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Dipole-Bound Anions of β-Alanine: Canonical and Zwitterionic Conformers

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The remarkable stabilities of the dipole-bound anions of the canonical and zwitterionic conformers of β-alanine are predicted at the high level of theories, in which the former is the global minimum and the latter, the anti zwitterionic anion, is the local minimum. In contrast to the dipole-bound anions of glycine, the gauche zwitterionic anion of β-alanine is an unstable conformer. The vertical electron detachment energies for the canonical and anti zwitterionic anions are 58 and 1145 meV, respectively. The photodetachment electron spectrum of the canonical anion is theoretically simulated on the basis of the Franck−Condon factor calculations.

1. Introduction

Novel properties of anionic species attract great interest of both experimental and theoretical studies. In particular, an excess electron can be captured and supported for a considerably long time by the molecular strong electrostatic fields regarding dipole and quadrupole moments (noted as dipole- and quadrupole-bound anions, respectively).[1] As far as biological molecules, both valence-bound (the excess electron occupies at one empty molecular orbital of the neutral) and dipole-bound anions can be formed for the free nucleic acid bases;[2] the dipole-bound anions are found for glycine and arginine conformers,[1,3] while the instabilities of valence-bound anions of the isolated amino acids have been proved.[3g] Amino acids have a quantity of conformers in gas phase due to the intramolecular rotation freedoms. Recently, a stability rule for the neutral isolated amino acids was derived from the experimental data and computational results, namely, the bifurcated $NH_2\cdots O$ (carbonyl) hydrogen bonding (HB) conformers are the most stable and the N$\cdots$HO bonding conformers have comparative stabilities.[4] In contrast to the gas-phase conformers, the amino acids usually exist as zwitterions $NH_3^+{-}CHR{-}COO{-}$ in the condensed phase.[5] However, instabilities of the gas-phase zwitterionic conformers of the neutral amino acids have been demonstrated.[6] The N$\cdots$HO bonding canonical and zwitterionic conformers of the neutral amino acids clearly have the large dipole moments; therefore, they can support the dipole-bound anions. The dipole-bound anions based on the canonical and zwitterionic structures of glycine and arginine are found to be stable.[3a,b,e,f] The electron-solvated zwitterion (the dipole-bound anion) of glycine is a local minimum, and it is 3167 cm^{-1} energetically higher than the singly HB (N$\cdots$HO) canonical anion, which is the global minimum.[3a] The vertical electron detachment energy (VDE) of the canonical glycine anion is predicted to be 668 cm^{-1} (ca. 83 meV),[3a] which is appealingly close to the experimental value of 95 meV.[3b] The VDE of arginine anion is measured to be 256 ± 30 meV, which may arise from the photodetachment of the zwitterionic anion; the shoulder at 180 meV in the photodetachment electron spectrum (PES) can be explained by the photodetachment of the canonical anion.[3e] Moreover, the theoretical calculations indicate that the canonical and zwitterionic anions of arginine are energetically degenerate but have distinctly different VDE values.[3f]

In this work, a theoretical approach of the dipole-bound anions of β-alanine is reported, which is potentially a reference of experimental work in the future. Furthermore, although the conformations and the stability order of β-alanine are similar to those of glycine, the extremely strong intramolecular HB N$\cdots$HO in β-alanine significantly affects the electronic structure of the neutral.[4b] Whether or how this intramolecular interaction affects the stability of the canonical anion is a very interesting topic. On the other hand, it is well-known that there are two, gauche and anti, zwitterionic conformers of β-alanine. About 20 kcal/mol energy difference between the gauche and anti conformers in gas phase is remarkably reduced within solvent effects, and the anti conformer is slightly preferred in solution.[7] Although neither of these two neutral zwitterions is stable in the gas phase,[7] whether they can be stabilized by an excess electron is another topic of this study.

2. Theoretical Methods

As demonstrated by Gutowski and co-workers,[8] electron correlation and proper basis set are important to describe the diffusely bounded electron of the dipole-bound anions. The geometrical parameters of all possible conformers (**A**, **B**, **B**$^-$, **Bz**$^-$, **Cz**$^-$) shown in Figure 1a were fully optimized with the second-order Møller−Plesset (MP2) perturbation method,[9] and the stationary points both of neutral and anions were examined by the harmonic vibrational frequency calculations. The Dunning's correlation consistent double-ζ basis set, aug-cc-pVDZ, was supplemented with the additional even-tempered 5s and 5p symmetry functions centered on N atom. The extra 5s5p diffuse set was built from the lowest s and p exponents included in the aug-cc-pVDZ, and the geometric progression ratio was set to 3.2, according to the previous work.[3a,3f,8] The energetic extrapolation calculations were carried out at the coupled cluster level of theory with singlet, double, and noniterative triple excitations CCSD(T).[10] In calculations for the doublet anion, the value of $\langle S^2\rangle$ never exceeded 0.7501 for the SCF wave

