

Electronic Supplementary Information

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

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Experimental Details

Materials. Hydrazine monohydrate ($\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$), benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$), 2-methoxybenzaldehyde ($(2\text{-CH}_3\text{O})\text{-C}_6\text{H}_4\text{CHO}$), 2-hydroxybenzaldehyde ($(2\text{-OH})\text{-C}_6\text{H}_4\text{CHO}$), cinnamaldehyde ($\text{C}_6\text{H}_5\text{C}=\text{CCHO}$), and acetophenone ($\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_3$) were purchased from Sigma-Aldrich, which were used without any further purification.

I. Instrumentation

General. Powder X-ray diffraction patterns were recorded with a Rigaku DMAX 2500 diffractometer ($\text{Cu K}\alpha$) operating at 40 kV and 150 mA. A Netzsch TG 209 F1 was used for the TGA analysis, and temperature is increased by 5 °C per minute from 25 to 150 °C. Nicolet 205 instrument was used to measure infrared spectra. Absorption spectra recorded on an Agilent 8453 UV-vis spectrophotometer. Melting point was measured with a SMP10, BIBBY. GC/MS data were recorded on Agilent 5973N, and elemental analyses were carried out using a Carlo Erba EA1180 at the Organic Chemistry Research Center in Sogang University.

^1H magic angle spinning (MAS) NMR spectra were acquired on a Unity INOVA 600 NMR spectrometer (Varian Inc.) using a 2.5 mm rotor spinning at 23 kHz spinning rate. ^{13}C cross-polarization (CP) MAS NMR experiments were performed on a 400 MHz Avance II⁺ spectrometer (Bruker BioSpin GmbH), using a 4 mm rotor spinning at 3 kHz, a proton pulse length of 3.7 μs (corresponding to 90° pulse length), a contact time of 2.5 ms, and a pulse repetition delay time of 3 s. ^1H NMR and ^{13}C NMR spectra in solution were recorded on a Varian 400-MHz Gemini operating at 400 MHz for ^1H and 100 MHz for ^{13}C , respectively. All chemical shifts were referenced to tetramethylsilane ($(\text{CH}_3)_4\text{Si}$).

X-ray crystallography. A single crystal of $\text{NH}_3^+\text{NHCO}_2^-$, was selected from polycrystalline powder by a nylon loop (Hampton Research Co.) placed on a handmade cooper plate mounted inside a liquid N_2 Dewar vessel at approximately $-40\text{ }^\circ\text{C}$ and mounted on a goniometer head in a N_2 cryostream. Data collections were carried out in a Bruker SMART AXS diffractometer equipped with a monochromator with a Mo $\text{K}\alpha$ ($\lambda = 0.71073\text{ \AA}$) incident beam. The charge-coupled device (CCD) data were integrated and scaled using the Bruker-S SAINT software package, and the structure was solved and refined using SHELXTL V 6.12.^{S1} Hydrogen atoms were located in the calculated positions. The crystal data for $\text{NH}_3^+\text{NHCO}_2^-$: $\text{CH}_4\text{N}_2\text{O}_2$, Orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 4.6021(2)$, $b = 7.3673(4)$, $c = 8.6802(5)\text{ \AA}$, $V = 294.30(3)\text{ \AA}^3$, $\mu = 0.161\text{ mm}^{-1}$, $\rho_{\text{calcd}} = 1.717\text{ g/cm}^3$, $R_1 = 0.0394$, and $wR_2 = 0.1422$ for 569 unique reflections and 47 variables. The crystallographic data for $\text{NH}_3^+\text{NHCO}_2^-$ are listed in Table S1, while Table S2 lists the selected bond distances and angles. CCDC-822062 for $\text{NH}_3^+\text{CH}_2\text{CO}_2^-$ contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Solid state NMR experiments. ^1H magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired on a Unity INOVA 600 NMR spectrometer (Varian Inc.) using a 2.5 mm rotor spinning at a rate of 23 kHz. ^{13}C cross-polarization (CP) MAS NMR experiments were performed on a 400 MHz Avance II⁺ spectrometer (Bruker BioSpin GmbH), using a 4 mm rotor spinning at 3 kHz, proton pulse length of 3.7 μs (corresponding to 90° pulse length), contact time of 2.5 ms, and pulse repetition delay time of 3 s. All the chemical shifts were referenced to tetramethylsilane.

