

## 3-(*tert*-Butyloxycarbonylamino)- bicyclo[1.1.1]pentanecarboxylic acid at 293 K

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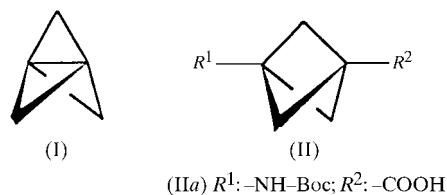
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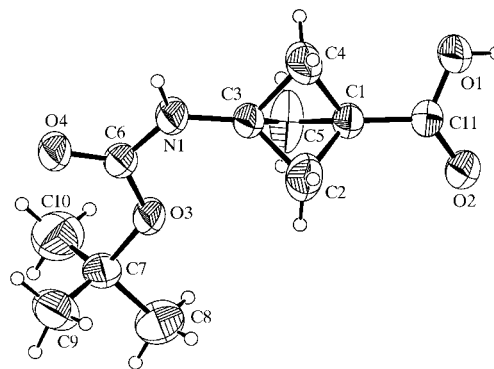
In the room-temperature X-ray structure of the *N*-Boc-protected derivative of the novel 3-aminobicyclo[1.1.1]pentanecarboxylic acid, C<sub>11</sub>H<sub>17</sub>NO<sub>4</sub>, the interbridgehead distance in the bicyclo[1.1.1]pentane cage is 1.852 (2) Å. The carboxyl and parts of the blocked amino group are almost in plane with one of the cage triangles. N—H···O and O—H···O hydrogen bonds generate infinite corrugated molecular chains in the crystal lattice.

### Comment

There is considerable interest in structural studies on the [1.1.1]propellane (I) and related bicyclo[1.1.1]pentane (II) derivatives in order to investigate the covalent or non-covalent nature of the interbridgehead linkage. A summary of X-ray analyses executed on this subject is given in the recent review article of Levin *et al.* (2000), reporting interbridge distances in the range 1.80–1.91 Å for type (II) derivatives and 1.46–1.50 Å for intercage C—C bonds for compounds of type (I). Charge-density studies of appropriate (I) and (II) derivatives should contribute to the bonding/non-bonding question in the intercage region. However, previous electron-difference-density studies have not yet allowed a definite conclusion to be drawn (Irgangtinger *et al.*, 1990; Seiler *et al.*, 1988).



The title compound is a protected derivative of the novel 3-aminobicyclo[1.1.1]pentanecarboxylic acid (Pätzelt *et al.*, 2000). This compound can be considered as a rigid analogue of the 4-aminobutyric acid, which acts as a neurotransmitter in

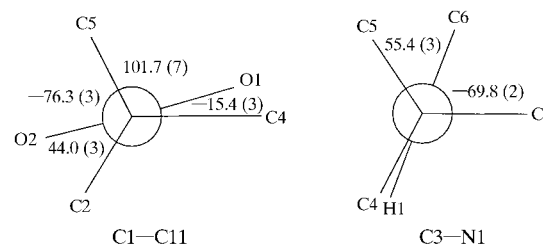


**Figure 1**  
The molecular structure (*ORTEP*II; Johnson, 1976) of the title compound showing the chosen numbering scheme.

