

Boc-AzAla-Ala-OMe

Cécile Abbas,^a Brigitte Jamart Grégoire,^a Régis Vanderesse^a and Claude Didierjean^{b*}

^aLaboratoire de Chimie Physique Macromoléculaire, UMR CRNS-INPL 7568, Nancy Université, BP 451, 54001 Nancy, France, and ^bLaboratoire de Cristallographie, Résonance Magnétique et Modélisations (CRM²), Nancy Université, UMR CNRS-UHP 7036, BP 70236, 54506 Vandoeuvre-lès-Nancy, France
Correspondence e-mail: claude.didierjean@crm2.uhp-nancy.fr

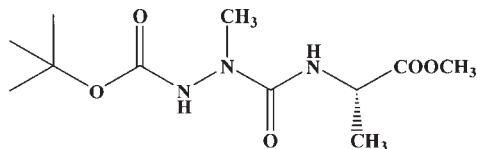
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.036; wR factor = 0.076; data-to-parameter ratio = 10.4.

The title compound (systematic name: *tert*-butyl 3-[[1-(methoxycarbonyl)ethyl]aminocarbonyl]-3-methylcarbazate), $\text{C}_{11}\text{H}_{21}\text{N}_3\text{O}_5$, is a precursor for the study of a new class of foldamer based on aza/ α -dipeptide oligomerization [Abbas *et al.* (2009). *Tetrahedron Lett.* **50**, 4158–4160]. The asymmetric unit consists of one molecule in an extended conformation which is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding.

Related literature

For the synthesis, see: Majer & Randad (1994); Brosse *et al.* (2001); Bouillon *et al.* (2004); Abbas *et al.* (2009). For the geometry of the aza-residue in azapeptides, see: Benatalah *et al.* (1991), André *et al.* (1996). For Boc-AzAla-Pro-NH₂, see: André *et al.* (1997). For the refinement procedure, see: Flack & Schwarzenbach (1988). For hydrogen-bond motifs, see: Etter (1990).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{21}\text{N}_3\text{O}_5$
 $M_r = 275.31$
Tetragonal, $P4_1$
 $a = 9.3194$ (4) Å
 $c = 17.4420$ (8) Å
 $V = 1514.86$ (12) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 100$ K
 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
14534 measured reflections
1847 independent reflections
1806 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.076$
 $S = 1.12$
1847 reflections
178 parameters
1 restraint
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.13$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1}\cdots\text{O2}^i$ | 0.86 | 2.18 | 2.972 (2) | 153 |
| $\text{N3}-\text{H3}\cdots\text{O3}^i$ | 0.86 | 2.03 | 2.850 (2) | 159 |
| $\text{C6}-\text{H6A}\cdots\text{O4}^{ii}$ | 0.96 | 2.55 | 3.303 (3) | 136 |
| $\text{C11}-\text{H11B}\cdots\text{O4}^{iii}$ | 0.96 | 2.41 | 3.346 (3) | 164 |

Symmetry codes: (i) $y, -x + 1, z - \frac{1}{2}$; (ii) $x - 1, y, z$; (iii) $y, -x + 2, z - \frac{1}{2}$.

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2501).

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Boc-AzAla-Ala-OMe

C. Abbas, B. Jamart Grégoire, R. Vanderesse and C. Didierjean

Comment

As part of our continuing studies on the synthesis and structure of hydrazino- and *N*-amino-peptides, we recently described the original and efficient synthesis of aza/ α -dipeptides *via* Mitsunobu and *trans*-protections protocols starting from *N*-*tert*-butyloxycarbonylamino-phthalimide (Abbas *et al.*, 2009; Majer & Randad 1994; Brosse *et al.* 2001; Bouillon *et al.* 2004). Aza-peptides are pseudopeptides, in which nitrogen has been substituted for at least one of the CH $^{\alpha}$ groups. Here we report the crystal structure of the pseudodipeptide Boc-AzAla-Ala-OMe (Fig. 1).

