Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Textural and calorimetric investigations on a homologous series of mesogenic azocompounds complexed with palladium(II)

C. C. Versace[ab]; R. Bartolino[bc]; M. Ghedini[d]; F. Neve[d]; S. Armentano[d]; M. Petrov[e]; N. Kirov[e]
[a] Dipartimento di Fisica, Università della Calabria, Cosenza, Italy [b] GNSM (CNR)-CISM (MPI)-INFM unità di Cosenza, [c] Istituto di Biochimica-Fisica e Patologia Molecolare e Cellulare Facolta di Medicina Università di Reggio Calabria, Catanzaro, Italy [d] Dipartimento di Chimica, Università della Calabria, Cosenza, Italy [e] Solid State Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria

To cite this Article Versace, C. C. , Bartolino, R. , Ghedini, M. , Neve, F. , Armentano, S. , Petrov, M. and Kirov, N.(1990) 'Textural and calorimetric investigations on a homologous series of mesogenic azocompounds complexed with palladium(II)', Liquid Crystals, 8: 4, 481 — 497

To link to this Article: DOI: 10.1080/02678299008047364

URL: http://dx.doi.org/10.1080/02678299008047364

LIQUID CRYSTALS, 1990, VOL. 8, NO. 4, 481–497

Textural and calorimetric investigations on a homologous series of mesogenic azocompounds complexed with palladium(II)

by C. C. VERSACE‡§, R. BARTOLINO¶§, M. GHEDINI†, F. NEVE†,
S. ARMENTANO†, M. PETROV|| and N. KIROV||

† Dipartimento di Chimica, Università della Calabria, Arcavacata di Rende,
87036 Cosenza, Italy
‡ Dipartimento di Fisica, Università della Calabria, Arcavacata di Rende,
87036 Cosenza, Italy
§ GNSM (CNR)—CISM (MPI)—INFM unità di Cosenza
|| Solid State Institute, Bulgarian Academy of Sciences Boulevard Lenin,
Sofia, Bulgaria
¶ Istituto di Biochimica-Fisica e Patologia Molecolare e Cellulare Facolta
di Medicina Università di Reggio Calabria, v.T. Campanella, Catanzaro,
Italy

(*Received 20 June 1989; accepted 23 March 1990*)

A comparative study of some mesogenic azobenzene compounds and their organometallic palladium(II) derivatives is reported. On the basis of the textural properties, calorimetric data and uniaxial order parameters (as deduced approximately from infrared spectroscopy), the main features induced by palladium complexation are (i) the transition temperatures increase, (ii) the number of ordered mesophases increases, (iii) the nematic uniaxial order parameter decreases, (iv) the textures are typical of highly ordered phases, and (v) an optical biaxiality appears in the nematic phase. The calorimetric data as well as the order parameters, if discussed in terms of molecular biaxiality result are interpreted at least qualitatively. Optical investigations show that macroscopical biaxial ordering can be achieved.

1. Introduction

In order to obtain new liquid-crystalline materials, we are currently concerned with the synthesis of transition metal complexes with mesomorphic properties [1–6]. In this paper we report a comparative study, carried out by calorimetric, optical and spectroscopic techniques, on two related series of compounds, namely the free ligands and their organometallic derivatives respectively. The ligands are alkyl-alkoxy azobenzenes whose general formula is depicted in figure 1 (*a*), while their organometallic liquid crystals derivatives are the products resulting from their reaction with $(PhCN)_2PdCl_2$. Remarkably, when the reacted ligand mesogens are the $n = 1$ and $m = 1, 2, 12$ or $n = 2$ and $m = 12$ members, their cyclopalladated complexes are 1 : 1 mixtures of the species having the general formula shown in figure 1 (*b*), or (*c*), while the alkyl-azoxy azobenzene with $n = 1$ and $m = 7$ only gives the complex with the molecular formula sketched in figure 1 (*b*) [7]. Thus, as far as the organometallic series is concerned, the materials investigated when $n = 1$ and $m = 1, 2, 12$ or $n = 2$ and $m = 12$, are actually isomeric mixtures.

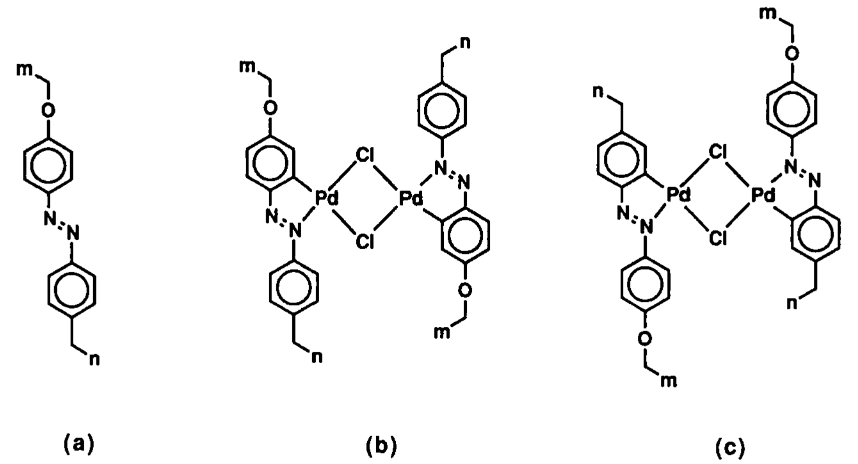


Figure 1. Formulas of: (*a*) the mesogenic ligands and (*b*) and (*c*) the isomeric organometallic derivatives.

2. Experimental results

2.1. *Phase diagrams and phase transitions*

The transition temperatures were determined by textural observations performed with a polarizing microscope (Leitz Orthoplan) the phase identification was confirmed also from miscibility [1] studies using terephthalylidene-bis(4-*n*-butylaniline) (TBBA) [8, 9] as a reference.

The thermal behaviour of the materials in both the ligand and organometallic series are summarized in table 1. The ligands, except for the compound with the shortest alkyl chains ($n = m = 1$) are mesogenic described previously [10], the mesomorphic behaviour displayed by the organometallic series which includes also the $n = m = 1$ member is therefore particularly noteworthy. Furthermore, comparing the data reported in table 1 it should be noted, as a general trend, that the transition temperatures for the organometallic complexes are significantly higher than those of the parent ligand, and for each series, that they decrease as the number of the aliphatic carbons increases (see figure 2). The clearing points, T_I, of the organometallic species, are constantly found at higher temperature with respect to the corresponding ligands. Moreover the effect of lengthening the chains is more enhanced for the organometallic complexes. In fact the difference ($\Delta T_I = T_I$ (organometallic) $- T_I$ (ligand)) decreases with of the alkyl chain length (see figure 3) showing that probably the entropic effect of the chains tends to be most important for longer chains [11, 12]. In particular, along the same series, the effect exerted by the chain length on the lowering of T_{NI} can be tentatively evaluated by showing the clearing temperatures T_I (expressed as T_I^*, which are scaled by normalizing T_I to the nematic–isotropic temperature of the shortest member of each series) versus the total length of the chains ($n + m$). Interestingly, the plot which results (see figure 4) shows that increasing ($n + m$) produces a lowering of T_I which is greater for the organometallic series than for the ligands (i.e. the slope of the curves obtained for the transition temperatures versus the total length of the aliphatic chains show that the ligand curve is smoother than for the organometallic. One of our objectives with the present investigation is the preparation of new materials suitable for practical applications and so particular attention has been paid to the properties of the nematic phase. Thus,

