

Hexahydrocycloocta[*b*]quinoxaline formation from 1,2-diacetoxycycloocta-5,6-dione

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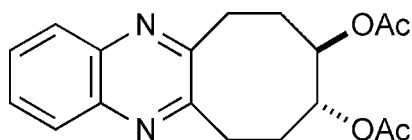
Received 4 May 2007; accepted 25 May 2007

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.041; wR factor = 0.089; data-to-parameter ratio = 14.0.

The reaction of 1,2-diacetoxycyclooctane-5,6-dione with *ortho*-phenylenediamine in acetic acid gave *trans*-6,7,8,9,10,11-hexahydrocycloocta[*b*]quinoxaline-8,9-diyl diacetate, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$. The saturated H atoms in the structure display almost perfect *gauche* orientations and the two acetoxy groups are oriented almost perfectly antiperiplanar. There are C—H...N bonding interactions linking the molecules into chains and intermolecular π – π stacking interactions between pyrazine rings [centroid–centroid distance = 3.6569 (9) Å and perpendicular distance = 3.426 Å].

Related literature

For related literature, see: Yates *et al.* (1972).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$	$V = 1642.5 (2) \text{ \AA}^3$
$M_r = 328.36$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.4108 (8) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 12.6470 (11) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 14.5249 (13) \text{ \AA}$	$0.40 \times 0.30 \times 0.10 \text{ mm}$
$\beta = 108.177 (2)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	3356 independent reflections
Absorption correction: none	1960 reflections with $I > 2\sigma(I)$
9291 measured reflections	$R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	1 restraint
$wR(F^2) = 0.089$	H-atom parameters constrained
$S = 0.84$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
3356 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
240 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C16}-\text{H16A}\cdots\text{N2}^{\text{i}}$	0.98	2.60	3.523 (2)	156
$\text{C18}-\text{H18C}\cdots\text{N1}^{\text{ii}}$	0.98	2.59	3.529 (2)	160

Symmetry codes: (i) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the University of Urmia for financial support of the preparative aspects of this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YM2054).

References

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supplementary materials

Acta Cryst. (2007). E63, o3182 [doi:10.1107/S1600536807025482]

Hexahydrocycloocta[*b*]quinoxaline formation from 1,2-diacetoxycycloocta-5,6-dione

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Comment

We have been interested in exploiting the potential of the readily available *cis,cis*-1,5-cyclooctadiene (1) for the synthesis of heterocycles. Following earlier work (Yates *et al.*, 1972) we dihydroxylated the diene with hydrogen peroxide and formic acid, diacetylated the resulting diol (2) giving (3) and oxidized the remaining double bond to the 5,6-dione (4) using KMnO₄, CuSO₄, Cu(OAc)₂. Condensation of this diketone with *ortho*-phenylenediamine produced the corresponding quinoxaline (5) cleanly, and significantly, with no ammonolytic loss of the acetoxy groups. A crystal structure of the quinoxaline-diacetate (Figure 1) revealed a *trans* disposition of the acetoxy groups confirming the *trans* orientation of the two alcoholic groups in the initial dihydroxylation product. The two (CH₂CH₂) chains which lead away from the quinoxaline 2- and 3-positions align to place the H atoms in a close-to-perfect *gauche* relationship: the relevant torsion angles for the H atoms on carbons C2 and C3 are, to the nearest whole number, 49, 67, 51, and 166° and those for C7 and C6, 35, 81, 82, and 163°.

The dihedral angle between the two acetoxy groups is 155.9° - remarkably close to the 180° required for these two groups to be perfectly antiperiplanar.

One other significant aspect of the structure is intermolecular C—H...N hydrogen bonding of the two acetyl methyl groups to an adjacent quinoxaline nitrogen, linking the molecules into chains (Figure 2, Table 1). There is also intermolecular π - π -stacking of the N1—C1—C8—N2—C14—C9 rings linking pairs of molecules in adjacent H bonded chains, with a centroid-centroid distance of 3.6569 (9) Å and a perpendicular distance of 3.426 Å (symmetry operation $2 - x, 2 - y, -z$; Figure 2).