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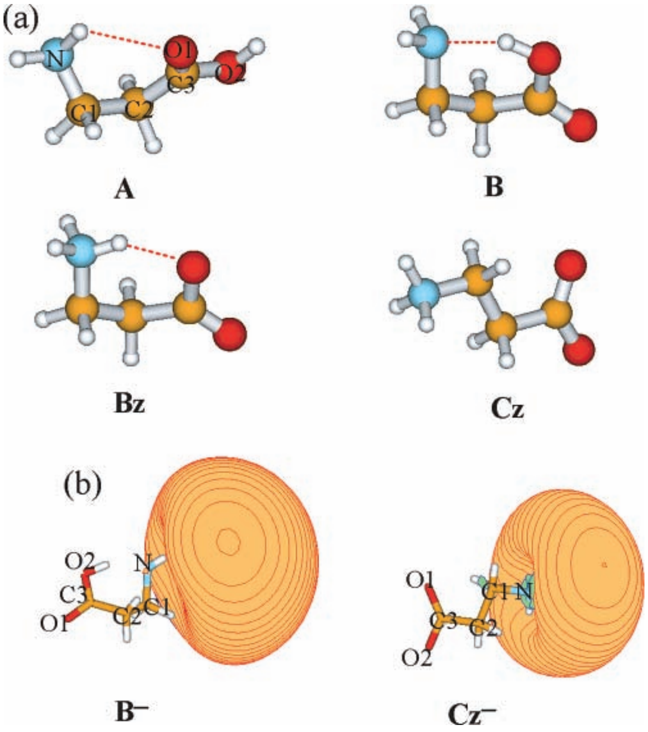

Figure 1. (a) Structures of the neutral β-alanine at the different stationary points on the MP2 potential energy surface. The artificial neutral state of **Bz** and **Cz** are shown with the geometries of the stable dipole-bound anions **B**$^-$ (the additional N−H bond length is 1.02 Å) and **Cz**$^-$, respectively. The broken lines represent the hydrogen bonds. (b) Singly occupied molecular orbital of the anionic β-alanine at the **B**$^-$ and **Cz**$^-$ stationary points.

TABLE 1: Energies (in meV) of the Neutral and Anionic Species with Respect to the Neutral A Conformer and the Dipole Moments of the Neutral β-Alanine (in D)

	MP2 + ZPVE[a]	CCSD(T)[b]	dipole moment[c]
A	0	0	1.42
B	25	20	6.57
B$^-$	−20	−36	6.63
Cz$^-$	959	1011	17.18

[a] With the zero-point vibrational energy correction. [b] Over the MP2 optimized geometries. [c] Over the respective (neutral or anionic) MP2 optimized geometries.

function. The reliability of the present theoretical methods was proven by reproducing the results of the dipole-bound canonical and zwitterionic anions of glycine,[3a] and the saturation of the basis set was examined by adding more diffuse functions. The above calculations were performed with the Gaussian 98 program.[11] Molecular orbital electron density maps were plotted using the MOLDEN program[12] with the contour values ±0.02 in arbitrary unit.

3. Results and Discussion

In Figure 1a, the neutral zwitterionic conformers **Bz** (gauche) and **Cz** (anti) are not at the minima of the electronic ground-state potential surface, in agreement with the previous conclusion.[6,7] Geometrical optimizations enforce the hydrogen atom binding with nitrogen atom in **Bz** or **Cz** to be rebounded with oxygen (O_2) atom (to form **B**) or to be depronated directly. The dipole-bound anions may be formed on the basis of the canonical structure of **B** and the zwitterionic structures of **Bz** and **Cz**, because their calculated dipole moments (6.57 D of **B** and 17.18 D of **Cz**) shown in Table 1 exceed the critical dipole of ca. 2.5 D required to bind an excess electron.[2,3] However, we failed in locating the stable dipole-bound anion **Bz**$^-$, and the geometrical optimization always moved downhill in energy to **B**$^-$. This is distinctly different from the zwitterionic anion of glycine, which is a local minimum on the potential energy surface.[3a] On the other hand, in our previous study of the β-alanine cations, the ionization for the highest occupied molecular orbital of **B** leads to the spontaneous hydrogen shift from O_2 to N atom, indicating the stability of the zwitterionic cation.[4b] A conclusion may be derived for **B** that the ionization can much more easily result in the intramolecular hydrogen shift than the slow-energy electron attachment. However, the anti zwitterionic anion **Cz**$^-$ (C_s symmetric) is found to be at the local minimum on the anionic potential energy surface.

