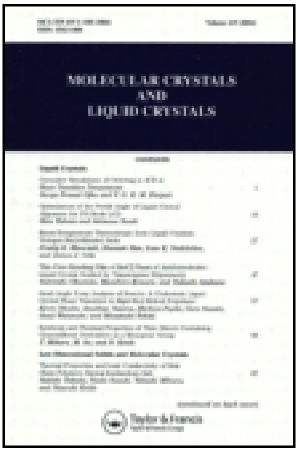

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QENS Experiments on a Palladium Containing Organometallic Mesogen†

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The cyclopalladation reaction of the liquid crystalline species p-dodecyloxy-p'-methylazobenzene (DOMAB) leads to the bimetallic metallo-mesogene [(DOMAB)Pd Cl]$_2$. Both the organic compound and its palladium organometallic complex have been investigated by quasielastic neutron scattering experiments in the nematic and smectic A phases. For DOMAB, the results exhibit a continuous rotation as expected for usual rod-like liquid crystals, while for [(DOMAB)Pd Cl]$_2$ they suggest a model wherein only some aliphatic protons can give a rotational diffusion.

INTRODUCTION

The metallo-mesogens, liquid-crystals incorporating transition metals, can be chemically classified as coordination compounds or organometallic complexes. The species we have synthesized so far, namely copper$^{1-5}$ and palladium species,$^{6-9}$ arise from reactions between appropriate rod-like thermotropic ligands and copper acetate (coordination compounds) or bis-(benzonitrile)-palladium chloride (organometallic complexes). The copper compounds are monometallic species, with a ligand to metal ratio of 2:1, while the palladium derivatives are chloro-bridged bimetallic complexes wherein the ligand to metal ratio is 1:1. Therefore, as far as the molecular shape is concerned, both these classes of compounds are featured by two roughly parallel long fragments, (i.e., the aliphatic chains which are part of the thermotropic ligands), whose separation is imposed by the metallic core (Figure 1). In principle such a structural inequality should be related to the molecular arrangements which the mesophases take up. Consequently, on the basis of previous investigations carried out either on copper or palladium mesogenes, we suggested two different packing modes: with strongly interdigitated molecules

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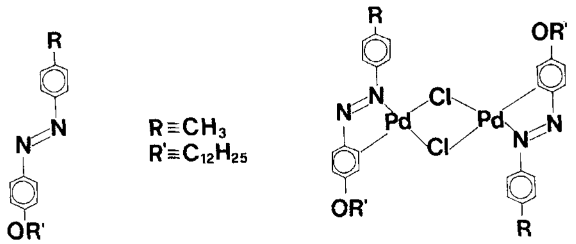

FIGURE 1 Molecular structure of DOMAB (1a) and [(DOMAB)Pd Cl]$_2$ (1b).

in the copper case and with the aliphatic chains partially melted in the palladium one.

Since it was expected that the dynamical properties displayed by the mesophases, could offer insights in the molecular packing, the discotic[10,11] and calamitic copper mesogenes[12] have been investigated recently by quasielastic neutron scattering (QENS). Here we report on the QENS results concerning p-dodecyloxy-p'-methylazobenzene (DOMAB) (Figure 1a) and its cyclopallated derivative [(DOMAB)Pd Cl)]$_2$ (Figure 1b).

The thermotropic properties of these compounds are[7]

$$\begin{array}{r} \text{DOMAB: C} \leftrightarrow 75.5^\circ\text{C(N)} \leftrightarrow 76.1\text{(I)} \\ \downarrow \\ 108.0^\circ\text{C(C)} \leftarrow 141.0^\circ\text{C(S}_c) \leftarrow 165.0^\circ\text{C(S}_a) \end{array}$$

$$[\text{(DOMAB)Pd Cl}]_2\text{: C} \rightarrow 150.4^\circ\text{C(N)} \leftrightarrow 174.0\text{(I)}$$

EXPERIMENTAL

The DOMAB and [(DOMAB)Pd Cl]$_2$ compounds were prepared as reported previously.[6] No deuteration was performed in this first approach.

The quasielastic neutron scattering experiments were performed at the Orphee reactor, of the Laboratoire Léon Brillouin, in Saclay (France) with the time-of-flight spectrometer Mibemol.

The incident neutron wavelength was $\lambda = 5$Å (3.25 meV) leading to an elastic resolution of 210 μeV. The detectors were placed at scattering angles 2θ between 44° and 103°. The sample put into a flat can was thermoregulated within ±1°C. The transmission of the sample was about 90%. With the used geometry and resolution we could consider to have access only to the rotational dynamics time scale and not to the translational one.[13]

After the standard corrections (empty can subtraction, normalization with a Vanadium run, energy dependence of the detector efficiency . . .) the spectra were fitted with pure rotational a model function $F(\omega)$ convoluted with the experimental resolution.

