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The ternary complex 4-(2-pyridyl)-pyridinium–3,5-dinitrobenzoate–3,5-dinitrobenzoic acid (1/1/1)

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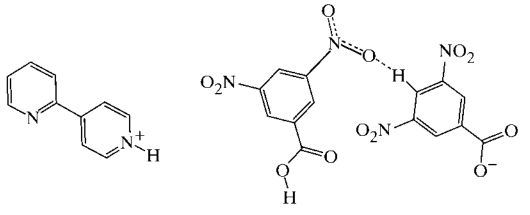
In the title ternary complex, $C_{10}H_9N_2^+ \cdot C_7H_3N_2O_6^- \cdot C_7H_4N_2O_6$, the pyridinium cation adopts the role of the donor in an intermolecular N—H···O hydrogen-bonding interaction with the carboxylate group of the 3,5-dinitrobenzoate anion. The molecules of the ternary complex form molecular ribbons perpendicular to the *b* direction, which are stabilized by one N—H···O, one O—H···O and five C—H···O intermolecular hydrogen bonds. The ribbons are further interconnected by three intermolecular C—H···O hydrogen bonds into a three-dimensional network.

Comment

In the crystals of adducts of carboxylic acids with organic amine bases, there is complete or occasionally only partial transfer of H atoms from the acid to the base (Burchell *et al.*, 2001). In our previous study of such bases, the trigonally substituted 3,5-dinitrobenzoic acid, $(O_2N)_2C_6H_3COOH$, readily formed the anion $(O_2N)_2C_6H_3COO^-$ and therefore can act as a multiple acceptor of hydrogen bonds (Chantrapromma *et al.*, 2002). Our ongoing studies of 3,5-dinitrobenzoic acid complexes with amine bases led to the title adduct, (I), in which 2,4′-bipyridine was selected as the amine base. The crystal structure, hydrogen bonds and weak interactions are reported here for (I) from data collected at 153 K.

3,5-Dinitrobenzoic acid forms a 2:1 salt with 2,4′-bipyridine, in which one of the acid molecules transfers an H atom to the bipyridine, making a ternary complex involving a 3,5-dinitrobenzoate anion, a 4-(2-pyridyl)pyridinium cation and a neutral 3,5-dinitrobenzoic acid molecule (Fig. 1).

The bond lengths and angles in (I) are within normal ranges (Allen *et al.*, 1987). The values within the 3,5-dinitrobenzoate anion and neutral 3,5-dinitrobenzoic acid molecule agree with each other, except for those of the carboxylate group; O1—C17 is shorter than O7—C24, whereas O2—C17 is longer than O8—C24 (Table 1). This is due to the H-atom transfer process.



(I)

The benzoate anion and benzoic acid molecule are nearly planar. For the benzoate anion, the two O atoms of the nitro groups are slightly displaced from the aromatic ring, so that the O3/O4/N4/C15 and O5/O6/N3/C13 planes are twisted around the N—C bonds by angles of 8.3 (1) and 4.8 (1)°, respectively. Similarly, the O9/O10/N6/C22 and O11/O12/N5/C20 planes are twisted by 8.3 (1) and 3.5 (1)°, respectively, from the plane of the benzoic acid aromatic ring. Though the dihedral angle of the neutral carboxylic acid group (O7/O8/C24/C18) with respect to its attached aromatic ring is 6.9 (1)°, that of the carboxylate group (O1/O2/C17/C11) with respect to its attached aromatic ring is 22.7 (1)°. This implies that the H-atom transfer process leads to geometric changes in the carboxylate anion, but does not produce any significant changes in the pyridinium cation, since the C—N bonds within both the charged and uncharged heterocyclic rings are almost the same. This is due to the bond-length constraints within the aromatic rings.

Within the asymmetric unit of (I), both the benzoate anion and benzoic acid molecule are interconnected by an intermolecular C14—H14···O9 interaction (Table 2). The pyridinium cation is nearly planar; the dihedral angle between the two aromatic rings is 2.0 (1)°. In the packing, this cation is connected to the benzoate anion and benzoic acid molecule by one N—H···O and six C—H···O interactions, while the benzoate anion and benzoic acid molecule are linked by one O—H···O and one C—H···O interactions (see Table 2). The N2—H111···O1 and O7—H117···O1 hydrogen bonds, together with the five C—H···O hydrogen bonds (C1—H1···O5,

