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1,2,3,4-Tetrahydroisoquinolinium hydrogensquarate

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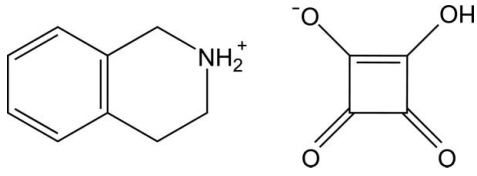
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.067; wR factor = 0.234; data-to-parameter ratio = 13.3.

The asymmetric unit of the title compound, $C_9H_{12}N^+\cdot C_4H_4O^-$, contains two independent 1,2,3,4-tetrahydroisoquinolinium cations and two independent hydrogensquarate anions. In one of the cations, the N atom is disordered over two positions with occupancies of approximately 0.8 and 0.2. The pyridinium rings adopt envelope conformations. The hydrogensquarate anions are linked to form cyclic tetramers through strong O—H···O hydrogen bonds. The tetrahydroisoquinolinium and hydrogensquarate ions are linked *via* N—H···O hydrogen bonds, forming a three-dimensional framework.

Related literature

For general background, see: Alexandrova *et al.* (2000); Anderson *et al.* (1998); Brzezinska (1994); Gargett & Wiley (1997); Loesel *et al.* (1987); Matsuhashi *et al.* (2002); Roqué-Rosell *et al.* (2006); Said *et al.* (2005). For related literature, see: Gilli *et al.* (2001); Kolev *et al.* (1997); Kolev *et al.* (2006); Kolev, Spiteller, Sheldrick & Mayer-Figge (2005); Kolev, Spiteller, Sheldrick, Mayer-Figge & Van Almsick (2005).



Experimental

Crystal data

$C_9H_{12}N^+\cdot C_4HO_4^-$
M_r = 247.24
Triclinic, $P\overline{1}$
a = 8.1456 (10) Å
b = 10.936 (2) Å
c = 13.6897 (12) Å
α = 77.81 (2)°
β = 78.170 (17)°
γ = 74.319 (13)°
V = 1133.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 290 (2) K
0.40 × 0.40 × 0.40 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
4773 measured reflections
4444 independent reflections
3226 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.234
S = 1.02
4444 reflections
335 parameters
12 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O33—H33···O42	0.82	1.66	2.476 (2)	176
O41—H41···O34^{i}	0.82	1.69	2.509 (3)	178
N1—H1A···O42	0.90	2.51	3.195 (3)	133
N2—H2A···O43^{ii}	0.90	2.30	2.943 (5)	128
N2—H2A···O33^{ii}	0.90	2.40	3.201 (6)	148
N2—H2B···O32^{iii}	0.90	1.87	2.773 (4)	177
N22—H22C···O32^{iii}	0.90	1.91	2.708 (2)	147
N22—H22D···O44^{iv}	0.90	1.82	2.72 (3)	174
N1—H1B···O31^{v}	0.90	2.21	2.910 (3)	134
N1—H1B···O42^{i}	0.90	2.36	2.992 (3)	127
N1—H1A···O34^{i}	0.90	2.27	3.027 (3)	142

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x, y-1, z$; (iii) $-x+1, -y+1, -z$; (iv) $-x+2, -y+1, -z$; (v) $-x, -y+2, -z+1$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2392).

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supplementary materials

Acta Cryst. (2007). E**63**, o3353-o3354 [**doi:10.1107/S1600536807030802**]

1,2,3,4-Tetrahydroisoquinolinium hydrogensquarate

T. Kolev, B. Shivachev, R. Petrova, I. Ivanov, S. Atanasova and S. Statkova

Comment

Isoquinoline derivatives have been used as building blocks in the synthesis of natural products (Roqué-Rosell *et al.*, 2006) and are of great interest due to their biological and pharmacological properties (Said *et al.*, 2005; Matsuhashi *et al.*, 2002; Alexandrova *et al.*, 2000; Anderson *et al.*, 1998; Gargett & Wiley, 1997; Brzezinska, 1994, Loesel *et al.*, 1987). In continuation of our investigations of biologically active hydrogensquarates (Kolev *et al.*, 1997; Kolev, Spiteller, Sheldrick & Mayer-Figge, 2005, 2006; Kolev, Spiteller, Sheldrick, Mayer-Figge & Van Almsick, 2005; Kolev, Yancheva *et al.*, 2006), we report here the structure of 1,2,3,4-tetrahydroisoquinolinium 2-hydroxy-3,4-dioxocyclobut-1-en-1-olate, (I).

