Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

A *B* *C*	*AB*	*BC*	*AC*	$A\hat{B}C$
N(2*A*)–H(2*A*)···Br(1*A*)	1·08	2·24	3·251 (4)	154·6
O(2′*A*)–H(2′*A*)···Br(1A^{i})	0·98	2·47	3·277 (4)	139·5
N(2*B*)–H(2*B*)···Br(2*B*)	1·17	2·05	3·207 (5)	168·9
O(2′B^{ii})–H(2′*B*)···Br(2*B*)	1·06	2·18	3·241 (4)	178·4

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

The authors thank C. H. Boehringer Sohn, Federal Republic of Germany, for providing the title compound and the Laboratorium voor Kristallografie, Universiteit van Amsterdam, The Netherlands, for collecting the X-ray data.

References

GELDERS, Y. G., DE RANTER, C. J. & KOKKES, M. (1980). *Acta Cryst.* B**36**, 1141–1146, and references therein.

GIGLIO, E. (1969). *Nature* (*London*), **222**, 339–341.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KARLE, I. L., GILARDI, R. D., FRATINI, A. V. & KARLE, J. (1969). *Acta Cryst.* B**25**, 1469–1479.

MERZ, H. & STOCKHAUS, K. (1979). *J. Med. Chem.* **22**, 1475–1483.

MOTHERWELL, S. (1974). *EENY*. Potential-energy calculation program – version of June 1974. Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.

STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1982). B**38**, 3171–3174

1,N^6-Ethenoadenosine

BY MARIUSZ JASKÓLSKI

Department of Crystallography, Institute of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6,
60-780 *Poznań, Poland*

(*Received* 15 *April* 1982; *accepted* 8 *July* 1982)

Abstract. $C_{12}H_{13}N_5O_4$, $M_r = 291\cdot3$, orthorhombic, $P2_12_12_1$, $a = 6\cdot4679\,(5)$, $b = 10\cdot4029\,(7)$, $c = 18\cdot277\,(2)$ Å, $V = 1229\cdot8\,(2)$ Å^3, $Z = 4$, $D_c = 1\cdot57$ Mg m^{-3}, μ(Cu $K\alpha$) = 1·04 mm^{-1}. $R = 0\cdot037$ for 977 observed $[I \geq 1\cdot96\sigma(I)]$ reflexions. Etheno-bridging introduces significant changes in the dimensions of the adenine base. The εadenine moiety is not planar but has a 'U' shape. The ribose ring is 2′-*endo* puckered with a g^+ side chain. The glycosidic torsion angle has an unusual value of 26·2 (4)° (*anti*), which is very rare in purine β-ribofuranosides. There is almost no base overlap in the structure.

Introduction. This paper presents the crystal and molecular structure of 1,N^6-ethenoadenosine (εAdo) and is the latest contribution to the studies of the fluorescent ethenocytidine (εCyd) and ethenoadenosine (εAdo) systems. In the case of the ethenocytidine system the structure of εCyd reported by Jaskólski, Krzyżosiak, Sierzputowska-Gracz & Wiewiórowski (1981) completed the series: Cyd (Furberg, Petersen & Rømming, 1965) → Cyd.H$^+$ (Mosset, Bonnet & Galy, 1979) → εCyd.H$^+$ (Wang, Barrio & Paul, 1976) → εCyd, and permitted a detailed discussion of the structural changes introduced by etheno-bridging and by protonation of Cyd and εCyd (Jaskólski *et al.*, 1981; Krzyżosiak, Jaskólski, Sierzputowska-Gracz & Wiewiórowski, 1982). In the case of the ethenoadenosine system, however, only the structure of a derivative of the εAdo.H$^+$ cation has been known (11-ethylethenoadenosine hydrochloride monohydrate; Wang, Dammann, Barrio & Paul, 1974). There is thus a strong need for the structure determination of εAdo (and also unmodified εAdo.H$^+$) if one wants to carry out comparative structural studies of the series: Ado (Lai & Marsh, 1972) → Ado.H$^+$ (Shikata, Ueki & Mitsui, 1973) → εAdo.H$^+$ → εAdo, simlar to those presented for the εCyd system. The main purpose of this paper is to provide the lacking data on neutral εAdo.

