Liquid-crystalline behaviour of di- and mono-palladium organyls: two ways of lyomesophase formation

Nadejda Usol'tseva,*[a,b] **Pablo Espinet,***[b,†] **Julio Buey**[b] **and José Luis Serrano**[c]

[a]*Liquid Crystal Laboratory, Ivanovo State University, C.I.S.-153025 Ivanovo, Russia*

[b]*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain*

[c]*Departamento de Química Orgánica, Facultad de Ciencias–ICMA, Universidad de Zaragoza–CSIC, 50009–Zaragoza, Spain*

Three members of a series of lath-like dinuclear complexes $[Pd_2(\mu\text{-}Cl)_2(C,N)_2]$ **1**, (C,N = orthopalladated imine $R^1{-}C_6H_3{-}CH{=}N{-}C_6H_4{-}R^2$; R^1 = alkoxy chain; R^2 = alkyl or alkoxy chain), a dinuclear cyclopalladated complex with mixed bridges (acetate/thiolate) **2** and a mononuclear orthopalladated complex incorporating a β-diketonate ligand **3**, have been synthesized and their lyotropic phase behaviour in mixtures with apolar organic solvents (linear alkanes, cycloocta-1,5-diene or limonene) has been studied. The lyotropic mesomorphism is determined by the combination of the length of the metalloorganyl side chains and the length of alkane used as solvent. Two ways of formation of lyotropic phases are found. The first case of lyotropic chiral nematic (cholesteric, N*) phase formation in a binary system composed of a non-chiral di- or mono-palladium organyl and a chiral apolar organic solvent is reported.

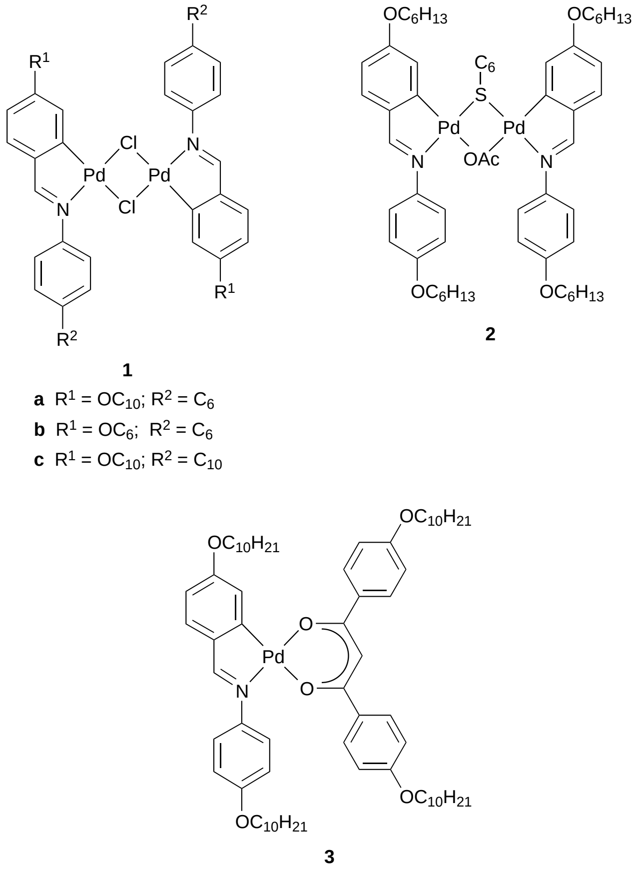
The geometrical proportions (shape, length, width, thickness) of mesogenic molecules are a main factor in determining their supramolecular packing in the mesophase. Thus, disc-like octasubstituted metal complexes of phthalocyanine and porphyrin derivatives,[1] or sheet-like tetra-metal organyls,[2] give the columnar type of supramolecular structure, both in thermotropic and in the lyotropic liquid crystalline phases. For rod-like metal-containing mesogens the layered kinds of thermotropic phases,[1a,3] and the lamellar or the hexagonal arrangements of lyotropic phases are typically formed.[1a,4]

Notwithstanding that, recently it has been shown that by elongating a porphyrin core along one axis through substitution at the 5 or 15 positions, the basically disc-shaped molecule behaves as a rod-like one, displaying smectic A or calamitic nematic thermotropic phases.[5] Moreover, the discovery of biforked mesogens, with a molecular form also intermediate between the two typical extreme shapes, showed their rich thermotropic polymorphism: nematic, lamellar, columnar and cubic thermotropic phases have been observed within the same series.[6] The lyotropic phase behaviour of these 'intermediate-form' mesogens was not studied.

