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SANS and SAXS studies on the structure of a liquid-crystalline palladium complex

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The neutron and X-ray small angle scattering data obtained from the cyclopalladated 4-dodecyloxy-4-methylazobenzene liquid crystal [(DOMAB)-PdCl]$_2$ are discussed. The results show that this compound forms several different solids whose nature should be related to different intermolecular contributions to the anisotropic intermolecular potential. Moreover in both the nematic and S_A phases, the characteristic lengths are found to be shorter than the theoretical values; in order to understand this peculiar behaviour, different interpretative models are discussed.

1. Introduction

The growing interest in metal containing liquid crystals, which has encouraged both the syntheses of new series of liquid-crystalline transition metal complexes, and the study of their structural and macroscopic properties, has been stimulated by the aim to prepare new stable materials [1–8]. In this context until now we have considered either mononuclear copper (II) Schiff's base coordination compounds or organometallic binuclear palladium 4,4′-disubstituted azobenzene complexes. The former series gives smectic textures [6] whereas the latter exhibits both smectic and nematic mesophases [7, 8]. Nevertheless, with reference to the molecular arrangement, while it is known that the copper containing species are characterized by highly interdigitated molecules [9–12], investigations concerning the palladium complexes have not yet been performed. Accordingly, in order to obtain an insight about this point, we have carried out X-ray and neutron small angle scattering experiments on a palladium mesogen, namely the cyclopalladated 4-dodecyloxy-4′-methylazobenzene (thereafter [(DOMAB)-PdCl]$_2$). Its molecular structure and mesomorphic behaviour are shown in

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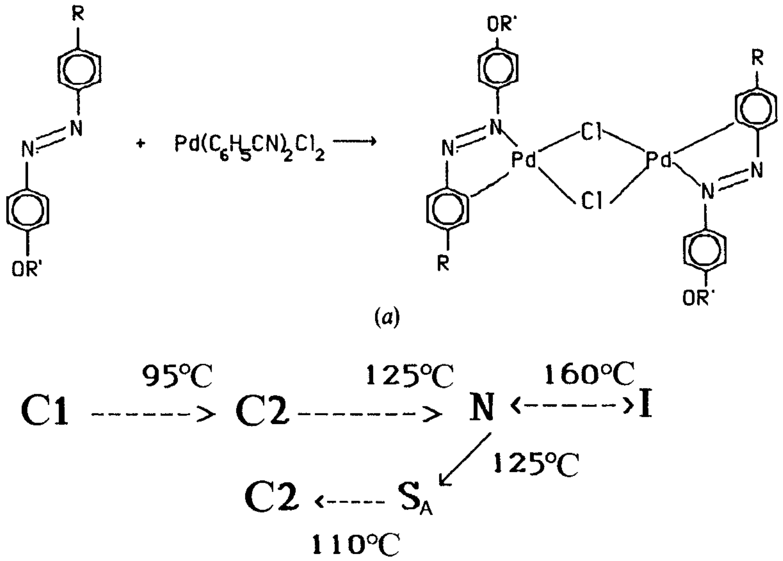


(*a*)

(*b*)

Scheme 1. Cyclopalladated 4-dodecyloxy-4′-methylazobenzene, [(DOMAB)-PdCl]$_2$: molecular structure and transition temperatures. The temperatures indicated came from microscopic observation. The temperatures found in our experiments are slightly different, because of a worse temperature control and the different measurement set-up.

scheme I. The synthesis [7], textural and calorimetric data [8] of a homologous series of thermotropic palladium azobenzene derivatives have been reported recently.

2. Experiments

The X-ray and small angle scattering (SAXS) measurements were carried out at the Laboratoire de Dynamique des Cristaux Moléculaires of Lille using the spectrometer previously described [13]. The incoming X-ray Cu–Kα beam ($\lambda = 1{\cdot}5418$ Å) was selected by the [002] reflection of a pyrolytic graphite monochromator. The scattered photons were detected by a curved linear position sensitive multidetector (INEL-CSP 120), covering 120° symmetrically with respect to the main beam, and equipped with a hollow beam catcher which absorbs the main beam to prevent it hitting the detector centre. The [(DOMAB)-PdCl]$_2$ sample was introduced into a 0·5 mm Lindeman glass capillary tube, 10 mm long, placed vertically on a goniometric head and set at the centre of the detector curvature. The sample was kept at a fixed temperature by a warm gas stream coming from the upper side, the precision of the temperature control was 2°C. Around the sample was placed an electromagnet providing a horizontal magnetic field, perpendicular to the incoming X-ray beam. In some cases the magnetic field, which could reach a magnitude of 0·8 T, was used to characterize the fluid phases. The small angle neutron scattering (SANS) experiments were performed at the spectrometer PAXY at the Orphée reactor in Saclay [14]. The samples were placed in a 1 mm thick, 15 mm diameter quartz cell. The cell was located in an evacuated oven which stabilized the temperature at about 1°C, and between the poles of an electromagnet which provided a 1·4 T horizontal magnetic field, orthogonal to the neutron beam. The scattered neutrons were detected by a 128 × 128 cell multidetector set 1·38 m from the sample. The neutron wavelength was 3·4354 Å.

3. SANS results

Some three dimensional images of the reconstructed neutrons scattered patterns are shown in figures 1, 2 and 3. Figures 1 and 2 are related to the spectra obtained by increasing the temperature. Qualitatively, in the pristine sample at 20°C, we can observe the presence of two different peaks later, this state will be reported as C1 (in the figures 1, 2 and 3, pA and pC indicate the lower and the higher angle peaks, respectively). When the sample is heated until about 96°C, the intensity of the narrowest pA peak increases and becomes higher than pC (figures 1 (*b*), (*c*) and 2 (*a*)), this state will be called C2. At higher temperatures (figure 2(*b*)) a further peak, pB, appears in between pA and pC, and an anisotropic orientational effect is observed. Finally at a still higher temperature (125°C) pB is the only remaining. Remarkably then the sample is very sensitive to the magnetic field (figure 2 (*c*)): the mesophase is a cybotatic nematic phase, exhibiting S_A-type short range correlations.

