Anthra- and Pentacenequinone Derivatives: Influence of Structure on the Formation of Columnar Liquid Crystal Phases

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Anthra- and Pentacenequinone Derivatives: Influence of Structure on the Formation of Columnar Liquid Crystal Phases

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We report the synthesis and mesophase characterization of a series of novel di- and tetra-aryl acenequinones. Diphenyl-acenequinones 1 and 2 exhibit monotropic mesophases while tetra-aryl acenequinones 4 and 5 exhibit stable columnar hexagonal mesophases. Compound 4 exhibits a more stable columnar mesophase than 5, consistent with a packing motif where molecules are stacked in perpendicular arrangement.

Compounds that exhibit columnar liquid crystal phases are attractive candidates for use as organic semiconductors because their extended π-stacked arrays allow transport of charge carriers along the columnar axis.[1-4] Anthraquinones were among the first compounds shown to exhibit columnar mesophases and these compounds have been studied extensively.[5-11] The anthraquinone core is amenable to π-stacking and the electron accepting ability of anthraquinones suggests that these compounds have potential as n-type semiconductors.[9, 10, 12] However, almost all of the columnar liquid crystalline anthraquinones are derived from rufigallol (1,2,3,5,6,7-hexahydroxyanthraquinone). Consequently, the structural diversity of anthraquinone liquid crystals has largely been limited to variations of the alkoxy side chains of the rufigallol core and alternative substitution patterns have received little attention. There is therefore incentive for the preparation of anthraquinone derivatives with distinctly different structures.

Given that there are several examples of liquid crystalline anthraquinone derivatives, the design of columnar liquid crystals derived from larger acenequinones such as tetracenequinone and pentacenequinone may also produce materials with properties suitable for organic semiconductors. Pentacenequinones are known to aggregate in solution, forming the basis for fluorescent sensors and nanoscale reactors.[13-15] Surprisingly, columnar liquid crystalline materials based on larger acenequinones have received little attention. Bhalla and coworkers recently reported an example of a liquid crystalline pentacenequinone.[15] However, the effect of extending the aromatic core in acenequinones on mesomorphic properties has not been examined. By extending the aromatic core, the molecular packing will be altered, which will influence the stability of the mesophase. Furthermore, the frontier molecular orbital energies can be tuned, which will affect the ability of these compounds transport charge. For example, recent studies have indicated that acenequinones such as substituted pentacenequinones can be used as potential semiconducting materials.[16] These acenequinones can also serve as precursors to the corresponding acenes, which are also promising candidates for organic semiconducting materials.[17, 18] Therefore, the preparation of liquid crystalline acenequinones, where organization of π-stacked arrays allows efficient charge transport, may provide access to materials that are suitable for applications as organic semiconductors.

Herein we report a general synthetic approach to liquid crystalline diphenylacenequinones (**1**-**3**) and tetraphenylacenequinones (**4**-**5**). By attaching 3,4-dialkoxyphenyl groups to anthraquinone, tetracenequinone, and pentacenequinone, we produce compounds that exhibit columnar liquid crystalline phases. These are among the first examples of liquid crystalline tetracene- and pentacenequinones and a comparison of this series of compounds allows us to probe the effect of extending the acenequinone core on mesomorphic properties.

Our synthesis of compounds **1**-**3** is outlined in Scheme 1. 2,3-Dibromoanthraquinone (**6**) was prepared by a reaction of 3,4-dibromothiophene-1,1-dioxide[19] with naphthoquinone as reported by Williams and coworkers.[20] Suzuki coupling of **6** with boronate ester **9**,[21] furnished compound **1** in modest yield. Compound **2** was prepared by Suzuki coupling of dibromotetracenequinone **7** with aryl boronate **9** to yield compound **2**. Compound **7** was prepared by a Cava reaction of

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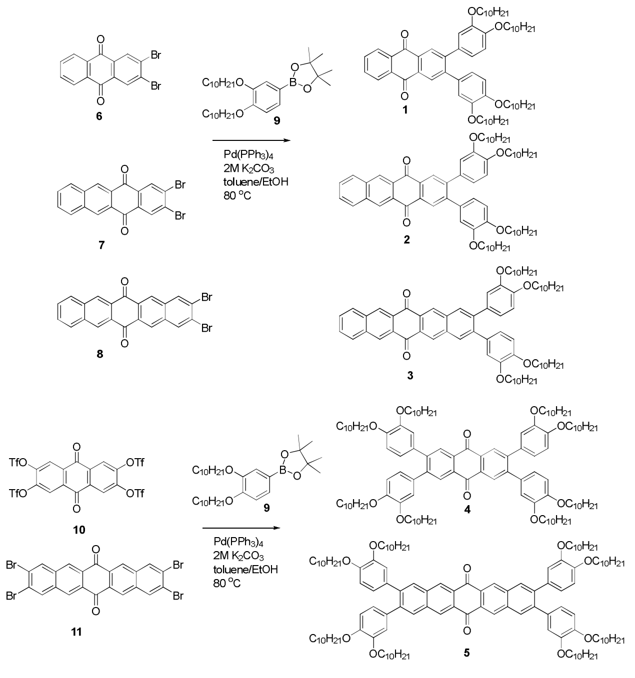
Electronic Supplementary Information (ESI) available: Experimental details including procedures, DSC traces, XRD data, CV data, and NMR spectroscopic data. See DOI: 10.1039/x0xx00000x α,α,α',α'-tetrabromo-*o*-xylene with 2,3-dibromonaphthoquinone.[20] Similarly, compound **3** was prepared from 2,3-dibromopentacenequinone (**8**).[22]

