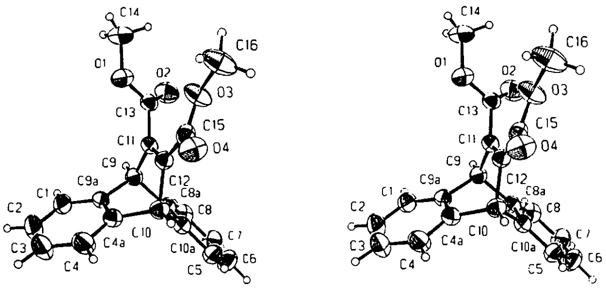

Fig. 1. Stereoview of the molecule.

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Structures of Two Polymorphic Forms of Diethyl Dibenzobarrelene-11,12-dicarboxylate

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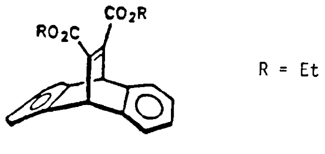
Abstract. Diethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate, $C_{22}H_{20}O_4$, $M_r = 348{\cdot}40$, $T = 295$ K; form *a*, monoclinic, $P2_1/c$, $a = 15{\cdot}037\,(2)$, $b = 29{\cdot}438\,(4)$, $c = 8{\cdot}186\,(1)$ Å, $\beta = 91{\cdot}06\,(1)°$, $V = 3623{\cdot}0\,(7)$ Å^3, $Z = 8$ (two molecules per asymmetric unit), $D_x = 1{\cdot}277$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å, $\mu = 0{\cdot}81$ cm^{-1}, $F(000) = 1472$, $R = 0{\cdot}041$ for 2680 unique observed reflections; form *b*, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}0157\,(5)$, $b = 13{\cdot}5253\,(9)$, $c = 14{\cdot}9749\,(7)$ Å, $V = 1826{\cdot}0\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}267$ g cm^{-3}, Cu $K\alpha_1$, $\lambda = 1{\cdot}54056$ Å, $\mu = 6{\cdot}7$ cm^{-1}, $F(000) = 736$, $R = 0{\cdot}035$ for 1602 unique observed reflections. The two ester groups have different orientations, with one group in each molecule not conjugated to the C═C double bond and the other fully conjugated.

Introduction. As part of a crystal and photochemical study of the di-π-methane rearrangement of dibenzobarrelene derivatives (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990*a*,*b*; Trotter & Wireko, 1991*a*) the structure of the symmetrical diethyl ester has now been determined. The material crystallizes in two crystal forms, one of which has two molecules per asymmetric unit.



Experimental. Crystals grown from ethanol exhibit two different morphologies, plate-like (Et/Et-*a*) and prisms (Et/Et-*b*). Approximate dimensions of cut crystals $0{\cdot}35 \times 0{\cdot}3 \times 0{\cdot}3$ mm for form *a* [$0{\cdot}30 \times 0{\cdot}33 \times 0{\cdot}29$ mm for form *b*]. Nonius CAD-4F diffractometer, monochromatized Mo $K\alpha$ [Cu $K\alpha$] radiation, lattice parameters from 25 reflections with $\theta = 10$–19 [30–56]°. Intensities for $\theta \leq 25$ [75]°; *hkl*: -17 to 17 [0 to 11], 0 to 34 [0 to 16], -9 to 0 [0 to 18]; ω–2θ scan, ω-scan width $(0{\cdot}65 + k\tan\theta)°$, $k = 0{\cdot}35$ [0·14] at 1·6–10 [1·1–10]° min^{-1}, extended 25% on each side for background measurement. Three standard reflections showed no significant variation. Lp but no absorption corrections. 6367 [2152] unique reflections, 2680 (42·1%) [1602 (74·4%)] with $I \geq 3\sigma(I)$ used in final refinement. Structure solved by direct methods, refined by full-matrix least-squares procedures. H atoms fixed [refined with isotropic thermal parametes], non-H atoms refined anisotropically. Refinement on F with $w = 1/\sigma^2(F)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}04I)^2$, S = scan, B_1 and B_2 = background counts. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102). Locally written, or locally modified versions of standard computer programs [*ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), *FORDAP* (Zalkin, unpublished) and *ORTEP*II (Johnson, 1976)]. Final $R = 0{\cdot}041$ [0·035], $wR = 0{\cdot}041$ [0·039], goodness of fit = 1·32 [1·47] for 469 [316] parameters, $R = 0{\cdot}146$ [0·056] for all 6367

0108-2701/91/061277-04$03.00

[2152] reflections, shift/e.s.d. in final cycle <0·001 (mean), 0·001 (maximum) [0·10, 1·7 (H parameters)], $\Delta\rho = -0{\cdot}25$ to $+0{\cdot}19$ [$-0{\cdot}20$ to $+0{\cdot}21$] e Å^{-3}, no extinction correction [correction, isotropic type I, $g = 2{\cdot}3\,(3) \times 10^4$].

