

10,11-Dihydroxy-4-azatricyclo-[5.2.2.0^{2,6}]undec-8-ene-3,5-dione

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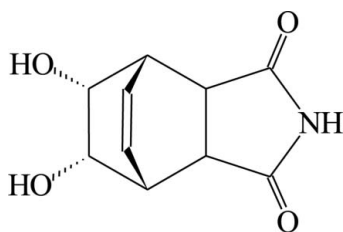
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.043; wR factor = 0.127; data-to-parameter ratio = 13.8.

The succinimide ring of the title compound, $\text{C}_{10}\text{H}_{11}\text{NO}_4$, is *endo-cis*-substituted to the bicyclooctene system. The hydroxyl groups of the diol fragment are *cis* oriented, the $\text{O}-\text{C}-\text{C}-\text{O}$ torsion angle being -20.7 (2)°. One of the OH groups is a double donor in two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to the second group, forming both a weak intramolecular hydrogen bond [$S(5)$ motif] and a centrosymmetric intermolecular dimer; the $\text{H}\cdots\text{O}$ distances are 2.34 and 2.10 Å for the intra- and intermolecular bonds, respectively. Accompanying intermolecular $\text{O}-\text{H}\cdots\text{O}_{\text{carbonyl}}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules into tapes parallel to the b axis and layers perpendicular to the c axis.

Related literature

For related structures, see: Kossakowski & Krawiecka (2000). See also the Cambridge Structural Database (Version 5.28 and upgrades; Allen, 2002) for the structures of simple succinimide derivatives with mono- or bicyclic hydrocarbon fragments, refcodes IHPEUG, PHYPHM, ODEMAL, YITBUY, QICWOO, PEMWOU, PEMWUA, PESVOZ, WEWCAC and YEXTUQ. For related literature, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{11}\text{NO}_4$
 $M_r = 209.20$
 Monoclinic, $P2_1/n$
 $a = 9.524$ (2) Å
 $b = 8.111$ (2) Å
 $c = 11.586$ (3) Å
 $\beta = 99.71$ (3)°
 $V = 882.2$ (4) Å³
 $Z = 4$
 Cu $K\alpha$ radiation
 $\mu = 1.04$ mm⁻¹
 $T = 295$ (2) K
 $0.53 \times 0.23 \times 0.23$ mm

Data collection

Kuma KM-4 four-circle diffractometer
 Absorption correction: none
 1973 measured reflections
 1891 independent reflections
 1410 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 3 standard reflections every 100 reflections
 intensity decay: 0.3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.127$
 $S = 1.07$
 1891 reflections
 137 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O11}-\text{H11}\cdots\text{O10}$	0.82	2.34	2.604 (2)	99
$\text{N4}-\text{H4}\cdots\text{O11}^{\text{i}}$	0.88	1.98	2.857 (2)	171
$\text{O10}-\text{H10}\cdots\text{O3}^{\text{ii}}$	0.82	1.96	2.768 (2)	166
$\text{O11}-\text{H11}\cdots\text{O10}^{\text{iii}}$	0.82	2.10	2.852 (2)	153
$\text{C11}-\text{H11C}\cdots\text{O5}^{\text{iv}}$	0.98	2.60	3.289 (2)	127
$\text{C10}-\text{H10C}\cdots\text{O5}^{\text{v}}$	0.98	2.58	3.303 (2)	130

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x, -y, -z + 1$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Data collection: *KM-4 Software* (Kuma Diffraction, 1999); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2155).

References

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supplementary materials

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10,11-Dihydroxy-4-azatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione

M. Krawiecka, I. Wawrzycka-Gorczyca, A. Galazka, J. Kossakowski and A. E. Koziol

Comment

A search for known structures of simple succinimide derivatives with mono- or bicyclic hydrocarbon moieties revealed several molecules having hydrophobic substituents (refcodes: IHEPUG, PHYPHM, ODEMAL, YITBUY, QICWOO, PEMWOU, PEMWUA, PESVOZ) as well as sulfinyl (WEWCAC) and sulfonfylamino (YEXTUQ) fragments (The Cambridge Structural Database, Ver. 5.28 and upgrades; Allen, 2002). Their preferred molecular association is a chain formed between imide groups through N—H \cdots O=C hydrogen bonds.

