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4,4′-Bipyridine–3-nitrobenzoic acid (1/2)

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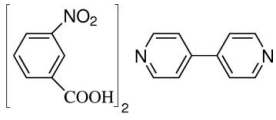
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.103; data-to-parameter ratio = 11.7.

The title compound, $C_{10}H_8N_2\cdot 2C_7H_5NO_4$,was obtained unintentionally as the harvested product of the hydrothermal reaction between $Co(OAc)_2\cdot 4H_2O$ and 4,4′-bipyridine in the presence of 3-nitrophthalic acid. In the reaction, 3-nitrophthalic acid is transformed into 3-nitrobenzoic acid by an *in situ* decarboxylation reaction, in which the carboxylate group is not deprotonated and is uncoordinated. In the crystal, the uncoordinated 3-nitrobenzoic acid and free 4,4′-bipyridine molecules are linked alternately by O—H···N hydrogen bonds into chains, which are assembled by C—H···O hydrogen bonds into a three-dimensional supramolecular network.

Related literature

For the use of 3-nitrophthalic acid in the self-assembly of coordination compounds, see: Deng *et al.* (2007*a*,*b*); Huang *et al.* (2007); Song *et al.* (2007); Wang *et al.* (2009).



Experimental

Crystal data

$C_{10}H_8N_2\cdot 2C_7H_5NO_4$
M_r = 490.42
Monoclinic, $C2/c$
a = 26.489 (7) Å
b = 6.7757 (14) Å
c = 13.291 (3) Å
β = 112.19 (3)°
V = 2208.8 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 113 K
0.20 × 0.12 × 0.10 mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.978, T_{max} = 0.989
7177 measured reflections
1935 independent reflections
1646 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.103
S = 1.09
1935 reflections
166 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N2^{i}	0.85 (1)	1.76 (1)	2.608 (2)	175 (2)
C5—H5···O3^{ii}	0.93	2.49	3.390 (2)	162
C9—H9···O4^{iii}	0.93	2.55	3.436 (2)	159
C12—H12···O1^{iv}	0.93	2.35	3.242 (2)	160

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2325).

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supporting information

Acta Cryst. (2010). E**66**, o546 [doi:10.1107/S1600536810003594]

4,4′-Bipyridine–3-nitrobenzoic acid (1/2)

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S1. Comment

3-nitrophthic acid acting as a multifunctional organic ligand has been widely used in the self-assembly of various coordination compounds (Deng *et al.*, 2007*a*,b; Huang *et al.*, 2007; Song *et al.*, 2007, Wang *et al.*, 2009). The title compound were obtained unintentionally as the harvested product of the hydrothermal reaction between $Co(oAc)_2.4H_2O$ and 4,4′-bipyridine in the presence of 3-nitrophthic acid. In the title compound, 3-nitrophthlic acid is transformed into 3-nitrobenzoic acid by *in situ* decarboxylation reaction, in which the carboxylate group is not deprotoned and is uncoordinated. The molecular structure of the title compound is illustrated in Fig. 1. The bond distances and angles are normal within experimental error.

The crystal packing of the title compound is illustrated in Fig. 2. The uncoordinated 3-nitrobenzoic acid and free 4,4′-bipyridine molecules are linked alternately by hydrogen bonds (O—H···O) into one-dimensional chains. Furthermore, these one-dimensional chains are assembled by hydrogen bonds(C—H···O) into three-dimensional supramolecular network.

S2. Experimental

A mixture of 3-nitrophthalic acid(0.020 g, 0.1 mmol), $Co(oAc)_2.4H_2O$(0.025 g, 0.1 mmol), 4,4′-bipyridine (0.019 g, 0.1 mmol), deionized water (8 ml) was sealed in a Teflon-lined stainless steel vessel (23 ml) and heated at 160 °C for 4 days under autogenous pressure and then cooled slowly to room temperature. The solution was filtered and after allowed to stand for a few weeks at room temperature, purple-red crystals were obtained.

