Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

1,10-Phenanthrolin-1-ium 2-carboxy-6-nitrobenzoate

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In the title salt, $C_{12}H_9N_2^+ \cdot C_8H_4NO_6^-$, one N atom of 1,10-phenanthroline is protonated [N—H = 1.00 (2) Å], while the other N atom is not. Protonation of the N atom causes the C—N—C angle to increase [122.3 (2)° in the protonated ring *versus* 116.2 (2)° in the unprotonated ring]. In the crystal structure, N—H···O and O—H···O hydrogen bonds and van der Waals forces stabilize the packing of the ions.

Received 12 April 2005
Accepted 9 May 2005
Online 14 May 2005

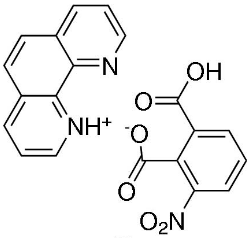
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.045
wR factor = 0.108
Data-to-parameter ratio = 12.6

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

Comment

The structures of the cation and anion of the title salt, (I), are shown in Fig. 1.



(I)

In the cation of the title salt, only one N atom of 1,10-phenanthroline is protonated. The C—N—C angle at the protonated N atom is significantly larger than the angle at the non-protonated N atom (see Table 1). The increase in the bond angle at the protonated N atom is not unexpected, as an

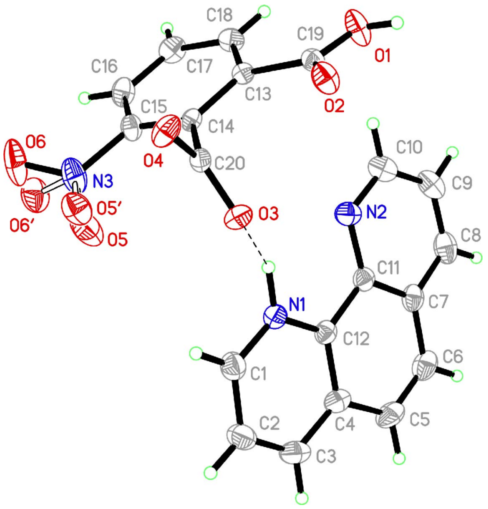


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates a hydrogen bond. Both disorder components are shown.

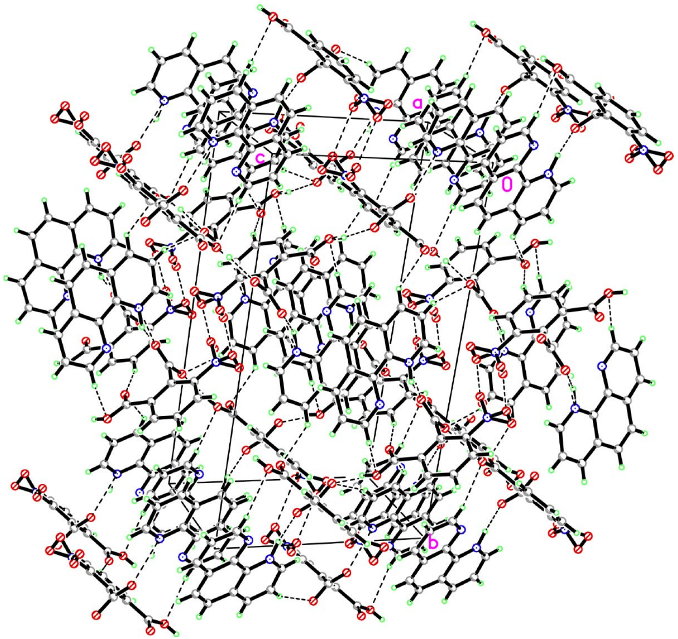


Figure 2
The packing, showing hydrogen-bond interactions as dashed lines, viewed approximately down the *a* axis.

analogous difference in the C—N—C bond angles was observed in previously reported monoprotonated phenanthrolines (*e.g.* Hensen *et al.*, 1998, 2000; Guo, 2005).

Positional disorder of the NO_2 group is observed. Each of the two O atoms bonded to N3 was successfully refined using a split-site model (O5/O5′ and O6/O6′), with occupancies of 0.880 (16) for O5 and O6, and 0.120 (16) for O5′ and O6′.

The two C—O bond distances (O1—C19 and O2—C19) of the 2-carboxy group are 1.300 (2) and 1.207 (2) Å, while the two C—O bond distances (O4—C20 and O3—C20) of the 1-carboxylate group are 1.265 (2) and 1.230 (2) Å. The C19/O1/O2 carboxy group is essentially coplanar with the central six-membered ring, while the C20/O3/O4 carboxy group is almost orthogonal to its attached ring. Selected geometric parameters are listed in Table 1.

Atom H1*A* is involved in an N1—H1*A*···O3 hydrogen bond, which joins the cations and anions into ion pairs, while atom H1*B* is responsible for formation of an O1—H1*B*···O4^{i} hydrogen bond (see Table 2 for symmetry codes), which links to another anion. These are further loosely aggregated into a three-dimensional framework *via* relatively weak C—H···O interactions (Table 2). A packing diagram for the structure of (I) is shown in Fig. 2.

