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Synthesis and structure of a highly fluorinated 7-bora-7*H*-benzo[*de*]anthracene

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Dedicated to François Mathey on the occasion of his 60th birthday

Abstract

1,8-Dilithionaphthalene·tmeda reacts with bis(pentafluorophenyl)boronfluoride·Et_2O in diethylether to afford 7-pentafluorophenyl-8,9,10,11-tetrafluoro-7-bora-7*H*-benzo[*de*]anthracene (**1**) in moderate yield. Compound **1**, which features a boron atom incorporated in a fused tetracyclic system with 16 π-electrons, has been characterized by multinuclear NMR spectroscopy, and its structure determined by single crystal X-ray crystallography. Cyclic voltammetry studies in THF show an irreversible reduction wave at -1.73 V versus Fc^+/Fc. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lewis acid; Boron; Fluorinated; *Anti*-aromatic

1. Introduction

Tris(pentafluorophenyl)borane [1,2] is a prototypical organoelement Lewis acid that has proved especially useful in olefin polymerization catalysis and organic synthesis [3–5]. While different fluorinated aryl substituents, such as perfluoronaphthyl [6,7] or perfluorobiphenyl [8,9] have been used in related boranes, the chemistry of these compounds has witnessed two recent developments aimed at improving the Lewis acidic properties. First, the synthesis of bidentate derivatives has received attention. While such compounds have been known for some time [10], a series of recent investigations has centered on the preparation and properties of bifunctional boranes holding two bis(pentafluorophenyl)boryl functionalities in close proximity. As a result of cooperative effects, these compounds exhibit unusual Lewis acidic properties and form tight chelate complexes with a series of anions [11–14]. The second development has been concerned with the incorporation of boron into potentially *anti*-aromatic ring systems. In this domain, the Lewis acidic properties of compounds such as boroles and borafluorenes [15–19] or 9,10-dihydro-9,10-diboranthracene [20,21] are especially noteworthy. Here we report the synthesis of 7-pentafluorophenyl-8,9,10,11-tetrafluoro-7-bora-7*H*-benzo[*de*]anthracene (**1**), which features a boron atom incorporated in a fused tetracyclic system with 16 π-electrons.

2. Results and discussion

2.1. Synthesis

The reaction of 1,8-dilithionaphthalene·tmeda [22] with two mole equivalents of bis(pentafluorophenyl)-boronfluoride·Et_2O [23] does not lead to the formation of a 1,8-diborylnaphthalene derivative [10b,24], but rather results in the formation of compound **1** (Scheme 1). The formation of **1** in this reaction can be rationalized by invoking the metathetical attachment of one bis(pentafluorophenyl)boryl group to the naphthalene backbone, followed by a nucleophilic substitution of an *ortho*-fluoride by the remaining carbanionic center. Nucleophilic aromatic substitutions are unusual at low temperatures. In the case of hexafluorobenzene, however, such a reaction readily occurs upon treatment with methyllithium or *n*-butyllithium [25]. In contrast,

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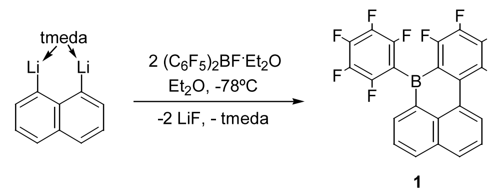

Scheme 1.

with less nucleophilic reagents such as 1-lithionaphthalene elevated temperatures are necessary [26]. According to ^{1}H- and ^{19}F-NMR spectroscopy of the reaction mixture, **1** forms in an approximate 30% yield as the only identifiable product. It can be isolated upon crystallization as a benzene solvate in a 17% yield. The crystallization of solvent-free **1** is possible from chloroform. Compound **1** is a bright yellow moisture-sensitive solid. It dissolves readily in polar solvents such as acetonitrile and THF and is sparingly soluble in unpolar solvents such as benzene. The ^{1}H-NMR spectrum of compound **1** exhibits six resonances, which reflects the presence of an unsymmetrically *peri*-substituted naphthalene derivative, whereas the ^{19}F-NMR spectrum shows seven signals and reveals the presence of a tetrafluoroaryl-system with four different fluorine atoms. The ^{11}B-NMR spectrum exhibits a single resonance at 52.7 ppm, confirming the presence of a boron atom in the complex.

