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## Structure Reports

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## Bis(adamantan-1-aminium) carbonate

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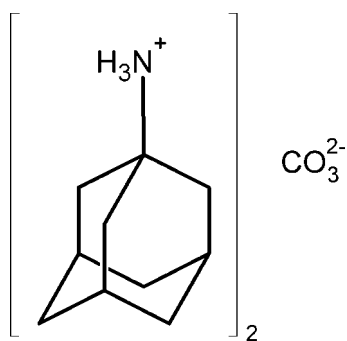
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 Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.042;  $wR$  factor = 0.107; data-to-parameter ratio = 14.0.

In the title compound,  $2\text{C}_{10}\text{H}_{18}\text{N}^+\cdot\text{CO}_3^{2-}$ , the adamantan-1-aminium cation forms three  $\text{N}-\text{H}\cdots\text{O}$  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  $\text{C}-\text{H}\cdots\text{H}-\text{C}$  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  $\text{CO}_2$  from the atmosphere, see: Yang *et al.* (2008).



## Experimental

## Crystal data

$2\text{C}_{10}\text{H}_{18}\text{N}^+\cdot\text{CO}_3^{2-}$   
 $M_r = 364.52$   
 Trigonal,  $P\bar{3}c1$   
 $a = 6.4340$  (6) Å  
 $c = 25.474$  (2) Å  
 $V = 913.25$  (14) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 173$  K  
 $0.30 \times 0.22 \times 0.08$  mm

## Data collection

Bruker APEXII CCD  
 diffractometer  
 3187 measured reflections

629 independent reflections  
 493 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.062$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.107$   
 $S = 1.08$   
 629 reflections  
 45 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.18$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}^{\text{i}}$	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.

The University of the Witwatersrand and the Molecular Sciences Institute are acknowledged for providing the infra-structure required for this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2467).

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## supporting information

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**Bis(adamantan-1-aminium) carbonate**

**Monika Nowakowska, Caryn Gamble and Demetrius C. Levendis**

**S1. 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<sub>2</sub>. We report the structure here. It is known that organic amines can trap CO<sub>2</sub> 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).

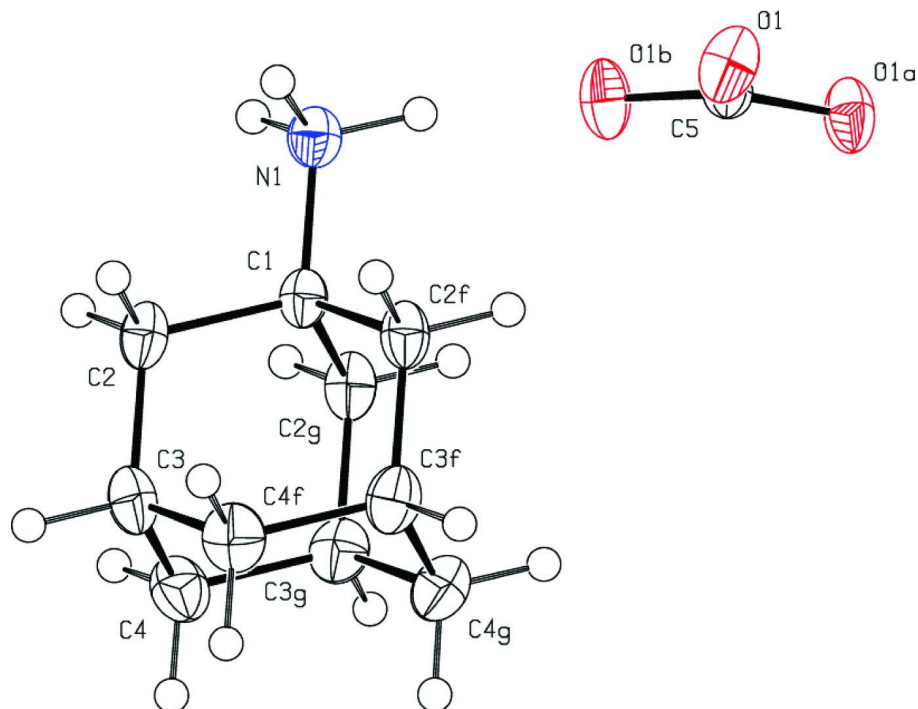
It is noted here that the structure of adamantan-1-aminium bicarbonate (Liu *et al.*, 2009) reported in the literature is isomorphous to adamantan-1-aminium nitrate (Zhao *et al.*, 2003). The former structure has unusually short H···H intermolecular contacts between NH<sub>3</sub><sup>+</sup> group H 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.

