Acta Cryst. (1974). **B30**, 1783

The Crystal Structure of *N*-(t-Butyloxycarbonyl)-L-proline

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(*Received* 10 *January* 1974; *accepted* 4 *March* 1974)

The crystal structure of the title compound has been determined by X-ray diffraction analysis. It crystallizes in the orthorhombic system, space group $P2_12_12_1$, $Z=4$, with unit-cell dimensions $a=12{\cdot}114$, $b=8{\cdot}153$, $c=12{\cdot}102$ Å. The structure has been solved by direct methods; refinement was carried out by full-matrix least-squares procedures including anisotropic thermal parameters. The molecule consists essentially of two planes: the carboxylic group and the remaining atoms with the exception of the methyl groups. The pyrrolidine ring is puckered at the β-carbon atom which deviates about 0·52 Å from the best plane formed by the four remaining atoms. The molecules are held together in the crystal in pairs by one hydrogen bond, O(2)···O(3) 2·63 Å. Bond lengths and valence angles are comparable with those of various related compounds.

Introduction

Recently the importance of deformations of the pyrrolidinic ring has been pointed out (Maigret, Pullman & Caillet, 1970) particularly in relation to the question of populations of allowed conformations of biological macromolecules containing the proline residue. By means of conformational analysis (Ajò, Cappelli, Damiani, Natale, Lapiccirella & Tomasi, 1971) it has been possible to confirm the existence of a large number of allowed conformations for the pyrrolidine ring which are approximately isoenergetic but which have differences not only in the values of the torsion angles but also in the values of the valence angles.

In order to gain more experimental evidence on the geometrical parameters as well as on the conformational flexibility of such ring systems, we have undertaken the X-ray crystal-structure determination of a simple derivative of L-proline: *N*-t-butyloxycarbonyl-L-proline (t-BOC-L-Pro).

Experimental

A sample of t-BOC-L-Pro* was obtained from Schwarz Bioresearch Inc. and crystals suitable for X-ray analysis were grown from aqueous solutions. A summary of crystal data is given in Table 1. Approximate unit-cell dimensions and space-group information were obtained from Weissenberg photographs. The crystals were found to belong to the orthorhombic system, space group $P2_12_12_1$. Precise lattice constants together with their estimated standard deviations were determined from a least-squares refinement (Busing & Levy, 1967) of the setting angles (θ,χ,φ) of eight high-angle reflexions on an automated diffractometer, using Cu $K\alpha$ radiation.

Table 1. *Crystal data of* t-BOC-L-PRO

Molecular formula	$C_{10}H_{17}NO_4$
Molecular weight	199·26
Space group	$P2_12_12_1$
Z	4
a	12·114 ± 0·005 Å
b	8·153 ± 0·007
c	12·102 ± 0·005
V	1195·2 Å^3
Density, flotation (CCl_4–n-heptane)	1·11 g cm^{-3}
Density, calculated	1·11 g cm^{-3}
Radiation	Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å; Ni-filtered
Number of independent reflexions	952
Temperature	23°, ambient

The data collection was carried out on a Siemens AED automatic single-crystal diffractometer equipped with a digital computer, scintillation counter and pulse-height analyser (Ni-filtered Cu $K\alpha$ radiation, $\lambda=1{\cdot}5418$ Å). The θ–2θ mode with the five-measurements technique was employed (Siemens AED manual, Bild 7). A fixed symmetrical scan range of 0·65° from the computed Cu $K\alpha$ peak was used. Intensity data were collected for the independent reflexions up to $\theta=60°$. A standard reflexion was measured at regular intervals to monitor crystal stability and crystal orientation. Its intensity remained essentially constant throughout the run (within 5%). In total, 1065 independent reflexions were collected, 113 of which were considered unobserved since their intensity was less than $3\sigma(I)$. The data were corrected for Lorentz and polarization effects and no absorption correction was applied because of the small size of the crystal used in the data collection.

Structure determination and refinement

An overall temperature factor ($B=4{\cdot}2$ Å^2) and scale factor were evaluated (Wilson, 1942) and used to compute normalized structure factors (E's) (Karle & Hauptman, 1956). The statistics of the E's confirmed

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* No attempt was made to determine the configuration by means of anomalous scattering.

an acentric structure. The structure was solved by direct methods by the application of the tangent formula in the form programmed by Germain, Main & Woolfson (1971). The 417 greatest E's were used to compute the reliabilities α_h of phases to be expected from the tangent formula refinement. The best starting set was selected by an iterative procedure, *CONVERGE*, and two additional starting phases were evaluated from a $\sum_1$ relationship (Hauptman & Karle, 1953). The starting set of phases was:

h	k	l	Phase	
0	4	2	π	from $\sum_1$ relationship
0	6	10	π	
0	7	1	$\pi/2$	origin-fixing
6	4	7	$\pi/4$ or $7\pi/4$	
1	7	1	$\pi/4$ enantiomorph-fixing	
1	8	1	$\pi/4$, $3\pi/4$, $5\pi/4$, $7\pi/4$	
5	2	8	$\pi/4$, $3\pi/4$, $5\pi/4$, $7\pi/4$.	

This choice produced 32 starting points. By iterative weighted tangent-formula refinement the phases of 377 E's were determined. Of all the 32 possible combinations, judging by probability characteristics such as the absolute figure of merit ($F_{\rm abs}$), the ψ_0, the sum of the residuals (R) and mostly from the combined figure of merit defined as

$$C=\frac{F_{\rm abs}-(F_{\rm abs})_{\rm min}}{(F_{\rm abs})_{\rm max}-(F_{\rm abs})_{\rm min}}+\frac{\psi_{0\,\rm max}-\psi_0}{(\psi_0)_{\rm max}-(\psi_0)_{\rm min}}+\frac{R_{\rm max}-R}{R_{\rm max}-R_{\rm min}},$$

only four sets of phases seemed to be correct. They presented differences in the shift of the origin. An E map computed with the 377 strongest E's from one of these four sets of phases revealed the whole structure apart from the hydrogen atoms.

The structure was then refined through a total of 15 least-squares cycles;* anisotropic thermal factors were assigned to all heavy atoms after the 10th cycle when the conventional R value $(=\sum|F_o|-|F_c|/\sum|F_o|)$ was 0·15. A difference Fourier synthesis calculated after the 13th cycle of refinement when the R value was 0·08 revealed the positions of all the hydrogen atoms. Their coordinates were then introduced in the last two cycles, assuming isotropic thermal parameters equal to those of the corresponding carrier atoms. The parameters of the hydrogen atoms were kept fixed. The atomic scattering factors for all atomic species were calculated from the analytical constants given by Moore (1963). Unit weight was experimentally found to be correct during the refinement. The refinement was ended when the maximum shifts in the atomic coordinates and anisotropic thermal parameters were less than one-fifth of the corresponding standard deviations. For all non-zero independent reflexions the final disagreement index was 0·050. The final atomic coordinates and thermal factors are listed in Table 2, while Table 3 contains a list of the observed and calculated structure factors.