There are two independent 1,2,3,4-tetrahydroisoquinolinium cations (A and B) and two independent hydrogensquarate anions in the asymmetric unit of (I) (Fig. 1). There are very few structural differences between the identical pairs of ions (A/B and C/D). The hydrogensquarate ions C and D are each planar with r.m.s. deviations of 0.031 and 0.010 Å, respectively. The C═O bonds have typical values around 1.22 Å while the different lengths for the C—O single bonds (Table 1) show the presence of a negative charge located on one of the oxygen atoms. In both isoquinolinium ions A and B the aromatic ring is nearly planar. The pyridinium rings adopt envelope conformations with atoms N1, N2 and N22 deviating from the mean planes through the remaining five atoms of the rings by 0.644 (4), 0.564 (7) and 0.25 (3) Å, respectively. The partial protonation of the secondary amino group in both A and B could be inferred from C—N bonds lengths (Table 1).

An extensive hydrogen bonding is observed in the crystal structure of (I) (Table 2). The strong O33—H33···O42 and O41—H41···O34^{i} hydrogen bonds [symmetry code (i): $1-x, 2-y, 1-z$) link hydrogensquarate moieties to form a cyclic tetramer. Similar motif (α-tetramer)(Gilli *et al.*, 2001) has been reported for guanidinium hydrogen squarate (Kolev *et al.*, 1997).

The tetrahydroisoquinolinium ions are hydrogen-bonded to hydrogensquarate ions through the only donor (N atom) present in the fragment (Fig. 2). In addition, weak C—H···O interactions (H···O = 2.30–2.57 Å and C···O = 3.251 (5)–3.402 (5) Å) stabilize the three-dimensional packing.

Experimental

A mixture of equimolar amounts of squaric acid (2 mmol, 228 mg) and 1,2,3,4-tetrahydroisoquinoline (2 mmol, 266.4 mg) in water (40 ml) was stirred at room temperature for 2 h. The resulting 1,2,3,4-tetrahydroisoquinolinium hydrogensquarate was isolated from the reaction mixture by filtration. Colourless crystals of (I) suitable for X-ray analysis were grown from water.

Refinement

The nitrogen atom of molecule B is disordered over two positions (N2 and N22) with occupancies of 0.796 (14) and 0.204 (14). The N—C distances involving the disordered atoms were restrained to be equal within 0.03 Å, and the U^{ij} components of the N22 atom were approximated to isotropic behaviour. The H atoms were placed in idealized positions,

with O—H = 0.82 Å, C—H = 0.93–0.97 Å and N—H = 0.90 Å. All H atoms were constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C or N) and U_{iso}(H) = 1.5U_{eq}(O).

Figures

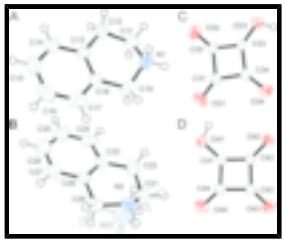


Fig. 1. The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. Both disorder components are shown.

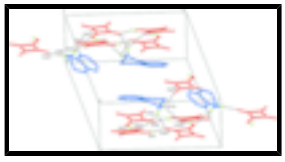


Fig. 2. A view of the molecular packing in (I). H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity. [Symmetry codes: (i) 1 − *x*, 1 − *y*, −*z*; (ii) *x*, *y* − 1,*z*; (iii) 1 − *x*, 2 − *y*, 1 − *z*; (iv) −*x*, 2 − *y*, 1 − *z*].

1,2,3,4-tetrahydroisoquinolinium 2-hydroxy-3,4-dioxocyclobut-1-en-1-olate

Crystal data

$C_9H_{12}N^+·C_4HO_4^-$	Z = 4
M_r = 247.24	F_{000} = 520
Triclinic, $P\overline{1}$	D_x = 1.449 Mg m^{-3}
Hall symbol: -P 1	Melting point: not measured K
a = 8.1456 (10) Å	Mo $K\alpha$ radiation λ = 0.71073 Å
b = 10.936 (2) Å	Cell parameters from 22 reflections
c = 13.6897 (12) Å	θ = 17.9–19.8º
α = 77.81 (2)º	μ = 0.11 mm^{-1}
β = 78.170 (17)º	T = 290 (2) K
γ = 74.319 (13)º	Block, colourless
V = 1133.4 (3) Å^3	0.40 × 0.40 × 0.40 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.042
Radiation source: fine-focus sealed tube	θ_{max} = 26.0º
Monochromator: graphite	θ_{min} = 1.5º
T = 290(2) K	h = 0→10
non–profiled ω/2θ scans	k = −12→13
Absorption correction: none	l = −16→16
4773 measured reflections	3 standard reflections
4444 independent reflections	every 120 min
3226 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.067$	H-atom parameters constrained
$wR(F^2) = 0.234$	$w = 1/[\sigma^2(F_o^2) + (0.1657P)^2 + 0.1541P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4444 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
335 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
12 restraints	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 $F^2 > 2\text{sigma}(F^2)$ 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}	Occ. (<1)
C11	0.5030 (4)	0.7057 (3)	0.6246 (2)	0.0522 (8)	
H11A	0.4125	0.6594	0.6488	0.063*	
H11B	0.5215	0.7383	0.6811	0.063*	
C12	0.6682 (4)	0.6146 (3)	0.5848 (2)	0.0482 (7)	
H12A	0.7655	0.6479	0.5883	0.058*	
H12B	0.6786	0.5318	0.6289	0.058*	
C13	0.6795 (3)	0.5948 (2)	0.4790 (2)	0.0369 (6)	
C14	0.8152 (4)	0.5022 (3)	0.4379 (3)	0.0488 (8)	
H14A	0.8942	0.4495	0.4784	0.059*	
C15	0.8344 (5)	0.4875 (3)	0.3385 (3)	0.0586 (9)	
H15A	0.9256	0.4252	0.3122	0.070*	
C16	0.7181 (5)	0.5654 (4)	0.2782 (3)	0.0650 (10)	
H16A	0.7321	0.5571	0.2106	0.078*	
C17	0.5813 (5)	0.6553 (4)	0.3177 (3)	0.0565 (8)	
H17A	0.5014	0.7060	0.2769	0.068*	
C18	0.5611 (3)	0.6713 (3)	0.4173 (2)	0.0385 (6)	
C19	0.4094 (4)	0.7697 (3)	0.4595 (2)	0.0487 (8)	

