

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

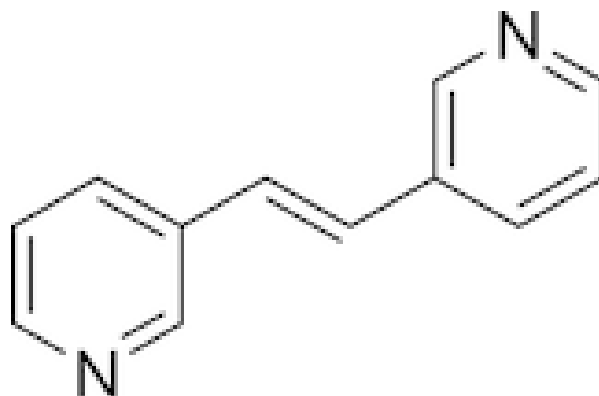
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The molecular structure of *trans*-bis(pyridin-3-yl)ethylene (**3,3-bpe**), C₁₂H₁₀N₂, as determined by single-crystal X-ray diffraction is reported. The molecule self-assembles into two dimensional arrays by a combination of C—H...N hydrogen bonds and edge-to-face C—H...π 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* = 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).



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).

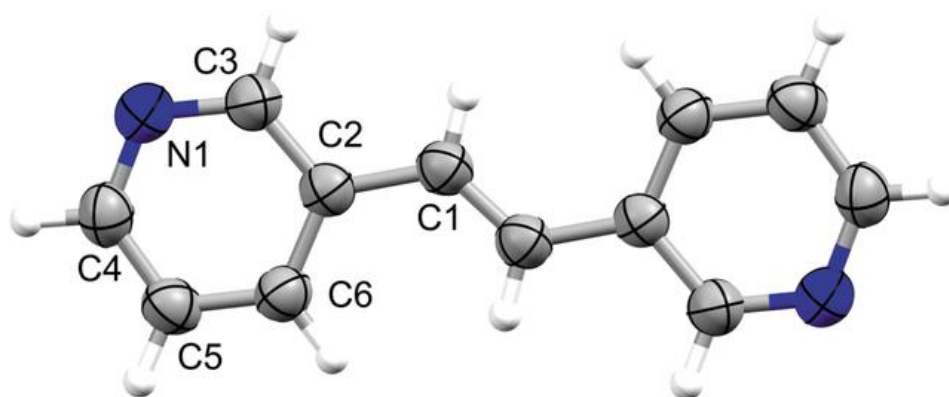


Figure 1: Single crystal structure for trans-bis(pyridin-3-yl)ethylene (**3,3-bpe**) with anisotropic displacement ellipsoids at 50% probability.

3. Supramolecular features

Adjacent **3,3-bpe** molecules interact primarily *via* edge-to-face C—H [$d(\text{C6 pyr})$ 3.58 Å; $\theta(\text{C6—H6 pyr})$ 131.8°] forces between pyridyl rings (Fig. 2). Those rings also participate

in C—H N [$d(\text{C4 N1})$ 3.59 Å; $\theta(\text{C4—H4 N1})$ 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 photodimerization and suggests that **3,3 -bpe** is photostable (Schmidt, 1971).

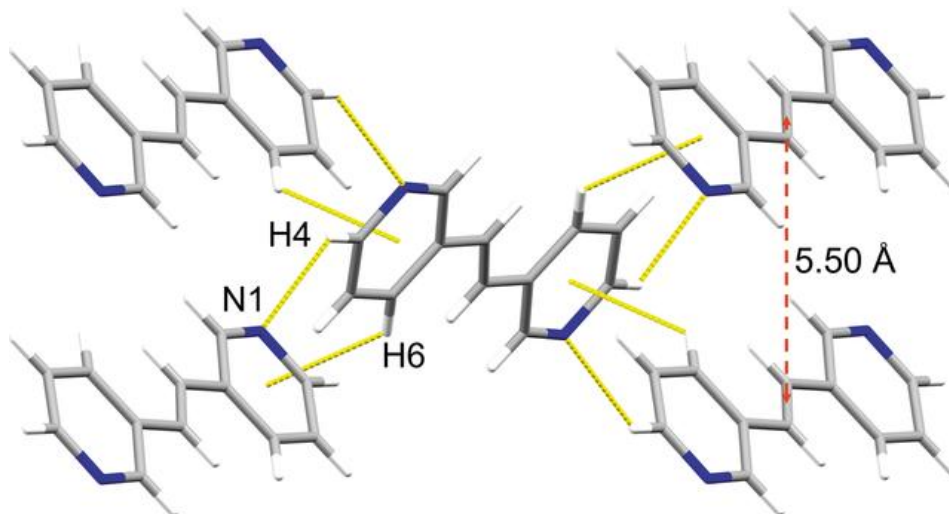


Figure 2: C—H N and edge-to-face C—H intermolecular interactions (both yellow dotted lines) highlighting nearest-neighbor alkene separations (red dashed arrow) (view along a).



