The addition of CO2 to four superbase ionic liquids: a DFT study


Published in:
Physical Chemistry Chemical Physics

Document Version:
Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
This journal is © the Owner Societies 2015. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence, which permits unrestricted use, distribution and reproduction in any medium, provided the author and source are cited.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access
This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: http://go.qub.ac.uk/oa-feedback
The addition of CO₂ to four superbase ionic liquids: a DFT study†

Maxime Mercy,a S. F. Rebecca Taylor,b Johan Jacquemin,b Christopher Hardacre,b Robert G. Bell* and Nora H. De Leeuw*a,c

The addition of carbon dioxide to four superbase ionic liquids, [P₃333][Benzim], [P₃333][124Triz], [P₃333][123Triz] and [P₃333][Bentriz] was studied using a molecular DFT approach involving anions alone and individual ion pairs. Intermolecular bonding within the individual ion pairs is characterised by a number of weak hydrogen bonds, with the superbase anion geometrically arranged so as to maximize interactions between the heterocyclic N atoms and the cation. The pairing energies show no correlation to the observed CO₂ adsorption capacity. Addition of CO₂ to the anion alone clearly resulted in the formation of a covalently-bound carbamate function with the strength of binding correlated to experimental capacity. In the ion pair however the cation significantly alters the nature of the bonding such that the overall cohesive energy is reduced. Formation of a strong carbamate function occurs at the expense of weakening the interaction between anion and cation. In the more weakly absorbing ion pairs which contain [123Triz]⁻ and [Bentriz]⁻, the carbamate-functionalised systems are very close in energy to adducts in which CO₂ is more weakly bound, suggesting an equilibrium between the chemi- and physisorbed CO₂.

A. Introduction

The limitation of anthropogenic CO₂ emissions is an issue of global importance. In particular there have been significant advances in the utilization of CO₂ as a chemical reagent to synthesize products with high added value. To be attractive, these processes depend on the economic sustainability of CO₂ capture. Thus an important field of research focuses on the capture of CO₂ from different sources of gas originating, for instance, from a power plant, an incinerator or a digester. Possibilities exist for CO₂ capture: e.g. amine based sorbents1–3 and microporous oxide and metal–organic frameworks.2,4 However, these methods have drawbacks in terms of sustainability and selectivity. Since the observation of CO₂ solubility in 1-butyl-3-methylimidazolium hexafluorophosphate [C₄mIm][PF₆] by Brennecke and co-workers,5 many ionic liquids (ILs) have been demonstrated. In this work the enthalpy was calculated according to their high pKₐ values. A wide range of absorption capacities was reported, up to a molar capacity of 1:1,6 with a link found between the pKₐ of the corresponding superbase and the absorption capacity. Calculated estimates of the absorption enthalpies were made using density functional theory (DFT), showing a link between the absorption capacity and the value of the enthalpy. In a perspective paper in 2012, the effect of different substitutions (–CH₃, –F, –CF₃, OCH₃, etc.) on four AHAs on their CO₂ capture capacity was calculated.9 A wide range of absorption enthalpies between CO₂ and these AHAs from −10 kJ mol⁻¹ up to −100 kJ mol⁻¹ was demonstrated. In this work the enthalpy was calculated according

* Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK. E-mail: r.g.bell@ucl.ac.uk
b QUILL, School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast, Northern Ireland BT9 5AG, UK
b School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK. E-mail: deleew@cardiff.ac.uk
c Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cp05153c
to Scheme 1. The cation was neglected as it is often assumed that the cation does not make a major contribution to the CO₂ absorption. In 2014, this tuning of SBILs was the subject of further experimental studies in which their high industrial potential was confirmed. Indeed the absorption of CO₂ by AHAs is fast and exothermic at atmospheric pressure and room temperature. The wide range of CO₂ absorption capacities possible in these systems make them tuneable. It was also shown that viscosity is low and is not significantly affected by absorption, in contrast to other task-specific ionic liquids such as the amino-acid based ionic liquids.

In the same year, Taylor et al. determined the absorption capacities for four superbase ionic liquids (SBILs) (Table 1). Absorption capacity was determined under both dry and wet conditions. Molar absorption capacities from 30% to 120% were observed using a gravimetric saturation technique for four SBILs in which the cation trihexyl-tetradecylphosphonium ([P₆₆₆,₁₄]+) was paired with the anions benzotriazolide ([Bentriz]), benzimidazolide ([Benzim]), 1,2,3-triazolide ([123Triz]), and 1,2,4-triazolide ([124Triz]) (Scheme 2).

