

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

X-ray diffraction study of some mesogenic copper, nickel and vanadyl complexes

Joaquin Barbera^{ab}; Anne-Marie Levelut^a; Mercedes Marcos^b; Pilar Romero^b; Jose Luis Serrano^b

^a Laboratoire de Physiques des Solides, L.A. 2 associé au C.N.R.S., Université Paris-Sud, Orsay, Cédex,

France ^b Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias,

Universidad de Zaragoza-C.S.I.C., Zaragoza, Spain

To cite this Article Barbera, Joaquin , Levelut, Anne-Marie , Marcos, Mercedes , Romero, Pilar and Serrano, Jose Luis(1991) 'X-ray diffraction study of some mesogenic copper, nickel and vanadyl complexes', *Liquid Crystals*, 10: 1, 119 – 126

To link to this Article: DOI: 10.1080/02678299108028235

URL: <http://dx.doi.org/10.1080/02678299108028235>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

X-ray diffraction study of some mesogenic copper, nickel and vanadyl complexes

by JOAQUIN BARBERA† and ANNE-MARIE LEVELUT*

Laboratoire de Physiques des Solides, L.A. 2 associé au C.N.R.S.,
Université Paris-Sud, 91405 Orsay, Cédex, France

and MERCEDES MARCOS, PILAR ROMERO and JOSE LUIS SERRANO

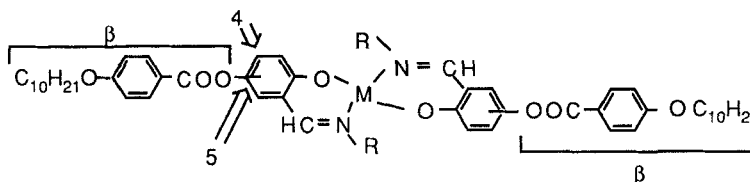
Química Orgánica, Instituto de Ciencia de Materiales de Aragón,
Facultad de Ciencias, Universidad de Zaragoza-C.S.I.C.,
50009 Zaragoza, Spain

(Received 19 November 1990; accepted 27 December 1990)

We present a comparative study of various metallomesogenic complexes, using X-ray diffraction methods. For a given ligand linked to different metal atoms (Cu, Ni, VO), the nature of this central atom influences mainly the magnetic susceptibilities of the mesophases. With different ligands, which keep the close neighbourhood of the metal atom unchanged, the apparent length of the mesogenic unit is longer for short ligands than for longer ones. This unexpected behaviour is qualitatively well explained by taking into account the global shape of the different complexes.

1. Introduction

The synthesis of metallo-organic complexes with mesomorphic properties offers a new field of liquid-crystalline compounds, the physical properties of which can be related to the presence of a central metal atom [1]. An important parameter is the geometry of the close neighbourhood of the metal since this geometry can be responsible for the structural properties of the mesophase and for the physical characteristics of the complexes. We present here a structural study of the mesophases of six different copper(II) ester-imine complexes. Moreover we give a comparative study of three nickel(II) and three vanadyl(II) complexes with the same ligands. The close neighbourhood of the metal is unchanged throughout the series, while the geometry of the complex varies with the chemical architecture of the ligands which are linked to the metal. The two ends of each ligand can be modified via the position of the *p*-*n*-decyloxybenzoate group β (4 or 5) and via the nature of the substituent linked to the



* Author for correspondence.

† Current address: Química Orgánica, Instituto de Ciencia de Materiales de Aragón,
Facultad de Ciencias, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain.

Table 1. Phase transition for the complexes studied and for one of the ligands. ● The phase exists; —, the phase does not exist.

