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Crystal structure of methyl 2-(1*H*-naphtho[1,8-*de*][1.3.2]diazaborinin-2(3*H*-yl)benzoate

C₁₈H₁₅BN₂O₂

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Abstract

C₁₈H₁₅BN₂O₂, monoclinic, *C*2/*c* (no. 15), *a* = 23.976(3) Å, *b* = 7.7690(9) Å, *c* = 32.940(4) Å, β = 95.17(1)°, *V* = 2482.26(15) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0525, *wR*_{ref}(*F*²) = 0.1415, *T* = 193 K.

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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:	0.44 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ _{max} , completeness:	54.1°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	32,343, 5654, 0.111
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2σ(<i>I</i> _{obs}), 3971
<i>N</i> (<i>param</i>) _{refined} :	417
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

In air Bpin–B(dan) (Bpin = Bis(pinacolato)diboron; B(dan) = naphthalene-1,8-diamino boronamide; 0.1 mmol; 1.0 eq.), methyl 2-aminobenzoate (0.2 mmol 2.0 eq.), TBAI (0.01 eq.), NaOAc (0.15 eq.) and benzoylperoxide (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. 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 were placed geometrically and refined without any constraints or restraints.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
B1	0.25359 (8)	0.0517 (3)	0.42812 (6)	0.0308 (5)
B2	0.25748 (8)	0.4684 (3)	0.32213 (7)	0.0323 (5)
C1	0.34121 (7)	−0.1085 (2)	0.44729 (5)	0.0304 (4)
C2	0.36867 (7)	−0.2552 (3)	0.46092 (6)	0.0356 (4)
H2A	0.347972	−0.356156	0.465833	0.043*
C3	0.42744 (7)	−0.2563 (3)	0.46765 (6)	0.0405 (5)
H3A	0.446038	−0.358012	0.477535	0.049*
C4	0.45818 (7)	−0.1139 (3)	0.46021 (6)	0.0395 (5)
H4A	0.497810	−0.117296	0.465186	0.047*
C5	0.43176 (7)	0.0384 (3)	0.44523 (5)	0.0332 (4)
C6	0.46171 (7)	0.1866 (3)	0.43518 (6)	0.0400 (5)
H6	0.501465	0.186198	0.438824	0.048*
C7	0.43422 (7)	0.3305 (3)	0.42026 (6)	0.0403 (5)
H7	0.455226	0.427669	0.412996	0.048*
C8	0.37547 (7)	0.3372 (3)	0.41548 (6)	0.0347 (4)
H8	0.357026	0.439269	0.405678	0.042*
C9	0.34476 (7)	0.1962 (2)	0.42498 (5)	0.0302 (4)
C10	0.37196 (7)	0.0426 (2)	0.43938 (5)	0.0295 (4)
C11	0.18792 (7)	0.0672 (2)	0.42894 (5)	0.0305 (4)
C12	0.16802 (7)	0.1215 (3)	0.46529 (6)	0.0361 (5)
H12	0.194054	0.148400	0.487859	0.043*
C13	0.11110 (7)	0.1373 (3)	0.46935 (6)	0.0412 (5)
H13	0.098503	0.175494	0.494351	0.049*
C14	0.07299 (7)	0.0971 (3)	0.43689 (7)	0.0445 (5)
H14	0.033993	0.105352	0.439713	0.053*
C15	0.09117 (7)	0.0452 (3)	0.40051 (6)	0.0411 (5)
H15	0.064698	0.018592	0.378178	0.049*
C16	0.14833 (7)	0.0312 (2)	0.39614 (6)	0.0320 (4)
C17	0.16820 (7)	−0.0220 (3)	0.35678 (6)	0.0354 (4)
C18	0.14121 (10)	−0.0963 (3)	0.28807 (6)	0.0564 (6)
H18A	0.107888	−0.091398	0.268548	0.085*
H18B	0.155795	−0.214146	0.289470	0.085*
H18C	0.169905	−0.018454	0.279194	0.085*
C19	0.33990 (7)	0.6592 (2)	0.33389 (5)	0.0307 (4)
C20	0.36321 (8)	0.8123 (3)	0.34715 (6)	0.0369 (5)
