

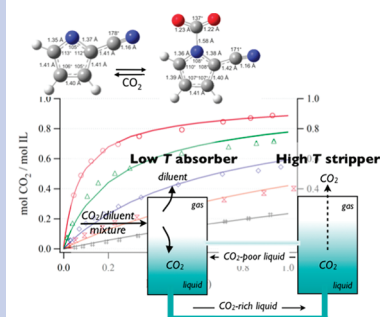
# Molecular Design of High Capacity, Low Viscosity, Chemically Tunable Ionic Liquids for CO<sub>2</sub> Capture

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**ABSTRACT** The discovery of materials that combine selectively, controllably, and reversibly with CO<sub>2</sub> is a key challenge for realizing practical carbon capture from flue gas and other point sources. We report the design of ionic liquids (ILs) with properties tailored to this CO<sub>2</sub> separation problem. Atomistic simulations predict that suitably substituted aprotic heterocyclic anions, or “AHAs,” bind CO<sub>2</sub> with energies that can be controlled over a wide range suitable to gas separations. Further, unlike all previously known CO<sub>2</sub>-binding ILs, the AHA IL viscosity is predicted to be insensitive to CO<sub>2</sub>. Spectroscopic, temperature-dependent absorption, rheological, and calorimetric measurements on trihexyl(tetradecyl)-phosphonium 2-cyanopyrrolide ([P<sub>66614</sub>][2-CNpyr]) show CO<sub>2</sub> uptakes close to prediction as well as insignificant changes in viscosity in the presence of CO<sub>2</sub>. A pyrazolide-based AHA IL behaves qualitatively similarly but with weaker binding energy. The results demonstrate the intrinsic design advantages of ILs as a platform for CO<sub>2</sub> separations.

**SECTION** Atmospheric, Environmental and Green Chemistry



The atmospheric concentration of CO<sub>2</sub> has increased unabated since the dawn of the industrial revolution, due primarily to CO<sub>2</sub> emissions from the combustion of fossil fuels, and this growing carbon burden has significant implications for the global climate.<sup>1</sup> While the development of a carbon-neutral energy infrastructure is the long-term solution to this problem, the increasing world demand for energy and the ready availability of fossil fuels—in particular coal—make it highly likely that fossil fuel combustion will continue to be a substantial fraction of the energy portfolio for the foreseeable future.<sup>2</sup> In this environment, alternative approaches to managing CO<sub>2</sub> emissions become essential.<sup>3</sup>

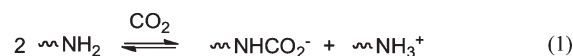
For coal-fired power plants and other point source emitters, postcombustion carbon capture is the most straightforward and promising route to limiting CO<sub>2</sub> release, but practical carbon capture depends on the discovery of energy-efficient means of separating CO<sub>2</sub> from the other gaseous components of a flue gas.<sup>4</sup> For example, a typical 500 MW coal-fired power plant produces on the order of 22 kmol s<sup>-1</sup> of flue gas containing ~15% CO<sub>2</sub> in N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and other trace gases at near ambient temperature and pressure.<sup>5</sup> Separating CO<sub>2</sub> from this stream is estimated to consume more than 30% of the power of the plant using presently available amine absorption technologies, far above the theoretical minimum work of separation.<sup>5</sup>

In absorption-based separations, CO<sub>2</sub> selectively dissolves into a liquid-phase absorbent from the flue gas mixture; a CO<sub>2</sub>-enriched stream is subsequently recovered either by vacuum or thermal desorption. Figure 1 illustrates schematically how the pressure- and temperature-dependent solubility of CO<sub>2</sub> in an absorbing liquid can be exploited to effect a separation. The

energy cost to drive this cycle is closely tied to CO<sub>2</sub>-absorbent equilibria, as embodied in the CO<sub>2</sub>-liquid isotherms, and means to control these isotherms are thus highly desirable.

