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4-Dimethylaminopyridinium–4-nitrophenolate–4-nitrophenol (1/1/1)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.065
Data-to-parameter ratio = 7.3

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

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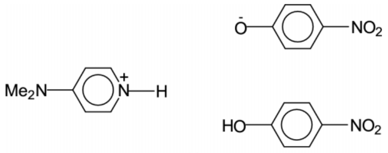
Within and between molecules of the title compound, $C_7H_{11}N_2^+\cdot C_6H_5NO_3^-\cdot C_6H_4NO_3$, there are C—H···O, C—H···N, O—H···O and N—H···O interactions, which generate rings of graph-set motifs $S(5)$, $R_2^1(5)$, $R_2^1(6)$, $R_2^1(7)$ and $R_1^2(4)$. The supramolecular aggregation is completed by the presence of three different π–π interactions and short van der Waals contacts.

Comment

The design of organic polar crystals for quadratic non-linear optical (NLO) applications is supported by the observation that the organic molecules containing π-electron systems asymmetrized by electron donor and acceptor groups are highly polarizable entities, in which problems of transparency and crystal growth may arise from their molecular crystal packing (Pecaut & Bagieu-Beucher, 1993). It is known that nitrophenols act not only as π-acceptors to form various π-stacking complexes with other aromatic molecules, but also as acidic ligands to form salts through specific electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). The bonding of electron-donor–acceptor complexes strongly depends on the nature of the partners. The linkage could involve not only electrostatic interactions, but also the formation of molecular complexes (Zaderenko *et al.*, 1997). It has been reported that proton-transfer thermochromic complexes are formed between phenols and amines in apolar solvents at low temperature, if an appropriate hydrogen-bonding network between phenols and amines is present to stabilize them (Mizutani *et al.*, 1998). Pyridinium picrate has been reported in two crystalline phases and it appears in both phases as an internally linked hydrogen-bonded ion pair. These two phases are termed as molecular crystals rather than salts, based on their structural arrangements (Botoshansky *et al.*, 1994). A similar structural arrangement has also been reported for 4-dimethylaminopyridinium picrate (Vembu *et al.*, 2003). It was reported (Evans *et al.*, 1998) that the reaction of 4-nitrophenol with 4-dimethylaminopyridine resulted in the formation of a new NLO material, whose crystal structure was determined from room-temperature data.



(I)

The X-ray structure determination of the title compound, (I), was undertaken at 120 K to study the role of hydrogen bonding and van der Waals interactions in stabilizing the

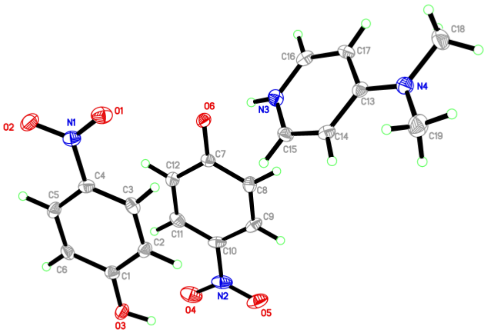


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids.

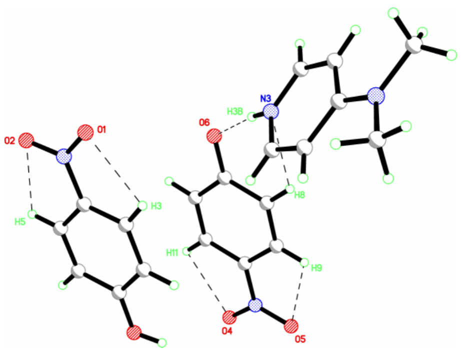


Figure 2
Diagram showing hydrogen bonds 1–6 (the numbers relate to the sequence of entries in Table 2).

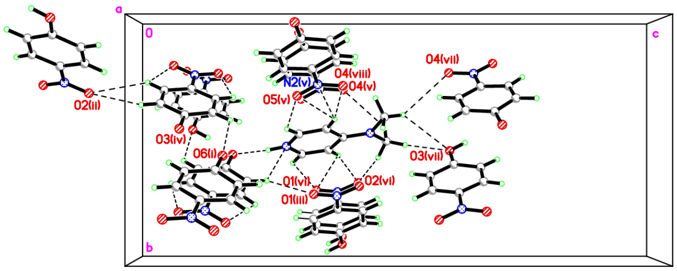


Figure 3
Diagram showing hydrogen bonds 7 and 9–23 (the numbers relate to the sequence of entries in Table 2).

crystal structure. This may serve as an initial study for assessing the optical properties of (I).

