Crystal structure of 4,4′-dimethoxy-2,2′-bipyridine

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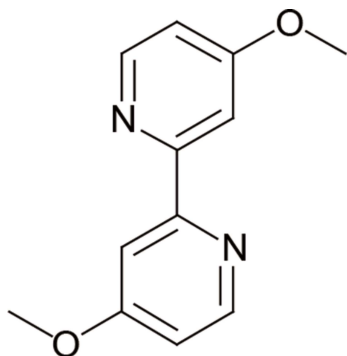
In the title compound, $C_{12}H_{12}N_2O_2$, the dihedral angle between the planes of the two pyridine rings is 5.8 (1)°. Neighbouring molecules are linked *via* C(Me)—H···N interactions, generating a two-dimensional sheet structure; C—H···π interactions further link the molecules into a three-dimensional network. An overlapped arrangement of parallel pyridine rings in neighbouring molecules [centroid-to-centroid distance = 3.6655 (15) Å] is observed in the crystal structure.

1. Related literature

For related structure of 4,4′-substituted 2,2′-bipyridines, see: Merritt & Schroeder (1956); Tynan *et al.* (2003); Pearson *et al.* (2004); Haberecht *et al.* (2005); Fujihara *et al.* (2005). For hydrogen-bonded motifs, see: Etter *et al.* (1990); Bernstein *et al.* (1995).

2. Experimental

2.1. Crystal data

$C_{12}H_{12}N_2O_2$	$V = 524.76$ (16) Å^3
$M_r = 216.24$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 6.4235$ (11) Å	$\mu = 0.10$ mm^{-1}
$b = 10.8139$ (18) Å	$T = 200$ K
$c = 8.0123$ (14) Å	$0.24 \times 0.07 \times 0.05$ mm
$\beta = 109.462$ (2)°	

2.2. Data collection

Bruker APEXII CCD area-detector diffractometer	5925 measured reflections
Absorption correction: multi-scan (*SADABS2014*; Bruker, 2014)	2301 independent reflections
$T_{min} = ?$, $T_{max} = ?$	2155 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.014$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	$\Delta\rho_{min} = -0.16$ e Å^{-3}
$wR(F^2) = 0.084$	Absolute structure: Flack x determined using 976 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
$S = 1.01$	
2301 reflections	
147 parameters	
1 restraint	Absolute structure parameter:
H-atom parameters constrained	0.7 (3)
$\Delta\rho_{max} = 0.20$ e Å^{-3}	

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

$Cg1$ and $Cg2$ are the centroids of the N1- and N2-rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11B···N1[i]	0.98	2.58	3.503 (3)	158
C12—H12B···N2[ii]	0.98	2.62	3.513 (3)	151
C1—H1···$Cg2$[iii]	0.95	2.68	3.515 (3)	146
C12—H12A···$Cg1$[iv]	0.98	2.72	3.439 (3)	134

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

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* and *XPREP* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *XCIF* (Bruker, 2014).

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supporting information

Crystal structure of 4,4′-dimethoxy-2,2′-bipyridine

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S1. Comment

The molecular structure of title compound (I) is illustrated in Fig. 1. In the crystal, all bond lengths and angles are similar to those of the other similar 4,4′-substituted 2,2′-bipyridines (Merritt & Schroeder, 1956; Tynan *et al.*, 2003; Pearson *et al.*, 2004; Haberecht *et al.*, 2005; Fujihara *et al.*, 2005). The dihedral angle between two pyridine rings is 5.8 (1)°. The neighbouring molecules are linked *via* intermolecular C–H···N interactions with an $R_2^2(16)$ ring motif (Etter *et al.*, 1990; Bernstein *et al.*, 1995), generating 2D sheet structure as shown in Fig. 2. An overlapped arrangement of parallel pyridine rings in neighbouring molecules [centroid-centroid distance = 3.6655 (15) Å] is observed in the crystal structure. Furthermore, intermolecular C–H···π interactions link the molecules into a three-dimensional network, as shown in Fig. 3.

