Reversible zwitterionic liquids, the reaction of alkanol guanidines, alkanol amidines, and diamines with CO_2

David J. Heldebrant,*[a] Phillip K. Koech,[a] M. Trisha C. Ang,[b] Chen Liang,[b] James E. Rainbolt,[a] Clement R. Yonker[a] and Philip G. Jessop[b]

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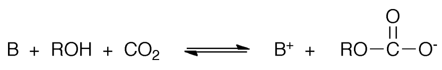
Alkanolamidines, alkanolguanidines and diamines each react with CO_2 to form reversible zwitterionic liquids. CO_2 is chemically bound to the alcohol on alkanolamidines and alkanolguanidines as zwitterionic alkylcarbonates, while CO_2 is chemically bound on diamines as zwitterionic carbamates. All three classes of zwitterionic liquids could be reverted to their non-ionic forms by thermally stripping the CO_2 at temperatures near 50 °C, while one derivative was found to irreversibly form a cyclic carbonate.

Introduction

Carbon dioxide chemistry is increasingly relevant to real-world issues, thanks to global warming. Key chemistry issues currently being studied are the capture, storage, and utilization of CO_2. While the relevance of capture and storage are obvious, the relevance of CO_2 utilization is less clear. Although CO_2 utilization is unlikely to consume significant quantities of CO_2, it can be a significant strategy for the development of sustainable processes. As part of our research efforts towards CO_2 utilization, some of us invented switchable solvents, meaning solvents that can switch reversibly from one version to another.[1] Our original version was a mixture of an amidine and an alcohol (eqn (1), where B is a liquid amidine), but since then we and others have developed others such as guanidine/alcohol mixtures (eqn (1), where B is a liquid guanidine),[2] amidine/primary amine mixtures,[3] and secondary amines (eqn (2)).[4] Switchable solvents of these types all convert from a low-polarity non-ionic liquid to a high-polarity ionic liquid form upon exposure to an atmosphere of CO_2 and revert back to the low polarity form when the CO_2 is removed by heat or flushing with inert gas. We also demonstrated that these switchable solvents can be used as reversible CO_2-binding organic liquids (CO_2BOLs) for CO_2 capture, and are more energy-efficient in that role than aqueous solutions of ethanolamine.[5]

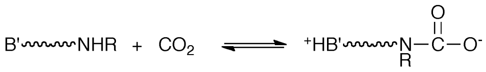


$$\mathrm{B} + \mathrm{ROH} + \mathrm{CO_2} \rightleftharpoons \mathrm{B^+} + \mathrm{RO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-} \quad (1)$$

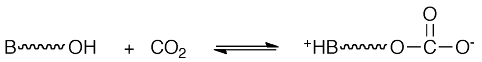
$$2\mathrm{R_2NH} + \mathrm{CO_2} \rightleftharpoons [\mathrm{R_2NH_2^+}][\mathrm{R_2NCO_2^-}] \quad (2)$$

Because these switchable solvents consist of a CO_2-capturing group (an alcohol in eqn (1) and one equivalent of amine in eqn (2)) and a base (B in eqn (1) and the second equivalent of amine in eqn (2)), we conjectured that a single molecule containing both a CO_2-capturing group and a basic functional group would also serve as a switchable solvent and CO_2BOL. These molecules could be an amidine–alcohol, a guanidine–alcohol, or a diamine (eqn (3) and (4)). The key differences in such switchable solvents compared to the earlier examples is that the polar, CO_2-containing form would be zwitterionic. If the reaction with CO_2 is reversible and the zwitterions are liquids, then these liquids could offer advantages over the previously-reported switchable solvents including the ease of use associated with having a single liquid component solvent rather than a mixture, and possibly an enhanced polarity difference between the ionic and non-ionic forms. There are very few reports of non switchable zwitterionic liquids in the literature,[6-10] and none that we could find on their polarity, so it was difficult to predict the polarity of these proposed switchable zwitterionic liquids. The zwitterionic switchable solvents could also have advantages for CO_2 capture in that the gravimetric CO_2 capacity may be higher than in the two-component systems.

It is important not to confuse these proposed zwitterionic liquids with the mythical amidine–CO_2 zwitterionic adducts. Some groups have proposed zwitterionic adducts of amidines and guanidines with CO_2 in which the basic nitrogen atom binds directly to the CO_2 carbon. However such adducts have never been isolated or even observed spectroscopically; reports of spectroscopic detection of such adducts in the past have been erroneous due to confusion with the bicarbonate salts, a result of failure to rigorously remove water from the system before study.[11-15] The zwitterions we report in this paper are entirely different in structure, having the CO_2 coordinated to an alkoxide oxygen (eqn (4)).



$$\mathrm{B'{\sim\sim}NHR} + \mathrm{CO_2} \rightleftharpoons \mathrm{{}^+HB'{\sim\sim}\underset{R}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-} \quad (3)$$



$$\mathrm{B{\sim\sim}OH} + \mathrm{CO_2} \rightleftharpoons \mathrm{{}^+HB{\sim\sim}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-} \quad (4)$$

To our knowledge, the only known switchable zwitterionic liquid was developed in our laboratory.[16] Our first generation switchable zwitterionic liquid was an alkanolamine, which reversibly captured SO_2 as an alkylsulfite salt. We hypothesized

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[a] Pacific Northwest National Laboratory, Richland, WA, USA 99352. E-mail: david.heldebrant@pnl.gov
[b] Department of Chemistry, Queen's University, Kingston, ON, Canada K7L 3N6

Table 1 NMR chemical shifts of **1** in $CDCl_3$ with and without CO_2

^{1}H	1 (OH)	2	3	4	5 (NH)	6	8, 10
1a	2.8 (s)	3.9 (t)	1.6 (m)	3.4 (t)	—	—	2.6 (s), 2.7 (s)
1b	—	4.2 (t)	1.8 (m)	3.7 (t)	6.0–7.0 (s)	—	2.8 (s)
^{13}C	1 (CO_2)	2	3	4	5	6	8, 10
1a	—	62.0	23.3	42.4	—	158.9	35.7, 37.0, 39.8
1b	152.2	66.3	23.3	42.5	—	161.3	36.9, 39.7

