Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 6375–6378

TETRAHEDRON
LETTERS

Synthesis of carbon dendron nano-chains with π-extended conjugation based on linear 1,4-phenylethynyl and 1,5-naphthylethynyl subunits

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Received 25 June 2003; revised 27 June 2003; accepted 27 June 2003

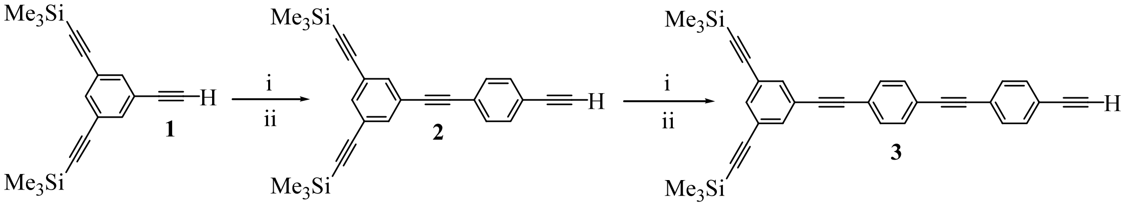
Abstract—A convenient and efficient synthesis of 3,5-di(trimethylsilylethynyl)phenylacetylene and *p*-[3,5-di(trimethylsilylethynyl)-1-phenylethynyl]phenylacetylene and the naphthylethynyl homologues terminal acetylenes of 5-(*N*,*N*-dimethylamino)naphthylethyne have been carried out. These terminal acetylene compounds serve to prepare nanometer-sized conjugated 1,3,5-tri(ethynylphenyl)benzene and 1,3,5-tri(ethynylnaphthyl)benzene oligomers, by means of heterocoupling with 1,3,5-triiodobenzene, catalysed by palladium, in excellent yields. Both the ethynylphenyl or ethynylnaphthyl homologues chains show fluorescence emission radiation, with important quantum yield.

Introduction

The synthesis and characterisation of nanometer-sized conjugated molecules of precise length and constitution, are of wide-spread interest, due to their inherent synthetic flexibility, which permits the design of molecular architectures with important properties.[1,2] Molecules showing π extended conjugation, in general exhibit high thermal stability and can present electroconductive, magnetic and optical properties.[3] A variety of potential applications such as artificial photosynthesis,[4] photocatalysis,[5] molecular photovoltaic cells,[6] molecular informatics,[7] and optoelectronic devices,[8,9] are beginning to emerge from this new field of research.

Conjugated systems integrated by 1,2-, 1,3-, 1,4-diethynyl and 1,3,5-triethynylphenyl units have been used in the preparation of aromatic monomers bearing multiple ethynyl groups with electroluminescence properties,[10] poly(phenylenevinylene) with fluorescence properties as well as dendrimers[11] with poly(yne) chain.[12] The triple bonds play the role of a wire while the polyaromatic systems behave as an energy relay subunit.

We now report the controlled synthesis of a novel family of rigid conjugated dendron nanostructures with a well defined geometry and the fluorescence properties.



Scheme 1. *Reagents and conditions*: (i) 4-(*p*-iodophenyl)-2-methylbut-3-yn-2-ol, $PdCl_2(PPh_3)_2$, Cu_2I_2, Et_3N; (ii) NaOH, toluene at reflux.

Keywords: trigonal geometry; 1,3,5-tri(ethynylphenyl)benzene and 1,3,5-tri(ethynylnaphthyl)benzene nanostructures; π-extended conjugation; 1,3,5-triiodobenzene; Sonogashira reaction; dendron base units.

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doi:10.1016/S0040-4039(03)01615-0

