Acid-base thermochemistry of gaseous aliphatic α-aminoacids.

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Supplementary Informations

Tables S1-S6: Total (Hartree) and relative (kJ/mol) $H°_0$, $H°_{298}$ and $G°_{298}$ calculated at the B3LYP/6-31G(d)// B3LYP/6-31G(d) and G3MP2B3 levels for the investigated conformers of **AAA**, **AAAH**$^+$ and **[AAA-H]**$^-$ (**AAA**= Gly, Ala, Val, Leu, Ile, Pro).

Figures S1-S6: B3LYP/6-31G(d) optimized geometries of the most stable conformers of **AAA**, **AAAH**$^+$ and **[AAA-H]**$^-$ (**AAA**= Gly, Ala, Val, Leu, Ile, Pro).

Table S1. Relative energies (kJ/mol) calculated for neutral, protonated and deprotonated glycine conformers[a,b,c].

Species	B3LYP/6-31G(d) $H°_0$	G3MP2B3 H^0_0	G3MP2B3 H^0_{298}	G3MP2B3 G^0_{298}
GlyI	0	0	0	0
GlyII	2.8	4.9	4.0	6.7
GlyIII	6.9	7.2	7.2	6.2
GlyIV	8.0	4.7	4.5	5.5
GlyHI	0	0	0	0
GlyHII	21.3	18.5	19.4	17.1
GlyI-H	0	0	0	0

a) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for the reference species **GlyI** are -284. , -284.066290 , -284.059608 and -284.09551 Hartree, respectively.
b) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for the reference species **GlyHI** are -284. , -284.401955 , -284.395330 and -284.431134 Hartree, respectively.
c) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for the reference species **GlyI-H** are -283.850794 , -283.521668, -283.515415 and -283.550125 Hartree, respectively.

Table S2. Relative energies (kJ/mol) calculated for neutral, protonated and deprotonated alanine conformers[a,b,c].

Species	B3LYP/6-31G(d) $H°_0$	G3MP2B3 H^0_0	G3MP2B3 H^0_{298}	G3MP2B3 G^0_{298}
AlaI	0	0	0	0
AlaII$_A$	0.4	2.7	1.9	4.3
AlaII$_B$	-1.3	3.8	2.8	5.8
AlaIII	6.1	6.3	6.2	4.5
AlaIV$_A$	8.1	4.8	4.6	5.7
AlaIV$_B$	6.7	4.4	4.2	5.1
AlaHI	0	0	0	0
AlaHII	17.4	15.8	16.2	15.1
AlaI-H$_A$	0	0	0	0
AlaI-H$_B$	-1.9	0.3	0.1	0.6

a) B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **AlaI** are -323.739642, -323.306690 , -323.298659 and -323.337793 in Hartree, respectively.
b) B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **AlaHI** are -324.103576, -323.647935 , -323.639932 and -323.679014 in Hartree, respectively.
c) B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **AlaI-H$_A$** are -323.168506, -322.763104 , -322.755457 and -322.793612 in Hartree, respectively.

Table S3. Relative energies (kJ/mol) calculated for neutral, protonated and deprotonated valine conformers[a,b,c].

Species[c]	B3LYP/6-31G(d) $H°_0$	G3MP2B3 H^0_0	G3MP2B3 H^0_{298}	G3MP2B3 G^0_{298}
Val-Ig+	2.4	2.8	2.7	2.7
Val-Ia	4.1	4.8	4.5	5.1
Val-Ig-	0	0	0	0
Val-II$_A$g+	5.5	7.9	7.2	6.7
Val-II$_B$g+	4.1	12.2	11.1	13.6
Val-II$_A$a	1.6	4.5	3.5	6.1
Val-II$_B$a	1.7	8.5	7.4	10.4
Val-II$_A$g-	1.2	3.5	3.0	3.1
Val-II$_B$g-	2.3	3.0	1.8	4.7
Val-IIIg+	6.2	4.2	4.4	2.8
Val-IIIa	8.8	9.0	8.8	9.0
Val-IIIg-	6.2	6.4	6.4	5.5
Val-IV$_B$g-[d]	7.0	5.2	5.1	5.6
Val-IV$_B$g+[d]	8.6	7.3	7.1	7.0
Val-IV$_B$a	8.5	4.6	7.4	8.1
Val-IV$_A$a	11.3	8.6	8.4	8.7
Val-HIg+	5.6	6.7	6.5	7.1
Val-HIa	4.2	5.0	4.9	5.5
Val-HIg-	0	0	0	0
Val-I-H$_A$g+	2.2	6.4	6.2	6.8
Val-I-H$_B$g+	6.1	13.7	13.3	13.5
Val-I-H$_A$a	2.5	4.0	3.9	4.3
Val-I-H$_B$a	2.5	8.0	7.4	9.5
Val-I-H$_A$g-	0	0	0	0
Val-I-H$_B$g-	3.6	5.5	5.6	5.5

a) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for the reference species **Val-Ig-** are -402.366851, -401.782527 , -401.771807 and -401.817082 Hartree, respectively.
b) B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **Val-IHg-** are -402.7350683, -402.128723 , -402.117943 and -402.163613 in Hartree, respectively.
c) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for the reference species **Val-I-H$_A$g-** are -401.799526, -401.242019 , -401.231698 and -401.276263 Hartree, respectively.
d) Tentatives of geometry optimization of conformers **Val-IV$_A$g-** and **Val-IV$_A$g+** lead to the corresponding conformers **Val-I**.

Table S4. Relative energies (kJ/mol) calculated for neutral, protonated and deprotonated leucine conformers[a,b].

Species	B3LYP/6-31G(d) $H°_0$	G3MP2B3 H^0_0	G3MP2B3 H^0_{298}	G3MP2B3 G^0_{298}
LeuIg+g+	0	0	0	0
LeuIg+a	5.3	7.1	7.2	6.1
LeuIg+g-	8.0	8.6	8.4	9.3
LeuIag+	8.7	8.1	7.8	9.0
LeuIaa	3.6	2.0	1.8	3.2
LeuIag-	11.9			
LeuIg-g+	9.6			
LeuIg-a	6.5	5.1	4.8	6.5
LeuIg-g-	17.1			
$LeuII_Ag+g+$	$leuII_Bg+g+$			
$LeuII_Bg+g+$	-0.7	4.3	3.2	6.3
$LeuII_Ag+a$	$leuII_Bg+a$			
$LeuII_Bg+a$	4.3	10.8	9.9	11.5
$LeuII_Ag+g-$	$leuII_Bg+g-$			
$LeuII_Bg+g-$	7.1	13.2	12.1	14.6
$LeuII_Aag+$	9.5			
$LeuII_Bag+$	$LeuII_Baa$			
$LeuII_Aaa$	1.1	2.9	1.9	5.3
$LeuII_Baa$	2.5	8.5	7.6	9.2
$LeuII_Aag-$	11.4			
$LeuII_Bag-$	15.5			
$LeuII_Ag-g+$	7.6			
$LeuII_Bg-g+$	6.8	9.2	7.9	12.1
$LeuII_Ag-a$	$LeuII_Bg-a$			
$LeuII_Bg-a$	3.5	6.5	5.0	10.7
$LeuII_Ag-g-$	14.7			
$LeuII_Bg-g-$	15.2			
LeuIIIg+g+	6.1	5.7	5.7	4.3
LeuIIIg+a	11.0			
LeuIIIg+g-	13.6			
LeuIIIag+	11.5			
LeuIIIaa	6.9			
LeuIIIag-	14.6			
LeuIIIg-g+	15.9			
LeuIIIg-a	11.1			
LeuIIIg-g-	22.1			

LeuIV$_B$g+g+[d]	8.5	5.6	5.4	6.3
LeuIV$_B$g+a[d]	15.5			
LeuIV$_B$aa[d]	8.8	5.5	5.2	7.1
LeuHIg+g+	0	0	0	0
LeuHIg+a	2.5	2.1	1.7	3.4
LeuHIg+g-	4.0	3.9	3.3	5.7
LeuHIag+	14.1			
LeuHIaa	5.0	4.7	4.6	5.5
LeuHIag-	16.8			
LeuHIg-g+	3.6	2.4	1.7	5.1
LeuHIg-a	4.5	3.9	3.3	6.7
LeuHIg-g-	10.7			
LeuI-H$_A$g+g+	4.1	1.7	2.4	-0.9
LeuI-H$_B$g+g+	4.5	3.3	3.8	0.6
LeuI-H$_A$aa	0	0	0	0
LeuI-H$_B$aa	3.2	4.2	4.6	2.9
LeuI-H$_A$g+a	6.1	8.1	8.7	5.7
LeuI-H$_B$g+a	3.4	7.3	7.3	6.6
LeuI-H$_A$g-a	3.7	4.3	4.3	4.1
LeuI-H$_B$g-a	6.8	5.7	5.6	6.1
LeuI-H$_A$g-g+	8.4	5.4	5.5	5.1
LeuI-H$_B$g-g+	7.9	6.5	6.4	6.8

a) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **LeuIg+g+** are: -441.680569, -441.018820 , -441.006717 and -441.056100 Hartree, respectively.
b) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **LeuHIg+g+** are: -442.04913328, -441.365309 , -441.353185 and -441.402486 Hartree, respectively.
c) Total B3LYP/6-31G(d) $H°_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **LeuI-H$_A$aa** are: -441.113766, -440.478066 , -440.466561 and -440.513862 Hartree, respectively.
d) Tentatives of geometry optimization of conformers **LeuIV$_A$xx** lead to the corresponding conformers **LeuIxx** (only xx=aa, g+g+ and g+a were considered since the relative energies of the other conformers are expected to be higher than 10 kJ/mol in view of the relative energies of the corresponding **LeuIxx** C-N rotamers).

Table S5. Relative energies (kJ/mol) calculated for neutral, protonated and deprotonated isoleucine conformers[a,b].

Species	B3LYP/6-31G(d) $H°_0$	G3MP2B3 H^0_0	G3MP2B3 H^0_{298}	G3MP2B3 G^0_{298}
IleIg+g+	7.0	4.3	4.3	4.6
IleIg+a	4.5	2.7	2.5	2.9
IleIg+g-	11.0			
IleIag+	15.7			
IleIaa	6.3	4.8	4.4	5.6

IleIag-	5.5	3.4	2.8	5.2
IleIg-g+	11.6			
IleIg-a	2.4	0	0	0
IleIg-g-	5.8	3.6	3.3	4.7
IleII_Ag+g+	10.1			
IleII_Bg+g+	9.2			
IleII_Ag+a	8.6			
IleII_Bg+a	7.6	13.9	12.5	15.8
IleII_Ag+g-	15.5			
IleII_Bg+g-	14.2			
IleII_Aag+	14.1			
IleII_Bag+	15.7			
IleII_Aaa	3.6	4.6	3.4	6.9
IleII_Baa	3.2	8.1	6.8	10.6
IleII_Aag-	2.3	3.4	2.0	6.3
IleII_Bag-	3.5	7.4	6.2	9.0
IleII_Ag-g+	IleII_Bg-g+			
IleII_Bg-g+	8.9			
IleII_Ag-a	IleII_Bg-a			
IleII_Bg-a	0	2.2	1.2	4.0
IleII_Ag-g-	IleII_Bg-g-			
IleII_Bg-g-	2.2	3.7	2.2	7.4
IleIIIg+g+	7.0	6.3	6.2	5.2
IleIIIg+a	8.2	4.3	4.3	3.5
IleIIIg+g-	11.0			
IleIIIag+	15.7			
IleIIIaa	11.2			
IleIIIag-	9.6			
IleIIIg-g+	18.3			
IleIIIg-a	8.4	6.0	5.9	5.4
IleIIIg-g-	10.0			
Ile-IV_Ag-a[d]	Ile-Ig-a			
Ile-IV_Bg-a	9.5	5.7	5.5	6.2
Ile-IV_Ag+a	20.8	17.6	17.0	17.1
Ile-IV_Bg+a	11.7	7.6	7.7	6.7
Ile-IV_Aag-	14.3	8.4	8.3	7.4
Ile-IV_Bag-	10.7	7.1	6.6	8.9

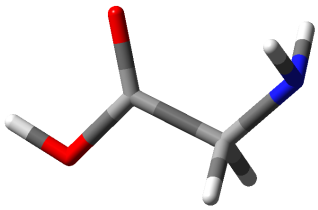
IleHIg+g+	7.7	8.5	8.2	8.2
IleHIg+a	6.8	7.5	7.5	7.3
IleHIg+g-	12.4			
IleHIg-g+	4.8	4.4	4.0	5.4
IleHIg-a	0.0	0	0	0
IleHIg-g-	3.1	3.8	3.1	5.5
IleHIag+	17.6			
IleHIaa	4.7	5.8	5.8	5.7
IleHIag-	3.6	3.9	3.9	4.0
IleI-H_Ag-a	0	0	0	0
IleI-H_Bg-a	6.3	5.2	5.2	4.9
IleI-H_Ag+a	2.4	6.0	6.1	5.3
IleI-HB_Ag+a	7.5	14.7	14.7	13.0
IleI-H_Aa g-	-2.5	0.8	0.2	2.9
IleI-H_Ba g-	2.5	5.3	4.7	7.3