In addition to the properties specific to the CO<sub>2</sub>-absorbent solubility, the ideal liquid will absorb CO<sub>2</sub> rapidly and reversibly and will have physical characteristics (high thermal stability, low volatility, low viscosity, low heat capacity) well suited to the separation process. Ionic liquids (ILs)—low-melting and virtually nonvolatile salts of bulky cations and anions—are an ideal platform for developing absorbents with these characteristics.<sup>6–9</sup> An essentially limitless number of ILs can be envisioned, and the challenge is to navigate this very large design space to identify optimal materials. We report here a molecular-simulation-driven design of new IL classes specifically tailored to the CO<sub>2</sub> separation problem.

Common ILs are intrinsically selective for CO<sub>2</sub> over O<sub>2</sub> and N<sub>2</sub>, but the physical solubility of CO<sub>2</sub> is modest and insufficient for flue-gas separations.<sup>10</sup> The most common approach to separating CO<sub>2</sub> from dilute gas streams involves selective and reversible reaction with aqueous amines:<sup>5</sup>

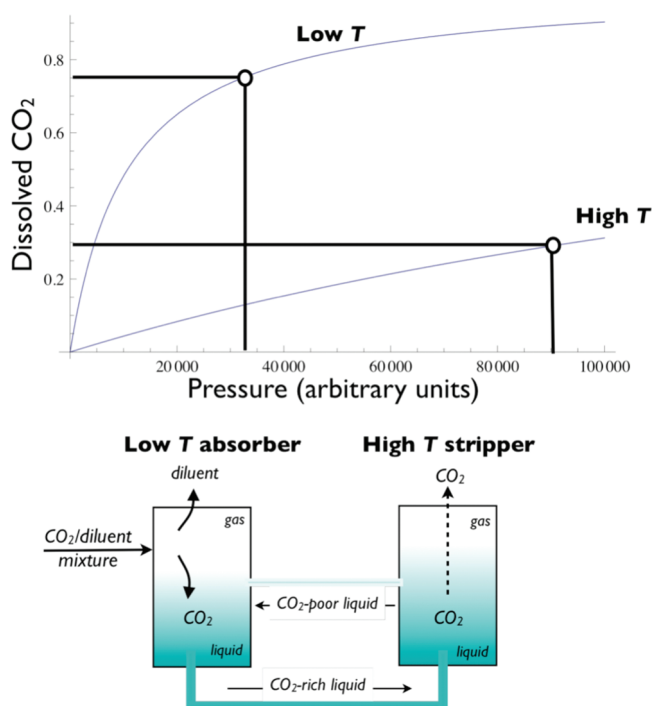


Initial attempts to increase the capacity of ILs for CO<sub>2</sub> involved tethering primary amine functionality to the IL

**Received Date:** November 11, 2010

**Accepted Date:** November 29, 2010

**Published on Web Date:** December 03, 2010



**Figure 1.** Absorption-based gas separation. Top: Isotherms relate partial pressure, temperature, and equilibrium concentration in an absorbing liquid that reacts selectively with CO<sub>2</sub>. Bottom: In a temperature-swing separation, the gas mixture is contacted with a cool, CO<sub>2</sub>-poor liquid, and the CO<sub>2</sub> selectively dissolves into the liquid phase up to a concentration dictated by the solubility isotherm; the diluent gases do not dissolve substantially in the absorbent and are emitted to the atmosphere. Raising the temperature of the CO<sub>2</sub>-laden liquid lowers the CO<sub>2</sub> solubility, and gas desorbs down to a concentration consistent with the higher temperature isotherm. The desorbed CO<sub>2</sub> is captured for subsequent sequestration.

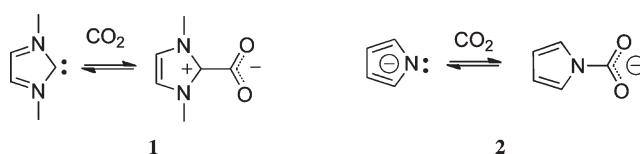
cation.<sup>11–15</sup> These functionalized ILs do indeed combine stoichiometrically and reversibly with CO<sub>2</sub> in a 2 amine:1 CO<sub>2</sub> proportion, but with large and generally undesirable increases in the liquid viscosity. Our atomistic molecular dynamics (MD) simulations trace this large viscosity increase to the formation of a pervasive salt bridge network connecting product carbamate and ammonium species.<sup>16</sup> Computed ion rotational relaxation times increase by 2–3 orders of magnitude, translational dynamics are greatly reduced, and radial distribution functions show the formation of a gel-like network.<sup>16</sup> We have recently shown that the stoichiometry of reaction between IL and CO<sub>2</sub> can be increased to nearly 1:1 simply by tethering the primary amine to the IL anion rather than the cation,<sup>17,18</sup> effectively doubling the molar efficiency of the separation:



Nonetheless, the viscosity changes remain, and systematic improvement of these materials remains illusive.

