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Boron(III)

Core-Expanded

Antiaromatic Boron(III) Subphthalocyanine Analogues**

Carbazosubphthalocyanines:

Joseph Y. M. Chan, Takahiro Kawata, Nagao Kobayashi,* and Dennis K. P. Ng*

Abstract: Condensation of 1,8-diamino-3,6-dichlorocarbazole with a series of disubstituted 1,3-diiminoisoindolines followed by the treatment with BF₃·OEt₂ led to the formation of the corresponding core-expanded boron(III) subphthalocyanine analogues. These airstable π -conjugated boron(III) carbazosubphthalocyanines possess two boron-containing seven-membered ring units and a 16 π -electron skeleton, which represent the first examples of antiaromatic boron(III) subphthalocyanine analogues as supported by spectroscopic and theoretical studies. The molecular structure of one of these compounds was also unambiguously determined by single-crystal X-ray diffraction analysis. In contrast to typical boron(III) subphthalocyanines which adopt a cone-shaped structure, the π skeleton of this compound is almost planar.

Antiaromatic porphyrinoids with a 4n m-electron core have received considerable attention.¹ Apart from their intrinsic interest from theoretical point of view, these compounds exhibit intriguing optical and electronic properties. They can serve as potential electrode-active materials in rechargeable batteries² and ambipolar semiconductors for field-effect transistors.3 To date, a number of antiaromatic porphyrins4 and their ring-expanded,5 ring-contracted (e.g. norcorroles⁶ and tetrahydronorcorroles⁷) and core-modified (e.g. isophlorins.1c.8 oxatriphyrins.9 and phenanthriporphyrin¹⁰) analogues have been reported. The aromaticity of these systems can be modulated through changing the physical and chemical environments, and by photo-switching the electronic states.1a Stacking of antiaromatic porphyrin molecules, for example, would diminish the inherent antiaromaticity and promote delocalization of the π electrons, thereby enhancing their two-photon absorption property.11 Despite the advances in the study of these systems, antiaromatic azaporphyrinoids are relatively scarce. To our knowledge, only a few such derivatives, including phthalocyanines,12 hemiporphyrazines,13 diazaporphyrins,14 and pentabenzotriazasmaraqdvrins¹⁵ have been reported so far. We report herein the first examples of antiaromatic boron(III) subphthalocyanine (SubPc) derivatives, namely boron(III) carbazosubphthalocyanines, which represent the smallest

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antiaromatic azaporphyrinoids reported so far. Typically, SubPcs contain three aza-linked isoindole units, forming a 14 m-electron aromatic skeleton around a boron center, and the molecules adopt a cone-shaped structure.¹⁶ Recently, we have reported two series of analogues in which one of the pyrrole units is replaced with a six- or seven-membered heterocycle without alternating the inner m-electron core (Figure 1).¹⁷ In contrast, these boron(III) carbazosubphthalocyanines are core-expanded having a 16 m-electron skeleton. The antiaromatic character of these compounds has been revealed by spectroscopic and theoretical studies as reported and discussed below.



a peripheral seven-membered ring (this work)

Figure 1. Molecular structures of SubPcs and their analogues.

These boron(III) carbazosubphthalocyanines were prepared in two steps as shown in Scheme 1. 1,8-Diamino-3,6dichlorocarbazole (1) was first treated with 2.1 equivalent of disubstituted 1,3-diiminoisoindolines 2a-d in refluxing ethanol overnight. The solvent was then removed, and the residue was mixed with BF3:Et2O and 1.8-diazabicvclo[5.4.0]undec-7-ene (DBU) in 1-chloronaphthalene. After stirring at 150 °C for 2 h, the corresponding boron(III) carbazosubphthalocyanines 3a-d were formed and isolated in 24-47% yield. Attempts were made to isolate the intermediate product of 1 and 2a, but its low solubility in common organic solvents and high polarity hindered this process. Based on the mass spectrometric data (Figure S1 in Supporting Information), it is likely that the 1:2 condensed product 4 was formed. Similar condensation reactions of diamines and 1,3-diiminoisoindolines have been reported previously.18 Addition of BF3·Et2O led to chelation followed by cyclization. In the absence of DBU, the yield was slightly reduced (to 25% for 3a). indicating that it might play a role in this reaction. Interestingly,

