Synthesis and Study of the Stability of Amidinium/Guanidinium Carbamates of Amines and α-Amino Acids

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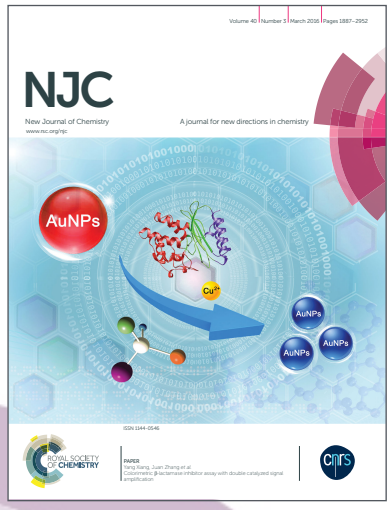

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Synthesis and Study of the Stability of Amidinium/Guanidinium Carbamates of Amines and α-Amino Acids

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Thermally stable amidinium/guanidinium *N,N*-dialkylcarbamates, including vacuum stable compounds, have been prepared, and then isolated in the solid state, by reaction of tetramethylguanidine (TMG) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with secondary amines under atmospheric pressure of CO_2. The same method has been successfully applied to α-amino acids, thus the corresponding carbamates of sarcosine, L-proline and L-phenylalanine have been obtained. All the products are highly moisture sensitive, and have been characterized by analytical and spectroscopic (IR, multinuclear NMR) techniques.

Introduction

Pioneering studies performed in aqueous solution in the first decades of the past century showed that amines reacted with CO_2 in 2:1 molar ratio (Eq. 1) affording alkylammonium alkylcarbamates, $[NH_2RR'][O_2CNRR']$.[1] This reactivity was confirmed in subsequent papers,[2] then the studies were extended to α-amino acids.[3]

$$CO_2 + 2\ NHRR' \rightleftharpoons [NH_2RR'][O_2CNRR'] \quad (1)$$

$$[NH_2RR'][O_2CNRR'] + H_2O \rightleftharpoons NHRR' + [NH_2RR'][HCO_3] \quad (2)$$

R, R' = H, alkyl

The formation of the bicarbonate ion is a competitive reaction in the presence of water (Eq. 2). Instead, under strictly anhydrous conditions, ammonium carbamates derived from primary alkylamines form quantitatively but can be isolated only under CO_2 atmosphere.[4] In fact, CO_2 uptake by some primary amines, NH_2R (R = Bu, ^{i}Pr, Cy), leads to colourless solids according to a CO_2/amine molar ratio close to 0.5, as expected for the predominant formation of $[NH_3R][O_2CNHR]$.[4] On the other hand, the carbonatation of secondary alkylamines is less favoured, and reaction molar ratios lower than 0.5 have been ascertained in hydrocarbon solution (e.g., 0.43 for $NHEt_2$, 0.08 for $NHBz_2$, 0.02 for $NHCy_2$).[4] It has been demonstrated that the possibility of obtaining stable ammonium carbamates does not depend only on the relative basicity of the amine, but also on other factors (*e.g.* amine steric hindrance and lattice energy of the salt).[5]

Due to the fast increase of atmospheric CO_2 level and its presumable impact on the world climate change,[6] the interest in the carbonatation of amines has seen a recent renaissance as a viable strategy to transform carbon dioxide into useful chemicals, e.g. ionic solvents.[7]

It has been recently shown that 1:1 mixtures of organic superbases[8] and amines[9] or α-amino acids[10] are more effective in the fixation of carbon dioxide than amines / α-amino acids alone. The most commonly employed superbases are tetramethylguanidine (TMG) (Fig. 1a) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Fig. 1b), affording guanidinium (Eq. 3) and amidinium (Eq. 4) carbamates, respectively.

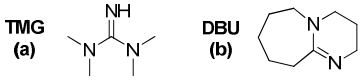


Figure 1. Structures of tetramethylguanidine (TMG, a) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, b).

$$NHRR' + TMG + CO_2 \rightarrow [TMGH][O_2CNRR'] \quad (3)$$

$$NHRR' + DBU + CO_2 \rightarrow [DBUH][O_2CNRR'] \quad (4)$$

The resulting systems exhibit a limited stability, as they generally release CO_2 by mild heating or even by bubbling N_2 through the liquid phase.[9c]. It is noteworthy that these systems have been called *reversible* (or switchable) with reference to the CO_2 release/uptake.[11]

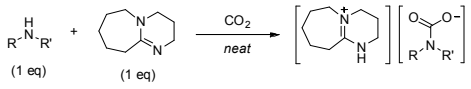
Only a small number of amidinium/guanidinium carbamates derived from primary alkylamines and α-amino acids have been isolated so far. However, the reported synthetic procedure makes use of high CO_2 pressure (5-60 bar) and requires long reaction times, and the authors did not specify to handle the products under anhydrous conditions.[9d,10]

In the present work, we describe the convenient synthesis and the solid state isolation, in the absence of CO_2 atmosphere, of amidinium/guanidinium carbamates. Being these compounds highly moisture sensitive, they have been manipulated under nitrogen/argon, and a study of their stability has been carried out too. The present class of carbamates has been extended to the analogous derivatives of secondary amines and secondary α-amino acids.

Results and Discussion

Preparation and characterization of carbamates

Under strictly anhydrous conditions, the reaction of CO_2 with an equimolar mixture of amine and DBU (Eq. 5) or TMG (Eq. 6) led to the formation of the corresponding carbamates as colourless solids (Table 1, compounds **1-6**). The carbonatation of α-amino acids in the presence of two equivalents of TMG (Eq. 7) was performed in THF suspension at 273 K in order to lower the solvent vapour pressure and to increase the CO_2 solubility. After filtration and evaporation of the solvent, colourless liquid carbamates were isolated (Table 1, compounds **7-9**).



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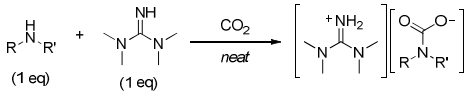

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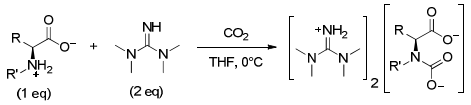

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Table 1. Carbamates prepared from alkylamines or α-amino acids discussed in this work.

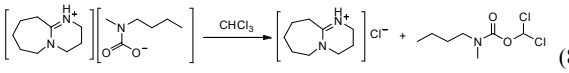
Cpd.	Eq.	Cation / Amine group type	R	R'
1	(5)	[DBUH$^+$] / Primary alkylamine	H	^{n}Bu
2		[DBUH$^+$] / Secondary alkylamine	Me	^{n}Bu
3	(6)	[TMGH$^+$] / Primary alkylamine	H	^{n}Bu
4		[TMGH$^+$] / Secondary alkylamine	Me	^{n}Bu
5		[TMGH$^+$] / Secondary alkylamine	Et	Et
6		[TMGH$^+$] / Secondary alkylamine	^{i}Pr	^{i}Pr
7	(7)	[TMGH$^+$] / Secondary α-amino acid	H	Me
8		[TMGH$^+$] / Secondary α-amino acid	$CH_2CH_2CH_2$	
9		[TMGH$^+$] / Primary α-amino acid	$PhCH_2$	H

Compounds **1-4** were prepared at super-atmospheric pressure of CO_2 according to the literature,[9d] while compounds **5-9** were obtained by bubbling CO_2 at atmospheric pressure for 30 minutes using common Schlenk glassware. All of the compounds were obtained in nearly quantitative yield and characterized by elemental analysis, IR and NMR spectroscopy.

