Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,2,4-Trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepin-5-ium 3,5-dihydroxybenzoate

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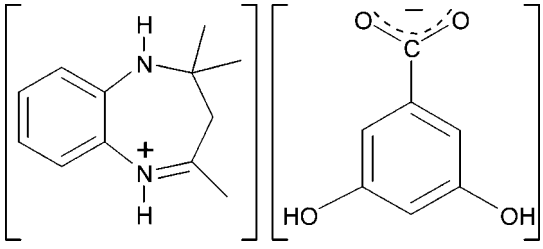
Received 11 November 2007; accepted 18 November 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.084; data-to-parameter ratio = 8.9.

In the crystal structure of the title compound, $C_{12}H_{17}N_2^+\cdot C_7H_5O_4^-$, the cations and anions are linked by O—H···O, N—H···O and C—H···O hydrogen bonds, resulting in a homochiral left-handed molecular helical extended structure. The O—H···O and N—H···O hydrogen bonds are involved in the formation of the helical backbone. The seven-membered ring adopts a half-chair conformation.

Related literature

For general background, see: Krapcho & Turk (1966); Essaber *et al.* (1998); Herbert & Suschitzky (1974); Morales *et al.* (1986); Balakrishna & Kaboudin (2001); Yadav *et al.* (2002); De & Gibbs (2005). For related structures, see: Thakuria *et al.* (2006); Burchell *et al.* (2001);



Experimental

Crystal data

$C_{12}H_{17}N_2^+\cdot C_7H_5O_4^-$
M_r = 342.39
Orthorhombic, $P2_12_12_1$
a = 18.718 (4) Å
b = 9.924 (2) Å
c = 9.696 (2) Å
V = 1801.1 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 298 (2) K
0.42 × 0.32 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.964, T_{max} = 0.981
9324 measured reflections
2028 independent reflections
1891 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.084
S = 1.09
2028 reflections
229 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1X···O4^{i}	0.87	2.11	2.981 (2)	174
N2—H2X···O1^{ii}	0.99	1.69	2.676 (2)	172
O3—H3···O1^{iii}	0.82	1.93	2.721 (2)	163
O4—H4···O2^{iii}	0.82	1.79	2.597 (2)	170
C2—H2···O4^{i}	0.93	2.59	3.366 (3)	142
C5—H5···O1^{ii}	0.93	2.55	3.264 (3)	134

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

PR thanks Dr B. R. Srinivasan, Goa University, and Dr Samar K. Das, University of Hyderabad, for useful discussions. Thanks are due to the National Single-Crystal X-ray Diffractometer Facility, School of Chemistry, University of Hyderabad.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2381).

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 doi:10.1107/S1600536807060424

supplementary materials

Acta Cryst. (2007). E**63**, o4909 [**doi:10.1107/S1600536807060424**]

2,2,4-Trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepin-5-ium 3,5-dihydroxybenzoate

P. Raghavaiah

Comment

Benzodiazepines and their polycyclic derivatives are an important class of bioactive compounds because of their pharmacological properties. These compounds are extensively used as anticonvulsant, antianxiety, analgesic, sedative, antidepressive, hypnotic, and anti inflamatory agents (Krapcho & Turk, 1966). In particular, 1,5-benzodiazepines are useful precursors for the synthesis of fused ring benzodiazepine derivatives (Essaber *et al.*, 1998) such as triazolo, oxadiazolo, oxazino and furano benzodiazepines. Benzodiazepines are prepared by the condensation of *o*-phenylenediamine with acetone in the presence of a catalytic amount of an organic acid. Numerous synthetic methods are available in the literature to prepare these compounds by condensation of *o*-phenylenediamine with acetone, including BF_3 etherate (Herbert & Suschitzky, 1974), polyphosphoric acid (Morales *et al.*, 1986), MgO/$POCl_3$ (Balakrishna & Kaboudin, 2001) and ionic liquid medium (Yadav *et al.*, 2002). The mechanism of the condensation reaction involves an intramolecular imine enamine cyclization promoted by 3,5-dihydroxybenzoic acid (De & Gibbs, 2005). The difficulties, encountered in the cyclization of these seven-membered heterocycles, have limited their structural studies. Recently, the synthesis of a series of organic salts with 1,5-benzodiazepine and various aliphatic and aromatic acids under solvent-free conditions at room temperature, using acetone and *o*-phenylene- diamine in the presence of a catalytic amount of an organic acid has been reported. The organic salts of trimesic acid and picric acid were characterized by single-crystal X-ray studies (Thakuria *et al.*, 2006). We report herein the crystal structure of the title compound, (I), which exhibits a homo chiral left handed molecular helical extended structure

The asymmetric unit of the title compound, (I), (Fig. 1) contains a 2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepin-5-ium cation and a 3,5-dihydroxybenzoate anion, in which the bond lengths and angles are in good agreement with the reported values (Thakuria *et al.*, 2006; Burchell *et al.*, 2001).