Table 2. *Final atomic parameters with their estimated standard deviations*

E.s.d.'s are in units of the last significant figure.

(*a*) Positional parameters

	x/a	y/b	z/c
O(1)	0·3139 (3)	0·5503 (4)	0·4369 (3)
O(2)	0·2084 (3)	0·7714 (4)	0·4149 (2)
O(3)	0·2442 (3)	0·2658 (3)	0·7038 (2)
O(4)	0·1193 (3)	0·4044 (3)	0·5978 (2)
N	0·2669 (3)	0·5347 (4)	0·6587 (3)
C(1)	0·2581 (4)	0·8578 (5)	0·4746 (3)
C(2)	0·2354 (4)	0·6799 (5)	0·5968 (3)
C(3)	0·3091 (4)	0·8114 (6)	0·6485 (4)
C(4)	0·4115 (5)	0·7196 (8)	0·6823 (5)
C(5)	0·3727 (4)	0·5522 (7)	0·7183 (4)
C(6)	0·2124 (3)	0·3909 (5)	0·6568 (3)
C(7)	0·0390 (4)	0·2679 (5)	0·5903 (3)
C(8)	−0·0520 (5)	0·3424 (7)	0·5203 (5)
C(9)	−0·0033 (5)	0·2250 (7)	0·7053 (4)
C(10)	0·0911 (5)	0·1232 (7)	0·5292 (5)
H(1)C(10)	0·135	0·152	0·461
H(2)C(10)	0·167	0·081	0·559
H(3)C(10)	0·025	0·051	0·558
H(1)C(9)	−0·037	0·380	0·733
H(2)C(9)	−0·070	0·144	0·700
H(3)C(9)	0·050	0·233	0·771
H(1)C(8)	−0·026	0·402	0·438
H(2)C(8)	−0·103	0·427	0·569
H(3)C(8)	−0·106	0·251	0·482
H(1)C(5)	0·124	0·487	0·295
H(2)C(5)	0·129	0·548	0·173
H(1)C(4)	0·456	0·743	0·617
H(2)C(4)	0·428	0·816	0·765
H(1)C(3)	0·371	0·847	0·594
H(2)C(3)	0·319	0·906	0·578
H(1)C(2)	0·150	0·720	0·607
H(1)O(2)	0·201	0·787	0·681

(*b*) Thermal parameters in the form:

$$T=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	7·4 (2)	6·5 (2)	5·5 (2)	3·6 (2)	−0·8 (1)	0·4 (2)
O(2)	7·5 (2)	5·0 (1)	3·5 (1)	2·4 (1)	−1·0 (1)	−0·4 (1)
O(3)	6·3 (2)	3·6 (1)	3·5 (1)	0·5 (1)	1·0 (1)	−0·4 (1)
O(4)	4·1 (1)	3·7 (1)	4·5 (1)	−0·6 (1)	0·6 (1)	−1·0 (1)
N	3·7 (1)	4·1 (1)	3·6 (1)	−0·4 (1)	0·9 (1)	−0·3 (1)
C(1)	4·6 (2)	4·0 (2)	3·7 (2)	0·3 (2)	−0·6 (2)	0·2 (2)
C(2)	4·7 (2)	3·1 (1)	3·7 (2)	−0·4 (2)	−0·1 (2)	−0·1 (1)
C(3)	6·2 (3)	4·7 (2)	6·0 (2)	−2·0 (2)	0·3 (2)	0·5 (2)
C(4)	6·0 (3)	7·3 (3)	8·1 (3)	−2·7 (3)	1·6 (3)	0·1 (3)
C(5)	5·0 (2)	6·3 (3)	6·0 (2)	−1·4 (2)	2·3 (2)	−0·5 (2)
C(6)	4·2 (2)	4·0 (2)	2·5 (1)	0·0 (2)	0·1 (1)	0·3 (1)
C(7)	4·3 (2)	3·7 (2)	3·8 (2)	−0·7 (2)	0·3 (2)	0·3 (2)
C(8)	5·0 (2)	6·1 (3)	7·3 (3)	−0·5 (2)	1·2 (2)	0·3 (3)
C(9)	6·7 (3)	6·6 (3)	5·4 (3)	−2·1 (3)	−1·3 (2)	−0·2 (2)
C(10)	6·5 (3)	5·8 (3)	7·2 (3)	0·0 (2)	−0·0 (3)	1·9 (3)

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* A set of crystallographic Fortran IV programs written by Immirzi (1967) was used. All the computations were carried out at the Centro Calcolo Elettronico della Facoltà di Scienze (IBM 360/44 PS) of the University of Naples, Italy.

Results and discussion

In Table 4 bond lengths, bond angles and torsion angles are reported together with their estimated