H19A	0.3802	0.8426	0.4066	0.058*	
H19B	0.3103	0.7321	0.4824	0.058*	
C21	0.7842 (5)	0.1957 (5)	0.0189 (3)	0.0763 (13)	
H21A	0.8145	0.2461	−0.0465	0.092*	0.796 (14)
H21B	0.8907	0.1450	0.0422	0.092*	0.796 (14)
H21C	0.8582	0.1265	0.0568	0.092*	0.204 (14)
H21D	0.8591	0.2409	−0.0300	0.092*	0.204 (14)
C22	0.6897 (4)	0.2857 (4)	0.0921 (3)	0.0645 (10)	
H22A	0.7410	0.3592	0.0785	0.077*	
H22B	0.7040	0.2418	0.1603	0.077*	
C23	0.4997 (4)	0.3332 (3)	0.0863 (2)	0.0439 (7)	
C24	0.3951 (5)	0.4308 (3)	0.1385 (2)	0.0574 (9)	
H24A	0.4456	0.4705	0.1742	0.069*	
C25	0.2221 (5)	0.4693 (4)	0.1385 (3)	0.0667 (10)	
H25A	0.1560	0.5341	0.1743	0.080*	
C26	0.1449 (5)	0.4134 (4)	0.0864 (3)	0.0693 (11)	
H26A	0.0260	0.4387	0.0877	0.083*	
C27	0.2438 (4)	0.3191 (3)	0.0318 (2)	0.0532 (8)	
H27A	0.1918	0.2825	−0.0054	0.064*	
C28	0.4209 (4)	0.2785 (3)	0.0320 (2)	0.0402 (6)	
C29	0.5227 (4)	0.1760 (3)	−0.0282 (3)	0.0556 (8)	
H29A	0.4550	0.1139	−0.0236	0.067*	0.796 (14)
H29B	0.5451	0.2146	−0.0988	0.067*	0.796 (14)
H29C	0.4949	0.2037	−0.0955	0.067*	0.204 (14)
H29D	0.4787	0.1008	−0.0003	0.067*	0.204 (14)
C31	0.0455 (3)	1.1145 (2)	0.3028 (2)	0.0341 (6)	
C32	0.1510 (3)	1.0709 (3)	0.20780 (19)	0.0340 (6)	
C33	0.3049 (3)	1.0510 (3)	0.25202 (19)	0.0340 (6)	
C34	0.2090 (3)	1.0895 (2)	0.34349 (19)	0.0322 (6)	
C41	0.9529 (3)	0.8286 (2)	0.35799 (18)	0.0328 (6)	
C42	0.8025 (3)	0.8920 (2)	0.31596 (18)	0.0313 (6)	
C43	0.8868 (3)	0.8533 (3)	0.2170 (2)	0.0381 (6)	
C44	1.0468 (3)	0.7868 (3)	0.2646 (2)	0.0377 (6)	
N1	0.4485 (3)	0.8144 (2)	0.54460 (19)	0.0476 (6)	
H1A	0.5331	0.8568	0.5218	0.057*	
H1B	0.3541	0.8696	0.5706	0.057*	
N2	0.6865 (5)	0.1096 (4)	0.0066 (4)	0.0567 (16)	0.796 (14)
H2A	0.6656	0.0583	0.0661	0.068*	0.796 (14)
H2B	0.7504	0.0590	−0.0383	0.068*	0.796 (14)
N22	0.7023 (16)	0.159 (2)	−0.0462 (17)	0.082 (7)	0.204 (14)
H22C	0.7490	0.0748	−0.0480	0.099*	0.204 (14)
H22D	0.7304	0.2017	−0.1086	0.099*	0.204 (14)
O31	−0.1074 (2)	1.1535 (2)	0.33295 (17)	0.0509 (6)	
O32	0.1216 (3)	1.0535 (2)	0.12745 (15)	0.0471 (5)	
O33	0.4673 (2)	1.0111 (2)	0.21660 (13)	0.0478 (6)	
H33	0.5244	0.9943	0.2626	0.072*	
O34	0.2468 (2)	1.0950 (2)	0.42759 (14)	0.0438 (5)	
O41	1.0005 (2)	0.8119 (2)	0.44593 (14)	0.0472 (6)	
H41	0.9183	0.8426	0.4863	0.071*	

