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4,4′-Bipyridine–cyanoacetic acid (1/2)

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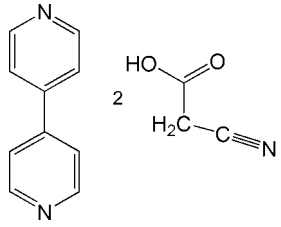
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.046; wR factor = 0.133; data-to-parameter ratio = 13.3.

Crystals of the title adduct, $C_{10}H_8N_2{\cdot}2C_3H_3NO_2$, were obtained from a methanol/water solution of cyanoacetic acid and 4,4′-bipyridine at room temperature. In the crystal structure, cyanoacetic acid and centrosymmetric 4,4′-bipyridine molecules are linked by O—H···N hydrogen bonds to form three-component supramolecular adducts. The acidic H atom is almost midway between the O and N atoms of the cyanoacetic acid and bipyridine molecules, with O—H and N—H distances of 1.19 (3) and 1.39 (3) Å, respectively, so that the H-atom transfer is best regarded as partial. The three-component adducts are further interconnected with neighboring molecules by weak intermolecular C—H···O and C—H···N hydrogen bonds and by π–π stacking interactions [centroid–centroid distance = 3.7200 (11) Å] to generate a three-dimensional supramolecular structure.

Related literature

For similar partial proton transfer from a carbonic acid towards a nitrogen base, see: Farrell *et al.* (2002*a*,*b*); For C—H···O and C—H···N hydrogen bonds, see: Balakrishna *et al.* (2005); Wang *et al.* (2008).



Experimental

Crystal data

$C_{10}H_8N_2{\cdot}2C_3H_3NO_2$
M_r = 326.31
Monoclinic, $P2_1/n$
a = 4.887 (2) Å
b = 21.383 (10) Å
c = 7.921 (4) Å
β = 100.664 (8)°
V = 813.4 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 291 (2) K
0.34 × 0.26 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.952, T_{max} = 0.982
3537 measured reflections
1487 independent reflections
1153 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.133
S = 1.04
1487 reflections
112 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7A···N2^{i}	0.97	2.92	3.420 (3)	113
C2—H2···O2^{ii}	0.93	2.62	3.361 (3)	137
C2—H2···N2^{iii}	0.93	2.75	3.322 (3)	121
O1—H1D···N1	1.19 (3)	1.39 (3)	2.566 (2)	170 (2)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2142).

References

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Wang, Y.-T., Tang, G.-M., Zhang, Y.-C. & Wan, W.-Z. (2008). *Acta Cryst.* E**64**, o1753.

supporting information

Acta Cryst. (2008). E**64**, o2058 [doi:10.1107/S1600536808031322]

4,4′-Bipyridine–cyanoacetic acid (1/2)

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S1. Comment

A view of the title structure is shown in Fig. 1. The asymmetric unit consists of one cyanoacetic acid molecule and half a 4,4′-bipyridine molecule. The H1D was found in a Fourier map and its position was refined freely. Within the asymmetric unit, atom H1D is almost mid-way between atoms O1 and N1, so that the H-atom transfer is best regarded as partial. The distances of O1—H1D and N1—H1D are 1.19 (3) Å and 1.39 (3) Å, respectively, which are comparable with literature data (Farrell *et al.*, 2002a,b). Cyanoacetic acid and 4,4′-bipyridine molecules are linked by these O—H···N hydrogen bonds to form 3-component supramolecular adducts.

The 3-compenent adducts interact with neigboring molecules *via* by weak intermolecular C—H···O and C—H···N hydrogen bonds, and by *π*-*π* stacking interactions. Within the asymmetric unit, the atoms C2 and C7 act as hydrogen-bond donors, *via* atoms H2, H2, and H7A, to atoms $O2^{ii}$, $N2^{iii}$ and $N2^{i}$, respectively (symmetry operators: i = *x* + 1/2,-*y* + 1/2,*z* + 1/2; ii = *x* - 1,*y*,*z* -1; iii = *x* - 3/2,-*y* + 1/2,*z* - 1/2). The bond lengths and angles of the above three hydrogen bonds (Table 1) are comparable with literature data (Balakrishna *et al.*, 2005; Wang *et al.*, 2008). These hydrogen bonds, albeit rather weak, link the 3-component supramolecular adducts into a three-dimensional supramolecular structure, which is further stabilized by weak intermolecular *π*-*π* stacking interactions, formed by adjacent bipyridine rings (centroid–centroid distance = 3.7200 (11) Å) (Fig. 2 and Fig. 3).