The infrared spectra of **1** and **2** display two intense absorptions at ca. 1640 cm^{-1}, assigned to the C=N bond stretching vibration in the [DBUH]$^+$ cation (1643 cm^{-1} in [DBUH]Cl), and at *ca.* 1610 cm^{-1}, assigned to the asymmetric stretching vibration of the carbamate group. Compounds **3-6** present one C=O stretching vibration in the 1580 cm^{-1} to 1540 cm^{-1} region; this absorption occurs at significantly lower wavenumbers respect to what found for **1** and **2**, in agreement with the stronger hydrogen bonds established within the [TMGH]$^+$ derivatives compared to the corresponding [DBUH]$^+$ salts.[12] An additional, strong absorption in the 1590-1600 cm^{-1} region, attributed to the C=N stretching of the tetramethylguanidinium ion, is observed in the spectra of **3-6**. Compounds **1-9** are highly hygroscopic, as shown by the progressive increase of the 3500 cm^{-1} and 1640 cm^{-1} IR bands upon brief air exposure (Fig. S1 and S2 given as Supporting Information).

All of the ammonium carbamates **1-9** were characterized by multinuclear NMR in $CDCl_3$ or CD_2Cl_2 solutions. Compounds **1-6** display a resonance around 165 ppm (C=N group belonging to the cation), whereas the resonance at approximately 163 ppm is related to the carbonyl group of the carbamate anion (Fig. 2, S3 and S4). On the other hand, the ^{13}C spectra of **7-9** show three resonances in the carbonyl region, assigned to the carboxylate group (ca. 175 ppm), the tetramethylguanidinium cation (ca. 162 ppm) and the carbamate group (160 ppm) (Fig. 2). The ^{1}H spectra are generally not well-resolved (Fig. 3 and S5), presumably due to the presence of strong hydrogen bonding between the cation and the anion.[9f]

Compounds **1-9** are well soluble in CH_2Cl_2, $CHCl_3$, toluene and almost insoluble in hexane. However, the stability in chlorinated solvents is limited. In fact, formation of [TMGH]Cl or [DBUH]Cl was observed when the carbamates were maintained in solution of CH_2Cl_2 or $CHCl_3$ at room temperature or 277 K for several days, as outlined by IR, NMR and X-ray analysis. In the case of **2**, ^{1}H and ^{13}C NMR spectra suggested the formation of the dichloromethyl carbamic ester derivative after some weeks in chloroform solution (Eq. 8).[13]



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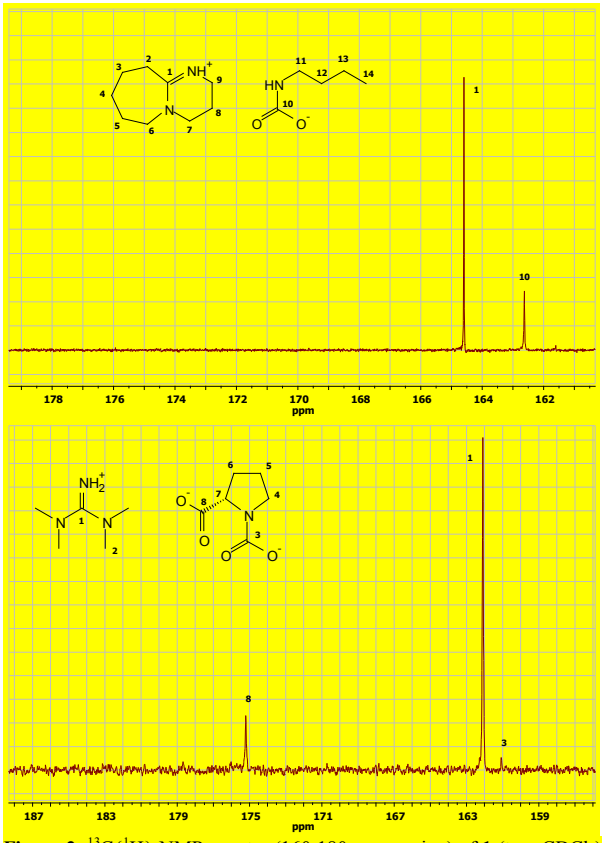


Figure 2. ^{13}C{^{1}H} NMR spectra (160-180 ppm region) of **1** (top, $CDCl_3$) and **8** (bottom, CD_2Cl_2).

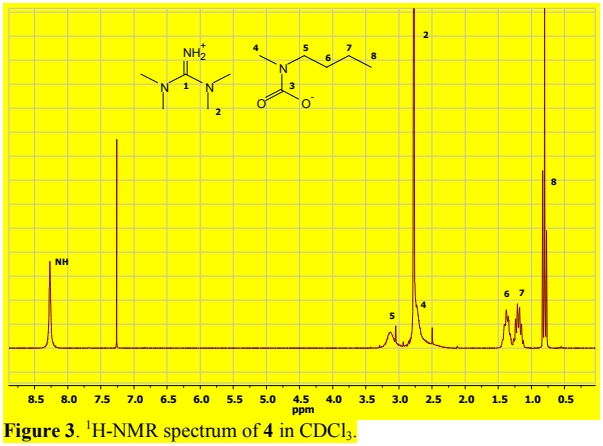


Figure 3. ^{1}H-NMR spectrum of **4** in $CDCl_3$.

Thermal and vacuum stability

At variance to the majority of ammonium carbamates reported in the literature,[4] the guanidinium/amidinium salts **1-9** are stable under N_2 atmosphere (Table 2) and did not undergo significant decomposition under high vacuum at room temperature for short periods of time.

Table 2. Thermal and vacuum stability of compounds **1-9** and of the corresponding ammonium carbamates.

