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Z-AzPro-AzPro-OBzl

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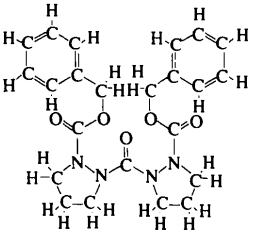
Abstract

The title compound, benzyl 1-(2-benzyloxycarbonyl-1-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 carbonylating 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.



(I)

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).

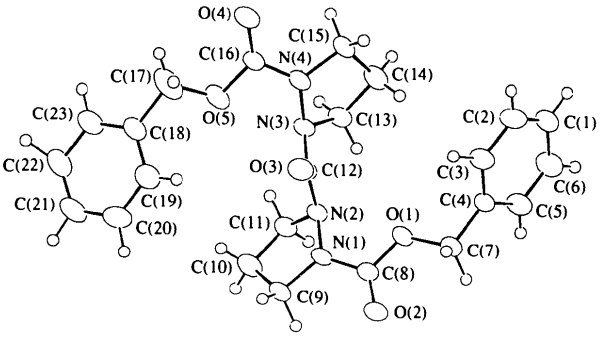


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the title molecule *A*, projected along the middle C═O pseudo-twofold axis, showing 50% probability displacement ellipsoids.

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 $\pm 100°$, 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*.

Of note is the *trans–cis* conformation of the urethane group, as already pointed out for the crystal structures of Z-AzPro-NH^{i}Pr and Z-AzPro-L-Ala-NH^{i}Pr (Lecoq, Boussard, Marraud & Aubry, 1993), and the *trans–trans* conformation of the AzPro-AzPro carbazide group. All four pyrrazolidine rings in molecules *A* and *B* assume an envelope conformation denoted by the small value of one of the intracyclic torsion angles (see Table 2).

Experimental

Crystal data

$C_{23}H_{26}N_4O_5$	Cu $K\alpha$ radiation
M_r = 438.48	λ = 1.5418 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1$	θ = 20–30°
a = 9.386 (1) Å	μ = 0.68 mm^{-1}
b = 27.912 (3) Å	T = 295 K
c = 9.463 (1) Å	Parallelepiped
β = 115.27 (2)°	0.4 × 0.3 × 0.3 mm
V = 2242 Å^3	Colourless
Z = 4	
D_x = 1.30 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.023
ω–2θ scans	θ_{max} = 70°
Absorption correction: none	$h = -11 \rightarrow 10$
4602 measured reflections	$k = 0 \rightarrow 34$
4509 independent reflections	$l = 0 \rightarrow 11$
4239 observed reflections [$I > 3\sigma(I)$]	2 standard reflections frequency: 90 min intensity decay: none

Refinement

Refinement on F	$w = 0.0316/[\sigma^2(F) + 0.00013F^2]$
R = 0.031	$(\Delta/\sigma)_{max}$ = 0.21
wR = 0.035	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
S = 2.37	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
4239 reflections	Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)
368 parameters	
Only coordinates of H atoms refined	