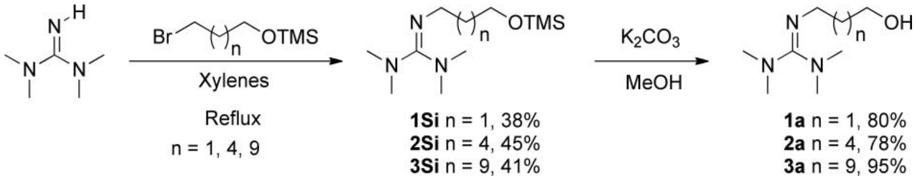
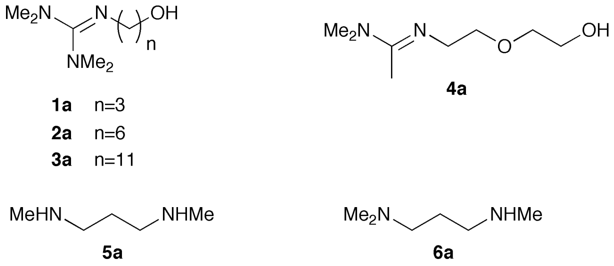


Fig. 1 Synthetic route to **1a** $n = 0$, **2a** $n = 4$, **3a** $n = 9$.

that a similar switchable zwitterionic liquid could be made with CO_2 if a sufficiently strong organic base such as a guanidine or amidine was paired with an alcohol in a single molecule (eqn (1), where "B" represents a basic group such as an amidine or guanidine). Alternatively, we also thought that a diamine, where one or both of the N atoms are secondary amines, would also react with CO_2 to give a zwitterionic liquid (eqn (3), where B′ represents a basic group such as an amine). Such systems could serve as either reversible CO_2-capturing agents or switchable solvents. We now report the preparation and study of these switchable zwitterionic liquids.

Results and discussion

We set out to synthesize a series of compounds (Scheme 1) that could react with CO_2 to make CO_2-activated switchable zwitterionic liquids.



Scheme 1 Candidate precursors for preparing switchable zwitterionic liquids.

(a) Alkanol-guanidines

Our recent interest in CO_2BOLs[1,2,5,17,18] led us to explore the functionalization of an amidine or guanidine with an alcohol to make a single component CO_2BOL. Combining the alcohol and the base components on one molecule (similar to alkanolamines) would simplify the binary alcohol/base solvent mixture into a unimolecular system, and potentially decrease component volatility through hydrogen bonding while increasing CO_2 weight capacities by using shorter alcohol chains. We chose 1,1,3,3-tetramethylguanidine (TMG) as our first substrate base because of its ease of functionalization.

Our first target molecules were alkanolguanidines (compounds **1a**, **2a**, and **3a** in Scheme 1) which were prepared from the reaction of 1,1,3,3-tetramethylguanidine with trimethylsilyl-protected bromoalkanols (Fig. 1). The resulting silyl-protected alkanolguanidines were then cleaved with K_2CO_3 in methanol.

Isolated compound **1a** was a clear and colorless non-viscous liquid. Spectroscopic characterization of **1a** was performed using both ^{1}H and ^{13}C NMR in $CDCl_3$ (Table 1). The ^{1}H NMR of **1a** in $CDCl_3$ showed two inequivalent CH_3 peaks (carbons 8 and 10 using the numbering scheme in Fig. 2) at 2.6 and 2.7 ppm which we attribute to the lack of free rotation around the C=N double bond. Two triplets were observed at 3.9 and 3.4 ppm, which we assign to the CH_2 carbons 2 and 4 respectively. Carbon 3 was visible at 1.6 pm as a multiplet and the alcohol O–H was observed at 2.8 ppm. The infrared (IR) spectrum of **1a** showed a broad O–H band at 3246 cm^{-1} as well as strong (C=N) absorption bands at 1654 and 1618 cm^{-1}.

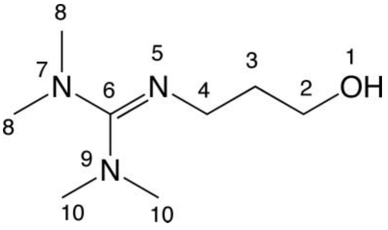


Fig. 2 Numerical assignment of **1a**.

The reaction of anhydrous **1a** with CO_2 lead to the formation of a highly viscous hazy liquid (**1b**), which we assigned the zwitterion structure (eqn (5)). The characteristic increase in viscosity has been observed when mixtures of amidines or guanidines and alcohols react with CO_2 to form their corresponding alkylcarbonate salts.[1,2,4,5,17,18] The zwitterion **1b** was soluble in common organic solvents such as $CDCl_3$ and MeCN and was characterized by NMR. The ^{1}H NMR spectrum ($CDCl_3$) showed no evidence of the free alcohol OH. The spectrum also showed downfield shifting of the R–CH_2–O protons from 3.9 to

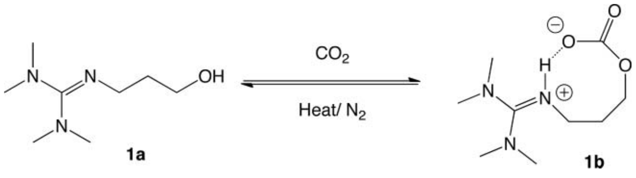
Table 2 NMR chemical shifts of **2a** in $CDCl_3$ with and without CO_2

^1H	1 (OH)	2	3	4	5 (NH)	6	8, 10
2a	(s)	3.5 (t)	1.5, 1.7	3.1 (t)	—	—	2.5, (s) 2.7 (s)
2b	—	3.8 (t)	1.3, 1.5, 1.6	3.7 (t)	8.8 (s)	—	2.8 (s)
^{13}C	1 (CO_2)	2	3	4	5	6	8, 10
2a	—	62.9	23.3	42.4	—	160.8	35.7, 37.0, 39.8
2b	158.6	65.1	23.3	42.5	—	163.2	36.9, 39.7

Table 3 NMR chemical shifts of **3a** in $CDCl_3$ with and without CO_2

^1H	1 (OH)	2	3	4	5 (NH)	6	8, 10
3a	—	3.6 (t)	1.5 (m) 1.3 (s)	3.1 (t)	—	—	2.5, (s) 2.7 (s)
3b	—	3.8 (t)	1.2 (s) 1.5 (m) 1.6 (m)	3.1 (t)	—	—	2.9 (s) broad
^{13}C	1 (CO_2)	2	3	4	5	6	8, 10
3a	—	62.8	26.0, 27.6, 29.7,32.9	49.7	—	160.4	39.0, 39.8
3b	158.9	64.9	25.9–32.9	45.5	—	161.6	40.0