S3. Refinement

The O-H hydrogen atom was found in a difference Fourier map and fixed during refinement at a O–H distance of 0.85 Å, with U_{iso}(H)=1.2 U_{eq}(O). The H atoms of C–H and N–H groups were treated as riding, with C–H = 0.97 Å and N–H = 0.86 Å and U_{iso} (H) = 1.2 U_{eq}(C,*N*).

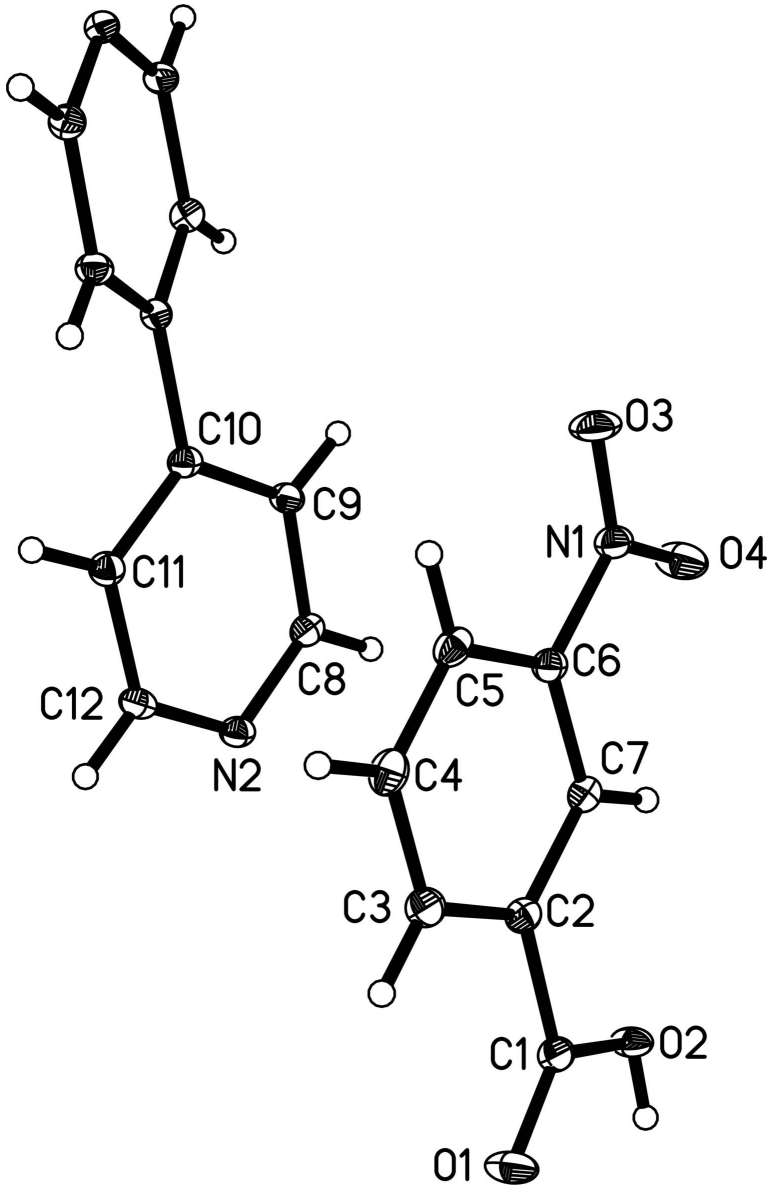

Figure 1

A view of the molecular structure of the title compound, showing the atom-numbering scheme. Dispacement ellipsoids are drawn at the 30% probability level.