O42	0.6533 (2)	0.95743 (19)	0.34911 (13)	0.0389 (5)
O43	0.8447 (3)	0.8715 (3)	0.13369 (15)	0.0576 (6)
O44	1.1933 (3)	0.7263 (2)	0.23680 (17)	0.0569 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0468 (18)	0.0601 (19)	0.0448 (17)	−0.0066 (15)	−0.0022 (13)	−0.0104 (14)
C12	0.0426 (17)	0.0480 (17)	0.0509 (17)	−0.0027 (13)	−0.0111 (13)	−0.0082 (13)
C13	0.0300 (13)	0.0327 (13)	0.0488 (16)	−0.0082 (11)	−0.0063 (11)	−0.0072 (11)
C14	0.0351 (16)	0.0397 (15)	0.071 (2)	−0.0025 (12)	−0.0089 (14)	−0.0149 (14)
C15	0.0517 (19)	0.0536 (19)	0.072 (2)	−0.0102 (15)	0.0040 (17)	−0.0303 (17)
C16	0.076 (3)	0.073 (2)	0.057 (2)	−0.025 (2)	−0.0041 (18)	−0.0291 (18)
C17	0.058 (2)	0.065 (2)	0.0494 (18)	−0.0150 (17)	−0.0180 (15)	−0.0064 (16)
C18	0.0308 (14)	0.0386 (14)	0.0450 (15)	−0.0086 (11)	−0.0062 (11)	−0.0038 (12)
C19	0.0314 (15)	0.0486 (17)	0.0583 (19)	0.0004 (13)	−0.0103 (13)	−0.0014 (14)
C21	0.0388 (19)	0.121 (4)	0.059 (2)	0.006 (2)	−0.0110 (16)	−0.022 (2)
C22	0.0431 (19)	0.103 (3)	0.053 (2)	−0.0139 (18)	−0.0088 (15)	−0.0277 (19)
C23	0.0470 (17)	0.0510 (17)	0.0346 (14)	−0.0104 (13)	−0.0054 (12)	−0.0117 (12)
C24	0.072 (2)	0.0558 (19)	0.0489 (18)	−0.0170 (17)	−0.0027 (16)	−0.0224 (15)
C25	0.061 (2)	0.059 (2)	0.064 (2)	0.0084 (17)	0.0049 (18)	−0.0197 (17)
C26	0.047 (2)	0.077 (3)	0.069 (2)	0.0066 (18)	−0.0076 (18)	−0.012 (2)
C27	0.0472 (18)	0.066 (2)	0.0489 (18)	−0.0156 (16)	−0.0131 (14)	−0.0066 (15)
C28	0.0435 (16)	0.0431 (15)	0.0325 (13)	−0.0065 (12)	−0.0037 (11)	−0.0101 (11)
C29	0.055 (2)	0.059 (2)	0.0529 (18)	0.0006 (16)	−0.0100 (15)	−0.0272 (16)
C31	0.0298 (13)	0.0357 (13)	0.0375 (13)	−0.0048 (10)	−0.0051 (10)	−0.0114 (11)
C32	0.0324 (13)	0.0386 (14)	0.0314 (13)	−0.0024 (11)	−0.0092 (10)	−0.0106 (10)
C33	0.0289 (13)	0.0416 (14)	0.0286 (12)	0.0001 (10)	−0.0068 (10)	−0.0084 (10)
C34	0.0283 (13)	0.0349 (13)	0.0331 (13)	−0.0031 (10)	−0.0051 (10)	−0.0105 (10)
C41	0.0258 (12)	0.0395 (14)	0.0314 (13)	−0.0026 (10)	−0.0045 (10)	−0.0093 (10)
C42	0.0243 (12)	0.0372 (13)	0.0323 (13)	−0.0041 (10)	−0.0037 (10)	−0.0104 (10)
C43	0.0330 (14)	0.0494 (16)	0.0335 (14)	−0.0077 (12)	−0.0061 (11)	−0.0122 (11)
C44	0.0328 (14)	0.0456 (15)	0.0342 (13)	−0.0041 (11)	−0.0040 (11)	−0.0133 (11)
N1	0.0331 (13)	0.0422 (13)	0.0601 (16)	−0.0029 (10)	0.0069 (11)	−0.0141 (12)
N2	0.067 (3)	0.056 (2)	0.036 (2)	0.0162 (18)	−0.0130 (17)	−0.0197 (19)
N22	0.092 (10)	0.077 (9)	0.057 (10)	−0.005 (7)	0.001 (7)	0.003 (7)
O31	0.0249 (10)	0.0641 (14)	0.0639 (14)	−0.0019 (9)	−0.0023 (9)	−0.0271 (11)
O32	0.0438 (12)	0.0605 (13)	0.0403 (11)	0.0000 (10)	−0.0177 (9)	−0.0202 (9)
O33	0.0278 (10)	0.0801 (15)	0.0286 (10)	0.0042 (9)	−0.0047 (8)	−0.0158 (10)
O34	0.0343 (11)	0.0662 (13)	0.0325 (10)	−0.0051 (9)	−0.0060 (8)	−0.0199 (9)
O41	0.0311 (10)	0.0732 (14)	0.0309 (10)	0.0081 (9)	−0.0092 (8)	−0.0169 (9)
O42	0.0251 (9)	0.0548 (12)	0.0361 (10)	−0.0007 (8)	−0.0064 (7)	−0.0159 (8)
O43	0.0468 (13)	0.0953 (18)	0.0313 (11)	−0.0076 (12)	−0.0088 (9)	−0.0212 (11)
O44	0.0351 (12)	0.0780 (16)	0.0488 (12)	0.0093 (11)	−0.0010 (9)	−0.0263 (11)

