ORGANIC LETTERS

2009
Vol. 11, No. 16
3726−3729

Synthesis of Substituted Trinaphthylenes via Aryne Cyclotrimerization

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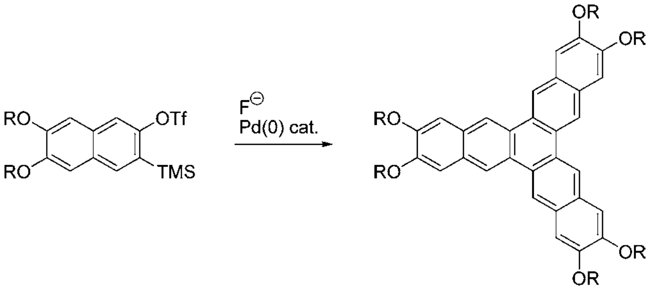
Received June 15, 2009

ABSTRACT



The first synthesis of a series of substituted trinaphthylene derivatives via a palladium-catalyzed aryne cyclotrimerization is reported. This method provides an approach for the preparation of novel disk-shaped polycyclic aromatic hydrocarbons that self-assemble via $\pi-\pi$ interactions and may form columnar liquid crystal phases. Although the trinaphthylenes prepared in this study do not exhibit columnar mesophases, variable concentration ^{1}H NMR studies provide evidence for aggregation in solution.

Polycyclic aromatic hydrocarbons (PAHs) are of considerable interest in materials science because their charge transport properties make them potentially useful in organic optoelectronic devices such as light-emitting diodes, field-effect transistors, and photovoltaics.[1] Efficient charge transport in PAHs stems from the low HOMO−LUMO gap of these compounds[2] but also requires effective $\pi-\pi$ overlap for charge conduction. Thus, an understanding of $\pi-\pi$ interactions in PAHs is important for the development of organic charge transporting materials. Indeed, many substituted PAHs show evidence of $\pi-\pi$ interactions either through aggregation in solution[3] or by forming columnar liquid crystal phases.[4] For example, substituted triphenylenes (**1**) (Figure 1) are known to exhibit columnar mesophases and show excellent charge transport properties.[5] The fluidity of columnar liquid crystals also facilitates alignment of the columns, which allows for optimal charge transport. However, to be useful for device applications, discotic liquid crystals should exhibit their mesophases over a broad temperature range. Consequently, there has been considerable effort toward the synthesis of new disk-shaped PAHs bearing periph-

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[2] Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891–4945.

[3] Chen, Z.; Lohr, A.; Saha-Möller, C. R.; Würthner, F. *Chem. Soc. Rev.* **2009**, *38*, 564–584.

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[5] (a) Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851–858. (b) Bacher, A.; Bleyl, I.; Erdelen, C. H.; Haarer, D.; Paulus, W.; Schmidt, H.-W. *Adv. Mater.* **1997**, *9*, 1031–1035. (c) Christ, T.; Glusen, B.; Greiner, A.; Kettner, A.; Sander, R.; Stumpflen, V.; Tsukruk, V.; Wenndorf, J. H. *Adv. Mater.* **1997**, *9*, 48–52. (d) Adam, D.; Schuhmacher, P.; Simmerer, J.; Haussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141–143. (e) Paraschiv, I.; Giesbers, M.; van Lagen, B.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Marcelis, A. T. M.; Zuilhof, H.; Sudhoelter, E. J. R. *Chem. Mater.* **2006**, *18*, 968–974.