Experimental

The title salt was prepared by mixing ethanol solutions of 3-nitrophthalic acid (0.4 g in 10 ml) and 1,10-phenanthroline (0.4 g in 10 ml). The reaction mixture 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 2 d at room temperature.

Crystal data

$C_{12}H_9N_2^+\cdot C_8H_4NO_6^-$
$M_r = 391.33$
Monoclinic, $P2_1/c$
$a = 7.623$ (3) Å
$b = 19.920$ (6) Å
$c = 11.558$ (4) Å
$\beta = 92.304$ (6)°
$V = 1753.8$ (10) Å^3
$Z = 4$
$D_x = 1.482$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 708 reflections
$\theta = 3.3$–22.4°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.20 × 0.18 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.960$, $T_{max} = 0.984$
10 088 measured reflections
3627 independent reflections
2223 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 26.5°$
$h = -9 \rightarrow 9$
$k = -24 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 1.01$
3627 reflections
287 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.1207P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.032 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C19	1.300 (2)	N3—O5′	1.206 (9)
O2—C19	1.207 (2)	N3—O5	1.213 (3)
O3—C20	1.230 (2)	N3—O6	1.223 (3)
O4—C20	1.265 (2)	N3—C15	1.466 (3)
N3—O6′	1.205 (8)	C13—C19	1.502 (3)
C1—N1—C12	122.27 (19)	O2—C19—C13	122.91 (18)
C10—N2—C11	116.22 (19)	O1—C19—C13	112.70 (17)
O6′—N3—O5′	119.7 (10)	O3—C20—O4	125.22 (18)
O5—N3—O6	123.2 (3)	O3—C20—C14	118.94 (17)
O2—C19—O1	124.38 (18)	O4—C20—C14	115.84 (16)
C12—N1—C1—C2	0.1 (3)	O5—N3—C15—C14	−25.9 (5)
C1—N1—C12—C4	−3.0 (3)	O6—N3—C15—C14	153.4 (5)
C1—N1—C12—C11	177.29 (18)	N3—C15—C16—C17	−179.06 (19)
C19—C13—C14—C20	1.8 (3)	C18—C13—C19—O2	166.34 (18)
C20—C14—C15—N3	−2.8 (3)	C14—C13—C19—O2	−13.0 (3)
O6′—N3—C15—C16	20 (2)	C18—C13—C19—O1	−12.9 (3)
O5′—N3—C15—C16	−176.3 (18)	C14—C13—C19—O1	167.81 (17)
O5—N3—C15—C16	154.6 (5)	C15—C14—C20—O3	100.2 (2)
O6—N3—C15—C16	−26.1 (5)	C13—C14—C20—O3	−81.8 (2)
O6′—N3—C15—C14	−161 (2)	C15—C14—C20—O4	−79.7 (2)
O5′—N3—C15—C14	3.3 (18)	C13—C14—C20—O4	98.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3	1.00 (2)	1.76 (2)	2.624 (2)	142 (2)
O1—H1*B*···O4^{i}	0.82	1.68	2.4878 (19)	166
C2—H2···O4^{ii}	0.93	2.49	3.378 (3)	160
C3—H3*A*···O2^{iii}	0.93	2.48	3.132 (3)	128
C10—H10···O1	0.93	2.52	3.304 (3)	143
C17—H17···O2^{iv}	0.93	2.48	3.382 (3)	163
C18—H18···O1	0.93	2.36	2.693 (2)	101

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

While determining the structure of (I), a potential ambiguity, *viz.* the group that is C19/O1/O2 could have been NO_2 and the group that is N3/O5/O6 could have been CO_2, was resolved by examining the bond distances C13—C19 [1.502 (3) Å] and N3—C15 [1.466 (3) Å] and the difference map, where an H atom is visible on the carboxylate at C19. If this assignment is changed, it results not only in less reasonable C—C and C—N bond distances but also in an increase in the values of *R* and *wR*. Each of the O atoms bonded to N3 is disordered over at least two sites. Refined occupancy factors for atoms O5/O5′ and O6/O6′ were 0.880 (16):0.120 (16). The H atom involved in O—H···O hydrogen bonds was found in a difference Fourier map; however, during refinement, O—H distances were fixed at 0.82 Å and the $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$(O), while the H atom bonded to atom N1 was 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 $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(N,C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; 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*.

References

Bruker (1997). *SMART* (Version 5.051) and *SAINT* (Version 5.A06). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Guo, M.-L. (2005). *Acta Cryst.* E**61**, o431–o433.

Hensen, K., Gebhardt, F. & Bolte, M. (1998). *Acta Cryst.* C**54**, 359–361.

Hensen, K., Spangenberg, B. & Bolte, M. (2000). *Acta Cryst.* C**56**, 208–210.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.