2.2. Structure of compound 1

The structure of compound **1** features a planar hitherto unknown 7-bora-7*H*-benzo[*de*]anthracene unit (Figs. 1 and 2). The coordination at the boron is slightly distorted trigonal planar ($\Sigma_{C-B-C} = 360.0°$). In comparison to the exocyclic angles C(1)–B–C(21) and C(11)–B–C(21) which are, respectively, equal to 120.0(4) and 122.9(4)°, the intracyclic C(1)–B–C(11) angle of 117.1(4)° appears relatively narrow. The internal B–C(1) and B–C(11) distances of 1.523(7) and 1.545(6) Å, respectively, are about 2–4% shorter than a typical B–C single bond (1.57–1.59 Å) [27–29], possibly indicating some multiple bonding at boron. The C_6F_5 ring is tilted out of the benzo[*de*]anthracene plane by 68.5°, precluding significant conjugation between the aryl and the 7-bora-7*H*-benzo[*de*]anthracene π-systems. It is interesting to note that the C(8)–C(12) bond distance of 1.494(6) Å falls in the range of a single bond. Hence, the π-systems of the tetrafluorophenylene and naphthalene units are essentially isolated. This distortion substantiates the *anti*-aromaticity of the 16 π-electron system.

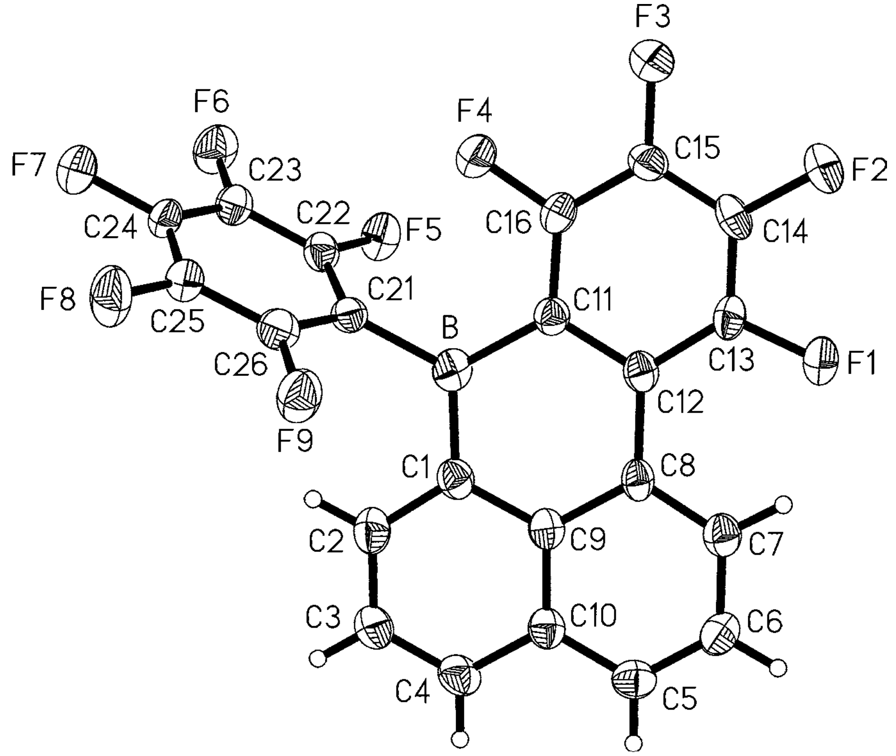

Fig. 1. Structure of **1** in the crystal. ORTEP drawing (50%). Relevant bond lengths are presented in Fig. 2. Selected bond angles (°): C(1)–B–C(11) 117.1(4), C(1)–B–C(21) 120.0(4), C(11)–B–C(21) 122.9(4), C(2)–C(1)–C(9) 118.6(4), C(2)–C(1)–B 121.3(4), C(9)–C(1)–B 120.1(4), C(7)–C(8)–C(9) 117.5(4), C(7)–C(8)–C(12) 122.0(4), C(9)–C(8)–C(12) 120.5(4), C(10)–C(9)–C(1) 118.9(4), C(10)–C(9)–C(8) 119.3(4), C(1)–C(9)–C(8) 121.8(4), C(16)–C(11)–C(12) 118.2(4), C(16)–C(11)–B 122.1(4), C(12)–C(11)–B 119.6(4), C(13)–C(12)–C(11) 116.1(4), C(13)–C(12)–C(8) 123.2(4), C(11)–C(12)–C(8) 120.7(4).

