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Structure of *cyclo*(-*N*-ε-Boc-L-Lys-L-Pro-)

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Abstract. $C_{16}H_{27}N_3O_4$, $M_r = 325·41$, orthorhombic, $P2_12_12_1$, $a = 10·400\ (3)$, $b = 10·647\ (3)$, $c = 15·970\ (4)$ Å, $V = 1768·5\ (5)$ Å^3, $Z = 4$, $D_x = 1·222$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·825$ mm^{-1}, $F(000) = 704$, $T = 295$ K, final $R = 0·039$, $wR = 0·051$ for 1757 observed reflections, $I \geq 3\sigma(I)$. The diketopiperazine (DKP) ring adopts a flattened boat conformation. Primary torsion angles are $\varphi_1 = -27·4$, $\psi_1 = 23·6$, $\omega_1 = 3·2$, $\varphi_2 = -28·4$, $\psi_2 = 24·8$, $\omega_2 = 2·3°$. The proline ring adopts an unusual conformation intermediate between half-chair and sofa forms and closest to a C_s–C^{β}-*endo* designation. The lysyl side chain extends away from the DKP ring in a zigzag *trans*-planar conformation. Prolyl side-chain torsion angles are $\chi_2^1 = -36·4$, $\chi_2^2 = 33·0$, $\chi_2^3 = -16·4$, $\chi_2^4 = -7·4$, $\theta = 27·7°$; those for lysine are $\chi_1^1 = 61·0$, $\chi_1^2 = -176·1$, $\chi_1^3 = -178·7$, $\chi_1^4 = 179·5°$. The urethane moiety, twisted perpendicularly to the lysyl side chain, is also planar. Two intermolecular hydrogen bonds, one each from the amide and urethane H atoms, to the DKP carbonyls are observed. Associated distances are N1···O2′ 2·839 (3), N_1^{ϵ}···O1′ 2·893 (3) Å.

Experimental. *Synthesis. cyclo*(-*N*-ε-Boc-L-Lys-L-Pro-) formed on storage of a methanol solution of H-ε-Boc-L-Lys-L-Pro-OMe, and crystallized as colorless tabloids as the solvent slowly evaporated. The crystal used for data collection had approximate dimensions 0·50 × 0·30 × 0·35 mm. Cell dimensions were determined from the angular settings of 25 reflections with $30 \leq 2\theta(\text{Mo}) \leq 35°$ measured on an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected in the range $2 \leq 2\theta \leq 60°$ with variable-speed ω–2θ scans using graphite-monochromated molybdenum radiation. Data were corrected for Lorentz and polarization effects but not for absorption. A correction for isotropic intensity loss (4·2% maximum) during the course of data collection was applied. The maximum correction factor was 1·043. A total of 2630 reflections were collected of which 1757 were considered observed [$I \geq 3\sigma(I)$] and used in the refinement; range of *hkl*: h 0→14, k 0→14, l 0→22.

