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Isolation and structural characterization of the elusive 1 : 1 adduct of hydrazine and carbon dioxide†

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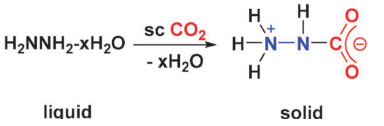
A solid hydrazine was isolated as a crystalline powder by reacting aqueous hydrazine with supercritical CO_2. Its structure determined by single crystal X-ray diffraction shows a zwitterionic form of $NH_3{}^+NHCO_2{}^-$. The solid hydrazine is remarkably stable but is as reactive as liquid hydrazine even in the absence of solvents.

Hydrazine is a volatile liquid that is extensively used as a rocket fuel,[1] blowing agent,[2] fuel cell,[3] and a precursor to make various high-value chemicals.[4,5] However, it is extremely hazardous and the risks of transportation and handling in its liquid form are a high deterrent to its extensive usage. This drawback can be overcome by preparing solid hydrazine whose usage can be considered chemically equivalent to liquid hydrazine. In this communication, we report the preparation of stable solid hydrazine by reacting aqueous hydrazine with supercritical CO_2 (sc CO_2). The product, formulated as $NH_3{}^+NHCO_2{}^-$, is a white crystalline powder that is quite stable but is as reactive as liquid hydrazine. Under mild conditions, the solid hydrazine readily produces anhydrous hydrazine *via* the decarboxylation process. This transportable solid hydrazine will lead to novel applications not only for the green synthesis of fine chemicals but also in energy-related fields such as hydrogen storage materials and fuels.[6]

Supercritical carbon dioxide (sc CO_2) has been widely used as an industrial solvent because of its environmentally benign nature and easy separation from products.[7,8] In recent years, sc CO_2 has also been considered to be an ideal synthetic feedstock.[9] Moreover, it is well documented that sc CO_2 can be an effective reagent for a variety of synthetic reactions. In particular, sc CO_2 reacts readily with amines, leading to the formation of carbamic acids.[10]



$$H_2NNH_2\text{-}xH_2O \xrightarrow[-\ xH_2O]{sc\ CO_2} H_3N^+\text{–}NH\text{–}CO_2^- \qquad (1)$$

Carbazic acid (NH_2NHCO_2H) has been known for a century,[11] but it does not exist in the free-state and is considered an intermediate compound. Carbazic acid has been presumed to form when a stream of CO_2 gas is passed through cold hydrazine in water. The sticky product thus formed probably comprises carbazic acid and hydrazinium carbazate ($N_2H_5{}^+CO_2N_2H_3{}^-$) that is ascribed to water present in liquid hydrazine. Pure carbazic acid can be considered as a simple 1 : 1 adduct of hydrazine and CO_2. However, its isolation and characterization have remained elusive[1,11] despite its great importance in various disciplines. This prompted us to employ sc CO_2 for the isolation of pure solid hydrazine. Our synthetic strategy was to exploit sc CO_2 as both a reactant and a solvent and to react sc CO_2 with hydrazine while sustaining its solvating capability under sc CO_2 conditions.

The reaction was conducted in a stainless steel reactor (eqn (1)). An aqueous solution of hydrazine was introduced into a reactor charged with dry ice (solid CO_2). The mixture was heated at 80 °C and 100 bar for 10 h (see ESI†). A colourless crystalline solid—zwitterionic hydrazinium carboxylate with the formula $NH_3{}^+NHCO_2{}^-$ (**1**)—was formed on the reactor wall. The solid hydrazine **1** is a remarkably stable solid and is almost insoluble in most solvents when stored in a closed bottle; its stability was carefully verified by X-ray powder diffraction (see Fig. S1, ESI†). Moreover, **1** remains intact even in the presence of water. Unlike amino acids, **1** slowly sublimes in air (see Fig. S2, ESI†) and reverts to NH_2NH_2 and CO_2 by various methods, which can thus be used as a source of anhydrous hydrazine.

