Synthesis of Hexacyanotriphenylene and Hexacyanotribenzylene

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Dedicated to Professor R. Neidlein on the occasion of his 70th birthday

Abstract: The synthesis of hexacyanotriphenylene (1) and hexacyanotribenzylene (2) with triangular geometry is described. The new hexanitriles 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.^{1,2} 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.³

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





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 ringclosure reaction. The possibility of formation of a spherical molecule built up from eight hexacyanotriphenylenes (1) was patented by $Oeste^3$ in 1991. The hypothetical spherical molecule (Figure 2, left side) consists of six phthalocyanine units, which are not totally planar.





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 2.4 Calculations with force field (MM+) methods gave promising results regarding the stability of these types of spheres.⁵

In the following, we report on the synthesis of the hexacyano substituted precursors 1 and 2.

Benzene rings carrying one or two cyano groups are easy to prepare based on several methods,⁶ the quite common route being the replacement of the bromine atoms in the aromatic ring by the cyano groups known as the Rosenmund–von Braun reaction.⁷ Dehydration of oximes and amides to nitriles also work well to obtain mono- or dinitriles in the aromatic series. Substitution of triflates and nonaflates with cyano groups are known for up to two groups.^{8,9} However, to our knowledge there are no reports on the preparation of aromatic compounds carrying more than three nitrile groups by direct substitution reaction. We report here two procedures, which we have standardized for the synthesis of hexacyanonitriles.

Hexacyanotriphenylene (1) was synthesized starting from triphenylene¹⁰ (3) (Scheme 2), which was selectively brominated with formation of 2,3,6,7,10,11-hexabromotriphenylene (4), using iron as catalyst.¹¹ The exchange of bromine with copper cyanide in a Rosenmund–von Braun reaction⁷ leads only to a partial exchange of the bromine atoms against the cyano groups. Under the usual conditions, the obtained product is a mixture of mono- to pentacyanobromotriphenylenes.

After several trials, the synthesis of hexacyanotriphenylene (1) from 4 was successfully achieved by reacting with potassium cyanide in 2-chloronaphthalene (2-ClNp) in the presence of dibenzo-18-crown-6 and tetrakis(triphenylphosphine)palladium(0) as catalyst.¹² Under these conditions, all six bromine atoms in 4 were exchanged with formation of 1 (41%), which was characterized by ¹H NMR, MS, IR, and elemental analyses. The hexanitrile 1 being planar and symmetric is very sparingly soluble in common organic solvents and hence we encountered the problem of carrying out the self-condensation reaction.

To improve further the solubility of the precursor with six cyano groups, we chose the tribenzylene system 2 containing a nine-membered ring with methylene bridges. Because the aromatic systems are separated by methylene bridges compound 2 has a non-planar structure. This would lead to a lower aggregation and increase the solubility. A way for building up such nine-membered ring-systems is the trimerization of veratryl alcohol (5) to cy-

clotriveratrylene (**6**),¹³ which after demethylation with boron tribromide,¹⁴ yields the catechol derivative **7** (Scheme 3).

To exchange the hydroxy with cyano groups, they were first converted to nonafluorosulfonates by reacting with nonaflyl fluoride (nonafluorobutanesulfonyl fluoride). The reaction was carried out in DMF with triethylamine in analogy to the preparation of other aromatic nonafluorobutanesulfonates.¹⁵ The obtained hexanonaflate **8** was characterized by ¹H and ¹³C NMR, MS, IR, and elemental analyses. The methylene protons inside and outside the nine-membered ring (designated as H_i , H_o) in compounds **2**, **6–8** show different chemical shifts.

The replacement of all the nonaflyl with cyano groups in **8** gave some problems, because the described palladiumcatalyzed cyanation with zinc cyanide^{8,9} for replacement of triflates failed due to the deactivation of the palladium catalyst Pd(PPh₃)₄ during the reaction. The replacement reaction of nonaflates with cyano groups was therefore optimized using 1,2-bis(nonaflyl)benzene (**10**) as the model compound (Scheme 4) using a slightly modified method.⁸ The bis-nonaflate **10** was obtained from catechol (**9**) by reacting with nonaflyl fluoride.

After several attempts, the optimum condition for the conversion was found by sequential addition of 15 to 20 equal portions of zinc cyanide to the reaction mixture over 6 hours. With this procedure, 1,2-bis(nonaflyl)benzene (10) was converted into phthalonitrile (11) in 83% yield. Applying this method to hexakis(nonaflyl)tribenzylene (8), pure 2 was obtained 32% yield.