Also of interest is that in the solid-state, one of the methyl groups lies directly over the pyrazine ring and close enough that one would anticipate the ¹H NMR chemical shift of that methyl group to be under the influence of the aromatic ring current. The methyl C16 lies just 4.14 Å from C9 and 4.16 Å from N1. However, solution-state ¹H NMR measurement showed only one, six-proton signal for the two acetyl methyl groups at δ 1.72 indicating that rapid ring flipping in solution must cause averaging of the stereochemical situation and hence magnetic environment of these two groups.

Experimental

1,2-Bis(acetoxy)cyclooctane-5,6-dione (0.5 g, 1.95 mmol) and *ortho*-phenylenediamine (0.21 g, 1.95 mmol) in acetic acid (10 ml) were heated at 368 K for 1 h. Water (20 ml) was added to the hot solution and, after cooling, the product was extracted with dichloromethane (3 x 15 ml). The solvent was evaporated from the extract giving *trans*-6,7,8,9,10,11-hexahydrocycloocta[*b*]quinoxaline-8,9-diyl diacetate (0.48 g, 75 percent) which was recrystallized from ethanol, m.p. 391–392 K.

Refinement

H atoms were included in calculated positions with C—H distances ranging from 0.95 to 1.00 Å and methyl H atoms allowed to rotate to give the best fit with the electron density. There is disorder of the atoms O1, O2, O3, C4 and C5 whose occupancies were constrained to sum to 1.0; the final occupancy of the highest occupancy component was 0.768 (4). The atoms of the lower occupancy fraction were refined isotropically. Restraints were applied to the C15—O1 and C15—O1B bond lengths.

Figures

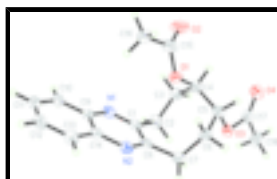


Fig. 1. Plot of the title compound with ellipsoids drawn at the 50% probability level; disordered atoms from the lower occupancy fraction have been omitted for clarity.

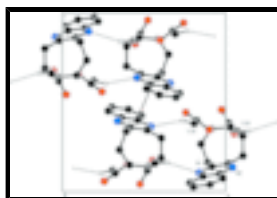


Fig. 2. Packing diagram viewed down the *a* axis with intermolecular C—H...N hydrogen bonds shown with dashed lines. Only H atoms involved in H bonding have been included.



Fig. 3. The synthesis of *trans*-6,7,8,9,10,11-hexahydrocycloocta [*b*]quinoxaline-8,9-diyl diacetate.