Single crystals of **1** were grown from the reaction mixture of $NH_2NH_2{\cdot}H_2O$ with sc CO_2 and the reactor was cooled very slowly down to 0 °C after the reaction was completed. As illustrated in Fig. 1, the solid-state structure of **1** determined by single crystal X-ray diffraction clearly reveals a zwitterionic form of $NH_3{}^+NHCO_2{}^-$, which is structurally analogous to the glycine molecule ($NH_3{}^+CH_2CO_2{}^-$) known as the smallest amino acid.[12] However, the N–C bond (1.398 Å) of **1** is considerably shorter than that of glycine (1.475 Å).[12a] In addition, a quasi-planar NCO_2 geometry is formed by the N(2), C(1), O(1), and O(2) atoms, which implies that the N–C bond is intermediate between single and double bonds. The N–N bond length

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† Electronic supplementary information (ESI) available: Experimental details, data for the solid hydrazine (**1**), characterization of azines (**2**), XRD and crystallographic data. CCDC 822062. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14542h

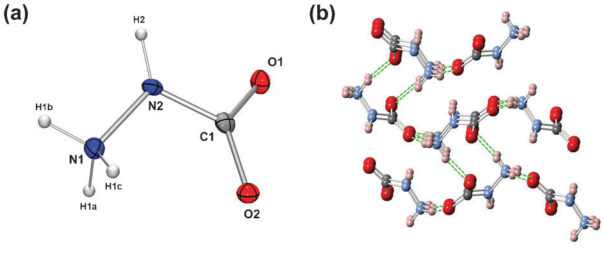


Fig. 1 X-Ray crystal structure of $NH_3^+NHCO_2^-$(**1**). (a) Molecular structure of **1**; here, thermal ellipsoids have 30% probability. The selected bond lengths and angles are as follows. O1–C1: 1.264(3) Å; O2–C1: 1.256(3) Å; N1–N2: 1.438(3) Å; N2–C1: 1.402(3) Å; C1–N2–N1: 114.1(2)°; O2–C1–O1: 126.8(2)°; O2–C1–N2: 117.8(2)°; O1–C1–N2: 115.3(2)°. (b) Illustration of hydrogen bonds in $NH_3^+NHCO_2^-$. Covalent bonds are linked by solid lines. Green dotted lines represent the hydrogen bonds in which the H···O distances are shorter than 2.0 Å. For clarity, other H···O distances longer than 2.0 Å are omitted. Red, blue, grey, and pale pink spheres represent O, N, C, and H atoms, respectively.

(1.438 Å) of **1** is similar to that of free hydrazine (1.450 Å). An important feature is that both O atoms of the CO_2^- group are involved in the formation of intermolecular hydrogen bonds with the H atoms in the NH_3^+ group. Each molecule ($NH_3^+NHCO_2^-$) is hydrogen-bonded to three neighbouring molecules, thereby forming a three-dimensional network (Fig. 1). The O(1) atom having a long C–O bond (1.258 Å) closely interacts with two different H atoms in the NH_3^+ groups; here, the two intermolecular O···H bond distances are 1.889 and 1.893 Å. The O(2) atom with a short C–O bond (1.250 Å) contacts an H atom in the NH_3^+ group, and the distance is 1.920 Å. In addition to the three short O···H bonds, the H atom attached to the NH group also weakly interacts with the two O atoms. However, their bond distances (2.467 and 2.573 Å) are considerably longer than those of the three short O···H bonds (Table S2, see ESI†). The considerable stability of **1** in the solid state is presumably associated with the intermolecular hydrogen bonding; this is well documented in the case of amino acids.[12]

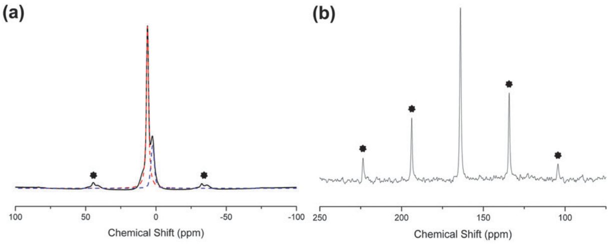
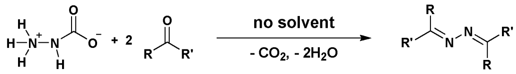
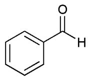
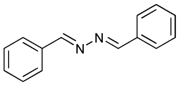
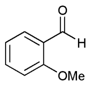
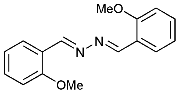
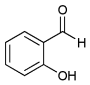
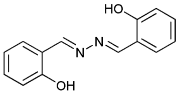
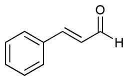
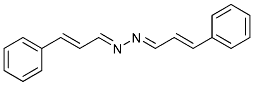
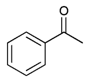
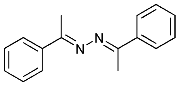


Fig. 2 Solid state NMR spectra of $NH_3^+NHCO_2^-$ (**1**) at 295 K. (a) ^1H magic angle spinning (MAS) NMR spectrum recorded at 14.1 T and 23 kHz spinning rate. The blue and red dotted lines correspond to two distinctive resonances at 7.2 and 10.2 ppm, respectively; they were obtained from the deconvolution of the peaks using a Voigt function. (b) ^{13}C CP MAS NMR spectrum recorded at 9.4 T and 3 kHz spinning rate. Asterisks (*) denote spinning side bands.

