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2-Aminoterephthalic acid dimethyl ester

Jürgen Brüning,[a] Jan W. Bats[b] and Martin U. Schmidt[a]*

[a]Institute of Inorganic and Analytical Chemistry, University of Frankfurt, Max-von-Laue-Strasse 7, D-60438 Frankfurt am Main, Germany, and [b]Institute of Organic Chemistry and Chemical Biology, University of Frankfurt, Max-von-Laue-Strasse 7, D-60438 Frankfurt am Main, Germany
Correspondence e-mail: m.schmidt@chemie.uni-frankfurt.de

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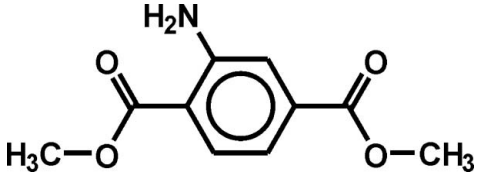
Key indicators: single-crystal X-ray study; T = 166 K; mean σ(C–C) = 0.005 Å; R factor = 0.054; wR factor = 0.134; data-to-parameter ratio = 11.6.

Single crystals of the title compound, $C_{10}H_{11}NO_4$, an intermediate in the industrial synthesis of yellow azo pigments, were obtained from the industrial production. The molecules crystallize as centrosymmetic dimers connected by two symmetry-related N—H···O=C hydrogen bonds. Each molecule also contains an intramolecular N—H···O=C hydrogen bond. The dimers form stacks along the *a*-axis direction. Neighbouring stacks are arranged into a herringbone structure.

Related literature

For studies on aminoterephthalic acid esters, see: Wegscheider *et al.* (1912); Clark *et al.* (1995); O'Connor *et al.* (1999); Lavalette *et al.* (2002); Jones *et al.* (2008). For syntheses wherein the title compound is used, see: Cordier & Coulet (1994); Metz & Weber (1999); Stengel-Rutkowski & Metz (2000); Jung *et al.* (2001); Herbst & Hunger (2004); Schweikart *et al.* (2007). For the crystal structure of the final product, Pigment Yellow 213, see: Schmidt *et al.* (2009).



Experimental

Crystal data

$C_{10}H_{11}NO_4$
M_r = 209.20
Monoclinic, $P2_1/c$
a = 4.7721 (12) Å
b = 16.928 (5) Å
c = 11.841 (5) Å
β = 93.88 (5)°
V = 954.4 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 166 K
0.75 × 0.32 × 0.04 mm

Data collection

Siemens SMART 1K CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.760, T_{max} = 0.995
11829 measured reflections
1687 independent reflections
884 reflections with $I > 2\sigma(I)$
R_{int} = 0.140

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.134
S = 0.96
1687 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O4	0.92 (4)	2.01 (4)	2.717 (4)	133 (3)
N1—H1B···O2^{i}	0.95 (4)	2.14 (3)	3.016 (4)	153 (3)

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

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FK2004).

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supporting information

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2-Aminoterephthalic acid dimethyl ester

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S1. Comment

2-Aminoterephthalic acid dimethyl ester (**I**, Fig. 1), $C_{10}H_{11}NO_4$, is used in the synthesis of industrial azo pigments like Pigment Yellow 213 (Metz & Weber, 1999; Stengel-Rutkowski & Metz, 2000; Herbst & Hunger, 2004; Schmidt *et al.*, 2009) (For synthesis of Pigment Yellow 213 see Fig. 1). Compound **I** is known since 1912 (Wegscheider *et al.*; 1912) and has been the subject of numerous investigations, *e.g.* as intermediate (Cordier & Coulet, 1994), antitumor drug (Clark *et al.*; 1995), drug against reflux disease (O′Connor *et al.*, 1999), in synthesis of pigments (Jung *et al.*, 2001; Herbst & Hunger, 2004; Schweikart *et al.*, 2007), in preparation of polymers (Lavalette *et al.*, 2002), and in parallel syntheses (Jones *et al.*, 2008); but its crystal structure has not been determined hitherto.

In order to determine the crystal structure of compound **I** and to search for different crystallographic phases, hydrates or solvates, a polymorph screening was performed. Different crystallization methods were used including (1) recrystallization from various solvents and solvent mixtures by heating and subsequent slow cooling, (2) overlaying a solution of the compound by an anti-solvent, (3) diffusion of an anti-solvent into a solution of the compound *via* the gas phase. The solvents included the most common organic solvents, *e.g.* dimethylsulfoxide, *N*,*N*-dimethylacetamide, *N*-methylpyrrolidone, ethers, esters, alcohols as well as acids, bases and water. According to X-ray powder diffraction no additional phases were formed.

