

The N...O distance is 2.78 Å and the N-H...O angle is 158°. The dihedral angle between the planes of the bridged molecules is 80°. There is also a hydrogen bond N(1)H(1)...O(6) which links oxalurate anions head to tail to form ribbons parallel to the *a* axis. This has an N...O distance of 2.91 Å and the NH...O angle is 175°. The oxalurate ribbons are crosslinked through pairs of N(3)H(3)...O(2) hydrogen bonds which are relatively weak. The N...O distances are 3.05 Å and NH...O angles are 155°.

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References

- ANDREWS, J. C. & SELL, I. T. (1955). *Arch. Biochem. Biophys.* **56**, 405–411.
 CRAVEN, B. M., MCMULLAN, R. K., BELL, J. D. & FREEMAN, H. C. (1977). *Acta Cryst.* **B33**, 2585–2589.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.
 SHIEH, H. S. & VOET, D. (1975). *Acta Cryst.* **B31**, 2192–2201.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WANG, A. C. & CRAVEN, B. M. (1979). *J. Pharm. Sci.* In the press.

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cyclo(-L-Prolyl-D-tert-leucyl-)

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Abstract. C₁₁H₁₈N₂O₂, orthorhombic, *P*2₁2₁2, *Z* = 4, FW 210.3, *a* = 10.942 (2), *b* = 16.438 (4), *c* = 6.452 (1) Å, *D_x* = 1.20, *D_m* = 1.14 Mg m⁻³, λ(Cu Kα) = 1.5418 Å (graphite monochromator); the final *R* = 0.046 on 794 observed reflexions [*F*_o² > 3σ(*F*_o²)] in the range 0 < 2θ ≤ 68°. The molecules are linked by hydrogen bonds to form chains [N(2)–H(1)...O(1): N(2)...O(2) = 2.894 (4), H(1)...O(1) = 2.053 (4) Å, ∠N(2)–H(1)...O(1) = 153 (3)°].

Introduction. Colourless transparent prismatic crystals of the title compound were prepared by Pospíšek & Bláha (1976) at the Institute of Organic Chemistry and Biochemistry, Praha. Our main interest was in the molecular conformation of the 2,5-piperazinedione ring with the bulky side chain of the *tert*-butyl group.

Measurement of integrated intensities of 2364 reflexions with *h* ≥ 0, *k* ≥ 0, *l* ≧ 0 was made on a Syntex *P*2₁ four-circle diffractometer. The scan range (2θ_{α₁} – 1°, 2θ_{α₂} + 1°) and a variable scan rate from 1.2 to 29.3° min⁻¹ were used. Three standard reflexions showed no unusual fluctuations. The data were corrected for background, Lorentz and polarization effects and for coincidence of pulses. The quality of the measurement was tested by

$$r = 2 \frac{\sum_{\substack{hkl \\ l > 0}} |I_{hkl} - I_{hk\bar{l}}|}{\sum_{\substack{hkl \\ l > 0}} I_{hkl} + I_{hk\bar{l}}} = 0.048$$

for both dependent sets of reflexions.

The structure was solved by direct methods with the tangent formula. For the set with the best figures of merit an *E* map was calculated and all non-hydrogen atoms were identified. They were refined anisotropically by full-matrix least squares to *R* = 0.102. An attempt to locate H atoms from a difference synthesis failed. We calculated positions for the H atoms with an isotropic temperature factor *B* = 3.4 Å². Positional and thermal parameters (anisotropic for non-hydrogen and isotropic for H atoms) were refined in three blocks (the last cycle in one block) to a final *R* = 0.046. Weights 1/σ(*F*_o²) were used. The final difference synthesis displayed no features > 0.2 e Å⁻³.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34026 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Scattering factors were taken from Cromer & Mann (1968). All calculations were performed on a Tesla 200 128 Kbyte computer with the *TLS* system (Sklenář, 1975). The figures were plotted with *UMCH* 108 (Šoler, 1974) and e.s.d.'s were obtained with *ORFFE* (Busing, Martin & Levy, 1964).