a) Total B3LYP/6-31G(d) H°$_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **IleIg-a** are: -441. 679798 (for **IleIIg-a**), -441.018097 , -441.005933 and -441.055026 Hartree, respectively.
b) Total B3LYP/6-31G(d) H°$_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **IleHIg-a** are: -442.048557, -441.365870 , -441.353732 and -441.402613 Hartree, respectively.
c) Total B3LYP/6-31G(d) H°$_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **IleI-H_Ag-a** are: -441.112350, -440.477772 , -440.466128 and -440.513909 Hartree, respectively.
d) converges on the IleIBxxx conformer.

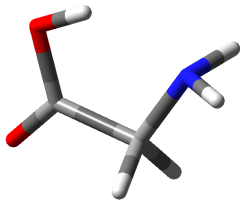
Table S6. Relative energies (kJ/mol) calculated for neutral, protonated and deprotonated proline conformers[a,b].

Species	B3LYP/6-31G(d) H°$_0$	G3MP2B3 H^0_0	G3MP2B3 H^0_{298}	G3MP2B3 G^0_{298}
ProII^{4}E(*endo-C4*)	0	0	0	0
ProII E$_4$(*exo-C4*)	2.7	3.0	3.2	1.6
ProIV^{4}E(*endo-C4*)	6.4	5.3	6.1	3.5
ProIV^{5}E(*endo-C5*)	6.2	5.3	6.3	2.4
ProH^{4}E*(endo-C4)*	0	0	0	0
ProH E$_4$*(exo-C4)*	2.0	2.6	2.9	2.0
ProII-H^{4}E*(endo-C4)*	0	0	0	0
ProII-H ^{5}E*(endo-C5)*	4.9	4.2	4.4	3.4
ProII-H ^{1}E*(endo-N)*	30.0	23.7	24.4	22.4

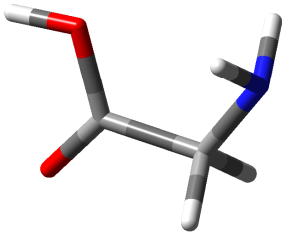
a) Total B3LYP/6-31G(d) H°$_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **ProIIendo** are: -401. 008800, -400.581392 , -400.573053 and -400.613686 Hartree, respectively.
b) Total B3LYP/6-31G(d) H°$_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **ProHIendo** are: -401.371706, -400.937781 , -400.929238 and -400.970206 Hartree, respectively.
c) Total B3LYP/6-31G(d) H°$_0$, G3MP2B3 enthalpy H^0_0, H^0_{298} and free energy G^0_{298} for reference species **ProII-H^{4}E** are: -400.585949, -400.039890 , -400.031691 and -400.072029 Hartree, respectively.



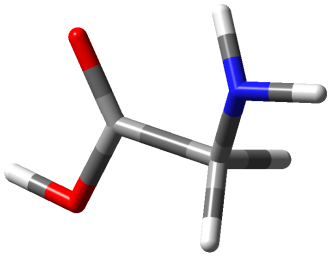
GlyI



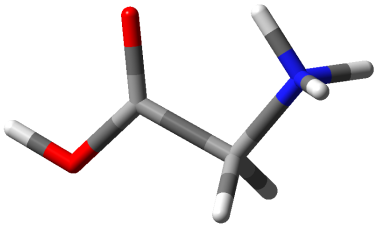
GlyII



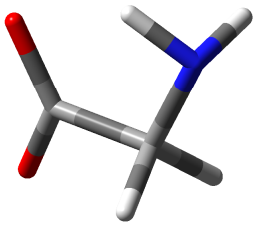
GlyIII



GlyIV

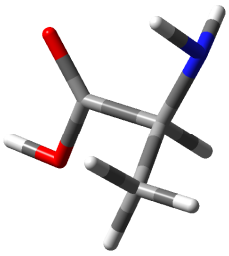


GlyHI

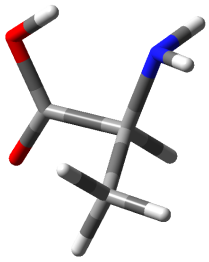


Gly-H

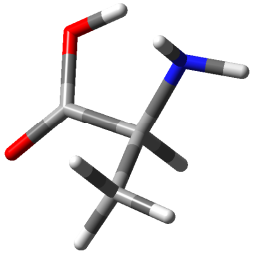
Figure S1. Most stable conformers of neutral, protonated and deprotonated glycine.



