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# 3*a*,6*a*-Bis(ethoxycarbonyl)glycoluril (diethyl 2,5-dioxoperhydroimidazo-[4,5-*d*]imidazole-3a,6a-dicarboxylate)

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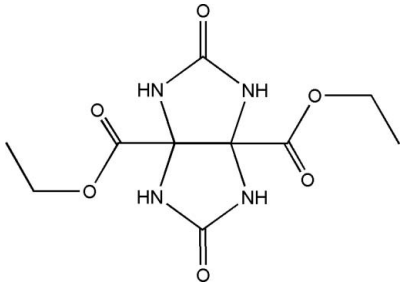
Key indicators: single-crystal X-ray study; $T$ = 292 K; mean $\sigma$(C–C) = 0.005 Å; disorder in main residue; $R$ factor = 0.068; $wR$ factor = 0.197; data-to-parameter ratio = 11.7.

The title compound, $C_{10}H_{14}N_4O_6$, crystallizes with two independent molecules in the asymmetric unit. An extensive network of N—H···O and C—H···O intermolecular hydrogen bonds stabilizes the crystal packing. One ethyl group is disordered over two positions; the site occupancy factors are 0.68 and 0.32.

## Related literature

For related literature, see: Burnett *et al.* (2003); Chen *et al.* (2007); Himes *et al.* (1978); Hof *et al.* (2002); Isaacs & Witt (2002); Kim *et al.* (2000); Li *et al.* (1994); Moon *et al.* (2003); Rowan *et al.* (1999); Wang *et al.* (2006, 2007); Wu *et al.* (2002).




## Experimental

### *Crystal data*

$C_{10}H_{14}N_4O_6$
$M_r$ = 286.25
Orthorhombic, *Pbca*
$a$ = 15.7555 (13) Å
$b$ = 11.2726 (9) Å
$c$ = 28.742 (2) Å
$V$ = 5104.7 (7) Å$^3$
$Z$ = 16
Mo $K\alpha$ radiation
$\mu$ = 0.12 mm$^{-1}$
$T$ = 292 (2) K
0.30 × 0.20 × 0.20 mm

### *Data collection*

Bruker SMART 4K CCD area-detector diffractometer
Absorption correction: none
29774 measured reflections
4501 independent reflections
2784 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.097

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.197
$S$ = 1.00
4501 reflections
385 parameters
6 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.42 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O2$^{i}$ | 0.86 | 2.15 | 2.963 (3) | 158 |
| N2—H2···O7$^{ii}$ | 0.86 | 2.10 | 2.927 (3) | 162 |
| N3—H3···O1$^{iii}$ | 0.86 | 2.11 | 2.937 (3) | 161 |
| N4—H4···O8$^{iv}$ | 0.86 | 2.21 | 2.879 (3) | 134 |
| N5—H5···O1$^{iv}$ | 0.86 | 2.22 | 2.870 (3) | 133 |
| N6—H6···O7$^{v}$ | 0.86 | 2.09 | 2.925 (3) | 164 |
| N7—H7···O2$^{ii}$ | 0.86 | 2.16 | 2.973 (3) | 158 |
| N8—H8···O8$^{vi}$ | 0.86 | 2.12 | 2.963 (3) | 165 |
| C16—H16*C*···O3$^{vii}$ | 0.96 | 2.51 | 3.087 (5) | 119 |
| C10—H10*B*···O11$^{v}$ | 0.96 | 2.32 | 3.162 (5) | 146 |

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

The authors are grateful to Central China Normal University for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2340).

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# supplementary materials

*Acta Cryst.* (2008). E**64**, o125 [ **doi:10.1107/S1600536807056292** ]

# 3α,6α-Bis(ethoxycarbonyl)glycoluril (diethyl 2,5-dioxoperhydroimidazo[4,5-*d*]imidazole-3a,6a-dicarboxylate)

**Y.-Z. Wang, Z.-G. Wang and L. Li**

## Comment

Glycoluril skeleton moiety (Fig. 3) is an important building block for both molecular and supramolecular chemistry. Its derivatives have been used as the basis for molecular capsules (Hof *et al.*, 2002), molecular clips (Rowan *et al.*, 1999), self-complementary facial amphiphiles (Isaacs *et al.*, 2002), and the cucurbit[*n*]uril (CB[*n*]) family (Kim *et al.*, 2000), and its utilization has been explored as a platform for studies of crystal engineering (Wang *et al.*, 2006; Chen *et al.*, 2007). However, relatively few crystal structures are known for glycoluril derivatives without N-substituents. The crystal structures of the reported glycoluril with different substituents exhibit two H-bonded types (Fig. 4). The mode A was found for (*R*=H) (Li *et al.*, 1994), (*R*=$CH_3$) (Himes *et al.*, 1978), (I, *R*=Ph) (Wu *et al.*, 2002), and so on, and the mode B was observed in the (*R*=Ph) (Moon *et al.*, 2003), (*R*=COO-n-$C_3H_7$) (Wang *et al.*, 2007). Herein, we report the crystal structure of the title compound (I), which exhibits the mode A of hydrogen bonding (Fig. 4).

The molecular structure of (I) (*R*=$COOC_2H_5$) is shown in Fig. 1. Its crystal structure exhibits the eight-membered rings H-bonding motifs (Fig. 4), which are entirely made up of *N*—*H*···*O*=*C*(imidazolone rings) (Table 1). The two-dimension hydrogen bonding network is shown in Fig. 2, In addition, intermolecular C10—H10B···O11, C16—H16C···O3 interactions (Table 1) contribute to the crystal structure stability.

## Experimental

The title compound was synthesized according to literature procedure (Burnett *et al.*, 2003) in 62% isolated yield. Crystals appropriate for data collection were obtained by slow evaporation of $CH_3OH$ solution at room temperature.

## Refinement

One ethyl group (C5—C6) was treted as disordered over two orientations with the occupancies refined to 0.683 (15) / 0.317 (15). All H-atoms were positioned geometrically (C—H 0.96, 0.97 Å; N—H 0.86 Å) and constrained to ride on their parent atoms, with $U_{iso}$(H) = 1.2–1.5$U_{eq}$ (parent atom).

