

# Design and Synthesis of Bismacrocylic Hexaazatriphenylene Derivatives

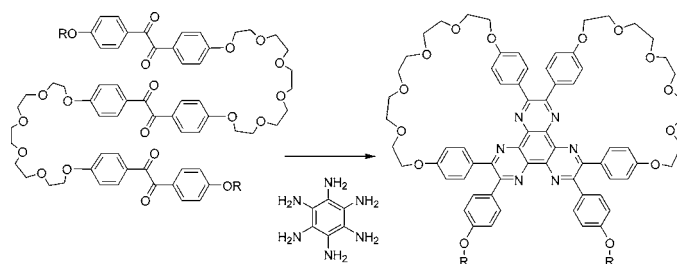
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## ABSTRACT



The first examples of bismacrocylic derivatives of 2,3,6,7,10,11-hexaphenyl-1,4,5,8,9,12-hexaazatriphenylene are described. They are obtained by the condensation of a linear trisbenzil precursor with hexaaminobenzene.

1,4,5,8,9,12-Hexaazatriphenylene (HAT) derivatives are disk-shaped aromatic molecules that are receiving considerable attention because of their easy synthetic accessibility, diversity in peripheral functionality, electron deficiency, coordination properties, and  $\pi$ -complexation ability. As a result of such versatility, HATs were exploited in a variety of applications, including discotic liquid crystals,<sup>1</sup> self-assembled organogels,<sup>2</sup> *n*-type semiconducting<sup>3</sup> and magnetic materials,<sup>4</sup> photoprobes and photoreagents of DNA,<sup>5</sup> fluorescent dyes,<sup>6</sup> and octupolar nonlinear optical chromophores.<sup>7</sup> The coordination chemistry of HATs is particularly rich.<sup>8</sup>

The appealing feature of these planar ligands is that they provide a symmetrical array of three bidentate diimine chelating sites, which renders them unique systems on which to base the generation of solid-state infinite coordination networks with intriguing topologies.<sup>8</sup> HATs also allowed building of discrete, low-nuclearity metal complexes with well-defined nanoscale architectures.<sup>9</sup> In light of these data, it occurred to us that HAT derivatives in which the phenanthroline-type subsites would be laterally bridged through the ortho positions to the nitrogen atoms could represent attractive building blocks for the generation of ordered structures with controlled nuclearity and topography and new topology.<sup>10</sup> Indeed, such systems could provide

(1) (a) Pieterse, K.; van Hal, P. A.; Kleppinger, R.; Vekemans, J. A. J. M.; Janssen, R. A. J.; Meijer, E. W. *Chem. Mater.* **2001**, *13*, 2675–2679.

(b) Arikainen, E. O.; Boden, N.; Bushby, R. J.; Lozman, O. R.; Vinter, J. G.; Wood, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2333–2336. (c) Gearba, R. I.; Lehman, M.; Levin, J.; Ivanov, D. A.; Koch, M. H. J.; Barberá, J.; Debije, M. G.; Piris, J.; Geerts, Y. H. *Adv. Mater.* **2003**, *15*, 1614–1618.

(2) Ishi-i, T.; Hirayama, T.; Murakami, K.; Tashiro, H.; Thiemann, T.; Kubo, K.; Mori, A.; Yamasaki, S.; Akao, T.; Tsuboyama, A.; Mukaiide, T.; Ueno, K.; Mataka, S. *Langmuir* **2005**, *21*, 1261–1268.

(3) Kaafarani, B. R.; Kondo, T.; Yu, J.; Zhang, Q.; Dattilo, D.; Risko, C.; Jones, S. C.; Barlow, S.; Domercq, B.; Amy, F.; Kahn, A.; Brédas, J.-L.; Kippelen, B.; Marder, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 16358–16359 and references therein.

(4) Marshall, S. R.; Rheingold, A. L.; Dawe, L. N.; Shum, W. W.; Kitamura, C.; Miller, J. S. *Inorg. Chem.* **2002**, *41*, 3599–3601.

(5) Blasius, R.; Moucheron, C.; Kirsch-De Mesmaeker, A. *Eur. J. Inorg. Chem.* **2004**, 3071–3979.

(6) (a) Hirayama, T.; Yamasaki, S.; Ameku, H.; Ishi-i, T.; Thiemann, T.; Mataka, S. *Dyes Pigm.* **2005**, *67*, 105–110. (b) Ishi-i, T.; Murakami, K.; Imai, Y.; Mataka, S. *Org. Lett.* **2005**, *7*, 3175–3178.

