Crystal Structure of Tertiarybutyl Ammonium Bis[(naphthalene-2,3-diolato)-borate] Dimethyl Sulfoxide Solvate

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The structure of tertiarybutyl ammonium bis[naphthalene-2,3-diolato)borate] dimethyl sulfoxide solvate was determined by X-Ray crystallography. The compound crystallized in a triclinic system, and was characterized to be in the space group *P*-1, with cell parameters a = 9.6282(9)Å, b = 11.0221(9)Å, c = 13.0273(12)Å, α = 91.050(4)^0, β = 109.419(4)^0, γ = 94.574(2)^0, Z = 2, and V = 1298.2(2)Å^3. The crystal packing is governed by intermolecular and intramolecular N–H···O hydrogen bonds. The B atom takes a distorted tetrahedral geometry with four O atoms of naphthalene-2,3-diolato ligands.

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By virtue of rapid development in technology, particularly, laser technology, microprocessing, space communication, and the modern military, borates have aroused interest notably concerning the aforementioned fields for the last several decades.[1] The wide application of borates stems from the structure-property relationship that renders possible their huge structural varieties and the functionality of the B–O units.[2] Hitherto, a series of borates possessing a planar B–O entity with outstanding optical properties have been reported, such as nonlinear optical (NLO) materials, β-BaB_2O_4.[3] The successful research of these rich structures can be ascribed to the uniqueness of a boron element forming a BO_3 triangle and a BO_4 tetrahedron with an oxygen atom, and further connected to each other by B–O–B, B–O–C, B–N–C, B–O–M–N to form various isolated, cage, chain, sheet and network structures.[4] Owing to the complexity of the possible structures, boron can form a wide diversity of compounds including non-metallic compounds.[5] The structures of these compounds can be displayed in a binary fashion composed of an anionic borate structural unit and a cationic interstitial complex.[6] The role of non-metal cations differs from metal cations due to the fact that they generally do not coordinate to oxygen in the same way, and may act instead as hydrogen-bond donors to the structural unit. As part of our progressing work on spiroborates,[7-9] the process of the self-assembly of organic and inorganic moieties has been performed under mild and aqueous solution conditions, and obtained original borate with organic amine associated with the solvent molecule, namely tertiarybutyl ammonium bis[(naphthalene-2,3-diolato)borate] dimethyl sulfoxide (Fig. 1).

The aforementioned compound (Fig. 2) was prepared utilizing an aqueous solution (10 mL) of boric acid (5 mmol), which was afterwards added dropwise to a solution of naphthalene-2,3-diol (10 mmol) in ethanol (10 mL) with stirring. The reaction mixture was allowed to be stirred at 50°C for 2 h, then following the addition of *tert*-butylamine (5 mmol) to this clear solution, in formation of a pink colored suspension resulted, which was stirred further for 3 h at 30°C. The crude product was crystallized from an acetone/DMSO mixture. Crystals of the title compound were obtained by slow evaporation.

X-ray crystallography was performed at 293 K on a Bruker D8 QUEST diffractometer (BRUKER APEX-II CCD) employing graphite-monochromated Mo $K\alpha$ radiation. Crystal data and details related to the data collection are given in Table 1. The structure was solved by an intrinsic phasing method and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were inserted at their calculated positions, and fixed there. The sulfur atoms were refined isotropically because of their severe disorder. The sulfur (S) atom was divided into two positions with occupation factors of 0.187 and 0.813. All calculations were carried out on a Window 7 Core i7 computer using SHELXT-2014/5 and SHELXL-2016/4. Crystallographic data have been deposited with Cambridge Crystallographic Data

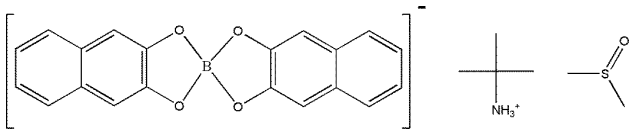

Fig. 1 Chemical diagram of the title compound.

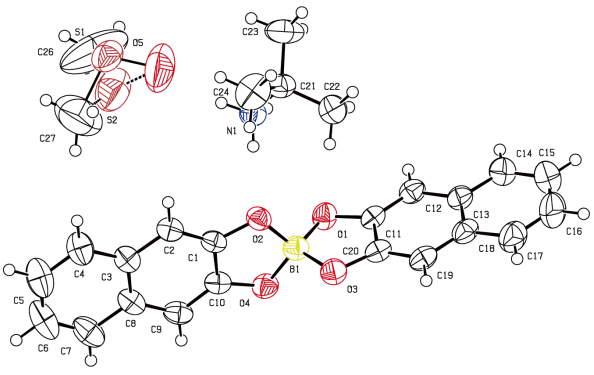

Fig. 2 ORTEP structure of compound **1** with ellipsoids shown at the 50% probability level.

