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Methyl 2-[(*E*)-(3-formyl-4-hydroxyphenyl)diazenyl]benzoate

Tushar S. Basu Baul,[a]‡ Smita Basu[a] and Edward R. T. Tiekink[b]*

[a]Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India, and [b]Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA
Correspondence e-mail: edward.tiekink@utsa.edu

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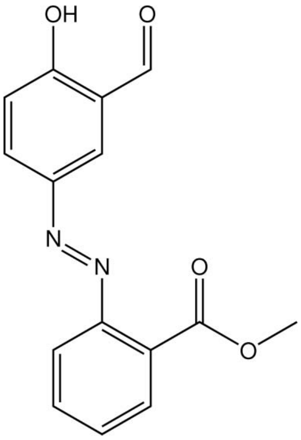
Key indicators: single-crystal X-ray study; *T* = 153 K; mean σ(C–C) = 0.002 Å; *R* factor = 0.046; *wR* factor = 0.129; data-to-parameter ratio = 13.6.

The title compound, $C_{15}H_{12}N_2O_4$, displays a twisted conformation as reflected in the dihedral angle between the aromatic rings of 59.77 (7)°. Intra- and intermolecular O—H⋯O interactions are found, with the latter leading to a double chain arranged about a zigzag chain of $\{O—H\cdots O\}_n$ interactions.

Related literature

For related literature, see: Basu Baul *et al.* (1996, 2006, 2004).



Experimental

Crystal data

$C_{15}H_{12}N_2O_4$
M_r = 284.27
Monoclinic, $P2_1/c$
a = 14.164 (2) Å
b = 4.6113 (8) Å
c = 21.067 (3) Å
β = 108.140 (4)°
V = 1307.6 (4) Å^3
Z = 4
Mo *K*α radiation
μ = 0.11 mm^{-1}
T = 153 (2) K
0.30 × 0.15 × 0.12 mm

Data collection

Rigaku AFC12K/SATURN724 diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.878, T_{max} = 1
11141 measured reflections
2638 independent reflections
2510 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.129
S = 1.08
2638 reflections
194 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O3—H3O⋯O4	0.84	1.94	2.6876 (16)	147
O3—H3O⋯O3^{i}	0.84	2.48	2.9810 (15)	119
C13—H13⋯O1^{ii}	0.95	2.36	3.268 (2)	160
C9—H9⋯N2^{iii}	0.95	2.66	3.596 (2)	167
C4—H4⋯O2^{iv}	0.95	2.84	3.677 (2)	147

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2251).

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‡ Additional correspondence author; e-mail: basubaul@nehu.ac.in.

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supplementary materials

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Methyl 2-[(*E*)-(3-formyl-4-hydroxyphenyl)diazenyl]benzoate

T. S. Basu Baul, **S. Basu** and **E. R. T. Tiekink**

Comment

The synthesis of the title compound (I) and their interactions with triorganotin(IV) moieties, have attracted much interest owing to their novel structural possibilities (Basu Baul *et al.*, 1996, 2006), and their significant biological activity towards mosquito larvae (Basu Baul *et al.*, 2004) and sea urchin early development stages (Basu Baul *et al.*, 2006).

Compound (I), Fig. 1, assumes an E-conformation. There is a twist in the molecule as seen in the N1—N2—C8—C9 and, in particular, the N2—N1—C7—C2 torsion angles of −163.77 (13) and −141.01 (14)°, respectively. This is also reflected in the dihedral angle of 59.77 (7)° formed between the C2—C7 and C8—C13 aromatic rings.

The hydroxyl group participates in an intramolecular O3—H···O4 hydrogen-bond and at the same time forms an intermolecular O3—H···O3 interaction with a centrosymmetric mate, Table 1, to form a double chain, Fig. 2. Additional stabilization to the chain are afforded by C—H···O1 contacts. Further, this arrangement allows for the close approach of the C=O4 carbonyl to the π-system of a translationally related C8—C13 ring; C12'=O4···*Cg*(C18—C13) = 3.2061 (13)^{ii} Å for ii: *x*, −1 + *y*, *z*. The double-chains stack in columns parallel to the *b* axis. Connections between columns are afforded by weak C—H···O contacts, involving an aromatic C4—H and O2 atoms, and weak C—H···N contacts involving aromatic C9—H and azo-N2 atoms, the latter leading to a eight-membered [···HCCN]$_2$ synthon.

