Anionic States of Six-Membered Aromatic Phosphorus Heterocycles As Studied by Electron Transmission Spectroscopy and ab Initio Methods

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The electron transmission spectra of 1,3,5-tri-*tert*-butylbenzene, 2,4,6-tri-*tert*-butylpyridine, 2,4,6-tri-*tert*-butylphosphabenzene, and 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene have been investigated and interpreted by means of quantum chemical calculations. Scaled virtual orbital energies obtained from calculations without employing diffuse functions provide good numerical values for the vertical electron attachment energies (VAEs). B3LYP/6-311+G* VAEs, calculated as the energy difference between the anion and the neutral molecule, were in good agreement with experiment, with the molecules investigated here having VAEs of less than about 1 eV. The first anion state of phosphabenzene is predicted to lie at the edge of stability. The gradual replacement of CH units by phosphorus in π systems results in a significant stabilization of the anionic states, which contrasts with the relative invariance of the electron donor properties. This behavior can be explained by considering that for the P═C π system both the interaction between the atomic levels (β) and the overlap are smaller than for the C═C π system.

Introduction

As an extension of the diagonal relationship between elements Li−Mg, Be−Al, and B−Si, the C−P diagonal relationship is now well established, as demonstrated by the recent book *Phosphorus the Carbon Copy.*[1] Thus, an extensive series of unsaturated organophosphorus compounds typified by phosphaalkynes, RCP, phosphaalkenes, $R_2C{=}PR'$, phosphabutadienes, $R_2C{=}CR{-}CR{=}PR'$, phosphaallenes, $R_2C{=}C{=}PR'$, phosphacyclopentadienyls, $P_nC_{5-n}R_{5-n}^-$, ($n = 1-5$) and phosphabenzenes, $P_nC_{6-n}R_{6-n}$ ($n = 1, 2, 3, 6$), have been synthesized and their chemistries studied. Furthermore, a wide range of their metal complexes are also known as well as many main group and transition metal complexes of phosphacyclopentadienyl anions, $P_nC_{5-n}R_{5-n}$ ($n = 1-5$), and phosphabenzenes, $P_nC_{6-n}R_{6-n}$ ($n = 1, 2, 3, 6$).[1,2]

The similarity between low coordinated phosphorus and unsaturated carbon is manifested not only in the similar chemical reactivity, e.g., in cycloaddition reactions, of the C═C and P═C bonds, but also in several spectroscopically measurable quantities. Thus the ionization energies (IEs) of analogous π systems with a P atom replacing a CH group were shown to have a linear correlation, with nearly unit slope, nearly zero intercept (0.2 eV), and a correlation coefficient of 0.98,[3] in line with the nearly equal IEs of the CH_3[4] and PH_2[5] radicals (9.843 and 9.824 eV, respectively). Considering this energy as the energy of an interacting p_z orbital at carbon or at phosphorus, it is apparent that the π molecular orbitals (MOs) formed either from P or from CH units have similar energies. Using the same argument, the π^*_{PC} anion states might be thought to have energies similar to those of their corresponding π^*_{CC} anion states; however, this appears not to be the case. For example, the π^*_{PC} negative ions of phosphabenzene[6] and *tert*-butylphosphaethyne[7] lie at sizably lower energies than the π^*_{CC} anion levels of the parent hydrocarbons, as deduced from electron transmission spectroscopy (ETS).

The relative large stability of the π^*_{PC} anion states has an important consequence on the chemical reactivity. Interestingly, Cloke and co-workers[8] have studied the redox behavior in solution of the bis(η^6-hetroarene)titanium complexes $[Ti(EC_5H_2{}^tBu_3)_2]$ (E = N, P), derived from 2,4,6-tri-*tert*-butylpyridine and 2,4,6-tri-*tert*-butylphosphabenzene, by cyclic voltammetry and showed that the half-wave potentials for the reversible reduction waves of the phosphaarene ring containing complex are at lower potential than those of the pyridine containing complex. The EPR spectra of 2,4,6-tri-*tert*-butylphosphabenzene[9] and 2,4,6-triphenylphosphabenzene[10] were reported, indicating the stability of these anions (in the presence of a corresponding counterion) in solution. Very recently Zenneck and co-workers, in unpublished work,[11] have observed experimentally the EPR spectrum of the 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene radical anion $P_3C_3R_3^-$ (R = ^{t}Bu) in solution and also studied its electrochemistry by cyclic voltammetry.

All these data indicate the pronounced electron-acceptor properties of the low-valent phosphorus derivatives in line with the above-mentioned gas-phase data. Systematic ETS studies[12] of saturated and unsaturated hydrocarbons substituted by main group heteroatoms of normal valency also showed that third-row (or heavier) elements increase the electron-acceptor proper-

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ties, i.e., stabilize adjacent π_{CC}* anion states and cause the presence of low-energy heteroatom−carbon σ* anion states.

In gas-phase collisions, an isolated molecule can temporarily attach an electron of appropriate energy and angular momentum to a vacant MO, the process being referred to as a shape resonance.[13] Electron transmission spectroscopy (ETS)[14] is one of the most suitable means for detecting the formation of these short-lived anions. Because electron attachment is rapid with respect to nuclear motion, temporary anions are formed in the equilibrium geometry of the neutral molecule. The impact electron energies at which electron attachment occurs are properly denoted as vertical attachment energies (VAEs) and are the negative of the vertical electron affinities (EAs).