4.2 ppm indicating that CO_2 was chemically bound through the alcohol. The spectrum showed a broad singlet centered at 6.5 ppm corresponding to the guanidinium C=N–H. The viscous liquid could not be a bicarbonate salt of **1** because water was not present. If **1b** was a bicarbonate, there would be no downfield shifting of the alcohol CH_2O protons. The neat ^{13}C spectrum of **1b** showed the guanidinium carbon at 161.3 ppm as well as the alkylcarbonate peak at 152.2 ppm. The guanidinium and carbonate peaks had the same integrated area, indicating stoichiometric absorption of CO_2. The ^1H and ^{13}C chemical shifts are in agreement with our previous studies of amidinium and guanidinium alkylcarbonates.[1,2,5,17,18,19]



(5)

The neat infrared (IR) spectrum of **1b** on NaCl plates showed strong bands at 1653 cm^{-1} and 1615 cm^{-1}, which are comparable to other protonated amidine and guanidine imines $[C=N–H]^+$ such as [DBUH]Cl (1645 cm^{-1})[1] and $[DBUH][OCO_2(CH_2)_5CH_3]$ (1648 cm^{-1}).[2] New strong bands appeared at 1590 cm^{-1}, 1403 cm^{-1}, and 1275 cm^{-1} which we assign to the (C=O) of the carbonate. We also observed medium intensity N–H stretching bands at 3160 cm^{-1}. The free O–H of **1a** was undetectable when CO_2 was bound.

Gravimetrically, 0.502 grams (3 mmol) of **1a** absorbed 0.130 grams (3 mmol) of CO_2, corresponding to 20.6% CO_2 by weight. The zwitterion **1b** did not off-gas, rather it slowly cyclized into a cyclic carbonate. All attempts to thermally release CO_2 were unsuccessful because of condensation of the carboxylate to the activated imine carbon (6) to produce the cyclic ester (Fig. 3). The cyclic ester ^{13}C spectrum ($CDCl_3$) showed a carboxylate peak at 153 ppm, the $N_3C–O$ tetra-coordinated carbon at 125 ppm, the $CH_2–OCO_2$ carbonate at 66 ppm, and the ^1H spectrum showed aliphatic $CH_2–OCO_2–$ hydrogens at 4.1 ppm and $CH_2–N$ hydrogens at 3.3 ppm. The CH_3 hydrogens were observed as an equivalent singlet at 2.7 ppm, and the internal $R–CH_2–R$ hydrogens were observed as a pentet at 1.7 ppm. The cyclic carbonate is a non-viscous liquid that boils at 100 °C and does not release CO_2. The cyclic carbonate is likely forming because of the length of the propanol chain of the alcohol allowing the carboxylate to be in proximity to form a thermodynamically favorable 8-membered ring. Compound **1a** is not a useful reversible zwitterionic liquid because of its inability to release CO_2.

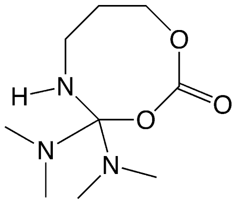


Fig. 3 The proposed structure of the cyclic carbonate product of **1b** heated above 25 °C.

We hypothesized that a longer alkyl spacer between the alcohol and guanidine would inhibit cyclization, so we synthesized two longer chained TMG derivatives (compounds **2a** and **3a** in Scheme 1 and Fig. 4). Isolated compounds **2a** and **3a** were both hazy white non-viscous liquids. The ^1H NMR spectra of compounds **2a** and **3a** (Tables 2 and 3) were nearly identical to the compound **1a**, with the only difference being the

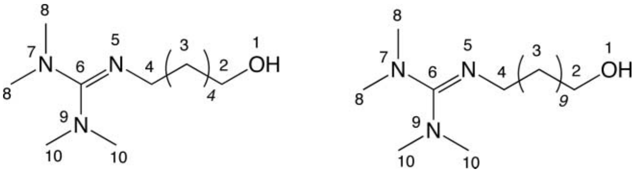
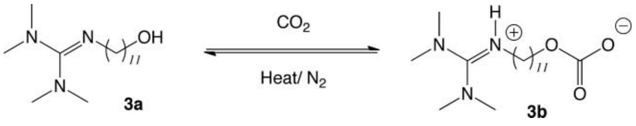


Fig. 4 Numerical assignment of positions in compounds **2a** and **3a**.

6 or 9 aliphatic carbons of the alcohol chains. The infrared (IR) spectrum of **2a** and **3a** showed broad O–H bands at 3356 cm^{-1} 3381 cm^{-1} as well as strong (C=N) absorption bands at 1604 cm^{-1}. and 1605 cm^{-1} respectively.

Compound **3a** converts to a slightly yellow waxy solid in the presence of CO_2 (**3b**, eqn (6)). The solid was soluble in common organic solvents such as $CDCl_3$ and MeCN and was characterized by NMR. The ^1H and ^{13}C spectra of this solid were similar to the propanol derivative **1b** except that only 74% CO_2 was absorbed.

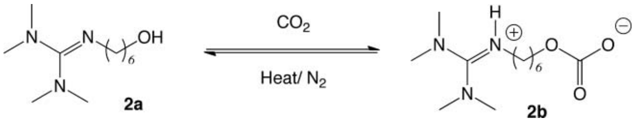


(6)

The IR spectrum of the crude **3b** on NaCl plates showed what appeared to be a mixture of carboxylated and non-carboxylated TMG–$(CH_2)_{11}$–OH. New (C=N) bands at 1695 cm^{-1}, 1670 cm^{-1}, 1605 cm^{-1}, and (C=O) bands at 1591 cm^{-1}, 1402 cm^{-1}, 997 cm^{-1}, and 833 cm^{-1} were observed for the carboxylated species. N–H stretching bands were not detected because of strong overlapping O–H bands at 3375 cm^{-1}. The solid does not melt, rather it decarboxylates completely at 65 °C. Attempts to crystallize the solid only yielded a waxy or gel like solid, which was not suitable for crystallographic analysis.

