

1,10-Phenanthroline-1-ium 2-carboxy-4-nitrobenzoate

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.056
 wR factor = 0.146
Data-to-parameter ratio = 12.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The cation of the title salt, $\text{C}_{12}\text{H}_9\text{N}_2^+\cdot\text{C}_8\text{H}_4\text{NO}_6^-$, is a monoprotonated 1,10-phenanthroline molecule, whereas its anion is a monodeprotonated 4-nitrophthalic acid molecule. There is a strong, almost symmetrical, intramolecular hydrogen bond linking the O atoms of neighbouring carboxylate groups within the anion [$\text{O}-\text{H} = 1.13$ (4) Å, $\text{H}\cdots\text{O} = 1.27$ (4) Å, $\text{O}\cdots\text{O} = 2.395$ (3) Å and $\text{O}-\text{H}\cdots\text{O} = 173$ (4) $^\circ$]. An $\text{N}-\text{H}\cdots\text{O}$ bond [$\text{N}-\text{H} = 1.00$ (3) Å, $\text{H}\cdots\text{O} = 1.70$ (3) Å, $\text{N}\cdots\text{O} = 2.668$ (3) Å and $\text{N}-\text{H}\cdots\text{O} = 160$ (3) $^\circ$] is responsible for formation of ion pairs, which are further loosely aggregated into a three-dimensional framework *via* $\text{C}-\text{H}\cdots\text{O}$ and $\pi-\pi$ interactions.

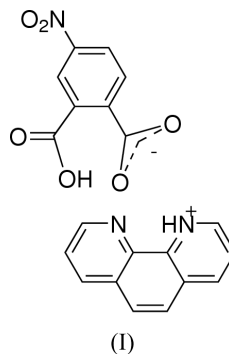
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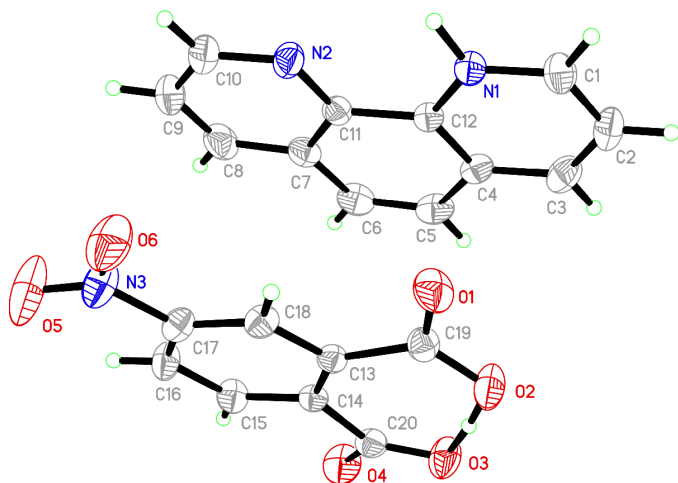
Comment

The title salt, (I), is composed of a cation which is a monoprotonated 1,10-phenanthroline molecule, and an anion, which is a monodeprotonated 4-nitrophthalic acid molecule. The structures of the cation and anion are shown in Fig. 1.

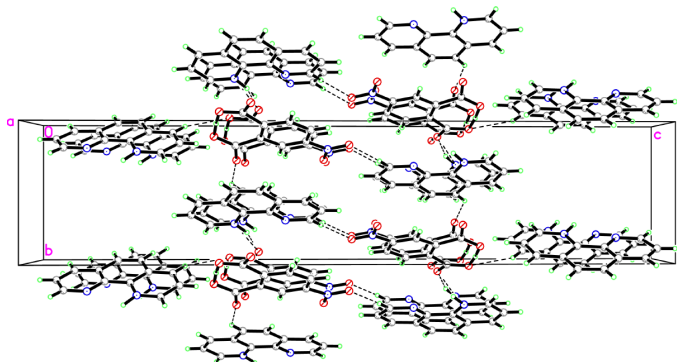


The protonation of atom N1 of the cation leads to a significant increase of the $\text{C}1-\text{N}1-\text{C}12$ angle [122.0 (2) $^\circ$], as compared with the $\text{C}11-\text{N}2-\text{C}10$ angle [116.4 (2) $^\circ$] at the non-protonated atom N2. The increase in the bond angle at the protonated N atom is not unexpected, as an analogous difference in the $\text{C}-\text{N}-\text{C}$ bond angles was observed in previously reported monoprotonated phenanthrolines (*e.g.* Hensen *et al.*, 1998, 2000).

The anion features an almost symmetrical intramolecular $\text{O}2-\text{H}2\text{A}\cdots\text{O}3$ hydrogen bond (Table 2), linking the O atoms of the neighbouring carboxylate groups. Even though the difference between the $\text{O}2-\text{H}2\text{A}$ and $\text{H}2\text{A}\cdots\text{O}3$ distances barely exceeds 3σ , it is correlated with there being a more pronounced difference between the $\text{O}-\text{C}$ bond lengths in one of the carboxyl groups [$\text{O}1-\text{C}19 = 1.208$ (3) Å and $\text{O}2-\text{C}19 = 1.292$ (3) Å] than there is in the other group [$\text{O}4-\text{C}20 = 1.226$ (3) Å and $\text{O}3-\text{C}20 = 1.260$ (3) Å].


