

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0428$

$wR(F^2) = 0.1400$

$S = 1.088$

1426 reflections

210 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.6156P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.212 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.221 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0115 (36)

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Data collection: *CAD-4 EXPRESS Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 EXPRESS Software*. Data reduction: local programs. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: locally modified version of *ORTEPII* (Johnson, 1976; Mallinson & Muir, 1985). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
C1	0.6631 (7)	0.3219 (7)	0.56877 (10)	0.0482 (11)
C2	0.5240 (9)	0.2755 (8)	0.54120 (10)	0.0535 (12)
C3	0.5642 (9)	0.0856 (8)	0.52263 (11)	0.0555 (12)
C4	0.7441 (9)	-0.0548 (8)	0.53222 (11)	0.0537 (12)
C4a	0.8954 (8)	-0.0118 (7)	0.56031 (10)	0.0467 (11)
C5	1.0894 (8)	-0.1563 (7)	0.56915 (11)	0.0537 (12)
C6	1.2432 (8)	-0.1156 (7)	0.59522 (11)	0.0501 (12)
C6a	1.1960 (7)	0.0731 (7)	0.61370 (10)	0.0440 (11)
C7a	1.2304 (7)	0.3241 (7)	0.65208 (10)	0.0407 (10)
C8	1.3280 (7)	0.4370 (7)	0.68167 (10)	0.0442 (11)
C8a	1.1925 (7)	0.6374 (7)	0.69053 (10)	0.0407 (10)
C9	1.2736 (8)	0.7636 (7)	0.71762 (10)	0.0485 (12)
C10	1.1468 (8)	0.9508 (8)	0.72662 (11)	0.0522 (12)
C11	0.9411 (8)	1.0132 (8)	0.70911 (10)	0.0508 (12)
C12	0.8596 (7)	0.8897 (7)	0.68221 (10)	0.0451 (11)
C12a	0.9829 (7)	0.7020 (7)	0.67284 (10)	0.0404 (10)
C13	0.8855 (7)	0.5739 (7)	0.64359 (10)	0.0403 (10)
C13a	1.0319 (7)	0.3836 (6)	0.63334 (10)	0.0376 (9)
C13b	1.0077 (7)	0.2195 (7)	0.60734 (9)	0.0400 (10)
C13c	0.8508 (7)	0.1820 (7)	0.57907 (10)	0.0420 (10)
O7	1.3353 (5)	0.1374 (5)	0.64080 (7)	0.0480 (8)
O8	1.5060 (5)	0.3706 (5)	0.69703 (7)	0.0600 (9)
O13	0.6960 (5)	0.6258 (5)	0.63008 (7)	0.0558 (9)

Table 2. Selected geometric parameters (\AA , $^\circ$)

C1—C2	1.366 (6)	C8—O8	1.219 (4)
C1—C13c	1.399 (5)	C8—C8a	1.477 (6)
C2—C3	1.397 (6)	C8a—C9	1.400 (6)
C3—C4	1.361 (6)	C8a—C12a	1.402 (5)
C4—C4a	1.416 (6)	C9—C10	1.387 (6)
C4a—C13c	1.424 (6)	C10—C11	1.377 (6)
C4a—C5	1.426 (6)	C11—C12	1.386 (5)
C5—C6	1.359 (6)	C12—C12a	1.384 (5)
C6—C6a	1.395 (6)	C12a—C13	1.503 (5)
C6a—O7	1.379 (5)	C13—O13	1.210 (4)
C6a—C13b	1.388 (5)	C13—C13a	1.472 (5)
C7a—O7	1.357 (5)	C13a—C13b	1.450 (5)
C7a—C13a	1.367 (5)	C13b—C13c	1.434 (5)
C7a—C8	1.467 (6)		
O7—C6a—C13b	111.6 (4)	O13—C13—C13a	123.4 (4)
O7—C6a—C6	123.2 (4)	O13—C13—C12a	120.7 (4)
C13b—C6a—C6	125.2 (4)	C7a—C13a—C13b	106.1 (4)
O7—C7a—C13a	112.3 (4)	C7a—C13a—C13	119.4 (4)
O7—C7a—C8	120.7 (3)	C13b—C13a—C13	134.3 (3)
C13a—C7a—C8	127.0 (4)	C6a—C13b—C13c	118.9 (4)
O8—C8—C7a	122.4 (4)	C6a—C13b—C13a	104.5 (3)
O8—C8—C8a	123.9 (4)	C13c—C13b—C13a	136.6 (4)

H atoms were included at calculated positions (C—H 0.96 \AA) riding on their attached C atoms, with $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The refined value of the Flack (1983) absolute-structure parameter [0 (3)] indicates that the absolute configuration could not be determined reliably from the crystallographic data.

