Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dimethyl 2,5-bis[2-(2-hydroxybenzoyl)-hydrazino]cyclohexa-1,4-diene-1,4-dicarboxylate dimethylformamide disolvate

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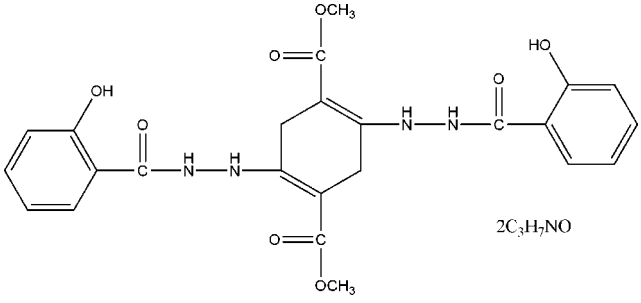
Received 13 September 2007; accepted 14 September 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.059; wR factor = 0.189; data-to-parameter ratio = 13.5.

The asymmetric unit of the title compound, $C_{24}H_{24}N_4O_8\cdot 2C_3H_7NO$, contains half of the centrosymmetric molecule of dimethyl 2,5-bis[2-(2-hydroxybenzoyl)-hydrazino]cyclohexa-1,4-diene-1,4-dicarboxylate and one dimethylformamide solvent molecule. There is a dihedral angle of 61.7 (1)° between the central and two outer rings. The crystal structure involves N—H···O, O—H···O and C—H···O hydrogen bonds.

Related literature

The crystal structures of cobalt and nickel complexes with a related aroylhydrazone derivative have been reported by Milway *et al.* (2004) and Liu *et al.* (2005), respectively. The crystal structure of 3-hydroxy-*N*-[phenyl(2-pyridyl)methylene]-2-naphthohydrazide was reported by Kang *et al.* (2007). For the catalytic and biological activities of aroylhydrazones, see Pouralimardan *et al.* (2007) and Patole *et al.* (2003), respectively.



Experimental

Crystal data

$C_{24}H_{24}N_4O_8\cdot 2C_3H_7NO$
M_r = 642.66
Monoclinic, $P2_1/n$
a = 6.227 (2) Å
b = 28.113 (9) Å
c = 9.376 (3) Å
β = 103.850 (14)°
V = 1593.6 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 (2) K
0.52 × 0.15 × 0.07 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.949, T_{max} = 0.993
7468 measured reflections
2800 independent reflections
1471 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.189
S = 1.00
2800 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5	0.86	2.03	2.827 (5)	153
N2—H2···O4	0.86	2.05	2.641 (4)	125
O2—H2*A*···O1	0.82	1.94	2.634 (4)	142
C15—H15*A*···O1^{i}	0.96	2.51	3.320 (6)	142

Symmetry code: (i) $x, y, z-1$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge the support of the National Natural Science Foundation of China (grant No. 20671048).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2302).

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  doi:10.1107/S1600536807045175

supplementary materials

Acta Cryst. (2007). E**63**, o4092 [**doi:10.1107/S1600536807045175**]

Dimethyl 2,5-bis[2-(2-hydroxybenzoyl)hydrazino]cyclohexa-1,4-diene-1,4-dicarboxylate dimethylformamide disolvate

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Comment

Aroylhydrazone and their metal complexes have been actively investigated for many years due to their wide spread applications in the fields of coordination chemistry (Milway *et al.*, 2004), bioinorganic chemistry (Patole *et al.*, 2003) and catalytic chemistry (Pouralimardan *et al.*, 2007). As an extension of our work on the structural characterization of aroylhydrazone derivatives (Liu *et al.*, 2005; Kang *et al.*, 2007), the title compound, (I), has been synthesized and structurally characterized.

In (I) (Fig. 1), the C8—C9 bond length of 1.354 (5) Å indicates that centrosymmetric aroylhydrazone moiety exists in the enol form with the formation of N2—H2···O4 hydrogen bond (Table 1). The central ring is essentially planar with the mean deviation of 0.0095 Å. The dihedral angle between the central ring and benzene ring C2—C7 is 61.7 (1)°. The intermolecular N—H···O hydrogen bonds and weak C—H···O interactions (Table 1) contribute to the crystal packing stability.

