Hao Zhu, Shi-Jun Chen, Yu-Xuann Lin, Qi-Di Zhong, Wu-Ji Sun and Xiu-Jun Zhang*

Crystal structure of 1,1'-dibenzyl-3,3'-dicyano-1,1',4,4'-tetrahydro-4,4'-bipyridine, $C_{26}H_{22}N_4$

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Abstract

$C_{26}H_{22}N_4$, monoclinic, $P2_1/c$ (no. 14), $a = 11.472(2)$ Å, $b = 6.0805(12)$ Å, $c = 29.787(6)$ Å, $\beta = 92.448(3)^\circ$, $V = 2075.9(7)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0427$, $wR_{ref}(F^2) = 0.0882$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Xiu-Jun Zhang, College of Psychology, North China University of Science and Technology, 063210 Caofeidian District, Tangshan, P.R. China, e-mail: zhangxiujun66@163.com

Hao Zhu and Wu-Ji Sun: School of Public Health, North China University of Science and Technology, 063210 Caofeidian District, Tangshan, P.R. China

Shi-Jun Chen, Yu-Xuann Lin and Qi-Di Zhong: School of Pharmacy, North China University of Science and Technology, 063210 Caofeidian District, Tangshan, P.R. China

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.25 \times 0.22 \times 0.20$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{max} , completeness:	25° , $>99\%$
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	11350, 3661, 0.031
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2871
$N(param)_{refined}$:	271
Programs:	Bruker programs [1], SHELX [2, 3]

Source of material

Add 1-benzyl-3-cyanopyridinium (0.9 mmol) to 200 mL of water, and then add Na_2CO_3 (47.2 mmol) and $Na_2S_2O_4$ (48.8 mmol), and slowly separate the bright yellow solid. Filter and wash with excess water. The solid was recrystallized from approximately equal volumes of ethanol and water to give a solid. Yield: 66% [4]. Some 1-benzyl-3-cyanopyridine-1,4-dihydropyridine (0.2 mmol) was dissolved in 50 mL of 0.1 M NH_3 –0.1 M NH_4Cl aqueous solution. This solution was electrolyzed at -1.20 V using a round mercury pool (area 20 cm²) as a working electrode with a saturated calomel electrode as reference, and a platinum gauze cylinder as a counter electrode. The solution was magnetically stirred and blanketed by a continuous nitrogen flux over its surface. Usually the electrolysis took about 3 h to get completion. After electrolysis, the mercury pool was covered by a yellow precipitate. The whole content of the cell was repeatedly extracted with CH_2Cl_2 . The gummy residue (0.5 g) was recovered by evaporating the dried organic layer was washed with cold water until solidification and the solid (0.4 g) was extracted three times with 10 mL of 95% ethanol at room temperature. Finally, the solution was evaporated to dryness in vacuo to give the title compound as colorless crystals [5].

Experimental details

All hydrogen atoms were placed in the calculated positions and all the non-hydrogen atoms were refined anisotropically.

Discussion

Reactions that couple two aromatic rings to make biaryls are among the most widely used processes in the pharmaceutical