trans-6,7,8,9,10,11-Hexahydrocycloocta[*b*]quinoxaline-8,9-diyl diacetate

Crystal data

C₁₈H₂₀N₂O₄

M_r = 328.36

Monoclinic, *P*2₁/*n*

a = 9.4108 (8) Å

b = 12.6470 (11) Å

c = 14.5249 (13) Å

β = 108.177 (2)°

V = 1642.5 (2) Å³

Z = 4

*F*₀₀₀ = 696

D_x = 1.328 Mg m⁻³

Melting point: 391–392 K

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 1632 reflections

θ = 2.3–24.0°

μ = 0.10 mm⁻¹

T = 100 (2) K

Plate, colourless

0.40 × 0.30 × 0.10 mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

1960 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.052

Monochromator: graphite $\theta_{\max} = 26.4^\circ$
 $T = 100(2)$ K $\theta_{\min} = 2.2^\circ$
 φ and ω scans $h = -11 \rightarrow 11$
 Absorption correction: none $k = -8 \rightarrow 15$
 9291 measured reflections $l = -17 \rightarrow 18$
 3356 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
 $R[F^2 > 2\sigma(F^2)] = 0.042$ H-atom parameters constrained
 $wR(F^2) = 0.089$ $w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 0.84$ $(\Delta/\sigma)_{\max} = 0.001$
 3356 reflections $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
 240 parameters $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
 1 restraint 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	1.0620 (2)	0.89998 (18)	0.34648 (13)	0.0291 (5)	0.768 (4)
O2	1.0940 (2)	0.75700 (19)	0.44192 (15)	0.0550 (8)	0.768 (4)
O3	0.72848 (19)	1.05380 (19)	0.32464 (12)	0.0277 (5)	0.768 (4)
O1B	1.1075 (8)	0.9328 (5)	0.3444 (5)	0.024 (2)*	0.232 (4)
O2B	1.1174 (6)	0.8335 (6)	0.4743 (4)	0.037 (2)*	0.232 (4)
O3B	0.7117 (7)	0.9997 (6)	0.3176 (5)	0.0285 (19)*	0.232 (4)
O4	0.69096 (16)	0.97625 (11)	0.45751 (10)	0.0554 (4)	
N1	0.98120 (15)	0.83903 (11)	0.10558 (10)	0.0268 (4)	
N2	1.10797 (15)	1.04284 (11)	0.13626 (10)	0.0267 (4)	
C1	0.91975 (18)	0.91665 (14)	0.13993 (11)	0.0249 (4)	
C2	0.77806 (18)	0.89132 (15)	0.16289 (12)	0.0308 (5)	

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H2A	0.7211	0.8376	0.1163	0.037*	
H2B	0.7158	0.9559	0.1538	0.037*	