Our third target alkanolguanidine was a hexanol-functionalized TMG. The isolated TMG–$(CH_2)_6$–OH **2a** was a clear and colorless non-viscous liquid. The ^1H and ^{13}C NMR spectra ($CDCl_3$) are presented in Table 3. The ^1H and ^{13}C NMR spectra showed the same trends as the propanol and undecanol derivatives. The infrared (IR) spectrum of **2a** showed a broad O–H band at 3356 cm^{-1} as well as strong (C=N) absorption bands at 1604 cm^{-1}.

The reaction of anhydrous **2a** with CO_2 leads to the formation of a highly viscous hazy liquid (**2b**, eqn (7)). The zwitterion was found to be soluble in $CDCl_3$ and MeCN as well as acetone. Nile red indicator dye was found to be insoluble in **2a** as well as **2b**, and no polarity data could be measured. No polarity measurements were performed on **1a**,**b** or **3a**,**b**. Table 3 lists the ^1H and ^{13}C NMR spectra of the zwitterion in $CDCl_3$. The ^1H and ^{13}C chemical shifts showed the same trends as the propanol and undecanol derivatives in the presence of CO_2.



(7)

The IR spectrum of **2b** on NaCl plates was a mixture of carboxylated and non-carboxylated material. We observed a new strong C=N band at 1618 cm^{-1}, strong C=O bands at 1600 cm^{-1}, 1403 cm^{-1}, and 1290 cm^{-1} and broad O–H stretching bands at 3379 cm^{-1}. The N–H band was not detected because it was dwarfed under the very broad and strong O–H peak of **2a**.

Gravimetrically, 0.452 grams (2 mmol) of **2a** absorbed 0.046 grams (1 mmol) of CO_2, corresponding to 10.2% CO_2 by weight. The 0.5 molar equivalent of chemically bound CO_2 were thermally stripped from **2b** at 70 °C. The **2a** was then re-contacted with CO_2 and then stripped for a total of three cycles. Each absorption cycle, **2a** bound 0.046 grams of CO_2, and each stripping released 0.046 grams of CO_2.

In our previous studies, dual component mixtures of TMG and linear alcohols in MeCN were unable to capture more than 0.47 molar equivalents of CO_2. Previous thermodynamic estimates of the energetics of CO_2 binding by mixtures of alcohols and TMG showed CO_2 binding was entropically unfavorable (on average $\Delta H = -160$ kJ mol^{-1} and $\Delta S = -530$ J mol^{-1}).[5]

The single component showed slightly similar thermodynamic properties to our dual component mixtures of alcohols and guanidines. We estimate values from the Van't Hoff plot of the integrations of the hydrogens of the bound (CH_2–O–CO_2) and unbound (CH_2–OH) in $CDCl_3$ as a function of temperature to be $\Delta H = -87.0$ kJ mol^{-1} and $\Delta S = -293$ J mol^{-1} for **2a** and $\Delta H = -87$ kJ mol^{-1} and $\Delta S = -291$ J mol^{-1} for **3a**. In the zwitterionic experiments, K is defined as $[\mathbf{2b}]/(P_{CO_2}[\mathbf{2a}])$, which is different from the K defined in our dual component systems. The estimated thermodynamics from the single component systems are similar to estimates of the dual component systems in that the binding of CO_2 is entropically controlled. This suggests that alkanolguanidines bind CO_2 in a similar manner as dual component systems. The entropically unfavored binding of CO_2 makes TMG a poor choice for a base component for switchable zwitterionic liquids at STP, however they may be applicable in high pressure applications. We are investigating the functionalization of an amidine base like DBU with a hexanol chain, which we predict is likely to be more thermodynamically favored and may bind up to 1 molar equivalent of CO_2 at STP. The thermodynamic estimates to date suggest that the limitation of CO_2 binding is due to the thermodynamics of the alkylcarbonate guanidinium binding mode of CO_2BOLs and not the carbamate-like binding mode of alkanolamines.

CO_2 is bound through the alcohol moiety in alkanolguanidines in contrast to its binding to the amine of an alkanolamine because of two factors: the reduced nucleophilicity of guanidines compared to amines, and the higher basicity of amidines and guanidines compared to amines. To our knowledge, there are no published accounts of isolated carbaguanidinium or carbamidinium zwitterions. We believe they are not isolable because amidines and guanidines are weak nucleophiles and weak hydrogen bond donors or acceptors[20] and are unable to react with CO_2 at standard temperature and pressure unless in the presence of a weak acid. The alcohol moiety of the alkanolguanidine is more nucleophilic than the delocalized guanidine component. Alcohols are known to react with CO_2 to form thermodynamically unstable alkylcarbonic acids.[21,22] Alkylcarbonic acids have been stabilized by the addition of strong bases, such as DBU or TMG as is the case with our previous systems.[1,2,5,17,19] We previously hypothesized that simple amines are not basic enough to accept the proton from alkylcarbonic acids and do not form alkylcarbonates[5] like amidine and guanidine bases.

(b) Alkanol-Amidines

Amidines are slightly less basic than guanidines but are still sufficiently basic to serve as the basic group in a

4a **4b** (8)

zwitterionic liquid precursor. *N*′-(2-Hydroxyethoxy)ethyl)-*N*,*N*-dimethylacetamidine (compound **4a** in Scheme 1 and Fig. 5) was prepared from aminoethoxyethanol by treatment with *N*,*N*-dimethylacetamide dimethylacetal and purified by vacuum distillation. The colorless liquid **4a** greatly increases in viscosity when CO_2 is bubbled through it. The product **4b** has been identified spectroscopically to be as shown in eqn (8).

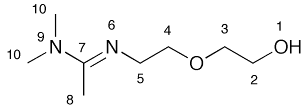


Fig. 5 Numerical assignment of positions in compound **4**.

