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Liquid-crystalline phenanthrolines

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The synthesis and mesomorphism of the first liquid-crystalline phenanthrolines are reported.

In studies of metallomesogens, there are reported many metal–ligand combinations; in some of these the ligand is mesomorphic, while in others it is not.[1] In the latter case coordination induces mesomorphism, often for structural reasons and the metal can be defined in a particular rôle. However, in the former case, we are presented with another opportunity, namely to study the effect of the metal on the mesomorphism of the ligand.

The first person to do this systematically with calamitic mesogens was Ghedini who took a range of mesomorphic azobenzene mesogens and complexed them *via* orthometallation to Pd(II).[2] In so doing, he created 'H-shaped' mesogens which had mesophases which were different from those shown by the ligand, although they were found at considerably higher temperatures. Since this work, published in the early 1980s, many groups have worked with this motif and a range of properties has been identified, including ferroelectric response.[1] Complexation of metals has the possibility to influence the properties of ligands in a number of ways. For example, we have shown how very high polarisability[3] and birefringence[4] are a consequence of complexation, while we and others have found that certain metal complexes are highly dichroic.[5]

In order that such studies advance, it is necessary continually to identify new ligand types, both mesomorphic and non-mesomorphic, which can bind to metals and generate mesomorphic complexes. The choice of ligand will determine the metals which can be complexed and in turn, these will determine which if any specific properties may be introduced. One of the ligands with the greatest range of coordination chemistry is 2,2′-bipyridine and we[6] and Ziessel[7] have shown that by appropriate 5,5′-substitution, it is possible to generate mesomorphic analogues. Subsequently, we used these to generate mesomorphic complexes.[8] One of the interesting features of 2,2′-bipyridine is that it exists in a *transoid* state when uncomplexed and so has no net dipole. However, on complexation, the conformation changes to *cisoid* in order to facilitate *N,N*-coordination (although *N,C*-coordination *via* orthometallation is known) conferring on the ligand a lateral dipole of the order of some 3.5 D (calculated for the gas-phase structure).[9]

By comparison 1,10-phenanthroline, which has a similarly wide coordination chemistry, has its conformation fixed by the exocyclic double bond, is ready set up for *N,N*-coordination and has a permanent lateral dipole. However, while Ziessel has recently reported the use of substituted non-mesogenic phenanthrolines to generate mesomorphic copper(I) complexes,[10] there are, to our knowledge, no reported examples of uncomplexed, mesomorphic phenanthrolines. Undoubtedly, one of the reasons for this is the relative unavailability of suitably substituted phenantholines from which to start. Much bipyridine chemistry is facilitated by the availability of various isomers, both symmetric and unsymmetric, of dimethyl derivatives which are readily accessed on a good scale using laboratory procedures. However, while certain substituted phenanthrolines are commercially available, none are available with a 3,8-substitution pattern which would be ideal for the realisation of calamitic mesogens. Nor are they easily made, and the classical Skraup syntheses do not cope readily with such a substitution pattern.

Like bipyridines, phenanthrolines are ligands to a number of photoactive complexes[11] and the photoactivity of these complexes has, however, found an outlet in, for example, the fast-growing field of dendrimer chemistry and in the construction of three-dimensional arrays. This has led to development of the chemistry of the bipy and phen ligands. Thus, we have used the reports by Siegel[12] and by Yamamoto[13] of improved syntheses for 3-bromo (**2**) and 3,8-dibromophenanthrolines (**3**) as the basis for the construction of new mesomorphic materials.

The bromophenanthrolines are obtained in a direct bromination[12] which leads to moderate yields of the 3-bromophenanthroline (38%, separated by column chromatography) and quite good yields[13] of the 3,8-dibromophenanthroline (60%). With the advent of many different protocols for performing cross-coupling reactions, having the bromo compounds in hand it is therefore a rather straightforward task to produce a range of substituted phenanthrolines. In order to demonstrate this concept, we now report the synthesis and mesomorphic properties of three derivatives which we believe represent the first examples of mesomorphic phenanthrolines.

