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# 4-Dimethylaminopyridinium 2,4-dinitrophenolate: supramolecular aggregation through N—H···O, C—H···O, C—H···$\pi$ and $\pi$–$\pi$ interactions

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**Key indicators**

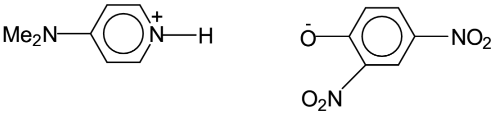
Single-crystal X-ray study
$T$ = 120 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.037
$wR$ factor = 0.067
Data-to-parameter ratio = 9.7

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

Within and between molecules of the title compound, $C_7H_{11}N_2^+ \cdot C_6H_3N_2O_5^-$, there are N—H···O and C—H···O interactions which generate rings of motifs $S(5)$, $D$, $D_1^2(4)$, $R_2^1(7)$, $R_2^1(5)$, $R_1^2(6)$, $R_2^2(10)$ and $R_2^2(14)$. The supramolecular aggregation is completed by the presence of C—H···$\pi$ and $\pi$–$\pi$ interactions.

## Comment

The design of organic polar crystals for quadratic non-linear optical (NLO) applications is supported by the observation that organic molecules containing $\pi$-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 $\pi$-acceptors, forming various $\pi$-stacking complexes with other aromatic molecules, but also as acidic ligands, forming salts through specific electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). The bonding of electron–donor acceptor complexes depends strongly 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-transferred 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 it (Mizutani *et al.*, 1998).



(I)

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 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, Nallu, Garrison & Youngs, 2003). The reaction of 4-nitrophenol with 4-dimethylaminopyridine results in the formation of a new NLO material, the crystal structure of which has been reported at room temperature (Evans *et al.*, 1998). Recently, we have reported the crystal structure of 4-dimethylaminopyridinium 4-nitrophenolate 4-nitrophenol (1/1/1) at 120 K (Vembu *et al.*, 2003). The X-ray structure determination of the title compound, (I), has been undertaken to study the nature of the interaction between

4-dimethylaminopyridine and 2,4-dinitrophenol in the solid state. This study may serve as a forerunner for assessing the optical properties of (I).

The asymmetric unit of (I) contains one 4-dimethylaminopyridinium cation and one 2,4-dinitrophenolate anion (Fig. 1). The bond lengths and angles of the phenolate and dimethylaminopyridinium moieties (Table 1) are comparable with 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···O and C—H···O interactions. The range of H···O distances (Table 2) found in (I) agrees with those found for N—H···O (Jeffrey, 1997) and C—H···O hydrogen bonds (Desiraju & Steiner, 1999). As shown in Fig. 2, each of the C3—H3···O3, C3—H3···O4 and C5—H5···O5 interactions generates an *S*(5) ring motif (Etter, 1990; Bernstein *et al.*, 1995). The *S*(5) rings generated by the C3—H3···O4 and C5—H5···O5 interactions are planar, whereas that generated by the C3—H3···O3 interaction is distorted from planarity, as atom O3 deviates by −0.284 (5) Å from the mean plane. The C3—H3···O3 and C3—H3···O4 interactions together constitute a pair of bifurcated donor bonds. The C12—H12C···O5 interaction generates a *D* motif linking the 4-dimethylaminopyridinium and 2,4-dinitrophenolate moieties together. The C13—H13*A*···O4 and C13—H13*A*···O5 interactions constitute a pair of bifurcated donor bonds generating a symmetrical three-centred hydrogen-bonded chelate (Desiraju, 1989) motif of graph set $D_1^2(4)$.

