Bis(adamantan-1-aminium) carbonate

Monika Nowakowska, Caryn Gamble and Demetrius C. Levendis*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, PO Wits 2050, South Africa
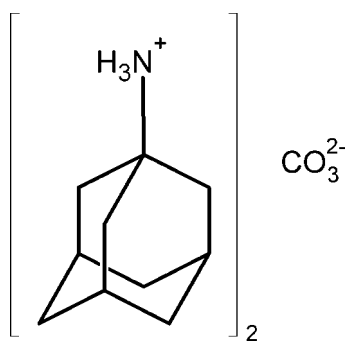Correspondence e-mail: demetrius.levendis@wits.ac.za

In the title compound, $2C_{10}H_{18}N^+ \cdot CO_3^{2-}$, the adamantan-1-aminium cation forms three N—H···O hydrogen bonds to three carbonate ions, resulting in a layer parallel to (001) with the adamantane groups located on its surface so that adjacent layers form only C—H···H—C contacts. The carbonate anions occupy special positions of 32 symmetry, whereas the adamantan-1-aminium cations occupy special positions of 3 symmetry.

Related literature

For related structures, see: de Vries *et al.* (2011); Mullica *et al.* (1999); He & Wen (2006); Liu *et al.* (2009); Zhao *et al.* (2003). For applications of adamantane–ammonium salts in virology, see: Hoffmann (1973); Dolin *et al.* (1982); Bright *et al.* (2005); Betakova (2007). For applications of amines for the capture of CO_2 from the atmosphere, see: Yang *et al.* (2008).

Experimental

Crystal data

$2C_{10}H_{18}N^+ \cdot CO_3^{2-}$	$Z = 2$
$M_r = 364.52$	Mo $K\alpha$ radiation
Trigonal, $P\bar{3}c1$	$\mu = 0.09$ mm^{-1}
$a = 6.4340$ (6) Å	$T = 173$ K
$c = 25.474$ (2) Å	$0.30 \times 0.22 \times 0.08$ mm
$V = 913.25$ (14) Å^3	

Data collection

Bruker APEXII CCD diffractometer	629 independent reflections
	493 reflections with $I > 2\sigma(I)$
3187 measured reflections	$R_{int} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.107$	
$S = 1.08$	
629 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
45 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.999 (16)	1.778 (15)	2.764 (1)	168.7 (18)

Symmetry code: (i) $-y + 1, x - y + 1, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

References

Betakova, T. (2007). *Curr. Pharm. Des.* **13**, 3231–3235.
Bright, R. A., Medina, M. J., Xu, X. Y., Gilda, P. O., Wallis, T. R., Davis, X. H. M., Povinelli, L., Cox, N. J. & Klimov, A. I. (2005). *Lancet*, **366**, 1175–1181.
Bruker (2005). *APEX2, SAINT-Plus* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dolin, R., Reichman, R. C., Madore, H. P., Maynard, R., Lindon, P. M. & Weber-Jones, J. (1982). *N. Engl. J. Med.* **307**, 580–584.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
He, Y.-H. & Wen, Y.-H. (2006). *Acta Cryst.* E**62**, o1312–o1313.
Hoffmann, C. E. (1973). *Selective Inhibitors of Viral Functions*, edited by W. A. Carter, p. 199. Cleveland, USA: CRC Press.
Liu, J.-F., Xian, H.-D., Li, H.-Q. & Zhao, G.-L. (2009). *Z. Kristallogr.* **224**, 69–70.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Mullica, D. F., Scott, T. G., Farmer, J. M. & Kautz, J. A. (1999). *J. Chem. Crystallogr.* **29**, 845–848.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Vries, E. J. C. de, Gamble, C. & Nowakowska, M. (2011). *Acta Cryst.* E**67**, o1339.
Yang, H., Xu, Z., Fan, M., Gupta, R., Bland, A. E. & Wright, I. J. (2008). *Environ. Sci.* **20**, 14–27.
Zhao, G.-L., Feng, Y.-L., Hu, X.-C. & Kong, L.-K. (2003). *Chin. J. Struct. Chem.* **22**, 321.

Bis(adamantan-1-aminium) carbonate

Monika Nowakowska, Caryn Gamble and Demetrius C. Levendis

Comment

It has been reported that 1-aminoadamantane hydrochloride (marketed as Symmetrel) is effective in the prevention and treatment of the influenza (A) virus (Hoffmann, 1973; Dolin *et al.*, 1982; Bright *et al.*, 2005). However recent studies suggest that the virus is becoming increasingly resistant to this anti-influenza drug (Betakova, 2007).

In an attempt to crystallize pure 1-aminoadamantane from ethanol we obtained instead adamantan-1-aminium carbonate, illustrated in Fig. 1, suggesting that the amine had captured atmospheric CO_2. We report the structure here. It is known that organic amines can trap CO_2 as the ammonium carbonate salt and this property is being explored as a way to capture carbon dioxide from the atmosphere (Yang *et al.*, 2008).