Amine	Ammonium carbamate	Guanidium and amidinium carbamates	
^{n}BuNH$_2$	[^{n}BuNH$_3$][O$_2$CNH^{n}Bu] [4] Stable under CO$_2$ atmosphere T_{dc}: 323 K	[DBUH][O$_2$CNH^{n}Bu], **1** Stable under vacuum (RT) T_{fus} = 373-375 K, T_{dc} = 382-383 K	[TMGH][O$_2$CNH^{n}Bu], **3** Stable under vacuum (RT) T_{fus} = 344-346 K, T_{dc} = 348-349 K
^{n}BuMeNH$_2$	[^{n}BuMeH$_2$][O$_2$CNMe^{n}Bu] Not reported	[DBUH][O$_2$CNMe^{n}Bu], **2** Stable under vacuum (RT, 313°C) T_{fus} = 500-502 K, T_{dc} = 514-516 K	[TMGH][O$_2$CNMe^{n}Bu], **4** Stable under N$_2$ (RT) T_{fus} = 326-329 K, T_{dc} = 332-334 K
Et$_2$NH	[Et$_2$NH$_2$][O$_2$CNEt$_2$] [4] Carbonatation yield: 86% in heptane Stable under CO$_2$ atmosphere Decomposition: 323 K	[TMGH][O$_2$CNEt$_2$], **5** Stable under N$_2$ (RT) T_{fus} = 337-338 K, T_{dc} = 342-345 K	
^{i}Pr$_2$NH	[^{i}Pr$_2$NH$_2$][O$_2$CN^{i}Pr$_2$] [4] Carbonatation yield: 14% in heptane Stable under CO$_2$ atmosphere Decomposition: 323 K	[TMGH][O$_2$CN^{i}Pr$_2$], **6** Stable under N$_2$ (RT) T_{fus} = 311-313 K, T_{dc} = 315-317 K	
Sarcosine	Not reported, observed in aqueous solution.[14]	[TMGH]$_2$[O$_2$CN(CH$_3$)CH$_2$CO$_2$], **7** Stable under N$_2$ (RT) T_{fus} < 298 K	
L-Proline	Not reported.	[TMGH]$_2$[O$_2$CNCH$_2$CH$_2$CH$_2$CHCO$_2$], **8** Stable under N$_2$ (RT) T_{fus} < 298 K	
L-Phenylalanine	Not reported, observed in aqueous solution.[15]	[TMGH]$_2$[O$_2$CNHCH(CH$_2$Ph)CO$_2$], **9** Stable under N2 (RT) T_{fus} < 298 K	

T_{fus}: melting temperature; T_{dc}: decomposition temperature.

For some of them, we measured the degradation in terms of mass loss at 0.5 mmHg residual pressure, respectively at room temperature and at 313 K (see Table 3). The results confirm the stability of these carbamates under vacuum, a rare property that is amenable in view of possible applications.[7]

In addition, it has to be pointed out that **1-9** are solid materials at room temperature, melting without decomposition. The melting temperatures range from a few degrees above room temperature (compound **6**) to T ≥ 373 K (compounds **1-2**). In each case, decomposition has been observed at 4-14 K above the melting temperature, accompanied by gas evolution. These results suggest the opportunity to modulate the thermal properties of the salts by an appropriate choice of the superbase and the amine.[9f,10] Compounds **7-9**, derived from the carbonatation of α-aminoacids, are (ionic) liquids at room temperature. It should be mentioned here that aminoacid-based ionic liquids are relatively rare, and currently investigated in view of possible applications in diverse fields.[16]

Table 3. Percentage of mass loss under vacuum (p = 0.5 mmHg) at different times.

Compound	Temperature	% mass loss (time)
2	295 K	0.8% (2 h), 0.9% (4 h)
	313 K	0.4% (2 h), 0.9% (4 h)
3	295 K	2 % (2 h), 11% (4 h), 12% (6 h)
	313 K	78% (2 h), 83% (4 h)
4	295 K	82% (2.5 h), 92% (5 h)

Role of the superbase in the formation and stability of carbamates

The mechanism of the formation of ammonium carbamates from amines/CO$_2$,[4,17] as well as the reverse reaction,[18] have been studied in detail. It is generally agreed that, in a first step, the amine reacts with CO$_2$ to afford the corresponding zwitterionic carbamate (Fig. 4a); this compound is in equilibrium (via proton exchange) with the neutral carbamic acid (Fig. 4b). In a second step, both these species can be deprotonated by a second equivalent of amine, yielding the ammonium carbamate (Fig. 4c). According to this model, it is possible to assume that a strongly Brönsted basic amine (*i.e.* an ammonium cation with a high value of pK$_a$) should enhance the stability of the carbamate. 1,1,3,3-Tetramethylguanidine and 1,8-diazabicyclo[5.4.0]undec-7-ene are stronger Brönsted bases than alkylamines (see comparison of pK$_a$ values in Table S1) but poor Lewis bases towards CO$_2$ in anhydrous conditions.[19] Therefore, DBU and TMG act as good Brönsted bases (Fig. 4c') and uncompetitive Lewis bases (Fig. 4a') in combination with alkylamines or α-amino acids. Indeed side reactions such as the formation of ammonium carbamates or the carbonatation of superbases have not been observed in our systems. The resulting guanidinium / amidinium carbamates display a remarkable vacuum and thermal stability, especially when compared to the respective ammonium carbamates. Reasonably, other factors than the pK$_a$ of the amidinium/guanidinium cation (*e.g.* lattice energy, hydrogen bonding) might contribute to the thermodynamic stability of these compounds.

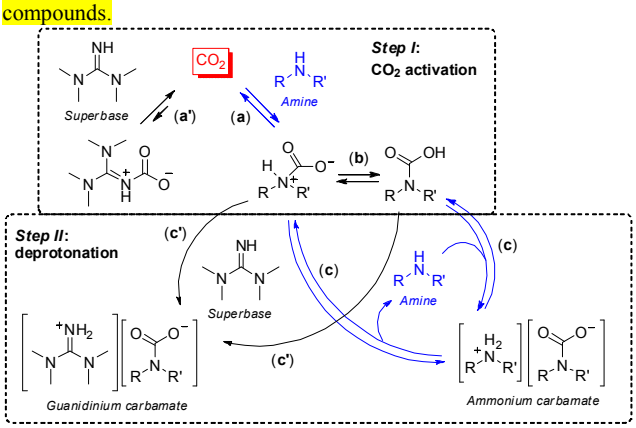


Figure 4. Possible reaction pathways in the three-component system under investigation (amine-superbase-CO$_2$).

Conclusions

Fixing carbon dioxide by reaction with amines is a long time investigated process that has aroused a great interest in the recent times due to environmental concerns. In this work, some primary and secondary amines were used in combination with tetramethylguanidine (TMG) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under CO$_2$ atmosphere to obtain highly moisture

sensitive solid carbamates. Some of the products resulted substantially stable under vacuum, even at temperatures above 298K. On the other hand, we have demonstrated that the compounds may undergo electrophilic attack by a chlorinated solvent. The carbonatation in the presence of a superbase was extended to primary (L-phenylalanine) and secondary (sarcosine and L-proline) α-amino acids. All the isolated carbamates showed low melting points, and in particular those carbamates obtained from α-amino acids are (ionic) liquids at room temperature.

Experimental

Materials, physicochemical measurements and analytical procedures. All the operations were carried out under an atmosphere of prepurified nitrogen or argon. The glass reaction vessels were oven dried at 140°C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. The autoclave reactor (EYELA PROCESS STATION PPV-4060 equipped with four autoclaves HIP-60) was purged with argon prior to use. Solvents (Sigma Aldrich), 1,1,3,3-tetramethylguanidine (TMG, Sigma Aldrich, 99%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Sigma Aldrich, 98%), butyl(methyl)amine (Sigma Aldrich, 96%), butylamine (Sigma Aldrich, 99.5%), diethylamine (Sigma Aldrich, 99.5%), diisopropylamine (Sigma Aldrich, 99%) were distilled from appropriate drying agents before use. Deuterated solvents (Cortecnet) were stored over 3Å molecular sieves under Ar. Sarcosine (Alfa Aesar, 98%), L-proline and L-phenylalanine (Apollo Sci, >98%) were stored under argon atmosphere as received. Once isolated, the products were stored in sealed glass tubes under nitrogen at 277 K.