Density functional theory calculations were carried out using the Minnesota density functional M06. This hybrid meta-exchange correlation functional is versatile and included in its construction is a non-local interaction term that makes it well-suited to the treatment of ionic and hydrogen bonding. Its predecessor M05 has been tested successfully for ILs. A Pople basis set 6-311+G(d,p) was used for all atoms. All cations, anions and ionic pairs were optimised using the software Gaussian 09 without symmetry constraints and, for each geometry, the nature of minima were checked with a frequency calculation. Energies were corrected for the zero-point energy and relative enthalpies were calculated at 298.15 K. Various tools were used to analyse the electronic density. Natural bond analysis (NBO) was carried out with NBO 3.124 as implemented with multiwfn.

There are multiple possibilities to arrange the cation and the anion to form each ionic pair. Two methods of building ionic pairs were followed in order to obtain local minima near to the global minimum on the potential energy surface. In the first, a molecular dynamics trajectory of five ns was generated at high temperatures. In the second part, addition of CO₂ to the four anions will be presented both with and without inclusion of an explicit cation; enthalpies of addition, geometrical and electronic properties of the anion–CO₂ bonding will be compared for both models and among the four anions. The different results are compared with observed absorption capacities.

### B. Simulation details – methodology

Density functional theory calculations were carried out using the Minnesota density functional M06. This hybrid meta-exchange correlation functional is versatile and included in its construction is a non-local interaction term that makes it well-suited to the treatment of ionic and hydrogen bonding. Its predecessor M05 has been tested successfully for ILs. A Pople basis set 6-311+G(d,p) was used for all atoms. All cations, anions and ionic pairs were optimised using the software Gaussian 09 without symmetry constraints and, for each geometry, the nature of minima were checked with a frequency calculation. Energies were corrected for the zero-point energy and relative enthalpies were calculated at 298.15 K. Various tools were used to analyse the electronic density. Natural bond analysis (NBO) was carried out with NBO 3.24 as implemented in Gaussian 09. Atoms in molecules (AIM) analysis was done with multiwfn.

There are multiple possibilities to arrange the cation and the anion to form each ionic pair. Two methods of building ionic pairs were followed in order to obtain local minima near to the global minimum on the potential energy surface. In the first, a molecular dynamics trajectory of five ns was generated at high temperatures. In the second part, addition of CO₂ to the four anions will be presented both with and without inclusion of an explicit cation; enthalpies of addition, geometrical and electronic properties of the anion–CO₂ bonding will be compared for both models and among the four anions. The different results are compared with observed absorption capacities.

### Table 1

<table>
<thead>
<tr>
<th>Ionic pair</th>
<th>CO₂ capacity (n mole CO₂ : n IL) at 22 °C</th>
<th>CO₂ capacity (n mole CO₂ : n IL) at 22 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[P₆₆₆,₁₄][Bentriz]</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>[P₆₆₆,₁₄][124Triz]</td>
<td>0.69</td>
<td>0.39</td>
</tr>
<tr>
<td>[P₆₆₆,₁₄][123Triz]</td>
<td>1.20</td>
<td>1.20</td>
</tr>
</tbody>
</table>

In the second part, addition of CO₂ to the four anions will be presented both with and without inclusion of an explicit cation; enthalpies of addition, geometrical and electronic properties of the anion–CO₂ bonding will be compared for both models and among the four anions. The different results are compared with observed absorption capacities.
temperature in the \textit{NVT} ensemble using the AMBER software with the GAFF force field.\textsuperscript{27} A large cell with one ionic pair was used. From the resulting trajectory, ten to twenty steps were extracted. These structures were optimized at DFT level with a small basis set, and the five most stable structure were then optimized at the M06-2X/6-311+G(d,p) level. In parallel, the tetraalkylphosphonium cation and the anion were positioned in different configurations by human chemical intuition and optimized. For each ion pair, multiple minima were found which were very close in energy to the most favourable structure. This can be attributed to the configurational flexibility of the cation’s alkyl chains. In the following analysis of the ionic pairing, only the most favourable structures are described. The geometries were created and monitored with Molden\textsuperscript{28} and VMD\textsuperscript{29} and the pictures were prepared with CYLview\textsuperscript{30} and VMD.

