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Dielectric study of the tilted columnar mesophase in three new chiral metallorganic discotic mesogens

BEATRIZ PALACIOS, M. ROSARIO DE LA FUENTE*,
MIGUEL ANGEL PÉREZ JUBINDO
Departamento de Física Aplicada II, Facultad de Ciencias,
Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain

RAQUEL IGLESIAS, JOSÉ LUIS SERRANO and TERESA SIERRA
Departamento de Química Orgánica, Facultad de Ciencias-I.C.M.A.,
Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain

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Chiral oxovanadium(IV), copper(II) and palladium(II) β-diketonates show a room temperature tilted columnar mesophase (rectangular $P2_1$). The dielectric response of these compounds was measured in the frequency range 10^{-2}–10^9 Hz. Three different relaxation processes have been observed in the columnar phase. One of them is only present in this mesophase and we suggest that it is a Goldstone-like mode, similar to the one present in the helical SmC* phases. In our case the presence of the helix was confirmed by circular dichroism studies.

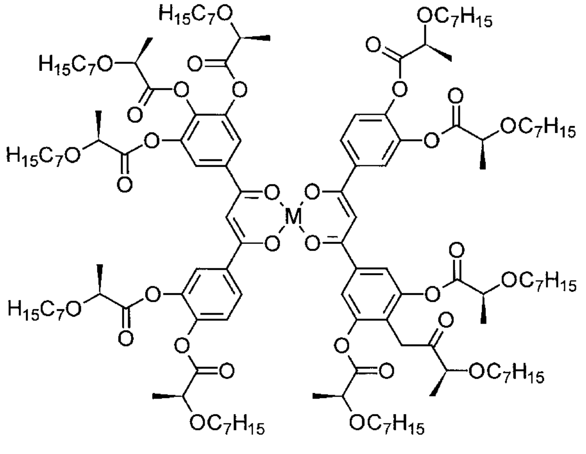
1. Introduction

Liquid crystals consisting of disc-shaped molecules were discovered by Chandrasekhar [1] 20 years ago. In this kind of compound, columnar mesophases [2] can appear when the molecules are suitably substituted with flexible side chains. The cores stack to form columns surrounded by the disordered aliphatic side chains. The centres of the cores form a rectangular (ordered or disordered) or hexagonal (ordered or disordered) lattice in the plane normal to the columnar axis. The occurrence of ferroelectricity in columnar phases was predicted by Prost in 1981 [3] and experimentally detected first in 1992 by Bock and Helfrich [4–9]. To show this phenomenon, the disk-shaped molecules have to be chiral and lie tilted with respect to the columnar axis. The macroscopic polarization is perpendicular to the column axis and the tilt plane and is due to the tilt-induced dipole moment of the chiral molecules. However, many questions regarding the molecular organization within the mesophase and the switching mechanism remain unanswered. Several authors [6] made claims for a helical arrangement in order to explain their results from switching experiments in terms of a process consisting of helix winding and unwinding. However, there is no other evidence (direct or indirect) for the existence of a helical arrangement inside the columns in these ferroelectric discotic liquid crystal materials.

It is the purpose of this paper to present the results of broadband dielectric studies (from 10^{-2} to 10^9 Hz) on three new chiral discotic liquid crystal materials with rectangular tilted columnar phases, Col_t^*, and hence ferroelectrics. One of the main results of this study is the presence of a Goldstone-like mode, similar to that present in SmC* phases, whose existence needs a helical arrangement. The helix was confirmed by circular dichroism studies [10, 11].

2. Results

The molecules of the three compounds consist of two penta-substituted 1,3-diphenylpropanedione ligands complexed to either vanadium(IV), copper(II) or palladium(II), thus giving rise to a disc-like core surrounded by ten flexible chiral tails derived from L-(-)-lactic acid.



M = VO, Cu, Pd

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*Author for correspondence.

Details of the chemistry of these materials, together with results from X-ray, circular dichroism, differential scanning calorimetry (DSC) and electro-optic switching studies have been published elsewhere [11]. These studies show that, upon cooling from their isotropic phases (I), these compounds form a wide temperature range columnar phase, identified as Col_r^* by X-ray, in which the molecular cores form a rectangular lattice ($P2_1$) in the plane normal to the columnar axis. These mesophases vitrify. The glass transitions have been found calorimetrically at around −70°C. On cooling from the isotropic liquid the mesophases display dendritic textures. When the mesophases are allowed to form at a very slow rate or annealed at 100°C for several hours, a texture with Maltese crosses often appears. The extinction brushes are tilted at a high angle with respect to the direction of the crossed polarizers, indicating a high tilt angle of the molecules with respect to the columnar axis. Circular dichroism studies have allowed us to deduce the existence of a helical order within the column (see figure 1). Only a non-parallel arrangement of the molecules within the column, together with the rotation of the molecular director along the column axis describing a helix, can account for the appearance of a positive exciton coupling corresponding to the π–π^* transition. Col_r^* phases are electro-optically switchable, but we could not measure the spontaneous polarization using the triangular wave method, probably because of the high value of the conductivity of the compounds at high temperatures and the high fields needed to invert the polarization at low temperatures.

