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1,4-Bis(3-pyridyloxy)benzene

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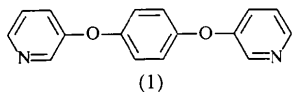
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Abstract

The centroid of the benzene ring of 1,4-bis(3-pyridyloxy)benzene, C₁₆H₁₂N₂O₂, lies on a crystallographic center of symmetry. The pyridine rings lie *trans* to each other at an angle of 66.9(1)° to the central benzene ring. π -Stacking interactions between the benzene and pyridine rings in adjacent molecules lead to a sinusoidal packing motif along the *b* axis.

Comment

We are currently studying certain metallocyclic transition metal complexes containing pyridine donor moieties in order to explore their potential as hosts for small molecules. The ability of some multinuclear palladium(II) complexes to bind small aromatic molecules has been demonstrated recently (Fujita & Ogura, 1996). We are interested in extending these studies to species containing various other transition metal centers. As the binding of potential guests will be promoted, at least in part, by π -stacking interactions, it was of interest to examine the nature of any stacking interactions in the free ligands. We have previously reported the preparation of a novel binuclear silver complex of 1,4-bis(2-pyridyloxy)benzene (Hartshorn & Steel, 1996), and have now prepared an isomeric ligand, 1,4-bis(3-pyridyloxy)benzene, (1), by an Ullman reaction between 3-hydroxypyridine and 1,4-dibromobenzene. In order to confirm the structure of this new ligand and to examine its conformation and molecular packing, a single-crystal X-ray determination was carried out.



The structure of the title molecule, which lies on a crystallographic center of inversion, is shown in Fig. 1. The pyridine rings lie *trans* to each other, with the dihedral angle between the pyridine and benzene rings being 66.9(1)°. The torsion angles about the O atom are -13.5(2) [C3ⁱ—C1—O1—C3ⁱ; symmetry code: (i) 2 - x, -y, 1 - z] and -60.60(17)° (C1—O1—C3ⁱ—C4ⁱ). The structure of (1) is similar to those of related 1,4-diheteroaryloxybenzenes (Drendel

& Sundaralingam, 1985; Katritzky *et al.*, 1996). The fact that the pyridine rings are not orthogonal to the benzene ring, thereby minimizing steric interactions [as observed in 1,4-diphenoxybenzene (Clayden *et al.*, 1990)], suggests a degree of conjugation between the rings mediated by the ether O atoms (Drendel & Sundaralingam, 1985).

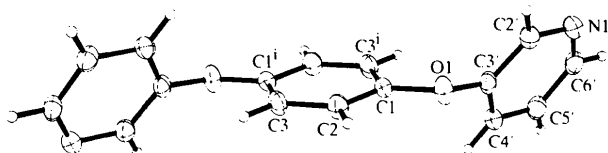


Fig. 1. Perspective view and atom labeling of the title ligand. (1). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. Symmetry code as in Table 1.

The molecules are arranged in a sinusoidal manner along the *b* axis as shown in Fig. 2, with the packing being controlled by a π -stacking interaction between the benzene ring of one molecule and the pyridine rings of two adjacent molecules. The distance between mean planes is 3.576(2) Å and there is a slight offset of the centroids of the rings. Stacking interactions between pairs of benzene rings or pairs of pyridine rings are not observed, consistent with the electrostatic nature of the π -stacking interaction (Hunter & Sanders, 1990).

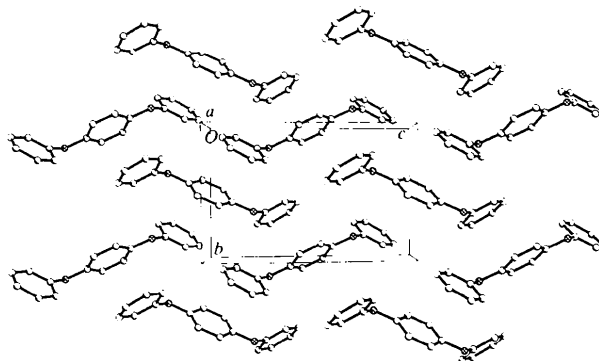


Fig. 2. The molecular packing diagram of (1).