II. Synthesis of solid hydrazine in super critical carbon dioxide

Hydrazinium carboxylate (1). The glass liner of an autoclave (Parr 4714, 45 mL) was charged with the hydrazine monohydrate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, 3.0 g, 60.0 mmol) with dry ice (15 g), and the gauge and gauge block assembly were attached. Subsequently, the autoclave was placed in an oil bath on a heater stirrer preset to the reaction temperature. After the appropriate time, the autoclave was removed from the oil and cooled to an ambient temperature. The excess gas was discharged and the system was disassembled. The white crystalline powders in the glass liner were filtered in air followed by washing with methanol (3×10 mL), diethylether (3×10 mL), and pentane (3×10 mL), and then dried under vacuum. The typical yield of **1** based on the used hydrazine hydrate was >95 %. Yield (4.33 g, 96 %). mp 99-100 °C. Elemental analysis (Found: C, 15.75; H, 5.31; N, 36.90. Calc. For $\text{C}_1\text{H}_4\text{N}_2\text{O}_2$: C, 15.79; H, 5.30; N, 36.84 %). $\lambda_{\text{max}}(\text{powder})/\text{nm}$ 201. $\nu_{\text{max}}(\text{powder})/\text{cm}^{-1}$ 3225w, 2966w, 2680w (NH/N⁺H₃, br.), 1666w, 1662w (NH/N⁺H₃), 1589m, 1477s (C=N/C=O), 1346s, 1219s (C-N). ¹H NMR (600 MHz, solid): δ (ppm) 7.2 (1H, NH), 10.2 (3H, H₃N⁺); ¹³C NMR (400 MHz, solid): δ (ppm) 164.

Precaution. The solid hydrazine, hydrazinium carboxylate (**1**), could be harmful for health due to its sublimation character. The equipment of effective ventilation is highly recommended for handling the solid hydrazine to avoid vapor inhalation.

III. Synthesis of azines by reactions of carbonyl compounds with solid hydrazine

Synthesis. A 10.0 mmol carbonyl compound was reacted with 0.38 g (5.0 mmol) of **1** in an opened vessel without any solvent in a 10 mL vial at 45 °C. Subsequently, CO₂ was evolved from the reaction mixture with stirring. After the time given in Table 3, 10 mL of diethyl ether and 20 mL of pentane were added to a small portion of the azine product (*ca.*

0.1 g). The produced crystalline solids were filtered, followed by washing with pentane (3 × 10 mL) and then dried under vacuum. All the products of the azines derivatives obtained from the reactions of **1** with carbonyl compounds exhibited >98 % purity and >97% yield, and they are assigned by comparing melting point, GC/MS, ¹H and ¹³C NMR with previously reported data.^{S2-S5}

1,2-Dibenzylidenehydrazine (2a, from benzaldehyde).^{S2} Yield (1.01 g, 97 %). mp 93 °C (ether/pentane, yellow crystal); lit. 93-94 °C.^{S2} Elemental analysis (Found: C, 80.67; H, 5.84; N, 13.41. Calc. For C₁₄H₁₂N₂: C, 80.74; H, 5.81; N, 13.45 %). λ_{max}(CHCl₃)/nm 303 (ε/dm³ mol⁻¹ cm⁻¹: 3.90 × 10⁴). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.47 (d, *J* = 8.4, 6H, CH-3, CH-4 and CH-5 in phenyl), 7.85 (m, 4H, CH-2 and CH-6 in phenyl), 8.68 (s, 2H, CH=N); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 128.71 (CH-2 and CH-6 in phenyl), 128.94 (CH-3 and CH-5 in phenyl), 131.33(C_{quart}-1), 134.23 (CH-4), 162.26 (CH=N). MS (EI+) *m/z* = 208[M⁺], 180, 152, 131, 104, 89, 77, 63, 51, 39.