### C. Results and discussion

#### C.1. The ionic pair

In order to avoid unnecessarily resource-intensive calculations and to decrease any error attributed to the alkyl chain configuration, we chose to use the tetrapropylphosphonium cation \( [\text{P3333}]^+ \) as a model for the experimental cation trihexyl-tetradecylphosphonium \( [\text{P666,14}]^+ \). We note here that the balance of forces would be expected to differ slightly between the two cations, with the cohesive energy of the ionic liquid being influenced more strongly by van der Waals interactions in the case of \( [\text{P666,14}]^+ \). In contrast, electrostatic forces would be more dominant for \( [\text{P3333}]^+ \). The four most stable ionic pairs are shown in Fig. 1. For all the ionic pairs, distances between anion nitrogen and hydrogen atoms of the cation are shown where they are less than, or close to, 2.75 Å, taken as the sum of the respective van der Waals radii.\textsuperscript{31} These invariably include the shortest cation–anion distance, given as \( r_{\text{SN}} \) in Table 2. For the ionic pairs \( [\text{P3333}]^+ [\text{Benzim}] \) (Fig. 1a), \( [\text{P3333}]^+ [\text{123Triz}] \) (Fig. 1c) and \( [\text{P3333}]^+ [\text{Bentriz}] \) (Fig. 1d), the anion is positioned in order to minimize the distance for both nitrogen atoms. All the nitrogen atoms exhibit short N–H distances, with H C\textsubscript{1} defined as a hydrogen bonded to a carbon adjacent to the phosphorus in the cation. For \( [\text{P3333}]^+ [\text{124Triz}] \) (Fig. 1b), the anion position allows nitrogen atoms N\textsubscript{1} and N\textsubscript{2} to be close to the phosphorus atom. The cation (\( [\text{P666,14}]^+ \)) in contrast, \( [\text{P3333}]^+ [\text{123Triz}] \) and \( [\text{P3333}]^+ [\text{Bentriz}] \), the anion position allows nitrogen atoms N\textsubscript{1} and N\textsubscript{2} to be close to the phosphorus atom.

The binding energy of the ionic pair \( \Delta E_{\text{IP}} \) is defined as the difference between the ionic pair energy and the sum of energies of the separate ions (optimised individually), \( \Delta E_{\text{IP}} = E_{\text{IP}} - (E_{\text{cation}} + E_{\text{anion}}) \). These are given in Table 2. All the pairing energies are weaker than 400 kJ mol\textsuperscript{-1}; our four cation/anion ionic-pair binding energies are thus low compared to typical ionic liquids. The ascending order of pairing strength is \( [\text{P3333}]^+ [\text{Benzim}] \) (a) < \( [\text{P3333}]^+ [\text{Bentriz}] \) (d) < \( [\text{P3333}]^+ [\text{124Triz}] \) (b) < \( [\text{P3333}]^+ [\text{123Triz}] \) (c). This order does not correlate with the CO\textsubscript{2} absorption capacity (Table 1). To obtain an electronic description of the interaction properties, an NBO analysis was carried on the different ionic pairs as well as on the anions treated alone. Natural atomic charge analysis indicates a small charge transfer (CT) from the cation to the anion of between 0.06 and 0.12 units (Table 2) when comparing the atomic charges in the ionic pairs with those in the separate moieties (the full NAO charges are shown in Table S1 in ESI\textsuperscript{1}). These are typical values for CT in ionic pairs as calculated accurately using a QM/MM approach for a variety of ILs in the liquid phase.\textsuperscript{32}

The influence of the cation may be seen in the adjustment of the anion natural charges in the ionic pair, compared to the monomer. Although on average the hydrogen charges become slightly more positive, there is a noticeable rearrangement of the atomic charges for each anion. For b, c, d, at least one nitrogen becomes more negative as a result of interaction with the cation (\( |\delta \delta| > 0.08 \)). These correspond to those interacting most closely with the cation and can be identified as one of the equivalent nitrogen atoms for b and c, and the central nitrogen of d.

![Fig. 1 Ionic pairs comprising a tetrapropylphosphonium cation, \( [\text{P3333}]^+ \), with the four anions: (a) \( [\text{P3333}]^+ [\text{Benzim}] \), (b) \( [\text{P3333}]^+ [\text{124Triz}] \), (c) \( [\text{P3333}]^+ [\text{123Triz}] \) and (d) \( [\text{P3333}]^+ [\text{Bentriz}] \). Dashed lines indicate intermolecular N–H distances less than or close to the sum of the vdW radii (2.75 Å). Colour code: blue – nitrogen; yellow – phosphorus; grey – carbon; white – hydrogen.](image)

