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Morpholin-4-ium 4-methoxybenzoate 4-methoxybenzoic acid monohydrate

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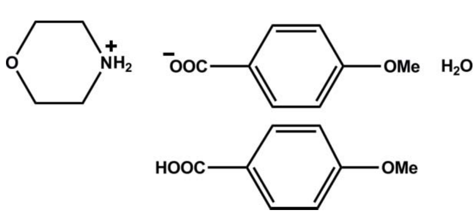
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.063; wR factor = 0.162; data-to-parameter ratio = 18.3.

In the crystal structure of the title compound, $C_4H_{10}NO^+\cdot C_8H_7O_3^-\cdot C_8H_8O_3\cdot H_2O$, cations, anions and neutral molecules are linked by intermolecular N—H⋯O and O—H⋯O hydrogen bonds into chains running parallel to the c axis. The $-CO_2$ groups make dihedral angles of 4.6 (3) and 5.7 (4)° with the attached ring in the 4-methoxybenzoic acid molecule and the 4-methoxybenzoate anion, respectively.

Related literature

For related studies on co-crystals of amino derivatives, see: Fu *et al.* (2010); Aminabhavi *et al.* (1986).



Experimental

Crystal data

$C_4H_{10}NO^+\cdot C_8H_7O_3^-\cdot C_8H_8O_3\cdot H_2O$
M_r = 409.43
Monoclinic, $P2_1/c$
a = 21.874 (4) Å
b = 11.753 (2) Å
c = 8.3618 (17) Å
β = 100.63 (3)°
V = 2112.9 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 K
0.30 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.910, T_{max} = 1.000
21489 measured reflections
4842 independent reflections
2453 reflections with $I > 2\sigma(I)$
R_{int} = 0.077

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.162
S = 1.03
4842 reflections
264 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O5^{i}	0.90	1.75	2.628 (3)	164
N1—H1B⋯O2	0.90	1.96	2.837 (3)	163
O1—H1⋯O1W^{i}	0.82	1.76	2.579 (2)	173
O1W—H1WA⋯O4	0.82	1.91	2.714 (2)	167
O1W—H1WB⋯O4^{ii}	0.82	1.91	2.712 (3)	164

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2614).

References

Aminabhavi, T. M., Biradar, N. S. & Patil, S. B. (1986). *Inorg. Chim. Acta*, **125**, 125–128.
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Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
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supplementary materials

Acta Cryst. (2011). E**67**, o1759 [**doi:10.1107/S1600536811023361**]

Morpholin-4-ium 4-methoxybenzoate 4-methoxybenzoic acid monohydrate

L.-P. Feng and **L. Zhao**

Comment

The amino derivatives have found wide range of applications in material science, such as magnetic, fluorescent and dielectric behaviors, and there has been an increasing interest in the preparation of amino co-crystal compounds (Aminabhavi *et al.,* 1986; Fu, *et al.* 2010). We report here the crystal structure of the title compound, morpholin-4-ium 4-methoxybenzoate 4-methoxybenzoic acid monohydrate.

The asymmetric unit of the title commpound is composed of one 4-methoxybenzoate anion, one morpholin-4-ium cation, one 4-methoxybenzoic acid molecule and one water molecule (Fig. 1). The morpholine ring is in a chair conformation. All geometric parameters are in the normal ranges. In the crystal structure, the H atoms bound to N and O atoms are involved in intermolecular N—H···O and O—H···O hydrogen bonds (Table 1) linking ions and neutral molecules into one-dimensional chains parallel to the *c*-axis (Fig. 2).

Experimental

A mixture of morpholine (0.4 mmol) 4-methoxybenzoic acid (0.8 mmol) was dissolved in distilled water (10 ml). Colourless crystals suitable for X-ray analysis were obtained after 3 days on slow evaporation of the solvent.

Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding, with C–H = 0.93-0.97 Å and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for methyl H atoms. The amine and carboxylic H atoms were located in a difference Fourier map and refined as riding, with the N–H = 0.90 (2) Å, O–H = 0.82 (2) Å, and with U_{iso}(H) = 1.2U_{eq}(N) or 1.5U_{eq}(O).

Figures

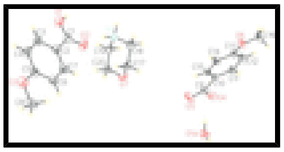

Fig. 1. The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

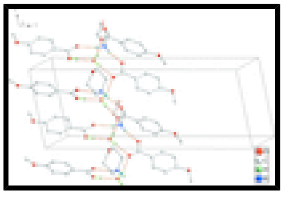

Fig. 2. The crystal packing of the title compound showing a one-dimensional chain (dashed line). Hydrogen atoms not involved in hydrogen bonding (dashed lines) are omitted for clarity.

