N—H···N hydrogen bond [the $N(2^{i})\cdots H(8^{ii})—N(1^{ii})$ angle is 165 (4)°].

The authors are grateful to Dr M. Muraoka of this University for helpful discussions. The authors also thank Professor M. Nagata for his continual interest throughout this investigation and the Ministry of Education for a grant towards the purchase of the diffractometer.

References

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–102. Birmingham: Kynoch Press.

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

Muraoka, M. & Takeshima, T. (1981). Private communication.

Muraoka, M., Yamamoto, T., Yamaguchi, S., Tonosaki, F., Takeshima, T. & Fukuda, N. (1977). *J. Chem. Soc. Perkin Trans.* 1, pp. 1273–1280.

Pauling, L. (1967). *The Chemical Bond*, p. 152. Ithaca Cornell Univ. Press.

Sakurai, T. & Kobayashi, K. (1978). *Rikagaku Kenkyusho Hokoku* (*Rep. Inst. Phys. Chem. Res.*, in Japanese), **55**, 69–77.

Wells, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 734. Oxford: Clarendon Press.

Acta Cryst. (1982). B**38**, 3168–3171

(—)-2′-Hydroxy-2-(4-methoxybutyl)-5,9-dimethyl-6,7-benzomorphan Hydrobromide*†

By O. M. Peeters, C. J. De Ranter‡ and N. M. Blaton

Laboratorium voor Analytische Chemie en Medicinale Fysicochemie,
Instituut voor Farmaceutische Wetenschappen, KU Leuven, Van Evenstraat 4, *B*-3000 *Leuven, Belgium*

(*Received* 18 *January* 1982; *accepted* 8 *July* 1982)

Abstract. $C_{19}H_{29}NO_2.HBr$, $M_r = 384{\cdot}36$, monoclinic, $P2_1$, $a = 12{\cdot}2567\,(9)$, $b = 8{\cdot}9898\,(9)$, $c = 17{\cdot}5559\,(9)$ Å, $\beta = 92{\cdot}63\,(1)^\circ$, $V = 1932$ Å^3, $D_m = 1{\cdot}32$, $D_c = 1{\cdot}32$ Mg m^{-3}, $Z = 4$, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 2{\cdot}97$ mm^{-1}, $F(000) = 808$. The structure refined to an R of 0·041 for 3035 observed reflections. The two molecules in the asymmetric unit have different N side-chain conformations.

Introduction. As part of our study of structure–activity relationships in the 6,7-benzomorphan series (Gelders, De Ranter & Kokkes, 1980), the *N*-[(tetrahydrofuryl)alkyl] and the *N*-(alkoxyalkyl) derivatives of (—)-normetazocine [(—)-2′-hydroxy-5,9α-dimethyl-6,7-benzomorphan] are interesting since some compounds of this series possess action profiles distinctly different from those of morphine and other classical opiates (Merz & Stockhaus, 1979). Three groups may be distinguished: (*a*) morphine-like agonists, (*b*) non-morphine-like agonists and (*c*) nalorphine-like agonist–antagonists. The title compound is of the morphine-like agonist type and shows an analgesic activity twice that of morphine in the writhing test. Crystals were grown from an ethanol–diethyl ether solution. Intensities were measured on a Nonius CAD-4 computer-controlled diffractometer with graphite-monochromated Cu $K\alpha$ radiation using θ–2θ scans ($\theta_{\max} = 65^\circ$). Cell dimensions were obtained by least-squares refinement of the setting angles of 14 reflections with $37^\circ < 2\theta < 44^\circ$. A total of 3377 independent reflections were measured of which 3035 were considered as observed [$I > 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The positions of 38 of the 46 non-H atoms present in the asymmetric unit were obtained from a Patterson synthesis followed by a superposition map (minimum function). The missing ones were obtained from a Fourier synthesis. Subsequent isotropic and anisotropic refinements by block-diagonal least squares using XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) lowered the R value to 0·067. 48 H atoms were then located from a difference synthesis and were included as fixed-atom contributions with the isotropic temperature factor of their carrier atoms. Further refinement converged at $R = 0{\cdot}041$. The weighting scheme employed was $w = (16{\cdot}0 + |F_o| + 0{\cdot}0125|F_o|^2)^{-1}$. The average and maximum parameter shifts during the final cycle were, respectively, 0·04 and 0·31 σ. The maximum electron density in a difference

---

* Structural Studies of Substituted 6,7-Benzomorphan Compounds. V. Part IV: Gelders, De Ranter & Kokkes (1980).

