

1,3-Diallyl-6-bromo-1*H*-imidazo[4,5-*b*]-pyridin-2(3*H*)-one

Siham Dahmani,^{a*} Youssef Kandri Rodi,^a Santiago V. Luis,^b Michael Bolte^c and Lahcen El Ammari^d

^aLaboratoire de Chimie Organique Appliquée, Université Sidi Mohamed, Ben Abdallah, Faculté des Sciences et Techniques, Route d'Immouzzar, BP 2202 Fès, Morocco, ^bDepartamento de Química Inorgánica & Organica, ESTCE, Universitat Jaume I, E-12080 Castellon, Spain, ^cInstitut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany, and ^dLaboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Université Mohammed V-Agdal, Avenue Ibn Battouta, BP 1014, Rabat, Morocco
Correspondence e-mail: s_dahmani12@yahoo.fr

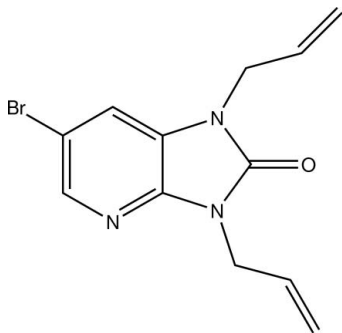
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Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.036; wR factor = 0.100; data-to-parameter ratio = 20.5.

In the molecule of the title compound, $\text{C}_{12}\text{H}_{12}\text{BrN}_3\text{O}$, the fused-ring system is essentially planar, the largest deviation from the mean plane being 0.0148 (3) Å. The two allyl groups are nearly perpendicular to the imidazo[4,5-*b*]pyridine plane [$\text{C}-\text{C}-\text{N}-\text{C}$ torsion angles of 81.6 (4) and -77.2 (4)°] and point in the same direction. The planes through the atoms forming each allyl group are nearly perpendicular to the imidazo[4,5-*b*]pyridin-2-one system, as indicated by the dihedral angles between them of 80.8 (5) and 73.6 (5)°.

Related literature

For background to the biological activity of substituted imidazopyridines and related compounds, see: Barraclough *et al.* (1990); Bavetsias *et al.* (2007, 2010); Coates *et al.* (1993); Liu *et al.* (2008); Ryabukhin *et al.* (2006); Schiffmann *et al.* (2006).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{12}\text{BrN}_3\text{O}$
 $M_r = 294.16$
 Orthorhombic, $Pna2_1$
 $a = 5.4110$ (3) Å
 $b = 25.4205$ (12) Å
 $c = 9.3170$ (4) Å
 $V = 1281.56$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.20$ mm⁻¹
 $T = 273$ K
 $0.52 \times 0.32 \times 0.14$ mm

Data collection

Bruker CCD three-circle diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\min} = 0.202$, $T_{\max} = 0.800$
 8789 measured reflections
 3201 independent reflections
 2361 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.100$
 $S = 1.03$
 3201 reflections
 156 parameters
 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.44$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³
 Absolute structure: Flack (1983),
 1494 Friedel pairs
 Flack parameter: 0.040 (17)

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2445).

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supplementary materials

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1,3-Diallyl-6-bromo-1*H*-imidazo[4,5-*b*]pyridin-2(3*H*)-one

S. Dahmani, Y. Kandri Rodi, S. V. Luis, M. Bolte and L. El Ammari

Comment

Substituted imidazopyridines and structurally related compounds are of pharmacological and therapeutical interest. They have been tested for their potential as anticancer, inotropic (Barraclough *et al.*, 1990), selective antihistamine (H1) agents and antibacterial activity (Liu *et al.*, 2008). Imidazo[4,5-*b*]pyridine derivatives were also reported as Aurora kinases (Bavetsias *et al.*, 2007); Bavetsias *et al.*, 2010), and cyclic PDE inhibitors (Coates *et al.*, 1993). The preparation of these compounds is usually straightforward, and a number of synthetic methods are already available (Ryabukhin *et al.*, 2006; Schiffmann *et al.*, 2006).

In this work, we report the synthesis of 1,3-diallyl-6-bromo-1,3-dihydroimidazo [4,5-*b*]pyridin-2-one *via* the reaction between 6-bromo-1,3-dihydro-imidazo [4,5 - *b*]pyridin-2-one and allylbromide in DMF using K₂CO₃ as base (scheme1).