Geometric parameters (Å, °)

C11—N1	1.475 (4)	C25—H25A	0.93
C11—C12	1.518 (4)	C26—C27	1.379 (5)

C11—H11A	0.97	C26—H26A	0.93
C11—H11B	0.97	C27—C28	1.391 (4)
C12—C13	1.491 (4)	C27—H27A	0.93
C12—H12A	0.97	C28—C29	1.494 (4)
C12—H12B	0.97	C29—N22	1.400 (12)
C13—C14	1.394 (4)	C29—N2	1.457 (5)
C13—C18	1.395 (4)	C29—H29A	0.97
C14—C15	1.376 (5)	C29—H29B	0.97
C14—H14A	0.93	C29—H29C	0.96
C15—C16	1.375 (5)	C29—H29D	0.96
C15—H15A	0.93	C31—O31	1.216 (3)
C16—C17	1.373 (5)	C31—C34	1.484 (3)
C16—H16A	0.93	C31—C32	1.497 (3)
C17—C18	1.382 (4)	C32—O32	1.235 (3)
C17—H17A	0.93	C32—C33	1.447 (3)
C18—C19	1.506 (4)	C33—O33	1.299 (3)
C19—N1	1.475 (4)	C33—C34	1.414 (3)
C19—H19A	0.97	C34—O34	1.268 (3)
C19—H19B	0.97	C41—O41	1.301 (3)
C21—N22	1.392 (13)	C41—C42	1.405 (3)
C21—N2	1.441 (6)	C41—C44	1.444 (3)
C21—C22	1.503 (5)	C42—O42	1.279 (3)
C21—H21A	0.97	C42—C43	1.479 (3)
C21—H21B	0.97	C43—O43	1.220 (3)
C21—H21C	0.96	C43—C44	1.513 (4)
C21—H21D	0.96	C44—O44	1.224 (3)
C22—C23	1.507 (4)	N1—H1A	0.90
C22—H22A	0.97	N1—H1B	0.90
C22—H22B	0.97	N2—H2A	0.90
C23—C28	1.382 (4)	N2—H2B	0.90
C23—C24	1.400 (4)	N22—H22C	0.90
C24—C25	1.358 (5)	N22—H22D	0.90
C24—H24A	0.93	O33—H33	0.82
C25—C26	1.361 (6)	O41—H41	0.82
N1—C11—C12	110.7 (2)	C25—C26—H26A	120.1
N1—C11—H11A	109.5	C27—C26—H26A	120.1
C12—C11—H11A	109.5	C26—C27—C28	120.3 (3)
N1—C11—H11B	109.5	C26—C27—H27A	119.9
C12—C11—H11B	109.5	C28—C27—H27A	119.9
H11A—C11—H11B	108.1	C23—C28—C27	120.3 (3)
C13—C12—C11	114.7 (2)	C23—C28—C29	121.3 (3)
C13—C12—H12A	108.6	C27—C28—C29	118.4 (3)
C11—C12—H12A	108.6	N22—C29—C28	116.8 (7)
C13—C12—H12B	108.6	N2—C29—C28	112.4 (3)
C11—C12—H12B	108.6	N22—C29—H29A	129.1
H12A—C12—H12B	107.6	N2—C29—H29A	109.1
C14—C13—C18	118.4 (3)	C28—C29—H29A	109.1
C14—C13—C12	120.1 (3)	N22—C29—H29B	77.2
C18—C13—C12	121.4 (2)	N2—C29—H29B	109.1