AlaI



AlaII$_A$



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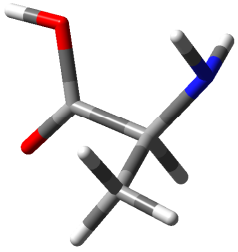
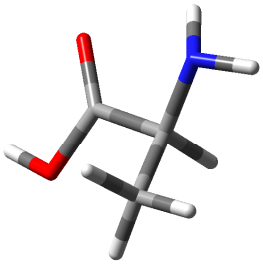
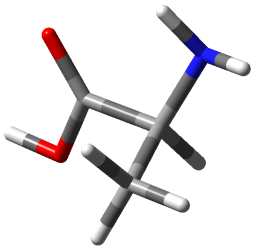


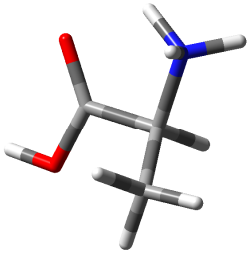
AlaIII



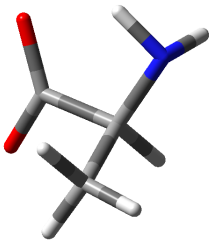
AlaIV$_A$



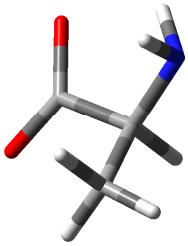
AlaIV$_B$



AlaHI

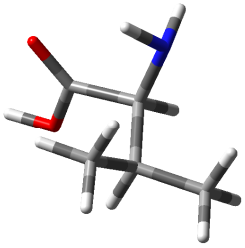


Ala-H_A

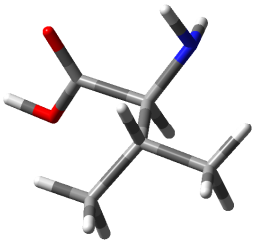


Ala-H_B

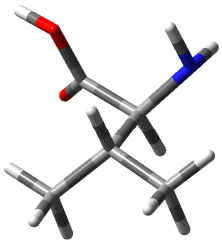
Figure S2. Most stable conformers of neutral, protonated and deprotonated alanine.



