In (II), (III) and (IV) all are directed to O atoms, usually O(7) of adjacent molecules, but in one case to the O of a water molecule. In both (I) and (V) one of the bonds is with the N(1) atom of a second molecule and the other with the O(7) of a third molecule.

(*c*) N(1) is always hydrogen-bonded to another N atom, variously equivalents of N(9), N(3) and N(1) [in (IV) a half-hydrogen is involved].

(*d*) The N(3)–H(18) group is always bonded. In two cases it bonds to an N(1) equivalent. In (I) the bond is with the O of a water molecule.

(*e*) The carbonyl oxygen O(7) forms one, two or three bonds. If water is absent all bonds are with N(9) equivalents. If water is present (I and III) O(7) forms hydrogen bonds with it.

As the above discussion indicates, the hydrogen bonding exhibited in the present structure is directionally compatible with the triple hydrogen-bond scheme for the pairing of guanine and cytosine in DNA as first suggested by Pauling & Corey (1956). However, in the present structure we find instead a double hydrogen-bond pattern between molecules within a ribbon, as occurs in crystalline *N*-methylcytosine (V). This preference could be associated with packing considerations due to the bulk of the methyl group and/or the tendency noted for the carbonyl O to form hydrogen bonds with water where present, as it is in most biological contexts.

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X-ray Structure Analysis and Molecular Conformation of *tert*-Butyloxycarbonyl-L-prolylproline (Boc-Pro-Pro)

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Abstract

$C_{15}H_{24}N_2O_5$ is orthorhombic, space group $P2_12_12_1$, with $a = 16{\cdot}968$ (1), $b = 14{\cdot}490$ (7), $c = 6{\cdot}664$ (9) Å, $V = 1638{\cdot}45$ Å^3, $M_r = 312{\cdot}39$, $D_o = 1{\cdot}2555$, $D_c = 1{\cdot}266$ Mg m^{-3}; $F(000) = 672$, $Z = 4$. The final $R = 3{\cdot}6\%$ for 1492 reflexions. Molecules are joined in pairs by a hydrogen bond O···OH, 2·613 Å. C$^\alpha$ is *cis* relative to the O atom of Boc and is *trans* relative to the C$^\alpha$ of the following ring. The absolute configuration of the non-centrosymmetric structure and the molecular conformation were determined by anomalous dispersion. The groups NC$^\alpha$C$^\gamma$C$^\delta$ of the two five-membered rings are fairly planar. In both cases C$^\beta$ is markedly displaced from the best plane and deviates by +0·45 and −0·57 Å, and N′ and C^γ for proline ring I as well as C^α and C^δ for ring II are on the same side as the carboxyl C′ atoms. Therefore, Boc-Pro-Pro is C_s-C^γ-*endo* (C^β-*exo*) for the two proline rings. This proline derivative belongs to conformation *B*, since the dihedral angles $\chi_{\rm I} = 27\cdot0°$ and $\chi_{\rm II} = 38\cdot4°$ have positive values.

Introduction

Proline, a cyclic amino acid, is regarded as a helix breaker because its presence at the amino terminal end of a polypeptide causes steric interactions for the preceding amino acids, especially when there is a C^β atom in its side chain. In addition to steric interactions from neighbouring amino acids at the terminal end, there are steric interactions of the carboxyl group of the proline and, in a polypeptide chain, of the amide of the carboxyl group with the pyrrolidine, notably its C^β—CH_2 group (Schimmel & Flory, 1968).

To study the cause of these neighbouring-group effects along a polypeptide chain after or before the position of a proline residue and eventually to come to some conclusions concerning protein conformations, it is essential to study peptides containing proline with different side residues at the amino and carboxyl termini of proline, or study model substances to generalize certain aspects, in particular to obtain the conformation of cyclic pyrrolidine systems in proline. The model system used here is *tert*-butyloxycarbonyl-L-prolylproline (Boc-Pro-Pro).

Experimental and results

The crystals were grown from ethyl acetate with a few drops of petroleum ether added. Approximate cell dimensions and space-group information were obtained from Weissenberg photographs. The θ–2θ mode with the three-measurements technique was adopted (Dreissig, 1969; Allen, Rogers & Troughton, 1971). 1628 reflexions were collected in the θ–2θ scan range 3–70° (Cu $K\alpha$ radiation, $\lambda = 1\cdot5418$ Å) of which 146 were considered unobserved with $I < 2\sigma(I)$. No absorption correction was applied (diameter of crystal <0·8 mm).

