

Crystal structure of 2,2'-bipyrrole

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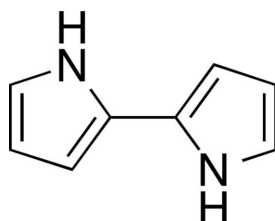
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The complete molecule of the title compound, C₈H₈N₂, is generated by a crystallographic center of symmetry. In the crystal, short N—H··· π [H··· π = 2.499 (19) Å] interactions link the molecules into a herringbone structure.

1. Chemical context

Bipyrrole, C₈H₈N₂, has been studied extensively over the years: the first reported synthesis was in 1962 (Rapoport & Castagnoli, 1962). The bipyrrole core occurs in naturally occurring compounds such as prodigiosin (Wasserman *et al.*, 1960). Functionalized bipyrroles have been shown to have anti-cancer activity (Manderville, 2001). Corrole rings contain a bipyrrole segment in the macrocycle (Aviv-Harel & Gross, 2009). Herein, we report on the crystal structure of the title compound, (I), synthesized by the oxidative coupling of pyrrole.

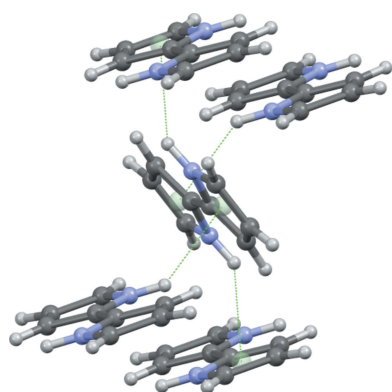


2. Structural commentary

The complete molecule of (I) is generated by a crystallographic center of symmetry (Fig. 1), and therefore the pyrrole rings are exactly parallel and the N—H groups face in opposite directions. The C2—C3 bond in (I) is 1.4151 (19) Å, *versus* the equivalent bond in pyrrole, which has a length of 1.423 (3) Å. The double bonds C1=C2 and C3=C4 in (I) are 1.3635 (19) and 1.3767 (17) Å, respectively, *versus* the double-bond length in pyrrole of 1.357 Å. The shortening of the C2—C3 bond and the lengthening of the adjacent C=C double bonds in (I) compared to pyrrole is consistent with stronger intermolecular interactions (see below).

3. Supramolecular features

In the crystal of (I), the molecules adopt an edge-to-face orientation: the distance between the N—H group and the centroid of the adjacent pyrrole ring generated by the 2₁ screw axis is 2.499 (19) Å (Table 1). A survey of the Cambridge Crystallographic Database (Groom *et al.*, 2016) showed that



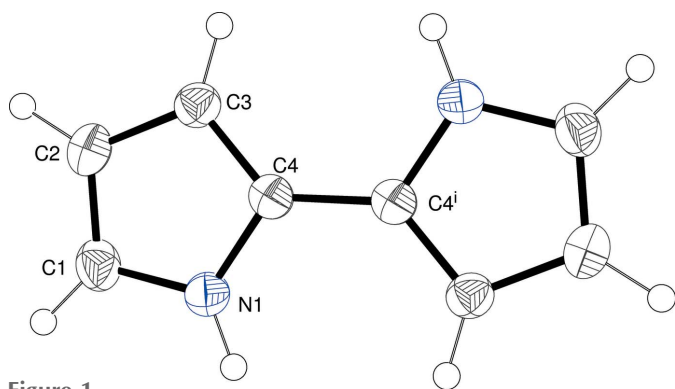


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $1 - x, 2 - y, -z$.]

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

C_g is the centroid of the N1/C1–C4 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots C_g1^i$	0.907 (16)	2.499 (19)	3.2275 (12)	138.1 (13)

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

the average $N-H\cdots\pi$ separation is 2.804 \AA and 13 out of 156 interactions (8.3%) had an $N-H\cdots\pi$ interactions shorter than 2.5 \AA . The crystal packing in (I) is similar to that of pyrrole, which has the same intermolecular $N-H\cdots\pi$ interactions (Goddard *et al.*, 1997). The edge-to-face interaction has been suggested to be a stabilizing factor in protein structures and polypeptides have been observed to have a separation of 2.42 \AA from the $N-H$ group to the phenyl ring

