

4-Dimethylaminopyridinium picrate: supramolecular aggregation through extensive N—H···O and C—H···O interactions

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Key indicators

Single-crystal X-ray study

$T = 100\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.072

wR factor = 0.155

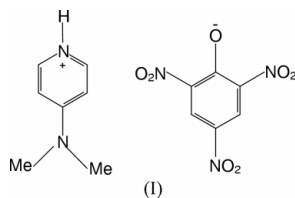
Data-to-parameter ratio = 12.5

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

The crystal structure of the title compound, $\text{C}_6\text{H}_2\text{N}_3\text{O}_7$ – $\text{C}_7\text{H}_{11}\text{N}_2$, contains two 4-dimethylaminopyridinium cations and two picrate anions in the asymmetric unit. The N—H···O and C—H···O interactions generate rings of graph set motifs $S(5)$, $R_1^1(6)$, $R_2^1(5)$, $R_1^1(4)$, $R_2^1(7)$, $R_2^1(6)$, $R_2^1(8)$, $R_2^1(10)$ and $R_2^1(14)$, which contribute to the supramolecular aggregation through bifurcated and trifurcated bonds.

Comment

The design of organic polar crystals for quadratic non-linear optical applications is supported by the observation that organic molecules containing π -electron systems asymmetricized 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 picric acid acts not only as an acceptor to form various π -stacking complexes with other aromatic molecules, but also as an acidic ligand to form salts through specific electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). The bonding of electron-donor-acceptor picric acid 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-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 can stabilize it (Mizutani *et al.*, 1998). Pyridinium picrate has been reported in two crystalline phases, and it occurs in both phases as an internally linked hydrogen-bonded ion pair; both phases are regarded as molecular crystals rather than salts, based on their structural arrangements (Botoshansky *et al.*, 1994). It has been reported that the reaction of 4-nitrophenol with 4-dimethylaminopyridine resulted in the formation of a new NLO material, which was found to be an association of three components, 4-nitrophenolate–4-nitrophenol–4-dimethylaminopyridinium (Evans *et al.*, 1998).



The X-ray structure determination of the title compound, (I), was undertaken to study the nature of the interaction

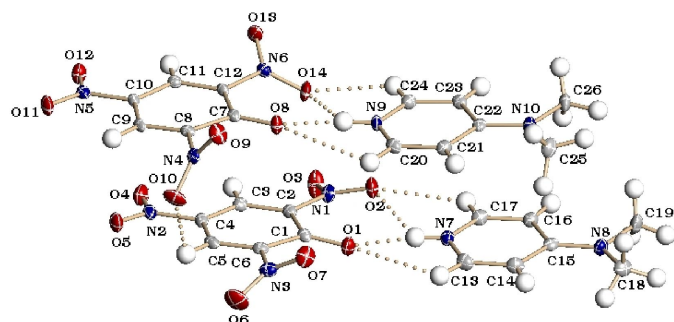


Figure 1

The contents of the asymmetric unit of (I), showing 50% probability displacement ellipsoids and N—H...O and C—H...O interactions.

between 4-dimethylaminopyridine and picric acid in the solid state. This study may serve as a forerunner for assessing the optical properties of the title compound.

The asymmetric unit of (I) contains two 4-dimethylaminopyridinium cations and two picrate anions (Fig. 1). The bond lengths and angles of the picrate and dimethylaminopyridinium moieties (Table 1) are comparable to those found in related structures reported in the Cambridge Structural Database (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 bonds (Desiraju & Steiner, 1999).