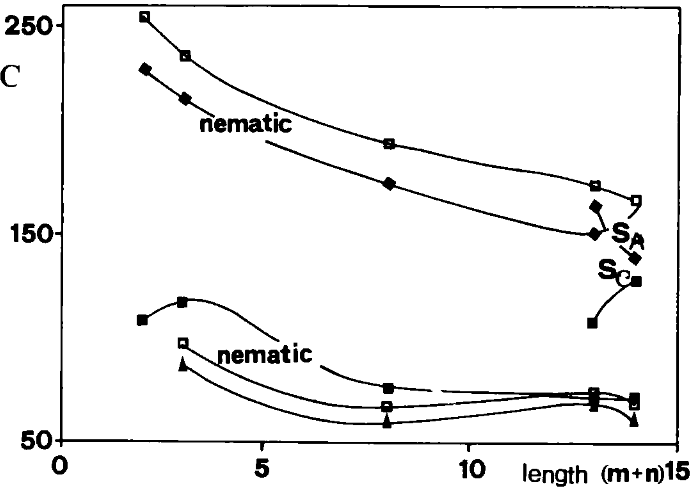


Figure 2. Transition temperatures versus the chain length $n + m$: the upper data are for the organometallic complexes and the lower for the ligands

Table 1. Thermal behaviour of the mesogenic ligands and organometallic series.

Carbons in the alkyl chains			
n	m	Mesogenic ligands	Organometallic complexes
1	1	$$\begin{tikzcd} C \arrow[rr, dash, "108^{\circ}C"] & & I \end{tikzcd}$$	$$\begin{tikzcd} C \arrow[r, dash, "229^{\circ}C"] & N \arrow[r, dash, "254^{\circ}C"] & I \end{tikzcd}$$
1	2	$$\begin{tikzcd} C \arrow[rr, dash, "117^{\circ}C"] \arrow[dr, dash, "87^{\circ}C"'] & & I \\ & N \arrow[ur, dash, "97^{\circ}C"'] & \end{tikzcd}$$	$$\begin{tikzcd} C \arrow[r, dash, "214^{\circ}C"] & N \arrow[r, dash, "235^{\circ}C"] & I \end{tikzcd}$$
1	7	$$\begin{tikzcd} C \arrow[rr, dash, "77^{\circ}C"] \arrow[dr, dash, "59{\cdot}3^{\circ}C"'] & & I \\ & N \arrow[ur, dash, "67{\cdot}5^{\circ}C"'] & \end{tikzcd}$$	$$\begin{tikzcd} C \arrow[r, dash, "175^{\circ}C"] & N \arrow[r, dash, "194^{\circ}C"] & I \end{tikzcd}$$
1	12	$$\begin{tikzcd} C \arrow[r, dash, "75{\cdot}5^{\circ}C"] \arrow[dr, dash, "69{\cdot}8^{\circ}C"'] & N \arrow[r, dash, "76{\cdot}1^{\circ}C"] & I \\ & N \arrow[ur, dash, "75{\cdot}2^{\circ}C"'] & \end{tikzcd}$$	$$\begin{tikzcd} C \arrow[rr, dash, "150{\cdot}4^{\circ}C"] \arrow[dr, dash, "108^{\circ}C"'] & & N \arrow[rr, dash, "174^{\circ}C"] & & I \\ & S_C \arrow[dr, dash, "141^{\circ}C"'] & & N \arrow[ur, dash, "174^{\circ}C"'] & \\ & & S_A \arrow[ur, dash, "165^{\circ}C"'] & & \end{tikzcd}$$
2	12	$$\begin{tikzcd} C \arrow[rr, dash, "70{\cdot}7^{\circ}C"] \arrow[dr, dash, "62{\cdot}1^{\circ}C"'] & & I \\ & S_A \arrow[dr, dash, "66{\cdot}8^{\circ}C"'] & \\ & & N \arrow[uu, dash, "69{\cdot}7^{\circ}C"'] \end{tikzcd}$$	$$\begin{tikzcd} C \arrow[rr, dash, "162{\cdot}5^{\circ}C"] \arrow[dr, dash, "129{\cdot}3^{\circ}C"'] & & N \arrow[rr, dash, "169{\cdot}1^{\circ}C"] & & I \\ & S_A \arrow[drr, dash, "140^{\circ}C"'] & & & \\ & & & N \arrow[uur, dash, "166{\cdot}9^{\circ}C"'] & \end{tikzcd}$$

it should be pointed out that the mesogenic ligands in table 1, namely $n = 1$ and $m = 2, 7$ or $n = 2$ and $m = 12$ display a monotropic nematic phase while all the organometallic complexes, $n = 1$ and $m = 1$ included, display such a phase upon heating.

The extent of the nematic ΔT_N ($\Delta T_N = T_{NI} - T_{NX}$, where T_{NI} is the clearing point of each compound and T_{NX} is the temperature at which the nematic phase appears)

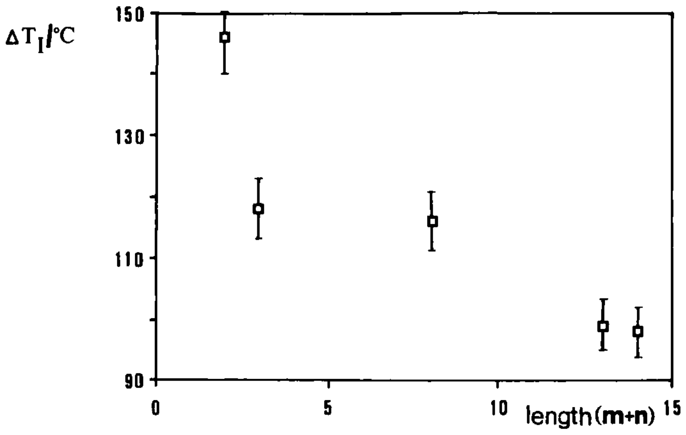


Figure 3. The difference between the clearing temperatures ΔT_I ($\Delta T_I = T_I$ (organometallic) $- T_I$ (ligand) versus the aliphatic chains length, expressed as the total number of carbon atoms ($n + m$).

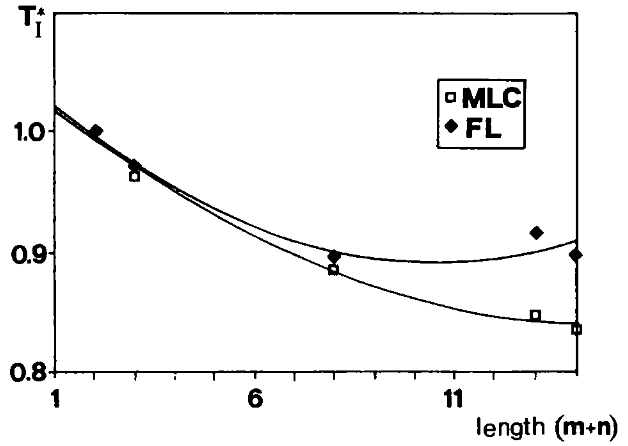


Figure 4. Clearing temperatures, reported as the scaled variable T_I^*, by normalizing T_I to the clearing temperature of the shortest member of each series versus the chains length ($n + m$); □ organometallic and ◆ ligand.

of both the ligands and the organometallic series are reported in figure 5 (*a*). Note that ΔT_N decreases with the length of the aliphatic chains, morever, the organometallic compounds exhibit a wider nematic range with respect to the corresponding length ($n + m$) of the ligand species (ΔT_N (organometallic) > ΔT_N (ligand)), and the difference ΔT_N (organometallic) $- \Delta T_N$ (ligand) decreases when the chain length ($n + m$) is increased, (see figure 5 (*b*)) thus indicating that for longer and longer chains the effect of the organic moiety prevails.

