C(5)	0.4618 (3)	0.1389 (4)	0.1475 (2)	3.32 (5)
C(6)	0.5146 (3)	−0.0568 (5)	0.1646 (2)	3.47 (5)
C(7)	0.6038 (3)	0.2923 (5)	0.1827 (2)	4.26 (6)
C(8)	0.6662 (3)	0.3149 (4)	0.3194 (2)	3.70 (5)
C(9)	0.8447 (4)	0.3774 (5)	0.3679 (3)	4.32 (6)
Cl(10)	1.0040 (1)	0.427	0.2739 (1)	6.96 (2)
C(11)	0.9041 (4)	0.4052 (6)	0.4909 (3)	6.14 (8)
C(12)	0.7805 (5)	0.3627 (7)	0.5684 (3)	6.9 (1)
C(13)	0.6067 (5)	0.2992 (7)	0.5235 (3)	6.70 (9)
C(14)	0.5477 (4)	0.2782 (6)	0.3987 (3)	5.26 (7)
C(15)	0.7113 (3)	−0.1161 (5)	0.2179 (3)	4.90 (7)
O(16)	−0.0182 (3)	0.0503 (3)	0.0150 (2)	4.51 (4)

Table 2. *Selected geometric parameters* (Å, °)

N(1)—N(2)	1.357 (3)	C(7)—C(8)	1.527 (3)
N(1)—C(6)	1.301 (4)	C(8)—C(9)	1.384 (3)
N(2)—C(3)	1.346 (4)	C(8)—C(14)	1.373 (4)
C(3)—C(4)	1.430 (4)	C(9)—Cl(10)	1.739 (3)
C(3)—O(16)	1.255 (3)	C(9)—C(11)	1.384 (4)
C(4)—C(5)	1.343 (3)	C(11)—C(12)	1.393 (5)
C(5)—C(6)	1.440 (4)	C(12)—C(13)	1.348 (5)
C(5)—C(7)	1.500 (4)	C(13)—C(14)	1.396 (4)
C(6)—C(15)	1.505 (3)		
C(4)···O(16^{i})	3.369 (3)	O(16)···O(16^{iii})	3.568 (3)
Cl(10)···O(16^{ii})	3.379 (3)	O(16)···O(16^{i})	3.568 (3)
N(1)···O(16^{iii})	3.458 (3)	C(3)···O(16^{iii})	3.592 (4)
C(15)···O(16^{iv})	3.477 (4)	N(2)···C(3^{iii})	3.690 (3)
N(2)···C(7^{v})	3.501 (3)	N(1)···C(5^{v})	3.684 (3)
N(1)···C(7^{v})	3.551 (3)	C(13)···C(14^{vii})	3.725 (6)
C(4)···Cl(10^{vi})	3.562 (3)		
N(2)—N(1)—C(6)	116.1 (2)	C(5)—C(7)—C(8)	113.8 (2)
N(1)—N(2)—C(3)	127.5 (2)	C(7)—C(8)—C(9)	120.9 (2)
N(2)—C(3)—C(4)	114.7 (2)	C(7)—C(8)—C(14)	121.7 (2)
N(2)—C(3)—O(16)	119.1 (2)	C(9)—C(8)—C(14)	117.4 (2)
C(4)—C(3)—O(16)	126.3 (3)	C(8)—C(9)—Cl(10)	120.4 (2)
C(3)—C(4)—C(5)	120.9 (3)	C(8)—C(9)—C(11)	122.4 (3)
C(4)—C(5)—C(6)	117.9 (2)	Cl(10)—C(9)—C(11)	117.2 (2)
C(4)—C(5)—C(7)	121.6 (3)	C(9)—C(11)—C(12)	118.3 (3)
C(6)—C(5)—C(7)	120.4 (2)	C(11)—C(12)—C(13)	120.4 (4)
N(1)—C(6)—C(5)	122.9 (3)	C(12)—C(13)—C(14)	120.3 (3)
N(1)—C(6)—C(15)	115.0 (3)	C(8)—C(14)—C(13)	121.1 (3)
C(5)—C(6)—C(15)	122.1 (2)		
C(4)—C(5)—C(7)—C(8)	111.0 (3)	C(5)—C(7)—C(8)—C(9)	149.7 (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(2)—H(2)···O(16^{iii})	0.78 (3)	1.96 (3)	2.725 (3)	170 (3)

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

Data reduction and other calculations were performed using *MolEN* (Fair, 1990). Lorentz and polarization corrections were applied to the data. The non-H atoms were located by direct methods using *MULTAN*11/82 (Main *et al.*, 1982). Molecular graphics were produced using *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: JZ1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cyclo-N-Acetyl-L-alanyl-*N*-methyl-L-alanyl (*cyclo-N*-Ac-L-Ala-*N*-Me-L-Ala)

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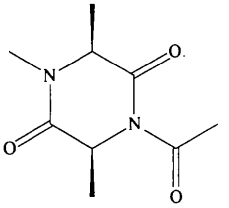
Abstract

The title compound, $C_9H_{14}N_2O_3$ (alternative name: 1-acetyl-3,4,6-trimethyl-2,5-piperazinedione), assumes a boat conformation with both methyl substituents in pseudo-axial orientations. The degree of folding of the diketopiperazine ring, defined by the angle between the planes containing the two endocyclic amide bonds, was found to be −29.1°.