C15—C14—C13	121.2 (3)	C28—C29—H29B	109.1
C15—C14—H14A	119.4	H29A—C29—H29B	107.8
C13—C14—H14A	119.4	N22—C29—H29C	101.8
C16—C15—C14	119.6 (3)	N2—C29—H29C	130.5
C16—C15—H15A	120.2	C28—C29—H29C	106.9
C14—C15—H15A	120.2	H29A—C29—H29C	84.1
C17—C16—C15	120.2 (3)	N22—C29—H29D	117.1
C17—C16—H16A	119.9	N2—C29—H29D	89.9
C15—C16—H16A	119.9	C28—C29—H29D	106.7
C16—C17—C18	120.7 (3)	H29B—C29—H29D	128.1
C16—C17—H17A	119.7	H29C—C29—H29D	106.6
C18—C17—H17A	119.7	O31—C31—C34	136.3 (2)
C17—C18—C13	119.9 (3)	O31—C31—C32	135.8 (3)
C17—C18—C19	119.9 (3)	C34—C31—C32	87.98 (19)
C13—C18—C19	120.1 (3)	O32—C32—C33	134.9 (2)
N1—C19—C18	111.1 (2)	O32—C32—C31	136.3 (2)
N1—C19—H19A	109.4	C33—C32—C31	88.76 (19)
C18—C19—H19A	109.4	O33—C33—C34	136.0 (2)
N1—C19—H19B	109.4	O33—C33—C32	131.2 (2)
C18—C19—H19B	109.4	C34—C33—C32	92.7 (2)
H19A—C19—H19B	108.0	O34—C34—C33	134.7 (2)
N22—C21—C22	122.9 (7)	O34—C34—C31	134.7 (2)
N2—C21—C22	113.7 (3)	C33—C34—C31	90.5 (2)
N22—C21—H21A	75.7	O41—C41—C42	135.8 (2)
N2—C21—H21A	108.8	O41—C41—C44	130.6 (2)
C22—C21—H21A	108.8	C42—C41—C44	93.5 (2)
N22—C21—H21B	124.3	O42—C42—C41	134.9 (2)
N2—C21—H21B	108.8	O42—C42—C43	134.4 (2)
C22—C21—H21B	108.8	C41—C42—C43	90.7 (2)
H21A—C21—H21B	107.7	O43—C43—C42	135.3 (3)
N22—C21—H21C	115.4	O43—C43—C44	136.8 (3)
N2—C21—H21C	91.2	C42—C43—C44	87.85 (19)
C22—C21—H21C	105.3	O44—C44—C41	135.5 (3)
H21A—C21—H21C	128.1	O44—C44—C43	136.6 (3)
N22—C21—H21D	99.5	C41—C44—C43	87.9 (2)
N2—C21—H21D	130.4	C11—N1—C19	111.3 (2)
C22—C21—H21D	106.0	C11—N1—H1A	109.4
H21B—C21—H21D	83.9	C19—N1—H1A	109.4
H21C—C21—H21D	106.1	C11—N1—H1B	109.4
C21—C22—C23	113.1 (3)	C19—N1—H1B	109.4
C21—C22—H22A	109.0	H1A—N1—H1B	108.0
C23—C22—H22A	109.0	C21—N2—C29	113.4 (4)
C21—C22—H22B	109.0	C21—N2—H2A	108.9
C23—C22—H22B	109.0	C29—N2—H2A	108.9
H22A—C22—H22B	107.8	C21—N2—H2B	108.9
C28—C23—C24	117.5 (3)	C29—N2—H2B	108.9
C28—C23—C22	121.2 (3)	H2A—N2—H2B	107.7
C24—C23—C22	121.3 (3)	C21—N22—C29	120.3 (12)
C25—C24—C23	121.8 (3)	C21—N22—H22C	107.2