These attempts to create chemically selective ILs fail to take advantage of the intrinsic nucleophilicity of the anion functionality. We reasoned that, by integrating the anion and CO<sub>2</sub> reaction functions, we could create a more atom-efficient

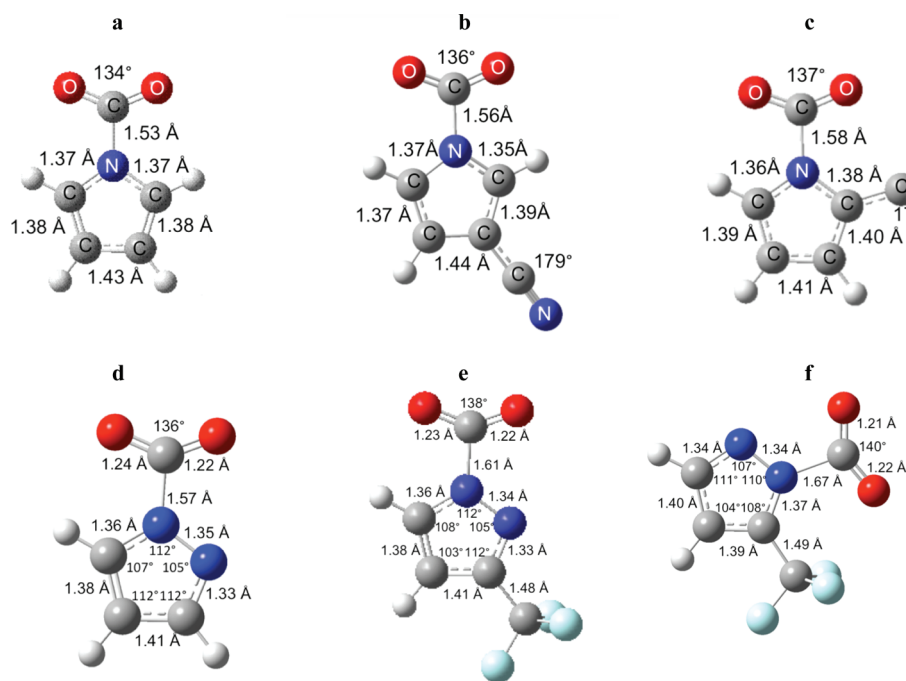
absorbent material. Further, to eliminate the viscosity changes, the ideal reaction should not create acidic protons. Most common IL anions (BF<sub>4</sub><sup>−</sup>, NO<sub>3</sub><sup>−</sup>, etc.) are too weakly nucleophilic to combine directly with CO<sub>2</sub>. However, *N*-heterocyclic carbenes (**1**) have been reported to reversibly form carboxylate adducts with CO<sub>2</sub>,<sup>19</sup> suggesting that the isoelectronic *N*-heterocyclic anions might be capable of the same chemistry:



Further, the pyrrolide (**2**) is effectively a tertiary amine, eliminating protons from the CO<sub>2</sub> capture chemistry. To our knowledge, these pyrrolide-based ILs and their reactions with CO<sub>2</sub> are unknown.