10.1021/ol9013443 CCC: $40.75
Published on Web 07/16/2009

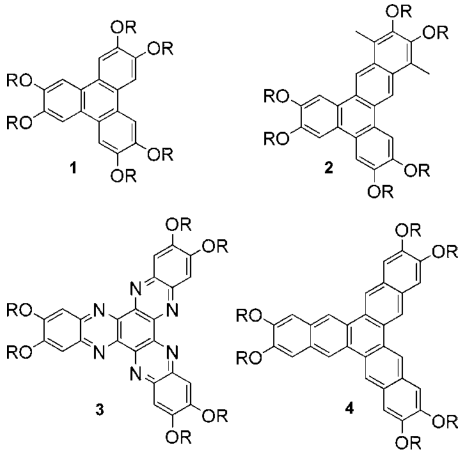


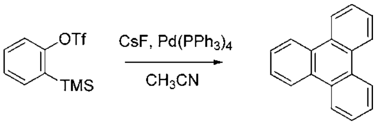
Figure 1. Disk-shaped hexaalkoxytriphenylenes and extended analogues.

eral alkyl or alkoxy side chains to discover compounds exhibiting columnar mesophases over a broad temperature range. Several studies suggest that increasing the size of the PAH core promotes broad liquid crystalline phases,[6] while other studies indicate that larger cores lead to improved charge transport properties.[7] Williams and co-workers have shown that a series of benzotriphenylenes (**2**), where the triphenylene core is extended by an additional aromatic ring on one side, exhibit broader columnar phases compared to the analogous triphenylenes.[6a] Meanwhile, Ong et al. have shown that some hexaazatrinaphthylenes (**3**) also exhibit mesomorphism.[8] Surprisingly, the closely related hexaalkoxytrinaphthylenes (**4**), where the triphenylene core is extended by one aromatic ring, have not been reported, possibly because no general synthetic methods provide access to these compounds.[9]

In this study, we report the first synthesis of substituted trinaphthylenes **4** using palladium-catalyzed aryne cyclotrimerization methods. We also report preliminary studies of the self-assembly of **4** through $\pi-\pi$ interactions.

Over the past decade, numerous developments in the transition-metal-catalyzed reactions of arynes have provided new routes toward substituted PAHs.[10] As a notable example, in 1998 Peña et al. reported the palladium-catalyzed cyclotrimerization of arynes to produce triphenylenes (Scheme 1).[10a]

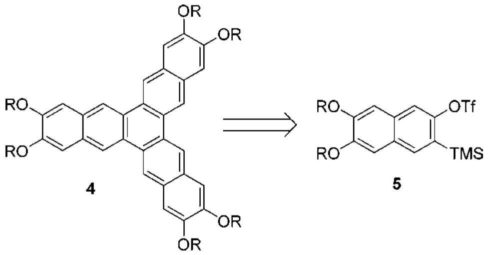
Scheme 1. Palladium-Catalyzed Aryne Cyclotrimerization Developed by Peña et al.[10a]



In this reaction, a trimethylsilylaryl triflate is treated with fluoride in the presence of a Pd(0) catalyst. The aryne generated in situ then undergoes cyclotrimerization catalyzed by palladium. The scope of this methodology is quite broad, having been applied to the synthesis of a wide variety of PAHs. Furthermore, similar conditions can be used in the cocyclotrimerization of arynes with alkynes to form phenanthrenes.[11] Indeed, this cocyclotrimerization methodology has recently been applied to the synthesis of a series of liquid crystalline tetrabenzopentaphenes.[12] However, the use of aryne cyclotrimerization for the synthesis of disk-shaped mesogens is still limited.

Given the versatility of this synthetic methodology, we sought to apply it to the synthesis of a series of novel hexaalkoxytrinaphthylenes and to explore the self-assembly of these compounds. We envisioned that the desired trinaphthylenes could be prepared from the appropriately substituted naphthalene (**5**) under conditions similar to those described by Peña et al. (Scheme 2) and that compound **5** could ultimately be derived from 2,3-dihydroxynaphthalene (**6**).