2.3. Lewis acidity

The Lewis acidic properties of **1** have been investigated in solution. ^{11}B-NMR of an equimolar mixture of **1** and MeCN in C_6D_6 leads to the detection of a signal at 41.5 ppm. In comparison to free **1**, this signal is shifted by 11.2 ppm to a higher field, which reflects the formation of a Lewis adduct [30]. The Childs method was used to further study the Lewis acidic properties of **1** [31]. When equimolar amounts of **1**, $B(C_6F_5)_3$, and MeCN were mixed in C_6D_6, formation of the adduct $MeCN{\cdot}B(C_6F_5)_3$ occurs quantitatively leaving **1** in an uncomplexed form as shown by ^{11}B- and ^{19}F-NMR spectroscopy. It can be concluded that compound **1** is a much weaker Lewis acid than $B(C_6F_5)_3$. This result can be rationalized on the basis of the structural rigidity of the fused ring system that impedes tetrahedralization of the boron center. Finally, we note that the cyclic voltammogram of compound **1** shows the presence of an irreversible reduction wave at -1.73 V versus Fc^+/Fc. For comparison, this reduction potential is less negative than that observed for triphenylborane and tri-α-naphthylborane ($E_{1/2} = -2.3$ and -2.4 V vs. Fc^+/Fc, respectively) [32,33]. It is also less negative than the reduction potential of pentaphenylborole ($E_{1/2} = -2.6$ V vs. Fc^+/Fc), another *anti*-aromatic boracycle [32,34]. The unusual redox properties of **1** most certainly result from the high degree of fluorination that increases electron deficiency and facilitates reduction. In that respect, it is interesting to note that $B(C_6F_5)_3$ has been recently shown to act as an one-electron oxidant [35–37].

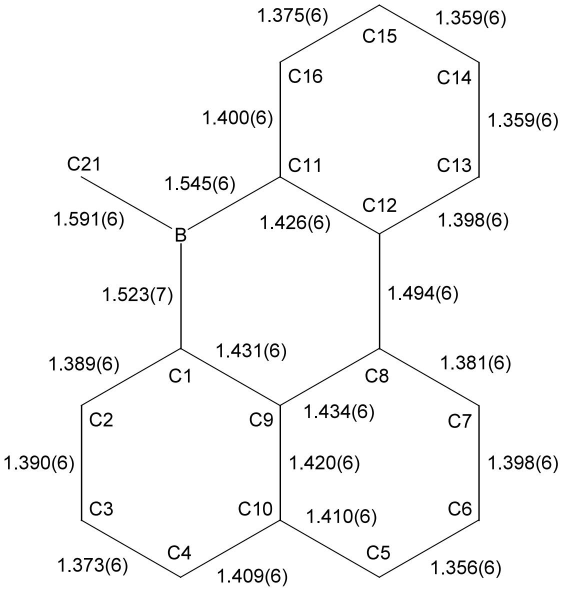

Fig. 2. Schematic drawing of the core of **1** showing the bond lengths (Å).

3. Experimental

3.1. General considerations

NMR spectra were obtained on a Varian Inova 400 spectrometer (399.67 MHz for ^{1}H, 128.23 MHz for ^{11}B, 100.50 MHz for ^{13}C, 376.02 MHz for ^{19}F). All spectra were recorded in C_6D_6. The proton and carbon signals of the deuterated solvent were used as internal standard for the ^{1}H- ($\delta = 7.16$ ppm) and ^{13}C- ($\delta = 128.06$ ppm) NMR spectra, respectively. Neat CCl_3F and neat $BF_3{\cdot}Et_2O$ were used as external standard for the ^{19}F- and ^{11}B-NMR spectra (both $\delta = 0.00$ ppm), respectively. The atom numbering scheme used to report the NMR data is in accordance with the IUPAC nomenclature for 7*H*-benzo[*de*]anthracene. Cyclic voltammetry studies were performed using a BAS100A electrochemical analyzer with a glassy carbon working electrode, a Pt auxiliary electrode, and a $Ag/AgNO_3$ reference electrode. The voltammogram was recorded at 250 mV s^{-1} with THF as solvent and Bu_4NPF_6 (0.1 M) as support electrolyte. All potential values are referred to the $E_{1/2}$ of Fc^+/Fc which was used as an internal standard. The microanalysis was performed by Atlantic Microlab, Norcross, GA. The melting point was measured on a sample in a sealed capillary and is uncorrected. All experiments were carried out under a dry inert atmosphere of N_2 using standard Schlenk technique or a glove box (Unilab, M. Braun). Diethylether was dried over Na, C_6H_6 was dried over K, C_6D_6 was dried over Na/K, and all solvents were distilled prior to use. 1,8-Dilithionaphthalene·tmeda [22] and bis(pentafluorophenyl)boronfluoride·Et_2O [23] were prepared according to published procedures.

