

C5A—C6A	1.374 (2)	C8B—C9B	1.450 (2)	Goud, B. S., Pathaneni, S. S. & Desiraju, G. R. (1993). <i>Acta Cryst.</i> C49 , 1107–1111.
C6A—F5A	1.340 (2)	C9B—O2B	1.251 (2)	Johnson, C. K. (1976). <i>ORTEPII</i> . Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
C7A—C8A	1.325 (3)	C9B—O1B	1.293 (2)	Leiserowitz, L. (1976). <i>Acta Cryst.</i> B32 , 775–802.
C8A—C9A	1.469 (2)	C10B—N1B	1.449 (2)	Motherwell, W. D. S. & Clegg, W. (1978). <i>PLUTO</i> . Program for Plotting Molecular and Crystal Structures. Univ. of Cambridge, England.
C9A—O2A	1.246 (2)	C11B—N1B	1.446 (2)	Sarma, J. A. R. P. & Desiraju, G. R. (1985). <i>J. Chem. Soc. Perkin Trans. 2</i> , pp. 1905–1912.
C2A—C1A—C6A	115.2 (2)	C7A—C8A—C9A	120.3 (2)	Schmidt, G. M. J. (1964). <i>J. Chem. Soc.</i> pp. 2014–2021.
C2A—C1A—C7A	119.6 (2)	O2A—C9A—O1A	123.6 (2)	Sharma, C. V. K., Panneerselvam, K., Pilati, T. & Desiraju, G. R. (1993). <i>J. Chem. Soc. Perkin Trans. 2</i> , pp. 2209–2217.
C6A—C1A—C7A	125.2 (2)	O2A—C9A—C8A	121.6 (2)	Sheldrick, G. M. (1990). <i>Acta Cryst.</i> A46 , 467–473.
F1A—C2A—C3A	117.2 (2)	O1A—C9A—C8A	114.9 (2)	Sheldrick, G. M. (1994). <i>SHELXL93</i> . Program for the Refinement of Crystal Structures. Univ. of Göttingen, Germany.
F1A—C2A—C1A	119.8 (2)	C6B—C1B—C2B	117.1 (2)	Weber, E., Hecker, M., Csoregh, I. & Czugler, M. (1989). <i>J. Am. Chem. Soc.</i> 111 , 7866–7872.
C3A—C2A—C1A	123.0 (2)	C6B—C1B—C7B	119.8 (2)	
F2A—C3A—C4A	119.9 (2)	C2B—C1B—C7B	123.0 (2)	
F2A—C3A—C2A	120.5 (2)	C3B—C2B—C1B	121.7 (2)	
C4A—C3A—C2A	119.6 (2)	C2B—C3B—C4B	120.8 (2)	
F3A—C4A—C3A	120.0 (2)	N1B—C4B—C5B	121.6 (2)	
F3A—C4A—C5A	120.4 (2)	N1B—C4B—C3B	121.1 (2)	
C3A—C4A—C5A	119.6 (2)	C5B—C4B—C3B	117.3 (2)	
F4A—C5A—C4A	119.8 (2)	C6B—C5B—C4B	121.1 (2)	
F4A—C5A—C6A	120.1 (2)	C5B—C6B—C1B	122.0 (2)	
C4A—C5A—C6A	120.1 (2)	C8B—C7B—C1B	128.0 (2)	
F5A—C6A—C5A	117.1 (2)	C7B—C8B—C9B	121.5 (2)	
F5A—C6A—C1A	120.4 (2)	O2B—C9B—O1B	122.5 (2)	
C5A—C6A—C1A	122.4 (2)	O2B—C9B—C8B	121.7 (2)	
C8A—C7A—C1A	128.4 (2)	O1B—C9B—C8B	115.8 (2)	