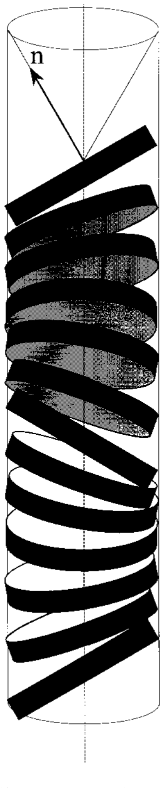

Figure 1. Schematic diagram of the molecular orientation in a column showing the helical structure.

The complex dielectric permittivity was measured over eleven decades of frequency (10^{-2}–10^9 Hz) using three different measuring systems: a Schlumberger 1260 frequency response analyser together with a high-impedance preamplifier of variable gain (10^{-2}–10^6 Hz), and two impedance analysers, the HP 4192A (10^2–10^7 Hz) and the HP 4191A (10^6–10^9 Hz). The cell consisted of two gold plated brass electrodes (diameter 5 mm) separated by 50 μm thick silica spacers. The details of the experimental set-up have been described elsewhere [12].

I–Col_r^* transition temperatures (deduced from the dielectric study) are 149°C for the palladium (Pd), 139°C for the copper (Cu) and 143°C for the oxovanadium (VO) complex. Dielectric spectra are quite similar for the three compounds (hereafter, unless necessary, we only mention the VO compound). Figure 2 is a plot of the complex dielectric permittivity versus the logarithm of the frequency in the I phase. Two clear relaxations are present at frequencies around 10^6 Hz (hereafter called mode l) and 10^9 Hz (hereafter called mode h). In the Col_r^* phase, together with modes h and l, a new mode (hereafter called the columnar mode) appears (see figure 3). To find the strengths, frequencies and activation energies of every process, the experimental data were fitted for each phase to:

$$\varepsilon(\omega)=\sum_k \Delta\varepsilon_k(\omega)+\varepsilon_\infty-\mathrm{i}\sigma_{\mathrm{d.c.}}/\omega\varepsilon_0 \qquad (1)$$

where $\sigma_{\mathrm{d.c.}}$ accounts for the d.c. conductivity and ε_∞ for the high frequency permittivity. Each dielectric mode,

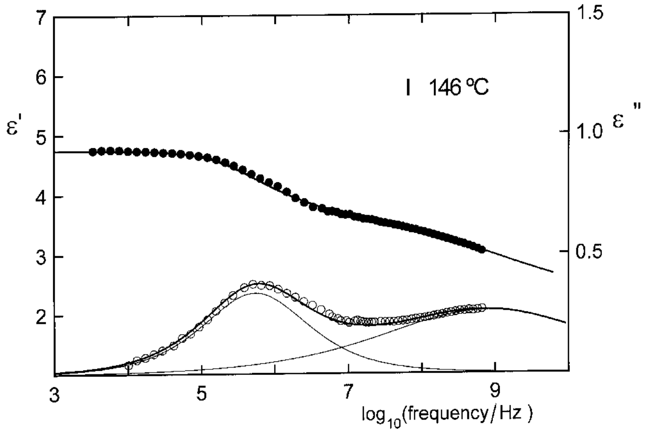

Figure 2. Real (●) and imaginary (○) components of the complex dielectric permittivity for the VO compound in the I phase. The continuous line is the fitting to equations (1) and (2).

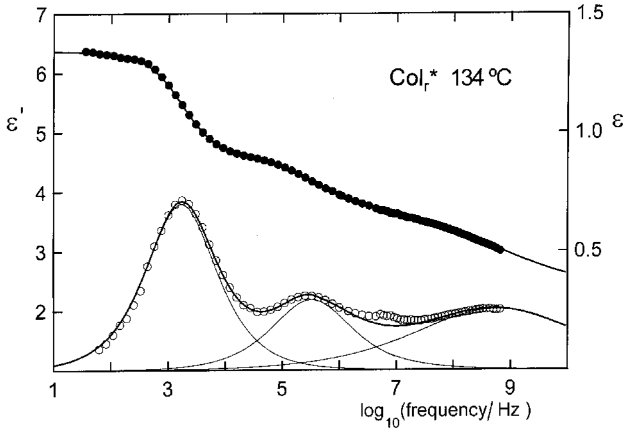

Figure 3. Real (●) and imaginary (○) components of the complex dielectric permittivity for the VO compound in the Col$_r^*$ phase. The continuous line is the fitting to equations (1) and (2).