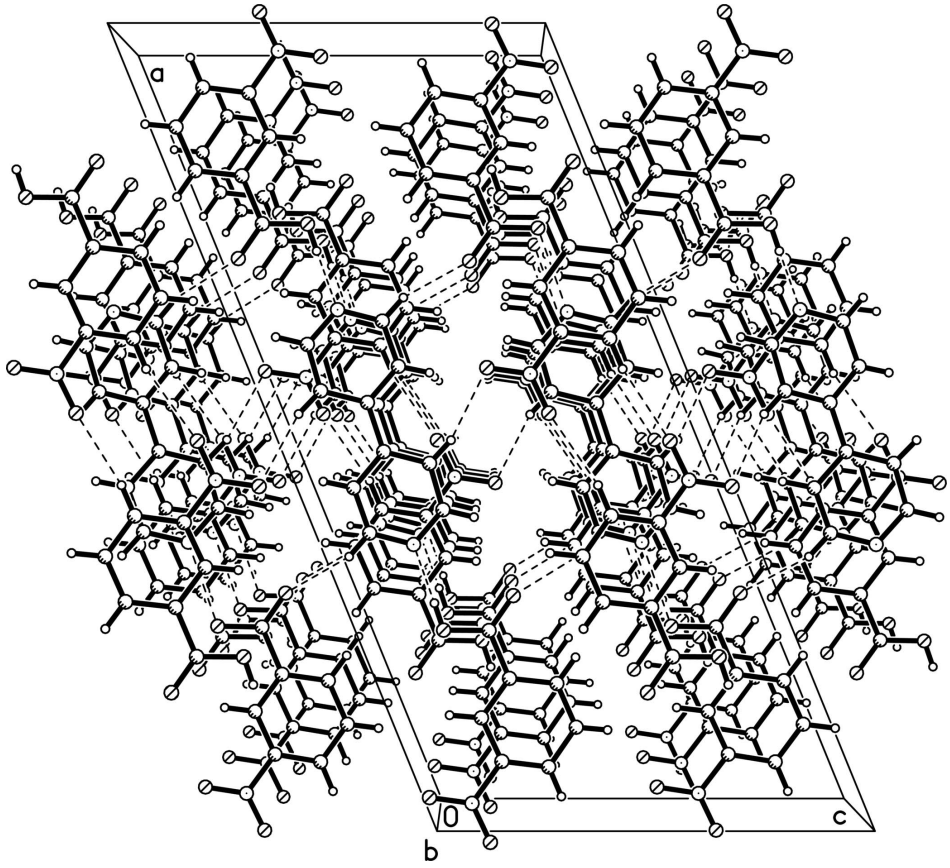

Figure 2

The crystal packing of the title compound along *b* axis. Hydrogen bonds are indicated by dashed lines.

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Crystal data

$C_{10}H_8N_2·2C_7H_5NO_4$
M_r = 490.42
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 26.489 (7) Å
b = 6.7757 (14) Å
c = 13.291 (3) Å
β = 112.19 (3)°
V = 2208.8 (9) Å^3
Z = 4
F(000) = 1016
D_x = 1.475 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2874 reflections
θ = 3.1–27.4°
μ = 0.11 mm^{-1}
T = 113 K
Plate, purple–red
0.20 × 0.12 × 0.10 mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
Radiation source: rotating anode
Confocal monochromator
Detector resolution: 7.31 pixels mm^{-1}
ω and *φ* scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.978, T_{max} = 0.989
7177 measured reflections
1935 independent reflections
1646 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 25.0°, θ_{min} = 3.1°
h = −31→31
k = −7→8
l = −13→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.103$
$S = 1.09$
1935 reflections
166 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.0461P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.30213 (4)	0.58310 (15)	0.39895 (8)	0.0316 (3)
O2	0.26214 (4)	0.60692 (13)	0.21797 (8)	0.0238 (3)
H2	0.2955 (4)	0.608 (2)	0.2257 (14)	0.036*
O3	0.01600 (4)	0.66151 (15)	0.13387 (9)	0.0328 (3)
O4	0.06802 (4)	0.65732 (16)	0.04209 (8)	0.0363 (3)
N1	0.06088 (4)	0.64662 (15)	0.12810 (10)	0.0223 (3)
N2	0.13751 (4)	0.10542 (14)	0.27135 (9)	0.0189 (3)
C1	0.26146 (5)	0.59392 (18)	0.31583 (11)	0.0204 (3)
C2	0.20523 (5)	0.59219 (17)	0.31772 (11)	0.0189 (3)
C3	0.19834 (5)	0.56014 (18)	0.41546 (11)	0.0231 (3)
H3	0.2287	0.5420	0.4791	0.028*
C4	0.14675 (6)	0.55513 (18)	0.41864 (12)	0.0247 (3)
H4	0.1427	0.5334	0.4843	0.030*
C5	0.10097 (5)	0.58232 (18)	0.32441 (11)	0.0224 (3)
H5	0.0661	0.5781	0.3256	0.027*
C6	0.10882 (5)	0.61589 (17)	0.22863 (11)	0.0188 (3)
C7	0.15989 (5)	0.62214 (17)	0.22295 (11)	0.0181 (3)
H7	0.1637	0.6458	0.1573	0.022*
C8	0.09648 (5)	0.14365 (18)	0.17646 (11)	0.0200 (3)
H8	0.1049	0.1696	0.1158	0.024*
C9	0.04234 (5)	0.14626 (18)	0.16471 (11)	0.0193 (3)
H9	0.0152	0.1758	0.0978	0.023*
C10	0.02882 (5)	0.10427 (17)	0.25412 (11)	0.0175 (3)
C11	0.07148 (5)	0.06255 (18)	0.35231 (11)	0.0195 (3)