A scrutiny of the crystal structure of (I) reveals the presence of strong O—H···O and N—H···O as well as weak C—H···O hydrogen-bond interactions between the cations and anions (Table 1, Fig. 2). The extended structure of (I) exhibits a homo chiral left handed molecular helix with a pitch length of 9.924 Å, which is identical to the crystallographic cell parameter b (Fig. 3). O—H···O and N—H···O hydrogen bonds are involved in the formation of the helical backbone. The imine nitrogen makes an H-donor bond with the hydroxyl oxygen O4 on one side, while the carboxylate oxygen O1 forms an H-acceptor bond with the amine N2 on the other side. The second oxygen O2 of this carboxylate anion is H-bonded to a symmetry related hydroxyl group. The carboxylate O atoms are moved away from the plane of the benzene ring by 28.12°, to complete the helical back bone.

Experimental

For the preparation of the title compound, 3,5-dihydroxybenzoic acid (465 mg, 3 mmol) dissolved in acetone (10 ml) was added to a methanolic solution (6 ml) of *o*-phenylenediamine (325 mg, 3 mmol). The reaction mixture was filtered and the filtrate was allowed to evaporate slowly at room temperature by covering the container with aluminium foil, which was punctured with holes. Single crystals suitable for X-ray analysis were obtained in 4 d (yield; 530 mg, 52% based on

o-phenylenediamine). Anal. Calcd (Found) (%): C, 66.65 (67.01); H, 6.48 (5.94); N, 8.18 (8.64). IR (KBr pellet, in cm^{-1}): 3327, 2975, 2627, 2178, 2068, 1688, 1537, 1497, 1362, 1285, 1165, 1009, 752.

Refinement

H atoms (for N_2) were located in a difference synthesis and constrained to ride on their parent atom [N—H = 0.8741 and 0.9917 Å and U_{iso}(H) = 1.2U_{eq}(N)]. The remaining H atoms were positioned geometrically, with O—H = 0.82 Å (for OH) and C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,*O*), where x = 1.5 for methyl H and OH H, and x = 1.2 for all other H atoms.

Figures

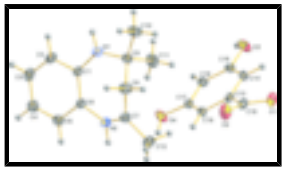

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

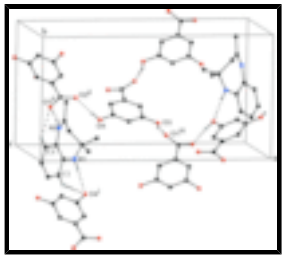

Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines [symmetry codes: (i) −x + 1/2, −y, z − 1/2; (ii) −x + 1/2, −y + 1, z + 1/2; (iii) −x + 1, y − 1/2, −z + 1/2]. Non-bonding H atoms are omitted for clarity.

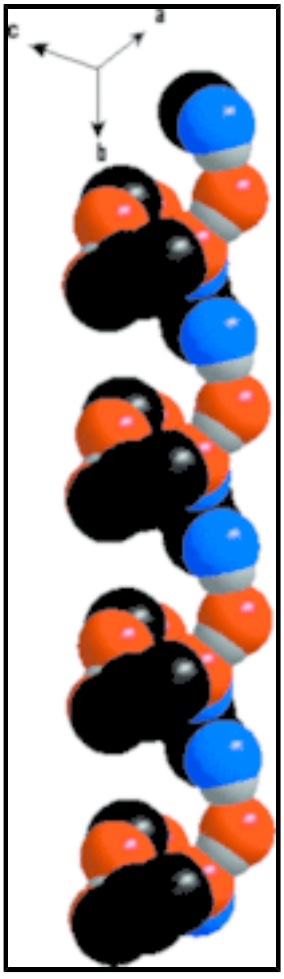

Fig. 3. A spacefill model of the helical back bone along *b* axis, formed by the N—H···O and O—H···O hydrogen-bond interactions.