Finally, it should be pointed out that some of the organometallic compounds, with respect to the mesogenic ligands, display a richer mesomorphism (see e.g. $n = 1$ and $m = 12$ or $n = 2$ and $m = 12$ in table 1). The additional mesophases, which have a lower symmetry (S_A and/or S_C), are detected only in the members having the longer aliphatic chains, so paralleling the trend usually observed in a homologous series of organic liquid crystals.

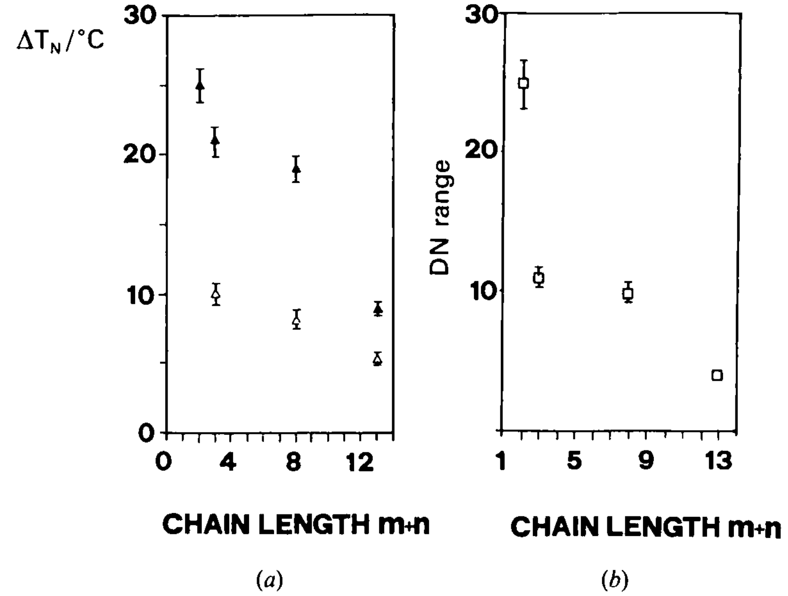


Figure 5. (*a*) Nematic range ΔT_N where $\Delta T_N = T_{NI} - T_{NX}$, where T_{NI} is the clearing point of the compound and T_{NX} is the temperature at which the nematic phase appears) versus the chain length ($n + m$); ◇ ligand and ◆ organometallic. (*b*) Differences between the width of the nematic ranges, ΔN versus the chain length $n + m$ ($\Delta N = \Delta T_N$ (organometallic) $- \Delta T_N$ (ligand)).

2.2. *Calorimetric data*

The calorimetric data for both the ligand and the organometallic series determined by an automatic Perkin–Elmer differential scanning calorimeter are reported in table 2. These data, for the solid–nematic CN, solid–isotropic CI, and nematic–isotropic NI phase transitions, show that both the CI and the CN transitions are always first order, as is well known. The NI phase transitions are also first order but with specific heats of about one order of magnitude smaller than the heats of the CN transitions. It is noteworthy, that the CN phase transition for the $n = 1$ and $m = 12$ organometallic compound has a small latent heat (four times smaller than the others), and, for the same compound, the NI specific heat is significantly low. Therefore it should be pointed out that such a value is comparable with that found for the NS_A transition which is usually considered second order when the nematic range is large and first order, or at the least partially first order when that range is narrow [13]. Finally, regarding the alkyl chains, it appears, as a general trend that (i) the two series behave similarly, (ii) the latent heat for the transitions in the organometallic series are smaller than for the ligands, and (iii) the difference between the latent heats of the two series, ΔH, increases when the chain length increases (see figure 6).

2.3. *Infrared spectroscopy and the major order parameter*

To see if the reduction of the symmetry of the mesophases reflects an increased order, we performed, in the nematic phase of the compound with $m = 1$ and $n = 12$, some approximate measurements of the major order parameter $\bar{P}_2$. The major order parameter is defined by

$$\bar{P}_2 = (3\overline{\cos^2\beta} - 1)/2$$

Table 2. Calorimetric data for the ligand and organometallic series.

Number of carbons in the alkyl chains		Ligands ΔH					Organometallic ΔH				
m	*n*	CI	C–N	N–I I–N	N–C	†N–S_A/ ‡S_A–C	C–N	N–I	N–S_A	S_A–S_C	§S_C–C ‖S_A–C
1	1	105·5	No	No	No	No	75·5	5·71	No	No	No
1	2	90·3	No	4·7¶	81·5	No	79·8	5·11	No	No	No
1	7	104·1	No	8·77¶	90·2	No	89·8	6·18	No	No	No
1	12	—		4·78	65·5	No	25·4	1·1	1·2¶	13·5¶	§11·9¶
2	12	91·3	—	4·81¶	No	†45·3¶ ‡39·7	95·4	4·13		No	‖49·3¶

¶ Monotropic phases.

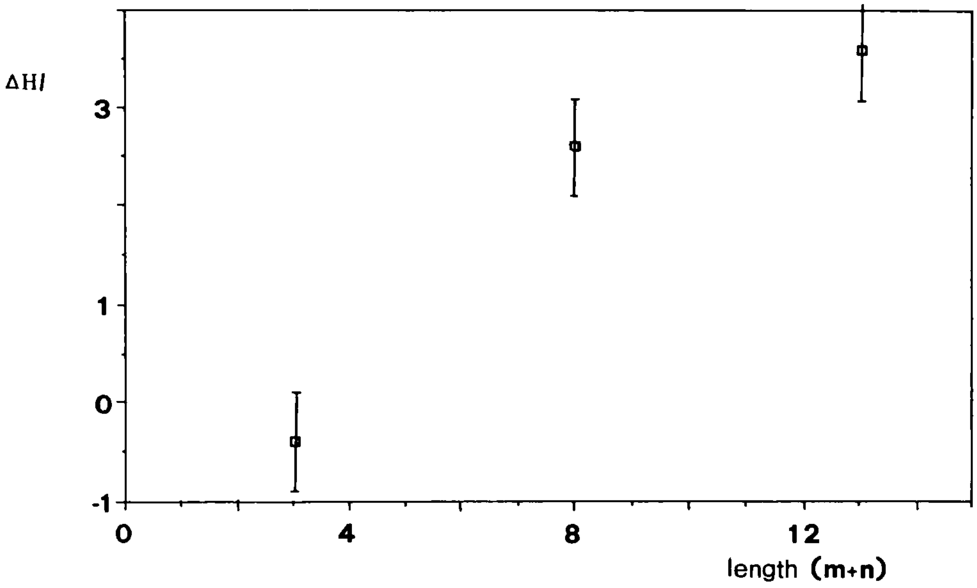


Figure 6. Differences between the latent heats at the nematic–isotropic phase transition $\Delta H = \Delta H_{\mathrm{NI}}$ (organometallic) $- \Delta H_{\mathrm{NI}}$ (ligand), versus the chain length $n + m$.

