Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Imidazolium 4-nitrophenolate 4-nitrophenol monohydrate

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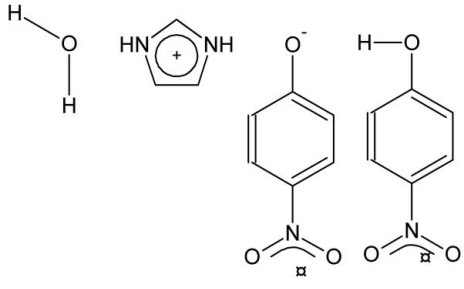
Received 1 August 2007; accepted 12 August 2007

Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.002 Å; R factor = 0.047; wR factor = 0.157; data-to-parameter ratio = 21.0.

In the title compound, $C_3H_5N_2^+\cdot C_6H_4NO_3^-\cdot C_6H_5NO_3\cdot H_2O$, the imidazolium ring is planar to within 0.002 Å and the nitro groups are approximately coplanar with the benzene rings to which they are bonded in both the 4-nitrophenolate and the 4-nitrophenol molecules [dihedral angles = 4.7 (1) and 1.1 (1)°, respectively]. An extensive network of O—H···O and N—H···O hydrogen bonds gives rise to one-dimensional zigzag chains running along the c axis, which are linked into layers in the (100) plane.

Related literature

For related literature, see: Vembu *et al.* (2003).



Experimental

Crystal data

$C_3H_5N_2^+\cdot C_6H_4NO_3^-\cdot C_6H_5NO_3\cdot H_2O$
M_r = 364.32
Monoclinic, $P2_1/c$
a = 20.6543 (3) Å
b = 3.7998 (1) Å
c = 21.6509 (3) Å
β = 100.832 (1)°
V = 1668.93 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 273 (2) K
0.32 × 0.22 × 0.20 mm

Data collection

Bruker APEX II CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.91, T_{max} = 0.98
64485 measured reflections
5070 independent reflections
3124 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.157
S = 1.04
5070 reflections
242 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{i}	0.86	1.76	2.6198 (18)	175
N2—H2···O7	0.86	1.81	2.667 (2)	172
O6—H6···O3	0.82	1.71	2.5213 (15)	169
O7—H7A···O6^{ii}	0.86 (2)	1.92 (2)	2.773 (2)	173 (3)
O7—H7B···O2^{iii}	0.82 (2)	2.09 (2)	2.858 (2)	156 (3)

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

This work was supported by Fundação para a Ciência e a Tecnologia (FCT).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2228).

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supplementary materials

Acta Cryst. (2007). E**63**, o4031 [**doi:10.1107/S1600536807039992**]

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Comment

Organic molecules with π electrons polarized by Lewis acid/base groups exhibit significant electric dipolar moments. This is convenient for the design of new materials with enhanced non-linear optical (NLO) properties. 4-Nitrophenol (4NP) can act as a π acceptor, forming π stacking compounds with other aromatic molecules, and is also a moderate acid which often gives rise to hydrogen-bonded compounds (Vembu *et al.*, 2003). The synthesis and structural characterization of the title compound was carried out in an attempt to prepare a new molecular crystalline material with significant NLO properties. However, the compound crystallizes in a centrosymmetric space group, and no significant second harmonic intensity is observed.

The asymmetric unit (Fig. 1) contains two 4NP molecules and one imidazole (IM) molecule. The positions of the protons were established taking into account the C—O distances in each acidic hydroxyl group of the 4NP molecules, the Fourier difference density map and the overall charge neutrality of the compound. O—H···O and N—H···O hydrogen bonds give rise to zigzag chains running parallel to the *c* axis. In these chains, the repeat sequence comprises an imidazolium cation, a water molecule, a 4NP molecule and a 4-nitrophenolate (4NP–) anion, the latter two lying in a tail-to-tail arrangement. The 4NP– anions connect two different chains (running in opposite directions) *via* atoms O2 and O3, which are acceptors of two hydrogen bonds. A 2-D hydrogen bonded network is therefore established in the (100) plane.

Experimental

Analytical grade imidazole (Aldrich) and 4-nitrophenol (Aldrich) were dissolved separately in water and methanol, respectively. The solutions were mixed in a 1:2 molar ratio and stirred at 323 K for several hours, then allowed to cool to room temperature. Crystals were obtained after two weeks by slow evaporation.

Refinement

All H atoms were visible in difference Fourier maps. Those bonded to C atoms and carboxyl O atoms were placed at idealized positions and refined as riding [C—H = 0.97 or 0.98 Å, O—H = 0.82 Å, U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O)]. Those belonging to the water molecule were included in their as-found positions and refined with the O—H distance restrained to be 0.89 (1) Å and with U_{iso}(H) = 1.5U_{eq}(O).