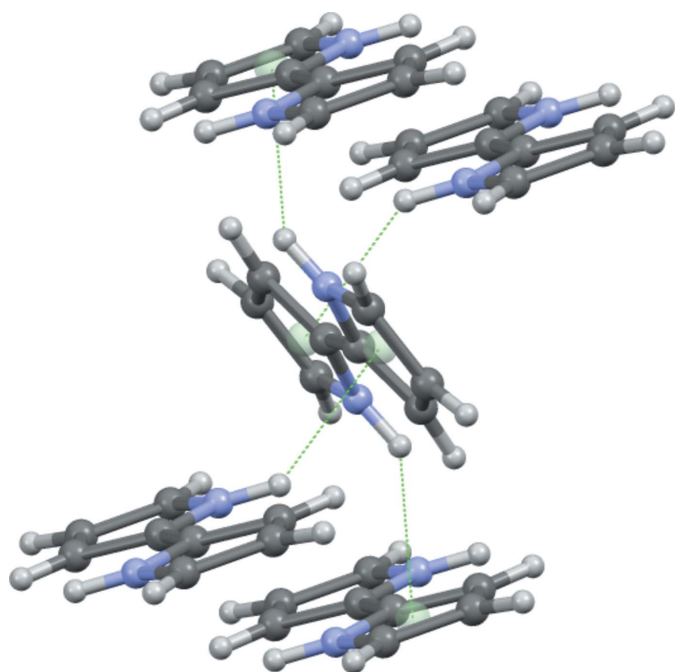


Figure 2
View of the $N-H\cdots\pi$ interactions and packing in the title compound.

(Steiner, 1998) and calculations corroborate these data (Levitt Perutz, 1988). It is notable that the $N-H$ bond of 2,2'-bipyrrole points almost directly at the midpoint of the $C2-C3$ bond. In the extended structure, the molecules are orientated by edge-to-face interactions generating a herringbone pattern, see Fig. 2.

4. Database survey

There are very few examples of similar compounds available in the literature. Most bipyrroles have carbonyl groups as substituents on the pyrrole ring in which the $N-H$ group forms hydrogen bonds with the oxygen atom of the carbonyl (Okawara *et al.*, 2015). So far as we are aware, there are no bipyrrole examples that exhibit the same packing and hydrogen-bonding pattern as the title compound; the closest example is pyrrole itself (Goddard *et al.*, 1997).

5. Synthesis and crystallization

230 μl (3.3 mmol) of pyrrole was added to dichloromethane (10 ml), degassed and cooled to 195 K. Trimethylsilyl bromide (290 μl , 2.2 mmol) and phenyl iodine trifluoroacetic acid (477 mg, 1.1 mmol in 1 ml dichloromethane) were added quickly to the cooled reaction. The mixture was stirred for 1 h then extracted with a saturated sodium bicarbonate solution and purified by column chromatography with a pentane/ethyl acetate (1:1) solution. Colourless blocks of (I) were obtained 7 d later by slow evaporation from an ethyl acetate solution.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_8N_2$
M_r	132.16
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (\AA)	5.9500 (2), 6.7650 (2), 8.4363 (3)
β ($^\circ$)	96.746 (2)
V (\AA^3)	337.22 (2)
Z	2
Radiation type	$\text{Cu } K\alpha$
μ (mm^{-1})	0.64
Crystal size (mm)	$0.11 \times 0.10 \times 0.06$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2004)
T_{\min}, T_{\max}	0.666, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1989, 590, 540
R_{int}	0.026
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.098, 1.08
No. of reflections	590
No. of parameters	62
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($\text{e } \text{\AA}^{-3}$)	0.18, -0.16

Computer programs: APEX2 and SAINT (Bruker, 2004), SHELXS97 and SHELXTL (Sheldrick, 2008) and SHELXL2014 (Sheldrick, 2015).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were located in difference maps and refined with isotropic displacement parameters.

