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4,5-Diaza-9,9′-spirobifluorene

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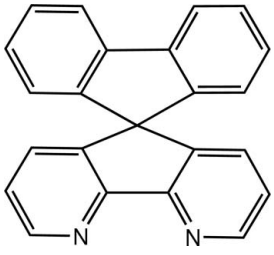
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.043; wR factor = 0.094; data-to-parameter ratio = 8.3.

In the title compound, $C_{23}H_{14}N_2$, biphenyl and 2,2′-bipyridine units are perpendicularly cross-linked by a C atom. The dihedral angle between the mean planes of the biphenyl and 2,2′-bipyridine units is 86.31 (4)°. The crystal structure is stabilized by intermolecular C—H···N interactions.

Related literature

For related literature on fluorene and its derivatives see: Scherf & List (2002); Li *et al.* (2004); Wong *et al.* (2005).



Experimental

Crystal data

$C_{23}H_{14}N_2$
M_r = 318.36
Orthorhombic, $P2_12_12_1$
a = 10.951 (2) Å
b = 11.885 (2) Å
c = 12.916 (2) Å
V = 1681.1 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 298 (2) K
0.33 × 0.15 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.974, T_{max} = 0.982
9237 measured reflections
1889 independent reflections
1193 reflections with $I > 2\sigma(I)$
R_{int} = 0.129

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.094
S = 1.00
1889 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 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
C21—H21···N1^{i}	0.93	2.58	3.383 (4)	145
C22—H22···N2^{i}	0.93	2.53	3.436 (4)	164

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); 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: GK2087).

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supplementary materials

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4,5-Diaza-9,9'-spirobifluorene

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Comment

Fluorene and its derivatives have an aromatic biphenyl structure. Due to a wide energy gap in the backbones and high luminescence efficiency, they have drawn much attention of the materials chemists and device physicists (Scherf & List, 2002; Li *et al.*, 2004).

Experimental

The title compound (m.p. 518 K) was prepared according to the published procedure (Wong *et al.*, 2005). Crystals suitable for X-ray diffraction were obtained during an attempt to prepare a metalorganic compound from 2,5-pyrindine dicarboxylic acid, 4,5-diaza-9,9'-spirobifluorene and zinc(II) nitrate hexahydrate by hydrothermal synthesis.

Refinement

Because the quality of the crystal was not good, and no facility was available for single-crystal structure determination at low temperature, the R_{int} value is quite high.

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances of 0.93 Å, and with $U_{iso}(H) = 1.2U_{eq}$ of the parent atoms. In the absence of significant anomalous scattering effects, Friedel pairs were averaged.

Figures

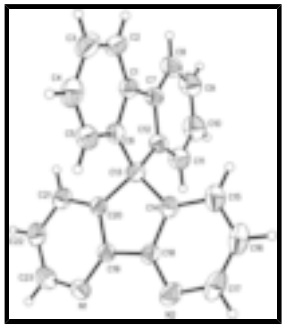

Fig. 1. The structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering schems.

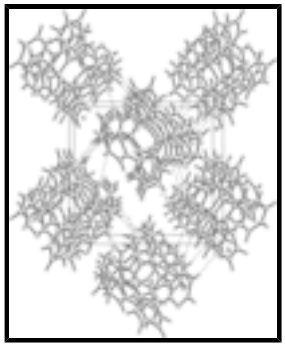

Fig. 2. The packing diagram shown along the *X* axis. Hydrogen bods are shown with dashed lines.