(7) Cho, B. R.; Lee, S. K.; Kim, K. A.; Son, K. N.; Kang, T. I.; Jeon, S. J. *Tetrahedron Lett.* **1998**, *39*, 9205–9208.

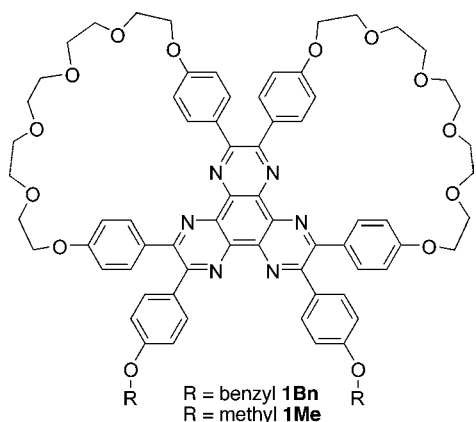
(8) Kitagawa, S.; Masaoka, S. *Coord. Chem. Rev.* **2003**, *246*, 73–88.

(9) (a) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.–Eur. J.* **1999**, *5*, 102–112. (b) Masaoka, S.; Furukawa, S.; Chang, H.-C.; Mizutani, T.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3817–3819. (c) Latterini, L.; Pourtois, G.; Moucheron, C.; Lazzaroni, R.; Brédas, J.-L.; Kirsch-De Mesmaeker, A.; De Schryver, F. *Chem.–Eur. J.* **2000**, *6*, 1331–1336.

(10) Frey, J. F.; Kraus, T.; Heitz, V.; Sauvage, J.-P. *Chem. Commun.* **2005**, 5310–5312.

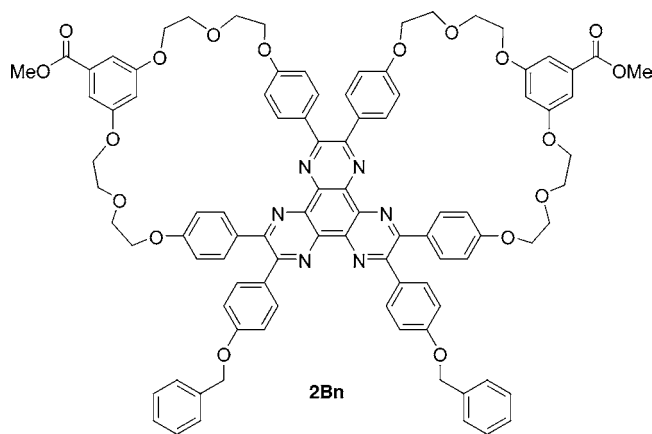
multivalent architectures<sup>11</sup> featuring the remarkable coordination properties of macrocyclic phenanthrolines, according to the pioneering work by Sauvage and co-workers.<sup>12</sup>

Here, we report the synthesis of three related tritopic ligands, **1R** (R = benzyl, methyl) and **2Bn**, as first examples of macrocyclic HAT derivatives in which only two of the three phenanthroline-type sites are each included in a lateral macrocycle. Pentaethyleneglycol chains were used to construct both 30-membered rings of the bismacrocycles **1R** (Figure 1).<sup>12</sup>



**Figure 1.** Structures of bismacrocycles **1Bn** and **1Me**.

The crown subunits in **2Bn** contain methyl 3,5-dihydroxybenzoate moieties which were shown recently to allow the anchoring of functional groups laterally to the ring of a rotaxane structure (Figure 2).<sup>13</sup> Moreover, as a result of their



**Figure 2.** Structure of bismacrocycle **2Bn**.

bismacrocyclic structure, compounds **1R** and **2Bn** are nonsymmetrical, which is quite rare in the HAT series.

(11) Badjic, J. D.; Nelson, A.; Cantrill, S. J.; Turnbull, W. B.; Stoddart, J. F. *Acc. Chem. Res.* **2005**, *38*, 723–732.

Actually, there are very few reports to date dealing with the synthesis of nonsymmetrical HATs.<sup>3,14</sup>

HAT derivatives are classically obtained from the condensation of benzil-type<sup>15</sup> precursors with hexaaminobenzene (HAB) in a 3:1 benzil/HAB molar ratio.<sup>16</sup> Although this route affords C<sub>3</sub> symmetrical derivatives in generally good yields, it has also been utilized to produce unsymmetrical species, such as 2,3-diphenyl- and 2,3,6,7-tetraphenyl-hexaazatriphenylene.<sup>14a</sup> Their formation involved competing condensation reactions between two  $\alpha$ -diketone derivatives and HAB, which inevitably led to a complex mixture of products.<sup>14a</sup> Two strategies can be envisaged for the synthesis of the nonsymmetrical macrocyclic systems **1R** and **2Bn**. The first one is based on a one-pot macrocyclization procedure starting from a preformed HAT precursor bearing six reactive peripheral functionalities. In that connection, a tris-crown-ether derivative of triphenylene was obtained upon reaction of hexahydroxytriphenylene with an appropriate ditosylate under high dilution conditions.<sup>17</sup>