Crystals suitable for X-ray analysis were obtained by precipitation (using ethanol) from aqueous solution. From symmetry and systematic absences on X-ray photographs the space group was established as $P2_12_12_1$. Unit-cell constants were determined by a least-squares fit of the setting angles of 15 counter reflexions. Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer using graphite-monochromated Cu $K\alpha$ radiation and a variable $\theta:2\theta$ scan for a crystal with dimensions 0·15 × 0·2 × 0·5 mm. 1075 independent reflexions were measured up to $\sin\theta/\lambda = 0\cdot562$ Å^{-1}; of these, 980 had $I \geq 1\cdot96\sigma(I)$ and were considered observed. For each reflexion the profile was measured and the background level as well as I and $\sigma(I)$ for each reflexion were calculated according to Lehmann & Larsen (1974) using the computer program *PRAN* (Jaskólski, 1979). The data were corrected for Lorentz and polarization effects but not for absorption and extinction.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971). All H atoms were located from a difference electron density (ΔF) map. They were allowed to contribute to F_c (with $B_{\rm iso}$ one unit greater than that of the carrier) but their parameters were kept fixed in the subsequent full-matrix least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weights were as follows: $w = (F_o/F_{\rm low})^2$ for $F_o < F_{\rm low}$, $w = 1$ for $F_{\rm low} \leq F_o \leq F_{\rm high}$, $w = (F_{\rm high}/F_o)^2$ for $F_o > F_{\rm high}$, with $F_{\rm low} = 6{\cdot}9$ and $F_{\rm high} = 16$. After the final refinement, which excluded the three most intense reflexions judged to suffer seriously from extinction, an additional ΔF map was calculated to redetermine the H-atom positions. The final agreement factors are $R = 0{\cdot}037$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0{\cdot}039$ for 977 reflexions.

All calculations were performed using original (*Syntex XTL Operation Manual*, 1973) or locally modified (Jaskólski, 1979) Syntex *XTL* programs on a Nova 1200 minicomputer.

Final positional parameters of non-H atoms are given in Table 1.*

Table 1. *Final fractional coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (*Willis & Pryor*, 1975) *for non*-H *atoms*

	x	y	z	$B_{\rm eq}$ (Å^2)
C(8)	6447 (6)	6431 (3)	449 (2)	2·6 (2)
N(7)	7961 (5)	6207 (3)	−23 (2)	2·7 (1)
C(5)	9113 (6)	5252 (3)	301 (2)	2·2 (1)
C(6)	10982 (6)	4642 (3)	99 (2)	2·3 (1)
N(6)	12253 (5)	4735 (3)	−464 (2)	3·1 (1)
C(10)	13860 (6)	3913 (4)	−304 (2)	3·6 (2)
C(11)	13586 (6)	3296 (4)	342 (2)	3·3 (2)
N(1)	11701 (5)	3751 (3)	611 (1)	2·5 (1)
C(2)	10714 (6)	3485 (3)	1260 (2)	2·7 (1)
N(3)	8987 (5)	4032 (3)	1454 (1)	2·4 (1)
C(4)	8290 (5)	4923 (3)	966 (2)	2·0 (1)
N(9)	6561 (5)	5686 (2)	1057 (1)	2·2 (1)
C(1′)	5105 (5)	5613 (3)	1663 (2)	2·3 (2)
C(2′)	5486 (5)	6505 (3)	2315 (2)	2·3 (1)
O(2′)	7131 (4)	6148 (2)	2777 (1)	2·9 (1)
C(3′)	3341 (6)	6471 (3)	2653 (2)	2·4 (1)
O(3′)	3011 (5)	5243 (3)	2979 (1)	3·5 (1)
C(4′)	1941 (6)	6545 (3)	1985 (2)	2·4 (1)
O(1′)	3149 (4)	5972 (2)	1392 (1)	2·7 (1)
C(5′)	1181 (6)	7852 (4)	1739 (2)	3·0 (2)
O(5′)	2819 (4)	8724 (2)	1594 (1)	3·5 (1)

Discussion. Bond distances and angles in the εAdo skeleton are given in Fig. 1. Etheno-bridging introduces significant changes in the molecular dimensions of the adenine moiety of the molecule. The following list summarizes the most significant differences in bond lengths of the base fragment between Ado and εAdo: N(1)—C(6) 0·046 (5) [increase on Ado → εAdo; *h*ighly *s*ignificant (*hs*) according to Cruickshank & Robertson (1953)], N(1)—C(2) 0·035 (5) (*hs*), C(2)—N(3) −0·028 (6) (*hs*), N(7)—C(8) 0·018 (6) (*s*), N(3)—C(4) 0·013 (5) (*s*), C(6)—N(6) −0·011 (5) Å (possibly significant). It can be thus concluded that introduction of the etheno bridge into the Ado molecule significantly changes the electronic structure of its base fragment and influences even such a distant part of the molecule as the N(7)—C(8) bond.