4,5-Diaza-9,9'-spirobifluorene

Crystal data

$C_{23}H_{14}N_2$	F_{000} = 664
M_r = 318.36	D_x = 1.258 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 1494 reflections
a = 10.951 (2) Å	θ = 2.3–18.2º
b = 11.885 (2) Å	μ = 0.07 mm^{-1}
c = 12.916 (2) Å	T = 298 (2) K
V = 1681.1 (5) Å^3	Acicular, orange
Z = 4	0.33 × 0.15 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer	1889 independent reflections
Radiation source: fine-focus sealed tube	1193 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.129
T = 298(2) K	θ_{max} = 26.0º
π and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	h = −13→13
T_{min} = 0.974, T_{max} = 0.982	k = −14→13
9237 measured reflections	l = −14→15

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0138P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.043	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.094	$\Delta\rho_{max}$ = 0.14 e Å^{-3}
S = 1.00	$\Delta\rho_{min}$ = −0.15 e Å^{-3}

1889 reflections
227 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
Extinction correction: SHELXL97
Extinction coefficient: 0.0065 (8)

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C19	0.0854 (2)	0.3926 (2)	0.34109 (19)	0.0457 (7)
C13	0.2359 (3)	0.2578 (2)	0.3985 (2)	0.0511 (7)
C18	0.1646 (3)	0.4480 (2)	0.4176 (2)	0.0502 (7)
N1	−0.0086 (2)	0.43886 (19)	0.29213 (18)	0.0584 (7)
C14	0.2477 (3)	0.3696 (2)	0.45536 (19)	0.0497 (7)
C20	0.1250 (2)	0.2819 (2)	0.3303 (2)	0.0439 (7)
C1	0.4017 (3)	0.1281 (2)	0.3718 (2)	0.0512 (7)
N2	0.1586 (3)	0.55576 (18)	0.44783 (18)	0.0655 (7)
C7	0.3194 (3)	0.0803 (2)	0.4506 (2)	0.0503 (7)
C21	0.0614 (3)	0.2127 (2)	0.2634 (2)	0.0568 (8)
H21	0.0843	0.1382	0.2535	0.068*
C23	−0.0681 (3)	0.3685 (3)	0.2293 (2)	0.0693 (9)
H23	−0.1360	0.3964	0.1945	0.083*
C12	0.2240 (3)	0.1545 (2)	0.4675 (2)	0.0507 (7)
C6	0.3520 (2)	0.2299 (2)	0.3381 (2)	0.0484 (7)
C5	0.4091 (3)	0.2924 (2)	0.2624 (2)	0.0615 (8)
H5	0.3762	0.3604	0.2402	0.074*
C11	0.1342 (3)	0.1312 (3)	0.5388 (2)	0.0698 (9)
H11	0.0716	0.1822	0.5516	0.084*
C2	0.5094 (3)	0.0908 (3)	0.3308 (2)	0.0637 (8)
H2	0.5433	0.0235	0.3538	0.076*
C8	0.3257 (3)	−0.0206 (3)	0.5047 (2)	0.0683 (9)
H8	0.3905	−0.0701	0.4950	0.082*
C3	0.5682 (3)	0.1531 (3)	0.2553 (3)	0.0770 (10)
H3	0.6422	0.1286	0.2281	0.092*
C4	0.5160 (3)	0.2522 (3)	0.2204 (2)	0.0753 (10)