Table 3. *Structure factors*

F_o and F_c aıe ×10.

```
K,L=  0,   0
  H   FO   FC
  6  375  384
  8  155  148
 12   32   36
 14   31   28

K,L=  1,   0
  H   FO   FC
 14   11    2
 13   13    9
 12   28   32
 11   32   34
  9   98   95
  8   45   51
  7  199  202
  6   81   81
  5   36   37
  4   76   71
  3  383  385

K,L=  2,   0
  H   FO   FC
  1  323  311
  2   58   69
  3  217  215
  4  486  491
  5   19   23
  6  108  113
  7   23   30
  9   51   48
 10   30   30
 11   84   89
 12   32   31

K,L=  3,   0
  H   FO   FC
 12   13    1
 11   49   47
 10   78   83
  9   87   89
  7  131  125
  5   67   68
  4  382  383
  3  147  147
  2  454  452
  1  147  152

K,L=  4,   0
  H   FO   FC
  0  194  185
  1  133  130
  2  110  108
  3  322  306
  4  243  240
  5   89   81
  6   28   31
  9   84   87
 10   14    7
 11   14    4
 12   12   11

K,L=  5,   0
  H   FO   FC
 12   20   16
 10   32   27
  9   23   28
  8   30   25
  7   62   67
  6   25   23
  5  166  173
  4   50   55
  3   51   45
  2  123  119
  1   28   29

K,L=  6,   0
  H   FO   FC
  0  144  148
  1   49   50
  2   28   30
  3   30   32
  4   96   95
  5   20   21
  6   56   57
  7   61   62
  8   18   20
  9   14    9
 10   36   31
 11   11    3

K,L=  7,   0
  H   FO   FC
  9   12   13
  7   14    5
  6   35   35
  5   14    4
  4   83   79
  3   90  110
  2   39   34
  1   27   32

K,L=  8,   0
  H   FO   FC
  0   16   12
  1   24   27
  2   26   27
  3   24   25
  4   14    8
  5   23   22
  6   19   18
  7   12    5

K,L=  9,   0
  H   FO   FC
  4   11    1
  3   37   37
  2   16   17
  1   12   11

K,L=  9,   1
  H   FO   FC
  0   12    2
  1   15   19
  2   28   24
  3   28   25
  4   11   10

K,L=  8,   1
  H   FO   FC
  7   24   21
  6   36   36
  5   62   62
  4   18   21
  3   45   42
  2   77   76
  1  132  128
  0   67   66

K,L=  7,   1
  H   FO   FC
  0  190  197
  1  170  175
  2  103   98
  3   73   74
  4   53   55
  5   62   66
  6   66   66
  7   43   43
  8   38   37
  9   22   22

K,L=  6,   1
  H   FO   FC
 11   14    9
  9   20   18
  8   56   59
  7   15   15
  6   72   75
  5   55   52
  4   14   12
  3   38   38
  2  108   99
  1   69   66
  0  119  112

K,L=  5,   1
  H   FO   FC
  0   92   89
  1   81   78
  2   69   66
  3  124  117
  4  103  106
  5   75   68
  6   67   69
  7   46   50
  8   99   97
  9   79   79
 10   55   50

 11   19   19
 12   15   11

K,L=  4,   1
  H   FO   FC
 12   18   19
 11   22   22
 10   52   49
  9   74   73
  8   97   90
  7  136  135
  6  131  130
  5   96   99
  3  223  225
  2  147  141
  1   96   82
  0   10    6

K,L=  3,   1
  H   FO   FC
  0  216  226
  1  176  166
  2  164  159
  3  284  267
  4  265  268
  5  226  230
  6  102   95
  8   64   63
  9  101  101
 10  115  115
 11   63   61
 12   37   34
 13   23   23

K,L=  2,   1
  H   FO   FC
 13   46   46
 12   41   42
 11  130  124
 10   54   56
  9   56   59
  8   60   58
  7   88   87
  6  224  223
  5  242  236
  3  251  228
  2  212  224
  1  279  283

K,L=  1,   1
  H   FO   FC
  3  342  330
  5  183  174
  6   91   93
  7   76   74
  8   21   23
  9   54   59
 10   22   26
 11   42   38
 12   64   60
 13   31   32
 14   14   16

K,L=  0,   1
  H   FO   FC
 14   11    5
 13   13    8
 11   17   11
 10  100   98
  9   24   21
  8   82   78
  7   58   48
  4   53   55
  2  118  124
  1  175  198

K,L=  0,   2
  H   FO   FC
  0  157  159
  5  243  242
  7  253  249
  8  143  148
  9  127  111
 10   32   27
 12   22   20
 14   26   26

K,L=  1,   2
  H   FO   FC
 14   11    7
 13   47   41
 12   45   56
 11   15    2
 10   24   23
  9   63   62
  8  170  182
  7  143  137
  6  243  250
  5  142  132
  4   59   57
  3  309  292
  2  215  221

K,L=  2,   2
  H   FO   FC
  0  113  104
  1   97  100
  2   79   86
  3  113   99
  5  143  132
  6  118  131
  7  101   93
  8   30   29
  9   49   44
 10   90   94
 12   48   47
 13   24   29

K,L=  3,   2
  H   FO   FC
 13   19   18
 12   27   29
 11   48   52
 10   35   39
  9  138  140
  8   68   73
  7   89   85
  6   47   44
  5  207  203
  4   96   90
  3  185  186
  1   95   96
  0  148  149

K,L=  4,   2
  H   FO   FC
  0  312  315
  3   66   65
  4  124  117
  5  136  129
  6  134  134
  9   75   70
 10  100   94
 11   84   80
 12   51   51

K,L=  5,   2
  H   FO   FC
 11   39   38
 10   65   65
  9   49   55
  8   67   71
  7   46   45
  6  119  115
  5   19   15
  4  137  128
  3   13   19
  2   63   48
  1   96   93
  0   36   24

K,L=  6,   2
  H   FO   FC
  0   98   89
  1   30   30
  2   81   85
  3  107  104
  5   68   73
  6   78   76
  7   58   54
  8   57   57
  9   32   35
 10   33   29

K,L=  7,   2
  H   FO   FC
  9   37   36
  8   34   35
  7   59   61

  5   35   34
  4   63   66
  3   97   92
  2   39   38
  1   88   86
  0   83   84

K,L=  8,   2
  H   FO   FC
  0   14    5
  1   17   17
  2   56   55
  3   21   23
  4   49   50
  5   13    3
  7   31   28

K,L=  9,   2
  H   FO   FC
  4   11    8
  3   54   53
  2   25   21
  1   47   47
  0   60   57

K,L=  9,   3
  H   FO   FC
  0   12    4
  1   13   12
  2   19   20
  3   16   14

K,L=  8,   3
  H   FO   FC
  7   14   17
  6   31   31
  5   29   29
  4   49   48
  3   48   49
  2   62   62
  1   40   38
  0   14    7

K,L=  7,   3
  H   FO   FC
  0  127  124
  1   59   59
  2  109  113
  3   40   42
  4   66   74
  5   20   17
  6   28   31
  7   13    6
  8   12   12
  9   27   27

K,L=  6,   3
  H   FO   FC
 10   20   21
  9   18   20
  8   46   46
  7   86   87
  6   45   47
  5  101  105
  4   78   77
  3   22   25
  2  113  113
  1  106  100

K,L=  5,   3
  H   FO   FC
  0   31   41
  3   54   55
  4   13   15
  5   32   35
  6  123  129
  7   94   93
  8   60   59
  9   47   47
 10   13    5
 11   39   39

K,L=  4,   3
  H   FO   FC
 12   23   23
 11   15   13
 10   43   41
  9   88   82
  8   60   62
  6   68   63
  5   92   96
  0  271  264

K,L=  3,   3
  H   FO   FC
  0   60   59
  1  258  262
  2   38   30
  3  227  215
  4  181  189
  5  158  143
  6   89   97
  8  104  104
 10   71   79
 11   31   29
 12   29   29
 13   15   14

K,L=  2,   3
  H   FO   FC
 13   19   15
 12   64   64
