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N,*N*-Dibutylanilinium hydrogen squarate

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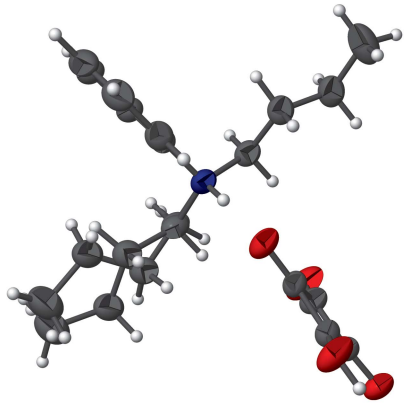
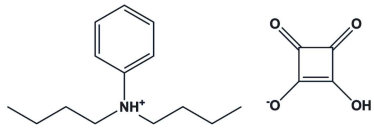
The title molecular salt, $C_{14}H_{24}N^{+}\cdot C_4HO_4^{-}$ [systematic name: *N*,*N*-dibutylbenzenaminium 2-hydroxy-3,4-dioxocyclobut-1-en-1-olate], is composed of a protonated *N*,*N*-dibutylaniline cation with a hydrogen squarate monoanion (common names). The disparate bond lengths within the squarate anion suggest delocalization of the negative charge over only part of the squarate moiety. In the crystal, the squarate anions are linked by pairs of O—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(10)$ ring motif. The dimers are linked to the cations on either side by N—H···O hydrogen bonds, and weak C—H···O hydrogen bonds. These cation–anion–anion–cation units are linked by further C—H···O hydrogen bonds, forming layers parallel to (102).

3D view



Chemical scheme



Structure description

Squaraine dyes have been studied extensively as materials for use in organic photovoltaic devices (Chen *et al.*, 2014, 2016; Feron *et al.*, 2016; Saccone *et al.*, 2016) as well as optical sensors (Sun *et al.*, 2016). The solid-state optical activity of these materials is highly dependent on intermolecular packing features. In the case of squaraine dyes, both van der Waals forces and possible hydrogen bonding play pivotal roles in the aggregation patterns of these materials (Kaczmarek-Kedziera & Kedziera, 2016). During the course of our studies of squaraine dyes, we synthesized a salt precursor to an asymmetrical squaraine. Herein, we report on the crystal structure of the title molecular salt, *N*,*N*-dibutylanilinium hydrogen squarate.

The structure of the title molecular salt is illustrated in Fig. 1. The asymmetric unit consists of an *N*,*N*-dibutyl anilinium cation with a hydrogen squarate anion. Positional disorder was modeled in one butyl group (C15–C18) over two positions with an appropriate mix of constraints and restraints. The pattern of observed C—C and C—O bond lengths in the squarate ring are consistent with the negative charge resonance-stabilized

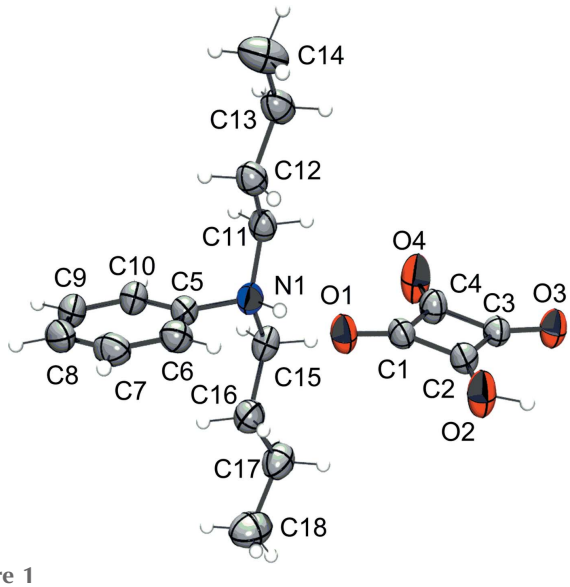


Figure 1
A view of the molecular structure of the title salt, showing the atom labeling. Displacement ellipsoid are drawn at the 50% probability level. Minor disorder component atoms have been omitted for clarity.