Continuing our studies (Kossakowski & Krawiecka, 2000) we designed a synthesis for several new derivatives containing the title compound (I). Molecule (I) has a bicyclooctene nucleus. One of its rings shares two C atoms with the *cis* bonded succinimide moiety, while the second ring has two hydroxyl substituents (Fig. 1). In the bicyclic hydrocarbon fragment, the six-membered rings adopt a distorted boat conformation. The hydroxyl groups are *cis* oriented to each other and linked by the weak intra-molecular O11—H \cdots O10 hydrogen bond (Table 1). The motif of this intra-molecular hydrogen bond is S(5) (Bernstein *et al.*, 1995) with the H \cdots O distance of 2.34 Å and the O—H \cdots O angle of 99°. The chemically equivalent C=O and C—N bonds of the succinimide system are not equal: C3=O3 1.219 (2) *versus* C5=O5 1.202 (2) Å and C3—N4 1.367 (2) *versus* C5—N4 1.384 (2) Å. Moreover, the five-membered succinimide ring is slightly puckered (torsion angles range from 1.0 (2)–8.4 (2)°).

Deviations from the expected bond lengths and the distorted conformation of rings are caused by the presence of different hydrogen bond patterns involving each of the carbonyl and hydroxyl groups (Table 1 and Fig. 2); for example: carbonyl O5 is involved in the C—H \cdots O contacts only, while the C \cdots O distances of the second carbonyl (*i.e.* O3) are longer than 3.35 Å. Strong inter-molecular O—H \cdots O and N—H \cdots O hydrogen bonds link hydroxyl, carbonyl and imide groups (Table 1), without typical imide \cdots imide interactions. The hydroxyl O11 is involved in both intra- and inter-molecular hydrogen-bonding to O10 of the second hydroxyl group. A cyclic dimer is formed as a result of the inter-molecular hydroxyl \cdots hydroxyl interaction around a center of symmetry (Fig. 2). The imide \cdots hydroxyl N4—H \cdots O11 hydrogen bond stabilizes the molecular tape running along the *b* axis (Fig. 3), while the hydroxyl \cdots carbonyl O10—H \cdots O3 bond links molecules lying in the neighbouring planes perpendicular to the *c* axis (Fig. 4). Numerous C—H \cdots O contacts are also observed.

Experimental

The Diels–Alder reaction was performed using a mixture of *cis*-3,5-cyclohexadiene-1,2-diole (30 cm³, 20% solution in ethyl acetate, 0.035 mol) and maleimide (5.14 g, 0.035 mol). After being refluxed for 2 h, the reaction mixture was cooled, the product was filtered off and recrystallized from ethyl acetate (m.p. 208–209°C).

Refinement

The hydroxyl and imide H atoms were found from ΔF map, and next they were fixed at the O—H and N—H distances of 0.82 and 0.88 Å, respectively. Carbon-bonded H atoms were positioned geometrically and fixed with alkene and methine C—H distances of 0.93 and 0.98 Å, respectively. The displacement parameters of the H atoms were $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C/O/N})$.

Figures

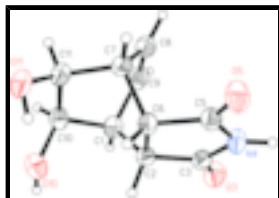


Fig. 1. Perspective view of (I). Displacement ellipsoids are drawn at the 50% probability level.

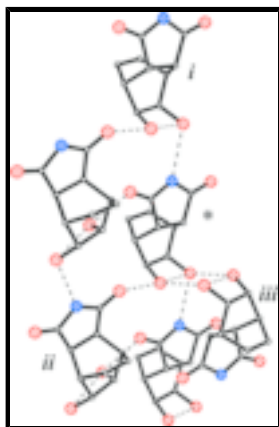


Fig. 2. The N—H \cdots O and O—H \cdots O hydrogen bond pattern involving the central molecule (*). Hydrogen atoms have been omitted for clarity. For the symmetry codes see Table 1.

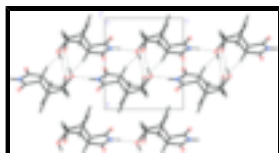


Fig. 3. View of the crystal packing down the c axis.

