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Structure of Bis(acetamidinium) Carbonate Monohydrate, $2(C_2H_7N_2^+).CO_3^{2-}.H_2O$, at 108 K

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Abstract. $M_r = 196{\cdot}21$, orthorhombic, $Pn2_1a$, $a = 10{\cdot}482(5)$, $b = 8{\cdot}546\ (5)$, $c = 11{\cdot}123\ (5)$, $V = 996{\cdot}4\ (9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}308\ (1)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}0$ cm^{-1}, $F(000) = 424$, $T = 108$ K, final $R = 0{\cdot}051$ for 1127 reflections. The title compound is shown to be the reaction product when acetamidine is exposed to air. The orientations of the methyl groups in the two symmetry-independent acetamidinium ions differ, most probably due to different intermolecular interactions. The different molecules in the structure are connected by hydrogen bonds, with the amino groups and the water molecule as hydrogen donors and the carbonate oxygens as acceptors.

Introduction. Pure crystalline acetamidine, which smells unpleasantly of mouse, can be prepared by a procedure recently described by Crossland & Grevil (1980). One of the problems with the pure compound is that it is not stable in air. When a crystalline specimen is exposed to air it reacts rapidly and gives a clear liquid. It was observed that this liquid gradually evaporates to give a colourless crystalline solid of yet unknown composition and without any obvious smell. In order to analyse the composition of this reaction product and to yield some information on the chemistry of acetamidine, a single-crystal structure determination has been carried out on the reaction product.

Experimental. Highly hygroscopic crystalline acetamidine exposed to air, liquid obtained evaporated after about 1 d at 293 K (40% relative humidity) to give colourless prisms of title compound; $0{\cdot}2 \times 0{\cdot}1 \times 0{\cdot}05$ mm, CAD-4 diffractometer with a cryogenic device (*cf.* van Bolhuis, 1971) operated at 108 K, graphite-monochromatized Mo $K\alpha$, lattice parameters from settings of 12 reflections with $7{\cdot}6 \geq \theta \geq 11{\cdot}2°$; absorption correction, transmission factors 0·93–0·97; 1665 reflections $(0,0,0 \leq h,k,l \leq 13,15,16)$, $\theta < 30°$, 1524 unique, 1127 with $\sigma(I)/I < 0{\cdot}33$ used for refinements; symmetry-equivalent reflections gave $R_{\rm int} = 0{\cdot}035$; two standard reflections (140 and 311), no significant intensity decrease during data collection; direct methods and subsequent $\rho_{\rm diff}$ to locate all atoms, least-squares minimization of $\sum w(\Delta F)^2$, anisotropic nonhydrogens, isotropic hydrogens, nitrogen–hydrogen and carbon–hydrogen bond distances constrained (Sheldrick, 1976) to be equal within each molecule, $R = 0{\cdot}051$, $wR = 0{\cdot}067$, w proportional to $[\sigma^2(F_o) + 0{\cdot}001|F_o|^2]^{-1}$, $\Delta_{\max}/\sigma = 0{\cdot}2$ (nonhydrogen parameters), 170 parameters refined, max. and min. $\Delta\rho$ excursions 0·25 and $-0{\cdot}52$ e Å^{-3}, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), programs *SHELX*76 (Sheldrick, 1976) and *XTAPL* (Norrestam, 1982).*

Discussion. An examination of the bond distances and angles for two of the symmetry-independent molecular entities found in the present structure at the stage when the nonhydrogens were located showed closer resemblances to the geometry observed for the protonated acetamidine ion (Cannon, White & Willis, 1976) rather than to that of acetamidine (Norrestam, Mertz & Crossland, 1983) itself. Furthermore, difference electron density maps gave probable hydrogen

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38942 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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positions in agreement with two acetamidinium ions. Another molecular entity with almost perfect threefold rotation symmetry had distances in agreement with a carbonate ion. In order to obtain electroneutrality, the only remaining nonhydrogen position indicated in an electron density map can thus be assumed to be a water molecule, although its hydrogen positions could not be located owing to large thermal vibrations. As is described below, the observed intermolecular hydrogen-bond scheme is also in agreement with the molecular composition diacetamidinium carbonate monohydrate. Furthermore, this composition is in agreement with the assumption of pure acetamidine as a very strong hygroscopic base, which would absorb carbon dioxide as well as water from the surrounding atmosphere to give the present hydrated carbonate.