Structure determination and refinement

The phase problem was solved with *MULTAN* 77 (Main, Woolfson, Lessinger, Germain & Declercq, 1977). An overall temperature factor ($B = 5\cdot0$ Å^2) and scale factor were evaluated (Wilson, 1942) and used to compute normalized structure factors (*E*'s) (Karle & Hauptman, 1956). From three reflexions in the starting set and 400 *E* values >1·8 all phases could be evaluated. The *E* statistics confirmed a non-centrosymmetric structure. *R* was 38·84%. All non-hydrogen atoms could be located. Least-squares refinement with an overall isotropic temperature factor of 5·0 Å^2 was carried out (Stewart, Kruger, Ammon, Dickinson & Hall, 1976). Anisotropic temperature factors for all heavy atoms were used for further refinement and all H atoms were located from a difference synthesis. Further refinement reduced *R* to 0·037.

Determination of the absolute configuration

At the end of the refinement additional cycles were required including dispersion to differentiate between

Table 1. *Atomic coordinates and temperature factors*

$T = \exp(-8\pi^2 U \sin^2\theta/\lambda^2)$ for H atoms and $B_{\rm eq} = 8\pi^2 U_{\rm eq}$ for O, N and C (Willis & Pryor, 1975).

	x	*y*	*z*	$B_{\rm eq}$ (Å^2)
O'_1	0·6023 (1)	0·3745 (1)	1·1699 (3)	5·1 (1)
O'_2	0·6376 (1)	0·4367 (2)	1·4702 (4)	6·7 (1)
O'_3	0·7296 (1)	0·1948 (1)	1·2531 (3)	5·5 (1)
O_4	0·7869 (1)	0·0418 (1)	0·8623 (4)	5·5 (1)
O_5	0·6856 (1)	−0·0543 (1)	0·8704 (4)	5·5 (1)
N'_1	0·7281 (1)	0·3833 (1)	1·2483 (4)	5·0 (1)
N'_2	0·6890 (1)	0·1905 (1)	0·9333 (4)	4·0 (1)
C_1	0·5178 (1)	0·3974 (2)	1·1824 (5)	5·1 (1)
C_2	0·4795 (2)	0·3437 (4)	1·3473 (8)	8·1 (3)
C_3	0·4879 (2)	0·3677 (3)	0·9810 (7)	7·0 (2)
C_4	0·5076 (2)	0·5007 (3)	1·2027 (8)	7·1 (3)
C'_5	0·6541 (2)	0·4016 (2)	1·3116 (5)	4·7 (1)
C^α_6	0·7466 (1)	0·3321 (2)	1·0669 (6)	4·9 (1)
C^β_7	0·8367 (2)	0·3384 (2)	1·0580 (1)	7·9 (4)
C^γ_8	0·8619 (2)	0·3498 (4)	1·2650 (1)	9·4 (5)
C^δ_9	0·7968 (2)	0·4020 (2)	1·3727 (8)	7·3 (3)
C'_{10}	0·7202 (1)	0·2330 (1)	1·0900 (4)	3·8 (1)
C^α_{11}	0·6577 (1)	0·0973 (2)	0·9504 (5)	4·3 (1)
C^β_{12}	0·5866 (2)	0·0992 (2)	0·8166 (7)	6·4 (2)
C^γ_{13}	0·6142 (2)	0·1568 (3)	0·6464 (7)	6·9 (1)
C^δ_{14}	0·6676 (2)	0·2295 (2)	0·7354 (5)	6·0 (1)
C'_{15}	0·7189 (2)	0·0270 (1)	0·8885 (4)	3·8 (0)
$H_1(O_5)$	0·720 (2)	−0·092 (3)	0·840 (6)	0·10 (1)
$H_1(C_2)$	0·502 (2)	0·362 (2)	1·462 (5)	0·07 (9)
$H_2(C_2)$	0·494 (3)	0·271 (4)	1·326 (7)	0·12 (2)
$H_3(C_2)$	0·423 (3)	0·361 (3)	1·327 (7)	0·11 (1)
$H_1(C_3)$	0·433 (2)	0·383 (3)	0·980 (6)	0·09 (1)
$H_2(C_3)$	0·522 (3)	0·402 (3)	0·860 (8)	0·11 (1)
$H_3(C_3)$	0·499 (2)	0·297 (3)	0·954 (5)	0·08 (1)
$H_1(C_4)$	0·452 (2)	0·517 (3)	1·178 (6)	0·09 (1)
$H_2(C_4)$	0·546 (4)	0·539 (4)	1·110 (1)	0·17 (3)
$H_3(C_4)$	0·523 (3)	0·515 (3)	1·350 (7)	0·11 (1)
$H_1(C^\alpha_6)$	0·720 (2)	0·363 (2)	0·948 (5)	0·07 (9)
$H_1(C^\beta_7)$	0·857 (2)	0·288 (3)	0·995 (6)	0·10 (1)
$H_2(C^\beta_7)$	0·852 (3)	0·400 (3)	0·969 (8)	0·12 (2)
$H_1(C^\gamma_8)$	0·910 (3)	0·379 (3)	1·265 (8)	0·13 (2)
$H_2(C^\gamma_8)$	0·861 (4)	0·282 (5)	1·360 (1)	0·17 (2)
$H_1(C^\delta_9)$	0·784 (2)	0·399 (3)	1·498 (6)	0·09 (1)
$H_2(C^\delta_9)$	0·809 (2)	0·465 (3)	1·353 (7)	0·10 (1)
$H_1(C^\alpha_{11})$	0·642 (2)	0·085 (2)	1·101 (5)	0·07 (8)
$H_1(C^\beta_{12})$	0·571 (3)	0·035 (4)	0·762 (8)	0·13 (2)
$H_2(C^\beta_{12})$	0·540 (3)	0·140 (3)	0·889 (8)	0·11 (1)
$H_1(C^\gamma_{13})$	0·650 (3)	0·110 (3)	0·562 (8)	0·13 (2)
$H_2(C^\gamma_{13})$	0·576 (3)	0·190 (3)	0·591 (8)	0·11 (1)
$H_1(C^\delta_{14})$	0·648 (2)	0·289 (3)	0·762 (7)	0·10 (1)
$H_2(C^\delta_{14})$	0·723 (3)	0·232 (3)	0·663 (7)	0·12 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

