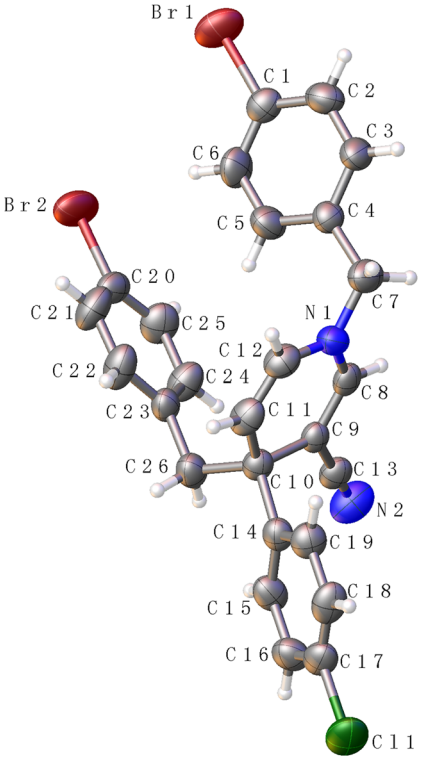
Han-Qiao Shao, Yin-Xin Wang, Hai-Yang Sun, Yu-Cai Wang and Wu-Ji Sun*

Crystal structure of 1,4-bis(4-bromobenzyl)-4-(4-chlorophenyl)-1,4-dihydropyridine-3-carbonitrile, $C_{26}H_{19}Br_2ClN_2$



https://doi.org/10.1515/ncrs-2021-0068
Received February 20, 2021; accepted March 11, 2021;
published online March 29, 2021

Abstract

$C_{26}H_{19}Br_2ClN_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.4830(12) Å, b = 10.2313(12) Å, c = 13.5948(18) Å, α = 111.234(2)°, β = 98.025(2)°, γ = 101.707(2)°, V = 1170.6(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0444, $wR_{ref}(F^2)$ = 0.1273, T = 296 K.

***Corresponding author: Wu-Ji Sun**, School of Pharmacy, North China University of Science and Technology, 063210 Caofeidian District, Tangshan, P. R. China, E-mail: sunwuji@yeah.net. https://orcid.org/0000-0002-9259-2490
Han-Qiao Shao, Yin-Xin Wang and Hai-Yang Sun, School of Pharmacy, North China University of Science and Technology, 063210, Caofeidian District, Tangshan, P. R. China
Yu-Cai Wang, School of Continuing Education, Jiamusi University, No. 148 Xuefu St., Jiamusi, Heilongjiang, P. R. China

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.23 × 0.20 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	3.59 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6017, 4093, 0.019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2659
$N(param)_{refined}$:	280
Programs:	Bruker [1], SHELX [2, 3]

CCDC no.: 2059793

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.

Source of material

Dissolve 3-cyanopyridine 4.16 g (40 mmol) in acetonitrile (40 mL), add 4-bromobenzyl bromide (40 mmol), and reflux the mixed system for 7 h. TLC monitors the end of the reaction. After the reaction is over, use acetonitrile (30 mL) to wash the product to obtain a white powder pyridine salt. Add 1-(4-bromobenzyl)-3-cyanopyridin-1-ium (10 mmol) to the reaction flask, add 70 mL of anhydrous tetrahydrofuran to obtain a suspension. At this time, avoid light on an ice bath, add 0.5 mmol CuI while stirring, add 10 mL of 4-chlorophenyl magnesium bromide under nitrogen – after 2 h, TLC analysis indicated the reaction was complete. Brine was then added, and the mixture extracted with ethyl acetate. The combined ethyl acetate layers were dried over magnesium sulfate. Finally, the obtained solution was evaporated to dryness in vacuum, and recrystallized from methanol to obtain the material for the next step [4, 5]. The 1-(4-bromobenzyl)-4-(4-chlorophenyl)-1,4-dihydropyridine-3-carbonitrile (5 mmol) was dissolved in dry tetrahydrofuran (30 mL) under stirring, placed in a quartz reactor and degassed. At room