N	Compound†		Polymorphism and transition temperatures/°C						
	M	R	Crystal	Smectic C	Nematic	Isotropic liquid			
1	Cu	CH ₃	●	174	●	178	●	224	●
2	Cu	<i>n</i> -C ₅ H ₁₁	●		—	105	●	147	●
3	Cu	<i>n</i> -C ₁₀ H ₂₁	●		—	113	●	132	●
4	Cu	CH ₃	●	190	●	240	●	260	●
5	Cu	<i>φ</i> -OCH ₃	●		—	170	●	276	●
6	Cu	<i>φ</i> -OC ₁₀ H ₂₁	●	164	●	248	●	249	●
7	Ni	<i>n</i> -C ₅ H ₁₁	●		—	127	●	172	●
8	Ni	<i>n</i> -C ₁₀ H ₂₁	●		—	132	●	155	●
9	Ni	<i>φ</i> -OCH ₃	●		—	190	●	214	●
10	VO	<i>n</i> -C ₅ H ₁₁	●		—	109	●	131	●
11	VO	<i>n</i> -C ₁₀ H ₂₁	●	92	●	103	●	118	●
12	VO	<i>φ</i> -OCH ₃	●		—	209	●	282	●
13	Organic ligand	<i>n</i> -C ₁₀ H ₂₁	●	67	●	72	●	80	●

† β group is in the 4 position for all the compounds except for compound 4 (β is in the 5 position).

nitrogen atom. The synthesis and the mesomorphic properties of the complexes have been reported earlier [2–5]. All of the compounds exhibit nematic mesomorphism and in four cases a smectic C phase also appears. However, a discussion of the influence of their chemical architecture upon the molecular packing in the liquid-crystalline phase cannot be undertaken unless some structural features characterizing the molecular organization in the mesophases are available.

In order to gain a better understanding of this organization, we have undertaken an X-ray diffraction study of a large number of members of these series. These compounds and their mesomorphic properties are listed in table 1. The ligand with $R = C_{10}H_{21}$ (compound 13), which is itself mesogenic, was also studied. The X-ray measurements were carried out on monodomains oriented by a magnetic field (0.3 or 1.7 T) either in the nematic or in the smectic C phase. The X-ray apparatus has been described elsewhere [6].

2. Results

Looking at the relative orientation of the diffraction patterns and of the magnetic field, we can divide the compounds into two groups.

In the first, the complexes orient with the director perpendicular to the magnetic field direction (Cu derivatives with $R = CH_3$, C_5H_{11} and $C_{10}H_{21}$). In this case a polydomain is obtained where the director can adopt any direction on the plane perpendicular to the field. A monodomain appears when the sample is subsequently rotated by an angle of $\pi/2$ around the capillary axis. This method has already proved to be effective for orienting some lyotropic and disc-like nematic phases [6, 7]. For the other complexes studied (Cu derivatives with $R = \phi-OCH_3$ or with the ester substituent in the 5 position, and all Ni and VO derivatives) we obtain a monodomain where the director adopts the magnetic field direction.

In figure 1 typical diffraction patterns of our complexes are shown. In general, we do not observe any outstanding difference compared to the diffraction pattern of classical liquid crystals. Basically the pattern consists of two large angle, diffuse crescents in the

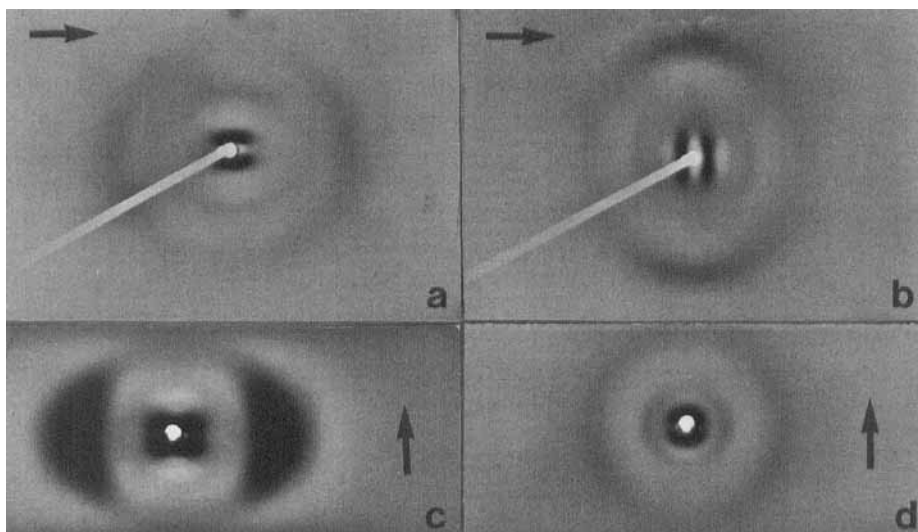


Figure 1. X-ray diffraction patterns of single domains of the nematic phase. The arrow indicates the magnetic field direction. (a) Complex of Cu **1** $B=0.3$ T, $T=200^\circ\text{C}$; sample was rotated around an axis perpendicular to the X-ray beam and to the magnetic field; (b) Complex of Ni **7**, $B=0.3$ T, $T=155^\circ\text{C}$; (c) Complex of Cu **5**, $B=1.7$ T, $T=180^\circ\text{C}$, (d) Complex of Ni **9**, $B=1.7$ T, $T=195^\circ\text{C}$.

