I3—I2—I1	177.88 (5)	C5—N1—C1	117.2 (15)
C10—N2—C6	121.2 (14)	C2—C1—N1	123.3 (16)
C3—C2—C1	118.9 (15)	C4—C3—C2	121.1 (15)
C5—C4—C3	114.9 (14)	C4—C5—N1	124.5 (14)
C6—C5—N1	115.3 (12)	C6—C5—C4	120.3 (13)
C5—C6—N2	114.3 (12)	C7—C6—N2	118.1 (15)
C7—C6—C5	127.6 (15)	C8—C7—C6	118.6 (18)
C9—C8—C7	122.4 (19)	C10—C9—C8	116.1 (18)
C9—C10—N2	123.5 (17)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
N2—HN···N1	1.13 (11)	1.83 (10)	124 (8)

All non-H atoms were refined anisotropically. H atoms attached to C atoms were placed in calculated positions with C—H = 0.95 Å and refined riding upon the C atom to which they were attached with a common group U_{iso}. The H atom attached to N2 was found in a difference map and refined isotropically. All computations were performed on the Sun SPARCserver (UNIX operating system) of the Computing Centre of the University of Aberdeen.

Data collection: *Nicolet P3 Software* (Nicolet XRD Corporation, 1980). Cell refinement: *Nicolet P3 Software*. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *XPUB* (Low, 1980).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Methylbenzylammonium 4-Methylbenzylcarbamate

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(Received 24 March 1995; accepted 9 October 1995)

Abstract

The title structure, $C_8H_{12}N^+.C_9H_{10}NO_2^-$, consists of infinite bilayers, parallel to the *ab* plane, incorporating both cations and anions. Within each bilayer, anions and cations are stacked in a herringbone fashion and the layers are generated by three N—H···O hydrogen bonds. The $NHCOO^-$ moiety displays near-planar geometry.

Comment

The chemical properties of organic carbamates have been studied widely, especially in view of their use as herbicides (Machemer & Pickel, 1994*b*) and insecticides (Machemer & Pickel, 1994*a*). The general synthetic route to carbamates is well established (Schering, 1901) and they are now easily prepared through the reaction of primary, secondary or aromatic amines with carbon dioxide. Furthermore, the reactions can be carried out at ambient temperature and pressure. Despite the ease with which organic carbamates can be made, there is a severe lack of X-ray single-crystal studies on organic compounds containing the *R*NHCOO$^-$ moiety. A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) uncovered only three organic compounds containing the uncoordinated *R*NHCOO$^-$ function, *i.e.* ammonium carbamate (Adams & Small,

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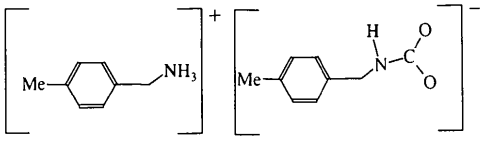
1973) and two polymorphs of *N*-(2-ammonioethyl)-carbamate (Garbauskas, Goehner & Davies, 1983), a zwitterionic compound.

We have recently initiated a program which will examine both the geometric features (*e.g.* planarity and degree of delocalization of the C—N bond) and hydrogen-bond preferences displayed by the *R*NHCOO$^-$ group in a series of organic carbamates. The first example in this study, 4-methylbenzylammonium (4-methylbenzyl)-carbamate, (I), was isolated during the slow recrystallization of 4-methylbenzylamine from an acidified aqueous solution. The subsequent single-crystal structure determination of (I) (Fig. 1, Table 1) represents an addition to a class of materials for which very little X-ray data is presently available.



(I)

The structure of (I) consists of bilayers of cations and anions (in the *ab* plane). Each bilayer is held together by three N—H···O hydrogen bonds between the NH_3^+ moiety of the cation and the two O atoms of the carboxylate moiety of the anion (one O atom acts as an acceptor for two hydrogen bonds; Fig. 2). Within each layer, cations and anions are stacked in columns forming a herringbone motif. The carbamate moiety is slightly twisted from a planar arrangement, with an O—C—N—H torsion angle of *ca* 10°. This value is in good agreement with the corresponding torsion angles observed previously, *i.e.* 7.6 (Adams & Small, 1973), 3.2 and 7.9° (Garbauskas, Goehner & Davies, 1983), for the three compounds mentioned above.

The C—N bond distance in the anion [1.365 (4) Å] indicates that a significant degree of delocalization is occurring in the C—N bond, which is in accordance with previous data, *i.e.* 1.361 (5) (Adams & Small, 1973), 1.353 (6) and 1.372 (9) Å (Garbauskas, Goehner & Davies, 1983).

