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The crystal structure of (*E*)-6-bromo-3,5-dimethyl-2-(1-phenylprop-1-en-2-yl)-3*H*imidazo[4,5*b*] pyridine, $C_{17}H_{16}BrN_3$

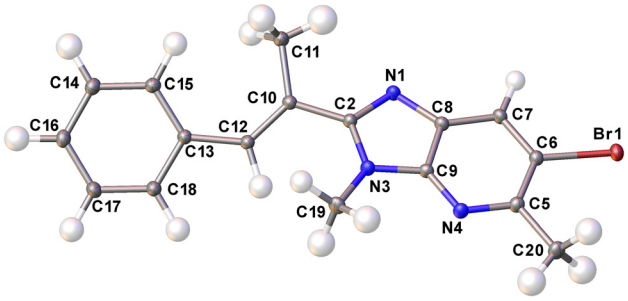

Figure 1: Molecular structure of the title compound, thermal ellipsoids at 50 % level. The hydrogen atoms were refined isotropically. π–π interactions, the lower molecule was generated by the symmetry code 1–X, 1–Y, 1–Z, the upper one with 1–X, 1–Y, 1–Z.

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Abstract

$C_{17}H_{16}BrN_3$, monoclinic, $P2_1/c$ (no. 14), a = 6.91863(13) Å, b = 7.17190(11) Å, c = 29.6309(5) Å, β = 93.9228(15)°, V = 1466.83(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0201, $wR_{ref}(F^2)$ = 0.0392, T = 100.0(1) 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 (Figure 1).

1 Source of material

The title compound was derived by an alkylation reaction of *E*)-6-bromo- 5-methyl-2-(1-phenylprop-1-en-2-yl)-3*H*imidazo-[4,5*b*]pyridine with methyl methanesulfonate (MMS) in a 1:1 molar ratio under basic conditions. The reaction occurs after 24 h under continuous stirring in dimethylformamide (DMF) at room temperature. After completed reaction (TLC control: dichloromethane/methanol, 9:1, R_f = 0.88) the mixture was treated with water, the precipitated product filtered under reduced pressure, washed three times with water, and dried at 70 ˚C. The title product was obtained as a white solid (45.2 mg, 86 %). Clear colorless crystals suitable for X-ray structure analysis were obtained after recrystallization from methanol and slowly evaporation of the solvent over a period of several days at 295–297 K. The melting point of the title compound is 413.4–414.9 K.

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size	0.23 × 0.20 × 0.04 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.80 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	32.3°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	63,301, 4996, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4406
$N(param)_{refined}$:	254
Programs:	CrysAlis^{PRO}[1], Olex2[2,4], SHELX[3]

2 Experimental details

A single crystal of the title compound was examined on a Rigaku Supernova diffractometer[1] using CuKα (λ = 0.71073 Å) radiation. The crystal was kept at 100.0(1) K during data collection. Using Olex2,[2] the structure was solved with the SHELXT[3] structure solution program using Intrinsic Phasing method and refined with the olex2.refine[4] refinement package using Gauss–Newton minimisation. Refinement using NoSpherA2, an implementation of NOn–SPHERical Atom-form-factors in Olex2[5] Hydrogen atoms were refined isotropically. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms were taken into account using a riding model. There is one molecule in the asymmetric unit. All geometric parameters are in the expected ranges.[5–7]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.323584 (15)	0.150853 (14)	0.412095 (3)	0.01640 (3)
N1	0.39492 (12)	0.33627 (12)	0.58837 (3)	0.01414 (15)
N3	0.72120 (11)	0.34886 (12)	0.58805 (3)	0.01353 (15)
N4	0.75840 (12)	0.26516 (12)	0.51033 (3)	0.01464 (16)
C2	0.55995 (14)	0.36597 (13)	0.61292 (3)	0.01305 (17)
C5	0.65740 (14)	0.21937 (14)	0.47162 (3)	0.01486 (18)
C6	0.45282 (14)	0.21349 (14)	0.46877 (3)	0.01359 (17)
C7	0.34311 (14)	0.25039 (13)	0.50530 (3)	0.01437 (18)
H7	0.1858 (18)	0.2447 (18)	0.5029 (4)	0.023 (3)*
C8	0.44914 (14)	0.29471 (13)	0.54561 (3)	0.01320 (17)
C9	0.65214 (14)	0.30059 (13)	0.54502 (3)	0.01283 (17)
C10	0.56568 (14)	0.40955 (13)	0.66157 (3)	0.01347 (17)
C11	0.38811 (16)	0.50491 (16)	0.67712 (4)	0.0201 (2)
H11a	0.341 (2)	0.435 (2)	0.7076 (5)	0.037 (4)*
H11b	0.419 (2)	0.649 (2)	0.6865 (5)	0.044 (4)*
H11c	0.277 (2)	0.502 (2)	0.6498 (5)	0.052 (5)*
C12	0.72061 (14)	0.35551 (14)	0.68876 (3)	0.01440 (17)
H12	0.8305 (19)	0.275 (2)	0.6733 (4)	0.033 (3)*
C13	0.76999 (14)	0.38514 (13)	0.73721 (3)	0.01411 (18)
C14	0.66289 (15)	0.48882 (14)	0.76727 (3)	0.01686 (19)
H14	0.525 (2)	0.552 (2)	0.7555 (5)	0.034 (4)*
C15	0.73233 (15)	0.51212 (14)	0.81226 (3)	0.01770 (19)
H15	0.648 (2)	0.592 (2)	0.8350 (5)	0.040 (4)*
C16	0.90893 (15)	0.43546 (14)	0.82805 (3)	0.01750 (19)
H16	0.963 (2)	0.460 (2)	0.8628 (5)	0.037 (4)*
C17	1.01598 (16)	0.33205 (15)	0.79895 (3)	0.0188 (2)
H17	1.154 (2)	0.277 (2)	0.8106 (5)	0.035 (4)*
C18	0.94655 (15)	0.30693 (14)	0.75416 (3)	0.01721 (19)
H18	1.033 (2)	0.226 (2)	0.7312 (5)	0.034 (4)*
C19	0.92419 (15)	0.39346 (15)	0.59890 (4)	0.01767 (19)
H19a	0.9358 (19)	0.5052 (19)	0.6243 (5)	0.030 (3)*
H19b	1.005 (2)	0.275 (2)	0.6111 (5)	0.044 (4)*
H19c	0.986 (2)	0.439 (2)	0.5683 (5)	0.043 (4)*
C20	0.77245 (16)	0.17169 (16)	0.43231 (3)	0.0194 (2)
H20a	0.739 (2)	0.268 (2)	0.4043 (5)	0.042 (4)*
H20b	0.918 (2)	0.174 (2)	0.4437 (5)	0.047 (4)*
H20c	0.735 (2)	0.032 (2)	0.4182 (5)	0.047 (4)*