C3	0.80500 (19)	0.84975 (14)	0.26634 (12)	0.0305 (4)	
H3A	0.7067	0.8452	0.2776	0.037*	
H3B	0.8441	0.7768	0.2691	0.037*	
C4	0.9107 (3)	0.9117 (2)	0.35072 (18)	0.0304 (7)	0.768 (4)
H4	0.9074	0.8774	0.4120	0.037*	0.768 (4)
C5	0.8866 (3)	1.03003 (19)	0.36028 (16)	0.0301 (7)	0.768 (4)
H5	0.9214	1.0470	0.4311	0.036*	0.768 (4)
C4B	0.8414 (10)	0.9287 (8)	0.3417 (7)	0.025 (3)*	0.232 (4)
H4B	0.8461	0.8922	0.4036	0.030*	0.232 (4)
C5B	0.9849 (9)	0.9962 (6)	0.3616 (5)	0.020 (2)*	0.232 (4)
H5B	1.0179	1.0113	0.4327	0.024*	0.232 (4)
C6	0.96715 (19)	1.10592 (14)	0.31121 (12)	0.0293 (4)	
H6A	1.0752	1.0890	0.3350	0.035*	
H6B	0.9552	1.1784	0.3334	0.035*	
C7	0.91850 (18)	1.10711 (14)	0.20033 (12)	0.0285 (4)	
H7A	0.8081	1.1017	0.1754	0.034*	
H7B	0.9471	1.1759	0.1788	0.034*	
C8	0.98452 (17)	1.02016 (14)	0.15627 (11)	0.0243 (4)	
C9	1.11112 (18)	0.86141 (14)	0.08546 (11)	0.0244 (4)	
C10	1.18255 (19)	0.78094 (15)	0.04906 (12)	0.0296 (4)	
H10	1.1418	0.7116	0.0396	0.036*	
C11	1.31064 (19)	0.80316 (15)	0.02752 (12)	0.0323 (5)	
H11	1.3592	0.7487	0.0036	0.039*	
C12	1.37116 (18)	0.90505 (16)	0.04022 (12)	0.0319 (5)	
H12	1.4598	0.9192	0.0242	0.038*	
C13	1.30442 (18)	0.98434 (15)	0.07531 (12)	0.0310 (5)	
H13	1.3461	1.0534	0.0833	0.037*	
C14	1.17343 (18)	0.96348 (14)	0.09967 (11)	0.0237 (4)	
C15	1.1460 (2)	0.8237 (2)	0.39717 (15)	0.0515 (6)	
C16	1.29052 (19)	0.80853 (15)	0.38052 (13)	0.0368 (5)	
H16A	1.3247	0.7357	0.3970	0.055*	
H16B	1.3640	0.8578	0.4213	0.055*	
H16C	1.2794	0.8220	0.3122	0.055*	
C17	0.6419 (2)	1.02199 (16)	0.38171 (14)	0.0356 (5)	
C18	0.4911 (2)	1.06620 (16)	0.34063 (14)	0.0440 (5)	
H18A	0.4299	1.0464	0.3815	0.066*	
H18B	0.4454	1.0383	0.2751	0.066*	
H18C	0.4974	1.1434	0.3379	0.066*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0267 (12)	0.0302 (13)	0.0305 (10)	0.0069 (10)	0.0091 (9)	0.0072 (9)
O2	0.0547 (13)	0.0587 (18)	0.0618 (15)	0.0211 (12)	0.0330 (11)	0.0354 (13)
O3	0.0290 (10)	0.0312 (13)	0.0259 (10)	0.0015 (10)	0.0129 (7)	0.0005 (9)
O4	0.0803 (11)	0.0572 (11)	0.0385 (9)	0.0237 (9)	0.0327 (8)	0.0129 (8)

