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Highly Electron-Deficient Dicyanomethylene-Functionalized Triarylboranes with Low-Lying LUMO and Strong Lewis Acidity

Guanming Liao, Xing Chen, Yali Qiao, Kanglei Liu, Nan Wang, Pangkuan Chen,* and Xiaodong Yin*



ricoordinated organoboranes are intrinsically electron-L deficient and Lewis-acidic because of the vacant p orbital of the boron atom. When incorporated into a π -conjugated skeleton, the $p-\pi^*$ interactions between boron and the jointing groups can tune the optical and electronic properties.¹ On the basis of these characteristics, numerous boroncontaining organic π -conjugated materials have been constructed for various applications, such as anion sensing, organic electronics,³ catalysis,⁴ and biological imaging.⁵ In particular, low-lying lowest unoccupied molecular orbital (LUMO) energy levels of conjugated materials with the introduction of electron-deficient boron are highly desirable in n-type or ambipolar semiconductor material.⁶ Thus far, in the development of boron-containing compounds with a low-lying LUMO, a variety of structural modifications have been explored, for example, introducing bulky protective groups with electron-withdrawing properties (e.g., 2,4,6-tri-(trifluoromethyl)phenyl (FMes)),7 embedding boron in polycyclic aromatic hydrocarbons (PAHs),⁸ and placing the triarylborane in conjugation with other strong electronacceptors.⁹ Because of the limited choices of the bulky group, the first method usually does not have a very pronounced effect, whereas the latter two usually suffer from the challenging synthesis and poor solubility of the extended π conjugated skeletons. The cyano group is widely used as a strong electron-withdrawing building block to improve the electron-accepting properties of compounds. Among the cyano-based acceptors, tetracyano-9,10-anthraquinonedimethane (TCAQ) has attracted increasing attention due to its applications in electrical materials.¹⁰ In addition, TCAQ achieves planarity and aromaticity during reduction, and the charge is dispersed on the two dicyanomethylene groups and the central anthracene.¹¹ On the basis of the above, we tried to combine the structural characteristic of TCAQ and triarylbor-

anes to develop a series of acceptors with strongly suppressed LUMOs and to further tune the electronic properties.

Herein we report the design and synthesis of a series of dicyanomethylene-functionalized triarylboranes (Figure 1a). Both 2,4,6-tri(t-butyl)phenyl (Mes*)^{7b,12} and ^FMes groups were used for the stabilization of the tricoordinated boron compound, and the dicyanomethylene was introduced in the ortho position relative to the boron on the phenylene groups to increase the electron deficiency. The resulting boron-doped six-membered ring has four π -electrons, which possibly exhibit antiaromatic character and thus enhance the Lewis acidity of boron.¹

The syntheses of FMesB-ACN and Mes*B-ACN are described in detail in the Supporting Information. TA was prepared according to the procedure reported by the Piers' group.¹⁴ As shown in Figure 1b, TA was treated with BCl₃ in CH₂Cl₂ to generate the chloroborane compounds (Cl-BA) and then directly used for the next step without purification beyond the removal of solvents and Me₂SnCl₂ byproduct. Then, crude Cl-BA was treated with ^FMes-Li and Mes*-Li in toluene to obtain ^FMesB-A and Mes*B-A, respectively. Oxidation of ^FMesB-A and Mes*B-A with CrO₃ in refluxing acetic acid produced carbonyl-functionalized triarylboranes ^FMesB-AQ and Mes*B-AQ, which were further transformed to dicyanomethylene-functionalized compounds under Knoevenagel conditions to yield ^FMesB-ACN and Mes*B-ACN, respectively. Dicyanomethylene-functionalized triarylboranes

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Figure 1. (a) Molecular design and (b) synthesis routes of dicyanomethylene-functionalized triarylboranes. ^aThe yield is estimated starting from TA. (c) ORTEP plots of ^FMesB-AQ, Mes*B-AQ, ^FMesB-ACN, and Mes*B-ACN with thermal ellipsoids drawn at 50% probability.

exhibited sufficient stability and could be purified by column chromatography on silica gel in an ambient atmosphere without noticeable decomposition. These molecular structures were fully characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry, and X-ray crystallography. Single crystals of FMesB-A, Mes*B-A, FMesB-AQ, Mes*B-AQ, FMesB-ACN, and Mes*B-ACN were obtained by the slow evaporation of hexane/dichloromethane solutions. The structures of these compounds are shown in Figure 1c and Figure S1. Selected bond lengths and angles are listed in Table S4. It is noteworthy that the dihedral angles between the two fused benzene rings of carbonyl-bridged triarylboranes are 6.1(1)° for ^FMesB-AQ and 8.94 (6)° for Mes*B-AQ, which indicates that the boraanthracene skeleton adopts an almost planar geometry. However, the dihedral angles between the two fused benzene rings of dicyanomethylene-functionalized compounds are 21.23(9)° for FMesB-ACN and 19.62(8)° for Mes*B-ACN, revealing a butterfly-like structure due to the steric hindrance between the dicyanomethylene moieties and the boraanthracene skeleton.