 11   46   43
 10   76   76
  9   80   80
  8   26   24
  7   23   24
  6  117  107
  5  166  172
  4  240  246
  3  318  324
  2  111   97
  1  432  453

K,L=  1,   3
  H   FO   FC
  0   85   82
  1  203  220
  3  323  329
  4  391  401
  5  109   96
  6   60   46
  7   86   77
  8  145  149
  9   31   24
 10   77   68
 11   85   85
 12   21   17
 13   17   20

K,L=  0,   3
  H   FO   FC
 13   31   40
 12   25   21
 11   62   54
  9   14    8
  8   56   55
  7   57   50
  6  124  128
  5  296  293
  3  267  261
  2  143  146

K,L=  0,   4
  H   FO   FC
  0  220  227
  2  369  381
  4   59   55
  6   32   40
  7   68   61
  8   41   37
  9   61   63
 11   27   23
 12   48   52
 13   12    1

K,L=  1,   4
  H   FO   FC
 13   46   43
 12   32   30
 11   34   37
 10   15   10
  9   73   63
  8   67   81
  6   49   46
  5  173  153
  4  163  161
  3   87   71
  2  304  297

  1  210  208
  0  366  391

K,L=  2,   4
  H   FO   FC
  1  133  146
  2  179  183
  3   87   93
  4  115  115
  5  100   93
  6  168  176
  7   99   90
  8  124  119
  9   79   83
 10   15    9
 11   27   26
 12   43   39

K,L=  3,   4
  H   FO   FC
 12   35   30
 11   39   42
 10   51   51
  9   37   39
  8   96   99
  7   85   89
  6   65   63
  5  201  214
  4  164  162
  3  271  275
  2  122  116
  1   71   67
  0  287  283

K,L=  4,   4
  H   FO   FC
  0   73   76
  1  241  252
  2   64   60
  3  121  116
  4  130  117
  5   49   46
  6   55   46
  7  141  145
  8   72   74
  9   47   46
 10   35   34
 11   24   21
 12   30   27

K,L=  5,   4
  H   FO   FC
 11   37   36
 10   22   19
  9   37   40
  8   49   65
  7   42   38
  6   69   69
  5   58   58
  4   86   85
  3   35   32
  2   13   13
  1  119  117
  0   78   76

K,L=  6,   4
  H   FO   FC
  0   86   77
  1   57   62
  2   65   73
  3  126  122
  4   66   61
  5   34   34
  7   21   23
  8   40   41
  9   19   13
 10   22   18

K,L=  7,   4
  H   FO   FC
  7   26   26
  6   14   26
  5   14   11
  3   66   55
  1   60   53
  0   29   25

K,L=  8,   4
  H   FO   FC
  0   19   20
  1   51   50
  2   32   32
  3   60   61
  4   15   20
  5   18   23
  6   20   23

K,L=  9,   4
  H   FO   FC
  2   27   27
  0   12   16

K,L=  8,   5
  H   FO   FC
  6   21   18
  5   50   49
  4   43   41
  3   48   48
  2   59   57
  1   13    1
  0   69   62

K,L=  7,   5
  H   FO   FC
  0   14    4
  1   90   92
  2   51   46
  3  107  105
  4   40   36
  5   35   38
  6   18   19
  8   11    6

K,L=  6,   5
  H   FO   FC
  9   22   24
  8   26   22
  7   59   57
  6   57   55
  5   53   51
  4   49   49
  3   40   41
  2   81   80
  0   78   68

K,L=  5,   5
  H   FO   FC
  0   13    9
  1   85   85
  3   90   86
  4  112  101
  5   76   78
  6   63   64
  7   45   46
  8   80   76
  9   28   26
 10   32   37
 11   11   10

K,L=  4,   5
  H   FO   FC
 11   13   12
 10   28   30
  9   63   57
  8   30   32
  7  118  124
  6   84   84

K,L=  5,   5
  H   FO   FC
  4  111  101

K,L=  4,   5
  H   FO   FC
  4   37   37
  3   34   35
  2  139  143
  1   62   60
  0   60   55

K,L=  3,   5
  H   FO   FC
  0  304  322
  1   81   87
  2  244  240
  3   27   20
  6  130  121
  8  168  162
  9   44   35

 10   14    7
 11   34   31
 12   12    6

K,L=  2,   5
  H   FO   FC
 12   35   31
 11   26   27
 10   73   70
  9   14   43
  8   29   23
  7   77   74
  6  208  197
  5   92   87
  4   53   47
  3  258  267
  2  105  108
  1  147  142
  0   12   10

K,L=  1,   5
  H   FO   FC
  0  356  348
  1  321  333
  2  293  283
  3   99  112
  4  337  344
  5  170  167
  6   55   58
  7   62   58
  8   14    8
  9   90   86
 10   15    8
 11   23   21
 12   28   34
 13   31   30

K,L=  0,   5
  H   FO   FC
 13   21   15
 12   13   11
 11   14   15
 10  118  119
  9   33   25
  8   28   25
  7  113   93
  6   17   21
  5   52   48
  4  110  100
  1  272  281

K,L=  0,   6
  H   FO   FC
  0  114  113
  1  144  134
  2   42   46
  3   46   64
  4  132  124
  5   12   21
  6  139  137
  7  102  102
  9   15    3
 10   14    0
 11   14    8
 12   48   46

K,L=  1,   6
  H   FO   FC
 12   24   21
 11   27   22
 10   20   22
  9   22   30
  8  167  164
  7   39   43
  6  104  104
  5  150  149
  4  225  226
  3  218  228
  2  116  118
  1  115  106
  0  203  216

K,L=  2,   6
  H   FO   FC
  0   96   79
  1  147  158
  2  148  142
  3  150  149
  4  191  192
  5   86   88
  6   65   52
  7  112  114
  8   23   25
  9   23   25
 10   30   31
 11   37   34
 12   21   16

K,L=  3,   6
  H   FO   FC
 12   23   22
 11   13    8
  9   65   64
  8   74   84
  6   89   89
  5   81   81
  4  104  104
  2  149  155
  1   68   60

K,L=  4,   6
  H   FO   FC
  0   82   81
  1  133  131
  2   71   73
  3   87   84
  4  124  121
  5   91   92
  6   33   32
  7   79   82
  8   90   90
  9   40   34
 10   20   19
 11   16   14

K,L=  5,   6
  H   FO   FC
 10   15   12
  9   42   39
  8   14   18
  7   69   63
  6   39   37
  5   29   34
  4   67   60
  2   41   34
  1   21   18
  0   79   75

K,L=  6,   6
  H   FO   FC
  0  104  100
  1   81   89
  2   58   49
  3   91   91
  4   35   34
  5  112  108
  6   33   35
  7   45   43
  8   31   30
  9   17   16

K,L=  7,   6
  H   FO   FC
  7   24   23
  6   42   42
  5   32   34
  4   31   29
  3   14   10
  2   64   58
  1   14   11
  0   21   20

K,L=  8,   6
  H   FO   FC
  0   13   14
  1   48   55
  2   33   30
  4   14   13
  5   14   15

K,L=  8,   7
  H   FO   FC
  3   17   17
  2   32   30
  1   13   13
  0   36   37

K,L=  7,   7
  H   FO   FC

  0   21   17
  1   23   24
  3   38   39
  4   15   12
  5   21   21
  6   11   14

K,L=  6,   7
  H   FO   FC
  8   11    1
  7   22   21
  6   23   18
  5   91   87
  4   52   48
  3   68   77
  2   22   22
  1   43   42
  0   15    8

K,L=  5,   7
  H   FO   FC
  0   25   32
  1   96   90
  2   41   38
  3   29   34
  4   86   97
  5   59   64
  6   97   95
  7   49   44
  8   33   29
  9   13   14

K,L=  4,   7
  H   FO   FC
 10   24   21
  9   16   11
  8   74   67
  7   58   54
  6  125  129
  5   16   16
  4   81   83
  3   33   35
  2  135  125
  1   91   81
  0  146  140

K,L=  3,   7
  H   FO   FC
  0  162  156
  1   13   22