**S2. 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<sub>2</sub>), at 423–428 K.

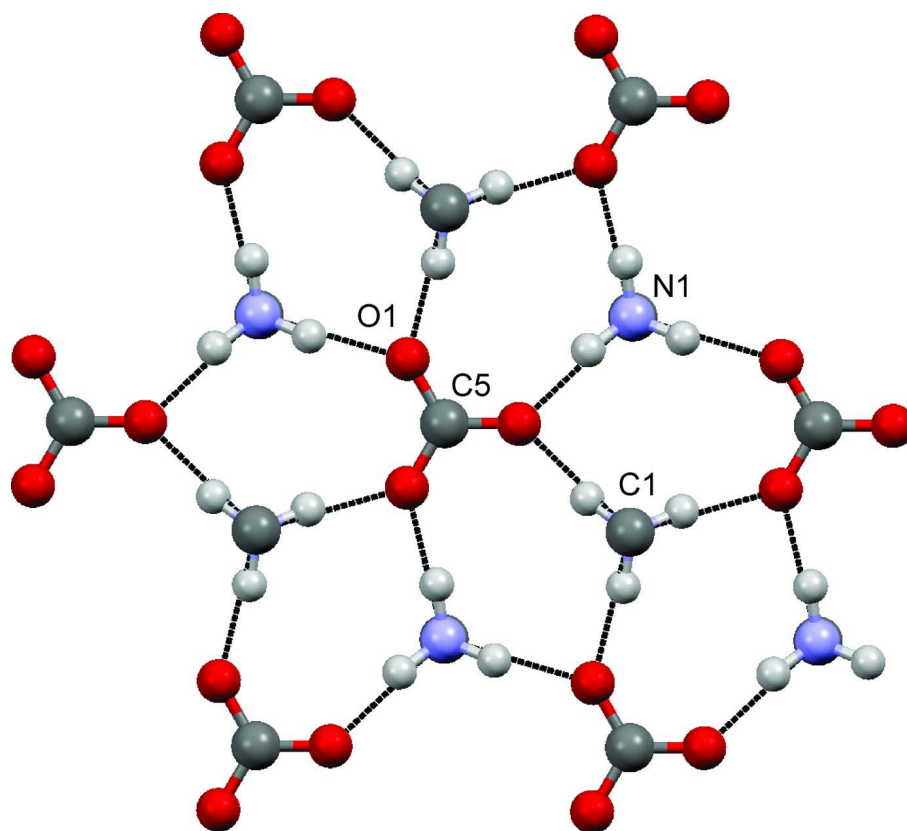
**S3. Refinement**

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<sub>2</sub>) and with  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}(\text{C})$ .



**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<sub>3</sub> and CO<sub>3</sub> groups for clarity.

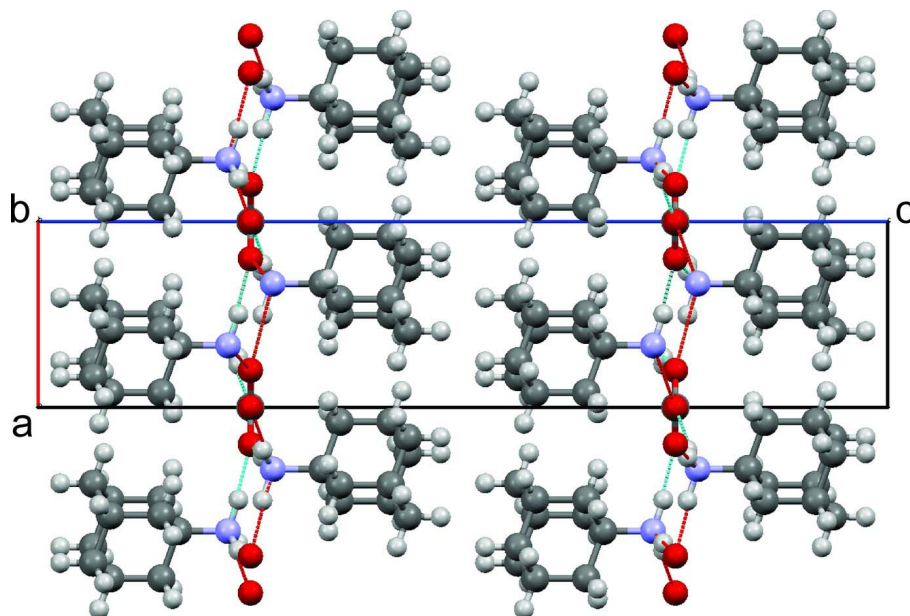


Figure 3

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

$2C_{10}H_{18}N^+ \cdot CO_3^{2-}$

$M_r = 364.52$

Trigonal,  $P\bar{3}c1$

Hall symbol:  $-P\ 3\ 2''c$

$a = 6.4340\ (6)\ \text{\AA}$

$c = 25.474\ (2)\ \text{\AA}$

$V = 913.25\ (14)\ \text{\AA}^3$

$Z = 2$

$F(000) = 400$

$D_x = 1.326\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 819 reflections

$\theta = 3.2\text{--}25.8^\circ$

$\mu = 0.09\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Prism, colourless

$0.30 \times 0.22 \times 0.08\ \text{mm}$

#### Data collection

Bruker APEXII CCD  
diffractometer

Graphite monochromator

$\varphi$  and  $\omega$  scans

3187 measured reflections

629 independent reflections

493 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\text{max}} = 26.4^\circ$ ,  $\theta_{\text{min}} = 1.6^\circ$

$h = -8 \rightarrow 5$

$k = -2 \rightarrow 8$

$l = -31 \rightarrow 31$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.107$

$S = 1.08$

629 reflections

45 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.010P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 ( $\text{\AA}$ ,  $^\circ$ )*

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 <sup>i</sup>	1.532 (2)	N1—H1	0.999 (16)
N1—C1—C2	109.13 (9)	C2—C3—C4	109.40 (12)
C2 <sup>ii</sup> —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 <sup>ii</sup> —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 <sup>iii</sup> —C5—O1	120
C4 <sup>i</sup> —C3—C2	109.29 (11)	C1—N1—H1	107.9 (11)
C4 <sup>i</sup> —C3—C4	109.58 (14)		
N1—C1—C2—C3	179.92 (8)	C1—C2—C3—C4	-59.84 (12)
C2 <sup>ii</sup> —C1—C2—C3	60.34 (13)	C4 <sup>i</sup> —C3—C4—C3 <sup>ii</sup>	-59.76 (18)
C2 <sup>i</sup> —C1—C2—C3	-60.50 (13)	C2—C3—C4—C3 <sup>ii</sup>	60.04 (15)
C1—C2—C3—C4 <sup>i</sup>	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, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 <sup>iv</sup>	0.999 (16)	1.778 (15)	2.7644 (11)	168.7 (18)

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