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cis-Perhydro-1,3-dimethyl-4,5-(epoxyethoxy)purine-2,6,8-trione

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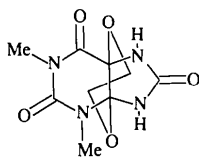
Abstract

The title compound, $\text{C}_9\text{H}_{12}\text{N}_4\text{O}_5$, adopts a distinct ring-twisted conformation defined by nearly orthogonal bridgehead torsion angles [C16—C15—C14—N19 -90.1 (2) and C26—C25—C24—N29 -87.8 (2) $^\circ$]. The antiperiplanar array [C17—O14—C14—N19 -158.0 (2)

and C27—O24—C24—N29 $-158.3(2)^\circ$] does not allow stereoelectronically controlled ring-opening at the C4—N9 bond.

Comment

As part of our extensive investigations of intermediates in enzymic uricolytic pathways, we were interested in the stereoelectronic effects controlling the ring opening of the purine system. The chemical model, the propellane (I), was completely stable toward acidic hydrolysis. The X-ray structure determination showed (I) to be the title compound, in which stereoelectronically controlled cleavage of the C4—N9 bond cannot occur.



(I)

An ORTEP (Johnson, 1965) drawing of the title molecule is shown in Fig. 1. The ring-twisted conformation, defined by nearly orthogonal bridgehead torsion angles [C16—C15—C14—N19 $-90.1(2)$ and C26—C25—C24—N29 $-87.8(2)^\circ$], corresponds to that found in the related compound *cis*-perhydro-4,5-dimethoxy-1-methylpurine-2,6,8-trione (Poje & Vicković, 1987). The 1,4-dioxane ring has a slightly distorted chair conformation, with the C7—O4 bond oriented antiperiplanar to the N9 atom. The most interesting features of the arrays at the ester aminal C4 and the hemiaminal ether C5 atoms, of the conformation and of the hydrogen-bonding are given in Tables 2 and 3. As a result of the conformationally rigid arrangement, the ester aminal function becomes locked into a configuration where cleavage of the C4—N9 bond is no longer stereoelectronically allowed.

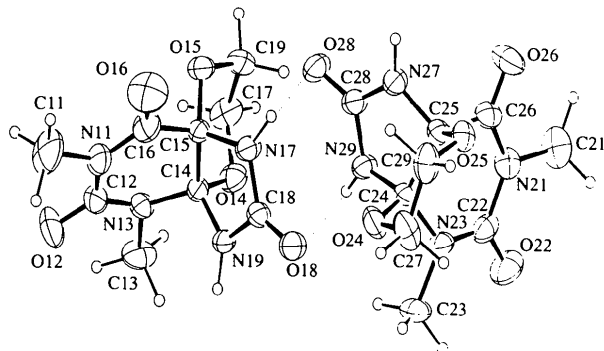


Fig. 1. View of the two independent molecules of (I) showing 50% probability displacement ellipsoids, the atom-numbering scheme and the dimeric association of imidazolone rings *via* a pair of hydrogen bonds (indicated by a dotted line).

Experimental

Crystals of (I) (m.p. 487–488 K, with decomposition) were obtained through the reaction of 5-chloro-1,3-dimethyl-5,7-dihydro-3*H*-purine-2,6,8-trione with anhydrous ethylene glycol (Modrić, Palković, Perina, Poje & Vicković, 1994; Poje, Palković & Poje, 1995). Recrystallization was from water.