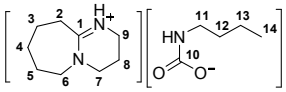
Infrared spectra were recorded at 298 K on a FTIR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. Infrared spectra of liquid compounds were recorded at 298 K on FT-IR Spectrum 100 Perkin Elmer. The samples were deposited on KBr pellets. Carbon, hydrogen and nitrogen analysis was performed on a Carlo Erba mod. 1106 instrument. ^{1}H and ^{13}C NMR spectra were recorded at 298 K through Bruker Avance II DRX 400 spectrometer. The ^{1}H and ^{13}C chemical shifts were fully assigned *via* DEPT experiments and $^{1}H,^{13}C$ correlation through gs-HSQC and gs-HMBC experiments.[20] Melting point and decomposition temperatures were measured on a Stuart mod. SMP10 instrument. The capillary containing the sample was prepared in nitrogen atmosphere and sealed. Mass loss on vacuum was determined placing *ca.* 1 g of the selected compound in a 5-mL round bottom Schlenk flask at 0.5 mmHg and at a specified temperature (298 K/room temperature or 313 K).

Preparation of carbamates from primary/secondary alkylamines

Procedure A: The autoclave was charged with a 1:1 mol/mol mixture of superbase (TMG or DBU) and amine. The colourless solution was magnetically stirred under a constant pressure of CO_2 (10 bar) for 4.5 hours at room temperature. The system was depressurized and purged with argon. The resulting solid was then transferred into a round-bottom Schlenk flask and dried *in vacuo*. In the case of DBU salts, compounds were dissolved in CH_2Cl_2 (10 mL) directly in the autoclave, the solution was transferred and the solvent was removed under vacuum.

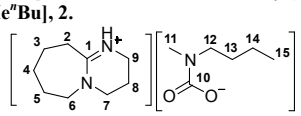
Procedure B: A 1:1 mol/mol mixture of TMG and amine was added to a Schlenk tube. Hence CO_2 at atmospheric pressure was introduced into the system and a colourless solid was obtained. When the absorption ceased (*ca.* 20 minutes), the system was purged with nitrogen. The resulting solid was dried *in vacuo*.

***1,8-Diazabicyclo[5.4.0]undec-7-enium butylcarbamate*, [DBUH][O_2CNH^nBu], 1.**



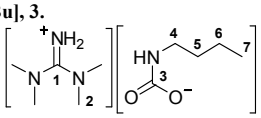
Colourless, extremely hygroscopic solid (14.397 g, 94%) obtained from DBU (8.694 g, 57.1 mmol) and $^{n}BuNH_2$ (4.224 g, 57.8 mmol) according to procedure A. Melting point: 373-375 K; decomposition temperature: 382-383 K. IR (solid state): ν = 3268w-br, 3029w, 2948m-sh, 2927s, 2858m, 1641s ($\nu_{C=N}$), 1609m-br ($\nu_{as,CO2}$), 1570m-br, 1455m, 1356m, 1318s, 1203m, 1155w, 1106w, 1088w, 983w, 832w, 810w, 728w, 690w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 11.1 (br, 1H, C1-NH), 4.89 (s, 1H, C10-NH), 3.07–3.00 (m, 4H, C7-H and C9-H), 2.91 (t, $^{3}J_{HH}$ = 5.7 Hz, 2H, C6-H), 2.56 (t, $^{3}J_{HH}$ = 6.9 Hz, 2H, C11-H), 2.41–2.28 (m, 2H, C2-H), 1.57–1.53 (m, 2H, C8-H), 1.35–1.09 (m, 6H, C3-H, C4-H and C5-H), 0.98–0.74 (m, 4H, C12-H and C13-H), 0.37 (t, $^{3}J_{H-H}$ = 7.1 Hz, 3H, C14-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 164.6 (C1), 162.6 (C10), 53.1 (C6), 47.6 (C7), 40.5 (C11), 37.2 (C9), 31.9 (C12), 31.1 (C2), 28.1 (C5), 26.0 (C4), 23.2 (C3), 19.2 (C13), 18.7 (C8), 13.0 (C14) ppm.

***1,8-Diazabicyclo[5.4.0]undec-7-enium butyl(methyl)carbamate*, [DBUH][O_2CNMe^nBu], 2.**



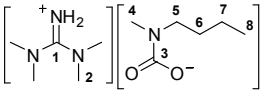
Colourless, extremely hygroscopic solid (15.3 g, 90%) obtained from DBU (9.176 g, 60.3 mmol) and $Me^{n}BuNH$ (5.313 g, 61.0 mmol) according to procedure A. Melting point: 500-502 K; decomposition temperature: 514-516 K. IR (solid state): ν = 3300-3100 w-br, 2925s, 2857s, 1643s ($\nu_{C=N}$), 1614s ($\nu_{as,CO2}$), 1556m, 1456m, 1419w, 1360s, 1304s, 1259m, 1203m, 1155w, 1109w, 1092w, 1057w, 1030w, 991w, 834w, 810w, 729w, 689w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 11.9 (br, 1H, NH), 3.33-3.21 (m, 6H, C-6, C-7 and C-9), 3.18-3.06 (m, 2H, C12-H), 2.78-2.62 (m-br, 5H, C2-H and C11-H), 1.88-1.75 (m, 2H, C8-H), 1.64-1.41 (m, 6H, C3-H, C4-H and C5-H), 1.40-1.24 (m, 2H, C13-H), 1.24-1.03 (m, 2H, C14-H), 0.74 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, C15-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 165.1 (C1), 163.7 (C10), 53.7 (C6), 48.6 (C12), 48.4 (C7), 38.5 (C9), 34.3 (C11), 32.3 (C2), 30.4 (C13), 29.1 (C5), 27.1 (C4), 24.3 (C3), 20.1 (C8), 20.0 (C14), 14.0 (C15) ppm.

***1,1,3,3-Tetramethylguanidinium butylcarbamate*, [TMGH][O_2CNH^nBu], 3.**



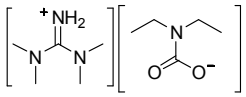
Colourless solid (13.478 g, 90%) obtained from TMG (7.521 g, 65.3 mmol) and $^{n}BuNH_2$ (4.730 g, 64.7 mmol) according to procedure A. Melting point: 344-346 K; decomposition temperature: 348-349 K. IR (solid state): ν = 3230w-br, 2951s, 2928s, 2868s, 1587s ($\nu_{C=N}$), 1564s ($\nu_{as,CO2}$), 1464s, 1435s, 1423s-sh, 1406m, 1383m, 1351m, 1304s-br, 1257m-sh, 1222w-sh, 1156 w, 1142w, 1097w-br, 1059w, 1034m, 891w, 816w, 727w, 687w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.88 (br, 2H, NH_2), 5.05 (s, 1H, NH), 2.77 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, C4-H), 2.63 (s, 12H, C2-H), 1.22-0.90 (m, 4H, C5-H and C6-H), 0.58 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, C7-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 162.8 (C1), 162.6 (C3), 40.9 (C4), 39.1 (C2), 32.5 (C5), 19.7 (C6), 13.5 (C7) ppm.

