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Article

Chloro and Hydroxo Forms of a Boron(III) Subtriazaporphyrin Macrocycle

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cis-3,4-Dicyano-3-hexene undergoes cyclotrimerization with BCl_3 to form the new subtriazaporphyrin chloro-[hexaethylsubtriazaporphyrinato]boron(III). The hydroxo derivative of this macrocycle has also been made, and the X-ray crystal structure of the hydroxy form was determined. Electronic absorption and magnetic circular dichroism spectra of the hydroxo monomer species were interpreted using time-dependent density functional theory calculations.

Introduction

The subphthalocyanine macrocycles[1] (SubPcs) have received a great deal of attention because of their interesting optical and nonlinear optical properties.[2] Only a handful of reports have appeared, however, describing the chemistry of the structurally related subtriazaporpyrins (SubTaps), which lack the peripheral benzo groups of the SubPcs. Formed from the cyclotrimerization of 1,2-dicyanoolefins with boron trihalides, SubTaps were first described by Rauschnabel and Hanack.[3] Kobayashi and co-workers later reported on the syntheses and spectroscopic characterization of a series of SubTaps.[4,5] However, detailed comparisons between experimental and theoretically expected properties are still scarce.[6,7] This is, in part, due to the difficulties in the synthesis of SubTAPs compared to the SubPcs. The dicyanoolefin precursors tend to undergo anionic polymerization under vigorous reaction conditions.[8] High reaction temperature must thus be avoided, and reactive reagents, such as BBr_3, must be employed very carefully in the synthesis of SubTAPs.

In this paper, we describe the synthesis of a new SubTap, **1**, derived from *cis*-3,4-dicyano-3-hexene[9] and BCl_3, and its hydroxo form, **2**, and the investigation of their spectroscopic properties with the aid of time-dependent density functional theory (DFT) calculations. The peripheral ethyl groups give the macrocycle good solubility in most organic solvents and, for the purposes of the spectroscopic and theoretical studies, give rise to much smaller structural and/or electronic substituent effects than are present in previously reported SubTAPs.[3−5] Finally, we report the X-ray crystallographic structure determination of **2**.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ (Aldrich) on a Bruker 300-MHz Avance spectrometer equipped with a broad-band probe. UV−visible spectra were

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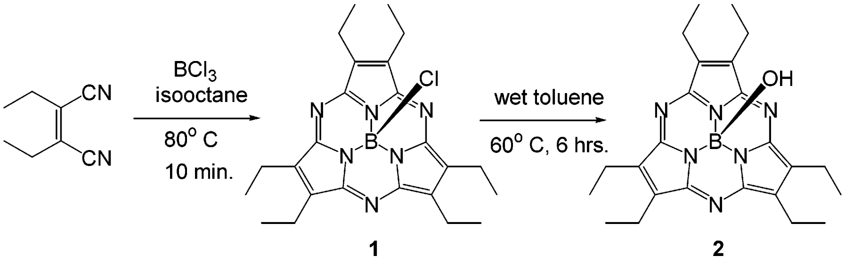
10.1021/ic051093u CCC: $33.50

Scheme 1. Synthetic Procedures for **1** and **2**



recorded on a Hitachi U-3410 spectrophotometer. High-pressure liquid chromatography was carried out in acetonitrile on a Hewlett-Packard series 1050, equipped with a 250-mm Econosil C18 column, with UV detection at 300 nm. Magnetic circular dichroism (MCD) spectra were run on a Jasco J-725 spectrodichrometer with a Jasco electromagnet that produced a magnetic field of up to 1.09 T. The magnitude of MCD features are expressed in terms of molar ellipticity per tesla, $[\theta]_M$/deg mol^{-1} dm^3 cm^{-1} T^{-1}. Mass spectra (fast atom bombardment, FAB) were obtained at the Michigan State University Mass Spectrometry Facility, which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health. Crystal structural analyses were performed on a Rigaku/MSC Mercury diffractometer with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SIR92) and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. The crystal data and experimental details are described in ref 10.