## Figures

Fig. 1. The content of asymmetric unit of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. Atoms of the minor disorder components are omitted for clarity.

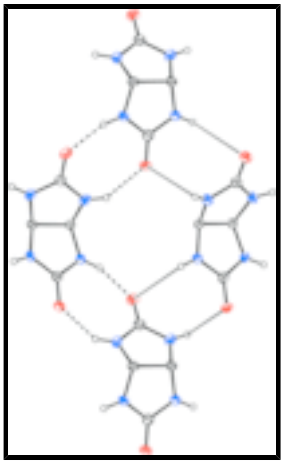


Fig. 2. The partial hydrogen bonding network in the crystal structure of the title compound. H-bond drawn as dashed lines. 3α,6α- Diethoxylcarbonyl are omitted for simplicity.

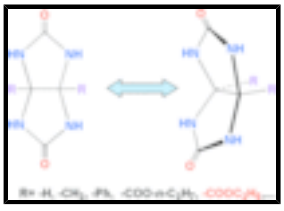


Fig. 3. The glycoluril skeleton moiety.

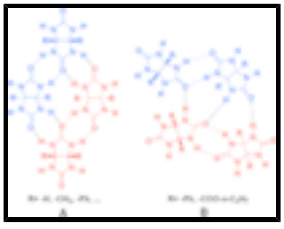


Fig. 4. Hydrogen-bonding modes A and B.

**diethyl 2,5-dioxoperhydroimidazo[4,5-*d*]imidazole-3a,6a-dicarboxylate**

*Crystal data*

| | |
|---|---|
| $C_{10}H_{14}N_4O_6$ | $F_{000}$ = 2400 |
| $M_r$ = 286.25 | $D_x$ = 1.490 Mg m$^{-3}$ |
| Orthorhombic, *Pbca* | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ac 2ab | Cell parameters from 2687 reflections |
| *a* = 15.7555 (13) Å | θ = 2.6–23.5º |
| *b* = 11.2726 (9) Å | μ = 0.12 mm$^{-1}$ |
| *c* = 28.742 (2) Å | *T* = 292 (2) K |
| *V* = 5104.7 (7) Å$^3$ | Block, colourless |
| *Z* = 16 | 0.30 × 0.20 × 0.20 mm |

*Data collection*

| | |
|---|---|
| Bruker SMART 4K CCD area-detector diffractometer | 2784 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int}$ = 0.097 |
| Monochromator: graphite | $\theta_{max}$ = 25.0º |

| | |
|---|---|
| $T$ = 292(2) K | $\theta_{min}$ = 1.9º |
| φ and ω scans | $h$ = −18→18 |
| Absorption correction: none | $k$ = −11→13 |
| 29774 measured reflections | $l$ = −34→29 |
| 4501 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.068 | H-atom parameters constrained |
| $wR(F^2)$ = 0.197 | ? |
| $S$ = 1.00 | $(\Delta/\sigma)_{max}$ < 0.001 |
| 4501 reflections | $\Delta\rho_{max}$ = 0.37 e Å$^{-3}$ |
| 385 parameters | $\Delta\rho_{min}$ = −0.42 e Å$^{-3}$ |
| 6 restraints | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*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.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C1 | 0.04208 (19) | 0.0660 (3) | 0.18565 (10) | 0.0315 (8) | |
| C2 | −0.0170 (2) | 0.4006 (3) | 0.18911 (10) | 0.0340 (8) | |
| C3 | 0.0813 (2) | 0.2558 (2) | 0.21072 (10) | 0.0304 (7) | |
| C4 | 0.1717 (2) | 0.2877 (3) | 0.22674 (12) | 0.0458 (9) | |
| C5 | 0.3149 (3) | 0.2426 (8) | 0.2249 (3) | 0.048 (2) | 0.683 (15) |
| H5A | 0.3278 | 0.2316 | 0.2576 | 0.058* | 0.683 (15) |
| H5B | 0.3233 | 0.3254 | 0.2170 | 0.058* | 0.683 (15) |
| C6 | 0.3700 (4) | 0.1644 (8) | 0.1953 (4) | 0.063 (3) | 0.683 (15) |
| H6A | 0.3601 | 0.0828 | 0.2033 | 0.095* | 0.683 (15) |
| H6B | 0.4286 | 0.1835 | 0.2007 | 0.095* | 0.683 (15) |
| H6C | 0.3566 | 0.1767 | 0.1631 | 0.095* | 0.683 (15) |
| C5' | 0.3127 (6) | 0.169 (2) | 0.2260 (7) | 0.082 (7) | 0.317 (15) |
| H5'1 | 0.3173 | 0.0833 | 0.2257 | 0.098* | 0.317 (15) |