The atoms composing the ring system of the εadenine fragment are non-coplanar with a maximum deviation of 0·064 (4) Å (plane I, χ^2 = 1396). Although the individual rings (II,III,IV) of the εadenine group (Fig. 1) show much smaller deviations from planarity, the pyrimidine ring (III) is slightly but significantly non-planar (χ^2 = 54·9) and only the other purine-system ring (IV) can be termed exactly planar (χ^2 = 3·57). Planes (II) and (IV) make angles of 2·8 (7) and 2·6 (6)° respectively with plane (III) and form a ‘U’ shape when looking from the edge side. The atoms of the two five-membered rings all lie on the same side of the best plane through the six-membered ring and the mode of deviation is exactly the same on both sides, the maximum deviations being as great as 0·097 (4) [C(10)] and 0·091 (3) Å [C(8)]. The shape of the εadenine moiety is similar to that observed in EtεAdo.H⁺ but the ‘U’ shape of the system was much less pronounced in the latter case. The C(1′) substituent deviates by as much as 0·087 (3) Å from plane (IV).

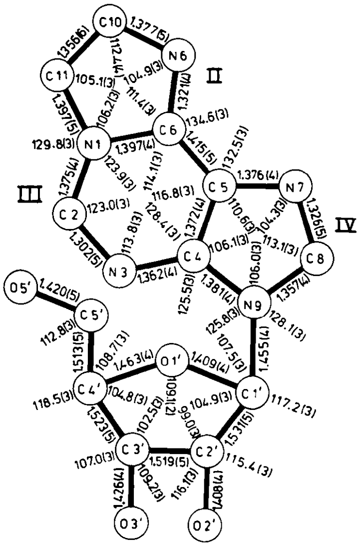

Fig. 1. Bond distances (Å) and angles (°) in the skeleton of εAdo. (II), (III) and (IV) label the rings of the εadenine system.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes, and Fig. 4 (projection of the structure down **b**) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38056 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The ribose ring is 2′-*endo* (^2E) slightly deformed towards 2′-*endo*-3′-*exo* ($^2T_3$). In terms of pseudorotation (Altona & Sundaralingam, 1972), the ribose conformation is characterized by $\nu_m = 44{\cdot}3$ and $P = 163{\cdot}5°$. A stereodrawing (Johnson, 1965) of the εAdo molecule is shown in Fig. 2, and the ribose torsion angles are given in Table 2. The torsion angles O(5′)—C(5′)—C(4′)—C(3′) (γ) and O(5′)—C(5′)—C(4′)—O(1′) indicate that the side chain assumes the preferred *gauche–gauche* conformation with the C(5′)—O(5′) bond rotated *ca* 3° out from the ideal staggered orientation towards C(4′)—C(3′). The glycosidic torsion angle [χ, O(1′)—C(1′)—N(9)—C(8)] which describes the relative orientation of the base with respect to the sugar is in the *anti* region and amounts to 26·2 (4)°. This value is quite unexpected since it falls outside the ranges characteristic of type S β-purines (Altona & Sundaralingam, 1972). According to a survey of nucleoside conformations by de Leeuw, Haasnoot & Altona (1980), only one purine with type S β-ribofuranose (Neidle, Achari, Sheldrick, Reese & Bridson, 1978) has been found to have the glycosidic angle similar to that observed in εAdo.

Figs. 3 and 4* show that regions of a nonpolar or hydrophobic nature (base moieties) alternate with those of a more polar character (sugar moieties) in the **c** direction. The nonpolar layers are located at $z = 0,\frac{1}{2},\ldots$ while the polar ones have $z = \frac{1}{4},\frac{3}{4},\ldots$. The structure contains a three-dimensional hydrogen-bond network consisting of three independent bonds and involving all available proton donors (ribose hydroxyl groups). The acceptor centers are N(6), N(7) and O(5′). Each molecule is involved in six hydrogen bonds. The hydrogen-bond network contains a cyclic

$$N(7^{ii})\cdots O(5'^{iii})\cdots O(2')\text{--}O(3')\cdots N(6^{ii})$$

pattern. Fig. 4 shows that all hydrogen bonds lie approximately in planes parallel to *bc* at $x = \frac{1}{4},\frac{3}{4}\ldots$ Comparison with Fig. 3 reveals that the two O···N hydrogen bonds are almost parallel to **c**. The geometry of the hydrogen bonds and their ΔHB parameters* are presented in Table 3. These data classify the three hydrogen bonds as relatively weak. Also the $\sum\Delta$ parameter* of 810 indicates that the total effect of the hydrogen bonds acting upon an εAdo molecule is not very strong. The structure contains two short intermolecular C—H···O(N) contacts: C(8)—H(8)···N(7) and C(2)—H(2)···O(2′). The C—H, H···*A*, C···*A* distances and the C—H···*A* angles for these contacts are 1·05, 2·41, 3·424 (4) Å and 164° [for C(8)···N(7)] and 1·03, 2·29, 3·309 (4) Å and 171° [for C(2)···O(2′)].