† *Chemical Abstracts* name: (—)-1,2,3,4,5,6-hexahydro-2,6-methano-3-(4-methoxybutyl)-6,11-dimethyl-3-benzazocin-8-ol hydrobromide.

‡ To whom correspondence should be addressed.

0567-7408/82/123168-04$01.00

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å²) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Br(1*A*)	−974 (1)	4999 (1)	9258 (1)	5·07 (1)
O(2′*A*)	6711 (3)	6419 (5)	8590 (2)	3·93 (3)
C(1′*A*)	4801 (4)	6079 (6)	8600 (2)	3·01 (4)
C(2′*A*)	5842 (4)	5620 (7)	8854 (2)	3·28 (4)
C(3′*A*)	5983 (4)	4473 (7)	9351 (3)	3·86 (5)
C(4′*A*)	5073 (4)	3697 (7)	9595 (3)	3·65 (4)
C(1*A*)	1959 (4)	3769 (7)	9365 (3)	3·70 (4)
N(2*A*)	1545 (3)	4885 (6)	9918 (2)	3·33 (3)
C(3*A*)	2199 (4)	6300 (6)	9937 (3)	3·42 (5)
C(4*A*)	2296 (4)	6926 (7)	9150 (3)	3·85 (5)
C(5*A*)	2735 (4)	5799 (7)	8571 (3)	3·52 (4)
C(6*A*)	3888 (4)	5297 (6)	8839 (2)	2·99 (4)
C(7*A*)	4025 (4)	4107 (6)	9342 (2)	3·18 (4)
C(8*A*)	3087 (5)	3158 (7)	9605 (3)	3·85 (5)
C(9*A*)	1953 (4)	4449 (7)	8560 (3)	3·98 (5)
C(10*A*)	2196 (6)	3262 (9)	7978 (4)	5·39 (6)
C(11*A*)	2695 (5)	6541 (8)	7780 (3)	4·47 (6)
C(12*A*)	1427 (5)	4233 (7)	10708 (3)	4·22 (5)
C(13*A*)	645 (5)	5070 (9)	11180 (3)	4·49 (5)
C(14*A*)	555 (6)	4243 (9)	11933 (4)	5·05 (6)
C(15*A*)	−318 (7)	4962 (11)	12406 (4)	6·40 (7)
C(16*A*)	−1212 (10)	4665 (14)	13552 (6)	9·80 (11)
O(17*A*)	−335 (6)	4181 (8)	13082 (3)	8·71 (5)
Br(2*B*)	4044 (1)	4009 (1)	5954 (1)	6·08 (1)
O(2′*B*)	11638 (3)	2974 (6)	5319 (2)	4·93 (3)
C(1′*B*)	9790 (4)	2996 (7)	5650 (3)	3·60 (4)
C(2′*B*)	10819 (4)	3649 (7)	5682 (3)	3·55 (5)
C(3′*B*)	10971 (4)	4998 (8)	6070 (3)	3·76 (4)
C(4′*B*)	10117 (4)	5645 (7)	6404 (3)	3·75 (5)
C(1*B*)	7063 (4)	5024 (8)	6723 (2)	3·55 (4)
N(2*B*)	6410 (3)	5541 (6)	6015 (2)	3·86 (4)
C(3*B*)	6943 (4)	5092 (10)	5289 (3)	4·55 (5)
C(4*B*)	7131 (5)	3446 (9)	5278 (3)	4·58 (6)
C(5*B*)	7805 (4)	2885 (7)	5992 (3)	3·78 (4)
C(6*B*)	8925 (4)	3634 (6)	6018 (3)	3·38 (4)
C(7*B*)	9087 (4)	4992 (7)	6395 (2)	3·31 (4)
C(8*B*)	8188 (4)	5756 (8)	6821 (3)	4·11 (5)
C(9*B*)	7167 (5)	3328 (7)	6686 (3)	3·93 (4)
C(10*B*)	7664 (6)	2765 (9)	7456 (4)	5·03 (6)
C(11*B*)	7884 (6)	1196 (9)	5923 (4)	5·57 (6)
C(12*B*)	6134 (5)	7165 (8)	5978 (4)	4·76 (6)
C(13*B*)	5547 (6)	7705 (9)	6659 (4)	5·23 (6)
C(14*B*)	5084 (7)	9259 (11)	6511 (4)	6·74 (7)
C(15*B*)	4813 (14)	10125 (13)	7139 (6)	12·05 (13)
C(16*B*)	5027 (14)	10471 (19)	8412 (7)	12·62 (14)
O(17*B*)	4605 (8)	9590 (7)	7807 (4)	10·20 (7)