Table 1. *Positional and equivalent isotropic thermal parameters and their e.s.d.'s*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
O_1'	0·5353 (2)	0·3474 (2)	0·3284 (1)	4·21 (4)
O_2'	0·2704 (2)	−0·0741 (2)	0·3745 (1)	4·71 (4)
O3	0·3898 (2)	0·4061 (2)	−0·1802 (1)	4·21 (4)
O4	0·4145 (2)	0·4981 (2)	−0·0529 (1)	4·55 (4)
N_1	0·4228 (2)	0·0303 (2)	0·3027 (1)	3·57 (4)
N_1^{ϵ}	0·3368 (3)	0·3024 (2)	−0·0660 (1)	4·84 (5)
N_2	0·4111 (2)	0·2271 (2)	0·4104 (1)	3·09 (4)
C_1^{α}	0·5204 (2)	0·1278 (2)	0·2942 (2)	3·10 (4)
C_1^{γ}	0·4218 (3)	0·2072 (3)	0·1579 (2)	3·76 (5)
C_1^{β}	0·5400 (2)	0·1582 (2)	0·2015 (2)	3·35 (5)
C_1^{ϵ}	0·3219 (3)	0·2802 (3)	0·0229 (2)	4·52 (6)
C_1'	0·4887 (2)	0·2441 (2)	0·3455 (1)	2·98 (4)
C_1^{δ}	0·4397 (3)	0·2286 (3)	0·0647 (2)	3·97 (5)
C_2^{γ}	0·2701 (3)	0·2691 (3)	0·5229 (2)	4·73 (6)
C_2^{δ}	0·3681 (3)	0·3305 (3)	0·4646 (2)	3·92 (5)
C_2'	0·3462 (2)	0·0133 (2)	0·3687 (1)	3·15 (4)
C_2^{α}	0·3599 (2)	0·1063 (2)	0·4382 (1)	3·04 (4)
C_2^{β}	0·2351 (3)	0·1454 (3)	0·4815 (2)	4·29 (6)
C3	0·3835 (2)	0·4093 (2)	−0·0959 (2)	3·53 (5)
C4	0·4506 (3)	0·5083 (2)	−0·2270 (2)	3·90 (5)
C5	0·4391 (4)	0·4658 (3)	−0·3168 (2)	5·58 (7)
C6	0·5897 (3)	0·5176 (4)	−0·2022 (2)	7·14 (9)
C7	0·3756 (4)	0·6281 (3)	−0·2151 (2)	7·20 (9)

Table 2. *Principal bond distances* (Å) *and angles* (°)

O_1'	C_1'	1·233 (3)	N_1^{ϵ}	C3	1·327 (3)	C_1^{ϵ}	C_1^{δ}	1·499 (4)
O_2'	C_2'	1·223 (3)	N_2	C_1'	1·326 (3)	C_2^{γ}	C_2^{δ}	1·526 (4)
O3	C3	1·349 (3)	N_2	C_2^{δ}	1·470 (3)	$C_2{}^{\gamma}$	C_2^{β}	1·518 (4)
O3	C4	1·463 (3)	N_2	C_2^{α}	1·462 (3)	C_2'	C_2^{α}	1·494 (3)
O4	C3	1·212 (3)	C_1^{α}	C_1^{β}	1·530 (3)	C_2^{α}	C_2^{β}	1·528 (4)
N_1	C_1^{α}	1·458 (3)	C_1^{α}	C_1'	1·520 (3)	C4	C5	1·509 (4)
N_1	C_2'	1·334 (3)	C_1^{γ}	C_1^{β}	1·505 (4)	C4	C6	1·503 (4)
N_1^{ϵ}	C_1^{ϵ}	1·447 (3)	C_1^{γ}	C_1^{δ}	1·518 (3)	C4	C7	1·507 (4)

C3	O3	C4	120·8 (2)	N_2	C_2^{δ}	C_2^{γ}	104·0 (2)
C_1^{α}	N_1	C_2'	125·9 (2)	O_2'	C_2'	N_1	123·2 (2)
C_1^{ϵ}	N_1^{ϵ}	C3	122·2 (2)	O_2'	C_2'	C_2^{α}	120·6 (2)
C_1'	N_2	C_2^{δ}	123·0 (2)	N_1	C_2'	C_2^{α}	116·1 (2)
C_1'	N_2	C_2^{α}	125·4 (2)	N_2	C_2^{α}	C_2'	113·1 (2)
C_2^{δ}	N_2	C_2^{α}	111·6 (2)	N_2	C_2^{α}	C_2^{β}	101·9 (2)
N_1	C_1^{α}	C_1^{β}	109·4 (2)	C_2'	C_2^{α}	C_2^{β}	115·8 (2)
N_1	C_1^{α}	C_1'	112·2 (2)	C_2^{γ}	C_2^{β}	C_2^{α}	103·3 (2)
C_1^{β}	C_1^{α}	C_1'	112·2 (2)	O3	C3	O4	125·0 (2)
C_1^{β}	C_1^{γ}	C_1^{δ}	113·9 (2)	O3	C3	N_1^{ϵ}	110·9 (2)
C_1^{α}	C_1^{β}	C_1^{γ}	114·3 (2)	O4	C3	N_1^{ϵ}	124·2 (2)
N_1^{ϵ}	C_1^{ϵ}	C_1^{δ}	114·1 (2)	O3	C4	C5	103·1 (2)
O_1'	C_1'	N_2	122·3 (2)	O3	C4	C6	109·3 (2)
O_1'	C_1'	C_1^{α}	121·5 (2)	O3	C4	C7	110·0 (2)
N_2	C_1'	C_1^{α}	116·3 (2)	C5	C4	C6	110·3 (3)
C_1^{γ}	C_1^{δ}	C_1^{ϵ}	113·0 (2)	C5	C4	C7	109·5 (3)
C_2^{δ}	C_2^{γ}	C_2^{β}	105·4 (2)	C6	C4	C7	114·2 (3)