| | | | | | |
|---|---|---|---|---|---|
| H5'2 | 0.3278 | 0.1970 | 0.2569 | 0.098* | 0.317 (15) |
| C6' | 0.3725 (8) | 0.223 (2) | 0.1899 (9) | 0.126 (12) | 0.317 (15) |
| H6'1 | 0.3641 | 0.1839 | 0.1605 | 0.190* | 0.317 (15) |
| H6'2 | 0.4302 | 0.2122 | 0.1997 | 0.190* | 0.317 (15) |
| H6'3 | 0.3607 | 0.3059 | 0.1866 | 0.190* | 0.317 (15) |
| C7 | 0.0685 (2) | 0.2544 (2) | 0.15577 (10) | 0.0314 (8) | |
| C8 | 0.1431 (2) | 0.2921 (3) | 0.12516 (13) | 0.0504 (10) | |
| C9 | 0.2477 (3) | 0.4440 (4) | 0.11294 (16) | 0.0836 (15) | |
| H9A | 0.2828 | 0.4932 | 0.1329 | 0.100* | |
| H9B | 0.2830 | 0.3815 | 0.1001 | 0.100* | |
| C10 | 0.2119 (3) | 0.5147 (4) | 0.07577 (17) | 0.0965 (17) | |
| H10A | 0.1835 | 0.4638 | 0.0540 | 0.145* | |
| H10B | 0.2565 | 0.5569 | 0.0601 | 0.145* | |
| H10C | 0.1721 | 0.5704 | 0.0885 | 0.145* | |
| C11 | 0.4936 (2) | 0.4078 (3) | 0.06138 (11) | 0.0347 (8) | |
| C12 | 0.52703 (19) | 0.0688 (3) | 0.06489 (10) | 0.0301 (7) | |
| C13 | 0.56575 (19) | 0.2511 (2) | 0.09612 (10) | 0.0296 (7) | |
| C14 | 0.6371 (2) | 0.2861 (3) | 0.12889 (12) | 0.0420 (9) | |
| C15 | 0.7460 (3) | 0.4299 (4) | 0.14264 (16) | 0.0771 (14) | |
| H15A | 0.7656 | 0.3726 | 0.1654 | 0.093* | |
| H15B | 0.7944 | 0.4544 | 0.1241 | 0.093* | |
| C16 | 0.7102 (3) | 0.5323 (4) | 0.16631 (17) | 0.0867 (16) | |
| H16A | 0.6913 | 0.5892 | 0.1437 | 0.130* | |
| H16B | 0.7526 | 0.5678 | 0.1858 | 0.130* | |
| H16C | 0.6629 | 0.5076 | 0.1850 | 0.130* | |
| C17 | 0.5822 (2) | 0.2525 (2) | 0.04197 (10) | 0.0296 (7) | |
| C18 | 0.6762 (2) | 0.2567 (3) | 0.02697 (11) | 0.0391 (8) | |
| C19 | 0.8066 (2) | 0.1494 (4) | 0.02685 (19) | 0.0847 (16) | |
| H19A | 0.8121 | 0.1722 | −0.0056 | 0.102* | |
| H19B | 0.8237 | 0.0671 | 0.0296 | 0.102* | |
| C20 | 0.8641 (3) | 0.2246 (4) | 0.05570 (17) | 0.0871 (16) | |
| H20A | 0.8512 | 0.3068 | 0.0505 | 0.131* | |
| H20B | 0.9220 | 0.2094 | 0.0471 | 0.131* | |
| H20C | 0.8561 | 0.2060 | 0.0880 | 0.131* | |
| N1 | 0.05846 (16) | 0.1358 (2) | 0.22301 (8) | 0.0332 (7) | |
| H1 | 0.0555 | 0.1110 | 0.2513 | 0.040* | |
| N2 | 0.04634 (17) | 0.1327 (2) | 0.14663 (8) | 0.0367 (7) | |
| H2 | 0.0368 | 0.1053 | 0.1192 | 0.044* | |
| N3 | 0.02328 (17) | 0.3466 (2) | 0.22512 (9) | 0.0389 (7) | |
| H3 | 0.0148 | 0.3650 | 0.2538 | 0.047* | |
| N4 | 0.00082 (17) | 0.3390 (2) | 0.14951 (9) | 0.0377 (7) | |
| H4 | −0.0254 | 0.3495 | 0.1236 | 0.045* | |
| N5 | 0.49893 (16) | 0.3389 (2) | 0.09994 (9) | 0.0361 (7) | |
| H5 | 0.4665 | 0.3463 | 0.1238 | 0.043* | |
| N6 | 0.53960 (17) | 0.3573 (2) | 0.02693 (9) | 0.0375 (7) | |
| H6 | 0.5428 | 0.3853 | −0.0009 | 0.045* | |
| N7 | 0.54036 (16) | 0.1301 (2) | 0.10487 (8) | 0.0341 (7) | |
| H7 | 0.5344 | 0.1003 | 0.1322 | 0.041* | |
| N8 | 0.54353 (16) | 0.1409 (2) | 0.02829 (8) | 0.0334 (7) | |