<table>
<thead>
<tr>
<th>Ionic pair</th>
<th>( \Delta E_{\text{IP}} ) (kJ mol\textsuperscript{-1})</th>
<th>( \delta_{\text{AHA}} )</th>
<th>CT</th>
<th>( r_{\text{SN}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>( [\text{P3333}]^+ [\text{Benzim}] )</td>
<td>-363.25</td>
<td>-0.94</td>
<td>0.06</td>
</tr>
<tr>
<td>b</td>
<td>( [\text{P3333}]^+ [\text{124Triz}] )</td>
<td>-374.50</td>
<td>-0.88</td>
<td>0.08</td>
</tr>
<tr>
<td>c</td>
<td>( [\text{P3333}]^+ [\text{123Triz}] )</td>
<td>-396.59</td>
<td>-0.93</td>
<td>0.07</td>
</tr>
<tr>
<td>d</td>
<td>( [\text{P3333}]^+ [\text{Bentriz}] )</td>
<td>-371.74</td>
<td>-1.00</td>
<td>0.12</td>
</tr>
</tbody>
</table>

---

\textsuperscript{1} ESI: Electronic supplementary information, available free of charge via the web.

\textsuperscript{2} A large cell with one ionic pair was used. From the resulting trajectory, ten to twenty steps were extracted. These structures were optimized at DFT level with a small basis set, and the five most stable structure were then optimized at the M06-2X/6-311+G(d,p) level. In parallel, the tetraalkylphosphonium cation and the anion were positioned in different configurations by human chemical intuition and optimized. For each ion pair, multiple minima were found which were very close in energy to the most favourable structure. This can be attributed to the configurational flexibility of the cation’s alkyl chains. In the following analysis of the ionic pairing, only the most favourable structures are described. The geometries were created and monitored with Molden\textsuperscript{28} and VMD\textsuperscript{29} and the pictures were prepared with CYLview\textsuperscript{30} and VMD.

---

\textsuperscript{3} PCCP Paper

---

\textsuperscript{4} View Article Online

---

\textsuperscript{5} This journal is © the Owner Societies 2015

---

\textsuperscript{6} Phys. Chem. Chem. Phys., 2015, 17, 28674--28682

---

\textsuperscript{7} Published on 25 September 2015. Downloaded on 24/11/2015 11:34:12.

---

\textsuperscript{8} Creative Commons Attribution 3.0 Unported Licence.
This behaviour is not observed for \( a \). The sum of the donor–acceptor interaction from second order perturbation analysis never exceeds 100 \( \text{kJ mol}^{-1} \) and this interaction is shared among multiple contributions. NBO analysis draws the interaction as a sum of numerous weak interactions, of which the most important can be identified as a nitrogen lone pair LP(N) of the anion pointing towards an empty \( \sigma \) bond orbital \( \sigma_{\text{in}}^* \) (C=H) or \( \sigma_{\text{in}}^* \) (P=C). The corresponding interaction energy \( \varepsilon_{\text{LP} \ldots \sigma} \) never exceeds 41 \( \text{kJ mol}^{-1} \) (Table S2, ESIf). Indeed, the short distance between the nitrogen and the cationic hydrogen as well as the various LP(N) \( \rightarrow \sigma_{\text{in}}^* \) (C=H) interactions, notably with hydrogen \( \text{He}_{16} \), are a good indication of multiple H-bonding interaction between the ions.

The H-bond can be described as a bifurcated/chelated H-bond. According to the 2015 review of Hunt et al.\(^{17}\) on H-bonds in ionic liquids, the \( E_{\text{LP} \ldots \sigma} \) NBO parameters indicate that H-bonding between AHAs and the tetraalkylphosphonium cation is very weak.

To gain more insight into these interactions, the electronic density was analysed within Bader’s theory of atoms in molecules (AIM). Properties of the intermolecular bond critical points (BCP) between the anion and the cation and ring critical points on the anion (RCP) are compiled in Table 3 and illustrated in Fig. 2. It is important to keep in mind that the critical point is dependent on the geometry and thus the results are specific to the interaction at this geometry. For all anions, multiple bond critical points are found between nitrogen of the anion and hydrogen atoms of the cation. Most of these BCPs are sited towards the hydrogen \( \text{He}_{16} \). At the BCPs, the density \( \rho(r) \) is low and the Laplacian \( \nabla^2 \rho(r) \) is positive as expected for non-covalent interactions in closed-shell systems. According to Hunt et al.\(^{17}\) where density \( \rho(r) < 0.02 \text{ a.u.} \) at the BCP, intermolecular interactions between cation and anion can be described as weak H-bonds. In the ion pairs discussed here we can therefore characterise the interionic bonding in terms of an array of such weak hydrogen bonds. From the topology analysis of the density, the H-bond energy \( E_{\text{HB}} \) can be estimated as half of the potential energy density \( V(r)^{13} \): \( E_{\text{HB}} = V(r)/2 \). Thus since \( E_{\text{HB}} \) is less than 16 \( \text{kJ mol}^{-1} \) for all anion–cation H-bonds, we can confirm the weak strength of the H-bonding.

