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Structures, Electron Affinities, and Harmonic Vibrational Frequencies of $C_6H_5X/C_6H_5X^-$ (X = N, S, NH, PH, CH_2, and SiH_2)

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The molecular structures and electron affinities of the $C_6H_5X/C_6H_5X^-$ (X = N, S, NH, PH, CH_2, and SiH_2) species have been determined using seven different density functional or hybrid Hartree−Fock density functional methods. The basis set used in this work is of double-ζ plus polarization quality with additional diffuse s- and p-type functions, denoted DZP++. These methods have been carefully calibrated (*Chem. Rev.* **2002**, *102*, 231). The geometries are fully optimized with each density functional theory (DFT) method, and discussed. Harmonic vibrational frequencies were found to be within 3.2% of available experimental values for most functionals. Three different types of the neutral−anion energy separations reported in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The most reliable adiabatic electron affinities, obtained at the DZP++ BPW91 level of theory, are 1.45 (C_6H_5N), 2.29 (C_6H_5S), 1.57 (C_6H_5NH), 1.51 (C_6H_5PH), 0.91 ($C_6H_5CH_2$), and 1.48 eV ($C_6H_5SiH_2$), respectively. Compared with the experimental values, the average absolute error of the BPW91 method is 0.04 eV. The B3LYP and B3PW91 functionals also gave excellent predictions, with average absolute errors of 0.06 and 0.07 eV, respectively.

Introduction

Phenylnitrene radical, phenylthio radical, C_6H_5PH radical, anilino radical, benzyl radical, and phenyl silyl radical have been studied both experimentally and theoretically because of their intrinsic interest from the point of view of chemical structure and bonding.[1−10] Phenylnitrene as a reactive intermediate produced upon thermal and photochemical decomposition of phenyl azide has long been a source of fascination to both organic and physical chemists.[11−14] Phosphorus compounds have the versatility and widespread use of organophosphorus compounds in such diverse applications as reagents in synthetic organic chemistry,[15] ligands in organotransition−metal complexes, [16] and pesticides and pharmaceuticals.[17] The electron affinity (EA) is both a key spectroscopic value and vitally important for use in the chemical cycle in order to determine bond dissociation energy. Over the past decades, there are many experimental studies for EA of above six radicals.[5−10] However, there have been few theoretical studies. The thermochemical properties and the ground or electronic states of the neutral and anion species are indispensable tools for understanding chemical reactivity and predicting the reaction mechanism. With this motivation, we have carried out a detailed study of structures, thermochemistry, and electron affinities of the above radicals and their anions using density functional theory (DFT).[18]

When predicting molecular energies, structures, and electron affinities, there are many theoretical approaches, but considering both reliability and computational expense, the GGA density functional theory is effective for predicting electron affinities of many organic species such as phenyl radical, phenoxyl radical, *o*-benzyne,[19] the radicals derived from the halide benzene,[20] and so on. The theoretical prediction of electron affinities has historically been generally difficult due to the desired result being a small difference between two large energies; but recent work has shown that some carefully chosen DFT methods are dependable for EA predictions. Though, for DFT calculations of anions, there are some problems[21,22] such as the unphysical asymptotic behavior of all their functionals and the lack of a complete basis set limit of some anions, DFT is indeed applicable to anions and provides EA predictions within experimental error and achieves satisfying results. For a general discussion of the reliability of DFT studies, the reader is referred to the 2002 review of Rienstra-Kiracofe et al.[19] They suggested that B3PW91 and BPW91 methods might outperform the B3LYP, BLYP, and BP86 functionals.

The object of the present study is to systematically apply seven contemporary forms of density functional theory[18] to determine the electron affinities and other properties of the C_6H_5X (X = N, S, NH, PH, CH_2, and SiH_2) species. Of specific interest is (a) the comparison of the theoretical electron affinities with available experimental results; (b) the relationship between the neutral C_6H_5X species and their anions as reflected by the three types of energy separations, e.g., the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy of the anion (VDE); (c) the predictions of other properties including vibrational frequencies; and (d) the comparison of the different DFT methods. In our paper, the experimental electron affinities are EA_{ad} which are available on the Internet as part of the NIST Chemistry Webbook.[23] We would like to establish reliable theoretical predictions for these C_6H_5X species in the absence of experimental results and in some cases to challenge existing experiments.

Theoretical Methods

The seven pure DFT or hybrid Hartree−Fock/DFT methods used in our study are (a) Becke's 1988 exchange functional[24] with Lee, Yang, and Parr's correlation functional[25] (BLYP); (b)

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the half and half exchange functional[26] with the LYP correlation functional (BHLYP); (c) Becke's three-parameter hybrid functional[27] with the LYP correlation functional (B3LYP); (d) Becke's 1988 exchange functional with Perdew's correlation functional[28] (BP86); (e) Becke's three-parameter hybrid functional with Perdew's correlation functional (B3P86); (f) Becke's three-parameter hybrid functional with Perdew and Wang's 1991 gradient-corrected correlation functional[29] (B3PW91); and (g) Becke's 1988 exchange functional with Perdew and Wang's 1991 gradient-corrected correlation functional (BPW91).

Restricted methods were used for all closed-shell systems, while unrestricted methods were employed for the open-shell species. All the electron affinities and molecular structures have been determined using the Gaussian 98 program suite.[30] The default numerical integration grid (75 302) of Gaussian 98 was initially applied.