Within the Koopmans theorem[15] (KT) approximation, VAEs are equal to the empty MO energies, just as the complementary IEs supplied by photoelectron spectroscopy are equal to the negative of the energies of the filled MOs. ETS has thus proved a powerful means for elucidating the empty level electronic structure. The KT approximation neglects correlation and relaxation effects, which tend to cancel out for the cations, but act in the same (stabilizing) direction for the anions. The virtual orbital energies (VOEs) calculated at the Hartree−Fock (HF) level for the neutral molecules consistently overestimate the measured VAEs by several electronvolts. However, it was noticed that the trends of the VOEs obtained with finite basis sets in molecules with similar structures parallel the experimental trends, whereas the use of diffuse functions in the basis set adversely affects the correlation.[16−18] In particular, Staley and Strnad[17] and Chen and Gallup[19] demonstrated that the π^*_{CC} VAEs measured in ETS are linearly correlated to the corresponding HF VOEs calculated with basis sets which do not include diffuse functions, and that this computational approach can be used for quantitative prediction of π* VAEs in unsaturated hydrocarbons. More recently, an analogous good linear correlation has also been found[20] with the Kohn−Sham VOEs supplied by B3LYP/6-31G* calculations. Koopmans electron affinities are also used to predict the stability of dianions against electron loss.[21]

VAEs can also be computed by more accurate methods than the approximate KT based approach; however, theoretical treatment of the unbound anion states observed in ETS involves difficulties not encountered for neutral or cation states.[16−19,22] The most correct approach is, in principle, the calculation of the total scattering cross section with the use of continuum functions, although further complications arise by the accurate description of the electron−molecule interactions.[23] For the description of a resonance state the complex Siegert energy[24] can be used, which can be computed using different approaches, as summarized in the recent work by Sommerfeld.[25,26] This methodology also provides information about the lifetime of the species, but it is computationally demanding.

The first VAE can be obtained as the energy difference between the lowest lying anion and the neutral state (both with the optimized geometry of the neutral species). This procedure (referred to as Δ technique) is computationally more demanding, but in principle more accurate than the KT approach. However, the description of resonance anion states (unstable with respect to electron loss) with standard bound state methods results in a difficult problem. The use of a finite basis set formed with (Gaussian) functions has the effect of confining the system within a box (termed as basis set confinement, BSC, approach[25]), accounting in some way for the fact that during a resonance process the extra electron is confined to the molecule by a potential barrier.[18] However, a proper description of the spatially diffuse electron distributions of anions requires a basis set with diffuse functions.[27,28] On the other hand, as the basis set is expanded the wave function ultimately describes a neutral molecule and an unbound electron in the continuum,[16−18] since this is the state of minimum energy. The choice of a basis set which gives a satisfactory description of the energy and nature of resonance processes is therefore a delicate task.

Despite all these theoretical problems it is a usual practice to use the BSC approach for the calculation of anionic states. Feuerbach and Cederbaum used basis sets with diffuse functions for dianions which lie at the edge of stability.[29] Schaefer and co-workers,[30] in a recent paper investigating benzene, naphthalene, and anthracene, obtained apparently good agreement between the VAEs (0.88, 0.20, and −0.58 eV, respectively) supplied by B3LYP calculations with a basis set containing diffuse functions (DZP++) and the corresponding experimental values of 1.12, 0.19, and −0.53 eV (i.e., EA = 0.53 eV). The agreement is least satisfactory for benzene, whose anion state is the most unstable of the trio with respect to electron detachment. Furthermore, the singly occupied MO (SOMO) of the benzene anion is predicted to be a spatially diffuse $\sigma^*(a_{1g})$ MO, instead of the valence $\pi^*(e_{2u})$ MO, and contrary to evidence from electron scattering. The first VAE (1.16 eV) calculated[20] at the B3LP/6-311+G* level (here less diffuse functions are added to the basis set than those of the DZP++ basis) is very close to experiment, but again the SOMO benzene anion is wrongly identified so that this energy comparison is irrelevant. The B3LYP/6-31G* calculation (without diffuse functions) predicts the SOMO to be of π* symmetry, but the computed VAE (2.31 eV) is far too high.[20]

In the following section we report the electron transmission (ET) spectra of the *tert*-butyl derivatives of benzene, pyridine, phosphabenzene, and 1,3,5-triphosphabenzene. Our goal was twofold. First, we wanted to obtain information about the electron-acceptor properties of the phosphabenzenes. The VAEs measured in these compounds and in related molecular systems are compared with those predicted by scaled KT−HF calculations. This constitutes a test for the use of the same linear equation found in hydrocarbons in these heteroatomic π systems. In turn, the scaled VOEs can allow evaluation of the positive EAs (not accessible in ETS). Second, in view of the above-mentioned difficulties, the VAEs supplied by B3LYP calculations with different basis sets are compared with experimental data to get more insight into the possible use of diffuse functions in the description of unstable anion states.

Experimental Section

The electron transmission apparatus used is in the format devised by Sanche and Schulz[14] and has been previously described.[31] To enhance the visibility of the sharp resonance structures, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the electron current transmitted through the gas sample is measured directly by a synchronous lock-in amplifier. Each resonance is characterized by a minimum and a maximum in the derivative signal. The energy of the midpoint between these features is assigned to the VAE. The present spectra were obtained by using the apparatus in the “high-rejection” mode[32] and are, therefore, related to the nearly total scattering cross section. The electron beam resolution was about 50 meV (fwhm). The energy scale was calibrated with reference to the $(1s^12s^2)^2S$ anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, depending on the number of decimal digits reported.