Each carbonate ion of the title compound forms hydrogen bonds to six adamantane-ammonium ions, as shown in Fig. 2, forming a two-dimensional layer of adamantan-1-aminium carbonates parallel to (001). The hydrophobic adamantane layers interact with the neighbouring layers of adamantane-ammonium molecules *via* C—H···H–C contacts (see Fig. 3).

It is noted here that the structure of adamantan-1-aminium bicarbonate (Liu *et al.*, 2009) reported in the literature is isomorphous to adamantan-1-aminium nitrate (Zhao *et al.*, 2003). The former structure has unusually short H···H intermolecular contacts between NH_3^+ group H atom and bicarbonate H atom of 1.50 Å In addition the geometry of the hydrogen carbonate ion is very similar to that of the nitrate ion. A re-investigation of these structures is warranted.

Experimental

Crystals were grown by slow evaporation of an ethanol solution of the title compound, 0.500 g in 10 ml of ethanol, and afforded colourless plates after three days under ambient conditions. Crystals decompose, with an emission of gas bubbles (presumably CO_2), at 423–428 K.

Refinement

The N-bound H atom was placed according to the observed electron density and was allowed to refine freely. The remaining H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H bond lengths of 1.00 (methine) and 0.99 Å (methylene CH_2) and with $U_{iso}(H) = 1.2$ times $U_{eq}(C)$.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), Mercury (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).
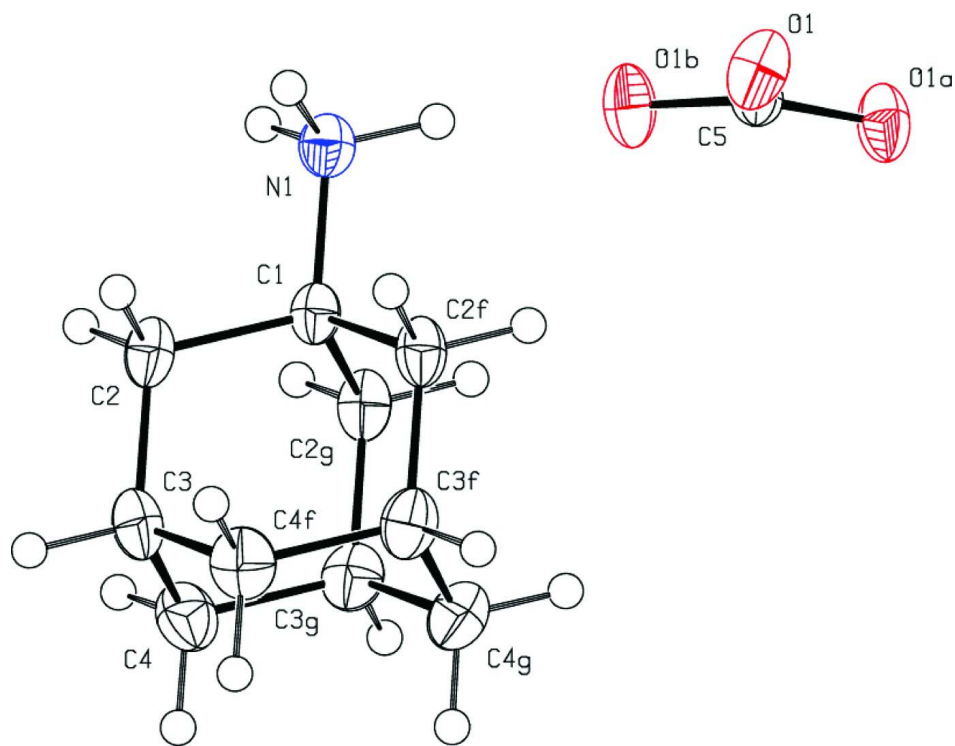
Figure 1

The molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. The atoms C2f to C4f are generated by the symmetry (1-*y*,*x*-*y*,*z*); C2g to C4g by (1-*x*+*y*, 1-*x*,*z*); O1a by (-*y*,*x*-*y*,*z*) and O2b by (-*x*+*y*,-*x*,*z*).
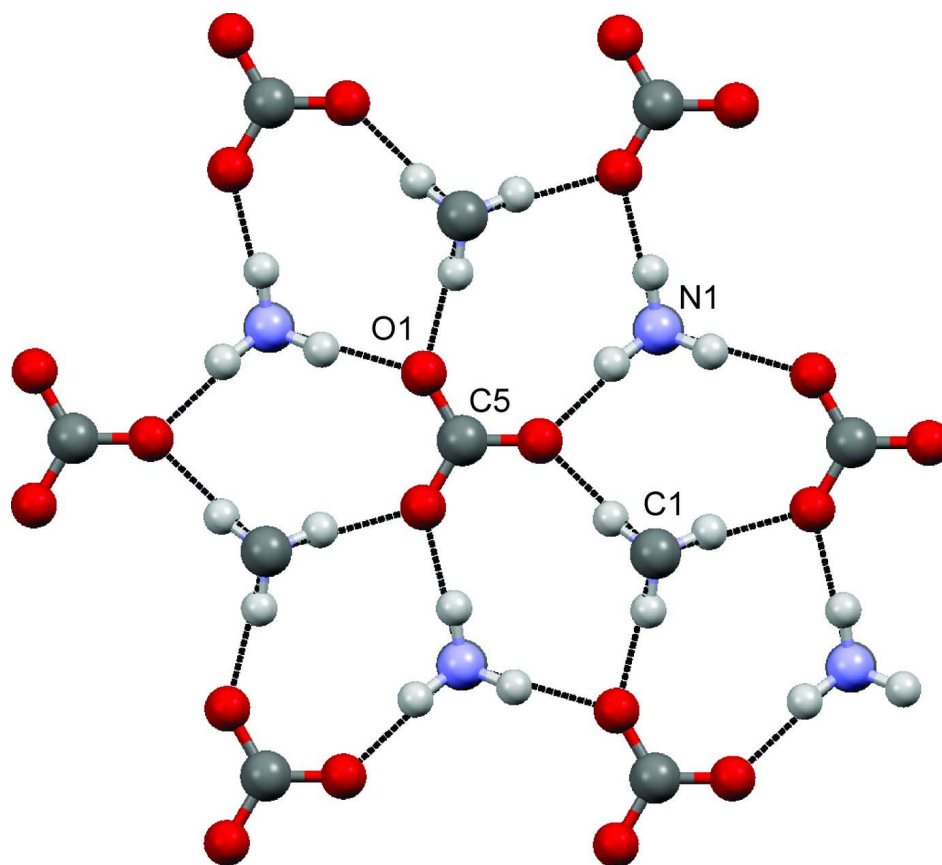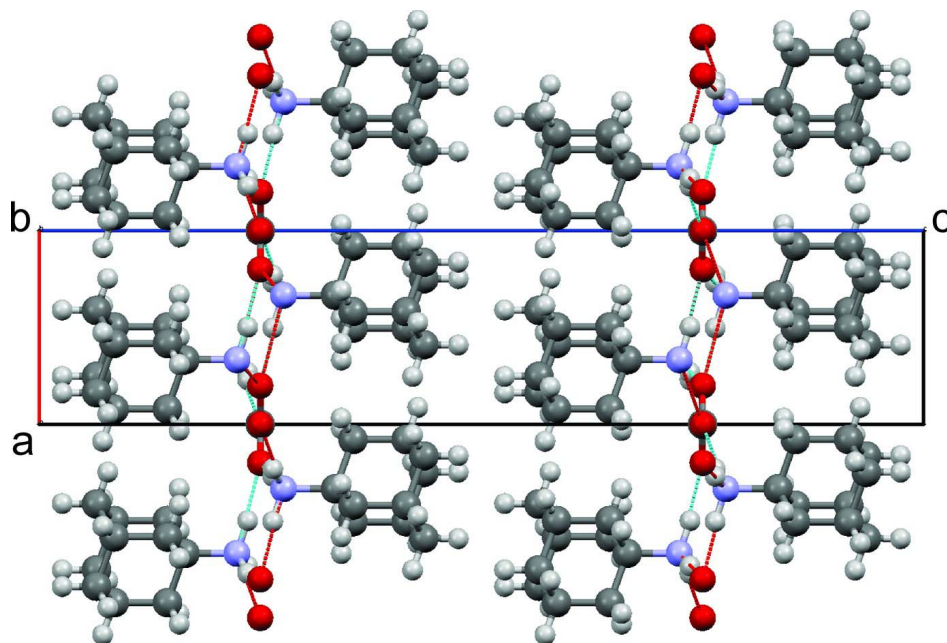
Figure 2

Intermolecular N—H···O hydrogen bonded (dashed lines) layers along [001] showing only the C-NH$_3$ and CO$_3$ groups for clarity.

Figure 3

A view down the *b* axis of the unit cell of the title compound showing the hydrogen bonded layers. Notice that the carbonate ions occupy sites with 32 symmetry whereas cations occupy the sites of 3 symmetry.