where β is the angle between the director and the long axes of the molecule can be determined from any physical quantity related to anistropic properties, i.e. dielectric constant, magnetic susceptibility or infrared dicroism (the ratio of the absorption coefficients of linear polarized infrared light measured along orthogonal directions: the reference axis is in this case the director). In the latter case the assignment of the frequencies to molecular modes is made according to the approximate symmetry of the molecule, namely modes pertaining to vibrations parallel and perpendicular to the molecular axis, and not present in the isotropic phase, can be found [14]. In particular the determination of the orientational order parameter by IR spectra for azo, azoxy and Schiff's base derivatives and their mesomorphic materials is not a very difficult task since most of the stretching vibrations and in-plane deformations of the aromatic part are well polarized along the long molecular axis (i.e. the major axis of alignment). Therefore the determinating $\bar{P}_2$ has been achieved by the infrared technique, operating with a standard IR-Jasco spectrophotometer.

For the free ligands we have chosen three well characterized vibration bands [15], i.e. 1598 cm^{-1}, 1512 cm^{-1} (assigned to the benzene ring stretching) and 1170 cm^{-1} (assigned to the in-plane deformation of the aromatic part). All of these lines are strongly longitudinally polarized and the calculation of $\bar{P}_2$ is easy. Although the frequencies of these bands change slightly in the spectra of the organometallic compounds their origin appears to us not to be alterated at all and therefore the same can be used also to determine $\bar{P}_2$ of the organometallic species: in fact it has been shown that the coupling of these stretching bonds with other molecular vibrations is very small, e.g. less than 10 per cent.

For more details on the vibrational potential energy distribution and on the assignment of such vibrations, as well as their general application to investigations of orientational order parameters the reader is referred to [14–16]. In figure 7, in order to compare the $\bar{P}_2$ data for the ligands and organometallic complexes, we report $\bar{P}_2$

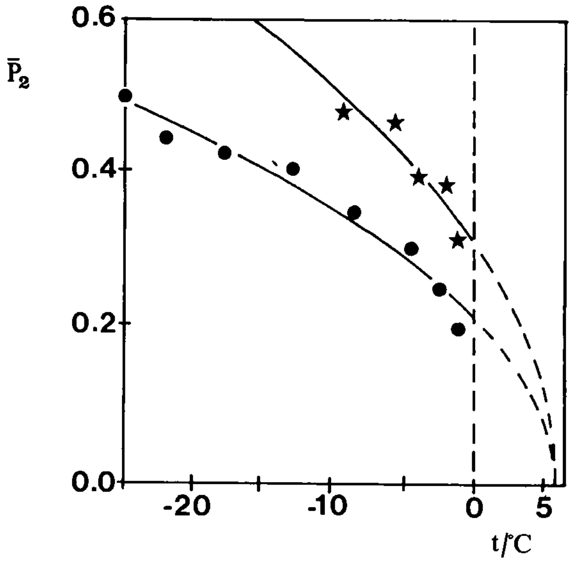


Figure 7. The major order parameter $\bar{P}_2$ versus t: the difference between the actual temperature and the clearing point ($t = T - T_{NI}$). ● organometallic and ★ ligands.

as a function of the difference between the actual temperature and the nematic–isotropic transition temperature ($t = T - T_{NI}$). The two curves, when the clearing point is approached, show a regular decrease in $\bar{P}_2$ and follow a similar fall to zero; moreover the $\bar{P}_2$ values for both ligand and organometallic complex, are well fitted by a square root law. As a mean field theory could suggest,

$$\bar{P}_2 = B\,(T_C - T)^b.$$

In the present case and within our accuracy, from the best fits we found critical exponent $b = 0{\cdot}5$, for both the order parameters and quite different B coefficients $B = 1{\cdot}6 \times 10^{-2}$ for the ligands and $B = 8{\cdot}0 \times 10^{-3}$ for the organometallic complex. Nevertheless, it must be observed that the values of the major order parameter for the organometallic compounds are systematically smaller than those determined for the ligand species.

Because of the metal complexation an increased order was expected, so to obtain more insight about this point the order parameter discontinuity, characteristic of a first order transition, was considered. For such a parameter, the Maier–Saupe molecular field theory [17] predicts that, at the transition, the discontinuity of the major parameter $\bar{P}_2$ should be about 0·43. Now at $t = -1$°C, we obtain $\bar{P}_2$ of 0·32 for the ligand, a value lower but close to some of the data reported in the literature (see for example [8, 18], and $\bar{P}_2 = 0{\cdot}20$ for the organometallic. Finally the virtual transition t^* (the temperature at which the transition becomes second order and the major order parameter is zero) is nearly 5·5°C for both compounds.

2.4. *Optical and textural observations*

These observations usually require several thermal cycles therefore only the compounds which combine a low clearing point with an high thermal stability, namely the ligands and organometallic compounds with $n = 1$ and $m = 12$, have been studied. The investigations with the optical microscope were performed in the nematic phase on oriented samples. We used an Hortoplan–Leitz microscope with a home made hot stage (temperature control to within ± 1°C) and equipped with an automatic photographic camera (Wild MPS). We operated with a magnification of 125 × and, for the sake of comparison, used cells whose thickness was controlled by thin mylar spacers of $50\,\mu$m. Moreover, in order to obtain conducting glasses, the spacers were placed between two optical glasses treated with SnO_2. Planar (homogeneous) orientation were achieved by coating the glass with a 1 per cent water solution of Surfine, or to obtain homeotropic orientations, with a 1 per cent water solution of DMOAP polymer.

Experimentally, the best and stable homeotropic orientations of the samples were realized on heating and cooling down from the isotropic to the nematic phase a few times. Thus, heating or cooling the organometallic sample (not for the ligand), a hysteresis near the clearing point was initially observed, then, after several thermal cycles, a well oriented nematic phase was obtained. Thereafter the nematic phase texture become stable and large regions with strong homeotropic anchoring, together with small islands with nematic schlieren textures (where the director is locally tilted) appear (see figure 8). Such islands decrease in size upon cooling. The oscillations of both the textures are related to the fixing of the organometallic system to the substrate and close to the nematic–isotropic transition ($t < 2$°C) only the schlieren texture is present. Therefore the organometallic molecules tilt at the nematic–isotropic interphase.

At the clearing point temperature, for both ligands and organometallic a first order transition occurs very strong for the former but much weaker for the latter. Moreover, at the clearing point when the planar orientation is obtained, this different behaviour between them is enhanced and easier to observe with the microscope: after stabilization, the organometallic transition appears to be nearly second order. As far as the behaviour on cooling is concerned the organometallic compound cooled to the S_A phase and shows a confocal texture with the focal conics parallel to the rubbing direction. Then when the freezing point is reached, the ligands form an usual polycrystalline solid (see figure 9(*a*)) while the organometallics, independent of the cooling rate, form a glassy smectic (see figure 9(*b*)), which, at room temperature, can be described as a supercooled liquid crystal. The solid phase of the glassy organometallic is optically very dark either in crossed or in parallel polarizers.