In the present study, the geometry of the aza-residue is similar to those observed for known azapeptides structures. In most of the cases, the α -nitrogen adopts a non-planar planar structure (André *et al.*, 1996; Benatalah *et al.* 1991). In the title compound, the deviation of the α -nitrogen out of the plane, defined by the three atoms bonded to it, is 0.268 (2) Å. The greatest difference from standard peptide group concern the bond lengths and bond angles around the α -nitrogen: (i) the N—N $^{\alpha}$ (N1—N2) and N $^{\alpha}$ —C $^{\beta}$ (N2—C6) bonds are shorter by about 0.06 Å than their homologous bonds in peptides; (ii) the N $^{\alpha}$ —C' (N2—C7) bond of 1.392 (3) Å is shorter than the homologous C $^{\alpha}$ —C' bond and exceeds the dimension of the amide bond; (iii) the bond angles around the α -nitrogen are larger by 5–6° than the bond angles around the α -carbon.

In the solid state, Boc-AzAla-Pro-NHiPr (André *et al.*, 1997) and the title compound Boc-AzAla-Ala-OMe adopt two distinct conformations with the N $^{\alpha}$ atoms having opposite configurations. In the former, the AzAla residue assumes the *R* chirality and the pseudodipeptide is folded by an intramolecular hydrogen bond between the (iPr)NH and the Boc(CO) groups. In the crystal of the title compound, the pseudodipeptides adopt an extended conformation which form infinite chains along the four fold axis. The N-H groups of AzaAla and Ala residues are engaged in intermolecular hydrogen bonds with the carbonyl groups of the N-terminal protecting group and the aza-residue, respectively, forming two C(4) chain motifs (Fig. 2, Etter 1990). Combination of these two motifs generates a new R 2_2 (12) pattern, shown in the Fig. 2. Finally, the third carbonyl group, C10=O4, is involved in weak CH \cdots O hydrogen bonds forming a threedimensional network structure.

Experimental

The title compound was prepared from *N*-*tert*-butyloxycarbonylamino-phthalimide (Abbas *et al.*, 2009), and was crystallized by slow evaporation of a diethyl ether solution.

Refinement

Because of the lack of any significant anomalous dispersion effects, the absolute configurations of the title compound could not be determined from the diffraction experiments but was known from the method of synthesis. The origin was fixed by floating-origin restraints (Flack & Schwarzenbach, 1988). All H atoms were located in difference Fourier maps. The C/N-bonded H atoms were placed at calculated positions and refined using a riding model, with C—H distances of 0.96–0.98

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Å and with N—H distance of 0.86 Å. The H-atom U_{iso} parameters were fixed at 1.2Ueq(C) for methine C—H, at 1.2Ueq(N) for the N—H group and at 1.5Ueq(C) for methyl C—H.

Figures

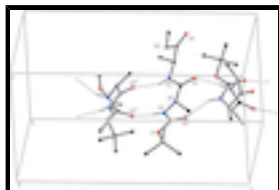


Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme. All non-H atoms are represented by 25% probability displacement ellipsoids.

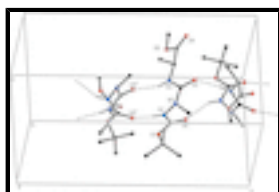


Fig. 2. Partial packing view of the title compound showing the formation of the C(4)C(4)[R²₂(12)] graph set motif parallel to [001]. H atoms not involved in hydrogen bondings have been omitted for clarity. H bonds are shown as dashed lines. [Symmetry code: (i) y, -x+1, z-1/4]

tert-butyl 3-[[1-(methoxycarbonyl)ethyl]aminocarbonyl]-3-methylcarbazate

Crystal data

C₁₁H₂₁N₃O₅

$M_r = 275.31$

Tetragonal, $P4_1$

Hall symbol: P 4w

$a = 9.3194(4)$ Å

$b = 9.3194(4)$ Å

$c = 17.4420(8)$ Å

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 1514.86(12)$ Å³

$Z = 4$

$F_{000} = 592$

$D_x = 1.207$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 14534 reflections

