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LETTERS

A Horner-Wadsworth-Emmons Approach to Dipolar and Non-Dipolar Poly(phenylenevinylene)dendrimers

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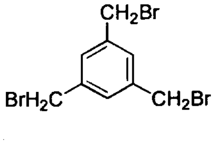
Abstract. The synthesis of first generation phenylenevinylene dendrimers is described. The Horner-Wadsworth-Emmons reaction is used for this purpose. The reported methodology permits the preparation of dipolar and non-dipolar structures. A second generation dendron bearing peripheral electron donor groups is also reported.

Polyphenylenevinylenes (PPV), polyphenylenes (PPP), polyfluorenes (PF) and other π-conjugated oligomers are important compounds due to their electrical, optical, non-linear optical, electroluminiscent and photophysic properties. This kind of conjugated polymer has received the interest of several research groups.[1] On the other hand, development of the dendrimer synthesis has provided efficient ways to a huge number of structures, some of them related to conjugated polymers, mainly PPP's.[2]

When growing dendrimers from 1,3,5-trisubstituted benzene cores, it is possible to obtain dipolar and non-dipolar structures with very good efficiency/transparency ratios, an interesting feature for NLO materials.[3] Some convergent approaches to phenylenevinylene dendrimers, also called stilbenoid dendrimers, have been recently reported.[4] In all cases non-dipolar dendrimers bearing alkyl or oxyalkyl peripheral groups are prepared. On the other hand, dendritic systems containing both strong π-donor and π-acceptor groups covalently bonded into their framework are especially attractive targets.[5]

The high number of commercially available benzyl bromides and benzaldehydes, and the efficient stereochemical control of the Horner-Wadsworth-Emmons reaction provides a versatile and useful methodology for the synthesis of dipolar and non-dipolar dendrimers bearing a 1,3,5-tris(phenylenevinylene)benzene core.

The strategy we have developed uses the readily available tribromide **1**[6] as a basic unit to form the core of the non-dipolar dendrimers as well as 1-acetyloxymethyl-3,5-bis(bromomethyl)benzene, **2**, and 1,3-bis(acetyloxymethyl)-5-bromomethylbenzene, **3** for the dipolar dendrimers. Compounds **2** and **3** were prepared by treatment of **1** with 1.5 equivalents of sodium acetate in DMF at 100 °C in a 33% and a 29% yield, respectively (62% overall).[7]



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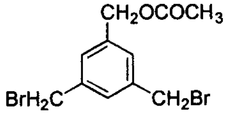

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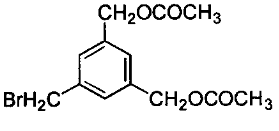

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The Arbuzov reaction of bromides **1-3** with triethyl phosphite at 140 °C gave the corresponding phosphonates in quantitative yield. Compound **4** reacted with several *para*-substituted benzaldehydes in

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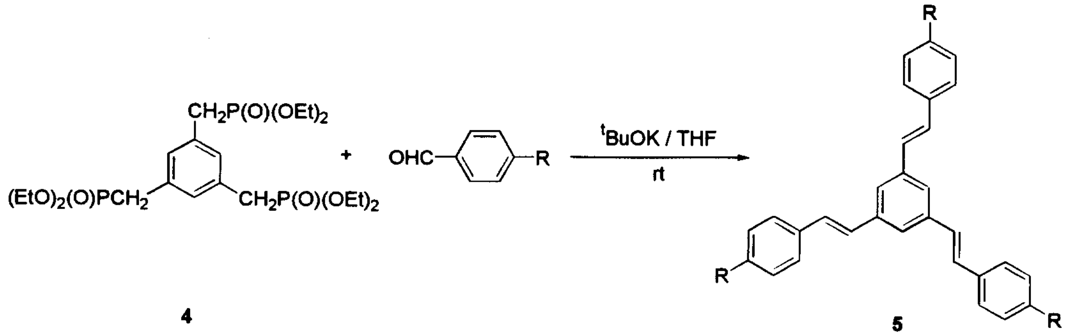
Bu^{t}OK/THF to yield the desired first generation dendrimers, **5** (see **Table**). Only the all-*trans* isomers were detected within the limits of NMR detection. ^{1}H and ^{13}C-NMR spectroscopy confirmed the threefold symmetry of compounds **5**.

Table. Preparation of non-dipolar first generation dendrimers



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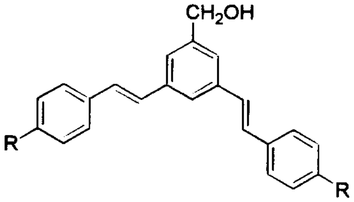
5

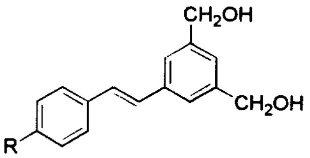
Compound[a]	R	Yield[b]
5a	CN	40
5b	OCH_3	85
5c	$N(CH_3)_2$	60
5d[c]	$CH(OCH_3)_2$	--
5e	CHO	40

[a] Only the all-*trans* isomers were observed by ^{1}H-NMR ($J_{trans} \cong 16.4$ Hz).
[b] Yield of pure, isolated product.
[c] Not isolated, it was *in situ* hydrolyzed in mild acid conditions to **5e**.