Finally, we report some qualitative remarks on the conoscopic pictures. In the homeotropic nematic phase, observations near the boundary defects show local conoscopic pictures and bulk conoscopic pictures appear in extended homogeneous homeotropic regions. In the ligand case, as expected for a uniaxial system, over all of the nematic range they consist of a set of local crosses typical of an uniaxially aligned system wherein the position and shape of the crosses do not depend on the temperature. Under the same conditions the organometallic gives a completely different behaviour: the conoscopic pictures are more complicated and depend on the temperature. In the nematic phase (and sometimes also in the S_A phase, but not in a reproducible way) the uniaxial crosses split slightly into isogyres in a stable and reversible manner, so reflecting a weak biaxial character [19]. Remarkably this effect is more evident when the homeotropic orientation is uniform and is enhanced when the sample is placed in a magnetic field. Some conoscopic pictures of organometallics obtained at different temperatures are shown in figure 10. The sample was placed between of two crossed polarizers, heated to the isotropic phase and then cooled very slowly in a quasi-equilibrium state (waiting several minutes before taking the picture,

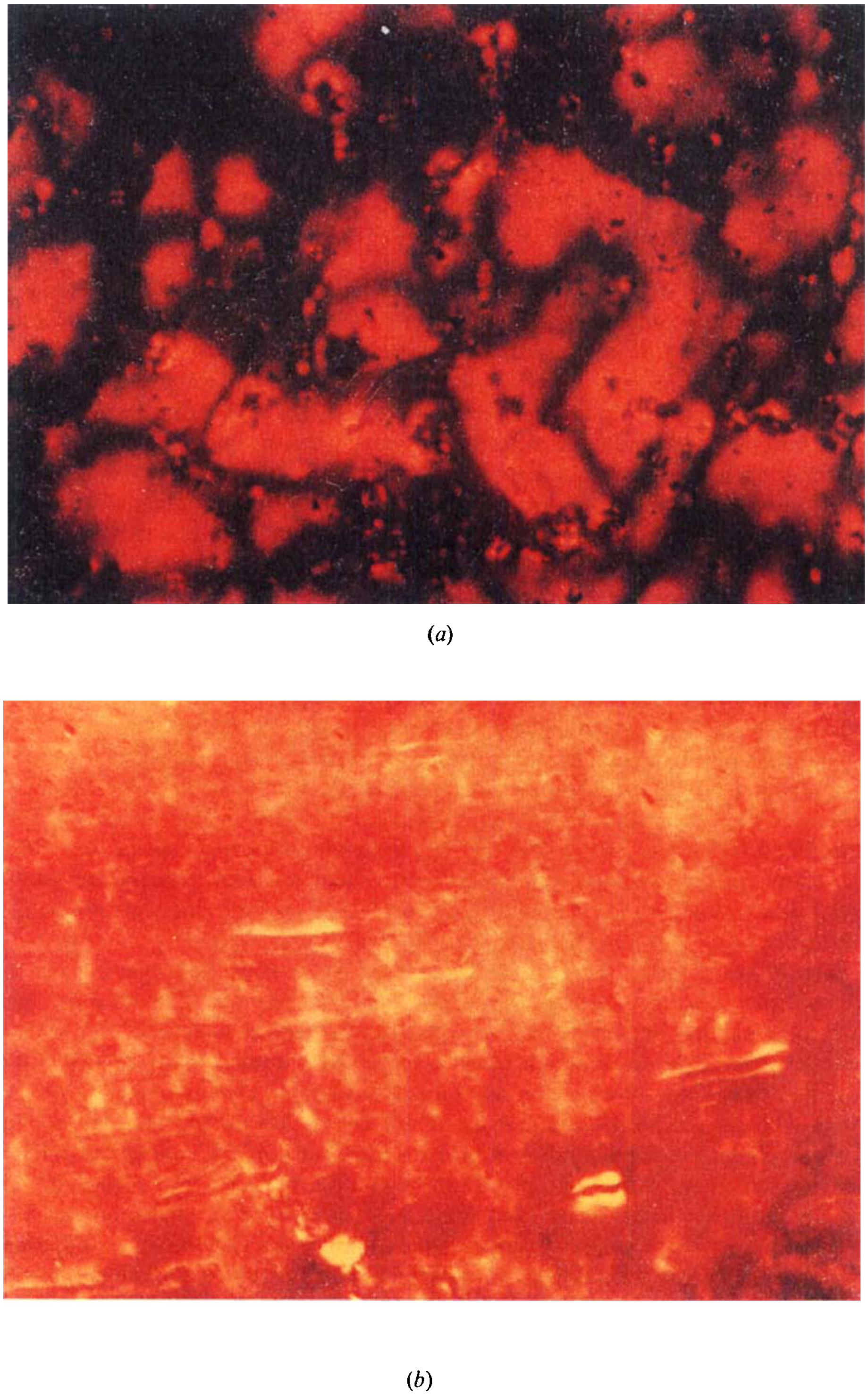
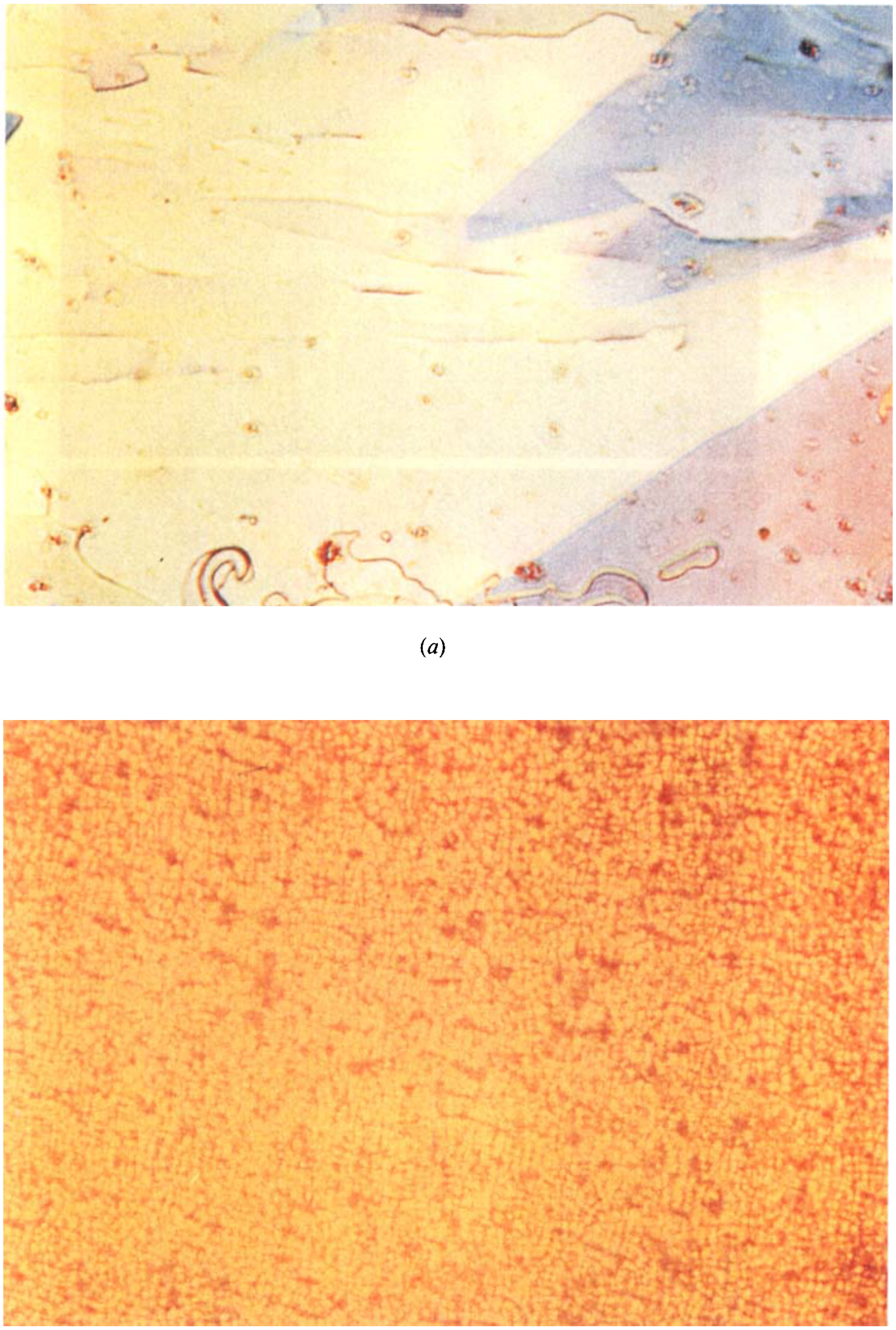