These model functions were of the form:

$$F(\omega) = (1 - c_1 - c_2)\delta(\omega) + c_1 \frac{\Gamma_1}{(\hbar\omega)^2 + \Gamma_1^2} + c_2 \frac{\Gamma_2}{(\hbar\omega)^2 + \Gamma_2^2}$$

i.e., a delta function and one ($c_2 = 0$) or two Lorentzians. The delta function accounts for all the motions that are too slow to be resolved within the instrumental resolution while each Lorentzian of width Γ_i corresponds to a different relaxation process of time $\tau_i = 2\hbar/\Gamma_i$.

RESULTS AND DISCUSSION

The qualitative behavior of the fits is quite different for the two different samples. While the $[(\mathrm{DOMAB})\mathrm{Pd\ Cl}]_2$ could be well fitted with only one Lorentzian over the entire Q-range in DOMAB a second Lorentzian was necessary to reproduce the Q-range above 1,45 Å^{-1}. Addition of further Lorentzians didn't give any improvement of the fit.

For DOMAB the FWHM (Γ_i) of the two Lorentzians is plotted against Q^2 (with Q the neutron momentum transfer). In Figure 2 the insert shows an example of the fit at $T = 76°\mathrm{C}$ taken at $Q = 0{,}8$ Å^{-1}.

For DOMAB, at small Q values, Γ_1 is roughly proportional to Q^2, Γ_2 is nearly constant with Q. On the other hand, the palladium complex behaves quite differently: Γ is almost independent of Q^2. This indicates that Γ_1 for DOMAB is related to some rotational motions which are almost forbidden in $[(\mathrm{DOMAB})\mathrm{Pd\ Cl}]_2$. Therefore qualitatively we conclude that $[(\mathrm{DOMAB})\mathrm{Pd\ Cl}]_2$ should be more hindered in the motion.

Further information on these rotational motions can be obtained from the analysis of the variations of the Elastic Incoherent Structure Factor (EISF) with Q. The experimental EISF data, $E(Q)$ are given by

$$E = [I_e/(I_e + I_{qe})] \tag{1}$$

where I_e and I_{qe} the intensity of the elastic and quasielastic peak respectively are obtained from the fits. The results are reported in Figures 3 and 4.

The calculation of the theoretical EISF values in agreement with the experimental data is not trivial and requires an appropriate rotational model. In the present case we have considered the simplest models suggested by Volino and Dianoux,[14–16] namely a rigid-rod freely continuous rotating around its long axis (continuous rotation on a circle of radius R) and a jump molecular rotation between different orientational positions.

For a continuous rotation $E(Q)$ is given by Equation 2:

$$E(Q) = J_0^2(Q^*R) \tag{2}$$

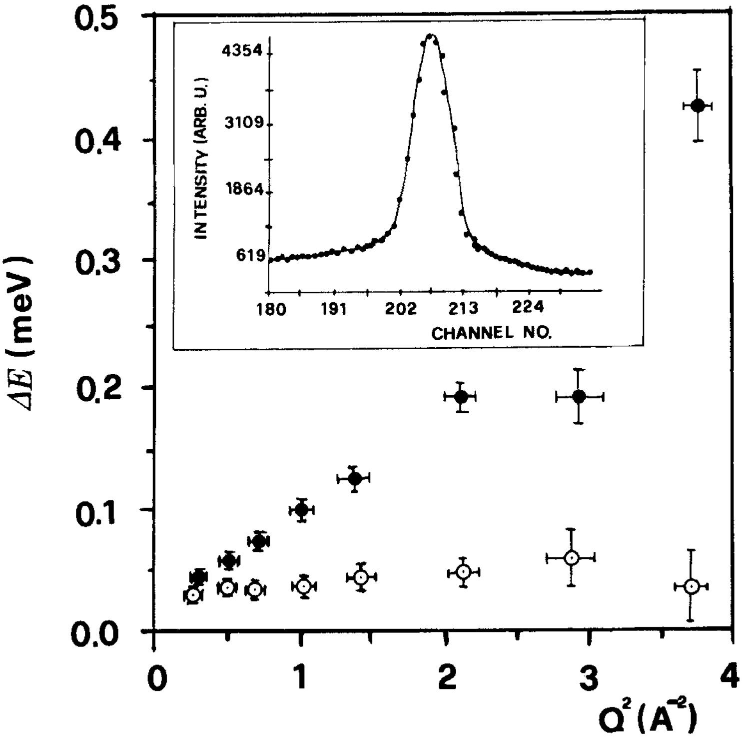

FIGURE 2 Behavior of the widths Γ_i of the two Lorentzian against Q^2 for one run of measurements on DOMAB at 75.8°C: the full dots are for Γ_1 and the open dots for Γ_2. In the insert is shown the fit of the spectrum with two Lorentzians.