| | | | | |
|---|---|---|---|---|
| H8 | 0.5323 | 0.1225 | −0.0001 | 0.040* |
| O1 | 0.02606 (15) | −0.04068 (18) | 0.18682 (7) | 0.0417 (6) |
| O2 | −0.06149 (16) | 0.48901 (19) | 0.19152 (7) | 0.0439 (6) |
| O3 | 0.18984 (19) | 0.3785 (3) | 0.24553 (10) | 0.0773 (9) |
| O4 | 0.22562 (15) | 0.2053 (3) | 0.21459 (10) | 0.0647 (8) |
| O5 | 0.17702 (17) | 0.3914 (2) | 0.14036 (9) | 0.0619 (8) |
| O6 | 0.1614 (3) | 0.2417 (2) | 0.09063 (13) | 0.1284 (18) |
| O7 | 0.45447 (16) | 0.50226 (19) | 0.05859 (8) | 0.0480 (7) |
| O8 | 0.50442 (15) | −0.03524 (18) | 0.06237 (7) | 0.0413 (6) |
| O9 | 0.6426 (2) | 0.2439 (2) | 0.16701 (10) | 0.0796 (10) |
| O10 | 0.68161 (17) | 0.3742 (2) | 0.11215 (9) | 0.0650 (8) |
| O11 | 0.70598 (17) | 0.3366 (2) | 0.00593 (10) | 0.0706 (9) |
| O12 | 0.71686 (14) | 0.1612 (2) | 0.04116 (10) | 0.0616 (8) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0399 (18) | 0.0296 (18) | 0.0250 (18) | −0.0046 (15) | 0.0030 (14) | 0.0008 (14) |
| C2 | 0.048 (2) | 0.0267 (18) | 0.0273 (18) | −0.0013 (15) | 0.0036 (15) | −0.0002 (14) |
| C3 | 0.0477 (19) | 0.0223 (16) | 0.0212 (17) | −0.0032 (14) | 0.0050 (14) | −0.0020 (13) |
| C4 | 0.054 (2) | 0.049 (2) | 0.034 (2) | −0.011 (2) | −0.0007 (17) | 0.0040 (18) |
| C5 | 0.036 (3) | 0.051 (5) | 0.056 (4) | −0.007 (3) | −0.010 (3) | −0.007 (4) |
| C6 | 0.032 (4) | 0.059 (6) | 0.099 (6) | −0.007 (3) | −0.006 (4) | −0.025 (5) |
| C5' | 0.098 (15) | 0.050 (12) | 0.098 (14) | −0.022 (11) | −0.021 (11) | 0.007 (11) |
| C6' | 0.16 (2) | 0.080 (18) | 0.14 (2) | −0.066 (16) | 0.005 (16) | −0.046 (18) |
| C7 | 0.0505 (19) | 0.0201 (16) | 0.0237 (18) | −0.0023 (14) | 0.0048 (14) | 0.0012 (13) |
| C8 | 0.080 (3) | 0.0243 (18) | 0.047 (2) | −0.0075 (18) | 0.028 (2) | 0.0016 (17) |
| C9 | 0.093 (3) | 0.084 (3) | 0.074 (3) | −0.043 (3) | 0.018 (3) | 0.020 (3) |
| C10 | 0.116 (4) | 0.104 (4) | 0.070 (3) | −0.037 (3) | 0.014 (3) | 0.021 (3) |
| C11 | 0.051 (2) | 0.0272 (18) | 0.0262 (18) | 0.0004 (16) | −0.0031 (15) | −0.0002 (14) |
| C12 | 0.0422 (18) | 0.0244 (17) | 0.0236 (17) | 0.0001 (14) | 0.0001 (14) | −0.0021 (13) |
| C13 | 0.0467 (19) | 0.0227 (16) | 0.0193 (16) | 0.0016 (14) | −0.0029 (14) | 0.0000 (13) |
| C14 | 0.068 (2) | 0.0253 (17) | 0.033 (2) | 0.0008 (17) | −0.0117 (18) | −0.0028 (16) |
| C15 | 0.075 (3) | 0.091 (3) | 0.065 (3) | −0.045 (3) | −0.010 (2) | −0.018 (3) |
| C16 | 0.126 (5) | 0.066 (3) | 0.068 (3) | −0.024 (3) | −0.025 (3) | 0.002 (3) |
| C17 | 0.0462 (18) | 0.0217 (16) | 0.0209 (17) | −0.0002 (14) | −0.0021 (14) | −0.0014 (12) |
| C18 | 0.051 (2) | 0.036 (2) | 0.030 (2) | −0.0069 (17) | 0.0047 (16) | −0.0019 (16) |
| C19 | 0.055 (3) | 0.075 (3) | 0.124 (4) | 0.008 (2) | 0.019 (3) | −0.028 (3) |
| C20 | 0.054 (3) | 0.119 (4) | 0.088 (4) | −0.010 (3) | 0.007 (2) | −0.002 (3) |
| N1 | 0.0568 (17) | 0.0260 (14) | 0.0167 (13) | −0.0072 (12) | 0.0020 (12) | 0.0029 (11) |
| N2 | 0.0675 (19) | 0.0236 (14) | 0.0190 (14) | −0.0060 (13) | 0.0017 (13) | −0.0022 (11) |
| N3 | 0.0638 (18) | 0.0330 (16) | 0.0200 (15) | 0.0150 (14) | 0.0035 (13) | −0.0003 (12) |
| N4 | 0.0609 (18) | 0.0311 (15) | 0.0210 (14) | 0.0071 (13) | −0.0028 (13) | −0.0015 (12) |
| N5 | 0.0539 (17) | 0.0299 (15) | 0.0244 (15) | 0.0095 (13) | 0.0050 (12) | 0.0032 (12) |
| N6 | 0.0602 (18) | 0.0292 (15) | 0.0231 (15) | 0.0072 (13) | 0.0018 (13) | 0.0023 (12) |
| N7 | 0.0615 (18) | 0.0248 (14) | 0.0160 (13) | −0.0035 (13) | −0.0016 (12) | 0.0017 (11) |
| N8 | 0.0534 (17) | 0.0297 (14) | 0.0170 (13) | −0.0078 (12) | −0.0035 (12) | −0.0005 (11) |
| O1 | 0.0726 (17) | 0.0228 (12) | 0.0297 (13) | −0.0122 (11) | 0.0029 (11) | 0.0000 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2 | 0.0629 (16) | 0.0333 (13) | 0.0355 (14) | 0.0145 (12) | 0.0033 (11) | −0.0008 (10) |
| O3 | 0.098 (2) | 0.0696 (19) | 0.065 (2) | −0.0339 (17) | −0.0148 (17) | −0.0141 (17) |
| O4 | 0.0439 (15) | 0.079 (2) | 0.071 (2) | 0.0037 (15) | −0.0027 (14) | −0.0057 (17) |
| O5 | 0.0844 (19) | 0.0537 (16) | 0.0475 (16) | −0.0306 (14) | 0.0233 (14) | 0.0021 (13) |
| O6 | 0.202 (4) | 0.067 (2) | 0.117 (3) | −0.056 (2) | 0.124 (3) | −0.054 (2) |
| O7 | 0.0780 (18) | 0.0339 (14) | 0.0320 (13) | 0.0195 (13) | −0.0011 (12) | 0.0031 (11) |
| O8 | 0.0710 (16) | 0.0255 (13) | 0.0273 (12) | −0.0093 (11) | −0.0039 (11) | −0.0007 (10) |
| O9 | 0.133 (3) | 0.0509 (17) | 0.0548 (19) | −0.0262 (17) | −0.0532 (19) | 0.0164 (14) |
| O10 | 0.0821 (19) | 0.0751 (18) | 0.0378 (15) | −0.0376 (16) | −0.0125 (14) | 0.0008 (14) |
| O11 | 0.0692 (19) | 0.083 (2) | 0.0593 (19) | −0.0114 (16) | 0.0114 (15) | 0.0253 (16) |
| O12 | 0.0470 (16) | 0.0454 (15) | 0.092 (2) | 0.0059 (12) | 0.0072 (14) | −0.0009 (15) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—O1 | 1.229 (4) | C11—N6 | 1.352 (4) |
| C1—N2 | 1.352 (4) | C11—N5 | 1.357 (4) |
| C1—N1 | 1.356 (4) | C12—O8 | 1.228 (3) |
| C2—O2 | 1.220 (4) | C12—N8 | 1.355 (4) |
| C2—N3 | 1.358 (4) | C12—N7 | 1.357 (4) |
| C2—N4 | 1.362 (4) | C13—N7 | 1.444 (3) |
| C3—N3 | 1.433 (4) | C13—N5 | 1.449 (4) |
| C3—N1 | 1.443 (3) | C13—C14 | 1.519 (4) |
| C3—C4 | 1.541 (5) | C13—C17 | 1.578 (4) |
| C3—C7 | 1.592 (4) | C14—O9 | 1.198 (4) |
| C4—O3 | 1.191 (4) | C14—O10 | 1.308 (4) |
| C4—O4 | 1.307 (4) | C15—C16 | 1.455 (6) |
| C5—O4 | 1.497 (5) | C15—O10 | 1.481 (4) |
| C5—C6 | 1.502 (7) | C15—H15A | 0.9700 |
| C5—H5A | 0.9700 | C15—H15B | 0.9700 |
| C5—H5B | 0.9700 | C16—H16A | 0.9600 |
| C6—H6A | 0.9600 | C16—H16B | 0.9600 |
| C6—H6B | 0.9600 | C16—H16C | 0.9600 |
| C6—H6C | 0.9600 | C17—N6 | 1.426 (4) |
| C5'—O4 | 1.469 (9) | C17—N8 | 1.452 (3) |
| C5'—C6' | 1.527 (10) | C17—C18 | 1.543 (5) |
| C5'—H5'1 | 0.9700 | C18—O11 | 1.182 (4) |
| C5'—H5'2 | 0.9700 | C18—O12 | 1.317 (4) |
| C6'—H6'1 | 0.9600 | C19—O12 | 1.478 (4) |
| C6'—H6'2 | 0.9600 | C19—C20 | 1.493 (6) |
| C6'—H6'3 | 0.9600 | C19—H19A | 0.9700 |
| C7—N2 | 1.440 (3) | C19—H19B | 0.9700 |
| C7—N4 | 1.442 (4) | C20—H20A | 0.9600 |
| C7—C8 | 1.529 (4) | C20—H20B | 0.9600 |
| C8—O6 | 1.179 (4) | C20—H20C | 0.9600 |
| C8—O5 | 1.314 (4) | N1—H1 | 0.8600 |
| C9—C10 | 1.448 (6) | N2—H2 | 0.8600 |
| C9—O5 | 1.488 (4) | N3—H3 | 0.8600 |
| C9—H9A | 0.9700 | N4—H4 | 0.8600 |
| C9—H9B | 0.9700 | N5—H5 | 0.8600 |