$\Delta\varepsilon_k(\omega)$, has been fitted to the Havriliak–Negami function:

$$\Delta\varepsilon_k(\omega)=\frac{\Delta\varepsilon_k}{[1+(i\omega\tau)^{\alpha}]^{\beta}} \tag{2}$$

where $\Delta\varepsilon_k$ is the dielectric strength, τ the relaxation time and α, β control the shape of the relaxation. $\alpha=\beta=1$ is the Debye function; $\beta=1$, $0<\alpha\leqslant1$ is the Cole–Cole function; $\alpha=1$, $0<\beta\leqslant1$ is the Cole–Davidson function. In general all these parameters are temperature dependent. The relaxation frequency, f_k, is related to τ, α and β, through: $f_k=\{\tan[\pi/2(\beta+1)]\}^{1/\alpha}/2\pi\tau$.

In figures 2 and 3 we have subtracted from the experimental points a spurious contribution due to the electrode polarization and also the d.c. conductivity contribution. The continuous lines are fits to equations (1) and (2). In the I phase, modes h and l are almost Cole–Cole ($\beta\approx1$) with $\alpha\approx0\cdot5$ ($0\cdot6$ for the Pd compound and $0\cdot7$ for the Cu compound) for mode h and $\alpha\approx0\cdot9$ for mode l. In the columnar phase the spectra are more complex. Modes h and l broaden continuously with decreasing temperature. For example at −40°C, mode h has $\alpha=0\cdot3$. Moreover, the appearance of the columnar mode with a much larger strength makes the analysis, above all of mode l, very difficult. However, due to the different thermal activation, we can confirm that at −80°C mode h is still active and mode l at −20°C. Figures 4 and 5 show, respectively, the temperature dependence of the dielectric strength and the frequency of the three modes. The analysis of modes h and l for the Pd and Cu compounds is more difficult than for the VO compound due to their smaller strength and also to the larger values for the columnar mode (3 for VO, 4 for Pd and 6 for Cu).

The frequency of mode h falls continuously on cooling and does not show any jump at the I–Col$_r^*$ transition.

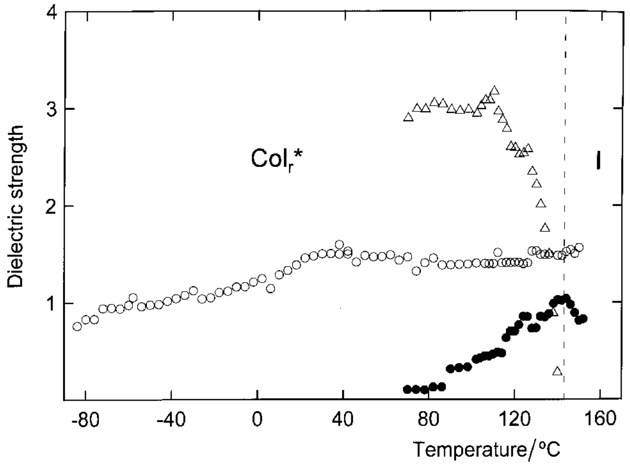

Figure 4. Dielectric strength of the different modes vs temperature for the VO compound: (○) mode h, (●) model l, (△) columnar mode.

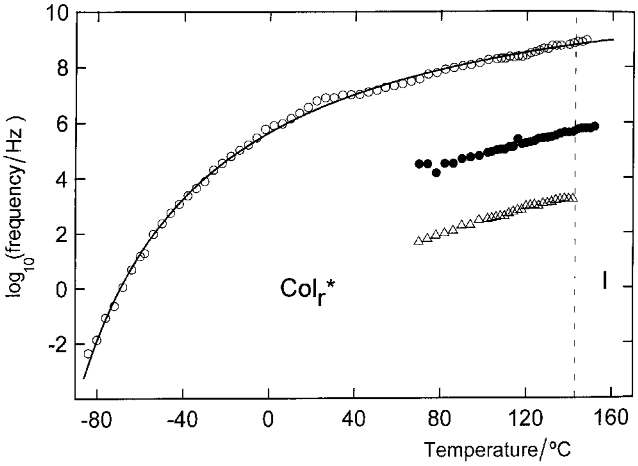

Figure 5. Frequency of the different modes vs. temperature for the VO compound: (○) mode h, (●) mode l, (△) columnar mode. The continuous line is the fitting to the VFT law.