at atoms O1 and O3 (Fig. 2). The C4—O4 bond distance of 1.216 (2) Å, is interpreted as a double bond, while the C3—O3 [1.255 (2) Å] and C1—O1 [1.249 (2) Å] bond lengths are indicative of bond orders between 1–2. Likewise, the C1—C2 [1.425 (2) Å] and C2—C3 [1.417 (2) Å] bond distances are shorter than bonds C1—C4 [1.490 (2) Å] and C3—C4 [1.492 (2) Å], consistent with the proposed dominant resonance structures (Fig. 2).

In the crystal, two unique intermolecular hydrogen bonds are present (Fig. 3, Table 1). The alcohol moiety (O2—H2) acts as a donor with an inversion-related hydrogen squarate O3 atom at ($-x$, $-y+1$, $-z+2$) as the acceptor. The inversion-related hydrogen squarate anions form an inversion dimer with an $R_2^2(10)$ ring motif. The protonated amine moiety (N1—H1) acts as a donor in a hydrogen bond with the acceptor O1 of the hydrogen squarate anion. Hence, the dimers are linked to the cations on either side by N—H···O hydrogen bonds (Fig. 3), and weak C15—H15*A*···O4 hydrogen bonds (Table 1). These cation–anion–anion–cation units are linked by C9—H9···O1^{ii} hydrogen bonds, forming layers parallel to plane (102); see Table 1 and Fig. 4.

While numerous other protonated amine salts of hydrogen squarate have been reported, only a few involve a cation with

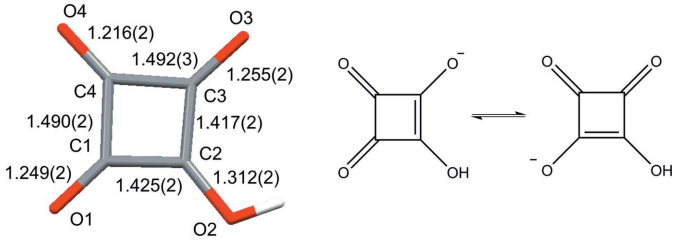


Figure 2
Intramolecular details (Å) of the hydrogen squarate anion and relevant resonance structures in the title compound.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3^{i}	0.91 (2)	1.68 (2)	2.543 (2)	157 (2)
N1—H1···O1	0.95 (2)	1.74 (2)	2.688 (2)	172 (2)
C15—H15*A*···O4	0.99	2.60	3.469 (5)	147
C9—H9···O1^{ii}	0.95	2.53	3.222 (2)	130

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

no other hydrogen-bond donors or acceptors, only the hydrogen squarate anion and no solvent. Examples include 4-phenylpyridinium hydrogen squarate (Kolev *et al.*, 2004) and 2-methylpyridinium hydrogen squarate (Korkmaz & Bulut, 2014), which have a similar hydrogen-bonding pattern with the $R_2^2(10)$ motif and capping N—H donors/squarate oxygen

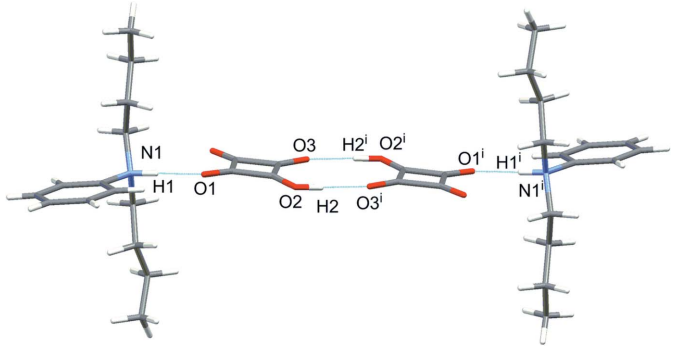


Figure 3
Intermolecular hydrogen-bonding (dashed lines; see Table 1). Minor disorder component atoms (C15′–C18′ and attached H atoms) have been omitted for clarity [symmetry code: (i) $-x, -y+1, -z+2$].

