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Structural and Electronic Properties of Amino Acid Based Ionic Liquids: A Theoretical Study

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The gas-phase ion pairs of the ionic liquids containing 1-ethyl-3-methylimidazolium ([emim]$^+$) and 20 natural amino acids ([AA]$^-$) are studied at the B3LYP/6-311+G (d,p) level. The optimized structures, energies, and natural population analysis are presented and analyzed in terms of their possible correlation with the interaction energies and the H-bond separations. It is found that all the ion pairs of [emim][AA] can form strong H-bond interactions, which are dominated by the side-chain structure and the functional group of amino acid anions. The calculations indicate that an increase of the alkyl side-chain length coincides with a gradual decrease of H-bond energy, while the functional groups lead to the different localized charges on the anions, consequently affecting the electrostatic force. In addition, the intramolecular H bond in [AA]$^-$ can weaken the interaction, due to the decrease of the proton-accepting ability of the carbonyl O atoms. The H-bond chemical nature of [emim][AA] is investigated by atoms in molecules and natural bond orbital analyses. The preliminary analysis of 20 kinds of [emim][AA] ion pairs provides some initial hints as to the relationship between the interaction energy and the experimental glass transition temperature.

I. Introduction

Recently, interest has tremendously increased in the room-temperature ionic liquids (RTILs),[1−5] which are ideal reaction solvents,[6] extraction solvents,[7] electrolyte materials,[8] and so on, due to their remarkable properties. To understand the properties of RTILs is, therefore, of fundamental importance not only for solvent alternatives but also for green chemistry.[9−11] However, commonly used RTILs are prepared with anions containing fluorine. Their utilization is usually associated with the release of HF and, consequently, jeopardizes the use of the liquids as "green" solvents. Obviously, the use of biologically relevant ions as precursors for preparing RTILs is a promising greener approach.

A novel concept of amino acid ionic liquids (AAILs), composed of natural amino acid ions, has thus been developed. For instance, Ohno et al.[12−19] first prepared the AAILs by coupling the 1-ethyl-3-methylimidazolium cation ([emim]$^+$) with 20 natural amino acid anions ([AA]$^-$). Kou et al.[20,21] reported a new generation of cations, which were directly derived from α-amino acids and their ester salts, and prepared novel natural ILs [AA]X (X = Cl$^-$, NO$_3^-$, BF$_4^-$, PF$_6^-$, ...) and [AAE]Y (Y = NO$_3^-$, BF$_4^-$, PF$_6^-$, Tf$_2$N$^-$, ...). The most exciting features of these AAILs are that they have chiral centers, biodegradable characteristics, and high biocompatibility. In addition, their physicochemical properties can be easily adjusted for a wide range of tasks, especially the hydrophobic ILs containing a chiral center.[14] The AAILs are, therefore, ideal candidates to act as a platform for "task-specific ILs" or "functional ILs".[16,17,21−25]

Although understanding the molecular-level interaction is important to predict the physicochemical properties and design of functional AAILs, theoretical studies on the AAILs are still limited. Recently, Mou et al.[26] investigated the AAILs formed from [emim]$^+$ and glycine anion [Gly]$^-$, and found that all the stable isomers were characterized by the intermolecular H bonds. Rong et al.[27] synthesized the glutamic acid based ILs, [Glu]X (X = BF$_4^-$, NO$_3^-$, Cl$^-$, PF$_6^-$, ...). The research indicated that the smaller the absolute value of binding energy between [Glu]$^+$ and acid anion is, the lower the melting point would be. Li et al.[28] explored the hydrophilic ability of HGlyBF$_4$, and due to the multiple water binding sites in HGlyBF$_4$, the hydrophilicity of HGlyBF$_4$ is relatively increased versus typical ILs based on the imidazolium cation.

Herein, we take a first step by a theoretical study on the gas-phase ion pairs of [emim][AA], containing 1-ethyl-3-methylimidazolium and 20 natural amino acids.[12] A systematic comparison on the structures and interactions of [emim][AA] ILs is presented. Density functional theory (DFT) methods were employed in our calculations. The calculated results indicated that the properties of [emim][AA] are dependent on the variety of [AA]$^-$. As the anion is changed from [Gly]$^-$, to [Ser]$^-$, or to other [AA]$^-$, the strength of cation−anion interaction and the local packing of ion pair are altered, producing interesting variations. These variations across different anion series are useful for understanding the structures and properties of amino acid anion based ILs in the liquid phase.

II. Computational Details

By use of the Gaussian 03 package,[29] the structures of the [emim][AA] ion pairs and the corresponding monomers are optimized by the B3LYP method, and 6-311+G(d,p) is chosen as basis set. It is well understood that polarizable and diffusive orbitals are needed to account for the H-bonded interactions. Vibrational frequencies are calculated to verify the stationary structure for all the ion pairs. The interaction energies are calculated without considering the deformation energies between the ion pairs and the isolated monomers, since the geometries of monomers in the complexes differ slightly from their optimal geometries when isolated. The zero-point vibrational energy corrections (ΔZPE) have been obtained within the harmonic approximation, and basis set superposition errors (ΔBSSE) have been determined using the counterpoise method.[30]

To give a further understanding of the orbital interaction of the [emim]$^+$ and [AA]$^-$, the NBO analyses are calculated by

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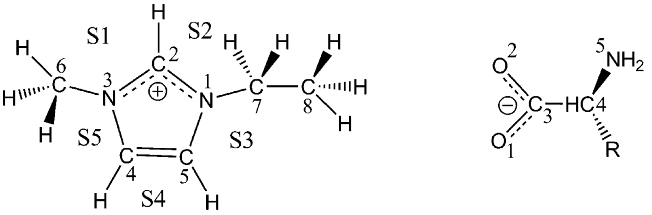
SCHEME 1: 1-Ethyl-3-methylimidazion Cation, [emim]$^+$, and Amino Acid Anions, [AA]$^-$



the B3LYP/6-311+G(d,p) method. In the NBO analysis, the stabilization energy $E(2)$ associated with delocalization $i \rightarrow j$ is estimated as[31]

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements, and $F(i, j)$ is the off-diagonal NBO Fork matrix element.

To gauge the bonding properties of [emim][AA] ion pairs, the AIM methodology[32] is applied to analyze the electron density ρ_c, its Laplacian $\nabla^2\rho_c$, and total energy density H_c at the critical point of $H^{\delta+}\cdots O^{\delta-}$ contact from the optimized results at the B3LYP/6-311+G(d,p) level. In general, a large electronic density (ρ_c) at the H-bond critical point (BCP) indicates a strong hydrogen bond, and a positive value of Laplacians ($\nabla^2\rho_c$) implies that the closed-shell (electrostatic) interaction is the major source in the H-bonded systems. Additionally, instead of the Laplacian, the total energy density H_c has been reported to be a more appropriate index to approach a better understanding of the weak nonbonded interactions.[33] The total energy density is the summation of kinetic [$G(r)$] and potential [$V(r)$] energy density, which obey the local virial theorem:[32]

$$(-\hbar^2/4m)\nabla^2\rho = 2G(r) + V(r)$$

The sign of H_c at the BCP assigns whether the interaction is electrostatic dominant ($H_c > 0$) or covalent dominant ($H_c < 0$). All AIM calculations have been performed using the AIM2000 program.[34]

III. Results and Discussion

A. The Favorable Location of H Bonds in the [emim][AA] Complexes. Dupont suggested that the pure ionic liquids based on the imidazolium cation are H-bonded polymeric supramolecules. Such structure is general for both the solid and liquid phase and is apparently maintained to a great extent even in the gas phase.[35] In the case of [emim][AA], the favorable sites of H bonds are located around the carbonyl oxygen atoms in [AA]$^-$,[26] and the C2−H, C4−H, and C5−H atoms in [emim]$^+$ (Scheme 1). The order of acidity is C2−H > C4−H > C5−H, and thus the C2−H···anion interaction is dominant in the ILs.[36−42] Five regions of S1, S2, S3, S4, and S5 are favorable for the formation of intermolecular H bond.[43] Accordingly, five configurations, [emim][AA]_S1, [emim][AA]_S2, [emim][AA]_S3, [emim][AA]_S4, and [emim][AA]_S5 can be proposed.