S2. Experimental

Cyanoacetic acid (0.2 mmol) and 4,4′-bipyridine (0.2 mmol) were dissolved in methanol (5 ml) and water (1 ml) at room temperature. The single crystals of the title compound were obtained from the solution after ten days.

S3. Refinement

H1D was found in a difference Fourier map and was refined with U_{iso}(H) = 1.5U_{eq}(O). All other H atoms were positioned geometrically and treated as riding, with C—H bonding lengths constrained to 0.93 (aromatic CH) or 0.97 Å (methylene CH_2), and with U_{iso}(H) = 1.2U_{eq}(C).

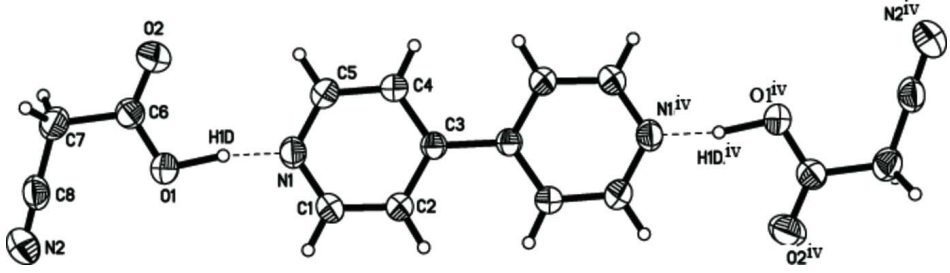

Figure 1

A view of the title compound, showing 30% probability displacement ellipsoids. Symmetry code: (iv) -*x*, 1 - *y*,-*z*.

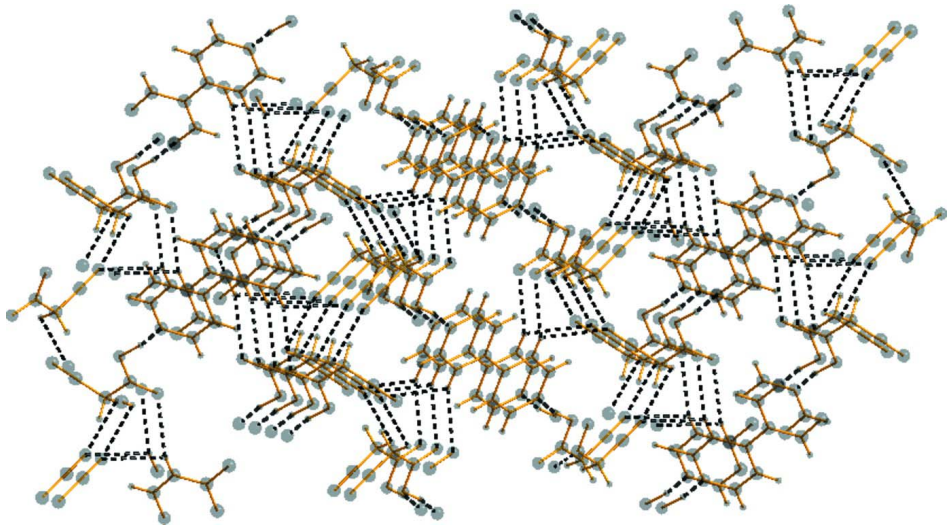

Figure 2

A view of the three-dimensional hydrogen-bonding pattern network.