C_1-C_2	1·495 (6)	$C^{\gamma}_{8}-C^{\delta}_{9}$	1·519 (6)
C_1-C_3	1·498 (6)	$C'_{10}-O'_3$	1·230 (4)
C_1-C_4	1·513 (5)	$C'_{10}-N'_2$	1·323 (4)
$C_1-O'_1$	1·474 (3)	$N'_2-C^{\alpha}_{11}$	1·456 (3)
$O'_1-C'_5$	1·348 (4)	$N'_2-C^{\delta}_{14}$	1·480 (4)
$C'_5-O'_2$	1·206 (4)	$C^{\alpha}_{11}-C^{\beta}_{12}$	1·500 (4)
$C'_5-N'_1$	1·351 (4)	$C^{\beta}_{12}-C^{\delta}_{13}$	1·484 (6)
$N'_1-C^{\alpha}_{6}$	1·453 (4)	$C^{\gamma}_{13}-C^{\delta}_{14}$	1·511 (6)
$N'_1-C^{\delta}_{9}$	1·456 (5)	$C^{\alpha}_{11}-C'_{15}$	1·512 (4)
$C^{\alpha}_{6}-C^{\beta}_{7}$	1·533 (4)	$C'_{15}-O_4$	1·186 (3)
$C^{\alpha}_{6}-C'_{10}$	1·512 (3)	$C'_{15}-O_5$	1·312 (3)
$C^{\beta}_{7}-C^{\gamma}_{8}$	1·454 (10)		