Scheme 2. Synthetic Approach for the Preparation of Substituted Trinaphthylenes



To prepare the requisite substituted naphthalyne precursor (**5**), our synthesis began with 2,3-dihydroxy-6,7-dibromonaphthalene (**7**), which can be prepared in two steps from 2,3-dihydroxynaphthalene as reported by Cammidge et al.[13] (see Scheme 3). Subsequent alkylation furnished the corre-

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(8) (a) Ong, C. W.; Liao, S.-C.; Chang, T. H.; Hsu, H.-F. *Tetrahedron Lett.* **2003**, *44*, 1477–1480. (b) Ong, C. W.; Liao, S.-C.; Chang, T. H.; Hsu, H.-F. *J. Org. Chem.* **2004**, *69*, 3181–3185.

(9) The standard oxidative coupling methods used for the synthesis of triphenylenes fails to produce the desired product and instead gives a complex mixture.

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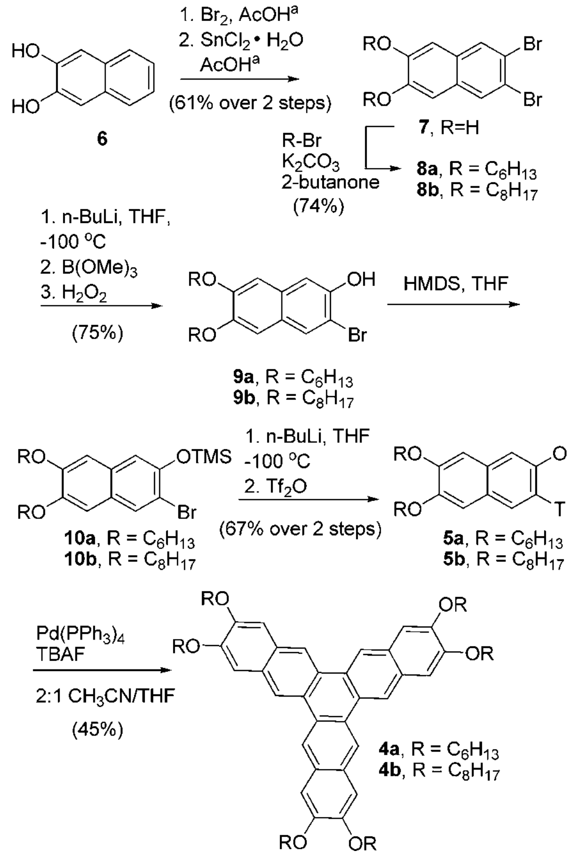
(13) Cammidge, A. N.; Chambrier, I.; Cook, M. J.; Garland, A. D.; Heeney, M. J.; Welford, K. *J. Porphyrins Phthalocyanines* **1997**, *1*, 77–86.

Scheme 3. Synthesis of Trinaphthylenes **4a** and **4b**



[a] Cammidge et al.[13]

sponding 2,3-dialkoxy-6,7-dibromonaphthalenes (**8**).[14] Compound **8** was subjected to lithium−halogen exchange using *n*-BuLi at −100 °C in THF (using a liq. N_2/Et_2O bath), and the aryllithium was trapped with trimethyl borate. The crude boronic acid was then oxidized using H_2O_2 to produce the desired substituted naphthol (**9**). To prevent aryne formation from the *ortho*-bromo-aryllithium, the lithium halogen exchange was carried out at −100 °C.[15] Following the approach developed by Peña et al., compound **9** was converted to the corresponding trimethylsilyl ether (**10**) using hexamethyldisilazane. After removal of volatiles under vacuum, compound **10** was used in the next step without further purification. Treatment of **10** with *n*-BuLi, followed by triflic anhydride, furnished the trimethylsilyl triflate aryne precursor (**5**). The palladium-catalyzed cyclotrimerization was carried out by slowly adding a solution of tetrabutylammonium fluoride to a mixture of **5** and 10% $Pd(PPh_3)_4$ in a 2:1 mixture of dry CH_3CN/THF. These conditions furnished the desired trinaphthylenes in moderate yield.