Figures 1−4 present the different interaction patterns between [emim]$^+$ and [AA]$^-$ (AA = Gly, Asn, Cys, and Glu) optimized by the B3LYP/6-311+G(d,p) method. These four anions are typical for confirming the H-bond interaction characters between [emim]$^+$ and [AA]$^-$. The interaction energetic data, including ΔE, ΔE_{ZPE} with zero-point correction, ΔE_{BSSE} considering basis set superposition error correction, and the available reported values[26] are listed in Table 1. Obviously, two short H-bond interactions are formed in all conformers and the carbonyl O atoms of [AA]$^-$ prefer to remain coplanar with the imidazolium ring. The [emim][AA]_S1 ion pairs have the shortest H bond (about 1.67 Å), to the most acidic C2−H, and a weaker interaction with the C6−H (about 2.06 Å). The [emim][AA]_S2 complexes also form the C2−H···anion interaction though they are slightly less stable than [emim][AA]_S1 (Table 1). Both isomers in the S1 and S2 regions can be considered as isoenergetic complexes.[26] Although the [AA]$^-$ can form a H bond with the hydrogen atoms in the S3, S4, S5 regions of [emim]$^+$, as presented in Figures 1−4, the distances of H bonds are much longer and the interaction energies are about 40 kJ/mol less than those of [emim][AA]_S1 and [emim][AA]_S2. Thus, the hydrogen atoms in the S1 region of [emim]$^+$ have a large stabilizing effect on the [AA]$^-$ anions and then produce the most stable isomers. The order of the H-bond energies is [emim][AA]_S1 > [emim][AA]_S2 > [emim][AA]_S3 > [emim][AA]_S5 > [emim][AA]_S4 for the [emim][AA] (AA = Gly, Asn, Cys, and Glu). The calculated results of [emim][Gly] are in good agreement with the previous report.[26]

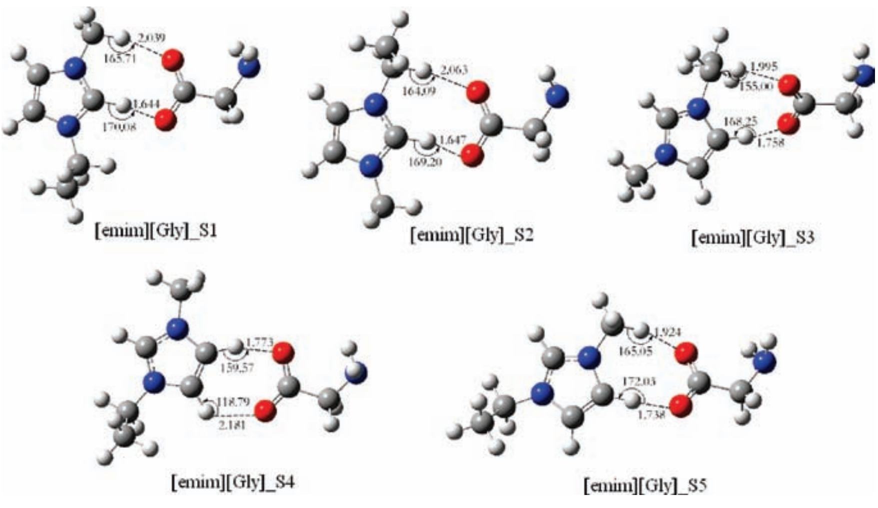


Figure 1. Optimized conformers of [emim][Gly], and key cation−anion distances and angles, calculated at the B3LYP/6-311+G(d,p) level. All distances are in angstroms, and all angles are in degrees.

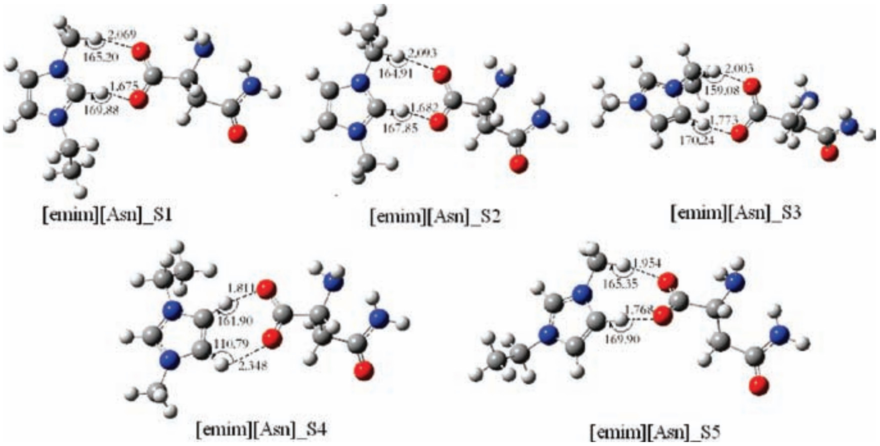


Figure 2. Optimized conformers of [emim][Asn], and key cation−anion distances and angles, calculated at the B3LYP/6-311+G(d,p) level. All distances are in angstroms, and all angles are in degrees.

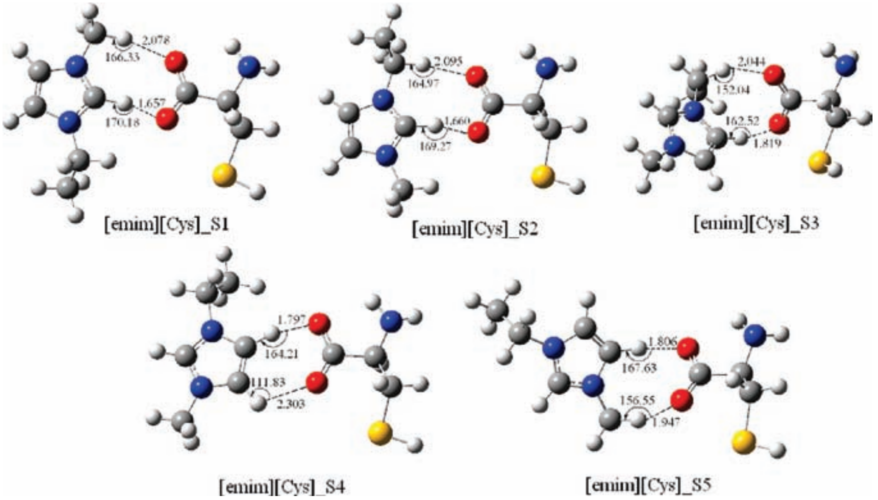


Figure 3. Optimized conformers of [emim][Cys], and key cation−anion distances and angles, calculated at the B3LYP/6-311+G(d,p) level. All distances are in angstroms, and all angles are in degrees.

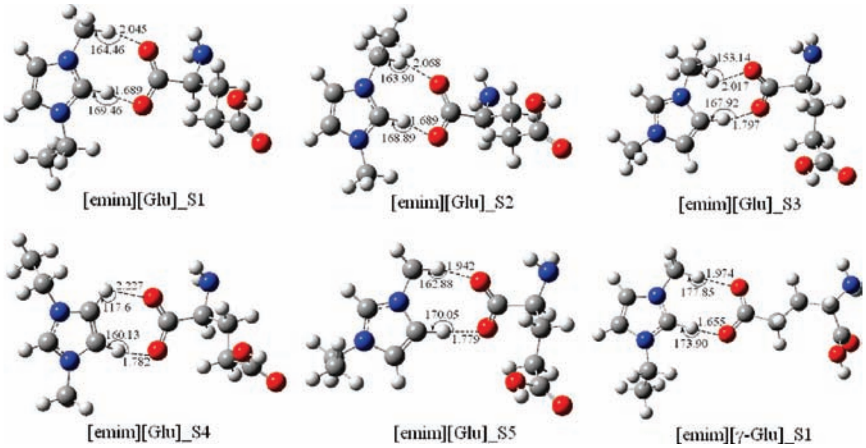


Figure 4. Optimized conformers of [emim][Glu], and key cation−anion distances and angles, calculated at the B3LYP/6-311+G(d,p) level. All distances are in angstroms, and all angles are in degrees.