  2   80   73
  3   34   32
  5   70   67
  6   33   35
  7  113  110
  8   14    7
  9   54   47
 10   16   12
 11   12   13

K,L=  2,   7
  H   FO   FC
 11   21   22
 10   50   44
  9   65   60
  8   25   23
  7   57   55
  6  111  108
  5   72   78
  4  187  190
  3   37   37
  2  226  228
  1   46   44

K,L=  1,   7
  H   FO   FC
  0   85   74
  1   93   83
  2  123  120
  3  234  227
  5   87   80
  6   49   42
  8   64   76
 10   48   40
 12   28   24

K,L=  0,   7
  H   FO   FC
 12   34   36
 11   23   25
 10   66   51
  9   50   44
  8   23   23
  6  121  129
  5  119  122
  4   16   10
  3   20   21
  2   34   33
  1   34   33

K,L=  0,   8
  H   FO   FC
  0  209  206
  1   27   14
  3  122  118
  4   70   74
  5   28   33
  6   23   17
  7   91   80
  8   15   13
  9  158  151
 10   17   16
 11   28   25

K,L=  1,   8
  H   FO   FC
 11   18   15
 10   17   15
  9   27   30
  8   67   62
  7   78   72
  6   15   17
  5   25   26
  4  139  138
  2   57   44
  1  121  104
  0   86   77

K,L=  2,   8
  H   FO   FC
  0   56   56
  1   74   69
  2  117  112
  3  113  120
  4  114  113
  5  176  187
  6  112  114
  7   62   46
  9   76   75
 10   13    7
 11   40   39

K,L=  3,   8
  H   FO   FC
 10   22   23
  9   13   19
  8   58   58
  7  104  105
  6   99  100
  5  152  154
  4  134  127
  3   78   77
  2  178  178
  1   50   50
  0  179  179

K,L=  4,   8
  H   FO   FC
  0  134  132
  1   41   37
  2   65   55
  3   21   22
  4   70   63
  5   54   46
  6   92   91
  7   51   31
  8   22   15
  9   13   13
 10   16   15

K,L=  5,   8
  H   FO   FC
  9   11    5
  8   35   31
  7   13   14
  6   14    9
  5   27   24
  4  112  108
  3   26   24

  2  118  114
  1   90   93
  0   56   60

K,L=  6,   8
  H   FO   FC
  1   25   24
  3   65   64
  4   35   32
  5   32   32
  6   12   10
  7   27   26

K,L=  7,   8
  H   FO   FC
  5   24   24
  4   12    2
  3   16   14
  2   16   12
  1   35   34
  0   45   50
 -1   29   34

K,L=  7,   9
  H   FO   FC
  0   12    5
  1   31   33
  2   21   28
  3   13   15

K,L=  6,   9
  H   FO   FC
  6   21   17
  5   46   48
  4   46   44
  3   58   56
  2   22   24
  1   50   51
  0   19   13

K,L=  5,   9
  H   FO   FC
  1  120  115
  2   68   68
  3   90   92
  4   69   66
  5   82   81
  7   43   49
  8   16   16

K,L=  4,   9
  H   FO   FC
  9   11    6
  8   27   27
  7   31   26
  6   86   84
  5   30   33
  4   60   55
  3   66   66
  2   72   74
  1   86   82
  0  129  128

K,L=  3,   9
  H   FO   FC
  0   28   32
  1  101   90
  2   32   29
  3   85   85
  4   77   75
  5  100   98
  6   16   14
  7   28   33
  8   15   14
 10   11    7

K,L=  2,   9
  H   FO   FC
  9   13   18
  7   49   46
  4  110  112
  3  104   97
  2   79   74
  1   30   27
  0   66   61

K,L=  1,   9
  H   FO   FC
  0   87   83
  1  110  101
  2   70   77
  3   43   39
  4   14   15
  5   14   18
  7   63   64
  8   14    8
  9   13    8
 10   12   13

K,L=  0,   9
  H   FO   FC
 11   18   19
 10   12    3
  9   14    0
  7   65   68
  6   29   33
  5   45   43
  4   38   33
  3   26   25
  2   88   83
  1   27   32

K,L=  0,  10
  H   FO   FC
  0  128  128
  1   15    5
  2   57   55
  3   14    7
  5   82   88
  6   44   43
  7   25   21
  8   13   82
  9   39   36
 10   19   17

K,L=  1,  10
  H   FO   FC
 10   11    9
  9   18   17
  8   37   38
  7   51   50
  6   92   87
  5   40   39
  4  107  114
  3  103   96
  2   45   44
  1   36   30
  0   34   32

K,L=  2,  10
  H   FO   FC
  1   41   33
  2   95   93
  3   73   71
  4  153  151
  5   76   73
  6   42   41
  7   31   36
  9   12    4

K,L=  3,  10
  H   FO   FC
  9   18   19
  8   13   14
  6   66   64
  5   39   34
  4   14   13
  3   58   57
  2   55   48
  1   97   97
  0   88   87

K,L=  4,  10
  H   FO   FC
  0   72   76
  1   57   56
  2   43   42
  3   65   62
  4   66   64
  5   64   59
  6   13    5
  7   34   31
  8   19   23

K,L=  5,  10
  H   FO   FC
  6   12    4
  5   31   32
  4   32   37

  3   61   54
  2   14    5
  1   36   34
  0   17   17

K,L=  6,  10
  H   FO   FC
  0   44   51
  1   34   37
  3   26   25
  4   26   27

K,L=  6,  11
  H   FO   FC
  1   11    0
  0   15   23

K,L=  5,  11
  H   FO   FC
  0   13   12
  1   23   23
  2   15   16
  3   36   35
  4   16   17
  5   32   35

K,L=  4,  11
  H   FO   FC
  6   46   46
  4   13   13
  2   26   25
  1   39   37
  0   16   15

K,L=  3,  11
  H   FO   FC
  0   48   51
  1   45   40
  2   47   47
  3   39   48
  4   42   40
  5   13   13
  6   27   26
  7   19   21

K,L=  2,  11
  H   FO   FC
  8   29   30
  7   17   14
  6   67   67
  5   59   59
  4   23   23
  3   60   52
  1   52   42
  0   23   13

K,L=  1,  11
  H   FO   FC
  0   15   13
  1   48   53
  2   74   75
  3   43   46
  4   35   34
  5   32   33
  6   35   34
  7   55   51
  8   14    8

K,L=  0,  11
  H   FO   FC
  9   26   26
  8   12    4
  7   17   17
  6   16   20
  5   14   11
  4   58   51
  3   30   30
  2   83   85
  1   48   47

K,L=  0,  12
  H   FO   FC
  0   69   68
  1   14    6
  2   50   51
  3   45   49
  4   22   27
  6   12    4
  7   29   24

K,L=  1,  12
  H   FO   FC
  7   25   24
  6   15   15
  5   52   47
  4   46   46
  3   40   41
  1   57   55

K,L=  2,  12
  H   FO   FC
  0   14    2
  1   31   31
  2   33   31
  3   21   20
  4   46   41
  5   38   41
  6   40   41
  7   33   31

K,L=  3,  12
  H   FO   FC
  6   28   28
  5   28   31
  4   65   65
  3   52   42
  2   13   14
  1   17   12
  0   18   18

K,L=  4,  12
  H   FO   FC
  0   12   10
  1   24   23
  2   19   17
  3   12   33
  4   11    3

K,L=  5,  12
  H   FO   FC
  1   37   37
  0   20   21

K,L=  3,  13
  H   FO   FC
  0   28   23
  1   30   26
  2   42   39
  3   15   16

K,L=  2,  13
  H   FO   FC
  4   19   18
  3   19   22
  2   36   35
  1   38   33
  0   13   14

K,L=  1,  13
  H   FO   FC
  1   13    3
  2   31   29
  3   24   31
  4   12   12
  5   20   19

K,L=  0,  13
  H   FO   FC
  5   35   35
  4   12    2
  3   13    1
  2   13    3
  1   31   31

K,L=  0,  14
  H   FO   FC
  0   17   21
  2   21   23

K,L=  1,  14
  H   FO   FC
  2   29   34
  1   30   30
```