$C_2-C_1-C_3$	111·2 (3)	$C^{\alpha}_{6}-C'_{10}-N'_2$	118·7 (2)
$C_2-C_1-C_4$	113·6 (3)	$C^{\alpha}_{6}-C'_{10}-O'_3$	118·6 (2)
$C_3-C_1-C_4$	109·0 (3)	$C^{\beta}_{7}-C^{\alpha}_{6}-C'_{10}$	110·9 (2)
$O'_1-C_1-C_2$	110·3 (3)	$C^{\beta}_{7}-C^{\gamma}_{8}-C^{\delta}_{9}$	106·9 (3)
$O'_1-C_1-C_3$	102·4 (2)	$O'_3-C'_{10}-N'_2$	122·7 (2)
$O'_1-C_1-C_4$	109·8 (2)	$C'_{10}-N'_2-C^{\alpha}_{11}$	121·1 (2)
$O'_1-C'_5-N'_1$	109·3 (3)	$C'_{10}-N'_2-C^{\delta}_{14}$	128·6 (2)
$C_1-O'_1-C'_5$	121·9 (2)	$N'_2-C^{\alpha}_{11}-C'_{15}$	110·7 (2)
$O'_2-C'_5-N'_1$	124·9 (3)	$N'_2-C^{\alpha}_{11}-C^{\beta}_{12}$	103·3 (2)
$O'_1-C'_5-O'_2$	125·8 (2)	$N'_2-C^{\delta}_{14}-C^{\gamma}_{13}$	103·3 (3)
$C'_5-N'_1-C^{\alpha}_{6}$	124·1 (2)	$C^{\alpha}_{11}-C^{\beta}_{12}-C^{\gamma}_{13}$	102·2 (3)
$C'_5-N'_1-C^{\delta}_{9}$	122·0 (3)	$C^{\alpha}_{11}-N'_2-C_{14}$	109·5 (2)
$N'_1-C^{\alpha}_{6}-C^{\beta}_{7}$	102·6 (3)	$C^{\alpha}_{11}-C'_{15}-O_4$	125·9 (2)
$N'_1-C^{\alpha}_{6}-C'_{10}$	109·7 (2)	$C^{\alpha}_{11}-C'_{15}-O_5$	109·5 (2)
$N'_1-C^{\delta}_{9}-C^{\gamma}_{8}$	102·7 (4)	$O_4-C'_{15}-O_5$	124·6 (2)
$C^{\alpha}_{6}-N'_1-C^{\gamma}_{9}$	113·3 (2)	$C^{\beta}_{12}-C^{\gamma}_{13}-O^{\delta}_{14}$	106·3 (3)
$C^{\alpha}_{6}-C^{\beta}_{7}-C^{\gamma}_{8}$	105·3 (4)	$C^{\beta}_{12}-C^{\alpha}_{11}-C'_{15}$	113·7 (2)

Table 3. *Torsion angles* (°)