Table 1 lists the energies of the neutral and anionic conformers with respect to the neutral **A**. Both the MP2 (including the zero-point vibrational energy (ZPVE) corrections) and energy extrapolated CCSD(T) calculations indicate that **B**$^-$ is the energetically lowest while **Cz**$^-$ is much higher in energy. **Cz**$^-$ and **Bz**$^-$ (the artificial anion **Bz**$^-$ is constructed with the dipole-bound anion **B**$^-$ structure) are predicted to be almost degenerate in energy at the MP2 level, which is similar to the relative stabilities between the neutral **Bz** and **Cz**.[7] **Cz**$^-$ is stable while **Bz**$^-$ is unstable. The dipole-bound anion **B**$^-$ should be at the global minimum of the electronic ground-state anionic potential surface. Thereby, the adiabatic electron affinity (EA_a) of **B** can be estimated to be 56 meV by the energy difference between **B** and **B**$^-$ at the CCSD(T) level. The diffuse character of the singly occupied molecular orbital (SOMO) describing the loosely bound electron is shown in Figure 1b. In Table 1, we find that the neutral dipole moment of the dipole-bound anionic structure of **B**$^-$ is slightly different from that of **B**, and this can be explained since the neutral equilibrium structure is relaxed after the excess electron attachment. This is an important factor that we may observe some weak vibrational structures in the PES of the dipole-bound anions.[3b,d,e] We will discuss this in the following text.

The MP2 energy profiles for the transitions between the neutral canonical **B** and zwitterionic **Bz**, and between the anionic **B**$^-$ and **Bz**$^-$ are shown in Figure 2a. The broad plateaus of the HB lengths 1.0−1.3 Å for N···HO are found for the neutral and anion. However, there are no stationary points in this range, indicating the instabilities of **Bz** and **Bz**$^-$. On the other hand, the formation of the stable zwitterionic anion **Cz**$^-$ is unlikely via the direct intramolecular hydrogen shift from the O_2H group to N atom. One possibility is to be produced through the intramolecular bond rotation, namely, the variance of the dihedral angle $D(C_3C_2C_1N)$. The MP2 energy profile in Figure 2b is obtained by scanning the relaxed potential energy surface of the dipole-bound anion from **B**$^-$ to **Cz**$^-$. Two main features should be addressed: there is a very low energy barrier for the transition from **Cz**$^-$ to **B**$^-$; the H atom can spontaneously shift from the O_2H group to N atom when the dihedral angle $D(C_3C_2C_1N)$ is about 77.5°. The latter is easily observed from the R(N···H) distance profile.

The VDE values of the stable **B**$^-$ and **Cz**$^-$ are calculated at the different levels of theory. In Table 2, one can find that the higher level consideration of electron correlation effect leads to the larger VDEs. The VDE (1145 meV) of **Cz**$^-$ is about two times larger than that (58 meV) of **B**$^-$, while the dipole moment (17.18 D) of **Cz** is three times larger than that (6.57 D) of **B**. Although the VDE values of the dipole-bound anions definitely increase with the increase of the dipole moments, they are also related to the chemical environments for the attached electron.[3f] The unexpected lower VDE[13] of **Cz**$^-$ is due to the excess