| | | | |
|---|---|---|---|
| C10—H10A | 0.9600 | N6—H6 | 0.8600 |
| C10—H10B | 0.9600 | N7—H7 | 0.8600 |
| C10—H10C | 0.9600 | N8—H8 | 0.8600 |
| C11—O7 | 1.233 (4) | | |
| O1—C1—N2 | 125.2 (3) | O9—C14—O10 | 126.8 (3) |
| O1—C1—N1 | 125.8 (3) | O9—C14—C13 | 121.2 (3) |
| N2—C1—N1 | 108.9 (3) | O10—C14—C13 | 111.5 (3) |
| O2—C2—N3 | 126.2 (3) | C16—C15—O10 | 110.3 (4) |
| O2—C2—N4 | 125.6 (3) | C16—C15—H15A | 109.6 |
| N3—C2—N4 | 108.2 (3) | O10—C15—H15A | 109.6 |
| N3—C3—N1 | 116.1 (3) | C16—C15—H15B | 109.6 |
| N3—C3—C4 | 109.7 (3) | O10—C15—H15B | 109.6 |
| N1—C3—C4 | 112.1 (3) | H15A—C15—H15B | 108.1 |
| N3—C3—C7 | 102.3 (2) | C15—C16—H16A | 109.5 |
| N1—C3—C7 | 101.7 (2) | C15—C16—H16B | 109.5 |
| C4—C3—C7 | 114.6 (2) | H16A—C16—H16B | 109.5 |
| O3—C4—O4 | 125.2 (4) | C15—C16—H16C | 109.5 |
| O3—C4—C3 | 123.9 (3) | H16A—C16—H16C | 109.5 |
| O4—C4—C3 | 110.8 (3) | H16B—C16—H16C | 109.5 |
| O4—C5—C6 | 105.5 (5) | N6—C17—N8 | 116.0 (2) |
| O4—C5—H5A | 110.6 | N6—C17—C18 | 110.0 (3) |
| C6—C5—H5A | 110.6 | N8—C17—C18 | 110.7 (2) |
| O4—C5—H5B | 110.6 | N6—C17—C13 | 103.3 (2) |
| C6—C5—H5B | 110.6 | N8—C17—C13 | 100.9 (2) |
| H5A—C5—H5B | 108.8 | C18—C17—C13 | 115.7 (2) |
| O4—C5'—C6' | 108.3 (9) | O11—C18—O12 | 126.0 (3) |
| O4—C5'—H5'1 | 110.0 | O11—C18—C17 | 123.2 (3) |
| C6'—C5'—H5'1 | 110.0 | O12—C18—C17 | 110.9 (3) |
| O4—C5'—H5'2 | 110.0 | O12—C19—C20 | 112.0 (4) |
| C6'—C5'—H5'2 | 110.0 | O12—C19—H19A | 109.2 |
| H5'1—C5'—H5'2 | 108.4 | C20—C19—H19A | 109.2 |
| C5'—C6'—H6'1 | 109.5 | O12—C19—H19B | 109.2 |
| C5'—C6'—H6'2 | 109.5 | C20—C19—H19B | 109.2 |
| H6'1—C6'—H6'2 | 109.5 | H19A—C19—H19B | 107.9 |
| C5'—C6'—H6'3 | 109.5 | C19—C20—H20A | 109.5 |
| H6'1—C6'—H6'3 | 109.5 | C19—C20—H20B | 109.5 |
| H6'2—C6'—H6'3 | 109.5 | H20A—C20—H20B | 109.5 |
| N2—C7—N4 | 115.3 (3) | C19—C20—H20C | 109.5 |
| N2—C7—C8 | 110.3 (3) | H20A—C20—H20C | 109.5 |
| N4—C7—C8 | 108.2 (2) | H20B—C20—H20C | 109.5 |
| N2—C7—C3 | 102.8 (2) | C1—N1—C3 | 113.4 (2) |
| N4—C7—C3 | 102.2 (2) | C1—N1—H1 | 123.3 |
| C8—C7—C3 | 118.1 (3) | C3—N1—H1 | 123.3 |
| O6—C8—O5 | 126.2 (3) | C1—N2—C7 | 113.0 (2) |
| O6—C8—C7 | 122.6 (3) | C1—N2—H2 | 123.5 |
| O5—C8—C7 | 111.0 (3) | C7—N2—H2 | 123.5 |
| C10—C9—O5 | 108.6 (4) | C2—N3—C3 | 113.5 (2) |
| C10—C9—H9A | 110.0 | C2—N3—H3 | 123.3 |
| O5—C9—H9A | 110.0 | C3—N3—H3 | 123.3 |

