(4S,5S)-4,5-Bis(pyrrolidinylcarbonyl)-2,2-dimethyl-1,3-dioxolane

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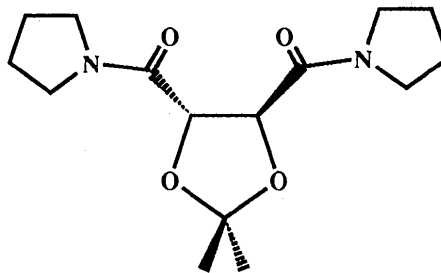
Abstract. $C_{15}H_{24}N_2O_4$, $M_r = 296\cdot4$, monoclinic, $C2$, $a = 28\cdot781$ (2), $b = 6\cdot1129$ (10), $c = 8\cdot9196$ (9) Å, $\beta = 99\cdot946$ (6)°, $V = 1545\cdot7$ (3) Å^3, $Z = 4$, $D_x = 1\cdot273$ g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1\cdot54184$ Å, $\mu = 7\cdot2$ cm^{-1}, $F(000) = 640$, $T = 299$ K, $R = 0\cdot045$ for 1740 observations with $I > 3\sigma(I)$ (of 1755 unique data). The molecule has approximate twofold symmetry, not coincident with the crystallographic symmetry axis. The pyrrolidine N atoms have nearly planar coordination, lying 0·016 (2) and 0·021 (2) Å out of the planes defined by the C atoms bonded to them. The N—C bonds within the pyrrolidine rings are in the range 1·463 (4)–1·479 (3) Å, and the C=O distances are 1·229 (3) and 1·232 (4) Å. The pyrrolidine rings have the half-chair conformation with the N atoms lying on the twist axis.

Experimental. The title compound was prepared by heating a solution of dimethyl (4S,5S)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate in dry pyrrolidine under reflux (Klein, Mohrs, Wild & Steglich, 1987; Seebach *et al.,* 1977). The starting material was the dimethyl (*S,S*)-tartrate (Musich & Rapoport, 1978) and the amide formation apparently does not lead to racemization since no *meso* compound is detected by NMR.

Crystals that deposited in the reaction flask, m.p. 426–428 K, were suitable; a clear, colorless crystal with dimensions 0·32 × 0·38 × 0·48 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Cu $K\alpha$ radiation and a graphite monochromator. Cell dimensions were determined from setting angles of 25 reflections having $30 > \theta > 25°$. The ω–2θ scans were designed for $I = 25\sigma(I)$, subject to maximum scan time = 90 s, scan rates varied from 0·75–3·30° min^{-1}. One quadrant of data having $h + k$ even, $2 < \theta < 75°$, $0 \le h \le 36$, $0 \le k \le 7$, $-11 \le l \le 11$ was measured and corrected for background, and Lorentz and polarization effects; ψ scans indicated no change in intensity with rotation about the diffraction vector, and no absorption corrections were made. Three standard reflections (1200, 020, 004) showed only a random fluctuation in intensity so no correction for decay was applied. The 0*kl* and 0*kl̄*

data were averaged, $R_{\text{int}} = 0\cdot013$. Systematic absences *hkl* with $h + k$ odd indicated possible space groups $C2$, Cm, or $C2/m$. No mirrors are present in the structure, and successful refinement in $C2$ demonstrated this to be the appropriate space group. The absolute configuration was not determined, but was chosen to correspond to that of the starting material. The structure was solved by direct methods and refined by full-matrix least squares based upon F, using data for which $I > 3\sigma(I)$, weights $w = 4F_o^2[\sigma^2(I) + (0\cdot02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Determination Package* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). Non-H-atom coordinates were refined with anisotropic thermal parameters; H-atom coordinates were located by ΔF synthesis and were constrained to lie 0·95 Å from the bonded C atom with isotropic $B = 1\cdot3B_{\text{eq}}$ for the C atom. Final $R = 0\cdot045$ for 1740 observed data (0·045 for all 1755 data), $wR = 0\cdot075$, $S = 2\cdot689$ for 190 variables. Maximum shift 0·11σ in the final cycle, max. residual density 0·23, min. $-0\cdot22$ e Å^{-3}, extinction coefficient $g = 1\cdot35$ (14) × 10^{-5} where the factor $(1 + gI_c)^{-1}$ was applied to F_c. A structural diagram of the title compound is shown below while the fractional coordinates are given in Table 1. Fig. 1 is a perspective drawing showing the atom numbering, and Fig. 2 is a stereoview of the unit cell. Bond distances, angles, and selected torsion angles are presented in Table 2.†