The atomic labels finally used and the intramolecular bond distances and angles obtained are shown in Fig. 1; the final atomic coordinates are given in Table 1. These bond distances and angles do not deviate by more than two e.s.d.'s between the two symmetry-independent acetamidinium ions. As mentioned above, the geometries agree with that found in an earlier study of the acetamidinium ion. The bond angles at the central carbon atom C(1) are closer to 120° than the corresponding angles in the neutral acetamidine molecule (Norrestam *et al.*, 1983), and the two C(1)—N bond distances are almost identical [average 1·311 (2) Å]. Thus, the π electrons are delocalized over the region N(1)—C(1)—N(2) with an estimated π-bond order of about 0·8 (*cf.* Norrestam *et al.*, 1983). The C(2)—C(1) distance and the N(1)—C(1)—N(2) bond angle found in acetamidinium chloride (Cannon *et al.*, 1976) were 1·477 (3) Å and 120·5° (2), respectively. The average values 1·498 (5) Å and 121·6 (3)° found in the present study indicate that the π-electron contribution is larger in the chloride; estimated C(1)—C(2) π-bond order of 0·2 in the chloride compared to 0·1 in the present study. This is possibly related to the strong interaction between the acetamidinium and the chloride ions in the crystal structure of acetamidinium chloride (*cf.* Cannon *et al.*, 1976).

The bond angles found in the present study for the carbonate ion are not significantly different from the ideal value 120°. However, the C—O bond lengths are slightly unequal, ranging from 1·269 (5) to 1·296 (5) Å.

The nonhydrogen atoms of the two symmetry-independent acetamidinium ions and of the carbonate ion deviate by less than two e.s.d.'s from the best planes through each of the ions. All three ions can thus be considered as planar. In view of the limited accuracy of the hydrogen positions obtainable from X-ray diffraction data, the possibly slightly pyramidal and twisted amino groups indicated in the present study cannot be considered as significant.

The methyl groups of the two symmetry-independent acetamidinium ions adopt different orientations. Thus,

Table 1. *Fractional atomic coordinates for the nonhydrogen atoms* (×10⁴) *and equivalent isotropic temperature parameters* (Å² ×10⁴), *estimated as one third of the trace of the orthogonalized U_{ij} tensor.*

The *y* coordinate of C(1*a*) was kept fixed at 0 to define the origin along the polar *b* axis.

	x	*y*	*z*	U_{eq}
C(1*a*)	−635 (4)	0	3166 (4)	155 (9)
C(2*a*)	37 (5)	−1417 (7)	2697 (4)	249 (11)
N(1*a*)	−1609 (3)	576 (7)	2578 (3)	165 (8)
N(2*a*)	−222 (4)	636 (6)	4170 (3)	190 (9)
C(1*b*)	3979 (4)	5056 (7)	3656 (4)	154 (9)
C(2*b*)	2700 (4)	5674 (7)	3281 (4)	212 (10)
N(1*b*)	4611 (3)	4136 (6)	2930 (3)	175 (8)
N(2*b*)	4429 (3)	5429 (6)	4721 (3)	195 (10)
C	2480 (4)	3648 (7)	498 (3)	122 (8)
O(1)	1900 (3)	4543 (6)	−230 (3)	223 (8)
O(2)	1841 (3)	2705 (6)	1183 (3)	159 (7)
O(3)	3706 (3)	3678 (6)	565 (3)	157 (7)
O(*w*)	2737 (7)	7587 (9)	388 (7)	903 (25)

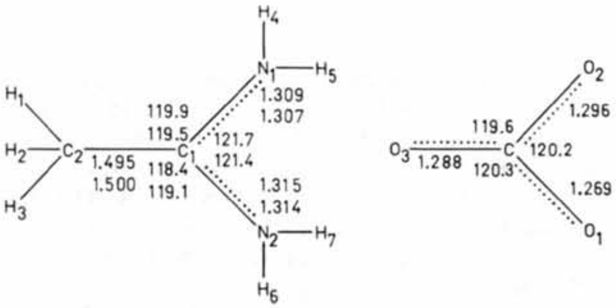

Fig. 1. Intramolecular bond distances (e.s.d.'s 0·005 Å) and angles (e.s.d.'s 0·3°) for the nonhydrogen atoms. The upper and lower numbers given for the acetamidinium ions refer to the two independent molecules designated *a* and *b* in Table 1. The C—H distances range from 0·97 to 1·10 Å and the N—H distances from 0·81 to 0·99 Å with e.s.d.'s of 0·05 Å.