As seen from Fig. 3, the C12—H12*B*···O4$^{\rm i}$ and C10—H10···O4$^{\rm i}$ interactions constitute a pair of bifurcated acceptor bonds generating an $R_2^1(7)$ motif. The C11—H11···O1$^{\rm ii}$ and N3—H3*A*···O1$^{\rm ii}$ interactions constitute a pair of bifurcated acceptor bonds generating an $R_2^1(5)$ motif. The C7—H7···O2$^{\rm ii}$ and N3—H3*A*···O2$^{\rm ii}$ interactions constitute another pair of bifurcated acceptor bonds generating an $R_2^1(5)$ motif. The N3—H3*A*···O1$^{\rm ii}$ and N3—H3*A*···O2$^{\rm ii}$ interactions constitute a pair of bifurcated donor bonds generating an $R_1^2(6)$ motif. The C7—H7···O2$^{\rm ii}$ and C11—H11···O1$^{\rm ii}$ interactions together generate an $R_2^2(10)$ motif. The C8—H8···O3$^{\rm iii}$ and C13—H13*B*···O3$^{\rm iii}$ interactions together generate a pair of bifurcated acceptor bonds generating an $R_2^1(7)$ motif. The C12—H12*B*···O4$^{\rm iv}$ and C11—H11···O3$^{\rm iv}$ interactions together generate an $R_2^2(14)$ motif. There are several other weak C—H···O interactions and a C—H···π interaction, which contribute to the supramolecular aggregation of (I) (Table 2).

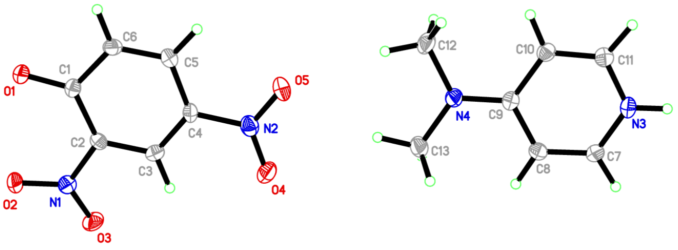


**Figure 1**
The molecular structure of (I), showing 50% probability displacement ellipsoids.

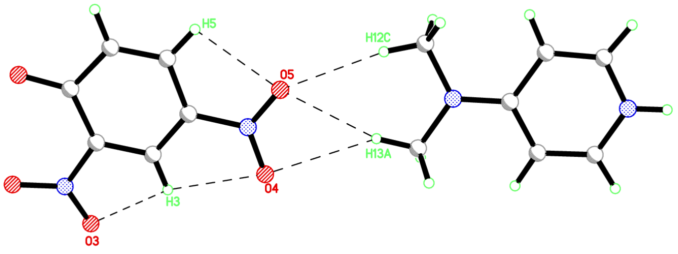


**Figure 2**
Hydrogen bonds 1–6 as dashed lines (the numbers correspond to the sequence of entries in Table 2).

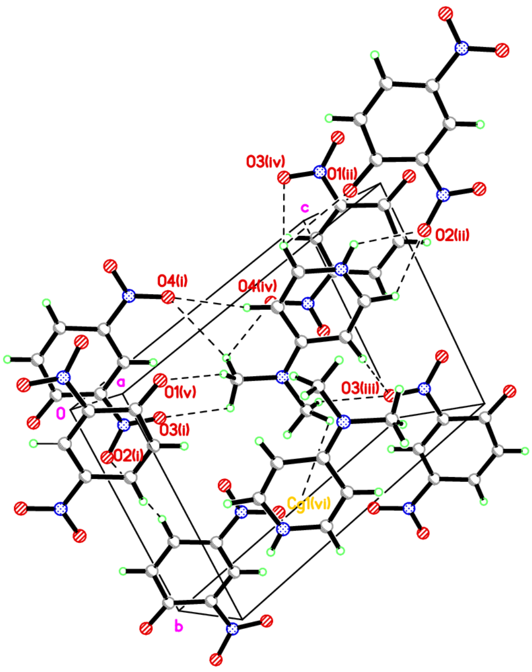


**Figure 3**
Hydrogen bonds 7–12 and 14–20 as dashed lines (the numbers correspond to sequence of entries in Table 2). Symmetry codes are as in Table 2.

