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The synthesis of bis(oligophenyleneethynylenes): novel potential nonlinear optical materials

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Abstract—Various functionalised phenyleneethynylene dimers **10** and trimers **12** were synthesised by palladium-catalyzed Sonogashira methodology. These dimers and trimers were coupled to 1,8-diido-10-methoxyanthracene to generate bis(oligophenyleneethynylenes) **17** and **18**. Preliminary results towards the construction of both phenyleneethynylene and phenylenevinylene hybrid motifs are presented.

1. Introduction

The effects produced by a nonlinear optical (NLO) response in a bulk material have applications in optical switching, modulation, amplification, beam steering, wavelength filters and image processing.[1] The most important contributions to this activity come from the second and third order optical susceptibilities, $\chi^{(2)}$ and $\chi^{(3)}$, and can be described on the molecular level by the first and second order hyperpolarizabilities β and γ. In order to achieve large $\chi^{(2)}$ and $\chi^{(3)}$, high values of β and γ and a high density of nonlinear optical chromophores is desired, and since the polarization of a molecule is a vector quantity, the alignment of molecular dipoles which reinforce each other is also important.

The design of NLO materials continues to present a significant challenge to organic chemists.[2] It is recognized that attributes which enhance β include high polarizability, large anharmonicity and extensive electron delocalization.[1] In order to exhibit high $\chi^{(2)}$, the molecules must also be non-centrosymmetric, and generally, the organic compounds which have shown the most promise are donor–acceptor molecules possessing conjugated spacers with a low HOMO–LUMO band-gap. However, the structural requirements for materials having significant γ and $\chi^{(3)}$ are less well understood; although a high degree of conjugation is again desirable, a non-centrosymmetric geometry is unimportant.[3]

Oligo- and poly(phenylenevinylene) molecules (OPVs and PPVs) are a well-known class of organic NLO materials, and have some of the highest $\chi^{(2)}$ and $\chi^{(3)}$ values recorded.[4] However, their alkynyl analogues, oligo(phenyleneethynylene)s (OPEs), have not been as thoroughly assessed for NLO activity, partly because of their poor solubility. Due to the absence of *E*–*Z* photoisomerization, OPEs offer the potential advantage of durability over their double bond counterparts,[5] but those previously studied have generally shown a lower NLO response in comparison,[6] which has usually been ascribed to a less effective electron delocalization along the OPE chain.[5]

Since the extent of conjugation is dependant on orbital overlap, coplanarity of the aryl moieties of the chain is an important factor for high β and γ.[7] Arylacetylenes are known to have a very low barrier (<1 kcal mol^{-1}) for rotation around their sp–sp^2 bonds,[8] hence OPEs exist in a conformational equilibrium of planar and various twisted forms.[9] It has been shown that properties such as fluorescence emission and $\chi^{(3)}$ can be altered or enhanced through coplanarity enforced by π-stacking[10] and hydrophobic/hydrophilic interactions[11] in Langmuir films, and by metal–metal bridging in related systems.[12] It is our aim to explore this theme by restricting the rotation of OPEs by covalent linking,[13] hydrogen bonding or steric bulk.

Earlier we reported the synthesis of the thiacyclophane **1** (Fig. 1) as well as some cyclophane precursors[14] and compared their absorption and emission spectra. However, the X-ray crystal structure of **1** and subsequent molecular modelling revealed that a consequence of the length of the 'arms' of the cyclophane was to induce some twisting of the OPE chains and this made the synthesis of

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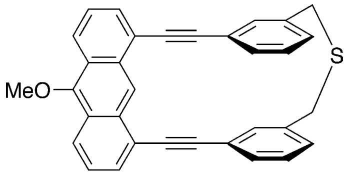

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Figure 1. A previously studied thiacyclophane.

dithiacyclophanes extremely challenging. We wished to prepare extended analogues of the precursors to thiacyclophane **1** with a view to exploring the effects of hydrogen bonding and steric bulk in the aryl spacer ‘arms’ on inducing coplanarity of the arylacetylene spacers. Herein we report the preparation of two bis(OPEs), after investigating various approaches for extension of OPE chains.