$C_1-O'_1-C_5-N'_1$	−171·0 (2)	
$O'_1-C'_5-N'_1-C^{\delta}_{9}$	−177·8 (3)	
$O'_1-C'_5-N'_1-C^{\alpha}_{6}$	−7·0 (4)	ω_1
$C'_5-N'_1-C^{\delta}_{9}-C^{\gamma}_{8}$	166·4 (3)	θ'''_1
$C'_5-N'_1-C^{\alpha}_{6}-C^{\beta}_{7}$	175·6 (3)	θ^{IV}_1
$C'_5-N'_1-C^{\alpha}_{6}-C^{\beta}_{7}$	175·6 (3)	θ^{IV}_1
$C'_5-N'_1-C^{\alpha}_{6}-C'_{10}$	−66·6 (3)	φ_1
$N'_1-C^{\alpha}_{6}-C'_{10}-O'_3$	−39·4 (3)	ψ_1
$N'_1-C^{\alpha}_{6}-C'_{10}-N'_2$	141·4 (2)	ψ_2
$N'_1-C^{\alpha}_{6}-C^{\beta}_{7}-C^{\gamma}_{8}$	27·0 (4)	χ_1
$C^{\alpha}_{6}-C^{\beta}_{7}-C^{\gamma}_{8}-C^{\delta}_{9}$	−31·1 (4)	χ_2
$C^{\beta}_{7}-C^{\gamma}_{8}-C^{\delta}_{9}-N'_1$	22·7 (4)	χ_3
$C^{\gamma}_{8}-C^{\delta}_{9}-N'_1-C^{\alpha}_{6}$	−5·3 (4)	χ_4
$C^{\gamma}_{8}-C^{\beta}_{7}-C^{\alpha}_{6}-C'_{10}$	−90·3 (4)	θ'_1
$C^{\delta}_{9}-N'_1-C^{\alpha}_{6}-C^{\beta}_{7}$	−12·9 (3)	θ_1
$C^{\delta}_{9}-N'_1-C^{\alpha}_{6}-C'_{10}$	104·9 (3)	θ''_1
$C^{\alpha}_{6}-C'_{10}-N'_2-C^{\delta}_{14}$	−7·0 (4)	
$C^{\alpha}_{6}-C'_{10}-N'_2-C^{\alpha}_{11}$	−175·8 (2)	ω_2
$C'_{10}-N'_2-C^{\delta}_{14}-C^{\gamma}_{13}$	−164·0 (3)	θ'''_2
$C'_{10}-N'_2-C^{\alpha}_{11}-C^{\beta}_{12}$	142·8 (3)	θ^{IV}_2
$C'_{10}-N'_2-C^{\alpha}_{11}-C'_{15}$	−95·1 (3)	φ_2
$N'_2-C^{\alpha}_{11}-C^{\beta}_{12}-C^{\gamma}_{13}$	38·4 (3)	χ_{11}
$C^{\alpha}_{11}-C^{\beta}_{12}-C^{\gamma}_{13}-C^{\delta}_{14}$	−35·7 (4)	χ_{22}
$C^{\beta}_{12}-C^{\gamma}_{13}-C^{\delta}_{14}-N'_2$	18·9 (4)	χ_{33}
$C^{\gamma}_{13}-C^{\delta}_{14}-N'_2-C^{\alpha}_{11}$	5·9 (3)	χ_{44}
$C^{\delta}_{14}-N'_2-C^{\alpha}_{11}-C^{\beta}_{12}$	−27·9 (3)	θ_2
$C^{\delta}_{14}-N'_2-C^{\alpha}_{11}-C'_{15}$	94·2 (3)	θ''_2
$N'_2-C^{\alpha}_{11}-C'_{15}-O_5$	−168·7 (2)	ψ_{22}
$N'_2-C^{\alpha}_{11}-C'_{15}-O_4$	12·1 (2)	ψ_{11}
$C'_{15}-C^{\alpha}_{11}-C^{\beta}_{12}-C^{\gamma}_{13}$	−81·6 (3)	θ'_2
$O_5-C'_{15}-C^{\alpha}_{11}-C^{\beta}_{12}$	−53·0 (3)	
$O_4-C'_{15}-C^{\alpha}_{11}-C^{\beta}_{12}$	127·9 (3)	

the two enantiomorphic forms of the structure. The atomic coordinates of the solved structure were used.

Corrections were taken into account by changing the sign of the imaginary part f''. R changed very little from the original 0·037 to R^{+} = 0·036, R^{-} = 0·036. The values for Cu $K\alpha$ radiation for O, C and N were taken from Cromer & Liberman (1970). The slight deviation of R from the original indicated that the proposed structure determined by *MULTAN* was in the correct orientation (Hamilton, 1956; Bijvoet, 1949).

Table 1 gives the atomic parameters, Table 2 bond lengths and angles and Table 3 torsion angles.*

Discussion and molecular conformation

Several five-membered ring systems, including pyrrolidine, are not planar. Their conformations can be described according to their symmetry elements such as C_s (envelope) or C_2 (half-chair) forms (Kilpatrick, Pitzer & Spitzer, 1947; Pitzer & Donath, 1960; Mitsui, Tsuboi & Iitaka, 1969; Sabesan & Venkatesan, 1971; Balasubramanian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran, 1971; Abraham & McLauchlan, 1962; Deslauriers & Smith, 1974; Ashida & Kakudo, 1974). Secondly, an approximate symmetry, in which C^{α}, C^{β} and very often C^{γ} are situated above or below a best plane of the ring is mostly encountered. A third factor is the direction of the shift of the atom from the plane in relation to the carboxyl C′ atom (*-endo* or *-exo*). Finally, proline rings can be divided into two classes. In class *A* the dihedral angle χ_1 takes negative values, while in class *B* the values are positive (Balasubramanian *et al.*, 1971).