Upon the reaction of **4a** with CO_2, the mass of the liquid phase increases by 20%. The theoretical mass increase, according to the stoichiometry of the equation and neglecting dissolved CO_2, is 25%. This gravimetric evidence, as well as the NMR evidence, show that the reaction is incomplete. ^{13}C NMR spectra of a solution of **4a** in DMSO (1 : 1 mixture by volume (Table 4)) show that, as CO_2 is bubbled through the solution, two small new peaks appear at 160.7 and 155.9 ppm, in addition to the peak for **4a** at 160.4 ppm. After further CO_2 treatment, the peaks have shifted to 161.6 and 156.2 and have become larger than the peak for **4a**. We attribute the new peaks to the protonated amidine group and the alkylcarbonate group of **4b**, respectively. In comparison, the alkylcarbonate peak of [DBUH][O_2COR] ionic liquid appears at 157–159 ppm depending on the alkyl group.[2] Heating the DMSO/**4b** mixture and bubbling argon through it restored the ^{13}C-NMR spectrum of **4a**.

A dilute solution of **4a** in DMSO failed to react significantly with CO_2, suggesting that DMSO as a solvent inhibits the reaction. The same effect was observed for a dilute solution of **4a** in C_6D_6.

To determine the polarity change upon conversion from the amidine alcohol to the zwitterionic liquid, the spectrum of a solution of solvatochromatic dye Nile Red in liquid **4a** was obtained before and after treatment with CO_2, The wavelength of maximum absorbance (λ_{max}) of a solution of Nile Red is indicative of the polarity of the solvent.[23] The λ_{max} value of Nile Red dissolved in neat **4a** was 544 nm before exposure to CO_2, indicating a polarity comparable to 1-octanol. After CO_2 was bubbled through the sample for 20 min at room temperature, the absorbance shifted to 554 nm, indicating a polarity that is greater than that of methanol. This amount of polarity change is comparable to that observed with the DBU/*n*-propanol switchable solvent,[2] showing that the amidine–alcohol single-component switchable solvent is just as effective as the DBU/*n*-propanol two-component switchable solvent and that there is no inherent advantage, in terms of increasing the size of the polarity change, to using a switchable zwitterionic liquid rather than a switchable ionic liquid.

(c) Diamines containing two secondary amines

Liquid secondary amines represent another kind of switchable solvent, wherein CO_2 is bound directly to the nitrogen atom in a carbamate salt rather than to an oxygen atom in an alkylcarbonate as is the case for alkanolguanidines and alkanolamidines.[4] Amines such as *N*-ethyl-*N*-butylamine, *N*-ethyl-*N*-propylamine, dipropylamine, and benzylmethylamine, are low-polarity non-ionic liquids that are switched, by exposure to CO_2, into carbamate ionic liquids of increased polarity (eqn (2)). By heating the viscous liquid to 60 °C and purging it with N_2, the liquid can switch back to the low polarity form. In most cases, especially for primary amines, solid carbamate salts are formed following the addition of CO_2.

We speculated that a diamine in which both amines were secondary would function as a switchable solvent and as a potential CO_2-capturing liquid (eqn (9)) However, only a liquid diamine that gave a liquid zwitterion would be acceptable for these applications. We screened the liquid diamines of the structure $RHN(CH_2)_nNHR$ where $n = 2$ (R = Me), $n = 3$ (R = Me, Et, i-Pr), and $n = 6$ (Me, Et, Bu). All gave solids upon reaction with CO_2. Note that in every case the diamines were used as received and not dried in any way. It is quite possible, for reasons explained below, that thoroughly dried amines might give liquids upon reaction with CO_2, but this possibility was not pursued because, for practical reasons, it is preferable to have a system that is water tolerant. The reaction

Table 4 NMR chemical shifts of **4** in DMSO-d_6 with and without CO_2

^{1}H	1 (OH)	2–5	6 (NH)	7	8	10
4a	4.7 (br)	3.23 (t), 3.4-3.5 (m)	—	—	1.82 (s)	2.78 (s)
4b	7.4 [a](br)	3.3-3.5 [a](m)	—	—	2.03 [a](br)	2.95 [a](br)
4a+HCl	5.6 (br)	3.45 (m), 3.48 (m), 3.56 (m)	9.19 (s)	—	2.31 (s)	3.17 (s), 3.22 (s)
^{13}C	1 (CO_2)	2–5	6	7	8	10
4a	—	51.1, 62.4, 73.0, 73.3	—	159.8[b]	12.7	38.0
4b	155.9	47.0, 62.8, 70.2, 70.7	—	160.7	13.3	38.6
4a+HCl	—	43.8, 60.0, 69.1, 72.3	—	164.7	15.0	41.0, 39.8

[a] These peaks are broadened due to high viscosity. [b] In very concentrated solution, this peak is at 160.4 ppm.

Table 5 NMR chemical shifts of **5** in $CDCl_3$ with and without CO_2

^1H	1	2 (NH)	3	4	5	6	7
5a	2.3 (s)	1.0 (br)	2.5 (t)	1.6 (quint)	—	—	—
5b	2.6 (br)	10.6 (br)	2.9 (br)[a]	1.9 (br)	3.4 (br)	2.8 (br)[a]	—

^{13}C	1	2 (NH)	3	4	5	6	7
5a	36.7	—	50.7	30.2	—	—	—
5b	32.1	—	44.7[a]	23.8	44.7[a]	34.2	163.9

[a] Overlapped.

of $MeHN(CH_2)_3NHMe$ (**5a**) with CO_2 is described here, and is representative of the behaviour of these amines.

The viscosity of neat liquid **5a** increased as CO_2 was bubbled through it. Upon completion of the reaction, the liquid turned into a white solid, to which we assign the zwitterionic structure $[MeH_2N^+CH_2CH_2CH_2N(Me)CO_2^-]$ (eqn (9)). The ATR-IR spectrum of the solid showed a band at 1545 cm^{-1}, which is characteristic of a carbamate anion.[24] No peak was observed at 835 cm^{-1}, which would have indicated the presence of a bicarbonate anion. The ^1H NMR spectrum of **5b** shows only minor changes in the chemical shifts of most carbon-bound protons except at positions 5 and 6 (see numbering scheme in Fig. 7), where the peaks have shifted downfield by 0.9 and ~0.6 ppm, respectively (Table 5). The N-bound proton has shifted from 1.0 ppm to 10.6 ppm, consistent with the change in charge on the N atom from neutral to positive. In the ^{13}C NMR spectrum of **5b**, a new peak appears at 163.9 ppm, which corresponds to the carbamate central carbon. Crystals of the product were grown by slow evaporation of a solution of the compound in hexanes under a CO_2 atmosphere. The crystal structure confirms the formation of a zwitterionic salt co-crystallized with one water molecule (Fig. 6). The water molecule is an integral part of the hydrogen-bonding network in the structure, which suggested to us that if the water had been absent, the salt might not have solidified. However, treating thoroughly-dried **5a** with CO_2 also created a solid.

