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Local Structures and Chemical Properties of Deprotonated Arginine

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The potential energy surface of gaseous deprotonated arginine has been systematically investigated by first principles calculations. At the B3LYP/6-31G(d) level, apart from the identification of several stable local structures, a new global minimum is located which is about 6.56 kJ/mol more stable than what has been reported. The deprotonated arginine molecule has two distinct forms with the deprotonation at the carboxylate group (COO^-). These two forms are bridged by a very high energy barrier and possess very different IR spectral profiles. Our calculated proton dissociation energy and gas-phase acidity of arginine molecule are found to be in good agreement with the corresponding experimental results. The predicted geometries, dipole moments, rotational constants, vertical ionization energies and IR spectra of low energy conformers will be useful for future experimental measurements.

Key words: Deprotonated arginine, Energy barrier, IR spectrum, Gas-phase acidity

I. INTRODUCTION

As the elemental building blocks of protein, the 20 common α-amino acids and their derivatives play an important role in diverse cellular functions and biosynthetic reactions [1]. A better understanding of these building blocks is certainly essential for obtaining a complete picture of the biological systems and their functions. It has only been possible to study gas phase amino acids and polypeptides in recent years owing to the development of effective experimental techniques [2]. The information about the intrinsic structure and properties of amino acids thus becomes available, which will at least help to verify and establish reliable theoretical tools for modeling more complicated biological systems. One important thing in the gas-phase study is to determine the most stable species of the given molecule, which have close relationship with its inherent optic, electronic and magnetic properties. Over the last decade, many experimental and theoretical studies on the amino acids and their derivatives have been reported [3−8]. But to the best of our knowledge, the deprotonated arginine has not been fully studied which might be due to the large number of internal rotational degrees of freedom involved in the arginine molecule. The low-cost computational methods such as force-field molecular mechanics can not give a proper description of the repulsive and attractive interactions in these molecules [9, 10] and more effective electronic structure algorithms are always required. For arginine, the situation becomes even more complicated since it consists of two distinct canonical tautomers and even a zwitterionic form. Moreover, the deprotonation of the arginine can take place at either the carboxylate group (COO^-) or the guanidine group (R^-), as shown in Fig.1.

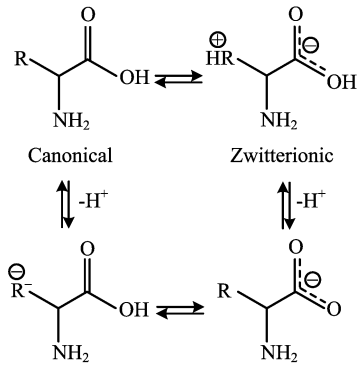

FIG. 1 Deprotonation reaction of arginine in the gas phase. "R" means the guanidine group in the side chain.

In this work, we provide a systematic study on the energy landscape of local structures and chemical properties of deprotonated arginine. Special attention is paid to the finding of the global minimum of the deprotonated arginine and the IR spectral characteristics of different configurations. The validity of the computational methods employed is verified by the good agreement between the theoretical and the experimental proton dissociation energy and gas-phase acidity of

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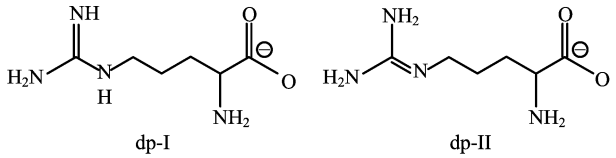

FIG. 2 Schematic structures of the deprotonated arginine dp-I and dp-II.

arginine molecule.

II. COMPUTATIONAL DETAILS

For arginine, two kinds of proton donor groups (OH and NH) coexist in its neutral form. Our first goal is to sort out the best donor group. The initial neutral forms were taken from a previous study [11], which presents the most accurate results up to date. More specifically, the conformers c1−c20 and z21−z25 in Ref.[11] were used to build up the deprotonated arginine at different deprotonation sites. The trial structures were optimized at the B3LYP/6-31++G(d,p) level of theory [12−14]. A large number of minima were located but only two deprotonated forms, named as dp-I and dp-II respectively, could stably exist as shown in Fig.2.