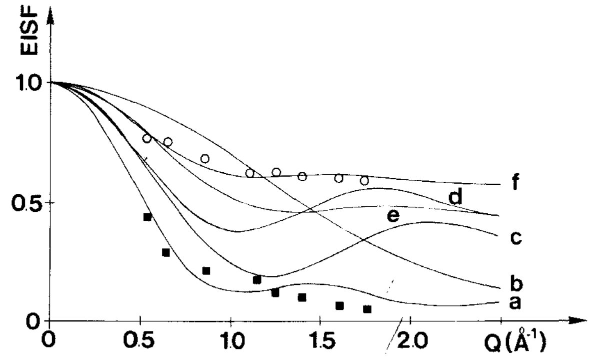

FIGURE 3 Experimental results on the Elastic Incoherent Structure Factor (EISF) of DOMAB in the nematic and solid phase (the squares are the experimental results in the nematic phase and the circles those in the solid phase). Theoretical calculations of different models are shown: free rotations of different order n with the same gyration radii, (a: R = 1Å; b: R = 2.1Å); jump rotations of order n with different gyration radii of R = 2.1Å (c: N = 4; d: N = 2); N is the number of steps in the jump model; and with a different fraction of standing protons, the remaining aliphatic protons rotating freely on an average radius of 2.1Å (e: 40% of standing protons; f: 60% of standing protons).

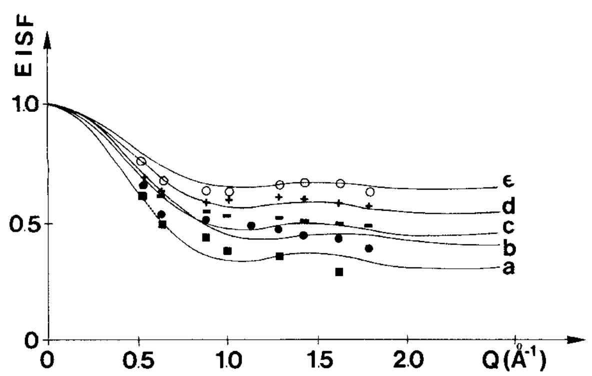

FIGURE 4 Elastic Incoherent Structure Factor (EISF) for [(DOMAB)Pd Cl]$_2$ at different temperatures (square and full dots for the nematic phase, lines and crosses for the Sa and open circles for the solid one): the full lines are calculated by considering a varying number of rotating protons: a: 75%; b: 63%; c: 57%; d: 51% and e: 43%.

(where $J_0(X)$ is the spherical Bessel function of order zero). For a jump rotation $E(Q)$ can be obtained from Equation 3:

$$E(Q) = \frac{1}{N}\sum_{n=1}^{N} J_0\left(Q^*R\sin\left(\frac{\pi_n}{N}\right)\right) \tag{3}$$

where R is the jump distance and N indicates the number of different possible orientational positions). Of course an improvement should consider for a powder sample (as in our case) an average of all the angular positions as numerically we done.

However, it should be pointed out that for a large number of positions (i.e., $N > 5$), Equation 3 becomes equivalent to Equation 2, and that the jump rotation can be treated analytically as an uniaxial rotation modulated by a sinusoidal potential which can be considered a "cage" formed by the surrounding molecules.

The goals of this preliminary work are: 1) to determine the possible differences between DOMAB and [(DOMAB)Pd Cl]$_2$ and 2) to propose a model for the rotational diffusion in this palladium-mesogen, even if it can only be a rough one. Accordingly, only free or jump rotations of the whole molecule, together with a combination of standing and freely rotating groups containing protons will be considered.

Figure 3 shows some calculations done for the DOMAB molecule. It gives the calculated EISF for a free rotation with different gyration radii (a: R = 1 Å; and b: R = 0.1 Å), for jump rotations with the same gyration radii of R = 2.1 Å (c: n = 4; d: n = 2) and for two different fractions of standing protons (e: 40%, f: 60%) with the remaining aliphatic protons rotating freely on a mean radius of 2.1 Å.

In the nematic phase, the best fits are obtained for the free rotor with a gyration radius of 2.1 Å (curve a), while for the solid phase good fits could be obtained either by progressively decreasing the gyration radii or by progressively freezing the aliphatic chains and preserving the same gyration radius (2.1 Å). The latter way seems more appropriate, and we conclude that the solid phase is best described by a fraction of 60% of standing protons. The remaining 45% are situated in the end groups of the aliphatic chains.