N1	0.0276 (8)	0.0302 (9)	0.0226 (8)	-0.0031 (7)	0.0077 (7)	-0.0002 (7)
N2	0.0297 (8)	0.0258 (9)	0.0262 (8)	-0.0013 (7)	0.0111 (7)	0.0033 (7)
C1	0.0250 (10)	0.0310 (11)	0.0178 (9)	-0.0021 (9)	0.0053 (7)	0.0027 (8)
C2	0.0269 (10)	0.0361 (12)	0.0301 (10)	-0.0065 (9)	0.0099 (8)	-0.0017 (9)
C3	0.0320 (10)	0.0275 (11)	0.0376 (11)	-0.0008 (9)	0.0189 (9)	0.0040 (9)
C4	0.0341 (18)	0.0317 (18)	0.0269 (14)	0.0038 (14)	0.0114 (13)	0.0082 (12)
C5	0.0313 (16)	0.0350 (16)	0.0217 (12)	0.0046 (13)	0.0050 (10)	0.0023 (12)
C6	0.0322 (10)	0.0232 (10)	0.0287 (10)	0.0001 (9)	0.0039 (8)	-0.0008 (9)
C7	0.0317 (10)	0.0270 (11)	0.0283 (10)	0.0031 (9)	0.0113 (8)	0.0046 (9)
C8	0.0256 (10)	0.0272 (11)	0.0192 (9)	0.0025 (9)	0.0054 (7)	0.0064 (8)
C9	0.0242 (10)	0.0294 (11)	0.0183 (9)	-0.0004 (8)	0.0049 (7)	0.0033 (8)
C10	0.0374 (11)	0.0281 (11)	0.0249 (10)	-0.0003 (9)	0.0119 (8)	0.0006 (8)
C11	0.0358 (11)	0.0383 (13)	0.0232 (10)	0.0095 (10)	0.0100 (8)	0.0026 (9)
C12	0.0247 (10)	0.0466 (13)	0.0252 (10)	0.0001 (9)	0.0090 (8)	0.0018 (9)
C13	0.0283 (10)	0.0353 (12)	0.0290 (10)	-0.0065 (9)	0.0084 (8)	-0.0001 (9)
C14	0.0249 (9)	0.0255 (10)	0.0196 (9)	0.0003 (8)	0.0052 (7)	0.0039 (8)
C15	0.0469 (13)	0.0754 (18)	0.0350 (13)	0.0269 (13)	0.0170 (10)	0.0208 (13)
C16	0.0370 (11)	0.0346 (12)	0.0385 (12)	0.0096 (10)	0.0113 (9)	0.0053 (9)
C17	0.0449 (12)	0.0364 (12)	0.0322 (11)	0.0029 (10)	0.0215 (9)	-0.0044 (10)
C18	0.0459 (13)	0.0441 (13)	0.0512 (13)	0.0050 (11)	0.0284 (11)	-0.0039 (11)