Table 2 lists the stabilization energies $E(2)$ of [emim][AA] (AA = Gly, Asn, Cys, and Glu) estimated from the natural bond orbital (NBO) analysis by B3LYP/6-311+G(d,p). The large stabilizing effect is due to the strong orbital interactions between the antibonding orbital of proton donor σ^*(C−H) and the lone pairs of proton acceptor lp(O). The $E(2)$ of lp(O) → σ^*(C−H) interaction of isomers in the S1 and S2 regions are much larger than those in the S3, S4, and S5 regions, which indicates the lp(O) → σ^*(C2−H) interaction contributes to the strong interaction between [emim]$^+$ and [AA]$^-$. Moreover, the $E(2)$ of isomers in the S1 region are slightly large compared to those in the S2 region, which is in accordance with the energetic data in Table 1. The results above indicate that the S1 region of [emim]$^+$ is the most acidic and the [AA]$^-$ in this region have a dramatic effect on the [emim]$^+$.

TABLE 1: Calculated Interaction Energies (kJ/mol) of [emim][Gly], [emim][Asn], [emim][Cys], and [emim][Glu] Ion Pairs at the B3LYP/6-311+G(d,p) Level[a]

	[emim][Gly]				[emim][Asn]			[emim][Cys]			[emim][Glu]		
	ΔE	ΔE_{ZPE}	ΔE_{BSSE}	ref[b]	ΔE	ΔE_{ZPE}	ΔE_{BSSE}	ΔE	ΔE_{ZPE}	ΔE_{BSSE}	ΔE	ΔE_{ZPE}	ΔE_{BSSE}
S1	−399.80	−398.69	−397.40	−396.11	−375.72	−373.96	−373.33	−391.22	−389.27	−388.03	−379.52	−377.35	−376.89
S2	−399.31	−398.09	−396.78	−395.42	−374.99	−373.17	−372.48	−390.55	−388.62	−387.27	−379.21	−376.98	−376.43
S3	−362.02	−360.00	−358.89	−356.73	−338.71	−337.06	−335.90	−355.27	−352.16	−351.42	−343.53	−340.95	−340.50
S4	−346.98	−346.06	−344.78	−346.07	−328.02	−326.28	−325.70	−341.55	−339.71	−338.79	−330.09	−328.53	−327.79
S5	−360.64	−358.57	−357.91	−355.56	−338.60	−336.43	−336.10	−351.85	−349.07	−348.78	−342.71	−340.00	−340.05
γ_S1											−393.83	−392.13	−391.40

[a] ΔE is the energy difference; ΔE_{ZPE} is the energy difference with the zero-point energy correction; ΔE_{BSSE} is the energy difference considering the basis set superposition error. [b] Reference 26.

TABLE 2: The Significant Natural Bond Orbital Interactions of [emim][Gly], [emim][Asn], [emim][Cys], and [emim][Glu] Ion Pairs and Their Second-Order Perturbation Stabilization Energies $E(2)$ (kJ/mol) Calculated at the B3LYP/6-311+G(d,p) Level[a]

		[emim][Gly]		[emim][Asn]		[emim][Cys]		[emim][Glu]	
S1	lp(O1) → σ^*(C2−H)	26.54	129.51	25.58	111.93	30.35	115.41	22.90	109.21
	lp(O2) → σ^*(C6−H)	14.61	18.54	13.19	16.45	12.89	16.07	14.90	15.91
S2	lp(O1) → σ^*(C2−H)	26.08	128.01	24.49	108.00	29.47	113.65	22.73	108.88
	lp(O2) → σ^*(C7−H)	13.94	16.45	12.77	14.07	12.56	14.57	14.19	14.32
S3	lp(O1) → σ^*(C5−H)	24.82	70.07	24.91	70.20	21.22	32.15	21.14	59.69
	lp(O2) → σ^*(C7−H)	13.14	21.31	13.14	19.72	10.97	19.88	12.56	17.20
S4	lp(O1) → σ^*(C4−H)	21.52[b]	75.31[b]	2.55	0.59	3.18	0.59	20.80	72.92
	lp(O2) → σ^*(C5−H)	6.28[c]	3.10[c]	18.00	62.71	19.21	68.78	5.02	2.26
S5	lp(O1) → σ^*(C4−H)	26.08	83.64	24.95	66.22	21.14	59.78	22.56	70.28
	lp(O2) → σ^*(C6−H)	16.83	31.23	15.82	29.80	16.79	19.67	16.62	26.87
γ_S1	lp(O1) → σ^*(C2−H)							23.74	123.95
	lp(O2) → σ^*(C6−H)							14.78	17.92

[a] σ^* denotes the formally empty antibonding orbital; lp denotes the occupied lone pairs. The labels of atoms are from Scheme 1. [b] The NBO interaction is lp(O2) → σ^*(C4−H). [c] The NBO interaction is lp(O1) → σ^*(C5−H).

TABLE 3: Electron Densities ρ_c (e/a_0^3), Laplacians $\nabla^2\rho_c$ (e/a_0^5), and Energy Densities H_c (a.u.) of [emim][Gly], [emim][Asn], [emim][Cys], and [emim][Glu] Ion Pairs within the AIM Theory[a]

		[emim][Gly]			[emim][Asn]			[emim][Cys]			[emim]Glu]		
		ρ_c	$\nabla^2\rho_c$	H_c	ρ_c	$\nabla^2\rho_c$	H_c	ρ_c	$\nabla^2\rho_c$	H_c	ρ_c	$\nabla^2\rho_c$	H_c
S1	C2−H···O1	0.0571	0.1348	−0.0100	0.0526	0.1335	−0.0074	0.0550	0.1367	−0.0086	0.0511	0.1304	−0.0067
	C6−H···O2	0.0222	0.0761	0.0022	0.0209	0.0710	0.0022	0.0205	0.0693	0.0021	0.0218	0.0754	0.0023
S2	C2−H···O1	0.0568	0.1348	−0.0098	0.0518	0.1330	−0.0069	0.0546	0.1364	−0.0084	0.0512	0.1306	−0.0067
	C7−H···O2	0.0214	0.0727	0.0022	0.0200	0.0676	0.0021	0.0200	0.0672	0.0020	0.0210	0.0720	0.0022
S3	C5−H···O1	0.0425	0.1236	−0.0023	0.0408	0.1218	−0.0016	0.0361	0.1158	0.0002	0.0388	0.1169	−0.0010
	C7−H···O2	0.0256	0.0852	0.0019	0.0249	0.0831	0.0020	0.0234	0.0765	0.0019	0.0244	0.0818	0.0020
S4	C4−H···O1	0.0415[b]	0.1215[b]	−0.0019[b]	0.0136	0.0505	0.0019	0.0147	0.0553	0.0021	0.0407	0.1203	−0.0016
	C5−H···O2	0.0183[c]	0.0671[c]	0.0024[c]	0.0379	0.1155	−0.0006	0.0392	0.1172	−0.0011	0.0167	0.0612	0.0023
S5	C4−H···O1	0.0445	0.1255	−0.0033	0.0411	0.1255	−0.0017	0.0379	0.1152	−0.0007	0.0405	0.1193	−0.0016
	C6−H···O2	0.0292	0.0967	0.0016	0.0274	0.0910	0.0018	0.0278	0.0943	0.0019	0.0280	0.0938	0.0018
γ_S1	C2−H···O1										0.0553	0.1333	−0.0090
	C6−H···O1										0.0222	0.0764	0.0023

[a] The labels of atoms refer to those used in Scheme 1. [b] The H-bond interaction is C4−H···O2. [c] The H-bond interaction is C5−H···O1.

