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Synthesis of soluble oligocarbazole derivatives

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Abstract—3,6-Disubstituted carbazole building blocks are coupled via copper-catalyzed Ullmann reactions to afford trimeric and heptameric carbazoles with excellent solubilites in organic solvents. Alternatively, oligomeric carbazoles with phenylene spacers, that are more stable towards oxidation, can be obtained via palladium-catalyzed Suzuki coupling reactions. © 2003 Elsevier Science Ltd. All rights reserved.

Carbazole derivatives are of interest as components in photorefractive polymer composites.[1,2] Recently, we reported on the photorefractive properties of bifunctional *N*-arylated carbazoles in a carbazole polymer host matrix.[3]

A number of reports on the Ullmann *N*-arylation of carbazoles with aryl halides (mainly iodides) at high temperatures describe the use of copper bronze as the catalyst.[4] The yields normally are low to fair, and several days of heating may be necessary. Recently, Pd-catalyzed reactions, using somewhat milder conditions, have also been described.[5] This gave some improvement but the catalyst and ligand are expensive and cumbersome to handle (glove box). Part of the problem of low yield with the copper bronze reactions may be caused by the low solubility of the *N*-arylcarbazoles, combined with their susceptibility to oxidative degradation. Therefore, we decided to start from a 3,6-disubstituted carbazole **1** with improved solubility and stability. 3,6-Bis(*t*-butyl)carbazole **1** was prepared in 40% yield by Friedel–Crafts alkylation of carbazole, adapting a published procedure.[6] The reaction of **1** with a series of aryl iodides **2a**–**c** in the presence of copper bronze gave excellent yields (92–98%) of *N*-arylcarbazoles **3a**–**c**, confirming our hypothesis about the low yield reported in the literature with unsubstituted carbazole. The reactions occur within 24 h at 160–170°C in nitrobenzene. The heterocyclic *N*-(2-thienyl) carbazole **3d** could be prepared in the same way in 52% yield. With **1** and an excess of 1,4-diiodobenzene the 4-iodophenyl derivative **3f** was formed in 80% yield, or alternatively a 2:1 ratio of reactants gave the biscarbazole **4** (55%). The same reaction with **1** and excess 1,4-dibromobenzene gives a slightly lower yield (55%) of the *N*-bromophenyl derivative **3e**. Compound **3f** was prepared earlier by Moore et al., using a five-step procedure, in connection with a study on carbazole dendrimers.[7] The iodide **3f** could be transformed to the aldehyde **3g** (80%) by lithiation and quenching with dimethyl formamide. Reaction of **1** with 1,3,5-tribromobenzene leads to the 3,5-dibromophenyl carbazole derivative **3h** (50%) when 2 equiv. of tribromobenzene are used. A 2:1 ratio of **1** and tribromobenzene gives the biscarbazole **5a** in 27% yield. Unfortunately, the completely substituted tris(carbazolyl)benzene **6** was not obtained when a slight excess of **1** was used, probably because of its instability towards oxidation (Figs. 1 and 2).

We also succeeded to obtain triscarbazoles **8a**,**b** (in 82 and 66% yield, respectively) which can be considered to be first generation carbazole dendrimers, from the copper bronze-catalyzed reaction of **1** with the known[8] 3,6-diiodo-9-substituted-carbazoles **7a**,**b**. The latter

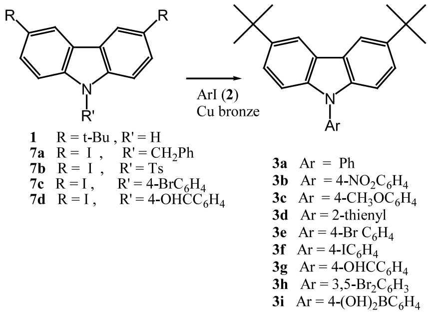

Figure 1. *N*-Arylation of 3,6-bis(*t*-butyl)carbazole.

Keywords: carbazoles; Ullmann coupling; oligomers; dendrimers.

