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2-[2,5-Dimethoxy-4-(3-nitropyridin-2-yl)phenyl]-3-nitropyridine

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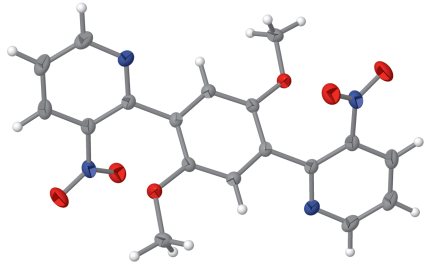
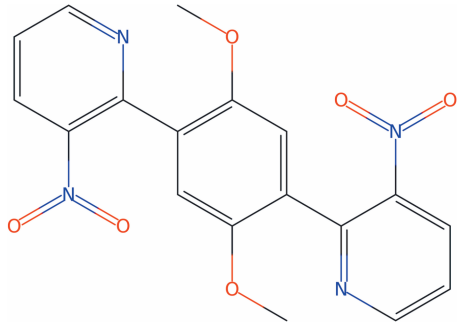
The title compound, $C_{18}H_{14}N_4O_6$, was prepared in a larger project on condensed heterocycles with a focus on the Cadogan reaction. Extension of this method to multiple Cadogan reactions was explored as a way to larger conjugated systems. A twofold Suzuki reaction on a central diboronic acid and chloronitropyridine gave the bis(3-nitropyridin-2-yl)benzene.

3D view



Chemical scheme



Structure description

The title compound, $C_{18}H_{14}N_4O_6$ (Fig. 1), was prepared in a larger project on condensed heterocycles (Nissen & Detert, 2011; Dassonneville *et al.*, 2011) with a focus on the Cadogan reaction (Letessier *et al.*, 2013, Limbach *et al.*, 2017, 2018). Extension of this method to multiple Cadogan reactions was explored as a way to larger conjugated systems (Wrobel *et al.*, 2012, 2017). A twofold Suzuki reaction on a central diboronic acid and chloronitropyridine gave the bis(3-nitropyridin-2-yl)benzene.

The unit cell is filled with one centrosymmetric molecule. The molecules form chains in the [10$\bar{1}$] direction, connected *via* hydrogen bridges (H5···O12: 2.481 Å) with a C—H···O angle of 133.31° (Table 1). Four substituents in *ortho*-positions of the dipyridylbenzene framework provoke torsion angles between the nitro group and the pyridine ring (O11—N10—C6—C1) of −33.41 (16)°, between the pyridine and phenylene (C6—C1—C7—C8) rings of −43.73 (17)° and between the methoxy group and the phenylene ring (C14—O13—C8—C7) of 169.47 (10)°. The packing is shown in Fig. 2.

Synthesis and crystallization

126.9 mg of 2-chloro-3-nitropyridine and 117.4 mg 2,5-dimethoxyphenylene-1,4-diboronic acid, 201.6 mg sodium bicarbonate 1.5 ml water and 1.5 ml 1,2-dimethoxyethane were mixed in a microwave vessel and the mixture was purged with nitrogen for 10 min. Tetrakis-triphenylphosphine palladium (46.2 mg) was added and the mixture was stirred while microwave irradiation, 100 W, 150°C, max. 10 bar for 15 min. The mixture

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O12^{i}	0.95	2.48	3.2077 (15)	133

Symmetry code: (i) $-x+2, -y+1, -z$.