Fig. 2 shows the ^1H magic angle spinning (MAS) NMR spectrum of **1** recorded at 295 K with a spinning rate of 23 kHz. Two broad signals with different intensities have been detected at 10.2 and 7.2 ppm. The integration ratio of the two peaks, which is estimated by the deconvolution of the peaks using a Voigt function of multi-peaks fitting, is very close to 3 : 1. The proton signals originating from the COOH group can typically be observed in the range of 11.0–18.1 ppm, while the signals of the N–H protons are observed at 6.3–10.3 ppm.[13] Hence, the assignment of the peaks in the ^1H MAS spectrum is straightforward. One peak at 7.2 ppm can be assigned to the NH proton signal while the other peak at 10.2 ppm can be ascribed to the signal of the NH_3^+ protons. The large values

Table 1 Reactions of solid hydrazine (**1**) with carbonyl compounds [a] †



Entry	Reactant	Product	Reaction time/h	Yield[b] (%)	Remark[c]
1			3	**2a**, >97	Yellow crystal
2			3	**2b**, >97	Yellow crystal
3			3	**2c**, >97	Yellow crystal
4			3	**2d**, >98	Yellow crystal
5			24	**2e**, >97	Yellow crystal

[a] Reaction conditions: 1 (5.0 mmol, 0.38 g), carbonyl reactant (10.0 mmol), no solvent, at 45 °C, in 10 mL vial. [b] Isolated yield based on **1**. [c] Crystals were obtained from the re-crystallization of powders in ether/pentane at ambient temperature.

of the chemical shifts of the NH_3^+ protons indicate that all the three protons are involved in strong hydrogen bonding with the O atoms in the CO_2^- group. As illustrated in Fig. 2, the ^{13}C cross polarization (CP) MAS NMR spectrum of **1** exhibits a sharp peak at 164.0 ppm along with side bands, and this corresponds to the carbon signal emanating from the CO_2^- group. The carboxylate carbon in amino acids is typically visible at the region of 167–173 ppm.[14] Further, the ^1H and ^{13}C solid-state NMR data are in good agreement with the solid state structure of **1** determined by a single crystal X-ray diffraction.

The reactivity of solid hydrazine was examined by the reaction of the liquid carbonyl compound with **1**, which was conducted in the absence of solvents. The addition of **1** to the carbonyl compounds yielded solid azines as the sole products with over 97% yields at 25 °C (Table 1 and ESI†). The reactions are essentially the condensation reactions of carbonyl compounds with **1**, and they appear to proceed *via* the dissociation of **1** into NH_2NH_2 and CO_2. A notable feature is that the reaction is highly selective without the production of any side products; this is probably a result of the generation of pure anhydrous hydrazine from **1**. As given in Table 1 (entry 4), the reaction of **1** with cinnamaldehyde produces exclusively the azine, **2d**. However, the same reaction performed with hydrazine hydrate gives a significant amount of unknown compounds (over 15%). It is noteworthy that hydrazine hydrate or hydrazine sulfate used as a hydrazine source often leads to the formation of byproducts[15,16] due presumably to the presence of water or acid in the reactant. However, all the reactions using **1** as a hydrazine source are environmentally benign "waste-free" processes in which no side products are generated except CO_2 and water. The solid hydrazine (**1**) will thus be beneficial for the extensive application of hydrazine to many organic syntheses, and this will not only enhance the selectivity but also reduce organic wastes.[17–19]

In summary, our solid hydrazine is a 1 : 1 adduct of hydrazine and CO_2 and is very stable. Moreover, its reactivity is similar to that of liquid hydrazine and exhibits better selectivity due probably to the absence of water. A remarkable benefit of solid hydrazine is that it can not only be transported safely but it also permits the production of anhydrous hydrazine at local areas because it readily produces anhydrous hydrazine *via* the decarboxylation process. This transportable solid hydrazine can be expected to significantly extend the current applications of liquid hydrazine and also lay the groundwork for major technological challenges in energy-related fields.

