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LETTERS

Poly-*ortho*phenylenes: Synthesis By Suzuki Coupling and Solid State Helical Structures

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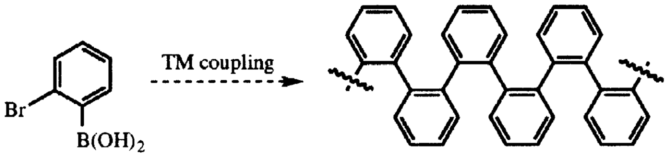
Abstract: The preparation of *ortho*-polyphenylene oligomers, having 3–9 rings, using a rational Suzuki coupling strategy, has been achieved, and a helical structure determined for a number of these products by X-ray crystallography.

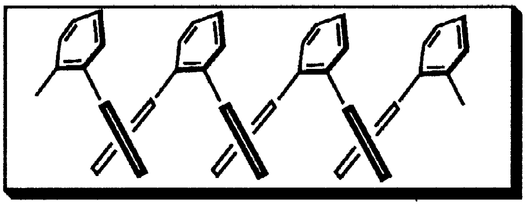
Although the helical motif is pre-eminent in double-stranded DNA, and also in α-helical polypeptides, other helical molecules of diverse structural types have also attracted considerable attention, mainly due to their potential in materials and polymer science.[1,2] Examples include helicenes,[3] polymeric isocyanides,[4] hydrogen bonded arrays,[5] and metal helicates.[6]

During our recent studies in the area of atropisomeric amide synthesis we had reason to examine the transition metal catalysed coupling of aromatic fragments to generate rather hindered systems, and became intrigued by the *ortho*-polyphenylene structure **2**. Although *para*-polyphenylenes and their heterocyclic relatives have been widely investigated, especially with regard to their potential as materials for electronic devices,[7] oligomers derived by *meta*- or *ortho*-linking of aromatic rings have been much less well examined. As part of a study of aromatic oligomers, Williams *et al.* described the X-ray structure of *meta*-deciphenyl (isolated from a mixture of oligomers by HPLC) which showed a helical structure with five aromatic rings to each turn of the helix.[8]

Molecular modelling of the *ortho*-polyphenylene structure **2**, which we envisaged would be available by a Suzuki coupling approach (e.g. using boronic acid **1**) suggested that the structure should adopt a tight helical conformation, which can be represented as **3**, having only three aromatic rings to each turn.[9,10]



(1) (2)



(3)

In this paper we describe the preparation of small *ortho*-polyphenylene oligomers, having 3–9 rings, using a rational Suzuki coupling strategy,[11,12] and report on the helical structure observed for a number of these products, as determined by X-ray crystal structures.

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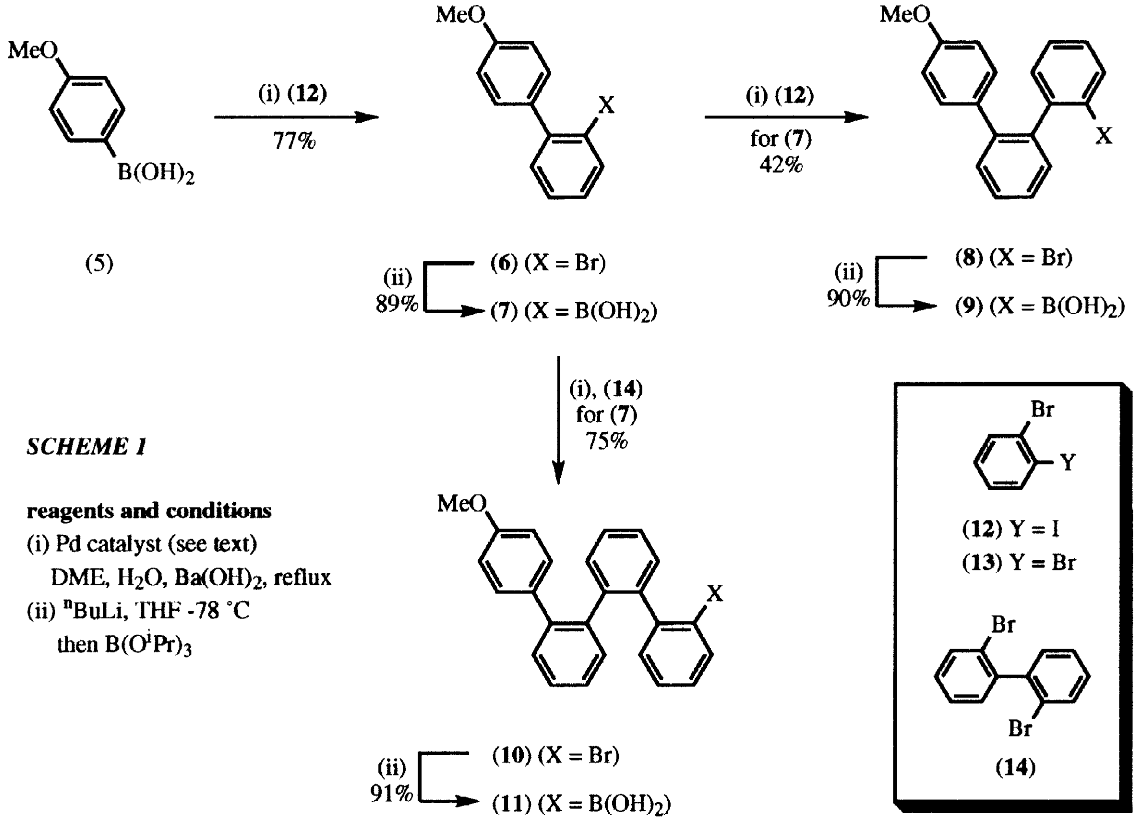
Our strategy for the synthesis of the required *ortho*-polyphenylene oligomers was to start with the commercially available boronic acid **5**, in which the methoxy group would act as a marker for ease of compound characterisation, and effect homologation to higher polyphenylene boronic acids, which could then be coupled to linking dihaloarenes. Suzuki coupling of **5** with 1-bromo-2-iodobenzene **12**, using *ca.* 3% of palladium catalyst [$(Ph_3P)_4Pd$ or $(Ph_3P)_2PdCl_2$] under typical conditions gave bromide **6**,[13] which could then be converted into boronic acid **7** by metal–halogen exchange, followed by quenching with triisopropylborate, Scheme 1.[14]