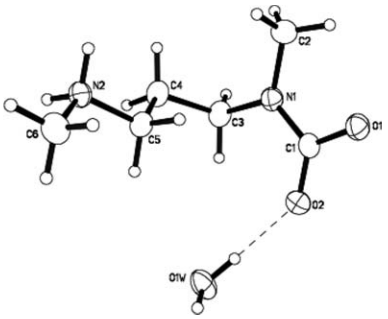
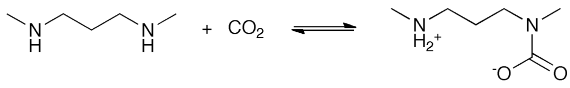


Fig. 6 Crystal structure of zwitterionic $[MeH_2N^+CH_2CH_2CH_2N(Me)CO_2^-]\cdot H_2O$ (**5b**). Displacement ellipsoids are drawn at the 50% probability level.

Fig. 7 Numerical assignment of positions in **5a** and **5b**.

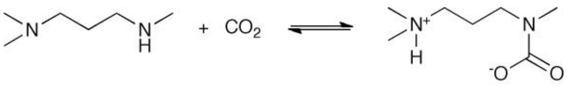


(9)

5a **5b**

(d) Diamines containing one secondary amine and one tertiary amine

Because all diamines having two secondary amines gave solids, a diamine containing one secondary and one tertiary amine was tested. Bubbling CO_2 through neat liquid *N*,*N'*-trimethyl-1,3-propanediamine (compound **6a**) increased the viscosity of the liquid greatly, but no solidification was observed. We assign the zwitterionic structure $[Me_2HN^+CH_2CH_2CH_2N(Me)CO_2^-]$ (**6b**) to the liquid product (eqn (10)). The ATR-IR spectrum of the solid showed the disappearance of the N–H band at 3298 cm^{-1} and the appearance of a band at 1545 cm^{-1}, which is characteristic of a carbamate anion.[24] No peak was observed at 835 cm^{-1}, which would have indicated the presence of bicarbonate anion. The ^1H NMR spectrum of **6b** shows only minor changes in the chemical shifts of most carbon-bound protons except at positions 5 and 7 (see numbering scheme in Fig. 8), where the peaks have shifted downfield by 0.6 and 0.4 ppm, respectively. The N-bound proton peak for the secondary amine disappears and a new peak at 10.6 ppm appears, consistent with a dialkylammonium cation (Table 6). In the ^{13}C NMR spectrum, a new peak appears at 163.9 ppm, which corresponds to the carbamate central carbon. High resolution ESI mass-spec (positive mode) of $[Me_2HN^+CH_2CH_2CH_2N(Me)CO_2^-]$ was measured and matched the expected M + 1 peak of 161.13 *m*/*z*.



(10)

6a **6b**

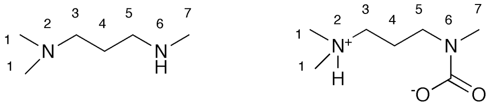


Fig. 8 Numerical assignment of positions in **6a** and **6b**.

The mass of liquid **6a** increased by 28 wt% due to uptake of CO_2. The theoretical increase in mass, assuming complete conversion but neglecting the mass of dissolved CO_2, should be 38%. The lower observed uptake suggests that the conversion of eqn (9) is incomplete, which may be the reason why the liquid did

Table 6 NMR chemical shifts of **6** in $CDCl_3$ with and without CO_2

^{1}H	1	2 (NH)	3	4	5	6	7
6a	2.2 (s)	—	2.3 (t)	1.6 (quint)	2.6 (t)	1.4 (br)	2.4 (s)
6b	2.3 (s)	10.5 (br)	2.4 (t)	1.8 (m)	3.2 (br)	—	2.8 (br)

^{13}C	1	2 (NH)	3	4	5	6 (CO_2)	7
6a	45.4	—	57.9	27.9	50.5	—	36.5
6b	44.8	—	56.7	25.1	47.2	161.1	34.0

not solidify. Removal of CO_2 and reversion of the liquid back to the neutral diamine form was achieved by bubbling argon through the viscous zwitterionic liquid at 60 °C. The reversion back to the diamine was confirmed by ^{1}H NMR spectroscopy.

To determine the polarity change upon conversion from the diamine to the zwitterionic liquid, the spectrum of the solvatochromatic dye Nile Red was obtained while the dye was in liquid **6** before and after treatment with CO_2, The λ_{max} value of Nile Red dissolved in neat **6a** was 523 before exposure to CO_2, indicating a polarity comparable to benzene. After CO_2 was bubbled through the sample with CO_2 for 20 min at room temperature, the absorbance shifted to 534 nm, indicating a polarity that is comparable to that of THF. This amount of polarity change is comparable to that observed with simple secondary amines such as ethyl butyl amine,[4] showing that there is no inherent advantage, in terms of increasing size of the polarity change, to using switchable zwitterionic liquids rather than switchable ionic liquids.

Experimental

All reactions were run under an atmosphere of argon, unless otherwise indicated. Flasks were oven-dried and cooled under vacuum. All secondary diamines, solvatochromatic dye, CO_2 (supercritical fluid chromatography grade), argon (99.98%), chlorotrimethylsilane, triethylamine, 3-bromo-1-propanol, 6-bromo-1-hexanol, 11-bromo-1-undecanol and 1,1,3.3-tetrametylguanidine were purchased from Sigma-Aldrich and used as received. High-resolution mass spectra (HRMS) ESI for compounds **2Si**–**3Si**, **1a**–**3a** were obtained on a Thermo Scientific Exactive (tm) Mass Spectrometer from Thermo Scientific Company as *m/z* (relative intensity). High-resolution mass spectrum (HRMS) ESI for **6b** was obtained on a Qstar XL QqTOF from Applied Biosystems/MDS Sciex. Accurate masses are reported for the molecular ion (M + 1) or a suitable fragment ion. IR measurements for compounds **1Si**–**3Si**, **1a**–**3b** were performed on NaCl disks using a Nicolet Magna-750 spectrometer running on OMNIC software. The IR spectra for compounds **5a**, **5b**, **6a**, and **6b** were obtained on a Varian Scimitar 1000 FTIR equipped with the Pike MIRacle™ ZnSe ATR accessory. Proton nuclear magnetic resonance (^{1}H NMR) spectra for compounds **1Si**–**3Si**, **1a**–**3b** were recorded with a Varian (300 MHz) spectrometer. Chemical Shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance ($^{13}C\{^{1}H\}$ NMR) spectra for compounds **1Si**–**3Si**, **1a**–**3b** were recorded with a Varian 300 (75.5 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. ^{1}H and ^{13}C NMR spectra for compounds **4a**–**6b** were obtained with a Bruker AVANCE-400 MHz NMR spectrometer where each sample is referenced to tetramethylsilane. The NMR spectra of the CO_2 treated amines were obtained by bubbling CO_2 into a septa capped NMR tube that had 0.1 mL amine in dry $CDCl_3$. Data collection for the crystal of **5b** was done on a Bruker SMART APEX II X-ray diffractometer.