Morpholin-4-ium 4-methoxybenzoate 4-methoxybenzoic acid monohydrate

Crystal data

$C_4H_{10}NO^+ \cdot C_8H_7O_3^- \cdot C_8H_8O_3 \cdot H_2O$	$F(000) = 872$
$M_r = 409.43$	$D_x = 1.287$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 4842 reflections
$a = 21.874$ (4) Å	$\theta = 3.0–27.5°$
$b = 11.753$ (2) Å	$\mu = 0.10$ mm^{-1}
$c = 8.3618$ (17) Å	$T = 298$ K
$\beta = 100.63$ (3)°	Needle, colourless
$V = 2112.9$ (7) Å^3	0.30 × 0.05 × 0.05 mm
$Z = 4$	

Data collection

Rigaku Mercury2 diffractometer	4842 independent reflections
Radiation source: fine-focus sealed tube	2453 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.077$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
CCD profile fitting scans	$h = -28 \rightarrow 27$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -15 \rightarrow 15$
$T_{min} = 0.910$, $T_{max} = 1.000$	$l = -10 \rightarrow 10$
21489 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.063$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.162$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.3115P]$ where $P = (F_o^2 + 2F_c^2)/3$
4842 reflections	$(\Delta/\sigma)_{max} < 0.001$
264 parameters	$\Delta\rho_{max} = 0.16$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ 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 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}
O4	0.30003 (8)	0.67567 (15)	0.28036 (19)	0.0575 (5)
C10	0.40047 (10)	0.61009 (19)	0.2544 (3)	0.0400 (5)
O6	0.56764 (7)	0.62620 (15)	0.0900 (2)	0.0653 (5)
C12	0.46359 (11)	0.6996 (2)	0.0826 (3)	0.0517 (6)
H12A	0.4682	0.7552	0.0067	0.062*
C14	0.50318 (12)	0.5405 (2)	0.2459 (3)	0.0556 (7)
H14A	0.5350	0.4887	0.2807	0.067*
C13	0.51084 (11)	0.6245 (2)	0.1353 (3)	0.0452 (6)
O5	0.34193 (10)	0.53418 (18)	0.4368 (3)	0.0845 (7)
C15	0.44880 (12)	0.5339 (2)	0.3038 (3)	0.0497 (6)
H15A	0.4441	0.4771	0.3780	0.060*
C11	0.40899 (11)	0.6921 (2)	0.1430 (3)	0.0486 (6)
H11A	0.3772	0.7438	0.1075	0.058*
C9	0.34312 (12)	0.6061 (2)	0.3279 (3)	0.0493 (6)
C16	0.57873 (13)	0.7102 (3)	−0.0241 (4)	0.0756 (9)
H16A	0.6193	0.6990	−0.0499	0.113*
H16B	0.5765	0.7846	0.0221	0.113*
H16C	0.5479	0.7038	−0.1215	0.113*
O1W	0.23075 (8)	0.74295 (15)	0.5012 (2)	0.0634 (5)
H1WA	0.2490	0.7132	0.4346	0.095*
H1WB	0.2567	0.7703	0.5746	0.095*
N1	0.26721 (9)	0.00361 (15)	0.1437 (2)	0.0462 (5)
H1A	0.2883	−0.0209	0.0674	0.055*
H1B	0.2299	−0.0308	0.1336	0.055*
O1	0.11518 (8)	−0.23024 (16)	0.0259 (2)	0.0703 (6)
H1	0.1514	−0.2296	0.0125	0.105*
O7	0.26402 (9)	0.14332 (16)	0.4181 (2)	0.0696 (6)
C1	0.10461 (12)	−0.1389 (2)	0.1073 (3)	0.0526 (6)
C2	0.04022 (11)	−0.1286 (2)	0.1359 (3)	0.0469 (6)
O2	0.14422 (8)	−0.06853 (17)	0.1541 (3)	0.0785 (6)
C5	−0.08025 (12)	−0.0989 (2)	0.1886 (3)	0.0550 (7)
O3	−0.14078 (8)	−0.09074 (17)	0.2062 (3)	0.0777 (6)
C7	0.02520 (12)	−0.0385 (2)	0.2269 (3)	0.0587 (7)
H7A	0.0560	0.0130	0.2708	0.070*
C4	−0.06580 (12)	−0.1890 (2)	0.0972 (4)	0.0661 (8)
H4A	−0.0968	−0.2402	0.0528	0.079*
C6	−0.03452 (12)	−0.0231 (2)	0.2543 (3)	0.0594 (7)
H6A	−0.0438	0.0378	0.3167	0.071*