Calculations were performed with the Gaussian 98 set of programs.[33] The vertical attachment energies (VAEs) were

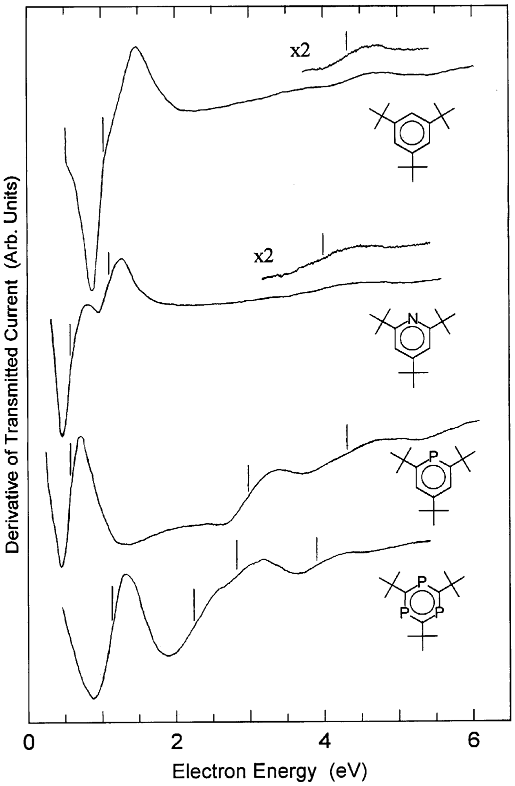

Figure 1. Derivative of transmitted current, as a function of electron energy, in 1,3,5-tri-*tert*-butylbenzene, 2,4,6-tri-*tert*-butylpyridine, 2,4,6-tri-*tert*-butyl-1-phosphabenzene, and 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene. The vertical lines locate the VAEs.

calculated as the difference of the total energy of the neutral state and the lowest anion state, both in the optimized geometry of the neutral state, using the B3LYP hybrid functional[34] with the standard 6-31G*, 6-31+G*, 6-311+G*, and aug-cc-pVTZ basis sets. Geometries were optimized for the parent rings under C_{2v} constraint, while for the ^{t}Bu-substituted systems no symmetry constraint was imposed. At the optimized structures, second derivatives were calculated to ensure that real minima were obtained. A stability check (searching for a wave function/density with a lower energy) has been carried out on the wave function of the open-shell anions to ensure that the minimum energy solution has been found.

The compounds 2,4,6-tri-*tert*-butylpyridine and 2,4,6-tri-*tert*-butylphosphabenzene, which were a gift from Professor F. G. N. Cloke, were made by the published procedures.[35] The 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, first reported by Binger and co-workers,[36] was made at Sussex as part of a series of studies, by the vanadium imide catalyzed cyclotrimerization of the phosphaalkyne PC^{t}Bu, described by Regitz and co-workers.[37]

Results

ET Spectra and Scaled VOEs. Figure 1 displays the ET spectra of 1,3,5-tri-*tert*-butylbenzene, 2,4,6-tri-*tert*-butylpyridine, 2,4,6-tri-*tert*-butyl-1-phosphabenzene, and 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, in the 0−6 eV energy range. The measured VAEs are given in the correlation diagram of Figure 2. Table 1 reports the π^* VAEs together with the calculated HF/6-31G π^* VOEs and the corresponding scaled values, obtained from the equation found in ref 17.

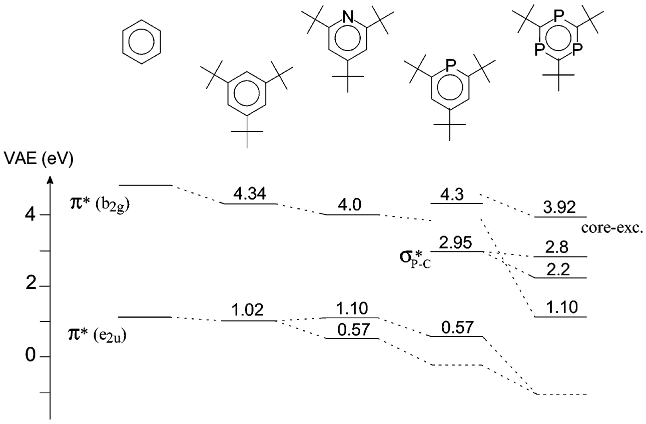

Figure 2. Correlation diagram of the VAEs measured in 1,3,5-tri-*tert*-butylbenzene, 2,4,6-tri-*tert*-butylpyridine, 2,4,6-tri-*tert*-butyl-1-phosphabenzene, and 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene.