The NH site of the anion is not involved in any hydrogen-bond interaction (Table 3), which is probably due to the overall imbalance (4:2) between hydrogen-bond donors and acceptors in (I). In ammonium carbamate (Adams & Small, 1973), only one H atom of the NH_2 moiety of the anion is involved in hydrogen bonding to the cation (the hydrogen-bond donor to acceptor ratio is 6:3) and the overall structure has a compact three-dimensional appearance (calculated density 1.376 Mg m^{-3}). In addition, the anions in ammonium carbamate are linked head-to-head to form a hydrogen-bonded eight-membered $R_2^2(8)$ ring (Etter, MacDonald & Bernstein, 1990).

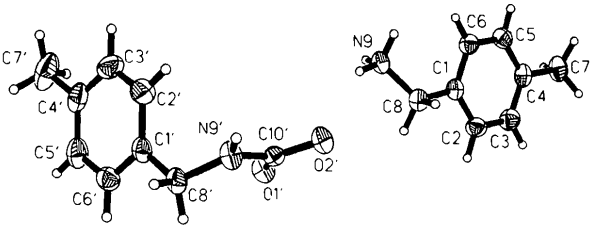


Fig. 1. Displacement ellipsoid plot (50% probability) of (I) showing the atom-numbering scheme for the ion pair.

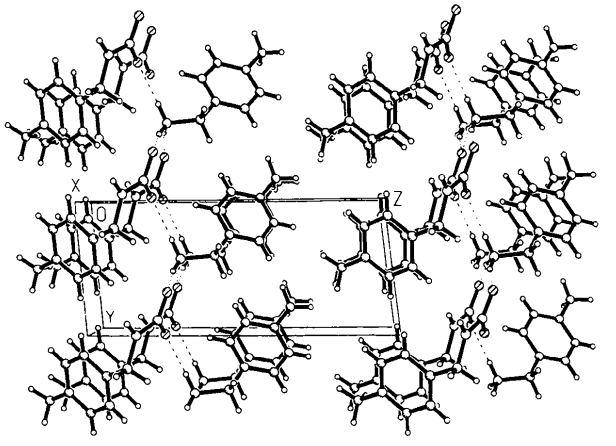


Fig. 2. A view of the bilayer of anions and cations, parallel to the *ab* plane, held together by three hydrogen bonds (indicated by dashed lines).

In contrast, in polymorph *B* of *N*-(2-ammonioethyl)-carbamate, each potential hydrogen-bond donor/acceptor is involved, including the NH group (one carboxylate O atom acts as an acceptor for three hydrogen bonds). The same is true for polymorph *A* (Garbauskas, Goehner & Davies, 1983), where all hydrogen-bond donors/acceptors are involved (each carboxylate O atom accepts two hydrogen bonds). Both polymorphs display an intricate three-dimensional structure, reflected in the high densities of 1.346 and 1.442 Mg m^{-3} for *A* and *B*, respectively, compared with the value of 1.259 Mg m^{-3} for the present compound.

Given the fact that the two polymorphs of *N*-(2-ammonioethyl)carbamate have been isolated and crystallographically characterized, we decided to examine the structural purity of the title compound (*i.e.* to establish that the chosen single crystal was representative of the bulk material). To this end, the X-ray powder diffraction pattern was simulated from the X-ray single-crystal data (using the *CERIUS*[2] package) and compared with the experimental X-ray powder pattern recorded on the bulk sample. The match between simulated and experimental pattern demonstrated that only one structural form of (I) was present (Aakeröy & Nieuwenhuyzen, 1995).

Experimental

Crystal data

$C_8H_{12}N^+.C_9H_{10}NO_2^-$
M_r = 286.37
Triclinic
$P1$
a = 4.829 (1) Å
b = 5.843 (1) Å
c = 13.610 (2) Å
α = 83.39 (1)°
β = 86.16 (1)°
γ = 82.63 (2)°
V = 377.8 (1) Å^3
Z = 1
D_x = 1.259 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 35 reflections
θ = 5–12.5°
μ = 0.083 mm^{-1}
T = 293 K
Plate
0.81 × 0.53 × 0.17 mm
Colourless

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
2666 measured reflections
2666 independent reflections
2418 observed reflections [$F > 4\sigma(F)$]

θ_{max} = 25°
$h = -5 \rightarrow 5$
$k = -6 \rightarrow 6$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 97 reflections
intensity variation: ±1%

