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A second monoclinic modification of benzimidazolium 3-carboxyphenoxyacetate 3-carboxyphenoxyacetic acid

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In the primitive monoclinic modification of the title compound, $C_7H_7N_2^+\cdot C_9H_7O_5^-\cdot C_9H_8O_5$, the two monoanions are connected by an 'acid' O—H···O hydrogen bond whose H atom does not lie on a special position. This acid hydrogen atom and the two monoanions comprise a carboxylate monoanion/neutral molecule in which the acid H atom is disordered between the two monoanionic units. The chains are connected into a layer structure through the $C_7H_7N_2^+$ cations *via* N—H···O hydrogen bonds.

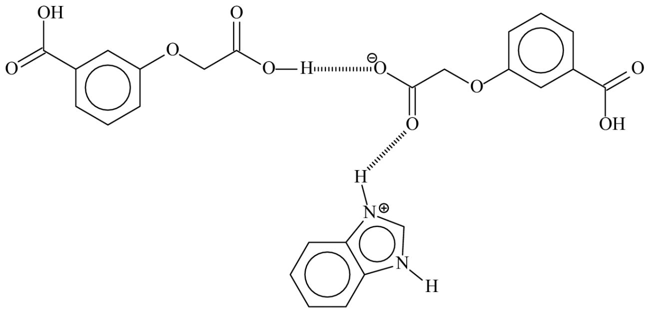
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.051
wR factor = 0.123
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In *C*-centered monoclinic $C_7H_7N_2^+\cdot CHO_2C_6H_4OCH_2CO_2^-\cdot CHO_2C_6H_4OCH_2CO_2H$, the $C_9H_7O_5^-$ anion and the $C_9H_8O_5$ molecule are linked through the carboxyl –CO_2H substituent of the aromatic ring into a hydrogen-bonded monoanion. The 'acid H' atom, which lies on an inversion center, connects adjacent monoanions into a linear chain [O—H = 1.241 (2) Å and O···O = 2.482 (2) Å] (Gao *et al.*, 2004). Whether this H atom is, in fact, equally bonded to both O atoms cannot be decided from the diffraction measurements, as the measurements represent a time-average position of this H atom. Interestingly, a special position is not imposed for the H atom in the title primitive modification (Fig. 1), and it is not exactly midway between the two O atoms [O···O = 2.511 (2) Å]. The H atom is actually disordered over two positions. The primitive and *C*-centered modifications have similar architectures; the primitive modification is, however, marginally less dense (1.490 *versus* 1.506 Mg m^{-3}), as noted from the calculated densities.



(I)

Experimental

Manganese chloride hexahydrate (4.68 g, 20 mmol) and benzimidazole (2.34 g, 20 mmol) were added to an aqueous solution of 3-carboxyphenoxyacetic acid (4.52 g, 20 mmol). The mixture was heated in a 15 ml Teflon-lined stainless steel bomb at 413 K for 3 d. The bomb was left to cool to room temperature. Colorless crystals

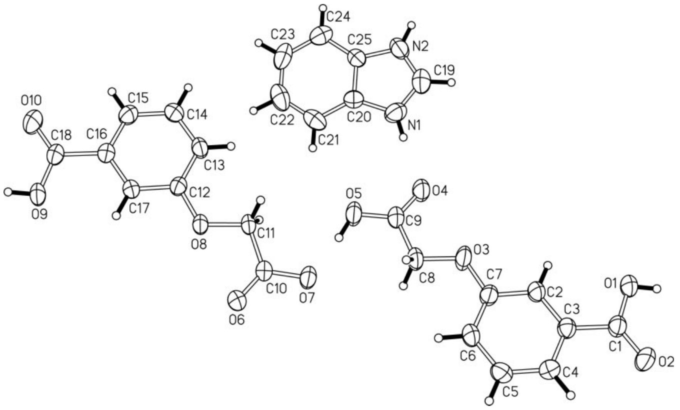


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. The disordered acid H atom is shown attached to the O5 atom.