The asymmetric unit of (I) contains one 4-dimethylaminopyridinium cation, one 4-nitrophenolate anion and one 4-nitrophenol molecule (Fig. 1). The bond lengths and angles of the phenolate and dimethylaminopyridinium ions (Table 1) are comparable to those found in related structures reported in the Cambridge Structural Database (Version 5.23; Allen, 2002; Bruno *et al.*, 2002). The crystal structure of (I) is stabilized by N—H$\cdots$O, O—H$\cdots$O, C—H$\cdots$O and C—H$\cdots$N interactions. The range of H$\cdots$O distances (Table 2) found in (I) agrees with those found for N—H$\cdots$O and O—H$\cdots$O (Jeffrey, 1997), and C—H$\cdots$O and C—H$\cdots$N hydrogen bonds (Desiraju & Steiner, 1999).

As shown in Fig. 2, each of the C3—H3$\cdots$O1, C5—H5$\cdots$O2, C9—H9$\cdots$O5 and C11—H11$\cdots$O4 interactions generates one $S(5)$ graph-set motif (Etter, 1990; Bernstein *et al.*, 1995). The C8—H8$\cdots$N3 and N3—H3*B*$\cdots$O6 interactions link the 4-dimethylaminopyridinium and 4-nitrophenolate ions together. As seen from Fig. 3, the C2—H2$\cdots$O6$^{\rm i}$ and O3—H3*A*$\cdots$O6$^{\rm i}$ interactions constitute a pair of hetero-electronic bifurcated acceptor bonds, generating a ring of graph-set $R^{1}_{2}(6)$. The C6—H6$\cdots$O2$^{\rm ii}$ and C5—H5$\cdots$O2$^{\rm ii}$ interactions form a pair of bifurcated acceptor bonds, generating an $R^{1}_{2}(5)$ motif (see Table 2 for symmetry codes). The C14—H14$\cdots$O4$^{\rm v}$ and C14—H14$\cdots$O5$^{\rm v}$ interactions constitute a pair of bifurcated donor bonds, generating a symmetrical three-center hydrogen-bonded chelate (Desiraju, 1989) of graph-set motif $R^{2}_{1}(4)$. The C14—H14$\cdots$O5$^{\rm v}$ and C15—H15$\cdots$O5$^{\rm v}$ interactions constitute a pair of bifurcated acceptor bonds, generating an $R^{1}_{2}(5)$ motif. The C14—H14$\cdots$O4$^{\rm v}$, C14—H14$\cdots$O5$^{\rm v}$ and C14—H14$\cdots$N2$^{\rm v}$ interactions together form a set of trifurcated donor bonds. The C17—H17$\cdots$O1$^{\rm vi}$ and C17—H17$\cdots$O2$^{\rm vi}$ interactions together form a pair of bifurcated donor bonds, generating another symmetrical three-center hydrogen-bonded chelate of graph-set motif $R^{2}_{1}(4)$. The C17—H17$\cdots$O1$^{\rm vi}$ and C16—H16$\cdots$O1$^{\rm vi}$ interactions constitute a pair of bifurcated acceptor bonds, generating an $R^{1}_{2}(5)$ motif. The C17—H17$\cdots$O2$^{\rm vi}$ and C18—H18*C*$\cdots$O2$^{\rm vi}$ interactions together form a pair of bifurcated acceptor bonds, generating an $R^{1}_{2}(7)$ motif. The $R^{1}_{2}(7)$ and $R^{1}_{2}(5)$ ring motifs are interlinked through the $R^{2}_{1}(4)$ chelate motif. The C19—H19*B*$\cdots$O3$^{\rm vii}$ and C19—H19*B*$\cdots$O4$^{\rm vii}$ interactions constitute a pair of bifurcated donor bonds. They link the 4-dimethylaminopyridinium moiety of an asymmetric unit with 4-nitrophenolate and 4-nitrophenol moieties of a neighboring asymmetric unit. The C19—H19*B*$\cdots$O3$^{\rm vii}$ and C18—H18*A*$\cdots$O3$^{\rm vii}$ interactions constitute a pair of bifurcated acceptor bonds, generating an $R^{1}_{2}(6)$ motif. There are several other C—H$\cdots$O interactions which contribute to the supramolecular aggregation. In the crystal structure (Figs. 4 and 5), the ions and molecules are stacked in layers held together by three different π–π interactions, with distances of 4.069 Å between the centroids of the 4-nitrophenol and 4-nitrophenolate ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$) rings, 4.046 Å between the centroids of the 4-nitrophenolate and 4-dimethylaminopyridinium ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$) rings, and 3.912 Å between the centroids of the 4-nitrophenol and 4-dimethylaminopyridinium rings. Other short intermolecular contacts are C1$\cdots$O1($x+1, y, z$) of 3.179 (2) Å, N1$\cdots$O3($x-1, y, z$) of 3.026 (2) Å, C7$\cdots$O5($x-1, y, z$) of 3.201 (3) Å and N2$\cdots$O6($x+1, y, z$) of 3.072 (2) Å. The view of the unit cell contents along the *c* axis (Fig. 4) shows the columnar arrangement. The 4-dimethylaminopyridinium cations are stacked in columns in between the columns of 4-nitrophenolate anions and 4-nitrophenol molecules. The interplay of strong O—H$\cdots$O and N—H$\cdots$O, and weak C—H$\cdots$O and π–π interactions and van der Waals forces with different strengths, directional preferences and dependence on distance presents a complex mosaic of interactions. The three-dimensional arrangement of the 4-nitrophenolate and 4-dimethylaminopyridinium ions and 4-nitrophenol molecules in the unit cell shows that (I) is an internally linked hydrogen-

