longueurs comparables aux longueurs moyennes généralement admises pour leurs homologues respectives. La Fig. 3 montre que le cycle *C* rappelle un cycle chaise. C(10) est à 0,717 (4) Å du plan moyen défini par C(5a), C(9b), C(11) et C(12), tandis que N(5), C(12a) et C(4a) sont de l'autre côté du même plan à des distances comprises entre 0,582 (3) et 1,552 (3) Å. De plus, le pentagone C(4a)N(5)C(5a)C(12)C(12a) est presque plan puisque les atomes N(5) et C(5a), les plus éloignés de son plan moyen, en sont à moins de 0,30 Å. C(12) est dans le plan du noyau *D* et N(5) en est distant seulement de 0,079 (6) Å. Les 'symétries dominantes', au sens de Duax & Norton (1975), sont la symétrie par rapport à la droite qui joint les milieux de C(4a)—N(5) et de C(10)—C(11) et la symétrie par rapport à un plan passant par C(4a) et C(10) et qui, dans le cas d'un cycle octogonal régulier, contiendrait l'axe perpendiculaire au plan de l'octogone en son centre. Les paramètres d'asymétrie $\Delta C_2^{4a,5}$ et ΔC_s^{4a} valent respectivement 14,9 et 49,6°. Dans le cycle *C*, la moyenne des angles dièdres est égale à 58,4°. La jonction des cycles *B* et *C* est du type *cis*.

La cohésion de la structure est due uniquement à des interactions de van der Waals.

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(6*S*)-1,4-Diazabicyclo[4.4.0]dec-8-ene-2,5-dione Monohydrate, $C_8H_{10}N_2O_2.H_2O$

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Abstract. $M_r = 184{\cdot}2$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 6{\cdot}888\ (1)$, $b = 26{\cdot}921\ (6)$, $c = 4{\cdot}852\ (4)$ Å, $V = 900\ (1)$ Å^3, $D_c = 1{\cdot}36$ Mg m^{-3}, $F(000) = 392$, $T = 295$ K, $\mu(\text{Mo }K\alpha) = 0{\cdot}113$ mm^{-1}. $R_w = 0{\cdot}028$ for 557 reflections with $I > 3\sigma(I)$ out of 960 independent measurements using Zr-filtered Mo radiation ($\theta_{\max} = 25°$). The piperidine ring has a half-chair conformation and the diketopiperazine ring a flattened twist-boat form. In the solid state the molecules do not dimerize but form chains in which three organic moieties are linked to one water molecule of crystallization.

Introduction. The title compound, shown in Fig. 1, contains the 2,5-diketopiperazine moiety (abbreviated as DKP). It is a cyclic dipeptide composed of L-baikain acid and glycine, also known as *cyclo*(-L-Bai-Gly-).

The biological and pharmacological properties of cyclic dipeptides together with their rigidity make DKP derivatives interesting model compounds for peptide conformational analysis. Typical aspects are the shape of the DKP ring and the tendency to form dimers through hydrogen bonding. The X-ray determination reported here is one of a series, the reports of which should be useful in the interpretation of NMR spectra and chemical activity.

Experimental. A good crystal of the title compound was obtained in an NMR tube after slow evaporation from the deutero-chloroform solution.

Intensities measured at room temperature, Enraf–Nonius CAD-4 diffractometer, pure ω scan; absorption correction omitted because of the small size of the crystal (0·2 × 0·1 × 0·1 mm) and the low absorption

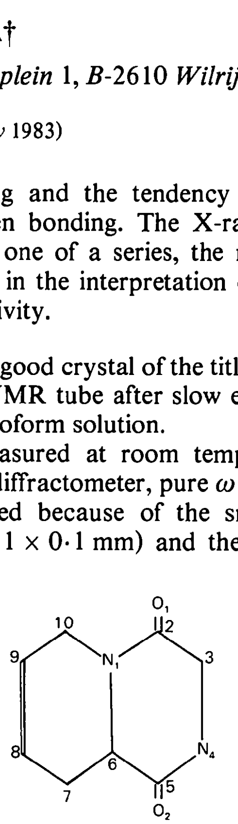

Fig. 1. Structural formula and numbering of atoms.