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

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Molecule *A*				
C(1)	0.2514 (3)	0.177	−0.3442 (4)	5.49 (9)
C(2)	0.2868 (3)	0.2233 (1)	−0.2975 (4)	5.87 (9)
C(3)	0.4273 (3)	0.2350 (1)	−0.1729 (3)	5.18 (8)
C(4)	0.5341 (3)	0.19979 (9)	−0.0942 (3)	4.04 (7)
C(5)	0.4969 (3)	0.1534 (1)	−0.1444 (4)	5.47 (9)
C(6)	0.3581 (4)	0.1419 (1)	−0.2660 (4)	6.4 (1)
C(7)	0.6874 (3)	0.2117 (1)	0.0406 (3)	4.70 (8)
O(1)	0.6545 (2)	0.21786 (7)	0.1755 (2)	4.66 (5)
C(8)	0.7810 (3)	0.22897 (9)	0.3088 (3)	4.22 (7)
O(2)	0.9150 (2)	0.22918 (7)	0.3247 (2)	5.21 (5)
N(1)	0.7377 (2)	0.23986 (8)	0.4243 (2)	4.43 (6)
C(9)	0.8499 (3)	0.2410 (1)	0.5903 (3)	4.46 (7)
C(10)	0.7474 (3)	0.2288 (1)	0.6730 (3)	5.79 (9)
C(11)	0.6011 (3)	0.2062 (1)	0.5487 (3)	4.67 (7)
N(2)	0.5824 (2)	0.23035 (8)	0.4052 (2)	3.96 (5)
C(12)	0.4804 (3)	0.26941 (9)	0.3465 (3)	3.72 (6)
O(3)	0.5184 (2)	0.30823 (7)	0.3189 (2)	5.65 (6)
N(3)	0.3301 (2)	0.25790 (7)	0.3258 (2)	3.66 (5)
C(13)	0.2547 (3)	0.2122 (1)	0.2589 (3)	4.52 (7)
C(14)	0.1456 (3)	0.2249 (1)	0.0919 (3)	5.31 (9)
C(15)	0.0951 (3)	0.2760 (1)	0.0995 (3)	4.67 (7)
N(4)	0.2148 (2)	0.29336 (7)	0.2502 (2)	3.96 (5)
C(16)	0.1817 (3)	0.32696 (9)	0.3335 (3)	4.16 (7)
O(4)	0.0692 (2)	0.35323 (7)	0.2794 (2)	5.10 (5)
O(5)	0.2942 (2)	0.32891 (6)	0.4810 (2)	5.02 (5)
C(17)	0.2881 (5)	0.3690 (1)	0.5725 (4)	7.1 (1)
C(18)	0.4236 (3)	0.36426 (9)	0.7286 (3)	4.70 (8)
C(19)	0.5745 (4)	0.3577 (1)	0.7452 (4)	5.89 (9)
C(20)	0.6967 (4)	0.3509 (1)	0.8900 (4)	6.2 (1)
C(21)	0.6694 (4)	0.3524 (1)	1.0197 (4)	6.3 (1)
C(22)	0.5214 (4)	0.3589 (1)	1.0065 (4)	6.7 (1)
C(23)	0.3984 (4)	0.3647 (1)	0.8605 (4)	5.85 (9)
Molecule *B*				
C(1)	−0.4687 (5)	0.5192 (3)	−0.2082 (5)	8.8 (1)
C(2)	−0.4520 (5)	0.5671 (3)	−0.2053 (5)	8.7 (1)
C(3)	−0.3214 (4)	0.5892 (2)	−0.0862 (4)	6.9 (1)
C(4)	−0.2087 (3)	0.5617 (1)	0.0249 (3)	5.32 (7)
C(5)	−0.2270 (4)	0.5126 (1)	0.0186 (5)	6.7 (1)
C(6)	−0.3570 (5)	0.4917 (2)	−0.0975 (6)	8.5 (1)
C(7)	−0.0662 (4)	0.5845 (1)	0.1512 (4)	6.28 (9)
O(1)	−0.0559 (2)	0.56790 (7)	0.3003 (2)	4.81 (4)
C(8)	0.0516 (3)	0.59030 (9)	0.4248 (3)	4.63 (6)
O(2)	0.1380 (2)	0.62172 (7)	0.4218 (3)	6.40 (6)
N(1)	0.0573 (3)	0.57240 (8)	0.5602 (3)	5.36 (6)
C(9)	0.1309 (4)	0.5967 (1)	0.7092 (4)	6.41 (9)
C(10)	0.0187 (5)	0.5899 (2)	0.7818 (5)	7.6 (1)
C(11)	−0.1170 (4)	0.5612 (1)	0.6682 (4)	5.62 (8)
N(2)	−0.0592 (3)	0.54041 (7)	0.5586 (2)	4.64 (5)
C(12)	−0.0079 (3)	0.49275 (9)	0.5778 (3)	4.05 (6)
O(3)	0.1196 (2)	0.47992 (7)	0.5904 (3)	6.11 (6)
N(3)	−0.1223 (2)	0.46290 (7)	0.5828 (2)	4.15 (5)
C(13)	−0.2900 (3)	0.4664 (1)	0.4782 (4)	5.49 (7)
C(14)	−0.3253 (5)	0.4216 (1)	0.3845 (5)	7.3 (1)
C(15)	−0.1930 (3)	0.3876 (1)	0.4633 (3)	5.19 (7)
N(4)	−0.0841 (2)	0.41396 (7)	0.6011 (2)	4.28 (5)
C(16)	−0.0203 (3)	0.39530 (9)	0.7467 (3)	4.12 (6)
O(4)	−0.0077 (2)	0.35270 (6)	0.7734 (2)	5.39 (5)
O(5)	0.0337 (2)	0.42984 (6)	0.8550 (2)	4.89 (4)
C(17)	0.1140 (4)	0.4144 (1)	1.0160 (3)	5.19 (7)
C(18)	0.2059 (3)	0.45686 (9)	1.1075 (3)	4.32 (6)
C(19)	0.2992 (4)	0.4833 (1)	1.0558 (3)	5.33 (7)
C(20)	0.3838 (4)	0.5222 (1)	1.1417 (4)	5.83 (8)
C(21)	0.3745 (4)	0.5350 (1)	1.2783 (4)	5.87 (8)
C(22)	0.2840 (3)	0.5084 (1)	1.3312 (3)	5.66 (8)
C(23)	0.1995 (3)	0.4696 (1)	1.2465 (3)	4.78 (6)