Discussion. Fractional coordinates are listed in Table 1. Figs. 1 and 2 give the bond lengths and angles.

Table 1. Atomic coordinates and their e.s.d.'s ($\times 10^4$)

	x	y	z
C(P1)	3300 (4)	2457 (3)	1011 (6)
O(1)	4141 (3)	2522 (2)	-245 (5)
N(1)	1435 (3)	1753 (2)	2277 (5)
C(A1)	2181 (4)	1970 (2)	451 (7)
C(B1)	2461 (4)	1142 (3)	-462 (8)
C(G1)	1269 (4)	678 (3)	-158 (8)
C(D1)	760 (4)	998 (3)	1905 (8)
C(P2)	1448 (3)	2126 (2)	4111 (7)
O(2)	788 (3)	1891 (2)	5574 (4)
N(2)	3342 (3)	2780 (2)	2938 (5)
C(A2)	2290 (4)	2846 (3)	4373 (7)
C(B2)	1686 (4)	3693 (2)	4271 (7)
C(1)	1234 (5)	3875 (4)	2079 (9)
C(2)	2594 (6)	4338 (3)	4922 (10)
C(3)	555 (6)	3720 (4)	5711 (12)
H(1)	4013 (37)	3051 (22)	3408 (61)
H(2)	2655 (36)	2805 (26)	5608 (61)
H(3)	1700 (36)	2327 (22)	-419 (65)
H(4)	3190 (38)	868 (20)	334 (67)
H(5)	2740 (38)	1162 (25)	-1622 (61)
H(6)	1406 (33)	40 (24)	-170 (62)
H(7)	616 (36)	829 (24)	-1228 (63)
H(8)	864 (39)	617 (22)	2966 (67)
H(9)	-131 (37)	1142 (23)	1960 (61)
H(10)	852 (38)	4455 (23)	2050 (67)
H(11)	573 (40)	3401 (25)	1623 (64)
H(12)	1818 (36)	3904 (27)	1051 (60)
H(13)	2177 (34)	4911 (22)	4943 (64)
H(14)	2839 (44)	4209 (25)	6169 (60)
H(15)	3366 (41)	4325 (23)	4045 (63)
H(16)	342 (40)	4351 (23)	5811 (70)
H(17)	-45 (39)	3296 (23)	5380 (68)
H(18)	926 (39)	3597 (25)	6983 (65)

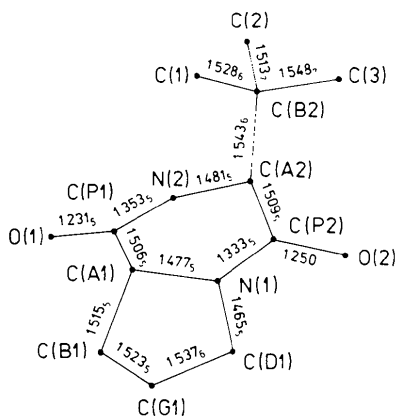


Fig. 1. Bond lengths (Å). E.s.d.'s are given as subscripts for the last digit listed.

The dimensions of the prolyl moiety lie within the range of those of other cyclic dipeptides with a prolyl ring, for example *cyclo*(-L-Pro-D-Leu-) (Karle, 1972), *cyclo*(-L-Pro-L-Pro-) (Benedetti, Goodman, Marsh, Rapoport & Musich, 1979) and *cyclo*(-L-Pro-L-Phe-) (Ramani, Venkatesan, Marsh & Hu Kung, 1976). C(A2)-N(2), C(P1)-N(2) are lengthened (Ramani, Sasisekharan & Venkatesan, 1977), probably due to the bulkiness of the *tert*-butyl side chain. The lengthening of C(P2)-O(2) reflects the effect of the hydrogen bonding and is also observed in *cyclo*(-L-Pro-L-Leu-) and *cyclo*(-L-Pro-D-Phe-). The molecular conformation of *cyclo*(-L-Pro-D-*tert*-Leu-) is similar to that of *cyclo*(-L-Pro-D-Phe-). The

