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Preliminary Communications

Thermotropic liquid crystal behaviour of 5,5′-[(4-hexadecyloxyphenyl)ethynyl]-2,2′-bipyridine

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5,5′-[(4-Hexadecyloxyphenyl)ethynyl]-2,2′-bipyridine was synthesized by a palladium(0) cross-coupling reaction. Its thermotropic liquid crystalline behaviour was analysed using differential scanning calorimetry, polarizing microscopy, and X-ray diffraction. Three enantiotropic tilted smectic phases were identified upon heating: S_F, S_I, and S_C.

Currently there is considerable interest in the search for new transition metal containing liquid crystals. These exhibit novel materials properties, mainly because of their redox, optical and magnetic characteristics [1].

Today the so-called *metallomesogens* can be classified as ionic, coordination, organo-element, and organometallic compounds [2]. Within the category of coordination metallomesogens, relatively little attention has been paid, so far, to oligopyridines (bipyridine, phenanthroline, terpyridine, naphthyridine, anthyridine...), although recent work has demonstrated the rich polymorphism of this kind of molecule [3–5].

Novel physical properties, based on the versatility of the chemistry of bipyridine and its complexation properties, may be expected in the near future. We recently developed a general procedure for large scale preparation of alkyne-substituted oligopyridines [6] and demonstrated that the alkyne modules behave as useful spacers allowing very efficient electronic coupling between two metal centres [7].

In a recent paper, the synthesis and liquid crystal behaviour of a homologous series of disymmetrically substituted 2,2′-bipyridines was studied [5]. Linkage between the complexation core and the alkoxy chain was ensured by a styrene connector. The present preliminary communication deals with the synthesis and study of the mesomorphic behaviour of a symmetrically substituted 2,2′-bipyridine (bpy), namely that 5,5′-disubstituted with 4-hexadecyloxyphenylethynyl (abbreviated to **16-ROPE-bpy**). Here the connection of the alkoxy chain is ensured by an ethynylphenyl sub-unit.

16-ROPE-bpy (1) was synthetized by a Pd(0) cross-coupling reaction between 5,5′-dibromo-2,2′-bipyridine [8] and 4-hexadecyloxyphenylacetylene [9], as previously described for analogous compounds [10,11] (see Scheme 1). This new compound was characterized by elemental analysis, IR, ^{1}H and ^{13}C {^{1}H} NMR and FAB-MS, by which means satisfactory results were obtained.

The thermotropic liquid crystalline polymorphism of **16-ROPE-bpy** was analysed by differential scanning calorimetry (Perkin–Elmer DSC-7, heating/cooling rates of 10°C min^{-1}). On heating from room temperature, the DSC traces show the presence of five sharp endothermic peaks indicative of first order transitions. The first two rather strong peaks at 113 and 125°C (21 and 43 kJ mol^{-1}, respectively) clearly correspond to transitions involving 'melting' of a crystal or strong disordering of a highly ordered liquid crystal phase; the next two weak peaks at 149 and 168°C (0·2 and 3 kJ mol^{-1}, respectively) correspond to transitions between liquid crystal phases; and the last one at 237°C (12 kJ mol^{-1}) corresponds to the final clearing point.

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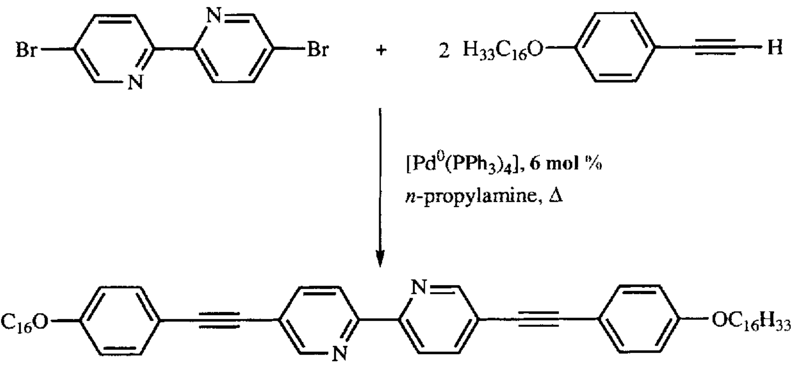

16-ROPE-bpy, **1** Isolated yield: 52 %

Scheme 1 Chemical structure and synthesis of the compound **16-ROPE-bpy**.