Discussion

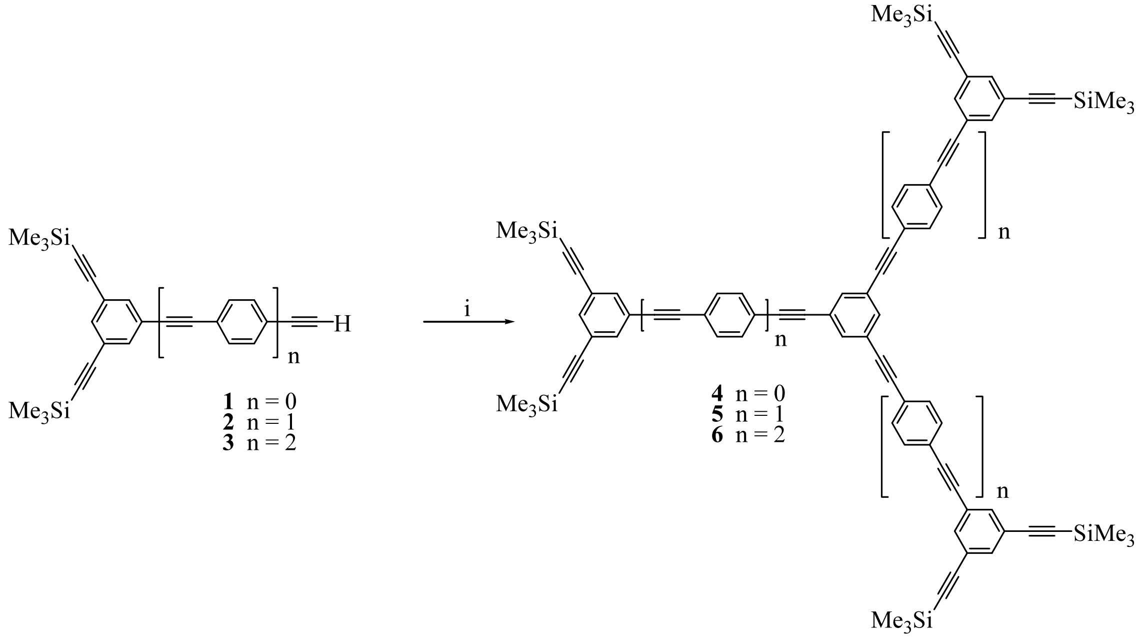
The 1,3,5-triiodobenzene was obtained by direct iodination giving a mixture of products that, in general, result in low yield and tedious purification.[13] A new practical synthesis of 1,3,5-triiodobenzene has been developed to obtain 1,3,5-tri(ethynylphenyl or ethynylnaphthyl)-benzene derivatives. Thus, by reduction of 1-iodo-3,5-dinitrobenzene with stannous chloride in ethyl acetate, was quantitatively isolated 1-iodo-3,5-diaminobenzene (123–125°C[14]) which, was transformed to the double diazonium salt with sodium nitrite/sulfuric acid, at −5 to −10°C, that was followed by treatment with potassium iodide at rt,[15] to give 1,3,5-triiodobenzene (184–186°C, 68%[13]).

Now, a new family of compounds have been synthesised starting of the terminal acetylene **3**, which was prepared by heterocoupling between the terminal acetylene homologue **2** and 4-(*p*-iodophenyl)-2-methylbut-3-yn-2-ol, followed by the specific deprotection of the propargylic group by treatment with powdered sodium hydroxide in dry toluene at reflux temperature.[16] Terminal acetylene **3** was isolated as a brown solid (148–150°C), in practically quantitative yield (Scheme 1).

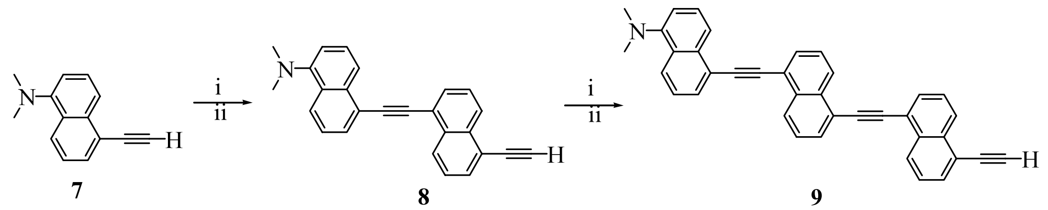
The heterocoupling of the terminal acetylenes **1**–**3** with 1,3,5-triiodobenzene gave the dendron nanostructures with a benzene core, which links a terminal 3,5-di(trimethylsilylethynyl)phenylacetylene, through a conjugated linear ethynylphenyl fragment giving **4**–**6** as yellow solids in good yield: **4** (118–120°C, 93%); **5** (143–146°C, 85%) and; **6** (199–203°C, 80%) (Scheme 2).