Crystal data

C ₉ H ₁₂ N ₄ O ₅	Cu $K\alpha$ radiation
$M_r = 256.218$	$\lambda = 1.54178 \text{ \AA}$
Orthorhombic	Cell parameters from 18 reflections
$Pna2_1$	$\theta = 12-21^\circ$
$a = 15.187(5) \text{ \AA}$	$\mu = 1.080 \text{ mm}^{-1}$
$b = 12.883(3) \text{ \AA}$	$T = 293 \text{ K}$
$c = 11.468(3) \text{ \AA}$	Prism
$V = 2243.8(11) \text{ \AA}^3$	$0.28 \times 0.24 \times 0.15 \text{ mm}$
$Z = 8$	Colourless
$D_x = 1.5169 \text{ Mg m}^{-3}$	
$D_m = 1.51 \text{ Mg m}^{-3}$	
D_m measured by flotation in $\text{CH}_3\text{Br}-\text{CH}_2\text{Cl}_2$	

Data collection

Philips PW1100/20 diffractometer	$\theta_{\max} = 69.95^\circ$
$\theta/2\theta$ scans	$h = 0 \rightarrow 18$
Absorption correction: none	$k = 0 \rightarrow 15$
1826 measured reflections	$l = 0 \rightarrow 13$
1826 independent reflections	3 standard reflections
1680 observed reflections	frequency: 120 min
$[I > 2\sigma(I)]$	intensity decay: none

Refinement

Refinement on F^2	Extinction correction: <i>SHELXL93</i> (Sheldrick, 1993)
$R(F) = 0.0426$	Extinction coefficient: 0.0065 (3)
$wR(F^2) = 0.0711$	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$S = 1.013$	Absolute configuration: Flack (1983) parameter = 0.15 (17)
1826 reflections	
328 parameters	
H-atom parameters not refined	
$w = 1/[\sigma^2(F_o^2) + 0.0121P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\max} = 1.355$	
$[U_{11}(\text{C11})]$	
$\Delta\rho_{\max} = 0.249 \text{ e \AA}^{-3}$	
$\Delta\rho_{\min} = -0.238 \text{ e \AA}^{-3}$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	x	y	z	U_{eq}
C11	0.2831 (4)	0.5163 (3)	0.8244 (4)	0.086
C12	0.3724 (2)	0.3592 (2)	0.7857 (2)	0.043
C13	0.4695 (2)	0.2165 (3)	0.7431 (3)	0.056
C14	0.3224 (1)	0.2226 (2)	0.6529 (2)	0.029
C15	0.2268 (1)	0.2639 (2)	0.6649 (2)	0.029
C16	0.2206 (2)	0.3733 (2)	0.7137 (2)	0.042
C17	0.2745 (2)	0.0663 (2)	0.7444 (3)	0.050
C18	0.2703 (2)	0.2650 (2)	0.4704 (2)	0.035
C19	0.1807 (2)	0.0957 (2)	0.7270 (3)	0.046

N11	0.2926 (2)	0.4115 (2)	0.7726 (2)	0.045
N13	0.3814 (1)	0.2622 (2)	0.7407 (2)	0.036
N17	0.1991 (1)	0.2612 (2)	0.5435 (2)	0.040
N19	0.3450 (1)	0.2552 (2)	0.5364 (2)	0.032
O12	0.4326 (2)	0.4020 (2)	0.8366 (2)	0.074
O14	0.3257 (1)	0.1137 (1)	0.6522 (2)	0.041
O15	0.1736 (1)	0.2072 (1)	0.7405 (2)	0.038
O16	0.1527 (2)	0.4212 (2)	0.7042 (3)	0.072
O18	0.2686 (1)	0.2770 (2)	0.3644 (2)	0.049
C21	0.0216 (2)	-0.0261 (2)	0.0390 (3)	0.056
C22	0.1231 (2)	0.1238 (2)	0.0444 (2)	0.041
C23	0.2287 (2)	0.2635 (4)	0.0526 (3)	0.063
C24	0.0817 (1)	0.2868 (2)	0.1419 (2)	0.033
C25	-0.0166 (1)	0.2561 (2)	0.1309 (2)	0.031
C26	-0.0318 (1)	0.1407 (2)	0.1064 (2)	0.035
C27	0.0530 (2)	0.4321 (3)	0.0182 (3)	0.054
C28	0.0208 (2)	0.2798 (2)	0.3247 (2)	0.038
C29	-0.0448 (2)	0.4158 (2)	0.0321 (3)	0.050
N21	0.0377 (2)	0.0838 (2)	0.0668 (2)	0.040
N23	0.1371 (1)	0.2267 (2)	0.0655 (2)	0.042
N27	-0.0478 (1)	0.2817 (2)	0.2470 (2)	0.038
N29	0.0977 (1)	0.2687 (2)	0.2644 (2)	0.037
O22	0.1796 (2)	0.0651 (2)	0.0070 (2)	0.061
O24	0.0957 (1)	0.3931 (2)	0.1211 (2)	0.046
O25	-0.0618 (1)	0.3061 (1)	0.0403 (2)	0.035
O26	-0.1037 (1)	0.1039 (2)	0.1241 (3)	0.056
O28	0.0154 (1)	0.2833 (2)	0.4318 (2)	0.049