The standard double-ζ plus polarization (DZP) basis sets are constructed from the Huzinage−Dunning−Hay[31] sets of contracted Gaussian functions by adding a set of five pure d-type polarization functions for C, N, P, S, and Si and a p-type polarization functions for H [$\alpha_p(\mathrm{H}) = 0.75$, $\alpha_d(\mathrm{C}) = 0.75$, $\alpha_d(\mathrm{N}) = 0.80$, $\alpha_d(\mathrm{S}) = 0.70$, $\alpha_d(\mathrm{P}) = 0.60$, and $\alpha_d(\mathrm{Si}) = 0.50$]. Since diffuse functions are important for the anions, the DZP basis was augmented with diffuse functions; each heavy atom received one additional s-type and one set of p-type functions and H atom received one s-diffuse function. The diffuse function orbital exponents were determined in an "even tempered sense" as a mathematical extension of the primitive set, according to the prescription of Lee and Schaefer.[32] [$\alpha_s(\mathrm{C}) = 0.0430$, $\alpha_p(\mathrm{C}) = 0.0363$, $\alpha_s(\mathrm{H}) = 0.04415$, $\alpha_s(\mathrm{Si}) = 0.02729$, and $\alpha_p(\mathrm{Si}) = 0.02500$]. The final basis sets are thus H (5s1p/3s1p); C, N (10s6p1d/5s3p1d); and Si, P, S (13s9p1d/7s5p1d). This extended basis will be denoted as "DZP++".

All C_6H_5X stationary point geometries were interrogated by the evaluation of their harmonic vibrational frequencies at each of the seven different levels of theory. Zero-point vibrational energies (ZPVEs) are evaluated at the seven levels (Table 1 of Supporting Information). These differences may be used as corrections to the adiabatic electron affinities. The total energy of six radicals and ZPVE corrected total energy are displayed in Table 2 of the Supporting Information.

The electron affinities are evaluated as the difference of total energies in the following manner: the adiabatic electron affinity is determined as $\mathrm{EA_{ad}} = E(\text{optimized neutral}) - E(\text{optimized anion})$; the vertical electron affinity, as $\mathrm{EA_{vert}} = E(\text{optimized neutral}) - E(\text{anion at optimized neutral geometry})$; and the vertical detachment energy of the anion, as $\mathrm{VDE} = E(\text{neutral at optimized anion geometry}) - E(\text{optimized anion})$.

Results and Discussion

A. C_6H_5N and $C_6H_5N^-$. Phenylnitrene, C_6H_5N is one interesting and important reactive intermediate in chemistry. There have been a number of studies of phenylnitrene in both gas and condensed phases.[1,33−36] Its gas-phase electron spectrum was first reported by Porter and Ward[33] in the late 1960s. In 1990, a discussion[1] of the photochemistry of the ground-state triplet phenylnitrene was reported in both gas and condensed phases.

In addition, elucidating the energies for different electronic states of phenylnitrene has been the goal of several experimental[5,37] and theoretical[2−4,38] studies. Theory and experiment are in good agreement on the relative ordering of the lowest energy states. On the theoretical aspect, there are several methods to study the properties of the C_6H_5N radical. For instance, Kim et al.[3] theoretically investigated the electronic spectra, structures, stabilities, and vibrational frequencies of phenylnitrene using ab initio quantum chemical techniques.

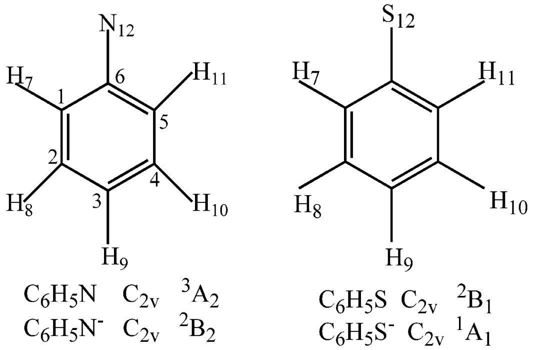

Figure 1. Optimized geometries for neutral C_6H_5N and anionic $C_6H_5N^-$ and for neutral C_6H_5S and anionic $C_6H_5S^-$. Carbon atoms are labeled from 1 to 6.

The equilibrium geometries of the ${}^3A_2$ ground states of neutral C_6H_5N with C_{2v} symmetry and the ${}^2B_2$ ground state of $C_6H_5N^-$ are displayed in Figure 1 and geometric parameters are in Table 3 of the Supporting Information. In our work, we also discover that B3LYP, BHLYP, B3P86, and B3PW91 results indicate the ${}^3A_2$ state is more stable than the ${}^1A_1$ state by about 2.08, 2.38, 1.44, and 1.49 eV, respectively. The ${}^3A_2$ state is the ground state and is in consistence with all previous work.

For the C_{2v} C_6H_5N molecular structure, there are no experimental geometries for comparison, but there are two theoretical values. Theoretical C−N bond length of 1.388 Å with the DZ+d basis sets at the CISD level of theory was reported by Kim et al. in 1992.[3] Subsequently, Hrovat et al.[2] predicted the C−N bond length to be 1.374 Å using the 3-21G basis set, 8-electron/8-orbit MCSCF calculations. Compared with the two ab initio bond length results, our present theoretical predictions (Table 3 of Supporting Information) of 1.331−1.340 Å are significantly shorter and might be more reliable.

The planar anion $C_6H_5N^-$ also has C_{2v} symmetry, with the C−N bond distances predicted to be 1.307−1.328 Å by the different DFT methods. From Table 3 of the Supporting Information, we can see that the neutral and anion geometries (C−N bond length) are indeed quite similar, with a slight decrease by about 0.015 Å from the neutral to the anion. In addition, the optimized geometries for the seven DFT methods vary only slightly among each other.