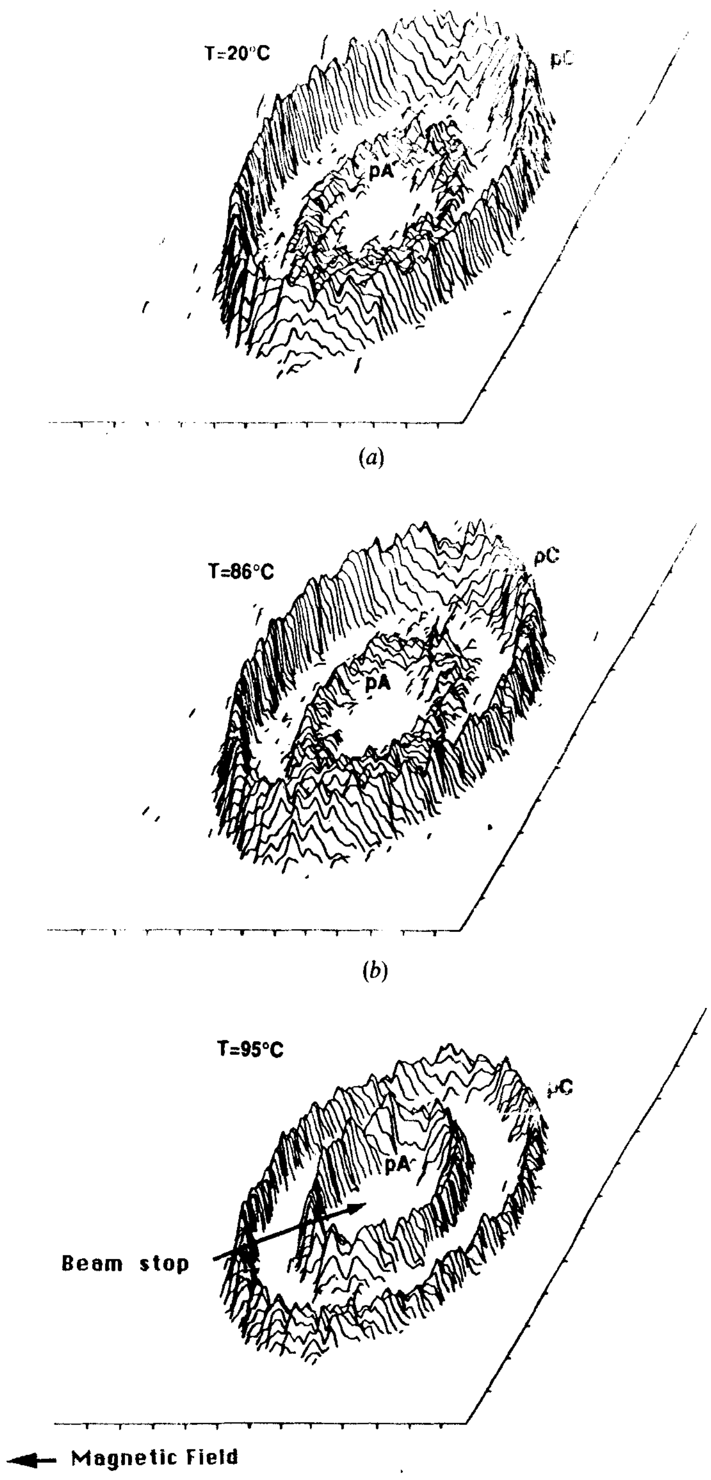
Figure 3 shows the spectra obtained by lowering the temperature from 108°C to 98°C. Figure 3 (*a*) (108°C) shows the same aligned nematic phase, as shown in figure 2 (*c*). A further oriented phase appears at about 100°C (figure 3 (*b*)). Noteworthy is the fact that the pA position is preserved, its width perpendicular to and along the magnetic field, decreases. Therefore, such a phase is different from the previous nematic. Moreover the presence and the character of this monotropic phases depends on the cooling rate. Thus, after several thermal cycles, differing by the cooling rate, this phase can either disappear or give rise, even at room temperature, to a glassy nematic or a S_A-like phase. In contrast, when the sample is cooled slowly, only the structure with $pA \gg pC$ (C2) can be reached and no transitions, nor the initial pristine structure are observed.

4. SAXS results

Some selected X-ray diffraction patterns are shown in figures 4, 5 and 6. Qualitatively these data parallel those found by neutron scattering while the transition temperatures are somewhat higher. At low temperatures two main peaks, pA and pC, are present; the most intense is pC. As previously described on heating the sample their intensity reverses until pA becomes one order of magnitude more intense than pC. At high temperatures a peak pB appears between the two former peaks: pB remains the only one in the smectic and nematic phases. Moreover since this experiment allows measurements at larger scattering angle, several additional peaks, pD, pE, pF (figures 4 and 5) were detected. These additional peaks are usually less intense than pA, pC and in the initial solid C_1 (figure 4 (*a*)) are rather broad; when the temperature increases, pF and pE become progressively narrow and their intensities comparable to that of pC.