### C.2. Interaction with \( \text{CO}_2 \)

The addition of \( \text{CO}_2 \) was explored according to Scheme 1. Addition to the individual anion monomers was first characterised, taking into account all non-equivalent nitrogen atoms. Subsequently \( \text{CO}_2 \) was added to ion pairs of each of the anions with tetrapropylphosphonium \( \text{[P}_{3333}^3 \) for each anion, the carbamate formation enthalpy \( \Delta H_f \) was calculated as well as the corresponding adduct formation enthalpy \( \Delta H_a \). We define an adduct as the combination of the anion and \( \text{CO}_2 \) in such a way that no bond is created but \( \text{CO}_2 \) loses its linearity and the distance between anion nitrogen and \( \text{CO}_2 \) carbon is less than 3 \( \text{Å} \). These occur as separate minima on the potential energy surface. \( \Delta H_f \) and \( \Delta H_a \) are defined as the enthalpy difference between the carbamate or adduct respectively and the separate \( \text{CO}_2 \) and superbase (either as monomer or taking the whole ion pair, depending on the model).

### C.3. Anion + \( \text{CO}_2 \)

Addition of \( \text{CO}_2 \) was simulated at all non-equivalent nitrogen atoms for the four anions. The enthalpy of carbamate formation is exothermic for both nitrogen and all anions (Table 4). It varies from \( \Delta H_a = -13.54 \text{ kJ mol}^{-1} \) for the weakest to \(-55.99 \text{ kJ mol}^{-1} \) for the strongest. Adducts were also obtained for anions except for \( \text{[124Triz]} \) \( b \). The enthalpy values obtained from this work for the anion alone are close to those previously published\(^{8,12}\) and show a correlation between measured absorption capacity\(^{14}\) and enthalpy of carbamate variation (Fig. 3). The more negative the reaction enthalpy, the better the absorption capacity is. For the anion \( \text{[124Triz]} \), as in the work of Seo et al.\(^ {12}\) we found a small difference between addition on \( \text{N}_1 \) and \( \text{N}_2 \) (\( |\Delta \Delta H_a| < 4 \text{ kJ mol}^{-1} \)) making the two configurations effectively isoenergetic. Also in agreement with the same authors, \( \text{CO}_2 \) was found to be more favourably coordinated at \( \text{N}_1 \) of \( \text{[123Triz]} \).

The bonding strength can be correlated to the carbamate bond length between the relevant nitrogen \( \text{N}_2 \) of the \( \text{SB} \) and the carbon \( \text{C}^* \) of the coordinated \( \text{CO}_2 \) moiety, \( d(\text{N}_2^* - \text{C}^*) \), and the angle of the \( \text{CO}_2 \) \( z(\text{OCO}) \) as illustrated in Fig. 4. From the natural atomic charge analysis, coordination of the \( \text{CO}_2 \) leads to the transfer of half the negative charge from the AHA...
moieties to the COO functions (Table 5). The stronger the carbamate bond, the more negative charge is transferred. The adduct formation enthalpies are less favourable than for carbamate formation, although for [Bentriz] the difference is less than 5 kJ mol⁻¹ suggesting a possible equilibrium between the two products. For the four anions, a scan of the d(Nₓ–C*) distance was conducted to identify the presence of any energetic barrier to CO₂ coordination (see Fig. S1 in ESI†). A barrier was found only for [Bentriz], in that case having a height of 4.5 kJ mol⁻¹. In these systems, we therefore consider CO₂ coordination to be an effectively barrierless process at ambient temperatures.

### C.4. Ionic pair + CO₂

The carbamate product and CO₂ adducts were also optimized including a [P3333]⁺ cation explicitly (Fig. 5–7). Calculated enthalpies and selected properties for (a) the carbamate formation for the anion alone xNₓ and (b) the respective adduct formation xNₓ* with a = [Benzim], b = [124Triz]⁺, c = [123Triz]⁺ and d = [Bentriz]⁻. Enthalpy ΔH in kJ mol⁻¹. Length of the carbamate bond d(Nₓ–C) in Å. CO₂ bending α(OCO) and torsion of the dihedral around the carbamate ω in °. nl = not located on the PES surface.