The photophysical properties of carbonyl- and dicyanomethylene-functionalized compounds were recorded in tetrahydrofuran (THF) (Figure 2a). A slight red shift in the absorption of the dicyanomethylene-functionalized derivatives compared with the carbonyl-bridged compounds can be



Figure 2. (a) UV–vis spectra $(1 \times 10^{-5} \text{ M in THF})$ and (b) cyclic voltammetry data of carbonyl- and dicyanomethylene-functionalized compounds in THF for Mes*B-AQ and CH₂Cl₂ for the rest.

observed (see Table 1). The electrochemical properties of these compounds were examined by cyclic voltammetry in

Table 1. Photophysical and Electrochemical Data of Carbonyl- and Dicyanomethylene-Functionalized Compounds

compound	λ_{onset} (nm)	$E_{\rm red}$ (V) ^{<i>a</i>}	LUMO (eV) ^b	LUMO (eV) ^c
^F MesB-AQ	368	-1.46	-3.34	-3.24
Mes*B-AQ	366	-1.73	-3.07	-2.84
^F MesB-ACN	395	-1.14	-3.66	-3.65
Mes*B-ACN	392	-1.28	-3.52	-3.38

^{*a*}Half-wave potentials of first reductive waves versus $Fc^{+/0}$. ^{*b*} E_{LUMO} = $-(4.8 + E_{red})/eV$.^{7b,16} ^{*c*}DFT-calculated results by Gaussian 09 at the B3PW91/6-311+G* level of theory.

CH₂Cl₂ and THF (for **Mes*B-AQ**), respectively (Figure 2b). In the carbonyl-bridged triarylboranes, the first reversible reduction waves were observed at $E_{1/2} = -1.46$ (^F**MesB-AQ**) and -1.73 V (**Mes*B-AQ**, vs Fc^{+/0}), which further positively shifted to -1.14 V vs Fc^{+/0} for ^F**MesB-ACN** and -1.28 V vs Fc^{+/0} for **Mes*B-ACN**, respectively. This observation clearly indicates that the dicyanomethylene group significantly contributes to lowering the LUMO levels of these compounds to ca. -3.66 eV for ^F**MesB-ACN**. These results demonstrate the strong electron-accepting ability of triarylboranes bearing a dicyanomethylene group among the majority of the reported triarylboranes.¹⁵ Density functional theory (DFT) calculations of ^F**MesB-AQ**, **Mes*B-AQ**, ^F**MesB-ACN**, and **Mes*B-ACN** were conducted using the Gaussian 09 D.01 soft package at the B3PW91/6-311+G*//B3LYP/6-31G** level of theory, respectively. The LUMO energy levels exhibited good agreement with the values estimated from CV data, as shown in Table 1 and Figure S12. Time-dependent (TD)-DFT calculations at the PBE0/6-311+G* level of theory were also conducted to get an in-depth understanding of the vertical transitions of the dicyanomethylene-functionalized compounds. (See Figures S13 and S14 and Table S7 for details.) In addition, all of these compounds are nearly nonemissive in THF solution, and the photoluminescence spectra are shown in Figure S9.

Encouraged by the excellent reversibility of the electrochemical reduction, spectro-electrochemistry was utilized to monitor the reduction processes of dicyanomethylenefunctionalized compounds. Figure S16b shows the different absorption spectra of Mes*B-ACN at sufficiently negative potentials to confirm the reduction reaction. The one-electron reduction of Mes*B-ACN to its radical anion results in new peaks growing around 682 nm. Further reduction is accompanied by spectral changes, with the emergence of a new absorption maxima at 551 nm, which is indicative of the generation of the dianionic species Mes*B-ACN²⁻. Reverting the applied voltage to 0 V resulted in the recovery of the absorption spectrum of the neutral species. The chemical reductions of Mes*B-ACN were carried out using CoCp*2 $(Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl) and KC₈ for single- and double-electron reduction, respectively (see Figure S16a). Upon the addition of 1.2 equiv of $CoCp_{2}^{*}$ to a solution of Mes*B-ACN in THF, the color of the solution changed from yellow to red, displaying broad absorption bands around 693 nm, which is consistent with the electrochemically reduced radical anion Mes*B-ACN-•. A solution of dianion Mes*B- ACN^{2-} was obtained by adding 2.4 equiv of KC₈, resulting in the appearance of the absorption bands at 518 nm. TD-DFT calculations of reduced products were conducted at the UPBE0/6-311+G* level of theory based on the optimized structures, as shown in Figure S16c and Table S9. The broad absorption peak of Mes*B-ACN^{-•} at ca. 700 nm can be assigned to a transition of highest occupied spin orbital (HOSO) \rightarrow lowest unoccupied spin orbital (LUSO) of both α and β spin orbitals. For Mes*B-ACN²⁻, the absorption at ca. 530 nm can be attributed to a transition of HOMO-1 \rightarrow LUMO+3. Electron paramagnetic resonance (EPR) data of Mes*B-ACN^{-•} were recorded in THF solution at room temperature, and the spectrum is shown in Figure S8, revealing a broad signal without a hyperfine structure. The spin density of Mes*B-ACN-• was calculated at the UB3LYP/6-31G** level of theory, which shows that the radical spin is mainly distributed over the dicyanomethylene part with a relatively smaller distribution on the boraanthracene skeleton. Therefore, the lack of a hyperfine structure in the EPR could be due to the conjugation over the boraanthracene skeleton. In addition, attempts to reduce FMesB-ACN by treatment with an excess of CoCp^{*}₂ or KC₈ in THF failed due to the poor stability of the reduction product.