Discussion. Final positional parameters are in Table 1 (the two independent molecules in form *a* are related approximately by the transformation: $x_2 \sim 0{\cdot}5 + x_1$, $y_2 \sim 0{\cdot}5 - y_1$, $z_2 \simeq 1{\cdot}16 - z_1$) and bond lengths and angles are in Table 2.* The dibenzobarrelene skeletons (Fig. 1) are similar to those in the parent hydrocarbon (Trotter & Wireko, 1990) and in related diester derivatives (Garcia-Garibay *et al.*, 1990*a*,*b*). The aromatic rings show slight, but not chemically significant, deviations from exact planarity and the angles external to the aromatic rings average 126·8°.

The two ester groups in all the Et/Et molecules have different orientations and different amounts of conjugation with the ring-system double bond; the torsion angles φ_1 = C12=C11—C13=O2 and φ_2 = C11=C12—C16=O4 (Table 3) indicate anticlinal and synperiplanar geometries for both molecules in form *a*, and synclinal/antiperiplanar in form *b*. Hence, in each molecule, one ester group (at C11) is not conjugated to the C11=C12 bond ($\cos^2\varphi_1$ = 0·13, 0·13, 0·01) and the other (at C12) is fully conjugated ($\cos^2\varphi_2$ = 0·99, 1·00, 0·99). The C11—C13 [1·488 (4), 1·496 (4), 1·487 (3), mean 1·490 Å] and C12—C16 [1·481 (4), 1·481 (4), 1·470 (4), mean 1·477 Å] bond lengths reflect this difference when compared with those for non-conjugated [1·497 (4) Å] and conjugated [1·470 (3) Å] systems (Allen, 1981).

The torsion angles C13—O1—C14—C15 and C16—O3—C17—C18 are −160·3 (3) and 167·5 (3)° for Et/Et-*a*, molecule 1, −159·2 (3) and 178·5 (2)° for Et/Et-*a*, molecule 2, and 81·1 (4) and −79·6 (4)° for Et/Et-*b*. Hence the ethyl groups in the Et/Et-*a* molecules lie approximately in the carboxyl planes, with the CH_2—CH_3 bonds *anti* to C—O; in Et/Et-*b* the CH_2—CH_3 bonds are approximately normal to the carboxyl planes.

The intermolecular environments of the two ester groups in each molecule also differ from each other,† but all contacts are of normal van der Waals type in both forms. As for the Me/Me derivative (Trotter & Wireko, 1991*a*), the two ethyl ester substituents are chemically identical, so that photolysis (solution or

Table 1. *Positional* (*fractional* × 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

U_{eq} = 1/3(trace of diagonalized U).

