Relationship between the magnetic field induced orientation in the mesophases of metallomesogens derived from Schiff's bases and their mesophase structure

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In this paper the orientation of the mesophase domains of metallomesogens derived from Schiff's bases by the effect of applied magnetic fields is analysed. Particular emphasis is put on the copper compounds; in this case, the orientation depends on the number of aromatic rings in the molecule (four or six) and, when four rings are present, it also depends on the type of molecular structure (2,4- versus 2,5-substitution). These differences are related to the order of the mesophase and can be explained by considering the additional ordering of the short axes. A strong indication of the existence of biaxial order in the mesophase is thus derived. This order is associated with the shape of the molecule which imposes geometrical constraints on the molecular packing.

1. Introduction

Macroscopic orientation of mesophases can be achieved using moderate magnetic fields. This phenomenon has been widely studied for conventional organic liquid crystals (LCs) and has been described as a coupling between the magnetic field and the director [1–3]. The macroscopic orientation is due to the co-operative effect of the molecular orientation in a domain (the molecules are bound together by the anisotropic interactions responsible for the order of the mesophase) and of the anisotropy of the molecular magnetic susceptibility, χ^M. Usually domains of calamitic organic LCs (in the N, S_A, S_C, ... phases) orient with the director parallel to the magnetic field. The resulting phase is uniaxial and the anisotropy of the domain susceptibility $\Delta\chi^D$ is given by:

$$\Delta\chi^D = S\Delta\chi^M \qquad (1)$$

where S is the Saupe order parameter and $\Delta\chi^M = \chi_z - (\chi_x + \chi_y)/2$ gives a measure of the anisotropy of the molecular susceptibility. Since $\Delta\chi^M > 0$, it follows that $\Delta\chi^D > 0$, which explains the observed behaviour.

The phenomenology is richer in the case of metallomesogens; orientations of the director both parallel and perpendicular to the magnetic field are found [4]. The competition between the paramagnetic contribution to the magnetic susceptibility due to the metal and the

diamagnetic contribution associated with the organic skeleton has been suggested as the reason for such behaviour [4, 5]. In particular there is a great deal of information about the orientational behaviour of some copper(II) and oxovanadium complexes derived from Schiff's bases (see the table). Oxovanadium complexes orient with the director parallel to the magnetic field, whereas it is found in Cu(II) complexes the orientation depends on the number of aromatic rings in the molecules (four or six) and, in the case where four rings are present, it also depends on the type of molecule (type III with 2,5-substitution versus types I and II with 2,4-substitution). In this paper we shall discuss these differences and relate them to the structure of the mesophases. As a main conclusion, we will propose that the observation of perpendicular orientation is likely to be related to the existence of biaxial ordering of the molecules in the mesophase, which is associated with the shape of the molecules that imposes geometrical constraints on the molecular packing.

2. Theory

For all the systems collected in the table, the metal core (see figure 1) can be described as planar and we have chosen the molecular axis frame (x_M, y_M, z_M) in such a way that the x_M axis is normal to the core plane and the z_M axis is along the long axis of the molecule. Thus the two aromatic rings in the central core (labelled as A) lie in the $y_M z_M$ plane and all the others (labelled

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Table. Some types of metallomesogens derived from Schiff's bases.

Type	Formula	Anisotropy for M = Cu	Oriented phase
I[a]		$\Delta\chi < 0$	S_A
II[b]		$\Delta\chi < 0$	N
III[c]		$\Delta\chi > 0$	S_C
IV[d]		$\Delta\chi > 0$	N
V[e]		$\Delta\chi > 0$	S_A

[a] Cu: $R_1 = OC_{10}H_{21}$, $R_2 = C_nH_{2n+1}$ [8, 9]; $R_1 = C_4H_9$, $R_2 = C_7H_{15}$ [8].
[b] Cu: $R = C_{10}H_{21}$, $n = 1$–10 [10]; $n = 1, 5, 10$ [12, 13]. VO: $R = C_{10}H_{21}$, $n = 5, 10$ [14].
[c] Cu: $R = C_{10}H_{21}$, $n = 1$ [12, 13].
[d] Cu: $R_1 = C_{10}H_{21}$, $R_2 = OCH_3$, $OC_{10}H_{21}$ [12–14]; $R_1 = C_4H_9$, $R_2 = OCH_3$, [15]. VO: $R_1 = C_{10}H_{21}$, $R_2 = OCH_3$, OC_2H_5, OC_5H_{11}, $OC_{10}H_{21}$ [12, 14].
[e] Cu: $R_1 = C_{10}H_{21}$, $R_2 = C_nH_{2n+1}$; $n = 1$–10 [9, 16].

