C(12)—C(13) bond distance of 1·533 (4) Å is significantly longer than the C(12)—C(14) bond distance of 1·513 (4) Å, and the bond angles 110·5 (2)° for N(2)—C(12)—C(14) and 110·1 (3)° for C(15)—C(12)—C(14) are larger than 107·3 (2)° for N(2)—C(12)—C(13) and 106·8 (2)° for C(15)—C(12)—C(13). Such asymmetry around the C^α atom of the Aib residue has been observed in other Aib-containing peptides. According to Paterson, Rumsey, Benedetti, Némethy & Scheraga (1981), the asymmetric geometries are sensitive to the backbone torsion angles of the Aib residue, and have a correlation with the helical conformation type. The present Aib residue has the torsion angles $\varphi_2 = -57·2\,(2)$, $\psi_2 = -31·4\,(3)$ and $\omega_2 = 178·5\,(2)°$, which are close to $\varphi = -60$, $\psi = -30$ and $\omega = 180°$ for an ideal right-handed 3_{10}-helix. The asymmetric covalent-bond geometry for the torsion angles corresponding to the right-handed helix is consistent with other data (Benedetti, Bavoso, Blasio, Pavone, Pedone, Crisma, Bonora & Toniolo, 1982). The Ala residue has the torsion angles $\varphi_1 = -125·5\,(2)$, $\psi_1 = 163·1\,(2)$ and $\omega_1 = 185·8\,(2)°$. The values are close to $\varphi = -113$ and $\psi = 165°$ in L-alanyl-L-alanine (Fletterick, Tsai & Hughes, 1971). The torsion angles for the N-terminal protected group are $-178·0\,(3)°$ for N(1)—C(8)—O(1)—C(7), $-138·3\,(3)°$ for C(8)—O(1)—C(7)—C(6) and $-80·0\,(3)°$ for O(1)—C(7)—C(6)—C(5). The molecular conformation differs from that of Boc-L-Ala-Aib-OH ($\varphi_1 = -66$, $\psi_1 = -24$, $\varphi_2 = -175$ and $\psi_2 = -170°$), and also differs from that of a similar C-terminal unprotected dipeptide Z-Aib-Aib-OH ($\varphi_1 = -65$, $\psi_1 = -26$, $\varphi_2 = 50$ and $\psi_2 = 45°$) (Benedetti, Pedone & Toniolo, 1980). Since the molecule has no intramolecular hydrogen bonds, the molecular conformation largely depends on intermolecular packing forces.

The crystal structure is shown in Fig. 2. The molecules are packed by three kinds of intermolecular hydrogen bonds, N(1)—H···O(4)($-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-z$) 2·859 (3), N(2)—H···O(2)($\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$) 2·912 (3), and O(5)—H···O(3)($-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-z$) 2·699 (3) Å. The hydrogen-bonded molecules form a layer perpendicular to the *c* axis. The molecules of the adjacent layers are close to each other with the usual van der Waals distances, the short intermolecular distances being 3·554 (5) Å between C(10) and C(14)($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$) and 3·368 (6) Å between C(2) and O(4)($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$).

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Structure of 8-Ethyl-9-methyladenine Dihydrate

By S. M. Tretyak, V. V. Mitkevich and L. F. Sukhodub

Physico-Technical Institute of Low Temperatures, Ukr. Academy of Sciences, 310164 *Kharkov, USSR*

and K. L. Wierzchowski

Institute of Biochemistry and Biophysics, Polish Academy of Sciences, 02-532 *Warszawa, Poland*

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Abstract. $C_8H_{11}N_5.2H_2O$, $M_r = 213·2$, triclinic, $P\bar{1}$, $a = 7·460\,(3)$, $b = 7·824\,(2)$, $c = 9·929\,(3)$ Å, $\alpha = 112·28\,(2)$, $\beta = 102·48\,(3)$, $\gamma = 89·06\,(3)°$, $V = 522·3\,(3)$ Å^3, $Z = 2$, $D_x = 1·36$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·12 mm^{-1}, $F(000) = 228$, $T = 105$ K, final $R = 0·083$, $wR = 0·067$ for 1337