The bromophenanthrolines were obtained as described previously and were then coupled (Scheme 1) with either acetylenes or phenylboronic acids, using Pd-catalysed procedures, to give a range of new mesogens. Some of these were then further reacted in a step-wise fashion to give mono- and di-methyl derivatives (**8** and **9**). The integrity and purity of the new compounds was established by NMR spectroscopy and by CHN analysis, while liquid crystal properties were determined by polarised optical microscopy and differential scanning calorimetry. Thermal data are collected in Table 1.

First, none of the 3-monosubstituted phenanthrolines (**4**, **5**) was mesomorphic and the compounds simply melted on heating. However, when symmetric, 3,8-disubstituted materials were made, the situation changed and materials with both smectic and nematic phases were found. Thus, the bis(acetylide) **6a** showed a wide-range nematic phase, while extension of the chain introduced a SmC phase. Neither of the two 3,8-diphenyl derivatives showed a nematic phase with **7a** showing a SmA phase and **7b** and SmC phase, with a monotropic crystal smectic phase observed on cooling. Note that in all these cases, the melting points were above 100 °C, while the clearing points approached 300 °C, often with decomposition.

These temperatures are clearly high and so it was of interest to seek strategies to see whether they could be reduced. Two

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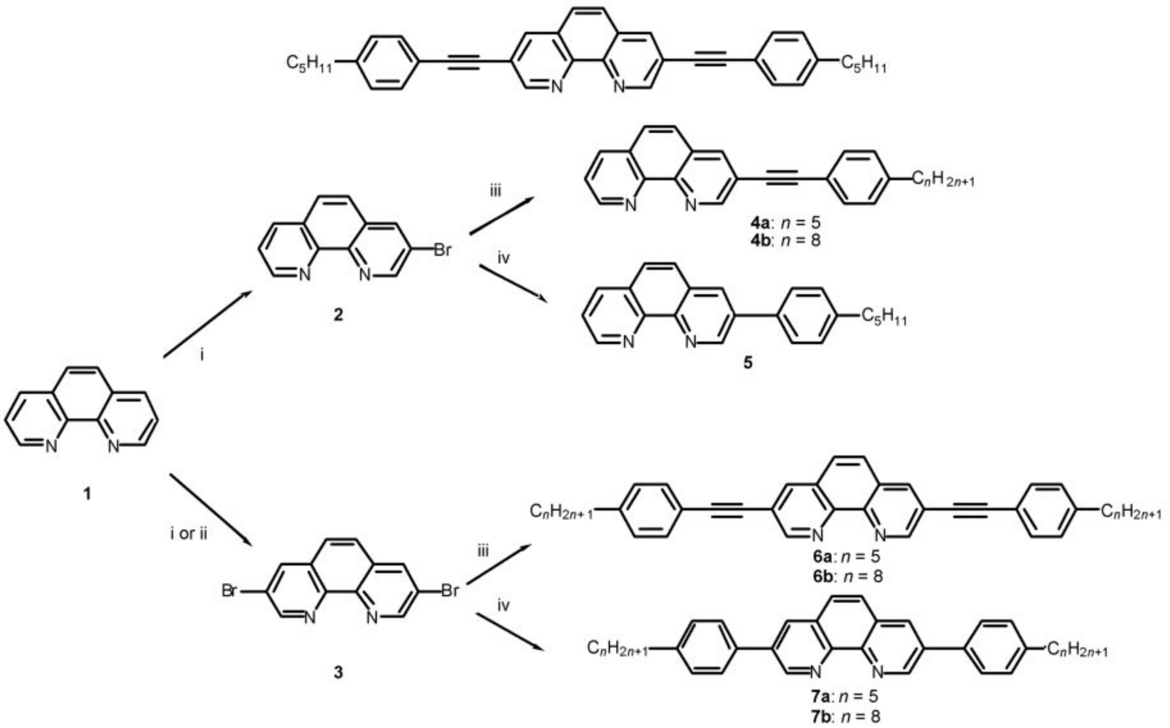
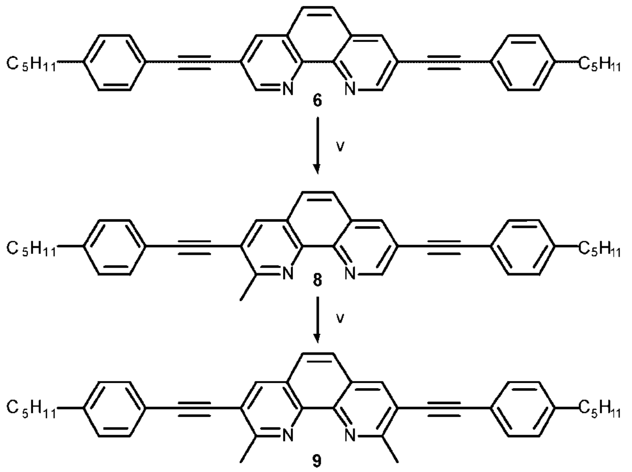