The theoretical $\mathrm{EA_{ad}}$, $\mathrm{EA_{vert}}$, and VDE, as well as the experimental electron affinity data, are listed in Table 1. The range of $\mathrm{EA_{ad}}$ corrected is predicted from 1.01 to 1.96 eV with the seven DFT methods. The BHLYP method predicts the smallest $\mathrm{EA_{ad}}$ (1.01 eV), and the B3P86 method predicts the largest $\mathrm{EA_{ad}}$ (1.96 eV). There are several experimental studies of the electron affinity for the phenylnitrene. In 1984, Drzaic and Brauman[39] reported the experimental adiabatic electron affinity of the triplet phenylnitrene neutral to be 33.7 ± 0.3 kcal/mol (1.461 ± 0.013 eV) via photodetachment spectroscopy. In 1992, Travers et al.[37] obtained the EA of phenylnitrene to be 1.450 ± 0.020 eV. Later (1993), McDonald and Davidson[5] reported the most accurate electron affinities to date for phenylnitrene, 1.429 ± 0.011 eV using negative ion photoelectron spectra. Our B3LYP (1.41 eV), BLYP (1.39 eV), B3PW91 (1.38), and BPW91 (1.45 eV) results are close to the more recent (and more reliable) experimental result (1.429 ± 0.011 eV). [5] The B3LYP and BPW91 result are closely matched by the experimental value (only deviating about 0.02 eV). From the above result, we can see that the application of the employed

TABLE 1: Adiabatic and Vertical Electron Affinities of the Neutral C_6H_5X and Vertical Detachment Energies of Their Anions in electronvolts (kilocalories per mole in parentheses)[a]

compd	method	EA_{ad}	corrected EA_{ad}	EA_{vert}	VDE
C_6H_5N	B3LYP	1.37 (31.6)	1.41	1.30 (30.0)	1.43 (33.1)
	BLYP	1.34 (30.8)	1.39	1.28 (29.5)	1.39 (32.1)
	BHLYP	0.98 (22.5)	1.01	0.89 (20.6)	1.05 (24.2)
	B3P86	1.92 (44.2)	1.96	1.85 (42.6)	1.99 (45.8)
	BP86	1.55 (35.7)	1.60	1.49 (34.4)	1.61 (37.0)
	B3PW91	1.34 (30.9)	1.38	1.27 (29.2)	1.41 (32.4)
	BPW91	1.41 (32.4)	1.45	1.35 (31.0)	1.46 (33.8)
	Expt.		1.429 ± 0.011[b]		
C_6H_5S	B3LYP	2.26 (52.2)	2.29	2.22 (51.3)	2.30 (53.1)
	BLYP	2.14 (49.3)	2.17	2.10 (48.5)	2.18 (50.3)
	BHLYP	2.03 (46.7)	2.05	1.98 (45.7)	2.07 (47.7)
	B3P86	2.83 (65.2)	2.86	2.79 (64.3)	2.87 (66.2)
	BP86	2.38 (54.9)	2.41	2.34 (54.0)	2.42 (55.7)
	B3PW91	2.27 (52.4)	2.30	2.23 (51.5)	2.31 (53.3)
	BPW91	2.25 (52.0)	2.29	2.22 (51.1)	2.29 (52.8)
	Expt.		2.26 ± 0.10[c] <2.470 ± 0.06[d]		
C_6H_5NH	B3LYP	1.50 (34.6)	1.54	1.45 (33.4)	1.55 (35.8)
	BLYP	1.44 (33.2)	1.49	1.39 (32.1)	1.49 (34.3)
	BHLYP	1.14 (26.3)	1.17	1.08 (24.9)	1.20 (27.7)
	B3P86	2.06 (47.4)	2.10	2.00 (46.2)	2.11 (48.7)
	BP86	1.66 (38.3)	1.71	1.61 (37.2)	1.71 (39.4)
	B3PW91	1.49 (34.3)	1.53	1.43 (33.0)	1.54 (35.6)
	BPW91	1.53 (35.2)	1.57	1.48 (34.1)	1.58 (36.3)
	Expt.		1.61 ± 0.13[e] 1.704 ± 0.0.30[f]		
C_6H_5PH	B3LYP	1.45 (33.3)	1.49	1.41 (32.6)	1.48 (34.1)
	BLYP	1.37 (31.6)	1.42	1.34 (30.9)	1.40 (32.4)
	BHLYP	1.16 (26.7)	1.20	1.12 (25.9)	1.20 (27.6)
	B3P86	1.99 (45.9)	2.04	1.96 (45.1)	2.03 (46.8)
	BP86	1.60 (36.9)	1.65	1.57 (36.1)	1.63 (37.6)
	B3PW91	1.44 (33.2)	1.48	1.41 (32.4)	1.48 (34.0)
	BPW91	1.47 (33.8)	1.51	1.43 (33.1)	1.50 (34.6)
	Expt.		1.52 ± 0.04[g]		
$C_6H_5CH_2$	B3LYP	0.80 (18.5)	0.87	0.75 (17.2)	0.86 (19.9)
	BLYP	0.77 (17.7)	0.84	0.72 (16.6)	0.82 (18.9)
	BHLYP	0.43 (10.0)	0.49	0.37 (8.49)	0.50 (11.5)
	B3P86	1.34 (30.8)	1.40	1.27 (29.4)	1.40 (32.3)
	BP86	0.97 (22.4)	1.05	0.92 (21.2)	1.02 (23.6)
	B3PW91	0.77 (17.8)	0.84	0.71 (16.4)	0.83 (19.2)
	BPW91	0.83 (19.2)	0.91	0.78 (18.0)	0.89 (20.4)
	Expt.		0.912 ± 0.006[h]		
$C_6H_5SiH_2$	B3LYP	1.45 (33.4)	1.52	1.06 (24.4)	1.93 (44.4)
	BLYP	1.37 (31.7)	1.44	1.02 (23.5)	1.80 (41.6)
	BHLYP	1.20 (27.7)	1.27	0.76 (17.6)	1.73 (40.0)
	B3P86	1.95 (45.0)	2.02	1.56 (35.9)	2.44 (56.3)
	BP86	1.56 (36.1)	1.63	1.20 (27.7)	2.00 (46.2)
	B3PW91	1.40 (32.3)	1.47	1.01 (23.3)	1.89 (43.5)
	BPW91	1.42 (32.7)	1.48	1.06 (24.4)	1.86 (42.9)
	Expt.		1.4354 ± 0.0043[i]		