TABLE 1: HF/6-31G π^* Virtual Orbital Energies (VOEs), Corresponding Scaled π^* VOEs (See Text), and Experimental VAEs[a]

	orbital	HF/6-31G VOE	scaled VOE	exptl VAE
benzene[b]	$\pi^*(b_{2g})$	9.94	5.01	4.82
	$\pi^*(e_{2u})$	4.03	1.15	1.12
1,3,5-tri-*tert*-butylbenzene	π^*_{O}	8.62	4.14	4.34
	π^*_{S}, π^*_{A}	4.20	1.26	1.02
pyridine[c]	π^*_{O}	9.50	4.72	4.48
	π^*_{A}	3.66	0.91	1.18
	π^*_{S}	3.33	0.69	0.72
2,4,6-tri-*tert*-butylpyridine	π^*_{O}	8.62	4.15	4.0
	π^*_{A}	4.02	1.14	1.10
	π^*_{S}	3.62	0.88	0.57
phosphabenzene[d]	π^*_{O}	8.37	3.98	4.21
	π^*_{A}	3.40	0.74	0.64
	π^*_{S}	1.91	−0.24	≤0
2,4,6-tri-*tert*-butyl-1-phosphabenzene	π^*_{O}	8.08	3.79	<4.3
	π^*_{A}	3.72	0.95	0.57
	π^*_{S}	2.28	0.01	≤0
1,3,5-triphosphabenzene	π^*_{O}	4.57	1.50	
	π^*_{S}, π^*_{A}	0.65	−1.06	
2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene	π^*_{O}	4.83	1.67	1.10
	π^*_{S}, π^*_{A}	1.21	−0.69	≤0
arsabenzene[d]	π^*_{O}	8.39	4.00	3.84
	π^*_{A}	3.48	0.79	0.62
	π^*_{S}	1.76	−0.33	≤0

[a] All values are in eV. [b] VAEs taken from ref 31. [c] VAEs taken from ref 38. [d] VAEs taken from ref 6.

The net energy perturbation brought about by the *tert*-butyl substituents on the benzene e_{2u} and b_{2g} empty π^* MOs (VAEs = 1.12 and 4.82 eV[31]) is due to the opposite hyperconjugative effects caused by interaction with the filled and empty $\sigma_{\mathrm{C-C}}$ orbitals of proper symmetry. Tri-*tert*-butyl substitution produces a sizable (0.5 eV) stabilization of the total antibonding benzene b_{2g} MO (closer in energy to the higher lying empty σ^*_{CC} orbitals) and a small (0.1 eV) stabilization of the e_{2u} LUMO (see Figure 2).

Replacement of a benzene CH group with a heteroatom results in C_{2v} symmetry and removes the degeneracy of the benzene LUMO into a symmetric (π^*_{S}) and an antisymmetric (π^*_{A}) component, of b_1 and a_2 symmetry, respectively. In pyridine (VAEs = 0.72, 1.18, and 4.48 eV[38]) the first (π^*_{S}) and third (π^*_{O}) anion states lie about 0.4 eV lower in energy than in benzene (in agreement with electronegativity considerations), whereas the second anion state (π^*_{A}), which has a node in the wave function at the position of the nitrogen atom, is nearly unperturbed. The ET spectrum of 2,4,6-tri-*tert*-butylpyridine shows that the stabilizing effects caused by the *tert*-butyl substituents on the π^* anions states of pyridine are similar to those observed in the benzene analogue (see Table 1).

In the phospha derivatives, the presence of the third-row element is expected to stabilize the π^* anion states and to give rise to low-energy σ^* anion states.[12] The ET spectrum of phoshabenzene reported by Burrow et al.[6] displays a single resonance (VAE = 0.64 eV) below 1.5 eV, assigned to electron attachment to the π^*_A MO, close in energy to the π^*_S (LUMO) resonance of pyridine.[38] The (π^*_S) LUMO of phosphabenzene was associated with a stable anion state (and thus not detectable in ETS). The present spectrum of 2,4,6-tri-*tert*-butylphosphabenzene displays the first resonance at 0.57 eV, in line with a small stabilizing effect exerted by the *tert*-butyl substituents on the π^*_A MO. Likewise, in the case of the parent compounds, this value is close to that of the π^*_S state of 2,4,6-tri-*tert*-butylpyridine. This fact again shows the relationship between the effect of the alkyl substituent and the energy of the interacting state. The second resonance, located at 2.95 eV (see Figures 1 and 2) is associated with σ^* MOs with mainly phosphorus character. Consistently, a corresponding resonance was observed at 3.51 eV in phosphabenzene[6] and at 2.7 eV in dimethylphenylphosphine.[39]

The next signal in the ET spectrum of 2,4,6-tri-*tert*-butylphosphabenzene, centered at 4.3 eV, owing to its broadness (fwhm ≥ 1.0 eV), is ascribed to the unresolved contributions from the highest lying π_O^* MO (VAE = 4.21 eV in phosphabenzene[6]) and a core-excited resonance, i.e., electron capture and simultaneous excitation of a valence electron.

The interpretation of the ET spectrum of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene is not as straightforward as that of the above compounds. Due to the presence of three heteroatoms, both the (degenerate) π^* LUMO and the π^*_O MOs are expected to be largely stabilized with respect to the monophospha analogue. While the π^* anionic ground state should be stable (thus not detectable in ETS), it is not obvious whether the π^*_O MOs gives rise to the first resonance (VAE = 1.10 eV) or to some higher lying signal.

As mentioned above, in a study of the use of KT calculations for the evaluation of VAEs, as a function of the basis set, Staley and Strnad[17] found good linear correlations between the π^*_{CC} VAEs measured in a large number of unsaturated hydrocarbons and the corresponding VOEs calculated for the neutral states with basis sets that do not include diffuse functions. The energies obtained with the D95V basis set gave the best correlations, ascribed to its proper degree of spatial diffuseness. The same linear equations were found to accurately reproduce the π^*_{CO} VAEs measured in mono- and diketones.[40] The D95V basis set, however, cannot be used for the present series of compounds because it is not defined for third-row or heavier elements. We thus use HF/6-31G calculations, which also supplied good results,[17,19] to assign the ET spectrum of the triphosphabenzene and verify those of the monoheteroatomic derivatives.