was filtered through celite, the filter cake was washed with ethyl acetate (75 ml) and the filtrate was washed with brine (20 ml) and dried over $MgSO_4$. Purification by chromatography on silica with petroleum ether/ethyl acetate/triethyl amine (1/1/0.025) as eluent (R_f = 1/5). Recrystallization from acetone gave 48.2 mg (31%) of an orange-red solid with m.p. = 542–544 K. ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.87 (*dd*, J = 4.7 Hz, J' = 1.5 Hz, 2 H, 6-H pyridine), 8.21 (*dd*, J = 8.2 Hz, J' = 1.5 Hz, 2 H, 4-H pyridine), 7.44 (*dd*, J = 8.1 Hz, J' = 4.7 Hz, 2 H, 5-H pyridine), 7.26 (*s*, 2 H, phenylene), 3.74 (*s*, 6 H, methoxy). ^{13}C-NMR ($CDCl_3$, 75 MHz): 152.44 (2 C, C-6 py), 150.84 (2 C), 1549.74 (2 C), 147.27 (2 C, C-3 py), 131.95 (2 C), 122.67 (2 C), 113.23 (2 C), 55.6 (2 C, OCH_3). IR (ATR) 3091, 3073, 3016, 2970, 2938, 2839, 2365, 1594, 1555, 1527, 1499, 1467, 1428, 1385, 1353, 1307, 1212, 1173, 1103, 1052, 1024, 862, 819, 802, 770, 717, 677 cm^{-1}. HRMS-ESI: found 383.1004, calculated for $C_{18}H_{14}N_4O_6$: 383.0992.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{14}N_4O_6$
M_r	382.33
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	193
a, b, c (Å)	4.5590 (4), 8.1530 (8), 11.6359 (10)
α, β, γ (°)	95.552 (7), 95.643 (7), 104.440 (7)
V (Å^3)	413.49 (7)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.80 × 0.40 × 0.10
Data collection	
Diffractometer	Stoe *IPDS* 2T
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4074, 1948, 1691
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.104, 1.08
No. of reflections	1948
No. of parameters	128
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.17

Computer programs: *X-AREA WinXpose*, *Recipe* and *Integrate* (Stoe & Cie, 2020), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2009).

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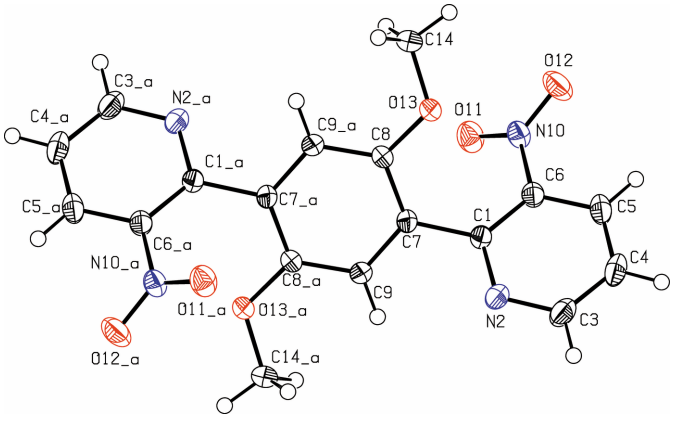

Figure 1
View (Spek, 2009) of the title compound. Atoms with suffix '_a' were generated using the symmetry operator $-x+1, -y+1, -z+1$. Displacement ellipsoids are drawn at the 50% probability level.

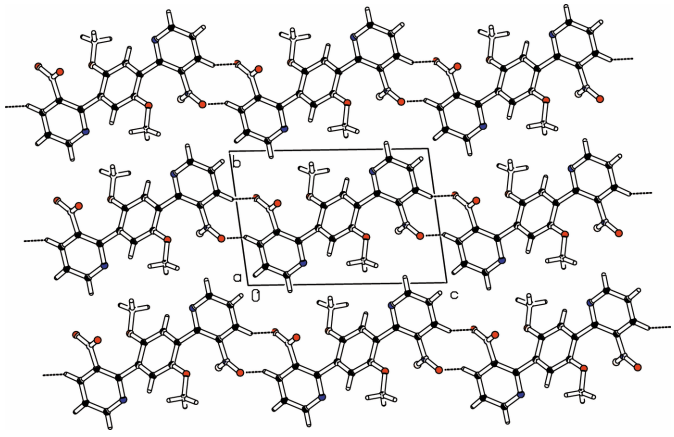

Figure 2
Part of the packing diagram. View along a-axis direction (Spek, 2009). C—H···O contacts are drawn as dashed lines.

full crystallographic data

IUCrData (2025). **10**, x250779 [https://doi.org/10.1107/S2414314625007795]