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

4. Database survey

For the ***n,n* -bpe** (where: $n = 2, 3$, 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 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

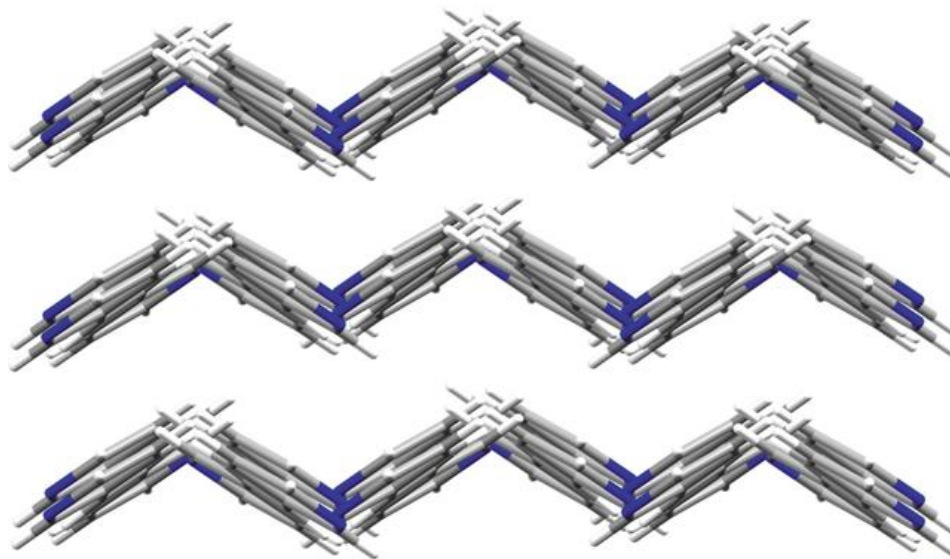


Figure 4: Herringbone arrangement of neighboring sheets of 3,3 -bpe molecules.

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

Compound	2,2 -bpe	3,3 -bpe	4,4 -bpe
Twist angle (°)	7.43	5.17	9.14
Solid-state packing assembly	corrugated chains	approximately planar sheets	planar sheets
Assembly forces	edge-to-face C—H	edge-to-face C—H , C—H N	C—H N, face-to-face
Nearest-neighbor alkene separation (Å)	6.09	5.5	5.72

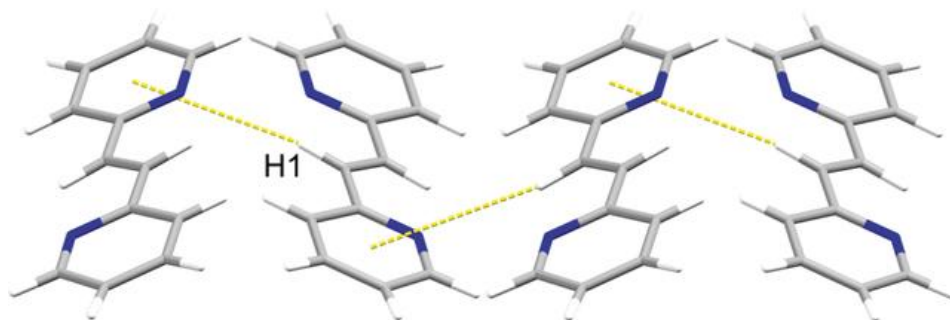


Figure 5: Corrugated, one-dimensional chains of 2,2 -bpe.

