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A PW91 Density Functional Study of Conformational Choice in 2-Phenylethanol, *n*-Butylbenzene, and Their Cations: Problems for Density Functional Theory?

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Absolute energies, geometric structures, harmonic vibrational frequencies, and partial charge distributions (NPA) are obtained from ab initio (HF/MP2) and density functional theory (DFT) calculations of stable conformers of neutral and cationic 2-phenylethanol and *n*-butylbenzene, model aromatic molecules with flexible side chains. We focus on exploring the conformational preferences of the cations and find that cationic conformational preference is more pronounced in the system with the strongly interacting side chain. The DFT calculations presented use the Perdew−Wang exchange and correlation functional, PW91. For the neutral conformers, PW91 performs extremely well compared to MP2, indicating that this functional will be highly useful for future computational studies of neutral aromatic molecules with flexible side chains. For the cationic conformers, PW91 again performs well compared to MP2 for *n*-butylbenzene, a system in which the side chain interacts only weakly with the aromatic ring. However, considerable discrepancies occur between the MP2 and DFT calculations for 2-phenylethanol$^+$. The results indicate that density functional theory does not provide a reliable description of the potential energy surface of 2-phenylethanol$^+$, and that high levels of theory may be necessary to accurately treat similar cations. The present study represents the first systematic comparison of HF, MP2, and DFT calculations of *cationic* conformers of aromatic molecules with flexible side chains.

1. Introduction

There has been great progress recently in understanding the factors governing conformational choice in unsolvated aromatic molecules with flexible side chains.[1] These advances have been achieved through the combined application of high-resolution molecular beam laser spectroscopy and ab initio theory.[2] Although there is a growing body of information on the conformations of neutral systems,[1,3] studies of the ionic analogues are rare and generally limited to photoionization studies of molecules with alkyl side chains that interact only weakly with the chromophore.[4−10] In this paper, we explore the issue of conformational preference in two prototype cationic systems, 2-phenylethanol$^+$ and *n*-butylbenzene$^+$ (Figure 1), using computational chemistry.

Much of the work on flexible aromatic molecules is motivated by their biological relevance,[1] and primary interest in the cationic analogues centers on their use as models for charge transfer in biological molecules.[8] In addition, aromatic groups with alkyl side chains are often used as the electron-donor moiety in electron-transfer experiments of bridged donor−acceptor molecules (e.g., anthracene−$(CH_2)_n$−aniline).[11] Elucidating an appropriate theoretical method for treating cationic aromatic molecules with flexible side chains is therefore an important preliminary to computational studies of model electron-transfer systems.

It is widely accepted that many current density functionals do not adequately describe through-space intersite electron correlation.[12,13] DFT calculations with local exchange-correlation functionals lead to overestimated binding energies of weakly bound systems, while nonlocal exchange-correlation functionals often underestimate the attraction. DFT calculations are therefore generally not expected to provide accurate structures and relative energies for the isomeric forms of molecules such as 2-phenylethanol and *n*-butylbenzene in which dispersion interactions should be important in determining conformational structure. However, recent studies[14−16] have demonstrated that the Perdew−Wang exchange and correlation functional (PW91)[17] can accurately predict the properties of van der Waals (vdW) dimers and hydrogen-bonded complexes. In this study, we perform ab initio (HF/MP2) and DFT calculations of the neutral (S_0) and

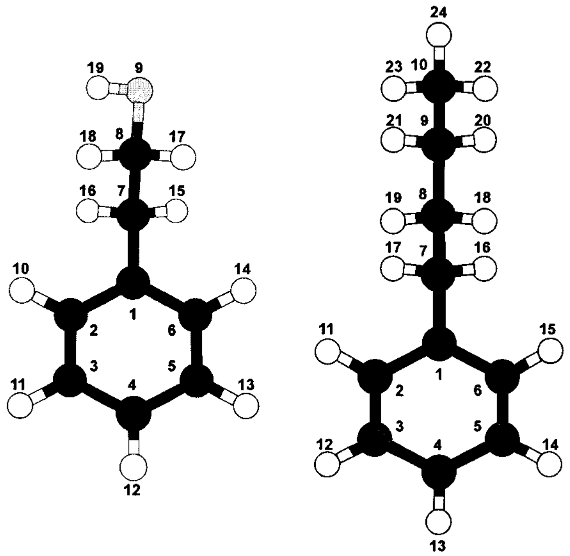

Figure 1. Schematic diagram of 2-phenylethanol (2PE) and *n*-butylbenzene (BB), illustrating the atom labeling schemes.

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cationic (D_0) ground states of aromatic molecules with flexible side chains to evaluate the functional performance for these systems. In particular, we are interested in whether PW91 performs as well for cationic molecules in which dispersion interactions influence conformational structure as it does in the previously studied neutral vdW complexes. 2-Phenylethanol (2PE) represents a model system with an end group that can interact strongly with the aromatic ring,[18−21] while in *n*-butylbenzene (BB) the alkyl side chain interacts only weakly.[22]

2. Theoretical Methods

Ab initio equilibrium geometries and energies of the neutral (S_0) and cationic (D_0) ground states of 2PE were calculated at the HF and MP2(fc) levels. DFT calculations were performed using the nonlocal exchange-correlation functional of Perdew and Wang, PW91.[17] Harmonic vibrational frequencies were calculated to confirm that conformers corresponded to local minima. Dunning's cc-pVDZ correlation-consistent basis set[23] was used for the 2PE system, while calculations were also conducted with Pople's 6-31G* basis set[24] for comparison. For BB, calculations employed 6-31G* because MP2/cc-pVDZ calculations were beyond the scope of our computational resources. All calculations were carried out on an IBM-RS6000 using Gaussian 98, version A.7,[25] with default or tight convergence criteria applied to the geometry optimizations. Zero-point energy (ZPE) corrections were computed from the harmonic vibrational frequencies and are reported unscaled. We note that ab initio calculations have been published previously for the S_0 state of 2PE,[8,18−21] and results for the neutral conformers are reported here primarily to evaluate the performance of PW91.