Table 2. Torsion angles ($^{\circ}$) in (a) *cyclo*(-L-Pro-D-*tert*-Leu-) and (b) *cyclo*(-L-Pro-D-Phe-)

	(a)	(b)	
ϕ_1	C(P1)-C(A1)-N(1)-C(P2)	-21.1 (5)	-17.1
ψ_1	N(2)-C(P1)-C(A1)-N(1)	14.1 (5)	14.9
ω_1	C(A2)-N(2)-C(P1)-C(A1)	13.7 (6)	2.8
ϕ_2	C(P2)-C(A2)-N(2)-C(P1)	-34.4 (3)	-19.0
ψ_2	N(1)-C(P2)-C(A2)-N(2)	26.5 (5)	16.6
ω_2	C(A1)-N(1)-C(P2)-C(A2)	0.6 (7)	0.7
χ_{11}	N(1)-C(A1)-C(B1)-C(G1)	-38.8 (4)	-37.9
χ_{12}	C(A1)-C(B1)-C(G1)-C(D1)	34.6 (5)	31.9
χ_{13}	C(B1)-C(G1)-C(D1)-N(1)	-16.6 (5)	-13.5
χ_{14}	C(G1)-C(D1)-N(1)-C(A1)	-8.3 (5)	-11.3

Table 3. Least-squares planes and atomic deviations (Å) for (a) *cyclo*(-L-Pro-D-*tert*-Leu-) and (b) *cyclo*(-L-Pro-D-Phe-)

Atoms marked by an asterisk are omitted from the calculation of the mean plane. The angles between the planes are: plane 1 \wedge plane 2 = 13.9 $^{\circ}$, plane 1 \wedge plane 3 = 8.3 $^{\circ}$, plane 2 \wedge plane 3 = 22.2 $^{\circ}$.

	(a)	(b)	
Plane 1			
A = 0.580	N(1)	-0.025	-0.002
B = -0.742	C(P1)	0.024	0.002
C = 0.336	N(2)	-0.025	-0.002
D = 0.833	C(P2)	0.025	0.002
	C(A1)*	0.202	0.188
	C(A2)*	0.356	0.210
	O(1)*	-0.113	-0.135
	O(2)*	-0.195	-0.147
Plane 2			
A = 0.757	N(1)	0.000	0.001
B = -0.583	C(P2)	0.000	-0.002
C = 0.294	C(A2)	0.000	0.000
D = 0.157	O(2)	0.000	0.001
	C(A1)*	-0.013	0.019
	C(D1)*	-0.137	-0.196
Plane 3			
A = 0.458	N(2)	-0.004	0.000
B = -0.819	C(P1)	0.012	-0.001
C = 0.347	C(A1)	-0.004	0.000
D = 1.551	O(1)	-0.005	0.000
	C(A2)*	0.245	0.058
	H(1)*	-0.05	0.00