In addition to the trialkyl derivatives analyzed here, the π^* VOEs are calculated and compared with experiment also for benzene, pyridine, phosphabenzene, and arsabenzene, for which ETS data are available. From results reported in Table 1, it is immediately apparent that the VOEs parallel the experimental trends on going from benzene to the aza, phospha, and arsa derivatives. The calculations also account for a significant stabilization of the highest lying ring π^*_O MO upon *tert*-butyl substitution, but seem to underestimate the stabilizing effect due to mixing with the σ^*_{CC} MOs (and/or to overestimate the opposite effect caused by mixing with the filled σ counterparts), so that a small destabilization is predicted for the lower lying empty π^* MOs (instead of the slight stabilization experimentally found).

A good linear correlation (VAE = 0.66431VOE − 1.65504, correlation coefficient = 0.989) is found between the calculated π^* VOEs and the corresponding measured VAEs (assigning the 1.1 eV resonance of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene to the π^*_O MO). Both the slope and shift terms are close to those of the equation (VAE = 0.65269VOE − 1.4793) found by Staley and Strnad[17] for the π^*_{CC} MOs of alkenes and benzenoid hydrocarbons, indicating that the same equation can be used for the present hetero-substituted compounds.

The scaled VOEs (see Table 1) reproduce the experimental VAEs within 0.2−0.3 eV, except for the low-energy π^* MOs of the *tert*-butyl derivatives. As noted above, *tert*-butyl substitution is erroneously predicted to destabilize the low-energy π^* MOs. Therefore, the scaled VOE (1.50 eV) of the π^*_O MO of (unsubstituted) triphosphabenzene can be considered an upper bound for the VAE of this MO in 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, indicating that the first resonance of the ET spectrum (VAE = 1.10 eV) is associated with the highest lying π^*_O MO. The two partially overlapped signals at 2.2 and 2.8 eV are thus assigned to electron attachment to σ^*_{P-C} MOs. In qualitative agreement, in contrast with the large stabilization of the π^*_O MO, the HF/6-31G calculations predict a small (0.2 eV) stabilization of the lowest σ^*_{PC} MO on going from 2,4,6-tri-*tert*-butyl-1-phosphabenzene to the triphospha analogue, and a reversed π^*_O/σ^*_{PC} MO energy sequence in the latter. The relatively narrow signal at 3.92 eV is likely associated with electron capture into the LUMO accompanied by HOMO−LUMO excitation.

In particular, according to the scaled VOEs electron capture into the LUMO of phosphabenzene, arsabenzene, and 1,3,5-triphosphabenzene gives rise to a stable anion state, the (positive) vertical EAs being predicted to be 0.2, 0.3, and 1.1 eV, respectively. Thus, monophospha substitution would increase the EA of benzene by about 1.3 eV, and triphospha substitution by about 2.2 eV. The EAs of the *tert*-butyl derivatives, owing to the small energy shift caused by the substituents on the low-energy π^* MOs, are expected to be nearly the same as those of the parent compounds.

Calculated VAEs. In Table 2 the measured VAEs are compared with those (negative values denote positive vertical EAs) calculated at the B3LYP level[41] using basis sets with (6-31+G*, 6-311+G*, and aug-cc-pVTZ) and without diffuse functions (6-31G* and cc-pVTZ). While in case of the 6-31+G* and 6-311+G* basis sets only s- and p-type diffuse functions are placed at the non-hydrogen atoms, the aug-cc-pVTZ basis set is augmented by further diffuse functions at the hydrogen atoms (likewise the DZP++ basis used by Schaefer et al.[30]) and by d- and f-type functions at the heavier atoms.

First we discuss the lowest energy anionic states only. With all basis sets, the anions of benzene and pyridine (as well as their *tert*-butyl derivatives) are predicted to be unstable against electron loss, whereas the first anionic state of triphosphabenzene and its alkyl derivative is stable. These results are in accordance with the conclusion obtained from the analysis of the ETS data and the scaled KT results. Phosphabenzene, its alkylated derivative, and arsabenzene seem to be borderline cases. It is immediately apparent that the calculated VAEs are significantly affected by the choice of the basis set. In particular, not only the 6-31G* but also the much larger cc-pVTZ basis set affords VAEs much higher than those experimentally measured, the lack of the diffuse functions preventing a proper description of the spatially diffuse anion states.[27−29]

In contrast, the aug-cc-pVTZ basis set, augmented with diffuse functions at the heavy atoms and hydrogens as well,