Experimental

The mixture of dimethyl-1,4-cyclohexanedione-2,5-dicarboxylate (2.28 g, 10 mmol) and salicylhydrazide (3.04 g, 20 mmol) in ethanol (30 ml) were refluxed for 6 h, and then the yellow precipitate was collected, washed with ethanol and dried in vacuo (yield 92%). The yellow solid was dissolved in DMF, then crystals suitable for X-ray diffraction were obtained after three weeks (m.p. 480–482 K). Elemental analysis: calcd. for $C_{30}H_{38}N_6O_{10}$: C 56.07, H 5.91, N 13.07%; found: C 56.15, H 5.59, N 13.13%.

Refinement

All H atoms were placed geometrically (O—H 0.82 Å, N—H 0.86 Å, C—H 0.93–0.97 Å) and treated as riding on their parent atoms, with U_{iso}(H) = 1.2–1.5U_{eq}(parent atom).

Figures

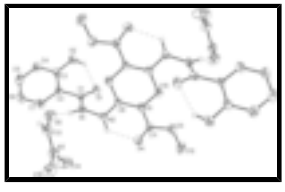


Fig. 1. A portion of the crystal structure of the title compound showing the atomic numbering and 30% probability displacement ellipsoids. Dashed lines denote hydrogen bonds. Unlabelled atoms are related to the labelled ones by symmetry operation (−*x*, −*y*, 1 − *z*). C-bound H atoms have been omitted for clarity.

Dimethyl 2,5-bis[2-(2-hydroxybenzoyl)hydrazino]cyclohexa- 1,4-diene-1,4-dicarboxylate dimethylformamide disolvate

Crystal data

$C_{24}H_{24}N_4O_8{\cdot}2C_3H_7NO$	$F_{000} = 680$
$M_r = 642.66$	$D_x = 1.339$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.227$ (2) Å	Cell parameters from 1492 reflections
$b = 28.113$ (9) Å	$\theta = 2.4$–25.3°
$c = 9.376$ (3) Å	$\mu = 0.10$ mm^{-1}
$\beta = 103.850$ (14)°	$T = 298$ (2) K
$V = 1593.6$ (9) Å^3	Stick, yellow
$Z = 2$	0.52 × 0.15 × 0.07 mm

Data collection

Siemens SMART CCD area-detector diffractometer	2800 independent reflections
Radiation source: fine-focus sealed tube	1471 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.064$
$T = 298$(2) K	$\theta_{max} = 25.0^\circ$
φ and ω scans	$\theta_{min} = 1.5^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -7 \rightarrow 7$
$T_{min} = 0.949$, $T_{max} = 0.993$	$k = -33 \rightarrow 32$
7468 measured reflections	$l = -11 \rightarrow 5$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.059$	H-atom parameters constrained
$wR(F^2) = 0.189$	$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 1.2201P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
2800 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
208 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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.

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 $F^2 > 2\text{sigma}(F^2)$ 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}
N1	0.0085 (5)	0.12965 (10)	0.4387 (3)	0.0401 (8)
H1	−0.0106	0.1403	0.3505	0.048*
N2	0.1573 (5)	0.09293 (10)	0.4882 (3)	0.0419 (8)
H2	0.2968	0.0989	0.5111	0.050*
N3	0.2346 (6)	0.12473 (12)	0.0477 (4)	0.0530 (9)
O1	−0.0940 (5)	0.13189 (9)	0.6539 (3)	0.0472 (7)
O2	−0.4852 (5)	0.17016 (9)	0.6376 (3)	0.0528 (8)
H2A	−0.3942	0.1486	0.6590	0.079*
O3	0.5415 (5)	−0.01121 (9)	0.7430 (3)	0.0591 (9)
O4	0.5249 (4)	0.06460 (9)	0.6729 (3)	0.0511 (8)
O5	−0.0794 (6)	0.13231 (13)	0.1286 (3)	0.0737 (10)
C1	−0.1059 (6)	0.14848 (12)	0.5312 (4)	0.0372 (9)
C2	−0.2469 (6)	0.18971 (12)	0.4759 (4)	0.0344 (9)
C3	−0.4309 (7)	0.19869 (13)	0.5337 (4)	0.0398 (9)
C4	−0.5660 (7)	0.23722 (14)	0.4857 (5)	0.0505 (11)
H4	−0.6889	0.2428	0.5235	0.061*
C5	−0.5186 (8)	0.26754 (14)	0.3816 (5)	0.0553 (12)
H5	−0.6099	0.2935	0.3496	0.066*
C6	−0.3375 (8)	0.25971 (14)	0.3248 (5)	0.0559 (12)
H6	−0.3061	0.2805	0.2553	0.067*
C7	−0.2032 (7)	0.22132 (13)	0.3708 (4)	0.0458 (10)
H7	−0.0813	0.2162	0.3317	0.055*
C8	0.0855 (6)	0.04753 (12)	0.5011 (4)	0.0359 (9)
C9	0.2168 (6)	0.01363 (12)	0.5801 (4)	0.0357 (9)
C10	0.1455 (6)	−0.03709 (12)	0.5836 (4)	0.0413 (10)
H10A	0.2463	−0.0569	0.5454	0.050*
H10B	0.1590	−0.0462	0.6852	0.050*
C11	0.4371 (6)	0.02576 (13)	0.6663 (4)	0.0384 (9)
C12	0.7623 (8)	−0.00190 (17)	0.8290 (6)	0.0767 (16)
H12A	0.8351	0.0197	0.7767	0.115*
H12B	0.8437	−0.0312	0.8463	0.115*
H12C	0.7550	0.0120	0.9213	0.115*
C13	0.0200 (8)	0.12140 (15)	0.0339 (5)	0.0543 (11)