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supporting information

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Crystal structure of 2,2'-bipyrrrole

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Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

2,2'-Bipyrrrole

Crystal data

$C_8H_8N_2$

$M_r = 132.16$

Monoclinic, $P2_1/c$

$a = 5.9500$ (2) Å

$b = 6.7650$ (2) Å

$c = 8.4363$ (3) Å

$\beta = 96.746$ (2)°

$V = 337.22$ (2) Å³

$Z = 2$

$F(000) = 140$

$D_x = 1.302$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 1086 reflections

$\theta = 7.5$ – 66.5 °

$\mu = 0.64$ mm⁻¹

$T = 173$ K

Cut-block, colorless

$0.11 \times 0.10 \times 0.06$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: Incoatec $I\mu S$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2004)

$T_{\min} = 0.666$, $T_{\max} = 0.753$

1989 measured reflections

590 independent reflections

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

$R_{\text{int}} = 0.026$

$\theta_{\max} = 66.5$ °, $\theta_{\min} = 7.5$ °

$h = -7 \rightarrow 4$

$k = -7 \rightarrow 8$

$l = -9 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.098$

$S = 1.08$

590 reflections

62 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.034P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.18$ e Å⁻³

$\Delta\rho_{\min} = -0.16$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.53346 (18)	1.09945 (15)	0.20670 (12)	0.0322 (4)
C1	0.7071 (2)	1.07425 (18)	0.32546 (15)	0.0352 (4)
C2	0.8665 (2)	0.95786 (18)	0.26832 (16)	0.0330 (4)
C3	0.7857 (2)	0.91019 (17)	0.10841 (15)	0.0297 (4)
C4	0.57828 (19)	0.99966 (16)	0.07196 (13)	0.0263 (4)
H1	0.704 (2)	1.135 (2)	0.4292 (17)	0.043 (4)*
H1N	0.407 (2)	1.170 (3)	0.2168 (17)	0.046 (4)*
H2	1.010 (3)	0.916 (2)	0.3269 (19)	0.041 (4)*
H3	0.859 (2)	0.831 (2)	0.0354 (16)	0.039 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0364 (6)	0.0295 (6)	0.0299 (6)	0.0075 (4)	0.0010 (5)	-0.0030 (4)
C1	0.0424 (8)	0.0320 (7)	0.0296 (7)	0.0003 (5)	-0.0028 (6)	-0.0038 (5)
C2	0.0299 (7)	0.0329 (7)	0.0347 (7)	-0.0016 (5)	-0.0023 (5)	0.0043 (5)
C3	0.0278 (7)	0.0307 (7)	0.0312 (7)	0.0005 (5)	0.0055 (5)	0.0021 (5)
C4	0.0306 (6)	0.0217 (6)	0.0270 (6)	-0.0017 (4)	0.0055 (5)	0.0025 (4)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.3628 (18)	C2—C3	1.4151 (19)
N1—C4	1.3748 (15)	C2—H2	0.979 (16)
N1—H1N	0.907 (16)	C3—C4	1.3767 (17)
C1—C2	1.3635 (19)	C3—H3	0.959 (14)
C1—H1	0.970 (15)	C4—C4 ⁱ	1.441 (2)
C1—N1—C4	110.02 (11)	C3—C2—H2	126.4 (9)
C1—N1—H1N	124.3 (9)	C4—C3—C2	107.93 (11)
C4—N1—H1N	125.6 (9)	C4—C3—H3	124.4 (8)
N1—C1—C2	108.12 (11)	C2—C3—H3	127.6 (8)
N1—C1—H1	121.2 (9)	N1—C4—C3	106.69 (11)
C2—C1—H1	130.7 (9)	N1—C4—C4 ⁱ	121.74 (13)
C1—C2—C3	107.23 (11)	C3—C4—C4 ⁱ	131.57 (13)
C1—C2—H2	126.4 (9)		
C4—N1—C1—C2	0.11 (14)	C1—N1—C4—C4 ⁱ	179.68 (12)
N1—C1—C2—C3	-0.15 (14)	C2—C3—C4—N1	-0.07 (13)

C1—C2—C3—C4	0.13 (14)	C2—C3—C4—C4 ⁱ	-179.73 (15)
C1—N1—C4—C3	-0.03 (13)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

C_g is the centroid of the N1/C1—C4 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots Cg1 ⁱⁱ	0.907 (16)	2.499 (19)	3.2275 (12)	138.1 (13)

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