Transition-state structures for interconversion of the S_0 state conformers of 2PE were located using the QST2 and QST3 routines in Gaussian 98.[25] Partially relaxed potential energy surfaces were obtained as a function of dihedral angle with fixed-ring and optimized side-chain geometries. Where indicated in the text, ZPE corrections have been added to the potential energy surfaces using the following methodology. In the ground vibrational state, the effective torsional potential is given (in $\mathrm{cm^{-1}}$) by eq 1,

$$V_{\mathrm{eff}}(\tau) = V_0(\tau) + \sum_{r=1}^{3N-7} [{}^{1}\!/_{2}\omega_r] \tag{1}$$

where $V_0(\tau)$ is the potential along the dihedral without including any vibrational modes, and ω_r are the vibrational frequencies.[26] Therefore, the ZPE along a normal coordinate is half the frequency of the normal mode corresponding to motion along that coordinate. Modes corresponding to relatively pure torsions were identified from the calculations as approximations to the internal coordinate frequencies.

Partial charge distributions in the S_0 and D_0 states were calculated using the natural population analysis (NPA) method of Weinhold,[27] in Gaussian 98.[25] An NPA analysis has been demonstrated to give reliable atomic charges in MP2 calculations of a similar system.[28] The calculated percent charge delocalizations presented in Tables 4 and 7 represent differences between the partial charges in the S_0 and D_0 states at a given atomic center summed over the atoms of the side chain. Percent charge delocalizations are presented for both the end group (OH or CH_3) and side chain (CH_2OH or $CH_2CH_2CH_3$) for comparison with previous results.[8,28]

3. Results and Discussion

I. 2-Phenylethanol. *A. Energies and Geometric Structures of the Neutral Conformers of 2PE.* Table 1 presents the relative and ZPE-corrected values for the neutral conformers of 2PE calculated at the HF, MP2, and PW91 levels. Five stable molecular conformers were identified (Figure 2)[8,18−21] with conformers **I**−**III** corresponding to gauche structures with a folded side chain and conformers **IV** and **V** representing anti conformers with extended side chains. The HF and MP2 relative energies presented generally agree well with the previous calculations.[8,18−21] At all levels of theory, conformer **II** is the most stable isomer because of the presence of an OH π hydrogen bond (Figure 3). The relative stabilization energy of this conformer increases significantly when electron correlation is included. For the anti conformers, the HF calculation predicts that conformer **V** is lower in energy than conformer **IV**, whereas the ordering is reversed in the MP2 calculations because of the greater importance of dispersion interactions in conformer **V**. Multiphoton ionization spectra of 2PE suggest that conformer **IV** is more stable than conformer **V**,[8,21] in agreement with the MP2 results.

Relative energies obtained from the PW91/cc-pVDZ calculations appear closer to the MP2 than to the HF results, with conformer **II** being stabilized by ∼550 $\mathrm{cm^{-1}}$ compared to conformers **I**, **III**, and **IV**, while conformer **V** lies approximately 100 $\mathrm{cm^{-1}}$ higher in energy. We note that the PW91/cc-pVDZ calculations provide more reliable relative energies, compared

TABLE 1: Relative Energies, ZPE-Corrected (ZPEC) Relative Energies, and Geometric Parameters of the S_0 Conformers of 2PE Calculated at the HF/cc-pVDZ, MP2/cc-pVDZ, and PW91/cc-pVDZ Levels of Theory[a,b]

	I	II	III	IV	V
			HF/cc-pVDZ		
energy[c]	392	0	613	304	241
ZPEC energy[c]	322	0	561	231	156
τ_1	105.1	87.9	107.2	90.8	89.4
τ_2	69.5	62.3	67.8	177.3	180.0
τ_3	189.7	293.2	69.8	66.3	180.0
$r_{O_9-C_1}$	3.025	3.010	3.098	3.771	3.724
$r_{H_{19}-C_1}$	3.813	2.716	3.519	4.047	4.437
A	3.5957	3.4304	3.6072	4.5015	4.5290
B	1.0609	1.0733	1.0496	0.8506	0.8525
C	0.8893	0.9389	0.8790	0.7614	0.7635
			MP2/cc-pVDZ		
energy[c]	653	0	704	650	769
ZPEC energy[c]	564	0	661	584	666
τ_1	105.4	90.0	109.9	89.4	88.2
τ_2	69.3	60.5	67.4	170.7	180.0
τ_3	191.4	298.4	66.5	63.3	180.0
$r_{O_9-C_1}$	2.988	2.952	3.0800	3.781	3.725
$r_{H_{19}-C_1}$	3.768	2.552	3.455	4.013	4.422
A	3.4842	3.3047	3.5099	4.3318	4.3679
B	1.0723	1.11022	1.0569	0.8487	0.8514
C	0.8919	0.9520	0.8757	0.7594	0.7619
			PW91/cc-pVDZ		
energy[c]	676	0	545	583	823
ZPEC energy[c]	558	0	509	531	691
τ_1	114.2	95.2	134.5	89.4	88.9
τ_2	71.9	61.0	69.9	176.0	180.0
τ_3	165.4	297.8	59.5	63.0	180.0
$r_{O_9-C_1}$	3.059	2.998	3.181	3.800	3.741
$r_{H_{19}-C_1}$	3.823	2.617	3.478	4.041	4.455
A	3.5805	3.3399	3.7134	4.3739	4.4124
B	1.0501	1.0910	1.0239	0.8406	0.8438
C	0.8644	0.9314	0.8319	0.7522	0.7552

[a] Energies in $\mathrm{cm^{-1}}$, angles in deg, distances in Å, and rotational constants in GHz. [b] τ_1 represents the $C_8C_7C_1C_2$ dihedral angle, τ_2 the $O_9C_8C_7C_1$ angle, and τ_3 the $H_{19}O_9C_8C_7$ angle. Atom labels are defined on Figure 1. [c] Total energies of conformer **II** are −383.658 396 (−383.485 619), −384.913 310 (−384.750 454), and −385.952 289 (−385.794 647) hartree at the HF, MP2, and PW91 level, respectively. ZPEC energies are given in parentheses.