To test this idea, we first used molecular electronic structure calculations at the *G3* level<sup>20</sup> to compute the structure and energetics of the pyrrolide and its CO<sub>2</sub> reaction product (details in the Supporting Information). The pyrrolide anion itself is planar and aromatic.<sup>21</sup> As shown in Figure 2a, it is calculated to combine with CO<sub>2</sub> through the N center to form a carbamate anion analogous to the carbene carboxylate. The planarity of the carbamate product and 39 kJ mol<sup>−1</sup> rotational energy barrier are both indicative of  $\pi$  conjugation that extends across the N–C bond.<sup>22</sup> The −109 kJ mol<sup>−1</sup> computed 298 K reaction enthalpy indicates strong affinity for CO<sub>2</sub>—greater than that, for instance, of the aqueous amines.<sup>23</sup> Further, the evident  $\sigma$  and  $\pi$  electronic communication between CO<sub>2</sub> and pyrrolide suggests that the ring–CO<sub>2</sub> bond energy should be sensitive to ring substitutions. We explored a large number of substituted pyrroles and found a strong effect on binding energies arising from a combination of inductive,  $\pi$  conjugation, and steric effects. The cyano-substituted compounds are representative: 3-substituted cyanopyrrolide (Figure 2b) forms a similar carbamate with CO<sub>2</sub> but with reaction enthalpy increased by 39 kJ mol<sup>−1</sup>; substitution in the 2 position introduces steric interference between N and CO<sub>2</sub> that raises the reaction enthalpy 21 kJ mol<sup>−1</sup> further, to −49 kJ mol<sup>−1</sup>. These results suggest a much wider range of tunability of the reaction enthalpy than is generally possible with the aqueous amines. Further, these absorption energies are in a window well suited to separations, between those normally associated with physically dissolved (−12 kJ mol<sup>−1</sup>)<sup>10</sup> and chemically bound (−80 kJ mol<sup>−1</sup>) CO<sub>2</sub>.<sup>23</sup>

To probe the viscosity of the pyrrolide-based IL in combination with CO<sub>2</sub>, MD simulations were carried out for an IL comprised of 2-cyanopyrrolide anions paired with tetrabutylphosphonium cations. A classical force field for the unreacted and reacted form of the anion (Figure 2c) was developed using a combination of electronic structure calculations and parameters from the generalized Amber force field.<sup>24</sup> MD simulations were carried out for the neat unreacted IL and for mixtures representing 25–100% extent of reaction. In contrast to the primary-amine-containing IL,<sup>16</sup> the simulations show that the ion translational and rotational dynamics are



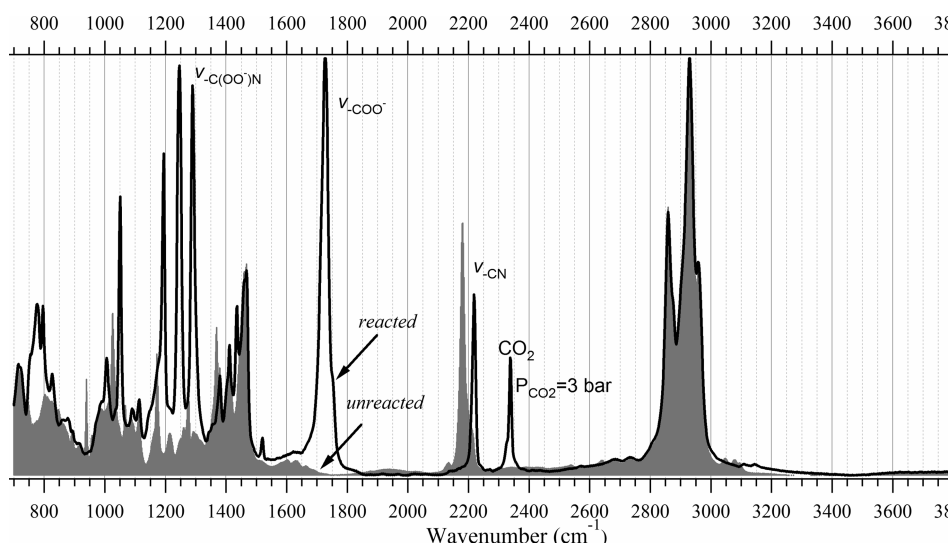
**Figure 2.** Computed products of  $\text{CO}_2$  reaction with aprotic heterocyclic anions (AHAs). G3-level geometry optimizations show that  $\text{CO}_2$  binds to pyrrolide N-heteroatom a.  $\text{CO}_2$  binds with slightly modified geometry and decreased binding energy upon cyano substitution in the 3- (b) or 2- (c) positions on the pyrrolide ring. Binding at a pyrazolide anion d is calculated to be about  $30 \text{ kJ mol}^{-1}$  weaker than the pyrazolide.  $\text{CF}_3$ -substitution on the pyrazolide creates two inequivalent  $\text{CO}_2$  binding sites, with the 1,3 substitution pattern e calculated to be  $27 \text{ kJ mol}^{-1}$  more strongly bound than the 1,2 pattern f.