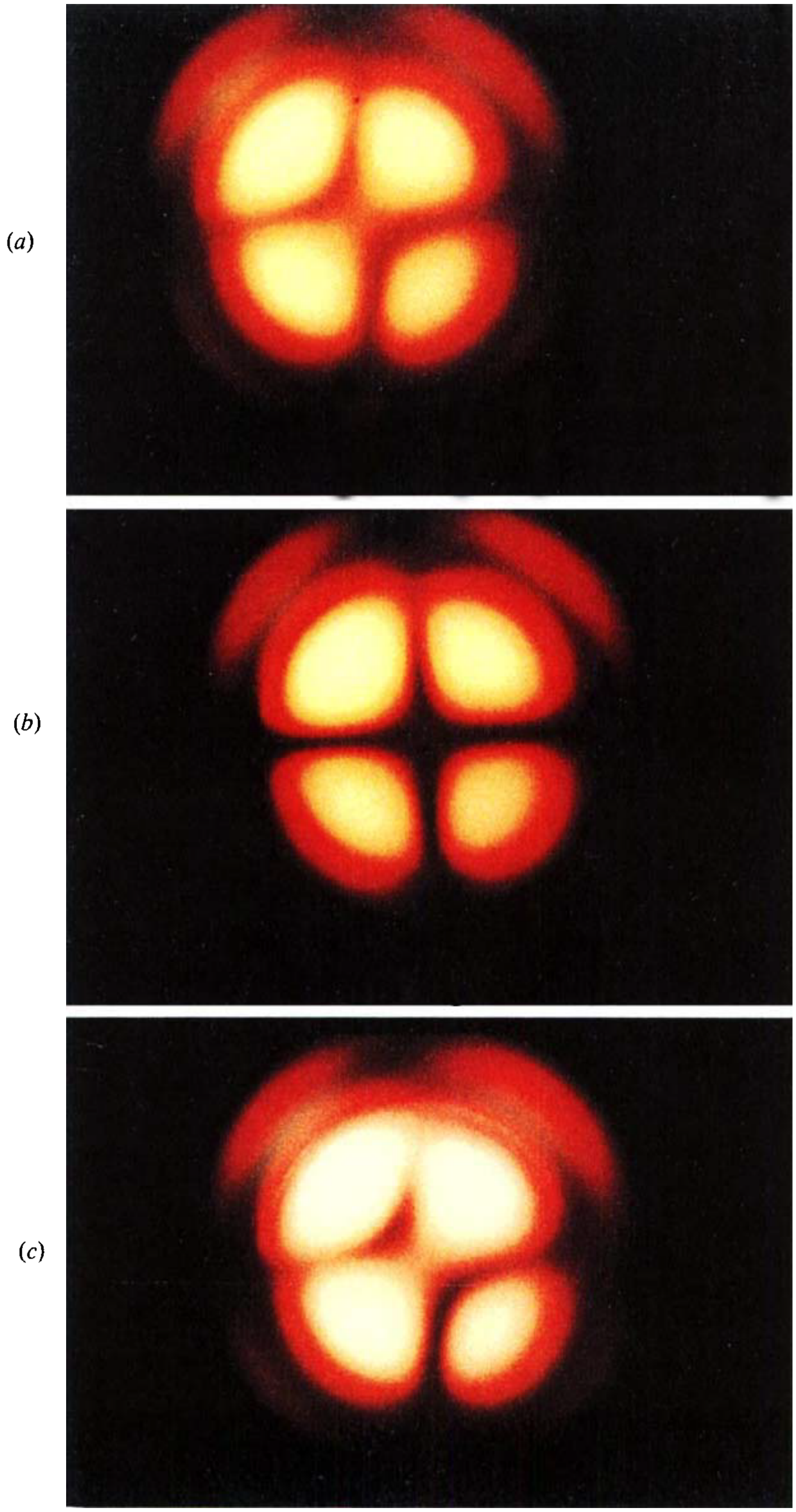
Figure 8. (*a*) Organometallic homeotropic texture, the picture has been taken at 170°C (nematic phase) between crossed polarizers. (*b*) Organometallic planar texture, at 168°C between crossed polarizers (nematic phase).



(*a*)

(*b*)

Figure 9. (*a*) Optical textures of the free ligand (20 μm cell) at room temperature. (*b*) the organometallic (20 μm cell) after cooling from 175°C to room temperature: a smectic texture is still visible.


(*a*)
(*b*)
(*c*)

even if the image appeared to be in equilibrium). In the nematic state the sample was rotated until the cross opens into a set of two hyperbolas and then cooling keeping the apparatus in a fixed position: figure 10 (*a*) is for the nematic, (*b*) for the smectic A (the cross is closed) and (*c*) for the glassy state (the cross is again open in two hyperbola).

3. Discussion

Some of the results can be conveniently analysed in the frame of the theory developed by Luckhurst *et al.* [20] for biaxial molecules. Briefly in this model the molecules are rigid interacting via second rank forces, the parameters required by such a model are the coefficients of the expansion of the contemplete pseudopotential. In particular two parameters which can be related to the molecular anisotropy must be considered:

$$C_{200} = (-2B(L^2 + W^2) - 2W(L^2 + B^2) + L(W^2 + B^2) + 8LBW)/3$$

and

$$C_{220} = (L^2 - BW)(B - W)/6^{1/2}.$$

Here L, W and B are, respectively, the length, the width and the breadth of the molecule. C_{220} is zero in the limit of cylindrical molecule ($W = B$) and the ratio $\lambda = C_{220}/C_{200}$ is related to the deviation from pure cylindrical symmetry ranges between 0 (for cylindrical symmetry) and 0·61 (fully biaxial molecule: $L \gg W \gg B$). These coefficients are related to the transition temperatures, to the order parameters and to the transitional entropy. Consequently, the value of the coefficient C_{200} is directly proportional to the nematic–isotropic transition temperature: therefore it is qualitatively obvious that a greater molecular anisotropy leads to a higher transition temperature.

