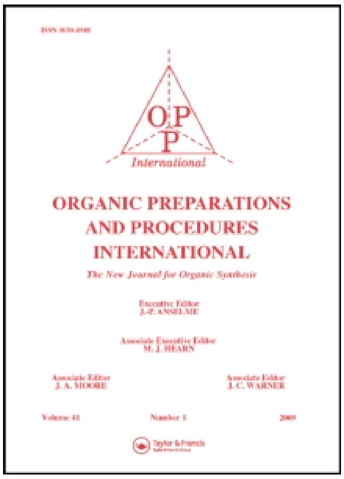

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SYNTHESIS OF A HEXAALKYNYLHEXAPHENYLBENZENE

John A. Hyatt[a]
[a] Research Laboratories, Eastman Chemical Co., Eastman Kodak Company, Kingsport, TN

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SYNTHESIS OF A HEXAALKYNYLHEXAPHENYLBENZENE

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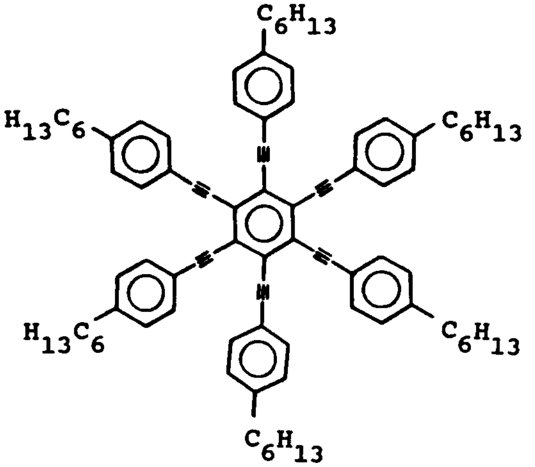
John A. Hyatt

Research Laboratories, Eastman Chemical Co.
Eastman Kodak Company, Kingsport, TN 37662

Recent publications by Praefcke and co-workers[1] have disclosed the occurrence of nematic-discotic mesophases in a series of hydrocarbons typified by the hexaalkynylbenzene **1**.[2] Such mesophases are rare but show interesting electrooptical effects.[3] It occurred to us that synthesis of the hexaphenylbenzene **4c**, an "inside-out" isomer of **1**, would be of interest. Unlike **1** for which models show the accessibility of a completely planar structure, acetylene **4c** should adopt the propeller-like conformation reported for unsubstituted hexaphenylbenzene.[4] Thus examination of **4c** might give an indication of the degree to which central disc planarity is required for discotic mesophase formation.



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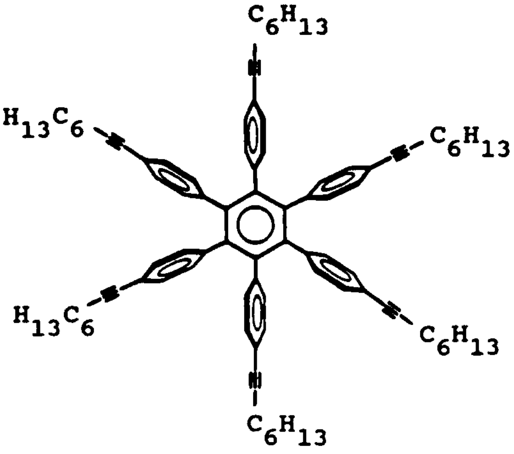
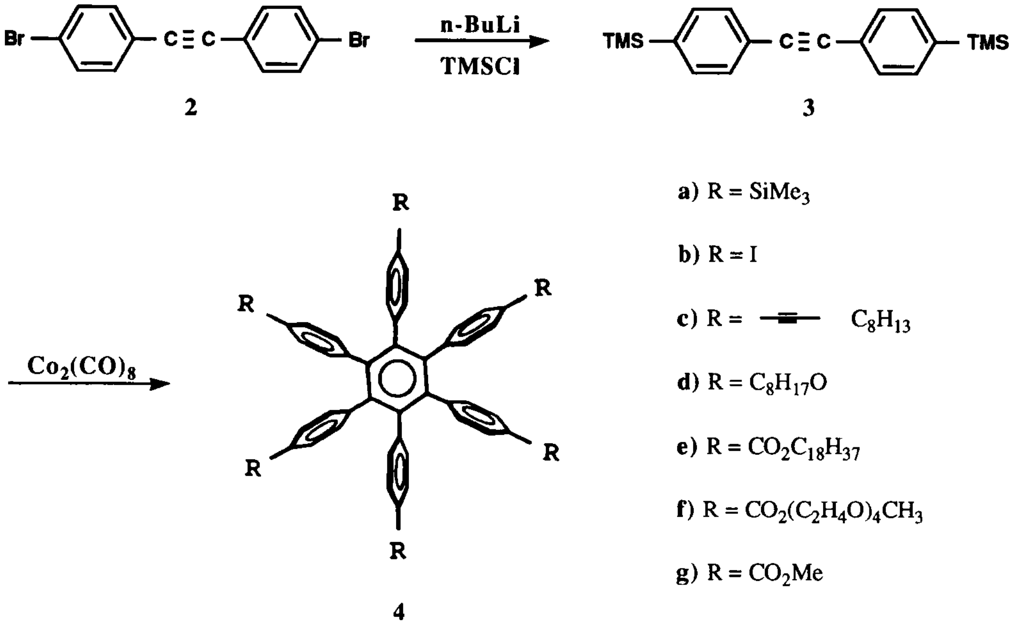