The C3—H3...O3 and C3—H3...O4 interactions constitute a pair of bifurcated donor bonds generating two fused rings, each of graph-set motif $S(5)$ (Etter, 1990; Bernstein *et al.*, 1995). A similar motif is generated by the C5—H5...O5 and C5—H5...O6 interactions. The C9—H9...O10 and C9—H9...O11 interactions form a pair of bifurcated donor bonds generating two fused rings, each of graph-set motif $S(5)$. A similar motif is generated by the C11—H11...O12 and C11—H11...O13 interactions. The N7—H'...O1 and N7—H'...O2 interactions constitute a pair of bifurcated donor bonds generating a ring of graph-set motif $R_1^2(6)$. The N7—H'...O1 and C13—H13...O1 interactions form a pair of bifurcated acceptor bonds, generating a ring of graph-set motif $R_2^1(5)$. The N7—H'...O2 and C17—H17...O2 interactions form a pair of bifurcated acceptor bonds, generating a ring of graph-set motif $R_2^1(5)$. The N9—H''...O8 and N9—H''...O14 interactions constitute a pair of bifurcated donor bonds, generating a ring of graph-set motif $R_1^2(6)$. The N9—H''...O8 and C20—H20...O8 interactions form a pair of bifurcated acceptor bonds, generating a ring of graph-set motif $R_2^1(5)$. The N9—H''...O14 and C24—H24...O14 interactions form a pair of bifurcated acceptor bonds, generating a ring of graph-set motif $R_2^1(5)$. The C5—H5...O10 interaction links the two anions present in the asymmetric unit.

The C11—H11...O4ⁱ and C11—H11...O12ⁱ interactions constitute a pair of bifurcated donor bonds involving acceptor O atoms from symmetry-related anions. The C9—H9...O2ⁱⁱ and C9—H9...O3ⁱⁱ interactions constitute a pair of bifurcated donor bonds and they generate a ring of graph-set motif $R_1^2(4)$. The C21—H21...O6ⁱⁱⁱ and C25—H25C...O6ⁱⁱⁱ interactions

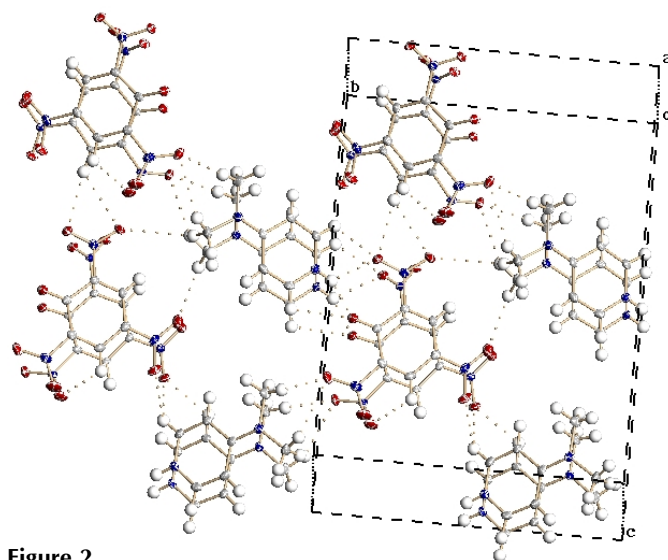


Figure 2

A view of the molecular packing of (I).

form a pair of bifurcated acceptor bonds, generating a ring of graph-set motif $R_2^1(7)$. The C16—H16...O5^{iv} and C17—H17...O5^{iv} interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph-set motif $R_2^1(5)$. The above motif can best be regarded as a three-center symmetrical hydrogen-bonded chelate (Desiraju, 1989; Vembu, Nallu, Garrison & Youngs, 2003b; Vembu, Nallu, Garrison & Youngs, 2003c; Vembu, Nallu, Garrison, Hindi & Youngs, 2003). The C17—H17...O11^{iv} and C17—H17...O5^{iv} interactions constitute a pair of bifurcated donor bonds. The C17—H17...O11^{iv} and C23—H23...O11^{iv} interactions form a pair of bifurcated acceptor bonds. The C19—H19B...O13^v and C16—H16...O13^v interactions form a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(7)$.