Whereas this route might be useful for the synthesis of electron-deficient HAT analogues of the triphenylene system, we surmised that its implementation under the statistical conditions needed to access partially cyclized species, such as ligands **1R** and **2Bn**, would not be convenient. Therefore, we turned our attention toward an alternative strategy involving the use of linear precursors, **3R** and **4Bn**, in which three benzil units are covalently linked by two flexible spacers (Schemes 1 and 2). Here, the stepwise creation of the six imine bonds, leading to the formation of the HAT core and the concomitant construction of the two lateral macrocycles, was reasoned to imply the wrapping of one molecule of **3R** or **4Bn** around the HAB nucleus in a sequence of one bimolecular and two intramolecular condensations.

The syntheses of the linear precursors mainly involve nucleophilic substitution reactions of phenols on primary iodides using conventional procedures. Compound **3Bn** was obtained in four steps according to a convergent approach, using 4,4'-dihydroxy-benzil (**5**) and its monobenzyl-substituted derivative (**6**) as starting building blocks (Scheme 1). In the case of **3Me**, a divergent route was followed (Scheme 1). The two terminal  $\alpha$ -diketone functionalities in **3Me** were constructed in a stepwise manner, subjecting the bisiodophenyl-terminated benzil-cored precursor (**9**) to a palladium-catalyzed cross-coupling reaction under Sonagashira conditions followed by the oxidation of the resulting bisacetylenic

(12) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795–810.

(13) Li, K.; Bracher, P. J.; Guldi, D. M.; Herranz, M. Á.; Echegoyen, L.; Schuster, D. I. *J. Am. Chem. Soc.* **2004**, *126*, 9156–9157.

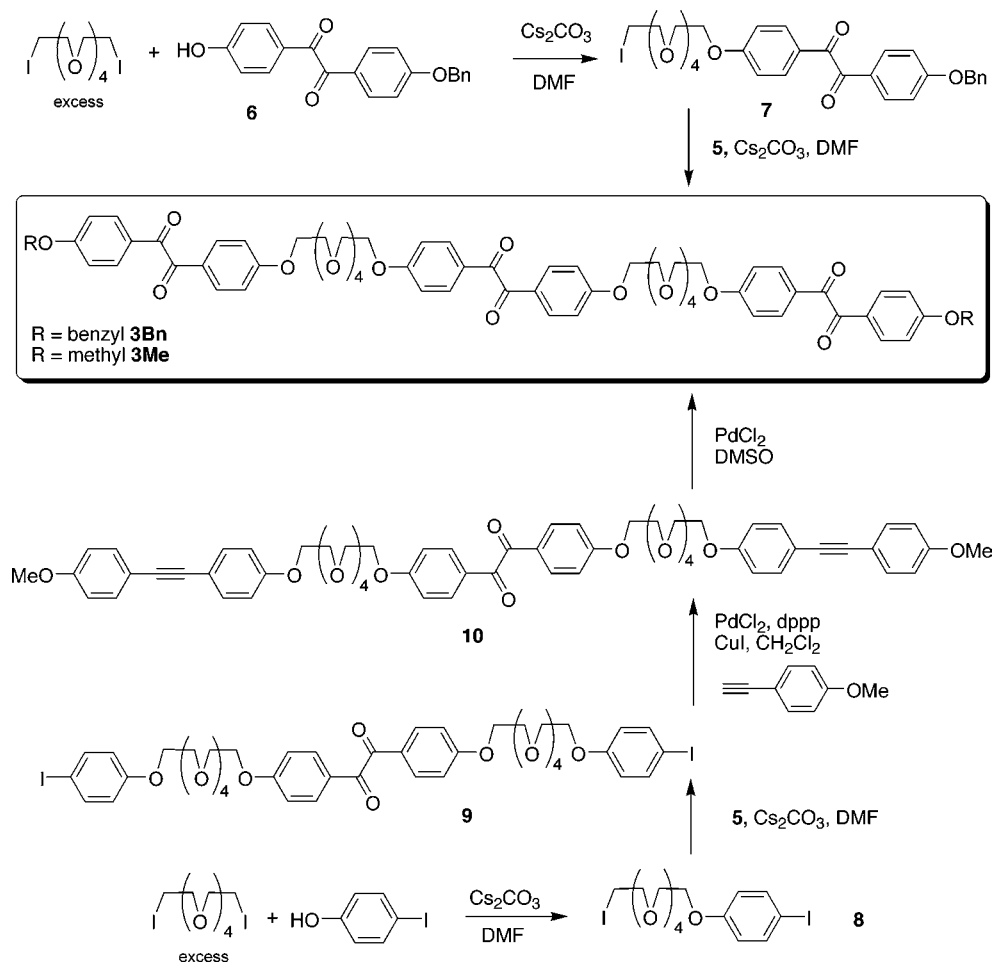
(14) (a) Nasielski, J.; Moucheron, C.; Verhoeven, C.; Nasielski-Hinkens, R. *Tetrahedron Lett.* **1990**, *31*, 2573–2576. (b) Moucheron, C.; Dietrich-Buchecker, C. O.; Sauvage, J.-P.; van Dorselaer, A. *J. Chem. Soc. Dalton Trans.* **1994**, 885–893. (c) Chang, T.-H.; Wu, B.-R.; Chiang, M. Y.; Liao, S.-C.; Ong, C. W.; Hsu, H.-F.; Lin, S.-Y. *Org. Lett.* **2005**, *7*, 4075–4078.