2,2,4-Trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepin-5-ium 3,5-dihydroxybenzoate

Crystal data

$C_{12}H_{17}N_2^+ \cdot C_7H_5O_4^-$	F_{000} = 728
M_r = 342.39	D_x = 1.263 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 6683 reflections
a = 18.718 (4) Å	θ = 2.2–26.0º
b = 9.924 (2) Å	μ = 0.09 mm^{-1}
c = 9.696 (2) Å	T = 298 (2) K
V = 1801.1 (6) Å^3	Block, yellow
Z = 4	0.42 × 0.32 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2028 independent reflections

Radiation source: fine-focus sealed tube	1891 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 298(2)$ K	$\theta_{max} = 26.0°$
φ and ω scans	$\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -21 \rightarrow 23$
$T_{min} = 0.964$, $T_{max} = 0.981$	$k = -12 \rightarrow 8$
9324 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.2759P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.084$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
$S = 1.09$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
2028 reflections	Extinction correction: none
229 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

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}
O1	0.40340 (8)	0.63504 (16)	0.02296 (16)	0.0480 (4)
O2	0.29131 (8)	0.56458 (18)	0.0434 (2)	0.0593 (5)
O3	0.53612 (7)	0.26295 (17)	0.25796 (16)	0.0503 (4)
H3	0.5459	0.2173	0.3259	0.075*
O4	0.30708 (8)	0.26504 (16)	0.47109 (16)	0.0519 (4)
H4	0.2740	0.3176	0.4847	0.078*
N1	0.15531 (12)	0.0043 (2)	0.0862 (2)	0.0573 (6)
H1X	0.1675	−0.0717	0.0471	0.069*

N2	0.11065 (9)	0.23045 (17)	0.28525 (17)	0.0389 (4)
H2X	0.1102	0.2811	0.3734	0.047*
C1	0.12226 (11)	−0.0126 (2)	0.2107 (2)	0.0403 (5)
C2	0.10747 (13)	−0.1463 (2)	0.2513 (3)	0.0527 (6)
H2	0.1200	−0.2160	0.1920	0.063*
C3	0.07561 (14)	−0.1778 (3)	0.3740 (3)	0.0573 (6)
H3A	0.0668	−0.2675	0.3961	0.069*
C4	0.05641 (15)	−0.0778 (3)	0.4652 (3)	0.0599 (7)
H4A	0.0351	−0.0988	0.5491	0.072*
C5	0.06944 (13)	0.0531 (3)	0.4295 (2)	0.0542 (6)
H5	0.0568	0.1213	0.4906	0.065*
C6	0.10124 (11)	0.0879 (2)	0.3033 (2)	0.0394 (5)
C7	0.12024 (11)	0.3003 (2)	0.1751 (2)	0.0420 (5)
C8	0.12468 (14)	0.2374 (3)	0.0365 (2)	0.0546 (6)
H8A	0.1350	0.3073	−0.0306	0.065*
H8B	0.0783	0.1998	0.0137	0.065*
C9	0.18117 (12)	0.1259 (2)	0.0225 (2)	0.0426 (5)
C10	0.19151 (16)	0.0941 (3)	−0.1312 (3)	0.0658 (7)
H10A	0.2229	0.0182	−0.1409	0.099*
H10B	0.2120	0.1709	−0.1767	0.099*
H10C	0.1461	0.0734	−0.1721	0.099*
C11	0.25198 (13)	0.1699 (3)	0.0851 (3)	0.0669 (8)
H11A	0.2456	0.1880	0.1816	0.100*
H11B	0.2684	0.2500	0.0396	0.100*
H11C	0.2866	0.0994	0.0737	0.100*
C12	0.12697 (14)	0.4493 (2)	0.1875 (3)	0.0545 (6)
H12A	0.1253	0.4744	0.2831	0.082*
H12B	0.0883	0.4918	0.1392	0.082*
H12C	0.1716	0.4777	0.1483	0.082*
C13	0.37873 (10)	0.46231 (19)	0.18369 (19)	0.0315 (4)
C14	0.44805 (10)	0.4115 (2)	0.17847 (19)	0.0343 (4)
H14	0.4804	0.4441	0.1137	0.041*
C15	0.46837 (10)	0.3121 (2)	0.27035 (19)	0.0339 (4)
C16	0.42097 (10)	0.2646 (2)	0.36872 (19)	0.0364 (4)
H16	0.4349	0.1977	0.4303	0.044*
C17	0.35227 (10)	0.3179 (2)	0.3743 (2)	0.0351 (4)
C18	0.33115 (9)	0.41684 (19)	0.2828 (2)	0.0337 (4)
H18	0.2853	0.4527	0.2876	0.040*
C19	0.35510 (10)	0.5624 (2)	0.0763 (2)	0.0366 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0535 (9)	0.0480 (9)	0.0426 (8)	−0.0128 (7)	−0.0097 (7)	0.0183 (8)
O2	0.0419 (8)	0.0614 (11)	0.0746 (11)	−0.0016 (8)	−0.0201 (8)	0.0290 (10)
O3	0.0368 (7)	0.0659 (11)	0.0483 (8)	0.0182 (7)	0.0052 (6)	0.0120 (8)
O4	0.0493 (8)	0.0505 (9)	0.0559 (9)	0.0159 (7)	0.0212 (7)	0.0222 (8)
N1	0.0795 (14)	0.0399 (11)	0.0525 (11)	−0.0069 (10)	0.0235 (11)	−0.0146 (9)