as B) can be rotated around the z_M axis. For type II, IV and V compounds, to consider z_M as the rotation axis for B-phenyl is an approximation. However, in principle our conclusions about the relationship between ordering and magnetic field induced orientation in these compounds will not be affected by this hypothesis. A scheme for the orientation of the aromatic rings in the molecule is given in figure 2.
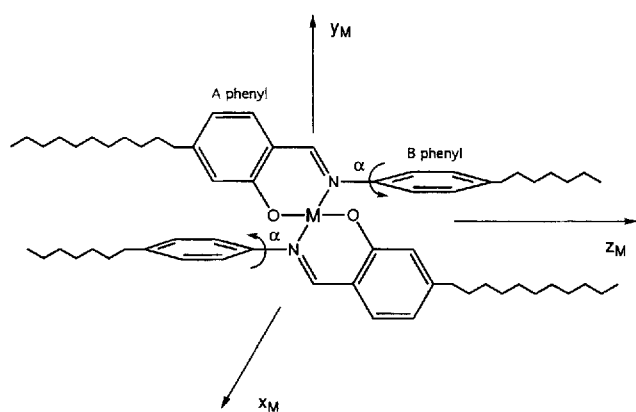
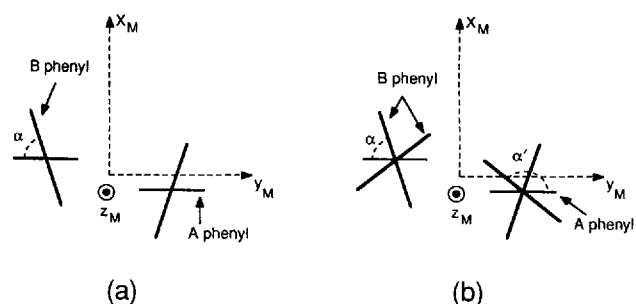Figure 1. Scheme for the metal-containing core of the molecules. The molecular axes are shown (see text).

Figure 2. Diagram showing the mean orientation of the phenyl rings (*a*) for type I, II and III compounds (four phenyl rings); (*b*) for type IV and V compounds (six phenyl rings).

Taking all these considerations into account we can estimate the anisotropy of the magnetic susceptibility in the following terms.

$$
\tilde{\chi}' = \begin{pmatrix} \chi_x' & & \\ & \chi_y' & \\ & & \chi_z' \end{pmatrix}
$$

$$
= \frac{\Delta\chi}{3}\begin{pmatrix} -1 & & \\ & -1 & \\ & & 2 \end{pmatrix} + \frac{\delta\chi}{2}\begin{pmatrix} 1 & & \\ & -1 & \\ & & 0 \end{pmatrix} \tag{2}
$$

where χ' represents the anisotropic part of the magnetic susceptibility χ and where $\Delta\chi = \chi_z - (\chi_x + \chi_y)/2$ and $\delta\chi = \chi_x - \chi_y$; χ_α ($\alpha = x, y, z$), being the principal values of the magnetic susceptibility, give a measure of its anisotropy.

The paramagnetic contribution, $\tilde{\chi}_p'$, is obtained from the *g*-values measured from the electron paramagnetic resonance (EPR) spectra. With our choice for the

molecular axes this is given by:

$$
\tilde{\chi}_p' = \frac{\Delta\chi_p}{3}\begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix} \tag{3}
$$

with

$$
\Delta\chi_p = \frac{\mu_B^2 S(S+1)}{3kT}(g_\parallel^2 - g_\perp^2) \tag{4}
$$

where μ_B is the Bohr magneton, $g_\parallel$ and $g_\perp$ are the principal *g*-values of the paramagnetic entity and $S = 1/2$.

The diamagnetic contribution, $\tilde{\chi}_d'$, to the anisotropy of the magnetic susceptibility is estimated by considering the molecular anisotropy of a phenyl ring. Diamagnetic contributions from other organic groups in the molecules are not taken into account since they are small compared with those of the aromatic rings. This is supported by previous studies on the magnetic susceptibility of diamagnetic mesogenic compounds where the experimental anisotropies agree very well with those calculated considering only the contributions from the phenyl rings [6, 7]. The diamagnetic susceptibility of the aromatic rings is described as axial with $\chi_\parallel = -91 \times 10^{-6}\,\text{emu mol}^{-1}$ and $\chi_\perp = -37 \times 10^{-6}\,\text{emu mol}^{-1}$, where $\parallel$ stands for the axis perpendicular to the plane of the phenyl ring and $\perp$ for any direction in this plane [2]. If $\Delta\chi_{ph} = \chi_\parallel - \chi_\perp = -54 \times 10^{-6}\,\text{emu mol}^{-1}$, the contribution of the two A phenyl rings to the anisotropy of the molecular magnetic susceptibility is:

$$
\chi_A' = 2\frac{\Delta\chi_{ph}}{3}\begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix} \tag{5}
$$

and the contribution for each pair of B phenyl rings is:

$$
\chi_B' = 2\frac{\Delta\chi_{ph}}{3}\begin{pmatrix} \frac{1}{2}+\frac{3}{2}\langle\cos 2\alpha\rangle & & \\ & \frac{1}{2}-\frac{3}{2}\langle\cos 2\alpha\rangle & \\ & & -1 \end{pmatrix} \tag{6}
$$

where $\langle\cos 2\alpha\rangle$ means the average of $\cos 2\alpha$ for all molecular conformations, α being the rotation angle of the B phenyl plane around the z_M axis (see figures 1 and 2).