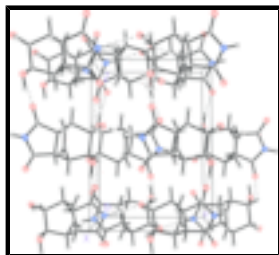


Fig. 4. View of the crystal packing down the a axis.

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Crystal data

$\text{C}_{10}\text{H}_{11}\text{NO}_4$
 $M_r = 209.20$

$F_{000} = 440$
 $D_x = 1.575 \text{ Mg m}^{-3}$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 9.524$ (2) Å

$b = 8.111$ (2) Å

$c = 11.586$ (3) Å

$\beta = 99.71$ (3)°

$V = 882.2$ (4) Å³

$Z = 4$

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 76 reflections

$\theta = 6$ – 17.5 °

$\mu = 1.04$ mm⁻¹

$T = 295$ (2) K

Prism, colourless

$0.53 \times 0.23 \times 0.23$ mm

Data collection

Kuma KM-4 four-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 295$ (2) K

$\omega/2\theta$ scans

Absorption correction: none

1973 measured reflections

1891 independent reflections

1410 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\text{max}} = 80.2$ °

$\theta_{\text{min}} = 5.6$ °

$h = -12 \rightarrow 12$

$k = 0 \rightarrow 10$

$l = 0 \rightarrow 14$

3 standard reflections

every 100 reflections

intensity decay: 0.3%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.127$

$S = 1.07$

1891 reflections

137 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.224P]$$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.34$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Extinction correction: SHELXL97 (Sheldrick, 1997),

$$F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.092 (5)

Special details

Experimental. ¹H NMR (DMSO): δ 11.02 (s, 1H, N—H); 6.08–6.06 (t, 2H, C9—H, C10—H); 4.93 (s, 2H, C6—OH, C7—OH); 3.50 (s, 2H, C6—H, C7—H), 3.11 (s, 2H, C5—H, C8—H), 2.93 (s, 2H, C1—H, C4—H) Elemental analysis, calculated for C₁₀H₁₁NO₄: C 57.42, H 5.26, N 6.72%; found: C 57.29, H 5.25, N 6.66%.

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.

supplementary materials

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.32529 (18)	0.2170 (2)	0.60092 (15)	0.0296 (4)
H1	0.3621	0.2298	0.6847	0.035*
C2	0.19096 (16)	0.3221 (2)	0.56282 (13)	0.0255 (4)
H2	0.1184	0.2947	0.6105	0.031*
C3	0.22198 (17)	0.5054 (2)	0.56929 (15)	0.0282 (4)
O3	0.28269 (15)	0.58212 (16)	0.65367 (11)	0.0396 (4)
N4	0.16905 (15)	0.57479 (17)	0.46334 (13)	0.0307 (4)
H4	0.1667	0.6815	0.4481	0.037*
C5	0.11373 (17)	0.4610 (2)	0.37877 (15)	0.0277 (4)
O5	0.06147 (15)	0.49537 (16)	0.27993 (11)	0.0391 (4)
C6	0.13289 (17)	0.29072 (19)	0.43262 (14)	0.0260 (4)
H6	0.0414	0.2327	0.4235	0.031*
C7	0.24300 (18)	0.1890 (2)	0.37810 (15)	0.0291 (4)
H7	0.2162	0.1817	0.2928	0.035*
C8	0.38806 (18)	0.2644 (2)	0.41258 (17)	0.0348 (4)
H8	0.4420	0.3021	0.3581	0.042*
C9	0.43268 (18)	0.2726 (2)	0.52713 (17)	0.0348 (4)
H9	0.5232	0.3097	0.5595	0.042*
C10	0.28118 (17)	0.0364 (2)	0.57016 (15)	0.0300 (4)
H10C	0.3581	-0.0380	0.6045	0.036*
O10	0.15352 (13)	-0.00595 (16)	0.61250 (11)	0.0359 (3)
H10	0.1659	0.0053	0.6838	0.043*
C11	0.25367 (18)	0.0168 (2)	0.43507 (15)	0.0302 (4)
H11C	0.3384	-0.0361	0.4142	0.036*
O11	0.13623 (14)	-0.08778 (14)	0.39332 (11)	0.0356 (3)
H11	0.0642	-0.0513	0.4142	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0298 (8)	0.0270 (8)	0.0297 (8)	0.0006 (6)	-0.0012 (6)	0.0010 (6)
C2	0.0278 (8)	0.0239 (8)	0.0252 (7)	0.0015 (6)	0.0054 (6)	0.0018 (6)
C3	0.0308 (8)	0.0263 (8)	0.0283 (8)	0.0031 (6)	0.0071 (6)	-0.0010 (6)
O3	0.0525 (8)	0.0326 (7)	0.0314 (7)	-0.0035 (6)	0.0008 (6)	-0.0061 (5)
N4	0.0368 (8)	0.0212 (7)	0.0330 (8)	0.0008 (5)	0.0026 (6)	0.0020 (5)
C5	0.0278 (7)	0.0252 (8)	0.0300 (8)	0.0013 (6)	0.0044 (6)	0.0015 (6)
O5	0.0480 (7)	0.0334 (7)	0.0322 (7)	0.0010 (5)	-0.0037 (5)	0.0061 (5)
C6	0.0269 (7)	0.0217 (7)	0.0291 (8)	-0.0002 (6)	0.0042 (6)	0.0014 (6)
C7	0.0349 (8)	0.0248 (8)	0.0285 (8)	0.0041 (6)	0.0079 (6)	0.0001 (6)
C8	0.0330 (8)	0.0275 (8)	0.0475 (10)	0.0004 (7)	0.0172 (7)	0.0015 (7)
C9	0.0267 (8)	0.0287 (9)	0.0483 (10)	0.0023 (6)	0.0046 (7)	-0.0007 (7)
C10	0.0294 (8)	0.0251 (8)	0.0338 (9)	0.0009 (6)	0.0000 (6)	0.0040 (6)
O10	0.0398 (7)	0.0358 (7)	0.0311 (6)	-0.0068 (5)	0.0032 (5)	0.0039 (5)
C11	0.0340 (8)	0.0230 (8)	0.0336 (8)	0.0027 (6)	0.0053 (6)	-0.0015 (6)

