Specific molecular interactions in Pd(II) complexes identify a new approach to the biaxial nematic phase

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Liquid-crystalline complexes of Pd(II) allow a new approach to the realisation of the biaxial nematic phase.

In the uniaxial nematic phase (N_u) of liquid crystals, there is no positional order and the unique axes of the molecules are oriented about a director, n. In the *biaxial nematic phase* (N_b) there is, additionally, a correlation of the other molecular axes in a direction perpendicular to n and so whereas in the N_u phase the physical properties in the plane perpendicular to n are angle-independent, this is not the case in the N_b phase. Since Freiser's[1] prediction of the existence of an N_b phase, this topic has attracted much interest. Yet despite experimentalists trying to make these predictions come to life, the N_b phase in low-molecular-mass thermotropic liquid crystals remains elusive.

Two main strategies have been developed in the search for the phase. One is based on single-component systems where 'shape biaxiality' is optimised,[2] while the other is suggests that mixtures of two uniaxial nematic phases with non-coincident directors, could lead to the formation of the N_b phase.[3] The latter approach is problematic as such mixtures phase-separate into two uniaxial nematics.

In this communication, we propose a different approach which exploits total *molecular* biaxiality, *i.e.* not simply a shape biaxiality. Thus, we are seeking systems where possibilities for biaxial intermolecular interactions can be built in that lead to the realisation of long-range, orientational correlation in two orthogonal directions.

Fluoro-substitution in thermotropic liquid crystals provides a way of modifying their physical properties.[4,5] Further, the ideas of amphiphilicity and microphase separation are also well-known in liquid crystals,[6] where it is recognised that like parts of a molecule prefer to associate. Indeed, the presence of perfluorocarbon and hydrocarbon chains within the same molecule produces micro-segregation at the molecular level. We wished to use these ideas to design some organopalladium(II) complexes which would, in addition to possessing shape biaxiality, generate localised segregation, so promoting correlations perpendicular to the main nematic director.

The complexes we chose for study are based on the well-known *ortho*-palladated mesogens. We took as our starting point a system described by Espinet and Buey[7] in which dimer **1** is cleaved with the anion of a β-diketonate (Fig. 1). We used trifluoroacetylacetonate (tfac) and obtained the target complex **2** as a 1:1 mixture of isomers as shown by the ¹H NMR spectrum.† We were able to obtain single crystals of the dimethoxy derivative (R = R′ = MeO) and found that a single isomer crystallised.‡ However, when the solid-state packing of the molecule was considered, we found that the fluorocarbon parts of the complex remained together (Fig. 2), supporting the approach we were taking.
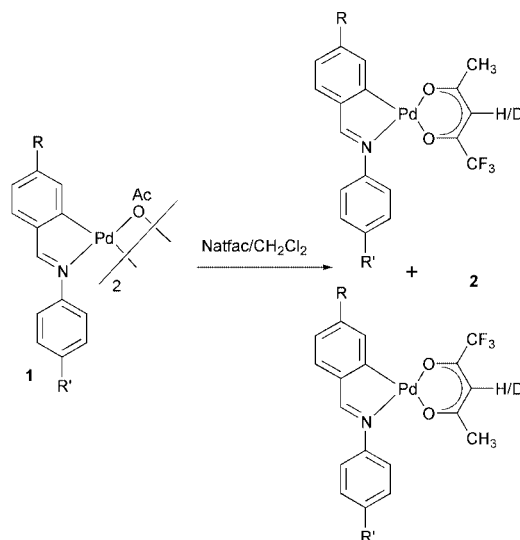

Fig. 1 Synthesis of the target complexes.

While we have made several derivatives of **2**, two are of particular note, namely with R = R′ = –OC₆H₁₃ (**2a**) and with R = –OC₆H₁₃, R′ = –C₆H₁₃ (**2b**). Both showed a monotropic nematic phase [**2a**: Cr • (62.6 • N) 91.6 • I; **2b**: Cr • (11.7 • N) • 67 • I; temp. in °C]; polarised optical microscopy showed each to have an ill-defined, marbled texture. We then evaluated the thermodynamics of the N–I transition as theory predicts[8] the N_b–I transition to be second order. The enthalpy changes were small [$\Delta H(\mathbf{2a}) = 0.20$ kJ mol⁻¹; $\Delta H(\mathbf{2b}) = 0.17$ kJ mol⁻¹] as were the corresponding entropy changes [$\Delta S/R(\mathbf{2a}) = 0.075$; $\Delta S/R(\mathbf{2b}) = 0.072$]. It is instructive to compare this behaviour with that of the non-fluorinated analogue of **2a** (*i.e.* prepared using acac) where the N–I transition showed $\Delta H = 1.0$ kJ mol⁻¹ and $\Delta S/R = 0.30$. This significant difference in the $\Delta S/R$ values shows that fluorination causes the transition to become much less strongly first order, providing further evidence supporting our approach.
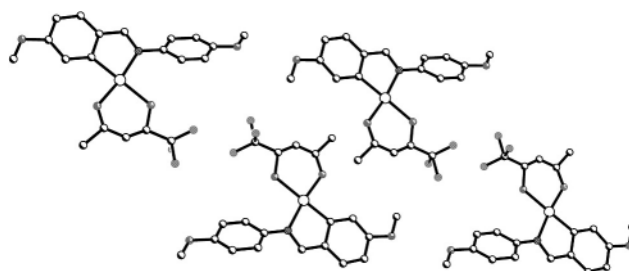