Table 4. *Molecular geometry*

E.s.d.'s are in units of the last significant figure.

(*a*) Bond distances (Å)

C(1)–O(1)	1·197 (6)
C(1)–O(2)	1·320 (5)
C(1)–C(2)	1·515 (6)
C(2)–C(3)	1·529 (7)
C(3)–C(4)	1·506 (8)
C(4)–C(5)	1·509 (8)
C(5)–N(1)	1·468 (6)
N(1)–C(2)	1·452 (5)
N(1)–C(6)	1·346 (5)
C(6)–O(3)	1·231 (5)
C(6)–O(4)	1·339 (5)
O(4)–C(7)	1·481 (5)
C(7)–C(8)	1·517 (7)
C(7)–C(9)	1·523 (7)
C(7)–C(10)	1·529 (7)

(*b*) Bond angles (°)

O(1)–C(1)–O(2)	124·3 (2)
O(1)–C(1)–C(2)	124·1 (2)
O(2)–C(1)–C(2)	111·5 (1)
C(1)–C(2)–C(3)	112·1 (2)
C(1)–C(2)–N(1)	111·0 (1)
C(2)–C(3)–C(4)	104·0 (2)
C(3)–C(4)–C(5)	105·8 (2)
C(4)–C(5)–N(1)	102·5 (2)
C(5)–N(1)–C(2)	113·6 (2)
N(1)–C(2)–C(3)	102·0 (2)
C(2)–N(1)–C(6)	124·9 (2)
C(5)–N(1)–C(6)	121·2 (2)
N(1)–C(6)–O(3)	124·1 (2)
N(1)–C(6)–O(4)	110·5 (1)
O(3)–C(6)–O(4)	125·3 (1)
C(6)–O(4)–C(7)	121·6 (1)
O(4)–C(7)–C(8)	102·1 (2)
O(4)–C(7)–C(9)	109·7 (2)
O(4)–C(7)–C(10)	109·8 (2)
C(8)–C(7)–C(9)	110·9 (2)
C(8)–C(7)–C(10)	109·8 (2)
C(9)–C(7)–C(10)	113·8 (2)

(*c*) Internal rotation angles (°)

O(1)–C(1)–C(2)–C(3)	100
O(1)–C(1)–C(2)–N(1)	−14
O(2)–C(1)–C(2)–C(3)	−81
O(2)–C(1)–C(2)–N(1)	166
C(1)–C(2)–C(3)–C(4)	−88
C(1)–C(2)–N(1)–C(5)	102
C(1)–C(2)–N(1)–C(6)	−72
C(2)–C(3)–C(4)–C(5)	−35
C(2)–N(1)–C(5)–C(4)	−4
C(2)–N(1)–C(6)–O(3)	175
C(2)–N(1)–C(6)–O(4)	−6
C(3)–C(4)–C(5)–N(1)	24
C(3)–C(2)–N(1)–C(5)	−17
C(3)–C(2)–N(1)–C(6)	168
C(4)–C(3)–C(2)–N(1)	31
C(4)–C(5)–N(1)–C(6)	171
C(5)–N(1)–C(6)–O(3)	1
C(5)–N(1)–C(6)–O(4)	180
N(1)–C(6)–O(4)–C(7)	185
C(6)–O(4)–C(7)–C(8)	178
C(6)–O(4)–C(7)–C(9)	60
C(6)–O(4)–C(7)–C(10)	−66
O(3)–C(6)–O(4)–C(7)	5

Table 5. *Least-squares planes*

The equations of the planes are of the form:

$$AX+BY+CZ-D=0$$

where X, Y and Z are coordinates (in Å) referred to the orthogonal axes and D is the origin-to-plane distance.