The electronic density ρ_c, its Laplacians $\nabla^2\rho_c$, and total energy density H_c at the bond critical points (BCP) for [emim][AA] (AA = Gly, Asn, Cys, Glu) are calculated by AIM2000 based on the optimized results at the B3LYP/6-311+G(d,p) level. It can be seen from Table 3 that all the values of $\nabla^2\rho_c$ are positive, implying that the C−H···O interactions for all the complexes have the electrostatic characters. The calculated electronic densities ρ_c range from 0.0136 to 0.0571 and are larger than those of a typical H-bond system (0.002−0.04) based on the AIM methodology,[44] which indicates that the strong H bonds are formed between $[\mathrm{emim}]^+$ and $[\mathrm{AA}]^-$. As shown in Table 3, the ρ_c values of C2−H···O are much larger than those of the other C−H···O, suggesting the strong C2−H···O interactions in the S1 and S2 regions of $[\mathrm{emim}]^+$. Moreover, all the H_c values of C2−H···O are negative, implying that the C2−H···O interactions have some covalent character. Compared with C4−H···O and C5−H···O, the negative H_c of C2−H···O is slightly small, indicating that the covalent character of C2−H···O is larger than those of C4−H···O and C5−H···O. All the H_c values of the interactions between the carbonyl O atoms and the hydrogen attaching to the alkyl side chain are positive, suggesting a dominant electrostatic character. These are in good agreement with the previous reported C−H···X (X = Cl or Br) interaction in the imidazolium halide ILs.[44]

Noted that some of amino acid anions, such as glutamic acid, have two carbonyl groups. The corresponding anion can be named as $[\alpha\_\mathrm{Glu}]^-$ and $[\gamma\_\mathrm{Glu}]^-$, in which the α and γ denote the position of carbonyl oxygen atoms. For simplicity, the $[\alpha\_\mathrm{Glu}]^-$ is replaced by $[\mathrm{Glu}]^-$. The calculated charge distributions of the carbonyl oxygen atoms are −0.793 and −0.791 for $[\mathrm{Glu}]^-$, and −0.783 and −0.796 for $[\gamma\_\mathrm{Glu}]^-$, respectively (see Supporting Information). Compared with the [emim][Glu]_S1 (1.689 and 2.045 Å), the two H-bond distances of [emim][γ_Glu]_S1 (1.655 and 1.974 Å) are slightly shorter, as presented in Figure 4. The difference of interaction energies ΔE_{ZPE} is around 15 kJ/mol with the relatively stronger value of [emim][γ_Glu]_S1,

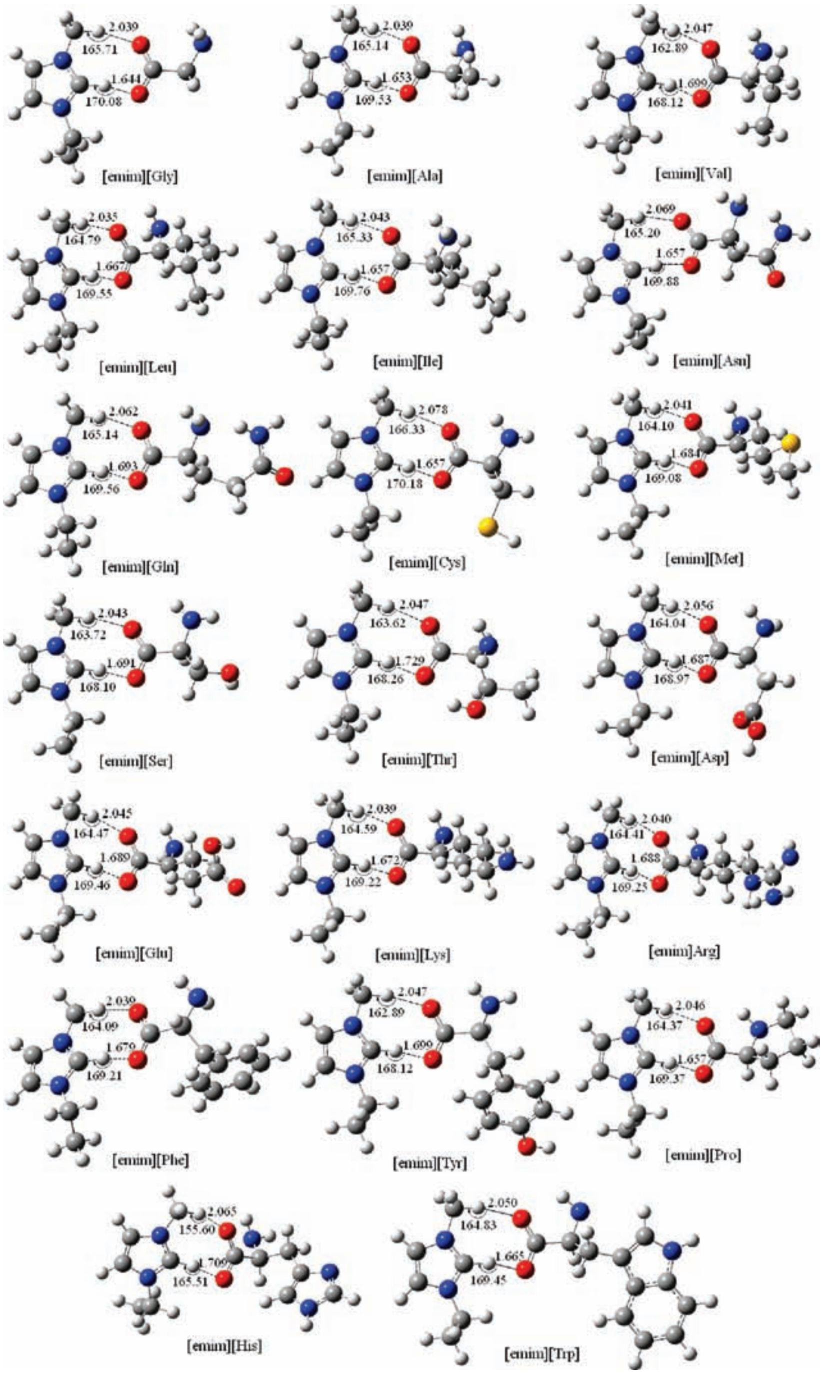


Figure 5. Optimized 20 kinds of AAIL ion pairs, and key cation−anion distances and angles, calculated at the B3LYP/6-311+G(d,p) level. All distances are in angstroms, and all angles are in degrees.

as listed in Table 1. The interaction between $[emim]^+$ and $[\gamma\_Glu]^-$ is only partly covalent in nature (Table 3) by AIM2000. Additionally, the second-order perturbation energy $E(2)$ of lp(O1) → σ^*(C2−H) (123.95 kJ/mol) of [emim][γ_Glu]_S1 is about 14 kJ/mol larger than the corresponding value of [emim][Glu]_S1 (109.21 kJ/mol). These results indicate that for the amino acid anions having two carbonyl groups, the carbonyl oxygen atoms far away the amide group are more favorable for proton attack.

B. Effects of the Amino Acid Anions on the Interaction Energy and Properties of AAILs. ***1. Optimized Geometries.*** Figure 5 shows the optimized geometries of the gas-phase ion pairs of the 20 novel AAILs at the B3LYP/6-311+G(d,p) level. In comparison, all the intermolecular H bonds are formed between the α carbonyl oxygen atoms of $[AA]^-$ and the H atoms in the S1 region of $[emim]^+$. We use the term "[emim][AA]" instead of "[emim][AA]_S1" for simplicity. Obviously, the geometries of the monomers in the complexes differ slightly from their isolated ones (see Supporting Information). For example, the distance of C2−H in the isolated $[emim]^+$ is 1.077 Å, while they are 1.132 and 1.120 Å in [emim][Gly] and [emim][Tyr], respectively. The deviation is not very large. Therefore, the deformation energies between the complexes and the isolated monomers are not taken into consideration when the H-bonded interaction energies are calculated. The calculated 20 ion pairs of [emim][AA] all form a strong H bond (r = 1.64−1.73 Å), to the most acidic C2−H, and a weaker interaction with the C6−H ($r \approx 2.0$ Å). The H-bonded interactions between $[emim]^+$ and $[AA]^-$ result in nearly linear hydrogen bonds, and the ranges of C2−H···O1 and C6−H···O2

TABLE 4: Calculated Interaction Energies (kJ/mol) of 20 Kinds of AAIL Ion Pairs[a]