Stable conformers of the gaseous deprotonated arginine can be characterized through rotating all the internal single-bond rotators like tryptophan, tyrosine and asparagine [15−17]. When all internal single bonds were rotated simultaneously, some (more than two) atoms may become so close that they will intercross to form rings. An effective way to solve this problem is to compute the distance between every two unbonded atoms in the molecule to determine if they are within a proper distance, which is about 0.2 Å larger than the summation of their respective radius. This simple excise can remove quite many improper structures and save considerably computational time.

Still, a total of 28698 for dp-I and 18302 for dp-II trial structures were generated with our in-house developed program written in Visual Basic 6.0 language, after abandoning 11320 unfavorable trial structures. The trial structures were first optimized by the semi-empirical PM3 method [18] and 4334 unique structures obtained were then reordered according to the HF/3-21G(d) single point energy since our extensive testing showed that the HF energy ordering is much better correlated with the DFT ordering than that of the PM3 calculations [19]. The low-energy structures were then further optimized at the B3LYP/6-31G(d), B3LYP/6-31++G(d,p) and MP2/6-31++G(d,p) levels of theory. Only the most stable conformers were then taken through to the next level of calculations. Frequency calculation at the B3LYP/6-31++G(d,p) level ensured the absence of imaginary frequencies in the minima.

The percentage shares of the different deprotonated conformers at 98, 198, 298, and 443 K are determined by the Boltzmann distribution function. The transition state between the two deprotonated forms was searched at the MP2/6-31++G(d,p) level. The IR spectra at 443 K for these two forms were simulated respectively and the IR spectra of canonical, zwitterionic and protonated arginine were also given for comparison. The proton dissociation energy (PDE) and gas-phase acidity (GA) of arginine were calculated and compared with the experimental data to unravel the deprotonation process. All the calculations were carried out with the Gaussian 03 quantum chemistry package [20].

III. RESULTS AND DISCUSSION

A. Conformers and energies

The twenty most stable conformers in dp-I form (dp1-I−dp20-I) and the ten unique conformers in dp-II form (dp21-II−dp30-II) selected from DFT calculations were finally optimized at the MP2/6-31++G(d,p) level to ensure the reliability of the energy order. It has been shown that MP2 method performs much better than the DFT methods for hydrogen-bonded molecules [11, 21, 22]. The calculated relative energy, relative zero-point vibrational energy (Δ_{ZPVE}) and the intra-molecular hydrogen bonding type (HB) for these stable conformers were all listed in Table I, together with the vertical ionization energies, the dipole moments and the rotational constants. The numbering accompanied with the label dp is coincident with the stability of the deprotonated species ordered by the MP2 electronic energy.

The intramolecular interactions, such as HBs and the stereoelectronic effects, determine the stability of a conformer. A cut-off distance of 2.80 Å for near-atom interactions among different groups is used as a geometric criterion for the existence of a hydrogen bond. Through analysis of all the stable conformers obtained, eight kinds of HBs were identified, named as A−H as illustrated in Fig.3. Notice that in most cases, at least two HBs existed in the low-energy conformers and the deprotonated carboxyl group (OCO) usually bridged the guanidine and the amino groups, leading to the formation of HBs and stabilization of these structures.

Conformer dp1-I is found to be the global minimum at both the B3LYP and MP2 levels. The previous global minimum found by Poutsma and coworkers [24], who performed *ab initio* and DFT calculations only on the 30−50 lowest energy structures located by the GMMX algorithm in PCModel, is similar to our conformer dp3-I. It is noted that at B3LYP/6-31G(d) level this conformer is only ordered at the ninth place and 6.56 kJ/mol higher in energy than that of the most stable structure.