5. Data analysis

To obtain quantitative information from these spectra, the data were processed as follows. The relevant parts of the *XY* neutron spectra were fitted by one or two dimensional gaussian or lorentzian functions. The small angle peaks of the X-ray spectra were fitted by ordinary gaussian or lorentzian functions. Thereafter the nature, position, width and relative intensity of the peaks were calculated. In figure 7, the positions of the diffraction peaks from the SANS experiment are reported versus the



(*a*)

(*b*)

(*c*)

Figure 1. Three dimensional diffraction patterns from the solid sample on increasing the temperature: (*a*) C1 at room temperature; (*b*) C2 at 86°C; (*c*) C2 at 95°C.

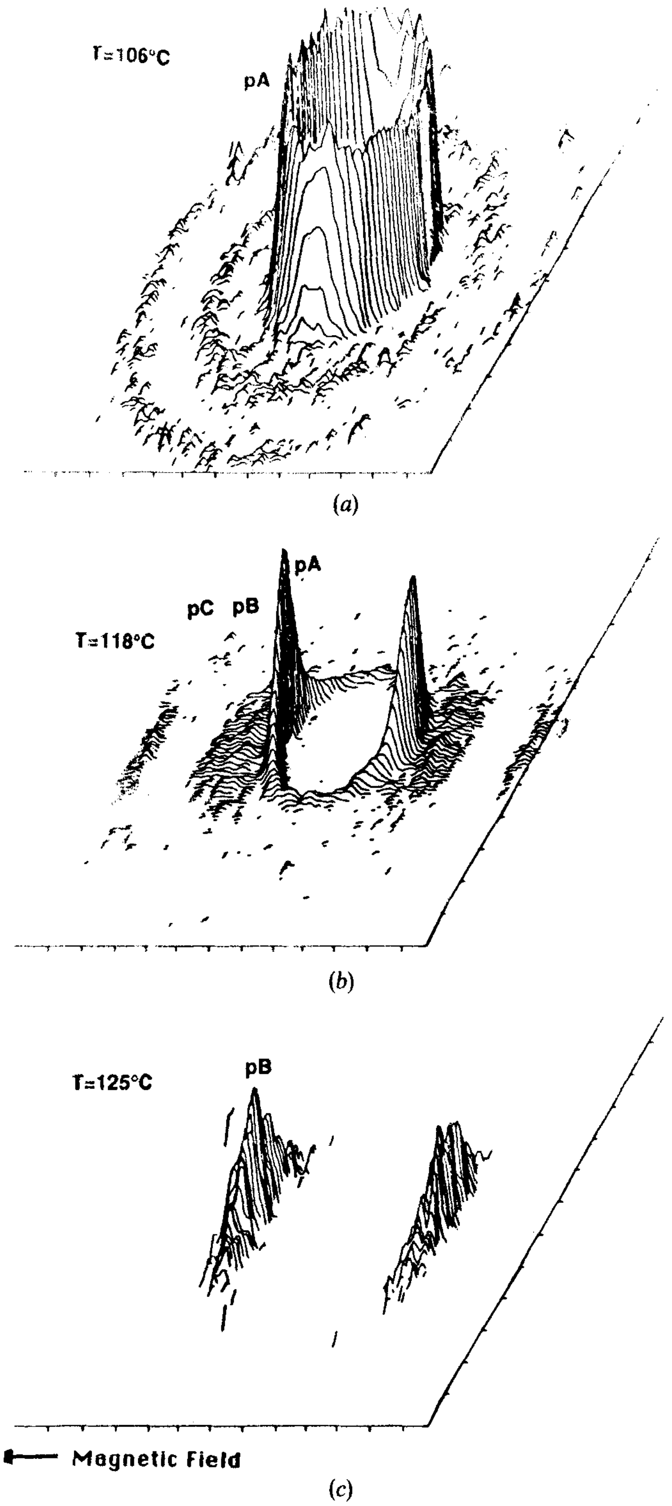


Figure 2. Three dimensional patterns increasing the temperature: (*a*) C2 at 106°C; (*b*) smectic A at 118°C; (*c*) nematic at 125°C.