The C26—H26C...O13^v and C26—H26C...O14^v interactions constitute a pair of bifurcated donor bonds, generating a ring of graph-set motif $R_1^2(4)$. The C19—H19B...O13^v, C16—H16...O13^v and C26—H26C...O13^v interactions can be collectively termed as trifurcated acceptor bonds. The C19—H19A...O7^{vi} and C18—H18A...O7^{vi} interactions form a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(6)$. The C25—H25A...O9^{vi} and C26—H26B...O9^{vi} interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(6)$. The C25—H25B...O12^{viii} and C26—H26A...O11^{viii} interactions generate a fork motif (Vembu, Nallu, Garrison & Youngs, 2003a) of graph set $R_2^2(8)$. The C26—H26A...O11^{viii} and C24—H24...O9^{viii} interactions generate a ring of graph set $R_2^2(14)$. Another $R_2^2(14)$ motif is formed by the C25—H25B...O12^{viii} and C24—H24...O9^{viii} interactions. The C25—H25A...O3^{ix} and C25—H25B...O4^{ix} interactions generate a ring of graph set $R_2^2(10)$. (Symmetry codes are given in Table 2.)

The three-dimensional arrangement of the picrate and the dimethylaminopyridinium ions in the unit cell shows that the title compound is an internally linked hydrogen-bonded ion pair, and hence can be regarded as a molecular crystal rather than a salt.

Experimental

Picric acid (5.2 mmol) dissolved in dichloromethane (25 ml) was added dropwise to 4-dimethylaminopyridine (5.7 mmol) in dichloromethane (25 ml). This solution was stirred constantly at room temperature for 2 h. The precipitated product was filtered off and recrystallized from aqueous ethanol.

Crystal data

| | |
|---------------------------------------|---|
| $C_7H_{11}N_2^+ \cdot C_6H_2N_3O_7^-$ | $D_x = 1.597 \text{ Mg m}^{-3}$ |
| $M_r = 351.28$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 5444 reflections |
| $a = 15.274 (4) \text{ \AA}$ | $\theta = 2.4\text{--}28.2^\circ$ |
| $b = 12.617 (3) \text{ \AA}$ | $\mu = 0.13 \text{ mm}^{-1}$ |
| $c = 19.795 (4) \text{ \AA}$ | $T = 100 (2) \text{ K}$ |
| $\beta = 129.996 (13)^\circ$ | Block, yellow |
| $V = 2922.4 (12) \text{ \AA}^3$ | $0.50 \times 0.40 \times 0.20 \text{ mm}$ |
| $Z = 8$ | |

Data collection

| | |
|---|--|
| Bruker CCD area-detector diffractometer | 6947 independent reflections |
| φ and ω scans | 5744 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $R_{\text{int}} = 0.069$ |
| $T_{\text{min}} = 0.937$, $T_{\text{max}} = 0.974$ | $\theta_{\text{max}} = 28.3^\circ$ |
| 24887 measured reflections | $h = -20 \rightarrow 19$ |
| | $k = -16 \rightarrow 16$ |
| | $l = -26 \rightarrow 26$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 2.9161P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.072$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.155$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 1.20$ | $\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$ |
| 6947 reflections | $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$ |
| 555 parameters | |
| All H-atom parameters refined | |