C3	−0.00622 (11)	−0.2043 (2)	0.0707 (3)	0.0571 (7)
H3A	0.0029	−0.2657	0.0089	0.069*
C19	0.30232 (12)	−0.0252 (2)	0.3071 (3)	0.0533 (7)
H19A	0.3443	0.0047	0.3197	0.064*
H19B	0.3050	−0.1072	0.3196	0.064*
C18	0.25775 (15)	0.1276 (2)	0.1291 (3)	0.0706 (8)
H18A	0.2314	0.1452	0.0255	0.085*
H18B	0.2975	0.1652	0.1328	0.085*
C20	0.27063 (14)	0.0242 (2)	0.4338 (3)	0.0671 (8)
H20A	0.2298	−0.0101	0.4253	0.081*
H20B	0.2944	0.0063	0.5405	0.081*
C8	−0.15903 (14)	0.0060 (3)	0.2886 (4)	0.0879 (10)
H8A	−0.2034	0.0060	0.2798	0.132*
H8B	−0.1463	0.0740	0.2404	0.132*
H8C	−0.1396	0.0030	0.4013	0.132*
C17	0.22811 (15)	0.1700 (2)	0.2644 (4)	0.0769 (9)
H17A	0.2230	0.2518	0.2550	0.092*
H17B	0.1872	0.1362	0.2555	0.092*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O4	0.0538 (11)	0.0730 (12)	0.0469 (10)	0.0087 (10)	0.0126 (8)	0.0003 (9)
C10	0.0456 (14)	0.0418 (13)	0.0326 (12)	−0.0019 (11)	0.0079 (11)	−0.0025 (10)
O6	0.0477 (11)	0.0712 (13)	0.0804 (13)	0.0108 (9)	0.0210 (10)	0.0273 (10)
C12	0.0467 (15)	0.0578 (16)	0.0495 (14)	0.0032 (12)	0.0063 (12)	0.0211 (12)
C14	0.0563 (16)	0.0518 (16)	0.0604 (16)	0.0163 (13)	0.0155 (14)	0.0141 (13)
C13	0.0406 (14)	0.0485 (15)	0.0465 (14)	0.0004 (11)	0.0082 (11)	0.0052 (12)
O5	0.0960 (16)	0.0856 (15)	0.0870 (15)	0.0203 (12)	0.0561 (13)	0.0340 (12)
C15	0.0636 (17)	0.0413 (14)	0.0459 (14)	0.0051 (12)	0.0146 (13)	0.0096 (11)
C11	0.0451 (15)	0.0513 (15)	0.0478 (14)	0.0083 (11)	0.0042 (12)	0.0115 (12)
C9	0.0592 (17)	0.0516 (16)	0.0387 (14)	−0.0028 (13)	0.0132 (13)	−0.0047 (12)
C16	0.0621 (19)	0.076 (2)	0.095 (2)	0.0011 (15)	0.0328 (17)	0.0317 (18)
O1W	0.0488 (10)	0.0806 (14)	0.0636 (12)	−0.0085 (9)	0.0179 (9)	−0.0138 (10)
N1	0.0494 (12)	0.0429 (11)	0.0500 (12)	−0.0063 (9)	0.0189 (10)	−0.0085 (9)
O1	0.0494 (11)	0.0678 (13)	0.0960 (15)	−0.0007 (9)	0.0197 (10)	−0.0159 (11)
O7	0.0921 (15)	0.0609 (13)	0.0555 (12)	0.0106 (10)	0.0132 (10)	−0.0171 (10)
C1	0.0443 (15)	0.0538 (17)	0.0588 (16)	0.0016 (13)	0.0075 (13)	0.0077 (13)
C2	0.0421 (14)	0.0471 (15)	0.0507 (14)	−0.0015 (11)	0.0061 (12)	0.0062 (12)
O2	0.0450 (11)	0.0735 (14)	0.1168 (17)	−0.0146 (10)	0.0145 (11)	−0.0202 (12)
C5	0.0444 (15)	0.0568 (17)	0.0662 (17)	−0.0019 (13)	0.0165 (13)	0.0060 (14)
O3	0.0516 (12)	0.0812 (14)	0.1071 (16)	−0.0047 (10)	0.0327 (11)	−0.0130 (12)
C7	0.0471 (16)	0.0622 (17)	0.0655 (17)	−0.0077 (13)	0.0070 (14)	−0.0077 (14)
C4	0.0475 (16)	0.0589 (18)	0.092 (2)	−0.0117 (13)	0.0143 (15)	−0.0122 (16)
C6	0.0594 (18)	0.0560 (17)	0.0636 (17)	−0.0009 (13)	0.0137 (14)	−0.0081 (13)
C3	0.0474 (16)	0.0486 (15)	0.0761 (19)	−0.0017 (12)	0.0137 (14)	−0.0067 (13)
C19	0.0523 (15)	0.0430 (14)	0.0625 (17)	0.0021 (12)	0.0051 (13)	−0.0009 (12)
C18	0.110 (2)	0.0468 (17)	0.0551 (17)	0.0088 (16)	0.0145 (17)	0.0071 (13)

