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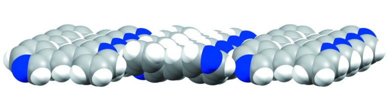

X-ray crystal structure of *trans*-bis(pyridin-3-yl)ethylene: comparing the supramolecular structural features among the symmetrical bis(*n*-pyridyl)ethylenes (*n* = 2, 3, or 4) constitutional isomers

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The molecular structure of *trans*-bis(pyridin-3-yl)ethylene (**3,3′-bpe**), $C_{12}H_{10}N_2$, as determined by single-crystal X-ray diffraction is reported. The molecule self-assembles into two dimensional arrays by a combination of C—H$\cdots$N hydrogen bonds and edge-to-face C—H$\cdots\pi$ interactions that stack in a herringbone arrangement perpendicular to the crystallographic *c*-axis. The supramolecular forces that direct the packing of **3,3′-bpe** as well as its packing assembly within the crystal are also compared to those observed within the structures of the other symmetrical isomers *trans*-1,2-bis(*n*-pyridyl)ethylene (***n*,*n*′-bpe**, where $n = n' = 2$ or 4).

1. Chemical context

Bis(pyridyl)ethylenes have arisen as somewhat of a natural extension of cinnamic acid as a series of molecules capable of undergoing [2+2] photodimerization in the solid state to generate cyclobutanes. Foundational work by Schmidt and coworkers on *trans*-cinnamic acids led to the formation of the 'Topochemical Postulate', which dictated that olefins within 4.2 Å of one another are capable of undergoing the photodimerization process. Unlike cinnamic acid, which crystallizes in such a way that the olefins are rendered photoactive (olefins within 4.2 Å of one another), the native crystalline forms of bis(pyridyl)ethylenes are photostable (olefins separated by distances > 4.2 Å in the crystal). To achieve photoreactivity of these olefins, it often becomes necessary to use a 'molecular template' that can interact with the olefin-containing bipyridine *via* supramolecular interactions such as hydrogen bonding, halogen bonding, argento- and aurophilic interactions, and dative N→B interactions. Analyses of the crystal structures of symmetric bis(pyridyl)ethylenes derivatives such as the *trans*-bis(*n*-pyridyl)ethylenes series of isomers (n = 2, 3 or 4) is necessary to understand the forces that govern their crystallization, why they are photostable, and why use templates to achieve photoreactivity (Campillo-Alvarado *et al.*, 2019; Chanthapally *et al.*, 2014; MacGillivray *et al.*, 2008; Pahari *et al.*, 2019; Sezer *et al.*, 2017; Volodin *et al.*, 2018).

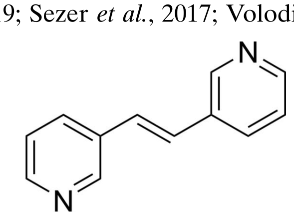

Table 1
Structural features of the ***n*,*n*′-bpe** series of constitutional isomers.

The twist angle is defined as the angle between the plane defined by the four alkene atoms and the plane defined by either pyridine ring.

Compound	**2,2′-bpe**	**3,3′-bpe**	**4,4′-bpe**
Twist angle φ (°)	7.43	5.17	9.14
Solid-state packing assembly	corrugated chains	approximately planar sheets	planar sheets
Assembly forces	edge-to-face C—H···π	edge-to-face C—H···π, C—H···N	C—H···N, face-to-face π–π
Nearest-neighbor alkene separation (Å)	6.09	5.50	5.72

2. Structural commentary

The alkene **3,3′-bpe** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (Fig. 1). The asymmetric unit consists of one-half molecule of **3,3′-bpe** with the C=C bond sitting on a crystallographic center of inversion. The pyridyl rings adopt an *anti*-conformation with respect to each other (Fig. 1).

3. Supramolecular features

Adjacent **3,3′-bpe** molecules interact primarily *via* edge-to-face C—H···π[d(C6···pyr) 3.58 Å; Θ(C6—H6···pyr) 131.8°] forces between pyridyl rings (Fig. 2). Those rings also participate in C—H···N [d(C4···N1) 3.59 Å; Θ(C4—H4···N1) 139.5°] hydrogen bonds (Fig. 2). The forces generate nearly planar sheets (Fig. 3), which aggregate into a herringbone arrangement of adjacent sheets (Fig. 4). Nearest-neighbor alkene C=C bonds of **3,3′-bpe** between adjacent sheets reveals a parallel, but offset orientation of the neighboring alkenes relative to one another at a distance of 5.50 Å. The distance exceeds the inter-alkene separation of Schmidt for photodimerizarion and suggests that **3,3′-bpe** is photostable (Schmidt, 1971).