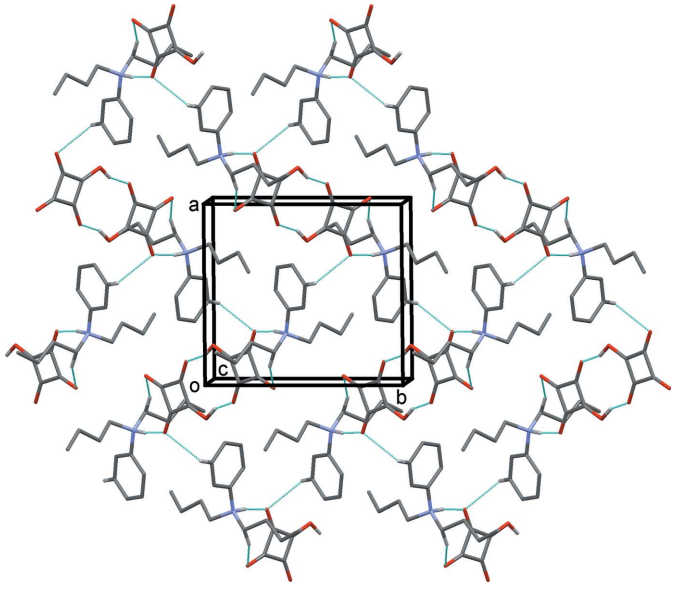


Figure 4
A view along the *c* axis of the crystal packing of the title salt. The hydrogen bonds are shown as dashed lines (see Table 1). For clarity, only the H atoms involved in hydrogen bonding have been included, and the minor disorder component atoms (C15′–C18′ and attached H atoms) have been omitted.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{24}N^+\cdot C_4HO_4^-$
M_r	319.40
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	10.3476 (16), 10.7877 (17), 16.922 (3)
β (°)	106.214 (8)
V (Å^3)	1813.9 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.33 × 0.23 × 0.15
Data collection	
Diffractometer	Rigaku XtaLAB mini
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.826, 0.988
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	14670, 3196, 2316
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.108, 1.03
No. of reflections	3196
No. of parameters	232
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.12, −0.16

Computer programs: *CrystalClear* (Rigaku, 2011), *CrystalStructure* (Rigaku, 2014), *SIR2004* (Burla *et al.*, 2005), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

acceptor [$D_1^1(2)$] motifs. Others, such as pyridinium hydrogen squarate (Modec, 2015) pack with a $C_1^1(5)$ chain motif of hydrogen squarate anions with dimer $D_1^1(2)$ motifs on the periphery of the hydrogen-bonded chains of hydrogen squarate anions. A more complex $R_4^4(2)$ tetramer hydrogen-bonded ring motif is found in the structure of 1,2,3,4-tetrahydroisoquinolinium hydrogen squarate (Kolev *et al.*, 2007).

Synthesis and crystallization

Under an argon atmosphere, squaric acid (1.5 g, 13.5 mmol) and *N*,*N*-dibutylanaline (6 ml, 26 mmol) were dissolved in a mixture of toluene (20 ml) and 1-butanol (20 ml). The reaction mixture was heated at 353 K with constant stirring for 8 h. During this time period, the solution turned a golden brown color. About 35 ml of azeotropic distillate was collected using a short path distillation setup with multiple flask take-off. The solution was purged with Ar and left to cool to rt (15 h). The solution was then reheated using an oil bath at 388 K for 6 h then allowed to cool to rt and stirred for 48 h under Ar. No additional color change was observed. Crystals grown from the reaction mixture were removed from the mother liquor three days after heating. The crystals were washed with 15 ml of hexanes, collected by vacuum filtration and stored in a vial at rt (yield 2.92 g, 9.2 mmol, 70%). ^{1}H NMR (600 MHz, CD_3OD): 8.03 (*s*, 1H), 7.23 (*br s*, 2H), 6.85 (*br s*, 2H), 6.70 (*br s*, 1H), 2.92 (*t*, 2H), 2.74 (*t*, 2H), 1.53 (*p*, 4H), 1.34 (*m*, 4H), 0.92 (*t*, 6H).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Positional disorder was modeled in one of the butyl groups over two conformations (C15–C18: C15′–C18′), which have a refined occupancy ratio of 0.825 (3): 0.175 (3). The 1,2 and 1,3 bond distances of the disordered components were restrained to be the same within standard uncertainties of 0.02 and 0.04 Å, respectively. The displacement parameters of the pairwise carbon atoms of the disordered components were constrained to be equal.