H11	0.0642	0.0326	0.4138	0.023*
C12	0.12465 (5)	0.06609 (17)	0.35760 (11)	0.0197 (3)
H12	0.1527	0.0400	0.4239	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0164 (5)	0.0538 (7)	0.0208 (6)	−0.0010 (4)	0.0028 (4)	0.0011 (4)
O2	0.0140 (5)	0.0381 (6)	0.0195 (5)	0.0001 (4)	0.0066 (4)	0.0023 (4)
O3	0.0145 (5)	0.0425 (6)	0.0437 (7)	0.0011 (4)	0.0134 (5)	−0.0002 (5)
O4	0.0229 (6)	0.0611 (7)	0.0243 (6)	0.0058 (5)	0.0083 (5)	0.0070 (5)
N1	0.0167 (6)	0.0213 (6)	0.0295 (7)	0.0001 (4)	0.0095 (5)	−0.0005 (5)
N2	0.0153 (6)	0.0180 (6)	0.0226 (6)	0.0008 (4)	0.0064 (5)	−0.0013 (4)
C1	0.0190 (7)	0.0219 (7)	0.0205 (7)	−0.0017 (5)	0.0075 (6)	−0.0003 (5)
C2	0.0185 (7)	0.0183 (6)	0.0203 (7)	−0.0013 (5)	0.0078 (6)	−0.0015 (5)
C3	0.0233 (7)	0.0260 (7)	0.0195 (7)	−0.0018 (5)	0.0076 (6)	0.0001 (5)
C4	0.0302 (8)	0.0256 (7)	0.0235 (8)	−0.0019 (6)	0.0161 (6)	0.0002 (6)
C5	0.0227 (8)	0.0179 (6)	0.0321 (8)	−0.0014 (5)	0.0167 (6)	−0.0026 (5)
C6	0.0169 (7)	0.0154 (6)	0.0233 (8)	−0.0005 (5)	0.0067 (6)	−0.0018 (5)
C7	0.0201 (7)	0.0166 (6)	0.0198 (7)	−0.0013 (5)	0.0100 (6)	−0.0018 (5)
C8	0.0189 (7)	0.0192 (7)	0.0233 (8)	−0.0017 (5)	0.0096 (6)	−0.0009 (5)
C9	0.0150 (7)	0.0197 (7)	0.0209 (7)	0.0005 (5)	0.0042 (6)	0.0006 (5)
C10	0.0153 (7)	0.0147 (6)	0.0220 (7)	−0.0007 (5)	0.0067 (6)	−0.0025 (5)
C11	0.0187 (7)	0.0200 (6)	0.0203 (7)	0.0009 (5)	0.0079 (6)	0.0001 (5)
C12	0.0150 (7)	0.0197 (7)	0.0211 (7)	0.0018 (5)	0.0030 (6)	−0.0009 (5)