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Notes and references

1 E. A. Schmidt, *Hydrazine and Its Derivatives: Preparation, Properties, Applications*, Wiley-Interscience, New York, 2001.
2 M. L. Berins, *SPI Plastics Engineering Handbook of the Society of the Plastics Industry*, Kluwer Academic Publishers, 2002, 11th edn, ch. 19, pp. 541–552.
3 (*a*) N. V. Rees and R. G. Compton, *Energy Environ. Sci.*, 2011, **4**, 1255; (*b*) K. Asazawa, K. Yamada, H. Tanaka, A. Oka, M. Taniguchi and T. Kobayashi, *Angew. Chem., Int. Ed.*, 2007, **46**, 8024.
4 (*a*) F. Loiseau, C. Clavette, M. Raymond, J.-G. Roveda, A. Burrell and A. M. Beauchemin, *Chem. Commun.*, 2011, **47**, 562; (*b*) V. B. Kurteva, S. P. Simeonov and M. Stoilova-Disheva, *Pharmacol. Pharm.*, 2011, **2**, 1; (*c*) W. Tang, Y. Xiang and A. Tong, *J. Org. Chem.*, 2009, **74**, 2163; (*d*) A. M. S. Silva, R. M. S. Sousa, M. L. Jimeno, F. Blanco, I. Alkorta and J. Elguero, *Magn. Reson. Chem.*, 2008, **46**, 859–864; (*e*) H. M. Nanjundaswamy and M. A. Pasha, *Synth. Commun.*, 2007, **37**, 3417.
5 (*a*) J.-S. Lee, M. V. Kovalenko, J. Huang, D. S. Chung and D. V. Talapin, *Nat. Nanotechnol.*, 2011, **6**, 348; (*b*) J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei and P. E. Sheehan, *Nano Lett.*, 2008, **8**, 3137.
6 A. D. Sutton, A. K. Burrel, D. A. Dixon, E. B. Garner III, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson and M. Vasiliu, *Science*, 2011, **331**, 1426.
7 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
8 C. A. Eckert, B. L. Knutson and P. G. Debenedetti, *Nature*, 1996, **383**, 313.
9 M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010, and references cited therein.
10 (*a*) A. Bandyopadhyay, *Clean Technol. Environ. Policy*, 2011, **13**, 269; (*b*) A. Sayari and Y. Belmabkhout, *J. Am. Chem. Soc.*, 2010, **132**, 6312; (*c*) J. B. Bossa, P. Theule, F. Duvernay, F. Borget and T. Chiavassa, *Astron. Astrophys.*, 2008, **492**, 719; (*d*) M. Aresta and E. Quaranta, *Tetrahedron*, 1991, **47**, 9489.
11 R. Stolle and K. Hofmann, *Ber. Dtsch. Chem. Ges.*, 1904, **37**, 4523.
12 (*a*) T. N. Drebushchak, E. V. Boldyreva and E. S. Shutova, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2002, **58**, 634; (*b*) Å. Kvick, W. M. Canning, T. F. Koetzle and G. J. B. Williams, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 115; (*c*) P.-G. Jönsson and Å. Kvick, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 1827.
13 (*a*) V. Chevelkov, B. J. van Rossum, F. Castellani, K. Rehbein, A. Diehl, M. Hohwy, S. Steuernagel, F. Engelke, H. Oschkinat and B. Reif, *J. Am. Chem. Soc.*, 2003, **125**, 7788; (*b*) E. Vinogradov, P. K. Madhu and S. Vega, *Chem. Phys. Lett.*, 1999, **314**, 443; (*c*) L. Zheng, K. E. Fishbein, R. G. Griffin and J. Herzfeld, *J. Am. Chem. Soc.*, 1993, **115**, 6254.
14 S. Ando, I. Ando, A. Shoji and T. Ozaki, *J. Am. Chem. Soc.*, 1988, **110**, 3380.
15 J. Safaria and S. Gandomi-Ravandia, *Synth. Commun.*, 2011, **41**, 645.
16 F. Toda, S. Hyoda, K. Okada and K. Hirotsu, *Chem. Commun.*, 1995, 1531.
17 F. Toda, *Organic Solid State Reactions*, Springer-Verlag, Berlin Heidelberg, 2005.
18 G. Kaupp and J. Schmeyers, *J. Phys. Org. Chem.*, 2000, **13**, 388.
19 A. V. Trask and W. Jones, *Top. Curr. Chem.*, 2005, **254**, 41.