

# Synthesis of Hexacyanotriphenylene and Hexacyanotribenzylene

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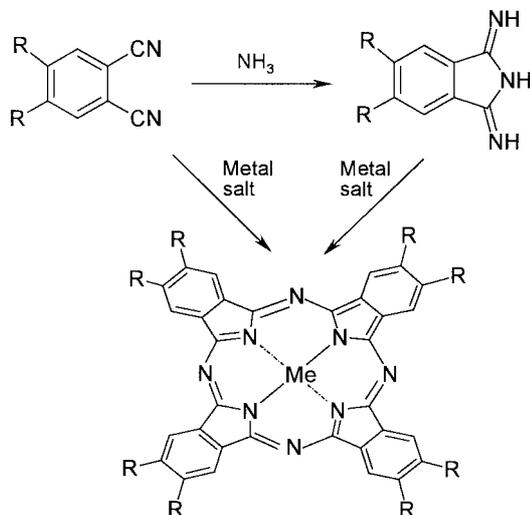
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Dedicated to Professor R. Neidlein on the occasion of his 70<sup>th</sup> birthday

**Abstract:** The synthesis of hexacyanotriphenylene (**1**) and hexacyanotribenzylene (**2**) with triangular geometry is described. The new hexanitrides are considered to be precursors for oligomeric, polymeric or spherical phthalocyanine systems.

**Key words:** phthalocyanines, triphenylenes, tribenzylenes, spheres, cyanation

Phthalocyanines and metalphthalocyanines have been widely used recently in materials science because they exhibit several interesting properties, e.g. semi conductivity, non-linear optical behavior and others. In addition, phthalocyanines are thermally and chemically quite stable, which is another advantage for their practical applications in the mentioned fields.<sup>1,2</sup> The basic reaction for preparing metalphthalocyanines is based on the reaction of phthalodinitriles or diiminoisoindolines with a metal salt as shown in Scheme 1.



Scheme 1

Starting with the appropriately modified phthalonitriles (Figure 1), it should be also possible to prepare polymeric phthalocyanines.<sup>3</sup>

We became interested in the hexacyano substituted systems **1** and **2** because the triangular geometry of these precursors should, in principle lead to 2- and 3-dimensional structures by reacting them according to Scheme 1. The

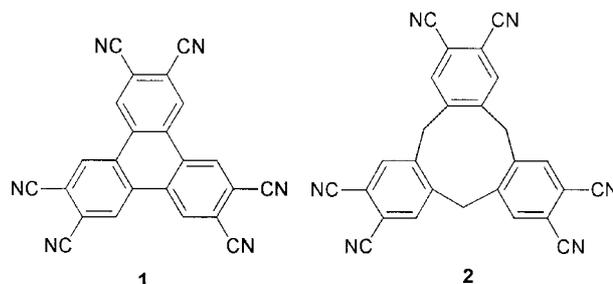


Figure 1

statistical reaction of **1** and **2** with phthalonitrile would lead to molecules with three phthalocyanine units (vide supra). The self-condensation of **1** would lead to products with polymer character.

Under the typical conditions for preparing phthalocyanines, it is in principle also possible to get branched structures similar to dendrimers. Under high dilution, the system could build spheres via a three dimensional ring-closure reaction. The possibility of formation of a spherical molecule built up from eight hexacyanotriphenylenes (**1**) was patented by Oeste<sup>3</sup> in 1991. The hypothetical spherical molecule (Figure 2, left side) consists of six phthalocyanine units, which are not totally planar.

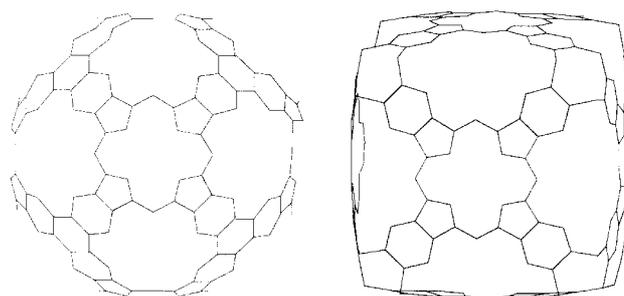
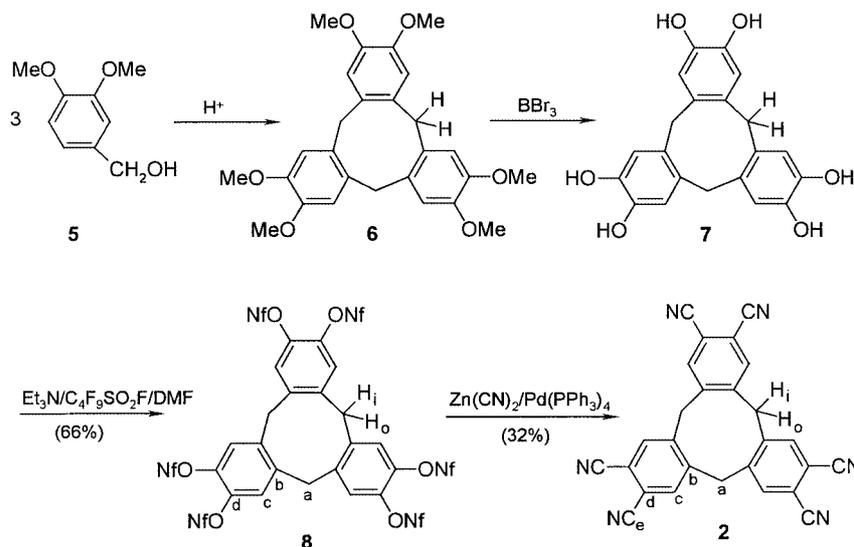