#### Table 5 Selected properties of the carbamate anion. Charges δ from NAO analysis of the carbamate with δ_AHA and δ_CO₂, the NAO charges split between the superbase and the CO₂ moieties respectively.

<table>
<thead>
<tr>
<th>Anion</th>
<th>δ_AHA</th>
<th>δ_CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>a⁻ N₁</td>
<td>−0.46</td>
<td>−0.54</td>
</tr>
<tr>
<td>b⁻ N₁</td>
<td>−0.46</td>
<td>−0.54</td>
</tr>
<tr>
<td>c⁻ N₁</td>
<td>−0.51</td>
<td>−0.49</td>
</tr>
<tr>
<td>d⁻ N₁</td>
<td>−0.53</td>
<td>−0.47</td>
</tr>
</tbody>
</table>
and geometric parameters for the carbamates and CO₂ adducts are reported in Table 6. The enthalpies Δ𝐻 are expressed taking the optimised ionic pair as reference (i.e. not including the pairing energy). For the four IPs, the carbamate formation enthalpy is weaker in all cases compared to the anion alone, and is even endothermic for cN₂ and dN₂. The ionic pair model also loses the trend between capacity and enthalpy of addition. For [P3333][Benzim], a, carbamate and adduct formation are 20 kJ mol⁻¹ less favourable. For [P3333][124Triz] b, the equivalence between N₃ and N₄ is lost as the carbamate formed on nitrogen N1, bN₁, is 24 kJ mol⁻¹ more stable than bN₄. Moreover bN₄ is also less stable than the two adducts bN₁ and bN₄: the adduct bN₁ is only 10 kJ mol⁻¹ above bN₄. For [P3333][123Triz] c, the carbamate pair cN₁ and the CO₂ adduct cN₁* are isoenergetic with a formation enthalpy around Δ𝐻 = −13 kJ mol⁻¹ and carbamate formation on N₂ is slightly exothermic. Finally, for [P3333][Bentriz] d, the most favourable product is the adduct on nitrogen N₂ dN₂, with Δ𝐻ₓ(dN₂*) = −15.66 kJ mol⁻¹. However, the formation enthalpies of the carbamate on N₁ dN₁ and of the CO₂ adduct dN₁* are still exothermic and within 5 kJ mol⁻¹ of the dN₂*, adduct. The inclusion of the cation makes the formation of N₂-carbamate dN₂ clearly endothermic Δ𝐻ₓ(dN₂) = +14.47 kJ mol⁻¹.

To get an energetic explanation of this important modification caused by the cation, the ionic pairing energy, Δ𝐸IPC₀₂, was calculated for the ionic pair-carbamate products (Table 7). This energy is defined with respect to the corresponding optimised anion – only carbamate product and optimised cation. For each separate anion, the most favourable carbamate is the one with the strongest resulting ionic pair. Elsewhere the difference
between the carbamate formation enthalpy on the four anions in the ionic pair model (xSNy) and in the anion-only model (xNy) is substantially similar to the energy difference between the ionic pairing energy after and before carbamate formation:

\[ \Delta H_f(xSNy) - \Delta H_f(xNy) = (\Delta E_{PCO2} - \Delta E_{PP}) \]

It can thus be seen that the formation of carbamate has a destabilizing effect on the ion pair, resulting in a close relationship between the carbamate formation enthalpy and the ionic pair strength. In the ionic pair model, the carbamate formation enthalpy does not correlate as well with the CO2 capacity as in the anion model. However, it is still consistent with the experimentally observed molar absorption capacities. Indeed for [P3333][Benzim] and [P3333][124Triz], N1-carbamate formation is strongly preferred suggesting a total conversion of CO2 to the carbamate. For [P3333][Bentriz] and [P3333][231Triz], carbamate formation is as favourable as the CO2 adduct formation and they are both relatively weakly bound. This is consistent with an equilibrium between coordinated and non-coordinated CO2. The explicit inclusion of the cation in the calculation results in a change in the geometry of the carbamate part. The superbase moiety shifts away somewhat from its optimal position in the ion pair, while the carbamate functions interact with the cation centre (Fig. 5 and 6). For example, on [P3333][Benzim], addition of CO2 on N1 increases the distance rSN from 2.19 Å to 2.62 Å whereas the shortest interionic oxygen–H(C1) distance, rSO, is 2.25 Å (Table 7). As a general feature, the N–H distances become longer and multiple O–H interactions are formed. In the adducts, the anion is less affected by the presence of CO2 (Fig. 7). The CO2 tends to be oriented with one oxygen pointing toward the cation and the carbon C* close to a nitrogen (d(N–C*) < 2.79 Å).