essentially insensitive to reaction with  $\text{CO}_2$ . For example, the simulations predict the bulky phosphonium cation and cyanopyrrolide anion in the unreacted IL to have a rotational time constants of 1.4 and 0.5 ns, respectively, at 333 K. Converting 100% of the anions to the  $\text{CO}_2$ -reacted form increases the cation rotational time constant to 1.7 ns while leaving the anion rotational dynamics virtually unchanged. The liquid structure in unreacted and  $\text{CO}_2$ -reacted states are also very similar; hydrogen bonding analysis and pair distribution functions show little change between the two. These simulations strongly suggest that the viscosity of pyrrolide-based ILs will be insensitive to reaction with  $\text{CO}_2$ .

On the basis of these findings, we synthesized trihexyl-(tetradecyl)phosphonium 2-cyanopyrrolide ( $[\text{P}_{66614}][2\text{-CNpyr}]$ ) by condensation of the phosphonium hydroxide with the protonated 2-cyanopyrrole and subsequent drying. Details can be found in the Supporting Information. We chose an asymmetric phosphonium cation rather than the tetrabutyl version used in the simulations to increase the likelihood that the IL would be liquid at room temperature. The product is, in fact, a stable room-temperature IL; NMR analysis (see Supporting Information) confirms its chemical identity. We exposed this IL at  $22^\circ\text{C}$  to  $\text{CO}_2$  gas in an in situ infrared spectrometer (Figure 3); results clearly indicate the formation of a chemically bound carbonate at lower pressure and additional physically absorbed  $\text{CO}_2$  at higher pressures. Upon application of vacuum, the carbamate asymmetric stretch disappears, and the original spectrum is restored. These results are all consistent with a 1:1 and reversible reaction between  $[2\text{-CNpyr}]^-$  and  $\text{CO}_2$ .

As shown in Figure 4a, the viscosity of  $[\text{P}_{66614}][2\text{-CNpyr}]$  before exposure to  $\text{CO}_2$  is less than 100 cP at typical flue-gas temperatures (approximately  $50^\circ\text{C}$ ) and, as expected, decreases with increasing temperature. More remarkably, the viscosity measured under 1 bar of  $\text{CO}_2$  atmosphere is nearly identical to the unreacted form. This behavior stands in stark contrast to all previously reported  $\text{CO}_2$ -complexing ILs.<sup>13,15,25</sup>  $[\text{P}_{66614}][\text{Isoleucinate}]$ , a primary amine-functionalized IL, is representative: its viscosity increases over 200-fold when exposed to 1 bar of  $\text{CO}_2$ ,<sup>25</sup> to a level much too large for the material to be useful in a liquid absorber/stripper such as the one shown in Figure 1. In fact, previous efforts to apply reactive ILs for  $\text{CO}_2$  capture have focused on fixing the ILs to a solid support.<sup>12,13</sup>  $[\text{P}_{66614}][2\text{-CNpyr}]$  is the first reported IL with both  $\text{CO}_2$  affinity and flow characteristics suitable for flue gas  $\text{CO}_2$  separations.

Isotherms measured at temperatures from  $22$  to  $100^\circ\text{C}$  are shown in Figure 4b. The steep initial slopes reflect chemical reaction between  $\text{CO}_2$  and the IL; gradual slopes at higher pressure reflect the contributions of weaker physical absorption. The uptake approaches 1 mol  $\text{CO}_2$  per mole  $[\text{P}_{66614}][2\text{-CNpyr}]$  at the highest pressures and lowest temperatures shown, consistent with a 1:1 reaction stoichiometry. At higher pressures (see Supporting Information) the uptake goes above 1 mol  $\text{CO}_2$  per mole of IL due to the continued increase in  $\text{CO}_2$  physical solubility with increasing pressure. A sample of  $[\text{P}_{66614}][2\text{-CNpyr}]$  that was saturated with approximately 6.3 wt % water did not show any diminished capacity per mole of  $[\text{P}_{66614}][2\text{-CNpyr}]$  at  $22^\circ\text{C}$ . Moreover, the chemical shifts of the protons on the cyanopyrrolide anion when