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independent reflections with $I \geq 1{\cdot}96\sigma(I)$. The molecular structure is similar to that observed in anhydrous crystals [Tretyak & Sukhodub (1988). *Kristallografiya*, **33**, 772–774]: the purine ring is essentially planar, with the ethyl group 2·8° out of this plane. Crystal packing in the dihydrate is characterized by stacking of centrosymmetrically related molecules along **a**. Within each layer the molecules form N(10)—H···N(1) hydrogen-bonded dimers. Water molecules occupy sites located in the *ab* plane between neighbouring dimers: one molecule bridges the base *via* N(10)—H···O(1) and O(1)—H···N(7) interactions, while the other forms O(2)—H···H(3) hydrogen bonds. Successive water layers are also hydrogen bonded to form cyclic water dimers. In air at room temperature the hydrated crystals are unstable.

Introduction. Structural studies of hydrated crystals of nucleic acid bases provide valuable information about the interaction of water molecules with the bases through hydrogen bonding and packing arrangements (Voet & Rich, 1970; Thewalt, Bugg & Marsh, 1971; Weber, Craven & McMullan, 1980; Tretyak, Mitkevich & Sukhodub, 1987). The results of these studies complement those on hydration of the bases under vacuum by field-ionization mass spectrometry (Sukhodub, Yanson, Shelkovski & Wierzchowski, 1982; Sukhodub, Shelkovski & Wierzchowski, 1984), and can be used to verify and parametrize empirical and semi-empirical atom–atom potentials for modelling intermolecular interactions in similar systems. We are particularly interested in the hydration of alkylated bases [*cf.* Sukhodub (1987) for a review], but no systematic data of this kind are available from structural X-ray diffraction studies of crystalline hydrates. We have therefore investigated the crystal structure of 8-ethyl-9-methyladenine dihydrate. A study of anhydrous crystals of this compound was recently reported (Tretyak & Sukhodub, 1988).

Experimental. The title compound was synthesized and purified (Dramański & Frass, 1987) and flat transparent needles suitable for X-ray measurements were grown by slow evaporation from aqueous solutions. They proved unstable in air at room temperature and decomposed slowly by loss of water of crystallization. At 298 K only the space group and unit-cell parameters could be determined as: triclinic, $P\overline{1}$, $a = 7{\cdot}521\ (4)$, $b = 7{\cdot}919\ (4)$, $c = 10{\cdot}049\ (4)$, Å, $\alpha = 111{\cdot}39\ (4)$, $\beta = 102{\cdot}80\ (4)$, $\gamma = 90{\cdot}14\ (4)$°, $V = 541{\cdot}2\ (5)$ Å^3, $D_x = 1{\cdot}31$ Mg m^{-3}. The structure determination was therefore performed at 105 K, a temperature at which the crystals were fully stable. Intensity measurements were carried out on a Syntex $P2_1$ automatic diffractometer, equipped with an LT-1 regulated temperature attachment, from a specimen $0{\cdot}05 \times 0{\cdot}2 \times 0{\cdot}3$ mm, using graphite-monochromated Mo $K\alpha$ radiation in θ–2θ scan mode for $\sin\theta/\lambda \leq 0{\cdot}6$ Å^{-1} ($2\theta \leq 50$°) with a scan rate of 3–29° min^{-1}. Intensities of two check reflections ($2\overline{1}1$ and 102) proved stable within 4% during the experiment.