In the I phase and in the high temperature side of the Col$_r^*$ phase, it can be fitted to the Arrhenius law, $f_h=f_{h\infty}\exp-E_a/kT$, the activation energy, E_a, being 52 kJ mol^{-1}. However, for lower temperatures the process becomes more activated with temperature and shows a non-Arrhenius behaviour. This temperature dependence can be well described by the empirical Vogel–Fulcher–Tammann (VFT) [13] law, $f_h=f_{h\infty}\exp\{-A/(T-T_0)\}$, over more than eleven decades of frequency, as shown by the continuous line in figure 5. In this expression T_0 is the so-called Vogel or ideal glass transition temperature (in general between 30 and 50 K below the calorimetric glass transition T_g), and A is a constant. In our case, $T_0=121$ K, $A=2235$ K and $f_{h\infty}=6\times10^{11}$ Hz.

The frequency of mode l does not show any jump at the I–Col_r^* phase transition and follows the Arrhenius law with an activation energy of $56\,\mathrm{kJ\,mol^{-1}}$ in both phases. Note that we could obtain this frequency only until 65°C, which opens the possibility of non-Arrhenius behaviour for lower temperatures.

The frequency of the columnar mode decreases with temperature, being around 10^3 Hz near the I–Col_r^* transition. We could characterize this mode properly down to 60°C because at this temperature the conductivity is still high and the relaxation frequency low.

3. Discussion

Now we discuss the possible origin of each mode. Modes h and l are present in the I and Col_r^* phases, and therefore they are not directly related to the columnar structure. Dielectric studies, for both chiral [14, 15] and achiral [16] discogens forming columnar non-tilted mesophases, also show these two modes. In these studies, the respective compounds showed a glass transition and being mode l related to the vitrification process. The authors assigned this relation to a motion of the discs around the column axis (which coincides with the molecular director for non-tilted columns). We think that the same explanation is valid in our case—a rotation around the molecular director (normal to the plane of the discs). In the Col_r^* phase there is a tilt induced dipole moment in the plane of the discs, perpendicular to the tilt direction and to the column axis, and therefore a rotation around the disc axis should contribute to the dielectric permittivity. The molecules have a symmetric structure, similar to one of the cases in references [16, 17]; then they do not necessarily have a net molecular dipole moment in the plane of the molecule in the I phase. Hence, the conformation of the carbonyl groups must be disordered leading to a mean square dipole moment in the plane of the molecule. Another possible explanation of the presence of mode l in the I phase is the existence of a local order, similar to that present in the columnar phase, producing a dipole moment lying in the disc plane in the same manner as in the Col_r^* phase. This last explanation would justify the increase of the dielectric strength in the I phase on cooling (see figure 4).

We think that mode h must be related to motions of the side groups of the discs. The side groups contain an ester linkage and a branch, which provide an important degree of rigidity for the chain from the point of attachment to the phenyl ring to the oxygen atoms bonded to the stereogenic carbon. These motions should be small angle (librations) and they are observed in the dielectric response over a wide range of temperature. This becomes broader and broader on cooling and shows non-Arrhenius behaviour, typical of an α process related to a glass transition. Moreover, in other cases, such lateral motions are explained as β relaxations, also active in the glassy state [14–20]. In our case the slowing down of the relaxation could be explained due to the proximity of part of the side group to the rigid part of the disc.

The so-called columnar mode was observed neither in achiral nor in chiral non-tilted columnar mesophases by other authors [14–20]. We think that it is related to the chiral and tilted character of the Col_r^* phase. It appears at the I–Col_r^* phase transition, and its strength is larger and its frequency smaller than those of the other modes. These facts suggest that it could be similar to the Goldstone mode in SmC* phase. The Goldstone mode is a collective mode related to the azimuthal fluctuations of the director around the helical axis. We think that in our case the same explanation is possible if a helical structure, consisting of tilted molecules whose tilt direction rotates along the columnar axis, is present (see figure 1). The columnar mode could be related to azimuthal fluctuations of the director around the helix axis that coincides with the columnar axis. The higher strength of this mode is due to the direct coupling of the macroscopic polarization and the field. As we have mentioned above, the presence of a helix is also confirmed by circular dichroism studies. The strength of the Goldstone mode in SmC* phases can be reduced by applying a bias field. This effect is due to the unwinding of the helix. We could not study the effect of a bias field on the strength of this mode because our low frequency set-up can only supply 10 V and the cells are thick (50 μm).

Summarizing, the synthesis of three new chiral discotic mesogens that show tilted colmnar phases, Col_r^*, has enabled us to investigate the influence of the chirality and the inclination of the molecules on the dielectric behaviour. As a result of both characteristics, a new relaxation, the columnar process, appears. We suggest that it is a Goldstone-like mode, similar to that present in SmC* phases, whose existence needs a helical arrangement. This helix was confirmed by circular dichroism studies.

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