H13	−0.0644	0.1098	−0.0549	0.065*
C14	0.3778 (9)	0.1427 (2)	0.1822 (6)	0.0914 (19)
H14A	0.3458	0.1757	0.1937	0.137*
H14B	0.5294	0.1393	0.1777	0.137*
H14C	0.3528	0.1250	0.2643	0.137*
C15	0.3392 (9)	0.1104 (2)	−0.0693 (5)	0.0854 (17)
H15A	0.2276	0.1008	−0.1539	0.128*
H15B	0.4377	0.0842	−0.0361	0.128*
H15C	0.4212	0.1367	−0.0947	0.128*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.047 (2)	0.0276 (16)	0.0475 (19)	0.0090 (15)	0.0152 (16)	0.0056 (14)
N2	0.0338 (18)	0.0298 (17)	0.064 (2)	0.0019 (14)	0.0156 (16)	0.0041 (15)
N3	0.052 (2)	0.067 (2)	0.043 (2)	0.0019 (19)	0.0161 (18)	−0.0044 (18)
O1	0.0589 (19)	0.0445 (15)	0.0371 (15)	0.0050 (14)	0.0093 (13)	0.0086 (13)
O2	0.0590 (19)	0.0457 (16)	0.0611 (19)	0.0037 (14)	0.0289 (15)	0.0114 (14)
O3	0.0461 (18)	0.0431 (16)	0.076 (2)	0.0007 (14)	−0.0090 (16)	0.0112 (15)
O4	0.0438 (18)	0.0359 (15)	0.072 (2)	−0.0034 (13)	0.0097 (15)	0.0013 (14)
O5	0.060 (2)	0.112 (3)	0.054 (2)	0.0068 (19)	0.0235 (17)	0.0052 (19)
C1	0.038 (2)	0.0284 (19)	0.045 (2)	−0.0047 (16)	0.0089 (19)	−0.0027 (17)
C2	0.040 (2)	0.0275 (18)	0.037 (2)	−0.0008 (17)	0.0125 (17)	0.0002 (16)
C3	0.049 (3)	0.032 (2)	0.038 (2)	−0.0014 (18)	0.0108 (19)	−0.0011 (17)
C4	0.054 (3)	0.044 (2)	0.056 (3)	0.008 (2)	0.019 (2)	−0.002 (2)
C5	0.071 (3)	0.037 (2)	0.055 (3)	0.019 (2)	0.010 (2)	0.004 (2)
C6	0.074 (3)	0.043 (2)	0.056 (3)	0.010 (2)	0.026 (2)	0.013 (2)
C7	0.056 (3)	0.036 (2)	0.049 (2)	0.0047 (19)	0.021 (2)	0.0047 (18)
C8	0.035 (2)	0.0287 (19)	0.047 (2)	0.0014 (17)	0.0158 (18)	−0.0045 (17)
C9	0.036 (2)	0.0266 (18)	0.044 (2)	0.0014 (16)	0.0085 (18)	0.0001 (16)
C10	0.040 (2)	0.033 (2)	0.050 (2)	0.0007 (17)	0.0081 (19)	0.0012 (17)
C11	0.041 (2)	0.030 (2)	0.045 (2)	0.0061 (18)	0.0137 (19)	0.0011 (17)
C12	0.053 (3)	0.060 (3)	0.097 (4)	−0.001 (2)	−0.022 (3)	0.009 (3)
C13	0.058 (3)	0.058 (3)	0.046 (3)	0.005 (2)	0.011 (2)	0.004 (2)
C14	0.065 (4)	0.134 (5)	0.075 (4)	−0.025 (3)	0.016 (3)	−0.037 (4)
C15	0.079 (4)	0.133 (5)	0.052 (3)	0.024 (3)	0.031 (3)	−0.001 (3)