C25—C24—H24A	119.1	C29—N22—H22C	107.2
C23—C24—H24A	119.1	C21—N22—H22D	107.2
C24—C25—C26	120.3 (3)	C29—N22—H22D	107.2
C24—C25—H25A	119.8	H22C—N22—H22D	106.9
C26—C25—H25A	119.8	C33—O33—H33	109.5
C25—C26—C27	119.7 (3)	C41—O41—H41	109.5
N1—C11—C12—C13	−38.3 (4)	C34—C31—C32—C33	−0.9 (2)
C11—C12—C13—C14	−172.6 (3)	O32—C32—C33—O33	3.1 (6)
C11—C12—C13—C18	10.6 (4)	C31—C32—C33—O33	−179.6 (3)
C18—C13—C14—C15	1.0 (4)	O32—C32—C33—C34	−176.4 (3)
C12—C13—C14—C15	−176.0 (3)	C31—C32—C33—C34	1.0 (2)
C13—C14—C15—C16	0.1 (5)	O33—C33—C34—O34	−3.1 (6)
C14—C15—C16—C17	−1.5 (6)	C32—C33—C34—O34	176.3 (3)
C15—C16—C17—C18	1.8 (6)	O33—C33—C34—C31	179.7 (3)
C16—C17—C18—C13	−0.6 (5)	C32—C33—C34—C31	−1.0 (2)
C16—C17—C18—C19	−179.5 (3)	O31—C31—C34—O34	3.8 (6)
C14—C13—C18—C17	−0.7 (4)	C32—C31—C34—O34	−176.3 (3)
C12—C13—C18—C17	176.2 (3)	O31—C31—C34—C33	−178.9 (3)
C14—C13—C18—C19	178.1 (3)	C32—C31—C34—C33	0.9 (2)
C12—C13—C18—C19	−5.0 (4)	O41—C41—C42—O42	−0.5 (6)
C17—C18—C19—N1	−154.1 (3)	C44—C41—C42—O42	−179.3 (3)
C13—C18—C19—N1	27.1 (4)	O41—C41—C42—C43	179.1 (3)
N22—C21—C22—C23	−1.0 (15)	C44—C41—C42—C43	0.3 (2)
N2—C21—C22—C23	−37.7 (5)	O42—C42—C43—O43	1.1 (6)
C21—C22—C23—C28	11.2 (5)	C41—C42—C43—O43	−178.5 (4)
C21—C22—C23—C24	−171.2 (3)	O42—C42—C43—C44	179.3 (3)
C28—C23—C24—C25	1.5 (5)	C41—C42—C43—C44	−0.3 (2)
C22—C23—C24—C25	−176.2 (4)	O41—C41—C44—O44	−0.6 (6)
C23—C24—C25—C26	−0.4 (6)	C42—C41—C44—O44	178.3 (4)
C24—C25—C26—C27	−1.3 (6)	O41—C41—C44—C43	−179.2 (3)
C25—C26—C27—C28	1.8 (6)	C42—C41—C44—C43	−0.3 (2)
C24—C23—C28—C27	−1.0 (5)	O43—C43—C44—O44	−0.1 (7)
C22—C23—C28—C27	176.7 (3)	C42—C43—C44—O44	−178.2 (4)
C24—C23—C28—C29	178.4 (3)	O43—C43—C44—C41	178.4 (4)
C22—C23—C28—C29	−3.9 (5)	C42—C43—C44—C41	0.3 (2)
C26—C27—C28—C23	−0.6 (5)	C12—C11—N1—C19	62.4 (3)
C26—C27—C28—C29	179.9 (3)	C18—C19—N1—C11	−55.9 (3)
C23—C28—C29—N22	−14.2 (13)	N22—C21—N2—C29	−55.8 (12)
C27—C28—C29—N22	165.2 (13)	C22—C21—N2—C29	58.4 (5)
C23—C28—C29—N2	22.0 (5)	N22—C29—N2—C21	56.1 (12)
C27—C28—C29—N2	−158.6 (4)	C28—C29—N2—C21	−48.9 (5)
O31—C31—C32—O32	−3.8 (6)	N2—C21—N22—C29	66.4 (17)
C34—C31—C32—O32	176.3 (3)	N2—C29—N22—C21	−66.0 (18)
O31—C31—C32—C33	178.9 (3)		