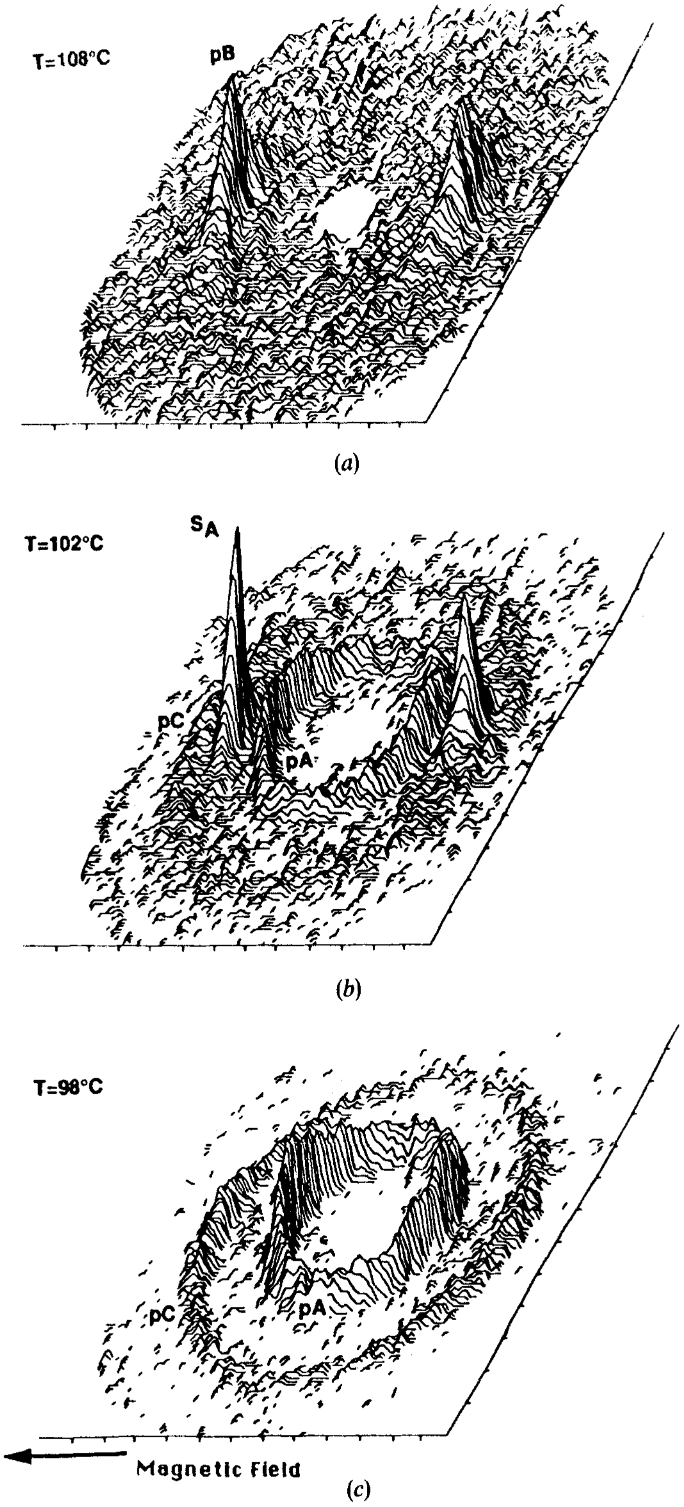


Figure 3. Three dimensional patterns found on decreasing the temperature: (*a*) nematic at 108°C; (*b*) smectic A at 102°C; (*c*) C2 at 98°C.

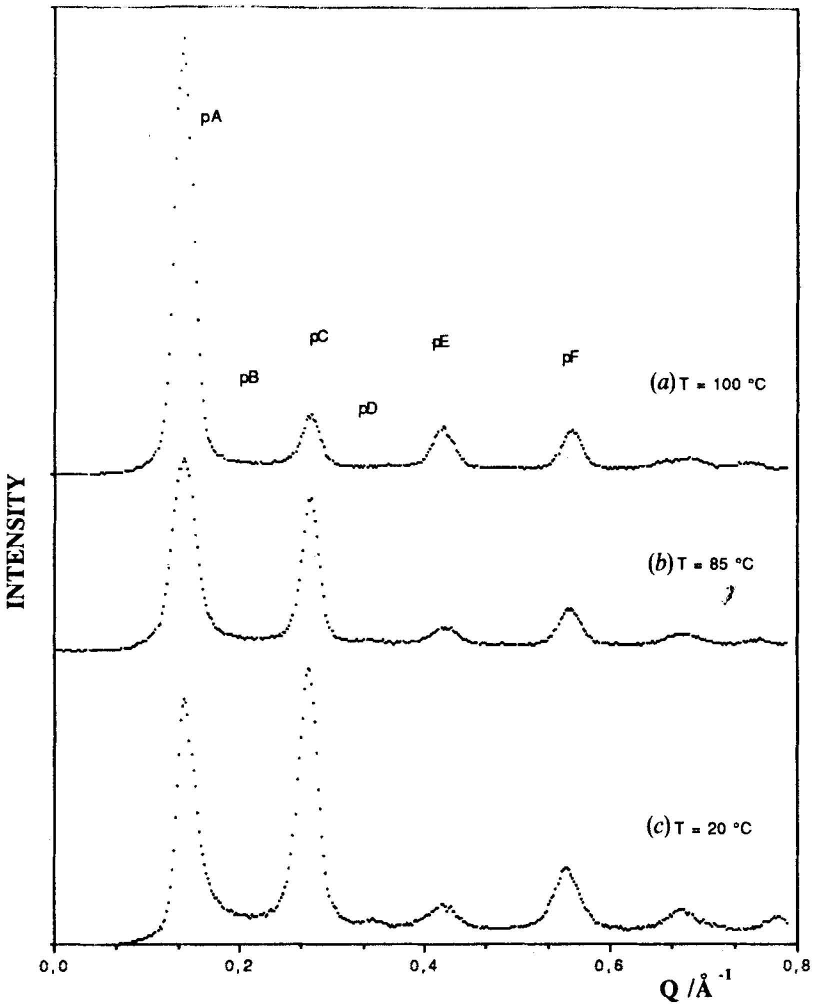


Figure 4. X-ray spectra observed at different increasing temperatures: (*a*) solid C1, room temperatures; (*b*) solid C1, 85°C; (*c*) solid C2, 100°C.

temperatures, heating the sample (figure 7 (*a*)) and cooling quickly (figure 7 (*b*)). When the shape appeared to be gaussian and at its narrowest ($\approx 0{\cdot}0077$ Å^{-1} for peak pE at about 145°C) the spectrometer resolution was considered to have been reached; these instrumental widths (in order to appreciate the peaks intrinsic widths) are shown in figure 8. The intensities are shown in figure 9. A look at figures 6 to 9 shows at least four regimes.

(*a*) At room temperature (20°C) the background is large and most of the peaks rather broad.

(*b*) At higher temperatures, up to about 100°C most of the peaks narrower and narrower: pD can be seen in most spectra.

