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Achiral banana-shaped mesogenic bidentate ligands and their Cu(II) and Pd(II) complexes

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The first achiral bent-core banana-shaped bidentate ligands and their Cu(II) and Pd(II) metal complexes have been synthesized and investigated for mesomorphic behaviour. The bidentate ligands exhibit only one enantiotropic mesophase. The ligand having C⁶-alkoxy chains shows a mesophase that has been assigned as a two-dimensional B¹ phase while the C⁸ and C¹⁰ homologues stabilize the fluid B² mesophase showing antiferroelectric switching characteristics. In contrast, their corresponding Cu(II) and Pd(II) metal complexes are non-mesomorphic.

1. Introduction

Since the discovery of switchable smectic mesophase formed by achiral bent-core, banana-shaped molecules in 1996 by Niori *et al.* [1], there has been increasing interest in the synthesis and characterization of such compounds. The majority of these compounds are symmetrical, consisting of an angular central core, usually having a phenyl ring nucleus, substituted with two identical linear Schiff's base mesogenic rigid cores at the 1,3-positions [2]. A large number of such compounds have been reported in the literature, perhaps owing to their ease of synthesis. Although these compounds exhibit interesting physical properties their stability to heat and moisture is reported to be poor.

In an attempt to obtain stable molecules and to understand structure–property relationships, non-symmetrical banana-shaped materials have been reported [3]. In these materials either the two halves of the molecule (i.e. the two mesogenic entities) or the two linking functional groups attached to the angular central core are different. In some examples the angular central core, the phenyl ring nucleus is substituted with chloro- or cyano-groups at either the 4- or 6-position making the molecule non-symmetric. Owing to difficult and long synthetic routes, only a few non-symmetrical banana-shaped compounds are known. It is also interesting to note that to date no metal atom has been incorporated in these compounds.

This prompted us to design non-symmetrical banana-shaped molecules that show stability to heat and moisture and can, at the same time, possibly accommodate a metal atom. In continuation of our work on banana-shaped compounds [4], here we report the synthesis and mesomorphic behaviour of the first banana-shaped bidentate ligands and their Cu(II) and Pd(II) metal complexes.

2. Experimental

The molecular structures of the intermediates (3–6), bidentate ligands (1a–c) and their metal complexes (2aCu, 2aPd, 2bCu, 2bPd, 2cCu and 2cPd) are shown in figure 1. The ligands and their metal complexes were prepared as described. Thus, firstly phenol 6 was coupled with 4-(4-*n*-decyloxybenzoyloxy)benzoic acid (5) in the presence of DCC to obtain the bent-shaped nitro-substituted compound 4, which upon catalytic hydrogenation gave the key intermediate amine 3. The condensation of 2-hydroxy-4-*n*-alkyloxybenzaldehydes with amine 3 yielded banana-shaped bidentate ligands 1a–c as yellow solids. These ligands, upon treating with either copper(II) acetate or palladium(II) chloride in a solvent medium gave brown coloured copper (2aCu, 2bCu, and 2cCu) or yellow coloured palladium (2aPd, 2bPd and 2cPd) metal complexes. The molecular structure of the intermediates, banana-shaped ligands and the metal complexes were confirmed by spectroscopic (IR, ¹H, ¹³C NMR and FAB Mass) analyses. As a representative case spectral data is given for the compounds 1c, 2cCu and 2cPd.

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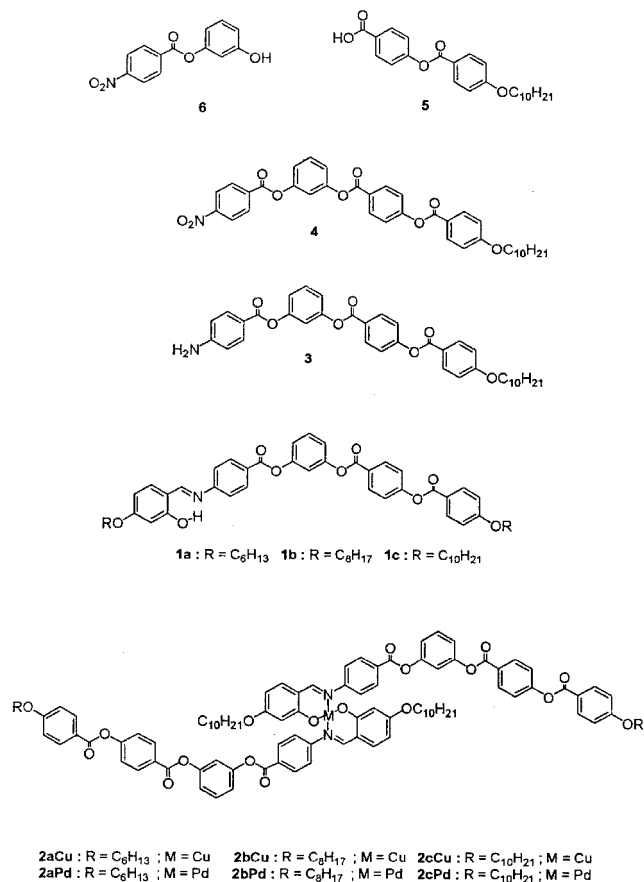