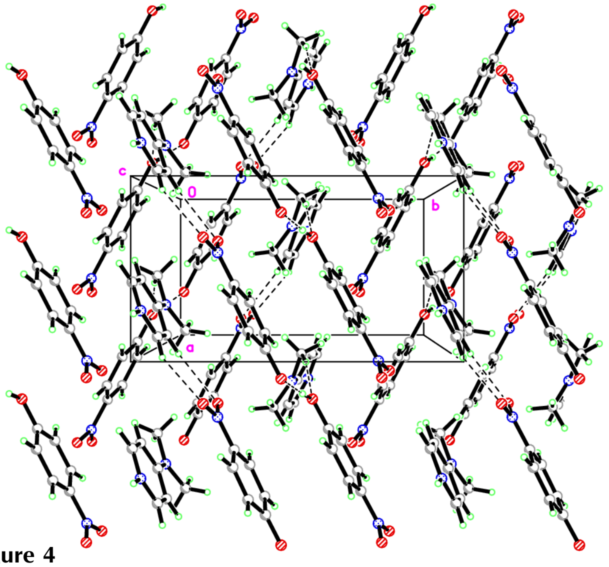


Figure 4
View of the molecules along the c axis in the unit cell, showing the zigzag chains of hydrogen bonds.

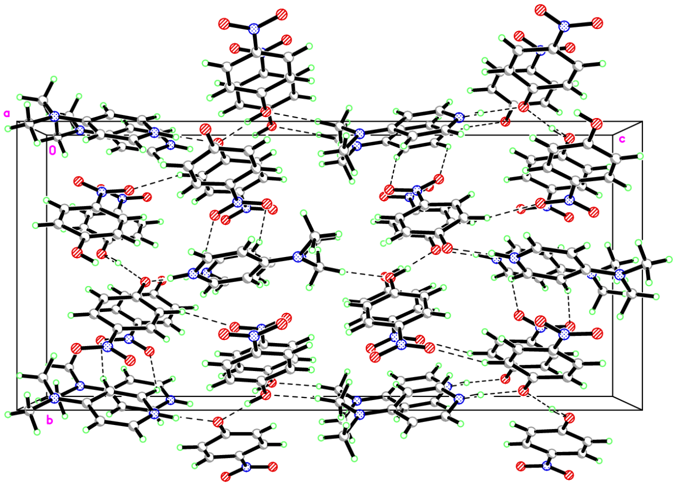


Figure 5
View of the molecules along the a axis in the unit cell, showing the network of O—H···O, N—H···O, C—H···O, C—H···N and π–π interactions.

bonded ion pair, and hence can be regarded as a molecular crystal rather than a salt.

Experimental

Dimethylaminopyridine (4.9 mmol) was dissolved in ethanol (25 ml). 4-Nitrophenol (5.0 mmol) was dissolved in ethanol (25 ml). The two solutions were mixed. The crystals of the title compound (I) (1.25 mmol, yield: 51%) were obtained by natural evaporation of the solvent at room temperature.

Crystal data

$C_7H_{11}N_2^+\cdot C_6H_4NO_3^-\cdot C_6H_5NO_3$
$M_r = 400.39$
Orthorhombic, $P2_12_12_1$
$a = 6.4168\ (16)$ Å
$b = 11.505\ (3)$ Å
$c = 24.943\ (6)$ Å
$V = 1841.4\ (8)$ Å^3
$Z = 4$
$D_x = 1.444$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 701 reflections
$\theta = 3.0$–$22.4°$
$\mu = 0.11$ mm^{-1}
$T = 120\ (2)$ K
Block, yellow
$0.20 \times 0.15 \times 0.11$ mm

Data collection

Bruker Proteum M diffractometer
ω scans
Absorption correction: none
12716 measured reflections
2355 independent reflections
1940 reflections with $I > 2\sigma(I)$

$R_{int} = 0.048$
$\theta_{max} = 27.2°$
$h = -8 \rightarrow 7$
$k = -13 \rightarrow 14$
$l = -19 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.065$
$S = 1.09$
2355 reflections
322 parameters

Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0196P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O3	1.336 (3)	C10—C11	1.388 (4)
C1—C6	1.397 (3)	C10—N2	1.439 (3)
C1—C2	1.398 (3)	C11—C12	1.377 (3)
C2—C3	1.384 (4)	N2—O5	1.236 (3)
C3—C4	1.383 (3)	N2—O4	1.241 (3)
C4—C5	1.383 (4)	C13—N4	1.342 (3)
C4—N1	1.454 (3)	C13—C14	1.410 (3)
C5—C6	1.371 (4)	C13—C17	1.416 (3)
N1—O1	1.232 (3)	C14—C15	1.359 (3)
N1—O2	1.238 (3)	C15—N3	1.342 (3)
C7—O6	1.316 (3)	C16—N3	1.346 (3)
C7—C12	1.408 (4)	C16—C17	1.356 (3)
C7—C8	1.411 (3)	C18—N4	1.464 (4)
C8—C9	1.371 (4)	C19—N4	1.458 (4)
C9—C10	1.385 (4)		
O1—N1—O2	122.6 (2)	O4—N2—C10	118.8 (2)
O1—N1—C4	119.0 (2)	C15—N3—C16	119.7 (2)
O2—N1—C4	118.5 (2)	C13—N4—C19	120.8 (2)
O5—N2—O4	122.6 (2)	C13—N4—C18	121.5 (2)
O5—N2—C10	118.6 (2)	C19—N4—C18	117.3 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O1	0.95 (2)	2.40 (2)	2.735 (3)	100.1 (17)
C5—H5···O2	0.97 (2)	2.42 (2)	2.715 (3)	97.2 (16)
C8—H8···N3	0.98 (3)	2.71 (2)	3.391 (3)	126.9 (18)
C9—H9···O5	0.92 (2)	2.41 (3)	2.712 (3)	99.3 (18)
C11—H11···O4	0.95 (2)	2.43 (2)	2.733 (3)	98.2 (17)
N3—H3B···O6	0.90 (2)	1.77 (3)	2.657 (3)	169 (2)
C2—H2···O6^{i}	0.98 (2)	2.88 (2)	3.470 (3)	119.2 (17)
O3—H3A···O6^{i}	0.89 (2)	1.63 (3)	2.516 (2)	171 (3)
C6—H6···O2^{ii}	0.94 (2)	2.71 (2)	3.407 (3)	131 (2)
C5—H5···O2^{ii}	0.97 (2)	2.89 (2)	3.484 (3)	120.5 (18)
C8—H8···O1^{iii}	0.98 (3)	2.41 (3)	3.206 (3)	138.0 (19)
C12—H12···O3^{iv}	0.93 (2)	2.63 (2)	3.265 (3)	126.0 (18)
C14—H14···O4^{v}	0.94 (2)	2.54 (2)	3.459 (3)	164 (2)
C14—H14···O5^{v}	0.94 (2)	2.74 (2)	3.291 (3)	117.6 (18)
C15—H15···O5^{v}	0.96 (2)	2.43 (2)	3.120 (3)	128.3 (18)
C14—H14···N2^{v}	0.94 (2)	3.00 (2)	3.788 (3)	141.8 (18)
C17—H17···O1^{vi}	0.93 (2)	2.80 (2)	3.390 (3)	122.3 (18)
C17—H17···O2^{vi}	0.93 (2)	2.65 (2)	3.548 (3)	164.1 (19)
C18—H18C···O2^{vi}	0.99 (3)	2.76 (3)	3.641 (4)	148 (2)
C16—H16···O1^{vi}	0.97 (3)	2.68 (2)	3.342 (3)	126.5 (18)
C19—H19B···O3^{vii}	0.95 (3)	2.85 (3)	3.593 (4)	136 (2)
C19—H19B···O4^{vii}	0.95 (3)	2.99 (3)	3.790 (4)	142 (2)
C18—H18A···O3^{vii}	0.98 (3)	2.52 (3)	3.475 (4)	164 (2)
C18—H18B···O4^{viii}	0.95 (3)	2.90 (3)	3.607 (4)	133 (2)

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

o1194 N. Vembu *et al.* • $C_7H_{11}N_2^+\cdot C_6H_5NO_3^-\cdot C_6H_4NO_3$ *Acta Cryst.* (2003). E**59**, o1192–o1195

All the H atoms were located from a difference Fourier map and their positional parameters were refined. Their $U_{\rm iso}$ parameters were set to $1.2U_{\rm eq}$ of their bonded partners. The C—H bond lengths are in the range 0.89 (2)–1.02 (3) Å and the O—H distance is 0.98 (2) Å. Friedel-pair reflections were merged before the final refinement, since the Flack (1983) parameter was 1.4 (11).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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