1,2-bis(2-methoxybenzylidene)hydrazine (2b, from 2-methoxybenzaldehyde).^{S3} Yield (1.31 g, 98 %). mp 143 °C (CHCl₃/ether, yellow crystal), lit. 143 °C.^{S4} Elemental analysis (Found: C, 71.64; H, 6.02; N, 10.54. Calc. For C₁₆H₁₆N₂O₂: C, 71.62; H, 6.01; N, 10.44 %). λ_{max}(CHCl₃)/nm 293, 341 (ε/dm³ mol⁻¹ cm⁻¹: 1.63 × 10⁴, 2.67 × 10⁴). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.85 (s, 6H, -OCH₃), 6.91 (d, *J* = 8.4, 2H, in phenyl), 7.00 (t, *J* = 7.6, 2H, in phenyl), 7.39 (td, *J* = 8.4, *J* = 1.6, 2H, in phenyl), 8.10 (dd, *J* = 7.6, *J* = 1.6, 2H, in phenyl), 9.06 (s, 2H, CH=N); ¹³C (100MHz, CDCl₃): δ (ppm) □ 55.58 (OCH₃), 111.18 (CH-3 in phenyl), 120.75 (CH-5 in phenyl), 122.81 (C_{quart}-1 in phenyl), 127.28 (CH-6 in phenyl), 132.36 (CH-4 in phenyl), 157.45 (C_{quart}-OCH₃ in phenyl), 159.08 (CH = N). MS (EI+) *m/z* =

268[M⁺], 253, 237, 207, 161, 150, 133, 119, 104, 91, 77, 64, 51, 44.

1,2-bis(2-hydroxybenzylidene)hydrazine (2c, from 2-hydroxybenzaldehyde).^{S3}

Yield (1.16 g, 97 %). mp 217 °C (CHCl₃/ether, yellowish crystal), lit. 213-214 °C.^{S2}
Elemental analysis (Found: C, 69.72; H, 4.89; N, 11.43. Calc. For C₁₄H₁₂N₂O₂: C, 69.99; H, 5.04; N, 11.66 %). λ_{\max} (CHCl₃)/nm 298, 361 (ϵ /dm³ mol⁻¹ cm⁻¹: 1.93 x 10⁴, 1.75 x 10⁴). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.97 (t, *J* = 7.2, 2H, in phenyl), 7.03 (d, *J* = 8.4, 2H, in phenyl), 7.35 – 7.41 (m, 4H, in phenyl), 8.71 (s, 2H, CH=N), 11.38 (s, 2H, OH); ¹³C NMR (100MHz, CDCl₃): δ (ppm) 117.14 (CH-4 in phenyl), 117.25 (CH-3 in phenyl), 119.70 (CH-5 in phenyl), 132.53 (CH-6 in phenyl), 133.42 (C_{quart}H-1 in phenyl), 159.78 (C_{quart}2-OH), 164.69 (CH=N). MS (EI⁺) *m/z* = 240[M⁺], 223, 207, 196, 165, 147, 121, 102, 93, 77, 65, 51, 44.

(1E,2E)-1,2-bis((E)-3-phenylallylidene)hydrazine (2d, from cinnamaldehyde).^{S5}

Yield (1.27 g, 98 %). mp 170-172 °C (CHCl₃/ether, yellow crystal), lit. 163-165 °C.^{S5}
Elemental analysis (Found: C, 83.30; H, 6.03; N, 10.84. Calc. For C₁₈H₁₆N₂: C, 83.05; H, 6.20; N, 10.76 %). λ_{\max} (CHCl₃)/nm 350 (ϵ /dm³ mol⁻¹ cm⁻¹: 4.08 x 10⁴). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.08 (m, 4H, C=CH-N and C-H in phenyl), 7.33 – 7.41 (m, 6H, CH=C-N and C-H in phenyl), 7.43 (br s, 2H, in phenyl), 7.44 (br s, 2H, in phenyl), and 8.29 (t, *J* = 4.4, 2H, CH=N); ¹³C NMR (100MHz, CDCl₃): δ (ppm) 125.37 (CH-C=N), 127.47 (CH-2 and CH-6 in phenyl), 128.92 (CH-3 and CH-5 in phenyl), 129.55 (CH=CH), 135.73 (C_{quart}H-1 in phenyl), 143.45 (CH-4 in phenyl), 163.73 (CH=N). MS (EI⁺) *m/z* = 260[M⁺], 245, 183, 157, 130, 115, 103, 89, 77, 63 51.