Single crystals were obtained from technical synthesis. The structure of the molecule is shown in Fig. 2. The central six-membered ring is planar [mean deviation from best plane: 0.002 (2) Å]. The angle between the plane of the six-membered ring and the planes of the carboxy groups attached to C3 and C6 is 3.3 (2) and 5.4 (2)°, respectively. The molecules form centrosymmetric dimers connected by two symmetry-related N—H···O═C hydrogen bonds (Table 1). The second H atom of the NH_2 group is involved in an intramolecular N—H···O═C hydrogen bond. The crystal packing is shown in Figures 3 and 4. The molecules stack along the crystallographic *a*-direction. The interplanar distance in the stack is 3.396 (2) Å. Neighbouring stacks show a herringbone arrangement.

S2. Experimental

The crystals of compound **I** were obtained from Clariant GmbH, Frankfurt am Main.

S3. Refinement

The H atoms attached to C atoms were geometrically positioned and were constrained using C_{planar}—H = 0.95 Å, C_{methyl}—H = 0.98 Å, $U_{iso}(H) = 1.2U_{eq}(C_{planar})$ and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$. The H atoms at the NH_2 group were taken from a difference Fourier synthesis and were refined. The torsion angles about the O—C_{methyl} groups were refined.

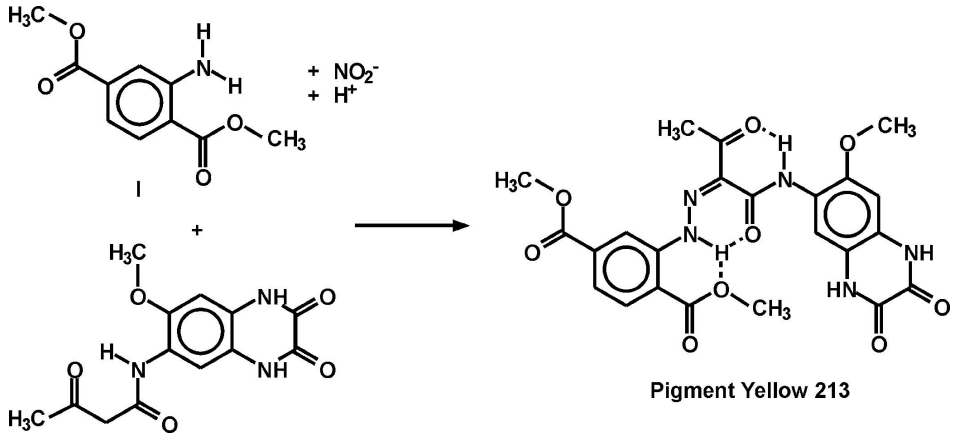

Figure 1

Preparation of Pigment Yellow 213 in which compound (I) is used as preproduct.

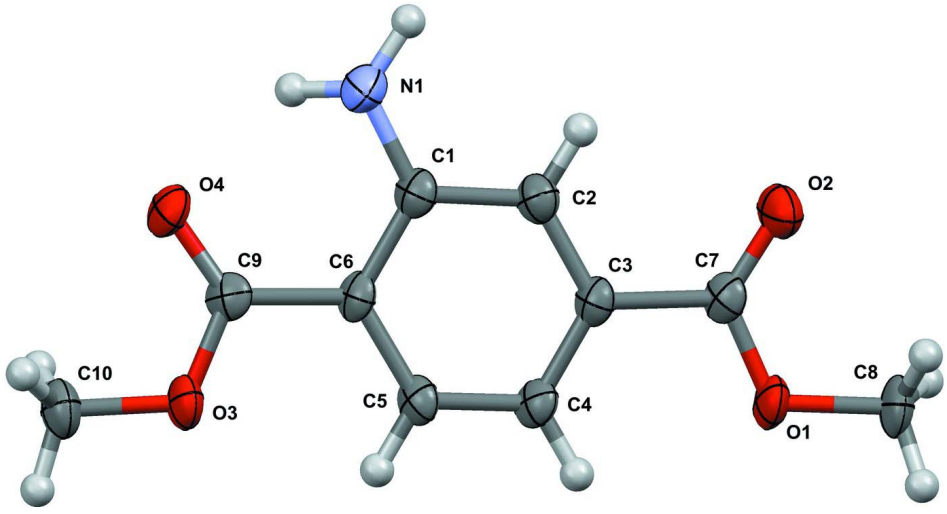

Figure 2

Molecular structure of compound **I**, with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level) for non-H atoms.