As already mentioned, the bonding strength of the carbamate can be characterised by its geometric properties. In the ionic pair model, the length of the carbamate N–C* bond is shorter than for the anion alone (e.g. for b, δd = −0.08 Å) and the bond angle of the CO2 moiety is lower (e.g. for b, δr = −5°) (Table 6). This means that, despite considerably more positive enthalpies \( \Delta H_f \) in the ionic pair, the CO2 forms a stronger carbamate bond. However, as pointed out in Section C.3, explicit inclusion of the cation increases the negative charge of one nitrogen atom in the ionic pair for b, c and d. This nitrogen corresponds to the most favourable CO2 coordination position. NBO analysis was carried for the carbamate ionic pair and selected electronic properties are summarized in Table 7 (detailed NAO charges are given in ESI† Table S1). Overall charge transfer between anion and cation is similar or slightly lower for the carbamate ionic pairs compared to the ion pairs by themselves. However, the partition of the charge on anions between the carbamate ionic pairs. Similar to the topology of the ionic pair before addition of CO2, we can identify a certain number of weak intermolecular H-bonds between the cation and the anion defined by BCPs with low values of \( \rho(r) \) and \( \nabla^2 \rho(r) \) (see Tables S3–S5 and Fig. S2–S4 in ESI†). However, the addition of CO2 results in the decrease of the number of N–H BCPs and creation of new O–H BCPs, especially with H(C1). At the carbamate function, the strong \( \rho(r) \) density and the negative value of its Laplacian \( \nabla^2 \rho(r) \) at the BCP between the nitrogen and the carbamate carbon (bcp N–C*) suggest the presence of a strong covalent bond (Table 8). Moreover, the NC* bond is the strongest for [P3333][Bentriz] followed by [P3333][124Triz]. Values for [P3333][231Triz] and [P3333][Bentriz] are

---

**Table 6** Selected properties for (a) carbamate formation on the ionic pair for each nitrogen xNy of each anion x (xSNy) and (b) the respective adduct formation xNy with a = [P3333][Bentriz], b = [P3333][124Triz], c = [P3333][231Triz] and d = [P3333][Bentriz]: enthalpies \( \Delta H_f \), length of the carbamate bond d(N–C), carbamate bond angle \( \alpha_{(OCO)} \), and torsion of the dihedral around the carbamate \( \beta(|CNCO|) \).

<table>
<thead>
<tr>
<th></th>
<th>xSNy</th>
<th>xNy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_f/kJ \text{ mol}^{-1} )</td>
<td>d(N–C)/Å</td>
<td>( \alpha_{(OCO)}^\circ )</td>
</tr>
<tr>
<td>aSNy</td>
<td>35.82</td>
<td>1.49</td>
</tr>
<tr>
<td>bSNy</td>
<td>32.62</td>
<td>1.51</td>
</tr>
<tr>
<td>cSNy</td>
<td>9.06</td>
<td>1.49</td>
</tr>
<tr>
<td>dSNy</td>
<td>13.50</td>
<td>1.57</td>
</tr>
<tr>
<td>cSNy</td>
<td>+1.91</td>
<td>1.52</td>
</tr>
<tr>
<td>dSNy</td>
<td>−13.03</td>
<td>1.55</td>
</tr>
<tr>
<td>dSNy</td>
<td>+14.47</td>
<td>1.62</td>
</tr>
</tbody>
</table>

**Table 7** Selected properties of the most stable ionic pair-carbamates: charges \( \delta \) from NAO analysis of the carbamate with \( \delta_{AHA} \) and \( \delta_{CO2} \), the NAO charges split between the superbase and the CO2 moieties respectively, \( r_{SO} \) and \( r_{SN} \) are respectively the shortest distances between N(anion) and H(cation) and between O(carbamate) and H(cation).