Upon cooling from the melt, the thermograms show five sharp (exothermic) peaks. The first three high temperature transitions at 234, 170, and 146°C (10, 4, and 0·2 kJ mol^{-1}, respectively) take place without hysteresis, as is usual for transitions between fluid phases; the fourth transition at 126°C is now weak (1·4 kJ mol^{-1}), suggesting the presence of an extra liquid crystal phase, monotropic in nature; the last one at 116°C involves a strong (43 kJ mol^{-1}) enthalpy change indicative of crystallization. Further cycles of heating and cooling do nothing but repeat the same sequence of transitions. These data are summarized in scheme 2, in which, for simplicity, the nature of the phases detected is specified now, before discussing the X-ray diffraction patterns.

The compound was then examined visually by polarizing optical microscopy (Leitz Orthoplan, Mettler FP82 hot stage). The observations confirm in every way all the phase transitions detected by DSC and furthermore provide evidence of an additional transition occurring just below the final clearing point. Upon slow cooling from the isotropic melt, a nematic mesophase appears first (spherical birefringent droplets coalescing into a very fluid and twinkling large schlieren texture) followed, one or two degrees below, by a distinct smectic C mesophase (less mobile fine schlieren texture). These two phases could not be seen separately by DSC, probably due to the narrowness of the nematic range and the weakness of the smectic to nematic phase transition. The next four transitions detected by DSC could all be observed by optical microscopy without difficulty. At the $S_C \rightarrow S_I$ transition, the pale-yellow schlieren texture of S_C becomes covered with an apparently liquid veil, turning suddenly into a range of pale rainbow colours randomly intermixed; at the $S_I \rightarrow S_F$ transition, the colours stop varying progressively and divide into separate coloured juxtaposed areas; at the $S_F \rightarrow$crystal G transition, the coloured areas become covered with fine radial striations and take up the general appearance of a broken fan texture; finally, at the G→Cr′ transition, the sample freezes to a solid, the optical field of view being rapidly crossed by a crystallization front.

The structure of the phases observed was finally investigated as a function of increasing temperature up to 200°C using X-ray diffraction (powder samples in Lindemann capillaries, Guinier focusing camera equipped with a bent-quartz monochromator using CuK$_{\alpha 1}$ radiation from an INEL X-ray generator, INSTEC hot stage, INEL CPS-120 curved position-sensitive detector). The X-ray patterns of the Cr phase contain a series of sharp Bragg reflections located both

$$\begin{tikzcd}
\mathrm{Cr} \arrow[r, "113(21)"] & \mathrm{X} \arrow[r, "125(43)"] & S_F \arrow[r, shift left, "149(0{\cdot}2)"] \arrow[d, "126(1{\cdot}4)"] & S_I \arrow[l, shift left, "146(0{\cdot}2)"] \arrow[r, shift left, "168(3)"] & S_C \arrow[l, shift left, "170(4)"] \arrow[r, shift left, dashed, "237(12)\dagger"] & \mathrm{I} \arrow[l, shift left, dashed, "234(10)"] \\
\mathrm{K'} & & \mathrm{SmG\ ?} \arrow[ll, "116(43)"'] & & &
\end{tikzcd}$$

† Via a short range nematic phase, see following results from polarizing optical microscopy.

Scheme 2 Polymorphic pathway for **16-ROPE-bpy**. Transition enthalpies (in parentheses) are given in kJ mol^{-1} and temperatures in °C. S_C, S_I and S_F, stand for smectic C, I, F phases, respectively, and G for an ordered crystal G phase. Cr and Cr′ represent crystal phases; I stands for isotropic liquid and X for a mixture of crystal and/or highly ordered smectic phases.

in the small and the wide angle region, indicative of a three-dimensional crystalline ordering of the molecules. The small angle reflections are all equidistant up to the seventh order, indicating a lamellar structure with a layer thickness of 58·8 Å. Slightly smaller than the overall length of the molecules in a fully extended all-*trans*-conformation (of about 67 Å as estimated from Biosym software run on a Silicon Graphics station managed by a MicroVax minicomputer), such a thickness suggests that the molecules are tilted with respect to the layers by about 29°. All these reflections are weak in comparison with the ground harmonic, but the third and sixth reflections are clearly missing completely from the patterns, in accordance with the fact that the thickness of the aromatic sub-layers is about one third of the lamellar period (the spacing of the oxygen atoms in the aromatic cores, 23·5 Å, is about one third of the overall length of the molecules).