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coefficient; structure solved using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by least-squares [$\sum w(\Delta F)^2$ minimized]; weighting scheme based on counting statistics. An unexpected water molecule of crystallization and all H atoms were found from difference electron density maps; the Debye–Waller temperature parameters of H atoms were kept fixed at 4 Å^2. Correction for extinction effects unnecessary; $R_w = 0{\cdot}028$, the maximum noise level in the final difference Fourier map was 0·2 e Å^{-3}, atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates and $B_{\rm iso}$ values* are listed in Table 1, the atomic numbering scheme is given in Fig. 1.

Bond lengths and valence angles, listed in Table 2, are similar to values found in analogous derivatives (Ramani, Sasisekhara & Venkatesan, 1977; Van Poucke & Lenstra, 1982*a,b*; Van Poucke, Geise & Lenstra, 1983). The piperidine ring has a half-chair conformation, while the DKP ring has a shallow twist-boat form with the pseudo twofold axis passing through the keto functions. Using the notation introduced by Boeyens (1978) the rings approach forms denoted as $^2H_1$ and $^1T_3$, respectively. The corresponding puckering parameters (Cremer & Pople, 1975) as well as the endocyclic torsion angles are presented in Table 3.

A parameter of interest to NMR spectroscopists is the angle between the C(3)C(2)N(1)C(6) and C(3)-N(4)C(5)C(6) planes. Its value is 12 (1)°, showing that the DKP ring in the title compound is rather flat. In similar compounds values in the range 18–26° are observed. The same conclusion also follows from a comparison of torsion angles and Cremer & Pople puckering parameters.

A pyramidal configuration around the peptide N(1) atom in a number of dipeptides has been observed (Sletten, 1970; Pattabhi, Venkatesan & Hall, 1973, 1974; Van Poucke & Lenstra, 1982*a,b*), whereas the planar configuration seems to occur less frequently (Van Poucke, Geise & Lenstra, 1983). In the title compound N(1) is insignificantly (*ca* 0·045 Å) above the C(2)C(6)C(10) plane. Nor do we observe in the surrounding valence and torsion angles (Tables 2, 3 and Fig. 2*a*) signs of an appreciable deviation from *sp*^{2} character. Note that in accordance with this view the N(1)–C(2) bond length (1·313 Å) is close to the lower limit of the range (1·30–1·38 Å) observed in DKP derivatives.

Table 1. *Positional parameters in fractions of the cell edges and isotropic temperature factors* (Å^2)

The e.s.d.'s given in parentheses refer to the last significant digit. Isotropic temperature factors are calculated from anisotropic temperature parameters assuming equal volume of the 50% probability region. All anisotropic temperature parameters were physically acceptable. $B_{\rm iso}$ for non-hydrogen atoms was calculated according to Lipson & Cochran (1968):

$B_{\rm iso} = 8\pi^2[U^0_{11}U^0_{22}U^0_{33}]^{1/3}$. H atom H ($j,x$) with j = 1,2 is attached to atom x.