***1,1,3,3-Tetramethylguanidinium butyl(methyl)carbamate*, [TMGH][O_2CNMe^nBu], 4.**



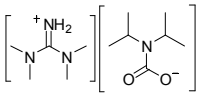
Colourless solid (12.836 g, 87%) obtained from TMG (6.942 g, 60.3 mmol) and $Me^{n}BuNH$ (5.249 g, 60.2 mmol) according to procedure A. Melting point: 326-329 K; decomposition temperature: 332-334 K. IR (solid state): ν = 3356w-br, 3013sh, 2954s, 2924s, 2870s, 2859s, 2815s, 2361w, 2340w, 1599s ($\nu_{C=N}$), 1574s ($\nu_{as,CO2}$), 1535s, 1458s-br, 1410s, 1363s, 1304s, 1250s, 1203m-sh, 1105m, 1065m, 1032s, 995w, 888w, 808w, 725w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.27 (s, 2H, NH_2), 3.21-3.03 (m-br, 1.5H, C5-H), 2.77 (s, 12H, C2-H), 2.76-2.66 (m-br, 3.5H, C4-H), 1.46-1.28 (m, 2H, C6-H), 1.29-1.09 (m, 2H, C7-H), 0.80 (t, $^{3}J_{HH}$ = 7.2 Hz, C8-H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 164.7 (C1); 162.9 (br, C3); 48.8 (br, C5); 39.4 (C2); 34.4 (br, C4); 30.5 (C6); 20.2 (C7); 14.1 (C8) ppm.

***1,1,3,3-Tetramethylguanidinium diethylcarbamate*, [TMGH][O_2CNEt_2], 5.**



Colourless solid (72%) obtained from TMG (1.032 g, 8.96 mmol) and $NHEt_2$ (0.93 mL, 8.96 mmol) according to procedure B. Anal. Calc. for $C_{10}H_{24}N_4O_2$: C, 51.7; H, 10.4; N, 24.1%. Found: C, 51.4; H, 10.3; N, 24.0%. Melting point: 337-338 K; Decomposition temperature: 342-345 K. IR (solid state): ν = 2958w-sh, 2927w, 2868w, 2817w, 1594vs ($\nu_{C=N}$), 1540vs ($\nu_{as,CO2}$), 1464m-s, 1455m-s, 1434m, 1395s, 1291s, 1207w, 1106w-m, 1071m-s, 1049m-s, 1032s, 887w, 804w-m, 772w, 727w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.16 (br, NH_2), 3.24-2.99 (m-br, CH_2), 2.72 (s, N-CH_3), 1.10-0.79 (br, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 165.2 (C=N), 162.2 (br, C=O), 40.4 (br, CH_2), 39.3 (N-CH_3), 14.2 (CH_3) ppm.

***1,1,3,3-Tetramethylguanidinium diisopropylcarbamate*, [TMGH][$O_2CN^iPr_2$], 6.**

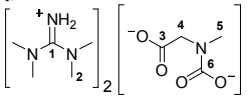


Colourless solid (55%) obtained from TMG (1.033 g, 8.97 mmol) and NH^iPr_2 (1.26 mL, 8.97 mmol) according to procedure B. Anal. Calc. for $C_{12}H_{28}N_4O_2$: C, 55.3; H, 10.8; N, 21.4%. Found: C, 55.1; H, 10.4; N, 21.0%. Melting point: 311-313 K; Decomposition temperature: 315-317 K. IR (solid state): ν = 2943w-m, 2842vw, 2789vw, 1597s-sh ($\nu_{C=N}$), 1577m-s ($\nu_{as,CO2}$), 1495w-m, 1458w-m, 1409m, 1373vs-sh, 1258m, 1196w, 1100w-m, 1064m, 1037m, 999m, 890w, 845w-m, 781m, 724m, 691m cm^{-1}.^{1}H NMR ($CDCl_3$): δ = 3.29 (br, 2H, NH), 2.81 (hept., $^3J_{H-H}$ = 6.4 Hz, 2H, CH), 2.64 (s, N-$(CH_3)_2$), 0.95 (d, $^3J_{H-H}$ = 6.1 Hz, 12H, C-$(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.9 (C=N), 45.2 (CH), 39.3 (N-CH_3), 23.4 (CH_3) ppm. ^{1}H NMR (CD_3CN): δ = 3.71 (br, 2H, NH), 2.85 (hept., $^3J_{H-H}$ = 6.4 Hz, 2H, CH), 2.65 (s, N-$(CH_3)_2$), 0.96 (d, $^3J_{H-H}$ = 6.1 Hz, 12H, C-$(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 168.0 (C=N), 45.9 (CH), 39.7 (N-CH_3), 23.8 (CH_3) ppm.

Preparation of carbamates from α-amino acids

General procedure: The appropriate α-amino acid was added to a solution of TMG (1:2 molar ratio) in 10 mL of tetrahydrofuran. The mixture was cooled at 273 K and carbon dioxide was introduced into the system (atmospheric pressure). When the absorption ceased (ca. 30 minutes), the solvent was removed *in vacuo* at room temperature. The mixture was filtered after addition of 15 mL of CH_2Cl_2. The solvent was removed from the filtrate solution affording a colourless highly viscous liquid.

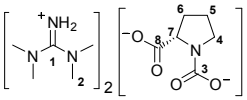
Bis*(1,1,3,3-tetramethylguanidinium) sarcosinecarbamate,* [TMGH]$_2$[$O_2CN(CH_3)CH_2CO_2$], 7.



Colourless liquid (4.0 g, 80% yield) obtained from TMG (0.42 mL, 3.37 mmol) and sarcosine (0.150 g, 1.68 mmol) according to general procedure.

IR (KBr pellets): ν = 3038s, 2960s, 2326w, 1654s-sh ($\nu_{as,CO2\text{-}carboxylate}$), 1601vs ($\nu_{C=N}$), 1568vs ($\nu_{as,CO2\text{-}carbamate}$), 1405s, 1374m-s, 1268m-s, 1143vw, 1101w-m, 1067m, 1038m, 971wv, 882w, 730vs , 696m-s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.55 (br, 4H, NH_2), 2.57 (m, 27H, C2-H and C5-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 174.9 (C3), 162.2 (C1), 159.8 (C6), 53.3 (C4), 39.1 (C2), 34.8 (C5) ppm.

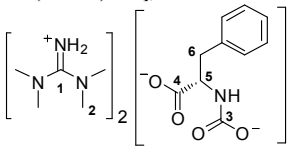
***Bis(1,1,3,3-tetramethylguanidinium) L-prolinecarbamate,* [TMGH]$_2$[$O_2CNCH_2CH_2CH_2CHCO_2$], 8.**



Colourless liquid (1.05 g, 73%) obtained from TMG (0.93 mL, 7.38 mmol) and L-proline (0.425 g, 3.69 mmol) according to general procedure.