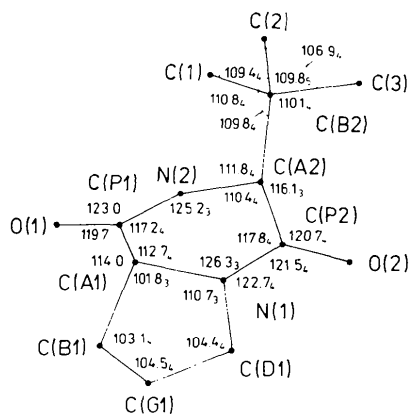
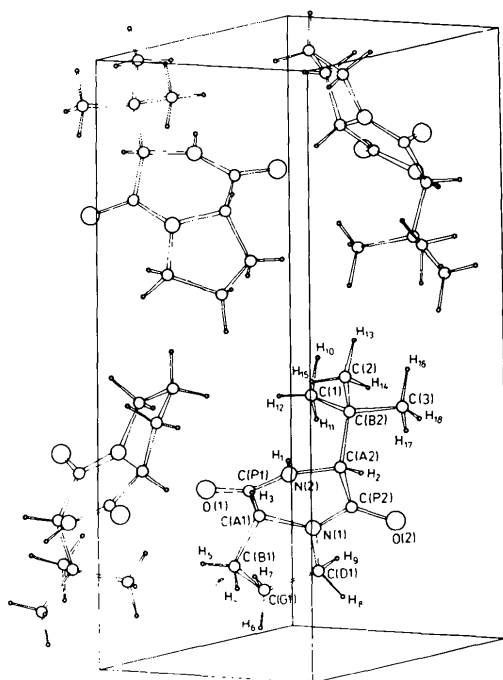
Fig. 2. Bond angles ($^{\circ}$).

Fig. 3. View of the molecular packing.

torsion angles and deviations from the least-squares planes are compared in Tables 2 and 3. There are no significant differences in the prolyl moieties. However, torsion angles and deviations from the least-squares moieties, are significantly larger in *cyclo(-L-Pro-D-tert-Leu-)*. It can also be seen that the 2,5-piperazinedione

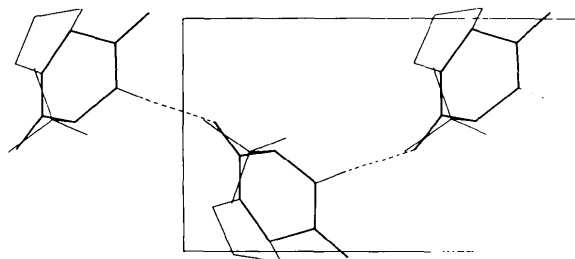


Fig. 4. Hydrogen-bonded chains in *cyclo(-L-Pro-D-tert-Leu-)* viewed along *b*. Covalent bonds are solid, hydrogen bonds are dashed. Of the four symmetrically-equivalent chains through the unit cell, only one is displayed.

ring of the present compound is less planar than in *cyclo(-L-Pro-D-Phe-)*.

The packing is shown in Fig. 3 (viewed approximately along [101]). There is only one hydrogen bond: N(2)–H(1)···O(1) with N(2)···O(2) = 2.894 (4), H(1)···O(1) = 2.053 (4) Å, and \angle N(2)–H(1)···O(1) = 153 (3) $^{\circ}$. Fig. 4 shows the linking of the molecules by hydrogen bonds (viewed along *b*). Except for the hydrogen bond, no significantly short contacts were observed. The shortest intermolecular distances are 3.560 (9) Å between C and C [between the C(2) atoms of molecule (I) at *x,y,z* and molecule (II) at *x,ȳ,z̄*], 3.073 (4) Å between O and N and 3.193 (6) Å between O and C.

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References

- BENEDETTI, E., GOODMAN, M., MARSH, R. E., RAPOPORT, H. & MUSICH, J. A. (1979). To be published.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- KARLE, I. L. (1972). *J. Am. Chem. Soc.* **94**, 81–84.
- POSPÍŠEK, J. & BLÁHA, K. (1976). *Peptides*. Proceedings of the Fourteenth European Peptide Symposium, Wépion, Belgium.
- RAMANI, R., SASISEKHARAN, V. & VENKATESAN, K. (1977). *Int. J. Pept. Protein Res.* **9**, 277–292.
- RAMANI, R., VENKATESAN, K., MARSH, R. E. & HU KUNG, W. J. (1976). *Acta Cryst.* **B32**, 1051–1056.
- SKLENÁŘ, I. (1975). *TLS* program system (unpublished).
- ŠOLER, J. (1974). *ÚMCH 108*. Institute of Macromolecular Chemistry, Praha.