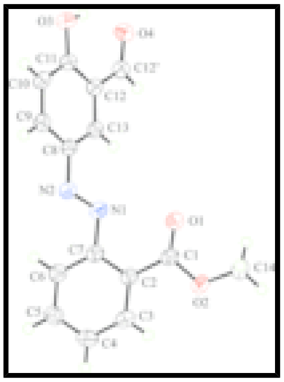
Experimental

2-[(*E*)-2-(3-Formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (2.0 g, 7.40 mmol), prepared as in the literature (Basu Baul *et al.*, 1996), was dissolved in anhydrous methanol (150 ml) and transferred to a three-necked round bottom flask equipped with a dropping funnel, water-cooled condenser and a guard tube, all placed in an ice/salt bath. The clear solution was allowed to cool as the stirring was continued. After sufficient cooling, $SOCl_2$ (1.62 ml, 22.19 mmol) was added drop-wise over 30 min. The whole reaction mixture was allowed to warm to room temperature, stirred for 20 h, and then the volatiles were removed using a rotary evaporator. Water was added to the residue and neutralized with aqueous $NaHCO_3$ solution. The product was extracted in ethyl acetate and the resulting two-phase system was mixed well and filtered, and the layers were separated. The ethyl acetate portion was washed with water, dried over Na_2SO_4, and the solvent was evaporated to one-fourth of its initial solvent volume and kept at room temperature to yield (I). The solid was washed with hexane, dried *in vacuo* and recrystallized from an ethyl acetate-methanol mixture (*v*/*v*, 1:1) which afforded the orange crystals (m.p. 333–335 K) in 85% (1.78 g) yield. Elemental analysis, found: C 63.41, H 4.27, N 9.87%; $C_{15}H_{12}N_2O_4$ requires C 63.37, H 4.25, N 9.85%. IR (KBr, cm^{-1}): 1725 ν(OCO)$_{asym}$. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ H: 11.37 [s, 1H, H4], 10.02 [s, 1H, H7], 8.41 [d, 2.6 Hz, 1H, H2], 8.19 [dd, 2.6, 8.8 Hz, 1H, H6], 7.83 [dd, 1.5, 7.7 Hz, 1H, H3'], 7.60 [dt, 1.5, 7.7 Hz, 2H, H4' & H6'], 7.51 [dt, 1.5, 7.7 Hz, 1H, H5'], 7.11 [d, 8.8 Hz, 1H, H5], 4.00 [s, 3H, H8'] p.p.m. ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ C: 196.9, 168.2, 164.6, 152.1, 146.4, 132.5, 131.1, 130.4, 130.3, 130.2, 129.0, 120.7, 119.2, 119.0, 52.8 p.p.m.

Refinement

All C-bound H atoms were included in the riding-model approximation, with C—H = 0.95 to 0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C). The hydroxyl-H atom was located from a difference map and included so that O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O).

Figures



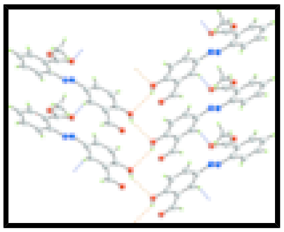
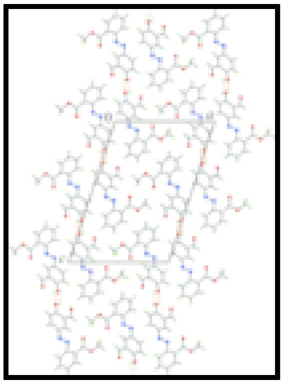


Figure 1 Molecular structure of (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level.
Figure 2 View of the supramolecular chain in (I) mediated by hydrogen bonds, shown as orange-dashed lines. Colour code: red (oxygen), blue (nitrogen), grey (carbon) and green (hydrogen).