Compounds **4** and **5** were prepared in an analogous manner by Suzuki coupling of **10** and **11**[22] with boronate **9** (Scheme 1). While 2,3,6,7-tetrabromoanthraquinone is known,[20] in our hands the preparation gave very low yields. We therefore carried out the Suzuki coupling using the corresponding triflate (**10**), which was prepared from 2,3,6,7-tetrahydroxyanthraquinone.[23]

The liquid crystalline properties of these compounds were studied by polarized optical microscopy, differential scanning calorimetry, and variable temperature powder X-ray diffraction (vt-XRD). The mesophase behaviour is summarized in Table 1.

Compounds **1** to **3** have wedge-shaped molecular structures that potentially self-organize into columnar mesophases as has been previously shown for other wedge-shaped compounds.[24-29] DSC data of all three compounds show only one larger transition on heating and cooling that is suggestive of reversible melting and crystallization transitions between crystalline and isotropic liquid phases. However, detailed POM and vt-XRD studies revealed more complex phase behaviour for anthraquinones **1** and **2**.

Scheme 1. Synthesis of Compounds 1-5.



Diaryl anthraquinone **1** melts from a crystalline phase directly into an isotropic liquid but the transition on cooling generates a monotropic mesophase of unknown structure that crystallizes into the initial crystal phase when kept between 25 ºC and 5 ºC for several days.

Table 1. Phase Behaviour of Compounds **1-5**.

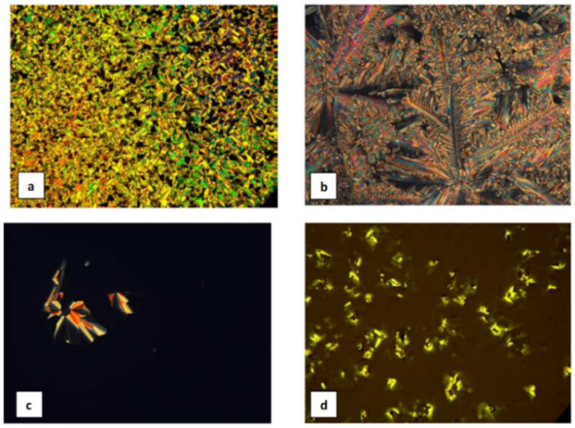
Compound	Transition Temperatures[a] in °C (Enthalpies of transitions in kJ/mol on heating and cooling)
1	Cr 52 (10.6) I 42 (-7.4) M_{Col} 25-5 (n.o.)[b] Cr
2	Cr 85 (9.0) I 78 (-10.0) Cr[c]
3	Cr/glass 64 (-13.6) Cr 98 (27.1) I 51 (-2.6) Cr/glass
4	Cr_2 -6 (2.7) Cr_1 9 (17.8) M_{Col} 74 (8.5) Col_h 174 (18.1) I 173 (-18.1) Col_h 74 (-6.9) M_{Col} 2 (18.3) Cr_1 -14 (-2.3) Cr_2
5	M_{Col} 109 (2.4) Col_h 145 (3.7) I 142 (-3.8) Col_h 103 (-2.8) M_{Col}

[a] Determined by DSC (peak position) and/or polarized optical microscopy on heating and cooling at 5 K/min, reproducible over three heating and cooling cycles. [b] Crystallization occurs at a temperature between 25 ºC and 5 ºC over a period of days as confirmed by POM and vt-XRD. [c] A metastable columnar rectangular mesophase is initially formed on cooling from the isotropic liquid but crystallizes over a period of a few hours as confirmed by POM and vt-XRD. Cr denotes a crystalline or soft crystal phase, Col_h a columnar hexagonal phase, M_{Col} a mesophase of unknown but likely columnar structure, Cr/glass a mixture of partially crystalline and partially glassy compound, and I an isotropic liquid.