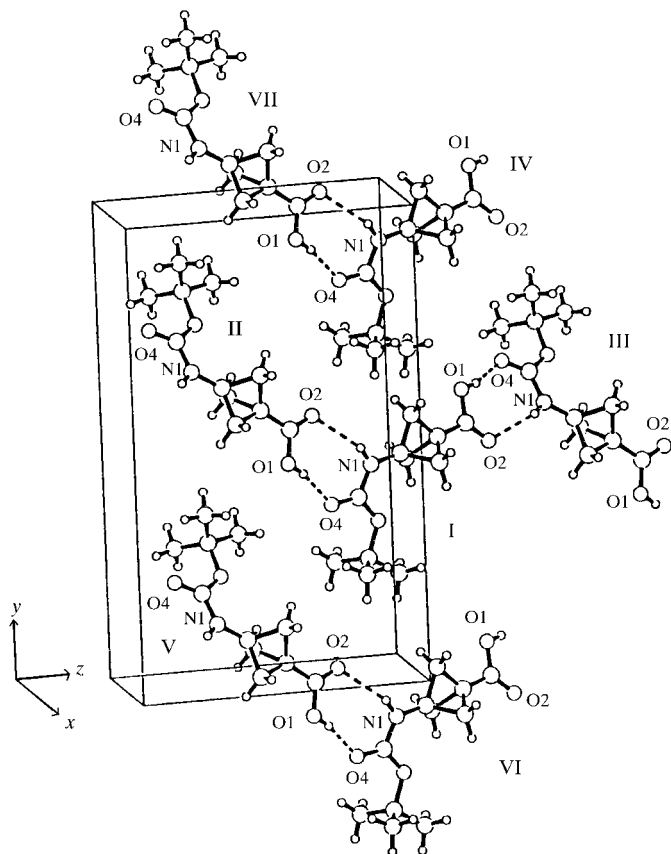
the brain. In our ongoing project of charge-density studies on the 20 naturally occurring amino acids, the title compound was considered as an interesting alternative of an unnatural example. Here we report as a first result on the room-temperature structure of the *N*-Boc-derivative, (IIa) (Boc = *tert*-butyloxycarbonyl).

The molecular structure with the chosen atomic numbering scheme is shown in the *ORTEP*II (Johnson, 1976) representation in Fig. 1. The bicyclo[1.1.1]pentane cage has dimensions as expected. The interbridge distance C1—C3, being 1.852 (2) Å, is in the recently reported range (Levin *et al.*, 2000), and not far from the value of 1.874 Å found in an electron-diffraction study (Almenningen *et al.*, 1971) for the unsubstituted parent type (II) cage. Also, all further bond lengths and angles in this cage and in the substituent regions are in normal ranges and need no further discussion. A local threefold symmetry in the bicyclo[1.1.1]pentane moiety is nicely realized. Having the line C1···C3 in common, the three triangles with C2, C4 and C5 as apices form interplanar angles which differ less than 1.5° from 60°.

The relative orientations of the carboxyl and the blocked amino group to the bicyclo[1.1.1]pentane fragment is illustrated in the two Newman projections of Fig. 2. The carboxyl group is almost in plane with the C1—C4—C3 triangle, as seen from the C4—C1—C11—O1 torsion angle of -15.4 (3)°. On the opposite side, the torsion angle C4—C3—N1—C6 of 173.5 (2)° indicates also an almost coplanar arrangement. This is in agreement with the recent findings of in-plane conformations for some aryl-substituted bicyclo[1.1.1]pentanes (Rehm *et al.*, 1999). For the torsions along N1—C6 and C6—O3, the angles differ by less than 10° from zero or 180°, so that a more or less planar molecular fragment exists where the only



**Figure 2**  
Newman projections (angles in °) along C1—C11 and C3—N1.



**Figure 3**  
Packing illustration in a projection of the lattice onto the  $yz$  plane (SCHAKAL; Keller, 1988). Symmetry codes are as follows: (I)  $x, y, z$ ; (II)  $-1+x, 1-y, -\frac{1}{2}+z$ ; (III)  $1+x, 1-y, \frac{1}{2}+z$ ; (IV)  $\frac{1}{2}+x, \frac{1}{2}+y, z$ ; (V)  $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (VI)  $\frac{1}{2}+x, -\frac{1}{2}+y, z$ ; (VII)  $-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$ .

(non-H) out-of-plane atoms are the methyl C atoms C9/C10 and the cage atoms C2/C5.

The crystal packing is shown in Fig. 3. Two hydrogen bonds with the carboxyl O1–H and the amino N1–H as donors connect molecules *via* the crystallographic glide plane  $[N1-H1 \cdots O2(-1+x, 1-y, -\frac{1}{2}+z): H \cdots O = 2.30, N \cdots O = 3.091(2) \text{ \AA}, N-H \cdots O = 153^\circ; O1-H10 \cdots O4(1+x, 1-y, \frac{1}{2}+z): H \cdots O = 1.78, O \cdots O4 = 2.588(2) \text{ \AA}, O-H \cdots O = 166^\circ]$ . These linkages establish infinite corrugated molecular chains in the  $[201]$  direction at  $y = 0, \frac{1}{2}, \text{etc.}$  No interchain contacts exist in the crystal lattice.