	x	y	z	$B_{\rm iso}$
O(1)	0·5018 (4)	0·1972 (1)	−0·2653 (7)	4·96
O(2)	0·8556 (4)	0·0951 (1)	0·5345 (7)	5·99
N(1)	0·4959 (4)	0·1330 (1)	0·0307 (8)	3·88
C(2)	0·5786 (5)	0·1719 (1)	−0·0817 (9)	3·79
C(3)	0·7767 (6)	0·1864 (1)	0·0116 (9)	4·68
N(4)	0·8503 (4)	0·1599 (1)	0·2465 (8)	3·92
C(5)	0·7788 (6)	0·1183 (1)	0·3445 (9)	4·44
C(6)	0·5915 (5)	0·0990 (1)	0·2238 (9)	3·66
C(7)	0·6235 (6)	0·0487 (1)	0·0810 (9)	4·56
C(8)	0·4439 (6)	0·0325 (1)	−0·0670 (9)	5·21
C(9)	0·2992 (6)	0·0627 (1)	−0·1182 (9)	5·00
C(10)	0·2998 (6)	0·1167 (1)	−0·0540 (9)	4·82
O(*W*)	0·1553 (4)	0·2144 (1)	0·4659 (8)	6·46
H(1,C3)	0·772 (4)	0·216 (1)	0·060 (6)	4·00
H(2,C3)	0·861 (4)	0·182 (1)	−0·132 (6)	4·00
H(N4)	0·959 (4)	0·170 (1)	0·351 (6)	4·00
H(C6)	0·487 (4)	0·100 (1)	0·391 (6)	4·00
H(1,C7)	0·648 (4)	0·025 (1)	0·218 (6)	4·00
H(2,C7)	0·747 (4)	0·052 (1)	−0·061 (6)	4·00
H(C8)	0·449 (4)	−0·004 (1)	−0·108 (7)	4·00
H(C9)	0·192 (4)	0·049 (1)	−0·220 (6)	4·00
H(1,C10)	0·253 (4)	0·147 (1)	−0·229 (6)	4·00
H(2,C10)	0·214 (4)	0·127 (1)	0·093 (6)	4·00
H(1,O*W*)	0·122 (4)	0·241 (1)	0·425 (6)	4·00
H(2,O*W*)	0·273 (4)	0·209 (1)	0·538 (6)	4·00

Table 2. *Bond lengths* (Å) *and valence angles* (°)

Estimated standard deviations are *ca* 0·005 Å and 0·4°, respectively.

N(1)–C(2)	1·313	C(5)–O(2)	1·234
N(1)–C(10)	1·478	C(6)–C(7)	1·534
N(1)–C(6)	1·469	C(7)–C(8)	1·495
C(2)–C(3)	1·489	C(8)–C(9)	1·310
C(2)–O(1)	1·242	C(9)–C(10)	1·486
C(3)–N(4)	1·438	N(4)–H	0·94 (8)
N(4)–C(5)	1·315	⟨C–H⟩	1·00 (5)
C(5)–C(6)	1·509		
N(1)–C(2)–C(3)	118·6	C(8)–C(7)–C(6)	110·8
C(2)–C(3)–N(4)	115·7	C(7)–C(6)–N(1)	109·1
C(3)–N(4)–C(5)	125·5	C(6)–N(1)–C(10)	113·6
N(4)–C(5)–C(6)	118·2	N(4)–C(5)–O(2)	122·9
C(5)–C(6)–N(1)	124·8	C(6)–C(5)–O(2)	118·8
C(6)–N(1)–C(2)	124·8	C(3)–C(2)–O(1)	117·7
N(1)–C(10)–C(9)	110·5	N(1)–C(2)–O(1)	123·6
C(10)–C(9)–C(8)	124·4	C(7)–C(6)–C(5)	110·8
C(9)–C(8)–C(7)	122·7	C(2)–N(1)–C(10)	121·2

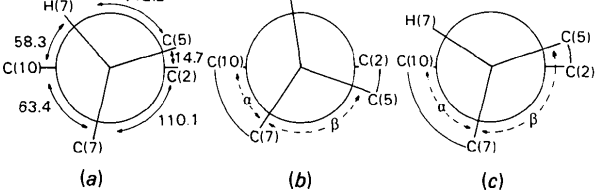

Fig. 2. Newman projections along C(6)–N(1) showing the type of fusion: (*a*) observed in *cyclo* (-L-Bai-Gly-), (*b*) *trans*-like fusion, (*c*) *cis*-like fusion. (Angles in degrees.)