† Lists of H-atom coordinates and thermal parameters, anisotropic thermal parameters, torsion angles, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53295 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Coordinates and equivalent isotropic thermal parameters*

The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation:

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

	x	*y*	*z*	$B_{eq}(\text{Å}^2)$
O1	0·39721 (5)	0	0·2011 (2)	4·29 (3)
O2	0·43696 (6)	−0·0366 (6)	0·0023 (2)	6·95 (6)
O3	0·32521 (8)	−0·3873 (4)	0·0857 (3)	5·70 (5)
O4	0·35116 (8)	0·0489 (4)	−0·2508 (2)	5·79 (4)
N1	0·29298 (6)	−0·0941 (4)	0·1794 (2)	3·66 (3)
N2	0·38780 (6)	−0·2603 (4)	−0·2998 (2)	3·48 (3)
C1	0·36285 (7)	−0·0403 (4)	0·0665 (2)	3·35 (4)
C2	0·39277 (8)	−0·1472 (5)	−0·0366 (2)	3·83 (4)
C3	0·44120 (7)	0·0422 (5)	0·1543 (2)	3·87 (4)
C4	0·4791 (1)	−0·0803 (8)	0·2582 (4)	6·19 (7)
C5	0·4508 (1)	0·2823 (8)	0·1524 (5)	6·99 (8)
C6	0·32515 (7)	−0·1893 (4)	0·1111 (2)	3·48 (4)
C7	0·25483 (8)	−0·2211 (5)	0·2304 (3)	4·41 (5)
C8	0·22419 (9)	−0·0518 (7)	0·2820 (4)	5·62 (6)
C9	0·2554 (1)	0·1366 (7)	0·3285 (4)	5·95 (7)
C10	0·29072 (9)	0·1375 (5)	0·2194 (3)	4·67 (5)
C11	0·37530 (7)	−0·1120 (4)	−0·2065 (2)	3·40 (4)
C12	0·41507 (9)	−0·4602 (5)	−0·2596 (3)	4·32 (5)
C13	0·4255 (1)	−0·5391 (7)	−0·4121 (3)	6·11 (7)
C14	0·3838 (1)	−0·4635 (8)	−0·5234 (3)	6·15 (7)
C15	0·3723 (1)	−0·2427 (7)	−0·4653 (3)	5·14 (6)

Related literature. The structures of $N,N,N',N',$-N'',N'',N''',N'''-octamethyl-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxamide at 273 K (Dock, Moras, Behr & Lehn, 1983), *tert*-butoxycarbonyl-L-alanyl-L-asparaginyl-L-proline benzyl ester (In, Doi, Ishida, Inoue & Tomita, 1987), and Boc-Asn[1]-Pro[2]-Ser[3](Bzl)-NHMe and Boc-Asn[1](Me)-Pro[2]-Ser[3](Bzl)-NHMe (Aubry, Abbadi, Boussard & Marraud, 1987) exhibit the single bond N1—C6 [1·335 (9); 1·309 (9); 1·346 (9); 1·334 (9); 1·302 (8); 1·364 (8); 1·307 (9); 1·341 (9), 1·340 (4), and 1·332 (7); 1·344 (7) Å respectively], and C6—O3 distances [1·194 (8); 1·208 (8); 1·217 (8); 1·202 (8); 1·244 (8); 1·233 (8); 1·274 (9); 1·196 (8), 1·222 (4), and 1·216 (7); 1·221 (7) Å respectively], as does the title compound [1·232 (4) Å]. The bond angle, N1—C6—O3 [122·6 (2)°] of the title compound is similar to the analogous bond angles of $N,N,N',N',N'',N'',N''',N'''$-octamethyl-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxamide, [120·2 (7); 125·4 (7); 121·7 (6); 123·2 (7); 119·9 (6);