3.2. Preparation of compound 1

To a solution of bis(pentafluorophenyl)boronfluoride·Et_2O (1.37 g, 3.12 mmol) in ether (20 ml) was added a solution of 1,8-dilithionaphthalene·tmeda (400 mg, 1.56 mmol) in ether (20 ml) at -78 °C and the resulting reaction mixture stirred for 15 h while the cooling bath slowly warmed to ambient temperature. The ether was evaporated in vacuo and the residue extracted with C_6H_6 (10 ml). Crystallization over 3 days yielded 130 mg (0.265 mmol, 17%) bright yellow plates of **1** as a solvate with half a mole equivalent of C_6H_6 (dec. 228–230 °C). Anal. Calc. for $C_{25}H_9BF_9$: C, 61.14; H, 1.85. Found: C, 61.14; H, 1.76%. NMR data for **1** (25°C). ^{1}H-NMR: δ 7.30 (dd, 1H, *H*-2 or *H*-5), 7.33 (dd, 1H, *H*-2 or *H*-5), 7.61 (dd, 1H, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 1$ Hz, *H*-1, *H*-3, or *H*-6), 7.79 (dd, 1H, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 1$ Hz, *H*-1, *H*-3, or *H*-6), 8.04 (dd, 1H, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 1$ Hz, *H*-1, *H*-3, or *H*-6), 8.94 (dd, 1H, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 1$ Hz, *H*-4). $^{11}B\{^1H\}$-NMR: δ 52.7. $^{13}C\{^1H\}$-NMR: δ 126.55, 126.92, 131.26, 132.64, 132.70, 133.11, 133.40, 139.59, 143.83, 146.83 (only ten assignable signals were detected). $^{19}F\{^1H\}$-NMR: δ -161.7 (m, 2F, *m-F*), -156.3 (m, 1F, *F*-9), -153.4 (m, 1F, *F*-11), -143.9 (m, 1F, *p-F*), -134.8 (m, 1F, *F*-10), -131.6 (dd, 2F, $^3J_{F,F} = 25$ Hz, $^4J_{F,F} = 9$ Hz, *o-F*), -125.1 (m, 1F, *F*-8).

3.3. Structural study of compound **1**

Due to the reactive nature of compound **1**, the crystals were handled under a blanket of dry mineral oil during mounting. A yellow crystal ca. 0.11 × 0.08 × 0.03 mm in size was selected for data collection, mounted on a glass fiber with apiezon grease, and rapidly transferred to the cold N_2 stream on the instrument. X-ray data for compound $\mathbf{1}\cdot 1/2C_6H_6$ were collected at 110(2) K on a Siemens SMART CCD diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) and 0.3°-wide ω-scans with a crystal to detector distance of 5.0 cm to yield a complete (98.6%) sphere of 5040 (3318 unique, $R_{int} = 0.0829$) data ($3.16 < 2\theta < 50.00°$). Other key crystallographic parameters are as follows: $C_{25}H_9BF_9$, $M = 491.13$, triclinic space group $P\bar{1}$; $a = 7.428(1)$, $b = 10.082(2)$, $c = 13.041(2)$ Å; $\alpha = 97.950(4)$, $\beta = 90.841(4)$, $\gamma = 97.775(4)°$; $V = 957.9(3)$ Å^3; $Z = 2$; $\mu = 0.159$ mm^{-1}. The structure was solved by direct method and refined by full-matrix least-squares against F^2 using the SHELXTL/PC (ver. 5.03) package. The refinement converged with residuals of R_1 (wR_2) = 0.1268 (0.1661) for 316 refined parameters and all 3318 reflections.

4. Supplementary material

The complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 165581 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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