

2-Methylquinolinium 2,4-dinitrobenzoate

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.036
wR factor = 0.108
Data-to-parameter ratio = 11.5

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

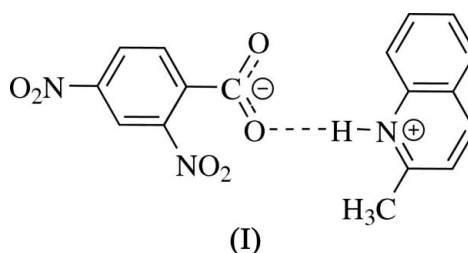
In the title salt, $\text{C}_{10}\text{H}_{10}\text{N}^+\cdot\text{C}_7\text{H}_3\text{N}_2\text{O}_6^-$, in addition to electrostatic interactions, the quinoldinium and 2,4-dinitrobenzoate ions are linked by $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds into a three-dimensional molecular network. The quinoldinium cations are stacked along the *a* axis with a centroid-centroid distance of 3.4662 (7) Å, indicating $\pi-\pi$ interactions.

Received 24 February 2006

Accepted 25 February 2006

Comment

Hydrogen bonding is a very important structural phenomenon and is still not fully understood, especially in phenol-benzoic acid systems. Interactions of organic acids with amine bases in the solid phase have been of interest due to their hydrogen-bonding interactions (Coupar *et al.*, 1997; Sobczyk *et al.*, 2000) and their important role in biological systems (Blow, 1976). We have been studying hydrogen-bonding interactions in the adducts of phenols and carboxylic acids with amines (Usman *et al.*, 2001; Chantrapromma *et al.*, 2002*a,b,c*, 2004, 2006; Chantrapromma & Fun 2004; Fun *et al.*, 2003; How *et al.*, 2005; Rosli *et al.*, 2006). 2,4-Dinitrobenzoic acid is an interesting acid since it readily forms the 2,4-dinitrobenzoate anion when co-crystallized with amine bases, by transferring a proton. This proton transfer leads to the formation of salt-like adducts consisting of 2,4-dinitrobenzoate anions and amine-based cations, in which the 2,4-dinitrobenzoate anion is expected to act as a multiple donor of hydrogen bonds *via* the nitro and carboxylate groups.



Our studies using 2,4-dinitrophenol and 3,5-dinitrobenzoic acid with some amines gave a number of proton-transfer compounds (Usman *et al.*, 2001; Chantrapromma *et al.*, 2002*a,b*, 2004; Fun *et al.*, 2003) and some of these undergo a phase transition (Fun *et al.*, 2003; How *et al.*, 2005). Owing to our interest in studying hydrogen bonding and in searching for further examples of phase transitions due to hydrogen bonding in the adducts of acids and amines (Fun *et al.*, 2003; How *et al.*, 2005), the title compound, (I), was prepared and we report its crystal structure here.

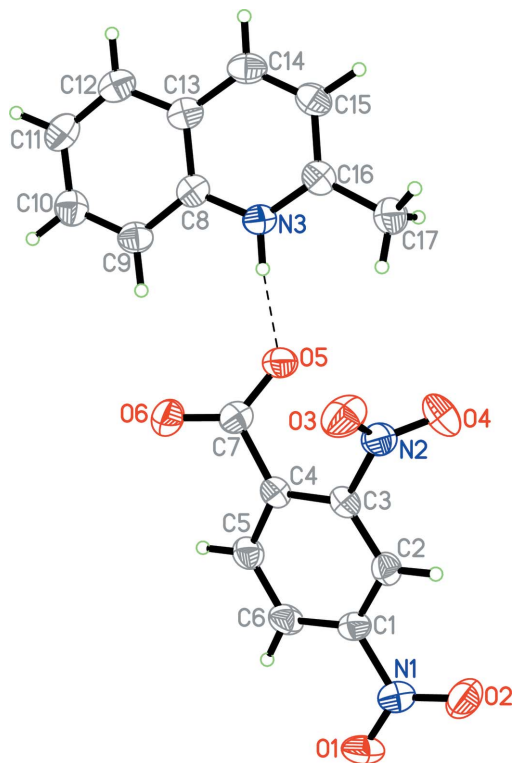


Figure 1
The asymmetric unit of (I), showing 80% probability displacement ellipsoids and the atomic numbering scheme. The dashed line indicates a hydrogen bond.

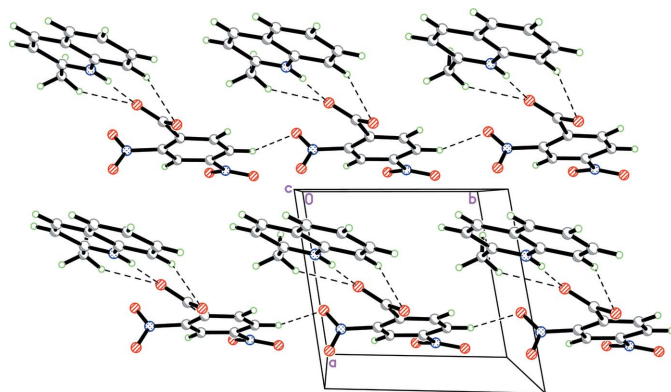


Figure 2
A view of the hydrogen-bonded (dashed lines) chain in the crystal structure of (I).