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

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H1A...O2B	0.98 (3)	1.64 (3)	2.618 (1)	173 (3)
O1B—H1B...O2A	0.90 (3)	1.74 (3)	2.626 (1)	169 (3)
C8A—H8A...O1A ⁱ	1.00 (2)	2.904 (19)	3.882 (4)	167 (1)
C2B—H2B...O1B ⁱⁱ	0.97 (2)	2.689 (18)	3.374 (4)	129 (1)
C3B—H3B...O2A ⁱⁱⁱ	0.99 (2)	2.872 (19)	3.820 (4)	159 (1)
C5B—H5B...O1A ⁱⁱⁱ	0.96 (2)	2.90 (2)	3.633 (4)	135 (1)
C6B—H6B...O2B ⁱⁱⁱ	0.97 (2)	2.92 (2)	3.571 (4)	125 (1)
C10B—H102B...O1B ^{iv}	1.03 (2)	2.91 (2)	3.318 (4)	105 (1)
C11B—H112B...O1A ⁱⁱⁱ	0.96 (2)	2.90 (2)	3.525 (4)	162 (2)
C11B—H113B...O1A ^{iv}	1.05 (2)	2.90 (2)	3.888 (4)	158 (2)
C2B—H2B...F2A ^v	0.97 (2)	2.687 (19)	3.420 (2)	133 (1)
C7B—H7B...F4A ⁱ	0.89 (2)	2.635 (19)	3.479 (4)	161 (1)
C8B—H8B...F1A ⁱ	0.94 (2)	2.781 (18)	3.556 (4)	141 (1)
C10B—H101B...F3A ^{vi}	1.04 (2)	2.76 (2)	3.607 (4)	152 (2)
C10B—H101B...F1A ⁱⁱ	1.04 (2)	2.80 (2)	3.491 (4)	124 (1)
C11B—H111B...F3A ^{vi}	0.96 (2)	2.39 (3)	3.346 (3)	175 (2)

Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $2 - x, 2 - y, 3 - z$; (iii) $2 - x, 1 - y, 3 - z$; (iv) $x, y, 1 + z$; (v) $2 - x, 2 - y, 2 - z$; (vi) $1 + x, y, 2 + z$.

Data collection: Syntex R3 diffractometer. Cell refinement: Syntex R3 diffractometer. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *ORTEPII* (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978). 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: HR1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,5-Diamino-6-(2-methylphenyl)-1,2,4-triazine Monohydrate: an Analogue of Lamotrigine

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Abstract

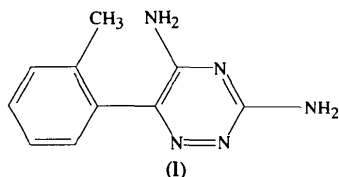
The asymmetric unit of $2C_{10}H_{11}N_5 \cdot H_2O$ contains two conformers of the triazine molecule and a water molecule; each conformer has distinct dihedral angles between the respective phenyl and triazine rings [100.8(1) and 61.7(1)°]. These two conformers exhibit significant differences in certain bond lengths and angles which may arise because of their different dihedral angles. Although crystallized from acetonitrile, the extensive hydrogen-bonding network that maintains the crystal structure incorporates a water molecule.

Comment

The molecule studied is an analogue of the anticonvulsant 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazine, known as lamotrigine (Janes, Lisgarten & Palmer, 1989), and was supplied by Wellcome Pharmaceuticals (UK). The structure was determined as part of an on-going investigation into structure–activity studies on a series of lamotrigine analogues (Janes & Palmer,

1995*a,b*). The single crystal was grown by slow evaporation from acetonitrile, but no precautions were taken to dry the solvent. As a result of previous studies where methanol solvent molecules had been included in the structure, the crystal was mounted in a capillary tube with mother liquor present as a precaution against possible drying and loss of crystallinity.

Two conformations of the 2-methylphenyl analogue (I) exist in the asymmetric unit, and a prime is added in the numbering scheme to the second conformer to distinguish between them. A water molecule was also found in the structure and it is probable that it came from the solvent. The ring moieties of both conformations are planar and the methyl substituent C atoms lie in the planes of their respective phenyl rings. The amino N5 atom is displaced 0.150 (1) Å from its triazine ring, while the remaining amino N atoms are planar with their rings. There is a marked difference between the dihedral angles of the two conformers; 100.8 (1)° for the first and 61.7 (1)° for the second. There are also differences in bond lengths, both within each phenyl ring and in comparisons between comparable bonds between the phenyl rings. Within the triazine rings the N1—N2 and N4—C5*t* bonds exhibit significant differences in length between the two conformers. Some of the corresponding angles within the phenyl and triazine ring moieties also exhibit differences. While the bonds of the amino groups in the first conformer are identical in length, those of the second conformer differ significantly.