In this respect it is difficult to predict the lyotropic mesomorphism of orthopalladated dinuclear complexes ('dipalladium organyls'), or palladium β-diketonato complexes ('monopalladium organyls'). Molecules of this type are known to show thermotropic behaviour similar to that of typical rod-like mesogens,[7] but they possess molecular structures somehow intermediate between disc-like and rod-like. By analogy with the nomenclature of some lyomesogens, such types of molecular shape could be classified as lath-like in order to stress that they are definitely bidimensional molecules, not just elongated molecules. The investigation presented here is the extension of previous research on the connection between the molecular structure of metal-containing compounds and the lyomesomorphism they display in binary and in multicomponent systems. We report and discuss the first data on the influence of the length of the lateral chains, or the composition of the mesogen–solvent system on the lyotropic properties of chloro-bridged dipalladium organyls **1**. We also compare the lyotropic mesomorphism of these compounds with the lyotropic phase behaviour of the dipalladium organyl **2** and the monopalladium organyl **3** in apolar organic solvents of different types.

Experimental

The dinuclear Pd^{II} complexes **1a–c** and monopalladium complex **3** have been reported previously.[7a,b] Complex **2** was



1

a $R^1 = OC_{10}$; $R^2 = C_6$

b $R^1 = OC_6$; $R^2 = C_6$

c $R^1 = OC_{10}$; $R^2 = C_{10}$

2

3

Scheme 1

---

† Email: espinet@cpd.uva.es

synthesized as described previously for similar compounds,[7c] and characterized by IR, ^{1}H NMR, and C,H,N analyses.† The phase behaviour of the compounds was investigated by polarizing microscopy employing a Leica DMRB microscope with crossed polarizers equipped with a Mettler FP 90 hot stage, at heating rates of 1–5 K min^{-1}, and by differential scanning calorimetry (Perkin Elmer DSC 7, heating rate 5 K min^{-1}). The photographs of textures shown were taken using a CCD Hitachi KP–C 501 video camera equipped with a Sony UP 5000 P videoprinter.

We applied the contact method to explore the lyomesophase behaviour of these palladium organyls with the following apolar organic solvents: linear alkanes (octane, decane, dodecane, pentadecane), cycloocta-1,5-diene and (*R*)-(+)-limonene. This method has been used successfully to identify mesophases in liquid-crystalline mixtures,[8a] in amphiphile–water systems,[8b] and in metallomesogen–organic solvent compositions.[2c,d] The phase diagram of the **1c**–pentadecane system was obtained on the basis of polarizing microscopy and DSC studies of eleven mixtures containing the dipalladium organyl between 15 and 89 mass% in the compositions. The preparation of homogeneous mixtures was achieved as described previously.[2c]

Results and Discussion

Thermotropic behaviour

Compound **1a** ($R^1 = OC_{10}$, $R^2 = OC_6$) exhibits a smectic A (S_A) phase with myelinic figures and spherulites, between 106.6 and 263.4 °C. Compound **1b**, with shorter chains but more similar in length ($R^1 = OC_6$, $R^2 = C_6$), also displays the S_A phase although in a shorter temperature range. **1c** ($R^1 = OC_{10}$, $R^2 = C_{10}$) possesses a smectic C (S_C) phase with a broken fan-shaped texture, as well as an S_A phase with myelinic figures and spherulites.

The non-planar dinuclear Pd complex **2** shows, besides the S_A phase, the schlieren texture of a nematic (N) phase between 168.9 and 173.2 °C. The monopalladium organyl **3** displays S_C, S_A and N phases, although the nematic phase is observed in a very short temperature range (*ca.* 1 °C only). The data of transition temperatures, together with their corresponding enthalpies and types of mesophases, are summarized in Table 1.

Lyotropic behaviour

The dipalladium organyl **1a** does not form any lyomesophase in contact preparations with the linear alkanes octane, decane, dodecane, or pentadecane. Only dissolution of the substance (on heating) or crystallization (on cooling) was observed. When **1b** or **1c** were mixed with the above-mentioned linear alkanes one type of lyomesophase was observed, with myelinic figures and spherulites in the contact area.