The mesomorphic properties of **4** were investigated by variable-temperature polarized optical microscopy. Surprisingly, neither compound showed any evidence of liquid crystallinity but rather showed distinct transitions between crystalline solid and isotropic liquid on both heating and cooling. In contrast, hexa(hexyloxy)triphenylene (HAT6) exhibits a columnar mesophase from 67 to 97 °C,[16] while the analogous hexaazatrinaphthylene **3** exhibits a broad mesophase range from 187 to 230 °C.[8b]

Although compounds **4a** and **4b** do not exhibit columnar mesophases, variable concentration ^1H NMR studies showed that the chemical shift of the aromatic protons changed as a function of concentration. Solutions of **4a** in $CDCl_3$ displayed upfield shifts at higher concentration, which is consistent with aggregation through $\pi-\pi$ stacking interactions. A plot of the chemical shift of the most deshielded aromatic signal as a function of concentration (Figure 2) was fitted to a curve for monomer−dimer aggregation[17] and yielded a dimerization constant, *K*, of 3.8 M^{-1}. A similar plot of the other aromatic resonance yielded a similar fit with the same equilibrium constant (see Supporting Information). It is noteworthy that the aggregation is still observed in benzene-d_6. The results are consistent with dimerization in solution and reflect a relatively weak self-association compared to other disk-shaped PAHs.[3] For example, some hexabenzocoronene derivatives show association constants up to 10^4 M^{-1}.[18] Although **4** possesses a large aromatic core that may be expected to favor π-stacking interactions, the core is also electron rich, which may electrostatically disfavor strong association. Furthermore, the shape of the core may allow for a staggered stacking arrangement where $\pi-\pi$ overlap is less effective.

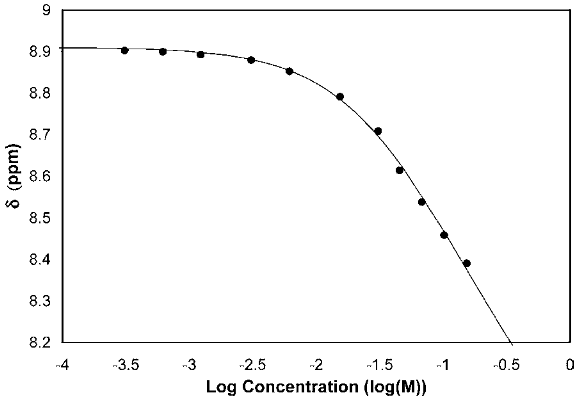


Figure 2. Plot of ^1H NMR chemical shift of aromatic signal vs log concentration (dots), fitted to a curve using a monomer−dimer model (line). See Supporting Information for more details.

In summary, we have prepared a series of novel trinaphthylenes via palladium-catalyzed aryne cyclotrimerization. Although these alkoxy-substituted trinaphthylenes did not

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(14) Chen, Z.; Swager, T. M. *Org. Lett.* **2007**, *9*, 997–1000.

(15) While the lithium−halogen exchange proceeded in good yield for **9a** and **9b**, the reaction failed for the derivatives with longer alkyl chains (decyl or dodecyl), presumably due to the insolubility of the reactants and corresponding aryllithium species at low temperatures.

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exhibit any mesomorphic properties, compounds of this type may exhibit interesting electronic properties. We are currently investigating the effect of structural modifications on the self-assembly as well as mesomorphic properties of these compounds.

Acknowledgment. The authors gratefully acknowledge financial assistance from Wilfrid Laurier University, the Science and Technology Endowment Program (STEP), the Natural Sciences and Engineering Research Council of Canada (NSERC), and a Research Corporation Cottrell Science College Award. The authors also gratefully acknowledge Dr. R. Smith at the University of Waterloo and Dr. A. Furtos at the Université de Montréal for mass spectrometric analysis.

Supporting Information Available: Experimental details, characterization data and spectra for new compounds, and variable concentration NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

OL9013443