[a] Values are corrected for ZPVE and were obtained with the DZP++ basis set. [b] Reference 5. [c] Reference 6. [d] Reference 40. [e] Reference 41. [f] Reference 7. [g] Reference 8. [h] Reference 9. [i] Reference 10.

DFT techniques to the Ph−N is better and satisfying. The theoretical vertical electron affinity $EA_{vert}(C_6H_5N)$ predicted by BPW91 is 1.35 eV, and the vertical detachment energy VDE ($C_6H_5N^-$) is 1.46 eV. The values of EA_{ad}, EA_{vert}, and VDE are close to each other due to the small differences in geometry between the neutral and the anion.

B. C_6H_5S and $C_6H_5S^-$. The phenylthio radical, or thiophenoxy radical, C_6H_5S, with C_{2v} symmetry for the $^2B_1$ ground state is a planar structure. The optimized geometries of the neutral and its anion (C_{2v} symmetry for the $^1A_1$ ground state) are given in Figure 1 and Table 4 of the Supporting Information. For the C−S bond length, our present theoretical predictions (1.712−1.735 Å) are quite acceptable. The BLYP method provides the longest bond distance (1.735 Å). There are no experimental data available.

The anion $C_6H_5S^-$ is also predicted to have a planar structure with C_{2v} symmetry. There are no experimental data available. Our results (Table 4 of the Supporting Information) predict the C−S bond distance to be between 1.733 and 1.757 Å. The geometries of the neutral and anion are quite similar, with the most noticeable difference being a decrease for the bond angle *A*(1,6,5) of about 3.0° from neutral to anion. This suggests the "last" electron in the anion electron resides at the electronegative sulfur atom, causing the decrease in angle to provide more space for the extra electron density. Indeed, the Mulliken atomic charge on the sulfur increases from −0.14 for the neutral to −0.77 for the anion. Compared with the neutral species data, the C−S bond length of the anion lengthened by about 0.021 Å.

The theoretical EA_{ad}, EA_{vert}, and VDE values, as well as the experimental results, are listed in Table 1. Richardson et al.[40] estimated an upper limit for EA_{ad} (C_6H_5S) to be <2.470 ± 0.060 eV. The experimental EA_{ad} was obtained to be 2.26 ± 0.10 eV by Taft and Bordwell[6] in 1988. We predicted the EA_{ad} value for the phenylthio radical ranges from 2.03 to 2.83 eV. The EA_{ad} value predicted by DZP++ B3LYP and BPW91 (2.29 eV with ZPVE) for the phenylthio radical is a noteworthy match of the experimental result (the average absolute error being 0.03

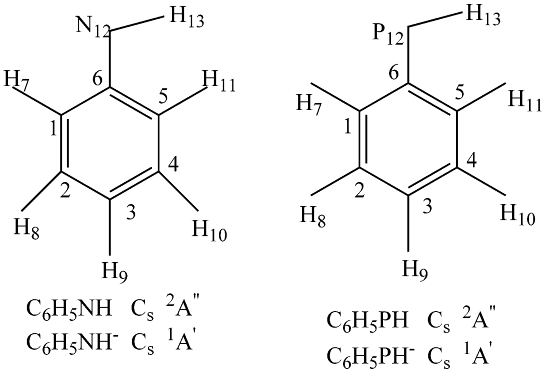

Figure 2. Optimized geometries for neutral C_6H_5NH and anionic $C_6H_5NH^-$ and for neutral C_6H_5PH and anionic $C_6H_5PH^-$. Carbon atoms are labeled from 1 to 6.

eV); B3PW91 (2.30 eV) and BPW91 (2.29 eV) predict more reasonable values within experimental error;[6] BLYP (2.17 eV) is also satisfying, having a little bigger deviation (0.09 eV). The EA_{vert} value is predicted to range from 1.98 to 2.79 eV, while the VDE values vary from 2.07 to 2.87 eV. Except for B3P86 and BHLYP, the predictions of the other DFT methods are reasonable. The values for EA_{ad}, EA_{vert}, and VDE are fairly close to each other, due to the small differences in geometry between neutral and anion.

C. C_6H_5NH and $C_6H_5NH^-$. Anilino radical, C_6H_5NH, has not received much theoretical attention. The C_s symmetry structure of the $^2A''$ ground state for the neutral anilino radical and the C_s symmetry structure of the $^1A'$ ground state for the anionic $C_6H_5NH^-$ are shown in Figure 2 and Table 2. There are no experimental bond angles and bond lengths. From the present study, the trend of the bond distances is BLYP > BP86 ∼ BPW91 > B3LYP > B3PW91 ∼ B3P86 > BHLYP (Table 2). It is interesting to compare the anion's geometries to those of the neutral. With an extra electron, the bond lengths of the C−N and N−H of the neutral and anion are still basically similar to the neutral species. It is also noteworthy that the geometries obtained via seven functionals are all similar. As for bond angles, for instance *A*(6,12,13), it is predicted to be 109.5 (BHLYP), 109.1 (B3LYP), 108.4 (BP86), 108.7 (BLYP), 108.4 (BPW91), 108.9° (B3P86), and 108.9° (B3PW91) for the neutral, while, for the anion, being 108.2, 107.9, 108.5, 107.8, 107.4, 107.8, and 107.4°, respectively. The bond angles are about 0.99° smaller than their neutral counterparts. Unlike *A*(6,12,13), *A*(1,6,5) and *A*(2,3,4) angles change about 3.9 and 3.1° between the neutral and the anion, respectively.