Table 1. *Postional parameters of non*-H *atoms* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10$)

The e.s.d.'s are given in parentheses. $B_{eq} = (1/24\pi^2)\sum_i\sum_j B_{ij}\overset{*}{a}_i\overset{*}{a}_j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
N(1)	4299 (5)	8791 (5)	6034 (4)	12 (2)
C(2)	4198 (7)	8566 (7)	7299 (5)	13 (2)
N(3)	3494 (5)	7098 (6)	7446 (4)	13 (2)
C(4)	2846 (6)	5739 (6)	6089 (5)	9 (2)
C(5)	2829 (6)	5763 (6)	4712 (5)	10 (2)
C(6)	3637 (6)	7392 (6)	4701 (5)	10 (2)
N(7)	2039 (5)	4109 (5)	3574 (4)	10 (2)
C(8)	1594 (6)	3119 (6)	4277 (5)	9 (2)
N(9)	2028 (5)	4049 (5)	5810 (4)	9 (2)
N(10)	3774 (6)	7617 (5)	3462 (4)	13 (2)
C(11)	733 (7)	1181 (6)	3582 (6)	13 (2)
C(12)	450 (8)	373 (7)	1886 (6)	19 (3)
C(13)	1707 (7)	3368 (7)	6935 (5)	13 (2)
O(1)	1557 (5)	4413 (5)	744 (4)	20 (2)
O(2)	5236 (5)	6887 (5)	10223 (4)	22 (2)

The unit-cell parameters were determined by the least-squares method using 15 reflections with $13 \leq 2\theta \leq 20$°. Out of 1887 ($0 \leq h \leq 8$, $-9 \leq k \leq 9$, $-11 \leq l \leq 11$) independent reflections measured, 1337 with $I \geq 1{\cdot}96\sigma(I)$ were used in structure solution and refinement. The structure was solved by direct methods (Germain, Main & Woolfson, 1971). Positions of H atoms were located from a difference Fourier map. Refinement was carried out by block-diagonal least-squares techniques using anisotropic thermal factors for non-H atoms and isotropic factors for H atoms. The final $R = 0{\cdot}082$, $wR = 0{\cdot}067$ and $w = \sigma_F^{-2}$. S {defined as $[\sum_w(F_o - F_c)^2/(m-n)]^{1/2}$} $= 2{\cdot}7$; the ratio of maximum least-squares shift to e.s.d. in final refinement cycle = 0·7. Maximum and minimum heights in the final difference Fourier synthesis are 0·36 and $-0{\cdot}42$ e Å^{-3}. The positional and equivalent isotropic thermal parameters are collected in Table 1.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The *XTL* system of programs (Syntex, 1976) was used for calculations.

Discussion. Bond distances and bond angles are shown in Fig. 1 and are in good agreement with those previously determined for the anhydrous tri-

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* Lists of anisotropic thermal parameters, interatomic distances and angles, structure factors, and coordinates of H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52116 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

clinic crystal (Tretyak & Sukhodub, 1988); the maximum difference in the bond lengths does not exceed 2σ. The maximum deviation of the non-alkyl atoms from the least-squares plane through the purine ring [equation: $0{\cdot}9021x - 0{\cdot}4299y + 0{\cdot}0389z = 0{\cdot}0556$] is 0·016 (4) Å, so the base is essentially planar. The ethyl-group C atoms, C(11) and C(12), deviate significantly from this plane, by 0·060 (5) and 0·129 (6) Å. The ethyl group is inclined to the purine ring at an angle of 2·8° by rotation about C(8)—C(11).

In the crystals of the dihydrate the molecules are packed in stacks along the *a* axis at an angle of 64·4° and related one with another by a centre of inversion. They are thus stacked in an alternating fashion. Each molecule is hydrogen bonded to an adjacent one in the same layer along the *b* axis through a pair of N(10)—H···N(1) bonds, as shown in Fig. 2 and Table 2. Molecules in a stack therefore alternately assume two somewhat different overlap patterns characterized by: (i) a high degree of purine ring overlap at an interplanar distance of 3·34 Å, and projection of the ethyl group over the 'interior' of a hydrogen-bonded pair (Fig. 3*a*); and (ii) partial base–base overlap, limited to the imidazole part of the purine ring only, and involving an interaction between the ethyl group and the pyrimidine part of a neighbouring purine ring (Fig. 3*b*). As a result of the 2·8° deviation of the ethyl group from the molecular plane the interplanar distance in cases (ii) is only slightly larger at 3·39 Å. The small deviation of the ethyl group from coplanarity thus allows for molecular stacking with an almost regular interplanar distance.