(*c*) A dramatic change occurs at 100°C: the intensity of pA overcomes that of pC by one order of magnitude and pE narrows sharply. pD remains visible until 120°C. Other changes are apparent at $Q \approx 0{\cdot}7$ Å^{-1} where a broad low

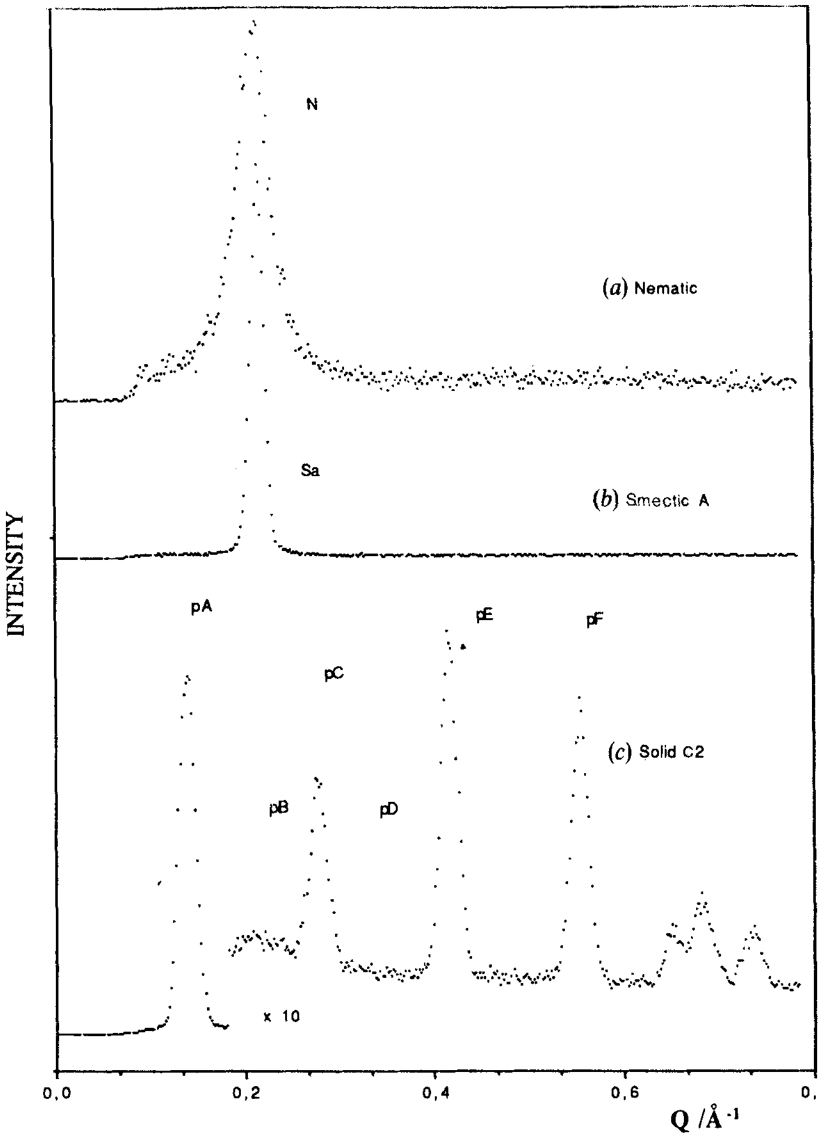


Figure 5. X-ray spectra found at different decreasing temperatures: (*a*) nematic phase at 150°C; (*b*) smectic phase at 120°C; (*c*) solid C2.

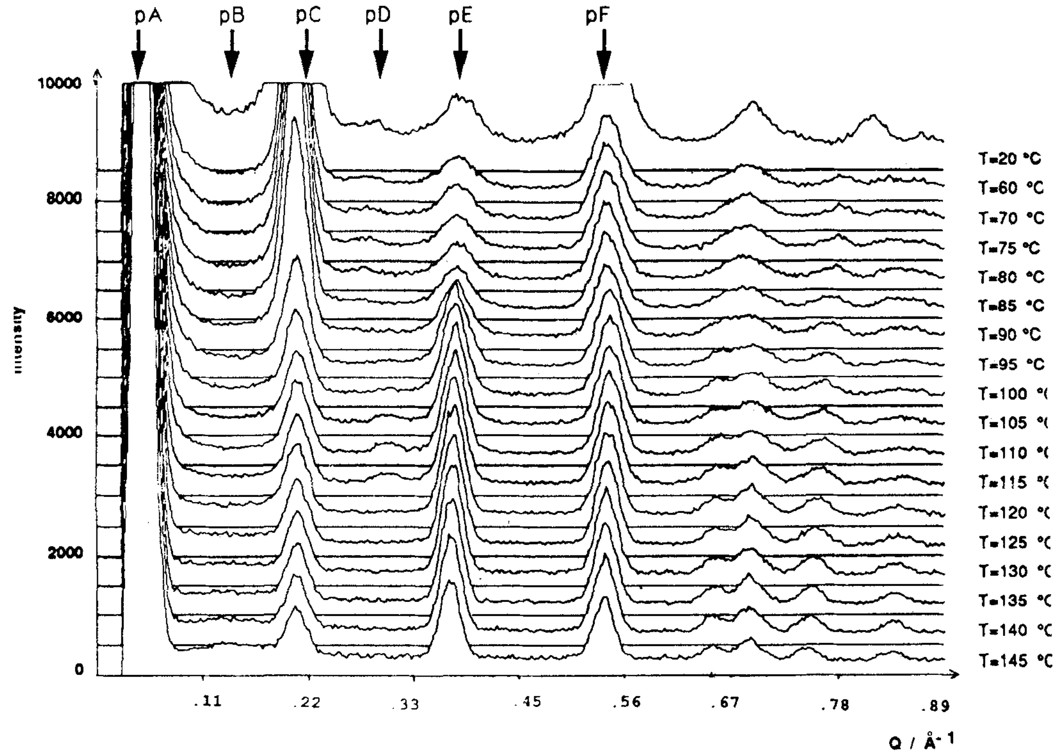


Figure 6. The intensity of some of the diffraction peaks versus temperature in the X-ray experiments.