As indicated in Table I, the relative energy ordering of the most stable conformers have noticeable differences between B3LYP and MP2 theories with the same basis set 6-31++G(d,p). It seems like that the

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TABLE I Relative electronic energies (ΔE), $\Delta_{\rm ZPVE}$, relative Gibbs free energies ($\Delta G_{298,\rm corr}$) and HB of the most stable conformers of the deprotonated arginine, together with the vibrational ionization energies (VIEs), the dipole moments (μ) and the rotational constants*.

Conf.	ΔE		$\Delta_{\rm ZPVE}$	$E_{\rm MP2}+\Delta G_{298,\rm corr}$	HB	VIE/eV	μ/D	Rotational constant/GHz		
	$E_{\rm B3LYP}$	$E_{\rm MP2}$						A	B	C
dp1-I	0.00	0.00	0.00	0.00	A	4.10	4.794	1.324	0.636	0.555
dp2-I	3.84	1.25	2.72	8.23	B	4.09	5.065	1.305	0.695	0.580
dp3-I	6.94	2.59	1.96	6.02	A	4.16	3.426	1.306	0.737	0.590
dp4-I	7.40	3.01	2.26	8.82	C	4.06	5.297	1.446	0.690	0.550
dp5-I	6.90	3.05	2.34	9.61	B	4.03	2.954	1.276	0.715	0.599
dp6-I	4.56	3.64	2.63	7.19	A	4.23	5.280	1.520	0.620	0.507
dp7-I	8.19	3.80	1.92	7.02	B	4.06	4.973	1.150	0.844	0.703
dp8-I	5.39	4.30	−0.29	3.38	A	4.04	4.005	1.301	0.659	0.578
dp9-I	15.34	4.51	2.84	10.57	C	4.08	4.543	1.373	0.762	0.625
dp10-I	10.32	4.68	2.84	8.82	D	4.02	2.981	1.417	0.711	0.567
dp11-I	10.28	4.81	1.96	10.53	C	4.01	2.980	1.420	0.709	0.563
dp12-I	7.23	4.93	2.63	9.15	A	4.16	2.729	1.485	0.639	0.518
dp13-I	8.40	5.31	1.55	8.11	B	4.07	5.040	1.280	0.730	0.618
dp14-I	6.73	5.64	2.21	8.74	A	4.20	6.152	1.369	0.675	0.542
dp15-I	9.95	5.68	2.36	11.90	D	4.10	7.490	1.235	0.768	0.637
dp16-I	5.22	6.06	−0.46	5.98	A	4.30	6.854	1.330	0.633	0.554
dp17-I	9.07	6.14	2.51	10.66	A	4.16	6.008	1.417	0.664	0.515
dp18-I	11.03	6.14	0.67	2.17	B	4.03	3.417	1.234	0.763	0.635
dp19-I	8.94	6.19	2.47	10.74	C	4.05	5.009	1.510	0.665	0.540
dp20-I	12.20	6.23	1.88	12.00	E	4.03	4.722	1.218	0.793	0.651
dp21-II	16.64	14.09	0.79	17.05	F	3.93	5.996	1.800	0.502	0.428
dp22-II	17.26	15.51	−0.67	14.59	F	3.87	5.643	1.828	0.499	0.425
dp23-II	33.73	15.92	2.21	23.24	G	3.79	2.898	1.185	0.887	0.751
dp24-II	16.97	16.76	−0.42	17.93	F	3.95	5.391	1.762	0.499	0.427
dp25-II	22.03	19.77	−0.29	20.52	F	3.88	5.816	1.849	0.499	0.439
dp26-II	23.20	20.27	0.00	21.74	F	3.93	5.122	1.837	0.507	0.442
dp27-II	26.21	20.98	−21	22.15	H	3.84	5.989	1.524	0.545	0.505
dp28-II	20.86	21.86	−0.79	23.03	F	4.19	6.757	1.778	0.497	0.423
dp29-II	30.93	22.19	0.67	25.79	H	3.85	2.273	1.363	0.729	0.600
dp30-II	29.72	23.62	0.17	24.95	F	3.95	5.301	1.485	0.584	0.501

* The electronic energies of dp1-I calculated at the B3LYP/6-31++G(d,p) and MP2/6-31++G(d,p) levels are −606.066 and −604.316 a. u., respectively. $\Delta_{\rm ZPVE}$ was calculated at the B3LYP/6-31++G** level and scaled by 0.9887 [23]. The thermal corrections of the Gibbs free energy were scaled by 0.9688 [23]. All the energies are given in kJ/mol.