Table 2. *Bond distances (Å), angles (°), and selected torsion angles (°)*

O1—C1	1·439 (2)	C1—C2	1·513 (3)
O1—C3	1·424 (3)	C1—C6	1·522 (3)
O2—C2	1·429 (3)	C2—C11	1·527 (3)
O2—C3	1·423 (3)	C3—C4	1·503 (4)
O3—C6	1·232 (4)	C3—C5	1·494 (6)
O4—C11	1·229 (3)	C7—C8	1·484 (5)
N1—C6	1·327 (3)	C8—C9	1·475 (5)
N1—C7	1·479 (3)	C9—C10	1·524 (4)
N1—C10	1·464 (4)	C12—C13	1·521 (4)
N2—C11	1·322 (3)	C13—C14	1·492 (4)
N2—C12	1·463 (4)	C14—C15	1·502 (6)
N2—C15	1·470 (3)		

C1—O1—C3	107·7 (2)	O2—C3—C4	110·6 (3)
C2—O2—C3	108·5 (2)	O2—C3—C5	107·9 (3)
C6—N1—C7	121·7 (2)	C4—C3—C5	112·4 (3)
C6—N1—C10	126·8 (2)	O3—C6—N1	122·6 (2)
C7—N1—C10	111·5 (2)	O3—C6—C1	121·1 (2)
C11—N2—C12	127·7 (2)	N1—C6—C1	116·3 (2)
C11—N2—C15	120·9 (2)	N1—C7—C8	104·0 (3)
C12—N2—C15	111·3 (2)	C7—C8—C9	105·4 (2)
O1—C1—C2	101·5 (2)	C8—C9—C10	105·3 (3)
O1—C1—C6	107·6 (2)	N1—C10—C9	102·4 (2)
C2—C1—C6	114·0 (2)	O4—C11—N2	123·1 (2)
O2—C2—C1	102·9 (2)	O4—C11—C2	120·2 (2)
O2—C2—C11	107·5 (2)	N2—C11—C2	116·7 (2)
C1—C2—C11	114·7 (2)	N2—C12—C13	103·0 (2)
O1—C3—O2	106·5 (2)	C12—C13—C14	103·7 (3)
O1—C3—C4	108·4 (2)	C13—C14—C15	104·3 (3)
O1—C3—C5	110·9 (2)	N2—C15—C14	103·5 (3)

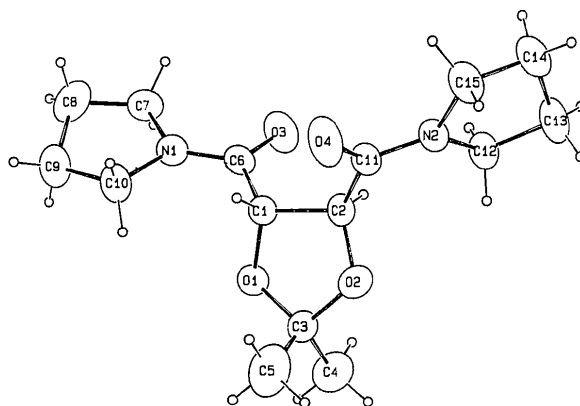|			
C3—O1—C1—C2	32·3 (2)	C1—O1—C3—O2	−17·3 (3)
C1—O1—C3—C5	99·8 (2)	C3—O2—C2—C1	25·8 (3)
C3—O2—C2—C11	147·3 (3)	C2—O2—C3—O1	−6·3 (3)
C7—N1—C6—O3	0·2 (3)	C10—N1—C7—C8	8·7 (3)
C7—N1—C10—C9	11·9 (3)	C15—N2—C11—O4	−1·3 (4)
C15—N2—C12—C13	12·8 (3)	C12—N2—C15—C14	10·3 (3)
O1—C1—C2—O2	−34·9 (2)	C6—C1—C2—C11	93·2 (3)
C2—C1—C6—O3	11·7 (3)	C1—C2—C11—O4	25·3 (4)
N1—C7—C8—C9	−26·6 (3)	C7—C8—C9—C10	34·7 (3)
C8—C9—C10—N1	−28·3 (3)	N2—C12—C13—C14	−31·0 (3)
C12—C13—C14—C15	38·1 (3)	C13—C14—C15—N2	−29·8 (3)