Figures

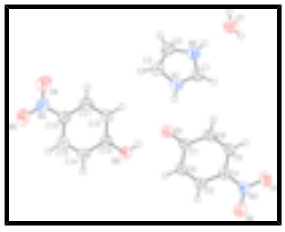

Fig. 1. Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level for non-H atoms.

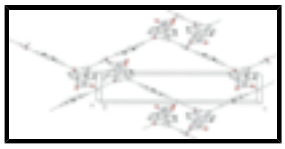

Fig. 2. Packing of molecules showing two zigzag chain running along the *c* axis. The 2-D network in the (100) plane is completed by integer translations along *b*.

Imidazolium 4-nitrophenolate 4-nitrophenol monohydrate

Crystal data

$C_3H_5N_2^+ \cdot C_6H_4NO_3^- \cdot C_6H_5NO_3 \cdot H_2O$	$F_{000} = 760$
$M_r = 364.32$	$D_x = 1.450$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8152 reflections
$a = 20.6543$ (3) Å	$\theta = 2.3$–28.0º
$b = 3.7998$ (1) Å	$\mu = 0.12$ mm^{-1}
$c = 21.6509$ (3) Å	$T = 273$ (2) K
$\beta = 100.832$ (1)º	Block, colourless
$V = 1668.93$ (6) Å^3	0.32 × 0.22 × 0.20 mm
$Z = 4$	

Data collection

Bruker APEX II CCD diffractometer	5070 independent reflections
Radiation source: fine-focus sealed tube	3124 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.037$
$T = 273$(2) K	$\theta_{max} = 30.5$º
φ and ω scans	$\theta_{min} = 1.0$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -28 \rightarrow 29$
$T_{min} = 0.91$, $T_{max} = 0.98$	$k = -5 \rightarrow 5$
64485 measured reflections	$l = -30 \rightarrow 28$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.157$	$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.4455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
5070 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
242 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
2 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}
N1	0.24632 (7)	0.5142 (4)	0.28812 (6)	0.0453 (3)
H1	0.2309	0.6083	0.2522	0.054*
C1	0.21230 (8)	0.4289 (5)	0.33129 (8)	0.0502 (4)
H1A	0.1671	0.4605	0.3280	0.060*
N2	0.25219 (7)	0.2912 (4)	0.38017 (7)	0.0501 (4)
H2	0.2409	0.2171	0.4141	0.075*
C2	0.31425 (9)	0.2867 (5)	0.36755 (9)	0.0538 (4)
H2A	0.3520	0.2024	0.3937	0.065*
C3	0.31050 (8)	0.4270 (5)	0.31036 (9)	0.0518 (4)
H3	0.3455	0.4593	0.2894	0.062*
O1	−0.08257 (6)	0.3716 (5)	0.14603 (6)	0.0713 (4)
O2	−0.06841 (7)	0.3946 (5)	0.05064 (7)	0.0805 (5)
N3	−0.04774 (7)	0.3245 (4)	0.10640 (7)	0.0488 (4)
C4	0.01766 (7)	0.1921 (4)	0.12502 (7)	0.0391 (3)
C5	0.05858 (8)	0.1678 (5)	0.08089 (7)	0.0449 (4)
H5	0.0433	0.2346	0.0394	0.054*
C6	0.12145 (8)	0.0447 (5)	0.09921 (7)	0.0457 (4)
H6A	0.1488	0.0305	0.0698	0.055*
C7	0.14569 (7)	−0.0610 (4)	0.16142 (7)	0.0384 (3)
O3	0.20579 (5)	−0.1830 (3)	0.17899 (5)	0.0489 (3)
C8	0.10277 (8)	−0.0309 (5)	0.20472 (7)	0.0443 (4)
H8	0.1175	−0.0983	0.2463	0.053*