**Figure 3.** Infrared analysis of 2-CNpyr IL reaction with CO<sub>2</sub>. Solid plot shows vibrational spectrum of unreacted [P<sub>66614</sub>][2-CNpyr] at 22 °C. The unreacted compound has a feature at 2183 cm<sup>-1</sup> characteristic of the cyano group. After exposure to 1 bar CO<sub>2</sub> (line plot), the cyano band shifts to 2220 cm<sup>-1</sup> and prominent features appear at 1728 and 1521 cm<sup>-1</sup>, indicative of the -NCOO<sup>-</sup> stretches. These observed features are in excellent agreement with those predicted from the computations for the carbamate (see Supporting Information). At higher CO<sub>2</sub> pressures (> 1 bar), a band due to physically dissolved CO<sub>2</sub> appears between 2370 and 2300 cm<sup>-1</sup>.

complexed with CO<sub>2</sub> were the same both with and without water present (see Supporting Information), suggesting similar reaction chemistry between the IL and the CO<sub>2</sub> in the presence of water.

A model that incorporates both the stoichiometric reaction and physical uptake nicely fits the isotherm data:



Total CO<sub>2</sub> uptake on a mole ratio basis ( $z = n_{\text{CO}_2}/n_{\text{IL}_0}$ ) is expressed as:

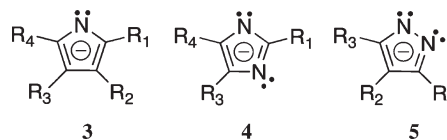
$$z = \frac{P_{\text{CO}_2}/H}{1 - P_{\text{CO}_2}/H} + \frac{k_1 P_{\text{CO}_2} C_3}{1 + k_1 P_{\text{CO}_2}} \quad (5)$$

where  $P_{\text{CO}_2}$  is the CO<sub>2</sub> pressure in bar,  $H$  is Henry's law constant in bar,  $k_1$  is the reaction equilibrium constant, and  $C_3$  is a measure of the reaction site density. We found it convenient to fix the Henry law constant by applying Beer's law to the physical absorption IR band. These values were determined at 22, 40, and 55 °C, and extrapolated to higher temperatures from the linear plot of  $\ln H$  versus  $1/T$  (K) (Figure 4c). The contribution from the physical dissolution is very small, never reaching more than 3% of the total uptake.

Reaction enthalpies and entropies can be determined from the temperature-dependence of the equilibrium constants, and the graph for the enthalpies is shown in Figure 4c. The close linearity of the van't Hoff plots lends credence to the model. The  $-10 \text{ kJ mol}^{-1}$  physical uptake enthalpy is consistent with that observed for nonreacting ILs; the chemical reaction enthalpy and entropy referenced to gas-phase CO<sub>2</sub> are found to be  $-43 \text{ kJ mol}^{-1}$  and  $-130 \text{ J mol}^{-1} \text{ K}^{-1}$ . The latter reflects the nearly complete loss of translational entropy associated with chemical complexation to the IL anion via reaction 3.