N2	0.0431 (9)	0.0371 (9)	0.0363 (8)	−0.0030 (8)	0.0025 (7)	−0.0094 (8)
C1	0.0416 (11)	0.0385 (11)	0.0409 (11)	−0.0051 (9)	−0.0006 (9)	−0.0094 (9)
C2	0.0605 (14)	0.0403 (12)	0.0573 (14)	−0.0063 (11)	0.0034 (12)	−0.0099 (11)
C3	0.0665 (15)	0.0422 (13)	0.0632 (15)	−0.0095 (12)	0.0025 (13)	0.0058 (13)
C4	0.0734 (16)	0.0559 (15)	0.0505 (13)	−0.0082 (13)	0.0147 (13)	0.0037 (13)
C5	0.0685 (15)	0.0508 (14)	0.0432 (12)	−0.0037 (12)	0.0132 (11)	−0.0082 (11)
C6	0.0412 (10)	0.0369 (11)	0.0402 (11)	−0.0039 (9)	0.0000 (9)	−0.0073 (10)
C7	0.0409 (11)	0.0426 (12)	0.0426 (11)	0.0031 (10)	−0.0022 (9)	−0.0032 (10)
C8	0.0681 (15)	0.0581 (15)	0.0376 (11)	0.0131 (13)	−0.0056 (11)	−0.0039 (12)
C9	0.0474 (11)	0.0445 (12)	0.0359 (10)	0.0000 (10)	0.0039 (9)	−0.0045 (10)
C10	0.0802 (18)	0.0746 (19)	0.0425 (13)	0.0098 (16)	0.0123 (13)	−0.0104 (13)
C11	0.0491 (14)	0.081 (2)	0.0705 (17)	−0.0072 (14)	0.0005 (13)	−0.0115 (16)
C12	0.0659 (15)	0.0427 (13)	0.0548 (14)	−0.0009 (12)	−0.0038 (12)	−0.0004 (12)
C13	0.0339 (9)	0.0275 (9)	0.0330 (9)	−0.0027 (8)	−0.0068 (8)	0.0000 (8)
C14	0.0333 (9)	0.0388 (11)	0.0309 (9)	−0.0023 (8)	0.0010 (8)	0.0012 (9)
C15	0.0301 (9)	0.0383 (10)	0.0335 (9)	0.0056 (8)	−0.0018 (8)	−0.0032 (8)
C16	0.0409 (11)	0.0345 (10)	0.0337 (9)	0.0091 (9)	−0.0019 (8)	0.0073 (9)
C17	0.0371 (10)	0.0330 (10)	0.0353 (9)	0.0015 (9)	0.0033 (8)	0.0026 (9)
C18	0.0282 (9)	0.0319 (10)	0.0409 (10)	0.0026 (8)	−0.0026 (8)	0.0036 (9)
C19	0.0416 (11)	0.0328 (11)	0.0352 (10)	−0.0025 (9)	−0.0088 (8)	0.0035 (9)

Geometric parameters (Å, °)