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full crystallographic data

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N,*N*-Dibutylanilinium hydrogen squarate

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(I)

Crystal data

$C_{14}H_{24}N^+·C_4HO_4^-$
M_r = 319.40
Monoclinic, $P2_1/c$
a = 10.3476 (16) Å
b = 10.7877 (17) Å
c = 16.922 (3) Å
β = 106.214 (8)°
V = 1813.9 (5) Å^3
Z = 4
$F(000)$ = 688.00
D_x = 1.170 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 11464 reflections
θ = 3.1–25.2°
μ = 0.08 mm^{-1}
T = 173 K
Prism, colorless
0.33 × 0.23 × 0.15 mm

Data collection

Rigaku XtaLAB mini diffractometer
Detector resolution: 6.849 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.826, T_{max} = 0.988
14670 measured reflections
3196 independent reflections
2316 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.042
θ_{max} = 25.0°, θ_{min} = 3.1°
h = −12→12
k = −12→12
l = −20→20

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.108
S = 1.03
3196 reflections
232 parameters
5 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
$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.2934P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C15	0.1766 (5)	0.1587 (3)	0.6843 (2)	0.0419 (8)	0.825 (3)
H15A	0.0963	0.1820	0.7019	0.050*	0.825 (3)
H15B	0.1480	0.0975	0.6391	0.050*	0.825 (3)
C16	0.2311 (3)	0.2736 (2)	0.65204 (15)	0.0488 (7)	0.825 (3)
H16A	0.2802	0.3252	0.6993	0.059*	0.825 (3)
H16B	0.2959	0.2477	0.6219	0.059*	0.825 (3)
C17	0.1218 (2)	0.3504 (2)	0.59581 (15)	0.0573 (7)	0.825 (3)
H17A	0.0700	0.3930	0.6289	0.069*	0.825 (3)
H17B	0.0594	0.2950	0.5563	0.069*	0.825 (3)
C18	0.1776 (4)	0.4460 (3)	0.5486 (2)	0.0762 (10)	0.825 (3)
H18D	0.2266	0.4041	0.5144	0.091*	0.825 (3)
H18E	0.2390	0.5015	0.5875	0.091*	0.825 (3)
H18F	0.1034	0.4944	0.5135	0.091*	0.825 (3)
C15′	0.153 (3)	0.1345 (16)	0.6716 (15)	0.0419 (8)	0.175 (3)
H15C	0.1599	0.0826	0.6248	0.050*	0.175 (3)
H15D	0.0652	0.1164	0.6822	0.050*	0.175 (3)
C16′	0.1585 (14)	0.2707 (11)	0.6498 (8)	0.0488 (7)	0.175 (3)
H16C	0.0710	0.2946	0.6114	0.059*	0.175 (3)
H16D	0.1712	0.3206	0.7005	0.059*	0.175 (3)
C17′	0.2693 (12)	0.3028 (11)	0.6109 (8)	0.0573 (7)	0.175 (3)
H17C	0.2808	0.2332	0.5753	0.069*	0.175 (3)
H17D	0.3548	0.3127	0.6548	0.069*	0.175 (3)
C18′	0.2419 (19)	0.4208 (15)	0.5596 (12)	0.0762 (10)	0.175 (3)
H18A	0.2033	0.4836	0.5882	0.091*	0.175 (3)
H18B	0.1783	0.4029	0.5060	0.091*	0.175 (3)
H18C	0.3263	0.4519	0.5516	0.091*	0.175 (3)
H1	0.2875 (17)	0.1574 (17)	0.7987 (11)	0.051 (5)*	
H2	0.148 (2)	0.525 (2)	1.0022 (14)	0.074 (7)*	
O1	0.28289 (11)	0.26494 (11)	0.87454 (7)	0.0467 (3)	
O2	0.20270 (13)	0.47939 (13)	0.97961 (9)	0.0567 (4)	
O3	−0.10897 (11)	0.37798 (11)	0.93017 (8)	0.0465 (3)	
O4	−0.02637 (13)	0.16806 (14)	0.81630 (9)	0.0669 (4)	
N1	0.27710 (14)	0.10014 (13)	0.75448 (9)	0.0394 (4)	
C1	0.17434 (16)	0.29656 (15)	0.88734 (10)	0.0375 (4)	
C2	0.13305 (16)	0.39029 (15)	0.93441 (10)	0.0372 (4)	
C3	−0.00209 (16)	0.34850 (15)	0.91360 (10)	0.0370 (4)	
C4	0.03317 (17)	0.25007 (16)	0.86125 (11)	0.0429 (4)	
C5	0.40968 (17)	0.08575 (15)	0.73863 (11)	0.0389 (4)	
C6	0.51639 (18)	0.15324 (16)	0.78593 (12)	0.0464 (4)	
H6	0.5047	0.2071	0.8278	0.056*	
C7	0.64118 (19)	0.14138 (18)	0.77141 (13)	0.0545 (5)	