Comment

The conformations of a number of diketopiperazines have been studied by X-ray diffraction (for examples and leading references, see Karle, 1981). In an attempt

to understand the effects of substituents on the conformations of simple diketopiperazines, we have determined the crystal structure of *cyclo-N*-Ac-L-Ala-*N*-Me-L-Ala, (1). To our knowledge, the conformations of diketopiperazines with both *N*-methyl and *N*-acetyl substituents have not been studied by X-ray crystallography.



(1)

The crystal structure determination of (1) reveals a boat conformation with the C^{α}-methyl substituents in pseudo-axial positions. The conformational parameters [following the conventions of the IUPAC–IUB Commission on Biochemical Nomenclature (1970)] are summarized in Table 3. It is interesting to note that the endocyclic amide groups deviate only slightly from planarity, exhibiting values of −1.3 (3) (ω_1) and −5.2 (4)° (ω_2). These compare favourably with the respective values for *cyclo-N*-Me-L-Ala-*N*-Me-L-Ala, (2) (0 and −10°) (Benedetti, Marsh & Goodman, 1976), and *cyclo-N*-Me-L-Ala-L-Ala, (3) (−5.3 and −9.3°) (Filhol & Timmins, 1976). The angle between the least-squares planes of the peptide bonds is frequently used as a measure of the folding in the diketopiperazine ring (Hooker, Bayley, Radding & Schellman, 1974); in this case it was found to be −29.1°, and in agreement with that of (2) (−25°).

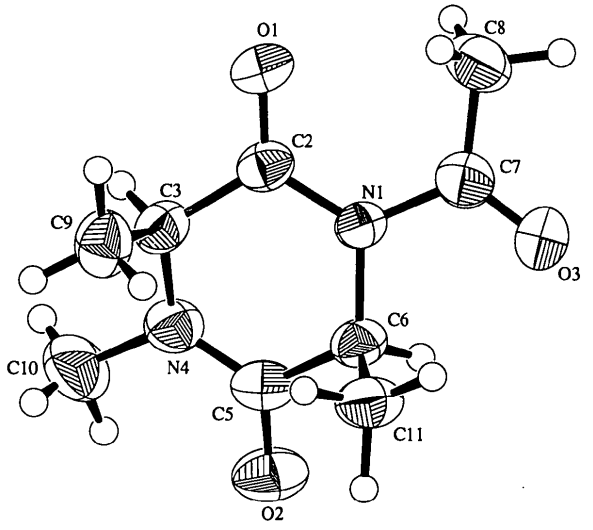


Fig. 1. View of *cyclo-N*-acetyl-L-alanyl-*N*-methyl-L-alanyl showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radii.

Bond lengths and angles involving the non-H atoms of (1) are generally comparable with those of (2) and (3). A notable difference lies in the length of the endocyclic amide bond adjacent to the *N*-acetyl substituent, which is almost 0.06 Å longer than the other amide bond in the molecule [1.389 (3) and 1.331 (3) Å, respectively]. This presumably reflects the nature of the *N*-substituent in the amide linkage: the double-bond character of the endocyclic amide bond adjacent to the *N*-acetyl substituent is diminished since the lone pair at the N atom can also delocalize onto the exocyclic amide bond. The bond angle C(6)—N(1)—C(2) is slightly smaller than C(3)—N(4)—C(5) and analogous angles in (2) and (3).

Experimental

cyclo-N-Me-L-Ala-L-Ala, (3), was synthesized from the corresponding dipeptide ester following the procedures of Slater (1969). The diketopiperazine was then treated with acetic anhydride (10 × mass) at 393 K for 4 h. The desired compound, (1), was purified by flash chromatography and recrystallized from a solvent mixture of ethyl acetate and petroleum spirit.