| | | | |
|---|---|---|---|
| C10—C9—H9B | 110.0 | C2—N4—C7 | 112.7 (3) |
| O5—C9—H9B | 110.0 | C2—N4—H4 | 123.7 |
| H9A—C9—H9B | 108.4 | C7—N4—H4 | 123.7 |
| C9—C10—H10A | 109.5 | C11—N5—C13 | 112.0 (2) |
| C9—C10—H10B | 109.5 | C11—N5—H5 | 124.0 |
| H10A—C10—H10B | 109.5 | C13—N5—H5 | 124.0 |
| C9—C10—H10C | 109.5 | C11—N6—C17 | 112.3 (2) |
| H10A—C10—H10C | 109.5 | C11—N6—H6 | 123.9 |
| H10B—C10—H10C | 109.5 | C17—N6—H6 | 123.9 |
| O7—C11—N6 | 125.7 (3) | C12—N7—C13 | 112.1 (2) |
| O7—C11—N5 | 125.4 (3) | C12—N7—H7 | 124.0 |
| N6—C11—N5 | 108.9 (3) | C13—N7—H7 | 124.0 |
| O8—C12—N8 | 125.7 (3) | C12—N8—C17 | 113.0 (2) |
| O8—C12—N7 | 125.5 (3) | C12—N8—H8 | 123.5 |
| N8—C12—N7 | 108.8 (2) | C17—N8—H8 | 123.5 |
| N7—C13—N5 | 115.5 (3) | C4—O4—C5' | 138.1 (10) |
| N7—C13—C14 | 110.0 (2) | C4—O4—C5 | 111.0 (4) |
| N5—C13—C14 | 108.2 (2) | C5'—O4—C5 | 32.5 (7) |
| N7—C13—C17 | 103.1 (2) | C8—O5—C9 | 117.9 (3) |
| N5—C13—C17 | 100.8 (2) | C14—O10—C15 | 118.2 (3) |
| C14—C13—C17 | 119.2 (3) | C18—O12—C19 | 116.9 (3) |
| N3—C3—C4—O3 | −4.5 (5) | C8—C7—N2—C1 | 128.3 (3) |
| N1—C3—C4—O3 | −134.9 (3) | C3—C7—N2—C1 | 1.5 (3) |
| C7—C3—C4—O3 | 109.9 (4) | O2—C2—N3—C3 | −170.9 (3) |
| N3—C3—C4—O4 | 179.0 (3) | N4—C2—N3—C3 | 9.1 (4) |
| N1—C3—C4—O4 | 48.6 (4) | N1—C3—N3—C2 | −112.5 (3) |
| C7—C3—C4—O4 | −66.6 (4) | C4—C3—N3—C2 | 119.2 (3) |
| N3—C3—C7—N2 | −123.9 (2) | C7—C3—N3—C2 | −2.8 (3) |
| N1—C3—C7—N2 | −3.6 (3) | O2—C2—N4—C7 | 167.8 (3) |
| C4—C3—C7—N2 | 117.5 (3) | N3—C2—N4—C7 | −12.1 (4) |
| N3—C3—C7—N4 | −4.0 (3) | N2—C7—N4—C2 | 120.5 (3) |
| N1—C3—C7—N4 | 116.3 (2) | C8—C7—N4—C2 | −115.5 (3) |
| C4—C3—C7—N4 | −122.6 (3) | C3—C7—N4—C2 | 9.8 (3) |
| N3—C3—C7—C8 | 114.5 (3) | O7—C11—N5—C13 | −165.3 (3) |
| N1—C3—C7—C8 | −125.2 (3) | N6—C11—N5—C13 | 13.4 (4) |
| C4—C3—C7—C8 | −4.1 (4) | N7—C13—N5—C11 | −127.2 (3) |
| N2—C7—C8—O6 | 20.6 (5) | C14—C13—N5—C11 | 109.0 (3) |
| N4—C7—C8—O6 | −106.4 (5) | C17—C13—N5—C11 | −16.9 (3) |
| C3—C7—C8—O6 | 138.3 (4) | O7—C11—N6—C17 | 175.8 (3) |
| N2—C7—C8—O5 | −165.0 (3) | N5—C11—N6—C17 | −2.9 (4) |
| N4—C7—C8—O5 | 68.0 (4) | N8—C17—N6—C11 | 101.9 (3) |
| C3—C7—C8—O5 | −47.4 (4) | C18—C17—N6—C11 | −131.5 (3) |
| N7—C13—C14—O9 | −30.6 (4) | C13—C17—N6—C11 | −7.4 (3) |
| N5—C13—C14—O9 | 96.5 (4) | O8—C12—N7—C13 | −179.4 (3) |
| C17—C13—C14—O9 | −149.3 (3) | N8—C12—N7—C13 | 1.2 (3) |
| N7—C13—C14—O10 | 157.0 (3) | N5—C13—N7—C12 | 99.5 (3) |
| N5—C13—C14—O10 | −75.9 (3) | C14—C13—N7—C12 | −137.6 (3) |
| C17—C13—C14—O10 | 38.3 (4) | C17—C13—N7—C12 | −9.5 (3) |
| N7—C13—C17—N6 | 133.5 (2) | O8—C12—N8—C17 | −170.5 (3) |

