Assessing the impact of anion-π effects on phenylalanine ion formation using IRMPD spectroscopy

Michael Burt, Kathleen Wilson, Rick Marta, Moaraj Hasan, W. Scott Hopkins and Terry McMahon

Supplementary Information

1. Optimized Structures. Figures S1a-g show larger versions of the optimized structures discussed in the article as well as the bond lengths (in Å) of any predicted anion-hydrogen or intramolecular hydrogen bonds. These minima were identified from candidate ions using B3LYP/6-311++G(d,p) density functional theory as implemented by Gaussian 09 (Revision C.01).[1]

2. $(PheF_5\text{-}HF)^-$ Carbene and Indolecarboxylate Comparison. Figure 3 demonstrates that the sequential removal of HCl and HF from chloride-bound pentafluorophenylalanine results in an indolecarboxylate structure that is 0.9 kJ/mol higher in energy than the most stable $PheF_5Cl^-$ isomer. It is also conceivable that a carbene isomer could be formed, but Figure S2 indicates that the lowest energy structure for this product is 130.0 kJ/mol less stable than the indolecarboxylate structure. It is therefore unlikely that it exists in the gas phase.

3. HCl, HF, and H_2 Thermochemistry. Table S1 lists the B3LYP/6-311++G(d,p), MP2(full)/6-311++G(2d,2p)//B3LYP/6-311++G(d,p), and MP2(full)/aug-cc-pVTZ//B3LYP/6-311++G(d,p) thermochemistry determined for HCl, HF, and H_2. These data were used to balance the reaction in Figure 3.

Table S1 Thermochemical information for HCl, HF, and H_2

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hcl
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B3LYP/6-311++G(d,p) optimization and frequency results:

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Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
Cl                -2.24824   1.13583   0.0
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H	-3.53824	1.13583	0.0

Zero-point correction= 0.006670 (Hartree/Particle)
Thermal correction to Energy= 0.009030
Thermal correction to Enthalpy= 0.009974
Thermal correction to Gibbs Free Energy= -0.011219
Sum of electronic and zero-point Energies= -460.827349
Sum of electronic and thermal Energies= -460.824989
Sum of electronic and thermal Enthalpies= -460.824045
Sum of electronic and thermal Free Energies= -460.845238

Single-point energies:
MP2(full)/6-311++G(2d,2p)// B3LYP/6-311++G(d,p) = -460.3284617
MP2(full)/aug-cc-pVTZ//B3LYP/6-311++G(d,p) = -460.3509096

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hf
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B3LYP/6-311++G(d,p) optimization and frequency results:
Charge = 0 Multiplicity = 1
Symbolic Z-Matrix:

F	-2.06089	0.7377	0.0
H	-2.94089	0.7377	0.0

Zero-point correction= 0.009331 (Hartree/Particle)
Thermal correction to Energy= 0.011691
Thermal correction to Enthalpy= 0.012636
Thermal correction to Gibbs Free Energy= -0.007076
Sum of electronic and zero-point Energies= -100.473052
Sum of electronic and thermal Energies= -100.470692
Sum of electronic and thermal Enthalpies= -100.469748
Sum of electronic and thermal Free Energies= -100.489459

Single-point energies:
MP2(full)/6-311++G(2d,2p)// B3LYP/6-311++G(d,p) = -100.3244775
MP2(full)/aug-cc-pVTZ//B3LYP/6-311++G(d,p) = -100.355065

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h_2
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B3LYP/6-311++G(d,p) optimization and frequency results:
Charge = 0 Multiplicity = 1
Symbolic Z-Matrix:

H	0.01134	2.49412	-0.03265
H	0.61134	2.49412	-0.03265

Zero-point correction= 0.010065 (Hartree/Particle)
Thermal correction to Energy= 0.012426
Thermal correction to Enthalpy= 0.013370
Thermal correction to Gibbs Free Energy= -0.001426
Sum of electronic and zero-point Energies= -1.169506
Sum of electronic and thermal Energies= -1.167146
Sum of electronic and thermal Enthalpies= -1.166202
Sum of electronic and thermal Free Energies= -1.180997

Single-point energies:
MP2(full)/6-311++G(2d,2p)// B3LYP/6-311++G(d,p) = -1.1627601
MP2(full)/aug-cc-pVTZ//B3LYP/6-311++G(d,p) = -1.1649922

4. Natural Bond Order Analyses of Phe25F$_2$Cl$^-$ and Phe35F$_2$Cl$^-$. Natural bond order (NBO) analyses were performed on the lowest energy Phe25F$_2$Cl$^-$ and Phe35F$_2$Cl$^-$ ring isomers to investigate the change in their relative stabilities.[2] Atomic charges are reported in Table S2 and correspond with the atoms labeled in Figure S3. Figure S3 also displays relative atomic charges by colouring the atoms in shades of red or green, which correspond to negative and positive charge; red is brightest at -1.000 and darkens as it approaches zero, green behaves the same, but is brightest at 1.000. The NBO results suggest that the aromatic carbons nearest to the chloride are more positive in the case of Phe25F$_2$Cl$^-$. This likely explains why its most stable ring isomer is more favourable than the analogous Phe35F$_2$Cl$^-$ structure.

Table S2 Atomic charges of Phe25F$_2$Cl$^-$ and Phe35F$_2$Cl$^-$ ring isomers.

Atom Label	**Atomic Charge**		
	2,5-A	*2,5-B*	*3,5*
1 (C)	0.401	0.407	-0.267
2 (C)	-0.251	-0.232	0.439
3 (C)	-0.270	-0.250	-0.333
4 (C)	0.395	0.406	0.434
5 (C)	-0.252	-0.237	-0.276
6 (C)	-0.042	-0.073	0.005
7 (C)	-0.402	-0.406	-0.403
8 (H)	0.213	0.218	0.218
9 (H)	0.238	0.207	0.193
10 (C)	-0.137	-0.100	-0.101
11 (H)	0.248	0.195	0.195
12 (C)	-0.859	-0.879	-0.880
13 (H)	0.364	0.398	0.400
14 (H)	0.350	0.342	0.335
15 (C)	0.792	0.800	0.801
16 (O)	-0.721	-0.716	-0.714
17 (H)	0.486	0.499	0.499
18 (O)	-0.663	-0.653	-0.653
19 (F/C)	-0.362	-0.372	0.214
20 (F/C)	0.214	0.214	-0.362
21 (C)	0.212	0.213	0.227
22 (F/C)	-0.370	-0.366	-0.362
23 (C)	0.257	0.227	0.229
24 (Cl)	-0.841	-0.842	-0.839

References

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