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
N1	0.60256(12)	0.4124(2)	0.21357(4)	0.0420(4)
N2	0.25003(16)	0.1055(3)	0.15290(6)	0.0724(6)
N3	0.67733(11)	0.5167(2)	0.03877(5)	0.0420(4)
N4	0.33300(14)	0.9482(3)	0.04197(5)	0.0530(4)
C1	0.92574(19)	−0.1558(4)	0.20064(8)	0.0736(7)
H1	0.9784	−0.2599	0.1909	0.088*
C2	0.8717(2)	−0.0152(4)	0.17052(7)	0.0735(7)
H2	0.8875	−0.0251	0.1402	0.088*
C3	0.79432(17)	0.1409(4)	0.18461(6)	0.0571(5)
H3	0.7585	0.2359	0.1638	0.069*
C4	0.76975(14)	0.1568(3)	0.22939(5)	0.0408(4)
C5	0.82433(15)	0.0121(3)	0.25937(6)	0.0490(5)
H5	0.8082	0.0197	0.2897	0.059*
C6	0.90193(17)	−0.1426(4)	0.24514(8)	0.0638(6)
H6	0.9382	−0.2381	0.2658	0.077*
C7	0.68857(16)	0.3291(3)	0.24684(6)	0.0494(5)
H7A	0.6477	0.2671	0.2717	0.059*
H7B	0.7349	0.4516	0.2584	0.059*
C8	0.50667(14)	0.2919(3)	0.20167(5)	0.0387(4)
H8	0.4929	0.1635	0.2176	0.046*
C9	0.43056(14)	0.3485(3)	0.16808(5)	0.0367(4)
C10	0.44945(14)	0.5428(3)	0.13734(5)	0.0367(4)
H10	0.3805	0.6377	0.1379	0.044*
C11	0.55217(16)	0.6703(3)	0.15584(6)	0.0472(5)
H11	0.5682	0.8048	0.1426	0.057*
C12	0.62146(16)	0.6048(3)	0.18969(6)	0.0448(4)
H12	0.6858	0.6910	0.1980	0.054*
C13	0.33075(16)	0.2120(3)	0.15976(6)	0.0467(5)
C14	1.08994(18)	0.6917(4)	0.09676(8)	0.0694(6)
H14	1.1564	0.7246	0.1144	0.083*
C15	1.04144(18)	0.8463(4)	0.06894(8)	0.0683(6)
H15	1.0751	0.9851	0.0674	0.082*
C16	0.94174(16)	0.7984(3)	0.04270(7)	0.0553(5)
H16	0.9089	0.9061	0.0239	0.066*
C17	0.89113(14)	0.5944(3)	0.04407(6)	0.0431(4)
C18	0.94252(19)	0.4402(4)	0.07228(8)	0.0733(7)
H18	0.9103	0.3001	0.0736	0.088*
C19	1.0413(2)	0.4895(5)	0.09870(9)	0.0838(8)
H19	1.0742	0.3834	0.1178	0.101*
C20	0.78539(14)	0.5382(3)	0.01437(6)	0.0478(5)
H20A	0.7746	0.6518	−0.0083	0.057*
H20B	0.7999	0.4009	−0.0010	0.057*
C21	0.59279(14)	0.6714(3)	0.03596(5)	0.0387(4)
H21	0.6053	0.7964	0.0188	0.046*
C22	0.49097(14)	0.6533(3)	0.05681(5)	0.0346(4)
C23	0.46370(14)	0.4641(3)	0.08782(5)	0.0344(4)
H23	0.3896	0.3986	0.0771	0.041*
C24	0.55712(15)	0.2944(3)	0.08389(5)	0.0409(4)
H24	0.5466	0.1593	0.0978	0.049*
C25	0.65373(15)	0.3241(3)	0.06200(5)	0.0424(4)
H25	0.7084	0.2112	0.0621	0.051*
C26	0.40473(15)	0.8184(3)	0.04851(5)	0.0392(4)

industry [6, 7]. Coupling of pyridines results in heterobiaryls, a privileged pharmacophore found in commercial drugs as well as numerous therapeutic candidates [8–10]. The title molecule is depicted in the figure. When the 3-position is a strong electron-withdrawing group such as a cyano group, the reaction is relatively easy to occur, and the methylene group in the *para* position can be activated by an electrochemical method to form a title compound. However, due to the steric hindrance effect, the two benzyl arrangements are not completely identical. In the crystal structure, several important bond angle data are derived as follows C8–N1–C12 = 117.59(14)°, C9–C10–C11 = 108.18(13)°, C22–C23–C24 = 107.97(13)°, C21–N3–C25 = 117.5(14)°. The bond lengths and angles are in the expected ranges.

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