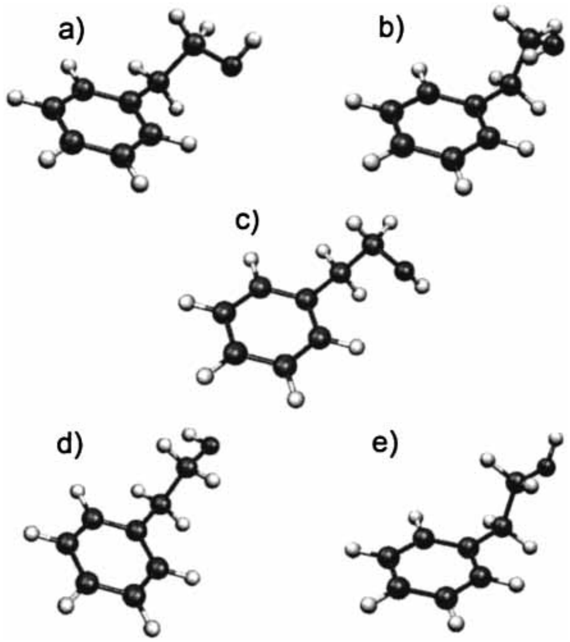

Figure 2. Stable conformers of the S_0 state of 2PE illustrating (a) conformer **I**, (b) conformer **II**, (c) conformer **III**, (d) conformer **IV**, and (e) conformer **V**.

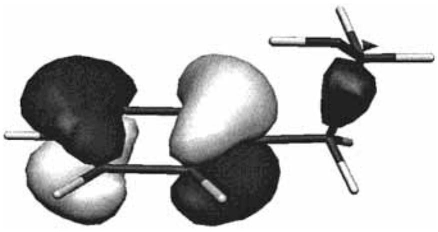

Figure 3. HOMO of conformer **II** of 2PE illustrating the OH$-\pi$ hydrogen bond. Orbital cutoffs are set at 5%.

to the MP2/cc-pVDZ benchmark, than previous B3LYP/6-31+G* calculations.[8] Nonetheless, it is necessary to view the relative energies of the ab initio and DFT neutral conformers with some caution because of the presence of conformationally differential basis set superposition error (BSSE). This could be of comparable magnitude to that in intermolecular complexes (up to 600 cm^{-1} for similar sized basis sets),[29-31] although cc-pVDZ tends to exhibit rather low BSSE compared to similar sized basis sets.[32] In fact, MP2/cc-pVDZ calculations generally predict good binding energies because BSSE cancels against the methodological underestimates of the binding energy, and the energies predicted here are indeed in line with experiment.[8,21]

Table 1 illustrates that the geometric parameters for the neutral conformers of 2PE obtained from the ab initio and DFT calculations are broadly similar. Comparing the ab initio results for gauche conformer **II**, we note that the $r_{H_{19}-C_1}$ distance is shorter in the MP2 calculation because of the inclusion of correlation energy. The PW91 prediction of $r_{H_{19}-C_1}$ is closer to the MP2 result, indicating that the functional describes the intersite electron correlation reasonably well. To a first approximation, the primary structural difference between the gauche and anti conformers is the orientation of the τ_3 dihedral angle, whereas conformers **II** and **IV** and conformers **I** and **V** differ in the orientation of τ_2. Figure 4 displays a schematic potential energy surface of 2PE, illustrating that the barriers for gauche$-$anti interconversion are substantial, while barrier heights between the various gauche and anti conformers are more modest. The small barrier height (~4 cm^{-1}) for conversion of conformer **I** into conformer **II** is notable.

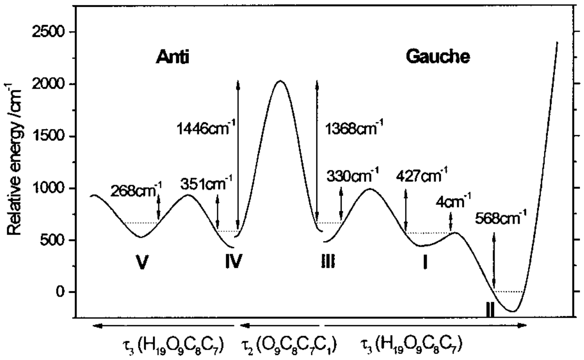

Figure 4. Schematic potential energy surface illustrating the S_0 state of 2PE with relative energies and barrier heights calculated at the MP2/cc-pVDZ level of theory.[47]

B. Energies and Geometric Structures of the Cationic Conformers of 2PE. i. HF/cc-pVDZ. Three stable cationic conformers of 2PE were identified at the HF/cc-pVDZ level of theory, with structures analogous to neutral conformers **II**, **IV**, and **V**. Table 2 presents the calculated relative energies for these conformers, illustrating that gauche conformer **II** is the most stable cationic conformer, with a significantly lower total energy than those of conformers **IV** and **V**. This result is somewhat surprising because the OH π interaction should become repulsive upon ionization.[7,33,34] BSSE effects may again be present for the cations and adversely stabilize the folded gauche conformations. We are unaware of any estimates of BSSE for similar cationic molecules, although in HF calculations of cationic intermolecular complexes it is on the order of 100$-$400 cm^{-1} for similar sized basis sets.[35] Expectation values of the S^2 operator were reasonable, with doublet values of 0.7602, 0.7642, and 0.7595, respectively, indicating that the calculated structures are essentially uncontaminated.

Geometric parameters for the HF/cc-pVDZ D_0 conformers are also presented in Table 2 facilitating a comparison of ionization-induced structural changes. For conformer **II**, the τ_2 dihedral angle is predicted to decrease by approximately 20°, as the CO bond rotates toward the ring, while the τ_3 angle increases, twisting the OH group toward the chromophore. The geometry changes for conformers **IV** and **V** are more modest with the OH group moving away from the aromatic ring in both cations.

ii. MP2/cc-pVDZ. The inclusion of electron correlation significantly alters the cationic potential energy surface obtained from the HF calculations. Anti conformer **V** is now predicted to represent the transition-state structure for interconversion of the cation **IV** enantiomers with a negative frequency of 350 cm^{-1} associated with the OH group rock. Gauche conformer **II** and anti conformer **IV** are again predicted to represent stable conformations, although the relative energies are notably different with the inclusion of correlation energy. Expectation values of the S^2 operator for **II**, **IV**, and **V** were 0.7638, 0.8598, and 0.7838, respectively.