^{1}H NMR (CD_2Cl_2): δ = 9.03 (br, NH_2), 3.86 (br, C7-H), 3.54 (br, C4-H), 3.16 (br, C6-H), 2.86 (s, C2-H), 1.94 (br, C5-H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 175.3 (C8), 162.1 (C1), 161.1 (C3), 61.1(C7), 46.4 (C4), 39.8 (C2), 30.0 (C6), 24.4 (C5) ppm.

Bis*(1,1,3,3-tetramethylguanidinium) L-phenylalaninecarbamate,* [TMGH]$_2$[$O_2CNHCH(CH_2Ph)CO_2$], 9.



Colourless liquid (0.89 g, 58%) obtained from TMG (0.88 mL, 7.05 mmol) and L-phenylalanine (0.582 g, 3.52 mmol) according to general procedure. ^{1}H NMR (CD_2Cl_2): δ = 8.52 (br, 4 H, NH_2), 7.23-6.94 (m, 5H, Ph), 3.54 (s, C5-H), 2.99 (m, C6-H), 2.79 (s, C2-H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 177.3 (C4), 162.4 (C1), 162.0 (C3), 140.5 (Ph), 129.9 (Ph), 127.9 (Ph), 125.7 (Ph), 58.4 (C5), 39.8 (C2), 38.5 (C6) ppm.

Preparation of DBU and TMG hydrochlorides.

37% HCl (1 mL) was added dropwise to a round-bottom flask containing DBU or TMG (1 mL) at 0°C. Excess HCl and water were removed under vacuum at 65°C, affording colourless solids.

***1,8-Diazabicyclo[5.4.0]undec-7-enium chloride*, [DBUH]Cl.**

IR (solid state): ν = 3201m, 3093m, 3029m, 2933m, 2859m, 2805m, 1643s ($\nu_{C=N}$), 1589m, 1471w, 1444w, 1321m, 1205w, 1105w, 983w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 11.19 (br, 1H), 3.52–3.42 (m, 4H), 3.37–3.31 (m, 2H), 2.94–2.87 (m, 2H), 2.02–1.91 (m, 2H), 1.73–1.59 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 166.1, 54.4, 48.7, 37.9, 32.1, 28.9, 26.8, 24.0, 19.5 ppm.

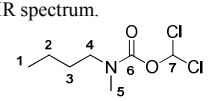
***1,1,3,3-Tetramethylguanidinium chloride*, [TMGH]Cl.**

IR (solid state): ν = 3330m-sh, 3216s-br, 3158s-br, 3045s, 2956m-sh, 2912m-sh, 2815w-sh, 1654m, 1602s ($\nu_{C=N}$), 1562s, 1450w, 1411s, 1319w, 1091m, 1064m, 1037m, 875w, 736w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.34 (s, 2H, NH_2), 2.81 (s, 12H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 161.2 (C=N), 39.9 (CH_3) ppm.

Instability of compound 2 in $CHCl_3$ solution.

Compound **2** was dissolved in $CHCl_3$ and the colourless solution was kept at 277 K for several weeks. Then, solvent was removed under vacuum and the residue was suspended in toluene. The suspension was filtered, the colourless precipitate was washed with toluene and dried under vacuum. NMR and IR spectra were in agreement with [DBUH]Cl.

Toluene was removed under vacuum from the filtrated solution, affording a colourless oily residue. NMR data (reported below) suggested the quantitative formation of dichloromethyl ester. Partial double-bond character of N-CO_2 bond may be responsible for the two sets of signals observed in the ^{13}C NMR spectrum.



^{1}H NMR ($CDCl_3$): δ = 5.64 (s, 1H, C7-H), 3.19–3.09 (m, 2H, C4-H), 2.82–2.72 (m, 3H, C5-H), 1.44–1.29 (m, 2H, C3-H), 1.25–1.09 (m, 2H, C2-H), 0.85–0.71 (m, 3H, C1-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 154.8 and 154.7 (C6), 81.0 (C7), 48.7 and 48.3 (C4), 34.3 and 33.8 (C5), 29.8 and 29.3 (C3), 19.7 and 19.5 (C2), 13.6 (C1) ppm.

Acknowledgements

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Synthesis and Study of the Stability of Amidinium/Guanidinium Carbamates of Amines and α-Amino Acids

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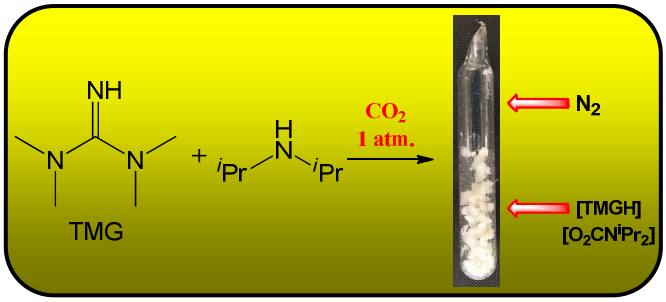
A convenient method for the synthesis and the solid state isolation of thermally stable *N,N*-dialkylcarbamates, including vacuum stable compounds, is proposed.



Synthesis and Study of the Stability of Amidinium/Guanidinium Carbamates of Amines and α-Amino Acids

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SUPPORTING INFORMATION

Figure S1. IR spectra of compound **2** recorded before (black line) and after (red line) exposing sample to air for 30 seconds, showing the increase in the absorptions at 3200-3200 and 1645 cm^{-1}.

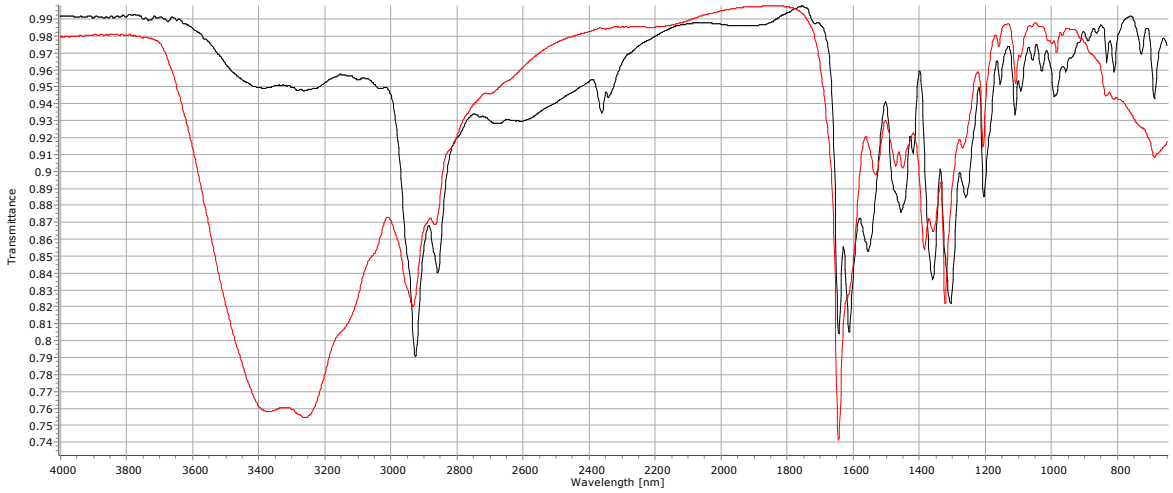

Figure S2. IR spectra of compound **7** recorded before (red line) and after (black line) exposing sample to air for 30 seconds, showing the increase in the absorptions at 3400 and 1650 cm^{-1}.