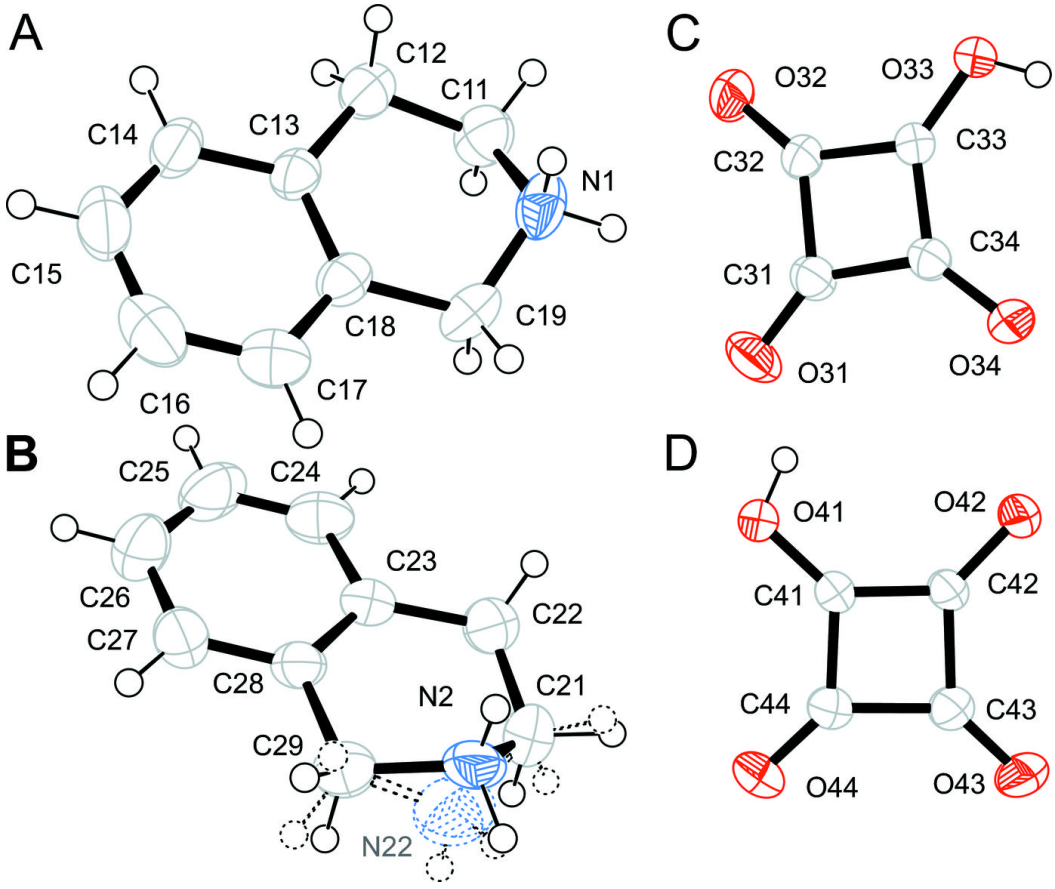
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O33—H33···O42	0.82	1.66	2.476 (2)	176

O41—H41···O34^{i}	0.82	1.69	2.509 (3)	178
N1—H1A···O42	0.90	2.51	3.195 (3)	133
N2—H2A···O43^{ii}	0.90	2.30	2.943 (5)	128
N2—H2A···O33^{ii}	0.90	2.40	3.201 (6)	148
N2—H2B···O32^{iii}	0.90	1.87	2.773 (4)	177
N22—H22C···O32^{iii}	0.90	1.91	2.708 (2)	147
N22—H22D···O44^{iv}	0.90	1.82	2.72 (3)	174
N1—H1B···O31^{v}	0.90	2.21	2.910 (3)	134
N1—H1B···O42^{i}	0.90	2.36	2.992 (3)	127
N1—H1A···O34^{i}	0.90	2.27	3.027 (3)	142

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

Fig. 1


A
C12
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C13
C14
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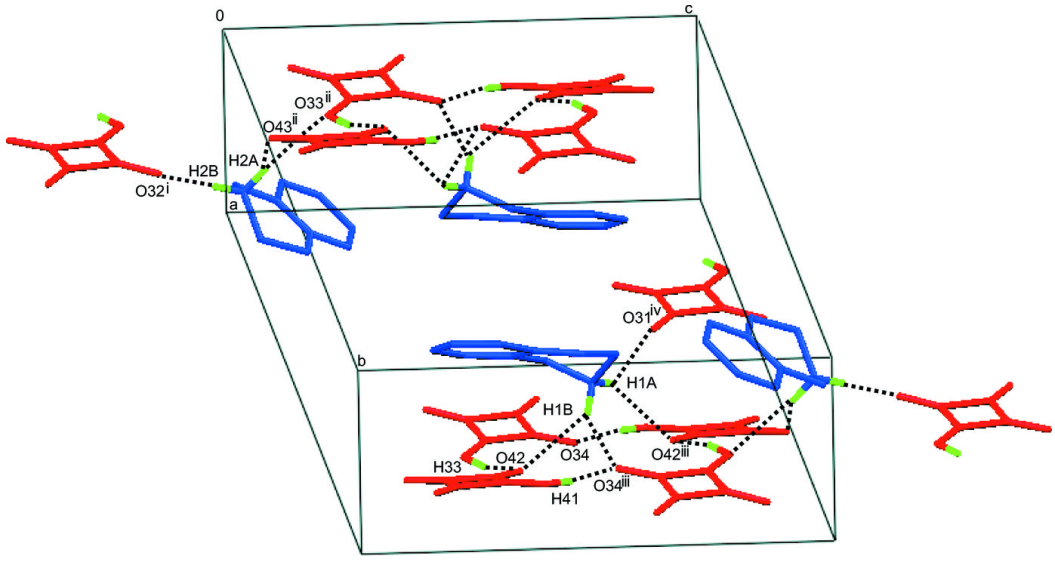
C15
C18
C19
C16
C17
B
C25
C24
C23
C26
C22
C27
C28
N2
C21
C29
N22
C
O32
O33
C33
C32
C34
C31
O31
O34
D
O41
O42
C41
C42
C44
C43
O44
O43

Fig. 2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c
a
b
O33ii
O43ii
H2A
H2B
O32i
O31iv
H1A
H1B
H33
O42
O34
O42iii
H41
O34iii