TABLE 2: First VAEs Calculated as the Energy Difference between the Anion State and Neutral State, Both with the Optimized Geometry of the Neutral State, at the B3LYP Level with Different Basis Sets, along with Experimental VAEs and Those Obtained from Scaled VOEs for Comparison[a]

	orbital	exptl VAE	scaled VOE	B3LYP/ 6-31G*	B3LYP/ 6-31+G*	B3LYP/ 6-311+G*	B3LYP/ cc-pVTZ	B3LYP/ aug-cc-pVTZ
benzene[b]	$\pi^*(e_{2u})$	1.12	1.15	2.31	1.38	1.16*	1.76	0.42*
1,3,5-tri-*tert*-butylbenzene	π^*_S, π^*_A	1.02	1.26	1.93	0.76	0.71[e]		
pyridine[c]	π^*_S	0.72	0.69	1.63	0.93	0.82	1.19	0.35*
2,4,6-tri-*tert*-butylpyridine	π^*_S	0.57	0.88	1.39	0.67	0.71[e]		
phosphabenzene[d]	π^*_S	≤0	−0.24	0.76	0.22	0.22	0.41	0.17
2,4,6-tri-*tert*-butyl-1-phosphabenzene	π^*_S	≤0	0.01	0.59	0.22	0.18[e]		
1,3,5-triphosphabenzene	π^*_S, π^*_A		−1.06	−0.49	−0.88	−0.74	−0.74	−0.93
2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene	π^*_S, π^*_A	≤0	−0.69	−0.41	−0.71	−0.74[e]		
arsabenzene[d]	π^*_S	≤0	−0.33	0.61	0.05	−0.02	0.24	−0.04

[a] All values are in eV. Values for the anionic ground states where the SOMO is a diffuse orbital are marked by asterisks (*). [b] VAEs taken from ref 31. [c] VAEs taken from ref 38. [d] VAEs taken from ref 6. [e] B3LYP/6-311+G*//B3LYP/6-31+G*.

predicts VAEs that are too low for the unstable anion states of benzene and pyridine (the above-mentioned DZP++ basis set used by Schaefer et al.[30] also provides too low a VAE for benzene). Apparently, the overly diffuse basis functions tend to describe the anion as the neutral species plus an electron in as much of the continuum as the basis set can emulate. The resulting solution for the wave function corresponds to an energy which is lower than that of the (unstable) resonance anion state, although higher than 0 eV (electron in the continuum). Accordingly, the extra electron in these cases resides on a diffuse orbital, the symmetry of the anionic system being A_1 and A_{1g} for pyridine and benzene, respectively. The VAEs associated with anion pseudostates where the extra electron is placed in a diffuse σ orbital are denoted by an asterisk in Table 2.

Such a description of the symmetry and localization properties of the benzene SOMO is not consistent with the ET spectral features. The large intensity of the first resonance and the presence of a sharp vibrational structure (which implies a relatively long lifetime) indicate that the symmetry of the empty MO where the added electron is accommodated determines high angular momentum components.[42] This requirement is fulfilled by the degenerate $\pi^*(e_{2u})$ MO, whereas for a diffuse MO of a_{1g} symmetry a large contribution from the $l = 0$ partial wave is expected. Moreover, ETS widely demonstrated[12,42] that substituents bearing group orbitals of π symmetry split the first resonance of benzene into its two components. The B3LYP/6-31G* (no diffuse functions) calculations, which on the other hand largely overestimate the VAE, correctly predict that the lowest anion state is associated with electron attachment to the degenerate $\pi^*(e_{2u})$ orbital.

The lowest lying anion state of pyridine is calculated to possess B_1 symmetry with all basis sets except for aug-cc-pVTZ, while for benzene the proper symmetry is predicted by all basis sets that contain no diffuse functions and the 6-31+G* basis set (the latter, however, supplies a solution with only 0.01 eV higher energy where the extra electron resides on a diffuse a_{1g} Kohn−Sham MO). It is noteworthy that the lowest anion of benzene is less stable against electron loss than that of pyridine. Consequently the calculations tend to describe the system as the neutral species plus a free electron in the continuum, even when only a relative smaller set of diffuse functions are available (6-311+G*). For example, in case of ethyne the B3LYP/6-311+G* VAE was about 1.3 eV lower than the experimental value, with the extra electron residing on the nonphysical diffuse orbital.[20] The first (π^*) anion state of ethyne, on the other hand, lies at higher energy (experimental VAE = 2.6 eV)[42] than that of benzene or pyridine. Clearly, other factors being the same, the applicability of a given basis set with diffuse functions depends on the instability of the anion. In contrast, this factor does not affect the KT 6-31G* scaled results, at least over a large energy range.

Interestingly, the basis set dependence of the calculated VAEs of the P and As derivatives is less pronounced than that of the benzene and pyridine derivatives. The VAEs calculated without diffuse functions in the basis set are too high, but not as much as for the carbon and nitrogen analogues. More importantly, addition of more diffuse functions (using the aug-cc-pVTZ vs the 6-31+G* basis set) does not significantly change the calculated anion energy, in contrast to the observations for benzene and pyridine. Although the phosphabenzene anion (and its alkyl derivative) is predicted to be unstable against electron loss, this instability is small: the calculated VAE ranges from 0.17 to 0.22 eV with those basis sets that include diffuse functions. In each case the anionic ground state has B_1 symmetry (including the aug-cc-pVTZ basis); i.e., the extra electron does not reside on the diffuse orbital representing the continuum.

The corresponding B_1 (π^*) anion of arsabenzene is predicted to be somewhat more stable than that of phosphabenzene at each level of theory, in line with the KT-scaled VOEs, and the predicted electron affinity is slightly positive at the highest level (B3LYP/aug-cc-pVTZ) used.