Computational Method. The *Gaussian 98* program[11] running on a NEC SX-4/128H4 supercomputing system operated by Tohoku University Supercomputing System Information Synergy Center was used to perform DFT calculations. The B3LYP with 6-31G(d) basis set was used for both geometry optimization and excited energy calculations.

Materials. Isooctane and cyclohexane were distilled from sodium. Dichloromethane was distilled from P_4O_{10}. Silica (technical grade, 230−400 mesh, Silicycle) was used for flash chromatography.

Synthesis. All synthetic procedures were carried out under an atmosphere of dry N_2(g). *cis*-3,4-Dicyano-3-hexene was prepared by the method of Fitzgerald et al.[9]

Cl[Et$_6$SubTap]B (1). A total of 0.10 g of *cis*-3,4-dicyano-3-hexene (0.75 mmol) was stirred in 5 mL of dry isooctane and cooled to 0 °C in an ice bath. A total of 0.37 mL of BCl_3 (2.0 M in isooctane, 0.75 mmol) was added to the mixture. The reaction mixture was heated to 80−90 °C with an oil bath for 10 min and then rotary evaporated to dryness. The crude product was dissolved in ethyl acetate/*n*-hexane (1:4) and flash chromatographed on silica, eluting with ethyl acetate/*n*-hexane (1:4). Slow evaporation of the solvent resulted in the formation of **1** as an orange microcyrstalline solid. Yield: 0.022 g (20%). Mp: 138−139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (t, $J = 7.5$ Hz, 18H), 3.19 (q, $J = 7.5$ Hz, 12 H). ^{13}C NMR (300 MHz, $CDCl_3$): 16.33, 18.32, 137.91, 155.84. HRMS (FAB): M$^+$ 448.2320 (calcd for $C_{24}H_{30}BClN_6$: 448.2318).

HO[Et$_6$SubTap]B (2). Heating **1** in wet toluene for 6 h at 60 °C resulted in the near-quantitative formation of **2**. Alternatively, recrystallization of **1** in aqueous ethanol resulted in the formation of **2**. Mp: 195−197 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (t, $J = 7.5$ Hz, 18H), 3.15 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 16.47, 18.20, 136.76, 157.04. UV−vis: $\lambda_{max} = 496$ nm ($\epsilon = 40\,000$ M^{-1} cm^{-1}), 481(sh), 324 (sh), 289 (35 000). MS (FAB): M$^+$ 430.32. Crystals of **2** were grown by slow evaporation of a $CHCl_3$/cyclohexane solution.

O([Et$_6$SubTap])$_2$ (3). Small quantities of the μ-oxo dimer were also produced in the conversion of **1** to **2**. They were identified by high-resolution mass spectrometry (HRMS) but could not be completely separated from **2**. HRMS (FAB): M$^+$ 842.5224 (calcd for $C_{48}H_{60}B_2N_{12}O$: 842.5214).

Results and Discussion

(a) Synthesis and Characterization. The cyclotrimerization of *cis*-3,4-dicyano-3-hexene proceeds under much milder conditions than those typically employed in SubPc syntheses (Scheme 1).[12] The modest yield of the chloro adduct, **1**, obtained using isooctane (2,2,4-trimethylpentane) as the solvent, can be attributed to the tendency of electron-deficient olefins to undergo anionic polymerization.[8] The axial chloride ligand in **1** is much more readily substituted than that in SubPcs, and heating **1** in wet toluene results in the near-quantitative formation of the hydroxy adduct **2** and the formation of small amounts of the μ-oxo dimer, **3**. Although **3** was identified using HRMS, we were unable to completely separate it from **2** and isolate it in sufficiently pure form for further spectroscopic characterization.