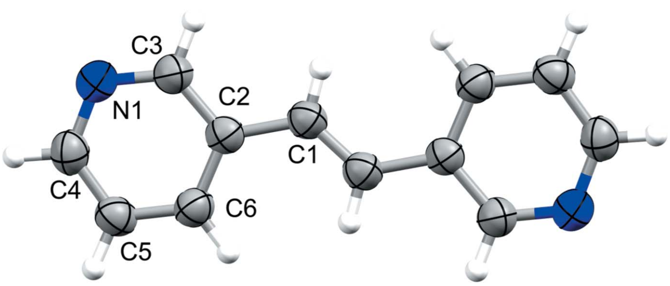

Figure 1
Single crystal structure for *trans*-bis(pyridin-3-yl)ethylene (**3,3′-bpe**) with anisotropic displacement ellipsoids at 50% probability.

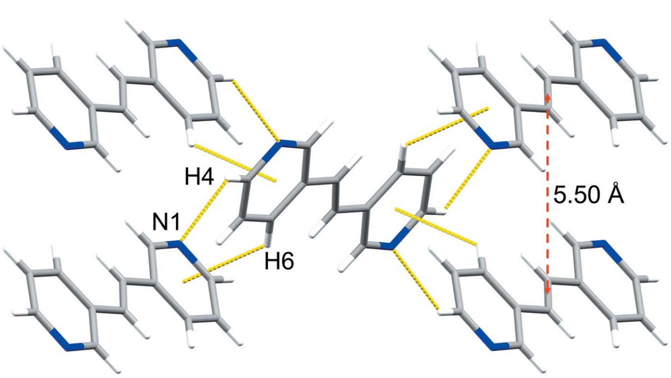

Figure 2
C—H···N and edge-to-face C—H···π intermolecular interactions (both yellow dotted lines) highlighting nearest-neighbor alkene separations (red dashed arrow) (view along a).

4. Database survey

For the ***n*,*n*′-bpe** (where: $n = n' = 2$, 3, or 4) series of symmetric alkenes, all three adopt nearly planar conformations (Table 1), with the pyridyl rings of **3,3′-bpe** and **2,2′-bpe** adopting *anti*-conformations with respect to each other. The packings of the symmetric alkenes are defined by combinations of C—H···π and/or C—H···N hydrogen bonds (Table 1) to form either one-dimensional chain (**2,2′-bpe**, Fig. 5) or two-dimensional sheet (**3,3′-bpe** and **4,4′-bpe**) structures (Fig. 6). Similar to **3,3′-bpe**, the alkene C=C bonds of **2,2′-bpe** (6.09 Å; Vansant *et al.*,

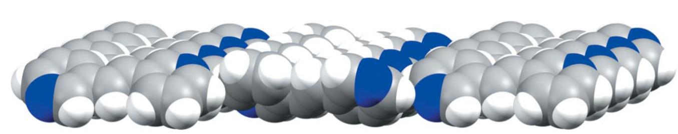

Figure 3
Edge-on view of sheets encompassing neighboring molecules of **3,3′-bpe** supported by C—H···N and C—H···π intermolecular interactions.

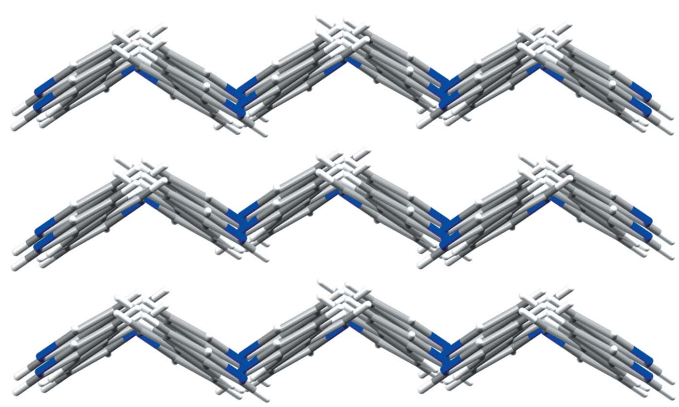

Figure 4
Herringbone arrangement of neighboring sheets of **3,3′-bpe** molecules.