	ΔE	ΔE_{ZPE}	ΔE_{BSSE}	ΔE_{SP}	T_g[b]
[emim][Gly]	−399.80	−398.69	−397.40	−401.94	−65
[emim][Ala]	−397.66	−396.17	−395.18	−400.03	−57
[emim][Val]	−392.17	−390.07	−389.65	−393.98	−52
[emim][Leu]	−390.97	−389.36	−388.30	−392.71	−51
[emim][Ile]	−391.69	−389.46	−389.14	−393.12	−52
[emim][Asn]	−375.72	−373.96	−373.33	−377.44	−16
[emim][Gln]	−368.45	−365.68	−366.06	−372.04	−12
[emim][Cys]	−391.22	−389.26	−388.03	−392.49	−19
[emim][Met]	−382.84	−380.80	−380.92	−387.45	−57
[emim][Ser]	−387.45	−385.19	−384.84	−390.57	−49
[emim][Thr]	−373.92	−370.94	−371.21	−370.07	−40
[emim][Asp]	−384.66	−382.42	−381.64	−385.26	5
[emim][Glu]	−379.52	−377.35	−376.89	−381.48	6
[emim][Lys]	−391.52	−389.37	−388.95	−396.91	−47
[emim][Arg]	−377.27	−375.06	−374.68	−381.03	−18
[emim][Phe]	−384.22	−382.28	−381.55	−386.78	−36
[emim][Tyr]	−382.54	−379.13	−379.97	−387.85	−23
[emim][His]	−384.85	−381.69	−381.92	−387.45	−24
[emim][Trp]	−387.90	−385.83	−385.25	−390.74	−31
[emim][Pro]	−395.24	−392.94	−392.13	−397.87	−48

[a] ΔE is the energy difference; ΔE_{ZPE} is the energy difference with the zero-point energy correction; ΔE_{BSSE} is the energy difference considering the basis set superposition error at the B3LYP/6-311+G(d,p) level. ΔE_{SP} is the single point energy difference at the B3LYP/AUG-cc-pVTZ level. [b] Experimental glass transition temperatures (T_g) from ref 12.

angles are 165.5−170.2° and 155.6−166.3°, respectively. Compared with typical ionic liquids, such as [emim]Cl, [emim][BF_4], and [emim][PF_6], the H-bond distances of [emim]-[AA] are much shorter.[45] For instance, the H-bond distances in [emim]Cl are 1.988 Å (C2−H···Cl) and 2.552 Å (C6−H···Cl, methyl hydrogen) by B3LYP/6-31G(d). As for [emim][BF_4] and [emim][PF_6], the shortest H-bond distances between the F atom and the C2−H are 2.083 and 2.210 Å, respectively, at the B3LYP/6-31+G(d) level. Nevertheless, the differences of the H-bond distances for the [emim][AA] are only about 0.5 Å. On the basis of these data, it is difficult to elucidate the effect of amino acid anion structures on the properties of AAILs. To further information, we have to rely on the other calculations, such as interaction energies, charge distributions, and so on.

2. Binding Energy. Table 4 lists the interaction energies ΔE, ΔE_{ZPE}, and ΔE_{BSSE} of 20 [emim][AA] ion pairs by the B3LYP/6-311+G(d,p) method. The single point energies ΔE_{SP} at the B3LYP/AUG-cc-pVTZ level based on the optimized results by B3LYP/6-311+G(d,p) are also presented. For the [emim][AA], the interaction energies with ZPE correction are ranging from −365.68 to −398.69 kJ/mol at the B3LYP/6-311+G(d,p) level. Generally, the H-bonded interaction energies of AAILs are comparable to conventional ionic liquids. Taking [emim]Cl, [emim][BF_4], and [emim][PF_6] as examples, the interaction energies are about −382.11, −345.80, and −364.68 kJ/mol, respectively, by the B3LYP/6-31+G(d) method.[45]

From the calucated results, we can find that the side-chain structure of the amino acids has the dominant influence on the H-bond energies. The H-bond interaction energies of [emim]-[Gly], [emim][Ala], [emim][Val], and [emim][Leu] are larger than those of other amino acid ILs. The values of ΔE_{BSSE} are −397.40, −395.18, −389.65, and −388.30 kJ/mol, respectively. An increase of the alkyl side-chain length produces a decrease of H-bond energy. It can be considered that with the size of the $[AA]^-$ alkyl side chains increasing, due to the van der Waals force between the cation and anions the $[AA]^-$ anion moves far away from the $[emim]^+$ and the H bonds of ion pairs become weaker. Accordingly, the H-bond distances of [emim][Gly], [emim][Ala], [emim][Val], and [emim][Leu] are gradually increasing, 1.644, 1.653, 1.660, and 1.667 Å, respectively. Another example is that the interaction energies ΔE_{BSSE} of [emim][Asp] and [emim][Glu] are −381.64 and −376.89 kJ/mol, respectively. The interaction energy of [emim][Asp] is at a much more favorable 4.75 kJ/mol due to one more $-CH_2$ side chain of the $[Glu]^-$ fragment. A similar effect has been expected in conventional ionic liquids, the larger the size of the anions is, the weaker the hydrogen bonds of the ion pairs would be.

Moreover, the functional groups of $[AA]^-$ can greatly influence the intermolecular H bonds. For instance, the [emim]-[Pro] with a pyrrolidine group has a strong H-bond energy, −392.94 kJ/mol. For the AAILs with phenyl and pentacyclic groups, their interaction energies are much less than those with alkyl side chains. This is possibly due to the hyperconjugation effect between the benzene ring and the carbonyl group in the $[AA]^-$. Such an effect makes the negative charge more delocalized over the anion and reduces the interaction energies, which will be explored in detail in the following part for the charge population analyses. Additionally, the intramolecular H bonds formed between the functional group and the carbonyl O atoms should decrease the proton-accepting ability of carbonyl O atoms and then weaken the H-bonded interaction energies. Taking [emim][Thr] as an example, the hydroxyl H atom forms an intramolecular H bond with one of the carbonyl O atoms (the distance is about 1.849 Å), which produces a relatively weaker interaction energy, −370.94 kJ/mol with ZPE correction. For [emim][Asn] and [emim][Gln] with amide groups, the H-bond interactions are relatively weak, −373.96 and −365.68 kJ/mol, due to the formation of intramolecular H bonds. The H-bond energies of six typical ion pairs have the following sequence: −392.94 kJ/mol ([emim][Pro]) < −389.37 kJ/mol ([emim][Lys]) < −389.26 kJ/mol ([emim][Cys]) < −385.19 kJ/mol ([emim][Ser]) < −382.42 kJ/mol ([emim][Asp]) < −373.96 kJ/mol ([emim][Asn]). The interaction energy of [emim][Pro] is about 20 kJ/mol stronger than that of [emim][Asn].

Therefore, the contributions of the side-chain structures of amino acid anions to the stabilities for AAILs are not negligible, via the alkyl side-chain length, different functional groups, intramolecular hydrogen bonds, and negative charge delocalization over anions. The balance of those four factors leaves the relative stability order of 20 amino acid ILs based on the imidazolium cation and provides some insights into the glass transition temperature (T_g) of amino acid ILs observed in experiments.

3. Correlation of Interaction Energy and Glass Transition Temperature. Melting point (T_m) or glass transition temperature (T_g) is one of the most important properties of ionic liquids and reflects the interactions of cations and anions and the molecular packing.[45] In terms of conventional ILs, gross "linear" trends relating interaction energy and melting point had been found, in which the smaller the absolute value of binding energy between ions is, the lower the melting point would be.[46] Interestingly, the presence of amino acid anions in ILs does introduce intricate links between interaction energy and glass transition temperature (T_g).