1,2-Bis(1-phenylethylidene)hydrazine (2e, from acetophenone).^{S2} Yield (1.15 g, 97 %). mp 122 °C (ether/pentane, yellow crystal), lit. 121-122 °C.^{S2} Elemental analysis (Found: C, 81.37; H, 6.86; N, 11.67. Calc. For C₁₆H₁₆N₂: C, 81.32; H, 6.83; N, 11.85 %). λ_{max} (CHCl₃)/nm 271 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$: 1.88 x 10⁴). ¹H NMR (400MHz, CDCl₃): δ (ppm) 2.30 (s, 6H, CH₃), 7.39 (m, 6H, CH-3, CH-4 and CH-5 in phenyl), 7.90 (m, 4H, CH-2 and CH-6 in phenyl); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 15.12 (CH₃), 126.70 (CH-2 and CH-6 in phenyl), 128.43 (CH-3 and CH-5 in phenyl), 129.71 (CH-4 in phenyl), 138.49 (C_{quart}-1 in phenyl), 157.80 (C=N). MS (EI+) m/z = 236[M⁺], 221, 194, 180, 159, 143, 132, 118, 103, 77, 51, 39.

Supplementary Figures and Tables

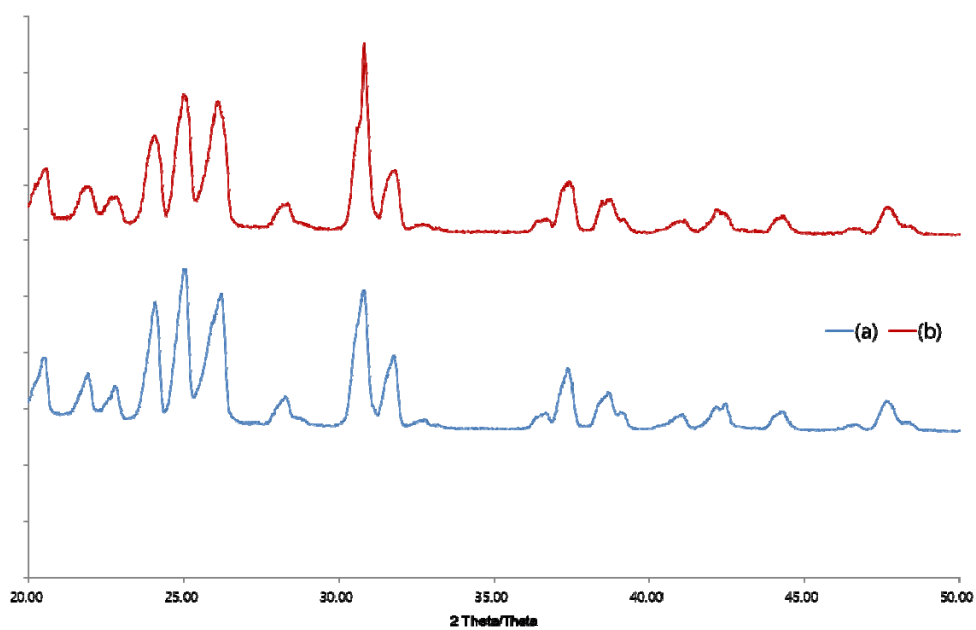


Fig. S1 X-ray powder diffraction (XRD) patterns of $\text{H}_3\text{N}^+\text{NHCO}_2^-$ (**1**): (a) XRD patterns of as-synthesized powders and (b) the same powders stored in a vial for 30 days.