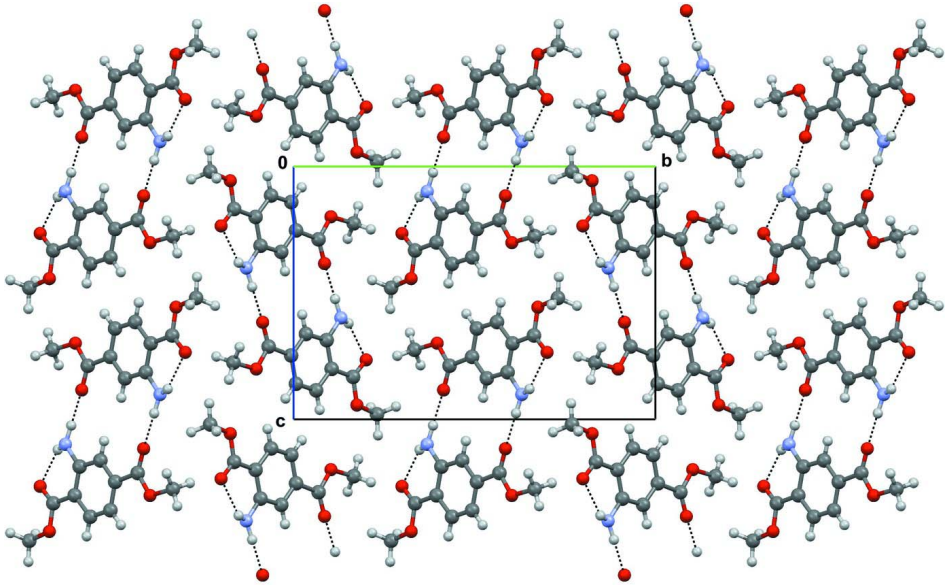

Figure 3

Molecular packing of compound **I** showing the hydrogen bond architecture; view direction [100]. The hydrogen bonds are drawn as dashed lines.

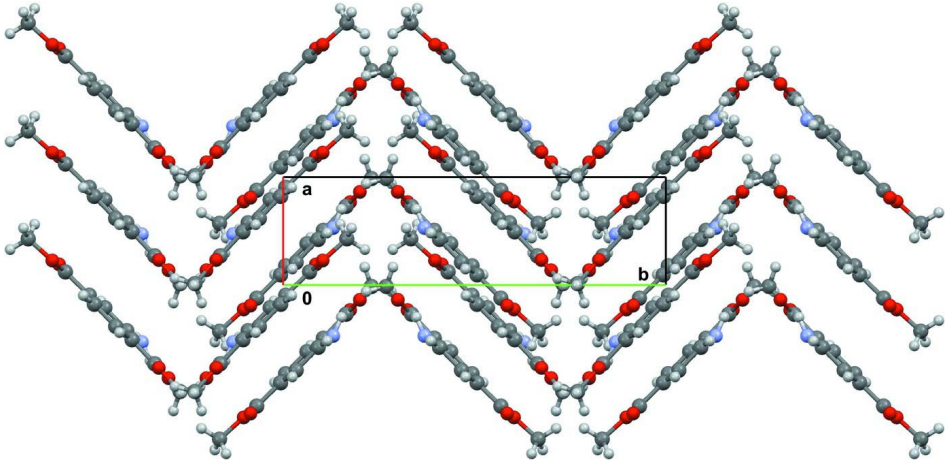

Figure 4

Molecular packing of compound **I**, showing the herringbone arrangement of the molecules. View direction [001].