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The structure was discovered with *MULTAN*80 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Initial atomic positions were refined by full-matrix least squares minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weights, w, were defined as $4F_o^2/S^2(I)$ with $S^2(I) = [\sigma^2(I_c) + (0\cdot06\ F_o)^2]$. Non-H atoms were refined with anisotropic thermal parameters. Positions for all of the H atoms were determined from successive difference Fourier maps and, except for those attached to the Boc group which were held at fixed calculated positions with fixed isotropic temperature factors, were refined along with the isotropic temperature factors. The refinement converged; max. Δ/σ in the final cycle was 0·03. The standard crystallographic agreement factors were $R = 0\cdot039$ and $wR = 0\cdot051$, GOF = 1·23 for 1757 observations and 281 variables. An extinction coefficient of the kind described by Zachariasen (1963) refined in the latter stages to $3\cdot89\ (1) \times 10^{-7}$. A final difference Fourier map showed maximum positive and negative excursions of 0·153 and 0·129 e Å^{-3}. A refinement using all 2419 data with $I \geq 0\cdot01\sigma(I)$ gave $R = 0\cdot056$, $wR = 0\cdot054$. Values of the neutral-atom scattering factors were employed as implemented in the Enraf–Nonius *SDP* (Frenz, 1987), a locally modified version of which was the source of all programs. Atomic coordinates are presented in Table 1.* Bond distances and angles are listed in Table 2. A view of the molecule is provided as Fig. 1.

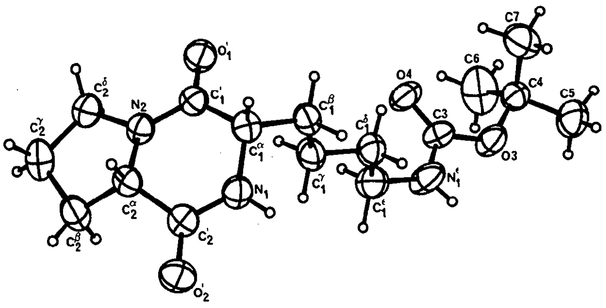

Fig. 1. *ORTEP* (Johnson, 1976) drawing of *cyclo*(-*N*-ε-Boc-L-Lys-L-Pro-). Non-H atoms are shown as principal ellipses at the 50% probability level, H atoms as small spheres of arbitrary size.

Related literature. Structures and conformations of diketopiperazines have been the subject of multitudinous publications. Much of this work has been reviewed and analyzed in a series of papers (Jankowska & Ciarkowski, 1987; Gdaniec, Liberek, Kolodziejczyk, Jankowska & Ciarkowski, 1987; Karle, 1979). Proline ring conformations have been analyzed and categorized by Ashida & Kakudo (1974).

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* Lists of structure factors, H-atom positions, bond distances and angles involving hydrogen and anisotropic librational parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52675 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Two Nitro-Substituted Aryl Carbonates

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Abstract. 2-Nitrophenyl 2-nitrophenoxyformate (I), $C_{13}H_8N_2O_7$, $M_r = 304\cdot2$, monoclinic, Pc, $a = 7\cdot887\ (3)$, $b = 10\cdot969\ (7)$, $c = 8\cdot113\ (5)$ Å, $\beta = 115\cdot11\ (4)°$, $V = 635\cdot5$ Å^3, $Z = 2$, $D_x = 1\cdot590$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1\cdot2$ cm^{-1}, $F(000) = 312$, $T = 173$ K, $R = 0\cdot0396$ for 1497 unique reflections

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