N,*N*,*N′*,*N′*-Tetramethyl-*N″*-(3-trimethylsilanyloxypropyl)-guanidine (1Si)

1,1,3,3-Tetramethylguanidine (TMG) (33.6 mL, 260.4 mmol) was charged into a 250 mL round bottom flask and then xylenes (25 mL) was added, this solution was heated to reflux. While maintaining the temperature (3-bromopropoxy)trimethylsilane[25] 25 g (118.39 mmol) was added. The resulting white suspension was refluxed overnight. After which the reaction was allowed to cool to room temperature and the resulting precipitate was filtered off, and the filtrate was distilled under vacuum, collecting xylenes followed by a second fraction compound **1a** as a colorless viscous liquid (9 g, 38%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (t, $J = 5.4$ Hz, 2H), 3.46 (t, $J = 5.4$ Hz, 2H), 2.00 (quin, $J = 5.3$ Hz, 2H), 0.09 (s, 9H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, neat) δ 160.4, 61.1, 45.9, 39.7, 39.0, 35.6, -0.3. FTIR (NaCl, film): 2940, 1661, 1653, 1495, 1366, 1249, 1091, 839 cm^{-1}

N″-(3-Hydroxypropyl)-*N*,*N*,*N′*,*N′*-tetramethylguanidine (1a)

1.3 g of compound **1Si** was charge into a clean dry 100 mL RB flask, and then anhydrous MeOH 20 mL was added. The solution was degassed by bubbling argon for 10 min and then K_2CO_3 1.46 g was added, this mixture was stirred at RT for 1 h. The reaction mixture was then filtered and the resulting filtrate was distilled under vacuum to afford compound **1a** as a colorless liquid (0.73 g 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (t, $J = 5.0$ Hz, 2H), 3.33 (t, $J = 5.0$ Hz, 2H), 2.72 (br s, 1H),2.19 (s, 6H), 2.58 (s, 6H) 1.64 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, neat) δ 158.9, 62.0, 42.4, 39.8, 39.0, 35.7, 23.3 FTIR (NaCl, film): 3246, 2927, 1653, 1611, 1496, 1455, 13609, 1330, 1178, 1132, 1062 cm^{-1} HRMS ESI (positive mode M + H^+) calculated for $C_8H_{19}N_3O$ 174.1600, found 174.1596.

N,*N*,*N*′,*N*′-Tetramethyl-*N*″-(6-trimethylsilanyloxyhexyl)-guanidine (2Si)

Following the same procedure as for **1Si** using, (6-bromohexoxy)trimethylsilane[27] (3.50 g, 13.90 mmol), TMG (3.80 mL, 30.55 mmol) and xylenes (5 mL) affords **2a** (1.8 g, 45%) as a pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.53 (t, $J = 7.0$ Hz, 2H), 3.06 (t, $J = 7.0$ Hz, 2H), 2.70 (s, 6H), 2.62 (s, 6H), 1.47 (m, 2H) 1.24 (m, 6H), 0.08 (s, 9H). ^{13}C{^{1}H} NMR (75.5 MHz) δ 160.1, 62.9, 49.6, 39.8, 39.0, 32.9, 27.4, 25.9, -0.3. FTIR (NaCl, film): 2931, 2859, 1663, 1494, 1453, 1363, 1243, 1095, 840 cm^{-1} HRMS ESI (positive mode M + H$^+$) calculated for $C_{14}H_{33}N_3OSi$ 288.2465, found 288.2453.

N″-(6-Hydroxyhexyl)-*N*,*N*,*N*′,*N*′-tetramethylguanidine 2a

Following the same procedure as for compound **1a** using compound **2Si** (1.70 g, 5.92 mmol), K_2CO_3 (1.63 g, 11.83 mmol), and MeOH (15 mL) provides **2a** (1.0 g, 78%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, $J = 6.7$H Hz, 2H), 3.06 (t, $J = 6.7$ Hz, 2H), 2.70 (s, 6H), 2.61 (s, 6H), 1.51 (m, 4H) 1.32 (m, 4H). ^{13}C{^{1}H} NMR (75.5 MHz) δ 160.8, 62.9, 42.4 39.8, 37.0, 35.7, 23.3. FTIR (NaCl, film): 3355, 2995, 2928, 1618, 1501, 1454, 13.74, 1238, 1137, 1102, 751 cm^{-1} HRMS ESI (positive mode M + H$^+$) calculated for $C_{11}H_{25}N_3O$ 216.2070, found 216.2061.

N,*N*,*N*′,*N*′-Tetramethyl-*N*″-(11-trimethylsilanyloxyundecyl)-guanidine (3Si)

Following the same procedure as for **1Si** using, (11-bromoundecanoxy)trimethylsilane[26] (8.1 g, 25.10 mmol), TMG (7.0 mL, 55.30 mmol) and xylenes (10 mL) provide compound **3Si** (3.70 g, 41%) as a pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ. 3.56 (t, $J = 7.2$ Hz, 2H), 3.04 (t, $J = 7.2$ Hz, 2H), 2.69 (s, 6H), 2.61 (s, 6H), 1.49 (quintet, $J = 7.2$ Hz, 4H), 1.23 (unresolved s, 14H), 0.24 (s, 9H). ^{13}C{^{1}H} NMR (75.5 MHz, neat) δ 62.8, 49.7, 39.8, 39.0, 32.9, 32.8, 29.7, 27.6, 25.9, 2.1 FTIR (NaCl, film): 2925, 2853, 1604, 1502, 1456, 1375, 1252, 1136, 1059, 845 cm^{-1}. HRMS ESI (positive mode M + H$^+$) calculated for $C_{19}H_{43}N_3OSi$ 358.3248, found 358.3256.