Starting from our X-rays and neutron scattering experiments [21] we evaluted approximately the C_{200}, C_{220} and λ parameters: we see that they are very different in the ligand and organometallic cases, such an evaluation repeated for all the materials gave similar results (with a small decrease of the molecular biaxiality when the terminal chains are increased in length). The λ values are 0 and 0·33 for the ligand and organometallic compounds, respectively.

3.1. *Transition temperatures*

The transition temperatures have been obtained from calorimetric investigations. They can be summarized as follows:

(1) In all of the alkyl-alkoxy mesogenic azocompounds studied the complexation with palladium produces new mesogenic compounds. Even for the ligand species without mesophases (e.g. in the case of short chains) the corresponding organometallic compounds show at least a nematic phase.
(2) As a general trend, the organometallic materials display a number of mesophases.
(3) The transition temperatures of the organometallics are dramatically higher than for the ligands.

Figure 10. (*a*) The conoscopic picture in the nematic phase (50 μm, 170°C), (*b*) the conoscopic picture in the smectic A phase (160°C), and (*c*) the conoscopic picture in the glassy phase at room temperature obtained by slow cooling.

Table 3. The measured [21] the dimensions of the compounds with $m = 12$, $n = 1$ and the calculated values of the anisotropy parameters

	L/Å	W/Å	B/Å	C_{220}/Å^3	C_{200}Å^3	λ
Ligand	30	5	5	0	2775	0
Organometallic	29·5	9	5	1396	4195	0·33

(4) The difference in the T_1 between the ligands and the organometallics is reduced as the chain length is increased.

(5) The complexation enlarges the nematic range and such a widening is chain length dependent.

Points (1)–(5) indicate (i) that metal complexation stabilizes the mesophases, and (ii) that in the organometallic compounds an orientational order, greater than in the organic ligands is probably present. This feature could be tentatively explained by taking into account several different contributions. First, the effects induced by the increased molecular anisotropies, either as dynamical or as purely conformational effects. In the former case (points (1) and (2)) we might assume that the introduction of a metallic core into the ligand structure prevents some free rotations and as supported by recent quasielastic neutron scattering measurements [22] causes a partially hindered array of the organometallic molecules. To discuss point (3) we refer to the theory given by Luckhurst *et al.* and to verify the influence of the steric anisotropy on the transition temperature, appropriate calculations have been performed [20]. In particular the calculated ratio of the temperature of the nematic–isotropic phase transitions between the organometallic and ligands by 1·5, while for our experimental data, this ratio varies from 1·38 (for the shortest member of the series) and 1·28 (for the longest). Therefore, at least qualitatively, a straight correlation between the high transition temperatures of the organometallics and their high molecular anisotropy has been found. In this respect also the reduction from 1·38 and 1·28 could be significant because for these molecules when the chain length is increased the biaxiality decreases. Quantitative improvements in the theory applied to linear oligomers have been made [23] and the results indicate a similar trend.

This discussion has been carried on the basis of the peculiar molecular geometry exhibited by these organometallic species. Other effects could be present: such as weak short range interactions of an electronic origin, these could either stabilize the structure or also induce mesophases, and so probably make the comparison more quantitative. Thus, for the organometallics, electronic interactions exerted by the metal centres on neighbouring molecules, as found in mesogenic copper containing materials [5, 24], cannot be excluded.

Concluding, with reference to point (4), qualitatively it is known [11, 12], that for high temperature liquid crystals, the entropic term in the free energy usually increases with the chain length (while the opposite occurs with low melting liquid crystals). Therefore, in this respect, organic and metallorganic mesogens with high transition temperatures behave similarly. To comment on this feature, it has been suggested [25] that the observed T_{NI} lowering as the chain length increases may result from a dilution effect in that the interaction between the mesogenic groups is reduced because their average separation is lowered as the chain length increases. This effect is clearly more important the stronger the mesogenic interaction and hence the higher T_{NI}.

3.2. *Calorimetry*

The model given by Luckhurst *et al.* (20) also provides a useful tool with which to discuss, at least qualitatively, the calorimetric data on the basis of the molecular biaxiality. For sake of simplicity, the discussion will be restricted to the nematic–isotropic transition of the compound most extensively studied ($n = 1$, $m = 12$).

The ΔH for the ligand and the organometallic are 0·45 kJ/mol and 0·18 kJ/mol respectively. For alkyl-alkoxyazobenzenes with a total chain length ranging from 2 to 12 [25] at the nematic–isotropic transitions the nematic–isotropic enthalpies are $0{\cdot}5 < \Delta H < 1{\cdot}05$ (kJ/mol). Accordingly while the value for the ligand is of the same order as expected that for the organometallic is much smaller. In order to understand the origin of such a discrepancy the entropy values, ΔS, have been calculated. For the alkyl-alkoxy azobenzenes [26] they are of few J/K mol as predicted also by the Saupe theory [17] for which ΔS is 3·5 J/K mol, but such a value should decrease with increasing molecular biaxiality [19]. In the present cases ΔS is 1·5 J/K mol for the ligand and 0·35 J/K mol for the organometallic. Again the ligand value is of the same order of magnitude of the previously mentioned compounds while the organometallic value is significantly smaller. Hence, according to [19] a large molecular biaxiality must be present. In fact, for $\lambda = 0{\cdot}33$ the theoretical ΔS value is 0·40 J/K mol, which is very close to the result for the organometallic.

3.3. *Order parameter*

Surprising for us the major order parameter determined for the organometallic are systematically smaller than those determined for the ligand. Furthermore, the critical exponents are roughly the same but both the critical coefficients, and the jump of the order parameters at the phase transition, are remarkably different. However, recalling the previous discussion, it is apparent that the introduction of a molecular biaxiality may change $\bar{P}_2$ at the transition. Thus, while according to the Maier–Saupe theory (when $\lambda = 0$) $\bar{P}_2$ is 0·43 and for $\lambda = 0{\cdot}2$ $\bar{P}_2$ is 0·34, with reference to the theory of Luckhurst *et al.*, for $\lambda = 0{\cdot}33$ $\bar{P}_2$ should be 0·17 qualitatively close to our experimental result of 0·2.

The residual difference between the theoretical and experimental data leads us to conclude that probably the organometallic molecule investigated is biaxial but the theory should be improved to modify the pseudopotential, or that the biaxial ordering simply exists on a local scale, so that the measured major order parameter is only one component of the tensor order parameter.

3.4. *Optical observations*

The optical observations show that ligands and organometallics orient on treating the cell surfaces, in the same way. Moreover conoscopy displays without any doubt that the organometallic can be macroscopically organized in a biaxial nematic phase. Regarding the metal containing liquid crystals the observations of a macroscopic biaxiality has been recently reported for a copper mesogen [27], so the main difference is worthwhile. At first (apart from the different compound which we are considering), as far as the stability of the material is concerned, in the organometallic case, the compound is mesogenic at a lower temperature and stable without any apparent decomposition, so that several runs of reproducible measurements, have been obtained. As a further difference, it may be considered that the biaxial–uniaxial phase transition was observed only for a mixture while such a transition is associated here with the smectic A–nematic transition which takes place in a pure organometallic compounds. Finally, it should be pointed out that our observations do not need the application of an orientating electric field, so bypassing the interpretative problems arising from the interaction of a biaxial material with the electric field.