The Plot of the title compound molecule is shown in Fig.1. The two fused five and six-membered rings are nearly planar with the maximum deviation of -0.014 (3)Å from N1. The two allyl chains (–C7–C8–C9) and (–C10–C11–C12) are almost perpendicular to the imidazo[4,5-*b*]pyridine system mean plane as indicated by the following torsion angles C8–C7–N2–C5 and C11–C10–N3–C4 of 81.6 (4)° and -77.2 (4)° respectively.

Experimental

To a stirred solution of 6-bromo-1,3-dihydro-imidazo[4,5 - *b*]pyridin-2- one (0.5 g; 2.33 mmol), K₂CO₃ (1.29 g; 9.34 mmol), and tetrabutylammonium bromide (0.07 g; 2.37 10⁻⁴ mol) in DMF, allylbromide (0.5 ml; 5.84 mmol) was added dropwise. Stirring was continued at room temperature for 24 h. After completion of reaction (monitored by TLC), the salt was filtered and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel using ethylacetate/hexane (1/1) as eluent. The crystals of the title compound are obtained by dissolving 80 mg of product in 4 ml of ethanol at about 353 K, followed by a slow evaporation of the solvent.

Refinement

The origin of the non centro symmetric space group is fixed by the *SHELXL* program and the 1495 Friedel opposite reflections are not merged. H atoms were located in a difference map and treated as riding with C—H = 0.93 Å and 0.97 Å for aromatic and methylene respectively. All H atoms with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (aromatic and methylene).

Figures

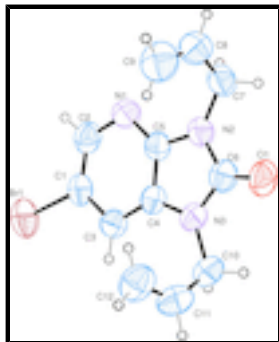


Fig. 1. : Plot of the molecule of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

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Crystal data

$C_{12}H_{12}BrN_3O$

$M_r = 294.16$

Orthorhombic, $Pna2_1$

Hall symbol: $p\ 2c\ -2n$

$a = 5.4110\ (3)\ \text{\AA}$

$b = 25.4205\ (12)\ \text{\AA}$

$c = 9.3170\ (4)\ \text{\AA}$

$V = 1281.56\ (11)\ \text{\AA}^3$

$Z = 4$

$F(000) = 592$

$D_x = 1.525\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3201 reflections

$\theta = 1.6\text{--}28.5^\circ$

$\mu = 3.20\ \text{mm}^{-1}$

$T = 273\ \text{K}$

Block, colourless

$0.52 \times 0.32 \times 0.14\ \text{mm}$

Data collection

Bruker CCD three-circle diffractometer

Radiation source: sealed tube graphite

phi and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 1997)

$T_{\min} = 0.202$, $T_{\max} = 0.800$

8789 measured reflections

3201 independent reflections

2361 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 28.5^\circ$, $\theta_{\min} = 1.6^\circ$

$h = -6 \rightarrow 7$

$k = -25 \rightarrow 34$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.100$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.2176P]$

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

$S = 1.03$	$(\Delta/\sigma)_{\max} < 0.001$
3201 reflections	$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
156 parameters	$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
1 restraint	Absolute structure: Flack (1983), 1494 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.040 (17)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against all reflections. The weighted R_w factor and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on all data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.99838 (6)	0.148410 (15)	0.99886 (11)	0.07396 (14)
N1	0.5607 (5)	0.19539 (10)	0.6617 (3)	0.0585 (6)
N2	0.2257 (4)	0.14754 (9)	0.5520 (3)	0.0541 (6)
N3	0.2480 (5)	0.07428 (9)	0.6813 (3)	0.0552 (6)
O1	-0.0599 (4)	0.08103 (10)	0.5080 (4)	0.0730 (6)
C1	0.7552 (5)	0.14820 (11)	0.8523 (3)	0.0515 (7)
C2	0.7283 (6)	0.19139 (12)	0.7678 (4)	0.0592 (8)
H2	0.8321	0.2199	0.7842	0.071*
C3	0.6043 (6)	0.10361 (12)	0.8374 (3)	0.0532 (7)
H3	0.6209	0.0739	0.8948	0.064*
C4	0.4298 (5)	0.10753 (12)	0.7306 (3)	0.0496 (6)
C5	0.4169 (6)	0.15329 (11)	0.6493 (4)	0.0489 (6)
C6	0.1188 (6)	0.09843 (13)	0.5717 (4)	0.0579 (7)
C7	0.1361 (6)	0.18683 (13)	0.4530 (4)	0.0621 (8)
H7A	0.1349	0.2207	0.5011	0.075*
H7B	-0.0331	0.1784	0.4274	0.075*
C8	0.2846 (7)	0.19138 (15)	0.3195 (4)	0.0706 (9)
H8	0.2371	0.2173	0.2548	0.090 (12)*
C9	0.4653 (9)	0.1641 (3)	0.2855 (6)	0.0939 (15)
H9A	0.5201	0.1376	0.3466	0.113*
H9B	0.5461	0.1701	0.1989	0.113*
C10	0.1712 (7)	0.02523 (13)	0.7497 (4)	0.0694 (9)
H10A	0.0091	0.0156	0.7137	0.083*
H10B	0.1562	0.0311	0.8522	0.083*
C11	0.3410 (8)	-0.01892 (15)	0.7256 (5)	0.0771 (10)
H11	0.3027	-0.0503	0.7717	0.129 (19)*