2-Aminoterephthalic acid dimethyl ester

Crystal data

$C_{10}H_{11}NO_4$
$M_r = 209.20$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 4.7721\ (12)$ Å
$b = 16.928\ (5)$ Å
$c = 11.841\ (5)$ Å
$\beta = 93.88\ (5)°$
$V = 954.4\ (6)$ Å^3
$Z = 4$

$F(000) = 440$
$D_x = 1.456$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 57 reflections
$\theta = 3–23°$
$\mu = 0.11$ mm^{-1}
$T = 166$ K
Plate, colourless
0.75 × 0.32 × 0.04 mm

Data collection

Siemens SMART 1K CCD diffractometer
Radiation source: normal-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.760, T_{max} = 0.995
11829 measured reflections
1687 independent reflections
884 reflections with $I > 2\sigma(I)$
R_{int} = 0.140
θ_{max} = 25.0°, θ_{min} = 2.1°
h = −5→5
k = −20→20
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.134
S = 0.96
1687 reflections
146 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	−0.2268 (4)	0.60319 (11)	0.30114 (17)	0.0341 (6)
O2	−0.1912 (5)	0.58551 (12)	0.11612 (18)	0.0421 (7)
O3	0.7681 (5)	0.32502 (11)	0.44342 (17)	0.0328 (6)
O4	0.8629 (4)	0.29952 (12)	0.26489 (18)	0.0333 (6)
N1	0.5292 (7)	0.36927 (18)	0.0986 (3)	0.0402 (8)
C1	0.4228 (7)	0.40860 (18)	0.1867 (3)	0.0280 (8)
C2	0.2108 (7)	0.46595 (17)	0.1622 (3)	0.0298 (8)
H2A	0.1487	0.4762	0.0857	0.036*
C3	0.0944 (6)	0.50678 (17)	0.2471 (3)	0.0258 (8)
C4	0.1783 (6)	0.49355 (17)	0.3592 (3)	0.0287 (8)
H4A	0.0967	0.5224	0.4175	0.034*
C5	0.3823 (6)	0.43779 (17)	0.3851 (2)	0.0277 (8)
H5A	0.4401	0.4281	0.4622	0.033*
C6	0.5072 (6)	0.39497 (17)	0.3004 (3)	0.0263 (8)
C7	−0.1217 (7)	0.56897 (17)	0.2121 (3)	0.0281 (8)

C8	−0.4282 (6)	0.66622 (18)	0.2753 (3)	0.0386 (9)
H8A	−0.3290	0.7134	0.2514	0.058*
H8B	−0.5277	0.6785	0.3429	0.058*
H8C	−0.5636	0.6492	0.2142	0.058*
C9	0.7296 (7)	0.33575 (17)	0.3320 (3)	0.0267 (8)
C10	0.9869 (7)	0.26942 (18)	0.4801 (3)	0.0381 (9)
H10A	0.9394	0.2170	0.4495	0.057*
H10B	1.0030	0.2670	0.5630	0.057*
H10C	1.1661	0.2867	0.4527	0.057*
H1A	0.702 (9)	0.348 (2)	0.120 (3)	0.074 (14)*
H1B	0.482 (7)	0.385 (2)	0.023 (3)	0.059 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0400 (15)	0.0187 (12)	0.0440 (14)	0.0105 (11)	0.0066 (11)	0.0034 (10)
O2	0.0606 (18)	0.0258 (14)	0.0392 (15)	0.0091 (12)	−0.0009 (12)	0.0034 (11)
O3	0.0391 (13)	0.0174 (11)	0.0416 (14)	0.0065 (11)	0.0000 (11)	0.0041 (10)
O4	0.0396 (14)	0.0177 (12)	0.0431 (14)	0.0031 (11)	0.0068 (11)	−0.0042 (10)
N1	0.049 (2)	0.0357 (19)	0.0361 (19)	0.0125 (16)	0.0027 (17)	−0.0045 (15)
C1	0.032 (2)	0.0169 (17)	0.0351 (19)	−0.0029 (16)	0.0028 (16)	−0.0014 (14)
C2	0.034 (2)	0.0208 (18)	0.0347 (19)	−0.0019 (16)	0.0017 (16)	0.0027 (15)
C3	0.0273 (19)	0.0148 (17)	0.0354 (19)	−0.0035 (15)	0.0038 (15)	0.0009 (14)
C4	0.037 (2)	0.0129 (17)	0.036 (2)	−0.0012 (16)	0.0058 (16)	−0.0015 (14)
C5	0.035 (2)	0.0139 (17)	0.0334 (18)	−0.0036 (15)	−0.0004 (15)	0.0010 (14)
C6	0.0305 (19)	0.0109 (16)	0.0376 (19)	−0.0015 (14)	0.0029 (16)	−0.0005 (14)
C7	0.034 (2)	0.0133 (18)	0.037 (2)	−0.0050 (15)	0.0053 (17)	0.0005 (16)
C8	0.040 (2)	0.0197 (19)	0.056 (2)	0.0112 (16)	−0.0004 (18)	0.0031 (16)
C9	0.035 (2)	0.0127 (17)	0.0329 (19)	−0.0090 (15)	0.0039 (16)	−0.0007 (14)
C10	0.041 (2)	0.0234 (18)	0.049 (2)	0.0059 (17)	−0.0031 (17)	0.0051 (17)