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

	Molecule *A*	Molecule *B*
C(1)—C(2)	1.355 (3)	1.35 (1)
C(1)—C(6)	1.373 (4)	1.358 (7)
C(2)—C(3)	1.381 (3)	1.404 (5)
C(3)—C(4)	1.374 (4)	1.364 (4)
C(4)—C(5)	1.372 (4)	1.380 (5)
C(4)—C(7)	1.497 (3)	1.502 (4)
C(5)—C(6)	1.358 (4)	1.376 (5)
C(7)—O(1)	1.446 (4)	1.448 (4)
O(1)—C(8)	1.348 (2)	1.335 (3)
C(8)—O(2)	1.201 (3)	1.203 (4)
C(8)—N(1)	1.353 (4)	1.355 (4)
N(1)—C(9)	1.471 (3)	1.447 (4)
N(1)—N(2)	1.416 (3)	1.406 (3)
C(9)—C(10)	1.515 (5)	1.494 (7)
C(10)—C(11)	1.513 (4)	1.501 (5)
C(11)—N(2)	1.458 (4)	1.478 (5)
N(2)—C(12)	1.400 (3)	1.400 (3)
C(12)—O(3)	1.204 (3)	1.205 (4)
C(12)—N(3)	1.377 (3)	1.376 (3)