Geometric parameters (Å, º)

O1—C1	1.2197 (17)	C4—H4	0.9300
O2—C1	1.3106 (17)	C5—C6	1.3839 (19)
O2—H2	0.850 (9)	C5—H5	0.9300
O3—N1	1.2242 (14)	C6—C7	1.3838 (18)
O4—N1	1.2294 (14)	C7—H7	0.9300
N1—C6	1.4695 (18)	C8—C9	1.3827 (18)
N2—C12	1.3402 (18)	C8—H8	0.9300
N2—C8	1.3430 (18)	C9—C10	1.3938 (19)
C1—C2	1.4991 (19)	C9—H9	0.9300
C2—C7	1.388 (2)	C10—C11	1.3950 (19)
C2—C3	1.3954 (19)	C10—C10^{i}	1.489 (2)
C3—C4	1.3835 (19)	C11—C12	1.3836 (18)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.388 (2)	C12—H12	0.9300
C1—O2—H2	106.5 (12)	C7—C6—N1	118.22 (12)
O3—N1—O4	123.21 (12)	C5—C6—N1	118.77 (11)
O3—N1—C6	118.74 (12)	C6—C7—C2	118.33 (13)
O4—N1—C6	118.05 (10)	C6—C7—H7	120.8
C12—N2—C8	117.68 (11)	C2—C7—H7	120.8

O1—C1—O2	124.35 (13)	N2—C8—C9	123.06 (13)
O1—C1—C2	121.85 (13)	N2—C8—H8	118.5
O2—C1—C2	113.79 (12)	C9—C8—H8	118.5
C7—C2—C3	119.66 (13)	C8—C9—C10	119.38 (12)
C7—C2—C1	120.54 (12)	C8—C9—H9	120.3
C3—C2—C1	119.80 (12)	C10—C9—H9	120.3
C4—C3—C2	120.68 (13)	C9—C10—C11	117.44 (12)
C4—C3—H3	119.7	C9—C10—C10^{i}	121.59 (14)
C2—C3—H3	119.7	C11—C10—C10^{i}	120.97 (15)
C3—C4—C5	120.38 (13)	C12—C11—C10	119.56 (13)
C3—C4—H4	119.8	C12—C11—H11	120.2
C5—C4—H4	119.8	C10—C11—H11	120.2
C6—C5—C4	117.93 (12)	N2—C12—C11	122.87 (12)
C6—C5—H5	121.0	N2—C12—H12	118.6
C4—C5—H5	121.0	C11—C12—H12	118.6
C7—C6—C5	123.01 (13)		

O1—C1—C2—C7	174.30 (12)	O4—N1—C6—C5	−173.13 (11)
O2—C1—C2—C7	−6.02 (16)	C5—C6—C7—C2	0.37 (18)
O1—C1—C2—C3	−5.73 (18)	N1—C6—C7—C2	−179.69 (10)
O2—C1—C2—C3	173.94 (10)	C3—C2—C7—C6	−1.03 (17)
C7—C2—C3—C4	0.92 (18)	C1—C2—C7—C6	178.94 (10)
C1—C2—C3—C4	−179.05 (11)	C12—N2—C8—C9	0.77 (17)
C2—C3—C4—C5	−0.11 (18)	N2—C8—C9—C10	−1.16 (18)
C3—C4—C5—C6	−0.54 (18)	C8—C9—C10—C11	0.43 (16)
C4—C5—C6—C7	0.42 (18)	C8—C9—C10—C10^{i}	−179.76 (8)
C4—C5—C6—N1	−179.52 (10)	C9—C10—C11—C12	0.59 (17)
O3—N1—C6—C7	−172.63 (10)	C10^{i}—C10—C11—C12	−179.22 (8)
O4—N1—C6—C7	6.93 (16)	C8—N2—C12—C11	0.33 (17)
O3—N1—C6—C5	7.31 (16)	C10—C11—C12—N2	−1.01 (18)

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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