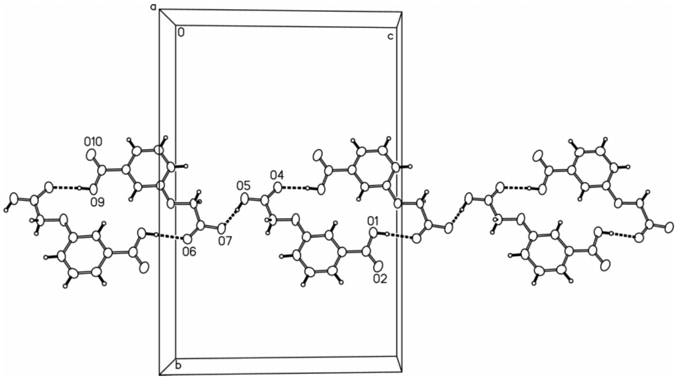


Figure 2
*ORTEP*II (Johnson, 1976) plot of the chains formed from the carboxylate anion and carboxylic acid. The acid H atom is disordered over two positions between atoms O5 and O7, and is represented as being attached to atom O5 in the figure.

were obtained from the filtered solution after a few days. Analysis calculated for $C_{25}H_{22}N_2O10$: C 58.82, H 4.34, N 5.49%; found: C 59.99, H 4.38, N 5.44%. Manganese was not incorporated into the product. The C-centered monoclinic modification of the organic compound was obtained when a cadmium salt was used in the hydrothermal synthesis (Gao *et al.*, 2004).

Crystal data

$C_7H_7N_2^+\cdot C_9H_7O_5^-\cdot C_9H_8O_5$
$M_r = 510.45$
Monoclinic, $P2_1/n$
$a = 7.647$ (2) Å
$b = 21.158$ (4) Å
$c = 14.122$ (3) Å
$\beta = 95.08$ (3)°
$V = 2276.1$ (8) Å^3
$Z = 4$

$D_x = 1.490$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 563 reflections
$\theta = 3.1$–27.2°
$\mu = 0.12$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.42 × 0.26 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.782$, $T_{\max} = 0.979$
21 472 measured reflections

5193 independent reflections
3394 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 8$
$k = -27 \rightarrow 27$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.123$
$S = 1.01$
5193 reflections
359 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 0.2455P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.322 (2)	O9—C18	1.309 (2)
O2—C1	1.210 (2)	O10—C18	1.201 (2)
O3—C7	1.373 (2)	N1—C19	1.315 (3)
O3—C8	1.414 (2)	N1—C20	1.387 (3)
O4—C9	1.243 (2)	N2—C19	1.313 (3)
O5—C9	1.261 (2)	N2—C25	1.377 (2)
O6—C10	1.219 (2)	C1—C3	1.489 (2)
O7—C10	1.296 (2)	C8—C9	1.513 (3)
O8—C12	1.373 (2)	C10—C11	1.512 (3)
O8—C11	1.408 (2)	C16—C18	1.491 (3)
C7—O3—C8	118.6 (1)	O6—C10—C11	122.3 (2)
C11—O8—C12	118.6 (1)	O7—C10—C11	115.2 (2)
C19—N1—C20	108.2 (2)	O8—C11—C10	107.2 (1)
C19—N2—C25	108.8 (2)	O8—C12—C13	124.8 (2)
O1—C1—O2	123.2 (2)	O8—C12—C17	114.7 (2)
O1—C1—C3	113.6 (2)	C15—C16—C18	118.9 (2)
O2—C1—C3	123.2 (2)	C12—C17—C16	119.6 (2)
C1—C3—C2	121.0 (2)	O10—C18—O9	123.6 (2)
C1—C3—C4	118.8 (2)	O9—C18—C16	113.9 (2)
O3—C7—C2	114.8 (2)	O10—C18—C16	122.5 (2)
O3—C7—C6	125.2 (2)	N1—C19—N2	110.7 (2)
O3—C8—C9	109.1 (2)	N1—C20—C21	131.6 (2)
O4—C9—O5	124.1 (2)	N1—C20—C25	106.2 (2)
O4—C9—C8	120.2 (2)	N2—C25—C20	106.1 (2)
O5—C9—C8	115.7 (2)	N2—C25—C24	132.2 (2)
O6—C10—O7	122.5 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O1—H1O···O6$^{\rm i}$	0.87 (2)	1.93 (2)	2.800 (2)	176 (2)
O5—H5O···O7	0.85 (2)	1.69 (3)	2.511 (2)	161 (7)
O7—H7O···O5	0.86 (2)	1.65 (2)	2.511 (2)	174 (4)
O9—H9O···O4$^{\rm ii}$	0.86 (2)	1.87 (2)	2.728 (2)	175 (2)
N1—H1N···O4	0.86 (2)	1.94 (2)	2.802 (2)	173 (3)
N2—H2N···O2$^{\rm iii}$	0.87 (2)	2.11 (2)	2.771 (2)	133 (2)

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

The occupancy of the acid H atom was refined to approximately 0.42 (7)/0.58 (7). Other H atoms were placed in calculated positions [C—H$_{\rm aromatic}$ = 0.93 Å, C—H$_{\rm aliphatic}$ = 0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The amine and carboxyl H atoms were located and refined with a distance restraint of 0.85 (1) Å.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku Corporation, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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