There is almost no base overlap in the structure. Only some overlap of the two five-membered rings is observed between **a**-translated molecules [C(8)—N(9) overlaps C(11)—C(10), plane-to-plane distance 3·41 Å]. This is in contrast to the large overlap of the εadenine bases found for EtεAdo.H⁺.

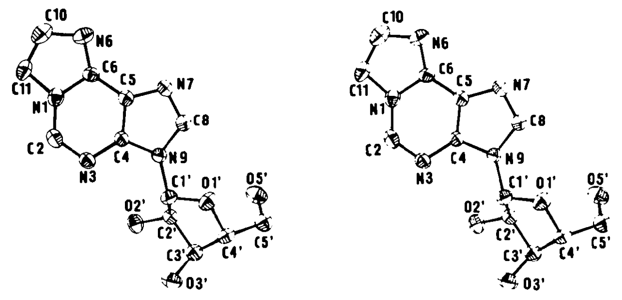

Fig. 2. Thermal-ellipsoid stereoscopic view of the εAdo molecule. H atoms have been omitted.

Table 2. *Torsion angles* (°) *at the ribose ring*

C(1′)–C(2′)–C(3′)–C(4′)	41·4 (4)	O(5′)–C(5′)–C(4′)–C(3′)	56·7 (4)
C(2′)–C(3′)–C(4′)–O(1′)	27·9 (3)	O(5′)–C(5′)–C(4′)–O(1′)	62·7 (3)
C(3′)–C(4′)–O(1′)–C(1′)	1·4 (3)	C(8)–N(9)–C(1′)–O(1′)	26·2 (4)
C(4′)–O(1′)–C(1′)–C(2′)	−25·7 (4)	C(8)–N(9)–C(1′)–C(2′)	91·5 (4)
O(1′)–C(1′)–C(2′)–C(3′)	41·8 (3)		

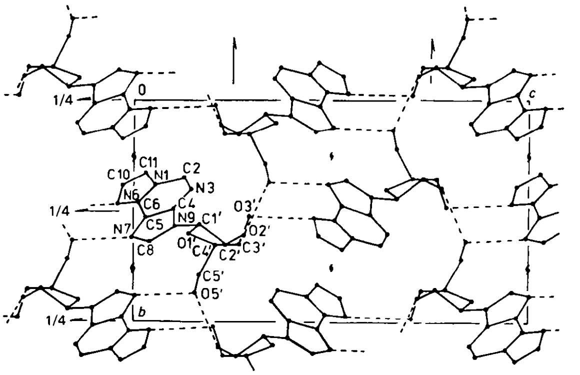

Fig. 3. Projection of the structure down **a**.

Table 3. *Geometrical features and* ΔHB *parameters characterizing the intermolecular hydrogen bonds*

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)	ΔHB*
O(3′)—H(O3′)···N(6^{i})	0·83	2·03	2·850 (4)	174	150
O(2′)—H(O2′)···O(5′^{ii})	0·89	1·90	2·772 (3)	167	128
O(5′)—H(O5′)···N(7^{iii})	0·64	2·26	2·873 (4)	162	127

Symmetry code: (i) $1{\cdot}5 - x$, $1 - y$, $0{\cdot}5 + z$; (ii) $1 - x$, $y - 0{\cdot}5$, $0{\cdot}5 - z$; (iii) $x - 0{\cdot}5$, $1{\cdot}5 - y$, $-z$.

* Jaskólski *et al.* (1981).

---

* Fig. 4 has been deposited. See previous footnote.

* For a *D*—H···*A* hydrogen bond the ΔHB parameter is defined as follows: $\Delta HB = |(rD + rA) - da| \times 10^3$, where *rD* (*rA*) is the proton–donor (–acceptor) van der Waals radius (Å) and *da* is the *D*···*A* distance (Å). $\sum\Delta$ is obtained for a given molecule as a sum of the ΔHB values for all hydrogen bonds in which it is involved (Jaskólski *et al.*, 1981).