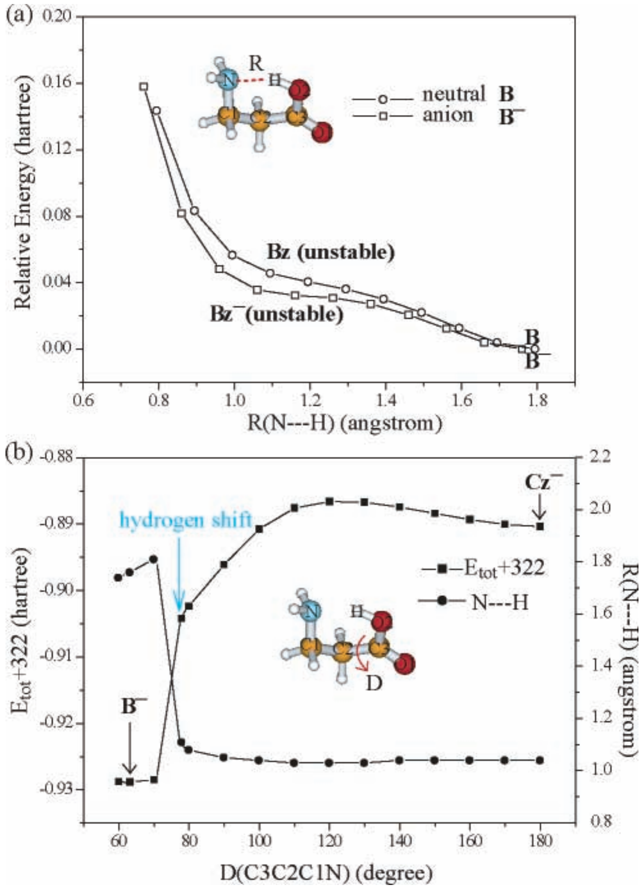

Figure 2. (a) MP2 energy profile for the neutral $\mathbf{B}^-$ and anion $\mathbf{B}^-$ for the hydrogen shift process. (b) The relaxed potential energy profile for the transition from $\mathbf{B}^-$ to $\mathbf{Cz}^-$ by varying the dihedral angle D(C3C2C1N) (■) and the corresponding N···H distances (●), predicted at the MP2 level. The details can be found in the text.

TABLE 2: Vertical Electron Detachment Energies (in meV)[a]

	MP2	MP3[b]	MP4(SDQ)[c]	CCSD(T)
$\mathbf{B}^-$	44	45	47	58
$\mathbf{Cz}^-$	1093	1102	1102	1145

[a] Over the MP2 optimized geometries. [b] The third-order perturbation method. [c] The forth-order perturbation using single, double, and quadruple substitution space.

TABLE 3: Geometrical Parameter Changes and Vibrational Frequency Shifts of $\mathbf{B}^-$ with Respect to B

	bond length ($\geq 10^{-3}$ Å)		angle ($\geq$0.02 deg)
O_2−H	+3.2	A(NC_1C_2)	−0.03
N···H	−1.9	A(C_3O_2N)	+0.21
		D(O_2HNC_1)	−0.02

mode	frequency shift (cm^{-1})	mode	frequency shift (cm^{-1})
υ_3($C_1C_2C_3$ bending)	+4.7	υ_{26}(C_3O_1stretching)	−7.7
υ_{11}(NH_2,O_2H wagging)	+5.6	υ_{31}(O_2H stretching)	−65.3
υ_{13}(O_2H wagging)[a]	+18.8	υ_{32}(NH_2 stretching)[c]	−7.5
υ_{14}(NH_2,CH_2 wagging)	+4.8	υ_{33}(NH_2 stretching)[d]	−9.5
υ_{23}(O_2H wagging)[b]	+8.6		

[a] Out-of-plane ($O_2C_3C_2$). [b] In-plane ($O_2C_3C_2$). [c] Symmetric. [d] Asymmetric.

TABLE 4: Theoretical Values of Franck−Condon Factors and Transition Energies (cm^{-1}) in the Photodetachment Electron Spectrum of the Canonical *β*-Alanine Anion ($\mathbf{B}^-$)[a]

transition	position	FC factor[b]
0_0^0	0	1.000
2_0^1	204	0.004
3_0^1	281	0.003
6_0^1	484	0.001
10_0^1	813	0.001
8_0^1	864	0.001
12_0^1	992	0.001
14_0^1	1021	0.002
16_0^1	1091	0.001
17_0^1	1241	0.001
19_0^1	1306	0.003
24_0^1	1485	0.001
25_0^1	1664	0.001
29_0^1	3131	0.003
30_0^1	3160	0.002
31_0^1	3254	0.003
32_0^1	3504	0.008

[a] Position of the 0−0 transition was set to 0 cm^{-1}. [b] In Figure 3, the transitions with the FC factors larger than 0.0001 are included. 2: $C_3C_2C_1N$ torsion; 3: $C_1C_2C_3$ bending; 14: NH_2,CH_2 wagging; 19: CH_2,NH_2 wagging; 29: C_1H_2 stretching (asymmetric); 30: C_2H_2 stretching (asymmetric); 31: O_2H stretching; 32: NH_2 stretching (symmetric).

electron density distribution that is a little delocalized. In Figure 1b, the bonding and anti-bonding relations with the main lobe of SOMO of $\mathbf{Cz}^-$ can be observed by the small amplitudes on the NH_3 group and C_1 atom. This case, similar to the zwitterionic dipole-bound anion of arginine,[3f] indicates that there is no clear border between the dipole-bound and valence-bound anions. As mentioned above, $\mathbf{Cz}^-$ may be produced via the rotation from $\mathbf{B}^-$ (see Figure 2b). However, this possibility can be ruled out because the VDE of $\mathbf{B}^-$ is much smaller than the energy difference between $\mathbf{B}^-$ and $\mathbf{Cz}^-$. The intramolecular rotation by varying D($C_3C_2C_1N$) angle can lead to the electron autodetachment of $\mathbf{B}^-$.