On heating, for the contact preparations of **1b** with octane or decane the phase transitions temperatures to the lyomesophase are lower (42 and 64.3 °C respectively) than for the analogous contact preparations of **1c** (76 and 80 °C respectively, see Fig. 1). However, for contact preparations with dodecane or pentadecane the reverse was observed: the phase transition temperatures with **1b** are higher (120 and 130.5 °C) than for **1c** (90 and 99 °C). On cooling, the lyomesophases stay in the contact preparations until 25–27 °C.

Table 1 Optical, thermal and themodynamic data for compounds **1–3**[a]

compound	transition	*T*/°C	Δ*H*/kJ mol^{-1}
1a	K–S_A	106.6	31.8
	S_A–I	263.4[c]	—
1b	K–K′	101.2	7.1
	K′–S_A[b]	127.5	26.1
	S_A–I	210.0[c]	—
1c	K–K′	95.0	26.7
	K′–S_C	112.4	3.3
	S_C–S_A[b]	135.0	—
	S_A–I	237.6[c]	—
2	K–S_A	154.4	13.7
	S_A–N	168.9	
	N–I	173.2	2.5[d]
3	K–S_C	80.0	61.9
	S_C–S_A[b]	150.0	0.4
	S_A–N	154.0	
	N–I	155.0	2.5[d]

[a]K,K′ = crystal; S_A = smectic A; S_C = smectic C; N = nematic; I = isotropic. [b]Optical microscopy data. [c]Decomposition. [d]Combined enthalpies.

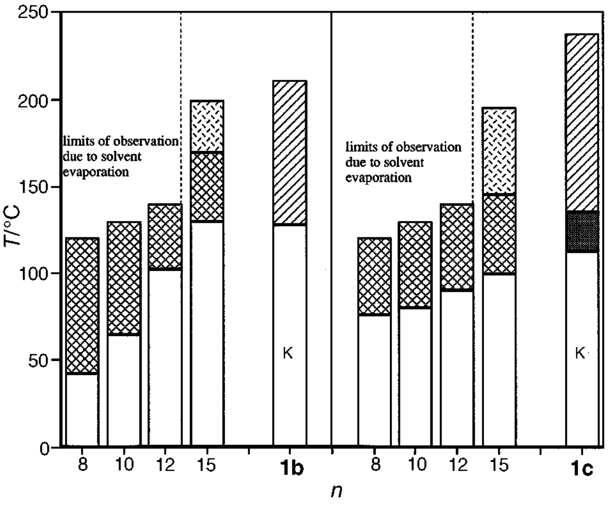


Fig. 1 Relationship of the lamellar phase existence with the chain length *n* of the solvent in the binary systems of dipalladium organyls **1b** or **1c** with linear alkanes, based on the observation of contact preparations on heating

Looking at the phase diagram of the **1c**–pentadecane system (Fig. 2) it is possible to conclude that the supramolecular packing in the lyotropic phase with myelinic figures remains basically the same as in the thermotropic smectic phase. This process is accompanied by a reduction of the S_C to S_A transition temperatures.

In the contact preparations of compound **2** with the above mentioned linear alkanes a nematic lyotropic phase with a schlieren texture appears. The widest temperature area of N phase existence was observed in the **2**–pentadecane system (48 °C on heating or 143 °C on cooling). Moreover, on cooling the nematic phase remains in this system until room temperature (Fig. 3). In the **3**–linear alkane systems the formation of a homeotropically oriented nematic phase and a lamellar phase with spherulites and myelinic figures was observed, the last one monotropically. In contrast to the thermotropic phase behaviour of compound **3**, displaying the nematic phase in a narrow range of temperatures, the lyotropic nematic area of **3**–linear alkane systems exists in a wide temperature range, *e.g.* 92 °C in the **3**–decane system, on heating. The temperature range of the nematic phase was smaller when the length of the solvent molecule and the length of the substituents in the metalloorganyl **3** were more different (Table 2).

