Isolation and structural determination of two derivatives of the elusive carbamic acid†

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The dibenzyl-substituted carbamic acid $(PhCH_2)_2NC(O)OH$ (1), its deprotonation product $[(PhCH_2)_2NH_2][(PhCH_2)_2NCO_2]$ (2) and $CoCl(NO)_2[PhP(OCH_2CH_2)_2NC(O)OH]\cdot 2MeCOMe$ ($3\cdot 2MeCOMe$) are reported, the diffractometric study showing the carbamic acids 1 and 3 to be paired through hydrogen bonds.

Carbamic acids $R_2NC(O)OH$ (R = alkyl, aryl) have been until now elusive compounds, even for primary amines,[1] owing to their tendency to undergo decarbonation[2] under reduced pressure of carbon dioxide [eqn. (1)] or deprotonation in the presence of amine [eqn. (2)]. Carbamic acid itself, $H_2NC(O)OH$, has not been isolated so far although it has been detected by IR at low temperature,[2] and some of its properties have been calculated theoretically.[3,4]

$$R_2NH + CO_2 \rightleftarrows R_2NC(O)OH \tag{1}$$

$$R_2NC(O)OH + R_2NH \rightleftarrows [R_2NH_2][R_2NCO_2] \tag{2}$$

Thus, although *N*-substituted carbamic species are believed to be key intermediates in biological carbonations,[5] and in the photosynthetic carbon cycle promoted by Rubisco (ribulose 1,5-biphosphate carboxylase),[6] no simple member of this class has been isolated and no crystal data are available. This paper covers this gap.

Secondary amines R_2NH (R = Bu^n, Pr^i, *c*-C_6H_{11}) as neat liquids were reacted with CO_2 at atmospheric pressure over reaction times of several hours up to constant volume, gas volumetric measurements showing the CO_2/R_2NH molar ratio to be close to 0.5, namely 0.56 (Bu^n, 9.6 °C), 0.44 (Pr^i, 19.3 °C) and 0.53 (*c*-C_6H_{11}, 24.9 °C). Accordingly, the corresponding dialkylammonium dialkylcarbamate is the predominant product of the reaction. By contrast, for R = $PhCH_2$, a $CO_2/(PhCH_2)_2NH$ molar ratio close to 1 was observed at 10.3 °C, showing the preferential formation of *N,N*-dibenzylcarbamic acid $(PhCH_2)_2NC(O)OH$ **1**. By operating in heptane at *ca.* 9 °C, the carbonation, monitored by gas volumetry, corresponded to the complete conversion to **1**. Well formed crystals of **1** were obtained from heptane (*vide infra*).

The carbonation of dibenzylamine was monitored by IR in a PCTFE medium. When dibenzylamine was submitted to a CO_2 atmosphere at room temperature, the spectrum corresponded to the formation of **2**. Cooling the PCTFE mull at *ca.* 5 °C under CO_2 led to the almost exclusive formation of **1** after several hours. The process can be reversed by increasing the temperature and/or reducing the partial pressure of CO_2. The $\nu(CO)$ band of the carbamic function at 1640 cm^{-1} suggests the presence of intermolecular hydrogen bonds, in substantial agreement with theoretical calculations and spectroscopic data at low temperature[2–4] for the NH_3/CO_2 system.

When the carbonation of dibenzylamine was conducted with a CO_2/amine molar ratio not exceeding 0.5, **2** was obtained.‡ The corresponding IR spectrum shows bands centred at 1530, 1432, 1410, 1330 and 1316 cm^{-1}. The 1530 cm^{-1} band is assigned to $\nu_{as}(CO)$ of the O_2CN moiety, which compares well with those at 1525 and at 1550 cm^{-1} for $[NH_4]O_2CNH_2]$[9] (thin film, −190 °C), and $[Me_2NH_2][O_2CNMe_2]$ (neat liquid), respectively.[10]

The structure of **1** consists of two crystallographically independent molecules‡ (Fig. 1), whose main bond distances and angles are listed in the figure legend. In agreement with earlier theoretical studies,[3] the molecule does not crystallize as its zwitterionic form. The adopted conformation meets the requirement of maintaining the bulky benzyl groups relatively far from the $-CO_2H$ function. The main difference between the two molecules is in the torsion angles N(1)–C(9)–C(10)–C(11) and N(2)–C(24)–C(25)–C(26) differing by 34°. Within the same molecule, the C–O bond distances differ by 0.08 or 0.06 Å, the longer distance being connected with the oxygen carrying the hydrogen. The carbamate moieties are substantially