$\theta = 2.5$ – 27.9°

$\mu = 0.10$ mm⁻¹

$T = 100$ K

Prism, colorless

$0.3 \times 0.2 \times 0.2$ mm

Data collection

Nonis KappaCCD
diffractometer

$T = 100$ K

CCD rotation images, thick slices scans

Absorption correction: none

14534 measured reflections

1847 independent reflections

1806 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\text{max}} = 27.8^\circ$

$\theta_{\text{min}} = 2.5^\circ$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 12$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

1 restraint

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.036$$

$$wR(F^2) = 0.076$$

$$S = 1.12$$

1847 reflections

178 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0164P)^2 + 0.7016P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| C1 | 0.3488 (2) | 0.0563 (2) | 0.63461 (13) | 0.0228 (4) |
| C2 | 0.2822 (3) | -0.0204 (3) | 0.56621 (14) | 0.0311 (5) |
| H2A | 0.1902 | 0.021 | 0.5551 | 0.047* |
| H2B | 0.2706 | -0.1204 | 0.578 | 0.047* |
| H2C | 0.3438 | -0.0103 | 0.5224 | 0.047* |
| C3 | 0.2529 (3) | 0.0415 (2) | 0.70463 (14) | 0.0279 (5) |
| H3A | 0.2995 | 0.0837 | 0.7482 | 0.042* |
| H3B | 0.235 | -0.0582 | 0.7145 | 0.042* |
| H3C | 0.1635 | 0.0898 | 0.6954 | 0.042* |
| C4 | 0.5016 (3) | 0.0058 (3) | 0.64752 (15) | 0.0308 (5) |
| H4A | 0.557 | 0.022 | 0.6019 | 0.046* |
| H4B | 0.5015 | -0.0948 | 0.6594 | 0.046* |
| H4C | 0.5431 | 0.0583 | 0.6894 | 0.046* |
| O1 | 0.35134 (16) | 0.20833 (15) | 0.60837 (9) | 0.0218 (3) |
| C5 | 0.3987 (2) | 0.3109 (2) | 0.65626 (12) | 0.0193 (4) |
| O2 | 0.43957 (17) | 0.29435 (17) | 0.72181 (9) | 0.0239 (3) |
| N1 | 0.39666 (19) | 0.44041 (18) | 0.61993 (11) | 0.0201 (4) |
| H1 | 0.3753 | 0.4464 | 0.5721 | 0.024* |
| N2 | 0.43006 (19) | 0.56280 (19) | 0.66214 (11) | 0.0200 (4) |
| C6 | 0.3156 (2) | 0.6117 (2) | 0.71325 (14) | 0.0259 (5) |
| H6A | 0.2304 | 0.63 | 0.6839 | 0.039* |
| H6B | 0.3451 | 0.6982 | 0.7386 | 0.039* |
| H6C | 0.2961 | 0.5389 | 0.7508 | 0.039* |
| C7 | 0.5716 (2) | 0.5760 (2) | 0.68660 (12) | 0.0189 (4) |
| O3 | 0.60321 (16) | 0.65021 (16) | 0.74280 (8) | 0.0221 (3) |
| N3 | 0.67193 (19) | 0.50835 (19) | 0.64451 (10) | 0.0209 (4) |
| H3 | 0.6487 | 0.4606 | 0.6042 | 0.025* |
| C8 | 0.8201 (2) | 0.5181 (2) | 0.66902 (13) | 0.0232 (4) |
| H8 | 0.8264 | 0.478 | 0.7209 | 0.028* |