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Crystal data

$C_{15}H_{12}N_2O_4$
M_r = 284.27
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc

F_{000} = 592
D_x = 1.444 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71070 Å
Cell parameters from 2012 reflections

a = 14.164 (2) Å

b = 4.6113 (8) Å

c = 21.067 (3) Å

β = 108.140 (4)°

V = 1307.6 (4) Å^3

Z = 4

θ = 2.9–30.2°

μ = 0.11 mm^{-1}

T = 153 (2) K

Block, orange

0.30 × 0.15 × 0.12 mm

Data collection

Rigaku AFC12K/SATURN724 diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 153(2) K

ω scans

Absorption correction: multi-scan (ABSCOR; Higashi, 1995)

T_{min} = 0.878, T_{max} = 1

11141 measured reflections

2638 independent reflections

2510 reflections with $I > 2\sigma(I)$

R_{int} = 0.021

θ_{max} = 26.5°

θ_{min} = 2.9°

$h = -17 \rightarrow 14$

$k = -5 \rightarrow 4$

$l = -21 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.046

$wR(F^2)$ = 0.129

S = 1.08

2638 reflections

194 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.3817P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}}$ = 0.21 e Å^{-3}

$\Delta\rho_{\text{min}}$ = −0.22 e Å^{-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.

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 > 2sigma(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*	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.60419 (8)	0.6564 (3)	0.46402 (5)	0.0425 (3)
O2	0.48259 (8)	0.7820 (3)	0.37164 (5)	0.0439 (3)
O3	0.99285 (8)	−0.2764 (2)	0.70389 (5)	0.0360 (3)
H3O	0.9518	−0.4018	0.7075	0.054*
O4	0.82006 (8)	−0.5682 (2)	0.67043 (5)	0.0387 (3)
N1	0.74996 (9)	0.3207 (3)	0.43726 (6)	0.0328 (3)
N2	0.84243 (9)	0.3272 (3)	0.46527 (6)	0.0304 (3)
C1	0.57480 (10)	0.6905 (3)	0.40427 (7)	0.0331 (3)
C2	0.63371 (10)	0.6449 (3)	0.35758 (7)	0.0313 (3)
C3	0.60542 (11)	0.7840 (3)	0.29581 (8)	0.0365 (4)
H3	0.5472	0.9006	0.2834	0.044*
C4	0.66068 (12)	0.7554 (4)	0.25217 (8)	0.0397 (4)
H4	0.6408	0.8533	0.2104	0.048*
C5	0.74493 (12)	0.5833 (4)	0.26977 (8)	0.0389 (4)
H5	0.7823	0.5599	0.2397	0.047*
C6	0.77477 (11)	0.4460 (3)	0.33085 (7)	0.0348 (3)
H6	0.8328	0.3286	0.3426	0.042*
C7	0.72068 (10)	0.4773 (3)	0.37562 (7)	0.0309 (3)
C8	0.87549 (10)	0.1598 (3)	0.52484 (7)	0.0286 (3)
C9	0.97161 (10)	0.2172 (3)	0.56704 (7)	0.0312 (3)
H9	1.0116	0.3564	0.5541	0.037*
C10	1.00897 (10)	0.0743 (3)	0.62710 (7)	0.0322 (3)
H10	1.0734	0.1202	0.6560	0.039*
C11	0.95250 (10)	−0.1370 (3)	0.64554 (7)	0.0295 (3)
C12	0.85650 (10)	−0.2015 (3)	0.60252 (7)	0.0286 (3)
C12'	0.79609 (11)	−0.4270 (3)	0.61856 (7)	0.0333 (3)
H12'	0.7336	−0.4681	0.5866	0.040*
C13	0.81883 (10)	−0.0505 (3)	0.54276 (7)	0.0291 (3)
H13	0.7538	−0.0919	0.5141	0.035*
C14	0.42299 (11)	0.8673 (5)	0.41328 (9)	0.0473 (4)
H14A	0.4272	0.7175	0.4470	0.071*
H14B	0.3537	0.8907	0.3855	0.071*
H14C	0.4478	1.0514	0.4354	0.071*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0320 (5)	0.0608 (8)	0.0328 (6)	0.0020 (5)	0.0070 (4)	0.0048 (5)
O2	0.0301 (5)	0.0631 (8)	0.0353 (6)	0.0097 (5)	0.0054 (5)	0.0033 (5)
O3	0.0390 (6)	0.0332 (6)	0.0303 (6)	−0.0002 (4)	0.0027 (5)	0.0029 (4)
O4	0.0432 (6)	0.0379 (6)	0.0359 (6)	−0.0005 (5)	0.0135 (5)	0.0037 (5)
N1	0.0312 (6)	0.0318 (7)	0.0333 (7)	0.0014 (5)	0.0068 (5)	0.0025 (5)
N2	0.0303 (6)	0.0298 (6)	0.0293 (6)	0.0018 (5)	0.0067 (5)	−0.0002 (5)
C1	0.0272 (7)	0.0355 (8)	0.0318 (8)	−0.0023 (6)	0.0021 (6)	0.0010 (6)