H7	0.7161	0.1866	0.8038	0.065*
C8	0.6563 (2)	0.06392 (18)	0.71004 (14)	0.0568 (5)
H8	0.7420	0.0557	0.7004	0.068*
C9	0.54816 (19)	−0.00196 (17)	0.66235 (13)	0.0528 (5)
H9	0.5594	−0.0543	0.6196	0.063*
C10	0.42343 (18)	0.00821 (16)	0.67682 (11)	0.0440 (4)
H10	0.3486	−0.0375	0.6447	0.053*
C11	0.22876 (17)	−0.01779 (15)	0.78457 (11)	0.0424 (4)
H11A	0.2135	−0.0813	0.7407	0.051*
H11B	0.1418	−0.0020	0.7965	0.051*
C12	0.32913 (18)	−0.06664 (17)	0.86129 (11)	0.0467 (5)
H12A	0.3594	0.0024	0.9006	0.056*
H12B	0.4088	−0.0991	0.8465	0.056*
C13	0.2707 (2)	−0.16874 (18)	0.90269 (12)	0.0531 (5)
H13A	0.1949	−0.1348	0.9210	0.064*
H13B	0.2347	−0.2353	0.8623	0.064*
C14	0.3739 (3)	−0.2230 (2)	0.97576 (14)	0.0786 (7)
H14A	0.3313	−0.2861	1.0018	0.094*
H14B	0.4109	−0.1571	1.0155	0.094*
H14C	0.4466	−0.2610	0.9574	0.094*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C15	0.037 (2)	0.0443 (18)	0.0425 (18)	0.0049 (13)	0.0073 (15)	−0.0079 (14)
C16	0.0466 (17)	0.0463 (12)	0.0529 (14)	0.0004 (13)	0.0130 (15)	−0.0023 (10)
C17	0.0616 (15)	0.0567 (15)	0.0521 (15)	0.0122 (12)	0.0136 (12)	0.0023 (12)
C18	0.094 (3)	0.0636 (19)	0.0656 (19)	0.0076 (19)	0.013 (2)	0.0120 (14)
C15′	0.037 (2)	0.0443 (18)	0.0425 (18)	0.0049 (13)	0.0073 (15)	−0.0079 (14)
C16′	0.0466 (17)	0.0463 (12)	0.0529 (14)	0.0004 (13)	0.0130 (15)	−0.0023 (10)
C17′	0.0616 (15)	0.0567 (15)	0.0521 (15)	0.0122 (12)	0.0136 (12)	0.0023 (12)
C18′	0.094 (3)	0.0636 (19)	0.0656 (19)	0.0076 (19)	0.013 (2)	0.0120 (14)
O1	0.0361 (7)	0.0524 (8)	0.0574 (8)	−0.0073 (6)	0.0225 (6)	−0.0147 (6)
O2	0.0412 (8)	0.0627 (9)	0.0724 (10)	−0.0127 (7)	0.0261 (7)	−0.0309 (7)
O3	0.0341 (7)	0.0515 (8)	0.0558 (8)	0.0015 (5)	0.0159 (6)	−0.0114 (6)
O4	0.0427 (8)	0.0726 (10)	0.0898 (11)	−0.0151 (7)	0.0260 (7)	−0.0417 (8)
N1	0.0397 (8)	0.0376 (8)	0.0434 (9)	0.0006 (6)	0.0158 (7)	−0.0051 (7)
C1	0.0357 (9)	0.0398 (9)	0.0400 (10)	−0.0018 (7)	0.0156 (8)	−0.0004 (7)
C2	0.0367 (9)	0.0398 (9)	0.0365 (9)	−0.0029 (7)	0.0125 (7)	−0.0026 (7)
C3	0.0351 (9)	0.0396 (9)	0.0376 (9)	0.0033 (7)	0.0122 (7)	0.0019 (7)
C4	0.0365 (10)	0.0444 (10)	0.0495 (11)	−0.0026 (8)	0.0148 (8)	−0.0079 (9)
C5	0.0383 (10)	0.0370 (9)	0.0439 (10)	0.0016 (8)	0.0155 (8)	0.0034 (8)
C6	0.0472 (11)	0.0425 (10)	0.0502 (11)	−0.0039 (8)	0.0150 (9)	0.0019 (8)
C7	0.0425 (11)	0.0502 (12)	0.0696 (14)	−0.0068 (9)	0.0136 (10)	0.0116 (10)
C8	0.0438 (12)	0.0527 (12)	0.0816 (15)	0.0084 (9)	0.0304 (11)	0.0201 (11)
C9	0.0539 (12)	0.0485 (11)	0.0639 (13)	0.0134 (9)	0.0296 (10)	0.0074 (9)
C10	0.0427 (10)	0.0431 (10)	0.0483 (11)	0.0046 (8)	0.0163 (8)	−0.0006 (8)
C11	0.0378 (10)	0.0411 (10)	0.0512 (11)	−0.0049 (8)	0.0173 (8)	−0.0051 (8)