X-ray crystallographic analysis confirmed the generation of the corresponding monoanion (Mes*B-ACN^{-•}) and dianionic species (Mes*B-ACN²⁻), as shown in Figure 3. Some selected bond lengths of the reduced products are given in Table S4. In the crystal structures, the B–C_{Mes*} bond length of Mes*B-ACN^{-•} (1.559(9) Å) is shorter than that in the neutral state (1.583(2) Å) or the dianionic species (1.597(6) Å). The dihedral angles between the two fused benzene rings of Mes*B-ACN^{-•} (2.1(8)°) and Mes*B-ACN²⁻ (4.2(2)°) are



[Mes*B-ACN]⁻ · [CoCp*₂]⁺ [Mes*B-ACN]²· K₂²⁺

Figure 3. ORTEP plots of (a) $[Mes^*B-ACN]^{-\bullet} [CoCp^*_2]^+$ and (b) $[Mes^*B-ACN]^{2-} K_2^{2+}$, with thermal ellipsoids drawn at 50% probability.

much smaller than those of Mes*B-ACN $(19.62(8)^{\circ})$, suggesting that the fused benzene rings of the two reduced products are nearly coplanar. It is noteworthy that the bond lengths of the C-C bond adjacent to the dicyanomethylene group are 1.442(8) Å for the Mes*B-ACN^{-•} and 1.497(5) Å for the **Mes*B-ACN**^{2–}, which are much longer than that in the neutral compound (1.365(2) Å), indicating the formation of single-bond character in dianionic species. As a result, the conformation changed from a butterfly to a coplanar structure during the reduction process. The elongated lengths of the C-C double bond in the reduced species result in an increment of torsion angles for the twisted dicyanomethylene group to boraanthracene skeleton from 44.1(8)° for Mes*B-ACN^{-•} to $68.3(6)^{\circ}$ for Mes*B-ACN²⁻, respectively. In addition, the bond lengths of C-N in cyano group exhibit pronounced elongation from 1.147(2) and 1.143(2) Å of neutral molecule to 1.160(8) and 1.168(7) Å for Mes*B-ACN^{-•} and 1.158(6) and 1.156(6) Å for Mes*B-ACN²⁻, which is similar to the reduction of TCAQ.^{10a,11} Proton and carbon NMR were recorded for dianionic species in THF- d_{8} , which exhibit a relative upfield shift in comparison with that of neutral compounds (see Figures S10 and S11).

NICS_zz values were calculated at the B3LYP/6-31G^{**} level of theory for the optimized structures, as shown in Figure S15.¹⁷ In the neutral molecule, the NICS(0)_zz value of the boron-doped six-member ring is 27.44 indicating pronounced antiaromaticity, whereas the NICS(1)_zz values are 9.34 and 6.41, respectively. For Mes*B-ACN^{-•}, the NICS(0)_zz value is ca. 9.76, and the NICS(1)_zz values are -8.07 and -8.15, signifying a decrease in the antiaromatic character. For Mes*B-ACN²⁻, the NICS(0)_zz value is ca. -11.43, and the NICS(1)_zz values are -28.27 and -26.30, revealing a dramatic switch to aromatic character, which is consistent with the reduction of TCAQ.^{10a,11}

The Lewis acidity of ^FMesB-ACN was first tested by the Gutmann–Beckett method¹⁸ to obtain the acceptor number (AN) at ca. 29 in CDCl₃ (Figure S2 and Table S5), which is higher than that of ^FMes containing borafluorene (AN = 14.1).¹⁹ In addition, the fluoride anion (F⁻) binding experiments were conducted via both UV–vis and NMR spectroscopy. The UV–vis absorption spectra showed that the absorption around 268 nm decreased, and a new band appeared at 318 nm, adding F⁻ to ^FMesB-ACN in THF (see Figure 4a). The fitting of the titration data indicated a very strong binding process with a binding constant toward F⁻ to be