Geometric parameters (Å, °)

N1—C1	1.355 (5)	C5—H5	0.9300
N1—N2	1.390 (4)	C6—C7	1.370 (5)
N1—H1	0.8600	C6—H6	0.9300
N2—C8	1.367 (4)	C7—H7	0.9300
N2—H2	0.8600	C8—C9	1.355 (5)
N3—C13	1.315 (6)	C8—C10^{i}	1.496 (5)
N3—C14	1.450 (6)	C9—C11	1.456 (5)
N3—C15	1.460 (5)	C9—C10	1.496 (5)
O1—C1	1.227 (4)	C10—C8^{i}	1.496 (5)

O2—C3	1.366 (4)	C10—H10A	0.9700
O2—H2A	0.8200	C10—H10B	0.9700
O3—C11	1.341 (4)	C12—H12A	0.9600
O3—C12	1.441 (5)	C12—H12B	0.9600
O4—C11	1.216 (4)	C12—H12C	0.9600
O5—C13	1.237 (5)	C13—H13	0.9300
C1—C2	1.472 (5)	C14—H14A	0.9600
C2—C7	1.401 (5)	C14—H14B	0.9600
C2—C3	1.403 (5)	C14—H14C	0.9600
C3—C4	1.379 (5)	C15—H15A	0.9600
C4—C5	1.380 (6)	C15—H15B	0.9600
C4—H4	0.9300	C15—H15C	0.9600
C5—C6	1.375 (6)		
C1—N1—N2	119.1 (3)	N2—C8—C10^{i}	115.4 (3)
C1—N1—H1	120.4	C8—C9—C11	120.2 (3)
N2—N1—H1	120.4	C8—C9—C10	122.6 (3)
C8—N2—N1	121.1 (3)	C11—C9—C10	117.1 (3)
C8—N2—H2	119.4	C8^{i}—C10—C9	115.3 (3)
N1—N2—H2	119.4	C8^{i}—C10—H10A	108.4
C13—N3—C14	120.6 (4)	C9—C10—H10A	108.4
C13—N3—C15	122.1 (4)	C8^{i}—C10—H10B	108.4
C14—N3—C15	117.2 (4)	C9—C10—H10B	108.4
C3—O2—H2A	109.5	H10A—C10—H10B	107.5
C11—O3—C12	115.7 (3)	O4—C11—O3	121.0 (4)
O1—C1—N1	121.9 (3)	O4—C11—C9	126.2 (3)
O1—C1—C2	121.8 (4)	O3—C11—C9	112.8 (3)
N1—C1—C2	116.3 (3)	O3—C12—H12A	109.5
C7—C2—C3	118.1 (3)	O3—C12—H12B	109.5
C7—C2—C1	123.2 (4)	H12A—C12—H12B	109.5
C3—C2—C1	118.6 (3)	O3—C12—H12C	109.5
O2—C3—C4	117.3 (4)	H12A—C12—H12C	109.5
O2—C3—C2	122.3 (3)	H12B—C12—H12C	109.5
C4—C3—C2	120.4 (4)	O5—C13—N3	125.7 (4)
C3—C4—C5	119.9 (4)	O5—C13—H13	117.2
C3—C4—H4	120.0	N3—C13—H13	117.2
C5—C4—H4	120.0	N3—C14—H14A	109.5
C6—C5—C4	120.6 (4)	N3—C14—H14B	109.5
C6—C5—H5	119.7	H14A—C14—H14B	109.5
C4—C5—H5	119.7	N3—C14—H14C	109.5
C7—C6—C5	120.0 (4)	H14A—C14—H14C	109.5
C7—C6—H6	120.0	H14B—C14—H14C	109.5
C5—C6—H6	120.0	N3—C15—H15A	109.5
C6—C7—C2	121.0 (4)	N3—C15—H15B	109.5
C6—C7—H7	119.5	H15A—C15—H15B	109.5
C2—C7—H7	119.5	N3—C15—H15C	109.5
C9—C8—N2	122.5 (3)	H15A—C15—H15C	109.5
C9—C8—C10^{i}	122.0 (3)	H15B—C15—H15C	109.5