Scheme 1 Synthesis of the phenanthroline mesogens: i) Br$_2$/PhNO$_2$; ii) Br$_2$, S$_2$Cl$_2$, Bu-Cl, py or Br$_2$/PhNO$_2$; iii) C_nH_{2n+1}–C_6H_4–C≡C–H/PrNH$_2$/[Pd(PPh$_3$)$_4$]; iv) C_nH_{2n+1}–C_6H_4–B(OH)$_2$/[Pd(PPh$_3$)$_4$]/PhH/Na$_2$CO$_3$(aq).

ways in which this can be achieved in liquid crystals is by reducing the symmetry and also by reducing the structural anisotropy. In phenanthroline chemistry, we saw a useful way to achieve this end by introducing methyl groups at the 2- and 9-positions, as in both cases, structural anisotropy would be reduced and in the case of the monomethyl derivative, the symmetry would be lowered, too. Thus, compounds **8** and **9** were obtained in a step-wise manner following procedures described by Sauvage and co-workers (Scheme 2).[14] For the monomethyl compound (**8**), the mesomorphism changed little from that of the parent material (**6a**), there being a small drop in the clearing/decomposition temperature. The mesomorphism of (**9**) also showed only a nematic phase, and once more, the melting point was little different from that of the parent compound (**6a**). However, the reduction in structural anisotropy did show itself in the lower clearing point, which did prevent decomposition. However, it is somewhat curious that these effectively lateral methyl groups did not have a more profound effect on the mesomorphic properties.

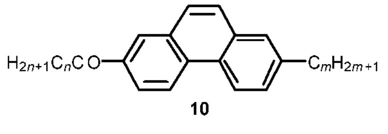


Scheme 2 Synthesis of the methylphenanthrolines: v) MeLi.

Table 1 Thermal data for the new phenanthroline compounds

Compound	Transition	T/°C	ΔH/ kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}
4a	Cr–I	120		
4b	Cr–I	69		
5	Cr–I	70		
6a	Cr–N	158	28.0	64
	N–decomp.	>309	—	—
6b	Cr–SmC	144	22.7	57
	SmC–N	232	1.1	2
	N–I	277	0.9	2
7a	Cr–SmA	188	18.1	39
	SmA–N	229	24.9	48
	N–I	295	1.56	3
7b	Cr–SmC	122	12.9	33
	(SmC–G/J)	113	—	—
	SmC–I	272	4.8	9
8	Cr–N	166	21.5	49
	N–decomp.	>280	—	—
9	Cr–N	134	6.6	16
	N–I	250	—	—

Comparisons with known systems are few and far between. Ziessel[15] reported analogous compounds of bipyridines using alkoxyphenylethynyl groups in the 5,5′-positions, but here the chains were very long and a polymorphic sequence was found. Some twenty years ago, Malthête[16] reported the synthesis and mesomorphism of some unsymmetric phenanthrene mesogens with the general structure (**10**) and here, the mesomorphism was exclusively that of the smectic A phase with an underlying crystal smectic E phase .



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