Carboxyl group

$$0{\cdot}8066X+0{\cdot}5859Y+0{\cdot}0780Z-6{\cdot}0975=0$$

Deviations of atoms from the plane (Å)

C(1)	$+0{\cdot}001_2$
C(2)	$-0{\cdot}000_4$
O(1)	$-0{\cdot}000_4$
O(2)	$-0{\cdot}000_4$

Pyrrolidine ring

$$-0{\cdot}4670X+0{\cdot}2298Y+0{\cdot}8539Z-6{\cdot}2489=0$$

Deviations of atoms from the plane (Å)

N	+0·040
C(2)	−0·150
C(3)	+0·212
C(4)	−0·190
C(5)	+0·089

Plane through N, C(2), C(4) and C(5)

$$-0{\cdot}458X+0{\cdot}390Y+0{\cdot}799Z-6{\cdot}5932=0$$

Deviations of atoms from the plane (Å)

N	−0·022
C(2)	+0·014
C(4)	−0·013
C(5)	+0·021

Amide group

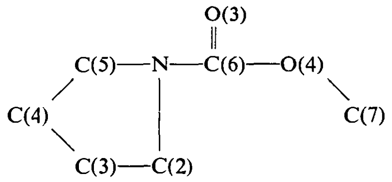
$$-0{\cdot}504X+0{\cdot}295Y+0{\cdot}812Z-6{\cdot}087=0$$

Deviations of atoms from the plane (Å)

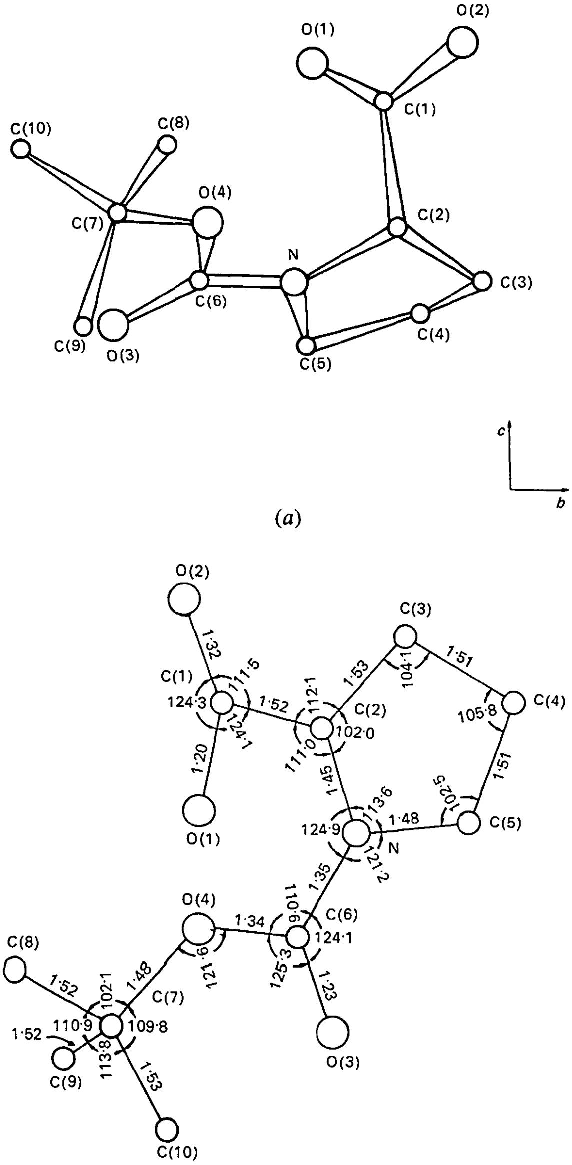
N	+0·031
C(2)	−0·037
C(5)	+0·013
C(6)	+0·001
O(3)	−0·031
O(4)	+0·022

standard deviations.* In Fig. 1 a schematic drawing and a view of the molecule along the *c* axis are shown. The geometrical parameters experimentally found in the present structure are comparable with the values found in other peptides or aminoacids containing the proline residue within the errors reported for those structures.

The molecule of t-BOC-L-Pro is essentially composed of two planes: the carboxyl group, formed by the atoms O(1), O(2), C(1) and C(2), and the plane of the residue:



However, the above residue has large deviations from a strictly planar arrangement. The equations of the least-squares planes and the distances of individual atoms from the planes are given in Table 5. As is commonly



(*a*)

(*b*)

Fig. 1. (*a*) A view of the molecule as seen along the [001] direction. (*b*) Schematic drawing of t-BOC-L-Pro with the final geometrical parameters. The C(9)–C(7)–O(4) and C(10)–C(7)–C(8) angles are 109·7 and 109·8° respectively.

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* The e.s.d.'s given in Table 4 have been calculated neglecting vibrational motion effects, which could play some role in inducing an additional error in the geometrical parameters. This may be particularly true where atoms which display larger anisotropic thermal parameters are involved. However, in our structure no unusually large vibrational motion seems to be present.

found in molecules containing proline residues, the pyrrolidine ring takes a puckered conformation and, surprisingly, the β-carbon atom C(3) is displaced from the plane of the four remaining atoms by 0·519 Å. In all reported crystal structures of compounds containing the pyrrolidine ring (Mathieson & Welsh, 1952; Leung & Marsh, 1958; Fridrichsons & Mathieson, 1962; Ueki, Ashida, Kakudo, Sasada & Katsube, 1969; Mitsui *et al.*, 1969; Matsuzaki & Iitaka, 1971; Kartha & Ambady, 1972; Shamala & Venkatesan, 1973) it has been found that the γ-carbon atom deviates from the plane formed by the remaining four atoms, except in the crystal structure of DL-proline hydrochloride (Mitsui *et al.*, 1969) in which the α-carbon atom is displaced from the best plane. In many cases large variations of internal rotation angles are possible because of the possibility of coupling of small bond-angle deformations or the simultaneous variation of bond angles and other internal rotation angles. An example of these changes is the five-membered ring of cyclopentane in which the conformation can vary almost continuously on an equipotential energy surface (Lifson & Warshel, 1968). Recently, several authors (Ramachandran, Lakshminarayanan, Balasubramanian & Tegoni, 1970; Balasubramanian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran, 1971; A. Damiani, private communication) have carried out calculations of the potential energy arising from bond-angle and torsion-angle strain, non-bonded and electrostatic interatomic energies in order to determine the favoured conformations of the prolyl residue. The results of such calculations show that the pyrrolidine ring must be considered rather flexible, and a large number of possible almost isoenergetic conformations can be predicted. In particular Ramachandran *et al.* (1970) have found two local minima in conformational space for the pyrrolidine ring, one with the C^{γ} displaced on the same side as C', which is lower in energy than the other with C^{γ} displaced on the side opposite to C' (denoted respectively as conformations *A* and *B*). The torsion angle θ tends to be much closer to zero than any other torsion angle, indicating that the atoms N, C^{α}, C^{β} and C^{δ} tend to be coplanar. Positive values of θ are associated with conformation *A* and negative values of θ with conformation *B*.