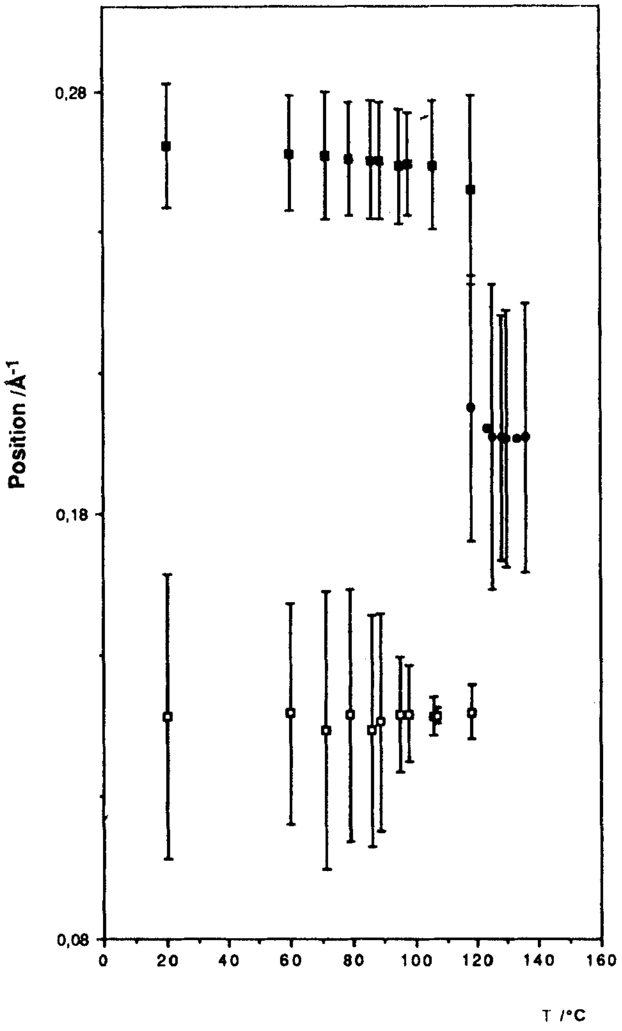
temperature peak divides in two, and at $Q \approx 1{\cdot}6\,\text{Å}^{-1}$ where two peaks well apart at low temperature merge into a single one.

(*d*) At the highest temperatures, above 120°C, the peak pD is always lacking, while pB is seen more and more clearly.

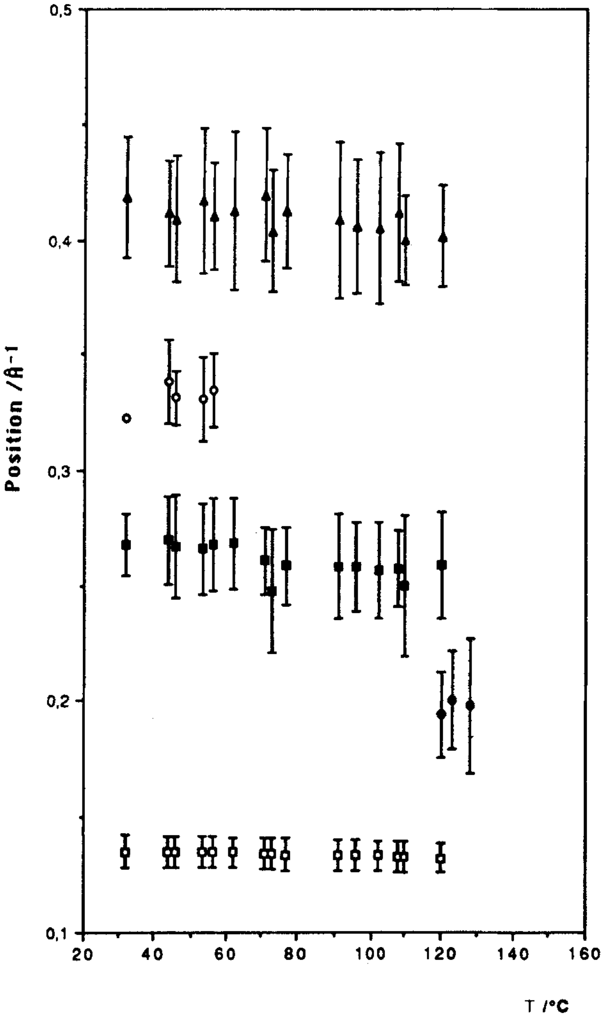
Data fitted for the temperatures 20, 80, 140°C are shown in the table. After melting ($T = 150$°C), the mesophases show only one main diffraction peak, with a characteristic length of 30 Å.

6. Discussion

The four peaks pA, pC, pE and pF can be seen in all of the crystalline phases. Their positions are commensurate and correspond to a distance of about 46 Å. They are the signature of a strongly layered organization of the solid, which remains through the temperature changes. Nevertheless the strong intensity and width modifications of these peaks indicate strong molecular reorganization. The low temperature solid (C1) must be considered as a paracrystal, as most of the peaks show a short correlation length, the temperature increase produces an annealing which increases the correlation length, mostly of the pC peak. The fact that this second order peak is better ordered than the first order pA may mean that the single layer organization with a 46 Å distance is far from being achieved, a half distance, being more visible. When the temperature increases a true phase transition occurs at about 100°C where the formation of 46 Å layers is accompanied by modifications inside the layers. The pD peak is probably a Bragg peak relevant to a direction different from the normal to the layers: its



(*a*)



(*b*)

Figure 7. Position of the diffraction peaks versus temperature (X-ray experiments). The lines are guides for eye: (*a*) increasing temperature. (□) pA; (●) pB; (■) pC. (*b*) decreasing temperature. (□) pA; (●) pB; (■) pC; (○) pD; (▲) pE.