B3LYP method overestimated the relative energies of most structures. However, unlike the most stable conformers of neutral or protonated arginine whose adopts the dp-II form in their side chain, the most stable deprotonated conformers take the dp-I form as illustrated in Fig.2. To be more specific, the most stable structure of the dp-II form (dp21-II) is found to be 14.09 kJ/mol higher in energy than the global minimum dp1-I at the MP2 theory. This resulted from the difference in HBs existing in those conformers, since the electronic energies of the most stable conformers are very close. As shown in Table I, due to the relative small zero-point energies and significant entropic contributions, one can conclude that dp1-I, dp8-I, and dp18-I conformers are the three most stable ones on the potential energy surface.

VIEs are important for understanding the charge transfer, electrophilicity and reactivity redox potential of biological molecules. Table I presents the VIE values for the 30 most stable conformers of deprotonated arginine at the B3LYP/6-31++G(d,p) level of theory, together with the dipole moments and rotational constants for the MP2/6-31++G(d,p) geometries due to the fact that the MP2 dipole moments for tryptophan agree well with the experiment [25]. Most of the VIEs in dp-I form are larger than those in dp-II form, while

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TABLE II Percent shares of the deprotonated arginine conformers in their respective equilibrium mixtures at various temperatures. Scaling factor 0.9688 was used for the frequencies.

T/K	Shares of dp-I/%							Shares of dp-II/%						
	dp1-I	dp3-I	dp6-I	dp7-I	dp8-I	dp16-I	dp18-I	dp21-II	dp22-II	dp24-II	dp25-II	dp26-II	dp27-II	dp28-II
98	98.1	0.3	0.1	0.1	0.9	0.1	0.1	23.0	26.8	15.9	7.0	5.5	4.8	4.3
198	71.3	2.8	1.3	1.4	7.8	2.1	7.1	21.3	31.6	15.6	7.3	5.4	4.7	4.1
298	44.6	3.9	2.5	2.6	11.4	4.0	18.5	19.1	37.0	15.0	7.4	5.3	4.8	3.7
443	27.5	4.0	3.1	3.2	12.2	5.0	28.5	15.5	45.4	13.9	7.4	4.9	4.5	3.2

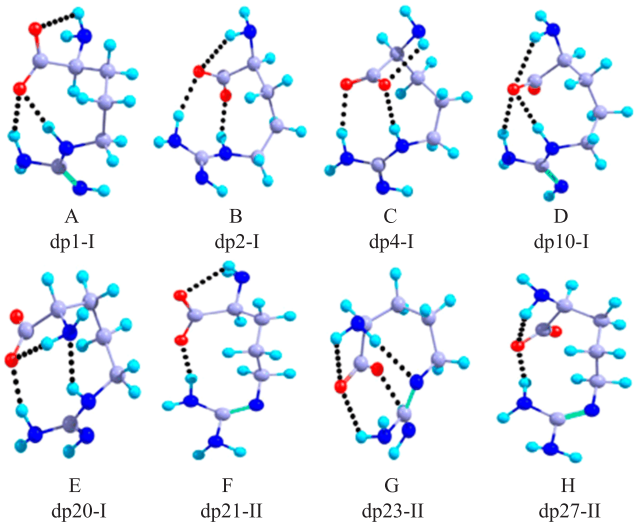

FIG. 3 Intramolecular hydrogen bonding types in the most stable conformers.

the average values for dp-I and dp-II forms are 4.10 and 3.92 eV, respectively. One can notice that conformers with the hydrogen bonding type A and F with almost unfolded structures usually have larger ionization energy.