Taking into account both paramagnetic and diamagnetic contributions, the anisotropy of the molecular

magnetic susceptibility is given by:

$$\chi'^M = \frac{\Delta\chi_P}{3}\begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix}$$

$$+ \frac{2\Delta\chi_{ph}}{3}\begin{pmatrix} \frac{n+3}{2} + \frac{3}{2}A_n & & \\ & \frac{n-3}{2} - \frac{3}{2}A_n & \\ & & -n \end{pmatrix} \quad (7)$$

with $n = 2$ (or 3) if the molecule has four (or six) phenyl rings, and

$$A_2 = \langle\cos 2\alpha\rangle \quad \text{or} \quad A_3 = \langle\cos 2\alpha\rangle + \langle\cos 2\alpha'\rangle \quad (8)$$

Thus, we obtain for the molecular magnetic susceptbility:

$$\Delta\chi^M = -\frac{\Delta\chi_p}{2} - n\Delta\chi_{ph} \quad \delta\chi^M = \Delta\chi_p + 2(1 + A_n)\Delta\chi_{ph}$$

$$(9)$$

Considering these values and using the order parameters introduced by Straley [17] in a general case, the anisotropy of the domain magnetic susceptibility is described by [4]:

$$\Delta\chi^D = -\frac{1}{2}(S + U)\Delta\chi_p - \{nS + U(1 + A_n)\}\Delta\chi_{ph}$$

$$\delta\chi^D = \frac{1}{2}(T - 2V)\Delta\chi_p + \{nT - 2V(1 + A_n)\}\Delta\chi_{ph}$$

$$(10)$$

For oxovanadium compounds, $\Delta\chi_p < 0$ from the EPR data because $g_\parallel < g_\perp$ [4]. So, $\Delta\chi^D > 0$ in each case, in agreement with the observed behaviour. In the following, we will restrict ourselves to the copper compounds. If we follow a classical description of the phase by assuming cylindrical symmetry for the orientation of the molecular long axis around the director and for the orientation of the x_M and y_M axes around the z_M axis, only the Saupe parameter S is necessary to describe such an order, and $T = U = V = 0$. Thus:

$$\Delta\chi^D = -S\left(\frac{\Delta\chi_p}{2} + n\Delta\chi_{ph}\right) = S\left(n|\Delta\chi_{ph}| - \frac{\Delta\chi_p}{2}\right)$$

$$(11)$$

This is true for N and S_A phases, but in the case of an S_C phase, a non-vanishing value for T is expected, whereas for a description of the molecules as being cylindrical, $U = V = 0$. As we will see later this is not relevant for our conclusions.

It is worth noting that for a uniaxial arrangement of the molecules in the domain, the magnetic susceptibility anisotropy does not depend on the actual orientation of

the B-phenyl rings around the long axis, but only on the number of pairs of aromatic rings in the molecule. This is in contrast with the behaviour observed in type I and type II metallomesogens as compared with those of type III (see the table). All these compounds have four aromatic rings in the molecules; however, whereas type III complexes orient in the mesophase with the director along the magnetic field ($\Delta\chi^D > 0$), type I and type II behave in the opposite sense ($\Delta\chi^D < 0$).

If we introduce the ratio $\eta = |\Delta\chi_{ph}|/\Delta\chi_p$, a perpendicular orientation of the domain ($\Delta\chi^D < 0$) would be reached if

$$\eta = \frac{|\Delta\chi_{ph}|}{\Delta\chi_p} < \frac{1}{2n} = \gamma_n \quad (12)$$

where $\gamma_n = 0.25$ (0.17) in the case of two (three) pairs of aromatic rings in the molecule.