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|------------|-------------|-------------|-------------|
| O1—C1 | 1.235 (3) | N2—C4 | 1.441 (3) |
| O2—N1 | 1.224 (3) | N3—C6 | 1.454 (3) |
| O3—N1 | 1.226 (3) | N4—C8 | 1.457 (3) |
| O4—N2 | 1.223 (3) | N5—C10 | 1.444 (3) |
| O5—N2 | 1.232 (3) | N6—C12 | 1.451 (3) |
| O6—N3 | 1.230 (3) | N7—C17 | 1.340 (3) |
| O7—N3 | 1.215 (3) | N7—C13 | 1.345 (3) |
| O8—C7 | 1.240 (3) | N8—C15 | 1.337 (3) |
| O9—N4 | 1.218 (3) | N8—C18 | 1.448 (3) |
| O10—N4 | 1.218 (3) | N8—C19 | 1.458 (3) |
| O11—N5 | 1.228 (2) | N9—C24 | 1.337 (3) |
| O12—N5 | 1.225 (3) | N9—C20 | 1.344 (3) |
| O13—N6 | 1.221 (3) | N10—C22 | 1.335 (3) |
| O14—N6 | 1.225 (3) | N10—C25 | 1.458 (3) |
| N1—C2 | 1.454 (3) | N10—C26 | 1.463 (3) |
| O2—N1—O3 | 122.4 (2) | O12—N5—C10 | 118.45 (18) |
| O2—N1—C2 | 119.45 (19) | O11—N5—C10 | 117.91 (19) |
| O3—N1—C2 | 118.2 (2) | O13—N6—O14 | 123.37 (19) |
| O4—N2—O5 | 123.5 (2) | O13—N6—C12 | 117.95 (19) |
| O4—N2—C4 | 118.7 (2) | O14—N6—C12 | 118.67 (19) |
| O5—N2—C4 | 117.8 (2) | C17—N7—C13 | 119.9 (2) |
| O7—N3—O6 | 123.1 (2) | C15—N8—C18 | 122.6 (2) |
| O7—N3—C6 | 119.1 (2) | C15—N8—C19 | 120.7 (2) |
| O6—N3—C6 | 117.8 (2) | C18—N8—C19 | 116.3 (2) |
| O9—N4—O10 | 123.4 (2) | C24—N9—C20 | 120.3 (2) |
| O9—N4—C8 | 118.23 (19) | C22—N10—C25 | 120.8 (2) |
| O10—N4—C8 | 118.3 (2) | C22—N10—C26 | 120.3 (2) |
| O12—N5—O11 | 123.6 (2) | C25—N10—C26 | 118.9 (2) |