Table 2. Structural characteristics of the mesophases. d , layer periodicity in the smectic range or in the smectic fluctuation in the nematic range; l , apparent molecular length measured on X-ray patterns; α , tilt angle in the smectic phase or in the smectic fluctuations.

Compound†			Measured distances					Estimated fully extended length/Å	
N	M	R	$\Delta\chi$ (sign)	Phase	$d/\text{Å}$	$l/\text{Å}$	Angle $\alpha/^\circ$	Ligand	Complex
1	Cu	CH_3	—	N	39	43.5	26	30	53
2	Cu	$n\text{-C}_5\text{H}_{11}$	—	N	28	37	41	35	53
3	Cu	$n\text{-C}_{10}\text{H}_{21}$	—	N	27.5	36.5	41	40.5	53
4	Cu	CH_3	+	S_C	37	45	35	29.5	53.5
5	Cu	$\phi\text{-OCH}_3$	+	N	34	39.5	31	36	53
6	Cu	$\phi\text{-OC}_{10}\text{H}_{21}$?	S_C	32	—	—	47	53
7	Ni	$n\text{-C}_5\text{H}_{11}$	+	N	29	39.5	43	35	53
8	Ni	$n\text{-C}_{10}\text{H}_{21}$	+	N	27.5	38	44	40.5	53
9	Ni	$\phi\text{-OCH}_3$	+	N	37	37	0	36	53
10	VO	$n\text{-C}_5\text{H}_{11}$	+	N	29	38.5	41	35	53
11	VO	$n\text{-C}_{10}\text{H}_{21}$	+	N	29	37	38	40.5	53
12	VO	$\phi\text{-OCH}_3$	+	N	33.5	39.5	32	36	53
13	Organic ligand	$n\text{-C}_{10}\text{H}_{21}$	+	N	30	37.5	37	40.5	—
				S_C	30				

† β group is in the 4 position for all the compounds except for compound 4 (β is in the 5 position).

equatorial region at a scattering angle 2θ of about 20° , and some spots at small angles in the meridian region (2θ between 2.3° and 3.2°) which are Bragg spots for the smectic C phase and diffuse spots for the nematic phase. From the radial position of the maximum in the scattered intensity at large angles we can estimate, using the Bragg relation [8], a distance perpendicular to the director of between 4.5 and 4.8 Å depending on the structure of the complex. In general, the existence in the nematic as well as in the smectic C phase of a four point pattern at small angles (see figure 1 (a), (b) and (c)) gives evidence of smectic C-like fluctuations in the nematic phase [9]. The four point pattern allows the measurement of the layer spacing d , and of the apparent molecular length l . The results of these measurements are quoted in table 2, together with the length of the ligand and of the complex as estimated from Dreiding stereomodels assuming a fully extended conformation of the paraffinic chains. Furthermore, from the layer spacing and the apparent molecular length, the tilt angle α in the smectic C phase or in the smectic C-like fluctuations can be obtained.

3. Discussion

The direction of alignment of the director by a magnetic field depends on the sign of anisotropy of the magnetic susceptibility ($\Delta\chi$). Thus, the diffraction patterns allow us to conclude that ($\Delta\chi$) is negative for complexes **1**, **2** and **3** (Cu derivatives with $R = \text{CH}_3$, C_5H_{11} and $\text{C}_{10}\text{H}_{21}$), and positive for the rest of the complexes studied (see table 2). Complex **6** (Cu derivative with $R = \phi\text{-OCH}_3$) did not give a good orientation in the very viscous smectic C mesophase and its smectic C–nematic transition temperature is too high and could not be reached with our experimental equipment; we cannot, therefore, determine the sign of the anisotropy of the magnetic susceptibility for this complex.