Experimental

1,4-Bis(3-pyridyloxy)benzene, (1), was prepared by a modification of literature procedures (Pavia *et al.*, 1988; Bacon & Stewart, 1965). 3-Hydroxypyridine (32 mmol), 1,4-dibromobenzene (32 mmol), K₂CO₃ (33 mmol) and Cu⁰ (2.5 mol%) were refluxed in dimethylacetamide (10 ml) under argon for 18 h. The reaction mixture was then diluted with diethyl ether, washed with dilute aqueous NaOH, water and brine, concentrated and chromatographed on silica (ethyl acetate–petroleum ether 1:1) to give the product as a light-brown solid (17%, m.p. 353–354 K). Analysis: C₁₆H₁₂N₂O₂ requires C 72.72, H 4.58, N 10.60%; found C 72.46, H 4.47, N 10.52%. ¹H

NMR (CDCl₃, 300 MHz, TMS) δ = 7.05 (s, 4H, H_{2,3,5,6}), 7.29 (m, 4H, H_{4',5'}), 8.37 (dd, 2H, J = 1.8, 3.9 Hz, H_{6'}), 8.41 (t, 2H, J = 1.5 Hz, H_{2'}). Recrystallization from ethyl acetate gave a mass of crystals from which a suitable crystal was cut.

Crystal data

C₁₆H₁₂N₂O₂

M_r = 264.28

Monoclinic

$P2_1/c$

a = 6.9174 (4) Å

b = 7.4267 (4) Å

c = 12.0693 (7) Å

β = 98.206 (3)°

V = 613.69 (6) Å³

Z = 2

D_x = 1.430 Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

λ = 0.71073 Å

Cell parameters from 2080 reflections

θ = 3.0–26.9°

μ = 0.096 mm⁻¹

T = 158 (2) K

Block

0.48 × 0.44 × 0.32 mm

Beige

Data collection

Siemens SMART CCD diffractometer

Exposures over 0.3° φ or ω rotation scans

Absorption correction: none

1988 measured reflections

903 independent reflections

823 reflections with

$I > 2\sigma(I)$

R_{int} = 0.047

θ_{max} = 25.85°

h = -3 → 8

k = -8 → 8

l = -9 → 14

No standard reflections

Intensity decay: 10%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)]$ = 0.037

$wR(F^2)$ = 0.105

S = 1.09

903 reflections

91 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.1532P]$

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

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

$\Delta\rho_{max} = 0.175 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{min} = -0.178 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C1—C2	1.379 (2)	N1'—C2'	1.339 (2)
C1—C3'	1.383 (2)	C2'—C3'	1.381 (2)
C1—O1	1.399 (2)	C3'—C4'	1.384 (2)
C2—C3	1.383 (2)	C4'—C5'	1.381 (2)
O1—C3'	1.380 (2)	C5'—C6'	1.382 (2)
N1'—C6'	1.334 (2)		
C2—C1—C3'	120.05 (13)	N1'—C2'—C3'	122.94 (13)
C2—C1—O1	115.98 (12)	O1—C3'—C2'	117.49 (13)
C3'—C1—O1	123.94 (13)	O1—C3'—C4'	122.73 (12)
C1—C2—C3	120.21 (13)	C2'—C3'—C4'	119.69 (13)
C1'—C3—C2	119.75 (13)	C5'—C4'—C3'	117.60 (13)
C3'—O1—C1	118.18 (10)	C4'—C5'—C6'	119.09 (13)
C6'—N1'—C2'	116.90 (12)	N1'—C6'—C5'	123.73 (14)

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

Crystal decay was monitored by measurement of duplicate reflections.

Data collection: SMART (Siemens, 1995). Cell refinement: SAINT. Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Pro-

gram(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXL93. Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1207). Services for accessing these data are described at the back of the journal.

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(-)-(2S)-Tifluadom Hydrochloride and Two of its (-)-(2S)-2-(Acylaminomethyl)-benzodiazepine Hydrochloride Analogues

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Abstract

The structures of three (-)-(2S)-(acylaminomethyl)-benzodiazepine hydrochlorides, namely, 5-(2-fluorophenyl)-1-methyl-2-(3-thenoylaminomethyl)-2,3-dihydro-1H-1,4-benzodiazepin-4-ium chloride [C₂₂H₂₁FN₃OS⁺.Cl⁻, (1), tifluadom], 1,7-dimethyl-5-phenyl-2-(3-thenoylaminomethyl)-2,3-dihydro-1H-1,4-benzodiazepin-4-ium chloride [C₂₃H₂₄N₃OS⁺.Cl⁻, (2)] and 5-(4-fluorophenyl)-1,8-dimethyl-2-(p-toluylaminomethyl)-2,3-