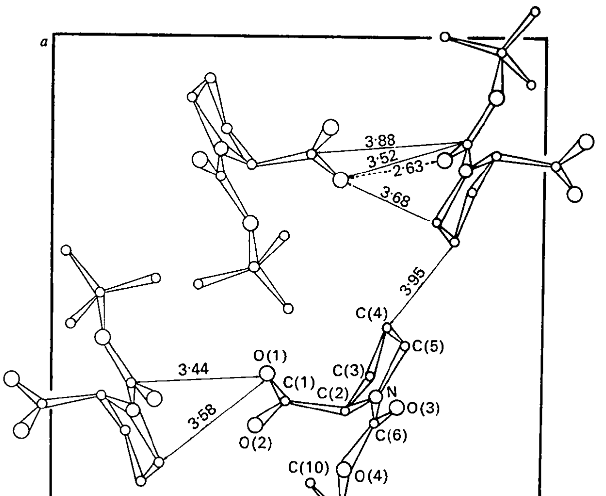
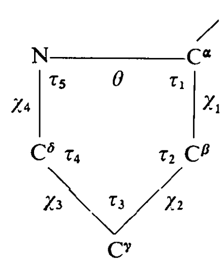


Fig. 2. Mode of packing of t-BOC-L-Pro along the [010] direction. The hydrogen-bond distances are indicated as broken lines. Some short intermolecular distances are reported.



However, the calculations indicate that χ_4 can also be small, meaning that the atoms C^{γ}, C^{δ}, N and C^{α} are also nearly coplanar as found in the present structure. A comparison of the bond angles and torsion angles experimentally found for t-BOC-L-Pro and one of the lowest-energy *B* conformations is reported in Table 6; the values are in very good agreement, showing that the conformation of the pyrrolidine ring observed in the crystal structure is very close to one of the conformations having minimal strain energy in the isolated state calculated from considerations of intramolecular interactions only. The t-BOC-L-Pro structure consists of hydrogen-bonded pairs of molecules, the hydrogen bond being formed between molecules related by a screw axis along **c**. The O(2)–O(3) distance between hydrogen-bonded atoms (see Fig. 2) is 2·63 Å. The need for hydrogen-bond formation coupled with crystal packing interactions in which the β-C atom is involved is probably also responsible for the experimentally found conformation of the pyrrolidine ring. In fact, no rather short intramolecular contact involving the pyrrolidine ring atoms seems to be present and on the other hand a planar conformation or a conformation in which the γ-carbon is out of the plane on either side of the ring would produce a poor hy-

Table 6. *Comparison of the bond angles and torsion angles of one of the lowest-energy B conformations (see text) and those of* t-BOC-L-Pro (°)

	τ_1	τ_2	τ_3	τ_4	τ_5	θ	χ_1	χ_2	χ_3	χ_4
t-BOC-L-Pro	102·0	104·1	105·8	102·5	113·6	−17	+31	−35	+24	−4
Conformation *B*	103	104	107	102	113	−15	+29	−33	+24	−5

drogen bond as far as the distance between oxygen atoms and directions of bond are concerned. The data available at present on crystal structures of molecules containing the pyrrolidine ring and those reported here thus confirm that this ring is a rather flexible one and its conformation is affected by various factors including intramolecular and/or intermolecular interactions such as hydrogen bonds. The orientation of the carboxylic group is such that the ketonic group C(1)–O(1) is in the preferred synplanar conformation with respect to the N–C(2) bond of the pyrrolidine ring, as has often been found (Dunitz & Strickler, 1966, 1968). The internal rotation angle N–C(2)–C(1)–O(1) is 13°.

The t-butyl group is in a staggered conformation with respect to the C(6)–O(3) bond. Accordingly, short contacts arise between the methyl groups C(9) and C(10) and the oxygen atom O(3) (3·02 and 3·04 Å respectively).

Finally the mode of packing in the crystal merits a short discussion. In Figs. 2 and 3 the views of the crystal structure along the [010] and [001] directions are shown. The structure consists of pairs of molecules linked by the formation of one hydrogen bond. The O(1) and O(4) atoms are not involved in any bonding other than van der Waals contacts. Some of the shortest intermolecular distances are reported in Figs. 2 and 3.

This work has been carried out with the support of Research Grant 71/01561 from the Italian C.N.R.

We are grateful to Professors P. A. Temussi and A. Damiani for helpful suggestions and criticism.

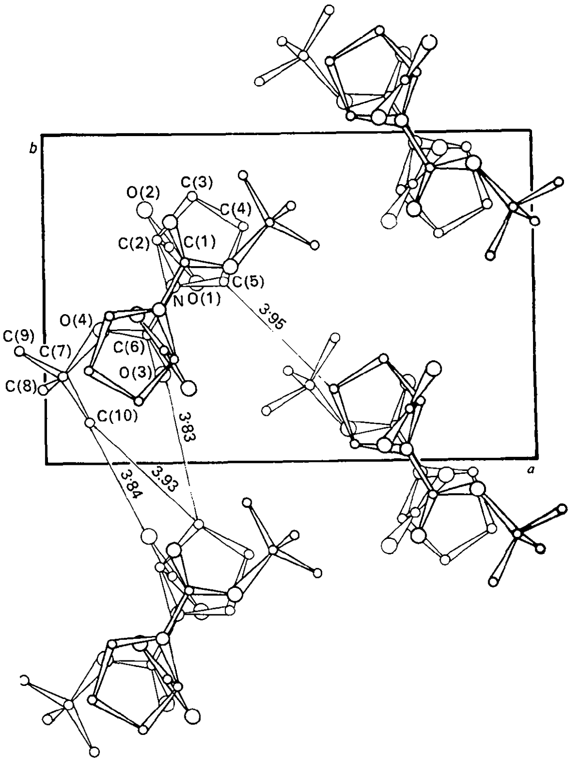


Fig. 3. Mode of packing of t-BOC-L-Pro along the [001] direction. Some of the shortest intermolecular distances are indicated.

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