The theoretical EA_{ad}, EA_{vert}, and VDE for C_6H_5NH, as well as the experimental electron affinity data, are given in Table 1. The range of EA_{ad} is predicted from 1.17 to 2.10 eV with the seven DFT methods. The BHLYP method predicts the smallest EA_{ad} (1.17 eV), and the B3P86 method predicts the largest EA_{ad} (2.10 eV). In 1979, experimental electron affinities of 1.61 ± 0.13 eV were reported by Bartmess et al.[41] with a pulsed ion cyclotron resonance spectrometer. After several years, Drzaic and Brauman[7] presented the experimental adiabatic electron affinity of the anilino radical to be 39.3 ± 0.7kcal/mol (1.704 ± 0.030 eV) via photodetachment spectroscopy. The BP86 still well predicts the electron affinity of anilino radical (0.006 eV higher) within experimental error, and our BPW91 (1.57 eV), B3LYP (1.54 eV), and B3PW91 (1.53 eV) results slightly underestimated the experimental value (1.704 ± 0.030 eV) and are also reasonable.

D. C_6H_5PH and $C_6H_5PH^-$. The equilibrium geometries of the $^2A''$ ground state of neutral C_6H_5PH and the $^1A'$ ground state of anion $C_6H_5PH^-$ are displayed in Figure 2 and Table 3. For the C_s C_6H_5PH planar structure, the theoretical C−P bond lengths are in the range from 1.789 to 1.813 Å. No experimental geometries are available for either C_6H_5PH or $C_6H_5PH^-$. The anion $C_6H_5PH^-$ also has C_s symmetry with planar structure. The C−P bond lengths are predicted from 1.795 to 1.818 Å. These distances are about 0.005 Å longer than their neutral counterparts; the P−H bond distance of the anion is also longer than the neutral's. This is different from the anilino radical (C_6H_5NH) species. The bond angle *A*(6,12,13) of the neutral and anion change about 0.1° compared with each other, while changes of the *A*(1,6,5) and *A*(2,3,4) angle are relatively large, being about 3.2 and 2.2° between the neutral and the anion species, respectively (Table 3).

Our theoretical neutral−anion energy separations for the phenylphosphide ion, as well as experimental electron affinity data, are shown in Table 1. The adiabatic electron affinity EA_{ad} is predicted to be 1.20−2.04 eV. Compared with the experimental value (1.52 ± 0.04 eV) given by Berger and Brauman[8] in 1992 from their electron photodetachment study, the present DZP++ BPW91 EA_{ad} value provides the most favorable comparison with the experimental result, of which the absolute error is only 0.01 eV. The B3LYP (1.49 eV) and B3PW91 (1.48 eV) methods are also considered to be the more reliable, deviating about 0.03 and 0.04 eV, respectively. The EA_{vert} ranges from 1.12 to 1.96 eV. The range of VDE is from 1.20 to 2.05 eV. The values for EA_{ad}, EA_{vert}, and VDE are fairly close to each other, due to the small differences in geometry between neutral and anion.

E. $C_6H_5CH_2$ and $C_6H_5CH_2^-$. The geometries of the $^2B_1$ ground state of benzyl radical and the $^1A_1$ state of its anion are shown in Figure 3 and Table 5 of the Supporting Information. Both are planar structures with C_{2v} symmetries. There are no experimental geometries available for either $C_6H_5CH_2$ or $C_6H_5CH_2^-$. There are a number of studies for benzyl radical; for example, Vanermen et al.[42] calculated (STO-3G level) the planar geometry of the benzyl radical and gained understanding that it was more stable than the tetrahedral configuration around the benzylic carbon atom. Spectra of the benzyl radical have been obtained in matrixes[43−45] and in the gas phase.[46,47] In 1992, the planar geometry and frequencies of the benzyl radical were again calculated at the 6-31G** level using Hartree−Fock methods by Gunion et al. [9] We find that the differences in geometries between the neutral and the anion are quite small, in particular bond lengths (Table 5 of the Supporting Information). The C_6−C_{12} bond length decreases slightly by about 0.013 Å from the neutral to the anion. The value of *A*(1,6,5) bond angle decreases 3.7°. The optimized geometries for the seven DFT methods vary only slightly among each other.