C12	0.0468 (11)	0.0461 (11)	0.0493 (11)	−0.0068 (8)	0.0167 (9)	−0.0018 (8)
C13	0.0624 (13)	0.0469 (11)	0.0546 (12)	−0.0112 (9)	0.0240 (10)	−0.0042 (9)
C14	0.0995 (19)	0.0695 (15)	0.0639 (15)	−0.0205 (13)	0.0182 (13)	0.0144 (12)

Geometric parameters (Å, º)

C15—N1	1.484 (4)	N1—C5	1.478 (2)
C15—C16	1.525 (4)	N1—C11	1.507 (2)
C15—H15A	0.9900	N1—H1	0.953 (19)
C15—H15B	0.9900	C1—C2	1.425 (2)
C16—C17	1.506 (3)	C1—C4	1.490 (2)
C16—H16A	0.9900	C2—C3	1.417 (2)
C16—H16B	0.9900	C3—C4	1.492 (2)
C17—C18	1.514 (4)	C5—C6	1.377 (2)
C17—H17A	0.9900	C5—C10	1.377 (2)
C17—H17B	0.9900	C6—C7	1.386 (3)
C18—H18D	0.9800	C6—H6	0.9500
C18—H18E	0.9800	C7—C8	1.375 (3)
C18—H18F	0.9800	C7—H7	0.9500
C15′—C16′	1.520 (16)	C8—C9	1.380 (3)
C15′—N1	1.66 (2)	C8—H8	0.9500
C15′—H15C	0.9900	C9—C10	1.384 (2)
C15′—H15D	0.9900	C9—H9	0.9500
C16′—C17′	1.513 (13)	C10—H10	0.9500
C16′—H16C	0.9900	C11—C12	1.513 (2)
C16′—H16D	0.9900	C11—H11A	0.9900
C17′—C18′	1.521 (14)	C11—H11B	0.9900
C17′—H17C	0.9900	C12—C13	1.519 (2)
C17′—H17D	0.9900	C12—H12A	0.9900
C18′—H18A	0.9800	C12—H12B	0.9900
C18′—H18B	0.9800	C13—C14	1.508 (3)
C18′—H18C	0.9800	C13—H13A	0.9900
O1—C1	1.2492 (19)	C13—H13B	0.9900
O2—C2	1.312 (2)	C14—H14A	0.9800
O2—H2	0.91 (2)	C14—H14B	0.9800
O3—C3	1.2555 (18)	C14—H14C	0.9800
O4—C4	1.216 (2)		
N1—C15—C16	112.7 (3)	C11—N1—H1	104.9 (11)
N1—C15—H15A	109.0	C15′—N1—H1	114.1 (14)
C16—C15—H15A	109.0	O1—C1—C2	135.67 (16)
N1—C15—H15B	109.0	O1—C1—C4	135.33 (15)
C16—C15—H15B	109.0	C2—C1—C4	88.99 (13)
H15A—C15—H15B	107.8	O2—C2—C3	136.17 (15)
C17—C16—C15	112.7 (3)	O2—C2—C1	130.13 (15)
C17—C16—H16A	109.0	C3—C2—C1	93.70 (13)
C15—C16—H16A	109.0	O3—C3—C2	137.20 (16)
C17—C16—H16B	109.0	O3—C3—C4	133.60 (15)

C15—C16—H16B	109.0	C2—C3—C4	89.19 (13)
H16A—C16—H16B	107.8	O4—C4—C1	135.54 (16)
C16—C17—C18	112.2 (2)	O4—C4—C3	136.38 (16)