C9	0.04013 (8)	0.0946 (5)	0.18709 (7)	0.0444 (4)
H9	0.0127	0.1146	0.2164	0.053*
O4	0.54689 (7)	0.4274 (5)	0.17607 (8)	0.0818 (5)
O5	0.54652 (7)	0.3441 (5)	0.07800 (8)	0.0848 (5)
N4	0.52012 (7)	0.3238 (4)	0.12386 (8)	0.0580 (4)
C10	0.45462 (8)	0.1720 (4)	0.11626 (8)	0.0443 (4)
C11	0.42407 (8)	0.1463 (5)	0.16755 (8)	0.0478 (4)
H11	0.4454	0.2222	0.2070	0.057*
C12	0.36168 (8)	0.0070 (5)	0.15963 (8)	0.0461 (4)
H12	0.3407	−0.0114	0.1939	0.055*
C13	0.32958 (7)	−0.1069 (4)	0.10057 (7)	0.0405 (3)
O6	0.26930 (5)	−0.2495 (4)	0.09096 (6)	0.0518 (3)
H6	0.2531	−0.2223	0.1224	0.078*
C14	0.36155 (8)	−0.0784 (5)	0.04971 (7)	0.0469 (4)
H14	0.3405	−0.1548	0.0102	0.056*
C15	0.42381 (8)	0.0612 (5)	0.05720 (8)	0.0498 (4)
H15	0.4450	0.0810	0.0230	0.060*
O7	0.20602 (7)	0.0530 (6)	0.47937 (7)	0.0836 (5)
H7A	0.2284 (14)	−0.045 (8)	0.5123 (11)	0.125*
H7B	0.1710 (11)	−0.045 (8)	0.4664 (15)	0.125*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0431 (7)	0.0532 (8)	0.0387 (7)	0.0022 (6)	0.0053 (6)	0.0022 (6)
C1	0.0390 (9)	0.0647 (11)	0.0467 (9)	0.0071 (8)	0.0079 (7)	0.0063 (8)
N2	0.0506 (8)	0.0570 (9)	0.0422 (8)	0.0052 (7)	0.0076 (6)	0.0069 (6)
C2	0.0425 (9)	0.0606 (11)	0.0541 (11)	0.0073 (8)	−0.0015 (8)	0.0010 (8)
C3	0.0389 (9)	0.0635 (11)	0.0536 (10)	0.0010 (8)	0.0103 (8)	−0.0019 (9)
O1	0.0507 (7)	0.1097 (12)	0.0596 (8)	0.0178 (8)	0.0265 (6)	0.0075 (8)
O2	0.0482 (8)	0.1416 (15)	0.0505 (8)	0.0238 (9)	0.0064 (6)	0.0204 (9)
N3	0.0396 (7)	0.0647 (9)	0.0439 (8)	0.0027 (6)	0.0121 (6)	0.0044 (7)
C4	0.0354 (8)	0.0449 (8)	0.0375 (8)	−0.0014 (6)	0.0086 (6)	0.0012 (6)
C5	0.0435 (9)	0.0617 (10)	0.0301 (7)	0.0036 (7)	0.0082 (6)	0.0062 (7)
C6	0.0420 (8)	0.0627 (10)	0.0349 (8)	0.0043 (7)	0.0139 (7)	0.0057 (7)
C7	0.0377 (8)	0.0418 (8)	0.0359 (8)	−0.0026 (6)	0.0071 (6)	0.0003 (6)
O3	0.0389 (6)	0.0672 (8)	0.0404 (6)	0.0060 (5)	0.0071 (5)	0.0079 (5)
C8	0.0497 (9)	0.0544 (9)	0.0292 (7)	0.0040 (7)	0.0083 (6)	0.0048 (6)
C9	0.0461 (9)	0.0544 (9)	0.0362 (8)	0.0023 (7)	0.0168 (7)	0.0032 (7)
O4	0.0519 (8)	0.1126 (13)	0.0765 (10)	−0.0197 (8)	0.0008 (7)	−0.0298 (9)
O5	0.0540 (8)	0.1253 (15)	0.0798 (11)	−0.0267 (9)	0.0246 (8)	−0.0126 (10)
N4	0.0405 (8)	0.0639 (10)	0.0682 (11)	−0.0034 (7)	0.0065 (8)	−0.0075 (8)
C10	0.0348 (8)	0.0479 (9)	0.0489 (9)	0.0017 (7)	0.0043 (7)	−0.0023 (7)
C11	0.0464 (9)	0.0543 (10)	0.0398 (8)	−0.0001 (7)	0.0002 (7)	−0.0051 (7)
C12	0.0467 (9)	0.0553 (10)	0.0371 (8)	−0.0020 (7)	0.0099 (7)	−0.0034 (7)
C13	0.0356 (8)	0.0449 (8)	0.0403 (8)	0.0038 (6)	0.0055 (6)	−0.0018 (6)
O6	0.0381 (6)	0.0737 (8)	0.0445 (7)	−0.0060 (6)	0.0101 (5)	−0.0105 (6)
C14	0.0432 (9)	0.0627 (10)	0.0341 (8)	−0.0011 (7)	0.0048 (7)	−0.0066 (7)