S2. Synthesis and crystallization

Crystals of (I) suitable for X-ray diffraction were obtained from solutions in acetone of a commercially available sample (Aldrich) by slow evaporation at 298 K. ^{1}H NMR (500MHz, CDCl$_3$): δ 4.10 (s, 6H, -OCH$_3$), 7.03(dd, 2H, py-5H), 8.37(d, 2H, py-H3), 8.56(d, 2H, py-H6).

S3. Refinement

The H atoms were included in calculated positions and treated as riding atoms: C—H = 0.95-0.98Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and = 1.2U_{eq}(C) for aromatic H atoms.
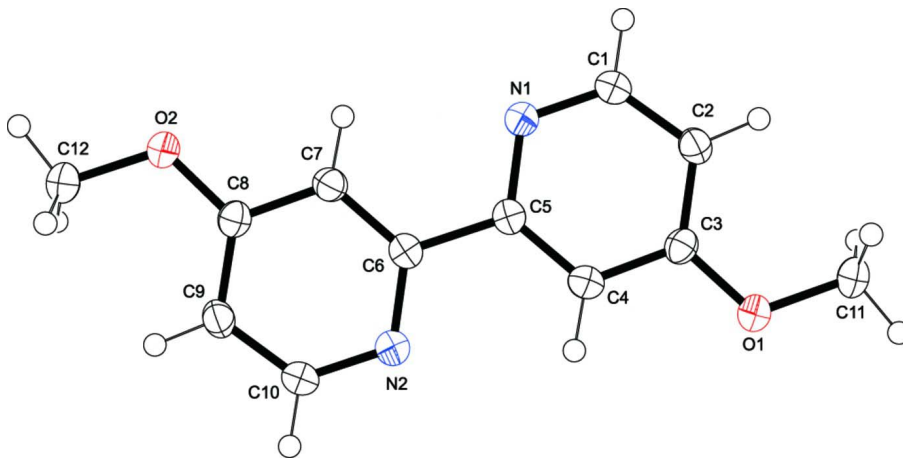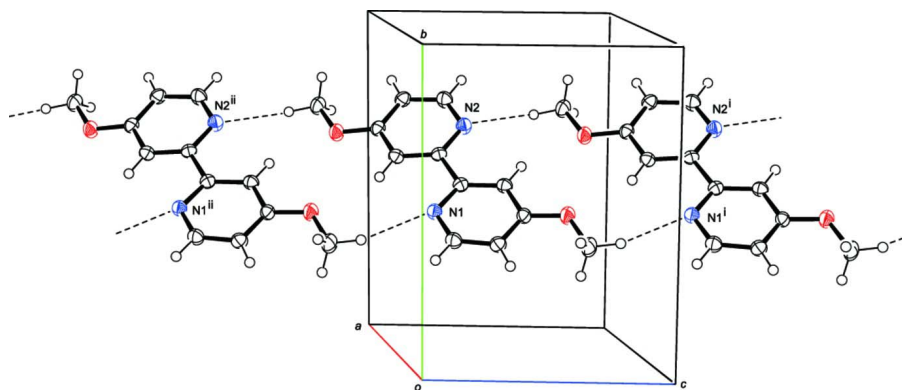

Figure 1

The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2

Part of the crystal structure of compound (I) showing the formation of 2D sheet. Dashed lines indicate the intermolecular C-H···N interactions. [Symmetry code: (i) *x*, *y*, 1+ *z*; (ii) *x*, *y*, -1+ *z*.]

Figure 3

Part of the crystal structure showing the intersheet stacking interactions and the weak C-H···π hydrogen bonds.

4,4′-Dimethoxy-2,2′-bipyridine

Crystal data

$C_{12}H_{12}N_2O_2$	$c = 8.0123$ (14) Å
$M_r = 216.24$	$\beta = 109.462$ (2)°
Monoclinic, $P2_1$	$V = 524.76$ (16) Å³
$a = 6.4235$ (11) Å	$Z = 2$
$b = 10.8139$ (18) Å	$F(000) = 228$

$D_x = 1.369$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3527 reflections

$\theta = 2.7$–28.3°

$\mu = 0.10$ mm^{-1}

$T = 200$ K

Plate, colourless

$0.24 \times 0.07 \times 0.05$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: Bruker TXS fine-focus rotating anode

Bruker Helios multilayer confocal mirror monochromator

Detector resolution: 8.333 pixels mm^{-1}

φ and ω scans

Absorption correction: multi-scan (*SADABS2014*; Bruker, 2014)