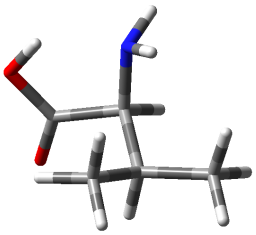
ValIg-



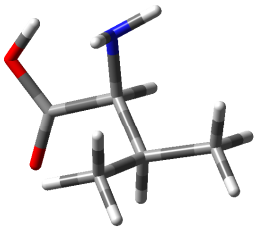
ValIg+



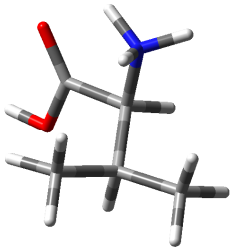
ValIIIg+



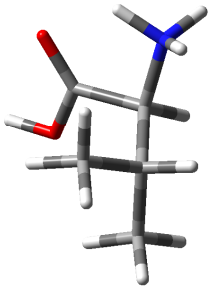
ValII$_A$g-



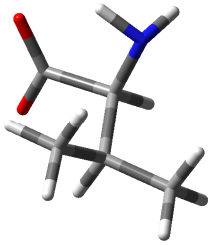
ValII$_B$g-



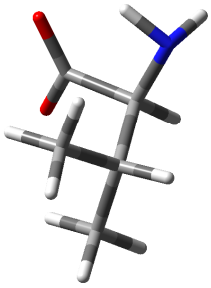
ValHIg-



ValHIa

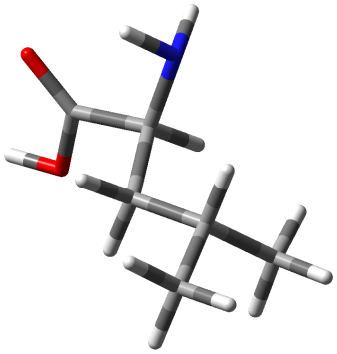


Val H_Ag-

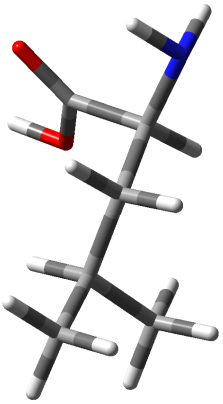


Val H_Aa

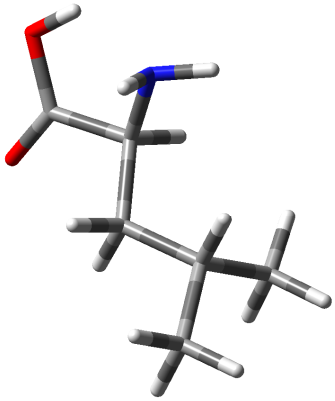
Figure S3. Most stable conformers of neutral, protonated and deprotonated valine.