C2	0.0284 (7)	0.0314 (7)	0.0304 (8)	−0.0028 (5)	0.0038 (6)	−0.0005 (6)
C3	0.0334 (7)	0.0377 (8)	0.0327 (8)	0.0015 (6)	0.0022 (6)	0.0010 (6)
C4	0.0430 (8)	0.0440 (9)	0.0281 (8)	−0.0021 (7)	0.0053 (6)	0.0038 (6)
C5	0.0410 (8)	0.0434 (9)	0.0328 (8)	−0.0030 (7)	0.0120 (6)	−0.0028 (7)
C6	0.0323 (7)	0.0360 (8)	0.0342 (8)	0.0009 (6)	0.0076 (6)	−0.0016 (6)
C7	0.0301 (7)	0.0295 (7)	0.0300 (7)	−0.0032 (5)	0.0051 (5)	0.0002 (5)
C8	0.0301 (7)	0.0271 (7)	0.0279 (7)	0.0036 (5)	0.0081 (5)	−0.0009 (5)
C9	0.0303 (7)	0.0285 (7)	0.0348 (8)	0.0002 (5)	0.0099 (6)	−0.0008 (6)
C10	0.0281 (7)	0.0306 (7)	0.0336 (8)	0.0009 (6)	0.0035 (6)	−0.0025 (6)
C11	0.0322 (7)	0.0266 (7)	0.0274 (7)	0.0047 (5)	0.0062 (5)	−0.0026 (5)
C12	0.0299 (7)	0.0263 (7)	0.0294 (7)	0.0010 (5)	0.0088 (5)	−0.0034 (5)
C12'	0.0333 (7)	0.0331 (8)	0.0331 (8)	0.0007 (6)	0.0096 (6)	−0.0001 (6)
C13	0.0277 (6)	0.0289 (7)	0.0289 (7)	0.0025 (5)	0.0063 (5)	−0.0032 (5)
C14	0.0317 (8)	0.0643 (11)	0.0468 (10)	0.0069 (8)	0.0136 (7)	0.0050 (8)

Geometric parameters (Å, °)