The dipole moments and rotational constants of gaseous deprotonated arginine depend on their structures and hydrogen bonding features. For example, conformer dp10-I differs from dp11-I only by the differences of their main-chain, so their dipole moments and rotational constants are quite similar. The calculated VIEs, dipole moments and rotational constants may be helpful for assigning the future microwave spectra and permanent electric dipole moments of gaseous deprotonated arginine [25−28].

B. Conformational distribution

The molecular partition functions have been determined by using the MP2/6-31++G(d,p) electronic energies and the B3LYP/6-31++G(d,p) harmonic frequencies. Table II presents the percentage shares of the two different gaseous deprotonated arginines at 98, 198, 298, and 443 K, respectively.

Conformer dp1-I is the dominant isomer in the dp-I form with more than 98% concentration at 98 K. With the temperature increasing, the population of the most stable conformers decreases rapidly, and the contents of many higher free energy conformers increases. It is worthy noticing that the concentrations of conformer dp8-I and dp18-I become quite large with the temperature increasing, mainly due to the favorable vibrational contributions to their free energies. However, at all temperatures, the concentration of conformers in the dp-II form does not change too much and the dp22-II is always the most important one.

In principle, the conformers with the dp-I and dp-II forms can be inter-exchanged. We have calculated the energy barrier between two representative structures dp22-II and dp18-I, with a value of 163.35 kJ/mol. This shows that once the molecule is fixed in a particular form, it is very difficult to convert to another form at room temperature.

TABLE III Theoretical proton dissociation energy and gas-phase acidity of gaseous arginine*.

	Dissociation energy		Gas-phase acidity	
	dp-I	dp-II	dp-I	dp-II
B3LYP	1356.19	1373.59	1320.17	1339.10
BHandHLYP	1377.56	1391.27	1344.66	1358.96
Experiment	1388.50(13) [29]		1359.50(13) [29]	
	1381.00(9.2) [24]		1352.00(9.6) [24]	

* All energies are in kJ/mol. All the theoretical data correspond to the reference state of 101 kPa and 298 K. The numbers in the parentheses are the absolute uncertainty.

C. Proton dissociation energy and gas-phase acidity

The theoretical proton dissociation energy (PDE) and gas-phase acidity (GA) of gaseous arginine are listed in Table III, together with the experimental data for comparison. The neutral arginine structures were selected from Ref.[11] and the electronic energies of all the conformers were determined at the MP2/6-31++G(d,p) level and the thermodynamic data were determined at the B3LYP/6-31++G(d,p) and BHandHLYP/6-31++G(d,p) with the suggested scal-

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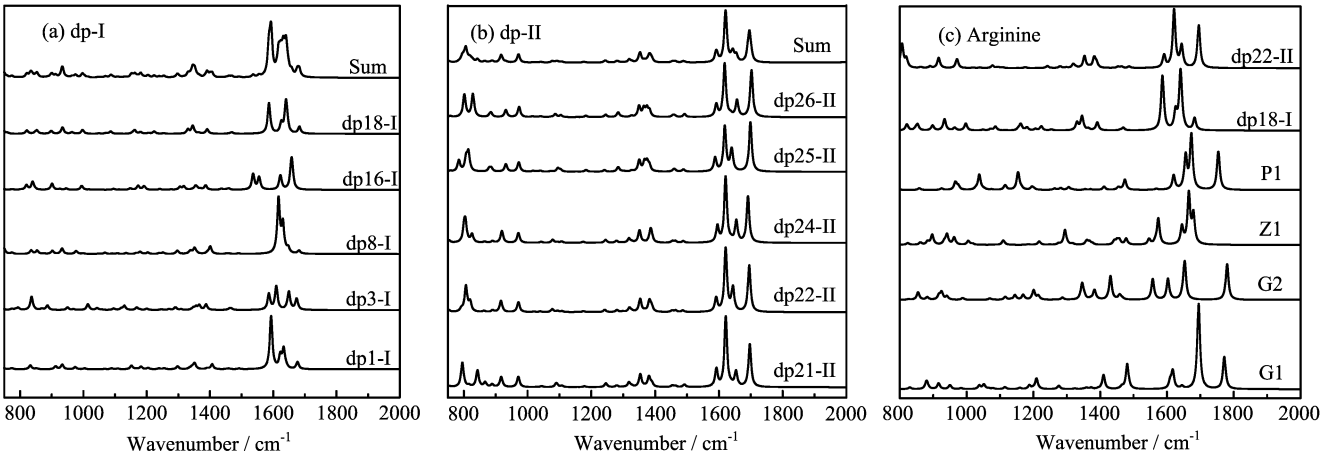