(15) For the sake of simplicity, the term benzil denotes the 1,2-diphenylethanedione unit throughout the text.

(16) Kohne, B.; Praefcke, K. *Liebigs Ann. Chem.* **1985**, 522–528.

(17) (a) Balzani, V.; Clemente-León, M.; Credi, A.; Lowe, J. N.; Badjic, J. D.; Stoddart, J. F.; Williams, D. J. *Chem.—Eur. J.* **2003**, *9*, 5348–5360. (b) Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845–1849.

**Scheme 1.** Synthesis of the Linear Precursors **3Bn** and **3Me**<sup>a</sup>



<sup>a</sup> **5**: 4,4'-dihydroxy-benzil. dppp: 1,3-bis(diphenylphosphino)propane.

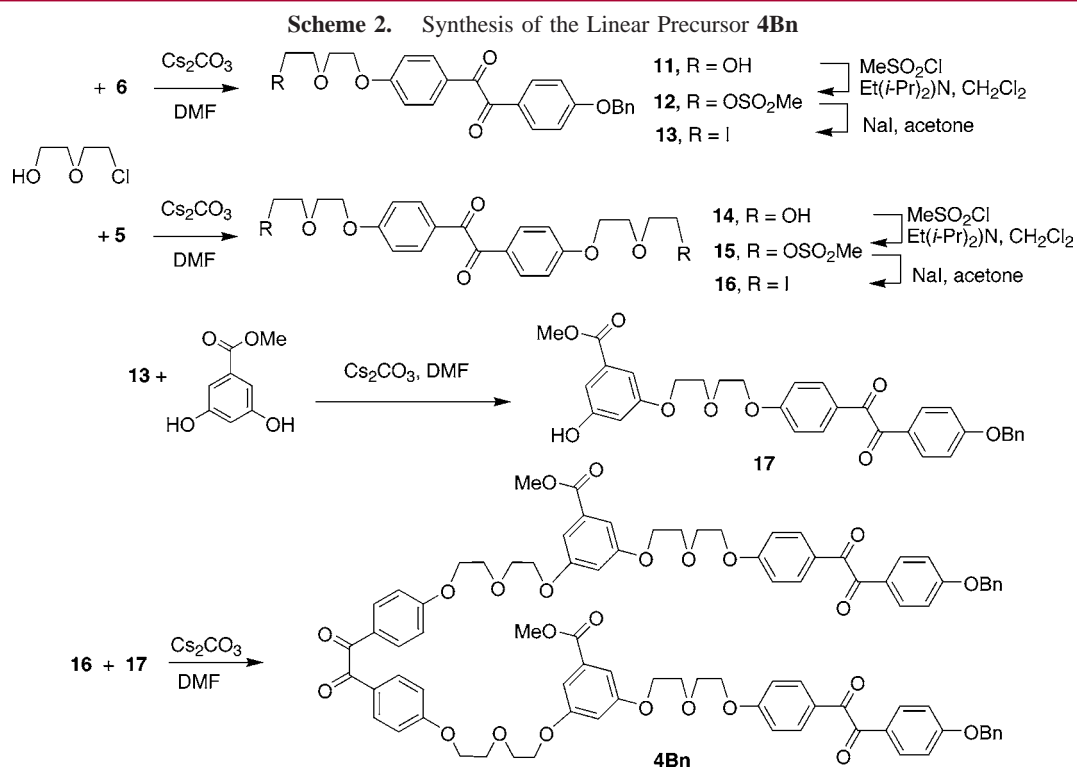
compound (**10**) with PdCl<sub>2</sub> in DMSO. The synthetic strategy toward compound **4Bn** was similar to that used for **3Bn** (Scheme 2). Cyclizations were carried out at 5–10 mM concentration with respect to the linear precursors, with 1 equiv of HAB, in acetic acid. The solutions were refluxed for 16 h under an argon atmosphere. After a few hours, TLC indicated in all cases the formation of a single, fast-running species displaying the characteristic fluorescence emission of the HAT nucleus. Simple column chromatography allowed us to isolate pure samples of the bismacrocyclic HATs **1R** and **2Bn** as yellow solids. The formation of very polar byproducts was also noticed. They consisted presumably of open-chained and cyclic oligomeric species and were not characterized. Compounds **1Bn**, **1Me**, and **2Bn** were obtained in 12, 25, and 6% yields, respectively. The reaction conditions were not yet optimized. However, we observed that decreasing the reaction time to 6 h gave an improved yield (18%) of **1Bn**, which may reflect the sensitivity of the benzyl group in refluxing acetic acid.