I wish to thank Professor M. Wiewiórowski for stimulating discussions and Dr W. Krzyżosiak for supplying the crystals.

References

ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698–705.

FURBERG, S., PETERSEN, C. S. & RØMMING, C. (1965). *Acta Cryst.* **18**, 313–320.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

JASKÓLSKI, M. (1979). Thesis, A. Mickiewicz Univ. Poznań.

JASKÓLSKI, M., KRZYŻOSIAK, W., SIERZPUTOWSKA-GRACZ, H. & WIEWIÓROWSKI, M. (1981). *Nucleic Acids Res.* **9**, 5423–5441.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory. Tennessee.

KRZYŻOSIAK, W., JASKÓLSKI, M., SIERZPUTOWSKA-GRACZ, H. & WIEWIÓROWSKI, M. (1982). *Nucleic Acids Res.* Submitted for publication.

LAI, T. F. & MARSH, R. E. (1972). *Acta Cryst.* B**28**, 1982–1989.

LEEUW, H. P. M. DE, HAASNOOT, C. A. & ALTONA, C. (1980). *Isr. J. Chem.* **20**, 108–126.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

MOSSET, A., BONNET, J. J. & GALY, J. (1979). *Acta Cryst.* B**35**, 1908–1910.

NEIDLE, S., ACHARI, A., SHELDRICK, G. M., REESE, C. B. & BRIDSON, P. K. (1978). *Acta Cryst.* B**34**, 2794–2798.

SHIKATA, K., UEKI, T. & MITSUI, T. (1973). *Acta Cryst.* B**29**, 31–38.

Syntex XTL Operation Manual (1973). Cupertino: Syntex Analytical Instruments.

WANG, A. H.-J., BARRIO, J. R. & PAUL, I. C. (1976). *J. Am. Chem. Soc.* **98**, 7401–7408.

WANG, A. H.-J., DAMMANN, L. G., BARRIO, J. R. & PAUL, I. C. (1974). *J. Am. Chem. Soc.* **96**, 1205–1213.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Acta Cryst. (1982). B**38**, 3174–3176

Ethyl 2-(Methylaminomethylene)-3-(2-methyl-6-oxopiperidino)-3-oxopropionate

BY INGEBORG CSÖREGH

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

AND LEVENTE PUSZTAY, GÁBOR HORVÁTH AND KÁLMÁN SIMON

CHINOIN Research Centre, H-1325 Budapest, POB 110, Hungary

(*Received* 29 *April* 1982; *accepted* 15 *July* 1982)

Abstract. $C_{13}H_{20}N_2O_4$, $M_r = 268{\cdot}17$, monoclinic, $P2_1/c$, $a = 10{\cdot}322\,(3)$, $b = 17{\cdot}218\,(6)$, $c = 8{\cdot}698\,(3)$ Å, $\beta = 112{\cdot}25\,(3)°$, $Z = 4$, $V = 1430{\cdot}72$ Å^3, $D_c = 0{\cdot}750$ Mg m^{-3}, $\mu(\text{Cu } K\alpha) = 0{\cdot}68$ mm^{-1}. $R = 0{\cdot}058$ for 1949 observed reflections. The geometry of the piperidine ring can be approximated to a flattened half-chair. The conformation of the ethyl 2-(methylaminomethylene)-3-oxopropionate side chain is stabilized by an intramolecular hydrogen bond. The crystal structure is held together by intermolecular hydrogen bonds besides the van der Waals forces.

Introduction. Among the homopyrimidazole derivatives, 3-ethoxycarbonyl-1,6-dimethyl-4-oxo-3,4,6,7,8,9-hexahydro-2*H*-pyrido[1,2-*a*]pyrimidinium methanesulphonate, Probon^R (Negwer, 1971), was found to be a new analgesic drug. However, it is believed that this drug must undergo biological metabolism to form the immediately active molecule (Simon, Mészáros & Sasvári, 1975). In the course of studies concerning the metabolism of Probon^R, the title compound (4 in Fig. 1) was isolated from alkaline solution (Mészáros, 1978). Because its structure could not be completely derived by spectroscopic methods, an X-ray structure analysis was undertaken.

The unit-cell dimensions were refined by least-squares fitting of the cell parameters to a powder pattern, taken in a Guinier–Hägg-type focusing camera with Cu $K\alpha_1$ ($\lambda = 1{\cdot}5405$ Å) radiation and KCl ($a = 6{\cdot}2930$ Å at 298 K) as internal standard. The intensity

0567-7408/82/123174-03$01.00