The ionization-induced structural changes predicted by the MP2 calculations for conformers **II** and **IV** are similar to the HF results. For conformer **II**, the OH group again moves closer to the aromatic ring in the cation, while it moves away from the aromatic ring upon ionization of isomer **IV**. Figure 5 illustrates the ionization-induced structural changes. A potential energy surface for the S_0 and D_0 states of the anti conformers of 2PE is displayed in Figure 6, illustrating that the cationic

TABLE 2: Relative Energies, ZPE-Corrected (ZPEC) Energies, and Geometric Parameters for the D_0 Conformers of 2PE Calculated at the HF/cc-pVDZ, MP2/cc-pVDZ, and PW91/cc-pVDZ Levels[a,b]

	II	III	IV	V
		HF/cc-pVDZ		
energy[c]	0		2031	2152
ZPEC energy[c]	0		1919	1887
τ_1	81.8		89.9	89.4
τ_2	44.1		177.7	180.0
τ_3	332.8		82.6	180.0
$r_{O_9-C_1}$	2.774		3.743	3.801
$r_{H_{19}-C_1}$	2.189		4.177	4.545
A	3.2760		4.4039	4.3981
B	1.1448		0.8663	0.8533
C	1.0292		0.7745	0.7663
		MP2/cc-pVDZ		
energy[c]	7102		0	
ZPEC energy[c]	5204		0	
τ_1	92.0		93.6	
τ_2	35.3		171.0	
τ_3	340.8		77.6	
$r_{O_9-C_1}$	2.686		3.735	
$r_{H_{19}-C_1}$	1.997		4.093	
A	3.2297		4.1833	
B	1.1884		0.8646	
C	1.0432		0.7664	
		PW91/cc-pVDZ		
energy[c]	280	0	169	
ZPEC energy[c]	259	0	245	
τ_1	96.5	99.7	90.4	
τ_2	74.6	70.0	172.1	
τ_3	256.3	85.7	83.8	
$r_{O_9-C_1}$	3.144	3.108	3.744	
$r_{H_{19}-C_1}$	3.270	3.721	4.158	
A	3.4194	3.4297	4.2640	
B	1.0291	1.0368	0.8496	
C	0.8766	0.8758	0.7549	

[a] Energies in cm^{-1}, angles in deg, distances in Å, and rotational constants in GHz. [b] τ_1 represents the $C_8C_7C_1C_2$ dihedral angle, τ_2 the $O_9C_8C_7C_1$ angle, and τ_3 the $H_{19}O_9C_8C_7$ angle. Atom labels are defined on Figure 1. [c] Total energy of conformer **II** is −383.333 144 (−383.163 542) hartree at the HF level, the total energy of conformer **IV** is −384.578 940 (−384.412 629) hartree at the MP2 level, and the total energy of conformer **III** is −385.628 340 (−385.471193) hartree at the PW91 level. ZPEC energies are given in parentheses.

conformer **IV** should be accessible in a vertical transition from the S_0 state and should therefore be amenable to study using photoelectron spectroscopy.[8,36,37]

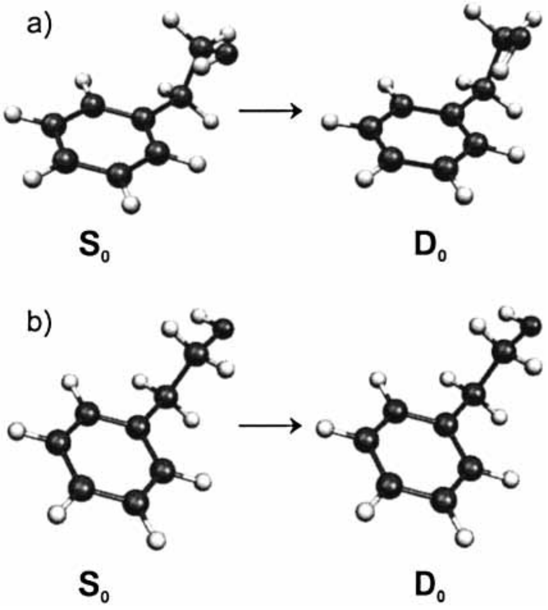

Figure 5. Structures of the stable cationic conformers of 2PE obtained at the MP2/cc-pVDZ level of theory displayed with the corresponding S_0 state structures to illustrate ionization-induced conformational changes for (a) conformer **II** and (b) conformer **IV**.

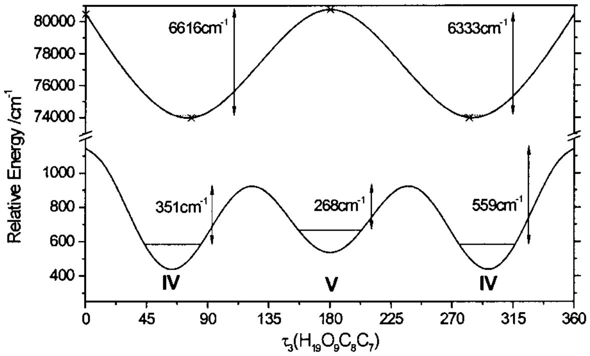

Figure 6. S_0 and D_0 state potential energy surfaces of the anti conformers of 2PE calculated at the MP2/cc-pVDZ level of theory. The D_0 state surface represents a spline fit to stationary points, while the S_0 surface is a spline fit of a partially relaxed potential energy surface with points calculated every 10°.[48]

The difference in the relative energies of conformers **II** and **IV** at the HF and MP2 levels merits further comment. Although BSSE contributions can differ in HF and MP2 calculations,[35] it is highly unlikely that this is the origin of the discrepancy. The energy ordering obtained from the MP2 calculations is in line with the intuitive expectation that conformer **II** should exist at a significantly higher energy because of the repulsive interaction between the OH group and the aromatic ring, which is on the order of 3500 cm^{-1}.[34] However, the MP2 energy difference between conformers **II** and **IV** is somewhat larger than this value, and it seems improbable that a stable cationic local minimum would occur ~7000 cm^{-1} above the absolute minimum. Note that this situation would imply that the barrier for cationic conformational change is approximately five times the barrier height on the neutral surface. It is therefore possible that the conformer **II** energy is a computational artifact.[38] An analysis of the charge redistribution in the $2PE^+$ conformers (section 3.I.B.vi) reveals that significant excess charge moves from the aromatic ring to the side chain in conformer **II**, indicating that the orbitals of the oxygen atom are interacting strongly with the aromatic π orbitals. In such a case, conformer **II** may not be well described by a single-determinant technique, and the structure obtained may include contributions from a cationic excited state. While fully optimized coupled-cluster calculations will establish the reliability of the MP2 results, such calculations are currently not possible for a molecule as large as $2PE^+$. Nonetheless, from comparison of the HF and MP2 results for $2PE^+$, it is clear that electron correlation plays an extremely important role in determining the stability of conformer **II** and that HF calculations are therefore not sufficient for treating this system.