Geometric parameters (Å, º)

O1—C7	1.330 (3)	C3—C4	1.379 (4)
O1—C8	1.455 (3)	C3—C7	1.512 (4)
O2—C7	1.195 (3)	C4—C5	1.376 (4)
O3—C9	1.333 (3)	C4—H4A	0.9500
O3—C10	1.450 (3)	C5—C6	1.403 (4)
O4—C9	1.216 (3)	C5—H5A	0.9500
N1—C1	1.365 (4)	C6—C9	1.489 (4)
N1—H1A	0.92 (4)	C8—H8A	0.9800
N1—H1B	0.94 (3)	C8—H8B	0.9800
C1—C6	1.398 (4)	C8—H8C	0.9800
C1—C2	1.418 (4)	C10—H10A	0.9800
C2—C3	1.368 (4)	C10—H10B	0.9800
C2—H2A	0.9500	C10—H10C	0.9800
C7—O1—C8	115.6 (2)	C1—C6—C9	120.5 (3)

C9—O3—C10	115.7 (2)	C5—C6—C9	119.9 (3)
C1—N1—H1A	111 (2)	O2—C7—O1	123.8 (3)
C1—N1—H1B	120 (2)	O2—C7—C3	124.3 (3)
H1A—N1—H1B	122 (3)	O1—C7—C3	111.9 (3)
N1—C1—C6	123.9 (3)	O1—C8—H8A	109.5
N1—C1—C2	118.4 (3)	O1—C8—H8B	109.5
C6—C1—C2	117.7 (3)	H8A—C8—H8B	109.5
C3—C2—C1	121.0 (3)	O1—C8—H8C	109.5
C3—C2—H2A	119.5	H8A—C8—H8C	109.5
C1—C2—H2A	119.5	H8B—C8—H8C	109.5
C2—C3—C4	121.3 (3)	O4—C9—O3	122.3 (3)
C2—C3—C7	117.0 (3)	O4—C9—C6	124.8 (3)
C4—C3—C7	121.7 (3)	O3—C9—C6	112.9 (3)
C5—C4—C3	118.7 (3)	O3—C10—H10A	109.5
C5—C4—H4A	120.6	O3—C10—H10B	109.5
C3—C4—H4A	120.6	H10A—C10—H10B	109.5
C4—C5—C6	121.6 (3)	O3—C10—H10C	109.5
C4—C5—H5A	119.2	H10A—C10—H10C	109.5
C6—C5—H5A	119.2	H10B—C10—H10C	109.5
C1—C6—C5	119.6 (3)		

N1—C1—C2—C3	179.4 (3)	C8—O1—C7—O2	−2.7 (4)
C6—C1—C2—C3	0.4 (4)	C8—O1—C7—C3	177.5 (2)
C1—C2—C3—C4	−0.1 (4)	C2—C3—C7—O2	−1.7 (4)
C1—C2—C3—C7	177.6 (3)	C4—C3—C7—O2	176.1 (3)
C2—C3—C4—C5	−0.3 (4)	C2—C3—C7—O1	178.1 (2)
C7—C3—C4—C5	−178.0 (3)	C4—C3—C7—O1	−4.1 (4)
C3—C4—C5—C6	0.5 (4)	C10—O3—C9—O4	2.2 (4)
N1—C1—C6—C5	−179.2 (3)	C10—O3—C9—C6	−178.6 (2)
C2—C1—C6—C5	−0.1 (4)	C1—C6—C9—O4	4.7 (4)
N1—C1—C6—C9	1.2 (5)	C5—C6—C9—O4	−175.0 (3)
C2—C1—C6—C9	−179.8 (3)	C1—C6—C9—O3	−174.5 (3)
C4—C5—C6—C1	−0.3 (4)	C5—C6—C9—O3	5.8 (4)
C4—C5—C6—C9	179.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O4	0.92 (4)	2.01 (4)	2.717 (4)	133 (3)
N1—H1*B*···O2^{i}	0.95 (4)	2.14 (3)	3.016 (4)	153 (3)

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