The mesophase displays fan-shaped textures observed by POM (Figure 1a) and its diffraction pattern consists of an intense small angle reflection at 29 Å, a broad halo for amorphous aliphatic chains at 4.4 Å, and a broad π-π stacking reflection at 3.4 Å, both POM and XRD data (Figure 2) suggest the presence of a columnar mesophase. The XRD pattern gradually changes over days to the pattern of the initial crystal phase at temperatures below 25 ºC but is stable for at least a week at a temperature of 30 ºC and above. We note that the crystal phase obtained by precipitation from solution is different to the crystal phase obtained from the melt.

Similarly complex is the phase behaviour of diaryl tetracenequinone 2, which exhibits a metastable mesophase on cooling, which is likely a columnar rectangular structure.

Figure 1. Representative polarized optical micrographs of (a) 1 at 42 °C,(b) 2 at 75 °C,(c) 4 at 170 °C, and (d) and 5 at 141 °C (polarizers at 70 ° angle).



Again, the single intense transition in the DSC graph on cooling suggests **2** fully crystallizes from the isotropic melt but vt-XRD and POM data confirm the initial formation of a metastable monotropic mesophase that crystallizes over a period of several hours. Polarized optical microscopy (Figure 1b) and powder XRD (see Electronic Supplementary Information) are consistent with a columnar rectangular mesophases although not all observed reflections could be indexed with certainty. Again, the crystal phase obtained from the melt is different to the crystal phase obtained from solution.

In contrast, diaryl pentacenequinone **3** did not display any mesomorphic behaviour based on DSC and POM. DSC data show a partial (10% of melting enthalpy) crystallization of **3** at a cooling rate of -5 K/min and a completion of the crystallization (50% of metling enthalpy) upon heating (cold crystallization), which confirms that this compound also crystallizes slowly but does not require hours or days as compounds **1** and **2**.

Overall, extending the aromatic core from anthraquinone to tetracenequinone to pentacenequinone in series **1-3** generates more rigid wedges that cover decreasing areas of an imaginary circle (more wedges are required for a helical or discotic stack). Expectedly, extension of the aromatic core increases the transition temperatures to the isotropic liquid phases and overall favours crystalline phases over mesophases. Only compound **1** forms a mesophase, although on cooling only (monotropic), while compound **2** displays a metastable monotropic mesophase. The extremely slow crystallization kinetics for compounds **1** and **2** make them difficult to detect by DSC and may be the result of high viscosity of their liquid phases combined with a complex packing structure. However, the dominating factor appears to be differences in packing structures as crystallization rates increase with increasing size of the aromatic core and, consequently, with increasing viscosity.

In an effort to produce materials with stable columnar mesophases, we turned our attention to compounds **4** and **5** where additional dialkoxyphenyl groups give the compounds a more disc-shape to promote columnar mesomorphism. Indeed, compounds **4** and **5** both exhibit stable columnar hexagonal mesophases on heating and cooling, as confirmed by POM, DSC and vt-XRD. POM images of fan-shaped textures featuring large homeotropically aligned domains (Figure 1c and 1d) and vt-XRD patterns are both consistent with a uniaxial columnar hexagonal phase, although the (11) reflection is not observed in either case (Figure 2, Table 1). The intercolumnar distance and the lattice area (Table 1) are consistent with one molecule per unit cell and the intercolumnar distances of 31.3 and 36.1 Å reasonably agree with the molecular structures of compounds **4** and **5**, respectively.

Upon cooling, the high temperature columnar hexagonal mesophases of compounds **4** and **5** transition into mesophases of unknown but likely columnar structures, and compound **4** eventually crystallizes upon further cooling (Table 1). In contrast to the usual trend observed for series **1-3**, where extending the aromatic core increased the phase transition temperature to the isotropic liquid, the clearing point of the smaller anthraquinone **4** is significantly higher than that of pentacenequinone **5**, suggesting that the columnar mesophase of compound **4** is more stable than that of **5**. The higher stability of the columnar hexagonal mesophase of **4** as compared to **5** is also supported by the fact that the XRD of **4** shows a diffraction peak at ca. 3.5 Å that corresponds to π-stacking of the cores, while this peak is absent for compound **5**, indicating that the stacking order within the columns is greater for **4**. It is noteworthy that even for the higher order columnar phase of **5** observed at lower temperatures, a diffraction peak corresponding to π-stacking is not observed (see ESI). While this result was surprising, it suggests that π-stacking is more effective for anthraquinone **4** than pentacenequinone **5** and is consistent with the greater mesophase stability of **4**. This result can be explained by considering the stacking motif within the columns of the mesophase. The aryl groups attached to the acenequinone cores adopt conformations where those rings are twisted with respect to the core due to steric constraints

Figure 2. Representative XRD Data for compounds 1, 4, and 5.