Bis(adamantan-1-aminium) carbonate

Crystal data

$2C_{10}H_{18}N^+ \cdot CO_3{}^{2-}$	$D_x = 1.326$ Mg m^{-3}
$M_r = 364.52$	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Trigonal, $P\bar{3}c1$	Cell parameters from 819 reflections
Hall symbol: -P 3 2"c	$\theta = 3.2–25.8°$
$a = 6.4340$ (6) Å	$\mu = 0.09$ mm^{-1}
$c = 25.474$ (2) Å	$T = 173$ K
$V = 913.25$ (14) Å^3	Prism, colourless
$Z = 2$	$0.30 \times 0.22 \times 0.08$ mm
$F(000) = 400$	

Data collection

Bruker APEXII CCD diffractometer	493 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.062$
φ and ω scans	$\theta_{max} = 26.4°$, $\theta_{min} = 1.6°$
3187 measured reflections	$h = -8{\rightarrow}5$
629 independent reflections	$k = -2{\rightarrow}8$
	$l = -31{\rightarrow}31$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.042$	
$wR(F^2) = 0.107$	
$S = 1.08$	Hydrogen site location: inferred from neighbouring sites
629 reflections	
45 parameters	H atoms treated by a mixture of independent and constrained refinement
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.010P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	0.6667	0.3333	0.16486 (9)	0.0236 (6)
C2	0.9213 (2)	0.5034 (2)	0.14518 (6)	0.0278 (4)
H2A	1.032	0.4505	0.1584	0.033*
H2B	0.977	0.6678	0.1583	0.033*
C3	0.9215 (2)	0.5033 (3)	0.08498 (6)	0.0309 (4)
H3	1.0877	0.614	0.0719	0.037*
C4	0.8365 (3)	0.2482 (3)	0.06502 (6)	0.0346 (4)
H4A	0.838	0.2474	0.0262	0.042*
H4B	0.9464	0.1932	0.0777	0.042*
C5	0	0	0.25	0.0219 (7)
N1	0.6667	0.3333	0.22372 (8)	0.0278 (5)
O1	0	0.1993 (2)	0.25	0.0343 (4)
H1	0.732 (4)	0.502 (3)	0.2358 (7)	0.060 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0198 (8)	0.0198 (8)	0.0312 (12)	0.0099 (4)	0	0
C2	0.0195 (8)	0.0205 (7)	0.0415 (9)	0.0087 (6)	−0.0018 (6)	−0.0014 (6)
C3	0.0217 (8)	0.0262 (8)	0.0404 (9)	0.0085 (6)	0.0061 (6)	0.0039 (6)
C4	0.0317 (9)	0.0350 (9)	0.0397 (8)	0.0185 (8)	0.0055 (6)	−0.0016 (7)
C5	0.0214 (10)	0.0214 (10)	0.0228 (15)	0.0107 (5)	0	0
N1	0.0253 (7)	0.0253 (7)	0.0328 (11)	0.0127 (3)	0	0
O1	0.0299 (8)	0.0221 (6)	0.0536 (10)	0.0149 (4)	−0.0091 (7)	−0.0045 (3)

Geometric parameters (Å, º)

C1—N1	1.500 (3)	C3—C4	1.534 (2)
C1—C2	1.5295 (14)	C3—H3	1
C2—C3	1.5335 (19)	C4—H4A	0.99
C2—H2A	0.99	C4—H4B	0.99
C2—H2B	0.99	C5—O1	1.2820 (13)
C3—C4^i	1.532 (2)	N1—H1	0.999 (16)

N1—C1—C2	109.13 (9)	C2—C3—C4	109.40 (12)
C2^{ii}—C1—C2	109.81 (9)	C2—C3—H3	109.5
C1—C2—C3	109.18 (12)	C4—C3—H3	109.5
C1—C2—H2A	109.8	C3^{ii}—C4—C3	109.57 (13)
C3—C2—H2A	109.8	C3—C4—H4A	109.8
C1—C2—H2B	109.8	C3—C4—H4B	109.8
C3—C2—H2B	109.8	H4A—C4—H4B	108.2
H2A—C2—H2B	108.3	O1^{iii}—C5—O1	120
C4^{i}—C3—C2	109.29 (11)	C1—N1—H1	107.9 (11)
C4^{i}—C3—C4	109.58 (14)		
N1—C1—C2—C3	179.92 (8)	C1—C2—C3—C4	−59.84 (12)
C2^{ii}—C1—C2—C3	60.34 (13)	C4^{i}—C3—C4—C3^{ii}	−59.76 (18)
C2^{i}—C1—C2—C3	−60.50 (13)	C2—C3—C4—C3^{ii}	60.04 (15)
C1—C2—C3—C4^{i}	60.13 (13)		

Symmetry codes: (i) −*y*+1, *x*−*y*, *z*; (ii) −*x*+*y*+1, −*x*+1, *z*; (iii) −*y*, *x*−*y*, *z*.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{iv}	0.999 (16)	1.778 (15)	2.7644 (11)	168.7 (18)

Symmetry code: (iv) −*y*+1, *x*−*y*+1, *z*.