Crystal structure of 4-(anthracen-9-yl)pyridine

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The title compound, $C_{19}H_{13}N$, which crystallizes in the monoclinic $C2/c$ space group with one half-molecule in the asymmetric unit, was synthesized by Suzuki–Miyaura cross-coupling reaction of 9-bromoanthracene with pyridin-4-ylboronic acid and purified by column chromatography on silica gel. Light-yellow crystals of 4-(anthracen-9-yl)-pyridine suitable for X-ray diffraction were collected by the solvent evaporation method. In the crystal, pairs of molecules are connected by intermolecular C—H···π (pyridine) interactions [d(H7···Cg) = 2.7391 (2) Å], forming cyclic centrosymmetric dimers, further resulting in an infinite one-dimensional linear chain along the c-axis direction. Weak face-to-face π–π stacking interactions [d(Cg···Cg) = 3.6061 (2) Å] link neighboring lamellar networks into the supramolecular structure.

1. Chemical context

Anthracene and its derivatives constitute a very famous class of fluorophores that have been widely used in the development of functional fluorescent chemosensors because of their intriguing photophysical properties and chemical stability (Martínez-Máñez *et al.*, 2003). One of the most important steps in the rational molecule design of anthracene-based chemosensors is the judicious combination with functional chemical recognition moieties, which can be used for monitoring and quantifying of abnormal physiological changes at the subcellular level (Densil *et al.*, 2018; Mondal *et al.*, 2014; Anand *et al.*, 2015; Shree *et al.*, 2019). It has been found that 9,10-distyrylanthracene derivatives with restricted intra-molecular rotations often lead to aggregation-induced emission characteristics (Lu *et al.*, 2010). In recent years, there has been an increased effort to combine anthracene derivatives with N- or O-coordinated single ligands and other attractive mixed ligands in order to construct tunable fluorescent ligands (Dey *et al.*, 2016; Yao *et al.*, 2019). As part of our studies in this area, we report herein the synthesis and crystal structure of a fluorescent monopyridine ligand, $C_{19}H_{13}N$.
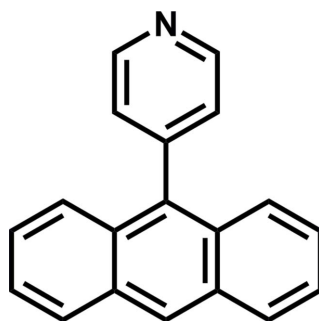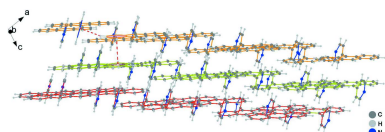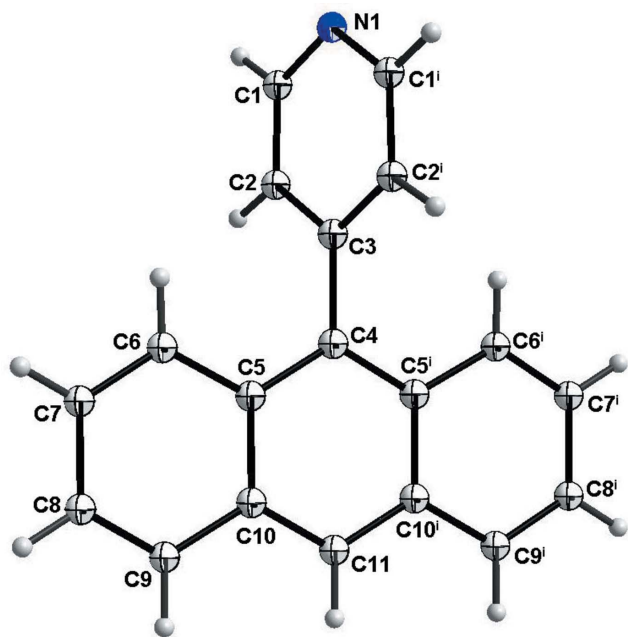
Figure 1
The molecular structure of 4-(anthracen-9-yl)-pyridine with displacement ellipsoids at the 50% probability level. Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