C1—N1	1.367 (3)	C11—H11A	0.9600
C1—C6	1.399 (3)	C11—H11B	0.9600
C1—C2	1.411 (3)	C11—H11C	0.9600
C2—C3	1.367 (3)	C12—H12A	0.9600
C2—H2	0.9300	C12—H12B	0.9600
C3—C4	1.377 (4)	C12—H12C	0.9600
C3—H3A	0.9300	C13—C18	1.385 (3)
C4—C5	1.367 (4)	C13—C14	1.393 (3)
C4—H4A	0.9300	C13—C19	1.505 (3)
C5—C6	1.403 (3)	C14—C15	1.382 (3)
C5—H5	0.9300	C14—H14	0.9300
C6—N2	1.436 (3)	C15—O3	1.364 (2)
C7—N2	1.286 (3)	C15—C16	1.385 (3)
C7—C8	1.484 (3)	C16—C17	1.392 (3)
C7—C12	1.489 (3)	C16—H16	0.9300
C8—C9	1.536 (3)	C17—O4	1.368 (2)
C8—H8A	0.9700	C17—C18	1.381 (3)
C8—H8B	0.9700	C18—H18	0.9300
C9—N1	1.440 (3)	C19—O2	1.236 (2)
C9—C11	1.522 (3)	C19—O1	1.267 (2)
C9—C10	1.535 (3)	N1—H1X	0.8741
C10—H10A	0.9600	N2—H2X	0.9917
C10—H10B	0.9600	O3—H3	0.8200
C10—H10C	0.9600	O4—H4	0.8201
N1—C1—C6	127.4 (2)	C9—C11—H11B	109.5
N1—C1—C2	116.8 (2)	H11A—C11—H11B	109.5

C6—C1—C2	115.8 (2)	C9—C11—H11C	109.5
C3—C2—C1	122.9 (2)	H11A—C11—H11C	109.5
C3—C2—H2	118.5	H11B—C11—H11C	109.5
C1—C2—H2	118.5	C7—C12—H12A	109.5
C2—C3—C4	120.5 (2)	C7—C12—H12B	109.5
C2—C3—H3A	119.8	H12A—C12—H12B	109.5
C4—C3—H3A	119.8	C7—C12—H12C	109.5
C5—C4—C3	118.4 (2)	H12A—C12—H12C	109.5
C5—C4—H4A	120.8	H12B—C12—H12C	109.5
C3—C4—H4A	120.8	C18—C13—C14	120.40 (17)
C4—C5—C6	122.0 (2)	C18—C13—C19	120.38 (16)
C4—C5—H5	119.0	C14—C13—C19	119.16 (17)
C6—C5—H5	119.0	C15—C14—C13	119.41 (18)
C1—C6—C5	120.2 (2)	C15—C14—H14	120.3
C1—C6—N2	126.12 (19)	C13—C14—H14	120.3
C5—C6—N2	113.60 (19)	O3—C15—C14	117.00 (17)
N2—C7—C8	122.3 (2)	O3—C15—C16	122.29 (18)
N2—C7—C12	118.7 (2)	C14—C15—C16	120.70 (17)
C8—C7—C12	119.1 (2)	C15—C16—C17	119.28 (18)
C7—C8—C9	114.90 (18)	C15—C16—H16	120.4
C7—C8—H8A	108.5	C17—C16—H16	120.4
C9—C8—H8A	108.5	O4—C17—C18	122.45 (17)
C7—C8—H8B	108.5	O4—C17—C16	116.89 (17)
C9—C8—H8B	108.5	C18—C17—C16	120.64 (18)
H8A—C8—H8B	107.5	C17—C18—C13	119.55 (17)
N1—C9—C11	111.2 (2)	C17—C18—H18	120.2
N1—C9—C10	106.6 (2)	C13—C18—H18	120.2
C11—C9—C10	109.7 (2)	O2—C19—O1	125.03 (19)
N1—C9—C8	109.53 (19)	O2—C19—C13	118.28 (18)
C11—C9—C8	111.0 (2)	O1—C19—C13	116.64 (16)
C10—C9—C8	108.69 (19)	C1—N1—C9	129.36 (19)
C9—C10—H10A	109.5	C1—N1—H1X	113.2
C9—C10—H10B	109.5	C9—N1—H1X	116.7
H10A—C10—H10B	109.5	C7—N2—C6	130.49 (18)
C9—C10—H10C	109.5	C7—N2—H2X	116.3
H10A—C10—H10C	109.5	C6—N2—H2X	113.2
H10B—C10—H10C	109.5	C15—O3—H3	109.5
C9—C11—H11A	109.5	C17—O4—H4	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1X···O4^{i}	0.87	2.11	2.981 (2)	174
N2—H2X···O1^{ii}	0.99	1.69	2.676 (2)	172
O3—H3···O1^{iii}	0.82	1.93	2.721 (2)	163
O4—H4···O2^{ii}	0.82	1.79	2.597 (2)	170
C2—H2···O4^{i}	0.93	2.59	3.366 (3)	142
C5—H5···O1^{ii}	0.93	2.55	3.264 (3)	134