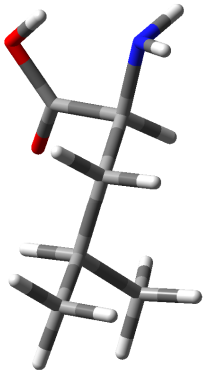
LeuIg+g+



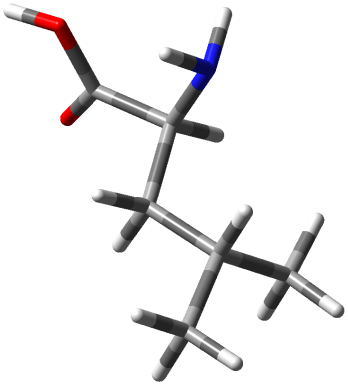
LeuIaa



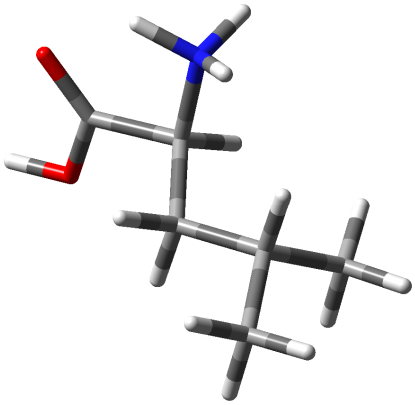
LeuII$_B$g+g+



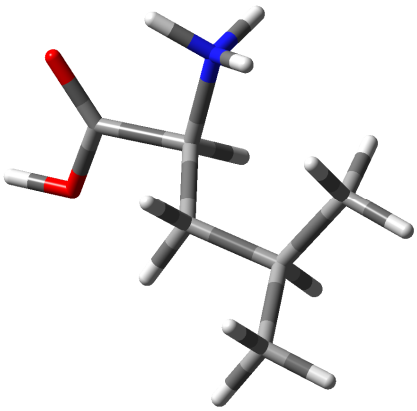
LeuII$_A$aa



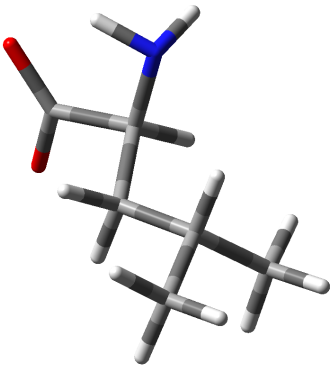
LeuIIIg+g+



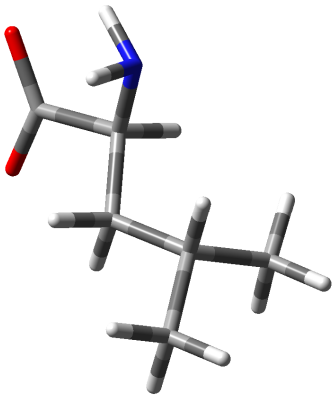
LeuHIg+g+



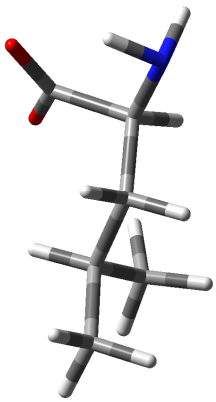
LeuHIg+a



Leu-H_Ag+g+

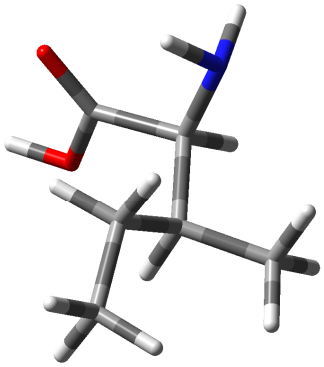


Leu-H_Bg+g+

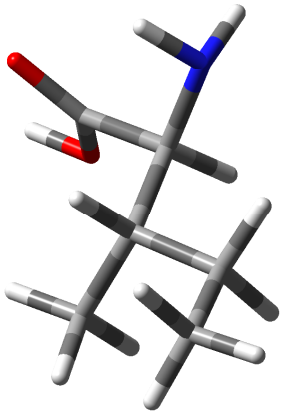


Leu-$H_A$aa

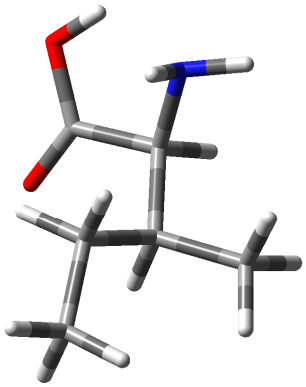
Figure S4. Mosts stable conformers of neutral, protonated and deprotonated leucine.