H4	0.5539	0.2922	0.1675	0.090*
C22	−0.0367 (3)	0.2578 (3)	0.2120 (2)	0.0670 (9)
H22	−0.0816	0.2141	0.1660	0.080*
C16	0.3234 (3)	0.5119 (4)	0.5654 (3)	0.0847 (11)
H16	0.3755	0.5373	0.6172	0.102*
C15	0.3284 (3)	0.4009 (3)	0.5330 (2)	0.0720 (10)
H15	0.3831	0.3499	0.5619	0.086*
C9	0.2333 (4)	−0.0450 (3)	0.5731 (3)	0.0780 (10)
H9	0.2341	−0.1135	0.6080	0.094*
C17	0.2412 (4)	0.5841 (3)	0.5208 (3)	0.0813 (11)
H17	0.2426	0.6587	0.5426	0.098*
C10	0.1400 (3)	0.0290 (3)	0.5910 (3)	0.0854 (11)
H10	0.0796	0.0108	0.6388	0.103*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C19	0.0524 (18)	0.0429 (15)	0.0418 (15)	−0.0013 (14)	−0.0013 (14)	0.0024 (13)
C13	0.0577 (19)	0.0476 (16)	0.0479 (15)	0.0030 (15)	0.0013 (14)	0.0026 (13)
C18	0.0657 (19)	0.0399 (16)	0.0449 (16)	−0.0034 (15)	0.0033 (15)	−0.0002 (13)
N1	0.0609 (16)	0.0585 (15)	0.0559 (15)	0.0055 (14)	−0.0094 (13)	0.0028 (13)
C14	0.0534 (18)	0.0533 (17)	0.0424 (15)	−0.0057 (15)	0.0029 (15)	0.0000 (14)
C20	0.0503 (17)	0.0414 (15)	0.0401 (15)	−0.0017 (14)	0.0011 (13)	0.0020 (13)
C1	0.0517 (19)	0.0525 (17)	0.0493 (17)	−0.0007 (16)	−0.0028 (14)	−0.0063 (14)
N2	0.092 (2)	0.0435 (15)	0.0608 (16)	−0.0072 (14)	0.0032 (15)	−0.0102 (13)
C7	0.0590 (19)	0.0438 (15)	0.0480 (17)	0.0017 (15)	−0.0049 (14)	0.0020 (14)
C21	0.065 (2)	0.0498 (16)	0.0561 (18)	−0.0119 (17)	0.0016 (17)	−0.0073 (15)
C23	0.059 (2)	0.080 (2)	0.069 (2)	−0.002 (2)	−0.0152 (18)	0.0069 (19)
C12	0.0546 (19)	0.0518 (17)	0.0456 (16)	0.0004 (15)	0.0007 (14)	0.0031 (14)
C6	0.0520 (17)	0.0505 (16)	0.0428 (15)	−0.0006 (15)	−0.0014 (14)	−0.0006 (14)
C5	0.064 (2)	0.0649 (19)	0.0551 (19)	−0.0057 (17)	0.0036 (17)	0.0100 (16)
C11	0.077 (2)	0.071 (2)	0.060 (2)	−0.0001 (18)	0.0120 (18)	0.0108 (18)
C2	0.064 (2)	0.0612 (19)	0.066 (2)	0.0088 (18)	0.0038 (18)	−0.0131 (18)
C8	0.084 (2)	0.0541 (19)	0.067 (2)	0.0031 (19)	−0.011 (2)	0.0070 (17)
C3	0.066 (2)	0.096 (3)	0.069 (2)	0.004 (2)	0.012 (2)	−0.022 (2)
C4	0.077 (3)	0.093 (3)	0.055 (2)	−0.014 (2)	0.0147 (19)	0.003 (2)
C22	0.072 (2)	0.072 (2)	0.057 (2)	−0.0157 (19)	−0.0134 (18)	−0.0079 (17)
C16	0.096 (3)	0.100 (3)	0.058 (2)	−0.021 (3)	−0.012 (2)	−0.022 (2)
C15	0.073 (2)	0.086 (2)	0.056 (2)	−0.009 (2)	−0.0142 (17)	−0.0092 (18)
C9	0.099 (3)	0.061 (2)	0.074 (2)	−0.008 (2)	−0.003 (2)	0.025 (2)
C17	0.104 (3)	0.073 (2)	0.067 (2)	−0.026 (2)	0.007 (2)	−0.027 (2)
C10	0.101 (3)	0.085 (3)	0.069 (2)	−0.010 (2)	0.010 (2)	0.026 (2)

Geometric parameters (Å, °)

C19—N1	1.327 (3)	C12—C11	1.375 (4)
C19—C20	1.393 (3)	C6—C5	1.378 (3)
C19—C18	1.470 (4)	C5—C4	1.376 (4)
C13—C12	1.522 (4)	C5—H5	0.9300