Figure 1. Molecular structures of the intermediates, banana-shaped bidentate ligands and their Cu(II)/Pd(II) metal complexes.

1c: IR (KBr Pellet): $\nu_{\max}/\text{cm}^{-1}$ 2920, 2853, 1714, 1593 and 1511; $^1\text{H NMR}$ (400 MHz, CDCl₃): 13.36 (s, 1H, -OH), 8.57 (s, 1H, CH=N), 8.28 (d, $J = 8.7$ Hz, 2H, Ar), 8.24 (d, $J = 8.4$ Hz, 2H, Ar), 8.15 (d, $J = 8.7$ Hz, 2H, Ar), 7.5 (t, $J = 8.1$ Hz, 1H, Ar), 7.36 (t, $J = 9.3$ Hz, 4H, Ar), 7.3 (d, $J = 9.2$ Hz, 2H, Ar), 7.2 (m, 2H, Ar), 7.0 (d, $J = 8.8$ Hz, 2H, Ar), 6.51 (m, 2H, Ar), 4.05 (t, $J = 6.6$ Hz, 2H, 1 × OCH₂), 4.01 (t, $J = 6.6$ Hz, 2H, 1 × OCH₂), 1.86–1.32 (m, 32H, 16 × CH₂) and 0.88 (t, $J = 6.7$ Hz, 6H, 2 × CH₃); ^{13}C (100 MHz, CDCl₃, Spin Echo FT): δ 164.25 (CO), 164.2 (C), 164 (C), 163.8 (C), 163.06 (CH=N), 155.47 (C), 153.31 (C), 151.48 (C), 151.14 (C), 135 (CH), 132.07 (CH), 131.7 (CH), 131.66 (CH), 129.78 (CH), 126.75 (C), 126.59 (C), 122.07 (CH), 121.19 (CH), 120.94 (CH), 119.22 (CH), 115.76 (CH), 114.4 (CH), 108.03 (CH), 101.57 (CH), 68.38 (OCH₂), 68.32 (OCH₂), 31.84 (CH₂), 29.5 (CH₂), 29.31 (CH₂), 29.26 (CH₂), 29.04 (CH₂), 29.02 (CH₂), 26.93 (CH₂), 22.62 (CH₂) and 14.05 (CH₃); FAB mass: m/z 869.6 [M]⁺.

2cCu: IR (KBr Pellet): $\nu_{\max}/\text{cm}^{-1}$ 2922, 2854, 1737, 1607, 1584 and 1522; FAB mass m/z 1800.43 [M]⁺.