2. Structural commentary

As shown in Fig. 1, single-crystal X-ray diffraction analysis reveals that 4-(anthracen-9-yl)-pyridine crystallizes in the monoclinic $C2/c$ space group with half molecule in the asymmetric unit (Table 1). In the structure of the title compound, the C–C bond lengths of the benzene ring range from 1.3534 (13) to 1.4352 (1) Å, and the C–N bond length is 1.3351 (11), which is comparable with the literature reported (Zhao *et al.*, 2016). The bond angle of N1–C1–C2 is 124.161 (7)°, closed to the ideal bond angle of 120° for benzene ring. The pyridine ring is inclined to the benzene ring at a dihedral angle of 71.64 (4)°.
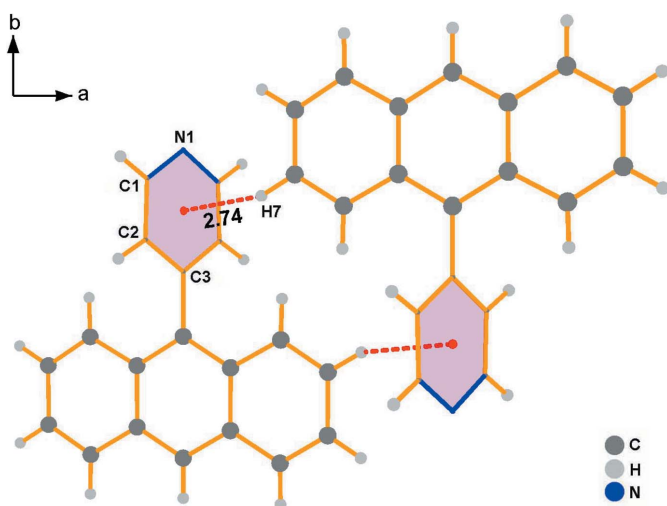

Figure 2
The hydrogen-bonded centrosymmetric dimer along the *c* axis. Dashed lines indicate C—H···π interactions.

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

Cg is the centroid of the pyridine ring.

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···Cg^i	0.93	2.74	3.5606 (12)	148
C7—H7···Cg^{ii}	0.93	2.74	3.5606 (12)	148

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

3. Supramolecular features

In the crystal, the hydrogen atom of anthracene ring contributes to the formation of a C7—H7···π contact with the pyridine ring (Table 1); the resulting cyclic centrosymmetric dimer is shown in Fig. 2. Subsequently, the paired C—H···π(pyridine) hydrogen-bonding interactions connect neighboring dimers, resulting in an infinite 1-D linear chain (Fig. 3), which is basis for extension of the dimensionality. As shown in Figs. 4 and 5, the crystal packing involves weak face-to-face π–π stacking interactions [$d(Cg···Cg) = 3.6095 (7)$ Å] between two benzene rings related by the symmetry operation $1 - x, y, \frac{1}{2} - z$.

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.41, update March 2021; Groom *et al.* 2016) revealed that this is the first example of a structurally characterized 4-(anthracen-9-yl)-pyridine. At the same time, a CSD search for compounds containing the 4-(anthracen-9-yl)-pyridine substructure identified only one compound, *viz.* $Ag_{12}(SCH_2C_6H_5)_6(CF_3COO)_6(L_4)_6$ [L_4 = 4-(anthracen-9-yl)-pyridine; Li *et al.*, 2018] in which the pyridine ring of this compound is inclined to the benzene ring at a dihedral angle of 73.28°.
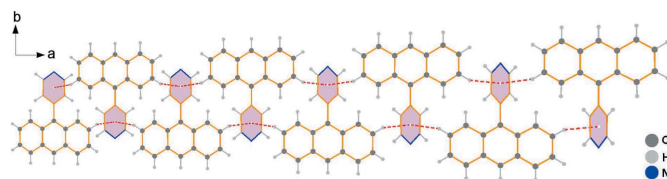

Figure 3
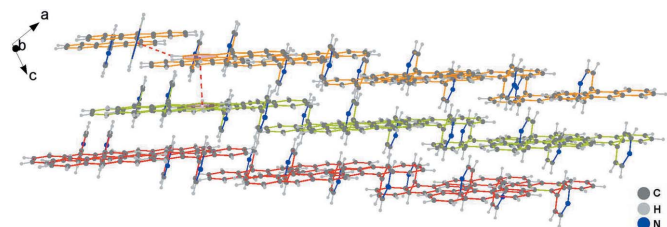View of the 1-D chain-like structure of the title compound along the *c* axis.

Figure 4
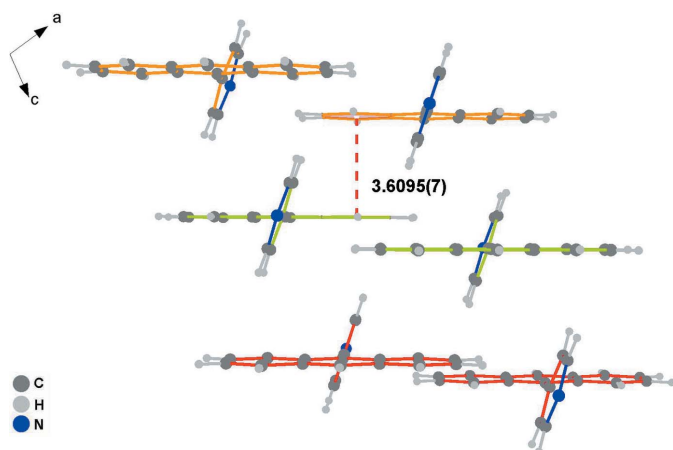Crystal packing projected *via* C—H···π and π–π stacking interactions.