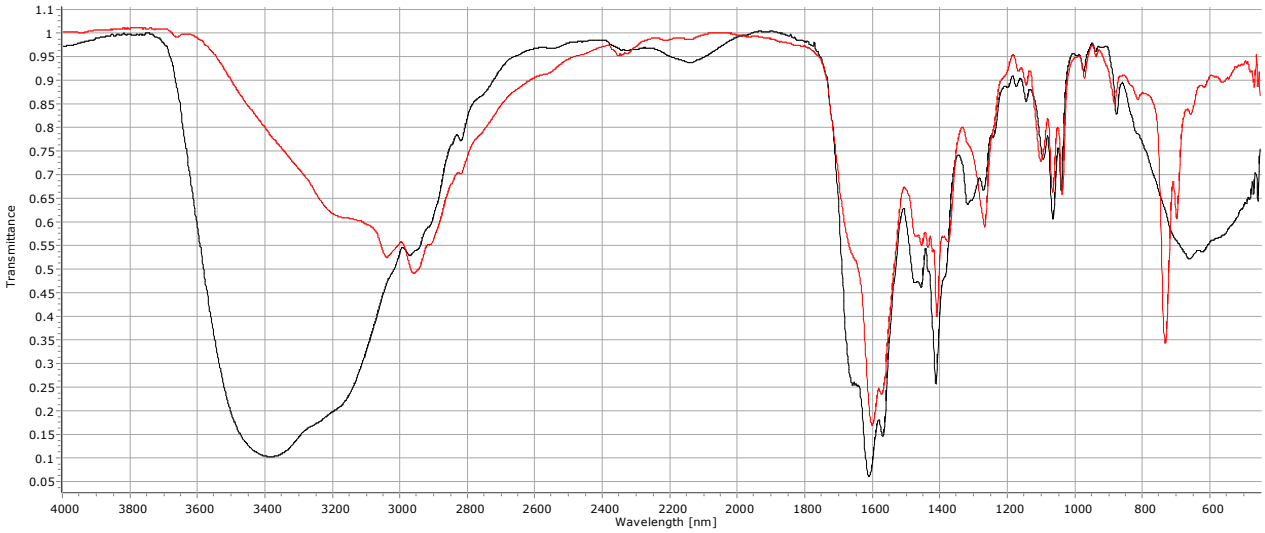

Figure S3. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

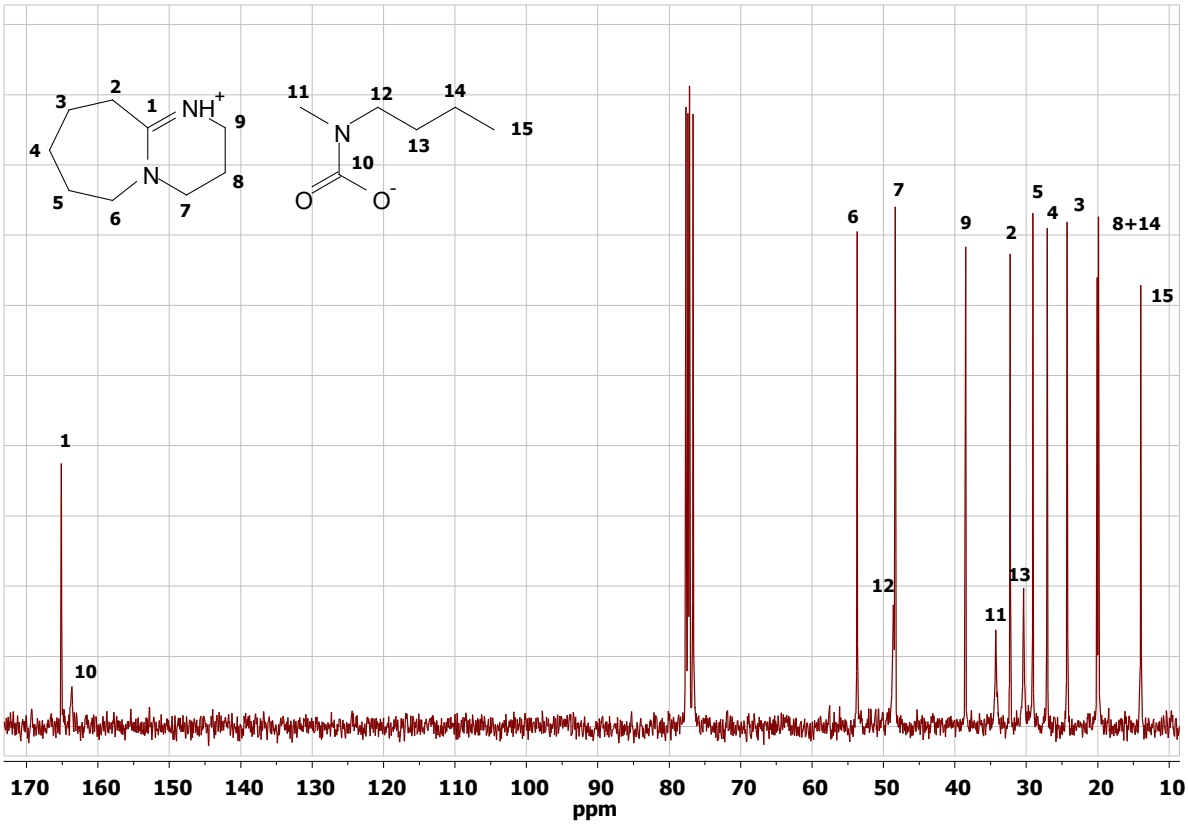

Figure S4. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

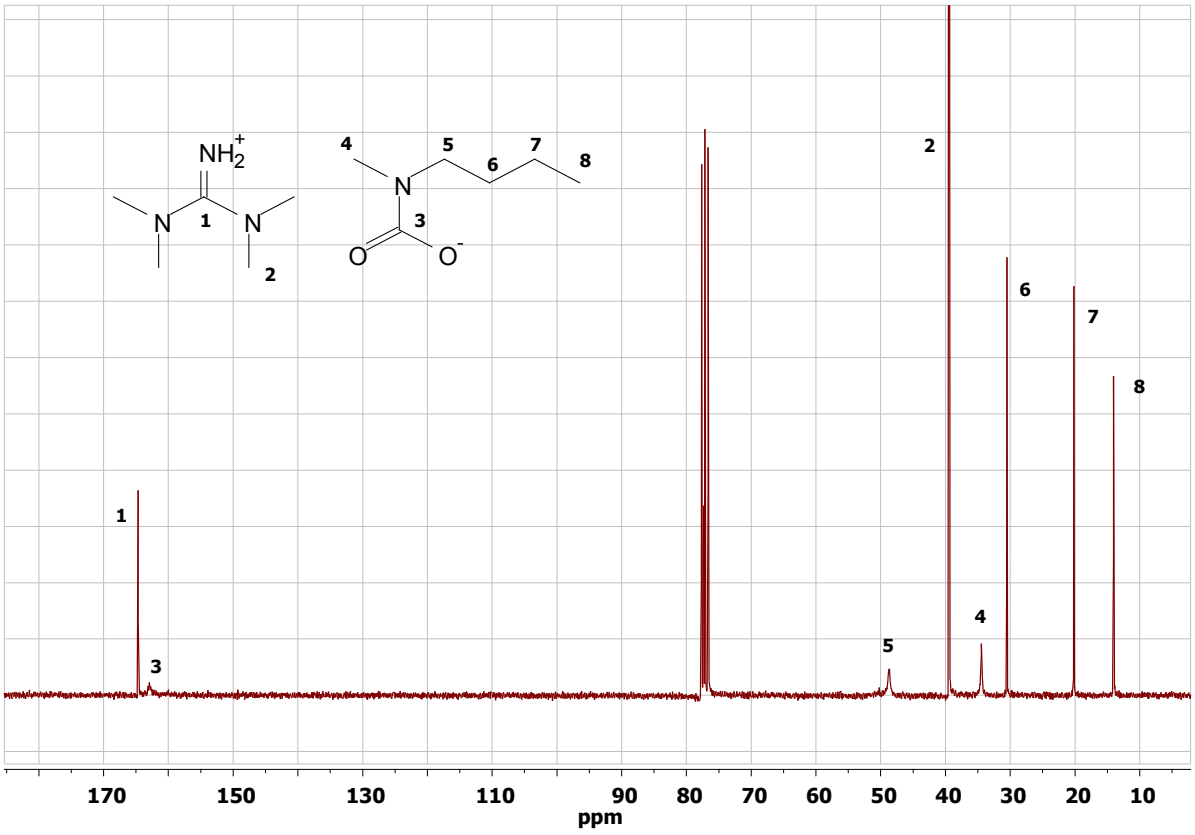

Figure S5. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

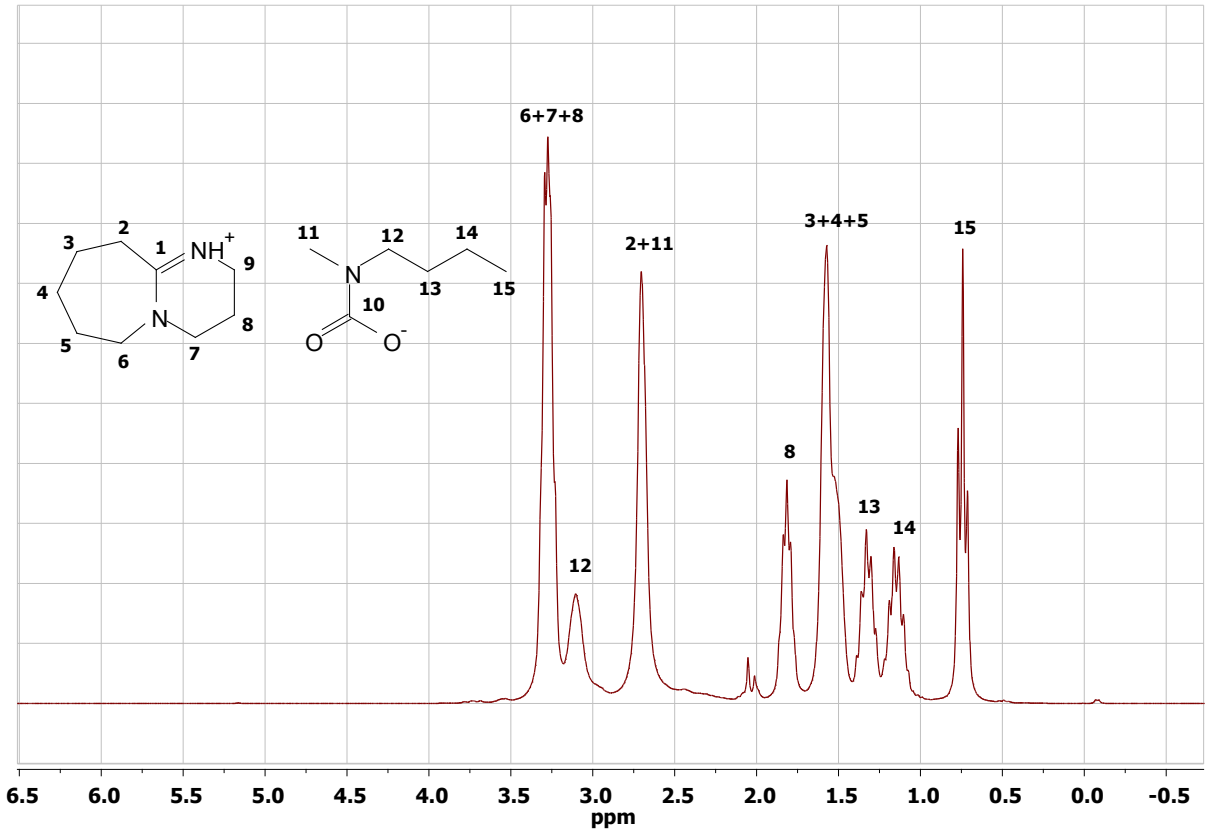

Table S1. pK_a values of TMG, DBU, the amines and α-aminoacids used in this work.

Ammonium cation	pK_a in H_2O	Reference
$Me^{n}BuNH_2^+$	10.8	P. L. Anelli, M. Brocchetta, S. Canipari, P. Losi, G. Manfredi, C. Tomba and G. Zecchi, *Gazz. Chim. Ital.* 1997, **127**, 135-142.
$^{n}BuNH_3^+$	10.8	J. W. Bunting and D. Stefanidis, *J. Am. Chem. Soc.* 1990, **112**, 779–786.