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|------|--------------|--------------|--------------|------------|
| C9 | 0.9146 (2) | 0.4274 (3) | 0.61671 (14) | 0.0296 (5) |
| H9A | 0.8853 | 0.3288 | 0.6198 | 0.044* |
| H9B | 1.0129 | 0.4358 | 0.6326 | 0.044* |
| H9C | 0.9052 | 0.4605 | 0.5648 | 0.044* |
| C10 | 0.8773 (2) | 0.6709 (3) | 0.67187 (13) | 0.0244 (4) |
| O4 | 0.97394 (18) | 0.7060 (2) | 0.71417 (11) | 0.0333 (4) |
| O5 | 0.81613 (16) | 0.75824 (17) | 0.62089 (9) | 0.0249 (3) |
| C11 | 0.8685 (3) | 0.9048 (3) | 0.62253 (16) | 0.0310 (5) |
| H11A | 0.8424 | 0.9487 | 0.6703 | 0.046* |
| H11B | 0.8267 | 0.9578 | 0.581 | 0.046* |
| H11C | 0.971 | 0.9048 | 0.6174 | 0.046* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.0313 (11) | 0.0171 (9) | 0.0199 (10) | -0.0034 (8) | 0.0039 (9) | 0.0017 (8) |
| C2 | 0.0429 (14) | 0.0269 (12) | 0.0236 (11) | -0.0138 (10) | 0.0058 (10) | -0.0039 (9) |
| C3 | 0.0345 (12) | 0.0232 (10) | 0.0261 (11) | -0.0033 (9) | 0.0091 (10) | -0.0012 (9) |
| C4 | 0.0339 (11) | 0.0269 (11) | 0.0317 (12) | 0.0044 (9) | 0.0059 (10) | 0.0039 (10) |
| O1 | 0.0288 (8) | 0.0190 (7) | 0.0178 (7) | -0.0036 (6) | -0.0026 (6) | 0.0000 (6) |
| C5 | 0.0183 (9) | 0.0217 (10) | 0.0180 (10) | -0.0021 (7) | 0.0011 (8) | -0.0017 (8) |
| O2 | 0.0304 (8) | 0.0240 (8) | 0.0172 (7) | -0.0031 (6) | -0.0033 (6) | 0.0007 (6) |
| N1 | 0.0251 (9) | 0.0199 (8) | 0.0155 (8) | -0.0020 (7) | -0.0033 (7) | -0.0001 (7) |
| N2 | 0.0217 (8) | 0.0204 (8) | 0.0178 (8) | -0.0010 (6) | 0.0005 (7) | -0.0014 (7) |
| C6 | 0.0224 (10) | 0.0256 (11) | 0.0295 (12) | 0.0017 (8) | 0.0029 (9) | -0.0037 (9) |
| C7 | 0.0213 (10) | 0.0190 (9) | 0.0164 (10) | -0.0028 (8) | 0.0009 (7) | 0.0023 (8) |
| O3 | 0.0240 (8) | 0.0256 (8) | 0.0165 (7) | -0.0023 (6) | 0.0026 (6) | -0.0024 (6) |
| N3 | 0.0197 (8) | 0.0273 (9) | 0.0157 (8) | -0.0014 (7) | 0.0003 (7) | -0.0035 (7) |
| C8 | 0.0212 (10) | 0.0306 (11) | 0.0179 (10) | 0.0013 (8) | -0.0020 (8) | 0.0005 (9) |
| C9 | 0.0231 (11) | 0.0413 (13) | 0.0243 (11) | 0.0049 (9) | 0.0008 (9) | -0.0043 (10) |
| C10 | 0.0186 (10) | 0.0357 (12) | 0.0188 (10) | 0.0012 (9) | 0.0007 (8) | -0.0009 (9) |
| O4 | 0.0263 (8) | 0.0421 (10) | 0.0316 (9) | -0.0027 (7) | -0.0105 (7) | -0.0012 (8) |
| O5 | 0.0228 (8) | 0.0301 (8) | 0.0217 (8) | -0.0039 (6) | -0.0038 (6) | 0.0018 (7) |
| C11 | 0.0283 (12) | 0.0330 (12) | 0.0317 (12) | -0.0052 (9) | -0.0019 (10) | 0.0031 (10) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-----------|--------|-----------|
| C1—O1 | 1.489 (2) | C6—H6A | 0.96 |
| C1—C4 | 1.517 (3) | C6—H6B | 0.96 |
| C1—C3 | 1.520 (3) | C6—H6C | 0.96 |
| C1—C2 | 1.523 (3) | C7—O3 | 1.235 (3) |
| C2—H2A | 0.96 | C7—N3 | 1.346 (3) |
| C2—H2B | 0.96 | N3—C8 | 1.448 (3) |
| C2—H2C | 0.96 | N3—H3 | 0.86 |
| C3—H3A | 0.96 | C8—C10 | 1.521 (3) |
| C3—H3B | 0.96 | C8—C9 | 1.524 (3) |
| C3—H3C | 0.96 | C8—H8 | 0.98 |
| C4—H4A | 0.96 | C9—H9A | 0.96 |
| C4—H4B | 0.96 | C9—H9B | 0.96 |