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Table 1 Crystal and experimental data

Chemical formula: $C_{26}H_{30}BO_5SN$	
Formula weight = 479.38	
T = 293 K	
Crystal system: triclinic	Space group: P-1
a = 9.6282(9)Å	α = 91.050(4)°
b = 11.0221(9)Å	β = 109.419(4)°
c = 13.0273(12)Å	γ = 94.574(2)°
V = 1298.2(2)Å^3	Z = 2
D_x = 1.226 g/cm^3	
Radiation Mo $K\alpha$ (λ = 0.71073 Å)	
μ(Mo $K\alpha$) = 0.160 mm^{-1}	F(0 0 0) = 508
Crystal size = 0.18 × 0.22 × 0.29 mm^3	
No. of reflections collected = 36973	
No. of independent reflections = 5359	
θ range for data collection: 2.881 to 26.584°	
Data/Restraints/Parameters = 5359/0/324	
Goodness-of-fit on F^2 = 1.107	
R indices [I >2σ(I)]: R1 = 0.0740, wR2 0.1680	
R indices (all data): R1 = 0.1040, wR2 = 0.1924	
$(\Delta/\sigma)_{max}$ = 0.000	
$(\Delta\rho)_{max}$ = 0.00 eÅ^{-3}	$(\Delta\rho)_{min}$ = –0.00 eÅ^{-3}
Measurement: Bruker APEX-II CCD	
Programs system: SHELXT 2014/5[11], Bruker SAINT	
Structure determination: SHELXL-2016/4[12]	
CCDC deposition number: 1862219	

Centre (Deposit numbers CCDC-1862219). Copies of the data can be obtained free of charge *via* http://www.ccdc.com.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK: Fax, +44 1223 336033: email, deposit@ccdc.cam.ac.uk). The crystal data and selected bond lengths and angles are summarized in Tables 1 and S1, respectively.

An ORTEP view of the compound is shown in Fig. 2. The sp^3-hybridized B atom is linked to four O atoms to form a distorted tetrahedral environment, where the B–O bond lengths range from 1.469(4) - 1.491(4)Å and the O–B–O angles are in the range 105.2(2) - 112.9(2)° (Table S1). The asymmetric unit of the abovementioned compound consists of a $[BO_4(C_{10}H_6)_2]^-$ anion, a $[C_4H_9NH_3)]^+$ cation and the dimethyl sulfoxide solvent. The $[BO_4(C_{10}H_6)_2]^-$ anion consists of one set of distorted $[BO_4]$ tetrahedra and two sets of $[C_{10}H_6]$ planes with oxygen atoms as sharing vertexes. The bond distances and angles are similar to those reported previously in related arylspiroborate compounds.[7-10] It should be noted that the cyclic ring structure induces a contraction of the O–B–O angles in the five-membered rings, with O1–B1–O4 112.9(2)° and O4–B1–O2 104.2(2)°. The exocyclic angles of O1–B1–O3 105.2(2)°, O4–B1–O3 111.8(2)°, O1–B1–O2 111.7(2)°, and O3–B1–O2 111.3(2)°, are dramatically larger. The borate rings are highly coplanar with the corresponding aryl rings [with 0.0320 Å r.m.s. deviation for Plane A (B1, O1, O3, C11–C20) and 0.0389 Å r.m.s. deviation for Plane B (B1, O2, O4, C1–C10). The coordination planes (Plane A and Plane B) intersect at an angle of 88.919(51)°. In the crystal structure the $[BO_4(C_{10}H_6)_2]^-$ anion and the $[C_4H_9NH_3]^+$ cation are discrete units, which interact both electrostatically and *via* intermolecular N–H···O hydrogen bonds (N1–H1A···O2 and N1–H1B···O5), where the H···O distance is 1.980 and 1.903 Å respectively (Fig. 3). Stabilization of the crystal structure arises from electrostatic interactions, and is assisted by intramolecular N–H···O hydrogen bonds (N1–H1C···O1 [–x+1, –y+1, –z+1] and N1–H1C···O4 [–x+1, –y+1, –z+1]), where the H···O distance is 2.607 and 2.096 Å, respectively, between the layers (Table S2).

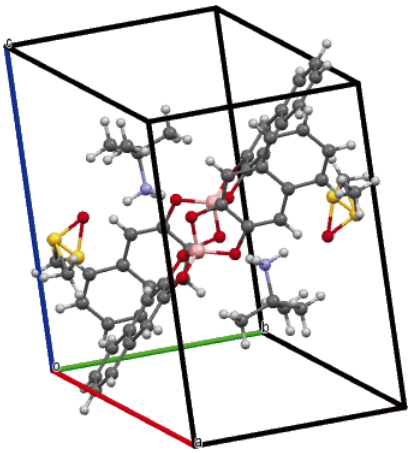

Fig. 3 Packing diagram of the title compound.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

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