The use of the high dilution technique can be envisaged, but the poor stability of HAB may represent a limitation to this end.<sup>18</sup>

Compounds **1R** and **2Bn** were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies, electrospray ionization mass spectrometry, and elemental analyses. The mass spectra in methanol containing ammonium acetate (3 mM) revealed a peak at *m/z* = 1372.1, 1219.7, and 1584.0 for **1Bn**, **1Me**, and **2Bn**, respectively, corresponding to the monocharged species [M + H]<sup>+</sup>. In the case of **1Me**, the adduct [M + NH<sub>4</sub>]<sup>+</sup> at *m/z* = 1237.2 could also be detected. Peaks at lower values of *m/z* could be assigned to doubly charged species [M + 2H]<sup>2+</sup>, [M + H + NH<sub>4</sub>]<sup>2+</sup>, and [M + 2NH<sub>4</sub>]<sup>2+</sup>. The <sup>1</sup>H NMR spectra of **1R** and **2Bn** in CDCl<sub>3</sub> were observed to be very close to those of their parent linear precursors, **3R** and **4Bn**, respectively. The main changes were observed for the shape and position of resonance patterns of the aromatic protons as a consequence of the conversion of the α-diketone groups into imine-containing aromatic moieties. In the aliphatic region, a downfield shift (Δδ = +0.06 ppm) could be observed for the resonance signal of the ε protons<sup>19</sup> in the polyoxyethylene units of both **1Bn** and **1Me** relative to the corresponding linear compounds **3Bn** and **3Me**. Simi-

(18) Rodgers, D. Z. *J. Org. Chem.* **1986**, *51*, 3904–3905.

(19) For atom numbering, see Supporting Information.



larly, a downfield shift ( $\Delta\delta = +0.12$  ppm) was also observed for the aromatic protons  $H_{10}$  of the methyl 3,5-dihydroxybenzoate moieties in the crown subunits of **2Bn**.<sup>19</sup> This effect common to the three compounds is diagnostic of the formation of the cyclized structures in which the hydrogen atoms of the crown chains are exposed to the deshielding effect of the HAT plane. <sup>13</sup>C NMR spectroscopy turned out to be more informative with respect to the structure and symmetry of molecules **1R** and **2Bn**. For example, the spectrum of **1Bn** did not show any carbonyl resonances and instead presented the signals characteristic of the quaternary carbon atoms of the HAT core. Noticeably, as compared to the situation with the averaged  $C_{3v}$  symmetrical hexabenzyl-substituted model compound, the carbon atoms of the HAT unit became anisochronous in **1Bn**, which is a consequence of the lowering of symmetry from  $C_{3v}$  to  $C_{2v}$ . The same features were observed for **1Me** and **2Bn**.

In summary, we report a simple approach to building HAT derivatives laterally bridged with two macrocyclic units. The

method, which involves the condensation of a linear trisbenzyl precursor with HAB acting as both a reagent and a template, allows the construction of bismacrocycles with different substituent groups and macrocyclic chains. Further extensions of this work are directed to improve the reaction conditions, synthesize new derivatives, including trismacrocyclic species, and investigate the coordination properties of the described and related bismacrocyclic HATs.

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**Supporting Information Available:** Synthetic procedures for new compounds, numbered figures and <sup>1</sup>H and <sup>13</sup>C NMR spectra of molecules **1R** and **2Bn**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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