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when BCl₃ and BBr₃, which are common reagents for SubPc synthesis, were used instead of BF₃-Et₂O, the desired boron(III) carbazosubphtalocyanines could not be obtained. It seems that the axial fluoro ligand can stabilize the expanded core as in the case of the SubPc analogues containing a peripheral seven-membered heterocycle.^{17b} Furthermore, when BF₃:Et₂O was added during the reaction of 1 and 2a, the one-pot reaction gave the metal-free phthalocyanine formed by self-cyclization of 2a in 18% yield, while only 4% yield of 3a was obtained. The experimental details and characterization data are given in the Supporting Information.



Scheme 1. Synthesis of boron(III) carbazosubphthalocyanines 3a-d.

Single crystals of 3a suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of 3a in CHCl₃. This compound crystallizes in the triclinic system with a P-1 space group with two molecules in a unit cell. The structure also contains two solvated CHCl₃ for each molecule. Figure 2(a) shows the top view of the molecular structure. Unlike typical SubPcs which have a cone-shaped structure, the π skeleton of 3a is almost planar [Figure 2(b)]. The central boron atom deviates from the mean plane defined by the three coordinating nitrogen atoms by 0.49 Å, which is significantly smaller than the values for typical SubPcs (0.59-0.66 Å).17b The sum of the N-B-N angles which is another parameter to reflect the extent of planarity, is 332°, which is also significantly larger than those for typical SubPcs (308-316°).17b With an essentially planar structure, the molecules stack in a head-to-tail manner with the axial fluoro ligands pointing each other in the crystal lattice (Figure S2 in Supporting Information). A close examination of the C-N bond distances along the inner core did not reveal significant bondlength alternation



Figure 2. Molecular structure of 3a. Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at the 30% probability level. (a) Top view (b) Side view.

The ¹H NMR spectrum of **3a** in CDCl₃ showed two doublets at δ 7.27 and 6.91 (with a ⁴J_{HH} of 2.4 Hz) for the two sets of carbazole protons, and two singlets at δ 6.69 and 6.58 for the two sets of isoindole protons. For **3b**, while the two doublets for the carbazole protons (at δ 7.13 and 6.92) were essentially unshifted, the isoindole protons' signals (at δ 7.90 and 7.83) were less upfield-

shifted compared with 3a. The spectrum of 3c was similar to that of 3a. The carbazole protons of 3d resonated at 5 7.03 and 6.68, while the isoindole protons resonated at 5 7.16 and 6.98. All these signals were slightly upfield-shifted when compared with those for carbazoles and phthalocyanines, which could be attributed to the paratropic ring current arising from the antiaromatic core of these compounds. The effect, however, was not as large as that of the previously reported porphyrincids based on the degree of upfield shift.⁵⁶ The relatively large upfield shift for the two isoindole protons' singlets for 3a, 3c, and 3d could be due to the additional anisotropic shielding effect by the neighboring aryl rings.

o provide further insight about the paratropic ring current of the one, we replaced the axial fluoro ligand of **3d** with a methoxy around by treating **3d** with NaOMe in 5% MeOH in tetrahydrofuran. The axial methoxy protons of the substituted product (compound or) resonated as a singlet at δ 3.73, which was significantly dow. field-shifted compared with that of the SubPc-OMe analogue (\sim 1.50).¹⁹ The signal also appeared at a more downfield pc diving the methoxy protons' signal typically in the range of δ 2.6-3.1.²⁰