C15	0.0433 (9)	0.0636 (11)	0.0441 (9)	0.0011 (8)	0.0127 (7)	−0.0024 (8)
O7	0.0493 (8)	0.1412 (16)	0.0569 (9)	−0.0156 (9)	0.0011 (7)	0.0356 (10)

Geometric parameters (Å, °)

N1—C1	1.311 (2)	C8—C9	1.365 (2)
N1—C3	1.364 (2)	C8—H8	0.930
N1—H1	0.860	C9—H9	0.930
C1—N2	1.321 (2)	O4—N4	1.226 (2)
C1—H1A	0.930	O5—N4	1.222 (2)
N2—C2	1.360 (2)	N4—C10	1.451 (2)
N2—H2	0.860	C10—C11	1.380 (2)
C2—C3	1.337 (3)	C10—C15	1.383 (2)
C2—H2A	0.930	C11—C12	1.374 (2)
C3—H3	0.930	C11—H11	0.930
O1—N3	1.2320 (18)	C12—C13	1.394 (2)
O2—N3	1.2316 (19)	C12—H12	0.930
N3—C4	1.427 (2)	C13—O6	1.3380 (18)
C4—C9	1.387 (2)	C13—C14	1.391 (2)
C4—C5	1.393 (2)	O6—H6	0.820
C5—C6	1.367 (2)	C14—C15	1.372 (2)
C5—H5	0.930	C14—H14	0.930
C6—C7	1.405 (2)	C15—H15	0.930
C6—H6A	0.930	O7—H7A	0.86 (2)
C7—O3	1.3125 (18)	O7—H7B	0.82 (2)
C7—C8	1.411 (2)		
C1—N1—C3	107.68 (14)	C9—C8—C7	121.58 (14)
C1—N1—H1	126.2	C9—C8—H8	119.2
C3—N1—H1	126.2	C7—C8—H8	119.2
N1—C1—N2	109.38 (15)	C8—C9—C4	119.44 (14)
N1—C1—H1A	125.3	C8—C9—H9	120.3
N2—C1—H1A	125.3	C4—C9—H9	120.3
C1—N2—C2	108.28 (15)	O5—N4—O4	122.41 (16)
C1—N2—H2	125.9	O5—N4—C10	118.82 (16)
C2—N2—H2	125.9	O4—N4—C10	118.77 (16)
C3—C2—N2	106.76 (15)	C11—C10—C15	121.46 (15)
C3—C2—H2A	126.6	C11—C10—N4	119.64 (15)
N2—C2—H2A	126.6	C15—C10—N4	118.89 (15)
C2—C3—N1	107.90 (15)	C12—C11—C10	119.15 (15)
C2—C3—H3	126.1	C12—C11—H11	120.4
N1—C3—H3	126.1	C10—C11—H11	120.4
O2—N3—O1	120.74 (14)	C11—C12—C13	120.49 (15)
O2—N3—C4	119.25 (13)	C11—C12—H12	119.8
O1—N3—C4	120.00 (14)	C13—C12—H12	119.8
C9—C4—C5	120.76 (14)	O6—C13—C14	118.35 (14)
C9—C4—N3	119.64 (13)	O6—C13—C12	122.46 (14)
C5—C4—N3	119.59 (14)	C14—C13—C12	119.18 (14)
C6—C5—C4	119.30 (14)	C13—O6—H6	109.5
C6—C5—H5	120.3	C15—C14—C13	120.68 (15)