synthesis was 0·81 e Å^{-3}. The atomic coordinates and their e.s.d.'s are given in Table 1.*

Discussion. The atomic-numbering system given in Fig. 1 is that commonly accepted for benzomorphans. Bond lengths and angles are given in Tables 2 and 3. While the values for the benzomorphan nucleus are within expected limits, some remarks have to be made for those of the N side chain. Namely for molecule *B* the bond lengths C(14)–C(15), C(15)–O(17) and C(16)–O(17) are markedly small. This probably arises from disorder in the crystal, shown by the high thermal parameters of the atoms concerned, causing the bond distances and angles computed for an average position to be considerably in error. The torsion angles listed in Table 4 show that the conformation of the benzomorphan nucleus is the same as in previously determined benzomorphan compounds (Gelders *et al.*, 1980). The two molecules in the asymmetric unit have different conformations in the N side chain. An

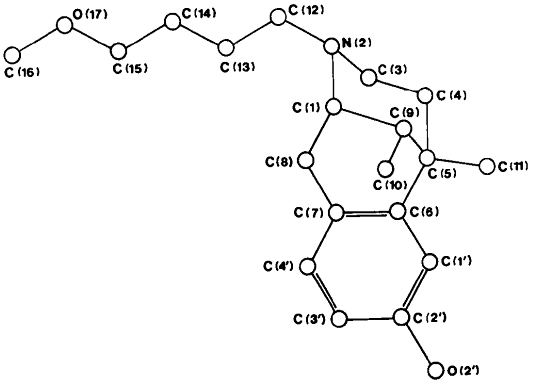

Fig. 1. Atomic-numbering scheme.

Table 2. *Bond lengths* (Å)

	Molecule *A*	Molecule *B*
O(2′)–C(2′)	1·382 (7)	1·357 (7)
C(1′)–C(2′)	1·396 (7)	1·390 (8)
C(1′)–C(6)	1·402 (7)	1·390 (8)
C(2′)–C(3′)	1·356 (8)	1·400 (9)
C(3′)–C(4′)	1·400 (8)	1·354 (8)
C(4′)–C(7)	1·390 (7)	1·392 (8)
C(1)–N(2)	1·500 (8)	1·520 (7)
C(1)–C(8)	1·528 (8)	1·530 (8)
C(1)–C(9)	1·539 (8)	1·532 (10)
N(2)–C(3)	1·503 (8)	1·513 (7)
N(2)–C(12)	1·519 (8)	1·499 (9)
C(3)–C(4)	1·502 (8)	1·498 (12)
C(4)–C(5)	1·549 (8)	1·553 (8)
C(5)–C(6)	1·537 (7)	1·528 (8)
C(5)–C(9)	1·546 (9)	1·530 (8)
C(5)–C(11)	1·539 (8)	1·526 (11)
C(6)–C(7)	1·393 (7)	1·398 (8)
C(7)–C(8)	1·520 (8)	1·522 (8)
C(9)–C(10)	1·517 (10)	1·542 (9)
C(12)–C(13)	1·499 (9)	1·504 (10)
C(13)–C(14)	1·525 (10)	1·526 (13)
C(14)–C(15)	1·529 (11)	1·403 (15)
C(15)–O(17)	1·380 (10)	1·303 (14)
C(16)–O(17)	1·451 (14)	1·404 (16)

---

* 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 38054 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°)