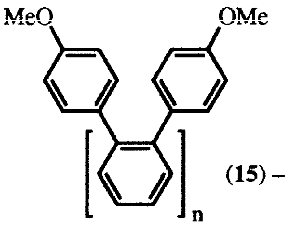
SCHEME 1

reagents and conditions
(i) Pd catalyst (see text)
DME, H_2O, $Ba(OH)_2$, reflux
(ii) ^nBuLi, THF -78 °C
then $B(O^iPr)_3$

Repetition of this sequence allowed the preparation of triphenylene boronic acid **9**, and terphenylene boronic acid **11** was available by a similar approach by using the readily available 2,2'-dibromobiphenyl **14** as coupling partner.[15] The boronic acids were then coupled with either 1,2-dibromobenzene **13** or **14**, to give the required polyphenylene products **15–20** as shown, Scheme 2.

SCHEME 2

(5) + **(13)** ⟶ **(15)** n = 1 (66%)
(5) + **(14)** ⟶ **(16)** n = 2 (15%) + **(8)** (39%)
(7) + **(13)** ⟶ **(17)** n = 3 (44%) + **(8)** (50%)
(7) + **(14)** ⟶ **(18)** n = 4 (32%) + **(10)** (35%)
(9) + **(13)** ⟶ **(19)** n = 5 (32%)
(11) + **(13)** ⟶ **(20)** n = 7 (23%)



(15) – **(20)**

In the case of couplings involving 1,2-dibromobenzene **13**, the typical Suzuki conditions were applied as before, whereas with the more sluggish reactions involving **14** we commonly employed the modified conditions described by Wright *et al.*, which involve addition of CsF to the reaction mixture.[16] None of the reactions has been optimised and, as can be seen, the yields at present are modest, often due to incomplete conversion of **13** or **14**.[17]

Each of the products **15–20** are solid, and so far it has proved possible to obtain X-ray structures for compounds **15–18**. The results for **18**, the longest oligomer determined by X-ray analysis to date, are representative, and two views are shown in Figures 1 and 2.[18]

FIGURE 1

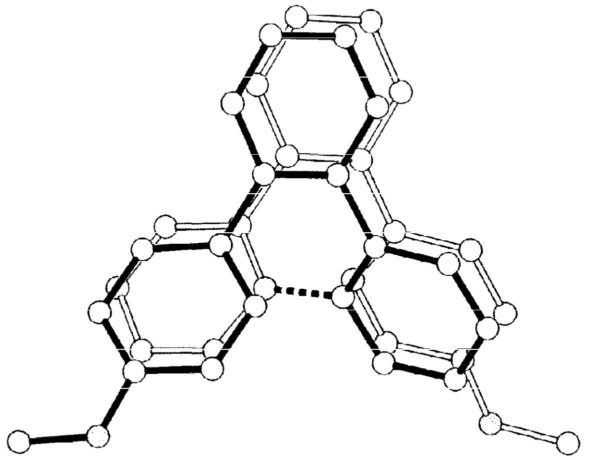
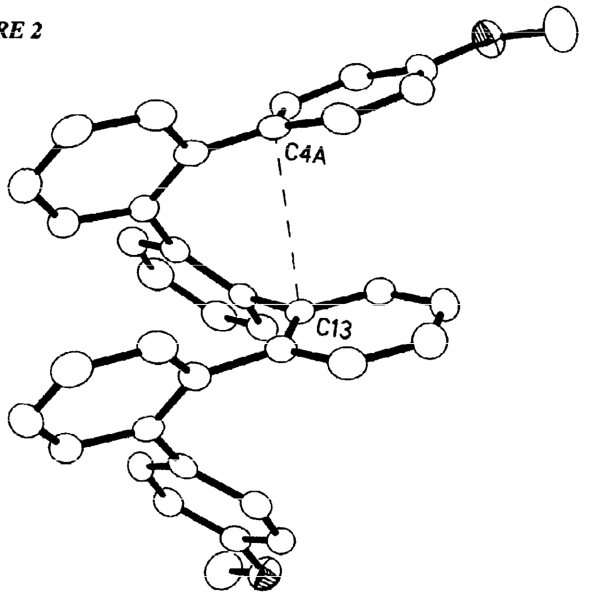