stronger evidence of antiaromaticity came from the ¹¹B and MR spectroscopic data. The ¹¹B NMR spectra of 3a, 3b, 3c. Job of the second state o $({}^{1}J_{BF} = 56.0 \text{ Hz}), 9.10 ({}^{1}J_{BF} = 54.9 \text{ Hz}), \text{ and } 9.13 ({}^{1}J_{BF} = 52.7 \text{ Hz}),$ respectively. Compared with the typical ¹¹B chemical shifts for S Jb, cs (δ-11 to -16), 17b, 19,21 these signals were largely dc " ,field-shifted. Similarly, the ¹⁹F NMR signals for **3a** (at δ -93.7), \sim (at δ -91.4), 3c (at δ -91.2), and 3d (at δ -91.0) were also significantly deshifted compared with those for boron supplicitly and our previously reported Supr'c derivatives (8 -149).17b The large downfield shift of these signals clearly indicates the presence of paratropic ring current. The ¹H NMR spectroscopic data are in accord with the result of nucleus-independent chemical shift (NICS) calculations using Live CAM-B3LYP/6-31G(d) basis set.22 As shown in Figure 3(a), the computed NICS values in the central core region of the density fing lonal theory (DFT)-optimized structure of 3a are all positive successting that paratropic ring current is exceeding over diatropic ring current, while in the outer rim region, the values become sma er and finally change to negative. This is further confirmed tropy of the current-induced density (ACID) calculations the CAM-B3LYP/6-31G(d) level,23 which show counterc ccl wise paratropic ring current flow in the inner core and crockwise diatropic ring current flow in the four fused benzo grou is [Figure 3(b)]. In contrast, clockwise diatropic ring current is shown for SubPcs both in the central core and the three ben o groups (Figure S3 in Supporting Information). The results indi ate that the effective chromophore region is that shown in bold lines in Figure 3(c) and the outer four fused benzo groups n ve little contribution in considering the theoretical absorption s, actroscopic aspect of this molecule. This can explain why these protons are not substantially upfield-shifted as observed for other antiaromatic porphyrin derivatives.5-8

Apart from 3a, we also computed the ¹H NMR data for the hypothetical boron-free analogue of 3a. The signals of the two inner pyrrole protons were predicted at 3 20.47, which were substantially downfield-shifted compared with those of the hypothetical boron-free SubPc analogue [at 8 0.76 (convex site)]

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and 5.78 (concave site)] (Figure S4 in Supporting Information). The NICS(0) values in the center of the boron-free analogue of **3a** and SubPc were calculated to be 8.33 and -13.5, respectively (Figure S5 in Supporting Information). In addition, we also calculated the chemical shifts of the OMe protons' signals of **5** and SubPc-OMe. They were found to appear at δ 4.21 (1 H) and 3.69 (2 H) (for **5**) and at δ 1.93 (1 H) and 1.06 (2 H) (for SuPc-OMe) (Figure S6 in Supporting Information), which were in good agreement with the experimental data. All these theoretical results further support the antiaromatic character of the carbazosubphthalocyanine core.



Figure 3. (a) Computed NICS values (in ppm) for the DFT-optimized structure of 3a at various positions (2.6-dimethylphenoxy groups were omitted for clarity). (b) Calculated ACID plot for 3a at an issoratue of 0.03. (c) The effective chromophore region according to the NICS calculations.

Figures 4(a) and 4(b) show the electronic absorption and magnetic circular dichroism (MCD) spectra of **3a** in CHCl₃. In contrast to the reported spectra of SubPcs, which have (4n+2)π type characteristics.¹⁶ it showed a very weak and broad absorption envelope in 600-900 nm and an intense peak at 416 nm with a tail extending to ca. 570 nm. The spectral features of **3b-d** and **5** were similar except that an additional band at 509 nm (for **3b**) or 504 nm (for **3c**) was also observed (Figure S7 in Supporting Information), which might be due to the n- π^* transition arising from the sulfur-containing substituents. These