Subtriazaporpyrins **1** and **2** are unambiguously identified by ^{1}H NMR and HRMS. The methylene resonance in the starting material undergoes a downfield shift from 2.42 to 3.19 ppm with the formation of the 14-π-electron aromatic macrocycle. Using FAB ionization, the parent ion is readily identified for both compounds. Second in intensity are peaks that correspond to the loss of the axial ligand, i.e., the three-coordinate cation.[13]

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(10) Crystallographic data for $C_{48}H_{62}N_{12}O_2B_2$, **2**: space group *Pc* (No. 7), monoclinic, with unit cell dimensions $a = 12.859(4)$ Å, $b = 10.915(4)$ Å, $c = 16.933(6)$ Å, $\beta = 93.780(6)°$, $V = 2371(1)$ Å^3, $Z = 2$, $D_{calc} = 1.205$ g/cm^3. A total of 22 151 reflections were measured and 5567 were independent. Final $R_1 = 0.046$, $R_w = 0.050$ [$I > 4.0\sigma(I)$], GOF = 1.14.

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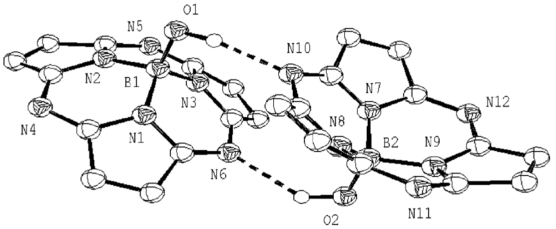

Figure 1. View of the molecular structure of **2**. Displacement ellipsoids are shown at the 50% probability level. The ethyl groups are omitted for clarity.

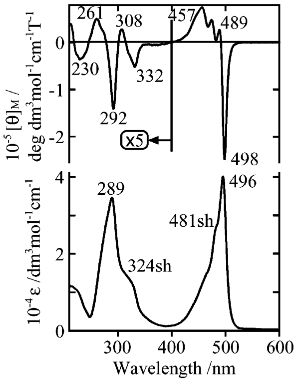

Figure 2. MCD (top) and absorption (bottom) spectra of **2** in hexane.

X-ray crystallography of **2** reveals the familiar cone shape of the SubPcs,[14−19] with the central boron atom in a nearly tetrahedral site bound to three nitrogen atoms and an axial hydroxy ligand (Figure 1). The asymmetric unit consists of two independent molecules located at general positions in the unit cell; the two molecules differ significantly only in the orientation of the peripheral ethyl groups. The B−N distances of the two molecules range from 1.500(5) to 1.514(5) Å and are comparable to 1.494 Å observed in the structure of the hydroxy-substituted SubPc.[16] Asymmetric units form dimers that are linked by hydrogen bonds between the axial hydroxy groups O1 and O2 and the ring nitrogen atoms N6 and N10.

(b) Spectroscopy. The simple spectral envelope in Figure 1 indicates the C_{3v} symmetry of **2**. Figure 2 shows MCD (top) and absorption (bottom) spectra of **2** in hexane. The absorption spectrum has the intense unsplit Q band at 496 nm. The corresponding MCD signal is a derivative-shaped Faraday *A* term with negative and positive envelopes at 498 and 489 nm, respectively, although the negative envelope shows a much greater intensity. Group theory suggests that SubPcs with C_{3v} symmetry have degenerate LUMOs, and the observed spectrum is consistent with this prediction. The spectral region between ca. 410 and 480 nm consists of several overlapping vibronic bands, and therefore the positive intensity of the *A* term is canceled partly by the superimposed Faraday *A* and *B* terms that arise from these vibronic bands. The relatively intense absorption band with molar absorption coefficients of ca. 3500 dm^3 mol^{-1} cm^{-1} appears in the Soret band region at 289 nm. However, the corresponding MCD signal has a smaller intensity than that of the Q band, supporting a smaller angular momentum change for the Soret band (note the magnification factor in the figure). The less extensive π-electron delocalization of the SubTaps, in comparison with the SubPcs, results in a blue shift for both the Q and Soret bands. Both features are also significantly diminished in intensity relative to the SubPcs.[4]

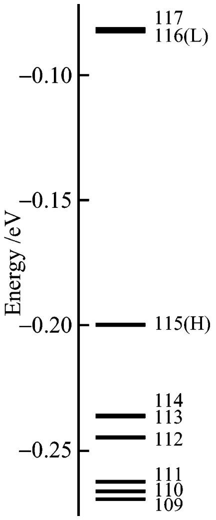

Figure 3. Partial MO energy diagram of **2**.