There have experimentally been a number of studies of the electron affinity for the benzyl radical, ranging from as low as 0.75887 eV to as high as 2.350 ± 0.069 eV.[7,9,41,48−52] Bartmess et al.[41] reported the adiabatic electron affinity of $C_6H_5CH_2$ radical to be 0.90 ± 0.10 eV in 1979. The EA value for the benzyl radical of 0.863 ± 0.013 eV was obtained by Drzaic and Brauman[7] with an electron photodetachment study in 1984. In the early 1990s, Gunion et al.[9] estimated the most accurate electron affinities to date for the $C_6H_5CH_2$ radical, 0.9120 ± 0.0060 eV using ultraviolet photoelectron spectra. The majority of these values place the electron affinity at about 0.90 eV. Perhaps the best results are those of Bartmess et al.[41] and Gunion et al.[9] Our theoretical neutral−anion energy separations for benzyl radical are given in Table 1. The adiabatic electron affinity EA_{ad} is predicted to be 0.49−1.40 eV. We can see that

TABLE 2: Optimized Geometry for the C_6H_5NH and the Corresponding Anion $C_6H_5NH^-$ [a]

	B3LYP	BLYP	BHLYP	B3P86	BP86	B3PW91	BPW91
C_6H_5NH							
c_1-c_2	1.389	1.399	1.380	1.385	1.396	1.386	1.395
c_1-c_6	1.440	1.454	1.428	1.435	1.450	1.437	1.448
c_5-c_6	1.439	1.452	1.426	1.434	1.448	1.435	1.447
c_6-n_{12}	1.346	1.356	1.338	1.341	1.352	1.343	1.351
$n_{12}-h_{13}$	1.029	1.039	1.017	1.027	1.039	1.028	1.037
A(2,3,4)	120.0	120.0	120.0	120.1	120.1	120.1	120.0
A(3,4,5)	120.4	120.4	120.3	120.3	120.4	120.3	120.4
A(1,6,5)	117.6	117.4	117.8	117.6	117.4	117.7	117.4
A(6,5,11)	117.4	117.4	117.6	117.4	117.3	117.4	117.3
A(6,12,13)	109.1	108.7	109.5	108.9	108.4	108.9	108.4
$C_6H_5NH^-$							
c_6-n_{12}	1.341	1.355	1.326	1.336	1.351	1.337	1.349
$n_{12}-h_{13}$	1.028	1.039	1.016	1.026	1.039	1.027	1.036
A(2,3,4)	117.0	117.1	116.8	116.9	117.0	116.9	117.0
A(3,4,5)	122.1	122.0	122.2	122.1	122.0	122.1	122.0
A(1,6,5)	113.7	113.8	113.8	113.7	113.7	113.6	113.6
A(6,5,11)	116.9	116.9	117.0	116.8	116.8	116.9	116.9
A(6,12,13)	108.2	107.9	108.5	107.8	107.4	107.8	107.4

[a] All bond distances are in angstroms, all bond angles are in degrees, and all results were obtained with the DZP++ basis set.

TABLE 3: Optimized Geometry for the C_6H_5PH and the Corresponding Anion $C_6H_5PH^-$ [a]

	B3LYP	BLYP	BHLYP	B3P86	BP86	B3PW91	BPW91
C_6H_5PH							
c_1-c_2	1.397	1.407	1.387	1.392	1.404	1.394	1.402
c_1-c_6	1.421	1.434	1.409	1.416	1.430	1.417	1.428
c_5-c_6	1.420	1.433	1.408	1.415	1.429	1.416	1.427
c_6-p_{12}	1.801	1.813	1.789	1.792	1.805	1.796	1.804
$p_{12}-h_{13}$	1.427	1.439	1.414	1.426	1.440	1.427	1.438
A(2,3,4)	119.7	119.7	119.7	119.7	119.7	119.7	119.7
A(3,4,50	120.3	120.3	120.3	120.2	120.3	120.3	120.3
A(1,6,5)	117.8	117.6	117.9	117.9	117.8	117.9	117.8
A(6,5,11)	119.4	119.3	119.5	119.4	119.3	119.4	119.3
A(6,12,13)	96.0	95.8	96.4	95.8	95.5	95.9	95.7
$C_6H_5PH^-$							
c_6-p_{12}	1.806	1.818	1.800	1.795	1.809	1.799	1.807
$p_{12}-h_{13}$	1.435	1.447	1.422	1.433	1.447	1.435	1.445
A(2,3,4)	117.5	117.5	117.6	117.5	117.5	117.5	117.5
A(3,4,5)	121.3	121.3	121.3	121.3	121.3	121.3	121.3
A(1,6,5)	114.7	114.6	114.9	114.7	114.6	114.5	114.6
A(6,5,11)	118.4	118.4	118.5	118.3	118.3	118.4	118.3
A(6,12,13)	95.9	95.9	96.0	95.7	95.6	95.8	95.7

[a] All bond distances are in angstrom, all bond angles are in degree, and all results were obtained with the DZP++ basis set.

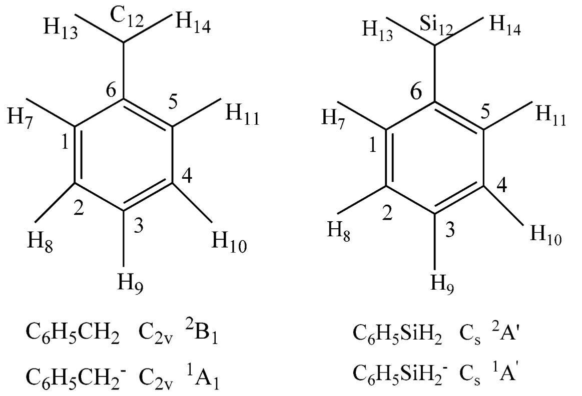

Figure 3. Optimized geometries for neutral $C_6H_5CH_2$ and anionic $C_6H_5CH_2^-$ and for neutral $C_6H_5SiH_2$ and anionic $C_6H_5SiH_2^-$. Carbon atoms are labeled from 1 to 6.

several theoretical values are in accord with each other, except for the B3P86 result (1.40 eV) and that of BHLYP (0.49 eV). Compared with the experimental value (0.9120 ± 0.0060 eV),[9] the BPW91 result (0.91 eV) is most reasonable and satisfactory, of which the absolute error is only 0.002 eV. In addition, the B3LYP, B3PW91, and BLYP methods also provided more reasonable prediction (0.87, 0.84, and 0.84 eV). The values of EA_{ad}, EA_{vert}, and VDE are fairly close to each other due to the small differences in geometry between the neutral and the anion.