Generally, an increase of the alkyl side-chain length results in a gradual increase of T_g,[12] such as [emim][Gly] (−65 °C), [emim][Ala] (−57 °C), [emim][Val] (−52 °C), and [emim][Leu] (−51 °C). This trend is associated with a decrease in the magnitude of the interaction energies. Such an observation corroborates that the T_g of AAILs is governed strongly by the

TABLE 5: Selected Partial Charges *q* (*e*), Charge Transfers CT (*e*), and Dipole Moment *μ* (Debye) from an NPA Analysis of 20 Kinds of AAIL Ion Pairs at the B3LYP/6-311+G(d,p) Level[a]

	$[\text{emim}]^+$								$[\text{AA}]^-$						
	N1	C2	C2−H	N3	C4	C4−H	C5	C5−H	O1	O2	C3	C4	N5	CT	μ
[emim][Gly]	−0.378	0.295	0.308	−0.362	−0.033	0.228	−0.039	0.227	−0.808	−0.790	0.772	−0.283	−0.845	0.130	12.1
[emim][Ala]	−0.378	0.295	0.306	−0.362	−0.033	0.228	−0.039	0.228	−0.807	−0.794	0.781	−0.117	−0.850	0.128	12.3
[emim][Val]	−0.377	0.295	0.306	−0.361	−0.032	0.229	−0.039	0.228	−0.802	−0.794	0.784	−0.109	−0.858	0.125	12.3
[emim][Leu]	−0.377	0.295	0.304	−0.361	−0.032	0.229	−0.039	0.228	−0.802	−0.797	0.780	−0.109	−0.845	0.125	12.4
[emim][Ile]	−0.377	0.295	0.306	−0.362	−0.032	0.229	−0.039	0.228	−0.804	−0.792	0.789	−0.111	−0.868	0.125	12.4
[emim][Asn]	−0.375	0.295	0.303	−0.361	−0.032	0.230	−0.036	0.229	−0.793	−0.789	0.781	−0.116	−0.877	0.117	13.3
[emim][Gln]	−0.375	0.295	0.303	−0.360	−0.031	0.230	−0.037	0.229	−0.796	−0.792	0.785	−0.111	−0.882	0.114	16.6
[emim][Cys]	−0.376	0.295	0.305	−0.362	−0.033	0.229	−0.037	0.228	−0.790	−0.783	0.795	−0.130	−0.863	0.120	10.7
[emim][Met]	−0.377	0.295	0.304	−0.360	−0.031	0.229	−0.038	0.228	−0.803	−0.794	0.777	−0.107	−0.846	0.120	13.8
[emim][Ser]	−0.376	0.297	0.305	−0.360	−0.032	0.229	−0.038	0.228	−0.804	−0.785	0.796	−0.138	−0.861	0.118	12.6
[emim][Thr]	−0.374	0.297	0.304	−0.358	−0.031	0.230	−0.036	0.229	−0.836	−0.774	0.786	−0.131	−0.846	0.106	13.8
[emim][Asp]	−0.375	0.297	0.304	−0.360	−0.032	0.229	−0.037	0.228	−0.791	−0.787	0.796	−0.113	−0.865	0.114	11.8
[emim][Glu]	−0.376	0.295	0.304	−0.360	−0.031	0.229	−0.038	0.229	−0.804	−0.791	0.778	−0.110	−0.848	0.117	13.7
[emim][Lys]	−0.377	0.295	0.305	−0.361	−0.031	0.229	−0.037	0.228	−0.800	−0.799	0.779	−0.107	−0.846	0.124	11.8
[emim][Arg]	−0.376	0.295	0.304	−0.360	−0.031	0.229	−0.038	0.228	−0.800	−0.797	0.777	−0.106	−0.846	0.119	14.8
[emim][Phe]	−0.377	0.295	0.305	−0.360	−0.032	0.229	−0.038	0.228	−0.815	−0.785	0.783	−0.104	−0.852	0.120	12.8
[emim][Tyr]	−0.375	0.297	0.305	−0.360	−0.031	0.229	−0.037	0.228	−0.806	−0.792	0.801	−0.105	−0.860	0.114	10.5
[emim][His]	−0.376	0.300	0.303	−0.359	−0.030	0.229	−0.039	0.228	−0.804	−0.792	0.795	−0.103	−0.851	0.111	12.5
[emim][Trp]	−0.377	0.296	0.305	−0.361	−0.032	0.229	−0.038	0.228	−0.803	−0.792	0.789	−0.108	−0.870	0.124	11.4
[emim][Pro]	−0.377	0.296	0.307	−0.362	−0.033	0.229	−0.039	0.228	−0.802	−0.791	0.792	−0.107	−0.706	0.125	11.6

[a] The labels of atoms refer to those used in Scheme 1.

van der Waals force between alkyl side chains, rather than the electrostatic interaction between anions and cations.[12] The relationship of experimental T_g and theoretical interaction energies for [emim][Ser] and [emim][Thr] and [emim][Asn] and [emim][Gln] further supports this assumption, as listed in Table 4. Moreover, the T_g values of [emim][Gly], [emim][Ala], [emim][Val], and [emim][Leu] are lower than those of other ILs, albeit with rather strong interaction energies. At the same time, [emim][Asp] and [emim][Glu] have the highest T_g, 5 and 6 °C, respectively, while the corresponding cation−anion interactions are relatively weaker, −382.42 and −377.35 kJ/mol with ZPE correction. And [emim][Asn] and [emim][Gln] have the weakest cation−anion H-bond interactions, −373.96 and −365.68 kJ/mol, but the T_g values of those two salts are relatively higher, −16 and −12 °C, respectively. Why might this be? This is possibly due to the presence of the extended 3D network of H bonds.[36,39,47,48] For the AAILs with carboxyl and amide groups, they are preferable to interact with H atoms of $[\text{emim}]^+$ or other $[\text{AA}]^-$ and then form the intermolecular H-bond networks. Such an extended network of H bonds undoubtedly restricts the release of single ions or ion pairs and thus has significantly increased the T_g. Additionally, in the case of the AAILs with groups to form conjugation structures, such as [emim][Phe], [emim][Trp], [emim][Tyr], the T_g values are also relatively higher (about −30 °C). It is possible that the intermolecular $\pi-\pi$ interaction occurs for the amino acid anions with benzene group and conjugated structures, and this $\pi-\pi$ interaction leads to the more effective molecular packing of ILs and thus increases the T_g.

Although the factors contributing to the T_g behavior of AAILs are relatively complicated, our preliminary analysis of a series of AAILs based on the imidazolium cation can provide some initial hints. Those are the anion−cation electrostatic attractions, van der Waals repulsions of the alkyl chains on the amino acid anions, a 3D network of H bonds, and intermolecular $\pi-\pi$ interactions. Further investigation of the liquid phase AAILs by molecular dynamics simulation should clarify the existence and nature of correlations with the glass transition temperature of AAILs, which is in consideration.

4. Charge Population Analysis. Table 5 lists the selected natural population analyses (NPA) of 20 AAILs. It is clear that the charge distributions in the cation and anions of ion pairs are qualitatively comparable to those of the isolated ions (see Supporting Information). Different amino acid anions located around the imidazolium ring have different effects on the charge distributions in the ring, albeit such differences are not very large. Taking the [emim][Asn] and [emim][Pro] ion pairs as references, the NPA of C2−H in $[\text{emim}]^+$ are 0.304 and 0.307*e*, respectively, and the difference is less than 0.003*e*. Additionally, it is found that the delocalization of negative charges varies with the different side-chain structures of $[\text{AA}]^-$. For example, the NPAs of O1, O2, C4, and N5 in $[\text{Phe}]^-$ are −0.799, −0.785, −0.112, and −0.878*e* (see Supporting Information), respectively, and comparing with the corresponding values in $[\text{Ala}]^-$, −0.793, −0.807, −0.128, and −0.885*e*, the negative charges are relatively more delocalized due to the functional group of benzene in $[\text{Phe}]^-$.