iii. PW91/cc-pVDZ. While PW91 calculations agreed well with the MP2 calculations for the neutral conformers of 2PE, the results for the cationic potential energy surface are notably different. Conformer **IV** was again identified as a stable minimum energy structure, along with an additional structure analogous to conformer **III**. A third stable conformer was identified with a geometric structure that corresponds broadly to neutral conformer **II** but with the hydroxyl hydrogen atom further removed from the aromatic ring than in the MP2 cation. Expectation values of the S^2 operator were 0.7534, 0.7534, and

TABLE 3: Harmonic Vibrational Frequencies (in cm^{-1}) of the Fifteen Lowest Frequency Modes and the OH Stretching Frequencies of Conformers II and IV of 2PE in the D_0 State Calculated at the MP2/cc-pVDZ Level of Theory

	conformer **II**		conformer **IV**	
no.	freq	assignment	freq	assignment
1	77	C_1−C_7 torsion	53	C_1−C_7 torsion
2	112	C_1−C_7 bend	88	C_1−C_7 bend
3	151	C_7−C_8 torsion	103	C_7−C_8 torsion
4	283	OH bend + ring bend	230	ring bend
5	340	side-chain twist	335	OH torsion
6	398	ring mode (16a)	346	ring mode (16a)
7	412	OH bend + CH_2 rock + ring mode (16b)	350	OH bend + CH_2 rock
8	494	ring mode (16b)	366	OH torsion (+ side-chain bend)
9	535	antisym. CH_2 rock + OH bend	385	ring mode (16b)
10	597	ring + OH torsion	544	ring bending mode
11	616	ring mode (6b)	611	sym. out-of-plane aromatic C−H bend
12	672	OH torsion + ring mode (4)	642	ring mode (6b)
13	711	sym. CH_2 rock + OH torsion	771	out-of-plane aromatic C−H bend
14	760	sym. out-of-plane aromatic C−H bend	800	antisym. side-chain CH_2 bend
15	776	ring mode (11)	814	ring + antisym. side-chain CH_2 bend
ν_{OH}	2772	OH stretch	3843	OH stretch
ν_{OH}	3816[a]	OH stretch	3844[a]	OH stretch

[a] The OH stretching frequencies of the S_0 states are displayed for comparison with IR−UV dip measurements.[20]

0.7535 for conformers **II**, **III**, and **IV**, respectively. The fact that PW91 predicts a greater number of stable minima than the MP2 calculations leads us to view the DFT results with some caution. Conformer **III** may appear as an artificially stable minimum because PW91 overestimates the long-range potential and electrostatic contributions.[14,15] The PW91 calculations predict that conformer **III** is the lowest energy conformer, followed by **IV** and then **II**, with all three conformers displaying similar total energies. This result is surprising because conformer **II** contains a repulsive interaction between the OH hydrogen atom and the aromatic π cloud.[33,34]

The DFT prediction of a greater number of stable cationic isomers than at the MP2 level is in line with previous studies of weakly bound cationic systems, such as Ar·NO$^+$ and CO·NO$^+$,[39,40] where DFT was revealed to be susceptible to overestimating the binding energy. For 2PE$^+$, this appears to result in cationic conformer **III** appearing stable in the PW91 calculations. These results are not specific to the PW91 functional, because B3LYP/6-31+G* calculations of 2PE$^+$ predicted the existence of four stable cationic conformers of 2PE$^+$.[8]

iv. HF, MP2, and PW91 Calculations with the 6-31G* Basis Set. To investigate the effect of changing the basis set, fully optimized calculations were performed on the S_0 and D_0 conformers of 2PE using 6-31G*. For the neutral system, the results obtained were very similar to those obtained using cc-pVDZ. At the HF level, the D_0 state results again agreed well with the cc-pVDZ results, that is, conformers **II**, **IV**, and **V** were identified as stable minima, with conformer **II** representing the lowest energy structure. However, MP2/6-31G* calculations of the cationic potential energy surface failed to locate a transition-state structure analogous to neutral conformer **V**. The S^2 expectation value was above 1.25 during this failed MP2/6-31G* optimization, considerably higher than during the MP2/cc-pVDZ optimization. This leads us to caution against the use of the 6-31G* basis set for cationic calculations in which spin contamination may be a problem. When the relative energies of the 6-31G* cationic conformers are compared, conformer **II** again represents the lower energy structure at the UHF/6-31G* level, with conformer **IV** appearing 2131 cm^{-1} (1991 cm^{-1} ZPEC) higher in energy. At the UMP2/6-31G* level, the relative energies again reverse with conformer **II** appearing 8370 cm^{-1} (6680 cm^{-1} ZPEC) higher in energy than conformer **IV**.