macrocycles.24,25 Corresponding to the weak absorption band in 600-900 nm, a negative MCD envelope was detected, while the sign of MCD signal changed from positive to negative on going from ca. 420-570 to ca. 325-420 nm. Since there are no degenerate states in neither the ground nor excited states due to low symmetry of the molecule, these are all Faraday B-terms appearing closely to the absorption peaks or shoulders and arise from mixing between closely related states linked by a magnetic dipole transition moment.²⁶ To reveal these spectral features, the absorption spectrum of 3a was simulated by time-dependent (TD)-DFT calculations at the CAM-B3LYP/6-31G(d) level [Figure 4(c)] with results for low-energy $\pi \rightarrow \pi^*$ transitions summarized in Table 1.27 Although the energies were slightly overestimated, the experimental spectrum was nicely reproduced. The data in Table 1 suggest that, a very weak, two weak, a medium, and an intense bands labelled respectively as S, CT, N1, and (P1+N2) bands are in ascending energy. The S band (the HOMO-LUMO transition) corresponds to an intrashell transition so that it carries no electric dipole oscillator strength and is therefore very weak. The CT band is characteristic of this system with transition occurs from an outer benzene ring to the inner ligand. The relationship between the N and P bands is similar to that of the Soret and Q bands in (4n+2)π porphyrinoids so that N bands are generally weak while P bands are stronger. In Figure 4(b), the absorptions in 600-900, 430-600, and 390-430 nm regions correspond to S, CT+N1, and P1+N2 bands, respectively. If we know the energy of six frontier orbitals labelled as h- (HOMO-2), h+ (HOMO-1), s- (HOMO), s+ (LUMO), I-(LUMO+1), and I+ (LUMO+2) of the "ligand perimeter", not only the intensity but also the MCD sign can often be reasonably explained.24,25



Figure 4. Experimental (a) MCD and (b) UV-Vis spectra of 3a in CHCI₃ and (c) a simulated UV-Vis spectrum of 3a calculated at the CAM-B3LYP/6-31G(d) level.

Figure 5 shows the energy diagram and the nodal patterns of some frontier molecular orbitals (MOs) of **3**a. Both the HOMO and LUMO have four nodal planes, indicating that they are originated from orbitals of angular momentum of ± 4 in a high-symmetry parent hydrocarbon perimeter, and that this is a 16 π system. The

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HOMO-1 and HOMO-2 may not correspond to the h+ and horbitals, respectively, since they have higher coefficient in the outer fused benzo moieties and only two nodes can be drawn for HOMO-2. The HOMO-3 and HOMO-4 may correspond to the h+ and h- orbitals, respectively, since three nodal planes can be drawn in the central part of their MOs (Figure S8 in Supporting Information) and the coefficients of MOs are large even in their central moieties. The relatively large contribution of these orbitals to the N1 and N2 bands (Table 1) may also support this assignment. Therefore, by assuming that the HOMO-4, HOMO-3. HOMO, LUMO, LUMO+1, LUMO+2 correspond to the h-, h+, s-, s+, l-, and l+ orbitals of the "ligand perimeter", respectively, and using the energy level values of these MOs, we can calculate the relative orbital energy differences as follows: $\Delta L = 0.99$, $\Delta S = 4.27$ $\Delta H = 0.19$, $\Delta LS = 4.04$, $\Delta HS = 3.40$, $\Delta HSL = 2(\Delta HS - \Delta LS) = -1.28$, $\Delta HL = \Delta H - \Delta L = -0.80$, and $\Sigma HL = \Delta H + \Delta L = 1.18$ eV. Furthermore. from the $|\Delta HSL| > \Sigma HL > |\Delta HL|$ relationship. C_{22} symmetry of the molecule, and the fact that the orbitals h- and l- do not have identical symmetry with respect to a plane of symmetry perpendicular to the molecular plane, we can infer that 3a can be classified as an orbital-shift-dominated system of S-perturbed perimeters.^{24a} Because ΔHSL is negative, the expected MCD sign pattern for the N1 and P1 (N2) transition is a +.- in ascending energy, which is consistent with the observed MCD signs in ca. 400-500 nm region