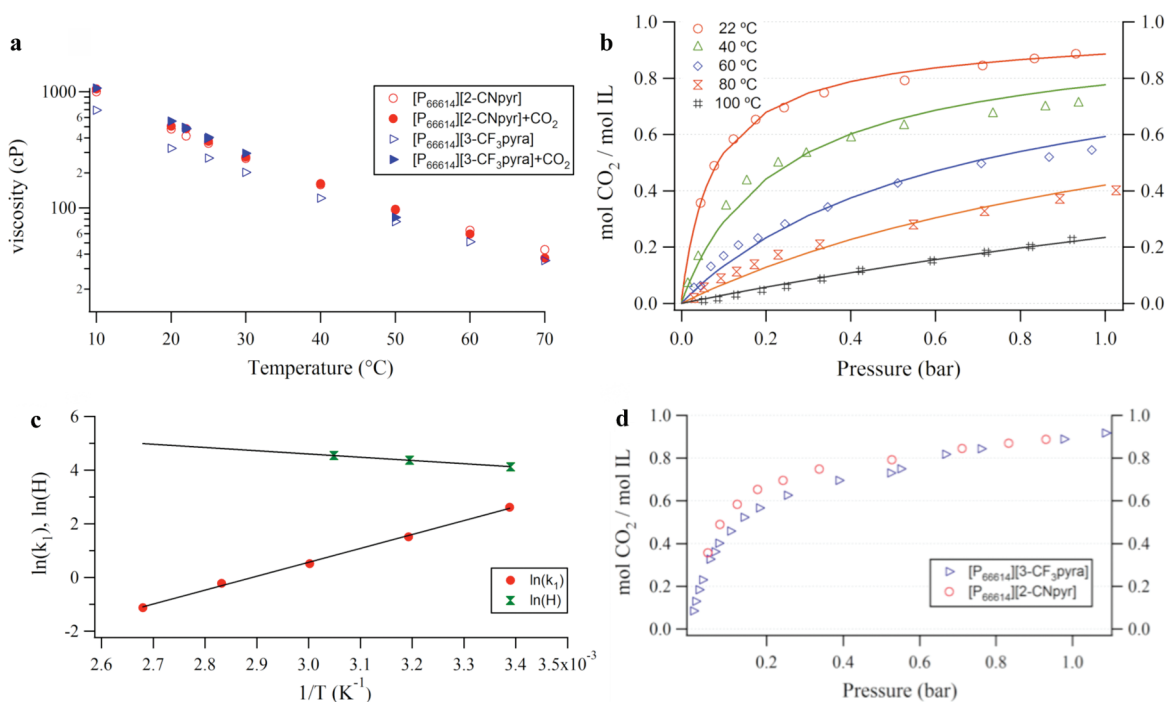
Differential calorimetry<sup>17</sup> gives a reaction enthalpy of  $-53 \text{ kJ mol}^{-1}$ , further corroborating the isotherm-derived thermodynamics. The calorimetry depends on the total amount of CO<sub>2</sub> uptake at a given temperature and pressure, which we take from the measured isotherms; we estimate the associated uncertainty to be  $\pm 5 \text{ kJ mol}^{-1}$ . These two independent measurements are thus in good agreement with one another and with the G3-computed reaction energy for the gas-phase anion ( $-49 \text{ kJ mol}^{-1}$ ), and are much less exothermic than the  $-80 \text{ kJ mol}^{-1}$  observed for [P<sub>66614</sub>][Prolinate] with the same method.<sup>17</sup> The very close agreement between the experimental liquid measurements and computed gas-phase reaction enthalpy can be understood by noting that the two differ by the *difference* in solvation enthalpies of the reactant and product anions (Figure 5), a quantity that is expected to be small for these rather large anions.

[P<sub>66614</sub>][2-CNpyr] thus has both physical and chemical properties superior to any previously reported chemically functionalized ILs for CO<sub>2</sub> separations. This general approach is not limited to the substituted pyrrolides (3): one can reasonably expect similar chemistry for imidazolides (4), pyrazolides (5), or any of many other aprotic heterocyclic anions, or AHAs:

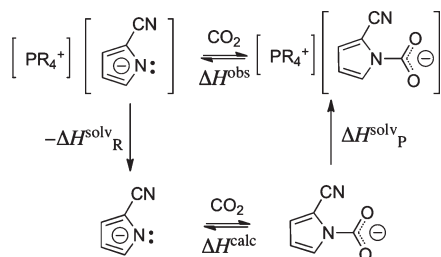


As demonstration of the generality of the approach, we prepared and characterized 3-(trifluoromethyl)pyrazolide ([P<sub>66614</sub>][3-CF<sub>3</sub>pyra]) following a similar protocol. Figure 4d compares absorption isotherms of [P<sub>66614</sub>][3-CF<sub>3</sub>pyra] with [P<sub>66614</sub>][2-CNpyr] at 22 °C. The two ILs exhibit similar CO<sub>2</sub> uptakes, although the [P<sub>66614</sub>][2-CNpyr] capacity is slightly





