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A simple "palladium-free" synthesis of phenyleneethynylene-based molecular materials revisited†

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Nucleophilic attack of acetylide anions at the two carbonyl moieties of *para*-quinones readily affords the corresponding diols. Subsequent reduction with stannous chloride affords a number of useful compounds, including 1,4-bis[(trimethylsilyl)ethynyl]benzene, 1,4-bis[(trimethylsilyl)ethynyl]naphthalene and 9,10-bis[(trimethylsilyl)ethynyl]anthracene. Sequential attack by different acetylide anions followed by reduction provides a useful route to differentially substituted compounds including 1-[(4-nonyloxyphenyl)ethynyl]-4-(phenylethynyl)benzene, a new luminescent liquid-crystalline material.

Introduction

Molecular and polymeric materials based on the phenyleneethynylene motif have been the subjects of considerable and varied interest in recent years.[1] The rigid rod-like structure of these compounds[2] and the ready decoration of the periphery by polar groups and aliphatic tails has led to the development of liquid-crystalline materials,[3] while the attachment of linear ethynyl moieties at controlled sites around the aryl ring has given an array of beautiful shape-persistent molecular architectures, and polymeric systems with controllable secondary architectures.[4]

Oligo(phenyleneethynylene)s are highly fluorescent, and the electroluminescent properties of these materials have recently been recognised,[1] leading several groups to begin to explore the potential of this class of material as the emitting material in OLED type devices.[5] The origin of the fluorescent properties of these systems, and the optical properties of these compounds in general, can be attributed to the extended linear π-system and are therefore intimately related to the molecular conformation. Theoretical calculations indicate a very low barrier to rotation of the aryl rings around the C(sp)–C(sp^2) single bond,[6] and the role of planar conformations in the ground and excited state on the optical properties of these systems has been investigated spectroscopically.[7] The linear conjugation pathway offered by poly(phenylethynyl)benzene derivatives has also been exploited in the preparation of a number of promising candidates for molecular electronic components,[8] as well as serving as a efficient bridging ligand capable of passing electronic effects and energy between metal centres located at the termini.[9]

Numerous routes have been reported for the synthesis of the prototypical 1,4-bis(phenylethynyl)benzene molecular framework, and closely related materials featuring ethynylaromatic moieties.[10] However, the most popular route used in the synthesis of these materials by far is based on the Sonogashira cross-coupling of aryl halides with terminal alkynes in the presence of a palladium and copper co-catalyst.[11] Oligo(arylethynylene) materials designed to exhibit functionality as a consequence of donor–acceptor substitution,[12,13] or to bind selectively to a surface at one end,[14,15] are differentially substituted at the peripheral ring systems by necessity. The preparation of such differentially substituted compounds often involves a multi-step synthesis based on disubstituted haloaromatic starting materials in conjunction with specific deprotection sequences,[16] use of an excess of dihaloarene necessitating chromatographic separation of the product from the unreacted reagent,[12a] or regiospecific reaction sequences of iodobromobenzenes.[17,18] Alternatively, a linear synthetic route requiring functional group inter-conversions to give halide (preferably iodide) derivatives for further cross-coupling reactions can be employed.[19,20] The synthetic utility of the method has been elegantly employed in an "iterative convergent/divergent approach" for the formation of very large oligomeric systems.[8a,21]

An older, yet surprisingly under exploited, reaction scheme makes use of the electrophilicity of carbonyl carbon centres in quinones.[22–24] While similar chemistry has been used for the preparation of mono-acetylenic compounds,[3b,25] and diethynyl derivatives of large polyaromatic hydrocarbons,[26] there has been far less emphasis on the use of quinone, naphthoquinone and anthraquinone directly as reagents for use in the preparation of simple oligo(arylethynylene)aromatic compounds; the preparation of differentially substituted systems by this route is, to the best of our knowledge, unreported.

We present here the direct synthesis of a number of useful and interesting bis(ethynyl)aromatic derivatives *via* the nucleophilic attack of quinones by lithiated acetylide anions. This method both limits the use of transition-metal catalysts and, importantly, allows preparation of differentially substituted materials without the need to resort to protection/deprotection sequences or chromatographic separation of excess reagents. The potential application of this protocol is illustrated by the one-pot preparation of 1-(4-nonyloxyphenylethynyl)-4-phenylethynylbenzene, a fluorescent material that exhibits a range of smectic and nematic liquid-crystalline phases at moderate temperatures.