Geometric parameters (Å, °)

O1—C15	1.317 (2)	C4B—C5B	1.546 (12)
O1—C4	1.452 (4)	C4B—H4B	1.0000
O2—C15	1.253 (3)	C5B—C6	1.553 (7)
O3—C17	1.390 (2)	C5B—H5B	1.0000
O3—C5	1.447 (3)	C6—C7	1.531 (2)
O1B—C5B	1.489 (10)	C6—H6A	0.9900
O1B—C15	1.566 (7)	C6—H6B	0.9900
O2B—C15	1.237 (6)	C7—C8	1.501 (2)
O3B—C17	1.326 (7)	C7—H7A	0.9900
O3B—C4B	1.467 (11)	C7—H7B	0.9900
O4—C17	1.201 (2)	C9—C14	1.406 (2)
N1—C1	1.314 (2)	C9—C10	1.410 (2)
N1—C9	1.372 (2)	C10—C11	1.366 (2)
N2—C8	1.314 (2)	C10—H10	0.9500
N2—C14	1.369 (2)	C11—C12	1.398 (2)
C1—C8	1.432 (2)	C11—H11	0.9500
C1—C2	1.506 (2)	C12—C13	1.364 (2)
C2—C3	1.537 (2)	C12—H12	0.9500
C2—H2A	0.9900	C13—C14	1.409 (2)
C2—H2B	0.9900	C13—H13	0.9500
C3—C4B	1.442 (10)	C15—C16	1.467 (3)
C3—C4	1.532 (3)	C16—H16A	0.9800
C3—H3A	0.9900	C16—H16B	0.9800
C3—H3B	0.9900	C16—H16C	0.9800
C4—C5	1.526 (4)	C17—C18	1.468 (2)
C4—H4	1.0000	C18—H18A	0.9800

supplementary materials

C5—C6	1.530 (3)	C18—H18B	0.9800
C5—H5	1.0000	C18—H18C	0.9800
C15—O1—C4	118.5 (2)	C5B—C6—H6B	132.9
C17—O3—C5	117.07 (17)	H6A—C6—H6B	107.2
C5B—O1B—C15	117.7 (5)	C8—C7—C6	114.43 (14)
C17—O3B—C4B	121.4 (6)	C8—C7—H7A	108.7
C1—N1—C9	116.98 (15)	C6—C7—H7A	108.7
C8—N2—C14	117.50 (15)	C8—C7—H7B	108.7
N1—C1—C8	122.05 (15)	C6—C7—H7B	108.7
N1—C1—C2	116.74 (16)	H7A—C7—H7B	107.6
C8—C1—C2	121.20 (16)	N2—C8—C1	121.52 (16)
C1—C2—C3	113.70 (13)	N2—C8—C7	116.51 (15)
C1—C2—H2A	108.8	C1—C8—C7	121.94 (15)
C3—C2—H2A	108.8	N1—C9—C14	121.09 (16)
C1—C2—H2B	108.8	N1—C9—C10	119.45 (16)
C3—C2—H2B	108.8	C14—C9—C10	119.46 (15)
H2A—C2—H2B	107.7	C11—C10—C9	119.70 (17)
C4B—C3—C4	25.4 (3)	C11—C10—H10	120.2
C4B—C3—C2	115.7 (4)	C9—C10—H10	120.2
C4—C3—C2	118.38 (16)	C10—C11—C12	120.79 (18)
C4B—C3—H3A	85.8	C10—C11—H11	119.6
C4—C3—H3A	107.7	C12—C11—H11	119.6
C2—C3—H3A	107.7	C13—C12—C11	120.74 (17)
C4B—C3—H3B	128.2	C13—C12—H12	119.6
C4—C3—H3B	107.7	C11—C12—H12	119.6
C2—C3—H3B	107.7	C12—C13—C14	119.81 (17)
H3A—C3—H3B	107.1	C12—C13—H13	120.1
O1—C4—C5	106.2 (2)	C14—C13—H13	120.1
O1—C4—C3	108.3 (2)	N2—C14—C9	120.83 (15)
C5—C4—C3	119.8 (2)	N2—C14—C13	119.68 (16)
O1—C4—H4	107.3	C9—C14—C13	119.49 (16)
C5—C4—H4	107.3	O2B—C15—O2	50.8 (3)
C3—C4—H4	107.3	O2B—C15—O1	99.8 (3)
O3—C5—C4	109.7 (2)	O2—C15—O1	121.3 (2)
O3—C5—C6	107.86 (17)	O2B—C15—C16	129.6 (3)
C4—C5—C6	117.6 (2)	O2—C15—C16	122.0 (2)
O3—C5—H5	107.1	O1—C15—C16	115.4 (2)
C4—C5—H5	107.1	O2B—C15—O1B	105.8 (4)
C6—C5—H5	107.1	O2—C15—O1B	141.2 (3)
C3—C4B—O3B	105.0 (6)	O1—C15—O1B	22.1 (2)
C3—C4B—C5B	120.7 (7)	C16—C15—O1B	96.8 (3)
O3B—C4B—C5B	108.7 (8)	C15—C16—H16A	109.5
C3—C4B—H4B	107.2	C15—C16—H16B	109.5
O3B—C4B—H4B	107.2	H16A—C16—H16B	109.5
C5B—C4B—H4B	107.2	C15—C16—H16C	109.5
O1B—C5B—C4B	110.4 (7)	H16A—C16—H16C	109.5
O1B—C5B—C6	112.2 (5)	H16B—C16—H16C	109.5
C4B—C5B—C6	116.5 (6)	O4—C17—O3B	114.1 (3)
O1B—C5B—H5B	105.6	O4—C17—O3	123.84 (18)