FIG. 4 Theoretical IR spectra of the two deprotonated forms of arginine and the spectral comparison among different forms of arginine. Conformer c5, c8, z22, and p1 [11] were selected to represent the canonical form G_1, G_2, the zwitterionic form Z1 and the protonated form P1. A Lorentzian profile with the half width at half maximum of 5 cm^{-1} is used to convolute the calculated spectra.

ing factors of 0.9688 and 0.9335 [23], respectively.

As shown in Table III, one can see that the B3LYP method slightly underestimates the two values in comparison with those from the BHandHLYP method. In general the calculated results are in excellent agreement with the respective experimental values [24, 29].

D. Vibrational spectra

The theoretical IR spectra of the two deprotonated arginine forms are given in Fig.4. In order to be more accessible for the future experiments, the comparison among spectra of the most stable conformers in the canonical (G1 and G2), the zwitterionic (Z1), the protonated (P1) and deprotonated (dp18-I and dp22-II) forms are also given in Fig.4(c). Naturally, there are some characteristic differences in the IR spectra of different species and even different isomers of the same specie. The frequency change reflects the internal structure changes, in particular the strength of the hydrogen bonds.

As shown in Fig.4 (a) and (b), for most deprotonated conforemrs in dp-I form (or in dp-II form), the symmetric and asymmetric carboxylate stretching modes at 1347 and 1639 cm^{-1} (or 1352 and 1620 cm^{-1}) are the dominate features, in consistent with the experimental infrared spectra of other amino acids [30]. The main difference between the two deprotonated forms is the position of the C=N stretching mode, which is at 1592 cm^{-1} in the dp-I form but blue shifted to 1695 cm^{-1} in the dp-II form. The peaks at 934 cm^{-1} for the dp-I and 806, 917, 971 cm^{-1} for the dp-II are mainly from the contribution of NH_2 scissoring which is not often observable in the IR experiment [30].

The strong peak at 1695 cm^{-1} of the canonical form G1 is attributed as the C=N stretching mode and is consistent with that of the dp-II form due to the same guanidine group in their side chain. For another canonical form G2, this mode has red-shifted to 1653 cm^{-1}, which is in the same trend as for the dp-I. Although the same deprotonated carboxylate group exists in the zwitterionic form, the energy difference between the symmetric and asymmetric carboxylate stretching modes (371 cm^{-1}) is much larger than that of the two deprotonated forms. This is mainly due to the different intramolecular hydrogen bonds. Another important thing is that the peak at 1754 cm^{-1} for P1 and 1773 and 1780 cm^{-1} for the two canonical forms, respectively, is the characteristic feature of the carbonyl stretching mode related to the COOH group.

IV. CONCLUSION

By combining theory of different levels, we have obtained the potential energy surface for the deprotonated arginine molecule. The usefulness and superiority of different methods are compared. A new global minimum of deprotonated arginine is discovered which is about 6.56 kJ/mol more stable in energy than the existing one. The conformational distributions at 98, 198, 298, and 443 K for the two deprotonated forms are estimated, which show that three most stable conformers (dp1-I, dp8-I and dp18-I) always present and can be used as representative structures of the dp-I form for the future studies. The basic structure, energy and IR spectra of different conformers are useful data for experimental structural identifications.

V. ACKNOWLEDGEMENTS

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