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecule, representing heavy atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radius.
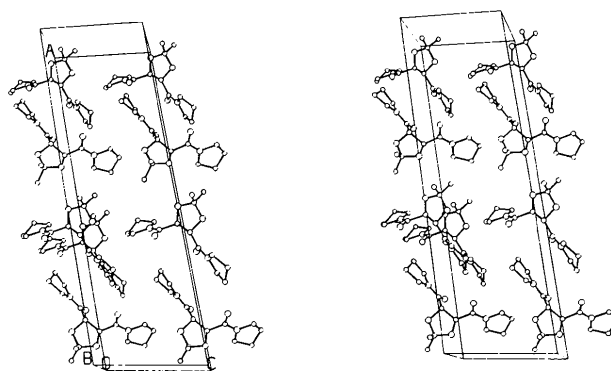

Fig. 2. Stereoview of the unit cell.

122·7 (6); 119·1 (6); 123·4 (6)°]. *tert*-Butoxycarbonyl-L-alanyl-L-asparaginyl-L-proline benzyl ester [120·7 (3)°], and Boc-Asn^1-Pro-^{2}-Ser^3(Bzl)-NHMe and Boc-Asn^1(Me)-Pro^2-Ser^3(Bzl)-NHMe [120·5 (4)°; 121·5 (4)°]. Torsion angles C7—C8—C9—C10 [34·7 (2)°], C12—C13—C14—C15 [38·1 (3)°], and O1—C1—C2—O2 [− 34·9 (2)°] of the title molecule show the similarity of the ring conformation adopted by the heterocyclic rings; namely, the two pyrrolidine and the 1,3-dioxolane rings.

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trans-1,5-Bicyclo[4.4.0]decadione*

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Abstract. $C_{10}H_{14}O_2$, $M_r = 166·2$, monoclinic, $P2_1/n$, $a = 7·4465$ (6), $b = 5·5949$ (3), $c = 10·9675$ (14) Å, $\beta = 106·776$ (8)°, $V = 437·48$ (7) Å^3, $Z = 2$, $D_x = 1·262$ g cm^{-3}; λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 6·6$ cm^{-1}, $F(000) = 180$, $T = 296$ K, $R = 0·033$ for 744 observations with $I > 3\sigma(I)$ (of 899 unique data). The molecule lies on an inversion center, and the *trans* fused cyclohexanone rings are in the chair conformation. The C=O bond length is 1·213 (2) Å, and the central bond has length 1·5474 (13) Å.

Experimental. The title compound was prepared by treating decalin-1,5-diol with 8N chromic acid in acetone at room temperature (Peet & Cargill, 1973). The *trans* isomer was formed by treatment with hydrochloric acid in chloroform (Hamon & Richards, 1973; Kleinfelter & Schleyer, 1973).

Crystals that deposited from the reaction flask, m.p. 426–428 K, were suitable; a clear colorless crystal with dimensions 0·12 × 0·20 × 0·30 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Cu $K\alpha$ radiation and a graphite

monochromator. Cell dimensions were determined from setting angles of 25 reflections having $30 > \theta > 25°$. The ω–2θ scans were designed for $I = 50\sigma(I)$, subject to maximum scan time = 120 s, scan rates varied in the range 0·57–3·30° min^{-1}. A full sphere of data having $2 < \theta < 75°$, $-9 \leq h \leq 9$, $-7 \leq k \leq 7$, $-13 \leq l \leq 13$ was measured and corrected for background, Lorentz and polarization effects, decay, and absorption. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 97·2%. Three standard reflections (200, 040, 006) decreased in intensity by 15·7% due to sublimation, and a linear correction was applied. A total of 3452 data was measured. Data from the four equivalent quadrants were averaged, $R_{int} = 0·013$, yielding 899 unique data. Systematic absences 0k0 with k odd and h0l with $h + l$ odd indicated space group $P2_1/n$. The structure was solved by direct methods, refined by full-matrix least squares based upon F, using data for which $I > 3\sigma)I$), weights $w = 4F_o^2[\sigma^2(I) + (0·02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Determination Package* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). C-atom coordinates were refined with anisotropic thermal parameters;

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* *trans*-Decalin-1,5-dione.
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