4c

The preparation of **4c** was carried out as follows. Conversion of the known 4,4'-dibromotolane **2**[5] to bis(trimethylsilyl) compound **3**, followed by cyclotrimerization[6] using dicobaltoctacarbonyl catalyst gave hexaphenylbenzene **4a** in 88% yield. Reaction of **4a** with bromine or with iodine gave complex mixtures of products, but iododesilylation[6,7] occurred smoothly with iodine monochloride in chloroform to give 74% of hexakis(*p*-iodophenyl)benzene **4b**. Coupling of 1-octyne with **4b** was achieved in the presence of Pd(II), Cu(I), triphenylphosphine and triethylamine[1] to afford pure **4c** in 51% yield. It should be pointed out that the propensity of transition metal catalysts to undergo oxidative addition to aryl bromides ruled out efficient cyclotrimerization of compounds such as **2**.



a) R = $SiMe_3$

b) R = I

c) R = —≡— C_8H_{13}

d) R = $C_8H_{17}O$

e) R = $CO_2C_{18}H_{37}$

f) R = $CO_2(C_2H_4O)_4CH_3$

g) R = CO_2Me

Hexaphenylbenzene **4c** melted at 176-178°; examination using a hot-stage polarizing microscope established that 4c did not form a mesophase. Thus it appears that one possible requirement for the formation of nematic mesophases in discotic compounds is the presence of a central molecular disc either thinner or more planar than that achievable in hexaphenylbenzenes. In further support of this assumption is the fact that neither hexakis(*p*-alkoxyphenyl) benzenes of the type **4d**[8] nor the novel esters **4e** and **4f** (which we prepared by ester interchange from the known ester **4g**) exhibit liquid crystalline behavior.

EXPERIMENTAL SECTION

Melting points were measured in open capillaries in a Thomas-Hoover apparatus and on a Carl Zeiss hot-stage microscope with crossed polarizers. NMR spectra were obtained using a Varian spectrometer operating at 300 (^1H) and 75 (^{13}C) MHz; samples were in $CDCl_3$ unless otherwise noted. Mass spectra were taken with a Vacuum Generators ZAB instrument operating in the field desorption mode. Elemental analyses were performed at the Eastman Research Labs.

4,4'-Bis(trimethylsilyl)diphenylacetylene (**3**).- A stirred slurry of 1.68 g (5.0 mmol) of 4,4'-dibromodiphenylacetylene[5] in 75 ml of dry tetrahydrofuran under an argon atmosphere was cooled in a Dry Ice-isopropanol bath and treated with 4.6 ml of 2.5 M n-butyllithium in hexane (11.5 mmol). After 5 min, 1.25 g (11.5 mmol) of freshly distilled trimethylsilyl chloride was added. The reaction was allowed to warm to room temperature over 2 hrs. The mixture was diluted with brine, extracted with ethyl acetate, and the extract dried ($MgSO_4$) and stripped of solvent. The solid residue was recrystallized from ethanol to give 1.15 g (74%) of product as lustrous plates, mp 135-137°. Repetition on a 6.7 g scale gave 4.97 g (77%) of 3. ^{1}H NMR: δ 7.51 (s, 4H); 0.27 (s, 9H).

Anal. Calcd. for $C_{20}H_{26}Si_2$: C, 74.45; H, 8.12. Found: C, 74.23; H, 8.34

Hexa(p-trimethylsilyphenyl)benzene (**4a**).- A mixture of 7.7 g of **3** (24.0 mmol), 0.20 g of dicobalt octacarbonyl and 150 ml of dioxane was stirred at reflux under argon for 18 hrs. The cooled reaction mixture was stripped of solvent and the residue extracted with ether (5 x 50 ml). The filtered ethereal solution was diluted with ethanol to precipitate the product **4a** (6.80g, 88%) as a chromatographically homogeneous white solid which did not melt below 330°. MS: m/e Calcd: 966. Found: 967. ^{1}H NMR: δ 6.96 (d, 2H), 6.76 (d, 2H), 0.10 (s, 9H).