$T_{min} = ?$, $T_{max} = ?$

5925 measured reflections

2301 independent reflections

2155 reflections with $I > 2\sigma(I)$

$R_{int} = 0.014$

$\theta_{max} = 27.1°$, $\theta_{min} = 2.7°$

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 13$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.084$

$S = 1.01$

2301 reflections

147 parameters

1 restraint

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.1642P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.20$ e Å^{-3}

$\Delta\rho_{min} = -0.16$ e Å^{-3}

Absolute structure: Flack x determined using 976 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)

Absolute structure parameter: 0.7 (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.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
- 3.4311 (0.0049) x + 8.4883 (0.0065) y - 0.9456 (0.0066) z = 4.1170 (0.0067)
* -0.0041 (0.0014) N2 * 0.0008 (0.0014) C6 * 0.0044 (0.0014) C7 * -0.0064 (0.0014) C8 * 0.0031 (0.0015) C9 * 0.0021 (0.0016) C10 -0.0086 (0.0030) O2 -0.0684 (0.0042) C12
Rms deviation of fitted atoms = 0.0039
- 3.4675 (0.0048) x + 8.7970 (0.0059) y - 0.1939 (0.0067) z = 4.4232 (0.0036)
Angle to previous plane (with approximate esd) = 5.832 (0.127)
* 0.0007 (0.0014) N1 * 0.0006 (0.0016) C1 * -0.0022 (0.0015) C2 * 0.0024 (0.0015) C3 * -0.0011 (0.0013) C4 * -0.0005 (0.0013) C5 0.0002 (0.0030) O1 -0.0031 (0.0045) C11
Rms deviation of fitted atoms = 0.0015
- 3.4311 (0.0049) x + 8.4883 (0.0065) y - 0.9456 (0.0066) z = 4.1170 (0.0067)
Angle to previous plane (with approximate esd) = 5.832 (0.127)
* -0.0041 (0.0014) N2 * 0.0008 (0.0014) C6 * 0.0044 (0.0014) C7 * -0.0064 (0.0014) C8 * 0.0031 (0.0015) C9 * 0.0021 (0.0016) C10 -3.3185 (0.0031) N1_$4 -3.3333 (0.0027) C1_$4 -3.4592 (0.0024) C2_$4 -3.5727 (0.0026) C3_$4 -3.5648 (0.0032) C4_$4 -3.4354 (0.0034) C5_$4
Rms deviation of fitted atoms = 0.0039
- 3.4675 (0.0048) x + 8.7970 (0.0059) y - 0.1939 (0.0067) z = 4.4232 (0.0036)
Angle to previous plane (with approximate esd) = 5.832 (0.127)
* 0.0007 (0.0014) N1 * 0.0006 (0.0016) C1 * -0.0022 (0.0015) C2 * 0.0024 (0.0015) C3 * -0.0011 (0.0013) C4 * -0.0005 (0.0013) C5 3.5634 (0.0029) N2_$3 3.4535 (0.0033) C6_$3 3.3280 (0.0034) C7_$3 3.3037 (0.0027) C8_$3 3.4295 (0.0025) C9_$3 3.5529 (0.0027) C10_$3
Rms deviation of fitted atoms = 0.0015

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.1486 (3)	0.4462 (2)	0.0875 (3)	0.0267 (5)
H1	−0.2534	0.4031	−0.0068	0.032*
C2	−0.1727 (4)	0.4400 (2)	0.2528 (3)	0.0266 (5)
H2	−0.2892	0.3940	0.2711	0.032*
C3	−0.0204 (3)	0.5037 (2)	0.3910 (3)	0.0229 (4)
C4	0.1487 (3)	0.56915 (19)	0.3571 (3)	0.0236 (4)
H4	0.2556	0.6130	0.4492	0.028*
C5	0.1577 (3)	0.56905 (19)	0.1864 (3)	0.0221 (4)
C6	0.3359 (3)	0.63676 (19)	0.1424 (3)	0.0217 (4)
C7	0.3547 (4)	0.6263 (2)	−0.0241 (3)	0.0238 (4)
H7	0.2539	0.5768	−0.1126	0.029*
C8	0.5240 (4)	0.68943 (19)	−0.0599 (3)	0.0235 (4)
C9	0.6663 (4)	0.7627 (2)	0.0716 (3)	0.0268 (5)
H9	0.7823	0.8081	0.0514	0.032*
C10	0.6319 (4)	0.7668 (2)	0.2337 (3)	0.0295 (5)
H10	0.7293	0.8166	0.3239	0.035*
C11	−0.1939 (4)	0.4392 (3)	0.5974 (3)	0.0356 (6)
H11A	−0.3380	0.4719	0.5251	0.053*
H11B	−0.1765	0.4482	0.7230	0.053*
H11C	−0.1846	0.3515	0.5698	0.053*