N(3)—C(13)	1.464 (3)	1.461 (3)
N(3)—N(4)	1.415 (3)	1.404 (3)
C(13)—C(14)	1.513 (4)	1.486 (5)
C(14)—C(15)	1.513 (4)	1.487 (5)
C(15)—N(4)	1.471 (3)	1.467 (3)
N(4)—C(16)	1.344 (4)	1.351 (3)
C(16)—O(4)	1.206 (3)	1.211 (3)
C(16)—O(5)	1.344 (2)	1.339 (3)
O(5)—C(17)	1.431 (4)	1.447 (3)
C(17)—C(18)	1.487 (4)	1.502 (4)
C(18)—C(19)	1.369 (5)	1.386 (5)
C(18)—C(23)	1.366 (5)	1.388 (4)
C(19)—C(20)	1.374 (4)	1.384 (4)
C(20)—C(21)	1.357 (6)	1.379 (6)
C(21)—C(22)	1.353 (6)	1.373 (5)
C(22)—C(23)	1.380 (4)	1.380 (4)
C(2)—C(1)—C(6)	118.9 (2)	120.0 (4)
C(1)—C(2)—C(3)	121.0 (3)	120.4 (4)
C(2)—C(3)—C(4)	120.2 (3)	119.8 (4)
C(3)—C(4)—C(5)	117.9 (2)	118.9 (3)
C(3)—C(4)—C(7)	121.1 (2)	120.7 (3)
C(5)—C(4)—C(7)	120.9 (2)	120.4 (3)
C(4)—C(5)—C(6)	121.7 (3)	120.5 (3)
C(1)—C(6)—C(5)	120.2 (3)	120.4 (5)
C(4)—C(7)—O(1)	106.8 (2)	107.9 (3)
C(7)—O(1)—C(8)	114.7 (2)	114.9 (2)
O(1)—C(8)—O(2)	125.1 (3)	125.7 (3)
O(1)—C(8)—N(1)	111.1 (2)	111.8 (2)
O(2)—C(8)—N(1)	123.8 (2)	122.4 (2)
C(8)—N(1)—C(9)	122.9 (2)	124.0 (3)
C(8)—N(1)—N(2)	120.2 (2)	120.5 (2)
C(9)—N(1)—N(2)	111.6 (2)	110.7 (3)
N(1)—C(9)—C(10)	102.9 (2)	104.6 (3)
O(3)—C(12)—N(3)	124.0 (2)	125.0 (2)
C(12)—N(3)—C(13)	122.7 (2)	124.5 (2)
C(12)—N(3)—N(4)	115.1 (2)	115.5 (2)
C(13)—N(3)—N(4)	105.4 (2)	107.1 (2)
N(3)—C(13)—C(14)	103.6 (2)	104.4 (3)
C(13)—C(14)—C(15)	104.9 (2)	108.3 (3)
C(14)—C(15)—N(4)	103.4 (2)	103.9 (3)
N(3)—N(4)—C(15)	111.2 (2)	109.5 (2)
N(3)—N(4)—C(16)	120.6 (2)	118.7 (2)
C(15)—N(4)—C(16)	121.8 (2)	123.4 (2)
N(4)—C(16)—O(4)	123.7 (2)	123.6 (2)
N(4)—C(16)—O(5)	111.2 (2)	111.2 (2)
O(4)—C(16)—O(5)	125.0 (2)	125.2 (2)
C(16)—O(5)—C(17)	116.3 (2)	116.7 (2)
O(5)—C(17)—C(18)	107.0 (3)	106.6 (2)
C(17)—C(18)—C(19)	122.0 (3)	120.7 (3)
C(17)—C(18)—C(23)	119.9 (3)	120.1 (3)
C(9)—C(10)—C(11)	105.0 (2)	106.7 (3)
C(10)—C(11)—N(2)	103.8 (2)	105.0 (3)
N(1)—N(2)—C(11)	105.1 (2)	105.1 (2)
N(1)—N(2)—C(12)	113.4 (2)	112.3 (2)
C(11)—N(2)—C(12)	121.3 (2)	119.4 (2)
N(2)—C(12)—O(3)	124.8 (2)	124.6 (3)
N(2)—C(12)—N(3)	111.1 (2)	110.4 (2)
C(19)—C(18)—C(23)	118.0 (2)	119.2 (2)
C(18)—C(19)—C(20)	121.0 (4)	120.0 (3)
C(19)—C(20)—C(21)	119.9 (3)	120.2 (3)
C(20)—C(21)—C(22)	120.2 (3)	119.9 (3)
C(21)—C(22)—C(23)	119.7 (4)	120.2 (3)
C(18)—C(23)—C(22)	121.1 (3)	120.4 (3)
C(4)—C(7)—O(1)—C(8)	−179.8 (2)	−170.7 (2)
C(7)—O(1)—C(8)—N(1)	172.5 (2)	−178.8 (3)
O(1)—C(8)—N(1)—N(2)	11.4 (3)	−10.5 (4)
O(1)—C(8)—N(1)—C(9)	163.5 (2)	−163.5 (3)
C(8)—N(1)—N(2)—C(12)	−93.2 (3)	101.1 (3)
N(1)—N(2)—C(11)—C(10)	33.4 (3)	−26.8 (3)
N(2)—C(11)—C(10)—C(9)	−32.0 (3)	16.1 (4)
C(11)—C(10)—C(9)—N(1)	18.1 (3)	0.1 (4)
C(10)—C(9)—N(1)—N(2)	2.5 (3)	−18.0 (3)
C(9)—N(1)—N(2)—C(11)	−22.9 (3)	28.5 (3)
N(1)—N(2)—C(12)—N(3)	178.2 (2)	177.2 (2)
N(2)—C(12)—N(3)—N(4)	−173.0 (2)	179.7 (2)
N(2)—C(12)—N(3)—C(13)	−42.4 (3)	43.4 (3)
C(12)—N(3)—N(4)—C(16)	−91.2 (3)	93.6 (4)
N(3)—N(4)—C(15)—C(14)	1.9 (3)	−16.0 (4)
N(4)—C(15)—C(14)—C13()	18.5 (3)	−0.1 (3)
C(15)—C(14)—C(13)—N(3)	−31.9 (3)	15.2 (5)
C(14)—C(13)—N(3)—N(4)	33.0 (3)	−25.2 (4)
C(13)—N(3)—N(4)—C(15)	−22.3 (3)	26.4 (3)
N(3)—N(4)—C(16)—O(5)	15.5 (3)	−16.1 (3)
N(4)—C(16)—O(5)—C(17)	168.6 (3)	−176.2 (3)
C(16)—O(5)—C(17)—C(18)	−179.1 (3)	162.5 (3)

Program used to solve the structure: *SHELXS*86 (Sheldrick, 1990). Refinement was by full-matrix least-squares methods using *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Five 3,3′-Bridged 2,2′-Dithiophenes

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Abstract

The crystal structures of the compounds 4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene, $C_9H_6S_2$ (I), spiro[4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-4,1′-cyclopentane], $C_{13}H_{12}S_2$ (II), 4*H*,6*H*-dithieno[3,2-*c*:2′,3′-*e*]oxepine, C_{10}-