Anal. Calcd. for $C_{60}H_{78}Si_6$: C, 74.46; H, 8.12. Found: C, 74.31; H, 8.22

Hexa(p-iodophenyl)benzene (**4b**).- To a solution of 6.40 g (6.6 mmol) of **4a** in 300 ml of chloroform was added in small portions over 0.5 hr 6.80 g (42.0 mmol) of iodine monochloride. The mixture was stirred at 25° with protection from moisture; after about 1 hr, the product began to precipitate. After 18 hrs, the product was collected and washed with dioxane and dried in vacuum to give 6.14 g (74%) of **4b** as a white solid which did not melt below 330°. MS: m/e Calcd: 1290; Found: 1290; ^{1}H NMR (pyridine-d_5): δ 7.43 (d, 2H), 6.89 (d, 2H). Correct elemental analysis was not obtained for this highly insoluble compound.

Hexa(p-(1-octynyl)phenyl)benzene (**4c**).- A mixture of 0.515 g (0.40 mmol) of **4b**, 0.10 g of bis(triphenylphosphine)palladium dibromide, 0.10 g of cuprous iodide, 0.20 g of triphenylphosphine, 0.80 g (7.2 mmol) of 1-octyne, and 75 ml of triethylamine was stirred under Ar in a 1000 oil bath for 17 hrs. The reaction mixture was cooled, decanted from the solids present, poured into 500 ml of water and 100 ml of ethyl acetate, and acidified with 10% HCl. The organic phase was washed with water until neutral, dried ($MgSO_4$), and stripped to give a tan semi-solid. It was triturated with ethanol to give a solid which was recrystallized from ethanol containing about 5% ether to give 0.24 g (51%) of **4c**, which crystallized with a mole of ethanol, mp 176-178°. MS: m/e Calcd: 1182; Found: 1183. ^{1}H NMR: δ 6.88 (d, 2H), 6.62 (d, 2H), 2.33 (2H, t), 1.6-1.2 (8H, complex m), 0.88 (3H, t). ^{13}C NMR: δ 140.4, 139.9, 131.5, 130.7, 121.4, 90.6, 80.9, 31.5, 28.8, 28.7, 22.6, 19.5, and 14.1.

Anal. Calcd. for $C_{90}H_{102}C_2H_5OH$: C, 89.84; H, 8.85. Found: C, 89.79; H, 8.81

Hexa(p-carbomethoxyphenyl)benzene (**4g**).- Compound **4g** was prepared using the sequence described for related esters in ref. 9 and did not melt below 330°. MS: m/e Calcd: 882; Found: 882. 1H NMR: δ 7.56 (d, 2H), 6.91 (d, 2H), 3.79 (s, 3H). ^{13}C NMR: δ 167.2, 144.6, 140.2, 131.5, 128.9, 128.3, 52.2.

Anal. Calcd. for $C_{54}H_{42}O_{12}$: C, 73.45; H, 4.79. Found: C, 73.19; H, 4.72

Hexaester (**4e**).- Ester **4g** (0.882 g, 1.0 mmol), 2.70 g (10 mmol) of 1-octadecanol, 50 ml of 1,2,4-trichlorobenzene, and ca. 0.05 g of titanium tetraisopropoxide were stirred under reflux (Ar atm) for 72 h, at which time TLC analysis disclosed the absence of **4g**. The reaction mixture was stripped of solvent under high vacuum and the residue flash-chromatographed on silica gel with 5% acetone in hexane elution. The major product was crystallized from hexane to give 1.0 g (43%) of **4e** as a waxy solid of mp 92-95°. MS: m/e Calcd: 2310; Found: 2311. ^{1}H NMR: δ 7.58 (d, 2H), 6.89 (d, 2H), 4.20 (t, 2H), 1.69 (t, 2H), 1.28 (br s, 30H), 0.87 (t, 3H).

Anal. Calcd. for $C_{156}H_{246}O_{12}$: C, 80.98; H, 10.72. Found: C, 81.18; H, 10.63

Hexaester (4f).- Ester **4g** (0.44 g, 5.0 mmol), 1.24 g (60 mmol) of tetraethylene glycol monomethyl ether, 10 ml of 1,2,4-trichlorobenzene, and 2 drops of titanium tetraisopropoxide were stirred at reflux under Ar for 19 hrs. The reaction mixture was stripped under high vacuum to leave a syrupy residue which was washed repeatedly with water followed by ether to remove excess glycol ether. A portion of the residue was further purified by prep TLC to give pure **4f** as a viscous liquid which tenaciously retained solvent and metal ions and did not give suitable elemental analysis. MS: m/e Calcd: M + Na, 1959. Found: 1960. ^{1}H NMR: δ 7.57 (d, 2H), 6.87 (d, 2H), 4.33 (t, 2H), 3.8-3.5 (m, 14H), 3.38 (s, 3H). ^{13}C NMR: δ 166.7, 144.6, 140.2, 131.4, 129.1, 128.2, 72.2, 70.8 (broad), 69.3, 64.3, 59.2.

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