2cPd: IR (KBr Pellet): $\nu_{\max}/\text{cm}^{-1}$ 2921, 2852, 1731, 1636, 1593 and 1522; $^1\text{H NMR}$ (400 MHz, CDCl₃): 8.27 (t, $J = 8.9$ Hz, 8H, Ar), 8.15 (d, $J = 8.9$ Hz, 4H, Ar), 7.6 (s, 2H, 2 × CH=N), 7.5 (m, 6H, Ar), 7.38 (d, $J = 8.8$ Hz, 6H, Ar), 7.22 (t, $J = 8.2$ Hz, 6H, Ar), 7.08 (d, $J = 8.9$ Hz, 2H, Ar), 6.9 (d, $J = 8.96$ Hz, 4H, Ar), 6.12 (dd, $J = 8.8$ Hz, $J = 2.32$ Hz, 2H, Ar), 5.55 (d, $J = 2.2$ Hz, 2H, Ar), 4.08 (t, $J = 6.6$ Hz, 2 × OCH₂), 3.8 (t, $J = 6.4$ Hz, 4H, 2 × OCH₂), 1.86–1.32 (m, 64H, 32 × CH₂) and 0.88 (m, 12H, 4 × CH₃); ^{13}C (100 MHz, CDCl₃, Spin Echo FT): δ 167.27 (CO), 165.79 (C), 164.35 (C), 164.1 (C), 163.9 (C), 161.01 (C), 155.56 (C), 154.56 (C), 151.53 (C), 135.76 (CH), 132.41 (CH), 131.81 (CH), 130.35 (CH), 129.83 (CH), 126.91 (C), 126.62 (C), 125.51 (CH), 122.13 (CH), 121.0 (C), 119.2 (CH), 119.13 (CH), 115.72 (CH), 114.47 (CH), 107.39 (CH), 102.11 (CH), 68.42 (OCH₂), 68.87 (OCH₂), 31.87 (CH₂), 29.52 (CH₂), 29.32 (CH₂), 29.09 (CH₂), 28.97 (CH₂), 25.96 (CH₂), 22.65 (CH₂) and 14.06 (CH₃); FAB mass: m/z 1843.3 [M]⁺.

The preliminary investigations on the samples to check the liquid crystalline behaviour were performed using the following techniques. The optical textures of the samples were observed using a polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90). The phase transition temperatures and associated enthalpies were obtained by differential scanning calorimetry (Perkin Elmer DSC7) and the results are summarized in the table. X-ray diffraction studies were carried out using an Image Plate Detector (MAC Science, Japan) equipped with double mirror focusing optics. The samples were contained in Lindemann capillary tubes. Spontaneous polarization and switching

Table. Phase transition temperatures ($T/^\circ\text{C}$)^a and corresponding enthalpy changes (in parentheses) ($\Delta H/\text{kJ mol}^{-1}$) for the 1-[*N*-(2-hydroxy-4-*n*-alkoxybenzylidene)-4-amino-benzoato]-3-[4-(4-*n*-decyloxybenzoyloxy)benzoyloxy]-benzenes and their Cu(II) and Pd(II) metal complexes. Cr = crystal; B¹ = a two-dimensional smectic phase; B² = a fluid smectic phase with antiferroelectric type switchable characteristics.

Compound	Phase sequence and transition temperature
1a	Cr 110.3 (21.1) B ¹ 132.5 (18.2) I
1b	Cr 82.5 (11) B ² 137.8 (15.1) I
1c	Cr 74.1 (26.5) B ² 141.9 (23.2) I
2aCu	Cr >110 decomposes
2aPd	Cr 228.3 (56.6) I
2bCu	Cr 170.1 (62.1) I
2bPd	Cr 168.7 (29.6) I
2cCu	Cr 162.2 (54.7) I
2cPd	Cr >145 decomposes

^a Peak temperatures in the DSC thermograms obtained during heating cycle at 5° min⁻¹.

time studies were carried out on samples sandwiched between ITO-coated glass plates treated with polyimide solution and rubbed unidirectionally.

3. Results and discussion

On cooling from the isotropic phase, the banana-shaped bidentate ligand **1a** shows a dendritic growth pattern that coalesces to give a mosaic texture with spherulitic domains. Such a textural pattern is usually seen from the B₁ phase, which was confirmed with the help of X-ray diffraction studies. Figure 2 shows the 2D-powder diffraction pattern and the 1D intensity against 2θ profile for sample **1a** recorded at 115°C. Two sharp reflections are seen at low angles, $2\theta = 3.24^\circ$ and 4.4° , which can be indexed as 20, 11 and whose d -spacings are in the ratio corresponding to reflections from a 2D rectangular lattice. The diffuse character of the peak at wide angle ($2\theta = 20^\circ$) corresponds to liquid-like ordering within the smectic layer. Additionally, we examined the material for electrical switching, by applying both triangular and square wave fields. The mesophase showed no kind of response to the applied field. These observations clearly indicate that the mesophase is of the B₁ type.