---

† Characterization data for complex **2**: yield: 73%. Elemental analysis: found: C, 60.51; H, 7.22; N, 2.48%. Calc. for $C_{58}H_{84}N_2O_6Pd_2S$: C, 60.57; H, 7.36; N, 2.43%. IR (KBr disc): 1605, ν(C=N); 1522, 1458 cm^{-1}, ν(C=O). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.95 (s, 2H, H–C=N), 7.10 (d, 2H), 6.59 (dd, 2H), 7.19 (d, 2H, cyclometallated ring), 7.25, 6.84 (8H, AA′XX′ system), 4.14–3.90 (m, 8H, OCH$_2$), 2.47 (m, 2H, SCH$_2$), 1.60 (s, 3H, CH$_3$–CO$_2$).

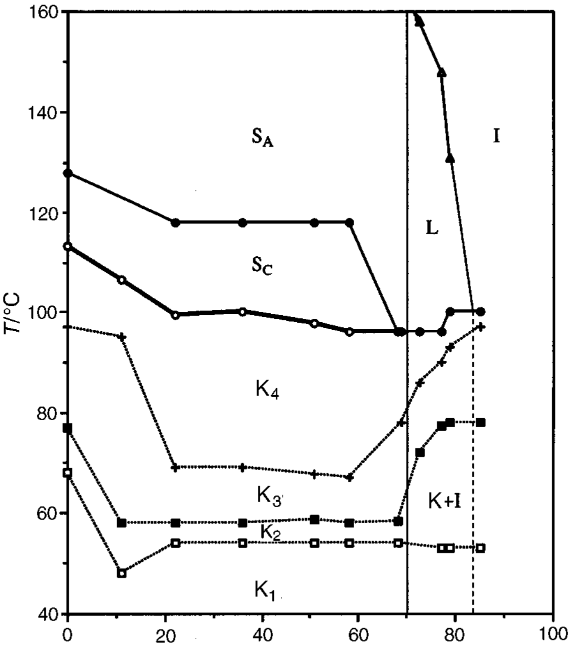


Fig. 2 Simplified phase diagram of the binary system **1c**–pentadecane in the region of lyomesophase formation, based on optical microscopy and DSC measurements of the mixtures with defined contents of the components (on heating): K_{1-4} = crystalline phases, S_C = smectic C phase, S_A = smectic A phase, L = lamellar phase, I = isotropic region

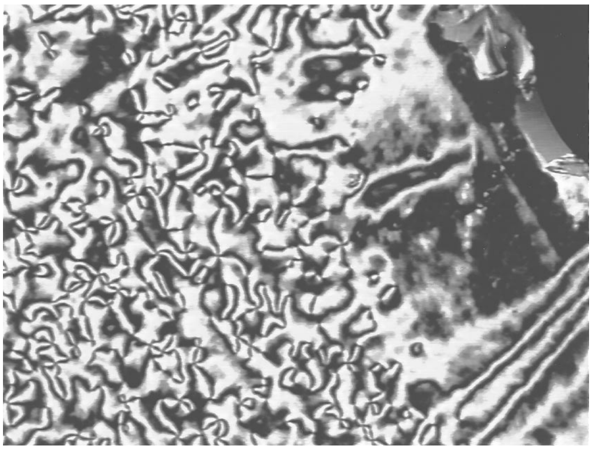


Fig. 3 Schlieren texture of the nematic phase in the binary system **2**–pentadecane; contact preparation, $T = 32$ °C, on cooling, magnification ×200

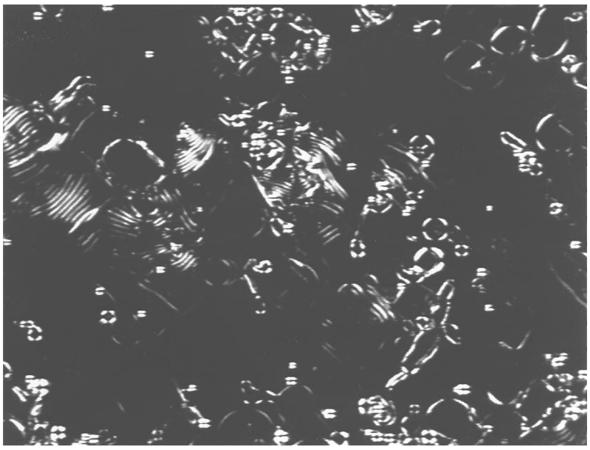


Fig. 4 Myelinic figures and spherulites in the binary system **1c**–(*R*)-(+)-limonene; contact preparation, $T = 32$ °C, on cooling, magnification ×200

In contact preparations with cycloocta-1,5-diene as solvent neither the dipalladium organyls **1** and **2**, nor the monopalladium organyl **3** display any lyomesophase. However, in binary systems with another cyclic solvent, (*R*)-(+)-limonene, the lyomesophase appearance and the type of lyomesophase depend on the structure of the palladium organyls. The **1a**/**1b**–(*R*)-(+)-limonene systems do not show lyomesomorphism, but a lyotropic phase with myelinic figures appears in the contact area of the **1c**–(*R*)-(+)-limonene system (Fig. 4).