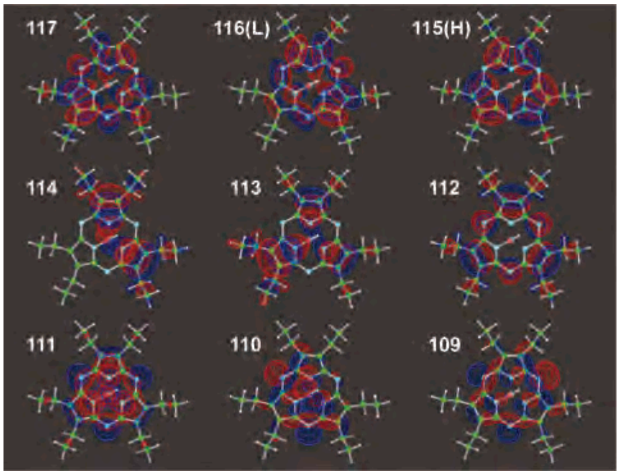

Figure 4. Frontier orbitals of **2** derived from B3LYP/6-31G(d) level DFT calculations.

(c) DFT Calculations. Figures 3 and 4 show the partial energy diagram and frontier orbitals of **2**, respectively. The LUMO (116) and LUMO+1 (117) are nearly degenerate; i.e., these have the *e* representation under the C_{3v} symmetry. Therefore, the Faraday *A* term in the MCD spectrum was observed for the Q band because the Q band is composed mainly of HOMO → LUMO (or LUMO+1) transitions (Table 1). The MO coefficients of the HOMO (115) have

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Table 1. Selected Transition Energies and Wavefunctions Calculated by the TDDFT [B3LYP/6-31G(d)] Method

no.	calcd (nm)	obsd (nm)	f	wavefunction
1	426	496	0.17	$0.607\|116 \leftarrow 115\rangle - 0.249\|117 \leftarrow 112\rangle + 0.123\|117 \leftarrow 111\rangle + ...$
2	424	496	0.16	$0.606\|117 \leftarrow 115\rangle + 0.251\|116 \leftarrow 112\rangle - 0.128\|116 \leftarrow 111\rangle + ...$
7	309	289	0.17	$0.507\|116 \leftarrow 112\rangle + 0.400\|116 \leftarrow 111\rangle + 0.152\|117 \leftarrow 110\rangle + ...$
9	307	289	0.17	$0.512\|117 \leftarrow 112\rangle + 0.381\|117 \leftarrow 111\rangle + 0.158\|116 \leftarrow 110\rangle + 0.114\|117 \leftarrow 109\rangle + ...$

a_2 character and are localized on the pyrrole α and β carbons with no significant coefficient on the meso nitrogens. This feature corresponds to the HOMO of typical D_{4h} metallo-Pcs with the a_{1u} representation.[20] The HOMO-1 of D_{4h} Pc usually belongs to the a_{2u} representation, in which large MO coefficients are located on the meso nitrogens. In the case of **2**, however, the corresponding orbital is not HOMO-1 (114) but HOMO-3 (112). Two nearly degenerate MOs are found between 115 and 112; these are not seen in the normal Pcs. The corresponding MOs were calculated as HOMO-3 and HOMO-4 by the PPP method.[4] As shown in Table 1, contributions of these two MOs (113 and 114) to the intense absorption band (Q and Soret bands) are negligible. Therefore, the origins of the Q and Soret bands of **2** are basically similar to the Pcs. The contributions of the ethyl groups to the frontier orbitals are very small.

Conclusions

In the present study, we have synthesized the new subtriazaporphyrin (SubTap), chloro[hexaethylsubtriazaporphinato]boron(III), **1**, and its hydroxo derivative, **2**. X-ray crystallography determined the conical macrocyclic structure of the hydroxo form unambiguously. Spectroscopic measurements and DFT calculations have succeeded in assigning the principal absorption bands.

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Supporting Information Available: Crystallographic data given in CIF and PDF formats. This material is available free of charge via the Internet at http://pubs.acs.org.

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