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.17965 (6)	−0.35193 (5)	0.11636 (5)	0.0797 (2)
Br2	0.67877 (6)	−0.35025 (5)	−0.02730 (5)	0.0887 (2)
C1	1.1809 (5)	−0.1564 (4)	0.1957 (3)	0.0504 (10)
C2	1.3033 (5)	−0.0638 (5)	0.2763 (4)	0.0602 (12)
H2	1.383229	−0.097581	0.293601	0.072*
C3	1.3059 (5)	0.0789 (5)	0.3309 (3)	0.0565 (11)
H3	1.388527	0.141614	0.385395	0.068*
C4	1.1883 (4)	0.1318 (4)	0.3067 (3)	0.0445 (9)
C5	1.0664 (5)	0.0355 (5)	0.2270 (3)	0.0585 (12)
H5	0.985221	0.068074	0.210377	0.070*
C6	1.0622 (5)	−0.1069 (4)	0.1718 (4)	0.0622 (12)
H6	0.978948	−0.170232	0.118120	0.075*
C7	1.1986 (5)	0.2892 (4)	0.3704 (4)	0.0611 (12)
H7A	1.214411	0.307240	0.446825	0.073*
H7B	1.284500	0.349228	0.361050	0.073*
C8	0.9575 (4)	0.3312 (4)	0.3923 (3)	0.0423 (9)
H8	0.968981	0.305939	0.451529	0.051*
C9	c	0.3621 (3)	0.3633 (3)	0.0379 (9)
C10	0.7975 (4)	0.4019 (4)	0.2664 (3)	0.0422 (9)
C11	0.9288 (5)	0.4009 (4)	0.2158 (3)	0.0530 (11)
H11	0.924613	0.423173	0.155157	0.064*
C12	1.0499 (5)	0.3704 (4)	0.2517 (3)	0.0522 (10)
H12	1.125874	0.373203	0.215401	0.063*
C13	0.7248 (5)	0.3554 (4)	0.4258 (3)	0.0467 (10)
C14	0.7736 (4)	0.5557 (4)	0.3063 (3)	0.0438 (9)
C15	0.6381 (5)	0.5809 (4)	0.3239 (3)	0.0528 (11)
H15	0.557719	0.501221	0.307738	0.063*
C16	0.6187 (5)	0.7177 (4)	0.3640 (3)	0.0578 (11)
H16	0.526779	0.730531	0.374585	0.069*
C17	0.7380 (5)	0.8369 (4)	0.3887 (3)	0.0536 (11)
C18	0.8722 (5)	0.8180 (4)	0.3733 (3)	0.0593 (12)
H18	0.951673	0.898466	0.389428	0.071*
C19	0.8907 (5)	0.6778 (4)	0.3332 (3)	0.0531 (10)
H19	0.983463	0.666126	0.324449	0.064*
C20	0.6781 (4)	−0.1517 (4)	0.0382 (3)	0.0538 (11)
C21	0.7218 (6)	−0.0596 (5)	−0.0093 (4)	0.0702 (13)
H21	0.754525	−0.092189	−0.072939	0.084*
C22	0.7171 (5)	0.0838 (5)	0.0381 (3)	0.0652 (13)
H22	0.747291	0.146973	0.005407	0.078*
C23	0.6692 (4)	0.1350 (4)	0.1317 (3)	0.0467 (10)
C24	0.6283 (5)	0.0393 (4)	0.1786 (3)	0.0587 (11)
H24	0.597341	0.072132	0.242972	0.070*
C25	0.6317 (5)	−0.1047 (4)	0.1330 (4)	0.0631 (12)
H25	0.603221	−0.168006	0.165849	0.076*
C26	0.6566 (5)	0.2892 (4)	0.1801 (3)	0.0544 (11)
H26A	0.572856	0.289083	0.213708	0.065*
H26B	0.635981	0.321094	0.121861	0.065*
Cl1	0.71559 (16)	1.01196 (11)	0.43980 (10)	0.0775 (4)
N1	1.0690 (4)	0.3347 (3)	0.3405 (3)	0.0484 (8)
N2	0.6382 (5)	0.3502 (4)	0.4761 (3)	0.0708 (11)

temperature, the light source (10 W, 410 nm, LED lamp) was 60 cm away from the sample. After 48 h, TLC analysis indicated the reaction was complete. The target derivative was formed, and the reaction solvent was removed by rotary evaporation. The silica gel column chromatography was used to obtain the title compound with high purity.

Experimental details

All hydrogen atoms were placed in the calculated positions.

Comment

Photochemical reactions have attracted much attention in the development of novel tandem reactions due to mild reaction conditions, efficient conversion, non-toxic, abundant and economy [6, 7]. In particular, six-membered rings with symmetrical double bond structure are often used as starting materials for photoreaction. For example, 1,4-dihydropyridine [8], 1,4-dihydropyrazine [9] and 1,4-oxazine. The group characteristics and structure-activity relationship of the photoreactive raw materials have a great influence on the yield of the title compound. When a strong electron withdrawing group is attached to the fourth group, the yield of the photoproduct is significantly improved. In the crystal structure, several important bond angle data are involved as follows C4—C7—N1 = 114.70(3) Å, C26—C10—C14 = 109.70(3) Å, C26—C10—C23 = 32.07 Å. The bond lengths and angles are in the expected ranges.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. BRUKER. SAINT. Version 8.23B; Bruker AXS Inc.: Madison, Wisconsin, USA, 2013.
2. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
3. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
4. Hilgeroth A., Baumeister U. Formation of novel photodimers from 4-aryl-1, 4-dihydropyridines. *Chem. Eur. J.* 2001, *7*, 4599–4603.
5. Paul C. E., Gargiulo S., Opperman D. J., Lavandera I., Gotor-Fernandez V., Gotor V., Taglieber A., Arends I. W. C. E., Hollmann F. Mimicking nature: synthetic nicotinamide cofactors for C=C bioreduction using enoate reductases. *Org. Lett.* 2013, *15*, 180–183.

6. Iguchi D., Erra-Balsells R., Bonesi S. M. Formation of 2,2-dimethylchroman-4-ones during the photoinduced rearrangement of some aryl 3-methyl-2-butenoate esters. A mechanistic insight. *Tetrahedron* 2016, *72*, 1903–1910.
7. Hoffmann N. Photochemical reactions as key steps in organic synthesis. *Chem. Rev.* 2008, *108*, 1052–1103.
8. Chen S., Zhong Q., Zhu H., Liu C., Zhuang P., Sun W. Visible-light-induced C–C coupling reaction to synthesize bipyridine from 3-cyano-1,4-dihydropyridines. *Front. Chem.* 2020, *7*, 940.
9. Xin H., Sun W., Yan H. Photochemical ring contraction of 1-aryl-1,4-dihydropyrazine to 1-aryl-1*H*-imidazole. *J. Photochem. Photobiol.* 2013, *267*, 49–54.