	x	y	z	U_{eq}
Et/Et-*a* (molecule 1)				
C1	3835 (2)	3569 (1)	7248 (4)	52
C2	4289 (2)	3906 (2)	6427 (5)	63
C3	3909 (3)	4328 (2)	6162 (4)	65
C4	3058 (2)	4419 (1)	6700 (4)	54
C4a	2601 (2)	4083 (1)	7494 (4)	41
C5	1560 (2)	4284 (1)	11285 (4)	51
C6	1740 (3)	4131 (1)	12876 (5)	61
C7	2118 (2)	3713 (1)	13149 (4)	61
C8	2323 (2)	3432 (1)	11855 (4)	49
C8a	2164 (2)	3585 (1)	10277 (4)	39
C9	2388 (2)	3336 (1)	8706 (4)	39
C9a	2995 (2)	3661 (1)	7781 (4)	41
C10	1665 (2)	4114 (1)	8174 (4)	40
C10a	1774 (2)	4007 (1)	9988 (4)	39
C11	1527 (2)	3311 (1)	7696 (4)	40
C12	1151 (2)	3714 (1)	7399 (4)	37
C13	1250 (2)	2859 (1)	7053 (4)	44
C14	188 (2)	2264 (1)	7235 (4)	55
C15	−762 (3)	2237 (1)	7652 (5)	73
C16	361 (2)	3762 (1)	6306 (4)	44
C17	−733 (3)	4255 (1)	5242 (5)	73
C18	−1111 (3)	4703 (2)	5564 (6)	93
O1	512 (1)	2710 (1)	7729 (3)	49
O2	1684 (2)	2652 (1)	6098 (3)	71
O3	58 (1)	4189 (1)	6254 (3)	52
O4	35 (2)	3459 (1)	5536 (3)	66
Et/Et-*a* (molecule 2)				
C1′	8861 (2)	1418 (1)	4326 (4)	55
C2′	9311 (3)	1080 (2)	5214 (5)	70
C3′	8901 (3)	671 (2)	5524 (4)	70
C4′	8031 (3)	586 (1)	4975 (4)	56
C4a′	7590 (2)	923 (1)	4119 (4)	42
C5′	6495 (2)	700 (1)	326 (4)	54
C6′	6669 (3)	831 (2)	−1264 (5)	65
C7′	7071 (3)	1241 (2)	−1587 (4)	66
C8′	7313 (2)	1530 (1)	−332 (5)	54
C8a′	7151 (2)	1402 (1)	1255 (4)	42
C9′	7412 (2)	1662 (1)	2811 (4)	41
C9a′	8006 (2)	1337 (1)	3794 (4)	42
C10′	6641 (2)	901 (1)	3415 (4)	41
C10a′	6743 (2)	989 (1)	1597 (4)	41
C11′	6566 (2)	1709 (1)	3783 (4)	40
C12′	6169 (2)	1315 (1)	4119 (4)	37
C13′	6315 (2)	2169 (1)	4399 (4)	46
C14′	5237 (3)	2757 (1)	4273 (4)	54
C15′	4272 (3)	2771 (1)	3856 (5)	71
C16′	5398 (2)	1283 (1)	5212 (4)	43
C17′	4348 (2)	799 (1)	6405 (5)	66
C18′	4098 (3)	320 (2)	6409 (6)	95
O1′	5564 (2)	2317 (1)	3719 (3)	50
O2′	6775 (2)	2376 (1)	5352 (3)	74
O3′	5112 (1)	853 (1)	5353 (3)	51
O4′	5071 (2)	1598 (1)	5907 (3)	64
Et/Et-*b*				
C1	16003 (3)	4855 (2)	4334 (2)	46
C2	16510 (4)	3886 (2)	4451 (2)	56
C3	15529 (4)	3103 (2)	4456 (2)	56
C4	14024 (4)	3262 (2)	4349 (2)	46
C4a	13509 (3)	4223 (2)	4246 (2)	40
C5	10921 (4)	4925 (3)	2543 (2)	53
C6	10993 (4)	5522 (3)	1799 (2)	60
C7	11970 (4)	6302 (3)	1768 (2)	62
C8	12907 (4)	6499 (2)	2484 (2)	50
C8a	12824 (3)	5909 (2)	3233 (2)	41
C9	13740 (3)	6007 (2)	4090 (2)	39
C9a	14503 (3)	5011 (2)	4224 (2)	39
C10	11904 (3)	4549 (2)	4143 (2)	41
C10a	11828 (3)	5118 (2)	3264 (2)	42
C11	12596 (3)	6078 (2)	4843 (2)	39
C12	11648 (3)	5316 (2)	4878 (2)	40
C13	12632 (3)	6980 (2)	5412 (2)	42
C14	13911 (5)	7795 (3)	6582 (3)	67
C15	12800 (7)	7868 (4)	7308 (3)	91
C16	10509 (3)	5121 (2)	5557 (2)	44
C17	9438 (4)	5667 (3)	6929 (2)	62
C18	7882 (5)	5895 (4)	6684 (3)	85
O1	13662 (2)	6920 (1)	6034 (1)	52
O2	11882 (3)	7692 (2)	5269 (1)	70
O3	10440 (3)	5825 (2)	6180 (1)	59
O4	9748 (3)	4387 (2)	5567 (2)	62