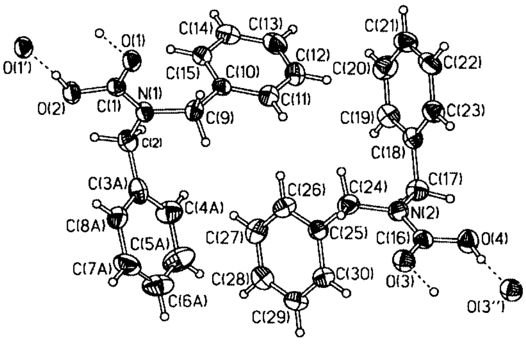

Fig. 1 The asymmetric unit of **1**. Thermal ellipsoids are at 50% probability. The hydrogen-bonded pairs are represented, together with the most populated positions of the disordered C(3)–C(8) ring. Relevant bond distances (Å) and angles (°). N(1)–C(2) 1.461(3), N(1)–C(9) 1.464(2), N(1)–C(1) 1.345(3), C(1)–O(1) 1.246(3), C(1)–O(2) 1.321(3), O(2)···O(1′) 2.556(2), N(2)–C(17) 1.465(3), N(2)–C(24) 1.468(3), N(2)–C(16) 1.340(3), C(16)–O(3) 1.254(3), C(16)–O(4) 1.315(3), O(3)···O(4″) 2.590(3); C(1)–N(1)–C(2) 123.5(2), C(1)–N(1)–C(9) 119.1(2), C(2)–N(1)–C(9) 117.5(2), O(1)–C(1)–N(1) 122.1(2), O(2)–C(1)–N(1) 115.1(2), O(1)–C(1)–O(2) 122.8(2), C(16)–N(2)–C(17) 123.1(2), C(16)–N(2)–C(24) 119.7(2), C(17)–N(2)–C(24) 116.8(2), O(3)–C(16)–N(2) 121.4(2), O(4)–C(16)–N(2) 115.8(2), O(3)–C(16)–O(4) 122.8(2). ′ = 3/2 − *x*, −1.2 − *y*, 1 − *z*; ″ = 2 − *x*, −*y*, 2 − *z*.

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planar (maximum deviation from planarity 0.07 Å). The N(1)–C(1) and N(2)–C(16) bond distances of 1.345 and 1.340 Å to the –C(O)OH function are substantially identical to the distance of 1.34 Å indicated by *ab initio* calculations.[3]

As in carboxylic acids, each molecule is connected through two end-on hydrogen bonds, which are shown in Fig. 1, in pairs related by an inversion centre.

Single crystals of **3** were obtained from an acetone solution of $CoCl(NO)_2[PhP(OCH_2CH_2)_2NH]$[11] upon carbonation at atmospheric pressure at −30 °C. The carbamic acid fragment‡ is paired through two end-on hydrogen bonds, similarly to **1**. The intermolecular O···O bond distance of 2.580 Å implies the existence of hydrogen atoms in between. The N–C(O)OH fragments in **1** and **3** do not differ significantly in bond distances and angles and, as expected, the C–O bonds are not equivalent.

Computational studies on the decomposition of ammonium carbamate[3,4] favour carbamic acid $H_2NC(O)OH$ as the intermediate, and its zwitterionic form as the transition state. The isolation of carbamic acids **1** and **3**, in the present study, shows for the first time that, under carbon dioxide at *atmospheric* pressure, carbonation of the secondary amine to the corresponding carbamic acid can be in fact a thermodynamically favourable process provided the appropriate substituents and reaction conditions are chosen, probably a determining factor in the stabilisation of the system being the hydrogen-bond network in the solid state, as previously observed in $Ag(O_3SOH)$.[12] The dialkylammonium carbamate may further slowly undergo carbonation to the acid or be kinetically or thermodynamically stabilized as such, depending on the nature of the group R. The zwitterionic form of the acid, $\{R_2NH^+CO_2^-\}$, may be a kinetically relevant intermediate undergoing fast deprotonation in the presence of amine.