For comparison, we have calculated the VAEs of phosphabenzene also with other functionals than B3LYP, indicated[41] as suitable for the calculation of electron affinities. At the BLYP/6-311+G*//BLYP/6-311+G* and B3PW91/6-311+G*//B3PW91/6-311+G* levels, VAEs of 0.31 and 0.21 eV have been obtained, respectively, with the extra electron residing on the b_1 MO in each case. These results indicate that the first VAE of phosphabenzene should be about 0.2−0.3 eV. In this case, the corresponding signal should be detectable in ETS (although partially overlapped with the electron beam signal), since the ET spectrum of naphthalene displays a detectable resonance at 0.19 eV.[30]

To get a more accurate result, we have carried out calculations for phosphabenzene at the wave function based CCSD(T)/aug-cc-pVTZ//B3LYP/cc-pVTZ and CASPT2(6,6)/aug-cc-pVTZ//B3LYP/cc-pVTZ levels.[43] The calculated VAEs (0.27 and 0.20 eV, respectively) are close to those obtained from the density functional studies. Especially noteworthy are the CASPT2 results, where in the CAS calculations only the valence but not the diffuse orbitals were considered; thus this solution had to converge to the appropriate π^* anion state where the electron has been attached to phosphabenzene. In addition, we have also calculated the CASPT2 energies for the $^2A_2$ (0.67 eV) and $^2B_1$ (4.1 eV) excited states, in very good agreement with the corresponding experimental VAEs[6] (0.64 and 4.21 eV, see Table 1). Thus we conclude that the density functional calculations are reliable in predicting the first vertical anion state of phosphabenzene at the edge of the stability, i.e., about 1 eV more stable than that of benzene.

The first anion state of triphosphabenzene is clearly stable against electron loss, as expected from the conclusions drawn from the analysis of the ETS data and the scaled KT results. The VAEs of the tri-*tert*-butyl derivatives are predicted to be equal to or slightly smaller than those of the parent compounds, again in agreement with the experimental data.

Discussion

The success of the scaled KT approximation in the assignment of the ET spectra underlines the fact that the energies of the anionic states provide relevant information on the electronic level structure of the molecules, and this also holds for the presently investigated molecules. Comparison of the electronic properties of the phosphorus and carbon containing compounds is particularly interesting, in view of the previously noted good linear correlation between the π ionization energies of the analogous C=C and P=C bonded compounds, where the phosphabenzene[45] and benzene[46] values were included.[3] The same relationship has been noted between the π photoelectron band positions of a chlorinated and a methylated phosphabenzene and those of the corresponding benzene derivatives.[47] The photoelectron spectra of 2,4,6-tri-*tert*-butylphosphabenzene[48] and that of 2,4,6-*tert*-butyl-1,3,5-triphosphabenzene[49] have also been reported in the literature. The vertical IEs from the π HOMO are 8.0 and 8.2 eV, respectively. Comparison with the corresponding IE of 1,3,5-tri-*tert*-butylbenzene (8.19 eV[50]) shows that replacement of ring CH groups with phosphorus atoms does not significantly change the electron-donor properties. Also, the π band positions in the spectrum of 2,4-di-*tert*-butyl-1,3-diphosphabenzene[49] properly fit those in the spectrum of 1,3-di-*tert*-butylbenzene.[50] While the carbon–phosphorus replacement hardly affects the IEs (by invoking Koopmans' theorem, the occupied MO energies), the unoccupied levels and thus the electron-acceptor properties are largely influenced. The stabilization of the anionic states of the phosphorus compounds with respect to their carbon analogues indicates that the above-mentioned diagonal relationship holds only for the occupied MOs. Those chemical reactions that are governed by the donor properties of the π system ought to be similar, in accordance with observations.[1,2] In reactions with nucleophilic partners, however, a considerably different behavior is expected between the phosphorus derivatives and their carbon counterparts.

As previously noted by Burrow et al.,[6] the stabilization of the π^* anion states of the phosphorus-containing species with respect to benzene cannot be explained on the basis of electronegativity considerations.

MS-Xα calculations, which reproduce satisfactorily the VAEs measured in phenylphosphine and related molecules,[33] predict a significant and large participation of the P 3d atomic orbitals to the π^* and σ^*_{PC} anion states, thus accounting for their stability (but this does not imply a significant contribution of the 3d orbitals to the bonding in the neutral molecules[51]).

We have investigated the participation of d orbitals in the wave function of the different phosphabenzene ionic states. Inspection of the AO coefficients in the lowest lying unoccupied b_1 6-31G* MOs of pyridine and phosphabenzene revealed that the contribution of the d orbitals is 0.01–0.02 in each molecule. For the π^* a_2 MO, however, the d orbital participation in pyridine remains 0.01, while it increases to 0.07 in phosphabenzene. The d orbital contribution to the corresponding half-filled MOs of the anions remains similar to that observed for the unoccupied MOs of the neutral molecules. Inspection of the Kohn–Sham orbitals (with the B3LYP functional) supplied similar results. The d orbital participation remained similar by using larger basis sets, up to aug-cc-pVTZ. As a result of the interaction between the a_2 and the proper d orbital, some stabilization can be expected for the A_2 π^* anion state. The experimentally observed a_2 VAEs of the pyridine–stibabenzene series[6] are in accord with the assumed d orbital participation. As noted before,[6] the a_2 π^* MO has a node through the heteroatom, and is expected to be relatively unperturbed throughout the pyridine–stibabenzene series. This assumption also holds for the occupied a_2 MO of the neutral molecules, as concluded from their photoelectron spectral investigation.[45] The a_2 π^* VAE of phosphabenzene, however, is stabilized by about 0.5 eV with respect to pyridine, while it remains nearly constant for arsabenzene and stibabenzene, i.e., in all those compounds where the heteroatom has d orbitals in the valence shell.