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

Fig. 1

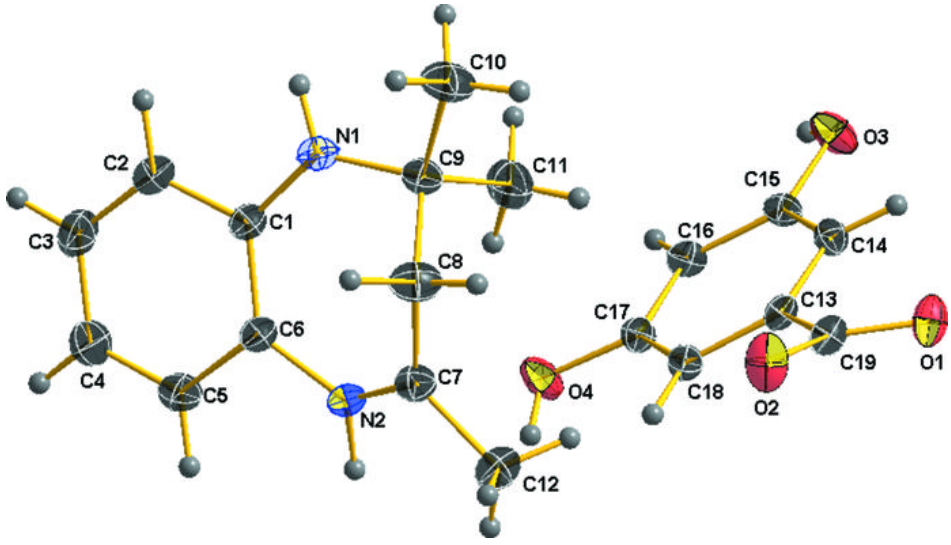

Fig. 2

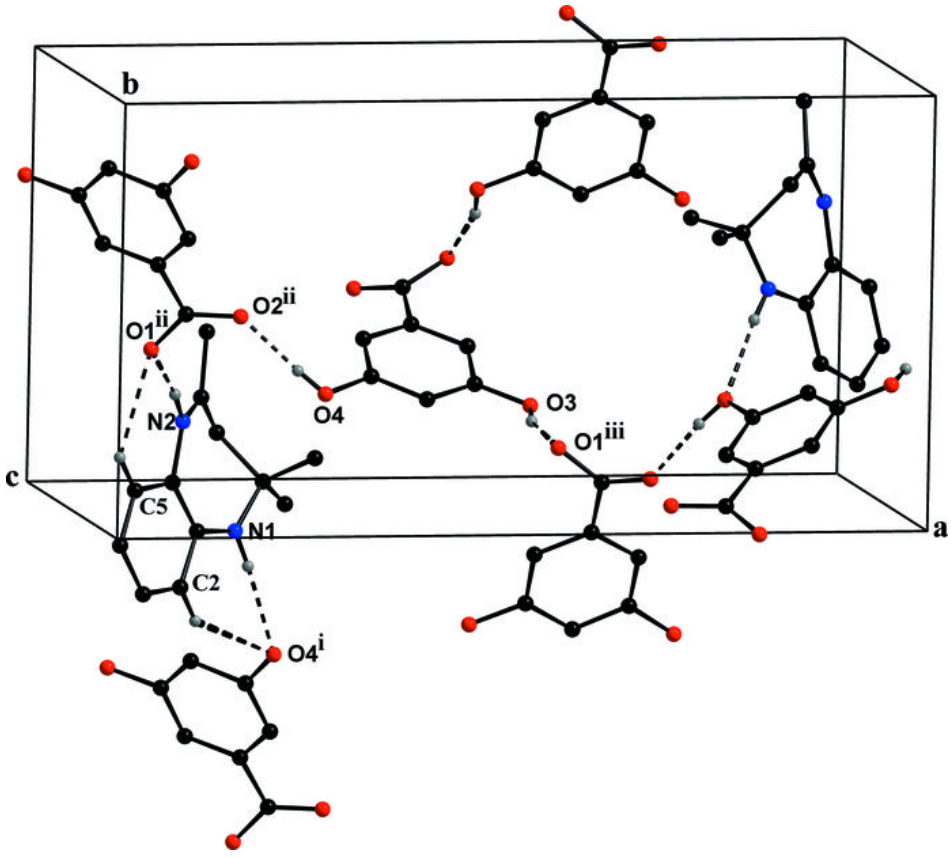

Fig. 3