Crystal data

$C_9H_{14}N_2O_3$	Cu $K\alpha$ radiation
M_r = 198.22	λ = 1.5418 Å
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	θ = 43.1–49.9°
a = 7.799 (1) Å	μ = 0.815 mm^{-1}
b = 11.2750 (8) Å	T = 213 K
c = 11.622 (1) Å	Sphere
V = 1022.0 (2) Å^3	0.24 × 0.22 × 0.18 mm
Z = 4	Colourless
D_x = 1.288 Mg m^{-3}	

Data collection

Rigaku AFC-6*R* diffractometer	830 observed reflections [$I \geq 3\sigma(I)$]
$\omega/2\theta$ scans	θ_{max} = 60.04°
Absorption correction: ψ scan	$h = 0 \rightarrow 8$
T_{min} = 0.907, T_{max} = 0.998	$k = 0 \rightarrow 12$
923 measured reflections	$l = 0 \rightarrow 13$
923 independent reflections	3 standard reflections monitored every 150 reflections
	intensity decay: 3.16%

Refinement

Refinement on F	$\Delta\rho_{max}$ = 0.11 e Å^{-3}
R = 0.029	$\Delta\rho_{min}$ = −0.10 e Å^{-3}
wR = 0.023	Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
S = 3.56	Extinction coefficient: 223 (8) × 10^{-5}
830 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
184 parameters	
All H-atom parameters refined	
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.003F_o^2)^2]$	
$(\Delta/\sigma)_{max}$ = 0.042	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O(1)	−0.6156 (3)	0.1781 (2)	−0.5425 (2)	0.0628 (7)
O(2)	−0.5475 (3)	−0.2623 (1)	−0.6902 (2)	0.0678 (7)
O(3)	−0.9112 (3)	0.0544 (2)	−0.8027 (2)	0.0934 (9)
N(1)	−0.6882 (3)	0.0415 (2)	−0.6802 (2)	0.0436 (6)
N(4)	−0.4530 (3)	−0.1134 (2)	−0.5782 (2)	0.0531 (8)
C(2)	−0.5872 (4)	0.0851 (2)	−0.5914 (2)	0.0448 (8)
C(3)	−0.4345 (4)	0.0127 (3)	−0.5560 (3)	0.0490 (9)
C(5)	−0.5440 (4)	−0.1561 (2)	−0.6658 (2)	0.0482 (9)
C(6)	−0.6436 (4)	−0.0707 (2)	−0.7387 (2)	0.0470 (9)
C(7)	−0.8301 (4)	0.1030 (3)	−0.7280 (3)	0.058 (1)
C(8)	−0.8776 (6)	0.2240 (4)	−0.6881 (4)	0.069 (1)
C(9)	−0.2702 (5)	0.0643 (4)	−0.6047 (4)	0.065 (1)
C(10)	−0.3473 (7)	−0.1946 (4)	−0.5087 (4)	0.078 (1)
C(11)	−0.5498 (6)	−0.0496 (3)	−0.8522 (3)	0.060 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

O(1)—C(2)	1.213 (3)	N(1)—C(7)	1.418 (4)
O(2)—C(5)	1.231 (3)	N(4)—C(5)	1.331 (3)
N(1)—C(2)	1.389 (3)		
C(2)—N(1)—C(6)	120.8 (2)	N(4)—C(3)—C(2)	113.9 (3)
C(3)—N(4)—C(5)	122.9 (2)	N(4)—C(5)—C(6)	118.5 (2)
N(1)—C(2)—C(3)	117.5 (2)	N(1)—C(6)—C(5)	114.3 (2)

Table 3. *Torsion angles* (°)

C(2)—N(1)—C(6)—C(5)	φ_1	27.1 (3)
C(5)—N(4)—C(3)—C(2)	φ_2	31.3 (4)
N(1)—C(6)—C(5)—N(4)	ψ_1	−24.1 (4)
N(4)—C(3)—C(2)—N(1)	ψ_2	−27.2 (4)
C(3)—C(2)—N(1)—C(6)	ω_1	−1.3 (3)
C(6)—C(5)—N(4)—C(3)	ω_2	−5.2 (4)

The θ-scan width used was $(0.80 + 0.3\tan\theta)°$ at a speed of 8.0° min^{-1} in ω. The weak reflections were rescanned a maximum of 4 times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. The structure was solved by direct methods and expanded using Fourier techniques (Beurskens *et al.*, 1992).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-3-Hydroxytricyclo[7.5.0.0^{3,8}]tetradec-1(9)-en-2-one

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Abstract

The stereochemistry at the single-bond ring junction in the title compound, $C_{14}H_{20}O_2$, indicates that in the transposition reaction leading to its formation the most stable *cis* product is produced. The cycloheptene ring is disordered over two positions related by a pseudo-mirror perpendicular to the ring-junction double bond. The hydroxyl group is involved in an intermolecular hydrogen bond.

Comment

As part of our research program dealing with the synthesis of polycyclic cyclopentane derivatives, we considered reactions of the type shown below, the mechanism of which has been reported elsewhere (Jamart-