C1—O1	1.2066 (19)	C5—H5	0.9500
C1—O2	1.3407 (17)	C6—C7	1.396 (2)
C14—O2	1.448 (2)	C6—H6	0.9500
O3—C11	1.3467 (17)	C8—C13	1.384 (2)
O3—H3O	0.8401	C8—C9	1.400 (2)
O4—C12'	1.2257 (18)	C9—C10	1.378 (2)
N1—N2	1.2582 (17)	C9—H9	0.9500
N1—C7	1.4298 (18)	C10—C11	1.390 (2)
N2—C8	1.4230 (18)	C10—H10	0.9500
C1—C2	1.490 (2)	C11—C12	1.4112 (19)
C2—C3	1.393 (2)	C12—C13	1.392 (2)
C2—C7	1.402 (2)	C12—C12'	1.452 (2)
C3—C4	1.387 (2)	C12'—H12'	0.9500
C3—H3	0.9500	C13—H13	0.9500
C4—C5	1.384 (2)	C14—H14A	0.9800
C4—H4	0.9500	C14—H14B	0.9800
C5—C6	1.377 (2)	C14—H14C	0.9800
C1—O2—C14	115.68 (12)	C13—C8—N2	124.14 (12)
C11—O3—H3O	107.5	C9—C8—N2	116.44 (12)
N2—N1—C7	112.28 (12)	C10—C9—C8	120.81 (13)
N1—N2—C8	114.16 (12)	C10—C9—H9	119.6
O1—C1—O2	122.71 (14)	C8—C9—H9	119.6
O1—C1—C2	126.03 (13)	C9—C10—C11	120.12 (13)
O2—C1—C2	111.25 (12)	C9—C10—H10	119.9
C3—C2—C7	118.68 (14)	C11—C10—H10	119.9
C3—C2—C1	119.63 (13)	O3—C11—C10	118.16 (12)
C7—C2—C1	121.60 (13)	O3—C11—C12	122.41 (13)
C2—C3—C4	121.18 (14)	C10—C11—C12	119.43 (13)
C2—C3—H3	119.4	C13—C12—C11	119.79 (13)
C4—C3—H3	119.4	C13—C12—C12'	118.77 (13)
C5—C4—C3	119.64 (14)	C11—C12—C12'	121.42 (13)
C5—C4—H4	120.2	O4—C12'—C12	124.63 (13)

C3—C4—H4	120.2	O4—C12'—H12'	117.7
C4—C5—C6	120.14 (15)	C12—C12'—H12'	117.7
C4—C5—H5	119.9	C8—C13—C12	120.39 (12)
C6—C5—H5	119.9	C8—C13—H13	119.8
C7—C6—C5	120.69 (14)	C12—C13—H13	119.8
C7—C6—H6	119.7	O2—C14—H14A	109.5
C5—C6—H6	119.7	O2—C14—H14B	109.5
C6—C7—C2	119.64 (13)	H14A—C14—H14B	109.5
C6—C7—N1	119.76 (13)	O2—C14—H14C	109.5
C2—C7—N1	120.42 (13)	H14A—C14—H14C	109.5
C13—C8—C9	119.41 (13)	H14B—C14—H14C	109.5

C7—N1—N2—C8	−176.49 (11)	N2—N1—C7—C2	−141.01 (14)
C14—O2—C1—O1	6.2 (2)	N1—N2—C8—C13	16.02 (19)
C14—O2—C1—C2	−172.67 (14)	N1—N2—C8—C9	−163.77 (13)
O1—C1—C2—C3	−157.39 (16)	C13—C8—C9—C10	−2.3 (2)
O2—C1—C2—C3	21.44 (19)	N2—C8—C9—C10	177.52 (12)
O1—C1—C2—C7	19.0 (2)	C8—C9—C10—C11	2.2 (2)
O2—C1—C2—C7	−162.17 (13)	C9—C10—C11—O3	178.37 (12)
C7—C2—C3—C4	1.0 (2)	C9—C10—C11—C12	−0.6 (2)
C1—C2—C3—C4	177.50 (14)	O3—C11—C12—C13	−179.87 (12)
C2—C3—C4—C5	0.7 (2)	C10—C11—C12—C13	−1.0 (2)
C3—C4—C5—C6	−1.3 (2)	O3—C11—C12—C12'	−1.0 (2)
C4—C5—C6—C7	0.2 (2)	C10—C11—C12—C12'	177.91 (13)
C5—C6—C7—C2	1.5 (2)	C13—C12—C12'—O4	−177.73 (13)
C5—C6—C7—N1	176.71 (13)	C11—C12—C12'—O4	3.4 (2)
C3—C2—C7—C6	−2.1 (2)	C9—C8—C13—C12	0.7 (2)
C1—C2—C7—C6	−178.52 (13)	N2—C8—C13—C12	−179.08 (12)
C3—C2—C7—N1	−177.23 (13)	C11—C12—C13—C8	0.9 (2)
C1—C2—C7—N1	6.3 (2)	C12'—C12—C13—C8	−178.02 (13)
N2—N1—C7—C6	43.86 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3O···O4	0.84	1.94	2.6876 (16)	147
O3—H3O···O3^{i}	0.84	2.48	2.9810 (15)	119
C13—H13···O1^{ii}	0.95	2.36	3.268 (2)	160
C9—H9···N2^{iii}	0.95	2.66	3.596 (2)	167
C4—H4···O2^{iv}	0.95	2.84	3.677 (2)	147