C4B—C5B—H5B	105.6	O3B—C17—O3	29.9 (3)
C6—C5B—H5B	105.6	O4—C17—C18	127.03 (18)
C5—C6—C7	117.86 (15)	O3B—C17—C18	115.1 (3)
C5—C6—C5B	38.4 (3)	O3—C17—C18	108.62 (17)
C7—C6—C5B	117.2 (3)	C17—C18—H18A	109.5
C5—C6—H6A	107.8	C17—C18—H18B	109.5
C7—C6—H6A	107.8	H18A—C18—H18B	109.5
C5B—C6—H6A	72.2	C17—C18—H18C	109.5
C5—C6—H6B	107.8	H18A—C18—H18C	109.5
C7—C6—H6B	107.8	H18B—C18—H18C	109.5
C9—N1—C1—C8	-0.2 (2)	C5B—C6—C7—C8	-37.7 (4)
C9—N1—C1—C2	-179.36 (14)	C14—N2—C8—C1	-0.4 (2)
N1—C1—C2—C3	88.39 (19)	C14—N2—C8—C7	177.43 (14)
C8—C1—C2—C3	-90.8 (2)	N1—C1—C8—N2	1.0 (2)
C1—C2—C3—C4B	78.1 (4)	C2—C1—C8—N2	-179.89 (14)
C1—C2—C3—C4	49.6 (2)	N1—C1—C8—C7	-176.75 (15)
C15—O1—C4—C5	136.7 (2)	C2—C1—C8—C7	2.4 (2)
C15—O1—C4—C3	-93.4 (2)	C6—C7—C8—N2	-93.89 (18)
C4B—C3—C4—O1	-160.1 (11)	C6—C7—C8—C1	84.0 (2)
C2—C3—C4—O1	-69.6 (2)	C1—N1—C9—C14	-1.0 (2)
C4B—C3—C4—C5	-38.2 (10)	C1—N1—C9—C10	179.58 (15)
C2—C3—C4—C5	52.4 (3)	N1—C9—C10—C11	179.01 (15)
C17—O3—C5—C4	72.6 (2)	C14—C9—C10—C11	-0.4 (2)
C17—O3—C5—C6	-158.2 (2)	C9—C10—C11—C12	-0.6 (3)
O1—C4—C5—O3	155.86 (18)	C10—C11—C12—C13	0.6 (3)
C3—C4—C5—O3	32.9 (3)	C11—C12—C13—C14	0.4 (3)
O1—C4—C5—C6	32.2 (3)	C8—N2—C14—C9	-0.8 (2)
C3—C4—C5—C6	-90.8 (3)	C8—N2—C14—C13	178.79 (15)
C4—C3—C4B—O3B	163.3 (14)	N1—C9—C14—N2	1.6 (2)
C2—C3—C4B—O3B	60.7 (6)	C10—C9—C14—N2	-179.01 (15)
C4—C3—C4B—C5B	40.2 (7)	N1—C9—C14—C13	-178.00 (15)
C2—C3—C4B—C5B	-62.4 (9)	C10—C9—C14—C13	1.4 (2)
C17—O3B—C4B—C3	126.7 (7)	C12—C13—C14—N2	179.01 (15)
C17—O3B—C4B—C5B	-102.8 (8)	C12—C13—C14—C9	-1.4 (2)
C15—O1B—C5B—C4B	-52.7 (8)	C4—O1—C15—O2B	-44.0 (4)
C15—O1B—C5B—C6	175.6 (4)	C4—O1—C15—O2	5.8 (4)
C3—C4B—C5B—O1B	-34.3 (10)	C4—O1—C15—C16	173.0 (2)
O3B—C4B—C5B—O1B	-155.6 (6)	C4—O1—C15—O1B	-152.0 (9)
C3—C4B—C5B—C6	95.1 (9)	C5B—O1B—C15—O2B	-30.8 (7)
O3B—C4B—C5B—C6	-26.2 (9)	C5B—O1B—C15—O2	15.1 (9)
O3—C5—C6—C7	-57.0 (2)	C5B—O1B—C15—O1	46.2 (6)
C4—C5—C6—C7	67.6 (3)	C5B—O1B—C15—C16	-165.3 (5)
O3—C5—C6—C5B	-156.5 (5)	C4B—O3B—C17—O4	-2.7 (8)
C4—C5—C6—C5B	-31.9 (5)	C4B—O3B—C17—O3	113.8 (10)
O1B—C5B—C6—C5	166.2 (8)	C4B—O3B—C17—C18	-162.3 (6)
C4B—C5B—C6—C5	37.6 (5)	C5—O3—C17—O4	-0.3 (3)
O1B—C5B—C6—C7	64.8 (6)	C5—O3—C17—O3B	-79.9 (6)
C4B—C5B—C6—C7	-63.8 (7)	C5—O3—C17—C18	172.02 (19)
C5—C6—C7—C8	-81.2 (2)		