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* Lists of anisotropic thermal parameters, H-atom parameters, torsion angles, structure factors and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53674 (55 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Packing diagrams in deposition material.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Et/Et-*a* Molecule 1	Et/Et-*a* Molecule 2	Et/Et-*b*
C1—C2	1·385 (5)	1·398 (5)	1·399 (4)
C1—C9a	1·372 (4)	1·370 (4)	1·378 (4)
C2—C3	1·383 (5)	1·378 (5)	1·380 (5)
C3—C4	1·388 (5)	1·398 (5)	1·383 (5)
C4—C4a	1·375 (4)	1·378 (4)	1·389 (4)
C4a—C9a	1·393 (4)	1·396 (4)	1·393 (4)
C4a—C10	1·525 (4)	1·531 (4)	1·520 (4)
C5—C6	1·399 (5)	1·387 (5)	1·378 (5)
C5—C10a	1·380 (4)	1·390 (4)	1·380 (4)
C6—C7	1·371 (5)	1·375 (5)	1·375 (5)
C7—C8	1·383 (5)	1·379 (5)	1·390 (5)
C8—C8a	1·384 (4)	1·379 (4)	1·379 (4)
C8a—C9	1·523 (4)	1·530 (4)	1·532 (4)
C8a—C10a	1·394 (4)	1·392 (4)	1·396 (4)
C9—C9a	1·532 (4)	1·527 (4)	1·526 (4)
C9—C11	1·525 (4)	1·519 (4)	1·532 (4)
C10—C10a	1·524 (4)	1·522 (4)	1·527 (4)
C10—C12	1·539 (4)	1·528 (4)	1·530 (4)
C11—C12	1·333 (4)	1·337 (4)	1·340 (4)
C11—C13	1·488 (4)	1·496 (4)	1·487 (3)
C12—C16	1·481 (4)	1·481 (4)	1·470 (4)
C13—O1	1·323 (4)	1·324 (4)	1·318 (3)
C13—O2	1·195 (3)	1·198 (4)	1·197 (3)
C14—C15	1·476 (5)	1·486 (5)	1·482 (6)
C14—O1	1·455 (4)	1·460 (4)	1·458 (4)
C16—O3	1·338 (4)	1·342 (4)	1·334 (3)
C16—O4	1·195 (4)	1·197 (4)	1·207 (3)
C17—C18	1·460 (5)	1·459 (5)	1·482 (6)
C17—O3	1·450 (4)	1·456 (4)	1·457 (4)
C2—C1—C9a	118·5 (3)	118·9 (4)	118·6 (3)
C1—C2—C3	120·9 (3)	120·1 (4)	120·7 (3)
C2—C3—C4	120·4 (3)	121·2 (4)	120·6 (3)
C3—C4—C4a	118·8 (3)	118·1 (4)	119·1 (3)
C4—C4a—C9a	120·4 (3)	120·9 (3)	120·2 (3)
C4—C4a—C10	127·0 (3)	126·6 (3)	126·9 (2)
C9a—C4a—C10	112·6 (3)	112·6 (3)	112·8 (2)
C6—C5—C10a	118·9 (3)	118·6 (3)	119·6 (3)
C5—C6—C7	120·8 (3)	121·0 (3)	120·5 (3)
C6—C7—C8	120·6 (3)	120·6 (4)	120·7 (3)
C7—C8—C8a	118·9 (3)	118·9 (4)	118·9 (3)
C8—C8a—C9	126·6 (3)	126·9 (3)	127·0 (3)
C8—C8a—C10a	120·8 (3)	121·0 (3)	120·3 (3)
C9—C8a—C10a	112·6 (3)	112·1 (3)	112·7 (2)
C8a—C9—C9a	105·1 (2)	105·3 (3)	106·0 (2)
C8a—C9—C11	106·4 (2)	106·1 (2)	105·0 (2)
C9a—C9—C11	105·6 (2)	105·6 (3)	105·2 (2)
C1—C9a—C4a	120·9 (3)	120·8 (3)	120·8 (2)
C1—C9a—C9	126·4 (3)	126·5 (3)	126·3 (2)
C4a—C9a—C9	112·6 (3)	112·7 (3)	112·9 (2)
C4a—C10—C10a	105·1 (2)	104·5 (2)	106·0 (2)
C4a—C10—C12	105·3 (2)	105·1 (3)	105·5 (2)
C10a—C10—C12	106·7 (2)	106·8 (2)	105·7 (2)
C5—C10a—C8a	119·9 (3)	119·8 (3)	120·0 (3)
C5—C10a—C10	127·3 (3)	126·6 (3)	127·3 (3)
C8a—C10a—C10	112·7 (3)	113·5 (3)	112·7 (2)
C9—C11—C12	114·1 (3)	114·1 (3)	114·1 (2)
C9—C11—C13	117·7 (3)	118·6 (3)	117·3 (2)
C12—C11—C13	128·0 (3)	126·9 (3)	128·5 (2)
C10—C12—C11	113·4 (3)	113·8 (3)	113·5 (2)
C10—C12—C16	124·5 (3)	123·5 (3)	118·8 (2)
C11—C12—C16	121·9 (3)	122·5 (3)	127·6 (2)
C11—C13—O1	112·3 (3)	112·0 (3)	111·7 (2)
C11—C13—O2	122·3 (3)	122·2 (3)	123·0 (2)
O1—C13—O2	125·2 (3)	125·8 (3)	125·1 (2)
C15—C14—O1	107·8 (3)	106·6 (3)	111·3 (3)
C12—C16—O3	112·3 (3)	111·6 (3)	112·8 (2)
C12—C16—O4	124·3 (3)	124·8 (3)	123·6 (3)
O3—C16—O4	123·4 (3)	123·6 (3)	123·6 (3)
C18—C17—O3	109·6 (3)	108·3 (3)	111·4 (3)
C13—O1—C14	117·5 (3)	116·8 (3)	117·2 (3)
C16—O3—C17	114·8 (3)	114·3 (3)	117·5 (3)