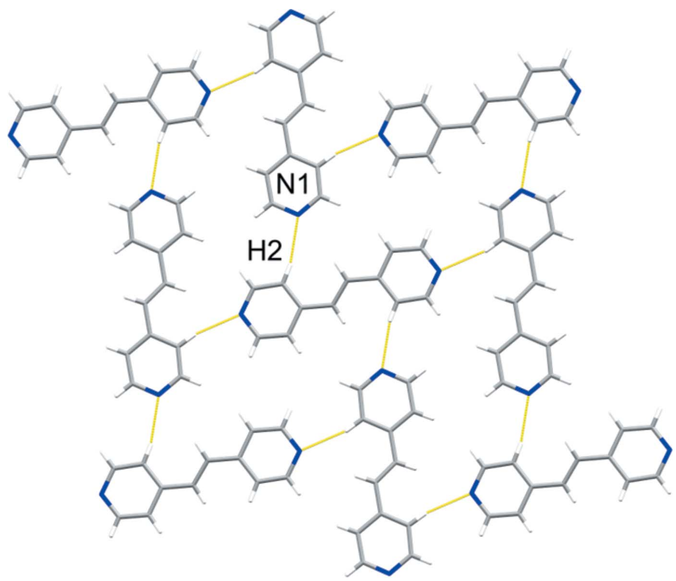

Figure 6
Planar, two-dimensional sheets of **4,4′-bpe.**

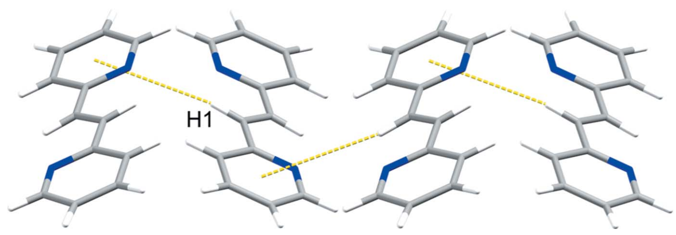

Figure 5
Corrugated, one-dimensional chains of **2,2′-bpe**.

1980) and **4,4′-bpe** (5.72 Å; Tinnemans *et al.*, 2018) (Table 1) are beyond the separation distance of Schmidt (1971).

5. Synthesis and crystallization

The alkene **3,3′-bpe** was prepared as described (Quentin *et al.*, 2020; Gordillo *et al.*, 2007, 2013) via a one-pot, aqueous Pd-catalyzed Hiyama-Heck cross-coupling between 3-bromo-pyridine and triethoxyvinylsilane (2:1 molar ratio) (Fig. 7). Flash chromatography (SiO_2, 10% MeOH/CH_2Cl_2) furnished **3,3′-bpe** as yellow crystals: 222.3 mg (23%). A portion of **3,3′-bpe** was dissolved in $CHCl_3$ and allowed to slowly evaporate at room temperature. Single crystals in the form of colorless plates suitable for single crystal X-ray diffraction formed within seven days.

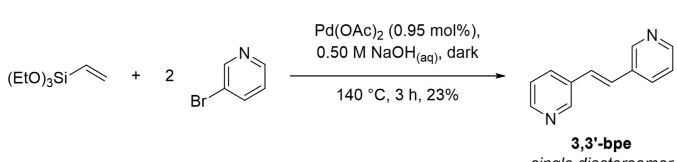

Figure 7
Synthesis of **3,3′-bpe** *via* Pd-catalyzed Hiyama–Heck cross-coupling.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{10}N_2$
M_r	182.22
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	7.4591 (7), 5.5045 (6), 11.7803 (12)
β (°)	99.638 (5)
V (Å^3)	476.86 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.18 × 0.12 × 0.06
Data collection	
Diffractometer	Bruker Nonius KappaCCD
Absorption correction	Multi-scan (*SADABS*; Krause et al., 2015)
T_{min}, T_{max}	0.989, 0.995
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2410, 836, 587
R_{int}	0.034
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.137, 1.07
No. of reflections	836
No. of parameters	84
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.13, −0.16

Computer programs: *COLLECT* (Nonius, 1988), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection and structure refinement details for **3,3′-bpe** are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the difference-Fourier map and freely refined with 0.93 < C—H < 0.99 Å. Refinement of the hydrogen atoms led to a data-to-parameter ratio of ~10. The single-crystal data were collected at room temperature to best reflect conditions under which photochemical reactions are typically conducted. Room-temperature data can also lead to fewer reflections and/or scaling anomalies.