There is pronounced distortion within the first conformer in the relative juxtapositions of the phenyl and triazine rings, particularly with respect to their common axis, denoted by C3*t*, C6*t*, C1 and C4. C4 is displaced 0.252 (1) Å from the triazine ring plane, while the non-bonding angle C3*t* · · C6*t* · · C4 is 170.6 (1)°. In comparison, the second conformer is far less distorted (Fig. 1).

There is an extensive hydrogen-bonding network within the crystal structure, incorporating the triazine rings of both conformers and the water molecule. However, while there are seven potential sites for hydrogen bonding around the triazine ring moiety, only five and six are utilized by the two conformers, respectively. Both conformers form dimers coupled by a centre of symmetry between their respective N4 and H31 atoms and this dimeric form has not been found in previous studies of related analogue structures (Janes, Lisgarten & Palmer, 1989; Janes & Palmer, 1995*a,b*). For both conformers H51 remains unused for hydrogen bonding, while H32 is not used in the first conformer.

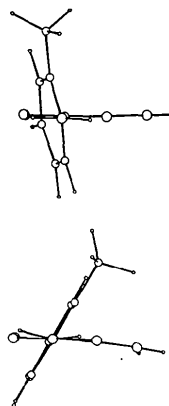


Fig. 1. View (SNOOPI; Davies, 1983) along the triazine ring atoms C3*t* and C6*t*, and C3*t*' and C6*t*' of the two conformers, illustrating both the differences in dihedral angles and the degree of distortion present in each of the molecules.

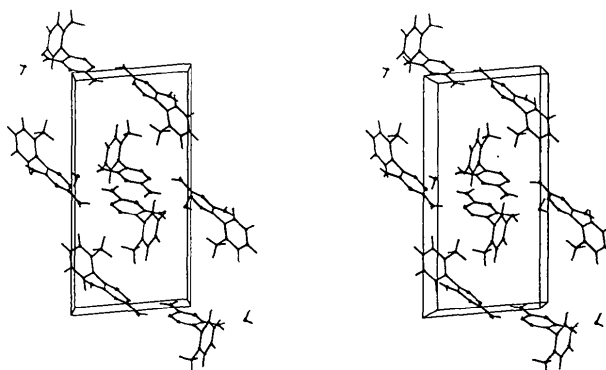


Fig. 2. Stereoview (SNOOPI; Davies, 1983) of the molecular packing along the *b* axis.

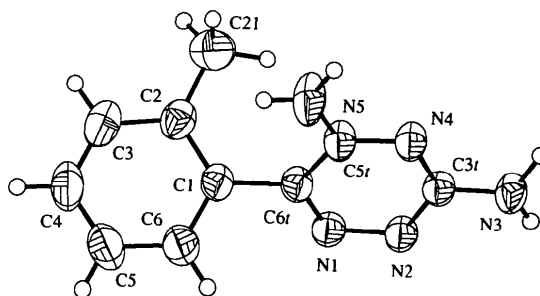


Fig. 3. Thermal ellipsoid plot (50% probability) of the title molecule showing the atomic labelling scheme.

Experimental

Crystal data

$2C_{10}H_{11}N_5 \cdot H_2O$
 $M_r = 420.4$
 Monoclinic
 $P2_1/n$
 $a = 9.672 (2) \text{ \AA}$
 $b = 11.690 (2) \text{ \AA}$
 $c = 19.184 (4) \text{ \AA}$
 $\beta = 95.12 (2)^\circ$

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 9-32^\circ$
 $\mu = 0.73 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Prismatic

$V = 2160.4 (6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.29 \text{ Mg m}^{-3}$

$0.30 \times 0.30 \times 0.30 \text{ mm}$
 Colourless
 Crystal source: crystallized
 from acetonitrile

Data collection

Enraf-Nonius CAD-4
 diffractometer

ω - 2θ scans

Absorption correction:
 none

8893 measured reflections

4107 independent reflections

3373 observed reflections
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.0081$