O11 0.0424 (7) 0.0243 (6) 0.0387 (7) -0.0019 (5) 0.0025 (5) -0.0044 (5)

Geometric parameters (Å, °)

C1—C9	1.508 (3)	C6—H6	0.9800
C1—C2	1.539 (2)	C7—C8	1.502 (2)
C1—C10	1.548 (2)	C7—C11	1.541 (2)
C1—H1	0.9800	C7—H7	0.9800
C2—C3	1.516 (2)	C8—C9	1.325 (3)
C2—C6	1.538 (2)	C8—H8	0.9300
C2—H2	0.9800	C9—H9	0.9300
C3—O3	1.219 (2)	C10—O10	1.428 (2)
C3—N4	1.367 (2)	C10—C11	1.551 (2)
N4—C5	1.384 (2)	C10—H10C	0.9800
N4—H4	0.8829	O10—H10	0.8200
C5—O5	1.202 (2)	C11—O11	1.422 (2)
C5—C6	1.514 (2)	C11—H11C	0.9800
C6—C7	1.550 (2)	O11—H11	0.8200
C9—C1—C2	106.39 (13)	C8—C7—C11	105.30 (14)
C9—C1—C10	109.62 (14)	C8—C7—C6	109.28 (13)
C2—C1—C10	106.13 (13)	C11—C7—C6	107.95 (13)
C9—C1—H1	111.5	C8—C7—H7	111.4
C2—C1—H1	111.5	C11—C7—H7	111.4
C10—C1—H1	111.5	C6—C7—H7	111.4
C3—C2—C6	104.22 (12)	C9—C8—C7	114.33 (16)
C3—C2—C1	112.56 (13)	C9—C8—H8	122.8
C6—C2—C1	109.50 (13)	C7—C8—H8	122.8
C3—C2—H2	110.1	C8—C9—C1	114.78 (15)
C6—C2—H2	110.1	C8—C9—H9	122.6
C1—C2—H2	110.1	C1—C9—H9	122.6
O3—C3—N4	124.28 (16)	O10—C10—C1	111.24 (14)
O3—C3—C2	127.05 (15)	O10—C10—C11	108.25 (13)
N4—C3—C2	108.67 (14)	C1—C10—C11	108.82 (13)
C3—N4—C5	113.57 (14)	O10—C10—H10C	109.5
C3—N4—H4	125.2	C1—C10—H10C	109.5
C5—N4—H4	121.3	C11—C10—H10C	109.5
O5—C5—N4	124.53 (15)	C10—O10—H10	109.5
O5—C5—C6	127.31 (15)	O11—C11—C7	113.81 (14)
N4—C5—C6	108.16 (14)	O11—C11—C10	113.20 (14)
C5—C6—C2	104.59 (13)	C7—C11—C10	109.07 (13)
C5—C6—C7	111.13 (13)	O11—C11—H11C	106.8
C2—C6—C7	109.37 (13)	C7—C11—H11C	106.8
C5—C6—H6	110.5	C10—C11—H11C	106.8
C2—C6—H6	110.5	C11—O11—H11	109.5
C7—C6—H6	110.5		
C9—C1—C2—C3	-54.17 (17)	C2—C6—C7—C8	-47.62 (17)
C10—C1—C2—C3	-170.87 (14)	C5—C6—C7—C11	-178.63 (13)
C9—C1—C2—C6	61.26 (16)	C2—C6—C7—C11	66.40 (16)
C10—C1—C2—C6	-55.44 (17)	C11—C7—C8—C9	-56.97 (19)