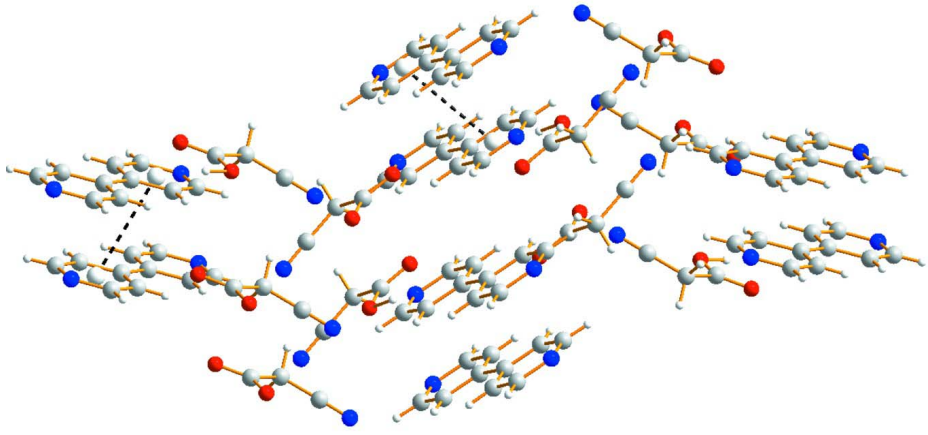

Figure 3

View of the π-π interactions between bipyridine rings in the crystal structure of the title compound.

4,4′-Bipyridine–cyanoacetic acid (1/2)

Crystal data

$C_{10}H_8N_2{\cdot}2C_3H_3NO_2$
M_r = 326.31
Monoclinic, $P2_1/n$
a = 4.887 (2) Å
b = 21.383 (10) Å
c = 7.921 (4) Å
β = 100.664 (8)°
V = 813.4 (7) Å^3
Z = 2
F(000) = 340
D_x = 1.332 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 1445 reflections
θ = 2.8–27.1°
μ = 0.10 mm^{-1}
T = 291 K
Block, colorless
0.34 × 0.26 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.952, T_{max} = 0.982
3537 measured reflections
1487 independent reflections
1153 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.5°, θ_{min} = 2.8°
h = −5→5
k = −25→24
l = −9→7

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.133
S = 1.04
1487 reflections
112 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.1963P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.9569 (3)	0.33450 (7)	0.35022 (19)	0.0763 (5)
H1D	0.779 (6)	0.3714 (12)	0.298 (3)	0.114*
O2	1.0674 (4)	0.40335 (8)	0.5596 (2)	0.1022 (6)
N1	0.5590 (3)	0.40726 (7)	0.21445 (19)	0.0595 (4)
N2	1.4242 (5)	0.21975 (10)	0.3693 (3)	0.1017 (7)
C1	0.3898 (4)	0.38664 (9)	0.0757 (3)	0.0729 (6)
H1	0.4196	0.3468	0.0354	0.087*
C2	0.1717 (4)	0.42138 (9)	−0.0118 (3)	0.0682 (6)
H2	0.0604	0.4052	−0.1100	0.082*
C3	0.1174 (3)	0.48036 (7)	0.04596 (19)	0.0464 (4)
C4	0.2939 (4)	0.50109 (9)	0.1930 (2)	0.0652 (5)
H4	0.2662	0.5402	0.2384	0.078*
C5	0.5109 (4)	0.46370 (9)	0.2722 (2)	0.0685 (6)
H5	0.6278	0.4787	0.3700	0.082*
C6	1.1058 (4)	0.35458 (9)	0.4903 (2)	0.0598 (5)
C7	1.3428 (4)	0.31156 (10)	0.5682 (3)	0.0707 (6)
H7A	1.5125	0.3360	0.5955	0.085*
H7B	1.3038	0.2948	0.6750	0.085*
C8	1.3896 (4)	0.25990 (10)	0.4580 (3)	0.0699 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0708 (9)	0.0714 (9)	0.0772 (9)	0.0193 (7)	−0.0112 (7)	−0.0097 (7)
O2	0.1424 (17)	0.0813 (11)	0.0760 (11)	0.0340 (11)	0.0021 (10)	−0.0164 (8)
N1	0.0558 (9)	0.0595 (9)	0.0611 (9)	0.0096 (7)	0.0053 (7)	0.0059 (7)
N2	0.1006 (16)	0.0809 (13)	0.1175 (17)	0.0300 (12)	0.0043 (13)	−0.0100 (12)
C1	0.0752 (14)	0.0532 (11)	0.0818 (14)	0.0146 (9)	−0.0073 (11)	−0.0079 (9)
C2	0.0700 (13)	0.0540 (10)	0.0708 (12)	0.0087 (9)	−0.0122 (10)	−0.0092 (9)
C3	0.0465 (9)	0.0460 (8)	0.0468 (8)	0.0003 (7)	0.0088 (7)	0.0027 (7)
C4	0.0685 (12)	0.0620 (11)	0.0592 (11)	0.0143 (9)	−0.0038 (9)	−0.0121 (8)
C5	0.0663 (13)	0.0744 (12)	0.0583 (11)	0.0123 (10)	−0.0051 (9)	−0.0077 (9)
C6	0.0676 (12)	0.0595 (10)	0.0536 (10)	0.0058 (9)	0.0143 (9)	0.0026 (8)
C7	0.0672 (13)	0.0827 (13)	0.0586 (11)	0.0084 (10)	0.0025 (9)	0.0020 (9)
C8	0.0613 (12)	0.0669 (12)	0.0773 (14)	0.0145 (10)	0.0021 (10)	0.0099 (10)