TABLE 4: Percent Charge Delocalization into the CH_2OH Side Chain and OH End Group of 2PE Calculated Using NPA Atomic Partial Charges

	conformer **II**		conformer **IV**	
	CH_2OH	OH	CH_2OH	OH
MP2/6-31G*	78.0	61.9	8.1	4.6
MP2/cc-pVDZ	78.6	58.2	8.0	4.4
PW91/6-31G*	29.4	18.1	30.2	20.6
PW91/cc-pVDZ	29.3	17.7	30.4	20.6
B3LYP/6-31+G*[a]	17.0		24.0	

[a] Calculated Mulliken charges from ref 8.

v. Harmonic Vibrational Frequencies of the Cationic Conformers of 2PE. Table 3 displays the harmonic vibrational frequencies obtained from the MP2/cc-pVDZ calculations of the D_0 state conformers to facilitate comparison with the threshold photoelectron spectrum of 2PE.[8] For conformer **IV**, vibrational modes displaying frequencies of 115 and 340 cm^{-1} were reported and appear to correspond to excitation of the C_7−C_8 torsion (103 cm^{-1}) and OH torsion (366 cm^{-1}). Excitation of these modes is in line with the $D_0 \leftarrow S_0$ geometric changes predicted by the ab initio calculations. The OH stretching frequencies of the S_0 and D_0 conformers of 2PE are also included in Table 3 for comparison with the S_0 state experimental values of 3626 and 3678 cm^{-1} for conformers **II** and **IV**, respectively.[20]

vi. Charge Delocalization in the Cationic Conformers of 2PE. Atomic partial charge distributions of the S_0 and D_0 conformers of 2PE calculated using a natural population analysis[28] are presented in Table 4. For conformer **IV**, the MP2 calculations predict that little charge delocalization occurs to the side chain and end group upon ionization, whereas in conformer **II**, substantial charge delocalization occurs. As noted above, the charge delocalization in conformer **II** indicates that the oxygen atom orbitals are interacting strongly with the aromatic π orbitals in this conformer. The substantial charge delocalization is responsible for the conformer **II** cation existing as a stable minima, because the excess charge moves from the chromophore to the OH group and allows the aromatic ring to solvate the electropositive hydroxyl hydrogen atom.[41] These results explain the different relative energies obtained for conformers **II** and **IV** at the HF and MP2 levels (section 3.I.B.ii), because intramolecular electron correlation should be crucial in charge delocalization and significantly alters the electronic structure of conformer **II**.

Percent charge delocalizations calculated with the PW91 functional are also presented in Table 4. DFT-calculated partial charges have been demonstrated to be unreliable for calculating charge delocalization in this type of system,[28] and the values presented for PW91 again deviate significantly from the MP2 results. Percent charge delocalizations obtained from a B3LYP calculation[8] are also displayed for comparison. Density functional theory does not deal well with localized variations in charge,[12] and its poor performance in calculating charge delocalization is therefore unsurprising.

vii. Further Comparison with Experiment. The $2PE^+$ system has been investigated experimentally with threshold photoelectron spectroscopy.[8,42] Anti conformer **IV** displayed a vibrationally resolved photoelectron spectrum,[8,42] indicative of a conformer in which only modest structural changes occur between the neutral species and the cation. Gauche conformer **II**,[8] by comparison, displayed a broad unresolved spectrum with a weak ionization onset, indicative of a substantial neutral-to-cation structural change. Two ionization energies have been reported for conformer **IV**, 8.49 eV[42] and 8.865 ± 0.002 eV,[8] while for conformer **II**, an upper limit on the adiabatic ionization energy is available, 8.870 ± 0.005 eV.[8] Spectra of conformers **I**, **III**, and **V** have not been obtained.

Threshold photoelectron spectroscopy therefore provides evidence for the existence of a single, stable cationic conformation, conformer **IV**. The three sets of calculations presented above all agree in predicting that neutral conformer **IV** has a corresponding cationic conformer that should be accessible in a vertical transition from the ground state. They also agree in predicting the existence of a stable cationic conformer **II**, with a geometry that differs significantly from the optimized neutral structure. All of the calculations therefore predict that photoexcitation of conformer **II** would be unlikely to result in a vibrationally resolved threshold photoelectron spectrum,[7] in line with experiment.[8]

Although the relative energies (and hence the calculated ionization energies) of conformers **II** and **IV** are different in the HF/MP2/PW91 calculations, the performance of the methods cannot be assessed on this basis because of ambiguities in the published experimental ionization energies for conformer **IV**.[8,42] Taking the ionization energy reported in ref 42 leads to relative energies that are most consistent with the MP2 results, while the ref 8 ionization energy is more consistent with the PW91 results. Further experiments would be useful to clarify this issue. Photoelectron spectroscopy is, in fact, of limited use in studies of such systems because detailed experimental data is only obtained when the neutral structure closely resembles the cationic structure accessed in photoexcitation. IR spectroscopy of cations generated in an electron impact ionization source is an excellent complementary experimental technique,[37,43] which can unambiguously identify the relative stabilities and geometric structures of numerous cationic isomers.[44] Such an experiment would be highly useful in this case to firmly establish the number and relative energies of the stable conformers of $2PE^+$.

TABLE 5: Relative Energies, ZPE-Corrected (ZPEC) Relative Energies, and Geometric Parameters of Two S_0 and D_0 Conformers of BB Calculated at the HF/6-31G*, MP2/6-31G*, and PW91/6-31G* Levels of Theory[a,b,c]

	S_0		D_0	
	I	**V**	**I**	**V**
	HF/6-31G*			
energy[d]	227	0	324.0	0.0
ZPEC energy[d]	275	0	333.0	0.0
$\langle S^2 \rangle$			0.9172	0.9218
τ_1	74.5	89.3	73.5	88.9
τ_2	65.9	180.0	65.3	180.0
τ_3	178.6	180.0	175.4	180.0
$r_{H_{21}-C_1}$	2.856	4.188	2.848	4.130
A	2.6055	3.7091	2.5166	3.4963
B	0.6893	0.5555	0.7016	0.5694
C	0.6663	0.5267	0.6778	0.5377
	MP2/6-31G*			
energy[d]	0	121	0.0	295.1
ZPEC energy[d]	0	73		
$\langle S^2 \rangle$			0.8650	0.8848
τ_1	75.3	88.3	74.6	87.9
τ_2	62.3	180.0	63.3	180.0
τ_3	179.0	180.0	175.3	180.0
$r_{H_{21}-C_1}$	2.728	4.172	2.765	4.129
A	2.4834	3.5813	2.4632	3.4600
B	0.7202	0.5613	0.7231	0.5758
C	0.6921	0.5328	0.6970	0.5438
	PW91/6-31G*			
energy[d]	99	0	591.6	0.0
ZPEC energy[d]	137	0	487.8	0.0
$\langle S^2 \rangle$			0.7546	0.7546
τ_1	76.6	88.9	71.8	89.2
τ_2	65.4	180.0	69.7	180.0
τ_3	179.7	180.0	174.2	180.0
$r_{H_{21}-C_1}$	2.819	4.201	2.898	4.109
A	2.5180	3.6109	2.5755	3.4400
B	0.6944	0.5506	0.6800	0.5728
C	0.6657	0.5218	0.6546	0.5412