supplementary materials

C6—C2—C3—O3	-172.16 (16)	C6—C7—C8—C9	58.76 (19)
C1—C2—C3—O3	-53.6 (2)	C7—C8—C9—C1	-4.5 (2)
C6—C2—C3—N4	8.35 (17)	C2—C1—C9—C8	-55.88 (19)
C1—C2—C3—N4	126.93 (15)	C10—C1—C9—C8	58.46 (19)
O3—C3—N4—C5	175.66 (16)	C9—C1—C10—O10	-163.83 (13)
C2—C3—N4—C5	-4.84 (19)	C2—C1—C10—O10	-49.31 (17)
C3—N4—C5—O5	179.71 (16)	C9—C1—C10—C11	-44.65 (17)
C3—N4—C5—C6	-0.98 (19)	C2—C1—C10—C11	69.87 (16)
O5—C5—C6—C2	-174.55 (16)	C8—C7—C11—O11	-167.72 (14)
N4—C5—C6—C2	6.17 (17)	C6—C7—C11—O11	75.64 (17)
O5—C5—C6—C7	67.5 (2)	C8—C7—C11—C10	64.83 (16)
N4—C5—C6—C7	-111.73 (15)	C6—C7—C11—C10	-51.81 (17)
C3—C2—C6—C5	-8.53 (15)	O10—C10—C11—O11	-20.65 (18)
C1—C2—C6—C5	-129.17 (14)	C1—C10—C11—O11	-141.68 (13)
C3—C2—C6—C7	110.57 (14)	O10—C10—C11—C7	107.15 (15)
C1—C2—C6—C7	-10.07 (17)	C1—C10—C11—C7	-13.88 (18)
C5—C6—C7—C8	67.34 (18)		

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>
O11—H11 \cdots O10	0.82	2.34	2.604 (2)	99
N4—H4 \cdots O11 ⁱ	0.88	1.98	2.857 (2)	171
O10—H10 \cdots O3 ⁱⁱ	0.82	1.96	2.768 (2)	166
O11—H11 \cdots O10 ⁱⁱⁱ	0.82	2.10	2.852 (2)	153
C7—H7 \cdots O5 ^{iv}	0.98	2.84	3.231 (2)	105
C8—H8 \cdots O5 ^{iv}	0.93	2.96	3.214 (2)	98
C11—H11C \cdots O5 ^{iv}	0.98	2.60	3.289 (2)	127
C1—H1 \cdots O5 ^v	0.98	2.73	3.279 (2)	116
C10—H10C \cdots O5 ^v	0.98	2.58	3.303 (2)	130

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1/2, y-1/2, -z+3/2$; (iii) $-x, -y, -z+1$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $x+1/2, -y+1/2, z+1/2$.