Figure 5
π–π stacking interactions of molecules in the crystal structure of the title compound.

5. Synthesis and crystallization

4-(Anthracen-9-yl)-pyridine was synthesized by the Suzuki–Miyaura cross-coupling reaction according to a previously reported protocol (Zhao *et al.*, 2019). As shown in Fig. 6, under a nitrogen atmosphere, 9-bromoanthracene (2.56 g, 10 mmol), pyridin-4-ylboronic acid (1.23 g, 10 mmol) and tetratriphenyl phosphine palladium (0.10 g, 0.1 mmol) were dissolved in toluene (90 mL) followed by the addition of potassium carbonate aqueous solution (22 wt%, 40 mL) under constant stirring. The reaction mixture was subsequently refluxed for 12 h, and the mixture was then further purified by column chromatography using petroleum/ethyl acetate (3:1, *v/v*) as eluent to give yellow solid 4-(anthracen-9-yl)pyridine (1.76 g, yield 69%).

Crystals of 4-(anthracen-9-yl)-pyridine suitable for X-ray analysis were obtained by the solvent evaporation method. In detail, solid 4-(anthracen-9-yl)-pyridine (0.013 g, 0.05 mmol) was dissolved in 0.5 mL of dichloromethane and 5 mL of ethyl acetate. The mixture solvent was evaporated slowly at room temperature for about 2 weeks. Light-yellow crystals of 4-(anthracen-9-yl)-pyridine suitable for X-ray diffraction were collected.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geome-
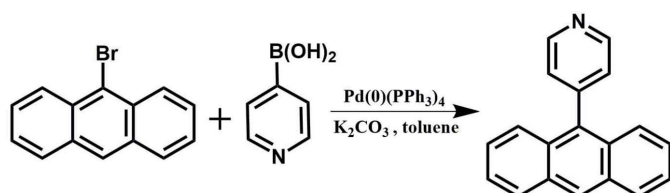

Figure 6
Synthesis of 4-(anthracen-9-yl)-pyridine.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{13}N$
M_r	255.30
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	296
a, b, c (Å)	6.0777 (4), 20.9211 (16), 10.2574 (7)
β (°)	102.476 (3)
V (Å^3)	1273.45 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	$0.18 \times 0.15 \times 0.13$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.699, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4703, 1144, 1022
R_{int}	0.029
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.105, 1.11
No. of reflections	1144
No. of parameters	94
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.15, −0.14

Computer programs: *APEX3* (Bruker, 2018), *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

trically (C—H = 0.93 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

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Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

4-(Anthracen-9-yl)pyridine

Crystal data

$C_{19}H_{13}N$	$F(000) = 536$
$M_r = 255.30$	$D_x = 1.332$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.0777$ (4) Å	Cell parameters from 2979 reflections
$b = 20.9211$ (16) Å	$\theta = 3.7–25.3°$
$c = 10.2574$ (7) Å	$\mu = 0.08$ mm^{-1}
$\beta = 102.476$ (3)°	$T = 296$ K
$V = 1273.45$ (16) Å^3	Bulk, light yellow
$Z = 4$	$0.18 \times 0.15 \times 0.13$ mm

Data collection

Bruker APEXII CCD diffractometer	1144 independent reflections
φ and ω scans	1022 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$R_{int} = 0.029$
	$\theta_{max} = 25.3°$, $\theta_{min} = 3.7°$
$T_{min} = 0.699$, $T_{max} = 0.745$	$h = -7 \rightarrow 6$
4703 measured reflections	$k = -22 \rightarrow 24$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.3319P]$
$wR(F^2) = 0.105$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
1144 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
94 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
0 restraints	