The present findings are believed to be relevant, *inter alia*, to the problem of carbon dioxide fixation by amino groups in biopolymers in the solid state.[13]

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Notes and references

‡ *Crystallography*: reflection intensities were collected on a Siemens P4 diffractometer for **1** and **2**, and on a Nonius CAD-4 diffractometer for **3**, both equipped with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). All data were collected in the ω–2θ scan mode.

Crystal data: for **2** at 173(2) K: $C_{29}H_{30}N_2O_2$; colourless monoclinic prisms. Cell parameters: a = 15.339(1), b = 8.850(1), c = 18.402(2) Å, β = 101.68(1)°, V = 5057.8(14) Å^3, Z = 4, D_c = 1.192 Mg m^{-3}, μ(Mo-Kα) = 0.084 mm^{-1}, space group $P2_1/n$ (no. 14), 3575 intensities collected between θ = 2.26 and 24.0° in the range $-17 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 8$, $-20 \leqslant l \leqslant 21$, and corrected for Lorentz and polarization effects; after merging (R_{int} = 0.0215), 3438 independent reflections; structure solved by direct methods (SIR92),[7] and refined (SHELXTL).[8] The nitrogen-bonded hydrogen atoms of the cation were located in the difference Fourier map, and were not refined; the other hydrogen positions were allowed to ride on the corresponding carbon atoms, obtaining R_1 [$I > 2\sigma(I)$] = 0.0447 and wR_2 = 0.1039 (298 parameters, without restraints).

For **1** at 173(2) K: $C_{15}H_{15}NO_2$; colourless needle-like prisms. Cell dimensions: a = 39.397(7), b = 5.545(1), c = 24.783(3) Å, β = 110.90(1)°, V = 2443.7(4) Å^3; monoclinic crystal, Z = 16, D_c = 1.267 Mg m^{-3}, μ(Mo-Kα) = 0.075 mm^{-1}, space group $C2/c$ (no. 15) or Cc, 4675 intensities collected between θ = 2.21 and 24.0° in the range $-44 \leqslant h \leqslant 1$, $-5 \leqslant k \leqslant 1$, $-26 \leqslant l \leqslant 28$, and corrected for Lorentz and polarization effects; after merging ($R_{int} = [\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)]$ = 0.0260), 3557 independent reflections; structure solved in the centrosymmetric space group (SIR92),[7] and refined (SHELXTL).[8] The abnormally large thermal ellipsoids of the aromatic ring suggested the presence of local rotational disorder. Two different phenyl rings of fixed geometry and rotated by slightly different angles around the C(2)–C(3) bond were then introduced in the same position, by fixing to unity the total occupancy of the site. The hydrogen within the C(O)OH group was located on the difference Fourier map and introduced in the calculations without refining; the other hydrogen atoms were introduced in calculated positions and allowed to ride on the corresponding carbon atoms. The final refinement cycles (353 parameters, no restraints) gave the reliability factors R_1 [$I > 2\sigma(I)$] = 0.0411 and wR_2 = 0.1012 (all data).

For **3** at 243(2) K: $C_{17}H_{26}ClCoN_3O_8P$; dark-brown prisms. Cell parameters: a = 9.612(2), b = 11.936(3), c = 12.371(4) Å, α = 73.34(2), β = 69.94(2), γ = 66.18(2)°, V = 1201.4(6) Å^3, Z = 2, D_c = 1.453 Mg m^{-3}, μ(Mo-Kα) = 0.937 mm^{-1}, triclinic, space group $P\bar{1}$ (no. 2), 3918 independent observed intensities collected between θ = 1.89 and 30.0° in the range $-12 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 10$, and corrected for Lorentz, polarization effects and absorption (ψ-scan method); structure solution by direct methods and refined (SHELXTL).[8] The asymmetric unit turned out to contain two acetone molecules, one of them being affected by some orientational disorder. The hydrogen atoms were introduced in calculated positions and allowed to ride on the connected atoms. The final refinement cycles with anisotropic thermal factors for heavy atoms and isotropic ones for hydrogen atoms (280 parameters, no restraints) gave R_1 [$I > 2\sigma(I)$] = 0.0915 and wR_2 = 0.1321.

CCDC 182/1613. See http://www.rsc.org/suppdata/cc/b0/b002479l/ for crystallographic files in .cif format.

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