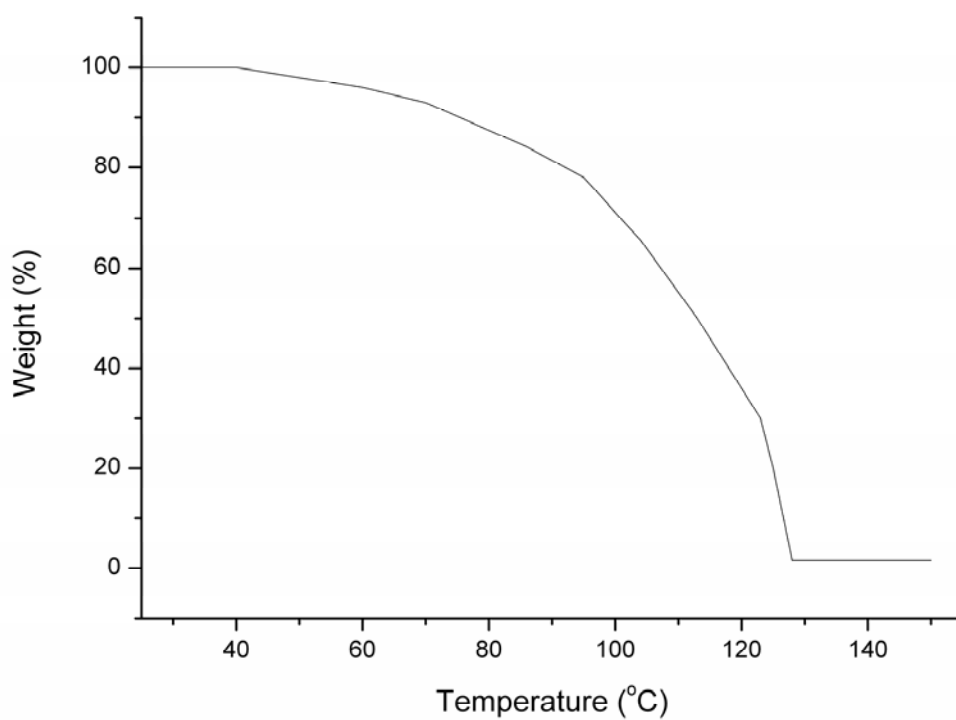


Fig. S2 The TGA data of H₃N⁺NHCO₂⁻ (**1**): the temperature is increased by 5 °C per minute from 25 to 150 °C.

Table S1. Crystal data for hydrazium carboxylate (**1**).

Formula sum	CH ₄ N ₂ O ₂
Formula weight	76.07
Crystal system	orthorhombic
Space group	<i>P</i> 21 21 21 (no. 19)
Unit cell dimensions	<i>a</i> = 4.5938(2) Å <i>b</i> = 7.3438(4) Å <i>c</i> = 8.6250(5) Å
Cell volume	290.97(3) Å ³
<i>Z</i>	4
Density, calculated	1.759 g/cm ³
R _{All}	0.040
Pearson code	oP36
Formula type	NO2P2Q4
Wyckoff sequence	a ⁹

Table S2. Selected bond distances and bond angles (Å, °) for hydrazium carboxylate (**1**).

O1—C	11.258(3)	N1—H1B	0.890
O2—C1	1.250(3)	N1—H1C	0.890
N1—N2	1.438(3)	N2—C1	1.398(3)
N1—H1A	0.890	N2—H2	0.860
N2—N1—H1A	109.50	C1—N2—N1	114.0(2)
N2—N1—H1B	109.50	C1—N2—H2	123.00
H1A—N1—H1B	109.50	N1—N2—H2	123.00
N2—N1—H1C	109.50	O2—C1—O1	126.5(2)
H1A—N1—H1C	109.50	O2—C1—N2	117.5(2)
H1B—N1—H1C	109.50	O1—C1—N2	115.0(2)

Supplementary References

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