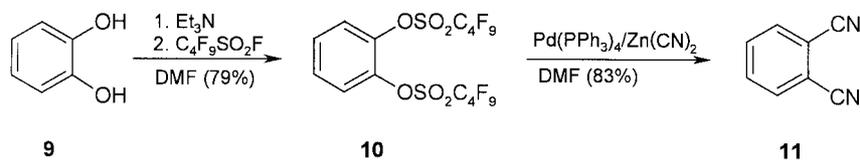
Figure 2

Molecule **2** which is not planar due to its methylene bridges would lead by self-condensation to the so-called phthalocuberenes as shown in Figure 2 (right side), which have a cubic symmetry and would be built up from eight molecules of **2**.<sup>4</sup> Calculations with force field (MM+)





Scheme 3



Scheme 4

are formed. Further studies on the preparation of substituted and more soluble hexanitrides corresponding to **1** and **2** and their conversion into the corresponding phthalocyanines are in progress.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at r.t. on a Bruker AC250 (<sup>1</sup>H: 250.1 MHz, <sup>13</sup>C: 62.9 MHz). Chemical shifts (δ) are given in ppm. EI/MS spectra were performed on Finnigan ISQ 70 (70eV)/ Varian MAT 711A. IR spectra were recorded as KBr pellets using a FT-IR spectrophotometer IFS 48 (Bruker). Elemental analyses were performed on a Carlo Erba Elemental Analyser 1106. All mps were determined with a heating rate of 2 K/min and are uncorrected. The course of reaction and the purity of products were followed by TLC analysis using Macherey-Nagel Alugram SII/UV<sub>254</sub> plates. Hexahydroxytribenzylene (**7**) was prepared according to literature procedure.<sup>12,13</sup>

#### 2,3,6,7,10,11-Hexacyanotriphenylene (**1**)

To a solution of 2,3,6,7,10,11-hexabromotriphenylene (**4**, 1 g, 1.4 mmol) in 2-chloronaphthalene (25 mL) were added KCN (0.62 g, 9.5 mmol), dibenzo-18-crown-6 (1.44 g, 4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (2.3 g, 2 mmol) under N<sub>2</sub>. The mixture was heated for 20 h at 140 °C, cooled to 60 °C, diluted with a mixture of warm heptane/toluene (1:1), and filtered at this temperature. The product was washed with toluene, and small amounts of Et<sub>2</sub>O and MeOH. Excess of KCN and other salts were removed by washing with H<sub>2</sub>O (1000 mL) and dried. To remove the Ph<sub>3</sub>P and the crown-ether, the product was extracted for 24 h with Et<sub>2</sub>O in a Soxhlet-extractor. The solvent was removed to give a green solid (220 mg, 41%).

<sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>CN): δ = 9.36 (s, 6 H).

IR (KBr): ν = 3123, 3092, 3058, 2237, 1610, 1593, 1564, 1499, 1435, 1408, 1236, 1126, 1097, 912, 800, 692 cm<sup>-1</sup>.

MS (EI): *m/z* = 378.3 (M<sup>+</sup>, 7), 353.2 (17), 328.2 (5).

#### 2,3,7,8,12,13-Hexakis(nonafluorobutoxy)tribenzylene (**8**)

A solution of hexahydroxytribenzylene (**7**, 2.5 g, 6.83 mmol) in DMF (30 mL) containing Et<sub>3</sub>N (12.4 g 123 mmol) was cooled to 0 °C. Then nonafluorobutoxy sulfonamide (37.1 g, 123 mmol) was added dropwise. The mixture was stirred under N<sub>2</sub> for 2 days, then filtered to remove the Et<sub>3</sub>N•HF. The solid was washed with CHCl<sub>3</sub> (20 mL) and the washings were combined with the filtrate. The combined organic layers were washed with NaOH (5%, 2 x 20 mL) and H<sub>2</sub>O (20 mL). After drying the organic phase (Na<sub>2</sub>SO<sub>4</sub>), the solvent was evaporated. The residue was purified by column chromatography on silica gel (CHCl<sub>3</sub>) to give a colorless powder (9.3 g, 66%), mp 132–133 °C.

IR (KBr): ν = 3084, 2883, 1593, 1501, 1431, 1356, 1294, 1238, 1204, 1145, 1126, 1034, 1011, 943, 895, 845, 806, 750, 700, 684 cm<sup>-1</sup>.

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 3.88 (d, *J* = 13.0 Hz, 3H<sub>i</sub>), 4.85 (d, *J* = 13.0 Hz, 3H<sub>o</sub>), 7.45 (s, 6H).

<sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>): δ = 36.3 (C<sub>a</sub>), 108–117 (C<sub>b</sub>, C<sub>4</sub>F<sub>9</sub>), 124.9 (C<sub>c</sub>), 139.2 (C<sub>b/d</sub>), 139.8 (C<sub>b/d</sub>).

MS (FD): *m/z* (%) = 2058.8 (M<sup>+</sup>, 100), 1776.5 (61).

Anal. calcd for C<sub>45</sub>H<sub>12</sub>F<sub>54</sub>S<sub>6</sub>O<sub>18</sub> (2058.8): C, 26.25; H, 0.58; S, 9.34; F, 49.83. Found: C, 26.20; H, 0.74; S, 9.2.67; F, 50.30.

**2,3,7,8,12,13-Hexacyanotribenzylene (2)**

A solution of 2,3,7,8,12,13-hexakisnonafluorocyclotribenzylene (**8**, 6.0 g, 2.9 mmol) in deoxygenated DMF (120 mL) was heated to 85 °C under N<sub>2</sub>. Pd(PPh<sub>3</sub>)<sub>4</sub> (in total 2.00 g, 1.73 mmol) and Zn(CN)<sub>2</sub> (in total 1.43 g, 12.2 mmol) were added in 15 to 20 equal portions over 6 h. The mixture was cooled to r.t., diluted with EtOAc (500 mL), and washed with dil. NaHCO<sub>3</sub> (2 x 200 mL), H<sub>2</sub>O, dil. HCl (200 mL), and finally with H<sub>2</sub>O (200 mL). After drying (Na<sub>2</sub>SO<sub>4</sub>) and concentrating in vacuo, the resulting solid was treated with hot hexane and crystallized from acetone. This provided a colorless solid material, which was recrystallized from MeCN (yield: 0.40 mg, 32%, mp > 350 °C).

IR (KBr):  $\nu = 3113, 3067, 3041, 2235, 1666, 1603, 1555, 1495, 1483, 1444, 1387, 1356, 1304, 1248, 1204, 1146, 1034, 935, 924, 898, 831, 783, 731, 604 \text{ cm}^{-1}$ .

<sup>1</sup>H NMR (250 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 4.00$  (d,  $J = 13.1$  Hz, 3H<sub>o</sub>), 5.20 (d,  $J = 13.1$  Hz, 3H<sub>i</sub>), 8.45 (s, 6H).

<sup>13</sup>C NMR (250 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 35.5$  (C<sub>a</sub>), 114.3 (C<sub>d</sub>), 116.4 (C<sub>e</sub>), 136.7 (C<sub>c</sub>), 144.9 (C<sub>b</sub>).

MS (EI):  $m/z$  (%) = 420.2 (M<sup>+</sup>, 7), 393.1 (22), 279.3 (5), 207.1 (24).

Anal. calcd for C<sub>27</sub>H<sub>12</sub>N<sub>6</sub> (420.44): C, 77.13; H, 2.88; N, 19.99. Found: C, 76.04; H, 2.85; N, 19.44.

**References**

- (1) Hanack, M.; Lang, M. *Adv. Mater.* **1994**, *6*, 819.
- (2) Hanack, M.; Subramanian, L. R. In *Handbook of Organic Conductive Molecules and Polymers*, Vol. 1; Nalwa, H. S., Ed.; Wiley: Chichester, 1997; pp 687–726.
- (3) Oeste, F. D. German Patent 4114536, 1991; *Chem. Abstr.* **1992**, *117*, 91076.
- (4) Keesmann, T.; Große-Wilde, H.; Hanack, M.; Mattmer, R.; Krempel, H. German Patent 19635058, 1997; *Chem. Abstr.* **1997**, *126*, 305594.
- (5) Karfunkel, H. R.; Dressler, T.; Hirsch, A. *J. Comput.-Aided. Mol. Des.* **1992**, *6*, 521.
- (6) Patai, S. *The Chemistry of the Cyano Group: 2*; Wiley-Interscience: Chichester, 1970; p 67.
- (7) Ellis, G. P.; Romney-Alexander, T. M. *Chem. Rev.* **1987**, *87*, 779.
- (8) Drechsler, U.; Hanack, M. *Synlett* **1998**, 1207.
- (9) Chambers, M. R. I.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1365. Selnick, H. G.; Smith, G. R.; Tebben, A. J. *Synth. Commun.* **1995**, *25*, 3255.
- (10) Präfcke, K.; Kohne, B.; Singer, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 177.
- (11) Bartle, H. D.; Heaney, H.; Jones D. W.; Lees, P. *Tetrahedron* **1965**, *21*, 3289.
- (12) Takagi, K.; Sasaki, K.; Sakakibara, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1118.
- (13) Yamato, T.; Hideshima, C.; Surya Prakash, G. K.; Olah, G. A. *J. Org. Chem.* **1991**, *56*, 2089.
- (14) Lindsey, A. S. *J. Chem. Soc.* **1965**, 1685.
- (15) Subramanian, L. R.; Garcia Martinez, A.; Herrera Fernandez, A.; Martinez Alvarez, R. *Synthesis* **1984**, 481.

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