Table 1. Calculated Transition Energies, Oscillator Strength f, Assignment, and Composition for 3a

Energy/eV (nm)	f	Assign.	Composition (weight %)
2.00 (620.8)	0.0031	S	H(s.)→L(s+) (95%)
3.23 (384.3)	0.0259	CT	H-1→L(s+) (74%),
			H-2→L(s+) (13%)
3.29 (367.7)	0.0150	CT	H-2→L(s+) (63%),
			H-4(h.)→L(s+) (15%)
3.35 (370.2)	0.2895	N ₁	H-3(h+)→L(s+)(86%),
			H-2→L+1(l.)(5%)
3.59 (345.6)	1.0200	P1	H(s.)→L+1(l.)(45%),
			H-4(h.)→L(s+)(31%)
3.76 (329.4)	0.0019	N ₂	H-4(h_)→L(s+)(42%),
			H(s-)→L+1(l-)(40%)
3.84 (322.9)	0.0202		H-16→L(s+)(78%),
			H-17→L+1(l-)(10%)
3.97 (312.2)	0.0247		H-13→L(s+)(75%),
			H-16→L+1(I.)(14%)
4.00 (309.8)	0.2140		H-13→L(s+)(54%),
			H-14→L(s+)(26%)
4.13 (300.6)	0.2033		H-14→L(s+)(55%),
			H-13→L(s+)(23%)

The redox behavior of **3a-d** and **5** was investigated using cyclic voltammetry in CH₂Cl₂ (for **3a**, **3d**, and **5**) or 1,2-dichlorobenzene (for **3b** and **3c**, which had limited solubility in CH₂Cl₂). All the compounds exhibited a reversible oxidation and a reversible reduction (Figure S9 and Table S1 in Supporting Information). Compared with boron(III) subphthalocyanine chloride,²⁸ the half-wave reduction potentials ($E_{1/2}^{red}$) of these compounds were substantially less negative (ca. -0.9 V vs. -1.7 V), showing that they are better oxidizing agents. The electrochemical HOMO-LUMO gap for these compounds (1.72-1.83 V) was in good agreement with the energy of the S-band absorption (ca. 1.75 eV).

In summary, we have synthesized a series of novel coreexpanded SuPc analogues through condensation of diamine 1 and 1,3-diminoisoindolines 2a-d, followed by boron-induced complexation and cyclization. This synthetic approach has rarely

been reported for the preparation of SubPc derivatives. The molecular structure of one of these compounds has been determined, which shows a planar π skeleton. Despite bondlength alternation is not noticeably in the inner core and the peripheral ring protons are not significantly upfield-shifted, the positive computed NICS values, counter-clockwise ring current flow as shown in the ACID plot in the core, calculated downfield chemical shift values for the inner pyrrole protons of the hypothetical boron-free analogue of **3a** and the axial methoxy protons of 5, as well as the large downshift shift of the ¹¹B and ¹⁹F NMR signals strongly suggest the presence of paratropic ring curry nt. The antiaromatic character of these compounds has also beer inferred by UV-Vis and MCD spectroscopic studies together with DFT calculations. To our knowledge, these boron(III) carbazosubphthalocyanines represent the first examples of anuaromatic SubPc derivatives and the smallest antiaromatic azaL prohyrinoids reported so far.



Figur + 5. (a) Energy diagram and some frontier MOs of 3a. (b) Nodal patterns

HOMO-3, HOMO, LUMO, and LUMO+1 of **3a** at an isovalue of 0.012.

K **:ywords:** Antiaromaticity • subphthalocyanines • boron • mag.ietic circular dichroism • ring expansion

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subphthalocyanine derivatives and the smallest antiaromatic azaporphyrinoids reported so far.

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Boron(III) Carbazosubphthalocvanines: Core-Expanded Antiaromatic Boron(III) Subphthalocyanine Analogues