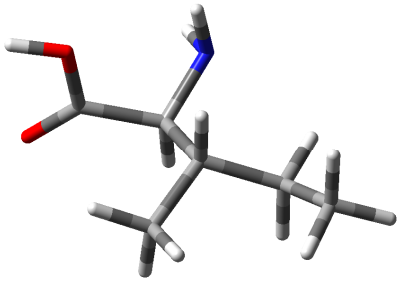
IleIg-a



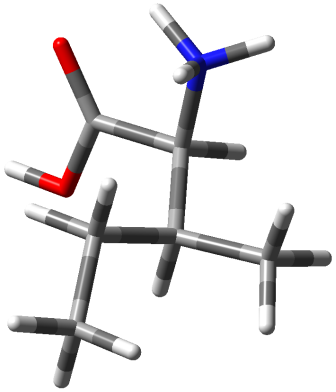
IleIg+a



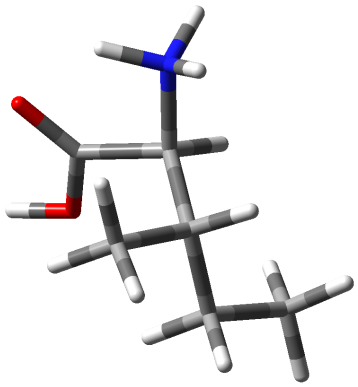
IleII$_B$g-a



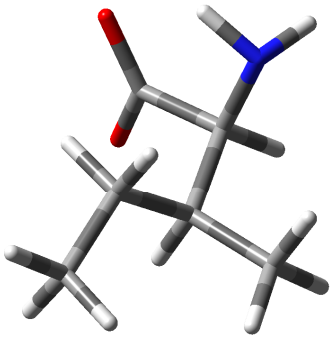
IleIIIg+a



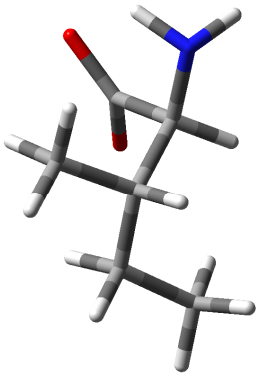
IleHIg-a



IleHIag-

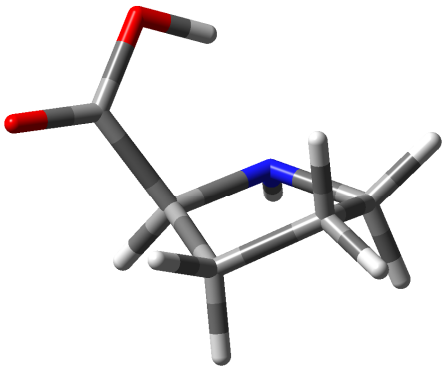


Ile-H_Ag-a

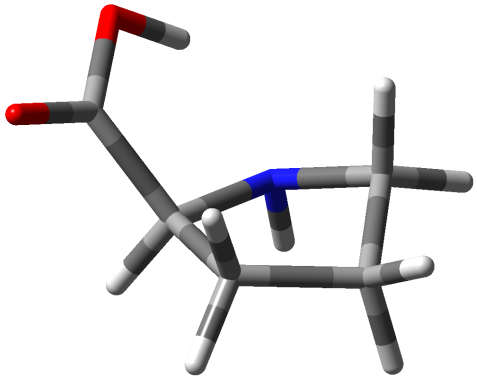


Ile-$H_A$ag-

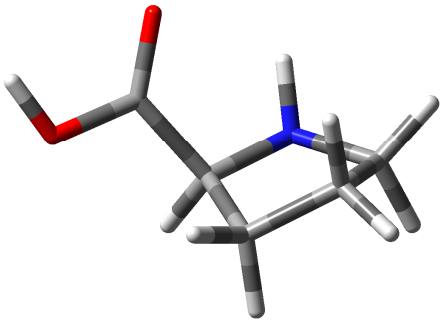
Figure S5. Most stable conformers of neutral, protonated and deprotonated isoleucine.



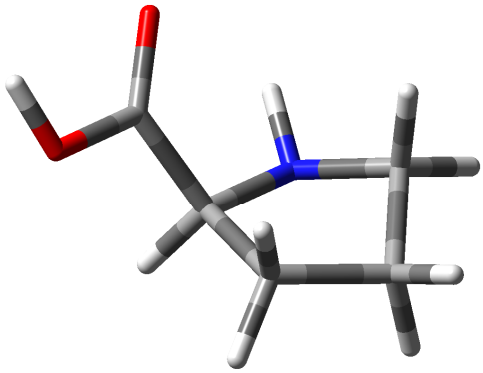
ProII^{4}E



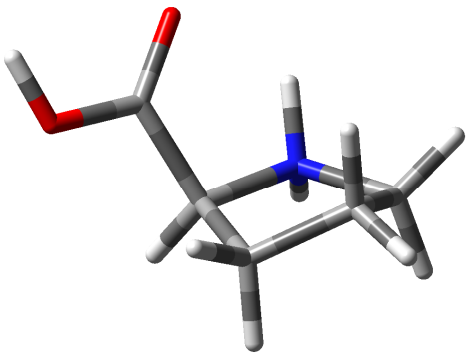
ProIIE$_{4}$



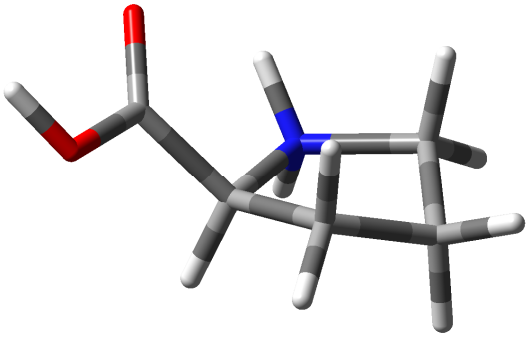
ProIV^{4}E



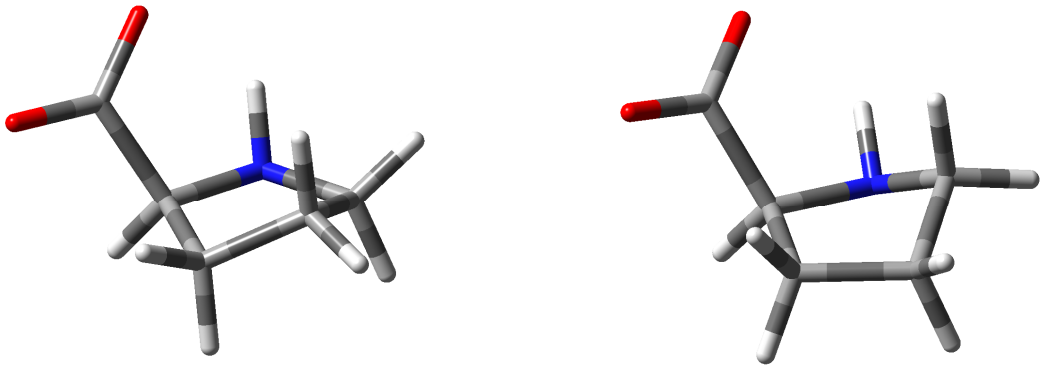
ProIV^{5}E



ProH^{4}E



ProHE$_{4}$



Pro-H^{4}E **Pro-H^{5}E**

Figure S6. Most stable conformations of neutral, protonated and deprotonated proline.