Two effects contribute mainly to the anisotropy of the magnetic susceptibility: the contribution of the paramagnetic entity due to the anisotropy of the g tensor and the strong anisotropic diamagnetic susceptibility of the benzene rings. A compromise between them is responsible for the actual orientation of the whole molecule in the presence of a magnetic field. EPR studies carried out for some complexes in these series have shown that the nickel derivatives are diamagnetic [3, 4] in the solid state at room temperature and in the mesophase. For the vanadyl complexes the EPR studies showed [10] that the anisotropy of paramagnetic contribution is small ($g_{\parallel} = 1.945$, $g_{\perp} = 1.980$ for $R = \text{C}_5\text{H}_{11}$); this favours the V–O bond being perpendicular to the magnetic field and so the molecules orientate with the main axis parallel to the magnetic field.

However, for the copper complexes [11], which have a higher g tensor anisotropy, there is a strong anisotropic paramagnetic contribution to the molecular magnetic susceptibility. Depending on which of two kinds of contribution (paramagnetic from the copper or diamagnetic from the ligands) dominates the molecular orientation will change. Thus, for complexes **1**, **2** and **3**, where R is an aliphatic group, the paramagnetic contribution is dominant. However, for complexes **5** and **6**, where R is aromatic, the greater number of benzene rings increases the diamagnetic contribution, which overcomes the paramagnetic contribution.

The different magnetic orientation of complexes **1** and **4** (for both of which $R = \text{CH}_3$), which can seem surprising at first sight, results from geometric effects. Both complexes have the same number of rings and only differ by their disposition: the β group (*p*-decyloxybenzoyloxy) occupies the 4 position of the salicylidene ring in complex **1** and the 5 position in complex **4**. From molecular models (see figure 2) we observe that the four benzene rings are practically coaxial in complex **4**, which is not the case in complex **1**. As a consequence in the former the diamagnetic contribution of the

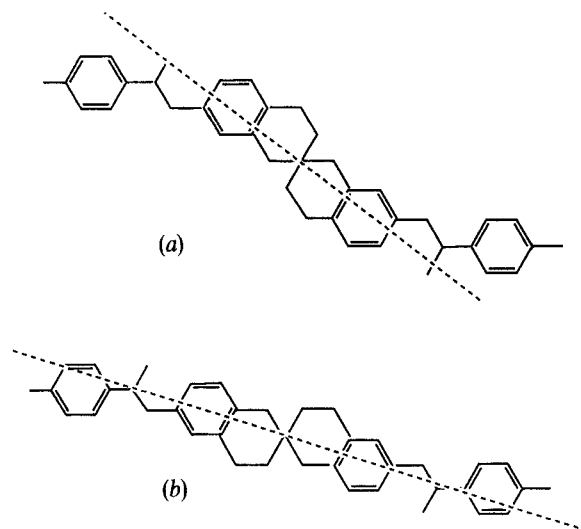


Figure 2. Schematic drawing of the complex core (a) compound **1** and (b) compound **4**.

rings is more efficient and, therefore, the molecules of complex **4** orient with their main axis parallel to the magnetic field. On the other hand, leaving aside the alignment direction, no significant differences are observed between the diffraction patterns of complexes **1** and **4** (see table 2).

It is noticeable from table 2 that the layer spacing d , the apparent length l and the tilt angle α in the complexes studied are practically independent of the metal and depend mainly on the R group. By comparing the apparent length values, we observe that the shortest length of substituent R ($R = \text{CH}_3$) corresponds to the largest apparent length. On the other hand with the largest ligands ($R = \text{C}_{10}\text{H}_{21}$ and $\phi\text{-OC}_{10}\text{H}_{21}$) the measured apparent length is slightly smaller than the fully extended ligand length and increases slightly from the Cu to VO and then to the Ni derivatives. This behaviour can be explained qualitatively. For the n -decyl derivatives neighbouring molecules are interdigitated, and the apparent length must be compared to the fully extended ligand length. In fact, the measured apparent length is even smaller than the fully extended ligand length, and is comparable to the apparent ligand length (compound **13**) in its smectic and nematic mesophases. The aliphatic chains are therefore far from an *all-trans* conformation in the mesomorphic state. For the N -methyl complexes, containing a shorter ligand, we find a structure more similar to a calamitic molecule (a rigid conjugated region and two flexible terminal chains) which should lead to the classic end-to-end packing typical of calamitic mesogens. The apparent length, smaller than the fully extended complex length, should also be due to the disordered conformations of the chains.