$Et_2NH_2^+$	10.9	R. A. Cherkasov, V. I. Galkin, N. G. Khusainova, O. A. Mostovaya, A. R. Garifzyanov, G. Kh. Nuriazdanova, N. S. Krasnova and E. A. Berdnikov, *Russ. J. Org. Chem*. 2005, **41**, 1481-1484.
$^{i}Pr_2NH_2^+$	11.0	N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.* 1932, **54**, 3469-3474.
Sarcosine	10.0	R.-S. Tsai, B. Testa, N. El Tayar and P.-A. Carrupt, *J. Chem. Soc. Perkin Trans. 2* 1991, 1797-1802.
L-Proline	10.7	E. S. Hamborg, J. P. M. Niederer and G. F. Versteeg , *J. Chem. Eng. Data* 2007, **52**, 2491-2502.
L-Phenylalanine	9.2	N. M. Arishy, R. A. Ammar and A. Al-Warthan , *Asian J. Chem.* 2014, **26**, 2395-2399.
$DBUH^+$	13.5	K. Kaupmees, A. Trummal and I. Leito, *Croat. Chem. Acta* 2014, **87**, 385–395.
$TMGH^+$	13.6	T. Ishikawa, *Superbases for Organic Synthesis*, 2009, John Wiley & Sons, Ltd, Publication.