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Crystal data

$C_{18}H_{14}N_4O_6$
M_r = 382.33
Triclinic, $P\overline{1}$
a = 4.5590 (4) Å
b = 8.1530 (8) Å
c = 11.6359 (10) Å
α = 95.552 (7)°
β = 95.643 (7)°
γ = 104.440 (7)°
V = 413.49 (7) Å^3
Z = 1
$F(000)$ = 198
D_x = 1.535 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7791 reflections
θ = 2.6–32.3°
μ = 0.12 mm^{-1}
T = 193 K
Plate, light orange
0.80 × 0.40 × 0.10 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
4074 measured reflections
1948 independent reflections
1691 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 28.0°, θ_{min} = 3.0°
h = −5→6
k = −10→10
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.104
S = 1.08
1948 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.0848P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Hydrogen atoms were placed at calculated positions and were refined in the riding-model approximation with $C_{aromatic}$–H = 0.95 Å or C_{methyl}–H = 0.98 Å and with U_{iso}(H) = 1.2 U_{eq}($C_{aromatic}$) or U_{iso}(H) = 1.5 U_{eq}($C_{aromatic}$).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O11	0.4116 (2)	0.60772 (12)	0.20547 (8)	0.0343 (2)
O12	0.7851 (2)	0.64907 (13)	0.10149 (9)	0.0394 (3)
O13	0.94900 (19)	0.65353 (10)	0.37295 (7)	0.0270 (2)
N2	0.6056 (3)	0.16286 (13)	0.29256 (9)	0.0286 (2)
N10	0.6193 (2)	0.56385 (14)	0.16322 (8)	0.0268 (2)
C1	0.6034 (2)	0.32632 (14)	0.28580 (9)	0.0220 (2)
C3	0.6787 (3)	0.07374 (16)	0.20193 (12)	0.0343 (3)
H3	0.671276	−0.042903	0.206503	0.041*
C4	0.7641 (3)	0.14116 (18)	0.10231 (11)	0.0351 (3)
H4	0.828474	0.075232	0.042713	0.042*
C5	0.7537 (3)	0.30699 (17)	0.09130 (10)	0.0300 (3)
H5	0.806523	0.357775	0.023507	0.036*
C6	0.6635 (3)	0.39632 (14)	0.18267 (9)	0.0236 (2)
C7	0.5471 (2)	0.41955 (14)	0.39427 (9)	0.0209 (2)
C8	0.7265 (2)	0.58398 (14)	0.43752 (9)	0.0212 (2)
C9	0.3237 (2)	0.33665 (14)	0.45786 (9)	0.0219 (2)
H9	0.204101	0.224369	0.429246	0.026*
C14	1.1013 (3)	0.82939 (15)	0.40204 (11)	0.0296 (3)
H14A	0.950412	0.896490	0.402626	0.044*
H14B	1.238818	0.865537	0.344292	0.044*
H14C	1.219809	0.847542	0.479277	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.0367 (5)	0.0389 (5)	0.0347 (5)	0.0189 (4)	0.0120 (4)	0.0094 (4)
O12	0.0466 (6)	0.0406 (5)	0.0376 (5)	0.0127 (4)	0.0191 (4)	0.0193 (4)
O13	0.0301 (4)	0.0225 (4)	0.0257 (4)	−0.0004 (3)	0.0124 (3)	0.0002 (3)
N2	0.0392 (6)	0.0218 (5)	0.0243 (5)	0.0074 (4)	0.0056 (4)	−0.0001 (4)
N10	0.0301 (5)	0.0311 (5)	0.0207 (5)	0.0087 (4)	0.0059 (4)	0.0061 (4)
C1	0.0230 (5)	0.0217 (5)	0.0200 (5)	0.0038 (4)	0.0043 (4)	0.0001 (4)
C3	0.0456 (7)	0.0250 (6)	0.0323 (6)	0.0119 (5)	0.0055 (5)	−0.0038 (5)
C4	0.0415 (7)	0.0369 (7)	0.0278 (6)	0.0142 (6)	0.0088 (5)	−0.0070 (5)
C5	0.0322 (6)	0.0373 (7)	0.0210 (5)	0.0092 (5)	0.0082 (4)	0.0011 (5)
C6	0.0240 (5)	0.0256 (6)	0.0210 (5)	0.0062 (4)	0.0041 (4)	0.0018 (4)
C7	0.0250 (5)	0.0210 (5)	0.0169 (5)	0.0059 (4)	0.0040 (4)	0.0017 (4)
C8	0.0233 (5)	0.0209 (5)	0.0195 (5)	0.0044 (4)	0.0061 (4)	0.0040 (4)
C9	0.0247 (5)	0.0188 (5)	0.0206 (5)	0.0031 (4)	0.0036 (4)	0.0011 (4)
C14	0.0339 (6)	0.0214 (6)	0.0315 (6)	0.0006 (5)	0.0107 (5)	0.0044 (4)