F. $C_6H_5SiH_2$ and $C_6H_5SiH_2^-$. The C_s symmetry structure of the $^2A'$ ground state for the neutral $C_6H_5SiH_2$ radical and the C_s symmetry structure of the $^1A'$ ground state for the anionic $C_6H_5SiH_2^-$ are shown in Figure 3 and Table 4. The structure of the phenyl is still basically planar, but SiH_2 and SiH_2^- both turn up a small angle. For the neutral $C_6H_5SiH_2$ radical, the C−Si bond distance is predicted to be 1.852 (BHLYP), 1.861 (B3LYP), 1.864 (BP86), 1.870 (BLYP), 1.865 (BPW91), 1.853 (B3P86), and 1.857 Å (B3PW91); the Si−H bond lengths are 1.476, 1.487, 1.499, 1.496, 1.497, 1.486, and 1.488 Å; and the bond angle A(13,12,14) is found to be 111.7, 111.6, 111.8, 111.5, 111.7, 111.8, and 111.7°, respectively. In the present work, we also found that the dihedral angle ($D(H_{11}-C_5-C_6-Si_{12})$) is only about 2.6°, while $D(C_5-C_6-Si_{12}-H_{14})$ is predicted to be about 28°. The $C_6H_5SiH_2^-$ displays C_s symmetry, and it has longer C−Si and Si−H bond distances than the neutral. We obtain an A(13,12,14) value of the anion to be about 96.7°, being reduced by about 15.0°. However, the dihedral angles ($D(H_{11}-C_5-C_6-Si_{12})$ and $D(C_5-C_6-Si_{12}-H_{14})$) increase by about 4.1 and 16.3°, respectively.

TABLE 4: Optimized Geometry for the $C_6H_5SiH_2$ and the Corresponding Anion $C_6H_5SiH_2^{-a}$

	B3LYP	BLYP	BHLYP	B3P86	BP86	B3PW91	BPW91
$C_6H_5SiH_2$							
c_6-si_{12}	1.861	1.870	1.852	1.853	1.864	1.857	1.865
$si_{12}-h_{13}(si_{12}-h_{14})$	1.487	1.496	1.476	1.486	1.499	1.488	1.497
A(13,12,14)	111.6	111.5	111.7	111.8	111.8	111.7	111.7
D(11,5,6,12)	−2.6	−2.7	−2.7	−2.6	−2.7	−2.6	−2.6
D(5,6,12,14)	28.4	28.5	28.5	28.1	28.1	28.2	28.1
$C_6H_5SiH_2^-$							
c_6-si_{12}	1.938	1.946	1.933	1.925	1.935	1.930	1.935
$si_{12}-h_{13}(si_{12}-h_{14})$	1.535	1.545	1.524	1.534	1.546	1.536	1.545
A(6,12,13)	97.8	98.2	97.5	97.5	97.9	97.6	98.0
A(13,12,14)	96.8	96.9	96.8	96.6	96.7	96.6	96.7
D(11,5,6,12)	−6.6	−7.3	−5.8	−6.6	−7.2	−6.6	−7.2
D(5,6,12,14)	44.5	44.7	44.0	44.6	44.8	44.6	44.8

[a] All bond distances are in angstroms, all bond angles are in degrees, and all results were obtained with the DZP++ basis set.

The theoretical EA_{ad}, EA_{vert}, and VDE, as well as the experimental electron affinity data, are listed in Table 1. The range of EA_{ad} is from 1.27 to 2.02 0 eV from the seven different functionals. In 1988, the experimental electron affinity of phenylsilyl radical was first reported by Damrauer et al.[53] and found to be 1.34 ± 0.22 eV. Compared with the more accurate experimental value (1.4354 ± 0.0043 eV) given by Wetzel et al.[10] in 1989 from gas-phase equilibria and electron photodetachment spectroscopy, the BLYP method (1.44 eV) predicts the most reliable and reasonable value; the absolute error is only 0.0046 eV. The B3PW91, BPW91, and B3LYP methods should also be recognized as the more reliable value based on the above studies, and their results are 1.47, 1.48, and 1.52 eV, respectively. The B3P86 method predicts the largest corrected EA_{ad} (2.02 eV), which deviates 0.58 eV higher, while the BHLYP method predicts the smallest corrected EA_{ad} (1.27 eV), which deviates 0.17 eV lower.

The geometries of six anion molecules are fairly similar to their corresponding neutral species. Furthermore, each DFT functional predicted overall geometries consistent with the other functionals. The BLYP method usually gave the longest bond distances, and the BHLYP method usually predicted the shortest bond lengths. We confirm that DFT may predict very good geometries for both the neutral and anionic basic aromatic radicals.

The BPW91, B3PW91, and B3LYP methods gave excellent agreement with experimental electron affinities in all species. Nonetheless, we can rank the functionals by the average absolute error with ZPVE correction from experiment (in electronvolts): BPW91 (0.04), B3LYP (0.06), B3PW91 (0.07), BLYP (0.09), BP86 (0.13), BHLYP (0.35), and B3P86 (0.52). Obviously, BPW91, B3LYP, and B3PW91 methods are outstanding choices for electron affinity predictions including the phenyl radical's organic rings. The accuracy of these three DFT method functionals is impressive.