| | | | |
|-------------|-------------|---------------|--------------|
| C4—H4C | 0.96 | C9—H9C | 0.96 |
| O1—C5 | 1.344 (2) | C10—O4 | 1.210 (3) |
| C5—O2 | 1.215 (3) | C10—O5 | 1.334 (3) |
| C5—N1 | 1.363 (3) | O5—C11 | 1.450 (3) |
| N1—N2 | 1.393 (2) | C11—H11A | 0.96 |
| N1—H1 | 0.86 | C11—H11B | 0.96 |
| N2—C7 | 1.392 (3) | C11—H11C | 0.96 |
| N2—C6 | 1.463 (3) | | |
| O1—C1—C4 | 109.01 (17) | N2—C6—H6A | 109.5 |
| O1—C1—C3 | 110.01 (17) | N2—C6—H6B | 109.5 |
| C4—C1—C3 | 113.9 (2) | H6A—C6—H6B | 109.5 |
| O1—C1—C2 | 102.26 (17) | N2—C6—H6C | 109.5 |
| C4—C1—C2 | 110.7 (2) | H6A—C6—H6C | 109.5 |
| C3—C1—C2 | 110.32 (19) | H6B—C6—H6C | 109.5 |
| C1—C2—H2A | 109.5 | O3—C7—N3 | 122.0 (2) |
| C1—C2—H2B | 109.5 | O3—C7—N2 | 121.24 (19) |
| H2A—C2—H2B | 109.5 | N3—C7—N2 | 116.72 (18) |
| C1—C2—H2C | 109.5 | C7—N3—C8 | 118.14 (18) |
| H2A—C2—H2C | 109.5 | C7—N3—H3 | 120.9 |
| H2B—C2—H2C | 109.5 | C8—N3—H3 | 120.9 |
| C1—C3—H3A | 109.5 | N3—C8—C10 | 113.75 (18) |
| C1—C3—H3B | 109.5 | N3—C8—C9 | 109.84 (18) |
| H3A—C3—H3B | 109.5 | C10—C8—C9 | 109.64 (19) |
| C1—C3—H3C | 109.5 | N3—C8—H8 | 107.8 |
| H3A—C3—H3C | 109.5 | C10—C8—H8 | 107.8 |
| H3B—C3—H3C | 109.5 | C9—C8—H8 | 107.8 |
| C1—C4—H4A | 109.5 | C8—C9—H9A | 109.5 |
| C1—C4—H4B | 109.5 | C8—C9—H9B | 109.5 |
| H4A—C4—H4B | 109.5 | H9A—C9—H9B | 109.5 |
| C1—C4—H4C | 109.5 | C8—C9—H9C | 109.5 |
| H4A—C4—H4C | 109.5 | H9A—C9—H9C | 109.5 |
| H4B—C4—H4C | 109.5 | H9B—C9—H9C | 109.5 |
| C5—O1—C1 | 119.40 (17) | O4—C10—O5 | 124.0 (2) |
| O2—C5—O1 | 126.7 (2) | O4—C10—C8 | 122.3 (2) |
| O2—C5—N1 | 123.66 (19) | O5—C10—C8 | 113.58 (18) |
| O1—C5—N1 | 109.64 (18) | C10—O5—C11 | 114.71 (18) |
| C5—N1—N2 | 118.43 (18) | O5—C11—H11A | 109.5 |
| C5—N1—H1 | 120.8 | O5—C11—H11B | 109.5 |
| N2—N1—H1 | 120.8 | H11A—C11—H11B | 109.5 |
| C7—N2—N1 | 116.51 (17) | O5—C11—H11C | 109.5 |
| C7—N2—C6 | 118.49 (18) | H11A—C11—H11C | 109.5 |
| N1—N2—C6 | 114.46 (17) | H11B—C11—H11C | 109.5 |
| C4—C1—O1—C5 | -65.6 (2) | C6—N2—C7—N3 | 168.95 (18) |
| C3—C1—O1—C5 | 60.0 (2) | O3—C7—N3—C8 | 3.2 (3) |
| C2—C1—O1—C5 | 177.16 (18) | N2—C7—N3—C8 | -179.09 (18) |
| C1—O1—C5—O2 | -1.3 (3) | C7—N3—C8—C10 | -60.0 (3) |
| C1—O1—C5—N1 | 177.86 (17) | C7—N3—C8—C9 | 176.65 (19) |
| O2—C5—N1—N2 | -6.4 (3) | N3—C8—C10—O4 | 153.4 (2) |

