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The crystal structure of 2-(3,5-difluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine, C₁₆H₁₁BF₂N₂

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Abstract

C₁₆H₁₁BF₂N₂, monoclinic, *P*₂/c (no. 14), *a* = 9.0978(14) Å, *b* = 18.580(3) Å, *c* = 15.476(2) Å, β = 99.516(5)°, *V* = 2580.0(7) Å³, *Z* = 8, *R*_{gt}(*F*) = 0.0406, *wR*_{ref}(*F*²) = 0.1307, *T* = 193 K.

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The asymmetric unit of the title crystal 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.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.12 × 0.10 × 0.10 mm
Wavelength:	Ga Kα radiation (1.34139 Å)
μ:	0.56 mm ⁻¹
Diffractionmeter, scan mode:	Bruker D8 VENTURE, φ and ω
θ _{max} , completeness:	60.5°, 99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	18,536, 5913, 0.038
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4678
<i>N</i> (<i>param</i>) _{refined} :	379
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
F1	0.65030 (11)	0.44574 (4)	0.91923 (6)	0.0491 (2)
F2	0.82361 (9)	0.60077 (5)	0.71944 (5)	0.0407 (2)
F3	0.66160 (9)	0.83072 (5)	0.76644 (6)	0.0460 (2)
F4	0.85937 (12)	0.99546 (5)	0.58781 (7)	0.0550 (3)
N1	0.25288 (11)	0.65270 (5)	0.87459 (7)	0.0270 (2)
H1	0.239360	0.606131	0.880014	0.032*
N2	0.40367 (11)	0.75151 (6)	0.83989 (7)	0.0275 (2)
H2	0.483344	0.767404	0.820519	0.033*
N3	1.24200 (11)	0.78243 (5)	0.61543 (7)	0.0268 (2)
H3A	1.256626	0.828842	0.609374	0.032*
N4	1.09297 (11)	0.68519 (6)	0.65584 (7)	0.0274 (2)
H4	1.013959	0.669976	0.676462	0.033*
C1	0.00754 (14)	0.67475 (7)	0.91065 (8)	0.0299 (3)
H1A	−0.012363	0.624560	0.910543	0.036*
C2	−0.09890 (14)	0.72407 (8)	0.93156 (8)	0.0331 (3)
H2A	−0.190373	0.706617	0.945396	0.040*
C3	−0.07305 (14)	0.79633 (8)	0.93232 (8)	0.0324 (3)
H3	−0.144563	0.828376	0.949220	0.039*
C4	0.05952 (14)	0.82419 (7)	0.90812 (8)	0.0279 (3)
C5	0.08857 (15)	0.89890 (7)	0.90410 (9)	0.0328 (3)
H5	0.019724	0.932490	0.920828	0.039*
C6	0.21466 (16)	0.92305 (7)	0.87638 (9)	0.0353 (3)
H6	0.231370	0.973365	0.872982	0.042*
C7	0.32028 (15)	0.87472 (7)	0.85277 (9)	0.0320 (3)
H7	0.406444	0.892544	0.832593	0.038*
C8	0.29903 (13)	0.80169 (7)	0.85884 (8)	0.0254 (3)
C9	0.16712 (13)	0.77490 (6)	0.88591 (7)	0.0240 (2)
C10	0.14001 (13)	0.69935 (7)	0.89042 (7)	0.0248 (2)
C11	0.51468 (13)	0.62207 (7)	0.83877 (8)	0.0255 (2)
C12	0.52851 (14)	0.55698 (7)	0.88557 (8)	0.0301 (3)
H12	0.461959	0.545936	0.924959	0.036*
C13	0.63944 (15)	0.50933 (7)	0.87381 (9)	0.0330 (3)
C14	0.73990 (14)	0.52170 (7)	0.81801 (9)	0.0328 (3)
H14	0.814746	0.487777	0.810227	0.039*
C15	0.72478 (14)	0.58644 (7)	0.77426 (8)	0.0295 (3)
C16	0.61640 (13)	0.63643 (7)	0.78259 (8)	0.0273 (3)
H16	0.610843	0.680197	0.750481	0.033*
C17	1.48033 (14)	0.75841 (7)	0.57088 (8)	0.0308 (3)
H17	1.498485	0.808500	0.566233	0.037*
C18	1.58526 (14)	0.70797 (8)	0.55092 (9)	0.0339 (3)
H18	1.674391	0.724643	0.533177	0.041*
C19	1.56189 (14)	0.63571 (8)	0.55647 (8)	0.0326 (3)
H19	1.633062	0.602853	0.540826	0.039*
C20	1.43240 (14)	0.60938 (7)	0.58536 (8)	0.0275 (3)
C21	1.40539 (15)	0.53480 (7)	0.59541 (9)	0.0324 (3)
H21	1.474340	0.500438	0.580464	0.039*
C22	1.28122 (16)	0.51209 (7)	0.62635 (9)	0.0348 (3)
H22	1.265892	0.462026	0.633568	0.042*
C23	1.17562 (15)	0.56130 (7)	0.64774 (9)	0.0321 (3)
H23	1.090083	0.544388	0.669370	0.039*
C24	1.19612 (13)	0.63430 (7)	0.63733 (8)	0.0257 (3)
C25	1.32566 (13)	0.65970 (6)	0.60648 (7)	0.0239 (2)