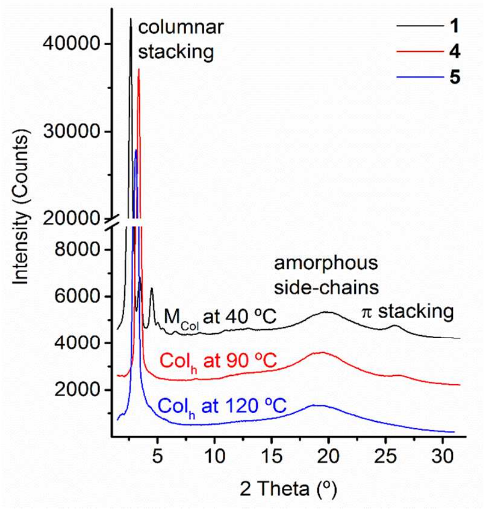


Table 2. Summary of XRD data for compounds **4** and **5**.

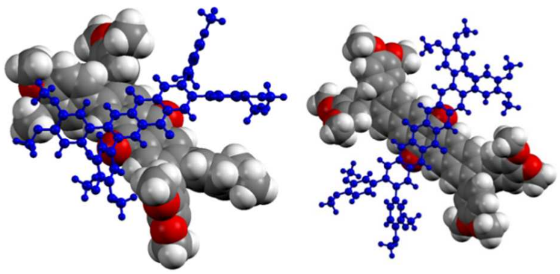
Compound	T[°C]	dobs[Å]^a	I[%]^b	hk^c	dcalc[Å]^a	Mesophase and parameters^d
4	150	27.1	100	10	27.1	Colh
		10.5	4.2	21	10.2	ah = 31.3 Å
		4.8	10.4	halo^e		sh = 848 Å2
		3.5	4.4	001^f		
5	120	31.3	100	10	31.3	Colh
		4.6	6.7	halo^e		ah = 36.1 Å
						sh = 1131 Å2

[a] d_{obs} and d_{calc} are the observed and calculated diffraction spacings; [b] I is the relative intensity of the diffraction signal; [c] hk is the indexation of the two-dimensional lattice; [d] a_h is the lattice vector of a hexagonal mesophase and s_h is the lattice area = 2√3(d_{10})^2; [e] broad reflection of amorphous aliphatic side chains; [f] reflection of π-stacking along the column. For compound **4**, a broad reflection is also observed at 12-14° (not indexed). This reflection is likely due to stacking of the alkoxyphenyl groups.

Consequently, a direct 'parallel' stacking of adjacent molecules is disfavoured and an offset stacking such as a perpendicular orientation is likely (Figure 3). In such an arrangement, compound **4** can stack effectively, while for compound **5**, where the aspect ratio of the core is significantly longer, producing much more free volume when the compound stacks in the mesophase. Consequently, the π-stacked mesophase of **5** is disfavoured compared to **4**, where the free volume is much lower. Thus, π-stacking is more effective with the smaller anthraquinone core of **4**, whereas the pentacenequinone core of **5** shows relatively little overlap with adjacent molecules and packing is not optimal, leading to a destabilization of the mesophase of **5** despite the fact that it has an extended core. It is also plausible that the closer contacts of the pendant aryl groups in **4** contribute to a stabilization of the mesophase.

The electrochemistry of compounds **1-5** were also investigated by cyclic voltammetry (see ESI). All of the compounds studied exhibited two reversible reduction peaks. The addition of the electron-rich dialkoxyphenyl groups onto the acenequinone core had only a slight effect on the reduction potentials, shifting them to slightly more negative potentials. Similarly, altering the size of the core had only a modest effect on reduction potentials, with the anthraquinone derivatives (**1** and **4**) having the least negative reduction potentials. These compounds also exhibited quasi-reversible oxidation peaks, which varied little between compounds **1-5**.

Figure 3. Representations of the proposed perpendicular stacking motif for compounds 4 and 5.



In summary, we have prepared the first examples of diphenyl- and tetraphenylacenequinones that exhibit columnar liquid crystal phases. Diphenylanthraquinone **1** and **2** exhibit monotropic mesophases of likely columnar structures but the mesophase of **2** is only metastable. Diphenylpentacenequinone **3** does not display any mesomorphic behaviour. Tetraphenylanthraquinone **4** and tetraphenylpentacenequinone **5** both exhibit stable columnar hexagonal mesophases. Although the larger core of **5** was expected to stabilize the mesophase through improved π-stacking interactions, compound **4** showed a broader mesophase temperature range and higher clearing point. These observations are consistent with a packing motif where molecules are stacked in perpendicular arrangement.

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The mesomorphic properties of novel acenequinones reveals that a perpendicular packing motif is an important factor for determining mesophase stability.


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