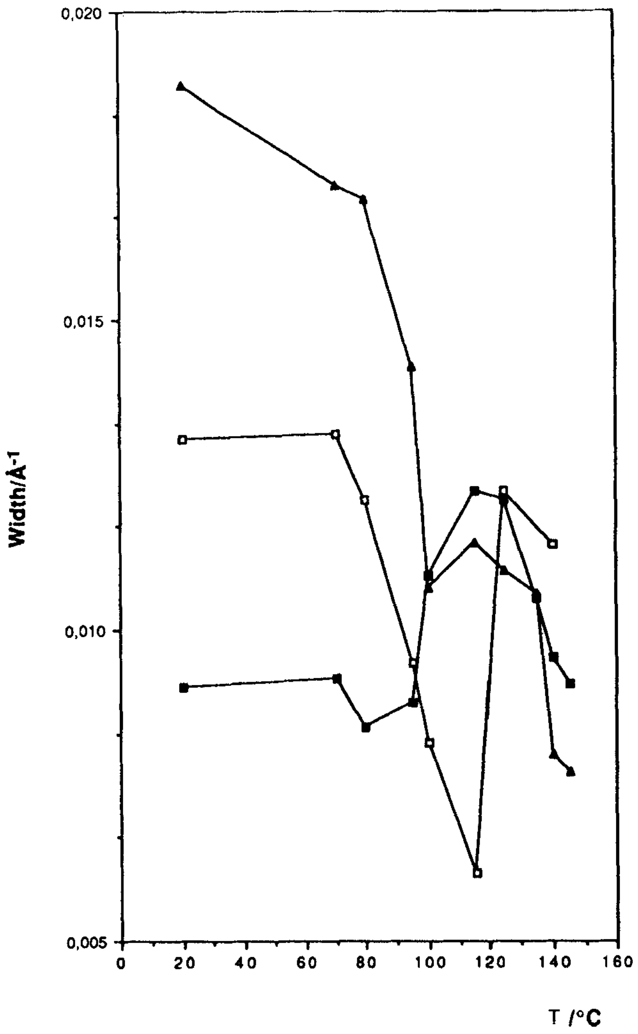


Figure 8. The experimental behaviour of the widths of some peaks versus temperature (X-ray experiments). (□) pA; (■) pC; (▲) pE.

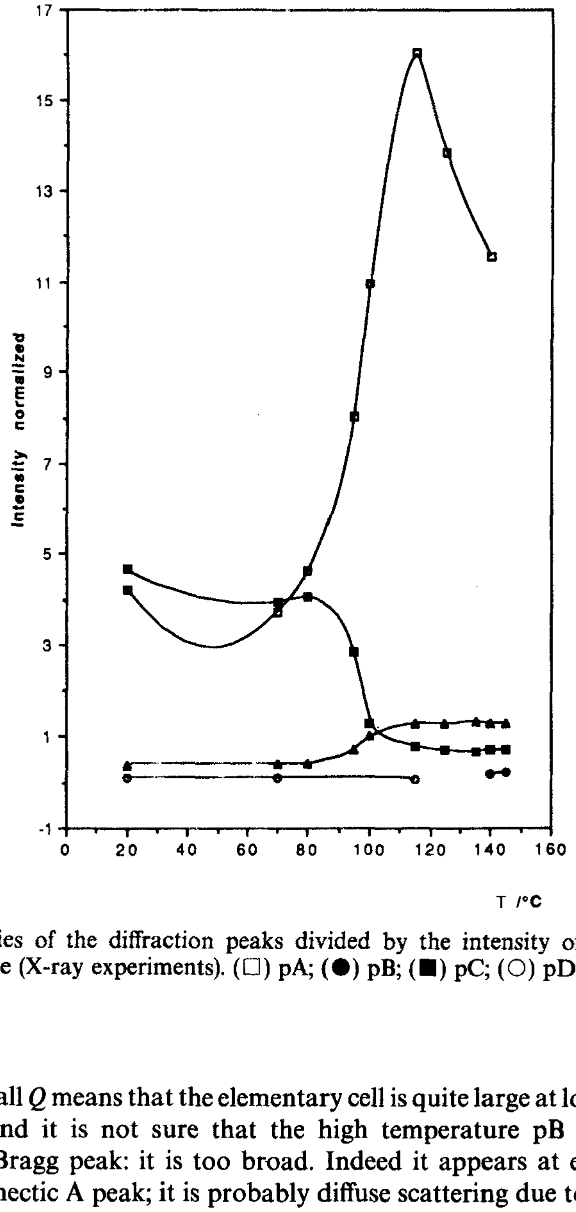


Figure 9. Intensities of the diffraction peaks divided by the intensity of peak pF versus temperature (X-ray experiments). (□) pA; (●) pB; (■) pC; (○) pD; (▲) pE.

appearance at small Q means that the elementary cell is quite large at low temperatures. On the other hand it is not sure that the high temperature pB peak should be considered as a Bragg peak: it is too broad. Indeed it appears at exactly the same position as the smectic A peak; it is probably diffuse scattering due to pretransitional smectic-like fluctuations of the molecules. At this stage of the investigation we do not think that we can simply apply the same model of molecular interdigitation as for the Cu complexes [9–11] to explain the apparent shortening of the molecules in the mesophases for two reasons. First because it seems to us that the larger width of the molecules makes for unsuccessful close packing and secondly because the apparent shortening is present only in the mesophases and another packing is present in the solids.