<table>
<thead>
<tr>
<th></th>
<th>( \Delta E_{PCO2}/kJ \text{ mol}^{-1} )</th>
<th>( \delta_{AHA} )</th>
<th>( \delta_{CO2} )</th>
<th>CT</th>
<th>rSO/Å</th>
<th>rSN/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>aSNy</td>
<td>−34.18</td>
<td>−0.35</td>
<td>−0.59</td>
<td>0.06</td>
<td>2.62</td>
<td>2.25</td>
</tr>
<tr>
<td>bSNy</td>
<td>−351.68</td>
<td>−0.38</td>
<td>−0.55</td>
<td>0.08</td>
<td>2.29</td>
<td>2.18</td>
</tr>
<tr>
<td>cSNy</td>
<td>−328.37</td>
<td>−0.37</td>
<td>−0.55</td>
<td>0.07</td>
<td>2.15</td>
<td>2.15</td>
</tr>
<tr>
<td>dSNy</td>
<td>−363.09</td>
<td>−0.45</td>
<td>−0.50</td>
<td>0.05</td>
<td>2.43</td>
<td>2.15</td>
</tr>
<tr>
<td>dSNy</td>
<td>−354.17</td>
<td>−0.43</td>
<td>−0.52</td>
<td>0.05</td>
<td>2.44</td>
<td>2.14</td>
</tr>
<tr>
<td>dSNy</td>
<td>−340.58</td>
<td>−0.50</td>
<td>−0.46</td>
<td>0.04</td>
<td>2.50</td>
<td>2.14</td>
</tr>
</tbody>
</table>
the lowest and equivalent. This order corresponds to the CO₂ absorption capacity and confirms the previous experimental observations.  

### D. Conclusions

CO₂ addition to four superbase tetraalklyphosphonium ionic liquids was studied using a molecular DFT approach. This has enabled us to explore in detail the nature of bonding in these complexes, and in particular to describe the carbamate function which results from the chemical bonding of CO₂ to these aprotic heterocyclic anions. The influence of the cation was found to be significant in determining the overall strength of binding.

The electronic properties of the ionic pairs were described both before and after the addition of CO₂. No direct relation between the pairing energy and the observed absorption capacity was evident and, in terms of the chemisorption energy, the models of CO₂ addition on the ion pairs do not reproduce the experimental trend as well as when the anion alone is considered. However, from the geometric and AIM topology analyses, it is possible to estimate the relative strength of the carbamate function. Thus it is evident that a more strongly bound carbamate, characterised by shorter N–C* bond and more acute O–C–O angle correlates with a higher CO₂ capture capacity. However, the global enthalpy of reaction is less favourable, which is due to a weakening of the ion pairing energy as a result of CO₂ addition. From this result [P₆₆₆₆][Bentriz] is predicted to be the best absorbent followed by [P₃₃₃₃][124Triz]. For both these IPs a strong enthalpy of reaction is in agreement with the 1 : 1 experimental molar capacity. [P₃₃₃₃][123Triz] and [P₃₃₃₃][Bentriz] possess the same weak enthalpy of reaction in agreement with a sub-maximal absorption capacity. For [P₃₃₃₃][Bentriz], the adduct formation is even slightly more favourable as the CO₂ chemisorption competes strongly with ion pair binding. Overall it is clear that the experimental order of increasing CO₂ capacity [P₆₆₆₆][Bentriz] < [P₆₆₆₆][123Triz] < [P₆₆₆₆][124Triz] < [P₆₆₆₆][Benzim] may be directly related to the enthalpy of formation of the most favoured carbamate product in each case. This is in turn correlated to the strength of the carbamate bond itself, characterised by the degree to which the nitrogen is able to donate charge into the CO₂ unit. The anions with three neighbouring aromatic nitrogen atoms are seen to show less basicity towards CO₂ than the other anions.

Finally, the influence of the cation was highlighted. The most notable effect is the reaction site on the anion [124Triz]⁻. In the ionic pair, the cation causes an increase in negative charge on one nitrogen, thus enhancing the reactivity on N₁ whereas for the anion-only model the enthalpy of reaction is virtually identical on both nitrogen atoms. Also, as noted above, including the cation in our calculation results in an overall destabilization of the carbamate (though the carbamate function itself is not necessarily more weakly bound) due to a reduction of the ionic pairing energy. Further investigation is needed to establish if the cation effect is moderated by including more ionic pairs in the calculation and/or simulating the equilibrium dynamics of the system. Considering alternative cations, such as those based on ammonium, will enable the influence of the cation to be probed more deeply.

### Acknowledgements

This work was carried out as part of the “4CU” programme grant, aimed at sustainable conversion of carbon dioxide into fuels, led by the University of Sheffield and carried out in collaboration with the University of Manchester; Queen’s University Belfast; and University College London. The authors therefore gratefully acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for supporting this work financially (Grant No. EP/K001329/1). The authors acknowledge the use of the UCL Legion High Performance Computing Facility (Legion@UCL), and associated support services, in the completion of this work.

### References

This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.