The X-ray patterns recorded in the temperature range from 113 to 130°C are complex. In the small angle region, they show a diffuse scattering around the direct beam and two (sometimes more) non-equidistant sharp reflections; in the wide-angle region, they contain a set of rather sharp reflections superimposed on a diffuse ring. Apparently out of equilibrium, the system comprises more than one phase in coexistence and is difficult to analyse precisely.

Above 130°C, the observed phases are smectic in nature. Their patterns contain a sharp reflection in the range from 39 to 45 Å related to the smectic period and a more or less wide band in the wide angle region related to the lateral correlations of the molecules within the smectic layers. The layer thickness measured (figure 1) is smaller than that for the low temperature crystal and decreases still more on further heating. The molecules are therefore arranged with their long axes tilted with respect to the smectic layers. By disregarding the effect of the cross-sectional area of the molecules (larger in the smectic than in the crystal, and increasing slowly with temperature due to thermal agitation) on the thickness of the smectic layers [12], one may evaluate the tilt of the molecules from a simple comparison of the smectic period with the molecular length; one then finds that the tilt grows from about 29° in the crystal to about 48° in the smectic at 135°C up to about 54° at 200°C. The observed transition between the smectic phases shows up clearly in the sharp change of the profile of the wide angle ring in the X-ray patterns (figure 2). This is a rather narrow band for S_F, a cusp-like peak for S_I, and a broad band for S_C. As already described and discussed in the literature [13], the lateral packing of the molecules in the S_F and S_I phases is hexagonal, with a coherence length extending farther for the latter phase than for the former; the difference between the two phases lies in the fact that the molecules are tilted towards an edge of the hexagonal net for S_F and towards a corner for S_I. From the spacing of the wide angle peak (4·55 Å), the cross-sectional area of the molecules in S_F and S_I can easily be evaluated at about 23·9 Å^2, in agreement with values found for smectic phases with lamellar order [13].

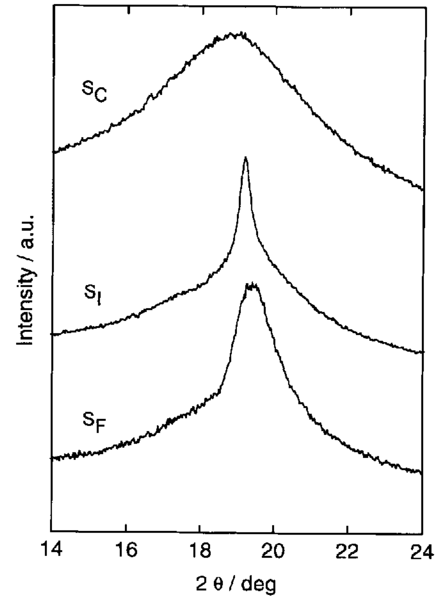

Figure 1. Layer thickness as a function of temperature. Symbols Cr, S_F, S_I, and S_C stand for crystal and smectic F, I, and C, respectively.

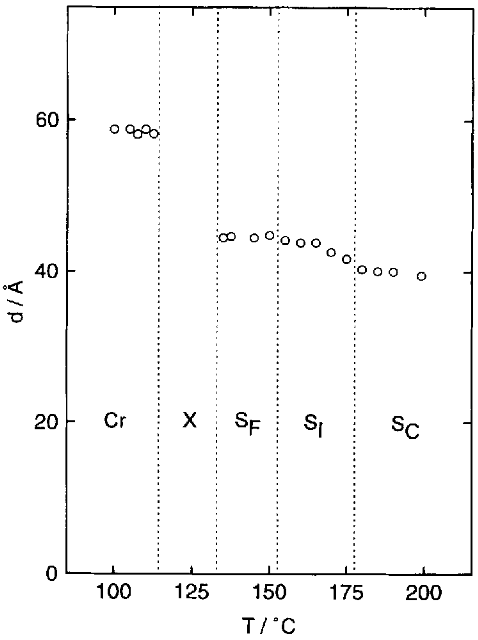

Figure 2. Profile as a function of Bragg angle of the outer ring of smectic F, smectic I, and smectic C, respectively.

Further systematic work on the liquid crystalline behaviour of **16-ROPE-bpy** is in progress; the structures of the smectic F and I mesophases will be thoroughly discussed and the structure of the nematic and G phases, detected only by differential scanning calorimetry and/or polarizing optical microscopy, will be established more completely. In addition, the liquid crystalline behaviour of the homologous series of ***n*-ROPE-bpy** ($n=6$, 8, 10, 12 and 14) will also be investigated in detail. Further developments including complexation of this ligand are underway, addressing conditions required for the preparation of metal-containing liquid crystals.

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