C13—C14	1.523 (4)	C11—C10	1.392 (5)
C13—C20	1.527 (4)	C11—H11	0.9300
C13—C6	1.529 (4)	C2—C3	1.383 (4)
C18—N2	1.340 (3)	C2—H2	0.9300
C18—C14	1.391 (4)	C8—C9	1.375 (4)
N1—C23	1.335 (3)	C8—H8	0.9300
C14—C15	1.388 (4)	C3—C4	1.384 (4)
C20—C21	1.381 (3)	C3—H3	0.9300
C1—C2	1.367 (4)	C4—H4	0.9300
C1—C6	1.395 (4)	C22—H22	0.9300
C1—C7	1.473 (4)	C16—C17	1.370 (5)
N2—C17	1.350 (4)	C16—C15	1.385 (5)
C7—C12	1.385 (4)	C16—H16	0.9300
C7—C8	1.391 (4)	C15—H15	0.9300
C21—C22	1.372 (4)	C9—C10	1.368 (4)
C21—H21	0.9300	C9—H9	0.9300
C23—C22	1.378 (4)	C17—H17	0.9300
C23—H23	0.9300	C10—H10	0.9300
N1—C19—C20	125.8 (3)	C1—C6—C13	110.7 (2)
N1—C19—C18	126.3 (2)	C4—C5—C6	118.5 (3)
C20—C19—C18	107.9 (2)	C4—C5—H5	120.7
C12—C13—C14	115.4 (2)	C6—C5—H5	120.7
C12—C13—C20	114.9 (2)	C12—C11—C10	117.9 (3)
C14—C13—C20	100.5 (2)	C12—C11—H11	121.1
C12—C13—C6	101.2 (2)	C10—C11—H11	121.1
C14—C13—C6	111.4 (2)	C1—C2—C3	120.0 (3)
C20—C13—C6	114.0 (2)	C1—C2—H2	120.0
N2—C18—C14	124.8 (3)	C3—C2—H2	120.0
N2—C18—C19	126.5 (3)	C9—C8—C7	117.9 (3)
C14—C18—C19	108.7 (2)	C9—C8—H8	121.0
C19—N1—C23	114.1 (2)	C7—C8—H8	121.0
C15—C14—C18	119.4 (3)	C2—C3—C4	119.5 (3)
C15—C14—C13	129.5 (3)	C2—C3—H3	120.2
C18—C14—C13	111.1 (2)	C4—C3—H3	120.2
C21—C20—C19	117.9 (3)	C5—C4—C3	121.2 (3)
C21—C20—C13	130.6 (2)	C5—C4—H4	119.4
C19—C20—C13	111.5 (2)	C3—C4—H4	119.4
C2—C1—C6	119.8 (3)	C21—C22—C23	119.3 (3)
C2—C1—C7	132.1 (3)	C21—C22—H22	120.4
C6—C1—C7	108.1 (2)	C23—C22—H22	120.4
C18—N2—C17	114.1 (3)	C17—C16—C15	119.7 (3)
C12—C7—C8	120.5 (3)	C17—C16—H16	120.1
C12—C7—C1	109.0 (2)	C15—C16—H16	120.1
C8—C7—C1	130.5 (3)	C16—C15—C14	116.6 (4)
C22—C21—C20	117.7 (3)	C16—C15—H15	121.7
C22—C21—H21	121.1	C14—C15—H15	121.7
C20—C21—H21	121.1	C10—C9—C8	121.6 (3)
N1—C23—C22	125.1 (3)	C10—C9—H9	119.2
N1—C23—H23	117.4	C8—C9—H9	119.2

C22—C23—H23	117.4	N2—C17—C16	125.3 (3)
C11—C12—C7	121.2 (3)	N2—C17—H17	117.4
C11—C12—C13	128.0 (3)	C16—C17—H17	117.4
C7—C12—C13	110.9 (2)	C9—C10—C11	120.9 (3)
C5—C6—C1	120.8 (3)	C9—C10—H10	119.5
C5—C6—C13	128.5 (3)	C11—C10—H10	119.5
N2—C18—C19—N1	−2.9 (5)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C21—H21···N1^{i}	0.93	2.58	3.383 (4)	145
C22—H22···N2^{i}	0.93	2.53	3.436 (4)	164