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

Fig. 1

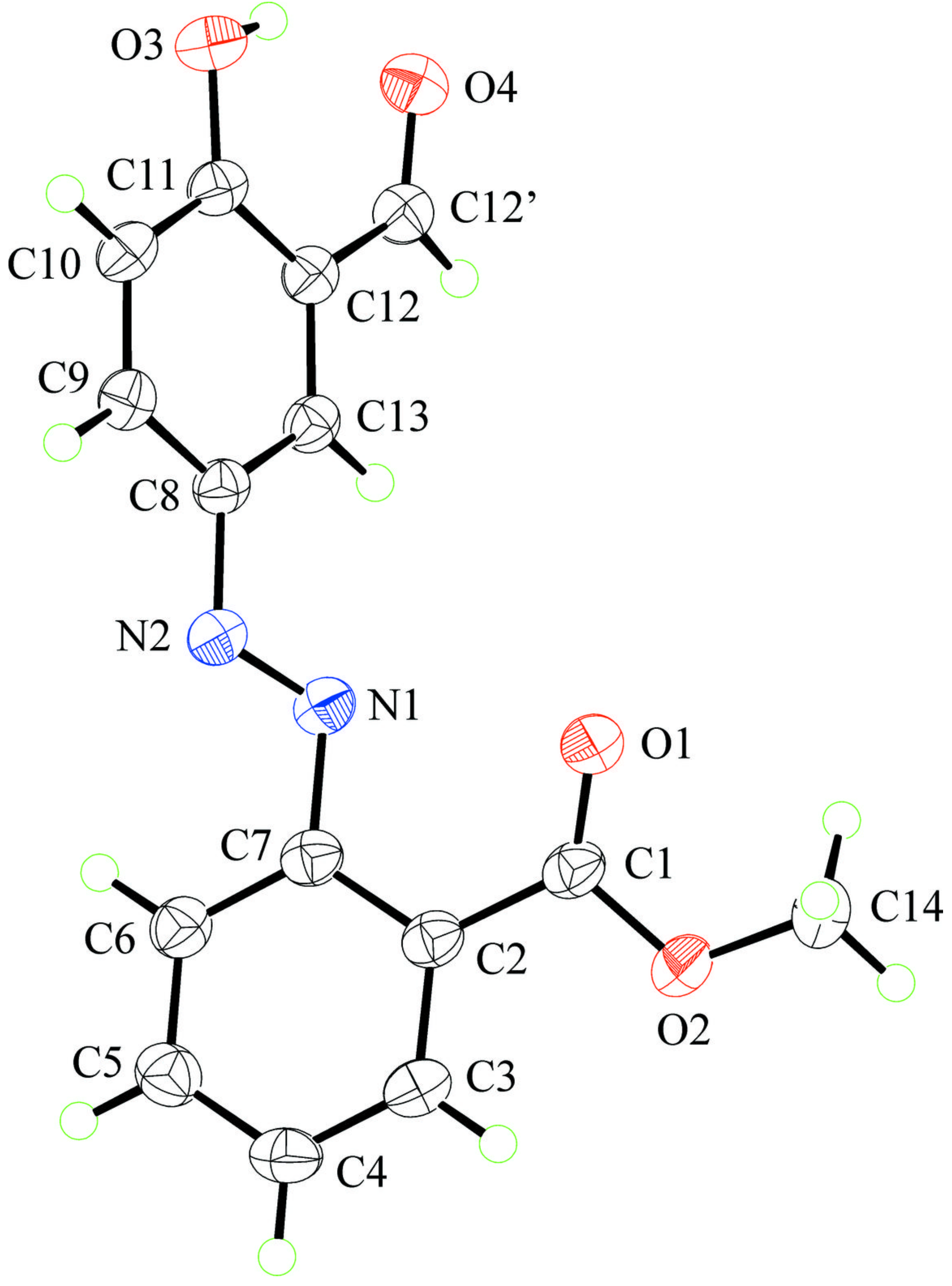

Fig. 2

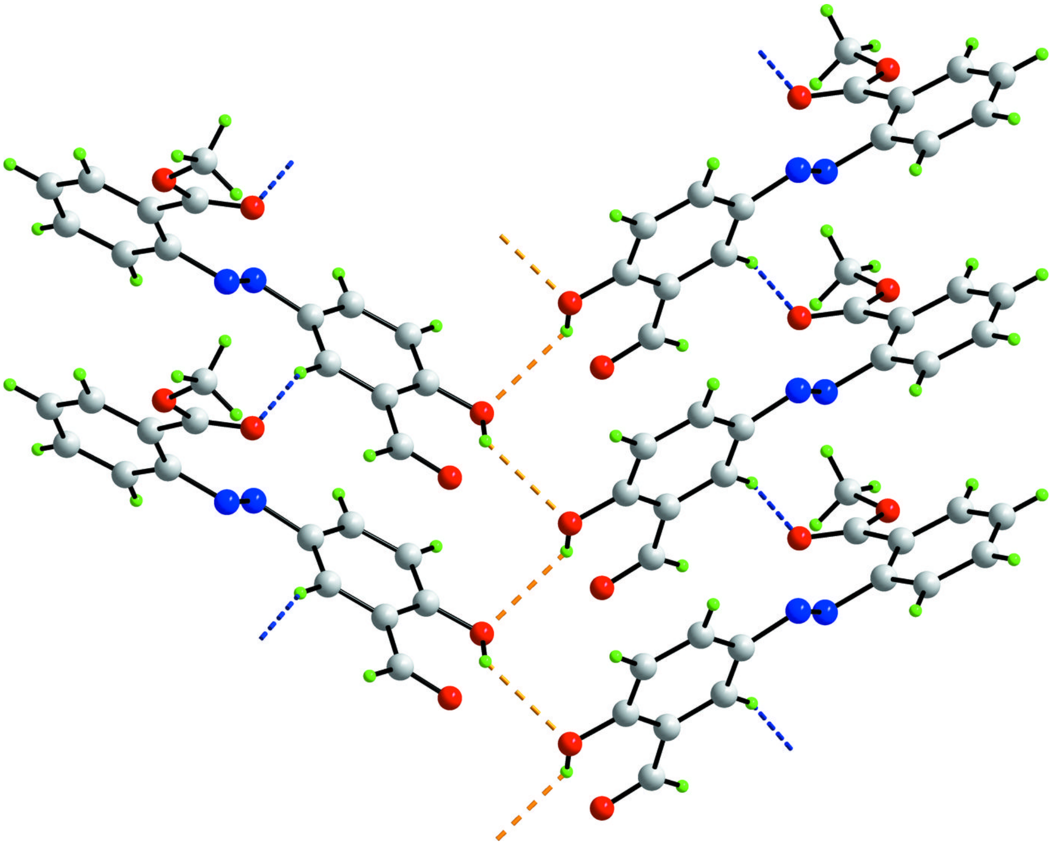

Fig. 3