Taking into account the value quoted above for $\Delta\chi_{ph}$ and an estimation of $\Delta\chi_p$ in the mesophase of the copper(II) complexes of about 180×10^{-6} emu mol^{-1} (from the EPR data), we obtain for η a value around 0.3. Therefore, in the approximation of classical uniaxial ordering, we would expect for all families collected in the table an orientation of the domains with the director parallel to the magnetic field. Thus, to explain the behaviour of type I and type II copper complexes, we have to consider another contribution to the anisotropy of the magnetic susceptibility. According to equation (10), some other order parameters besides the Saupe order parameter, S, must take values different from zero. Besides, if we consider the competition between the metal paramagnetic contribution and the diamagnetic contribution, perpendicular orientation of the mesophase of the copper complexes will be achieved when $\chi'_x > \chi'_z$, so (see equation (2)):

$$\delta\chi^D > 2\Delta\chi^D \quad (13)$$

Combining this equation with equation (10), it follows that:

$$\frac{|U - V|}{S + T/2} > \frac{2n\eta - 1}{|1 - 2\eta(1 + A_n)|} \quad (14)$$

Introducing the mean value of $\cos^2\alpha$ for all the B-aromatic rings in the molecule, that is $\langle\cos^2\alpha\rangle$ for $n = 2$ and $(\langle\cos^2\alpha\rangle + \langle\cos^2\alpha'\rangle)/2$ for $n = 3$, the former inequality is given by

$$\frac{|U - V|}{S + T/2} > \frac{4\eta - 1}{|1 - 4\eta\langle\cos^2\alpha\rangle|} \quad \text{for } n = 2$$

and

$$\frac{|U - V|}{S + T/2} > \frac{6\eta - 1}{|1 + 2\eta - 8\eta\langle\cos^2\alpha\rangle|} \quad \text{for } n = 3$$

$$(15)$$

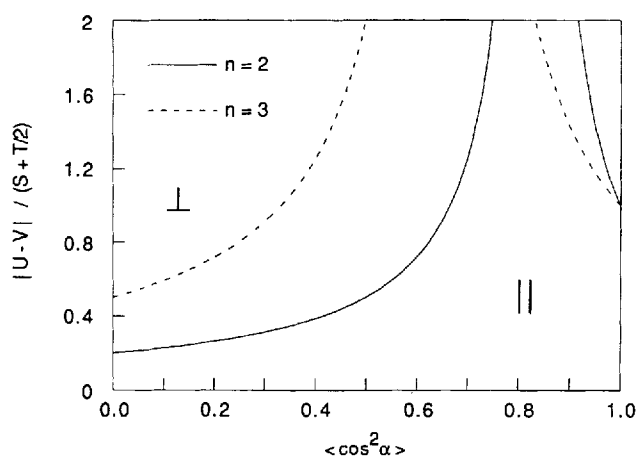The opposite is valid if the domains orient with the mean direction of the molecular long axis parallel to the magnetic field.

Figure 3. Plot of the regions defined by equations (15) corresponding to an orientation of the mesophase domains with the director parallel ($\parallel$) or perpendicular($\perp$) to the magnetic field. Solid line for $n = 2$ and broken line for $n = 3$.

3. Results and discussion

In figure 3 we show a graphical picture of these results, using the previously quoted value of $\eta \approx 0.3$. As a first conclusion, it is important to note that for a perpendicular orientation of the domains, $|U - V|$ has to be different from zero, regardless of the mean orientation of the B-phenyl rings. This implies, as has been pointed out above, an order of the molecular short axes (the x_M and y_M axes) in the mesophase, in addition to the order considered in a classical description of calamitic mesophases.

Besides, if the B-phenyl rings were able to rotate freely around the z_M molecular axis $\langle \cos^2 \alpha \rangle = 1/2$; however, as a consequence of spatial impediments, this value is an upper limit of the actual value of $\langle \cos^2 \alpha \rangle$. For these values of $\langle \cos^2 \alpha \rangle$, the differences observed in the orientational behaviour of type IV and type V compounds (six phenyls) as compared with type I and type II (four phenyls), whose order in the mesophase is expected to be similar, can be understood after examination of figure 3. For instance, for $\langle \cos^2 \alpha \rangle = 0.4$, a perpendicular orientation is expected for compounds with $n = 2$ if $|U - V| > 0.39 \ (S + T/2)$, whereas in the case of compounds with $n = 3$, this orientation occurs when $|U - V| > 1.25 \ (S + T/2)$. Thus, a higher degree of order of orientation of the short axes would be needed to achieve a perpendicular orientation of the director in the case of compounds with six phenyl rings than in the case of those having only four rings in their molecules.

Another important point for discussion is the difference between the orientational behaviour of type III compounds as compared with type I and type II complexes. In the first case, the molecular shape is more linear than in the second case, in which the molecule

can be better described as two rods bound by the metal core. These differences have previously been pointed by Marcos *et al.* [18] and impose differences in the molecular packing in the mesophase in such a way that type III molecules are more free to rotate around their molecular long axis than are type I and type II molecules. Thus lower values for the U and V parameters are expected for the former mesogenic compounds than for the latter. Consequently, our model explains, at least qualitatively, the differences observed in the orientational behaviour.

As a final point, we conclude that the description of the mesophase of some metallomesogenic compounds needs to be revisited and that some order in addition to the calamitic order should be considered.

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