C12	0.7110 (4)	0.7348 (2)	−0.2653 (3)	0.0321 (5)
H12A	0.7009	0.8244	−0.2509	0.048*
H12B	0.7005	0.7164	−0.3876	0.048*
H12C	0.8526	0.7048	−0.1844	0.048*
N1	0.0100 (3)	0.50795 (19)	0.0503 (2)	0.0244 (4)
N2	0.4729 (3)	0.70612 (19)	0.2732 (2)	0.0275 (4)
O1	−0.0221 (3)	0.50643 (16)	0.5595 (2)	0.0307 (4)
O2	0.5337 (3)	0.67463 (15)	−0.2257 (2)	0.0304 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0250 (10)	0.0285 (11)	0.0256 (10)	−0.0048 (10)	0.0069 (8)	−0.0029 (9)
C2	0.0252 (10)	0.0274 (11)	0.0292 (11)	−0.0049 (10)	0.0118 (9)	−0.0023 (10)
C3	0.0256 (10)	0.0222 (10)	0.0227 (10)	0.0027 (9)	0.0105 (8)	0.0002 (9)
C4	0.0224 (10)	0.0225 (10)	0.0242 (11)	−0.0003 (8)	0.0055 (8)	−0.0007 (9)
C5	0.0210 (9)	0.0208 (10)	0.0248 (10)	0.0015 (8)	0.0082 (8)	0.0014 (8)
C6	0.0201 (10)	0.0196 (10)	0.0252 (10)	0.0019 (8)	0.0071 (8)	0.0017 (8)
C7	0.0229 (10)	0.0234 (10)	0.0250 (10)	−0.0012 (8)	0.0077 (8)	−0.0016 (8)
C8	0.0239 (10)	0.0239 (11)	0.0235 (10)	0.0023 (9)	0.0090 (8)	0.0024 (8)
C9	0.0244 (10)	0.0279 (11)	0.0296 (11)	−0.0040 (9)	0.0112 (9)	0.0018 (9)
C10	0.0267 (11)	0.0338 (13)	0.0267 (11)	−0.0074 (9)	0.0071 (9)	−0.0046 (9)
C11	0.0397 (13)	0.0443 (14)	0.0292 (12)	−0.0120 (12)	0.0200 (10)	−0.0030 (11)
C12	0.0345 (12)	0.0370 (13)	0.0287 (12)	−0.0063 (10)	0.0158 (10)	0.0006 (10)
N1	0.0241 (8)	0.0265 (9)	0.0229 (9)	−0.0015 (7)	0.0081 (7)	−0.0003 (7)
N2	0.0257 (9)	0.0321 (10)	0.0252 (9)	−0.0040 (8)	0.0091 (7)	−0.0014 (8)
O1	0.0333 (8)	0.0362 (9)	0.0254 (8)	−0.0085 (7)	0.0137 (6)	−0.0025 (7)
O2	0.0325 (9)	0.0366 (9)	0.0256 (8)	−0.0094 (7)	0.0144 (7)	−0.0042 (7)

Geometric parameters (Å, º)