Refinement

Refinement on F^2
$R(F)$ = 0.0658
$wR(F^2)$ = 0.1714
S = 1.039
2666 reflections
193 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1325P)^2 + 0.0651P]$
where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	−0.2353 (6)	0.2550 (5)	0.4872 (2)	0.028 (1)
C(2)	−0.3443 (7)	0.3031 (6)	0.5807 (3)	0.036 (1)
C(3)	−0.5279 (8)	0.1660 (7)	0.6342 (3)	0.039 (1)
C(4)	−0.6084 (7)	−0.0235 (6)	0.5960 (3)	0.033 (1)
C(5)	−0.5028 (7)	−0.0695 (6)	0.5024 (3)	0.035 (1)
C(6)	−0.3167 (7)	0.0662 (6)	0.4488 (3)	0.033 (1)
C(7)	−0.8072 (8)	−0.1733 (7)	0.6551 (3)	0.043 (1)
C(8)	−0.0237 (6)	0.4027 (6)	0.4359 (3)	0.032 (1)
N(9)	−0.0179 (5)	0.4261 (5)	0.3258 (2)	0.029 (1)
C(1′)	1.3388 (7)	1.2736 (6)	0.0674 (2)	0.030 (1)
C(2′)	1.2894 (8)	1.1248 (6)	−0.0006 (3)	0.040 (1)
C(3′)	1.0988 (9)	1.2011 (8)	−0.0736 (3)	0.047 (1)
C(4′)	0.9561 (8)	1.4247 (7)	−0.0809 (3)	0.043 (1)
C(5′)	1.0089 (8)	1.5688 (7)	−0.0128 (3)	0.044 (1)
C(6′)	1.1982 (8)	1.4947 (6)	0.0594 (3)	0.037 (1)
C(7′)	0.7451 (10)	1.5040 (11)	−0.1588 (3)	0.066 (2)
C(8′)	1.5508 (7)	1.2023 (6)	0.1453 (3)	0.032 (1)
N(9′)	1.5804 (5)	0.9599 (5)	0.1841 (2)	0.031 (1)
C(10′)	1.3833 (6)	0.8634 (5)	0.2464 (2)	0.024 (1)
O(1′)	1.1467 (4)	0.9774 (4)	0.2570 (2)	0.032 (1)
O(2′)	1.4477 (4)	0.6594 (4)	0.2878 (2)	0.031 (1)

Table 2. *Selected geometric parameters (Å, °)*

C(1)—C(6)	1.385 (5)	C(1)—C(2)	1.389 (5)
C(1)—C(8)	1.506 (5)	C(2)—C(3)	1.385 (5)
C(3)—C(4)	1.385 (5)	C(4)—C(5)	1.383 (5)
C(4)—C(7)	1.512 (5)	C(5)—C(6)	1.389 (5)
C(8)—N(9)	1.487 (4)	C(1′)—C(6′)	1.376 (5)
C(1′)—C(2′)	1.392 (5)	C(1′)—C(8′)	1.511 (5)
C(2′)—C(3′)	1.395 (6)	C(3′)—C(4′)	1.393 (6)
C(4′)—C(5′)	1.378 (6)	C(4′)—C(7′)	1.513 (6)
C(5′)—C(6′)	1.382 (5)	C(8′)—N(9′)	1.446 (4)
N(9′)—C(10′)	1.365 (4)	C(10′)—O(1′)	1.255 (4)
C(10′)—O(2′)	1.268 (4)		
C(6)—C(1)—C(2)	117.9 (3)	C(6)—C(1)—C(8)	123.7 (3)
C(2)—C(1)—C(8)	118.2 (3)	C(3)—C(2)—C(1)	121.2 (3)
C(4)—C(3)—C(2)	120.9 (3)	C(5)—C(4)—C(3)	117.9 (3)
C(5)—C(4)—C(7)	121.5 (3)	C(3)—C(4)—C(7)	120.6 (3)
C(4)—C(5)—C(6)	121.4 (3)	C(1)—C(6)—C(5)	120.7 (3)
N(9)—C(8)—C(1)	115.1 (3)	C(6′)—C(1′)—C(2′)	118.3 (3)
C(6′)—C(1′)—C(8′)	119.8 (3)	C(2′)—C(1′)—C(8′)	121.8 (3)
C(1′)—C(2′)—C(3′)	119.8 (4)	C(4′)—C(3′)—C(2′)	121.7 (3)
C(5′)—C(4′)—C(3′)	117.5 (3)	C(5′)—C(4′)—C(7′)	121.3 (4)
C(3′)—C(4′)—C(7′)	121.2 (4)	C(4′)—C(5′)—C(6′)	121.2 (4)
C(1′)—C(6′)—C(5′)	121.6 (3)	N(9′)—C(8′)—C(1′)	115.8 (3)
C(10′)—N(9′)—C(8′)	123.0 (3)	O(1′)—C(10′)—O(2′)	123.7 (3)
O(1′)—C(10′)—N(9′)	118.5 (3)	O(2′)—C(10′)—N(9′)	117.8 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
N(9)—H(91)···O(2^{ii})	1.935 (4)	2.810 (3)	167 (1)
N(9)—H(92)···O(2′^{iii})	1.910 (6)	2.766 (3)	161 (1)
N(9)—H(92)···O(1′^{iii})	1.995 (4)	2.883 (4)	175 (2)

Symmetry codes: (i) $x-2, y, z$; (ii) $x-1, y, z$; (iii) $x-1, y-1, z$.