In a similar way, phosphonates derived from compounds **2** and **3** gave alcohols **6** and **7**, respectively, in good overall yields, after *in situ* hydrolysis of the ester moiety with NaOH / H_2O.

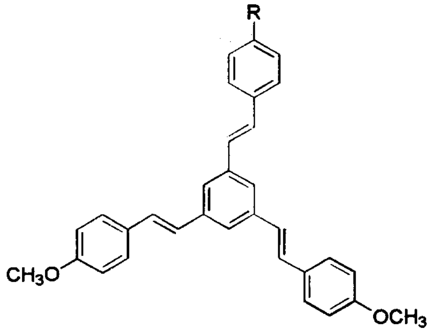


6a R = CN (58%)
6b R = OCH_3 (78%)
6c R = $N(CH_3)_2$ (80%)



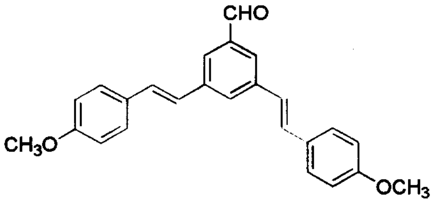
7b R = OCH_3 (82%)
7c R = $N(CH_3)_2$ (52%)

These alcohols can serve as building blocks for generating the first generation dipolar dendrimers. Thus, for example, bromination of **6b** with CBr_4/PPh_3 in CH_3CN followed by reaction with $P(OEt)_3$ and coupling with different aldehydes under the same experimental conditions described above gave compounds **8**. Again, only the all-*trans* isomers could be detected by ^{1}H-NMR. Dendritic structures **8** which possess a C_{2v} symmetry are excellent candidates to present NLO properties[8] as well as good transparency to UV.[3]



8a R = CN (31%)
H_3O^+ **8b** R = $CH(OCH_3)_2$ ---
8c R = CHO (25%)

Finally, we considered the synthesis of a second generation dendron bearing peripheral electron donor groups. PCC oxidation of **6b** gave the aldehyde **9** in a 85% yield. Horner-Wadsworth-Emmons reaction of this compound with the diphosphonate derived from **2**, followed by *in situ* hydrolysis with NaOH / H_2O, gave compound **10**[9] in a 86% overall yield. Since the above reactions can be repeated in a iterative fashion the alcohol **10** may be regarded not only as a precursor for non-dipolar second generation dendrimers, but also as the starting material for the synthesis of third and higher generation dendrons.



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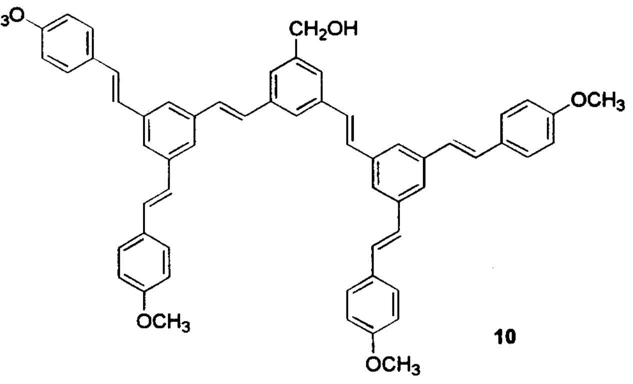

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In conclusion, the simple strategy depicted here provides a short route to construct phenylenevinylene first generation dendrimers with different electron donor and electron withdrawing substituents at the periphery. It also provides the synthesis of second generation dendrons which in turn are suitable building blocks for the preparation of both dendrimers and dendrons of higher generations. Work to determine the scope of this methodology as well as NLO properties for these structures is now in progress.

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6. Several procedures for the synthesis of **1** have been described starting from 1,3,5-tris(hydroxymethyl)benzene. Here, it was obtained by reaction with an excess of a 35% HBr solution in acetic acid in a 97% yield. Brominations using either PBr_3 (Boekelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3201) or 3 equivalents of Ph_3P/CBr_4 (Ashton, P. R.; Shibata, K.; Shipway, A. N.; Stoddart, J. F. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2781) have also been reported to proceed in good yields. 1,3,5-tris(hydroxymethylbenzene) was prepared by reduction with lithium aluminium hydride in refluxing THF of the commercially available 1,3,5-trimethyl benzenetricarboxylate according to a modification of the procedure reported by Cochrane, W. P.; Pauson, P. L.; Stevens, T. S. *J. Chem. Soc. (C)* **1968**, 630.
7. Although the presence of starting material **1** as well as the corresponding triacetate was also observed in the crude mixture, all the products were easily separated by column chromatography.
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9. ^{1}H-NMR ($CDCl_3$) δ: 3.83 (s, 12H, 4xOCH_3); 4.79 (s, 2H, C$\underline{H_2}$OH); 6.91 (d, 8H, J = 8.7 Hz, Ar); 6.98 (d, 4H, J = 16.5 Hz, 4xCH=); 7.13 (d, 4H, J = 16.5 Hz, 4xCH=); 7.18 (s, 4H, 2xCH=CH); 7.44-7.60 (m, 17H , Ar). ^{13}C-NMR ($CDCl_3$) δ: 159.4, 141.8, 138.4, 138.0, 137.8, 130.1, 129.2, 128.7, 128.6, 127.8, 126.3, 124.2, 123.8, 123.4, 114.2, 65.2 (CH_2OH), 55.3 (OCH_3).