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--------------------------------|----------|--------------|--------------|----------------|
| N7—H ⁱ ···O1 | 0.86 (3) | 1.83 (3) | 2.640 (3) | 156 (3) |
| N7—H ⁱ ···O2 | 0.86 (3) | 2.41 (3) | 2.986 (3) | 125 (2) |
| N9—H ⁱⁱ ···O8 | 0.89 (3) | 1.84 (3) | 2.669 (3) | 154 (2) |
| N9—H ⁱⁱ ···O14 | 0.89 (3) | 2.34 (3) | 2.934 (3) | 124 (2) |
| C3—H3···O3 | 0.93 (3) | 2.38 (3) | 2.661 (3) | 97 (2) |
| C3—H3···O4 | 0.93 (3) | 2.42 (3) | 2.718 (3) | 99 (2) |
| C5—H5···O5 | 0.95 (3) | 2.45 (3) | 2.696 (3) | 94.2 (17) |
| C5—H5···O6 | 0.95 (3) | 2.37 (3) | 2.701 (3) | 99.6 (18) |
| C5—H5···O10 | 0.95 (3) | 2.72 (3) | 3.237 (3) | 114.6 (19) |
| C9—H9···O10 | 0.96 (2) | 2.68 (2) | 2.860 (3) | 91.0 (15) |
| C9—H9···O11 | 0.96 (2) | 2.47 (2) | 2.712 (3) | 94.1 (15) |
| C11—H11···O12 | 0.94 (3) | 2.40 (3) | 2.702 (3) | 98.2 (18) |
| C11—H11···O13 | 0.94 (3) | 2.41 (3) | 2.681 (3) | 96.0 (18) |
| C13—H13···O1 | 0.95 (3) | 2.87 (3) | 3.201 (3) | 102 (2) |
| C17—H17···O2 | 0.93 (3) | 2.51 (3) | 3.090 (3) | 121 (2) |
| C20—H20···O8 | 0.94 (3) | 2.94 (3) | 3.232 (3) | 99.2 (17) |
| C24—H24···O14 | 0.92 (3) | 2.40 (3) | 3.007 (3) | 123 (2) |
| C11—H11···O4 ⁱ | 0.94 (3) | 2.56 (3) | 3.430 (3) | 153 (2) |
| C11—H11···O12 ⁱ | 0.94 (3) | 2.66 (3) | 3.195 (3) | 116.7 (19) |
| C9—H9···O2 ⁱⁱ | 0.96 (2) | 2.56 (2) | 3.501 (3) | 169.5 (19) |
| C9—H9···O3 ⁱⁱ | 0.96 (2) | 2.89 (2) | 3.552 (3) | 127.7 (17) |
| C14—H14···O10 ⁱⁱⁱ | 0.92 (3) | 2.32 (3) | 3.186 (3) | 156 (2) |
| C21—H21···O6 ⁱⁱⁱ | 0.93 (3) | 2.45 (3) | 3.328 (3) | 159 (3) |
| C13—H13···O5 ⁱⁱⁱ | 0.95 (3) | 2.86 (3) | 3.733 (3) | 153 (2) |
| C25—H25C···O6 ⁱⁱⁱ | 1.03 (3) | 2.94 (3) | 3.579 (3) | 121 (2) |
| C17—H17···O5 ^{iv} | 0.93 (3) | 2.78 (3) | 3.140 (3) | 104.3 (19) |
| C23—H23···O11 ^{iv} | 0.95 (2) | 2.58 (2) | 3.163 (3) | 119.7 (18) |
| C16—H16···O11 ^{iv} | 0.93 (3) | 2.45 (3) | 3.156 (3) | 133 (2) |
| C16—H16···O5 ^{iv} | 0.93 (2) | 2.68 (3) | 3.098 (3) | 107.9 (18) |
| C19—H19B···O13 ^v | 0.93 (3) | 2.48 (3) | 3.188 (3) | 133 (3) |
| C16—H16···O13 ^v | 0.93 (2) | 2.94 (3) | 3.784 (3) | 151 (2) |
| C26—H26C···O13 ^v | 0.95 (3) | 2.77 (3) | 3.524 (3) | 137 (2) |
| C26—H26C···O14 ^v | 0.95 (3) | 2.98 (3) | 3.245 (3) | 97 (2) |
| C19—H19A···O7 ^{vi} | 0.85 (4) | 2.42 (4) | 3.273 (3) | 177 (3) |
| C26—H26B···O9 ^{vi} | 0.94 (3) | 2.46 (3) | 3.398 (3) | 176 (2) |
| C18—H18A···O7 ^{vi} | 0.95 (4) | 2.84 (4) | 3.695 (4) | 151 (3) |
| C25—H25A···O9 ^{vi} | 0.96 (3) | 2.85 (3) | 3.706 (3) | 149 (2) |
| C18—H18C···O3 ^{vii} | 0.98 (3) | 2.95 (3) | 3.857 (4) | 153 (2) |
| C25—H25B···O12 ^{viii} | 0.97 (3) | 2.74 (3) | 3.406 (3) | 126 (2) |
| C24—H24···O9 ^{viii} | 0.92 (3) | 2.88 (3) | 3.380 (3) | 116 (2) |
| C26—H26A···O11 ^{viii} | 0.95 (3) | 2.76 (3) | 3.363 (3) | 122 (2) |
| C25—H25A···O3 ^{ix} | 0.96 (3) | 2.87 (3) | 3.651 (3) | 139 (2) |
| C25—H25B···O4 ^{ix} | 0.97 (3) | 2.64 (3) | 3.578 (3) | 164 (2) |

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

H atoms were located in a difference Fourier map and both positional and isotropic displacement parameters were refined. The ranges of C—H and N—H bond lengths are 0.92 (3)–1.04 (4) \AA and 0.86 (3)–0.89 (3) \AA , respectively, and U_{iso} values range from 0.003 (5) to 0.058 (12) \AA^2 .

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

NV thanks the University Grants Commission—SERO, Government of India, for the award of a Faculty Improvement Programme Grant [TFTNBD097 dated 07.07.99].

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