Anhydrous and dihydrate crystals of 8-ethyl-9-methyladenine have generally similar structures. However, in the dihydrate the stacks of bases are separated by *ab* layers of water. Each hydrogen-bonded base pair is separated from its neighbours in the same layer along **c** by four water molecules (Fig. 2), hydrogen bonded to N(7) and N(10)—H simultaneously, and to N(3) by one bond only (see Table 2 for the hydrogen-bond parameters). There are also

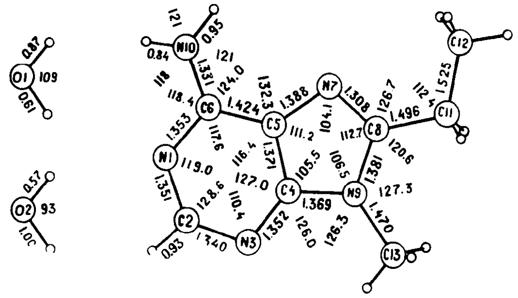

Fig. 1. Bond distances (Å) and bond angles (°) in 8-ethyl-9-methyladenine. The e.s.d.'s for distances and angles involving heavy atoms are about 0·007 Å and 0·4°, while those involving H atoms are about 0·07 Å and 5°, respectively.

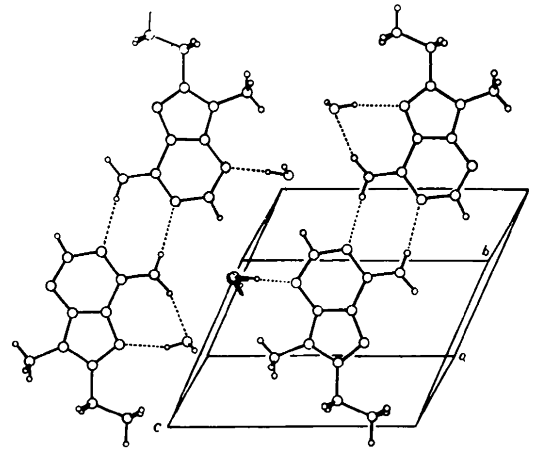

Fig. 2. A partial view of a layer formed by hydrogen-bonded base pairs and water molecules of hydration; the projection is on the mean molecular plane. Broken lines indicate hydrogen bonds.

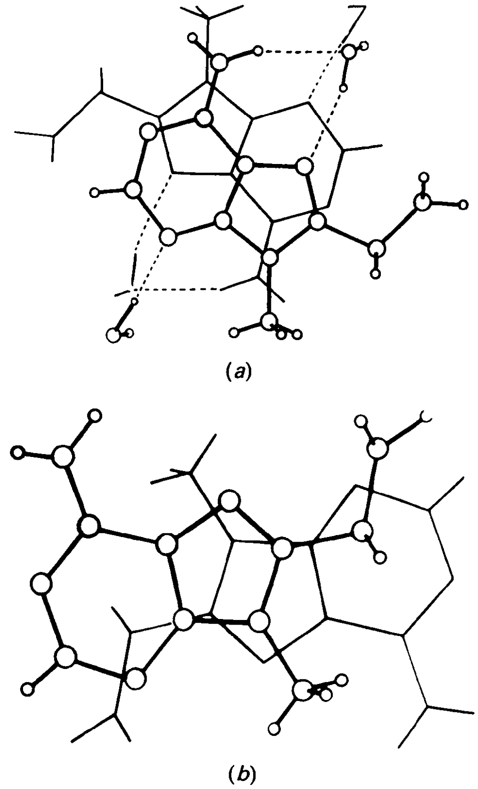

Fig. 3. (*a*) Stacking pattern of the molecules involving large overlap of their purine rings and projection of the C(8) ethyl group over a region forming an 'interior' of hydrogen-bonded base pairs. (*b*) Stacking pattern of the molecules characterized by limited overlap of their purine rings and large overlap of the pyrimidine parts of the latter with the ethyl group at C(8).