**Figure 4.** Observed CO<sub>2</sub>-uptakes in AHA ILs. (a) Viscosities of [P<sub>66614</sub>][2-CNpyr] and [P<sub>66614</sub>][3-CF<sub>3</sub>pyra] are nearly unchanged before and after reaction with CO<sub>2</sub>. Viscosities are measured in a closed rheometer under either N<sub>2</sub> or CO<sub>2</sub> (reacted samples). Reacted samples are withdrawn from uptake measurements performed at 22 °C and 1 bar of CO<sub>2</sub>. (b) CO<sub>2</sub> uptake capacity of [P<sub>66614</sub>][2-CNpyr] measured in a closed, stirred, variable temperature volumetric absorption cell. Lines indicate fits to a Langmuir-type isotherm model. (c) van't Hoff plots of fitted Henry's law and equilibrium constants for CO<sub>2</sub> with [P<sub>66614</sub>][2-CNpyr]. (d) Comparison of 22 °C absorption isotherms shows [P<sub>66614</sub>][3-CF<sub>3</sub>pyra] exhibits slightly lower uptake than [P<sub>66614</sub>][2-CNpyr]. Measurements performed in room-temperature volumetric uptake apparatus.



**Figure 5.** Thermodynamic cycle relating liquid- and gas-phase reaction enthalpies. Experimentally observed absorption enthalpies  $\Delta H^{\text{obs}}$  are related to calculated gas-phase enthalpies  $\Delta H^{\text{calc}}$  by ion solvation and desolvation steps,  $\Delta H^{\text{solv}}$ . While the absolute solvation enthalpies are large, differences between reactant and product solvation are small. Test calculations with implicit solvent or explicit counter cations estimate  $\Delta H^{\text{solv}}_{\text{P}} - \Delta H^{\text{solv}}_{\text{R}}$  at approximately  $-5 \text{ kJ mol}^{-1}$ .

greater than that of [P<sub>66614</sub>][3-CF<sub>3</sub>pyra] at pressures below about 0.75 bar. This difference is consistent with a slightly more positive [P<sub>66614</sub>][3-CF<sub>3</sub>pyra] reaction enthalpy with CO<sub>2</sub>, measured calorimetrically to be  $-46 \text{ kJ mol}^{-1}$ . The Langmuir-type isotherm model used to fit the [P<sub>66614</sub>][2-CNpyr] data does an equally good job of representing the [P<sub>66614</sub>][3-CF<sub>3</sub>pyra] data. Like [P<sub>66614</sub>][2-CNpyr], [P<sub>66614</sub>][3-CF<sub>3</sub>pyra] shows no measurable increase in viscosity when fully complexed with CO<sub>2</sub> at 1 bar pressure (Figure 4a).

The [3-CF<sub>3</sub>pyra]<sup>-</sup> anion offers two distinct CO<sub>2</sub> binding sites. The 1,3-substituted product (Figure 2e) is more stable and forms with a 298 K G<sub>3</sub> reaction enthalpy of  $-54 \text{ kJ mol}^{-1}$ ,

while the more sterically congested 2,3-substituted product (Figure 2f) binds a more modest  $-28 \text{ kJ mol}^{-1}$ . Both likely contribute to the observed uptake and account for the net weaker absorption energy than observed with [2-CNpyr].

In summary, we have used a computational molecular design approach to identify a new class of ILs based on the AHAs, which experiments show to react stoichiometrically and reversibly with CO<sub>2</sub> and to not suffer the large viscosity increases that have plagued previous attempts to create CO<sub>2</sub>-complexing ILs. The AHA platform provides a number of chemical handles for tuning CO<sub>2</sub> binding. The results are a promising step forward in the search for energy-optimal carbon capture materials.

**SUPPORTING INFORMATION AVAILABLE** Complete description of electronic structure simulations, molecular dynamics simulations, synthesis, characterization, and capacity measurement results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**ACKNOWLEDGMENT** This material is based upon work supported by the Department of Energy under Award Number DE-FC-07NT43091.

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