Table 3. C═C *distances* (Å) *and ester torsion angles* (°) *in dibenzobarrelene diesters*

Compound	C11═C12	φ_1*	φ_2*	Ref.
Dibenzobarrelene	1·316 (4)			*a*
Me/Me diester	1·333 (2)	115·7 (2)	164·2 (2)	*b*
Et/Et-*a* (1)	1·333 (4)	111·1 (4)	−4·8 (5)	*c*
(2)	1·337 (4)	110·9 (4)	−1·3 (5)	*c*
Et/Et-*b*	1·340 (4)	−83·6 (4)	−175·9 (3)	*c*
^{i}Pr/^{i}Pr-*a*	1·328 (5)	64·1 (7)	−164·3 (5)	*d*
^{i}Pr/^{i}Pr-*b*	1·339 (6)	36.1 (9)	−134·1 (6)	*d*
Me/^{i}Pr	1·334 (4)	45.6 (4)	−144·4 (3)	*e*
Me/Ph	1·336 (3)	−134·9 (4)	−145·0 (3)	*f*

References: (*a*) Trotter & Wireko (1990); (*b*) Trotter & Wireko (1991*a*); (*c*) this work; (*d*) Garcia-Garibay *et al.* (1990*b*); (*e*) Garcia-Garibay *et al.* (1990*a*); (*f*) Trotter & Wireko (1991*b*).

* φ_1 = C12═C11—C═O; φ_2 = C11═C12—C═O.

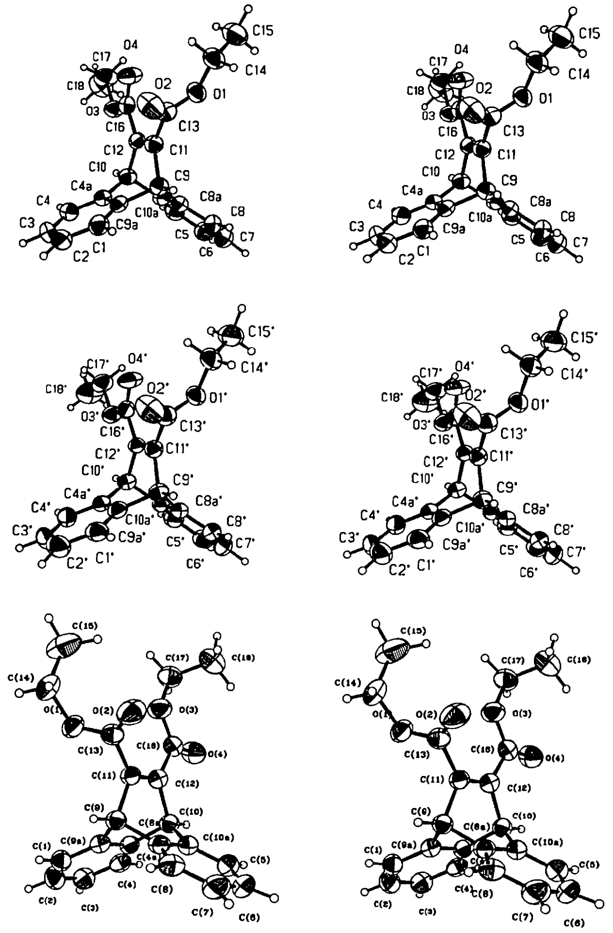

Fig. 1. Stereoviews of the molecules of Et/Et-*a*, molecule (1) (top), molecule (2) (centre) and Et/Et-*b* (bottom).

solid state) results in only one semibullvalene photoproduct (Garcia-Garibay *et al.*, 1990*a*,*b*).