The asymmetric unit of compound (I) (Fig. 1) contains a $C_{10}H_{10}N^+$ cation and a $C_7H_3N_2O_6^-$ anion. The 2,4-dinitro-carboxylic acid molecule has transferred a proton to the hetero-N atom of quinaldine. All bond distances and angles in (I) show normal values (Allen *et al.*, 1987). Selected bond distances and angles are given in Table 1.

The proton transfer from the carboxyl group results in a slight distortion of the functional groups of the 2,4-dinitrobenzoate ion. In this anion, the carboxylate and the two nitro groups are twisted away from the plane of the benzene ring, with torsion angles $O1-N1-C1-C2 = 167.17(12)^\circ$, $O3-N2-C3-C4 = 63.09(17)^\circ$ and $C3-C4-C7-O5 =$

$32.66(18)^\circ$. The dihedral angle between the planes of the adjacent carboxylate and nitro groups is $63.4(2)^\circ$. The C4–C7 bond distance [$1.5280(18) \text{ \AA}$] is relatively long compared with the corresponding distance in 3,5-dinitrobenzoic acid [$1.5019(10) \text{ \AA}$; Rosli *et al.*, 2006]. The maximum deviation from planarity in the essentially planar quinaldinium cation (C8–C17/N3) is $0.029(1) \text{ \AA}$ for atom C15. The dihedral angle between the plane of the benzene ring of the anion and the plane of the quinaldinium cation is $18.83(5)^\circ$.

In the crystal structure of (I), in addition to electrostatic interactions, the quinaldinium and 2,4-dinitrobenzoate ions are linked by $N3-H1N3 \cdots O5$, $C9-H9 \cdots O6$ and $C17-H17C \cdots O5$ hydrogen bonds, with the quinaldinium cation acting as a hydrogen-bond donor and the 2,4-dinitrobenzoate anion acting as a multiple hydrogen-bond acceptor. The $C6-H6 \cdots O4^i$ hydrogen bonds link the cation–anion pairs into a chain along the *b* axis (Fig. 2). These chains are interconnected through $C12-H12 \cdots O1^{ii}$ and $C12-H12 \cdots O3^{iii}$ hydrogen bonds (symmetry codes are given in Table 2) into a three-dimensional molecular network. The quinaldinium cations are stacked along the *a* axis with a centroid–centroid distance of $3.4662(7) \text{ \AA}$, indicating π – π interactions.

Experimental

Compound (I) was prepared by mixing equimolar amounts of quinaldine (0.07 ml, 0.5 mmol) and 2,4-dinitrobenzoic acid (0.11 g, 0.5 mmol) in ethanol (40 ml) with a few drops of water. The mixture was warmed until a clear solution was obtained. The solution was then filtered and left to evaporate slowly at ambient temperature. Pale-yellow block single crystals of (I) were obtained from the solution after a few days (m.p. 455–457 K).

Crystal data

$C_{10}H_{10}N^+ \cdot C_7H_3N_2O_6^-$
 $M_r = 355.30$
 Triclinic, $P\bar{1}$
 $a = 7.3823(2) \text{ \AA}$
 $b = 7.8262(2) \text{ \AA}$
 $c = 13.9272(3) \text{ \AA}$
 $\alpha = 79.062(1)^\circ$
 $\beta = 76.801(1)^\circ$
 $\gamma = 78.810(1)^\circ$
 $V = 759.54(3) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.554 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3305 reflections
 $\theta = 1.5$ – 27.0°
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 100.0(1) \text{ K}$
 Block, pale yellow
 $0.53 \times 0.23 \times 0.12 \text{ mm}$

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.938$, $T_{\max} = 0.985$
 10878 measured reflections

3295 independent reflections
 2850 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\max} = 27.0^\circ$
 $h = -9 \rightarrow 9$
 $k = -9 \rightarrow 6$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.108$
 $S = 1.09$
 3295 reflections
 287 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.2328P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O5—C7	1.2675 (17)	O6—C7	1.2354 (17)
C16—N3—C8	123.35 (12)	O6—C7—O5	128.64 (13)
O2—N1—C1—C2	−13.52 (18)	O4—N2—C3—C4	−120.05 (14)
O1—N1—C1—C6	−13.13 (18)	N2—C3—C4—C7	9.15 (19)
O2—N1—C1—C6	166.18 (12)	C5—C4—C7—O6	35.48 (18)
O4—N2—C3—C2	61.47 (16)	C3—C4—C7—O6	−150.15 (13)
O3—N2—C3—C2	−115.40 (13)	C5—C4—C7—O5	−141.71 (13)

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>
N3—H1N3...O5	0.90 (2)	1.74 (2)	2.6363 (15)	171 (2)
C6—H6...O4 ⁱ	0.972 (16)	2.438 (16)	3.1623 (18)	131 (1)
C9—H9...O6	0.982 (17)	2.570 (17)	3.4986 (17)	158 (1)
C12—H12...O1 ⁱⁱ	0.953 (17)	2.419 (16)	3.2418 (18)	144 (1)
C12—H12...O3 ⁱⁱⁱ	0.953 (17)	2.552 (17)	3.2086 (17)	126 (1)
C17—H17C...O5	0.95 (2)	2.55 (2)	3.2987 (19)	137 (2)

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

All H atoms were located in a difference Fourier map and refined isotropically.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

The authors thank the Malaysian Government and Universiti Sains Malaysia for Scientific Advancement Grant Allocation (SAGA) grant No. 304/PFIZIK/653003/A118. SC also thanks the Prince of Songkla University for partial financial support.

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