In the same way, the 5-(*N*,*N*-dimethylamino)naphthylethynyl terminal acetylenes **7**–**9** were synthesised from **7**.[17] Compounds **8** (145–147°C) or **9** (210–211°C), were satisfactory prepared by heterocoupling between **7** or **8** with 4-(5-iodo-1-naphthyl)-2-methylbut-3-yn-2-ol,[15] catalysed by palladium, giving the propargylic intermediates in good yield (87 and 88%, respectively), followed by treatment with sodium hydroxide in dry toluene at reflux temperature, to give the terminal acetylenes in quantitative yield (Scheme 3).

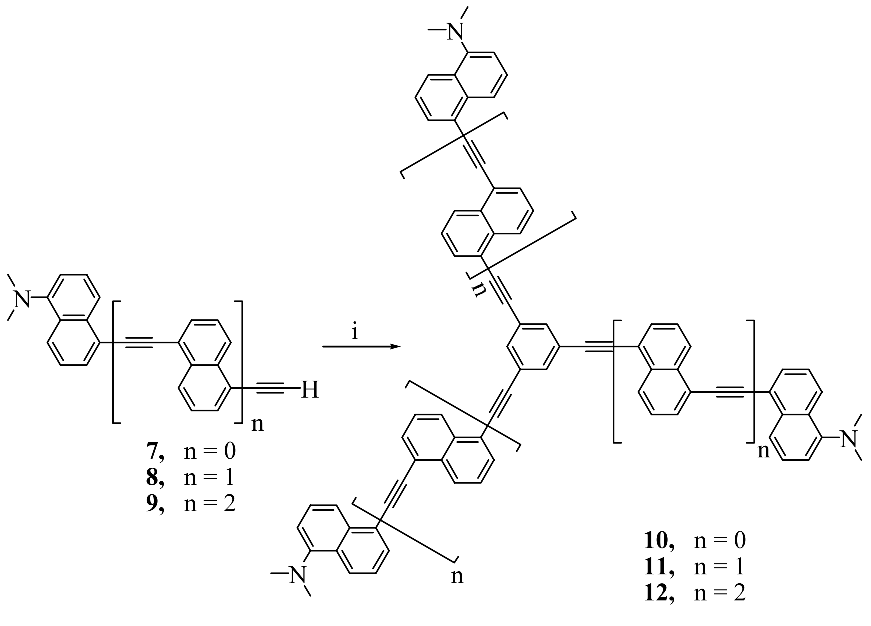
The heterocoupling reaction between the terminal acetylenes **7**–**9** with 1,3,5-triiodobenzene, catalysed by palladium, affords to the 5-(*N*,*N*-dimethylamino)naphthylethynyl dendron nanostructures **10**–**12**, as orange solids; compound **10** (193–195°C, 85%); compound **11** (237–238°C, 81%) (Scheme 4). The terminal acetylene **9** was treated with 1,3,5-triiodobenzene under



Scheme 2. *Reagents and conditions*: (i) 1,3,5-triiodobenzene, $PdCl_2(PPh_3)_2$, Cu_2I_2, Et_3N.



Scheme 3. *Reagents and conditions*: (i) $PdCl_2(PPh_3)_2$, Cu_2I_2, Et_3N, 4-(5-iodo-1-naphthyl)-2-methylbut-3-yn-2-ol; (ii) NaOH, toluene reflux.



Scheme 4. *Reagents and conditions*: (i) 1,3,5-triiodobenzene, $Cl_2Pd(PPh_3)_2$, Cu_2I_2, Et_3N.

Table 1. UV/vis and fluorescence spectra of the dendron structures **4**, **5**, **6**, and **10**, **11**, **12**[18]

Compd.	UV/vis[a] (CH_2Cl_2) λmax (nm)	ε (M^{-1} cm^{-1})	F[b] (CH_2Cl_2) λmax (nm)	Φ_f
4	308	87400	353, 367	0.16[c]
5	351	143700	356, 377	0.48[c]
6	347	187500	377, 398	0.80[c]
10	356	81400	504	0.43[d]
11	364	10650	527	0.21[d]
12	370	96800	530	<0.10[d]

[a] At room temperature.

[b] At room temperature and $[c] \cong 10^{-8}$ M.