G. Vibrational Frequencies. Harmonic vibrational frequencies of $C_6H_5X/C_6H_5X^-$ predicted with each functional are available in Tables 6−11 of the Supporting Information. Travers et al.[37] gave two vibrational mode frequencies for the neutral phenylnitrene radical: 515 (ring-breathing) and 1300 cm^{-1} (C−N distortion). Later, Mcdonald and Davidson[5] also confirmed ring-breathing vibrational mode. In 1990, the first complete infrared spectrum of phenylnitrene radical was reported by Hayes and Sheridan.[54] They did not give vibrational modes but reported tentative assignment or approximate value.

Table 6 of the Supporting Information lists the experimental IR harmonic vibrational requencies[54] for the C_6H_5N radical. Our theoretical frequencies agree quite well with experiment. Among the various functionals, BPW91, BLYP, and BP86 predict values slightly below or near the experimental values, while the others consistently overpredict values, with BHLYP being the highest, as it might expect because of its 50% Hartree−Fock exchange. Comparison of our results for the neutral with Hayes and Sheridan's IR frequencies[54] allows us to rank the methods according to average absolute percent error from experiment: BPW91 (0.8%), BLYP (1.1%), BP86 (1.2%), B3LYP (2.1%), B3PW91 (2.5%), B3P86 (2.6%), and BHLYP (5.7%). These results are quite good excluding that of BHLYP. Clearly, the result of the BPW91 method shows excellent agreement; those of the BLYP and BP86 methods are acceptable; the results of B3LYP, B3PW91, and B3P86 are slightly worse but also reasonable. The three pure methods give substantially better frequency predictions in this case.

The theoretical harmonic vibrational frequencies for neutral phenylthio radical is listed in the Supporting Information, Table 7. Shibuya et al.[55] assigned three experimental frequencies in the gas by LIF: 430 ± 20 (C−S stretch), 610 ± 20 (ring deformation), and 1165 ± 20 cm^{-1} (C−H deformation). BHLYP predicted the largest harmonic vibrational frequencies.

Our theoretical results of anilino radical's harmonic vibrational frequencies are given (see Table 8 of the Supporting Information). The predication values of the BPW91, BP86, and BLYP methods is very similar, while those of three hybrid DFT methods are consistent each other. The BHLYP method still displays the largest values. In 1987, Tripathi and Schuler[56] obtained three vibrational frequencies of the ground state, that is, 1505 (C−S stretch), 533 (ring deformation), and 1167 cm^{-1} (C−H deformation).

The theoretical vibrational frequencies for the neutral C_6H_5-PH radical and its anion species are shown Table 9 of the Supporting Information. For the BP86 result of the anion, there are two vibrational frequencies that are doubtful and are not in agreement with results of other methods. BHLYP predicts the highest harmonic vibrational frequencies

Our predicted harmonic vibrational frequencies for both the benzyl radical and its anion are presented in Table 10 of the Supporting Information. In 1993, Baskir et al.[57] assigned frequencies for 14 IR-active fundamentals of the benzyl radical from an infrared argon matrix absorption spectrum. We compared our frequencies to those of Baskir et al. Ranking the methods according to average absolute percent deviation from experiment we obtain the following: BPW91 (1.4%), BP86 (1.4%), BLYP (1.8%), B3PW91 (3.6%), B3P86 (3.8%), B3LYP (3.9%), and BHLYP (7.0%). Our predicted harmonic vibrational frequencies for the neutral radical show good agreement with the experimental results. As in the case of C_6H_5N, we can see that three pure DFT methods give the best agreement and are very similar, while the BHLYP frequencies again show the largest disagreement with experiment.

The theoretical vibrational frequencies for the neutral phenylsilyl radical and anion species are reported in Table 11 of the Supporting Information. The BHLYP again predicts the highest harmonic vibrational frequencies.

In any case, the theoretical frequency values for the anion are smaller than those for the corresponding neutral radicals, and this is consistent with the fact that anions have weaker bonds than neutral radicals, since the anions have longer equilibrium separation than the neutrals.

In general, there is good agreement between available experimental frequencies and predicted harmonic vibrational frequencies. All functionals except for BHLYP consistently gave reasonable predictions, never exceeding more than a 3.9% average absolute error. The BHLYP method had large errors and consistently predicted vibrational frequencies with the highest magnitude deviations from experiment. The three pure DFT methods achieved the remarkable success at predicting vibrational frequencies aspect.

Conclusions

Carefully selected DFT methods applied with the DZP++ basis set are capable of reliably predicting the structures and EAs of six C_6H_5X species. The BPW91 method is the most reliable method for predicting the electron affinities for these molecular systems. The adiabatic EAs (with ZPVE) are predicted to be 1.45 (C_6H_5N), 2.29 (C_6H_5S), 1.57 (C_6H_5NH), 1.51 (C_6H_5PH), 0.91 ($C_6H_5CH_2$), and 1.48 eV ($C_6H_5SiH_2$); The B3LYP and B3PW91 method are also the more reasonable for predicting the electron affinities for C_6H_5X species. In addition, the BLYP method is regarded as reasonable. The B3P86 method gives the most deviation (the average absolute error being 0.52 eV). Our theoretical EA values are in good agreement with the available experimental results.

All functionals predict reasonable geometries for the neutral and anion species and show relatively small variations among themselves. In addition, harmonic vibration frequencies also show very reasonable agreement with available experimental data, excluding BHLYP. The HF/DFT hybrid functionals produce higher vibrational frequencies than the pure DFT exchange functionals, which has also been observed in the present studies.

We hope that our theoretical predictions will provide strong motivation for further experimental studies of these important phenyl species and their anions.

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Supporting Information Available: Tables showing ZPVEs, total energies, optimized geometries, and predicted harmonic vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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