| | | | |
|---|---|---|---|
| N5—C13—C17—N6 | 13.9 (3) | N7—C12—N8—C17 | 8.9 (4) |
| C14—C13—C17—N6 | −104.2 (3) | N6—C17—N8—C12 | −124.7 (3) |
| N7—C13—C17—N8 | 13.3 (3) | C18—C17—N8—C12 | 109.1 (3) |
| N5—C13—C17—N8 | −106.4 (2) | C13—C17—N8—C12 | −13.9 (3) |
| C14—C13—C17—N8 | 135.5 (3) | O3—C4—O4—C5' | 18.8 (11) |
| N7—C13—C17—C18 | −106.2 (3) | C3—C4—O4—C5' | −164.8 (9) |
| N5—C13—C17—C18 | 134.2 (3) | O3—C4—O4—C5 | −3.3 (6) |
| C14—C13—C17—C18 | 16.0 (4) | C3—C4—O4—C5 | 173.1 (4) |
| N6—C17—C18—O11 | −0.3 (4) | C6'—C5'—O4—C4 | −96 (2) |
| N8—C17—C18—O11 | 129.2 (3) | C6'—C5'—O4—C5 | −55.2 (16) |
| C13—C17—C18—O11 | −116.8 (4) | C6—C5—O4—C4 | −160.8 (7) |
| N6—C17—C18—O12 | 179.1 (3) | C6—C5—O4—C5' | 47.1 (14) |
| N8—C17—C18—O12 | −51.4 (3) | O6—C8—O5—C9 | −2.7 (7) |
| C13—C17—C18—O12 | 62.6 (3) | C7—C8—O5—C9 | −176.8 (3) |
| O1—C1—N1—C3 | 175.7 (3) | C10—C9—O5—C8 | 84.3 (5) |
| N2—C1—N1—C3 | −4.2 (4) | O9—C14—O10—C15 | −0.1 (6) |
| N3—C3—N1—C1 | 114.9 (3) | C13—C14—O10—C15 | 171.7 (3) |
| C4—C3—N1—C1 | −118.0 (3) | C16—C15—O10—C14 | −94.1 (4) |
| C7—C3—N1—C1 | 4.8 (3) | O11—C18—O12—C19 | −4.2 (5) |
| O1—C1—N2—C7 | −178.5 (3) | C17—C18—O12—C19 | 176.4 (3) |
| N1—C1—N2—C7 | 1.4 (4) | C20—C19—O12—C18 | 78.4 (5) |
| N4—C7—N2—C1 | −108.8 (3) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O2$^{i}$ | 0.86 | 2.15 | 2.963 (3) | 158 |
| N2—H2···O7$^{ii}$ | 0.86 | 2.10 | 2.927 (3) | 162 |
| N3—H3···O1$^{iii}$ | 0.86 | 2.11 | 2.937 (3) | 161 |
| N4—H4···O8$^{iv}$ | 0.86 | 2.21 | 2.879 (3) | 134 |
| N5—H5···O1$^{iv}$ | 0.86 | 2.22 | 2.870 (3) | 133 |
| N6—H6···O7$^{v}$ | 0.86 | 2.09 | 2.925 (3) | 164 |
| N7—H7···O2$^{ii}$ | 0.86 | 2.16 | 2.973 (3) | 158 |
| N8—H8···O8$^{vi}$ | 0.86 | 2.12 | 2.963 (3) | 165 |
| C16—H16C···O3$^{vii}$ | 0.96 | 2.51 | 3.087 (5) | 119 |
| C10—H10B···O11$^{v}$ | 0.96 | 2.32 | 3.162 (5) | 146 |

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) −*x*+1/2, *y*−1/2, *z*; (iii) −*x*, *y*+1/2, −*z*+1/2; (iv) −*x*+1/2, *y*+1/2, *z*; (v) −*x*+1, −*y*+1, −*z*; (vi) −*x*+1, −*y*, −*z*; (vii) *x*+1/2, *y*, −*z*+1/2.

**Fig. 1**

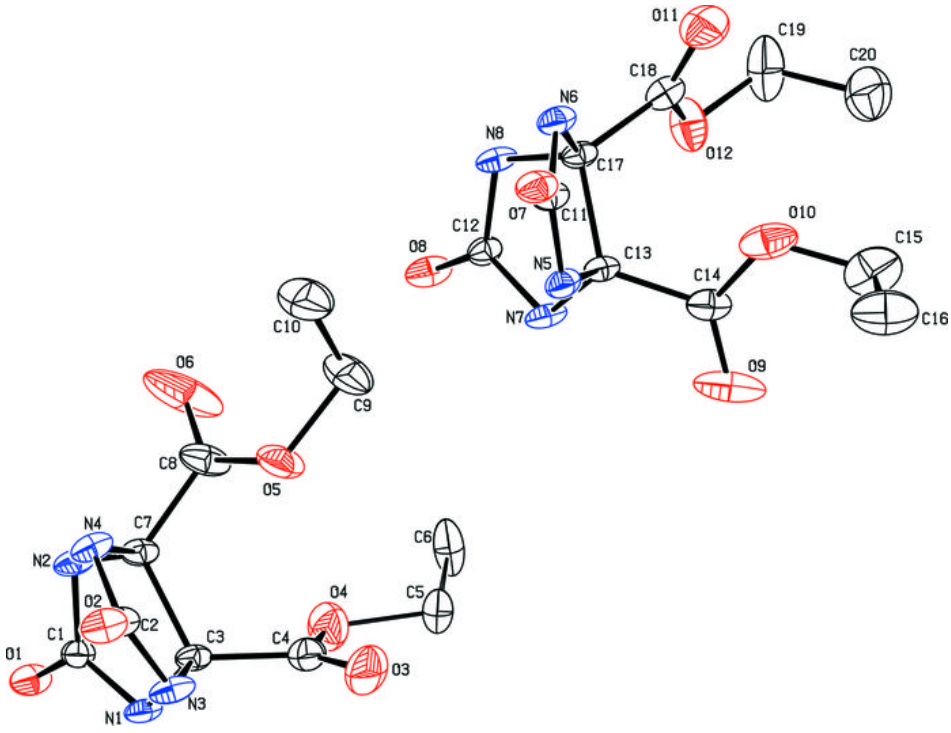

O11
C19
C20
C18
N6
N8
C17
O12
O7
C11
C12
O8
N5
C13
O10
C15
C14
N7
C16
O9
C10
O6
C9
C8
O5
N4
C7
C6
N2
O4
C5
O2
C1
C2
C3
C4
O1
O3
N1
N3