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C26	1.35129 (13)	0.73475 (7)	0.59717 (7)	0.0246 (2)
C27	0.98409 (13)	0.81523 (7)	0.65740 (8)	0.0255 (2)
C28	0.97720 (15)	0.88287 (7)	0.61715 (8)	0.0298 (3)
H28	1.049601	0.896295	0.582397	0.036*
C29	0.86475 (16)	0.92983 (7)	0.62826 (9)	0.0336 (3)
C30	0.75671 (15)	0.91447 (7)	0.67804 (9)	0.0345 (3)
H30	0.680490	0.947813	0.685237	0.041*
C31	0.76640 (14)	0.84771 (7)	0.71663 (9)	0.0316 (3)
C32	0.87544 (14)	0.79806 (7)	0.70790 (8)	0.0288 (3)
H32	0.876620	0.752567	0.736008	0.035*
B1	0.38777 (15)	0.67658 (8)	0.85030 (9)	0.0256 (3)
B2	1.10881 (15)	0.75983 (8)	0.64320 (9)	0.0256 (3)

Source of material

In air, Bpin {Bis(pinacolato)diboron}–B(dan) {naphthalene-1,8-diamino boronamide}; (0.1 mmol, 1.0 eq.), 3,5-difluoroaniline (0.2 mmol, 2.0 eq.), TBAI (tetrabutylammonium iodide; 0.01 eq.), NaOAc (0.15 eq.), and BPO (0.01 eq.) were sequentially weighed and added to a screw-capped Schlenk tube containing a magnetic stir bar. The vessel was evacuated and refilled with nitrogen for three times. tBuONO (0.2 eq.) and MeCN (0.6 mL) were added in turn under N₂ atmosphere using syringes through a septum which was temporarily used to replace the screw cap. The reaction mixture was then vigorously stirred at 80 °C for the indicated time. The resulting mixture was filtered through a pad of Celite, and the filter cake was washed with ethyl acetate (3 mL × 2). The combined filtrate was evaporated under vacuum to dryness and the residue was purified by column chromatography to yield the desired product as colorless solid.

Experimental details

All the H atoms on the benzene rings were placed geometrically and refined without any constraints or restraints.

Comment

In recent years, organoborons have always been a hot topic for chemists, because of their widely use in drug science, materials discovery and synthetic chemistry [5]. Existing

chemical reactions can efficiently convert the carbon–boron bonds into various carbon–carbon or carbon–heteroatom bonds; therefore, this strategy can be applied to the construction of special molecules with more complex structures [6, 7]. In numerous organoboron compounds, the naphthalene-1,8-diamino boronamide (Bdan), using the naphthalene-1,8-diaminato (dan) ligand as the masking group [8, 9], are less reactive than other derivatives, such as Bpin {Bis(pinacolato)diboron}, thus avoiding some side reactions. Because of this characteristic, Bdan compounds are often used in the iterative cross-coupling reactions as modular synthetical building blocks [10–12]. Now, we report the crystal structure of the title compound (*cf.* Figure).

All bonds and angles in the crystal structure are within the normal range. In conclusion, we have developed a facile process for the synthesis of 2-(3,5-difluorophenyl)-2,3-dihydro-1H-naphtho [1,8-*de*][1,3,2]diazaborinine.

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