As the forming of the hydrogen bonds, the charges are transferred from the amino acid anions to the $[\text{emim}]^+$ cation. The "extra" electron density is distributed over the N1, N3, C4−H, and C5−H centers, and the C2−H which is the most acidic becomes more positive. Those results are similar to those of typical IL [bmim]Cl.[49] On the other hand, when adding the $[\text{emim}]^+$, the charges of $[\text{AA}]^-$ will be also redistributed and the electrons transferred to the cation mainly come from the C3 atom of carbonyl group and the N5 atom of amide group. For example, the NPAs of C3 and N5 atoms of the isolated $[\text{Gly}]^-$ are 0.744 and −0.885*e*, and for the [emim][Gly] complex the corresponding NPAs are 0.772 and −0.845*e*, respectively. Gross trend relating the amount of charge transfers and the H-bonded stability of AAIL can be found. The more stable a cation−anion interaction of AAIL is, the more charges between the cation and anions are transferred. For instance, with alkyl side-chain length of [emim][Gly], [emim][Ala], [emim][Leu], and [emim][Ile] increasing, both the absolute values of the interaction energies and the transferred charges from $[\text{AA}]^-$ to $[\text{emim}]^+$ are decreased gradually. The transferred charges are 0.130 to 0.128, 0.125, and 0.125*e*, respectively. Overall, for

TABLE 6: The Significant Second-Order Perturbation Stabilization Energies, $E(2)$ (kJ/mol), and the Electron Occupation Differences of C−H Antibonding Orbital from an NBO Analysis of 20 Kinds of AAIL Ion Pairs at the B3LYP/6-311+G(d,p) Level[a]

	$E(2)$		$E(2)$			
	lp(O1) → σ^*(C2−H)		lp(O2) → σ^*(C6−H)		$\Delta\sigma^*$(C2−H)[b]	$\Delta\sigma^*$(C6−H)[b]
[emim][Gly]	26.54	129.51	14.61	18.54	0.0851	0.0193
[emim][Ala]	25.16	125.41	14.99	17.46	0.0839	0.0190
[emim][Val]	24.20	119.80	15.36	16.62	0.0820	0.0186
[emim][Leu]	23.36	118.84	15.40	17.00	0.0818	0.0190
[emim][Ile]	25.66	122.78	14.94	16.83	0.0825	0.0186
[emim][Asn]	25.58	111.93	13.19	16.45	0.0767	0.0175
[emim][Gln]	24.03	105.36	14.15	14.90	0.0740	0.0170
[emim][Cys]	30.35	115.41	12.89	16.07	0.0793	0.0173
[emim][Met]	22.94	111.22	15.15	16.03	0.0778	0.0182
[emim][Ser]	23.02	105.74	15.07	15.78	0.0748	0.0178
[emim][Thr]	28.13	81.33	15.11	14.78	0.0658	0.0174
[emim][Asp]	26.83	103.10	14.23	15.49	0.0741	0.0174
[emim][Glu]	22.90	109.21	14.90	15.91	0.0765	0.0180
[emim][Lys]	23.32	117.04	15.28	16.58	0.0807	0.0187
[emim][Arg]	22.52	109.92	15.28	16.03	0.0773	0.0183
[emim][Phe]	23.86	113.02	15.03	16.58	0.0780	0.0183
[emim][Tyr]	23.15	100.76	14.86	15.28	0.0724	0.0175
[emim][His]	21.35	94.31	12.89	13.69	0.0703	0.0166
[emim][Trp]	25.16	118.80	14.82	15.74	0.0806	0.0180
[emim][Pro]	25.41	122.23	15.03	16.20	0.0820	0.0183

[a] σ^* denotes the formally empty antibonding orbital, lp denotes the occupied lone pairs. The labels of atoms refer to those used in Scheme 1. [b] The electron occupation differences of C−H antibonding orbital of ion paris relative to that of isolated [emim]$^+$.

amino acid ILs the average amount of transferred charges (about 0.12*e*) is not large relative to that for typical ILs. The computed charge transfers for [bmim]Cl[49] and [mmim]Cl[50] are 0.16 and 0.22*e*, respectively. Although the changes in charge on any individual atom and transferred charges between cation and anion are small, the combined effect is more significant. The dipole moments of the gas-phase ion pairs of AAILs are large and vary between 10.5 and 16.6 D, as listed in Table 5. However, in the liquid phase anions will surround each cation, and hence some of these polarization effects are likely to cancel each other out, and T_g will decrease.[49]

Table 6 presents the stabilization energy $E(2)$ calculated at the B3LYP/6-311+G(d,p) level for each donor NBO of the [AA]$^-$ and acceptor NBO of the [emim]$^+$. Obviously, for all 20 AAILs, the lp(O) → σ^*(C2−H) orbital interactions between the carbonyl O lone pairs and the C2−H antibonding orbital are seen to give the strongest stabilization. Correspondingly, the electron transfers mainly from the lp(O) of [AA]$^-$ to the σ^*(C2−H) of [emim]$^+$, as listed in Table 6, which is in agreement with the results by Mou et al.[26] Furthermore, there is a rough correlation between the lp(O) → σ^*(C2−H) orbital interaction and intermolecular H-bonded interaction; that is to say, the less the orbital interaction energy is, the smaller the absolute value of H-bonded energy between ions would be, as presented in Tables 4 and 6.

The electronic density ρ_c, its Laplacians $\nabla^2\rho_c$, and total energy density H_c are calculated by AIM2000 using the optimized results at the B3LYP/6-311+G(d,p) level. As listed in Table 7, the calculated results indicate that the values of ρ_c of all 20 AAILs are large, about 0.05 for C2−H···O and 0.02 for C6−H···O, respectively. Especially for the C2−H···O interaction, the electronic density ρ_c is about 0.01 more than the maximal typical H-bond value (0.002−0.04). This is obviously attributed to the most acidic C2−H in [emim]$^+$ and the more negative charges of carbonyl O atoms in [AA]$^-$. Moreover, the calculated values of $\nabla^2\rho_c$ are positive, indicating that the C−H···O interactions of AAILs have the electrostatic character. Additionally, the H_c values of the C2−H···O are all negative, suggesting that the C2−H···O interactions have some covalent character. At the same time, all the H_c values of the C6−H···O are positive, indicating the dominant electrostatic character.

TABLE 7: Electron Densities ρ_c (e/a_0^3), Laplacians $\nabla^2\rho_c$ (e/a_0^5), and Energy Densities H_c (a.u.) of 20 Kinds of AAIL Ion Pairs within the AIM Theory[a]

	O1···C2−H			O2···C6−H		
	ρ_c	$\nabla^2\rho_c$	H_c	ρ_c	$\nabla^2\rho_c$	H_c
[emim][Gly]	0.0571	0.1348	−0.0100	0.0222	0.0761	0.0022
[emim][Ala]	0.0560	0.1339	−0.0094	0.0222	0.0763	0.0022
[emim][Val]	0.0543	0.1326	−0.0085	0.0222	0.0769	0.0023
[emim][Leu]	0.0541	0.1321	−0.0083	0.0223	0.0770	0.0023
[emim][Ile]	0.0554	0.1340	−0.0090	0.0220	0.0756	0.0022
[emim][Asn]	0.0526	0.1335	−0.0074	0.0209	0.0710	0.0022
[emim][Gln]	0.0505	0.1308	−0.0063	0.0211	0.0725	0.0022
[emim][Cys]	0.0550	0.1367	−0.0086	0.0205	0.0693	0.0021
[emim][Met]	0.0518	0.1306	−0.0071	0.0220	0.0762	0.0023
[emim][Ser]	0.0509	0.1308	−0.0066	0.0218	0.0761	0.0023
[emim][Thr]	0.0549	0.1587	−0.0074	0.0199	0.0640	0.0019
[emim][Asp]	0.0512	0.1324	−0.0066	0.0213	0.0735	0.0023
[emim][Glu]	0.0511	0.1304	−0.0067	0.0218	0.0754	0.0023
[emim][Lys]	0.0534	0.1316	−0.0080	0.0221	0.0764	0.0023
[emim][Arg]	0.0514	0.1300	−0.0069	0.0220	0.0765	0.0023
[emim][Phe]	0.0524	0.1317	−0.0074	0.0221	0.0766	0.0023
[emim][Tyr]	0.0497	0.1306	−0.0059	0.0217	0.0753	0.0023
[emim][His]	0.0486	0.1294	−0.0053	0.0212	0.0731	0.0023
[emim][Trp]	0.0543	0.1336	−0.0083	0.0217	0.0745	0.0022
[emim][Pro]	0.0553	0.1341	−0.0089	0.0218	0.0752	0.0022

[a] The labels of atoms refer to those used in Scheme 1.