C4—C5—H5	120.3	C15—C14—H14	119.7
C5—C6—C7	121.61 (14)	C13—C14—H14	119.7
C5—C6—H6A	119.2	C14—C15—C10	119.03 (15)
C7—C6—H6A	119.2	C14—C15—H15	120.5
O3—C7—C6	121.74 (13)	C10—C15—H15	120.5
O3—C7—C8	120.94 (14)	H7A—O7—H7B	113 (3)
C6—C7—C8	117.31 (14)		
C3—N1—C1—N2	0.1 (2)	C5—C4—C9—C8	−0.9 (3)
N1—C1—N2—C2	−0.3 (2)	N3—C4—C9—C8	−179.83 (15)
C1—N2—C2—C3	0.4 (2)	O5—N4—C10—C11	179.88 (18)
N2—C2—C3—N1	−0.4 (2)	O4—N4—C10—C11	−0.2 (3)
C1—N1—C3—C2	0.2 (2)	O5—N4—C10—C15	−1.1 (3)
O2—N3—C4—C9	−176.55 (17)	O4—N4—C10—C15	178.77 (18)
O1—N3—C4—C9	4.4 (3)	C15—C10—C11—C12	0.1 (3)
O2—N3—C4—C5	4.5 (3)	N4—C10—C11—C12	179.04 (16)
O1—N3—C4—C5	−174.57 (17)	C10—C11—C12—C13	0.0 (3)
C9—C4—C5—C6	0.3 (3)	C11—C12—C13—O6	178.85 (16)
N3—C4—C5—C6	179.24 (16)	C11—C12—C13—C14	0.1 (3)
C4—C5—C6—C7	0.6 (3)	O6—C13—C14—C15	−179.06 (16)
C5—C6—C7—O3	179.24 (16)	C12—C13—C14—C15	−0.3 (3)
C5—C6—C7—C8	−0.8 (3)	C13—C14—C15—C10	0.3 (3)
O3—C7—C8—C9	−179.85 (16)	C11—C10—C15—C14	−0.2 (3)
C6—C7—C8—C9	0.2 (3)	N4—C10—C15—C14	−179.21 (16)
C7—C8—C9—C4	0.6 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3^{i}	0.86	1.76	2.6198 (18)	175
N2—H2···O7	0.86	1.81	2.667 (2)	172
O6—H6···O3	0.82	1.71	2.5213 (15)	169
O7—H7A···O6^{ii}	0.86 (2)	1.92 (2)	2.773 (2)	173 (3)
O7—H7B···O2^{iii}	0.82 (2)	2.09 (2)	2.858 (2)	156 (3)

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

Fig. 1

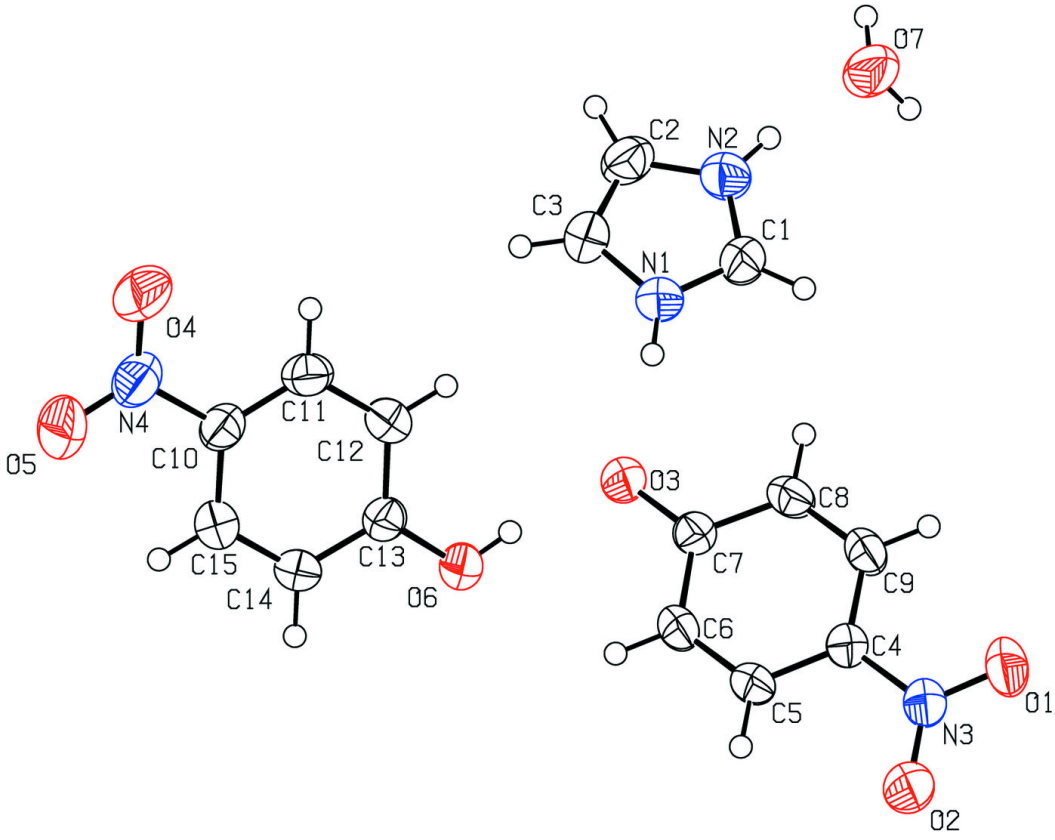
O7
C2
N2
C3
C1
N1
O4
N4
C11
C12
O5
C10
C15
C13
C14
O6
O3
C8
C7
C9
C6
C4
C5
O1
N3
O2

Fig. 2