 18.0% and 32.0, 16.0%, respectively. In contrast, the HOMO of the *ortho*-phosphanyl ketone has a comparable bonding weight (35.0%), but a smaller component from C=O (10.0%). The contribution from C=O presents a small paramagnetic effect. The larger bonding compositions of the π orbitals make a positive contribution, whereas C=O makes a negative contribution to the aromaticity of the phosphanyl ketone.

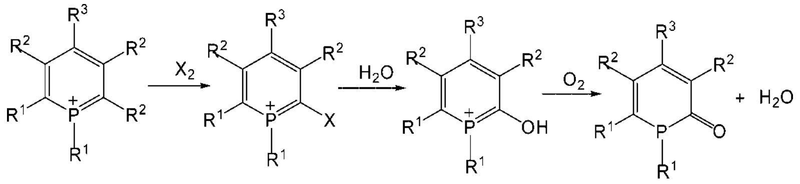
In general, for this type of compound, the enol-type resonance structures have an aromatic character. If valence bond theory gives them a larger percentage, then the compound would show a strong tendency to be aromatic.[30] The calculated NRT results show that the percentages of the resonance structures of enol-type I are 33.2, 31.5, and 17.3%, respectively. The contributions of the resonance structures similar to the Kekulé structures are 23.5, 15.3, and 8.0% for the *ortho*-, *meta*-, and *para*-phosphanyl ketones, respectively. This also implies a tendency for a reduction of aromaticity. However, the aromaticity of these phosphanyl ketones is not consistent with their geometric characters, that is, inconsistent with the conventional assumption that an aromatic molecule has a planar conformation. We must emphasize that aromaticity is an overall characteristic of these planar molecules. The planarity of these molecules is mainly determined by the delocalization of the lone pair of electrons of the tricoordinated phosphorus atom. The delocalization of the lone pair of electrons is only one aspect of many factors affecting aromaticity.

Planar molecules containing a tricoordinated phosphorus atom can be used as an excellent building block for aromatic compounds. As mentioned above (in the ELF results), the degree of planarity in the phosphanyl ketone compounds bears a close relationship to the delocalization of lone pair of electrons of the tricoordinated phosphorus atom. The fact that the pyramidality of a tricoordinated phosphorus atom can be reduced by the introduction of some substituent groups[31] has been proved. In this paper, we also examine the effect of some substituent groups, for example, $\text{-Ph(CH}_3)_2$, $\text{-C(CH}_3)_3$, and -BH_2, on the planarity of *ortho*- and *para*-phosphanyl ketones. The optimized structures show that substituent groups can greatly enhance the planarity of these molecules, as shown in Table 3, especially with the $\mathrm{BH_2}$ group, for which the sum of the bond angles around the tricoordinated phosphorus is increased to 347.0 and 360.0° for the *ortho*- and *para*-phosphanyl ketones, respectively. Therefore, we believe that it is possible to obtain planar phosphanyl ketones through substitution.

Table 3. The sum of the bond angles about the tricoordinated phosphorus atom in *ortho*- and *para*-phosphanyl ketones and their derivatives.

R[a]	H	$\mathrm{C(CH_3)_3}$	$\mathrm{Ph(CH_3)_2}$	$\mathrm{BH_2}$
Σa[b] [°]	304.1/301.0	317.9/355.9	322.0/317.8	347.0/360.0

[a] The substituent groups attached to the tricoordinated phosphorus. [b] The sum of the bond angles about the tricoordinated phosphorus atoms; the values before the slash are for the *ortho*-phosphanyl ketone and its derivatives, and the values after the slash are for the *para*-phosphanyl ketone and its derivatives.



Scheme 2. Synthetic route to the three target products by using the phosphininium cation as the starting reactant. X is a halogen, such as Cl, Br, or I.

The Hypothetical Synthetic Route

For over a century, the rich chemistry of organophosphorus compounds has been developed.[32] Various phosphides with different valences have been reported and chemists have found some familiar synthetic routes to them. Although the existence of phosphininiums has long been known, owing to their higher reactivity (they readily transform to λ^5-phosphinines) few data are available on their structures and electronic properties. Recently, Moores et al.[12] chose a substituted phosphinine as a precursor and successfully synthesized a 1-methylphosphininium complex – the first stable planar phosphininium. On the basis of this synthetic route, we can obtain a series of products with tricoordinate phosphorus atoms in a hexagonal structure through substitution, hydrolysis, and oxidation reactions. We have designed a simple synthetic route to the three target products by using the phosphininium cation as the starting reactant, as shown in Scheme 2.

Conclusions

By using the B3LYP/6-31+G(2d,2p) level of theory, we have studied the structures and electronic properties of phosphanyl ketones. The results show that the planar *meta*-phosphanyl ketone is a minimum on the PES, but the planar structures of the *ortho*- and *para*-phosphanyl ketones are transition states. The large negative NICS$_{c\pi}$ values show that their planar conformations are aromatic. According to CMO analyses, the contribution of a MO to aromaticity or antiaromaticity in phosphanyl ketones depends on two factors. On the one hand, the larger the bonding weight of a π MO is, the stronger the diamagnetic effect. On the other hand, the high proportion of electron-absorbing groups in orbitals can reduce the contribution of molecular orbitals to aromaticity. The delocalization of the tricoordinated phosphorus lone pair of electrons strongly depends on the relative positions of the two important groups (the carbonyl group and the tricoordinated phosphorus atom) in the molecules and determines the nature of the stationary point. The delocalization of the lone pair of electrons on the phosphorus atom determines the planarity of the phosphanyl ketone. Introduction of σ-donor, π-acceptor, and bulky substituents at the phosphorus atom can drastically enhance the planarity of the *ortho*- and *para*-phosphanyl ketones. We expect that phosphanyl ketones have potential applications in chemistry similar to their nitrogen analogue, pyridone.

Supporting Information (see footnote on the first page of this article): Atomic coordinates and total energies of the optimized geometries computed for the planar and stable conformations of the three compounds investigated at the B3LYP/6-31+G(2d,2p) level of theory and the atomic coordinates, lowest frequencies, and total energies for the planar conformations of the three compounds investigated at the QCISD/6-31+G(d,p) level of theory.

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