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C12	0.5362 (7)	-0.01882 (17)	0.6479 (6)	0.0832 (12)
H12A	0.5828	0.0116	0.5995	0.100*
H12B	0.6313	-0.0491	0.6400	0.100*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.05433 (18)	0.1026 (3)	0.0649 (2)	0.00262 (14)	-0.01189 (13)	-0.0127 (2)
N1	0.0564 (13)	0.0460 (14)	0.0731 (17)	-0.0070 (11)	-0.0083 (14)	0.0032 (13)
N2	0.0478 (13)	0.0545 (14)	0.0599 (15)	-0.0015 (10)	-0.0090 (11)	0.0029 (10)
N3	0.0493 (13)	0.0476 (13)	0.0686 (15)	-0.0089 (10)	-0.0042 (12)	0.0025 (11)
O1	0.0564 (12)	0.0847 (15)	0.0781 (16)	-0.0178 (10)	-0.0148 (16)	-0.0040 (16)
C1	0.0412 (14)	0.0642 (18)	0.0489 (15)	0.0007 (13)	-0.0024 (12)	-0.0096 (13)
C2	0.0507 (16)	0.0556 (17)	0.071 (2)	-0.0074 (13)	-0.0041 (15)	-0.0080 (15)
C3	0.0489 (15)	0.0567 (17)	0.0539 (16)	0.0026 (13)	0.0034 (14)	0.0046 (13)
C4	0.0416 (14)	0.0549 (17)	0.0522 (16)	-0.0013 (11)	0.0038 (12)	-0.0024 (13)
C5	0.0446 (14)	0.0454 (16)	0.0566 (17)	0.0003 (11)	-0.0005 (14)	-0.0055 (13)
C6	0.0531 (17)	0.0630 (18)	0.0575 (17)	-0.0051 (14)	-0.0016 (15)	-0.0051 (15)
C7	0.0550 (17)	0.0651 (19)	0.0662 (19)	0.0019 (13)	-0.0108 (15)	0.0016 (15)
C8	0.077 (2)	0.083 (2)	0.0523 (17)	-0.0094 (19)	-0.0090 (18)	0.0031 (17)
C9	0.092 (4)	0.119 (4)	0.071 (3)	0.003 (2)	0.017 (2)	-0.005 (3)
C10	0.065 (2)	0.062 (2)	0.081 (2)	-0.0164 (15)	0.0003 (19)	0.0097 (17)
C11	0.089 (3)	0.056 (2)	0.086 (3)	-0.0155 (18)	0.004 (2)	0.0058 (18)
C12	0.086 (3)	0.066 (3)	0.098 (3)	-0.0118 (17)	0.008 (2)	-0.014 (2)

Geometric parameters (\AA , $^\circ$)