[a] Energies in cm^{-1}, angles in deg, distances in Å, and rotational constants in GHz. [b] τ_1 represents the $C_8C_7C_1C_2$ dihedral angle, τ_2 the $C_9C_8C_7C_1$ angle, and τ_3 the $C_{10}C_9C_8C_7$ angle. Atom labels are defined in Figure 1. [c] ZPE-corrected relative energies have been omitted for the D_0 MP2 calculations because of the presence of an imaginary frequency in the conformer **V** calculations. See text for discussion. [d] Total energy of S_0 conformer **V** is −386.873 881 (−386.647 371) hartree at the HF level, the total energy of S_0 conformer **I** is −388.236 153 (−388.021 272) hartree at the MP2 level, and the total energy of S_0 conformer **V** is −389.321 243 (−389.111 726) hartree at the PW91 level. Total energy of D_0 conformer **V** is −386.607 819 (−386.383 303) hartree at the HF level, the total energy of D_0 conformer **I** is −387.909 144 hartree at the MP2 level, and the total energy of D_0 conformer **V** is −389.023 601 (−388.816 111) hartree at the PW91 level. ZPEC energies are given in parentheses.

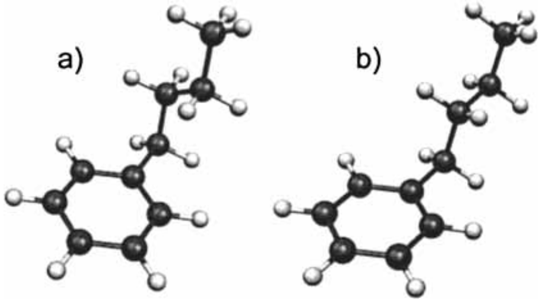

Figure 7. Geometric structures of the S_0 states of conformers (a) **I** and (b) **V** of BB obtained at the MP2/6-31G* level of theory.

II. *n*-Butylbenzene. *A. Energies and Geometric Structures of the Neutral Conformers of BB.* Only two conformers of BB were studied for simplicity corresponding to the dominant isomers in multiphoton ionization experiments.[22,45] Table 5 presents the relative energies and ZPE-corrected values, while Figure 7 displays the structures of conformers **I** and **V**, illustrating that the former corresponds to a gauche, C_1 symmetry structure, while the later represents an extended anti conformer with C_s symmetry. The MP2 calculations predict that conformer **V** is less stable than gauche conformer **I**, in which dispersion interactions are more important, whereas the ordering reverses

TABLE 6: Harmonic Vibrational Frequencies (in cm^{-1}) of the Fifteen Lowest Frequency Modes of Conformers I and V of BB in the D_0 State Calculated at the HF/cc-pVDZ Level of Theory

	conformer **I**		conformer **V**		
no.	freq	assignment	freq	sym[a]	assignment
1	39	C_1-C_7 torsion (τ_a)	39	a″	C_1-C_7 torsion
2	62	C_1-C_7 bend	73	a′	C_1-C_7 bend (β)
3	85	C_8 centered bend	75	a″	C_7-C_8 torsion
4	151	side-chain bend	128	a″	side-chain twist
5	220	side-chain bend (β)	192	a′	ring mode (10b)
6	262	C_9-C_{10} torsion (τ_b)	259	a″	C_9-C_{10} torsion
7	273	side-chain bend	273	a′	side-chain stretch (σ)
8	382	ring mode (16a)	378	a″	ring mode (16a) + CH_2 rock (C_7)
9	392	CH_2 rock (C_7)	386	a″	ring mode (16a) + CH_2 rock (C_7)
10	430	ring mode (16b)	398	a′	ring mode (16b) + side-chain stretch
11	461	ring stretching mode	472	a″	ring stretching mode
12	499	side-chain stretch + ring	484	a′	ring bending mode + side-chain bend
13	551	ring mode (6a)	587	a′	aromatic out-of-plane C−H bend
14	694	aromatic out-of-plane C−H bend	693	a′	aromatic out-of-plane C−H bend
15	785	side-chain CH_2 rock	792	a″	side-chain CH_2 rock

[a] Symmetries are only displayed for the C_s symmetry conformer **V**.

in the HF calculations. The PW91/6-31G* calculations also predict that conformer **V** is the lower energy isomer, although the two conformers lie closer in energy than in the HF calculations. However, it is important to note that the relative energy differences are small at all levels and possibly within the BSSE error limits.[29]

The geometric structures of the S_0 conformers studied were similar in the ab initio and DFT calculations, with dihedral angles generally differing by only 1°. The subtle effects of dispersion interactions in determining the conformations of BB are evident, however, in the $H_{21}-C_1$ intramolecular distances. For conformer **I**, H_{21} is closer to the aromatic ring in the MP2 calculation compared with the HF result because of the favorable dispersion interaction with the π electrons, with the PW91 result lying between the HF and MP2 results. In the anti conformer **V**, dispersion interactions of the side chain with the aromatic ring are less important and there is little variation in the $H_{21}-C_1$ distance.

B. Energies and Geometric Structures of the Cationic Conformers of BB. Table 5 presents relative energies and ZPE-corrected values for the cationic isomers of BB. Two stable isomers, with structures similar to the corresponding neutral isomers, were obtained in both the HF and PW91 calculations. It is notable that PW91 performs better for the cationic BB conformers than the 2PE analogues.

In the MP2 calculations, a stable cation corresponding to conformer **I** was obtained, but a negative frequency was obtained for the conformer **V** cation. The frequency of this mode was substantial (-628.4 cm^{-1}) and corresponded to a ring distortion, making it highly unlikely that this structure represents a true transition state. Furthermore, it was possible to obtain a ZEKE photoelectron spectrum of this conformer,[45] indicating that a stable cationic structure must exist with a geometry close to the neutral structure. Spin contamination (Table 5) was high in this calculation and may have produced an unreliable result. In $2PE^+$, spin contamination problems were overcome by using the cc-pVDZ basis set instead of 6-31G*. Although this was not possible for BB because of computational limitations, it would be useful to explore this issue further in subsequent work with improved resources.