Preliminary studies of the reaction of **1** with an excess of tetraphenylphthalonitrile and nickel acetate in hexanol gave products with phthalocyanine groups. The UV spectra showed a Q band with a maximum at 748 nm and the IR-spectra contained peaks typical of phthalocyanine substructures. Because of the high molecular weight and the insolubility of the reaction product, the isolation and characterization was difficult. Also the self-condensation of **1** in refluxing dimethylaminoethanol containing DBU yields phthalocyanines as seen by the Q-band with a maximum at 890 nm.

In conclusion, we have synthesized for the first time two different aromatic hexanitriles, which may be capable of forming spherical phthalocyanines of interest. Preliminary investigations on **1** have shown that phthalocyanines



Scheme 2

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Scheme 3

Scheme 4

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

¹H and ¹³C NMR spectra were recorded at r.t. on a Bruker AC250 (¹H: 250.1 MHz, ¹³C: 62.9 MHz). Chemical shifts ($\delta\delta$) are given in ppm. EI/FD mass 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 SIL/UV₂₅₄ plates. Hexahydroxytribenzylene (**7**) was prepared according to literature procedure.^{12,13}

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(PPh₃)₄ (2.3 g, 2 mmol) under N₂. 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 Et₂O and MeOH. Excess of KCN and other salts were removed by washing with H₂O (1000 mL) and dried. To remove the Ph₃P and the crown-ether, the product was extracted for 24 h with Et₂O in a Soxhlet-extractor. The solvent was removed to give a green solid (220 mg, 41%).

¹H NMR (250 MHz, CD₃CN): δ = 9.36 (s, 6 H).

IR (KBr): v = 3123, 3092, 3058, 2237, 1610, 1593, 1564, 1499, 1435, 1408, 1236, 1126, 1097, 912, 800, 692 cm⁻¹. MS (EI): *m/z* = 378.3 (M⁺, 7), 353.2 (17), 328.2 (5).

2,3,7,8,12,13-Hexakis(nonaflyl)tribenzylene (8)

A solution of hexahydroxytribenzylene (7, 2.5 g, 6.83 mmol) in DMF (30 mL) containing Et_3N (12.4 g 123 mmol) was cooled to 0 °C. Then nonafluorobutanesulfonyl fluoride (37.1 g, 123 mmol) was added dropwise. The mixture was stirred under N₂ for 2 days, then filtered to remove the Et_3N •HF. The solid was washed with CHCl₃ (20 mL) and the washings were combined with the filtrate. The combined organic layers were washed with NaOH (5%, 2 x 20 mL) and H₂O (20 mL). After drying the organic phase (Na₂SO₄), the solvent was evaporated. The residue was purified by column chromatography on silica gel (CHCl₃) to give a colorless powder (9.3 g, 66%), mp 132–133 °C.

IR (KBr): v = 3084, 2883, 1593, 1501, 1431, 1356, 1294, 1238, 1204, 1145, 1126, 1034, 1011, 943, 895, 845, 806, 750, 700, 684 cm⁻¹.

¹H NMR (250 MHz, CDCl₃): δ = 3.88 (d, *J* = 13.0 Hz, 3H_o), 4.85 (d, *J* = 13.0 Hz, 3H_i), 7.45 (s, 6H).

¹³C NMR (250 MHz, CDCl₃): δ = 36.3 (C_a), 108–117 (C,C₄F₉), 124.9 (C_c), 139.2 (C_{b/d}), 139.8 (C_{b/d}).

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

Anal. calcd for $C_{45}H_{12}F_{54}S_6O_{18}$ (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-hexakisnonaflylcyclotribenzylene (8, 6.0 g, 2.9 mmol) in deoxygenated DMF (120 mL) was heated to 85 °C under N₂. Pd(PPh₃)₄ (in total 2.00 g, 1.73 mmol) and Zn(CN)₂ (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. NaHCO₃ (2 x 200 mL), H₂O, dil. HCl (200 mL), and finally with H₂O (200 mL). After drying (Na₂SO₄) 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): v = 3113, 3067, 3041, 2235, 1666, 1603, 1555, 1495, 1483, 1444, 1387, 1356, 1304, 1248, 1204, 1146, 1034, 935, 924, 898, 831, 783, 731, 604 cm⁻¹.

¹H NMR (250 MHz, DMSO- d_6): $\delta = 4.00$ (d, J = 13.1 Hz, $3H_0$), 5.20 (d, J = 13.1 Hz, $3H_i$), 8.45 (s, 6H).

¹³C NMR (250 MHz, DMSO- d_{δ}): δ = 35.5 (C_a), 114.3 (C_d), 116.4 (C_e), 136.7 (C_c), 144.9 (C_b).

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

Anal. calcd for $C_{27}H_{12}N_6$ (420.44): C, 77.13; H, 2.88; N, 19.99. Found: C, 76.04; H, 2.85; N, 19.44.

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