These two kinds of organization are represented schematically in figure 3. For the complexes containing ligands with medium length ($R = \text{C}_5\text{H}_{11}$ and $\phi\text{-OCH}_3$) we find an intermediate situation, where the apparent length measured from the patterns is smaller than the fully extended complex length, but slightly larger than the fully extended ligand length. Therefore, it appears that the apparent length of the complex in

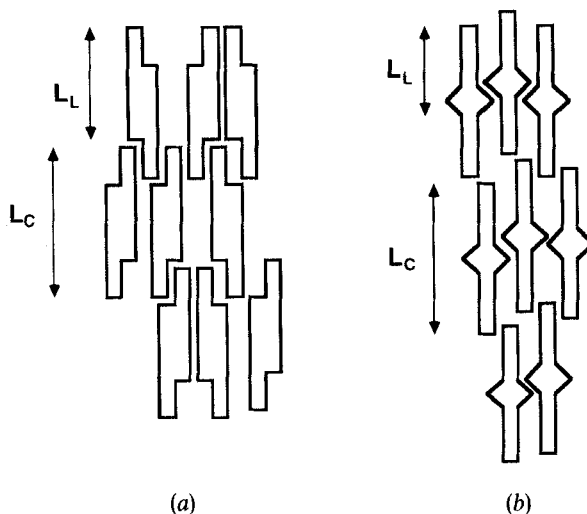


Figure 3. Schematic representation of the molecular stacking along the director (a) large ligands and (b) short ligands. L_L and L_C are, respectively, the lengths of the ligand and of the complex in a fully extended conformation.

the mesophase can be related to its geometry. Moreover it seems that the neighbourhoods close to the metal are very similar since the apparent length is only ligand dependent.

As we have noted the diffraction patterns on the equatorial plane are similar to the diffraction patterns of purely organic liquid crystals. This is in contrast with the phenomenon observed in other copper salicylideneamine complexes [12] and in some palladium complexes [13], where a diffuse intensity corresponding to a distance of approximately 8.5 \AA appears. This means that in the present case there is no evidence of a local coupling of molecules in pairs or in ribbons in a side-by-side array. Although there is only one intensity maximum in the equatorial plane, we can appreciate an unusual extension of the diffuse scattering in the low angle side of the peak at $2\theta \sim 20^\circ$. Furthermore some patterns exhibit diffuse lines parallel to the equatorial plane in the meridian region. This supports the evidence of a local array which is specific to these complex molecules, the shape of which is far from that of a simple rod.

The only exception to this general behaviour is found for the Ni derivative with $R = \phi\text{-OCH}_3$ (see figure 1 (d)), where a diffuse crescent in the equatorial region appears corresponding to a distance perpendicular to the director of 11.5 \AA . The diffraction pattern of this compound shows other peculiarities as compared to the pattern for the rest of the complexes: we do not find the four point pattern, which seems to exclude the existence of smectic C-like fluctuations. Furthermore, the crescents at large angles show a greater angular extension and appear at a slightly smaller angle (therefore they correspond to a slightly greater distance perpendicular to the director) than for the other complexes studied. This suggests that the nematic phase in this compound exhibits a somewhat different local order, namely smectic A ordering fluctuations and local side-by-side association characterize the nematic molecular organization. The peculiar behaviour of the nickel complex with $R = \phi\text{-OCH}_3$ (complex 9) raises two questions.

The first concerns the close neighbourhood of the metal atom. The geometry of the four organic atoms linked to the metal should be square planar for copper and square pyramidal for vanadyl, while it could be tetrahedral or square planar (or an intermediate situation) for the nickel. A tetrahedral neighbourhood would imply that the rigid part of the two ligands are far from being parallel. Such a difference between the different metals must act upon the organization in these mesophases whatever the ligands. The stability range of the nematic phase is the same, but the transition temperatures are about 20° higher for the nickel than for the copper derivatives. If there is some difference in the architecture of the complex, this difference does not change the structural features of the mesophases with $R = C_nH_{2n+1}$ because of the great disorder in the mesophase. The rigidity of the substituent $R = \phi-OCH_3$ might explain the smaller stability range and the difference in molecular organization of the nickel complex compared to the copper and vanadyl analogues.