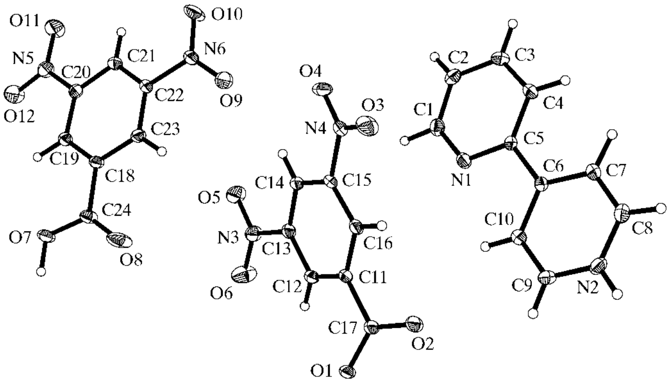


Figure 1
The structure of the title ternary complex, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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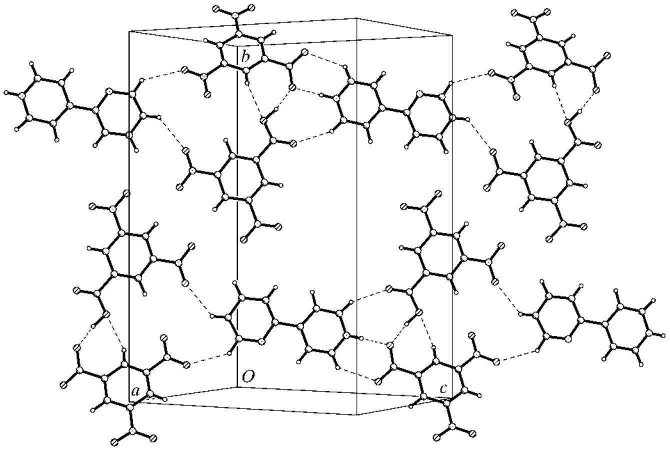

Figure 2
Packing diagram of the title ternary complex, showing the molecular ribbons perpendicular to the *b* direction.

C2—H2···O12, C8—H8···O8, C9—H9···O2 and C12—H12···O7) interconnect the molecules into molecular ribbons perpendicular to the *b* direction (Fig. 2). There are three other hydrogen bonds (C3—H3···O10, C7—H7···O4 and C14—H14···O9), which interconnect the ribbons into a three-dimensional molecular arrangement.

Experimental

3,5-Dinitrobenzoic acid (1.06 g, 5 mmol) and 2,4′-bipyridine (0.39 g, 2.5 mmol) were mixed thoroughly and dissolved in acetone (40 ml), after which, water (2 ml) was added. The resulting mixture was stirred and warmed for 15 min. The clear light-yellow solution obtained was filtered and left to evaporate slowly in air. Single crystals of (I) suitable for X-ray diffraction studies were obtained after a few days.

Crystal data

$C_{10}H_9N_2^+ \cdot C_7H_3N_2O_6^- \cdot C_7H_4N_2O_6$
$M_r = 580.43$
Monoclinic, $P2_1/c$
$a = 9.0193\ (1)$ Å
$b = 20.6107\ (2)$ Å
$c = 13.6609\ (3)$ Å
$\beta = 104.372\ (1)^\circ$
$V = 2460.01\ (7)$ Å^3
$Z = 4$
$D_x = 1.567$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5786 reflections
$\theta = 2.5$–28.3°
$\mu = 0.13$ mm^{-1}
$T = 153\ (2)$ K
Block, colorless
0.40 × 0.40 × 0.30 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.950$, $T_{\max} = 0.962$
14 651 measured reflections
5931 independent reflections
4473 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.088$
$\theta_{\max} = 28.3^\circ$
$h = -11 \rightarrow 12$
$k = -27 \rightarrow 19$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.144$
$S = 0.98$
5931 reflections
444 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.040 (3)

Table 1
Selected interatomic distances (Å).

O1—C17	1.2896 (18)	N1—C1	1.334 (2)
O2—C17	1.2361 (18)	N1—C5	1.3539 (19)
O3—N4	1.2235 (18)	N2—C9	1.341 (2)
O4—N4	1.2262 (18)	N2—C8	1.345 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H111···O1$^{\rm i}$	0.91 (2)	1.76 (2)	2.671 (2)	177 (2)
O7—H117···O1$^{\rm ii}$	1.01 (3)	1.59 (3)	2.579 (2)	164 (3)
C1—H1···O5$^{\rm iii}$	1.00 (2)	2.55 (2)	3.360 (2)	138 (2)
C2—H2···O12$^{\rm iv}$	0.92 (2)	2.47 (2)	3.176 (2)	134 (2)
C3—H3···O10$^{\rm v}$	0.98 (2)	2.58 (2)	3.399 (2)	142 (2)
C7—H7···O4$^{\rm v}$	0.99 (2)	2.39 (2)	3.272 (2)	148 (2)
C8—H8···O8$^{\rm vi}$	0.97 (2)	2.40 (2)	3.311 (2)	155 (2)
C9—H9···O2$^{\rm i}$	0.92 (2)	2.52 (2)	3.211 (2)	132 (2)
C12—H12···O7$^{\rm vii}$	0.94 (2)	2.44 (2)	3.087 (2)	126 (2)
C14—H14···O9	0.92 (2)	2.43 (2)	3.269 (2)	152 (2)

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

All H atoms were located from difference Fourier maps and were refined isotropically; C—H distances were in the range 0.91 (2)–1.00 (2) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1113). Services for accessing these data are described at the back of the journal.

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