In **2**/**3**–(*R*)-(+)-limonene preparations the existence of a chiral nematic lyomesophase (cholesteric, N*) is observed. This phase displays fingerprint, Grandjean and focal-conic cholesteric textures (Fig. 5). Qualitatively, the cholesteric pitch in the **2**–(*R*)-(+)-limonene system is larger than in the **3**–(*R*)-(+)-limonene system (at the same temperatures).

In both these compositions the N* phase exists in a very broad range of temperatures, including room temperature on cooling (Table 2). When a two-component mixture (limonene–pentadecane) was used as the solvent, the increase of the content of the pentadecane in this mixture (1:1, 1:2 or 1:3 mol%) caused an increase of the cholesteric pitch in the contact area.

The occurrence of myelinic figures in the contact preparations of **1b**, **1c** and **3** with apolar organic solvents is connected most probably with the formation of a lamellar lyotropic phase. In this case the general symmetry of the layered structure of the thermotropic smectic phase is kept in the lamellar lyotropic one, and lyotropic phase formation could be associated with an expansion of the arrangement existing in the absence of solvent (swollen process). The same manner of lyotropic nematic phase appearance is possible for the metalloorganyls **2** and **3**, which display nematic mesomorphism both in the thermotropic and in the lyotropic state. This is the first way of lyotropic phase formation in the metalloorganyls **1**–, **2**– and **3**–apolar organic solvent systems. Note that all contact preparations **3**–apolar organic solvent developed a very strong homeotropic orientation of the director in the nematic phase. The dark nematic pseudo-isotropic area on the border with the isotropic solution can be detected because of the strong thermal fluctuations, or by the schlieren texture existing 2–3 s after shearing of the sample. Usually, a special surface treatment is necessary for such an orientation of the nematogens.[9]

Table 2 Lyotropic phase behaviour of metalloorganyls **2**/**3**–apolar organic solvent systems[a]

		solvent				
compound	cycle	octane	decane	dodecane	pentadecane	(*R*)-(+)-limonene
2	heating	K 86 I	K 100 N 145 I	K 114 N 150 I	K 125 N 173 I	K 93 N* 147 I
	cooling	I 79 N(r.t.)	I 115 N 82 N+K(r.t.)	I 118 N 89 N+K(r.t.)	I 165 N(r.t.)	I 143 N*(r.t.)
3	heating	K 60 N 110 I	K 58 N 150 I	K 57 N 96 I	K 70 S 85 N 100 I	K 65 N* 136 I
	cooling	I 106 N 38 S(r.t.)	I 131 N 50 L 26 K	I 90 N 40 L 25 K	I 81 N 51 L 25 K	I 120 N*(r.t.)

[a] N = nematic phase; N* = chiral nematic phase; L = lamellar phase; S = smectic phase; K = crystalline phase; I = isotropic phase; (r.t.) = mesophase maintained at room temperature.

Table 3 Types of lyomesophases displayed in the binary systems of palladium organyls **1**–, **2**– and **3**–apolar organic solvent[a]

	compound (R^1, R^2)				
solvent	**1a** (OC_{10}, C_6)	**1b** (OC_6, C_6)	**1c** (OC_{10}, C_{10})	**2** (OC_6, OC_6, $R^3 = \mathrm{C}_6$)	**3** (OC_{10}, OC_{10})
octane	—	L	L	N (m)	N
decane	—	L	L	N	N, L (m)
dodecane	—	L	L	N	N, L (m)
pentadecane	—	L	L	N	N, L (m)
cycloocta-1,5-diene	—	—	—	—	—
(*R*)-(+)-limonene	—	—	L	N*	N*

[a] N = nematic phase; N* = chiral nematic phase; L = lamellar phase; (m) = monotropic.