In his spectroscopic studies, Oster (1973) stated that the C^{α} atom of proline peptides of Boc-amino acids that do not possess a C^{β} atom at their side chains (Boc-Pro-Pro inclusive) shows *cis–trans* isomers and that *trans* is normally preferred. It is confirmed in the present paper that C^{α} in Boc-Pro-Pro takes the rare *cis* configuration for ring I and *trans* for ring II. The dihedral angles $\omega_1 = -7{\cdot}0$ and $\omega_2 = -175{\cdot}8°$ are comparable to the normal ±0 and ±180° for peptide bonds with a *cis* and *trans* configuration, respectively. In this structure $O'_1-C'_5-N'_1$ and $C^{\alpha}_{6}-C'_{10}-N'_2$ are *109·3* and *118·7°*, respectively, the latter being comparable with the normal 118° of bonds with a *cis* configuration (Pauling, 1960). This effect in the latter case can be attributed to steric repulsion between the C^{α}_{6} and the H atoms bonded to C^{δ}_{14} of pyrrolidine ring II (Fig. 1). C^{γ}_{13} is deformed. The angle $O'_2-C'_5-N'_1$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36034 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is 124·9° which is in agreement with that cited by Corey & Pauling (1953); O'_3—C'_{10}—N'_2 is 122·7°, almost equal to that reported by Marsh & Donohue (1967), where it is 123·5°. N'_1—C^{α}_6—C'_{10} and N'_2—C^{α}_{11}—C'_{15} are 109·7 and 110·7°, respectively, which are comparable to the usual 110°. The molecules are joined in pairs by a hydrogen bond O···OH, 2·613 Å.

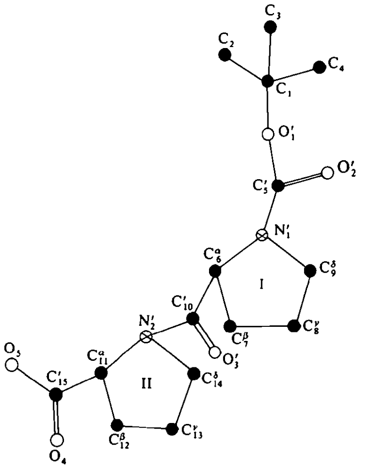

Fig. 1. Schematic drawing of Boc-Pro-Pro.

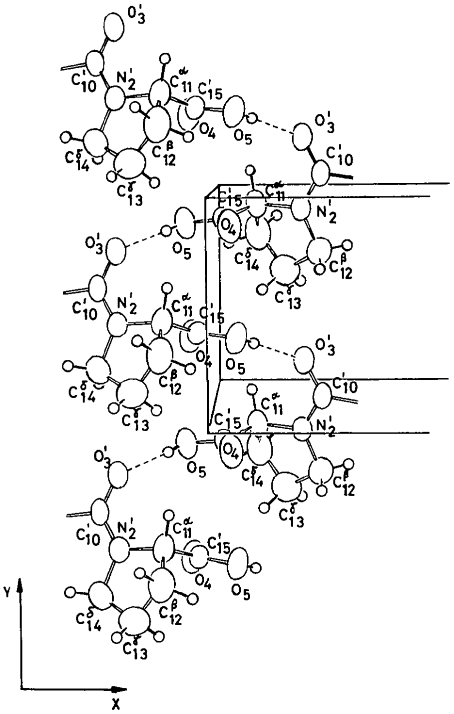

Fig. 2. Intermolecular hydrogen-bond scheme in Boc-Pro-Pro. Projection on the (001) plane. $O'_3 \cdots O_5$ 2·613, $O'_3 \cdots H_1(O_5)$ 1·818 Å.