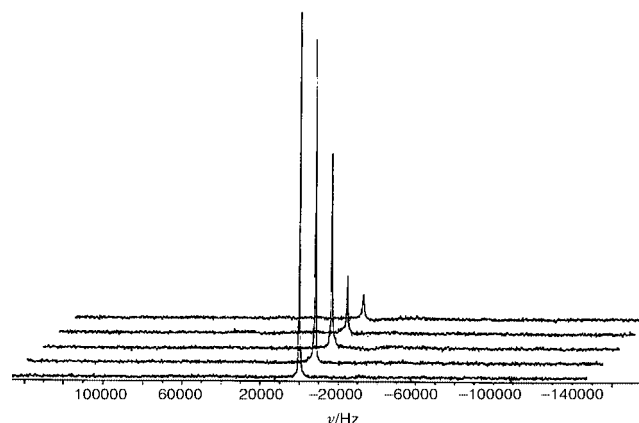**Fig. 2** The packing of **2a** in the solid state.

Fig. 3 ^{1}H NMR spectrum of **2a** in the isotropic phase between 365 K (most intense signal) and 335 K (least intense signal).

However, with the biaxial nematic phase, it is characterisation which is at the heart of the question[9] and the one technique which appears to offer unequivocal identification of the N_b phase is ^{2}H NMR spectroscopy.[10] It was, therefore, necessary to introduce deuterium into the complex which we did at the position shown in Fig. 1. Thus, Na$^+$tfac$^-$ was deuteriated by stirring in CD_3OD–D_2O at room temperature for 4 h before the solvents were removed *in vacuo*. After reaction with **1**, deuteriated **2a** was obtained with 80% deuterium incorporation.

The spectra were measured using a quadrupolar echo sequence, and the sample was brought into the isotropic phase and then cooled slowly; a strong singlet corresponding to the isotropic phase was recorded. However the signal intensity decreased with temperature and 90% of the magnetisation was lost before the nematic phase was reached (Fig. 3). This behaviour normally suggests that the compound is either crystallising or decomposing in the probe, but after the experiment, the sample was checked visually and then by polarised optical microscopy and also by ^{1}H NMR spectroscopy, none of which suggested that either of the two processes had occurred. No definite explanation has yet been given for this experimental observation, although we cannot yet rule out vitrification.

The sample was then further cooled and at the isotropic-to-nematic transition a doublet was observed. The spectra (Fig. 4) showed a small biphasic region and allowed the measurement of the transitional quadrupolar splitting, $\Delta\nu$, even if the signal was rather weak. From the quadrupolar splitting it is possible to calculate S, the order parameter of the long molecular axis and in so doing we made the assumption that the angle between the molecular long axis and the C–D bond was 90°. On calculating values of S, it was found that at the N–I transition, it had a value of 0.105. This compares with typical transition values for a *uniaxial* nematic phase of around 0.35. Note that S is expected
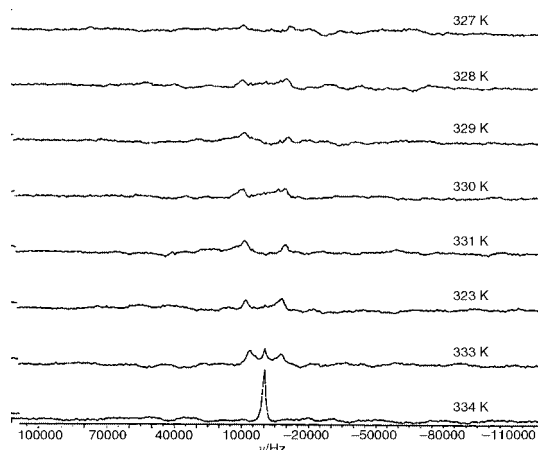
to start at zero for a *biaxial* nematic phase if the I → N_b transition is directly at the so-called Landau point. Our results indicate, therefore, a very low order parameter for this nematic phase consistent with the low transitional entropy ($\Delta S/R$), although we cannot say that the phase is biaxial.

By comparison, a very similar complex named 'Azpac' (as **2a** but containing an acac ligand and with the imine link replaced by an azoxy function) was studied by ^{2}H NMR spectroscopy some years ago.[11] The deuterons were introduced *via* the aromatic rings of the ligand, here, the order parameter close to the N–I transition was found to be *ca.* 0.4. These results provide further evidence in support of our approach to the generation of biaxial materials.

Further support for this strategy comes from recent results of Monte Carlo simulations by Berardi and Zannoni[12] in which they employed a Gay–Berne potential, modified to enhance side-to-side interactions of Gay–Berne particles. Using this approach, they too were able to stabilise a biaxial nematic phase, although interestingly, when face-to-face interactions were enhanced, a biaxial smectic phase was found. The recent identification[13] of the biaxial SmA phase using such an approach experimentally lends support to their simulations and further lends support to the approach we have identified.

Notes and references

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Fig. 4 ^{1}H NMR spectra in the nematic phase.