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

Fig. 1

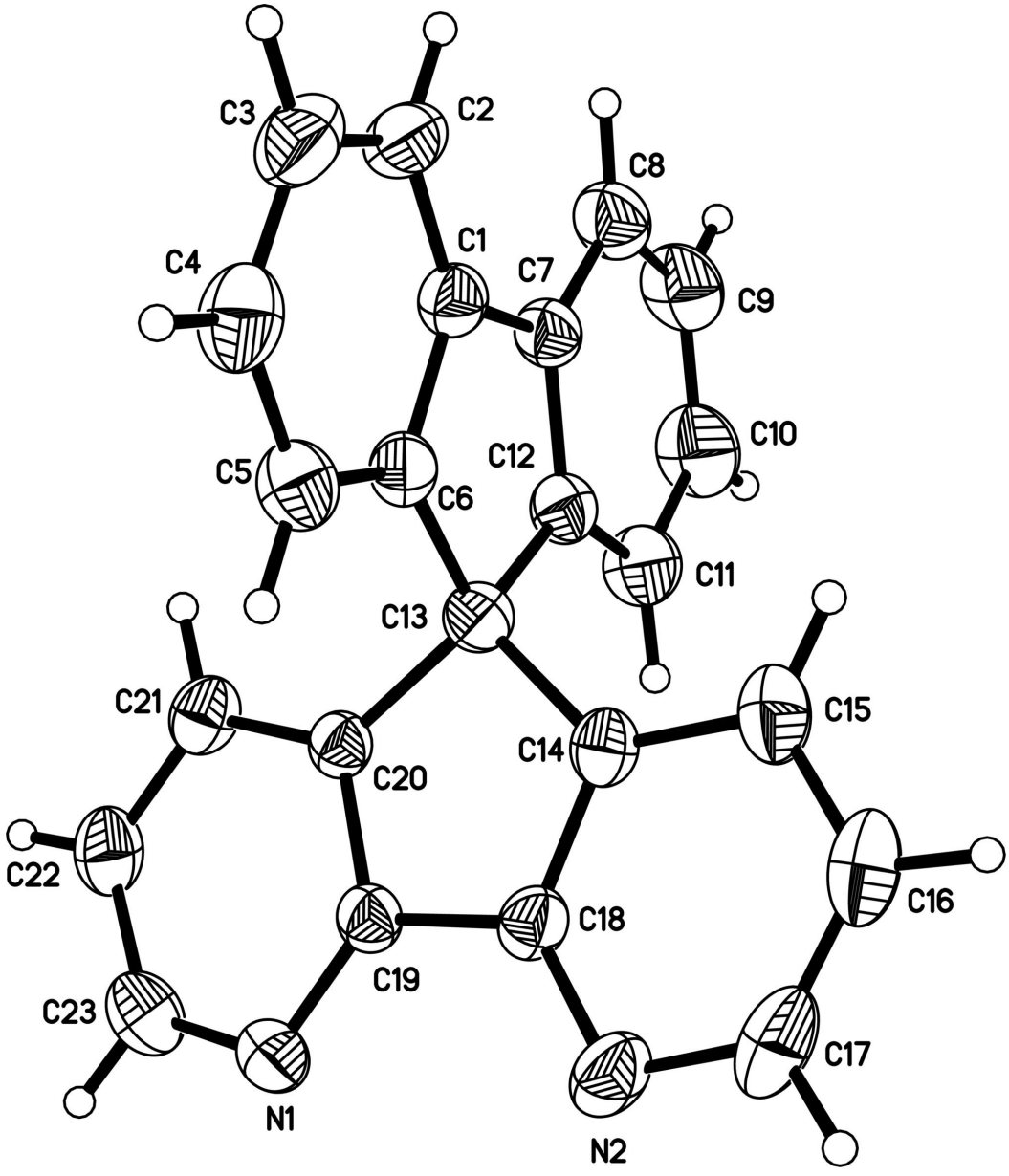
C3
C2
C8
C4
C1
C7
C9
C10
C5
C12
C6
C11
C13
C21
C15
C14
C20
C22
C16
C18
C19
C23
C17
N1
N2

Fig. 2