2. Results and discussion

The arylacetylene building blocks **2** (Fig. 2) required to generate the OPEs have been reported previously, or are commercially available.[15] In general, they were synthesized by palladium-catalyzed coupling of trimethylsilylacetylene (TMSA) with the corresponding aryl iodides, followed by protodesilylation under mild conditions.[16] The basic repeating unit of the OPE chains, the iodide **3a**,[17] was obtained in 65% overall yield from methyl *o*-anthranilate[18] by following established procedures for similar monomers[19] (Scheme 1). Alternatively, the triflate **3b** could be used.[20]

The OPE segments could be constructed in one of two ways: (a) the suitably functionalized monomers could be sequentially added to the anthracene template, extending the bis(OPE) one unit at a time; or (b) OPEs could be synthesized independently, then attached to the anthracene template. The ester side-arm acts as a handle that allows for further elaboration to groups, which may restrict the rotation of the aryl rings through hydrogen bonding or steric bulk, as well as to increase the solubility of the bis(OPE) products.[21] Monomer units containing only one ester side-arm were utilized for the development of OPE and bis(OPE) synthesis since the precursors were readily available.

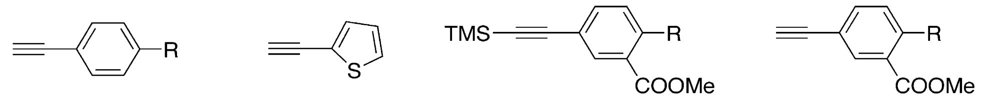
Based on previous reports, route (a) was initially investigated.[14] Protodesilylation of **3b** with potassium fluoride in methanol gave the terminal alkyne **4a** in quantitative yield; these conditions proved more efficient than either potassium carbonate–methanol or TBAF. Coupling of **4a** with **5**[22] using piperidine as a base, even when diluted with DMF, afforded the unexpected product **7**, which represents an example of an unusually facile Pd-catalyzed aryl amination reaction[23] (Scheme 2). It was believed that the formation of **7** was a consequence of the extended conjugation of the desired intermediate **6**. However, further experiments with different primary and secondary amines revealed that this reaction was specific for piperidine. The ditriflate **6** was isolated in 47% yield when the base was changed to triethylamine.

Disappointingly, the reaction of **5** with the phenolic alkyne **4b**[24] gave a complex mixture of products, which were not separable by chromatography, either directly or after attempted derivatization of the phenolic groups.[25]

A longer route for chain extension involving alternating addition of the alkynyl and aryl moieties was then explored. Reaction of **6** with an excess of TMSA afforded the disilane **8** in 74% yield; however, deprotection of **8** gave low yields of the corresponding unstable terminal bis-alkyne (Scheme 2).

The alternative route (b) to bis(OPE) formation proved to be more efficient. Sonogashira coupling of the arylacetylenes **2a**–**2g** with **3a** afforded the dimers **9a**–**9g** in 58–100% yields (Scheme 3).[26] Removal of the TMS groups was readily achieved with potassium carbonate–methanol to yield the terminal alkynes **10a**–**10g** without need for purification.[27]

Further coupling of **10a**–**10e** with **3a** gave the trimers **11a**–**11e** in good yields (Scheme 4), which again were



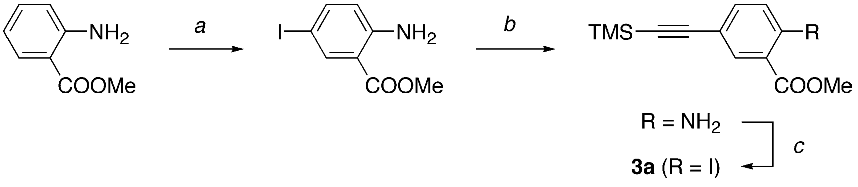
2a (R = H)
2b (R = NO$_2$)
2c (R = OMe)
2d (R = NHBoc)
2f (R = Br)
2g (R = SCH$_2$CH$_2$TMS)

2e

3a (R = I)
3b (R = OTf)

4a (R = OTf)
4b (R = OH)

Figure 2. Monomeric building blocks for constructing OPEs.



Scheme 1. Conditions: (a) BnMe$_3$NICl$_2$, NaHCO$_3$, 100%; (b) TMSA, Pd(PPh$_3$)$_2$Cl$_2$, CuI, 88%; (c) (i) BF$_3$·OEt$_2$, *t*-BuONO; (ii) NaI, I$_2$, 74%.