Figure 4. UV–vis absorption spectral changes upon the addition of TBAF·3H₂O to a THF solution of (a) ^FMesB-ACN and (b) Mes*B-ACN ($c = 1.0 \times 10^{-5}$ M). Inset: Illustration of F-bonded ^FMesB-ACN and Mes*B-ACN from DFT calculations at the B3LYP/6-31+G(d,p) level of theory.

much higher than 1×10^7 M⁻¹ (see Figure S5).²⁰ The ¹¹B NMR signal shifted to ca. 2.6 ppm in THF- d_{8} , indicating the formation of tetracoordinated borate, whereas ¹H NMR spectrum also exhibited a clean and completely conversion (see Figure S3). It is noteworthy that treatment with water cannot convert the F⁻ complex of the NMR sample back to the tricoordinated boron, revealing the strong F⁻ affinity. The electrospray ionization (ESI) mass spectrometry was also able to detect the ion peaks of ^FMesB-ACN- F^- (Figure S4). The Mes*-substituted boranes seldom show adequate anion binding owing to the steric hindrance of the Mes* group.9a Interestingly, we observed that Mes*B-ACN was able to form coordination complexes with the fluoride anion via both UVvis spectra and ¹¹B NMR (Figure 4b, Figure S6). On the basis of this spectral change, the binding constant of Mes*B-ACN toward \hat{F}^- was determined to be $K = 7.20 \times 10^5 \text{ M}^{-1}$ (log K =5.86; see Figure S7),²⁰ which is remarkable because the binding constant of other Mes*-functionalized boranes toward F⁻ usually cannot be determined. In the ¹¹B NMR spectrum, a new signal appeared at 3.3 ppm upon the addition of ca. 2.0 equiv of fluoride ions in THF- d_8 ; however, ¹H NMR spectroscopy showed complex signals for the fluoride ionbinding products, which indicates evidence of side reactions (Figure S6). The fluoride ion affinities (FIAs) were computationally evaluated for ^FMesB-ACN and Mes*B-ACN at M06-2X/6-311+G(d,p)//B3LYP/6-31+G(d,p) to ca. 386.8 (92.44 kcal/mol) and 292.5 kJ/mol (69.9 kcal/mol), respectively. (See Table S11 for details.) The FIA of ^FMesB-ACN exhibits pronounced affinity for the fluoride anion, which is in line with the highest values previously reported in triarylboranes.^{19,21}

In this work, we reported the synthesis of a series of dicyanomethylene-functionalized triarylboranes. The introduction of the dicyanomethylene group dramatically enhances the electron-deficient character, as evidenced by low-lying LUMO energy levels. The single-crystal structures exhibit the typical quinoidal character with a butterfly-like structure. The spectroscopy and structural character during the reduction of the dicyanomethylene-functionalized compounds were studied. The mono- and dianion species of Mes*B-ACN were obtained via reduction with $CoCp_2^*$ and KC_8 , respectively, which exhibited a molecular configuration transformation from a butterfly-like to a planar skeleton with an aromatization of the boron-doped six-membered ring reflected via DFT calculations. The fluoride anion titration confirmed the pronounced Lewis acidity of these compounds, with the binding constant of ^FMesB-ACN to fluoride anion in THF of >1 \times 10⁷ M⁻¹. This work presents a series of highly electron-deficient triarylborane compounds with a novel skeleton and therefore could improve the structural and functional diversity of boron-containing molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01983.

Experimental procedures, X-ray analysis, UV-vis spectra, electrochemical data, computational studies, and characterization data like NMR and high-resolution mass spectrometry (HRMS) spectra (PDF)

Accession Codes

CCDC 2010875, 2013629–2013630, and 2068081–2068085 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc. cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Xiaodong Yin Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China; orcid.org/ 0000-0001-7644-6744; Email: vinxd18@bit.edu.cn
- Pangkuan Chen Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China; orcid.org/ 0000-0002-8940-7418; Email: pangkuan@bit.edu.cn

Authors

Guanming Liao – Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China; School of Chemistry and Chemical Engineering, Jiangxi Science and Technology Normal University, Nanchang, Jiangxi 330013, P. R. China

- Xing Chen Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China
- Yali Qiao Beijing National Laboratory for Molecular Sciences, Key Laboratory of Green Printing, CAS Research/ Education Centre for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (ICCAS), Beijing 100190, P. R. China
- Kanglei Liu Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China
- Nan Wang Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China; Ocid.org/ 0000-0001-5973-4496

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c01983

Notes

The authors declare no competing financial interest.

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