Results and discussion

Addition of the diones benzoquinone (**1**), naphthoquinone (**2**) or anthraquinone (**3**) to two molar equivalents of lithium trimethylsilylacetylide readily afforded the corresponding enediols **4a**, **5a**, **6a**, obtained as a mixture of *syn* and *anti* isomers

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† Electronic supplementary information (ESI) available: full description of all experimental procedures and spectroscopic data, and the DSC thermogram for 1-[(4-nonyloxyphenyl)ethynyl]-4-(phenylethynyl)benzene. See http://dx.doi.org/10.1039/b502950c

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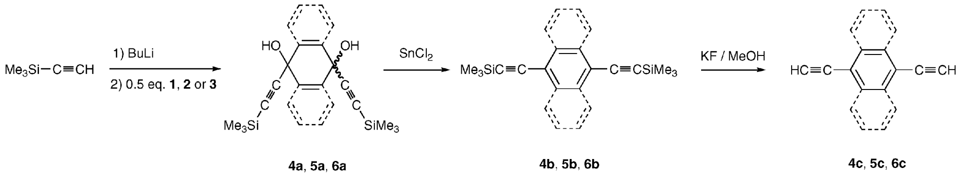

Scheme 1 The synthesis of diethynyl aromatic compounds from the aromatic diones **1**, **2** and **3**.

in an approximately 1 : 2 ratio, which may be separated by column chromatography, and are sufficiently pure for subsequent reduction (Scheme 1, Chart 1).[27,28] As both isomers are readily reduced by tin(II) chloride in ethanolic acetic acid giving the desired diethynyl aromatic compounds, which precipitate directly from the reaction mixture, chromatographic separation of the isomeric diols is not an essential part of the synthetic protocol.‡

This protocol allows a remarkably simple and cost effective synthesis of useful compounds such as 1,4-bis[(trimethylsilyl) ethynyl]benzene (**4b**),[29] 1,4-bis[(trimethylsilyl)ethynyl]naphthalene (**5b**)[9a] and 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**6b**),[9a,30] (Table 1) which may in turn be protodesilylated to give the 1,4-bis(ethynyl)aromatic compounds **4c–6c** in essentially quantitative yield (Scheme 1). While the unprotected ethynyl compounds are valuable synthetic reagents which, for example, have recently been used in the preparation of interesting π-conjugated, metal-containing polymers,[9a,f] these compounds are somewhat thermally and photochemically unstable, and degrade over time, compound **6c** being especially sensitive in this regard. Hence, large scale preparation and storage of the air-stable bis(trimethylsilyl) derivatives is recommended. A sequence of reactions entirely analogous to those represented in Scheme 1 can also be used in the preparation of the highly luminescent bis(phenylethynyl)aromatic compounds **7b**,[7b,31] **8b** and **9b**,[23,32] *via* reduction of the intermediate diols **7a**, **8a** and **9a**, respectively (Table 1, Chart 1) formed from reactions of **1**, **2** and **3** with lithium phenyl acetylide. These observations give us confidence that a wider range of diethynyl benzenes, naphthalenes and anthracenes can be prepared from **1**, **2** and **3**, with the obvious proviso that the substituent groups are stable to the lithiation and reduction conditions. However, we note that our attempts to perform similar reactions with ethynyl Grignards or sodium acetylide were complicated by competition from Michael addition reactions, giving intractable mixtures of products.

It has been noted that the addition of lithium acetylides to **1** proceeds in a stepwise fashion under kinetic control such that at −78 °C only monosubstitution occurs, even in the presence of excess acetylide reagent. Only at temperatures above −40 °C will addition of the second equivalent of nucleophile take place.[27] It was therefore a simple matter to prepare differentially substituted diene-diols, such as **10a** and **11a** *via* sequential addition of different lithiated acetylides with the necessary care taken to ensure regulation of the reaction temperature (Scheme 2).

The versatility introduced by the sequential reaction of the lithiated acetylides allows the rapid assembly of the carbon skeleton of differentially substituted 1,4-bis(ethynyl)diols in one-pot, with subsequent reduction affording the dialkynyl aromatics. The ready availability of the starting materials and ease of the synthetic manipulations permits the simple preparation of these compounds on a large scale. For example, sequential reaction of 1,4-benzoquinone with lithium phenylacetylide followed by lithium trimethylsilylacetylide gave diol **10a**, with subsequent reduction giving trimethylsilyl ethynyl tolane **10b** in 61% overall yield, from a 27 mmol scale reaction. This compares favourably with synthesis of this compound based upon a sequence of Sonogashira palladium/copper catalysed coupling reactions with 1-bromo-4-iodobenzene described previously which afford **10b** in 53% overall yield (10 mmol scale).[33] While compounds such as **10b** are useful intermediates in the preparation of more highly functional materials, the methodology described in Scheme 2 is also amenable to the preparation of functional compounds directly. For example, a 4-nonyloxy tail can be introduced to the elementary 1,4-bis(phenylethynyl)benzene framework to give 1-[(4-nonyloxyphenyl)ethynyl]-4-(phenylethynyl)benzene (**11b**), a fluorescent compound exhibiting liquid-crystal phase behaviour.