Figure 1

A view of the cation and anion in the structure of (I), showing the atom-numbering scheme; displacement ellipsoids are drawn at the 30% probability level.


Figure 2

A packing diagram of (I), viewed along the *a* axis, showing hydrogen bonds and C—H...O interactions (dashed lines).

Atom H1A is involved in an N1—H1A...O4^{iv} bond [Table 2; symmetry code: (iv) $1 + x, -1 + y, z$], which joins the cations and anions into ion pairs. These are further loosely aggregated into a three-dimensional framework *via* relatively weak C—H...O interactions (Table 2), as well as π – π interactions between the N2/C10/C9/C8/C7/C11 and C13^v–C18^v rings [symmetry code: (v) $x, y - 1, z$]. The interplanar spacing is *ca* 3.43 Å, the ring-centroid separation is 3.730 (2) Å and the dihedral angle is 1.95 (4)°. A packing diagram for the structure of (I) is shown in Fig. 2.

Experimental

The title salt was prepared by mixing ethanol solutions of 4-nitrophenthalic acid (0.4 g in 10 ml) and 1,10-phenanthroline (0.4 g in 10 ml). The solution was stirred at room temperature for 10 min, after which the crystalline product was separated by filtration (0.7 g, yield 87.5%). The pure product (0.5 g) was heated and dissolved in water (25 ml). Single crystals were obtained from this aqueous solution by slow concentration over a period of five days at room temperature.

Crystal data

$C_{12}H_9N_2^+ \cdot C_8H_4NO_6^-$
 $M_r = 391.33$
 Monoclinic, $P2_1/c$
 $a = 6.328$ (2) Å
 $b = 7.696$ (3) Å
 $c = 35.175$ (12) Å
 $\beta = 92.678$ (6)°
 $V = 1711.0$ (11) Å³
 $Z = 4$

$D_x = 1.519$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 784 reflections
 $\theta = 2.9$ – 25.4 °
 $\mu = 0.11$ mm⁻¹
 $T = 293$ (2) K
 Block, yellow
 $0.26 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.959$, $T_{\max} = 0.989$
 9498 measured reflections

3486 independent reflections
 2198 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 26.4$ °
 $h = -6 \rightarrow 7$
 $k = -9 \rightarrow 8$
 $l = -42 \rightarrow 43$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.146$
 $S = 1.05$
 3486 reflections
 271 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.6995P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.17$ e Å⁻³
 $\Delta\rho_{\min} = -0.16$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0069 (12)

Table 1

Selected geometric parameters (Å, °).

O1—C19	1.208 (3)	N1—C12	1.356 (3)
O2—C19	1.292 (3)	N2—C10	1.322 (3)
O2—H2A	1.13 (4)	N2—C11	1.355 (3)
O3—C20	1.260 (3)	N3—C17	1.466 (3)
O3—H2A	1.27 (4)	C13—C19	1.526 (3)
O4—C20	1.226 (3)	C14—C20	1.526 (4)
N1—C1	1.327 (3)		
C1—N1—C12	122.0 (2)	O1—C19—C13	119.4 (2)
C10—N2—C11	116.4 (2)	O2—C19—C13	119.2 (2)
O5—N3—O6	122.8 (3)	O4—C20—O3	123.0 (3)
O5—N3—C17	118.0 (3)	O4—C20—C14	116.5 (2)
O6—N3—C17	119.2 (3)	O3—C20—C14	120.4 (2)
O1—C19—O2	121.4 (3)		
C11—N2—C10—C9	−0.8 (5)	O5—N3—C17—C16	2.7 (5)
C10—N2—C11—C7	−0.6 (4)	C14—C13—C19—O1	166.7 (3)
C8—C7—C11—N2	1.7 (4)	C18—C13—C19—O2	169.0 (2)
C1—N1—C12—C4	−2.0 (4)	C13—C14—C20—O4	−176.6 (3)
O6—N3—C17—C18	1.5 (4)	C15—C14—C20—O3	−172.8 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C10—H10...O5 ⁱ	0.93	2.58	3.507 (4)	177
C5—H5...O1 ⁱⁱ	0.93	2.50	3.206 (3)	133
C3—H3...O3 ⁱⁱⁱ	0.93	2.51	3.216 (4)	132
O2—H2A...O3	1.13 (4)	1.27 (4)	2.395 (3)	173 (4)
N1—H1A...O4 ^{iv}	1.00 (3)	1.70 (3)	2.668 (3)	160 (3)

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

H atoms bonded to the O and N atoms were located in a difference Fourier map and refined in the isotropic approximation. H atoms bonded to C atoms were included in the refinement in the riding-model approximation, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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