supplementary materials

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C16—H16A···N2 ⁱ	0.98	2.60	3.523 (2)	156
C18—H18C···N1 ⁱⁱ	0.98	2.59	3.529 (2)	160

Symmetry codes: (i) $-x+5/2, y-1/2, -z+1/2$; (ii) $-x+3/2, y+1/2, -z+1/2$.

Fig. 1

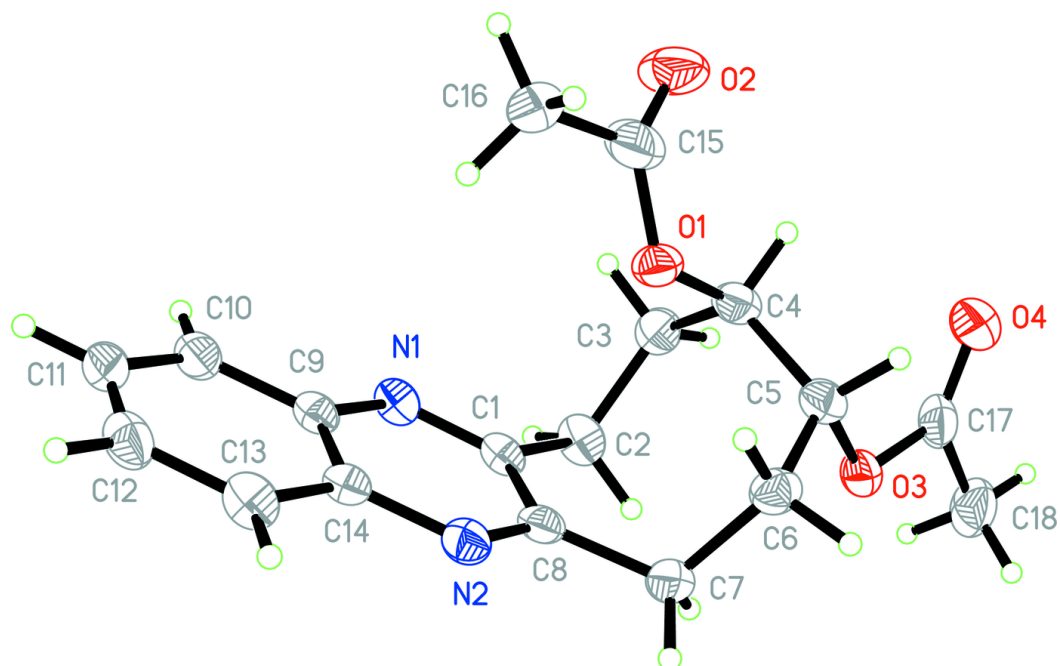


Fig. 2

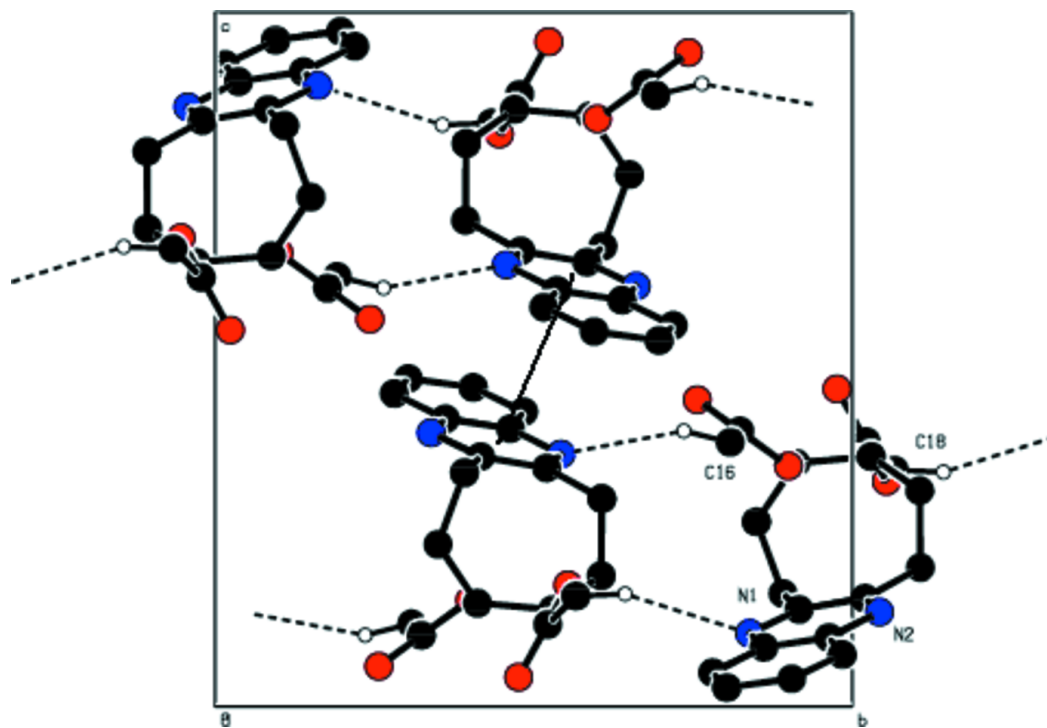


Fig. 3