In order to assess the influence of the introduction of the nonyloxy group on the optical properties of the 1,4-bis(phenylethynyl)benzene framework, the absorption, excitation and emission spectra of **11b** were recorded in dilute cyclohexane solution (Fig. 1). The absorption profile and emission spectrum arising from an excitation at 326 nm (Stokes shift 2400 cm^{-1})

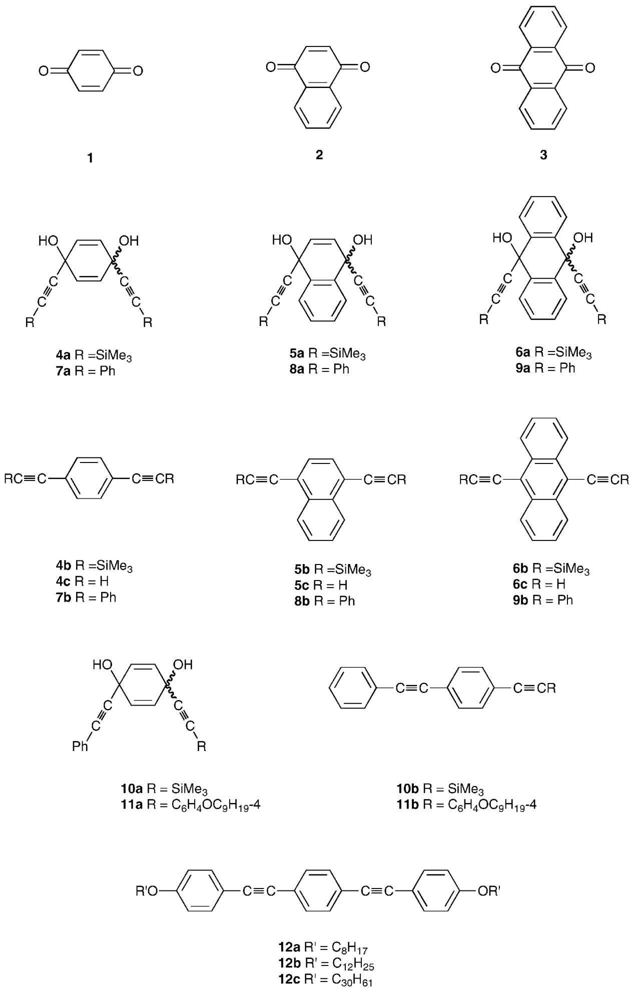

Chart 1 The key compounds and intermediates used in this work.

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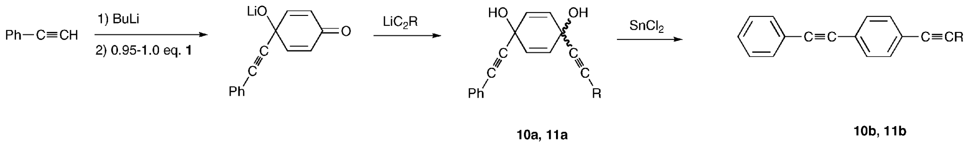
‡ An alternative attempt to reduce the diols by refluxing in ethanol with hydrazine monohydrate proved unsuccessful. Others have noted hydroiodic acid[23a] or powdered zinc[3b,25] can be used as reductants in similar transformations.