Fig. 1

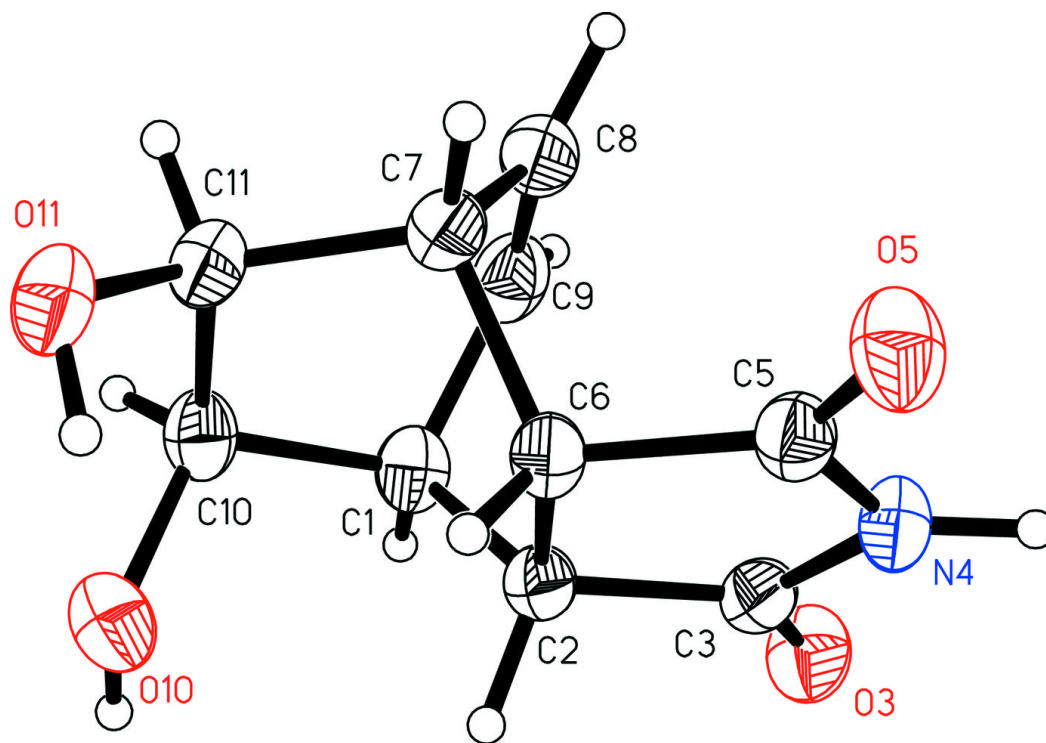


Fig. 2

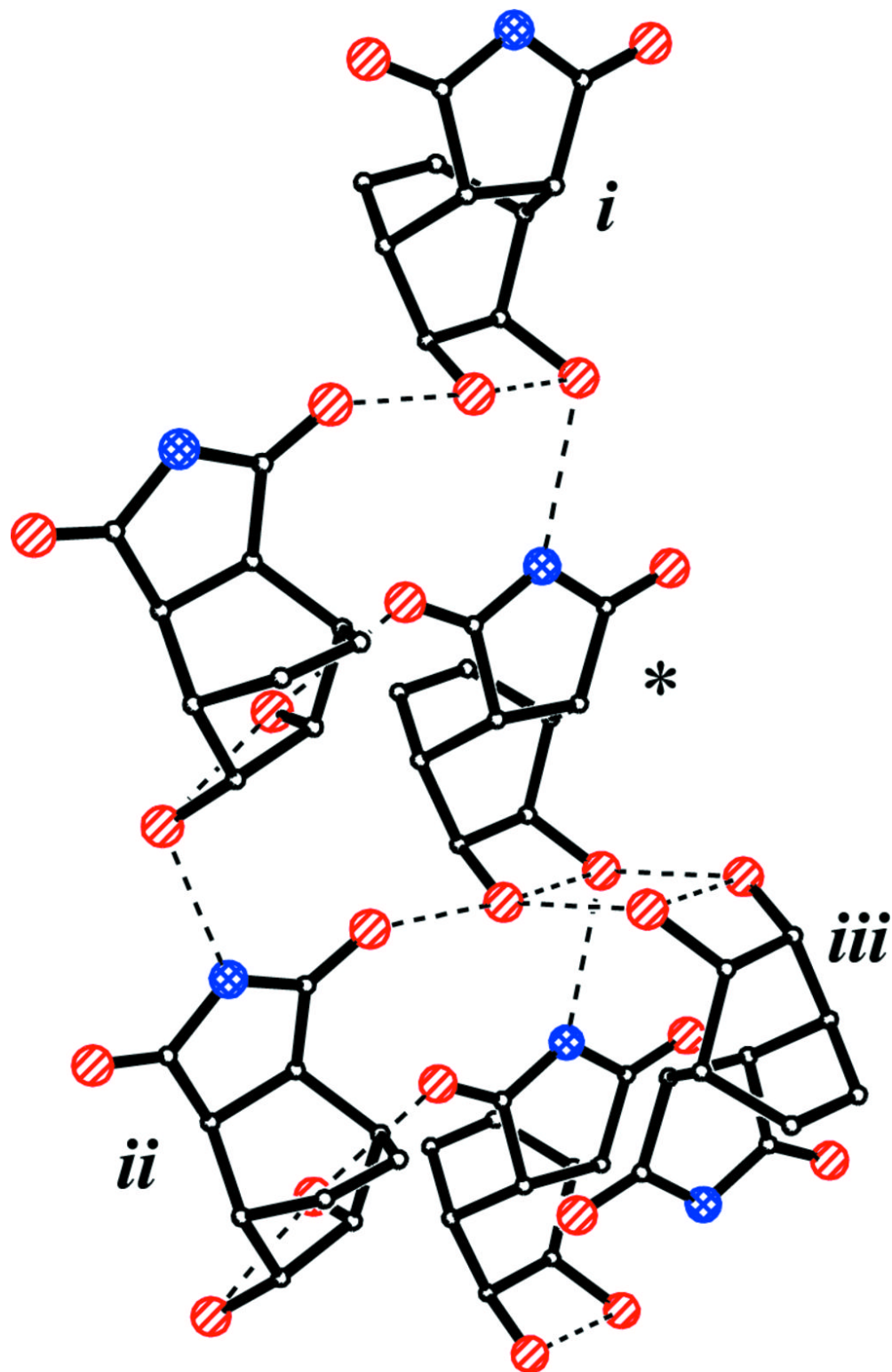