The groups $NC^{\alpha}C^{\gamma}C^{\delta}$ of the two rings (I and II) are fairly planar. In both cases C^{β} is markedly displaced from the best plane and deviates by 0·45 and −0·57 Å, respectively. N'_1 and C^{γ}_8 for ring I and C^{α}_{11} and C^{δ}_{14} for ring II are on the same side as the carboxyl C'_{10} and C'_{15}. The displacements from their respective best plane $NC^{\alpha}C^{\gamma}C^{\delta}$ are: $N'_1 = -0{\cdot}0299$, $C^{\alpha}_6 = 0{\cdot}0186$, $C^{\gamma}_8 = -0{\cdot}0168$, $C^{\delta}_9 = 0{\cdot}0280$, $C^{\beta}_7 = 0{\cdot}4471$ and $C'_{10} = -1{\cdot}3579$ Å; and $N'_2 = -0{\cdot}0388$, $C^{\alpha}_{11} = 0{\cdot}0218$, $C^{\gamma}_{13} = -0{\cdot}0203$, $C^{\beta}_{12} = -0{\cdot}5682$ and $C'_{15} = 1{\cdot}4425$ Å. This prolyl residue can, therefore, be regarded as C_s-C^{γ}-*endo* (C^{β}-*exo*). The positive torsion angles $\chi_1 = 27{\cdot}0°$ and $\chi_{11} = 38{\cdot}4°$ imply that Boc-Pro-Pro belongs to conformation *B*. The other dihedral angles are $\chi_2 = -31{\cdot}1$, $\chi_3 = 22{\cdot}7$, $\chi_4 = -5{\cdot}3$, $\theta_1 = -12{\cdot}9$, $\omega_1 = -7{\cdot}0$, $\varphi_1 = -66{\cdot}6$, $\psi_1 = -39{\cdot}4$, $\psi_2 = 141{\cdot}4°$ (ON group) and $\chi_{22} = -35{\cdot}7$, $\chi_{33} = 18{\cdot}9$, $\chi_{44} = 5{\cdot}9$, $\theta_2 = -27{\cdot}9$, $\omega_2 = -175{\cdot}8$, $\varphi_2 = -95{\cdot}1$, $\psi_{22} = -168{\cdot}7$ (OH group), $\psi_{11} = 12{\cdot}1°$. It is noted that $\varphi_2 = -95{\cdot}1°$ and $\theta_2 = -27{\cdot}9°$ are widened more than usual [−45 to −75° and 15°, respectively, according to Balasubramanian *et al.* (1971)]. The negative value of ψ_1 indicates that Boc-Pro-Pro belongs to the α-helix type of proline compounds, whereas the collagen-type prolines exhibit positive ψ_1 values in the range +150 to +180° (Hospital, Courseille, Leroy & Roques, 1979). Boc-Pro-Pro can be compared to *N*-propionylproline (Kamwaya, Oster & Bradaczek, 1981) and Boc-Gly-Pro (Marsh, Murthy & Venkatesan, 1977), where ψ_1 is −5·8° and −24·7° respectively, but differs from Boc-Ala-Pro/H_2O (Kamwaya, 1980) which shows collagen-like peculiarities with $\psi_1 = 160{\cdot}9°$.

Fig. 2 is a packing diagram.

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The Structure of the 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Bis(dimethyl sulphone) Complex

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Abstract

$C_{12}H_{24}O_6.2C_2H_6O_2S$ is monoclinic, $P2_1/n$, with $a = 8.852\ (4)$, $b = 16.440\ (8)$, $c = 8.389\ (2)$ Å, $\beta = 107.39\ (2)°$, $U = 1165.0$ Å^3, $Z = 2$, $D_m = 1.26$, $D_c = 1.29$ Mg m^{-3}. Final $R = 0.049$ for 1902 observed reflections. The centrosymmetrical 18-crown-6 molecule has approximately D_{3d} symmetry; one methyl group of each dimethyl sulphone molecule yields three C—H···O contacts of 2·47 (4), 2·48 (4) and 2·62 (4) Å to alternate O atoms.

Introduction

The macrocyclic polyether, 18-crown-6, which was first synthesized by Pedersen (Pedersen, 1967) has proved a versatile complexing agent, not only for cations of suitable radius, approximately 0·8 Å and larger, but also as an acceptor of hydrogen bonds from O—H, N—H, and even C—H groups, as in the compounds formed with the dimethyl ester of acetylenedicarboxylic acid (Goldberg, 1975) or that with malononitrile (Kaufman, Knöchel, Kopf, Oehler & Rudolph, 1977); the compound can be purified *via* its complex with acetonitrile (Gokel, Cram, Liotta, Harris & Cook, 1974). Recently, Vögtle & Müller (1980) have reported a variety of molecular complexes with this and other crown ethers observing, as had Pedersen (1971) in his investigation of thiourea/crown interactions, a variety of stoichiometries. A crystalline complex having stoichiometry (2:1) dimethyl sulphone:18-crown-6 is the subject of the present study.

It was necessary to coat the crystals in Araldite to lessen decomposition in air; even so, two crystals were required for complete collection of intensities. Observations were collected on an Enraf–Nonius CAD-4 diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å). No absorption correction was

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