Table 1 Selected experimental data[a]

	Yield[b] (%)	ν(C≡C)/cm^{-1} (Nujol) (lit.)	Mp/°C (lit.)	Ref.
4a	95	2184	[g]	27
4b	57	(2155)	125 (122)	29*a*
5a	90	2164	[g]	This work
5b	69	(2155)	92	9*a*
6a	98[c]	2171, 2157	[g]	22*c*
6b	39[d]	(2152)	242	9*a*, 30
7a	74	2217	[g]	22*d*
7b	63	(2185)	183 (180–181)	12*a*
8a	67	2224	[f]	23*b*
8b	76	[f]	156 (157–158)	23*b*
9a	47[e]	2254	[g]	23
9b	65[d]	[f]	253 (253–255)	23*a*, 32
10a	82	2219, 2162	[g]	This work
10b	74[d]	2152	119	33
11a	35	2223	[g]	This work
11b	33[b]	2285, 2210	153	This work

[a] Full synthetic details and spectroscopic data are available in the ESI.† [b] Purified by chromatography on silica. [c] Crude yield, used without purification. [d] Crystallised from toluene. [e] Crystallised from CH_2Cl_2–hexane. [f] Not observed. [g] Mixture of *syn* and *anti* isomers giving a broad, ill-defined melting point.



Scheme 2 The preparation of differentially substituted diethynyl benzenes from **1**.

were similar to those of the parent material 1,4-bis(phenylethynyl)benzene **7b**,[7b] with the alkoxy substituent causing only a small bathochromic shift of the absorption and emission maxima. The quantum efficiency and lifetime of fluorescence in **11b** ($\phi_F = 0.95$, $\tau = 0.60$ ns) were measured to be approximately 10% greater than those of **7b**.[7b]

The thermal behaviour of **11b** was studied using differential scanning calorimetry (DSC) and the different phases detected were characterised from their characteristic optical textures observed by transmitted polarised light microscopy. The DSC thermogram exhibits transitions at 96 and 117 °C and, because no melting of the sample was observed under the microscope in this temperature region nor does the sample exhibit any shear or deformation when probed mechanically, these transitions are assigned as crystal–crystal phase transitions. The material melted to give a liquid-crystalline phase with platelet type texture indicative of smectic behaviour above 144.6 °C, with a further transition to a nematic phase at 147.8 °C, before finally melting into the isotropic liquid at 152.7 °C. Curiously, simple mono-alkoxyl derivatives of the rigid rod-like 1,4-bis(phenylethynyl)benzene moiety are virtually unknown,[10a,b] although the liquid-crystalline phase behaviour of 1,4-bis[(alkoxylphenyl)ethynyl]benzenes have been reported.[3d,34] For the comparison, we note that the bis(alkoxy) derivatives **12a** and **12b** also exhibit both smectic and nematic mesophases, with the smectic phases forming at somewhat lower temperatures (118–128 °C) than **11b**.[3d] The nematic phases associated with **12a** and **12b** are found above 180 °C, with the compounds melting to the isotropic liquid at much higher temperatures [217.7 (**12a**) and 188.9 °C (**12b**)] than **11b**. The introduction of very long (**12c**) alkoxy groups eliminates the nematic phase behaviour with only the more ordered smectic phase being observed between 126.3 and 141.4 °C. It would appear that while compounds such as **12** form more ordered smectic phases more readily than mono(alkoxy) derivatives such as **11b**, the mono-substituted compounds give rise to nematic phases at temperatures lower than the bis(alkoxy) derivatives. Further investigations of the liquid-crystalline phase behaviour of this class of compound are underway and will be reported in due course.

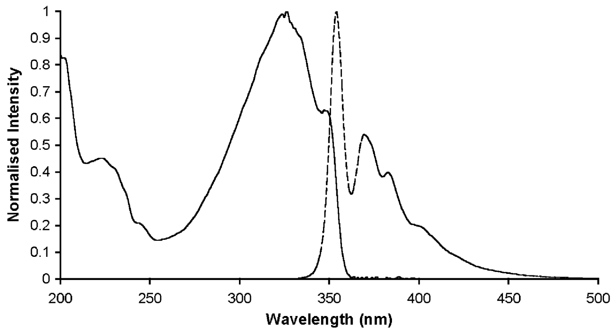


Fig. 1 The absorption (—) and emission (——, λ_{ex} 326 nm) spectra of **11b**.

Conclusion

A simple sequence of reactions based upon sequential nucleophilic attack on the carbonyl groups in diones by acetylide anions has afforded alkynyl ene-diones, which in turn are readily reduced by stannous chloride to give diethynyl aromatic compounds in good yield. These simple reaction steps have been used to prepare an example of a mono-alkoxyl substituted derivative of 1,4-bis(phenylethynyl)benzene, which was found to be a highly luminescent material with nematic phase behaviour at relatively low temperature. The route appears to be particularly useful for the preparation of compounds that are differentially substituted around the central aromatic core, with the obvious proviso that the subsitutents are stable to the reactions conditions.