C1—N1	1.332 (3)	C8—O2	1.359 (3)
C1—C2	1.385 (3)	C8—C9	1.390 (3)
C1—H1	0.9500	C9—C10	1.389 (3)
C2—C3	1.391 (3)	C9—H9	0.9500
C2—H2	0.9500	C10—N2	1.338 (3)
C3—O1	1.354 (3)	C10—H10	0.9500
C3—C4	1.398 (3)	C11—O1	1.436 (3)
C4—C5	1.388 (3)	C11—H11A	0.9800
C4—H4	0.9500	C11—H11B	0.9800
C5—N1	1.355 (3)	C11—H11C	0.9800
C5—C6	1.496 (2)	C12—O2	1.436 (3)
C6—N2	1.349 (3)	C12—H12A	0.9800
C6—C7	1.384 (3)	C12—H12B	0.9800
C7—C8	1.393 (3)	C12—H12C	0.9800
C7—H7	0.9500		
N1—C1—C2	125.1 (2)	C9—C8—C7	119.02 (19)

N1—C1—H1	117.4	C10—C9—C8	117.2 (2)
C2—C1—H1	117.4	C10—C9—H9	121.4
C1—C2—C3	117.7 (2)	C8—C9—H9	121.4
C1—C2—H2	121.2	N2—C10—C9	125.3 (2)
C3—C2—H2	121.2	N2—C10—H10	117.4
O1—C3—C2	124.60 (19)	C9—C10—H10	117.4
O1—C3—C4	116.61 (18)	O1—C11—H11A	109.5
C2—C3—C4	118.79 (19)	O1—C11—H11B	109.5
C5—C4—C3	118.80 (18)	H11A—C11—H11B	109.5
C5—C4—H4	120.6	O1—C11—H11C	109.5
C3—C4—H4	120.6	H11A—C11—H11C	109.5
N1—C5—C4	123.02 (19)	H11B—C11—H11C	109.5
N1—C5—C6	115.79 (17)	O2—C12—H12A	109.5
C4—C5—C6	121.18 (17)	O2—C12—H12B	109.5
N2—C6—C7	123.39 (19)	H12A—C12—H12B	109.5
N2—C6—C5	116.19 (17)	O2—C12—H12C	109.5
C7—C6—C5	120.41 (17)	H12A—C12—H12C	109.5
C6—C7—C8	118.92 (19)	H12B—C12—H12C	109.5
C6—C7—H7	120.5	C1—N1—C5	116.58 (18)
C8—C7—H7	120.5	C10—N2—C6	116.14 (19)
O2—C8—C9	125.1 (2)	C3—O1—C11	117.47 (18)
O2—C8—C7	115.88 (18)	C8—O2—C12	117.40 (17)
N1—C1—C2—C3	0.3 (4)	C6—C7—C8—C9	−1.1 (3)
C1—C2—C3—O1	−180.0 (2)	O2—C8—C9—C10	−179.9 (2)
C1—C2—C3—C4	−0.5 (3)	C7—C8—C9—C10	1.0 (3)
O1—C3—C4—C5	179.94 (18)	C8—C9—C10—N2	−0.1 (4)
C2—C3—C4—C5	0.4 (3)	C2—C1—N1—C5	−0.1 (3)
C3—C4—C5—N1	−0.2 (3)	C4—C5—N1—C1	0.0 (3)
C3—C4—C5—C6	−179.56 (19)	C6—C5—N1—C1	179.41 (18)
N1—C5—C6—N2	174.7 (2)	C9—C10—N2—C6	−0.5 (4)
C4—C5—C6—N2	−5.8 (3)	C7—C6—N2—C10	0.4 (3)
N1—C5—C6—C7	−5.5 (3)	C5—C6—N2—C10	−179.92 (19)
C4—C5—C6—C7	173.9 (2)	C2—C3—O1—C11	−0.2 (3)
N2—C6—C7—C8	0.4 (3)	C4—C3—O1—C11	−179.7 (2)
C5—C6—C7—C8	−179.28 (17)	C9—C8—O2—C12	3.0 (3)
C6—C7—C8—O2	179.70 (18)	C7—C8—O2—C12	−177.8 (2)

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the N1- and N2-rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···N2	0.95	2.50	2.813 (3)	99
C7—H7···N1	0.95	2.46	2.789 (3)	100
C11—H11*B*···N1^i	0.98	2.58	3.503 (3)	158
C12—H12*B*···N2^ii	0.98	2.62	3.513 (3)	151

C1—H1···*Cg*2[iii]	0.95	2.68	3.515 (3)	146
C12—H12*A*···*Cg*1[iv]	0.98	2.72	3.439 (3)	134

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