The [(DOMAB)Pd Cl$]_2$ complex was investigated in a similar way. The results in the nematic and in the smectic phases are far away to be fitted either by a free rotator model or a jump model. Therefore, by analogy with the more ordered phases of the usual liquid crystals, we considered that only some protons can rotate, we assume that the number of rotating protons is temperature dependent. Figure 4, shows our experimental results together with the EISF curves calculated using the DOMAB gyration radii having a different fraction of rotating protons as the only fit parameter. These curves represent a simultaneous fit to the five data sets covering all the phases studied, i.e., the nematic phase (at 170 and 166°C), the smectic A phase (T = 160 and 150°C) and the solid phase. Although not perfect this result is good enough given the roughness of the models.

The choice of the present model was motivated by previous results obtained from X-ray and small angle neutron scatterig measurements carried out on [(DOMAB)Pd Cl$]_2$. Those data were taken as evidence that at the transition from the solid to the mesophase the aliphatic chains melt and bend to fill up space. Moreover, we assumed that such a bending enlarges with increasing temperature. Owing to the high molecular width (about 2.5 times wider than in the usual rod-like liquid crystals), the rotation should then be inhibited even if, in principle, the melting of the aliphatic chains should ease the rotational diffusion.

In order to check this point the logarithm of the fraction of moving protons has been plotted against $1/T$ (where T is the temperature) (Figure 5). Due to the bending, we expect that the aliphatic chains should have a continuous distribution of the gyration radii from R = 0.0 Å for the CH_2 group bound to the benzene ring (practically standing) to R = 5.0 Å for the terminal CH_3 group.[23,24] Instead of a detailed distribution of gyration radii we adopted a mean value (R = 2.1 Å). The data are in agreement with an Arrhenius plot $N = N_0\, e^{-U/KT}$ where U is the activation energy for the rotation around the C—C axis, N_0 is the total number of protons in the molecules and N is the fraction of them that are rotating. From the best fit we calculate $U \cong 2.3\ 10^{-2}$ eV/bond, a value that seems quite appropriate

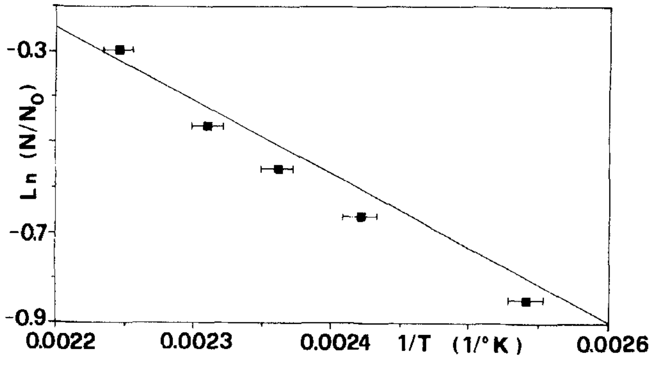

FIGURE 5 Arrhenius plot of the fraction of moving protons for [(DOMAB)Pd Cl$]_2$.

for the contribution of a single bond to the activation energy required for a rotational diffusion process.

The most important difference between DOMAB and [(DOMAB)Pd Cl]$_2$ lies in the number of Lorentzians needed for the fit to the experimental data: one at the lower Q-values and an additional one at the higher Q-values for DOMAB, and just one, over the entire Q range for [(DOMAB)Pd Cl]$_2$. Remarkably, such a feature reveals that the coupling of different motions is more important in usual liquid crystals than the palladium-mesogenes and that the organometallic rigid core (i.e., the four aromatic rings and the palladium-chlorine bridge) does not rotate. Moreover, for DOMAB, in the nematic phase a rotational diffusion is observed at the high Q-values and the whole molecules rotates freely. In contrast in [(DOMAB)Pd Cl]$_2$ only the aliphatic chains rotate, and the number of rotating C—C bonds increases with temperature. Finally, although DOMAB and [(DOMAB)Pd Cl]$_2$ are calamitic, uniaxial or biaxial, molecules some similarities between our results and those reported for disk-like molecules[10,11] are worth noting. In the discotic phase—as has been proved by experiments carried out on samples with a selectively deuteration on the alkyl chains—the only way to fit the results was to consider a linear distribution of the gyration radii with respect to the distance from the rigid core.

Considering the different roles played by the intermolecular forces on the packing mode our model for the calamitic case comes rather closely to the one for the discotic case. Both models describe the aliphatic chains as a mixture of standing and moving groups by means of an average gyration radius. However a more quantitative comparison between the two models will be possible when selective deuterated samples will be available. Moreover some further improvements to the models of calamitic mesophases can be made by taking into account the calculations of Leadbetter and Richardson[17–19] which show that not all of the protons are equivalent (e.g., the aromatic ones should have a different dynamical behavior than the aliphatic ones) and the suggestion of Janik[20–22] that the aliphatic gyration radii depend on their distances from the aromatic rings (see also the experimental results of References 10 and 11). Other models are also currently developed.[23–24]

Further experiments devoted to study in depth the theoretical implications related to the adopted model are still in progress.

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