	Molecule *A*	Molecule *B*
C(2′)—C(1′)—C(6)	119·2 (5)	121·1 (5)
O(2′)—C(2′)—C(1′)	116·5 (5)	118·8 (5)
O(2′)—C(2′)—C(3′)	122·2 (5)	122·1 (4)
C(1′)—C(2′)—C(3′)	121·2 (5)	119·1 (5)
C(2′)—C(3′)—C(4′)	119·8 (5)	119·6 (5)
C(3′)—C(4′)—C(7)	120·5 (5)	122·2 (6)
N(2)—C(1)—C(8)	113·0 (4)	113·5 (5)
N(2)—C(1)—C(9)	109·9 (5)	108·1 (4)
C(8)—C(1)—C(9)	111·2 (4)	110·9 (5)
C(1)—N(2)—C(3)	112·6 (4)	112·0 (4)
C(1)—N(2)—C(12)	112·5 (4)	116·2 (5)
C(3)—N(2)—C(12)	112·3 (4)	109·2 (5)
N(2)—C(3)—C(4)	111·1 (4)	110·3 (5)
C(3)—C(4)—C(5)	113·8 (5)	112·8 (5)
C(4)—C(5)—C(6)	109·4 (4)	108·9 (5)
C(4)—C(5)—C(9)	106·7 (4)	106·6 (4)
C(4)—C(5)—C(11)	108·1 (5)	107·0 (5)
C(6)—C(5)—C(9)	109·5 (5)	110·7 (4)
C(6)—C(5)—C(11)	113·2 (4)	112·4 (5)
C(9)—C(5)—C(11)	109·6 (4)	111·0 (5)
C(1′)—C(6)—C(5)	119·8 (4)	120·5 (5)
C(1′)—C(6)—C(7)	120·0 (4)	119·1 (5)
C(5)—C(6)—C(7)	120·1 (4)	120·4 (5)
C(4′)—C(7)—C(6)	119·3 (5)	118·8 (5)
C(4′)—C(7)—C(8)	117·1 (5)	118·7 (5)
C(6)—C(7)—C(8)	123·6 (4)	122·4 (5)
C(1)—C(8)—C(7)	113·7 (5)	114·8 (5)
C(1)—C(9)—C(5)	108·9 (4)	109·8 (5)
C(1)—C(9)—C(10)	110·3 (5)	108·6 (5)
C(5)—C(9)—C(10)	114·9 (5)	114·6 (5)
N(2)—C(12)—C(13)	113·7 (5)	113·3 (5)
C(12)—C(13)—C(14)	107·9 (6)	110·3 (6)
C(13)—C(14)—C(15)	110·1 (6)	118·3 (8)
C(14)—C(15)—O(17)	106·9 (7)	124·5 (9)
C(15)—O(17)—C(16)	112·1 (7)	113·1 (10)

ORTEP (Johnson, 1965) stereoview of molecule *A* is shown in Fig. 2. The attachment of the side chain on the N atom in molecule *B* [synclinal for C(1)—N(2)—C(12)—C(13) and antiplanar for N(2)—C(12)—C(13)—C(14)] is found in several substituted 6,7-benzomorphan compounds (Gelders *et al.*, 1980). The antiplanar conformations of C(1)—N(2)—C(12)—C(13) and N(2)—C(12)—C(13)—C(14) in molecule *A* are similar to those in (—)-cyclazocine.HBr.H_2O [2-(cyclopropylmethyl)-2′-hydroxy-5,9-dimethyl-6,7-benzomorphan hydrobromide monohydrate] (Karle, Gilardi, Fratini & Karle, 1969). Intramolecular potential-energy calculations using the program *EENY* (Motherwell, 1974) and empirical constants from Giglio (1969) show that both conformations correspond to energy minima in the energy map for varying C(1)—N(2)—C(12)—C(13) and N(2)—C(12)—C(13)—C(14) angles.

The packing of the molecules in the crystal is essentially achieved by hydrogen bonds between Br, O and N. Each Br^- ion is bonded to a phenolic O of one molecule and an N atom of another molecule. Endless chains are thus formed parallel to **a** (Fig. 3). Hydrogen-bond distances and angles are given in Table 5.

