ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Ionic liquids containing fluorinated β-diketonate anions: synthesis, characterization and potential applications

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Force field development

Non-bonded interactions are described by a pairwise-additive Lennard–Jones (12-6) plus point charge functional form. The [choline]$^+$ cation was modeled based on the force field parameters developed by Morrow and Maginn.[1] However no force field parameters are available in the literature for the β-diketone anions such as [hfac]$^-$. The Lennard-Jones (L-J) parameters for the different functional groups in [hfac]$^-$ were transferred from analogous groups previously modeled in OPLS-AA and AMBER. While the bonded parameters for [choline]$^+$ cation were obtained from the force field of Morrow and Maginn, the bonded parameters between the different interaction sites in the anion were based on the AMBER harmonic bond stretching and angle bending potential. The dihedral parameters for the different angles were fit to reproduce the energetics of conformational scan obtained from HF/6-31+g(d,p) using Gaussian 09,[2] as shown in Fig. S1. The point charges for the different functional group in [hfac]$^-$ anion were obtained from CHELPG population analysis on an optimized [choline][hfac] geometry performed at the HF level of theory and 6–31+g(d,p) basis set.

The CO_2 molecule was modeled using the three site model developed by Potoff et al.[3] The LJ and partial charges for CO_2 were optimized based on reproduction of vapor liquid coexistence curves and the quadropole moment of CO_2. Partial point charges were centered at each LJ site with an equilibrium C–O bond length of 1.16 Å, and equilibrium O–C–O bond angle of 180° with harmonic potentials governing the conformational dynamics. The Hamiltonian (V_{total}) of the system is given by equation 1.

$$V_{Total} = K_b \left(b - b_O\right)^2 + K_\theta \left(\theta - \theta_O\right)^2 + K_\chi \left[1 + cos\left(n\chi - \delta\right)\right] +$$
$$\varepsilon_{i,j} \left[\left(\frac{R_{min\,i,j}}{r_{i,j}}\right)^{12} - 2\left(\frac{R_{min\,i,j}}{r_{i,j}}\right)^6\right] + \frac{q_i q_j}{r_{i,j}} \tag{1}$$

A list of the non-bonded and bonded parameters for the [hfac]⁻ anion can be found in **Table S1** and **Table S2** respectively.

Table S1. Non-bonded force field parameters and partial charges for the interaction sites within the [hfac]⁻ anion.

| site	ε (kcal/mol)	R_{min} (Å)	Partial charge q (e)
C	−0.0200	2.300	0.53
F	−0.0970	1.600	−0.25
C$_2$/C$_3$	−0.1027	2.106	0.75
C$_4$	−0.0560	2.010	−0.82
O	−0.2079	1.666	−0.67
H	−0.0560	2.010	0.10

Table S2. Bonded force field parameters comprising of harmonic bond stretching, bond angle and torsional cosine series functional form for [hfac]$^-$ anion.

Bond	k_b (kcal/mol)	b_0 (Å)	
C–F	441.9	1.323	
C–C$_2$/ C–C$_3$	250.0	1.520	
C$_2$–C$_4$/ C$_3$–C$_4$	222.50	1.534	
C$_2$–O/ C$_3$–O	700.00	1.215	
C$_4$–H	309.00	1.111	
Angle	K_θ (kcal/mol)	θ_0 (degrees)	
F–C–C$_2$/C$_3$	44.0	112.0	
F–C–F	93.3	107.1	
C–C$_2$–O	75.0	122.0	
C$_2$–C$_4$–H	50.0	109.5	
O–C$_2$–C$_4$	75.0	122.0	
C$_2$-C$_4$-C$_3$	35.0	116.0	
Dihedral Angle	K_χ (kcal/mol)	n (multiplicity)	δ (degrees)
F–C–C$_2$–O	0.2	3	0
F–C–C$_2$–C$_4$	0.2	3	0
C–C$_2$–C$_4$–C$_3$	0.2	3	0
O–C$_2$–C$_4$–C$_3$	0.065	3	180.0
O–C$_2$–C$_4$–H	0.10	3	0

Table S3. Heats of reaction computed at the B3LYP/6-311+g(d,p) level of theory and basis set for the interaction of the [hfac]$^-$ anion with CO_2. (Note: To convert to kcal mol^{-1}, $\Delta G_{rxn} = (\Delta G_{product} - \Delta G_{reactant})*627.50$)

	Reactant [hfac]$^-$ (hartrees)	Reactant CO_2 (hartrees)	Product $CO_2 \cdot$[hfac]$^-$ (hartrees)	ΔG_{rxn} (kcal mol^{-1})
Configuration 1	−940.76353545	−188.59039262	−1129.32586779	17.61
Configuration 2	−940.46353545	−188.59039262	−1129.32962642	4.46

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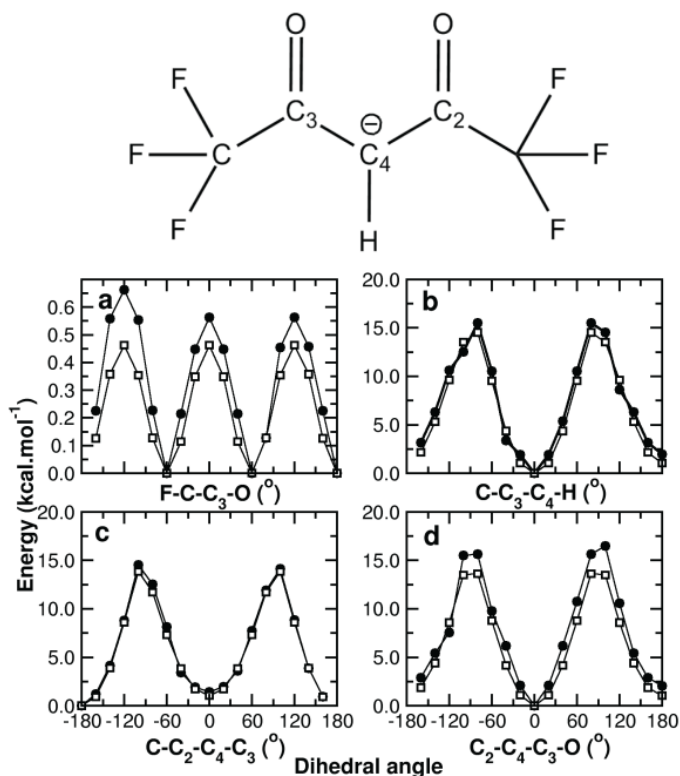
Figure S1. Chemical structure of [hfac]⁻ anion is shown with the different atom names as a means for identifying the different dihedral angles present in the anion. Potential energy scans for the different governing dihedral angles in increments of 20° performed using Gaussian 09 at the HF/6-31+g(d,p) level of theory and basis set. Open squares represent force field predictions in comparison to the filled circles being representative of quantum mechanical energetics corresponding to different dihedral conformations.

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