H20	0.339794	0.903344	0.354709	0.044*
C21	0.42158 (8)	0.8358 (3)	0.34965 (6)	0.0394 (5)
H21	0.437322	0.942023	0.359276	0.047*
C22	0.45582 (7)	0.7073 (3)	0.33836 (6)	0.0403 (5)
H22	0.495089	0.726197	0.339679	0.048*
C23	0.43369 (7)	0.5465 (3)	0.32473 (5)	0.0343 (4)
C24	0.46764 (7)	0.4084 (3)	0.31320 (6)	0.0422 (5)
H24	0.506840	0.424918	0.312748	0.051*
C25	0.44472 (8)	0.2529 (3)	0.30280 (6)	0.0457 (5)
H25	0.468134	0.162026	0.295147	0.055*
C26	0.38678 (7)	0.2243 (3)	0.30320 (6)	0.0387 (5)
H26	0.371565	0.113915	0.296563	0.046*
C27	0.35233 (7)	0.3554 (3)	0.31312 (5)	0.0313 (4)
C28	0.37479 (7)	0.5205 (2)	0.32353 (5)	0.0294 (4)
C29	0.19223 (7)	0.4373 (2)	0.31499 (6)	0.0319 (4)
C30	0.17255 (7)	0.3788 (3)	0.27623 (6)	0.0385 (5)
H30	0.198815	0.354355	0.257076	0.046*
C31	0.11602 (8)	0.3552 (3)	0.26476 (6)	0.0425 (5)
H31	0.104020	0.314014	0.238252	0.051*
C32	0.07735 (8)	0.3919 (3)	0.29202 (6)	0.0460 (5)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H32	0.038487	0.378438	0.284163	0.055*
C33	0.09511 (7)	0.4479 (3)	0.33066 (6)	0.0410 (5)
H33	0.068258	0.472438	0.349386	0.049*
C34	0.15214 (7)	0.4695 (2)	0.34280 (6)	0.0319 (4)
C35	0.17026 (7)	0.5195 (2)	0.38530 (6)	0.0332 (4)
C36	0.13949 (8)	0.6047 (3)	0.44854 (6)	0.0514 (6)
H36A	0.154642	0.721773	0.450852	0.077*
H36B	0.167050	0.523481	0.461268	0.077*
H36C	0.105005	0.598268	0.462333	0.077*
N1	0.28281 (6)	−0.0999 (2)	0.44083 (5)	0.0350 (4)
H1	0.263317	−0.193354	0.444861	0.042*
N2	0.28626 (5)	0.1981 (2)	0.42147 (4)	0.0331 (4)
H2	0.268986	0.295362	0.414785	0.040*
N3	0.29445 (6)	0.3338 (2)	0.31391 (5)	0.0351 (4)
H3	0.280314	0.230524	0.309010	0.042*
N4	0.28210 (6)	0.6312 (2)	0.33078 (5)	0.0352 (4)
H4	0.259957	0.719190	0.334372	0.042*
O1	0.21712 (5)	−0.0419 (2)	0.35101 (4)	0.0477 (4)
O2	0.12658 (5)	−0.0446 (2)	0.32767 (4)	0.0515 (4)
O3	0.12742 (5)	0.5614 (2)	0.40618 (4)	0.0515 (4)
O4	0.21832 (5)	0.52131 (18)	0.40037 (4)	0.0397 (3)

Comment

Organoboron chemistry has always been one of the hot topics in medicinal or material chemistry [5]. Such reagents can be used to form new C–C or C–X bonds [6, 7]. The most common boron-containing group Bpin has relatively high activity therefore it is not easy to control the reactivity in the chemical reactions. The naphthalene-1,8-diamino boronamide has a weak reactivity and has received much attention because it is robust enough to avoid the side reactions. The reagent will be converted to the corresponding boric acid under acidic hydrolysis conditions in order to participate in the following reactions [8–11].

There are two molecules in the symmetric unit (see Figure). All bonds and angles in the crystal structure are within the normal ranges [8, 9, 12, 13]. The molecules are connected by hydrogen bonds to form a chain along the [010] direction. In conclusion we have shown that a further diazaborinin compound: methyl 2-(1*H*-naphtho[1,8-*de*] [1.3.2] diazaborinin-2(3*H*-yl)benzoate can be easily obtained.

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