N″-(11-Hydroxyundecyl)-*N*,*N*,*N*′,*N*′-tetramethylguanidine (3a)

Following the same procedure as for compound **1a** using compound **3Si** (2.80 g, 7.83 mmol), K_2CO_3 (2.12 g, 16.79 mmol), and MeOH (20 mL) provides **3a** (2.16 g, 95%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ. 3.57 (t, $J = 7.5$ Hz, 2H), 3.04 (t, $J = 7.5$ Hz, 2H), 2.85 (s, 1H), 2.70 (s, 6H), 2.62 (s, 6H), 1.49 (quintet, $J = 6.8$ Hz, 4H), 1.23 (unresolved s, 14H).^{13}C{^{1}H} NMR (75.5 MHz, neat) δ 62.8, 49.6, 39.7, 38.9, 32.9, 37.7, 29.6 27.6, 25.9. FTIR (NaCl, film): 3381, 2921, 2852, 1605, 1501, 1455, 1375, 1145, 1063 cm^{-1}. HRMS ESI (positive mode M + H$^+$) calculated for $C_{16}H_{35}N_3O$ 286.2853, found 286.2855.

Preparation of *N*′-(2-hydroxyethoxy)ethyl)-*N*,*N*-dimethylacetamidine (4a)

Aminoethoxyethanol (6.1 g) was charged into a round bottom flask. *N*,*N*-Dimethylacetamide dimethylacetal (8.0 g) was added to reaction mixture, which was then heated to 75 °C, stirred for 30 min, cooled, and concentrated in a rotary evaporator. A clear colorless liquid was recovered after vacuum distillation (yield 82%). ESI-MS (positive mode, M + H$^+$) observed: 175.1447, calculated for $C_8H_{19}N_2O_2$: 175.1441. IR (neat, cm^{-1}): 3365 m, 2864 s, 1612 s, 1390 m, 1128 m, 1063 m, 1013 w, 891 w, 574 w.

Treatment of *N*′-(2-hydroxyethoxy)ethyl)-*N*,*N*-dimethylacetamidine (4a) with CO_2

Carbon dioxide was bubbled, *via* a syringe needle, through a sample of **4a** in a test tube. Although the liquid became quite viscous after only 0.5 h, the bubbling was continued for another 3 h to ensure maximum possible conversion. IR (neat, cm^{-1}): 3366 m, 2871 m, 1646 s, 1396 m, 1287 m, 1126 m, 1066 m, 1013 m, 836 w, 621 w. NMR data given in Table 4. ESI-MS (negative mode, M+H$^+$) observed: 217.1200, calculated for $C_9H_{17}N_2O_4$: 217.1188.

IR spectroscopic data for the bases before and after CO_2 treatment

***N*,*N*′-Dimethyl-1,3-propanediamine (5a).** (neat, cm^{-1}) Before CO_2 treatment: 3280 m, 2929 m, 2879 m, 2841 m, 2786 s, 2694 w, 1473 s, 1446 s, 1124 s, 739 s. After CO_2 treatment: 3289 w, 2928 m, 2840 m, 2787 m, 2405 m, 2361 m, 1545 s, 1471 s, 1372 s, 1034 s, 1255 s, 1038 s, 807 s, 757 s.

***N*,*N*,*N*′-Trimethyl-1,3-propanediamine (6a).** (neat, cm^{-1}) Before CO_2 treatment: 3298 w, 2940 s, 2857 m, 2814 s, 2783 s, 2764 s, 1739 w, 1460 s, 1376 w, 1263 w, 1150 m, 1122 m, 1041 s, 839 s, 743 s. After CO_2 treatment: 2941 m, 2814 m, 2762 m, 2462 w, 1683 w, 1624 w, 1545 w, 1460 s, 1376 s, 1305 m, 1262 s, 1040 s, 808 m.

Gravimetric uptake of CO_2 by *N*,*N*,*N*′-trimethyl-1,3-propanediamine (6a)

Compound **6a** (0.3 mL, 2.05 mmol) was added to a flame-dried 1 dram vial sealed with a rubber septa and massed. CO_2 was bubbled into the amine at room temperature and 1 bar to form the zwitterion. Mass was taken at 10 min intervals for 100 min although no further mass increase was observed after the first 10 min.

Polarity measurement of *N*,*N*,*N*′-trimethyl-1,3-propanediamine (6a)

Approximately 3 mL of the amine was placed in a 1 cm quartz cuvette where it was dotted with Nile red on a needle tip to give an absorbance between that of 0.5 and 1.0. The cuvette was then bubbled with atmospheric CO_2 for a period of 20 min or until the viscosity of the amine changed. A UV/visible spectrum was measured again. The experiment was done in triplicate, where the average of all three is the reported measurement.

Conclusions

Compounds **2a**, **4a**, and **6a** are switchable solvents, in that they react reversibly with CO_2 to form zwitterionic liquids. Any of these three compounds can serve as switchable solvents and as organic CO_2-capturing agents (CO_2BOLs). The liquid zwitterionic salts were all highly viscous and polar. The change in polarity, upon conversion of the neutral molecule to the zwitterion, was comparable to that observed with non-zwitterionic switchable solvents. In terms of gravimetric CO_2-capturing capacity, these liquids are comparable to the two-component CO_2-binding liquids reported previously.

For alkanolguanidines, the chain length of the alkyl group between the alcohol and guanidine has an affect on the physical properties and regeneration of the alkanolguanidines. Short alkyl chains promoted cyclization of the carbonate to form the cyclic carbonate. Longer alkyl chains produced a reversible zwitterionic liquid, while very long alkyl chains produced reversible zwitterionic wax-like materials.

Di-secondary diamines and a secondary/tertiary diamine were found to form reversible zwitterionic carbamate salts, although only the secondary/tertiary diamine gave a liquid salt.

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