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

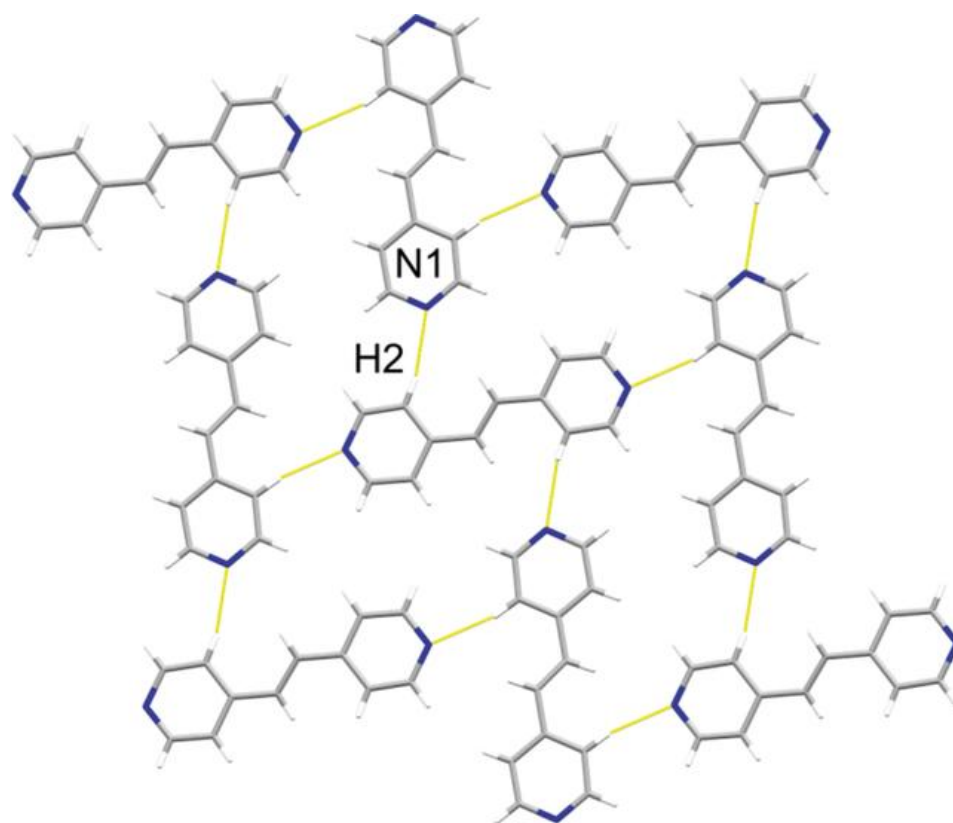


Figure 6: Planar, two-dimensional sheets of 4,4'-bpe.

3-bromopyridine and triethoxyvinylsilane (2:1 molar ratio) (Fig. 7). Flash chromatography (SiO_2 , 10% $\text{MeOH}/\text{CH}_2\text{Cl}_2$) 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.

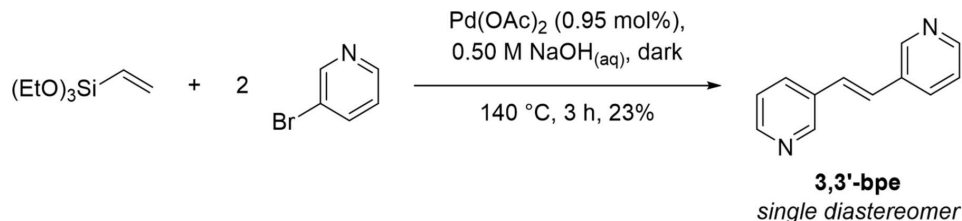


Figure 7: Synthesis of 3,3' bpe via Pd-catalyzed Hiyama–Heck cross-coupling.

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 $0.93 < \text{C}-\text{H} < 0.99 \text{ \AA}$. 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.

Crystal data	Information
Chemical formula	C ₁₂ H ₁₀ N ₂
Mr	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)
(°)	99.638 (5)
V (Å ³)	476.86 (8)
Z	2
Radiation type	Mo K
(mm ⁻¹)	0.08
Crystal size (mm)	0.18 × 0.12 × 0.06
NA	NA
Data collection	NA
Diffractometer	Bruker Nonius KappaCCD
Absorption correction	Multi-scan (SADABS; Krause et al., 2015)
Tmin, Tmax	0.989, 0.995
No. of measured, independent and observed [I > 2 (I)] reflections	2410, 836, 587
Rint	3.4000000000000002E-2
NA	NA
Refinement	NA
R[F ² > 2 (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
Δ max, Δ min (e Å ⁻³)	0.13, -0.16