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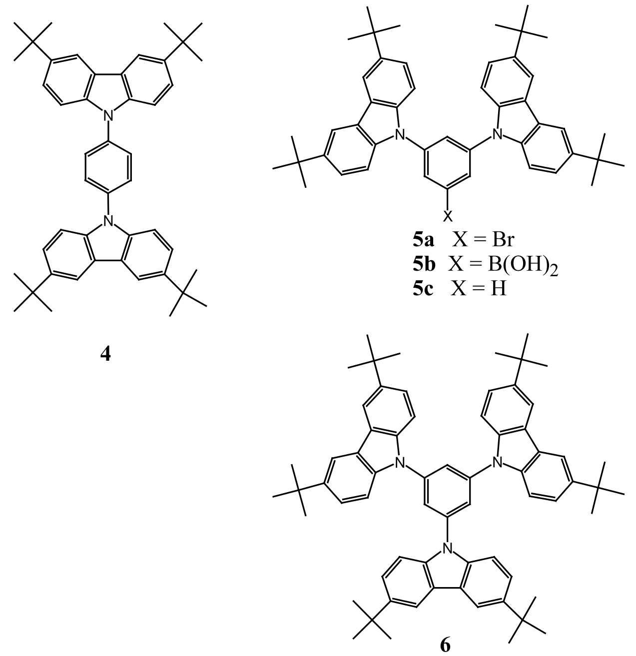

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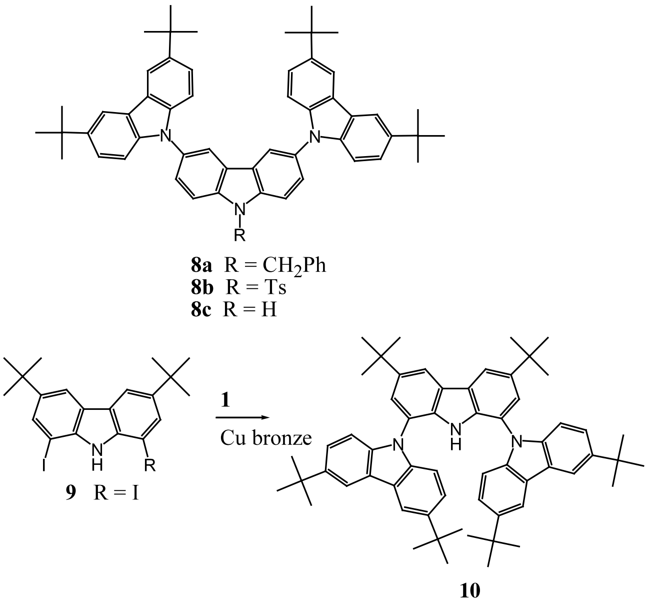
5a X = Br
5b X = B(OH)$_2$
5c X = H

6

Figure 2. Bis- and triscarbazolylbenzenes.

compounds can in the same way be seen as monomers for dendron synthesis.

The Ullmann reaction can even be applied to prepare a sterically encumbered triscarbazole **10** in 80% yield from **1** and the 1,8-diiodo-3,6-bis(*t*-butyl)carbazole **9**, which could itself be prepared in good yield (65%) from **1** and the potassium iodide/potassium iodate reagent.[8] Obviously the large 1,8-substituents prevent further Ullman reaction of the iodides with the remaining carbazole nitrogen of **10** (Fig. 3).



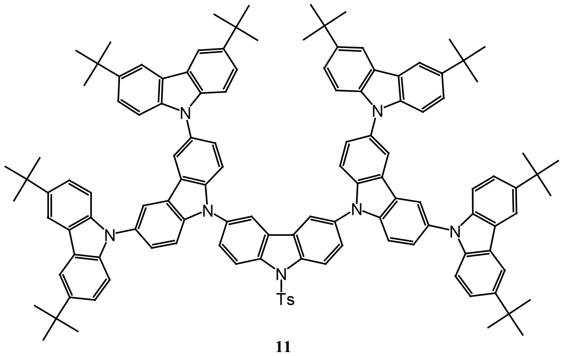
8a R = CH$_2$Ph
8b R = Ts
8c R = H

9 R = I

10

Figure 3. Synthesis of triscarbazoles.

Dendritic oligocarbazoles of higher generation are more difficult to prepare because of the inherent sensitivity of the materials towards oxidation. Deprotection of **8a** using a known procedure[6] failed, but the derivative **8b** was cleaved with aq. NaOH to afford the free carbazole dendron **8c** in 60% yield. The coupling of this derivative **8c** to the monomer **7b** was somewhat more problematic due to extensive oxidative breakdown of the second generation dendron **8c** under the relatively harsh reaction conditions, but still a yield of 14% of the heptameric second generation dendron **11** could be obtained.