IV. Conclusions

By a systematic study of the gas-phase ion pairs of amino acid anion based ILs, [emim][AA], some new insights into the structure, interaction energy, H-bond nature, and the factors contributing to the experimental T_g were revealed from the DFT/B3LYP calculations with 6-311+G(d,p) basis set. Here, the [emim][AA] ILs were formed by coupling the imidazolium cation [emim]$^+$ with 20 kinds of natural amino acid anions, [AA]$^-$.

All the ion pairs of [emim][AA] can form strong H-bond interactions, which are dominated by the side-chain structure and the functional group of amino acid anions. The calculations indicate that an increase of the alkyl side-chain length produces a decrease of H-bond energy, while the functional groups lead to the different localized charges on the anion, consequently affecting the electrostatic force. In addition, the intramolecular H bond in amino acid anions can weaken the interaction, due to the decrease of the proton-accepting ability of carbonyl O atom. The H-bond chemical nature of [emim][AA] is investigated by atoms in molecules (AIM) and natural bond orbital (NBO) analyses. The preliminary analysis of 20 kinds of [emim][AA] ion pairs provides some initial factors contributing to the T_g of AAILs: the anion−cation electrostatic attractions, van der Waals repulsions of the alkyl chains on the amino acid anions, 3D network of H bonds, and intermolecular $\pi-\pi$ interactions. How factors such as those are interplayed to affect the properties of AAILs, in terms of local packing, ionic motion, and cohesive energy, should be interesting subjects for further studies.

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Supporting Information Available: Three tables listing the selected bond distances (Å), bond angles (deg), and dihedral angles (D, deg) of $[\text{emim}]^+$ cation in 20 kinds of AAIL ion pairs and the corresponding isolated $[\text{emim}]^+$, the selected bond distances (Å) and bond angles (deg) of amino acid anions in 20 kinds of AAIL ion pairs and the corresponding isolated $[\text{AA}]^-$, and selected partial charges q (e) from an NPA analysis of isolated cation $[\text{emim}]^+$ and 20 kinds of amino acid anions $[\text{AA}]^-$. All calculations have been performed by the B3LYP/6-311+G(d,p) method. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, *13*, 965.
(2) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 5962.
(3) Bao, W. L.; Wang, Z. M.; Li, Y. X. *J. Org. Chem.* **2003**, *68*, 591.
(4) Huang, J.; Jiang, T.; Gao, H. X.; Han, B. X.; Liu, Z. M.; Wu, W. Z.; Chang, Y. H.; Zhao, G. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 1397.
(5) Dai, L. Y.; Yu, S. Y.; Shan, Y. K.; He, M. Y. *Eur. J. Inorg. Chem.* **2004**, *2*, 237.
(6) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
(7) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierbicki, A.; Davis, J. H., Jr.; Rogers, R. D. *Chem. Commun.* **2001**, *1*, 135.
(8) Yoshizawa, M.; Narita, A.; Ohno, H. *Aust. J. Chem.* **2004**, *57*, 139.
(9) Holbrey, J. D.; Seddon, K. R. *Clean Products Processes* **1999**, *1*, 223.
(10) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.
(11) Avalos, M. R.; Babiano, R.; Cintas, P.; Jiménez, J. L.; Palacios, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 3904.
(12) Fukumoto, K.; Yoshizawa, M.; Ohno, H. *J. Am. Chem. Soc.* **2005**, *127*, 2398.
(13) Kagimoto, J.; Fukumoto, K.; Ohno, H. *Chem. Commun.* **2006**, *21*, 2254.
(14) Fukumoto, K.; Ohno, H. *Chem. Commun.* **2006**, *29*, 3081.
(15) Fukumoto, K.; Kohno, Y.; Ohno, H. *Chem. Lett.* **2006**, *35*, 1252.
(16) Ohno, H.; Fukumoto, K. *Acc. Chem. Res.* **2007**, *40*, 1122.
(17) Ohno, H. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1665.
(18) Fukumoto, K.; Ohno, H. *Angew. Chem., Int. Ed.* **2007**, *49*, 1852.
(19) Minami, I.; Watanabe, N.; Nanao, H.; Mori, S.; Fukumoto, K.; Ohno, H. *Chem. Lett.* **2008**, *37*, 300.
(20) Tao, G. H.; He, L.; Sun, N.; Kou, Y. *Chem. Commun.* **2005**, *28*, 3562.
(21) Tao, G. H.; He, L.; Liu, W. S.; Xu, L.; Xiong, W.; Wang, T.; Kou, Y. *Green Chem.* **2006**, *8*, 639.
(22) Brégeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A. -C. *Amino Acids* **2008**, *35*, 175.
(23) Gao, H. S.; Hu, Z. G.; Wang, J. J.; Qiu, Z. F.; Fan, F. Q. *Aus. J. Chem.* **2008**, *61*, 521.
(24) Jiang, Y. Y.; Wang, G. N.; Zhou, Z.; Wu, Y. T.; Geng, J.; Zhang, Z. B. *Chem. Commun.* **2008**, *4*, 505.
(25) Ni, B. K.; Garre, S.; Headley, A. D. *Tetrahedron Lett.* **2007**, *48*, 1999.
(26) Mou, Z. X.; Li, P.; Wang, W.; Shi, J.; Song, R. *J. Phys. Chem. B* **2008**, *112*, 5088.
(27) Rong, H.; Li, W.; Chen, Z. Y.; Wu, X. M. *J. Phys. Chem. B* **2008**, *112*, 1451.
(28) Li, W.; Qi, C. S.; Wu, X. M.; Rong, H.; Gong, L. F. *J. Mol. Struct.: THEOCHEM* **2008**, *855*, 34.
(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *GAUSSIAN 03, revision a.1*, Gaussian, Inc.: Pittsburgh, PA, 2003.
(30) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(31) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(32) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.
(33) Arnold, W. D.; Oldfield, E. *J. Am. Chem. Soc.* **2000**, *122*, 12835.
(34) Biegler-Koning, F.; Schoenbohm, J. *AIM2000, 2.0 ed.*; Buro fur lnnovative software: Bielefeld, Germany, 2002.
(35) Dupont, J. *J. Braz. Chem. Soc.* **2004**, *15*, 341.
(36) Hardacre, C.; Holbrey, J. D.; McMath, S. E.; Bowron, D. T.; Soper, A. K. *J. Chem. Phys.* **2003**, *118*, 273.
(37) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Johnston, S.; Seddon, K. R.; Rogers, R. D. *Chem. Commun.* **2003**, *14*, 1636.
(38) Gutowski, K. E.; Holbrey, J. D.; Wogers, R. D.; Dixon, D. A. *J. Phys. Chem. B* **2005**, *109*, 23196.
(39) Urahata, S.; Riberiro, M. *J. Chem. Phys.* **2004**, *120*, 1855.
(40) Liu, Z.; Huang, S.; Wang, W. *J. Phys. Chem. B* **2004**, *108*, 12978.
(41) Del Popolo, M. G.; Lynden-Bell, R. M.; Kohanoff, J. *J. Phys. Chem. B* **2005**, *109*, 5895.
(42) Hunt, P. A.; Gould, I. R. *J. Phys. Chem. A* **2006**, *110*, 2269.
(43) Wang, Y.; Li, H.; Han, S. *J. Chem. Phys.* **2005**, *123*, 174501.
(44) Wang, Y.; Li, H.; Han, S. *J. Chem. Phys.* **2006**, *124*, 044504.
(45) Dong, K.; Zhang, S. J.; Wang, D.; Yao, X. Q. *J. Phys. Chem. A* **2006**, *110*, 9775.
(46) Turner, E. A.; Pye, C. C.; Singer, R. D. *J. Phys. Chem. A* **2003**, *107*, 2277.
(47) Mele, A.; Tran, C. D.; De Paoli Lacerda, S. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4364.
(48) Del Popolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 1744.
(49) Hunt, P. A.; Kirchner, B.; Welton, T. *Chem.−Eur. J.* **2006**, *12*, 6762.
(50) Bühl, M.; Chaumont, A.; Schurhammer, R.; Wipff, G. *J. Phys. Chem. A* **2005**, *109*, 18591.

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