Geometric parameters (Å, º)

O11—N10	1.2218 (13)	C4—C5	1.3824 (19)
O12—N10	1.2293 (13)	C4—H4	0.9500
O13—C8	1.3640 (12)	C5—C6	1.3840 (15)

O13—C14	1.4198 (14)	C5—H5	0.9500
N2—C3	1.3388 (15)	C7—C9	1.3942 (14)
N2—C1	1.3451 (15)	C7—C8	1.4003 (15)
N10—C6	1.4646 (15)	C8—C9^{i}	1.3889 (14)
C1—C6	1.4000 (15)	C9—H9	0.9500
C1—C7	1.4872 (14)	C14—H14A	0.9800
C3—C4	1.3794 (19)	C14—H14B	0.9800
C3—H3	0.9500	C14—H14C	0.9800

C8—O13—C14	117.88 (9)	C5—C6—N10	116.39 (10)
C3—N2—C1	118.87 (11)	C1—C6—N10	121.94 (9)
O11—N10—O12	123.78 (11)	C9—C7—C8	119.47 (9)
O11—N10—C6	117.99 (10)	C9—C7—C1	118.98 (9)
O12—N10—C6	118.16 (10)	C8—C7—C1	121.42 (9)
N2—C1—C6	119.33 (10)	O13—C8—C9^{i}	124.35 (10)
N2—C1—C7	115.02 (10)	O13—C8—C7	115.99 (9)
C6—C1—C7	125.60 (10)	C9^{i}—C8—C7	119.64 (10)
N2—C3—C4	123.92 (12)	C8^{i}—C9—C7	120.89 (10)
N2—C3—H3	118.0	C8^{i}—C9—H9	119.6
C4—C3—H3	118.0	C7—C9—H9	119.6
C3—C4—C5	118.38 (11)	O13—C14—H14A	109.5
C3—C4—H4	120.8	O13—C14—H14B	109.5
C5—C4—H4	120.8	H14A—C14—H14B	109.5
C4—C5—C6	117.56 (11)	O13—C14—H14C	109.5
C4—C5—H5	121.2	H14A—C14—H14C	109.5
C6—C5—H5	121.2	H14B—C14—H14C	109.5
C5—C6—C1	121.60 (11)		

C3—N2—C1—C6	2.91 (18)	O12—N10—C6—C1	149.52 (12)
C3—N2—C1—C7	−174.74 (11)	N2—C1—C7—C9	−42.07 (15)
C1—N2—C3—C4	2.5 (2)	C6—C1—C7—C9	140.45 (12)
N2—C3—C4—C5	−4.7 (2)	N2—C1—C7—C8	133.75 (12)
C3—C4—C5—C6	1.3 (2)	C6—C1—C7—C8	−43.73 (17)
C4—C5—C6—C1	4.01 (18)	C14—O13—C8—C9^{i}	−12.41 (17)
C4—C5—C6—N10	−172.96 (11)	C14—O13—C8—C7	169.47 (10)
N2—C1—C6—C5	−6.26 (18)	C9—C7—C8—O13	177.20 (10)
C7—C1—C6—C5	171.13 (11)	C1—C7—C8—O13	1.40 (16)
N2—C1—C6—N10	170.55 (10)	C9—C7—C8—C9^{i}	−1.02 (18)
C7—C1—C6—N10	−12.07 (18)	C1—C7—C8—C9^{i}	−176.82 (10)
O11—N10—C6—C5	143.55 (11)	C8—C7—C9—C8^{i}	1.03 (18)
O12—N10—C6—C5	−33.52 (16)	C1—C7—C9—C8^{i}	176.93 (10)
O11—N10—C6—C1	−33.41 (16)		

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

Hydrogen-bond geometry (Å, º)

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

C5—H5···O12^{ii}	0.95	2.48	3.2077 (15)	133

Symmetry code: (ii) $-x+2, -y+1, -z$.