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Conformation of *cyclo*-Bis(-L-valyl-L-prolyl-D-alanyl-), a Synthetic Cyclic Hexapeptide

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Abstract. $C_{26}H_{42}N_6O_6$, $M_r = 534{\cdot}7$, monoclinic, $C2$, $a = 20{\cdot}526\,(2)$, $b = 4{\cdot}923\,(1)$, $c = 17{\cdot}092\,(2)$ Å, $\beta = 126{\cdot}37\,(1)°$, $V = 1390{\cdot}9$ Å^3, $Z = 2$, D_m not measured, $D_x = 1{\cdot}28$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 7{\cdot}1$ cm^{-1}, $F(000) = 576$, $R = 0{\cdot}050$, $wR = 0{\cdot}049$ for 1012 reflections $[I > 2\sigma(I)]$, 1501 unique reflections measured at room temperature (296 K). The synthetic cyclic hexapeptide, *cyclo*-bis(-L-Val-L-Pro-D-Ala-), exhibits exact C_2 symmetry in the crystalline state with *cis* peptide links $[\omega = -13{\cdot}1\,(7)°]$ between Val and Pro residues; there are no intramolecular hydrogen bonds. The cyclic ring consists of two type VI*b* *cis* proline turns fused at the D-Ala residue. The backbone dihedral angles are all in the extended range except for ψVal $[72{\cdot}9\,(5)°]$ and φPro $[-78{\cdot}9\,(5)°]$ on either side of the *cis* peptide link. The carbonyl O atoms and the amide N atoms in the extended portion of the cyclic peptide form intermolecular hydrogen bonds with another cyclic hexapeptide molecule translated by a cell edge along the crystallographic *b* axis, forming an infinite stretch of β-sheets. The parallel β-sheet structures are separated by about 3·15 Å.

Introduction. Cyclic hexapeptides are good model compounds to study β-turns since a cyclic hexapeptide can be constructed by fusing two β-turns. We have studied the conformation of a number of cyclic hexapeptides of the general type *cyclo*-bis(-L-*Xxx*-L-Pro-D-*Yyy*-) in solution and the crystalline state. In solution, these peptides exist in two conformations (Kopple, Schamper & Go, 1974; Kopple, Sarkar & Giacometti, 1981), one with all-*trans* and the other with two *cis* *Xxx*-L-Pro peptide links. In the all-*trans* form, these hexapeptides are found to contain two β-turns with the L-Pro and D-*Yyy* residues at the corners and 4→1 type intramolecular hydrogen bonds. In the two *cis* forms, however, there are no intramolecular hydrogen bonds. Examples of the *trans* forms can be found in the crystal structures of *cyclo*-bis(-Gly-Pro-D-Phe-) (Brown & Yang, 1979), *cyclo*-bis(-Ala-Pro-D-Phe-) (Brown & Teller, 1976), *cyclo*-bis(-Gly-Pro-D-Ala-) (Kostansek, Lipscomb & Thiessen, 1979) and *cyclo*-bis(-L-Phe-L-Pro-D-Gln-) (Bhandary & Kopple, 1985). Two *cis* forms are found in the crystal structures of two crystal forms of *cyclo*-bis(-L-Phe-L-Pro-D-Ala-) (Kartha, Bhandary, Kopple, Go & Zhu, 1984; Bhandary, Kartha & Kopple, 1986), a second form of *cyclo*-bis(-L-Phe-L-Pro-D-Gln-) (Bhandary & Kopple, 1987) and in an Mg^{2+} complex of *cyclo*-bis(-Pro-Pro-Gly-) (Karle & Karle, 1981). In the crystal structure of the uncomplexed *cyclo*-bis(-Pro-Pro-Gly-), however, there are one *trans* and one *cis* Pro-Pro peptide linkages (Czugler, Sasvari & Hollosi, 1982). In this paper we report another example of a cyclic hexapeptide containing two *cis* L-Xxx-L-Pro peptide links.

Experimental. Needle-shaped crystal, 0·12 × 0·12 × 0·4 mm in size, of the synthetic cyclic hexapeptide, *cyclo*-bis(-L-Val-L-Pro-D-Ala-), grown by slow

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