Br1—C1	1.896 (3)	C4—C5	1.390 (4)
N1—C5	1.328 (4)	C7—C8	1.485 (5)
N1—C2	1.345 (4)	C7—H7A	0.9700
N2—C5	1.383 (4)	C7—H7B	0.9700
N2—C6	1.388 (4)	C8—C9	1.240 (6)
N2—C7	1.444 (4)	C8—H8	0.9300
N3—C4	1.376 (4)	C9—H9A	0.9300
N3—C6	1.381 (4)	C9—H9B	0.9300
N3—C10	1.461 (4)	C10—C11	1.467 (6)
O1—C6	1.218 (4)	C10—H10A	0.9700
C1—C2	1.359 (4)	C10—H10B	0.9700
C1—C3	1.404 (4)	C11—C12	1.281 (6)
C2—H2	0.9300	C11—H11	0.9300
C3—C4	1.375 (5)	C12—H12A	0.9300
C3—H3	0.9300	C12—H12B	0.9300
C5—N1—C2	113.5 (3)	N2—C7—C8	114.0 (3)
C5—N2—C6	108.7 (2)	N2—C7—H7A	108.7
C5—N2—C7	126.6 (2)	C8—C7—H7A	108.7
C6—N2—C7	124.5 (3)	N2—C7—H7B	108.7
C4—N3—C6	109.6 (3)	C8—C7—H7B	108.7
C4—N3—C10	125.6 (3)	H7A—C7—H7B	107.6

C6—N3—C10	123.9 (3)	C9—C8—C7	126.6 (4)
C2—C1—C3	122.2 (3)	C9—C8—H8	116.7
C2—C1—Br1	119.3 (2)	C7—C8—H8	116.7
C3—C1—Br1	118.5 (2)	C8—C9—H9A	120.0
N1—C2—C1	124.0 (3)	C8—C9—H9B	120.0
N1—C2—H2	118.0	H9A—C9—H9B	120.0
C1—C2—H2	118.0	N3—C10—C11	114.1 (3)
C4—C3—C1	114.4 (3)	N3—C10—H10A	108.7
C4—C3—H3	122.8	C11—C10—H10A	108.7
C1—C3—H3	122.8	N3—C10—H10B	108.7
C3—C4—N3	133.4 (3)	C11—C10—H10B	108.7
C3—C4—C5	119.3 (3)	H10A—C10—H10B	107.6
N3—C4—C5	107.3 (3)	C12—C11—C10	127.0 (4)
N1—C5—N2	125.5 (3)	C12—C11—H11	116.5
N1—C5—C4	126.7 (3)	C10—C11—H11	116.5
N2—C5—C4	107.8 (2)	C11—C12—H12A	120.0
O1—C6—N3	126.9 (3)	C11—C12—H12B	120.0
O1—C6—N2	126.4 (3)	H12A—C12—H12B	120.0
N3—C6—N2	106.6 (3)		
C5—N1—C2—C1	1.8 (5)	N3—C4—C5—N1	-179.7 (3)
C3—C1—C2—N1	-1.2 (5)	C3—C4—C5—N2	-179.1 (3)
Br1—C1—C2—N1	-179.5 (3)	N3—C4—C5—N2	0.5 (3)
C2—C1—C3—C4	0.2 (4)	C4—N3—C6—O1	-176.8 (4)
Br1—C1—C3—C4	178.6 (2)	C10—N3—C6—O1	-7.0 (5)
C1—C3—C4—N3	-179.4 (3)	C4—N3—C6—N2	0.7 (3)
C1—C3—C4—C5	0.0 (4)	C10—N3—C6—N2	170.5 (3)
C6—N3—C4—C3	178.7 (3)	C5—N2—C6—O1	177.2 (4)
C10—N3—C4—C3	9.2 (6)	C7—N2—C6—O1	1.4 (5)
C6—N3—C4—C5	-0.7 (3)	C5—N2—C6—N3	-0.4 (3)
C10—N3—C4—C5	-170.3 (3)	C7—N2—C6—N3	-176.1 (3)
C2—N1—C5—N2	178.2 (3)	C5—N2—C7—C8	81.6 (4)
C2—N1—C5—C4	-1.6 (5)	C6—N2—C7—C8	-103.5 (3)
C6—N2—C5—N1	-179.9 (3)	N2—C7—C8—C9	2.7 (6)
C7—N2—C5—N1	-4.3 (5)	C4—N3—C10—C11	-77.2 (4)
C6—N2—C5—C4	-0.1 (3)	C6—N3—C10—C11	114.7 (4)
C7—N2—C5—C4	175.5 (3)	N3—C10—C11—C12	-3.3 (6)
C3—C4—C5—N1	0.8 (5)		

Fig. 1