$\theta_{\text{max}} = 60^\circ$

$h = 0 \rightarrow 11$

$k = -14 \rightarrow 14$

$l = -23 \rightarrow 23$

3 standard reflections

frequency: 60 min

intensity decay: <10%

Refinement

Refinement on F

$R = 0.0566$

$wR = 0.0767$

$S = 1.37$

3373 reflections

341 parameters

All H-atom parameters
 refined

$w = 1.0/[\sigma^2(F)$
 $+ 0.010180(F)^2]$

$(\Delta/\sigma)_{\text{max}} = 0.640$

$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering fac-
 tors from *SHELX76*
 (Sheldrick, 1976)

C1—C6 t	1.493 (3)	C6 t —N1	1.310 (3)
N1—N2	1.341 (2)	N2—C3 t	1.346 (3)
C3 t —N4	1.344 (3)	N4—C5 t	1.338 (3)
C5 t —C6 t	1.432 (2)	C3 t —N3	1.334 (3)
C5 t —N5	1.333 (3)	C2—C21	1.494 (4)
C1 t —C2 t	1.411 (3)	C2 t —C3 t	1.395 (3)
C3 t —C4 t	1.398 (4)	C4 t —C5 t	1.355 (4)
C5 t —C6 t	1.384 (3)	C6 t —C1 t	1.391 (3)
C1 t —C6 t	1.485 (2)	C6 t —N1 t	1.300 (2)
N1 t —N2 t	1.355 (2)	N2 t —C3 t	1.341 (2)
C3 t —N4 t	1.347 (2)	N4 t —C5 t	1.327 (2)
C5 t —C6 t	1.439 (3)	C3 t —N3 t	1.342 (2)
C5 t —N5 t	1.331 (2)	C2 t —C21 t	1.497 (4)
C1—C2—C3	118.5 (2)	C1 t —C2 t —C3 t	117.7 (2)
C2—C3—C4	121.0 (2)	C2 t —C3 t —C4 t	121.5 (2)
C3—C4—C5	120.5 (3)	C3 t —C4 t —C5 t	120.1 (2)
C4—C5—C6	119.4 (3)	C4 t —C5 t —C6 t	120.0 (3)
C5—C6—C1	120.6 (2)	C5 t —C6 t —C1 t	121.2 (2)
C6—C1—C2	119.9 (2)	C6 t —C1 t —C2 t	119.6 (2)
C2—C1—C6 t	119.9 (2)	C2 t —C1 t —C6 t	122.2 (2)
C6—C1—C6 t	119.8 (2)	C6 t —C1 t —C6 t	118.2 (2)
C1—C6 t —N1	116.3 (2)	C1 t —C6 t —N1 t	119.1 (2)
C6 t —N1—N2	121.7 (2)	C6 t —N1 t —N2 t	121.1 (2)
N1—N2—C3 t	117.7 (2)	N4 t —C3 t —N3 t	121.7 (2)
N2—C3 t —N4	125.0 (2)	N2 t —C3 t —N4 t	125.9 (2)
C3 t —N4—C5 t	116.3 (2)	C3 t —N4 t —C5 t	115.6 (2)
N4—C5 t —C6 t	120.3 (2)	N4 t —C5 t —C6 t	120.4 (2)
C5 t —C6 t —N1	118.9 (2)	C5 t —C6 t —N1 t	119.5 (2)
C5 t —C6 t —C1	124.7 (2)	C5 t —C6 t —C1 t	121.4 (2)
N2—C3 t —N3	115.8 (2)	N2 t —C3 t —N3 t	116.8 (2)
N4—C3 t —N3	119.2 (2)	N1 t —N2 t —C3 t	117.2 (2)
N4—C5 t —N5	119.6 (2)	N4 t —C5 t —N5 t	118.6 (2)
C6 t —C5 t —N5	120.1 (2)	C6 t —C5 t —N5 t	121.0 (2)
C1—C2—C21	121.6 (2)	C1 t —C2 t —C21 t	123.2 (2)
C3—C2—C21	119.9 (2)	C3 t —C2 t —C21 t	119.1 (2)