C16—C17—H17A	109.2	C1—C4—C3	88.08 (13)
C18—C17—H17A	109.2	C10—C5—C6	121.77 (16)
C16—C17—H17B	109.2	C10—C5—N1	119.98 (15)
C18—C17—H17B	109.2	C6—C5—N1	118.24 (15)
H17A—C17—H17B	107.9	C5—C6—C7	118.91 (18)
C17—C18—H18D	109.5	C5—C6—H6	120.5
C17—C18—H18E	109.5	C7—C6—H6	120.5
H18D—C18—H18E	109.5	C8—C7—C6	119.85 (19)
C17—C18—H18F	109.5	C8—C7—H7	120.1
H18D—C18—H18F	109.5	C6—C7—H7	120.1
H18E—C18—H18F	109.5	C7—C8—C9	120.68 (18)
C16′—C15′—N1	110.3 (13)	C7—C8—H8	119.7
C16′—C15′—H15C	109.6	C9—C8—H8	119.7
N1—C15′—H15C	109.6	C8—C9—C10	119.98 (18)
C16′—C15′—H15D	109.6	C8—C9—H9	120.0
N1—C15′—H15D	109.6	C10—C9—H9	120.0
H15C—C15′—H15D	108.1	C5—C10—C9	118.81 (18)
C17′—C16′—C15′	114.4 (15)	C5—C10—H10	120.6
C17′—C16′—H16C	108.7	C9—C10—H10	120.6
C15′—C16′—H16C	108.7	N1—C11—C12	111.78 (14)
C17′—C16′—H16D	108.7	N1—C11—H11A	109.3
C15′—C16′—H16D	108.7	C12—C11—H11A	109.3
H16C—C16′—H16D	107.6	N1—C11—H11B	109.3
C16′—C17′—C18′	113.3 (11)	C12—C11—H11B	109.3
C16′—C17′—H17C	108.9	H11A—C11—H11B	107.9
C18′—C17′—H17C	108.9	C11—C12—C13	112.46 (15)
C16′—C17′—H17D	108.9	C11—C12—H12A	109.1
C18′—C17′—H17D	108.9	C13—C12—H12A	109.1
H17C—C17′—H17D	107.7	C11—C12—H12B	109.1
C17′—C18′—H18A	109.5	C13—C12—H12B	109.1
C17′—C18′—H18B	109.5	H12A—C12—H12B	107.8
H18A—C18′—H18B	109.5	C14—C13—C12	112.17 (16)
C17′—C18′—H18C	109.5	C14—C13—H13A	109.2
H18A—C18′—H18C	109.5	C12—C13—H13A	109.2
H18B—C18′—H18C	109.5	C14—C13—H13B	109.2
C2—O2—H2	109.6 (14)	C12—C13—H13B	109.2
C5—N1—C15	112.2 (2)	H13A—C13—H13B	107.9
C5—N1—C11	112.66 (13)	C13—C14—H14A	109.5
C15—N1—C11	113.90 (17)	C13—C14—H14B	109.5
C5—N1—C15′	114.2 (11)	H14A—C14—H14B	109.5
C11—N1—C15′	102.8 (6)	C13—C14—H14C	109.5
C5—N1—H1	107.7 (11)	H14A—C14—H14C	109.5
C15—N1—H1	104.6 (11)	H14B—C14—H14C	109.5
N1—C15—C16—C17	−165.9 (3)	C2—C3—C4—O4	−178.1 (2)