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38455 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Endocyclic torsion angles and Cremer & Pople ring puckering parameters*

(*a*) Torsion angles (°), using the sign convention of IUPAC (1974). E.s.d.'s are about 0·8°.

DKP ring		Piperidine ring	
N(1)–C(2)–C(3)–N(4)	−8·2	N(1)–C(6)–C(7)–C(8)	−46·2
C(2)–C(3)–N(4)–C(5)	15·5	C(6)–C(7)–C(8)–C(9)	14·6
C(3)–N(4)–C(5)–C(6)	−7·1	C(7)–C(8)–C(9)–C(10)	4·3
N(4)–C(5)–C(6)–N(1)	−7·6	C(8)–C(9)–C(10)–N(1)	9·5
C(5)–C(6)–N(1)–C(2)	14·7	C(9)–C(10)–N(1)–C(6)	−43·9
C(6)–N(1)–C(2)–C(3)	−6·5	C(10)–N(1)–C(6)–C(7)	63·5

(*b*) Ring-puckering parameters, using the sequences N(1)C(2)C(3)N(4)C(5)C(6) and N(1)C(6)C(7)C(8)C(9)C(10). E.s.d.'s are calculated according to Norrestam (1981).

	DKP ring	Piperidine ring
q_2(Å)	0·163 (12)	0·388 (13)
q_3(Å)	−0·001 (12)	−0·294 (13)
Q (Å)	0·163 (12)	0·487 (13)
φ (°)	322 (4)	216 (2)
θ (°)	90 (4)	127 (2)

Table 4. *Hydrogen bonding in the title compound* (*D*: *donor*, *A*: *acceptor*)

D–H	*A*	*A* at	*D*···*A*(Å)	H···*A*(Å)	*D*–H···*A*(°)
N(4)–H(N4)···	O(*W*)	1+*x*,*y*,*z*	2·774 (5)	1·80 (3)	155 (2)
O(*W*)–H(1,O*W*)···	O(1)	$-\frac{1}{2}+x,\frac{1}{2}+y,-z$	2·780 (5)	2·02 (3)	169 (3)
O(*W*)–H(2,O*W*)···	O(1)	*x*,*y*,1+*z*	2·759 (5)	1·87 (3)	172 (3)

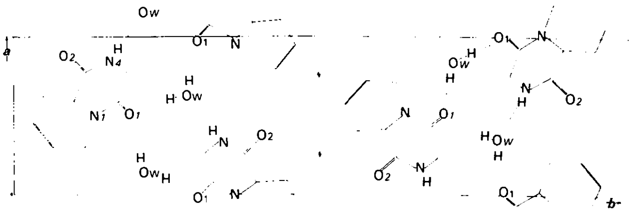

Fig. 3. Crystal packing of the title compound projected along the *c* axis.

A difference between the title compound and most other bicyclic dipeptides containing the DKP ring is the way the two rings are fused. The fusion (see Fig. 2) is *cis*-like in *cyclo*(-L-Bai-Gly-), but *trans*-like in most others.

The type of fusion and the hybridization of N(1) will depend upon the value of $\gamma = 180 - \alpha - \beta$ (Fig. 2*b*,*c*). One expects a *trans*-like fusion if $\gamma > 0°$, a *cis*-like fusion if $\gamma < 0°$ and a greater deviation from sp^2-hybridization the more $|\gamma|$ deviates from *ca* 15°. Here $\gamma = -8{\cdot}2°$. It follows that the double bond between C(8) and C(9), by way of its accompanying torsion angles in the piperidine ring, dominates the shape of the DKP ring. The packing is shown in Fig. 3. In contrast to many other crystalline DKP derivatives the title compound does not form dimers, but double chains, in which three DKP moieties are held together by one water molecule of crystallization. The H-bridging scheme is presented in Table 4.

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