Table 2. Selected geometric parameters (Å, °)

C14—C15	1.552 (2)	C24—C25	1.550 (2)
C14—N13	1.441 (3)	C24—N23	1.440 (3)
C14—N19	1.442 (3)	C24—N29	1.445 (3)
C14—O14	1.404 (3)	C24—O24	1.406 (4)
C15—C16	1.519 (4)	C25—C26	1.531 (4)
C15—N17	1.455 (3)	C25—N27	1.451 (3)
C15—O15	1.392 (3)	C25—O25	1.402 (3)
N13—C14—N19	113.3 (2)	N23—C24—N29	114.0 (2)
N13—C14—O14	109.6 (2)	N23—C24—O24	109.4 (2)
N19—C14—O14	106.1 (2)	N29—C24—O24	107.3 (2)
N17—C15—O15	114.6 (2)	N27—C25—O25	114.6 (2)
C12—N13—C14—N19	82.5 (3)	C22—N23—C24—N29	76.7 (3)
C16—C15—C14—N13	32.0 (3)	C26—C25—C24—N23	34.3 (3)
C16—C15—C14—N19	-90.1 (2)	C26—C25—C24—N29	-87.8 (2)
C17—O14—C14—N19	-158.0 (2)	C27—O24—C24—N29	-158.3 (2)
N17—C15—C14—N19	28.4 (2)	N27—C25—C24—N29	29.7 (2)
O14—C14—C15—O15	38.6 (3)	O24—C24—C25—O25	38.7 (3)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N17—H17...O28	0.992 (2)	2.117 (2)	3.083 (3)	164.1 (1)
N29—H29...O18	0.994 (2)	1.895 (2)	2.840 (3)	157.7 (1)
N19—H19...O28'	0.980 (2)	2.012 (2)	2.895 (3)	148.8 (1)
N27—H27...O18''	0.992 (2)	2.357 (2)	3.187 (3)	140.7 (1)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Mean (Δ/σ) is 0.359. The relatively large displacement parameters for the *N*-methyl C11 atom can be attributed to slight disorder.

Data collection: Philips PW1100/20 software. Cell refinement: Philips PW1100/20 software. Data reduction: local program. Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *CSU* (Vicković, 1988, 1994).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and intra- and intermolecular contact distances, have been deposited with the IUCr (Reference: KA1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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DL-Glutamine

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Abstract

In the structure of DL-glutamine (3,5-diamino-5-oxopentanoic acid, C₅H₁₀N₂O₃), the molecules aggregate into double layers involving head-to-tail sequences stabilized by hydrogen bonds between main-chain atoms. The double layers are stacked along *a* with the help of hydrogen bonds between side-chain atoms. This pattern is fundamentally different from that in the structure of L-glutamine, but is very similar to those in the structures of DL-methionine and hydrated L-arginine D-glutamate. The essential features of different possible aggregation patterns of amino acids appear to be determined by interactions involving main-chain atoms.

Comment

Glutamine is among the very few amino acids for which the crystal structure of only the L isomer is known. We felt it important to determine the structure of the racemate for two reasons. Firstly, a comparison of the structures of L- and DL-amino acids provides useful insights into the effect of chirality on molecular aggregation (Soman & Vijayan, 1989). Secondly, our long-term program on the study of crystalline complexes involving amino acids and peptides (Vijayan, 1988; Prasad & Vijayan, 1993; Suresh, Prasad & Vijayan, 1994; Suresh & Vijayan, 1995), aimed at elucidating the geometrical features of biologically and evolutionary important interactions, involves the comparison of the