3 Comment

The described herein single crystal structure of the title compound was obtained according to our previous re-crystallization procedures.[6,7] Within the present work, an amide coupling with subsequent intermolecular cyclization reaction between 5-bromo-6-methylpyridine-2,3-diamine and (*E*)-2-methyl-3-phenylacrylic acid was conducted in a 1:1 molar ratio under basic conditions in order to obtain the imidazo[4,5*b*]pyridine core structure of the title compound. The title compound crystallizes centrosymmetrically and the crystal structure contains six molecules per crystal unit cell, representing (*E*)-isomers with an antiparallel orientation in the crystal packing (Figure 1). The compound is assembled by an imidazo[4,5*b*]pyridine core and a phenyl moiety connected via an 2-methylbutene spacer. Formation of hydrogen bonds between the molecules within the crystal unit cell are not observed. The intramolecular bond lengths of the imidazo[4,5*b*]pyridine core and the phenyl moiety are between 1.3 and 1.4 Å indicating a delocalization of the double bonds within both structural units. The significant shorter bonds of the corresponding five and six-membered rings are N1–C2 (1.328(1) Å) and C9–N4 (1.329(1) Å), respectively. The distance between C10–C12 (1.353(1) Å) atoms indicates the localization of the spacer double bond. The methyl group C13 is *trans* to the second methyl group C11 in the position C10 of the core structure. The imidazo [4,5*b*]pyridine core is almost planar including the following atoms: N1, C2, N3, N4, C5, C6, C7, C8, and C9 from the main core as well as bromine Br1 and the methyl group in positions C5 and C6, respectively. The styryl unit forms a second planar moiety consisting of C2, C10, C12, C13, C14, C15, C16, C17, and C18. The tilt angle between the main imidazo[4,5*b*]pyridine plane and the second styryl planar arrangement is 31.08(0)°. The styryl and the imidazopyridine moiety form bond angles of N1–C2–C10 = 122.31(8)° and of N3–C2–C10 = 124.83(8)°.

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References

1. Rigaku, O. D. *CrysAlis^{Pro} 1.171.43.96a*: Abingdon, Oxfordshire, England, 2023.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
3. Sheldrick, G. M. *SHELXT* – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, *A71*, 3–8.
4. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment - Olex2 Dissected. *Acta Crystallogr.* **2015**, *A71*, 59–75.
5. Kleemiss, F.; Dolomanov, O. V.; Bodensteiner, M.; Peyerimhoff, N.; Midgley, M.; Bourhis, L. J.; Genoni, A.; Malaspina, L. A.; Jayatilaka, D.; Spencer, J. L.; White, F.; Grundkoetter–Stock, B.; Steinhauer, S.; Lentz, D.; Puschmann, H.; Grabowsky, S. Accurate Crystal Structures and Chemical Properties from NoSpherA2. *Chem. Sci.* **2021**, *12*, 1675–1692.

6. Tzvetkov, N. T.; Neumann, B.; Stammler, H.–G.; Mattay, J. Crystal Structure of (7a'*SR*)-7a'-Prop-2-Ynyl-1′,2′,4′,6′,7′,7a′-Hexahydrospiro [1,3-Dioxolan- 2,5′-indene], $C_{14}H_{18}O_2$. *Z. Kristallogr. N. Cryst. Struct.* **2006**, *221*, 479–480.

7. Tzvetkov, N. T.; Neumann, B.; Stammler, H.–G.; Mattay, J. Crystal Structure of (1a*SR*,3a*RSv,7a SR*)-3a-But-2-Ynyl-1a,2,3,3a,4,5-hexahydro-1*H* -cyclopropa[*c*]inden-6(7*H*)-one, $C_{14}H_{18}O$. *Z. Kristallogr. N. Cryst. Struct.* **2006**, *221*, 481–482.