Experimental

General conditions

Reactions involving lithium reagents were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Benzoquinone, naphthoquinone and anthraquinone, phenylacetylene (Aldrich), trimethylsilylacetylene (Fluorochem) and *n*-butyl lithium (1.6 M in hexanes, Acros) were purchased and, with the exception of napthoquinone which was purified by chromatography on alumina (dichloromethane) prior to use, were used as received. Solvents were dried and deoxygenated using an Innovative Technologies Inc. Solvent Purification System. The compound 4-nonyloxyphenylacetylene was prepared by modification of the literature methods.[35] IR spectra were recorded on an Nicolet Avatar spectrometer from nujol mulls supported between NaCl plates. NMR spectra were recorded from $CDCl_3$ solutions on a Bruker Avance 400 spectrometer, and referenced against solvent resonances. Mass spectra were recorded on Autospec EI and Micromass Quattro II spectrometers. UV-Vis absorption spectra were recorded on an ATI Unicam UV-2 spectrophotometer. Steady-state and time-correlated fluorescence measurements were performed at room temperature in dilute solutions, with an absorbance of <0.1, using a Horiba-Jobin-Yvon Fluorolog 322 Tau3 spectrofluorimeter, using conventional 90° geometry. Fluorescence quantum yields were determined at room temperature, relative to double matched standards (quinine sulfate in 0.1 M H_2SO_4 and 2,2′-(1,4-phenylene)bis(5-phenyloxazole) in cyclohexane).[36] Fluorescence lifetimes were recorded operating in the phase-modulation mode. The phase shift and modulation were recorded over the frequency range 1–300 MHz, and the data fitted using the Jobin-Yvon software package. A Perkin Elmer Pyris 1 DSC operating at a heating rate of 10 °C min^{-1}, and fitted with a Cryofill cooling system was used to record the thermal behaviour of the sample and an Olympus BX51 microscope fitted with a Linkam THMS 600 hotstage and a Linkam TMS 94 temperature controller was used to examine the phase behaviour of the materials. Melting points were obtained using the same apparatus.

Syntheses

A representative synthesis of the diols: preparation of 1,4-bis[(trimethylsilyl)ethynyl]-2,5-cyclohexadiene-1,4-diol (4a). To trimethylsilylacetylene (7.82 mL, 5.44 g, 54.4 mmol) in THF (50 mL) at −70 °C, *n*-butyllithium (33 mL, 53 mmol) was added slowly while stirring, and the reaction mixture was then allowed to warm to room temperature. The reaction mixture was then cooled to −70 °C and a solution of 1,4-benzoquinone (3.00 g, 27.7 mmol) in THF (50 mL) was added dropwise. The solution was then allowed to warm slowly to room temperature and stirred overnight. The reaction mixture was treated with a saturated solution of ammonium chloride and extracted with ethyl acetate. The organic solvents were removed under reduced pressure and the product was isolated following column chromatography on silica gel with a CH_2Cl_2/EtOAc gradient. Yield 95%. ^1H NMR: δ 6.02 (s, 4H, C_6H_4); 2.34 (s, 2H, OH); 0.15 (s, 18H, CH_3). ^{13}C NMR: δ 129.7 (CH) 104.5/90.1 ($-C{\equiv}C-$), 61.2 (C(OH)), −0.29 (Si(CH_3)$_3$). IR: ν(OH) 3314; ν(C≡C) 2184 cm^{-1}. MS (EI): m/z (%) 304 (38) [M]$^+$; 286 (3) [M − H_2O]$^+$; 255 (100) [M − CH_3 − $2H_2O$]$^+$.

Representative reduction procedure: preparation of 1,4-bis[(trimethylsilyl)ethynyl]benzene (4b). Compound **4a** (7.58 g, 24.9 mmol) was dissolved in absolute EtOH (30 mL) and added dropwise to a solution of $SnCl_2 \cdot 2H_2O$ (11.23 g, 49.8 mmol) in 50% acetic acid (30 mL) at 60 °C (10 min) and the precipitate formed was collected by filtration and washed with water and dried to afford **4b** (3.81 g, 14.1 mol, 57%). ^1H NMR: δ 7.39 (s 4H, C_6H_4); 0.26 (s, 18H, CH_3). ^{13}C NMR: δ 132.1, 123.5 (Ar); 104.9, 96.7, ($-C{\equiv}C-$); 0.3 (Si(CH_3)$_3$). MS (EI): m/z (%) 270 (51) [M]$^+$; 255 (100) [M − CH_3]$^+$.

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