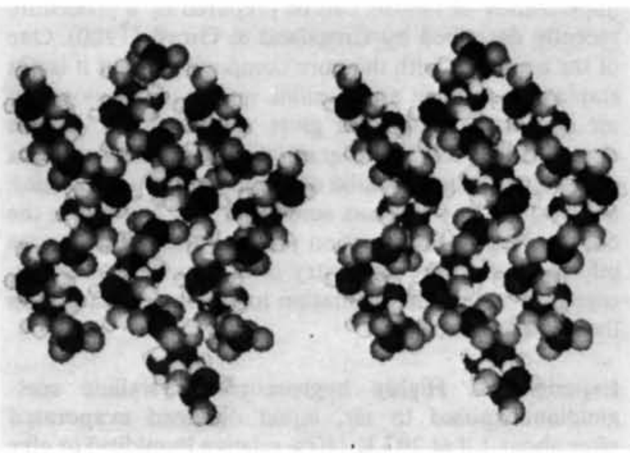

Fig. 2. Raster plot representation (Norrestam, 1981) of the molecular packing along the *b* direction. The molecules can be considered as forming a pleated-sheet arrangement perpendicular to the *a* axis. The oxygen and nitrogen atoms are grey, the carbon atoms black and the hydrogen atoms white.

in the molecules labelled *a* in Table 1 a methyl hydrogen is almost coplanar with the nonhydrogen atoms, but perpendicular to them in the molecules labelled *b*. The average torsion angles (modulo 60°) over the C(1)—C(2) bond and relative to any of the nitrogen atoms are 6 (9) and 28 (9)°, respectively. The methyl rotational barrier for this type of compounds is very low. Different types of calculations indicate a magnitude of a few kJ mol^{-1} and the methyl-group orientation is most probably determined by intermolecular interactions. For further discussions on this subject on similar molecules, see *e.g.* Hagler, Leiserowitz & Tuval (1976); Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople (1980); Norrestam *et al.* (1983).

The molecular packing in the crystal structure is shown in Fig. 2. The structure is held together by *inter alia* an extensive net of intermolecular hydrogen bonds. The four symmetry-independent amino groups are hydrogen donors to two hydrogen bonds each, while the oxygen atoms of the carbonate ions are acceptors of three hydrogen bonds each. The N···O distances range from 2·757 (5) to 2·864 (5) Å. The water molecule at O(*w*) participates (as hydrogen donor) in only one hydrogen bond, 2·830 (4) Å, to one of the carbonate oxygen atoms, O (1). Thus, the water molecule is rather loosely bonded in the structure. This is also reflected by the significantly higher thermal vibration parameter of O(*w*), $U_{\text{eq}} = 0{\cdot}090$ (2) Å^2, compared with the average value 0·018 (1) Å^2 of the other atoms.

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Thujaplicatin Methyl Ether, $C_{21}H_{24}O_7$

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Abstract. $M_r = 388{\cdot}4$, monoclinic, $P2_1$, $a = 11{\cdot}715$ (2), $b = 10{\cdot}815$ (1), $c = 7{\cdot}411$ (1) Å, $\beta = 92{\cdot}66$ (1)°, $V = 983{\cdot}0$ (2) Å^3, $Z = 2$, $D_m = 1{\cdot}365$ (5), $D_x = 1{\cdot}375$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}87$ mm^{-1}, $F(000) = 412{\cdot}0$, $T = 298$ K, $R = 0{\cdot}033$ for 1314 unique reflections. The lactone ring has a twist conformation [torsion angle C—C—C—O 27·6 (3)°] and the substituent carbon atoms at the 2- and 3-positions are *trans* to one another. Intermolecular O—H···O hydrogen bonding involving both the carbonyl and phenolic groups stabilizes the crystal structure. The absolute configuration assigned previously by circular dichroism studies has been confirmed.

Introduction. *Podocarpus saligna* D. Don is one of three species of *Podocarpus* native to Chile. The constituents daucosterin, fern-9(11)-ene, isofernene, β-sitosterol and *n*-nonacosane (Bhakuni, Bittner, Sammes & Silva, 1974) as well as more than ten nor- and bisnorditerpene dilactones (Zabel, Watson, Silva,

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