C20	0.091 (2)	0.065 (2)	0.0461 (15)	0.0022 (16)	0.0145 (15)	0.0004 (14)
C8	0.069 (2)	0.108 (3)	0.095 (2)	0.0141 (19)	0.0372 (19)	−0.009 (2)
C17	0.097 (2)	0.0520 (17)	0.079 (2)	0.0267 (16)	0.0081 (18)	−0.0102 (15)

Geometric parameters (Å, °)

O4—C9	1.256 (3)	C1—O2	1.209 (3)
C10—C11	1.377 (3)	C1—C2	1.476 (3)
C10—C15	1.389 (3)	C2—C7	1.379 (3)
C10—C9	1.496 (3)	C2—C3	1.384 (3)
O6—C13	1.364 (3)	C5—O3	1.362 (3)
O6—C16	1.425 (3)	C5—C6	1.376 (3)
C12—C13	1.369 (3)	C5—C4	1.377 (4)
C12—C11	1.383 (3)	O3—C8	1.424 (3)
C12—H12A	0.9300	C7—C6	1.379 (3)
C14—C15	1.367 (3)	C7—H7A	0.9300
C14—C13	1.384 (3)	C4—C3	1.374 (3)
C14—H14A	0.9300	C4—H4A	0.9300
O5—C9	1.246 (3)	C6—H6A	0.9300
C15—H15A	0.9300	C3—H3A	0.9300
C11—H11A	0.9300	C19—C20	1.487 (3)
C16—H16A	0.9600	C19—H19A	0.9700
C16—H16B	0.9600	C19—H19B	0.9700
C16—H16C	0.9600	C18—C17	1.490 (4)
O1W—H1WA	0.8204	C18—H18A	0.9700
O1W—H1WB	0.8203	C18—H18B	0.9700
N1—C18	1.474 (3)	C20—H20A	0.9700
N1—C19	1.478 (3)	C20—H20B	0.9700
N1—H1A	0.9004	C8—H8A	0.9600
N1—H1B	0.9004	C8—H8B	0.9600
O1—C1	1.315 (3)	C8—H8C	0.9600
O1—H1	0.8206	C17—H17A	0.9700
O7—C20	1.411 (3)	C17—H17B	0.9700
O7—C17	1.412 (3)		
C11—C10—C15	117.5 (2)	C6—C5—C4	119.7 (2)
C11—C10—C9	121.9 (2)	C5—O3—C8	118.2 (2)
C15—C10—C9	120.5 (2)	C2—C7—C6	121.5 (2)
C13—O6—C16	118.19 (19)	C2—C7—H7A	119.3
C13—C12—C11	119.6 (2)	C6—C7—H7A	119.3
C13—C12—H12A	120.2	C3—C4—C5	120.8 (2)
C11—C12—H12A	120.2	C3—C4—H4A	119.6
C15—C14—C13	119.9 (2)	C5—C4—H4A	119.6
C15—C14—H14A	120.1	C5—C6—C7	119.3 (2)
C13—C14—H14A	120.1	C5—C6—H6A	120.3
O6—C13—C12	125.0 (2)	C7—C6—H6A	120.3
O6—C13—C14	115.1 (2)	C4—C3—C2	120.1 (2)
C12—C13—C14	119.8 (2)	C4—C3—H3A	120.0
C14—C15—C10	121.5 (2)	C2—C3—H3A	120.0
C14—C15—H15A	119.2	N1—C19—C20	109.8 (2)