C15—C16—C17—C18	−166.5 (3)	O3—C3—C4—C1	−178.62 (19)
N1—C15′—C16′—C17′	75 (2)	C2—C3—C4—C1	1.40 (13)
C15′—C16′—C17′—C18′	156.9 (15)	C15—N1—C5—C6	113.9 (2)
C16—C15—N1—C5	−47.2 (4)	C11—N1—C5—C6	−115.94 (17)
C16—C15—N1—C11	−176.7 (3)	C15′—N1—C5—C6	127.2 (7)
C16—C15—N1—C15′	−149 (6)	C15—N1—C5—C10	−64.9 (2)
C16′—C15′—N1—C5	−77.4 (19)	C11—N1—C5—C10	65.3 (2)
C16′—C15′—N1—C15	6 (4)	C15′—N1—C5—C10	−51.6 (7)
C16′—C15′—N1—C11	160.2 (15)	C10—C5—C6—C7	−0.8 (3)
O1—C1—C2—O2	2.3 (3)	N1—C5—C6—C7	−179.56 (15)
C4—C1—C2—O2	−178.97 (19)	C5—C6—C7—C8	0.6 (3)
O1—C1—C2—C3	−177.3 (2)	C6—C7—C8—C9	0.3 (3)
C4—C1—C2—C3	1.47 (14)	C7—C8—C9—C10	−0.9 (3)
O2—C2—C3—O3	−1.0 (4)	C6—C5—C10—C9	0.2 (3)
C1—C2—C3—O3	178.6 (2)	N1—C5—C10—C9	178.92 (15)
O2—C2—C3—C4	179.0 (2)	C8—C9—C10—C5	0.7 (3)
C1—C2—C3—C4	−1.47 (14)	C5—N1—C11—C12	56.46 (19)
O1—C1—C4—O4	−3.1 (4)	C15—N1—C11—C12	−174.3 (3)
C2—C1—C4—O4	178.1 (2)	C15′—N1—C11—C12	179.9 (11)
O1—C1—C4—C3	177.4 (2)	N1—C11—C12—C13	167.88 (15)
C2—C1—C4—C3	−1.39 (13)	C11—C12—C13—C14	176.11 (17)
O3—C3—C4—O4	1.9 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3^{i}	0.91 (2)	1.68 (2)	2.543 (2)	157 (2)
N1—H1···O1	0.95 (2)	1.74 (2)	2.688 (2)	172 (2)
C15—H15*A*···O4	0.99	2.60	3.469 (5)	147
C9—H9···O1^{ii}	0.95	2.53	3.222 (2)	130

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