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Charge-transfer complexes of 4-(dimethylamino)pyridine with 2,4-, 3,4-and 3,5-dinitrobenzoic acid

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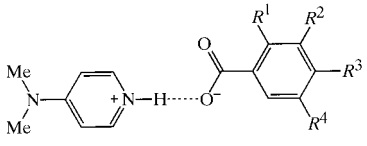
In the three title crystal structures 4-(dimethylamino)-pyridinium 2,4-dinitrobenzoate, (I), 4-(dimethylamino)pyridinium 3,4-dinitrobenzoate, (II), and 4-(dimethylamino)-pyridinium 3,5-dinitrobenzoate, (III), all $C_7H_{11}N_2^+\cdot C_7H_3N_2O_6^-$, the ions are connected by an N—H···O hydrogen bond. Dihedral angles between the pyridine and phenyl rings are 69.9 (1), 26.7 (1) and 56.2 (1)° in (I), (II) and (III), respectively. Donor–acceptor π–π stacking is observed in (II) and (III), but not in (I).

Comment

The efficiency for second harmonic generation (SHG) of (III) was 0.1 relative to an SHG signal of urea (Ito *et al.*, 1998).



(I) $R^1 = R^2 = NO_2, R^3 = R^4 = H$
(II) $R^2 = R^3 = NO_2, R^1 = R^4 = H$
(III) $R^2 = R^4 = NO_2, R^1 = R^3 = H$

Dihedral angles between the pyridine and phenyl rings are 69.9 (1), 26.7 (1) and 56.2 (1)° in (I), (II) and (III), respectively.

Experimental

For the preparation of (I), (II) and (III), equimolecular mixtures of 4-(dimethylamino)pyridine and 2,4-, 3,4- or 3,5-dinitrobenzoic acid were recrystallized from acetone.

Compound (I)

Crystal data

$C_7H_{11}N_2^+\cdot C_7H_3N_2O_6^-$
M_r = 334.29
Triclinic, $P\overline{1}$
a = 8.785 (1) Å
b = 12.276 (2) Å
c = 7.696 (1) Å
α = 107.37 (1)°
β = 105.86 (1)°
γ = 77.01 (1)°
V = 752.7 (2) Å^3
Z = 2
D_x = 1.475 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12.0–14.9°
μ = 0.118 mm^{-1}
T = 298 (1) K
Prism, colourless
0.2 × 0.2 × 0.1 mm

Data collection

Rigaku AFC-7R diffractometer
θ–2θ scans
3604 measured reflections
3444 independent reflections
1740 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 27.5°
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 0$
$l = -10 \rightarrow 10$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.050
$wR(F^2)$ = 0.136
S = 0.98
3444 reflections
273 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—N7	1.218 (3)	O4—N8	1.225 (4)
O2—N7	1.215 (3)	O5—C11	1.254 (3)
O3—N8	1.220 (3)	O6—C11	1.227 (4)
O1—N7—O2	124.7 (3)	O5—C11—O6	127.4 (3)
O3—N8—O4	123.7 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N10—H10···O5	0.95 (4)	1.73 (4)	2.677 (4)	173 (3)

Compound (II)

Crystal data

$C_7H_{11}N_2^+\cdot C_7H_3N_2O_6^-$
M_r = 334.29
Monoclinic, $P2_1/n$
a = 8.102 (2) Å
b = 7.734 (1) Å
c = 24.218 (1) Å
β = 95.77 (1)°
V = 1509.7 (4) Å^3
Z = 4
D_x = 1.471 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.0–14.9°
μ = 0.117 mm^{-1}
T = 298 (1) K
Prism, yellow
0.5 × 0.3 × 0.3 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω scans
3708 measured reflections
3468 independent reflections
2383 reflections with $I > 2\sigma(I)$
$R_{int} = 0.005$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = -31 \rightarrow 31$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.112$
$S = 1.01$
3468 reflections
273 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.3113P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

O1—N7	1.210 (2)	O4—N8	1.212 (2)
O2—N7	1.219 (2)	O5—C11	1.262 (2)
O3—N8	1.216 (2)	O6—C11	1.233 (2)
O1—N7—O2	124.8 (2)	O5—C11—O6	126.9 (2)
O3—N8—O4	124.9 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N10—H10···O5	0.96 (2)	1.68 (2)	2.633 (2)	176 (2)

Compound (III)

Crystal data

$C_7H_{11}N_2^+ \cdot C_7H_3N_2O_6^-$
$M_r = 334.29$
Orthorhombic, $P2_12_12_1$
$a = 13.774$ (2) Å
$b = 18.615$ (1) Å
$c = 5.888$ (2) Å
$V = 1509.7$ (5) Å^3
$Z = 4$
$D_x = 1.471$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.6$–$13.5°$
$\mu = 0.117$ mm^{-1}
$T = 298$ (1) K
Needle, yellow
$0.8 \times 0.15 \times 0.1$ mm

Data collection

Rigaku AFC-7*R* diffractometer
θ–2θ scans
2409 measured reflections
2020 independent reflections
1452 reflections with $I > 2\sigma(I)$
$R_{int} = 0.006$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 18$
$k = 0 \rightarrow 24$
$l = -4 \rightarrow 8$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.093$
$S = 1.04$
2020 reflections
273 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

O1—N7	1.209 (4)	O4—N8	1.223 (4)
O2—N7	1.227 (3)	O5—C11	1.253 (4)
O3—N8	1.214 (4)	O6—C11	1.230 (3)
O1—N7—O2	123.3 (2)	O5—C11—O6	127.1 (2)
O3—N8—O4	123.6 (3)		

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N10—H10···O5	0.87 (3)	1.81 (3)	2.673 (3)	174 (3)

No Friedel opposites were measured for (III); anomalous dispersion effects are negligible. All H atoms were located from difference syntheses and were refined isotropically. In compounds (I)–(III), N—H bond lengths are in the range 0.87 (3)–0.96 (2) Å, and the C—H lengths are in the range 0.87 (6)–1.06 (4) Å.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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