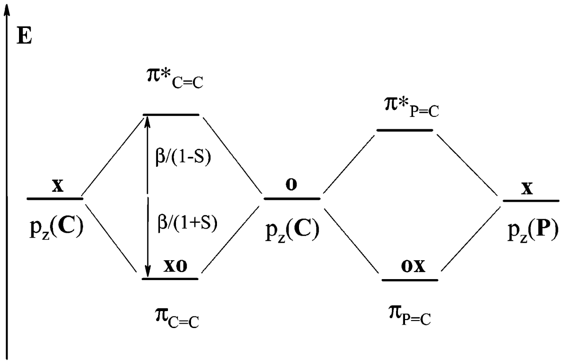

Figure 3. Schematic representation of the formation of the bonding and antibonding MOs of the P=C and C=C double bonds.

An alternative explanation for this behavior of the a_2 π^* anion states could result from possible mixing with a low-energy core-excited resonance of the same symmetry, the effect being significantly smaller in the case of pyridine. From CAS(10/14)/aug-cc-pVTZ calculations (where all the proper orbitals were included), however, it turns out the lowest lying a_2 anion state of phosphabenzene is described by a single configuration.

None of the above explanations, however, can account for the stabilization of the B_1 (π^*) anion state of phosphabenzene with respect to those of benzene and pyridine. The question is, why are the π^* states of the P=C systems more stable than those of the C=C systems, when the π states of the two systems have very similar energies?

Using Hückel theory, the stability of the π^* anion states of the phosphabenzenes could possibly be explained in a different way. When two levels with the same energy (α) interact (as mentioned above, the ionization energies of the PH_2[5] and CH_3[4] radicals are nearly equal), the resulting bonding and antibonding combinations are stabilized and destabilized (with respect to α) by $\beta/(1 + S)$ and $\beta/(1 - S)$, respectively, where the interaction parameter β is called a resonance integral and S is the overlap integral (see Figure 3). Larger values of both the β and S parameters for the C=C bond with respect to the C=P bond would account for the nearly equal energies of the filled π_{CC} and π_{CP} MOs and for the lower energy of the empty π^*_{CP} MOs relative to the π^*_{CC} counterparts.

Conclusions

The present electron transmission and theoretical results show that replacement of CH groups with phosphorus atoms causes a large increase of the electron-acceptor properties of the benzene ring, in contrast with the donating properties which remain nearly unchanged. This behavior can be explained if both the interaction (which can be related to the bond strength) and the overlap are smaller for the P═C than for the C═C bond. This is in accord with the results of Gordon[52] and Schleyer,[53] who have obtained smaller double bond energy for the P═C bond than for the C═C bond (43 and 65 kcal/mol, respectively).

Scaling of the virtual orbital energies supplied by simple KT−HF/6-31G calculations with an empirical linear equation calibrated with the π^* VAEs of unsaturated hydrocarbons leads to a satisfactory prediction of the π^* VAEs measured in pyridine and the phosphabenzenes.

According to this approach, the first VAE of phosphabenzene is slightly negative (−0.2 eV, in line with the absence of a corresponding signal in the ET spectrum), while high-level ab initio and density functional calculations predict a slightly positive value (0.2 eV). These data thus indicate that the vertical electron affinity of phosphabenzene is close to zero, i.e., significantly lower with respect to a previously reported evaluation,[6,44] but still considerably higher than that of benzene. Thus, while the chemical behavior of benzene is similar to that of its phospha derivatives, notable differences are expected when the electron-acceptor properties are involved.

The energies of formation of the lowest lying states have been computed using the B3LYP functional and different basis sets, as the energy difference between the anion and neutral states. The results show that for unstable anion states the calculated VAEs strongly depend on the choice of the basis set. As is well-known, if the basis set does not include diffuse functions, too high anion energies are obtained. Inclusion of diffuse functions lowers the calculated VAEs but does not solve the problem. The VAEs become increasingly smaller as the basis set is enlarged. In addition, the lowest lying anion state is often described (as for instance in benzene) by diffuse functions (that represent the neutral molecule with the electron in the continuum), which have no significance with regard to the resonance electron capture process.

The present results, however, indicate that the dependence of the calculated energies and localization properties on the addition of diffuse function to the basis set decreases with decreasing anion state energy. For phospha- and arsabenzene, where the first anion state lies close to zero energy, even addition of more diffuse functions does not significantly change the calculated VAE and (π^*) nature of the SOMO. Because of their relatively long lifetime, anion states close to zero energy (or stable) are associated with wave functions largely localized on the molecule, and the part representing the continuum is correspondingly small.

It is thus a hard task to decide a priori which basis set (if any) will be reliable for reproducing the energy and localization properties of unstable anion states. To establish whether a basis set is proper, a series of calculations (with increasingly diffuse functions) is needed, and the numerical agreement with the measured VAE is not the only requirement. It should also be investigated whether the electron is in a diffuse orbital. In the former case the continuum is strongly mixed in the wave function and the calculated anionic ground state does not reproduce the physical process of temporary anion formation. In these cases, more sophisticated computational methods are needed to evaluate the energy of the proper (excited) valence anion state.

For the crucial case of phosphabenzene, where the lowest energy anionic state is at the edge of stability, we have good results for both the ground and excited anionic π states by using the CASPT2 method, using the π-type valence orbitals in the active space. We will explore the use of this method in more detail in future work.

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