5. Conclusions

A comparative study has been carried on two homologous series of mesogenic compounds in order to elucidate (i) the differences between the free ligands and metallo-mesogens and (ii) the role played by the transition metal when organometallic liquid-crystalline derivatives are prepared by complexation of metals to mesogenic ligands. As expected, the two systems behave quite differently because of the dramatically different molecular structures, nevertheless a comparison gives some useful information. The calorimetric data as a whole indicate a greater molecular anistropy. As an example the organometallic transition temperatures are higher than those of the ligands, however the weak transition entropies are a possible indication of a large molecular biaxiality. The presence of additional ordered mesophases and the optical observations of the macroscopic ordering at the phase transitions suggest the hypothesis that the complexation modifies the molecular interactions (perhaps through the metal) creating a biaxial ordering and then a larger ordering. Nevertheless, while some results suggest a greater orientational order, the value of the major order parameter does not: the molecular biaxiality seems more appropriate to interpret these results. Remarkably, such a conclusion may be supported by the similar results obtained recently by Kiefer and Baur [28] on materials with a weak biaxiality ($0{\cdot}1 < \lambda < 0{\cdot}2$). On the other hand, preliminary optical observations seem to indicate a macroscopic biaxial ordering, consequently the usual order parameter measurements should be diagnostic of only a part of the total ordering. Therefore, in order to clarify this point, more accurate measurements, including the analysis of the biaxial character of the molecular ordering, are required.

Concluding, with reference to the packing mode of the organometallic mesophases, we suggest that, in addition to the usual long range orientational ordering (which prevails when the aliphatic chains are properly long) a two dimensional anisotropic liquid short range order (which could introduce further anisotropies in the local order) might be considered.

We wish to acknowledge the support of Professor M. Fontana in the I.R. measurements, Professor G. Durand for a critical reading of the manuscript and several suggestions, Professor E. Kats for the discussion on uniaxial and biaxial ordering, Professor E. R. Luckhurst for very important and helpful comments on the paper, the referees for a stimulating discussion and Johnson Matthey Ltd. for the loan of the palladium salt. This work was partially supported by INFM under the cover of National Project on new materials.

References

[1] Ghedini, M., Licoccia, S., Armentano, S., and Bartolino, R., 1984, *Molec. Crystals liq. Crystals*, **108**, 269.

[2] Ghedini, M., Armentano, S., Bartolino, R., Rustichelli, R., Torquati, G., Kirov, N., and Petrov, M., 1987, *Molec. Crystals liq. Crystals*, **151**, 75.

[3] Ghedini, M., Armentano, S., Bartolino, R., Kirov, N., Petrov, M., and Rosi, B., 1988, *J. molec. Liq.*, **5**, 128.

[4] GHEDINI, M., ARMENTANO, S., BARTOLINO, R., RUSTICHELLI, F., and TORQUATI, G., 1987, *Solid St. Commun.*, **64**, 1191.

[5] LEVELUT, A. M., GHEDINI, M., BARTOLINO, R., NICOLETTA, F. P., and RUSTICHELLI, F., 1989, *J. Phys.*, *Paris*, **50**, 113.

[6] TORQUATI, G., NICOLETTA, F. P., BARTOLINO, R., GHEDINI, M., and ARMENTANO, S., 1990, *Nuovo Cim.* D, **12** (in the press).

[7] GHEDINI, M., ARMENTANO, S., and NEVE, F., 1987, *Inorg. chim. Acta*, **134**, 23.

[8] DOUCET, J., 1978, Thèse d'état Orsay.

[9] ALBERTINI, G., DUBINI, B., MELONE, S., PONZI-BOSSI, M. G., PULITI, P., and RUSTICHELLI, F., 1980, *Nuovo Cim.* B, **56**, 157.

[10] HELKER, H., and HATZ, H., 1987, *Handbook of Liquid Crystals* (Verlag–Chemie).

[11] DE JEU, W. H., VAN DER VEEN, J., and GOOSSENS, W. J. A., 1973, *Solid St. Commun.*, **12**, 405.

[12] GRAY, G. W., 1976, *Advances in Liquid Crystals*, Vol. 2, edited by G. H. Brown, (Academic Press).

[13] MCMILLAN, W. L., 1971, *Phys. Rev.* A, **4**, 1238; 1975, *Ibid.* B, **12**, 345.

[14] (a) DOZOV, I., KIROV, N., and FONTANA, M. P., 1984, *J. chem. Phys.*, **81**, 2585. (b) KIROV, N., and SIMOVA, P., 1984, Vibrational Spectra of *Liquid Crystals* (Bulgarian Academy of Sciences).

[15] SIMOVA, P., KIROV, N., FONTANA, M. P., and RATAJCZAK, H., 1988, *Atlas of Vibrational Spectra of Liquid Crystals* (World Scientific).

[16] (a) BELLAMI, L. J., 1966, *The Infrared Spectra of Complex Molecules* (Methuen). (b) BULKIN B. J., 1974, *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnston and R. Porter (Academic Press).

[17] (a) DE GENNES, P. G., 1975, *The Physics of Liquid Crystals* (Oxford University Press). (b) SAUPE, A., 1964, *Z. Naturf.* (*a*), **19**, 161.

[18] DECOSTER, D., and BOUAMARA, M., 1980, *Springer Series on Chem. Phys.*, Vol. 81 (Springer-Verlag).

[19] GALERNE, Y., 1988, *Molec. Crystals liq. Crystals*, **165**, 180.

[20] LUCKHURST, G. R., ZANNONI, C., NORDIO, P. L., and SEGRE, U., 1975, *Molec. Phys.*, **30**, 1345.

[21] FORMOSO, V., PAGNOTTA, M. C., MARIANI, P., PEPY, G., MORE, M., and BARTOLINO, R., 1990, *Liq. Crystals* (in the press).

[22] CODDENS, G., PAGNOTTA, M. C., RUSTICHELLI, F., VERSACE, C. C., GHEDINI, M., NEVE, F., and BARTOLINO, R. (in preparation).

[23] KLOCZOWSKI, A., and LUCKHURST, G. R., 1988, *Liq. Crystals*, **3**, 95.

[24] ALBERTINI, G., GUIDO, A., MANCINI, G., STIZZA, S., GHEDINI, M., and BARTOLINO, R., 1990, *Europhysics Lett.* (in the press).

[25] LUCKHURST, G. R., (private communication).

[26] DEMUS, D., DIELE, S., GRANDE, S., and SACKMANN, H., 1983, *Advances in Liquid Crystals*, Vol. 6, edited by G. Brown (Academic Press).

[27] CHANDRASEKHAR, S., RATNA, B. R., SADASHIVA, B. K., and RAJA, V. N., 1988, *Molec. Crystals liq. Crystals*, **165**, 123.

[28] KIEFER, R., and BAUR, G., 1989, *Molec. Crystals liq. Crystals*, **174**, 101.