Fig. 3

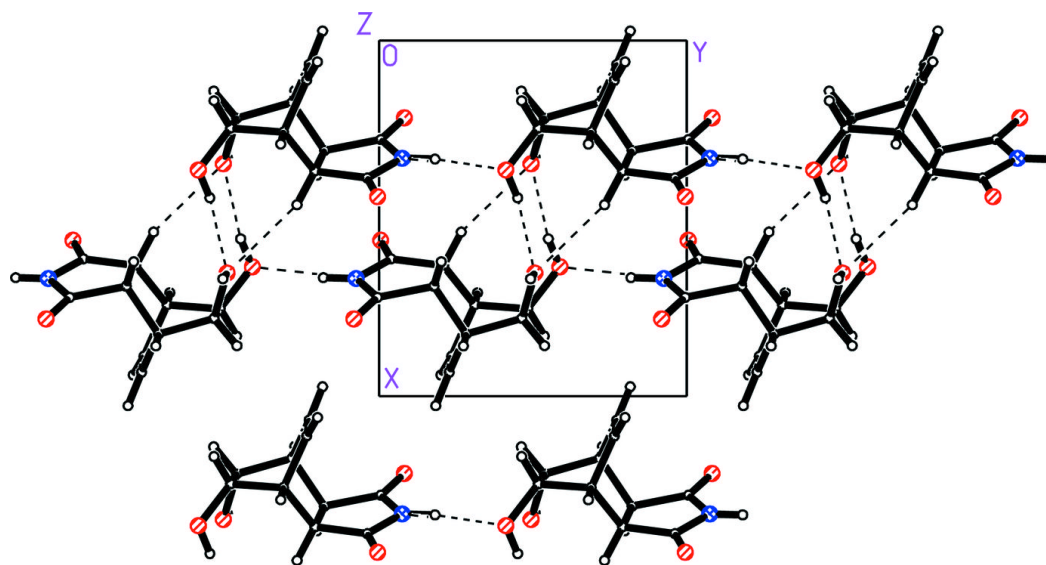


Fig. 4