Fig. 2

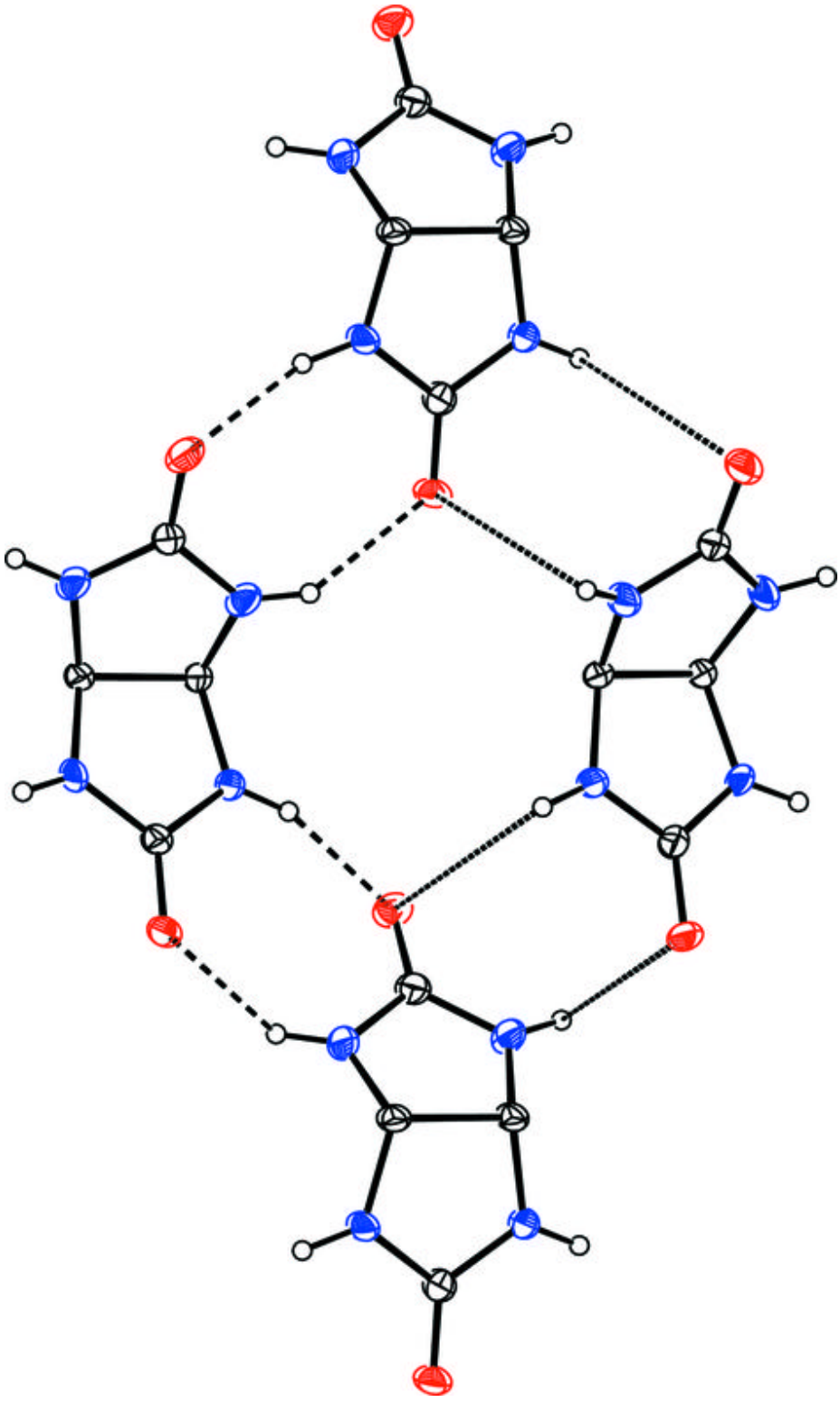
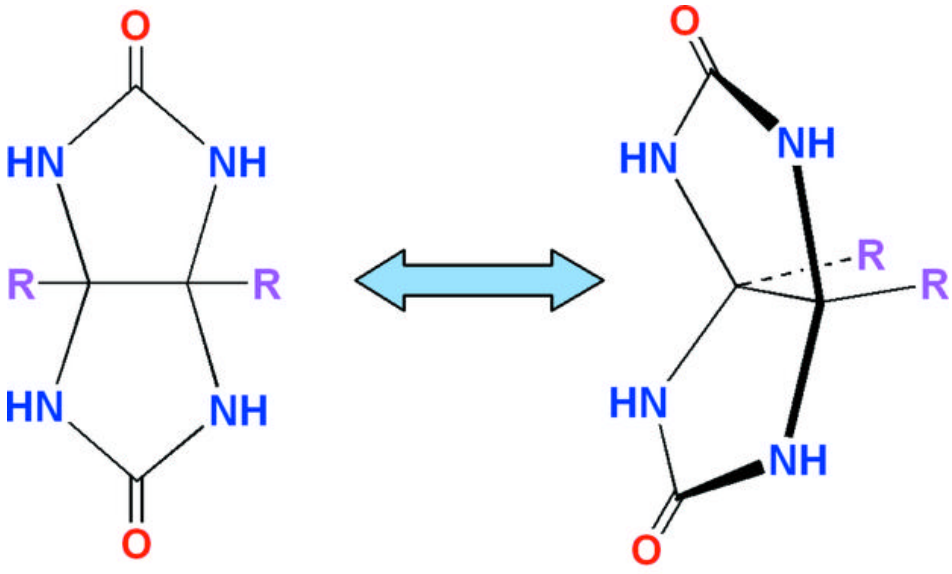


**Fig. 3**




**R= -H, -$CH_3$, -Ph, -COO-*n*-$C_3H_7$, -$COOC_2H_5$,...**

**Fig. 4**