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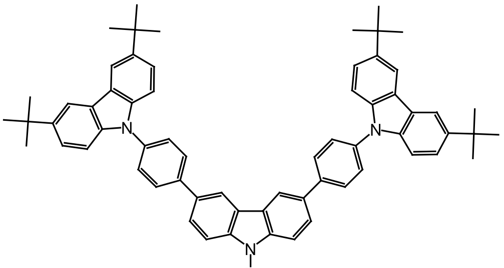
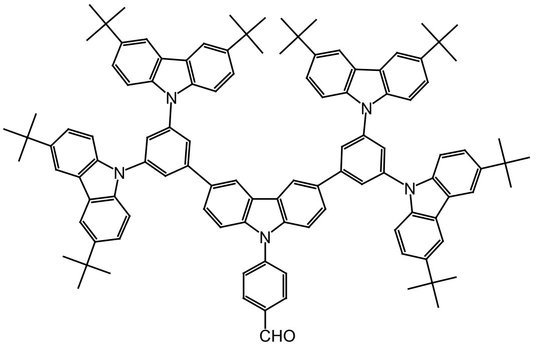
A way to increase the stability of the carbazole oligomers would be to have aryl spacers between the carbazole units. Thus, boronic acid **3i** was prepared (60% yield) starting from the *N*-arylcarbazole **3f** via the lithium derivative. Suzuki coupling of **3i** with the monomer **7b** again gave a triscarbazole **12a** (58%). The Suzuki coupling reaction (Pd(PPh$_3$)$_4$ as the catalyst) of the iodide functions of the alternative monomer **7c** with two equivalents of the boronic acid **3i** is specific, leaving the bromide function



12a R = Ts
12b R = 4-BrC$_6$H$_4$



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of **12b** (30%) intact. Analogously, the 1,3-bis(carbazolyl)benzene **5a** was converted into the boronic derivative **5b** (27%). This compound **5b** underwent Suzuki coupling with 3,6-diiodo-9-(4-formylphenyl)carbazole **7d** to give the pentakiscarbazole **13** (27%). A major side product was the *N*-phenylbiscarbazole **5c**, which is due to the instability of **5b**, which was already shown by the relatively low yield of its synthesis from **5a**. We hope in further work to convert **12b** and **13** to oligocarbazole materials of higher molecular mass.

All materials obtained were fully characterized by mass, ^{1}H and ^{13}C NMR spectral techniques.[9] The triscarbazoles **8a**,**b**,**c** and **10**, the heptacarbazole **11**, and the tris- and pentakiscarbazoles **12a**,**b** and **13** maintain excellent solubilities in many common organic solvents (THF, toluene, chlorinated solvents).

Acknowledgements

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References

1. Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127.
2. Kippelen, B.; Meerholz, K.; Peyghambarian, N. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S.; Mitaya, S., Eds.; 1997; p. 475.
3. Schaerlaekens, M.; Hendrickx, E.; Hameurlaine, A.; Dehaen, W.; Persoons, A. *Chem. Phys.* **2002**, *277*, 43.
4. Glaser, R.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2777.
5. Watanabe, M.; Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **2000**, *41*, 481.
6. Neugebauer, F. A.; Fischer, H. *Chem. Ber.* **1975**, *105*, 2686.
7. Zhu, Z.; Moore, J. S. *J. Org. Chem.* **2000**, *65*, 116–123.
8. Tucker, S. H. *J. Chem. Soc.* **1926**, 546–553.
9. ***Synthesis of 8b***: A mixture of 3,6-di-*t*-butylcarbazole (1.18 g, 4.25 mmol), 3,6-diiodo-*N*-tosylcarbazole **7b** (1 g, 1.7 mmol), potassium carbonate (1.17 g, 8.5 mmol), copper bronze (0.25 g) in nitrobenzene (7 ml) was heated overnight at 170°C. After cooling the reaction mixture at rt, chloroform was added and the solution was filtrated. Nitrobenzene was removed under reduced pressure and the residue was taken up in chloroform and chromatographed over silica gel with a mixture of hexane–chloroform (7:3–5:5) as the eluent. This gave **8b** as a white solid (1.4 g, 66%), mp >300°C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (d, $J=8.7$ Hz, 2H); 8.13 (d, $J=1.53$ Hz, 4H, carbazole H-4,5); 8.04 (d, $J=2.04$ Hz, 2H, carbazole H-4,5); 7.90 (d, $J=8.46$ Hz, 2H, tosyl); 7.71 (dd, $J=2.07$ and 8.7 Hz, 2H, carbazole 2,7-H); 7.43 (dd, $J=1.8$ and 8.7 Hz, 4H, carbazole 2,7-H); 7.28 (m, 8H, carbazole and tosyl); 2.39 (s, 3H, CH_3); 1.45 (s, 36H, *t*-Bu), ^{13}C NMR (300 MHz, $CDCl_3$): δ 145.90, 143.43, 139.92, 137.78, 135.42, 134.95, 130.49, 127.51, 127.18, 124.11, 123.80, 118.91, 116.73, 109.39, 35.16, 32.42, 22.11; MS (ES^{+}) 876 (MH).