Geometric parameters (Å, º)

O1—C6	1.283 (2)	C3—C4	1.388 (2)
O1—H1D	1.19 (3)	C3—C3^{i}	1.498 (3)
O2—C6	1.209 (2)	C4—C5	1.382 (3)
N1—C1	1.323 (2)	C4—H4	0.9300
N1—C5	1.327 (2)	C5—H5	0.9300
N2—C8	1.142 (3)	C6—C7	1.518 (3)
C1—C2	1.377 (3)	C7—C8	1.452 (3)
C1—H1	0.9300	C7—H7A	0.9700
C2—C3	1.384 (2)	C7—H7B	0.9700
C2—H2	0.9300		
C6—O1—H1D	109.8 (12)	C5—C4—H4	119.9
C1—N1—C5	117.80 (16)	C3—C4—H4	119.9
C1—N1—H1D	121.6 (10)	N1—C5—C4	122.65 (17)
C5—N1—H1D	120.6 (10)	N1—C5—H5	118.7
C1—N1—H1D	121.6 (10)	C4—C5—H5	118.7
C5—N1—H1D	120.6 (10)	O2—C6—O1	124.78 (19)
N1—C1—C2	123.03 (18)	O2—C6—C7	120.59 (19)
N1—C1—H1	118.5	O1—C6—C7	114.63 (17)
C2—C1—H1	118.5	C8—C7—C6	114.18 (17)
C1—C2—C3	120.22 (18)	C8—C7—H7A	108.7
C1—C2—H2	119.9	C6—C7—H7A	108.7
C3—C2—H2	119.9	C8—C7—H7B	108.7
C2—C3—C4	116.19 (16)	C6—C7—H7B	108.7
C2—C3—C3^{i}	121.79 (18)	H7A—C7—H7B	107.6
C4—C3—C3^{i}	122.02 (18)	N2—C8—C7	179.0 (2)
C5—C4—C3	120.11 (17)		
C5—N1—C1—C2	1.2 (3)	C3^{i}—C3—C4—C5	−178.96 (19)
H1D—N1—C1—C2	−179.1 (12)	C1—N1—C5—C4	−0.3 (3)

N1—C1—C2—C3	−1.2 (3)	H1D—N1—C5—C4	−180.0 (12)
C1—C2—C3—C4	0.2 (3)	C3—C4—C5—N1	−0.7 (3)
C1—C2—C3—C3^{i}	179.8 (2)	O2—C6—C7—C8	−170.9 (2)
C2—C3—C4—C5	0.7 (3)	O1—C6—C7—C8	9.4 (3)

Symmetry code: (i) −*x*, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*A*···N2^{ii}	0.97	2.92	3.420 (3)	113
C2—H2···O2^{iii}	0.93	2.62	3.361 (3)	137
C2—H2···N2^{iv}	0.93	2.75	3.322 (3)	121
O1—H1*D*···N1	1.19 (3)	1.39 (3)	2.566 (2)	170 (2)

Symmetry codes: (ii) *x*+1/2, −*y*+1/2, *z*+1/2; (iii) *x*−1, *y*, *z*−1; (iv) *x*−3/2, −*y*+1/2, *z*−1/2.