supplementary materials

| | | | |
|-------------|--------------|---------------|-------------|
| O1—C5—N1—N2 | 174.45 (17) | C9—C8—C10—O4 | -83.2 (3) |
| C5—N1—N2—C7 | 68.4 (2) | N3—C8—C10—O5 | -30.0 (3) |
| C5—N1—N2—C6 | -75.9 (2) | C9—C8—C10—O5 | 93.5 (2) |
| N1—N2—C7—O3 | -156.14 (19) | O4—C10—O5—C11 | -3.6 (3) |
| C6—N2—C7—O3 | -13.3 (3) | C8—C10—O5—C11 | 179.84 (19) |
| N1—N2—C7—N3 | 26.1 (3) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1 \cdots O2 ⁱ | 0.86 | 2.18 | 2.972 (2) | 153 |
| N3—H3 \cdots O3 ⁱ | 0.86 | 2.03 | 2.850 (2) | 159 |
| C6—H6A \cdots O4 ⁱⁱ | 0.96 | 2.55 | 3.303 (3) | 136 |
| C11—H11B \cdots O4 ⁱⁱⁱ | 0.96 | 2.41 | 3.346 (3) | 164 |

Symmetry codes: (i) $y, -x+1, z-1/4$; (ii) $x-1, y, z$; (iii) $y, -x+2, z-1/4$.

Fig. 1

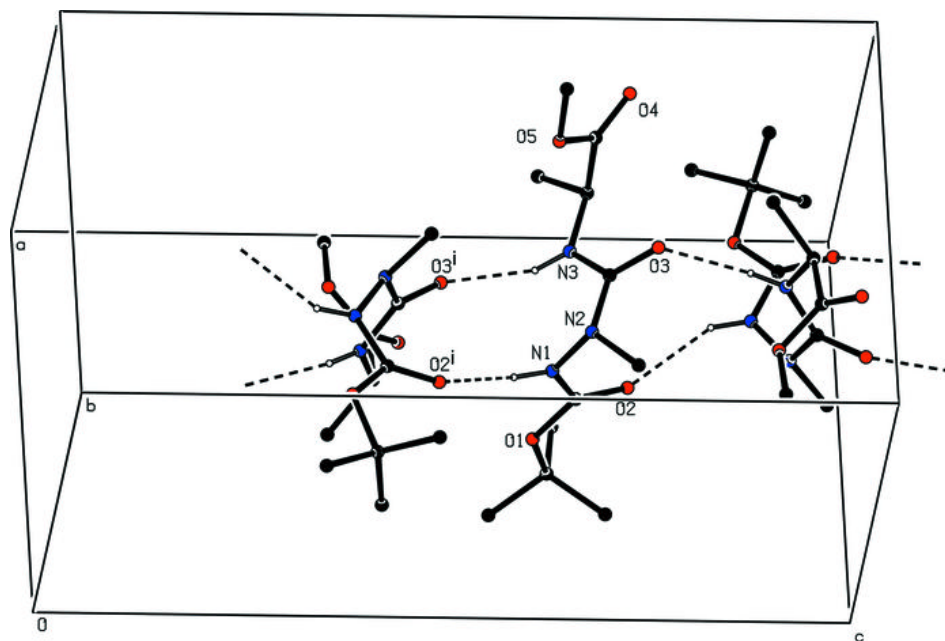


Fig. 2