C10—C15—H15A	119.2	N1—C19—H19A	109.7
C10—C11—C12	121.7 (2)	C20—C19—H19A	109.7
C10—C11—H11A	119.1	N1—C19—H19B	109.7
C12—C11—H11A	119.1	C20—C19—H19B	109.7
O5—C9—O4	123.9 (2)	H19A—C19—H19B	108.2
O5—C9—C10	117.0 (2)	N1—C18—C17	110.0 (2)
O4—C9—C10	119.1 (2)	N1—C18—H18A	109.7
O6—C16—H16A	109.5	C17—C18—H18A	109.7
O6—C16—H16B	109.5	N1—C18—H18B	109.7
H16A—C16—H16B	109.5	C17—C18—H18B	109.7
O6—C16—H16C	109.5	H18A—C18—H18B	108.2
H16A—C16—H16C	109.5	O7—C20—C19	112.0 (2)
H16B—C16—H16C	109.5	O7—C20—H20A	109.2
H1WA—O1W—H1WB	108.6	C19—C20—H20A	109.2
C18—N1—C19	110.12 (19)	O7—C20—H20B	109.2
C18—N1—H1A	109.9	C19—C20—H20B	109.2
C19—N1—H1A	109.6	H20A—C20—H20B	107.9
C18—N1—H1B	109.0	O3—C8—H8A	109.5
C19—N1—H1B	106.9	O3—C8—H8B	109.5
H1A—N1—H1B	111.3	H8A—C8—H8B	109.5
C1—O1—H1	109.2	O3—C8—H8C	109.5
C20—O7—C17	109.6 (2)	H8A—C8—H8C	109.5
O2—C1—O1	122.8 (2)	H8B—C8—H8C	109.5
O2—C1—C2	122.7 (3)	O7—C17—C18	111.7 (2)
O1—C1—C2	114.5 (2)	O7—C17—H17A	109.3
C7—C2—C3	118.6 (2)	C18—C17—H17A	109.3
C7—C2—C1	118.9 (2)	O7—C17—H17B	109.3
C3—C2—C1	122.4 (2)	C18—C17—H17B	109.3
O3—C5—C6	124.1 (2)	H17A—C17—H17B	107.9
O3—C5—C4	116.2 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O5^{i}	0.90	1.75	2.628 (3)	164
N1—H1B···O2	0.90	1.96	2.837 (3)	163
O1—H1···O1W^{i}	0.82	1.76	2.579 (2)	173
O1W—H1WA···O4	0.82	1.91	2.714 (2)	167
O1W—H1WB···O4^{ii}	0.82	1.91	2.712 (3)	164

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

Fig. 1

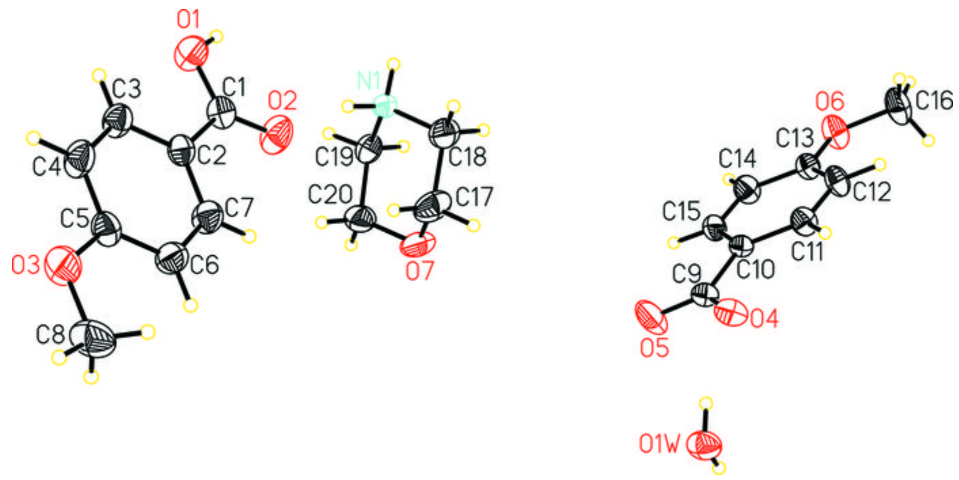
O1
C3
C1
O2
N1
C16
O6
C4
C2
C19
C18
C13
C14
C12
C7
C20
C17
C5
C15
C11
C6
C10
O3
O7
C9
O4
C8
O5
O1W

Fig. 2