FIGURE 2



As can be seen, the conformation of the product fulfils exactly our expectations of a tight helix, having a pitch of around 3.7–3.9 Å. Viewed from above (Figure 1) the first ring approximately overlays the fourth one, this pattern being repeated to generate a roughly triangular array of three stacks. Such overlaying rings show remarkably short contacts of about 3.2Å, with even closer contacts in the case of some particular interatomic distances, e.g. 3.13Å for the C4A to C13 distance highlighted (Figure 2). We interpret this as a function of the tight twist adopted by (or imposed upon) the molecule rather than a result of π–π stacking, although clearly such distances would suggest that the latter type of interaction could also be active.[19]

Studies are underway to further develop the synthesis of these novel compounds and to probe their conformations in solution. Applications in the areas of novel materials, chiral polymers, immobilised reagents and catalysts and functional scaffolds are also possibilities we hope to explore.

Acknowledgements

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References and Footnotes

1. Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 63. See also reference 3.
2. For recent examples, see (a) Tanatani, A.; Kagechika, H.; Azumaya, I.; Fukutomi, R.; Ito, Y.; Yamaguchi, K.; Shudo, K. *Tetrahedron Lett.* **1997**, *38*, 4425. (b) Dai. Y.; Katz, T. J.; Nichols, D. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *35*, 2109.
3. Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1.
4. Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, 11.
5. Geib, S. J.; Vicent, C.; Fan, E.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119.
6. Wiliams, A. *Chem. Eur. J.* **1997**, *3*, 15.
7. (a) Schlüter, A.-D. Synthesis of Poly(*para*-phenylenes) in Handbook of Conducting Polymers, Skotheim, T.; Elsenbaumer, R.; Reynolds, J. (eds.), Marcel Dekker, New York, 1997, p. 209–224. (b) Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017. (c) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. For some mixed heterocyclic systems, see (d) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8717. (e) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Commun.* **1996**, 2163.
8. Williams, D. J.; Colquhoun, H. M.; O'Mahoney, C. A. *J. Chem. Soc., Chem. Commun.* **1994**, 1643.
9. Modelling using Macromodel version 5.
10. Although *ortho*-polyphenylenes have been prepared previously, their conformation seems not to have been explored, see (a) Ozasa, S.; Fujioka, Y.; Fujiwara, M.; Ibuki, E. *Chem. Pharm. Bull.* **1980**, *28*, 3210. (b) Ibuki, E.; Ozasa, S.; Fujioka, Y.; Okada, M.; Yanagihara, Y. *Chem. Pharm. Bull.* **1982**, *30*, 2369.
11. (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
12. Frahn, J.; Karakaya, B.; Schäfer, A.; Schlüter, A.-D. *Tetrahedron* **1997**, *53*, 15459.
13. Selective cross-coupling at C–I rather than C–Br bonds is well documented, see reference 14 and references therein.
14. Frahn, J.; Schlüter, A.-D. *Synthesis* **1997**, 1301.
15. The boronic acids **7**, **9** and **11** were employed without purification.
16. Wright, S. W.; Hageman, D. L.; McLure, L. D. *J. Org. Chem.* **1994**, *59*, 6095.
17. Structure assignment of the higher oligomers **19** and **20** rests largely on mass spectrometric evidence, since NMR spectra are complex due to the presence of rotamers.
18. *X-ray structure determination for 18*

    A crystal was encapsulated in a film of RS3000 perfluoropolyether oil and mounted on a glass fibre before transfer to the diffractometer.

    Crystal data. $C_{38}H_{30}O_2$, M = 518.6, orthorhombic, a = 9.273(4), b = 16.287(6), c = 9.111(5) Å, U = 1376.2(11) Å^3, T = 150(2) K, space group $P2_12_12$ (No. 18), Z = 2, D_c = 1.252 g cm^{-3}, μ(Mo-Kα) = 0.076 mm^{-1}, 2851 reflections measured, 2405 unique (R_{int} = 0.042) which were used in all calculations. Final R_1 [1993 $F \geq 4\sigma(F)$] = 0.0633 and wR_2(all F^2) was 0.169.
19. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.