In the crystal structure of (I) (Fig. 4), the molecules are stacked in layers held together by pairs of π–π interactions, with a distance of 3.697 (1) Å between the centroids of the pyridinium ring and the benzene ring of the inversion-related 2,4-dinitrophenolate at (1−*x*, 1−*y*, 1−*z*), and a distance of 3.561 (1) Å between the centroids of the benzene rings at (*x*, *y*, *z*) and (1−*x*, 2−*y*, −*z*). The interplay of strong N—H···O and weak C—H···O, C—H···π and π–π interactions with different strengths, directional preferences and distances presents a complex mosaic of interactions. The three-dimensional arrangement of 2,4-dinitrophenolate and 4-dimethylaminopyridinium moieties in the unit cell shows that (I) is an internally linked hydrogen-bonded ion pair, and hence can be regarded as a molecular crystal rather than a salt.

## Experimental

4-Dimethylaminopyridine (4.9 mmol) in ethanol (25 ml) was added to 2,4-dinitrophenol (4.9 mmol) dissolved in ethanol (25 ml). The

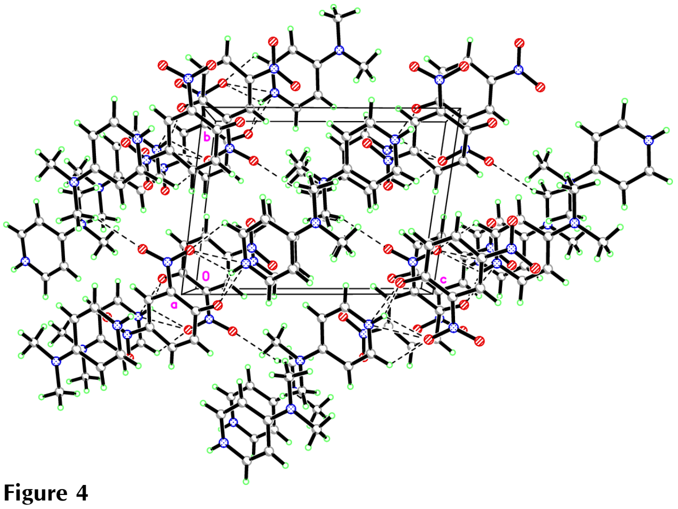


**Figure 4**
Packing of the molecules in the unit cell of (I), viewed along the *a* axis, showing the N—H···O, C—H···O, C—H···$\pi$ and $\pi$–$\pi$ interactions as dashed lines.

precipitate, (I) (3.9 mmol, yield 79%), was filtered and recrystallized from a 1:1 mixture of petroleum ether and acetone.

### *Crystal data*

$C_7H_{11}N_2^+ \cdot C_6H_3N_2O_5^-$
$M_r$ = 306.28
Triclinic, $P\overline{1}$
$a$ = 7.7246 (9) Å
$b$ = 8.1665 (10) Å
$c$ = 10.8838 (13) Å
$\alpha$ = 96.916 (3)°
$\beta$ = 92.630 (3)°
$\gamma$ = 101.618 (3)°
$V$ = 665.88 (14) Å$^3$

$Z$ = 2
$D_x$ = 1.528 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 763 reflections
$\theta$ = 2.6–27.0°
$\mu$ = 0.12 mm$^{-1}$
$T$ = 120 (2) K
Block, yellow
0.15 × 0.15 × 0.12 mm

### *Data collection*

Bruker Proteum *M* diffractometer
$\omega$ scans
3781 measured reflections
2332 independent reflections
1444 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.037
$\theta_{\rm max}$ = 25°
$h = -9 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 11$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.067
$S$ = 0.80
2332 reflections
241 parameters

Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.20 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C1—O1 | 1.262 (2) | N2—O4 | 1.2438 (19) |
| C2—N1 | 1.445 (2) | C7—N3 | 1.344 (2) |
| C4—N2 | 1.440 (2) | C9—N4 | 1.347 (2) |
| N1—O3 | 1.2393 (19) | C11—N3 | 1.348 (2) |
| N1—O2 | 1.240 (2) | C12—N4 | 1.459 (3) |
| N2—O5 | 1.2354 (18) | C13—N4 | 1.461 (3) |
| | | | |
| O3—N1—O2 | 121.66 (16) | O4—N2—C4 | 119.24 (17) |
| O3—N1—C2 | 118.94 (17) | C7—N3—C11 | 120.24 (19) |
| O2—N1—C2 | 119.40 (17) | C9—N4—C12 | 120.52 (17) |
| O5—N2—O4 | 122.57 (17) | C9—N4—C13 | 120.30 (17) |
| O5—N2—C4 | 118.19 (17) | C12—N4—C13 | 118.69 (17) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C3—H3···O3 | 0.954 (17) | 2.350 (16) | 2.665 (2) | 98.6 (12) |
| C3—H3···O4 | 0.954 (17) | 2.421 (17) | 2.728 (3) | 98.3 (11) |
| C5—H5···O5 | 0.977 (17) | 2.406 (17) | 2.732 (2) | 98.8 (11) |
| C12—H12*C*···O5 | 0.990 (19) | 2.60 (2) | 3.576 (3) | 170.0 (14) |
| C13—H13*A*···O4 | 1.03 (2) | 2.78 (2) | 3.697 (3) | 147.9 (14) |
| C13—H13*A*···O5 | 1.03 (2) | 2.62 (2) | 3.628 (3) | 164.5 (14) |
| C12—H12*C*···O3$^{\rm i}$ | 0.990 (19) | 2.972 (18) | 3.541 (3) | 117.6 (13) |
| C12—H12*B*···O4$^{\rm i}$ | 1.02 (2) | 2.920 (18) | 3.457 (3) | 113.6 (13) |
| C10—H10···O4$^{\rm i}$ | 0.968 (17) | 2.585 (18) | 3.533 (2) | 166.3 (15) |
| C5—H5···O2$^{\rm i}$ | 0.977 (17) | 2.772 (17) | 3.558 (2) | 137.9 (13) |
| C11—H11···O1$^{\rm ii}$ | 0.989 (17) | 2.731 (17) | 3.126 (2) | 104.3 (11) |
| C7—H7···O2$^{\rm ii}$ | 0.983 (18) | 2.369 (17) | 2.986 (3) | 120.2 (12) |
| N3—H3*A*···O1$^{\rm ii}$ | 0.913 (19) | 1.791 (19) | 2.624 (2) | 150.4 (17) |
| N3—H3*A*···O2$^{\rm ii}$ | 0.913 (19) | 2.238 (19) | 2.865 (2) | 125.4 (15) |
| C8—H8···O3$^{\rm iii}$ | 0.968 (17) | 2.688 (18) | 3.555 (2) | 149.3 (14) |
| C13—H13*B*···O3$^{\rm iii}$ | 0.94 (2) | 2.51 (2) | 3.233 (3) | 133.8 (14) |
| C12—H12*B*···O4$^{\rm iv}$ | 1.02 (2) | 2.94 (2) | 3.683 (3) | 130.3 (13) |
| C11—H11···O3$^{\rm iv}$ | 0.989 (17) | 2.858 (18) | 3.401 (3) | 115.3 (13) |
| C12—H12*A*···O1$^{\rm v}$ | 0.968 (19) | 2.74 (2) | 3.646 (3) | 156.1 (15) |
| C13—H13*C*···*Cg*1$^{\rm vi}$† | 0.993 (18) | 3.22 (2) | 3.745 (2) | 114.4 (14) |

Symmetry codes: (i) $x, y-1, z$; (ii) $1+x, y-1, 1+z$; (iii) $1-x, 2-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 1-y, -z$; (vi) $2-x, 1-y, 1-z$. † *Cg*1 denotes the centroid of the pyridine ring.

All H atoms were located from difference Fourier maps and their positional parameters were refined, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom). The C—H bond lengths are in the range 0.95 (2)–1.03 (2) Å.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); 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*.

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