The second question regards the relation between the side-by-side local array and the smectic A ordering. It is obvious that S_A fluctuations will be more compatible with a side-by-side array than a plain nematic ordering. A correlation between this local array and the smectic A ordering could be established at least for a series of mononuclear complexes (the palladium binuclear complexes [13] behave differently). However, the correlation length of the side-by-side array is rather short and cannot be taken as proof of any biaxial symmetry. Moreover a relation between the geometry of the complex and a smectic A or C local ordering is not obvious.

In conclusion, in a series of copper, vanadyl and nickel imine complexes, our structural analysis has shed light on the role of the substituent linked to the nitrogen atom upon the molecular organization of the mesophases of the complexes. On the other hand, no differences have been found between similar homologues of the three metal complexes, with the exception of a rigid environment for the metallic atom. However, our structural studies must be supported by a spectroscopic study of the structure of the metal neighbourhood in the mesophase and by anomalous X-ray scattering experiments in order to extract a metal-metal correlation pair function.

References

- [1] PIECHOCKI, C., SIMON, J., SKOULIOS, A., GUILLON, D., and WEBER, P., 1982, *J. Am. chem. Soc.*, **104**, 5245. TAKAHASHI, S., TAKAI, Y., MORIMOTO, H., and SONOGASHIRA, K., 1984, *J. chem. Soc. chem. Commun.*, 3. EASTMAN, M. P., HORNG, M. L., FREIHA, F., and SHEN, K. W., 1987, *Liq. Crystals*, **2**, 223. MOORE, J. S., and STUPP, S. I., 1988, *Polymer Bull.*, **19**, 251. ESPINET, P., ETXEBARRIA, J., MARCOS, M., PEREZ, J., REMON, A., and SERRANO, J. L., 1989, *Angew. Chem., Int. Ed. Engl.*, **28**, 1065.
- [2] MARCOS, M., ROMERO, P., SERRANO, J. L., BARBERA, J., and LEVELUT, A. M., 1990, *Liq. Crystals*, **7**, 251.
- [3] MARCOS, M., ROMERO, P., and SERRANO, J. L., 1989, *J. chem. Soc. chem. Commun.*, p. 1641.
- [4] MARCOS, M., ROMERO, P., and SERRANO, J. L., 1990, *Chem. Mater.*, **2**, 495.
- [5] SERRANO, J. L., ROMERO, P., MARCOS, M., and ALONSO, P. J., 1990, *J. chem. Soc. chem. Commun.*, p. 859.
- [6] LEVELUT, A. M., HARDOUIN, F., GASPAROUX, H., DESTRADE, C., and NGUYEN HUU TINH, 1981, *J. Phys., Paris*, **42**, 147.
- [7] CHARVOLIN, J., LEVELUT, A. M., and SAMULSKI, E. T., 1979, *J. Phys. Lett., Paris*, **40**, L 587.
- [8] For these complex molecules, the only valuable information must be given by an atomic pair correlation function. The value of 4.5–4.6 Å deduced from a simple Bragg law is only indicative.
- [9] DE VRIES, A., 1970, *Molec. Crystals liq. Crystals*, **10**, 31.

- [10] ALONSO, P. J., SANJUAN, M. L., ROMERO, P., MARCOS, M., and SERRANO, J. L., 1990, *J. Phys. Cond. Matter*, **2** (in the press).
- [11] ALONSO, P. J., ROMERO, P., MARCOS, M., and SERRANO, J. L. (unpublished data).
- [12] LEVELUT, A. M., GHEDINI, M., BARTOLINO, R., NICOLETTA, F. P., and RUSTICHELLI, F., 1989, *J. Phys., Paris*, **50**, 113.
- [13] ESPINET, P., PEREZ, J. MARCOS, M., ROS, M. B., SERRANO, J. L., BARBERA, J., and LEVELUT, A. M., 1990, *Organometallics*, **9**, 2028.