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supporting information

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Computing details

Data collection: *HKL SCALEPACK* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* (Nonius, 1998); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); 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).

trans-1,2-Bis(pyridin-3-yl)ethene

Crystal data

$C_{12}H_{10}N_2$
M_r = 182.22
Monoclinic, $P2_1/n$
a = 7.4591 (7) Å
b = 5.5045 (6) Å
c = 11.7803 (12) Å
β = 99.638 (5)°
V = 476.86 (8) Å^3
Z = 2
F(000) = 192
D_x = 1.269 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1169 reflections
θ = 1.0–26.7°
μ = 0.08 mm^{-1}
T = 296 K
Plate, colourless
0.18 × 0.12 × 0.06 mm

Data collection

Bruker Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
CCD phi and ω scans
Absorption correction: multi-scan (SADABS; Krause et al., 2015)
T_{min} = 0.989, T_{max} = 0.995
2410 measured reflections
836 independent reflections
587 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.0°, θ_{min} = 3.0°
h = −8→8
k = −6→6
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.137
S = 1.07
836 reflections
84 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.13 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	0.5400 (2)	0.7577 (3)	0.63093 (15)	0.0609 (6)
C2	0.2479 (2)	0.5639 (3)	0.57302 (15)	0.0459 (5)
C3	0.3752 (3)	0.7464 (4)	0.56601 (17)	0.0537 (6)
C6	0.2998 (3)	0.3821 (4)	0.65272 (17)	0.0529 (6)
C4	0.5835 (3)	0.5788 (4)	0.70678 (19)	0.0564 (6)
C1	0.0695 (3)	0.5737 (4)	0.49890 (16)	0.0509 (6)
C5	0.4688 (3)	0.3894 (4)	0.71993 (19)	0.0556 (6)
H4	0.705 (3)	0.590 (3)	0.7528 (19)	0.062 (6)*
H3	0.345 (3)	0.875 (4)	0.507 (2)	0.068 (6)*
H5	0.504 (3)	0.265 (4)	0.7803 (18)	0.063 (6)*
H6	0.215 (3)	0.250 (4)	0.6607 (17)	0.066 (6)*
H1	0.051 (3)	0.706 (4)	0.4498 (19)	0.071 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0566 (11)	0.0569 (11)	0.0674 (11)	−0.0077 (8)	0.0048 (9)	0.0012 (9)
C2	0.0493 (11)	0.0476 (11)	0.0416 (10)	−0.0010 (9)	0.0103 (8)	−0.0024 (8)
C3	0.0562 (13)	0.0522 (13)	0.0519 (12)	−0.0045 (9)	0.0068 (10)	0.0027 (10)
C6	0.0491 (12)	0.0522 (13)	0.0585 (13)	−0.0029 (9)	0.0120 (10)	0.0048 (10)
C4	0.0465 (12)	0.0671 (14)	0.0551 (12)	0.0010 (10)	0.0069 (10)	−0.0019 (11)
C1	0.0553 (12)	0.0526 (12)	0.0448 (11)	−0.0034 (8)	0.0085 (9)	0.0020 (10)
C5	0.0517 (12)	0.0591 (13)	0.0570 (12)	0.0067 (9)	0.0117 (10)	0.0095 (10)

Geometric parameters (Å, º)

N1—C3	1.336 (3)	C6—H6	0.98 (2)
N1—C4	1.333 (3)	C4—C5	1.374 (3)
C2—C3	1.395 (3)	C4—H4	0.98 (2)
C2—C6	1.382 (3)	C1—C1^{i}	1.320 (4)
C2—C1	1.465 (3)	C1—H1	0.93 (2)
C3—H3	0.99 (2)	C5—H5	0.99 (2)
C6—C5	1.372 (3)		
C4—N1—C3	116.54 (18)	N1—C4—C5	123.4 (2)
C3—C2—C1	119.85 (19)	N1—C4—H4	115.2 (11)
C6—C2—C3	116.44 (19)	C5—C4—H4	121.4 (11)
C6—C2—C1	123.71 (18)	C2—C1—H1	115.3 (13)
N1—C3—C2	124.8 (2)	C1^{i}—C1—C2	127.1 (3)

N1—C3—H3	116.6 (12)	C1^{i}—C1—H1	117.4 (13)
C2—C3—H3	118.6 (12)	C6—C5—C4	119.1 (2)
C2—C6—H6	119.4 (12)	C6—C5—H5	120.0 (11)
C5—C6—C2	119.80 (19)	C4—C5—H5	120.8 (11)
C5—C6—H6	120.8 (12)		
N1—C4—C5—C6	−0.5 (3)	C6—C2—C3—N1	−0.7 (3)
C2—C6—C5—C4	0.2 (3)	C6—C2—C1—C1^{i}	4.7 (4)
C3—N1—C4—C5	0.1 (3)	C4—N1—C3—C2	0.5 (3)
C3—C2—C6—C5	0.3 (3)	C1—C2—C3—N1	178.62 (17)
C3—C2—C1—C1^{i}	−174.6 (2)	C1—C2—C6—C5	−178.96 (17)

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