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.000000	0.36240 (5)	0.250000	0.0360 (4)
C1	0.12815 (18)	0.39626 (5)	0.18480 (11)	0.0359 (3)
H1	0.219495	0.374032	0.138423	0.043*
C2	0.13369 (17)	0.46237 (5)	0.18183 (10)	0.0324 (3)
H2	0.226472	0.483317	0.134422	0.039*
C3	0.000000	0.49724 (7)	0.250000	0.0266 (4)
C4	0.000000	0.56870 (6)	0.250000	0.0267 (4)
C5	0.18833 (15)	0.60220 (5)	0.32231 (9)	0.0279 (3)
C6	0.38307 (17)	0.57083 (5)	0.39762 (10)	0.0308 (3)
H6	0.387809	0.526405	0.399226	0.037*
C7	0.56176 (18)	0.60434 (5)	0.46706 (11)	0.0357 (3)
H7	0.686262	0.582594	0.515636	0.043*
C8	0.56061 (19)	0.67201 (5)	0.46633 (12)	0.0405 (3)
H8	0.683709	0.694491	0.514440	0.049*
C9	0.38025 (19)	0.70397 (5)	0.39555 (11)	0.0407 (4)
H9	0.381857	0.748415	0.394805	0.049*
C10	0.18747 (17)	0.67085 (5)	0.32198 (10)	0.0325 (3)
C11	0.000000	0.70319 (7)	0.250000	0.0371 (4)
H11	0.000002	0.747643	0.250003	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0410 (8)	0.0233 (7)	0.0417 (7)	0.000	0.0045 (6)	0.000
C1	0.0393 (6)	0.0281 (6)	0.0414 (6)	0.0039 (4)	0.0110 (5)	−0.0046 (4)
C2	0.0351 (6)	0.0280 (6)	0.0363 (6)	−0.0016 (4)	0.0123 (4)	−0.0006 (4)
C3	0.0274 (7)	0.0243 (7)	0.0269 (7)	0.000	0.0026 (5)	0.000
C4	0.0323 (8)	0.0235 (8)	0.0262 (7)	0.000	0.0108 (5)	0.000
C5	0.0328 (6)	0.0261 (6)	0.0268 (6)	−0.0010 (4)	0.0110 (4)	−0.0001 (3)
C6	0.0351 (6)	0.0260 (6)	0.0320 (6)	−0.0004 (4)	0.0085 (4)	0.0000 (4)
C7	0.0333 (6)	0.0362 (7)	0.0364 (6)	−0.0006 (4)	0.0050 (4)	0.0003 (4)
C8	0.0391 (7)	0.0359 (7)	0.0443 (7)	−0.0109 (5)	0.0039 (5)	−0.0035 (5)
C9	0.0479 (7)	0.0250 (6)	0.0473 (7)	−0.0073 (4)	0.0062 (6)	−0.0017 (4)
C10	0.0393 (7)	0.0255 (6)	0.0333 (6)	−0.0029 (4)	0.0091 (5)	−0.0004 (4)
C11	0.0467 (9)	0.0209 (7)	0.0427 (9)	0.000	0.0075 (7)	0.000

Geometric parameters (Å, º)

N1—C1	1.3345 (12)	C6—H6	0.9300
N1—C1ⁱ	1.3345 (12)	C6—C7	1.3579 (15)
C1—H1	0.9300	C7—H7	0.9300
C1—C2	1.3840 (15)	C7—C8	1.4158 (16)
C2—H2	0.9300	C8—H8	0.9300
C2—C3	1.3881 (12)	C8—C9	1.3534 (16)
C3—C4	1.4951 (19)	C9—H9	0.9300
C4—C5ⁱ	1.4088 (12)	C9—C10	1.4284 (15)
C4—C5	1.4088 (12)	C10—C11	1.3920 (13)
C5—C6	1.4259 (14)	C11—H11	0.9300
C5—C10	1.4362 (16)		
C1—N1—C1ⁱ	115.86 (12)	C7—C6—C5	121.52 (10)
N1—C1—H1	117.9	C7—C6—H6	119.2
N1—C1—C2	124.14 (10)	C6—C7—H7	119.6
C2—C1—H1	117.9	C6—C7—C8	120.73 (10)
C1—C2—H2	120.2	C8—C7—H7	119.6
C1—C2—C3	119.63 (10)	C7—C8—H8	120.0
C3—C2—H2	120.2	C9—C8—C7	119.95 (10)
C2ⁱ—C3—C2	116.60 (13)	C9—C8—H8	120.0
C2—C3—C4	121.70 (6)	C8—C9—H9	119.3
C2ⁱ—C3—C4	121.70 (6)	C8—C9—C10	121.38 (11)
C5ⁱ—C4—C3	119.84 (6)	C10—C9—H9	119.3
C5—C4—C3	119.83 (6)	C9—C10—C5	118.80 (9)
C5—C4—C5ⁱ	120.33 (13)	C11—C10—C5	119.30 (10)
C4—C5—C6	122.77 (10)	C11—C10—C9	121.90 (11)
C4—C5—C10	119.61 (9)	C10ⁱ—C11—C10	121.84 (14)
C6—C5—C10	117.62 (9)	C10ⁱ—C11—H11	119.1
C5—C6—H6	119.2	C10—C11—H11	119.1

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

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the pyridine ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C7—H7⋯*Cg*ⁱⁱ	0.93	2.74	3.5606 (12)	148
C7—H7⋯*Cg*ⁱⁱⁱ	0.93	2.74	3.5606 (12)	148

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