The canonical anion $\mathbf{B}^-$ is only one to be detected experimentally. To simulate its PES, first we compare the geometrical parameters and harmonic vibrational frequencies of $\mathbf{B}^-$ with those of the neutral **B** at the MP2 level. As shown in Table 3, the geometrical parameters are almost unchanged. The angle A(C_3O_2N) is widened with 0.21°, correspondingly, the HB length R(N···H) is a little shortened. It is interesting that the frequency blue-shifts and red-shifts are predicted for the XH (X = C, N, O) wagging and stretching modes of $\mathbf{B}^-$ with respect to the corresponding ones of **B**. In particular, the small elongation (+0.0032 Å) of the bond O_2−H leads to the significant red-shift (−65.3 cm^{-1}) of the O_2−H stretching frequency. The Franck−Condon (FC) factors (i.e., the squares of the overlap integrals between vibrational wave functions of $\mathbf{B}^-$ and **B**) are calculated in the harmonic approximation. The theoretical details can be found in ref 14. The intensity for the 0−0 transition is normalized to one and the others are scaled accordingly. The FC factors, transition assignments, and energy positions respective to the 0−0 transition are listed in Table 4. There are only a few vibrationally excited levels populated in the photodetachment experiments, because of the similarity of the equilibrium structures between $\mathbf{B}^-$ and **B**. The 0−0 transition energy corresponding to the EA_a is 56 meV calculated at the CCSD(T) level. In the simulated PES shown in Figure 3, the 0−0 transition predominatea, while the others are extremely weak. If we enlarge the spectrum in 0.1−0.6 eV of the electron binding energy, one can find several peaks around 0.2 and 0.5 eV that are due to the excitation transitions related to XH_2 (X = C, N) wagging and stretching modes, respectively. These scenarios are in line with the above-mentioned active vibration

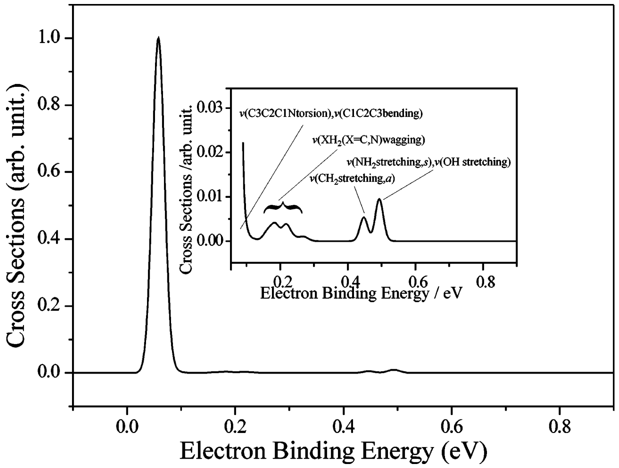

Figure 3. Theoretical photodetachment electron spectrum of the canonical anion of β-alanine simulated with the Franck−Condon factors (larger than 0.0001). Each transition is convoluted with the Gaussian profile shape (fwhm = 20 meV). The italic *s* and *a* represent the symmetric and asymmetric vibrational modes, respectively.

modes (e.g., they show the vibrational frequency shifts). Moreover, the similar structures are also observed in the experimental PES of the canonical dipole-bound anion of glycine.[2b,d] However, the intensities of XH_2 ($X = C, N$) wagging and stretching modes that appeared in the PES[2b,d] are a little higher. As proposed by Bailey et al.,[15] resonant and vibronic effects together with the FC factors may play role in the photodetachement of the dipole-bound anions.

4. Conclusion

The remarkable stabilities of the dipole-bound anions of the canonical and zwitterionic conformers of β-alanine are demonstrated by the high-level calculations, in which the former (**B**$^-$) is the global minimum and the latter, an anti zwitterionic anion (**Cz**$^-$), is the local minimum. In contrast to the dipole-bound anions of glycine,[3a,b] the gauche zwitterionic anion **Bz**$^-$ of β-alanine is an unstable conformer on the basis of the analyses of the potential energy surface of the dipole-bound anion. The vertical VDEs calculated at the CCSD(T) level for the canonical and zwitterionic anions are 58 and 1145 meV, respectively. The photodetachment electron spectrum of the canonical anion **B**$^-$ is simulated with the Franck−Condon factor calculations, in which the XH_2 ($X = C, N$) wagging and stretching modes are predicted to be excited by the electron detachment.

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