Ligands **1b** and **1c** show, on cooling from the isotropic phase spherulitic domains exhibiting a fringe pattern superposed on a focal-conic texture appearing spontaneously. On further cooling, new layers aggregate outside the initially formed spherulites and some of these show a clear Maltese cross. The texture is similar to the one reported for the B₂ banana phase of several materials reported in the literature. In order to confirm that it is indeed a B₂ phase, X-ray studies were performed on both samples (**1b** and **1c**). These compounds show an identical X-ray pattern and as a representative case, we show in figure 3, the 2D powder diffraction pattern and

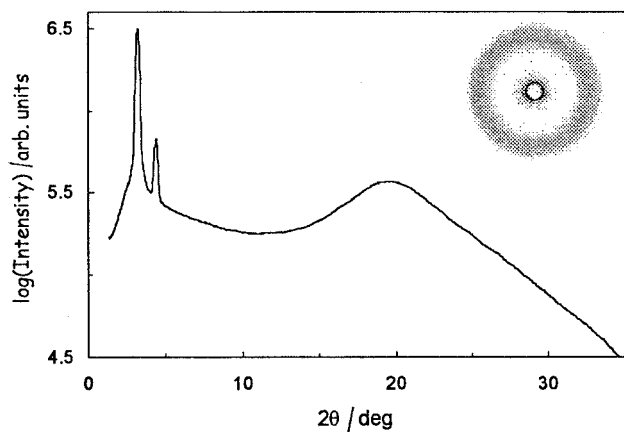


Figure 2. 2D powder X-ray diffraction pattern (inset) and the 1D intensity against 2θ profile for compound **1a** recorded at 115°C.

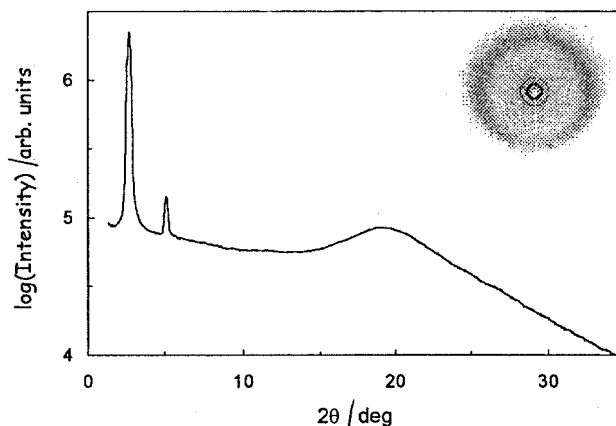


Figure 3. X-ray diffraction pattern (inset) and the intensity against 2θ profile of compound **1b** at 130°C.

the 1D intensity against 2θ profile for sample **1b**. Two sharp reflections are seen at angles $2\theta = 2.67^\circ$ and 5.09° with corresponding d -spacings of 3.63 and 1.81 nm, respectively. The ratio of the two spacings is of the order of 2, which is due to the dimeric nature of the molecule. The diffuse peak seen at $2\theta \sim 19.4^\circ$ with $d = 0.46$ nm indicates liquid-like ordering within the smectic layer.

Ligands **1b** and **1c** were then subjected to electrical switching studies. The two compounds respond to electrical fields in a similar manner. Here we present electrical switching measurements for sample **1b** as a representative case. A triangular wave electrical field ($40 \text{ V } \mu\text{m}^{-1}$) was applied at 111°C to the sample and the two-peak profile per half cycle obtained clearly shows antiferroelectric-type switching characteristics, which is commonly observed for the B₂ phase (figure 4). The combined area under the two peaks is a direct measure of the spontaneous polarization (P_s). The voltage required to switch the molecules in the B₂ phase is an order of magnitude greater than that required for the symmetric analogue of these materials [4a]. It is possible that this is due to the asymmetry of the molecular

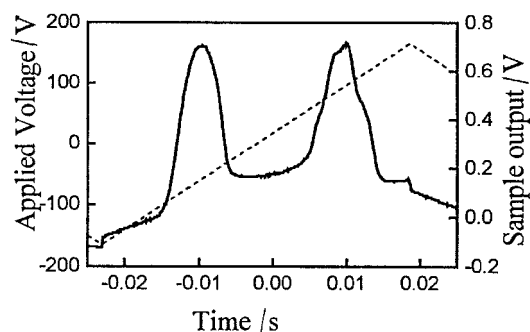


Figure 4. The current response peak of compound **1b** at 111°C when a triangular wave electrical field ($40 \text{ V } \mu\text{m}^{-1}$) was applied (solid line—sample output; dashed line—applied voltage).

structure; another reason could be the formation of hydrogen bonds. However, no experimental data are available to resolve this ambiguity. The thermal variation of P_s obtained by integrating the area under the peaks is shown in figure 5. The high value of P_s ($\sim 600 \mu\text{C cm}^{-2}$) is typical for banana-shaped compounds. P_s has a weak temperature dependence far away from the isotropic transition, but on approaching it, shows a precipitous drop and vanishes in the isotropic phase.