*C. Harmonic Vibrational Frequencies of the Cationic Conformers **I** and **V** of BB.* Table 6 displays the harmonic vibrational frequencies obtained from the HF/cc-pVDZ calculations for the D_0 state of conformers **I** and **V** for comparison with the ZEKE photoelectron spectra of these isomers.[45] For conformer **I**, vibrational modes displaying frequencies of 38, 203, 247, and 512 cm^{-1} were observed, which appear to correspond to excitation of τ_a (39 cm^{-1}), β (220 cm^{-1}), τ_b (262 cm^{-1}), and the 6a ring mode (551 cm^{-1}). For conformer **V**, vibrational modes displaying frequencies of 71, 179, and 257 cm^{-1} were observed corresponding to excitation of β (73 cm^{-1}), the 10b ring mode (192 cm^{-1}), and σ (273 cm^{-1}). Excitation of these modes is in line with $D_0 \leftarrow S_0$ calculated geometric changes.

TABLE 7: Percent Charge Delocalization into the $CH_2CH_2CH_3$ Side Chain and CH_3 End Group of BB Calculated Using NPA Atomic Partial Charges

	conformer **I**		conformer **V**	
	$CH_2CH_2CH_3$	CH_3	$CH_2CH_2CH_3$	CH_3
MP2/6-31G*	7.4	3.7	8.4	3.2
PW91/6-31G*	19.6	7.9	22.2	8.4

*D. Charge Delocalization in the Cationic Conformers **I** and **V** of BB.* Atomic partial charge distributions of the S_0 and D_0 states of conformers **I** and **V** of BB were obtained from MP2/6-31G* NPA calculations. Table 7 illustrates that there is little charge delocalization in either conformer, consistent with the high ionization energy of the alkyl side chain. PW91/6-31G* results are also included in Table 7 to further illustrate the unreliability of DFT-calculated partial charges for these systems.[28]

4. Conclusions

For the neutral conformers of 2PE and BB, the variations in the HF and MP2 results follow well-documented patterns. The PW91 exchange and correlation density functional describes intersite electron correlation reasonably well and provides conformeric energies and geometries close to the MP2 results. We note that the PW91 calculations presented here represent a considerable improvement on previously published B3LYP results,[8] which neglect intersite electron correlation.[14,15] The PW91 functional should therefore prove to be highly useful for future computational studies of neutral aromatic molecules with flexible side chains because it gives results comparable to MP2 at a considerably reduced computational cost.

The MP2 calculations of $2PE^+$ differ significantly from HF calculations of this system. Three cationic conformers were identified as stable minima at the HF level, with conformer **II** representing the lowest energy conformer. In contrast, only two minima are identified at the MP2 level, with conformer **II** occurring at a substantially higher energy than conformer **IV**.

While this qualitative isomer ordering is entirely in line with expectation,[33,34] the very high total energy of conformer **II** suggests that this conformer may be a computational artifact,[38] possibly due to the system not being accurately described by a single-determinant method. Fully optimized coupled-cluster calculations and further experiments will be necessary to settle this point. The overall pattern of fewer stable isomers occurring at the MP2 level compared to HF mirrors results for the related 3-phenylpropionic acid cation,[38] in which only two stable MP2 conformers were identified compared to five HF conformers.

PW91 calculations of the $2PE^+$ conformers produced a number of discrepancies compared to the MP2 benchmark. The functional predicted the existence of a conformer (**III**) that was unstable at the MP2 level, and the total energies of the stable PW91 conformers were predicted to be similar, a surprising result given that conformer **II** includes a repulsive electrostatic interaction between the OH hydrogen atom and the aromatic π cloud. The PW91 results for $2PE^+$ follow a trend observed in B3LYP calculations of $2PE^+$, in which four stable cationic conformers were identified. It therefore appears that these functionals do not give a reliable representation of the potential energy surface of $2PE^+$. Similar problems are likely to occur for PW91 and B3LYP calculations of the potential energy surfaces of larger positively charged molecules (e.g., peptide cations[46]), and caution should generally be exercised in applying density functional theory to cationic aromatic systems with strongly interacting side chains.

The discrepancies observed in the PW91 calculations of $2PE^+$ indicate that accurate intersite electron correlation is crucial in obtaining a proper representation of the potential energy surface. A variety of soft intramolecular interactions between the side chain and the aromatic ring (e.g., dispersion and distributed ion-induced dipole) combine to determine the conformeric structures of $2PE^+$. These interactions will clearly be strongly influenced by the extent of charge delocalization from the chromophore to the side chain. The origin of the discrepancies between the MP2 and DFT results therefore appears to lie in a combination of factors, including charge delocalization and the overestimation of long-range and electrostatic contributions. It should be noted that PW91 (and B3LYP)[8] does a reasonable job of calculating the structure of the anti conformer **IV** of $2PE^+$, in which the conformeric structure is dominated by a strong ion−dipole interaction.[8]

Overall, the results illustrate the importance of routinely testing ionic systems when density functionals are evaluated.[14−16] The future development of reliable functionals for treating cationic systems is, nonetheless, highly desirable given the substantially lower computational demands of DFT calculations compared to the open-shell MP2 harmonic frequency analyses presented here.

The comparative studies of BB^+, the system with the weakly interacting side chain, illustrated that comparable geometric structures could be obtained using HF, MP2, and PW91. Either HF or PW91 calculations are therefore likely to be sufficient for analyzing the spectra of similar cations.[4,6] It is of note that both gauche conformer **I** and anti conformer **V** of BB have corresponding cationic conformers that display only minor geometry changes compared to the neutral, and it is highly probable that this result would also apply to conformers **II**−**IV** of BB. For 2PE, although there are five neutral minima, there are only two stable cations at the MP2/cc-pVDZ level. Cationic conformational preference is therefore more pronounced for the system with the more strongly interacting side chain, reflecting previous MP2 results for benzyl and salicyl alcohol in which only a single cationic conformation was located for either system.[7]

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