Lorentz and polarization corrections were applied. The absolute configuration was not determined. The structure was solved by direct methods and the non-H atoms were refined with anisotropic displacement parameters. H-atom positions were located from difference Fourier maps and a riding model with fixed displacement parameters [U_{eq} = 1.2U_{eq}(riding atom)] was used for subsequent refinement.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC XP*.

Generous financial support from NIDevR is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,8-Dimethyl-5,11-dipropyl-1,4,5,6,7,10,11,12-octahydroimidazo[4,5-*h*]-imidazo[4,5-*c*][1,6]diazecine Hexahydrate

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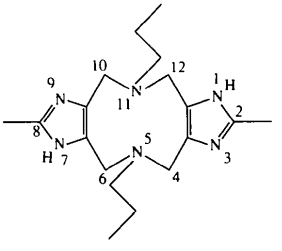
Abstract

Crystals of the title compound, $C_{18}H_{30}N_6.6H_2O$, are composed of molecules of pronmeim (the condensation product of 2-methylimidazole, *n*-propylamine and formaldehyde) and water linked together by hydrogen bonds to form a two-dimensional network. The diazecine ring is in a chair conformation. Bond lengths and angles are within the normal ranges.

Comment

The chemistry of imidazole is of special interest because of its wide occurrence in biological compounds, notably as part of the amino acid histidine and metabolites like histamine. Synthetic imidazole derivatives are also used as antihistamine drugs. New imidazole-containing compounds are being developed by our group in order to study their properties in relation to the role played by the imidazole group in different enzymes (Bouwman, Driessen & Reedijk, 1990). The development of simple processes for the synthesis of new imidazole derivatives is, therefore, a matter of constant research.

The Mannich reaction, which is one such powerful and simple process, is a one-step method for attaching aminomethylene groups to the imidazole ring (Stocker, Kurtz, Byron & Forsyth, 1970). The reaction of aldehydes, in particular formaldehyde, with different substrates and conditions has been used widely in organic synthesis. Some of these reactions involve coordinated amino acids (Teo, Ng & Tiekink, 1993; Berndt, 1970), coordinated amines (Geue, Höhn, Ralph, Sargeson & Willis, 1994), aromatic rings and secondary amines (Karunakaran & Kandaswamy, 1994) and secondary amines and 2,4(5)-disubstituted imidazoles (Baumann, Summers, Hutchinson, Zubieta & Marzilli, 1984; Stocker *et al.*, 1970). We used this reaction under basic conditions to condense propylamine, formaldehyde and 2-methylimidazole. A double addition of formaldehyde on the 4 and 5 positions of imidazole and a further condensation with propylamine resulted in the title compound, pronmeim, a novel heterocyclic 10-membered hexahydrodiazecine ring with two imidazole rings fused through the bond between C4 and C5. The crystal and molecular structure of this compound (which crystallized as the hexahydrate) are described here. The results of this study were required for comparative studies with analogous compounds containing different amine moieties and their coordination complexes (Mendoza-Díaz, Driessen & Reedijk, 1994).



Pronmeim

The molecular structure of the title compound is shown in Fig. 1. The 2-methyl group and the methylene C atoms attached directly to the imidazole ring lie essentially in the plane of the imidazole ring, with deviations from the least-squares plane through the ring of 0.088 (11), 0.006 (10) and −0.033 (14) Å for C7, C8 and the 2-methyl group, respectively. The slight twist of C7 out of this plane possibly results from it being part of the the diazecine ring. The angles made by the bonds C4—C7 and C5—C8 and the least-squares plane of the imidazole ring are 3.33 (14) and 0.26 (14)°, respectively, whereas the angle made by the bond between the 2-methyl group and the imidazole moiety (C2–C6) and this plane is 1.21 (14)°. The ten-membered diazecine ring has a chair-type conformation. The distance between the two centres of mass of the imidazole rings is 4.5897 Å. The angles at the nitrogen bridge in the diazecine ring sum to 334.1°, indicating a pyramidal conformation.

Crystals of the title compound consist of pronmeim and water molecules in the ratio 1:6. The water molecules form a two-dimensional network of hydrogen bonds along the crystallographic planes (100) and (010). Four of these water molecules (containing O50 and O51, but not O52) form a hydrogen-bond ring between two adjacent pronmeim molecules, shown in Fig. 2(*a*).

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