Table 4. *Torsion angles* (°)

	Molecule *A*	Molecule *B*
Ring *A*		
C(7)—C(6)—C(1′)—C(2′)	1·9 (8)	3·1 (9)
C(6)—C(1′)—C(2′)—C(3′)	−2·6 (8)	−2·2 (9)
C(1′)—C(2′)—C(3′)—C(4′)	2·2 (9)	−0·3 (8)
C(2′)—C(3′)—C(4′)—C(7)	−1·0 (9)	2·0 (9)
C(3′)—C(4′)—C(7)—C(6)	0·3 (7)	−1·1 (9)
C(4′)—C(7)—C(6)—C(1′)	−0·7 (8)	−1·4 (8)
Ring *C*		
C(8)—C(1)—C(9)—C(5)	−63·8 (6)	−62·1 (6)
C(1)—C(9)—C(5)—C(6)	58·1 (6)	56·5 (6)
C(9)—C(5)—C(6)—C(7)	−29·9 (7)	−27·4 (8)
C(5)—C(6)—C(7)—C(8)	5·3 (8)	2·5 (8)
C(6)—C(7)—C(8)—C(1)	−8·9 (8)	−7·1 (8)
C(7)—C(8)—C(1)—C(9)	37·8 (7)	36·4 (7)
Ring *E*		
C(9)—C(1)—N(2)—C(3)	−57·5 (6)	−58·7 (6)
C(1)—N(2)—C(3)—C(4)	52·2 (6)	55·1 (7)
N(2)—C(3)—C(4)—C(5)	−53·0 (6)	−55·2 (6)
C(3)—C(4)—C(5)—C(9)	57·2 (6)	58·4 (7)
C(4)—C(5)—C(9)—C(1)	−60·3 (6)	−61·7 (6)
C(5)—C(9)—C(1)—N(2)	62·1 (6)	62·9 (6)
N side chain		
C(1)—N(2)—C(12)—C(13)	−157·9 (5)	−55·0 (7)
C(3)—N(2)—C(12)—C(13)	73·9 (6)	177·1 (5)
N(2)—C(12)—C(13)—C(14)	176·6 (5)	−168·1 (6)
C(12)—C(13)—C(14)—C(15)	−174·5 (6)	−160·6 (10)
C(13)—C(14)—C(15)—O(17)	−178·7 (7)	−22·1 (20)
C(14)—C(15)—O(17)—C(16)	−174·2 (8)	141·5 (15)

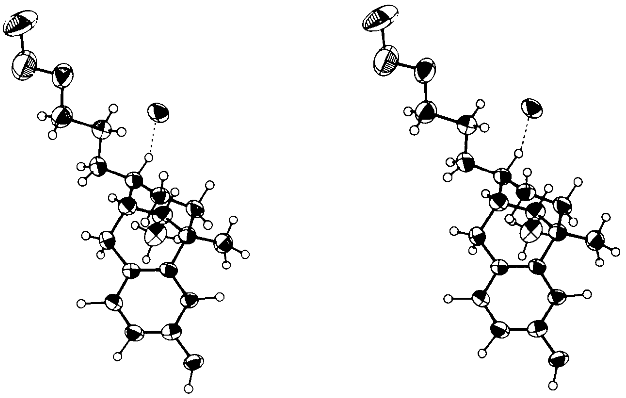

Fig. 2. Stereoscopic view of molecule *A* with 50% probability thermal ellipsoids for the non-H atoms.

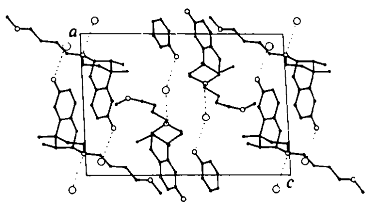

Fig. 3. Packing of the molecules. Hydrogen bonds are shown with broken lines.

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

$A \quad B \quad C$	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(1*A*$^{\rm i}$)	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*$^{\rm ii}$)–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 = 291·3, orthorhombic, $P2_12_12_1$, a = 6·4679 (5), b = 10·4029 (7), c = 18·277 (2) Å, V = 1229·8 (2) Å^3, Z = 4, D_c = 1·57 Mg m^{-3}, μ(Cu $K\alpha$) = 1·04 mm^{-1}. R = 0·037 for 977 observed [$I \geq 1{\cdot}96\sigma(I)$] 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 θ:2θ scan for a crystal with dimensions 0·15 × 0·2 × 0·5 mm. 1075 independent reflexions were measured up to sin θ/λ = 0·562 Å^{-1}; of these, 980 had $I \geq 1{\cdot}96\sigma(I)$ and were considered observed. For each reflexion the profile was measured and the background level as well

0567-7408/82/123171-04$01.00