The switching time τ in the B₂ phase was studied by monitoring the current response of the sample when a square wave field was applied to the sample. A typical time dependence of the sample output is shown in figure 6. Using such curves, τ was estimated from the time elapsed between the appearance of the maximum in the current signal and the field reversal. The plot of temperature versus switching time τ is shown in figure 7. τ decreases gradually as the sample temperature increases, going to zero at the B₂-isotropic phase transition. It may be mentioned here that the B₂ phase on cooling from the isotropic shows racemic domains which change over to chiral domains [5] on application of electric fields $> 60 \text{ V } \mu\text{m}^{-1}$.

The molecular structures of the metal complexes clearly indicate that banana-mesophases cannot be stabilized in such structures owing to the square planar

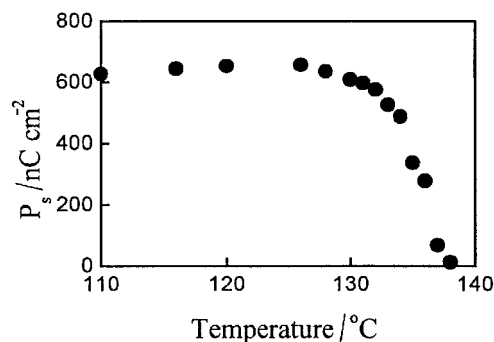


Figure 5. The thermal variation of P_s for compound **1b**.

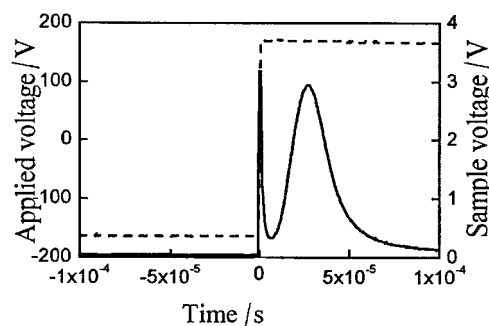


Figure 6. A typical time dependence of the sample response for compound **1b** when a square wave field of $42 \text{ V } \mu\text{m}^{-1}$ is applied at 111°C (solid line—sample output; dashed line—applied voltage).

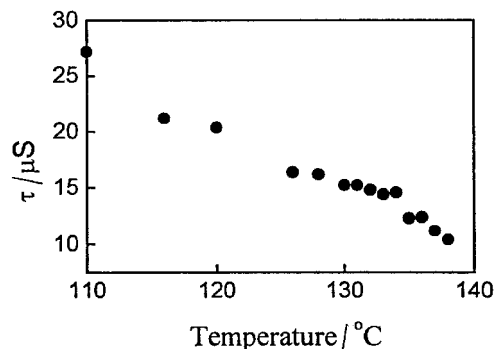


Figure 7. The plot of temperature versus switching time τ . Note that τ decreases gradually as the sample temperature increases, going to zero at the B₂-isotropic phase transition.

geometry of the complexes. In this geometry the two banana-shaped molecules pair-up to incorporate a metal atom in which the bend directions of the molecules are reversed. However, the stabilization of mesophases exhibited by conventional molecules cannot be ruled out. Surprisingly, neither of the metal complexes show liquid crystalline properties. It appears that we need to choose an appropriate banana-shaped ligand and metal atoms such that, in the resulting metal complex, the banana-shaped molecules pair-up to incorporate the metal atom in such a way that their bend direction is common.

4. Conclusions

We have presented the synthesis and characterization of the first examples of banana-shaped bidentate ligands and their Cu(II) and Pd(II) metal complexes. The bidentate banana-shaped ligands exhibit either a B₁ or a B₂ phase while their metal complexes do not show mesomorphism. Presently we are working on such systems so as to realize metal-containing banana-shaped mesogenic molecules.

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