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

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

	x	y	z	U_{eq}
C1	-0.1122 (2)	0.4359 (2)	-0.1331 (1)	0.047 (1)
C2	-0.0946 (2)	0.4560 (2)	-0.2028 (1)	0.054 (1)
C3	-0.1416 (3)	0.5607 (2)	-0.2326 (1)	0.065 (1)
C4	-0.2049 (3)	0.6407 (2)	-0.1938 (2)	0.071 (1)
C5	-0.2282 (3)	0.6184 (3)	-0.1253 (2)	0.070 (1)
C6	-0.1809 (3)	0.5167 (2)	-0.0947 (1)	0.060 (1)
C21	-0.0219 (4)	0.3721 (3)	-0.2456 (2)	0.082 (2)
N1	0.0897 (2)	0.3437 (2)	-0.0792 (1)	0.055 (1)
N2	0.1615 (2)	0.2597 (2)	-0.0450 (1)	0.057 (1)
C3 t	0.0912 (2)	0.1658 (2)	-0.0280 (1)	0.046 (1)
N4	-0.0451 (2)	0.1482 (1)	-0.0445 (1)	0.046 (1)
C5 t	-0.1142 (2)	0.2323 (2)	-0.0798 (1)	0.043 (1)
C6 t	-0.0440 (2)	0.3352 (2)	-0.0966 (1)	0.047 (1)
N3	0.1651 (2)	0.0867 (2)	0.0091 (1)	0.058 (1)
N5	-0.2488 (2)	0.2193 (2)	-0.0999 (1)	0.056 (1)
C1 t	0.8190 (2)	0.1842 (2)	0.1726 (1)	0.045 (1)
C2 t	0.8365 (2)	0.2283 (2)	0.2412 (1)	0.051 (1)
C3 t	0.9337 (3)	0.1752 (2)	0.2887 (1)	0.065 (1)
C4 t	1.0133 (3)	0.0828 (3)	0.2690 (2)	0.072 (1)
C5 t	0.9967 (3)	0.0427 (2)	0.2025 (2)	0.072 (2)
C6 t	0.8984 (3)	0.0913 (2)	0.1546 (1)	0.058 (1)
C21 t	0.7545 (3)	0.3271 (3)	0.2653 (2)	0.073 (1)
N1 t	0.6164 (2)	0.1665 (1)	0.0913 (1)	0.044 (1)
N2 t	0.5211 (2)	0.2060 (1)	0.0409 (1)	0.045 (1)
C3 t	0.5309 (2)	0.3161 (2)	0.0224 (1)	0.041 (1)
N4 t	0.6306 (2)	0.3899 (1)	0.0469 (1)	0.045 (1)
C5 t	0.7267 (2)	0.3474 (2)	0.0935 (1)	0.047 (1)
C6 t	0.7157 (2)	0.2320 (2)	0.1184 (1)	0.043 (1)
N3 t	0.4354 (2)	0.3548 (2)	-0.0271 (1)	0.050 (1)
N5 t	0.8346 (2)	0.4129 (2)	0.1151 (1)	0.070 (1)
O1A	-0.4651 (2)	0.0562 (2)	-0.0804 (1)	0.077 (1)

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

C1—C2	1.384 (3)	C2—C3	1.408 (3)
C3—C4	1.373 (4)	C4—C5	1.378 (4)
C5—C6	1.386 (4)	C6—C1	1.401 (3)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N3—H31...N4 i	0.98 (4)	2.11 (4)	3.080 (3)	170.8 (3.2)
N5—H52...O1A ii	0.85 (3)	2.06 (3)	2.880 (3)	161.9 (2.9)
N3 i —H31 i ...N4 iii	0.95 (3)	2.15 (3)	3.068 (3)	162.4 (2.3)
N3 i —H32 i ...N2 ii	1.00 (4)	1.95 (4)	2.865 (3)	151.3 (3.0)
N5 i —H52 i ...N1 iii	0.88 (3)	2.17 (4)	3.032 (3)	167.7 (2.7)
O1A—H1A...N2 iv	0.92 (4)	2.10 (4)	2.925 (3)	148.5 (2.9)
O1A—H2A...N1 vi	0.86 (5)	2.20 (5)	2.985 (3)	152.7 (4.6)