Table 2. *Hydrogen-bond parameters with e.s.d.'s in parentheses*

X—H···Y	d(H···Y) (Å)	d(X···Y) (Å)	∠(X—H···Y) (°)
N(10)—H(10*a*)···N(1^{i})	2·16 (5)	2·995 (6)	176 (4)
N(10)—H(10*b*)···O(1^{ii})	2·16 (5)	3·063 (6)	159 (4)
O(1)—H(11*w*)···N(7^{ii})	2·02 (7)	2·856 (5)	161 (7)
O(1)—H(12*w*)···O(2^{iii})	2·28 (7)	2·804 (5)	146 (8)
O(2)—H(21*w*)···O(1^{iii})	2·33 (7)	2·804 (5)	144 (9)
O(2)—H(22*w*)···N(3^{ii})	1·85 (7)	2·848 (5)	176 (6)

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

hydrogen bonds between water molecules in adjacent layers. The cyclic water dimer formed in this way (Table 2) exhibits a shortened transannular H···H van der Waals contact of 1·86 Å. Hydrogen bonding between water molecules is thus expected to be rather weak.

The crystal packing found in 8-ethyl-9-methyladenine dihydrate may explain the decomposition of the crystals in air at room temperature. The presence of holes along the *ab* planes filled by weakly bound water molecules facilitates diffusion of the latter to the crystal surface.

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Structure of the Zwitterionic 10-[2-(2-Dimethylsulfonioethoxy)ethoxy]undecahydro-7,8-dicarba-*nido*-undecaborate(1−)

BY V. ŠUBRTOVÁ, V. PETŘÍČEK AND L. HUMMEL

Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 *Praha* 8, *Czechoslovakia*

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Abstract. $C_8H_{25}B_9O_2S$, $M_r = 282·64$, orthorhombic, $P2_12_12_1$, $a = 8·799$ (3), $b = 11·268$ (3), $c = 16·012$ (4) Å, $V = 1587·5$ (2) Å^3, $Z = 4$, $D_m = 1·180$, $D_x = 1·183$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·184$ mm^{-1}, $F(000) = 600$, $T = 293$ K, $R = 0·037$ for 1910 observed independent reflections. The O—C—C—O—C—C (derived from opening of a dioxane ring) is bound to the *nido* eleven-vertex carbaborane cage which has negative charge [B—O = 1·420 (3) Å], and to the $S(CH_3)_2$ group (positive charge [C—S = 1·803 (2) Å]. In the carbaborane cage, mean B—B = 1·774 (3), mean C—B = 1·672 (3) Å and the C—C bond is 1·536 (4) Å.

Introduction. Crystals of the title zwitterionic compound were prepared in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences as part of a study of carbaborane derivatives which are being screened for chemotherapeutic activity. The compound represents a whole new class, generally accessible by opening of a dioxane ring bound to the skeletal B atom by a dative bond. The reaction of 7,8-$C_2B_9H_{13}$ in the dioxane solution (373 K, 20 hours) with Lewis base $(CH_3)_2S$ opens the dioxane ring producing $(CH_3)_2S$—$CH_2CH_2OCH_2CH_2O$—7,8-$C_2B_9H_{11}$ (Plešek, Štíbr & Heřmánek, 1989). Other β-dialkyl ether derivatives show the same behaviour.

Experimental. Transparent colourless crystal 0·3 × 0·3 × 0·5 mm; D_m by flotation; Hilger & Watts diffractometer; Mo $K\alpha$ radiation, Nb filter; cell parameters and standard deviations by least squares from 33 reflections ($6 < \theta < 19°$) (Shoemaker, 1970); 1997 unique independent reflections by learnt profile method (Clegg, 1981) measured by $\theta/2\theta$ scans to $\sin\theta/\lambda = 0·6387$ Å^{-1} for $h = 0$–10, $k = 0$–13, $l = 0$–20. 1910 reflections with $I > 1·96\sigma(I)$ regarded as observed. Intensities of three standards (400, 008, 051) measured every 30 reflections, no significant

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