C1—N1—N2—C8	76.3 (4)	C1—C2—C7—C6	−178.8 (4)
N2—N1—C1—O1	−5.3 (5)	N1—N2—C8—C9	−163.9 (3)
N2—N1—C1—C2	175.2 (3)	N1—N2—C8—C10^{i}	18.7 (5)
O1—C1—C2—C7	153.0 (4)	N2—C8—C9—C11	5.5 (6)
N1—C1—C2—C7	−27.5 (5)	C10^{i}—C8—C9—C11	−177.3 (3)
O1—C1—C2—C3	−25.3 (5)	N2—C8—C9—C10	−174.5 (3)
N1—C1—C2—C3	154.2 (3)	C10^{i}—C8—C9—C10	2.7 (6)
C7—C2—C3—O2	−179.3 (3)	C8—C9—C10—C8^{i}	−2.6 (6)
C1—C2—C3—O2	−1.0 (5)	C11—C9—C10—C8^{i}	177.4 (3)
C7—C2—C3—C4	1.1 (5)	C12—O3—C11—O4	−1.4 (6)
C1—C2—C3—C4	179.4 (4)	C12—O3—C11—C9	179.0 (4)
O2—C3—C4—C5	179.5 (4)	C8—C9—C11—O4	−2.4 (6)
C2—C3—C4—C5	−0.9 (6)	C10—C9—C11—O4	177.6 (4)
C3—C4—C5—C6	0.1 (7)	C8—C9—C11—O3	177.2 (3)
C4—C5—C6—C7	0.5 (7)	C10—C9—C11—O3	−2.8 (5)
C5—C6—C7—C2	−0.2 (7)	C14—N3—C13—O5	−0.4 (7)
C3—C2—C7—C6	−0.5 (6)	C15—N3—C13—O5	179.1 (4)

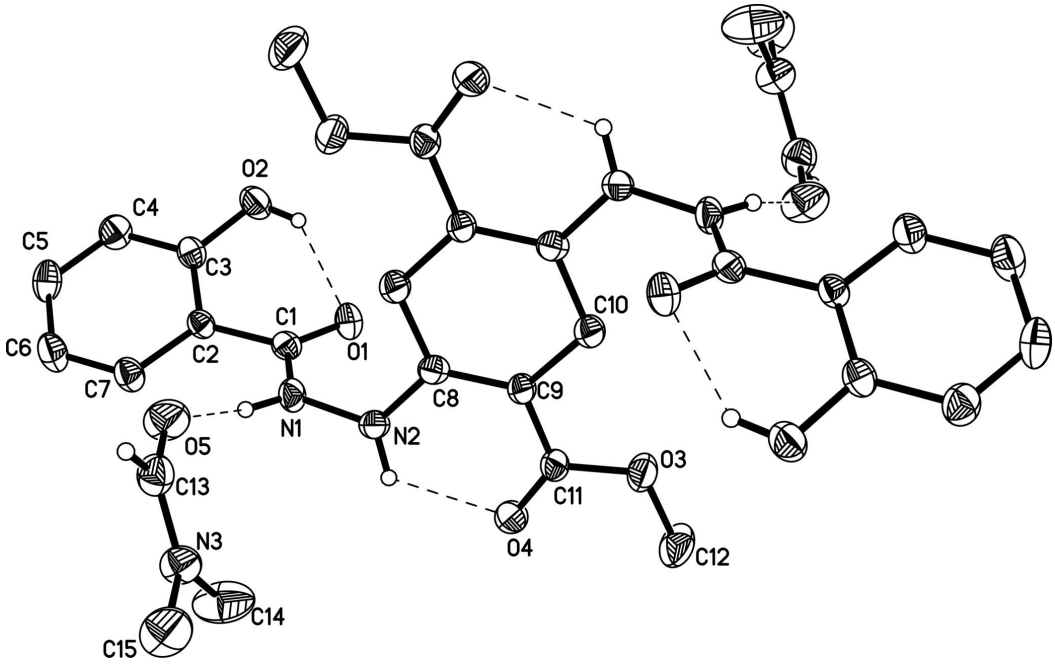
Symmetry codes: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5	0.86	2.03	2.827 (5)	153
N2—H2···O4	0.86	2.05	2.641 (4)	125
O2—H2A···O1	0.82	1.94	2.634 (4)	142
C15—H15A···O1^{ii}	0.96	2.51	3.320 (6)	142

Symmetry codes: (ii) *x*, *y*, *z*−1.

Fig. 1


O2
C4
C5
C3
C1
C10
C6
C2
O1
C7
C8
C9
N1
N2
O5
O3
C13
C11
N3
O4
C12
C14
C15