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

All H atoms of the phenyl rings were positioned from geometry constraints, while the remaining H atoms were located in difference maps.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989).
 Program used to solve structure: *SHELX76* (Sheldrick, 1976).
 Program used to draw figures: *SNOOPI* (Davies, 1983).
 Additional molecular geometry calculations: *XANADU*
 (Roberts & Sheldrick, 1975) and *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Z-AzPro-AzPro-OBzl

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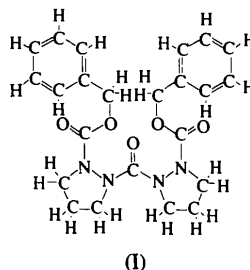
Abstract

The title compound, benzyl 1-(2-benzyloxycarbonyl-pyrazolidinylcarbonyl)pyrazolidine-2-carboxylate, $C_{23}H_{26}N_4O_5$, derived from the α -aza analogue of proline, crystallizes with two independent molecules per asymmetric unit, adopting two quasi mirror-image conformations. Because of steric hindrance and unfavourable polar interactions between the carbonyl groups connected to the same pyrazolidine ring, the N atoms lose part of their sp^2 character so that they are far from being planar and the N—CO bonds are noticeably longer than in peptides.

Comment

Aza peptides are peptide analogues where an N atom is substituted for the α -C atom in one or several constituent α -amino acids (Niedrich, 1967; Niedrich & Köller, 1974; Dutta & Morley, 1975; Gante, 1989), but their conformational properties have not been investigated until very recently. We have shown by X-ray diffraction and spectroscopic analysis that α -azaproline (AzPro) behaves as an 'anti-proline' residue, in the sense that it induces folding of the preceding sequence instead of the following sequence (Lecoq, Boussard, Marraud & Aubry, 1992, 1993). During the synthesis of AzPro derivatives using triphosgene as carbonyl-

ating agent, we obtained a secondary product which was shown to be an AzPro 'dimer' of formula Z-AzPro-AzPro-OBzl (I). Single crystals were obtained by slow evaporation of an ethyl acetate solution.



The unit cell contains two independent molecules with quasi-mirror-image conformations. Each of the molecules adopts an S-shaped structure in which the middle carbonyl bond can be considered as lying on a quasi-twofold axis (Fig. 1).

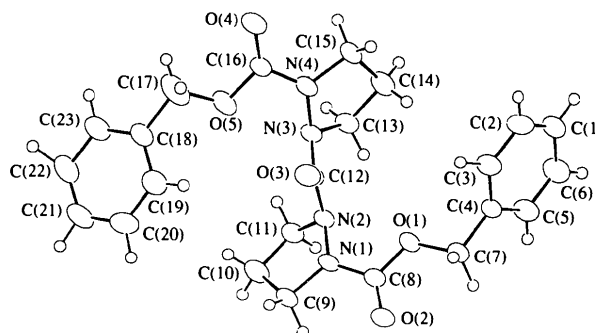


Fig. 1. ORTEP drawing (Johnson, 1965) of the title molecule A, projected along the middle C=O pseudo-twofold axis, showing 50% probability displacement ellipsoids.

Although both N atoms in the AzPro residue are acylated, their bond angles show that they are not strictly in the sp^2 electronic state, thus reducing the electronic conjugation of the N-atom lone pair with the carbonyl π -orbitals. This ensures that the N—CO bond is longer than the usual value (Benedetti, 1979) and that the N-atom lone pair is accessible to hydrogen bonding (Lecoq, Boussard, Marraud & Aubry, 1993). A planar conformation of the N atoms would induce severe steric hindrance between the carbonyl groups connected to the same pyrazolidine ring. The N—CO bonds tend to adopt antiperiplanar orientations with a C(=O)—N—N—C(=O) torsion angle of nearly $\pm 100^\circ$, thus conferring a chiral structure on the N atoms. Both (*R,R*)- and (*S,S*)-chiralities are equally possible for the prochiral AzPro residue and depend on the peptide sequence (Lecoq, Boussard, Marraud & Aubry, 1993). In the present case, the (*S,S*)-chirality is observed for molecule A and the (*R,R*)-chirality for molecule B.