7. Conclusions

The phase structures of the liquid-crystalline palladium complex, $[(\mathrm{DOMAB})\text{-}\mathrm{PdCl}]_2$, have been investigated by neutron and X-ray small angle scattering. These

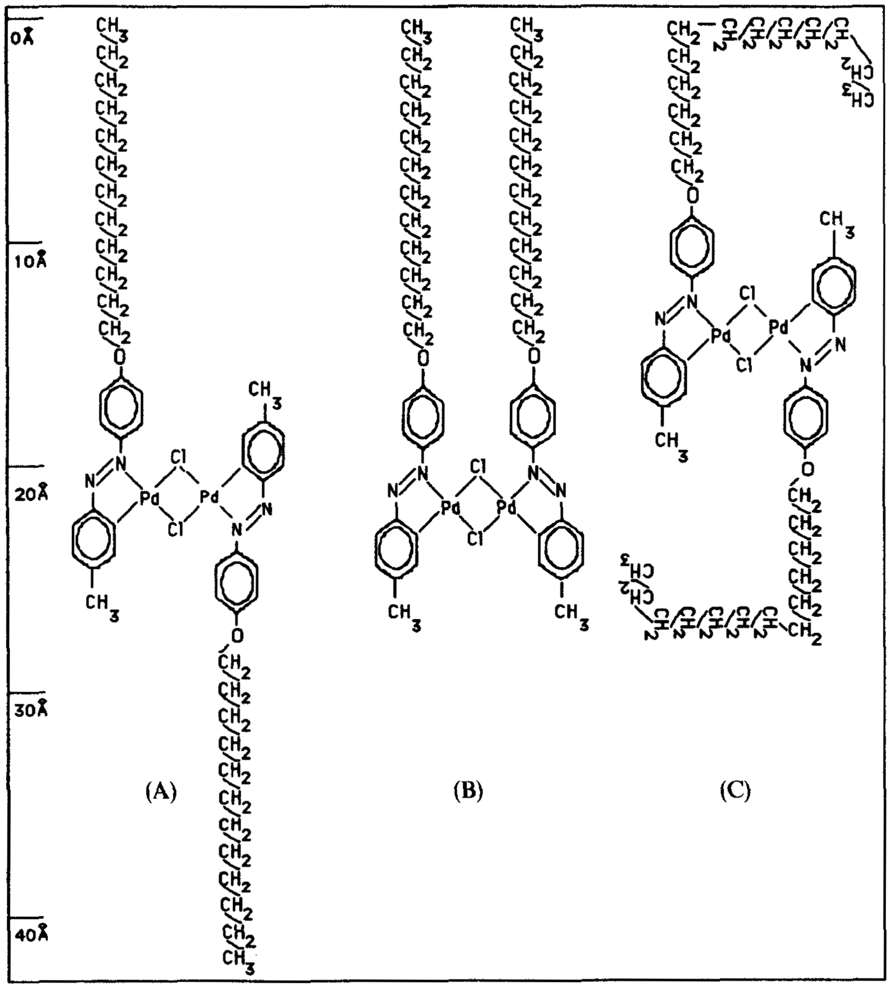
Typical values of the position and the width of the diffraction peaks from the X-ray pattern. We also report the calculated values for the correlation length obtained after the correction of the peak width for the instrumental resolution

$T=20°$C X-ray	Intensity	Position/Å^{-1}	Position/Å	HWHM/Å^{-1}	Correlation length/Å
pA	9317	0·13656	46	0·01306	149
pB	—	—	—	—	—
pC	10060	0·26464	24	0·00909	327
pE	840	0·40594	16	0·01879	92
pF	2162	0·53810	12	0·01533	119
$T=80°$C X-ray					
pA	6470	0·13333	47	0·01208	169
pB	—	—	—	—	—
pC	5700	0·26323	24	0·00845	454
pE	733	0·40281	16	0·01695	105
pF	1771	0·53397	12	0·01358	141
$T=140°$ X-ray					
pA	16391	0·13120	48	0·01136	190
pB	241	0·19645	32	0·03677	44
pC	988	0·26371	24	0·00955	279
pE	1818	0·39757	16	0·00799	732
pF	1416	0·53097	12	0·00830	508

results show that there are two different solid forms, a nematic phase and a monotropic smectic A phase. Moreover, the solids appear to possess a relatively complex intermolecular correlation. The structure, albeit not yet completely clear, is surely positionally three dimensional for the pristine solid and in the high temperature mesophase (the nematic) we observe peaks at $Q=0{\cdot}65\,\text{Å}^{-1}$ and $Q=0{\cdot}75\,\text{Å}^{-1}$. These correspond to typical distances of the order of 8–9 Å, roughly corresponding to a molecular width. This feature probably indicates a loss of positional ordering and an increase of orientational ordering due to the biaxial nature of the molecules. In our opinion the final (high temperature) solid should take into account both properties (decrease of positional order and increase of a biaxial orientational order). This indicates that probably some part of the anisotropic interaction potential is averaged to zero as, increasing the temperature, the positional disorder is enhanced but some parts not. The understanding of the different correlation lengths and directions of the ordering in the two solids, requires high resolution observation of the diffraction peak shapes, for instance with a cold neutron diffractometer. The apparent strong shortening of the molecule at the solid–mesophase transition can be attributed to four different reasons.

(*a*) The growing of a competitive ordering in a direction different to that existing in the unheated solid.

(*b*) A thermal trans to cis transition (scheme 2(B)).



Scheme 2. Sketch of possible $[(DOMAB):PdCl]_2$ structures: (A) Trans; (B) Cis; (C) Chain-melts.

(*c*) A nearly total chain fusion which fills more efficiently the empty space present in the molecules (scheme 2 (C)).

(*d*) A molecular interdigitation.

New experiments designed to elucidate these points are in progress, however at present the chain-melt molecular array (scheme 2 (C)) is suggested.

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