[c] Fluorescence quantum yield was in dichloromethane relative to 2-aminopyridine in 0.1N H_2SO_4.

[d] Fluorescence quantum yield in dichloromethane relative to quinine sulfate in 1N H_2SO_4.

the same conditions, but in pyridine, at reflux temperature to give **12** in low yield (212–214°C, 30%).

From Table 1 was observed an important increasing of the quantum yield for each ethynylphenyl fragment (**4**–**6**) or also an important decreasing for each ethynylnaphthyl fragment (**10**–**12**). The ethynylphenyl chains show two fluorescence wavelength emission bands while the ethynylnaphthyl chains show an unique emission band such as for **5** and **10** as the reference homologues, at 356, 377 nm and at 504 nm, respectively. The wavelength bands for these homologues exhibit a bathochromic shift for each ethynylphenyl or for each ethynylnaphthyl fragment in the conjugated chain, respectively.

Acknowledgements

J.G.R. will be always grateful to his father Natalio Rodriguez Menéndez (deceased on 01/06/03) for his ethical advice on life. We are indebted to CICYT of Spain (project PB97-0060).

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18. All the new compounds were recrystallised in hexane or hexane/dichloromethane and give satisfactory elemental analyses. Select spectra data of the new nanostructure dendrons are given (^{1}H NMR was registered in CDCl$_3$ at 300 MHz, and the chemical shifts are given in δ with TMS as an internal reference and constants coupling J are given in Hz). Compound **4**: ^{1}H NMR: 7.58 (s, 3H), 7.56 (d, 6H, $J=1.6$), 7.54 (t, 3H, $J=1.6$), 0.25 (s, 54H). MS m/z (relative intensity): 954.0 (M$^+$, 57), 73 (100). Compound **5**: ^{1}H NMR: 7.67 (s, 3H), 7.57 (d, 6H, $J=1.6$), 7.54 (t, 3H, $J=1.6$), 7.52 (d, 6H, $J=8.9$), 7.48 (d, 6H, $J=8.9$), 0.25 (s, 54H). MS (FAB): 1255.1 (M$^+$, 100). Compound **6**: ^{1}H NMR: 7.67 (s, 3H), 7.56 (d, 6H, $J=1.6$), 7.53–7.55 (m, 15H), 7.50 (d, 6H, $J=8.6$), 7.49 (d, 6H, $J=8.6$), 0.25 (s, 54H). MS (FAB): 1555.6 (M$^+$, 80). Compound **10**: ^{1}H NMR: 8.33 (d, 3H, $J=8.7$), 8.22 (d, 3H, $J=7.8$), 7.93 (s, 3H), 7.83 (d, 3H, $J=6.9$), 7.58 (t, 3H, $J=8.1$), 7.51 (dd, 3H, $J=8.7$, $J=6.9$), 7.17 (d, 3H, $J=7.5$), 2.93 (s, 18H). MS: 657 (M$^+$, 100), 643 (3), 328 (13). Compound **11**: ^{1}H NMR: 8.63 (d, 3H, $J=8.4$), 8.54 (d, 3H, $J=8.4$), 8.32 (d, 3H, $J=8.4$), 8.27 (d, 3H, $J=8.7$), 7.96 (d, 3H, $J=5.7$), 7.95 (s, 3H), 7.89 (d, 3H, $J=7.2$), 7.71–7.50 (m, 12H), 7.17 (d, 3H, $J=6.6$), 2.93 (s, 18H). MS (FAB): 1108.0 (M$^+$, 100). Compound **12**: ^{1}H NMR: 8.82 (d, 3H, $J=8.4$), 8.65 (d, 3H, $J=8.7$), 8.54 (d, 3H, $J=8.4$), 8.32 (d, 3H, $J=8.1$), 8.30 (d, 3H, $J=8.1$), 8.26 (d, 3H, $J=8.1$), 8.02 (d, 3H, $J=7.2$), 8.01 (d, 3H, $J=7.2$), 7.96 (d, 6H, $J=6.6$), 7.89 (d, 3H, $J=7.2$), 7.75 (d, 3H, $J=7.2$), 7.72–7.50 (m, 18H), 7.17 (d, 3H, $J=7.8$), 2.93 (s, 3H). MS (FAB): 1557.0 (M$^+$, 100).