## Experimental

The synthesis of (IIa) was described by Pätzel *et al.* (2000). Crystals suitable for X-ray analysis were prepared by slow evaporation from diethyl ether.

### Crystal data

$C_{11}H_{17}NO_4$   
 $M_r = 227.26$   
Monoclinic,  $Cc$   
 $a = 6.0851(2) \text{ \AA}$   
 $b = 18.3460(4) \text{ \AA}$   
 $c = 11.3499(6) \text{ \AA}$   
 $\beta = 94.020(3)^\circ$   
 $V = 1263.95(8) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.194 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 10385 reflections  
 $\theta = 2.22\text{--}32.13^\circ$   
 $\mu = 0.091 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
Prism, yellow  
 $0.40 \times 0.40 \times 0.18 \text{ mm}$

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

|             |              |              |             |
|-------------|--------------|--------------|-------------|
| C1–C11      | 1.482 (2)    | N1–C6        | 1.335 (2)   |
| C1–C5       | 1.524 (3)    | C6–O4        | 1.227 (2)   |
| C1–C4       | 1.541 (3)    | C6–O3        | 1.329 (2)   |
| C1–C2       | 1.544 (3)    | O3–C7        | 1.476 (2)   |
| C1–C3       | 1.852 (2)    | C7–C9        | 1.499 (4)   |
| C2–C3       | 1.535 (3)    | C7–C10       | 1.508 (4)   |
| C3–N1       | 1.434 (2)    | C7–C8        | 1.526 (3)   |
| C3–C5       | 1.517 (3)    | C11–O2       | 1.209 (2)   |
| C3–C4       | 1.533 (3)    | C11–O1       | 1.305 (2)   |
| C11–C1–C4   | 127.15 (16)  | C3–C2–C1     | 73.98 (14)  |
| C4–C1–C2    | 86.43 (18)   | N1–C3–C4     | 123.37 (15) |
| C5–C1–C3    | 52.33 (12)   | C4–C3–C2     | 87.02 (18)  |
| C4–C1–C3    | 52.77 (11)   |              |             |
| C5–C3–N1–C6 | 55.4 (3)     | C6–O3–C7–C9  | –62.4 (3)   |
| C4–C3–N1–C6 | 173.5 (2)    | C6–O3–C7–C10 | 64.0 (3)    |
| C2–C3–N1–C6 | –69.8 (3)    | C6–O3–C7–C8  | –178.7 (2)  |
| C3–N1–C6–O4 | –174.2 (2)   | C5–C1–C11–O1 | 101.7 (3)   |
| C3–N1–C6–O3 | 6.7 (3)      | C4–C1–C11–O1 | –15.4 (3)   |
| O4–C6–O3–C7 | 3.5 (3)      | C2–C1–C11–O1 | –137.9 (3)  |
| N1–C6–O3–C7 | –177.36 (18) |              |             |

### Data collection

CCD area-detector diffractometer  
 $\omega$  and  $\varphi$  scans  
10385 measured reflections  
4017 independent reflections  
2444 reflections with  $F > 4\sigma(F_o)$   
 $R_{\text{int}} = 0.027$

$\theta_{\text{max}} = 32.13^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -24 \rightarrow 27$   
 $l = -16 \rightarrow 16$   
Intensity decay: 2.0%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.139$   
 $S = 1.007$   
4017 reflections  
149 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 0.0246P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$

H atoms were refined with a riding model ( $C-H = 0.96\text{--}0.97 \text{ \AA}$ ). The Flack parameter (Flack, 1983), refined close to zero, was not significant.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SHELXTL (Siemens, 1996) and SAINT-Plus (Siemens, 1996); program(s) used to solve structure: SHELXS86 (Sheldrick, 1987); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SCHAKAL88 (Keller, 1988) and ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1400). Services for accessing these data are described at the back of the journal.

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