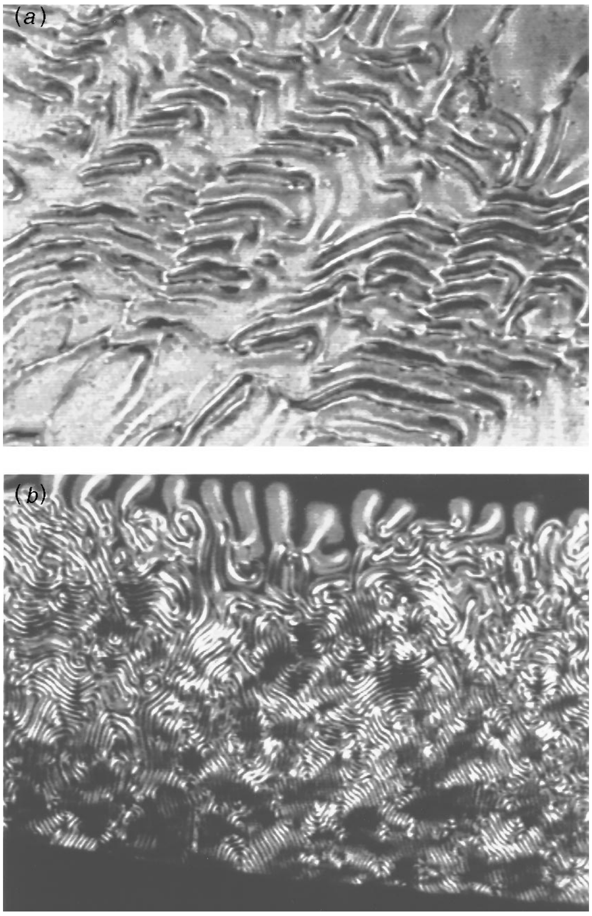


Fig. 5 Fingerprint textures formed in contact preparations of metalloorganyls with (*R*)-(+)-limonene: (*a*) chiral nematic phase of the **2**–(*R*)-(+)-limonene system, $T = 22\,^\circ\mathrm{C}$, on cooling; (*b*) chiral nematic phase of the **3**–(*R*)-(+)-limonene system, $T = 59\,^\circ\mathrm{C}$, on cooling; magnification ×200

More interesting is the occurrence of a new type of supramolecular organization in the lyotropic state, not found in the pure substance, which is the second way of lyotropic phase formation. This is the case of the formation of a lyotropic cholesteric phase in the systems composed of di- or mono-palladium organyls **2** and **3** with the chiral apolar organic solvent (*R*)-(+)-limonene. It is usual for the lyotropic aqueous compositions of amphiphiles that chiral nematic phases appear by adding chiral dopants (*e.g.* brucine sulfate) to the solvent forming a lyotropic nematic phase,[10a–c] or by dissolving chiral mesogens in aqueous media.[10d–f] Recently, one of us reported the first case of the lyotropic twisted nematic (N*) phase induced by a chiral charge-transfer complex composed of sheet-like tetrapalladium or tetraplatinum organyls with (+)- or (−)-TAPA [TAPA = 2-(2,4,5,7–tetranitro–9–fluorenylideneaminooxy) propionic acid] in apolar organic solvents.[2d,10g] The case reported here is the first case of lyotropic twisted nematic phase formation in the binary system non-chiral lath-like di- or mono-palladium organyl–chiral apolar organic solvent.

Conclusions

Dipalladium organyls of types **1** and **2** and monopalladium organyl **3** can display both thermotropic (Table 1) and lyotropic (with apolar organic solvents; Table 3) mesomorphic properties.

Both the ratio of the metallomesogen chain lengths to the length of alkanes used, and the structure of the apolar organic solvent, seem to have significant influences on the type of lyomesophase formed and on the temperatures of the phase transitions (see Table 2, Fig. 2). Two ways of lyotropic phase formation are possible in these above-mentioned lyotropic binary systems: (1) the preservation in the lyotropic mesomorphic state of the general symmetry existing in the thermotropic mesophase; and (2) the occurrence in binary systems of a new type of supramolecular packing, not typical for the thermotropic state of the pure substance, in this case a twisted nematic one. The size of the cholesteric pitch in these systems can be changed *via* addition to the chiral solvent of controlled amounts of the above mentioned linear alkanes.

Financial support of this work by the Spanish Dirección General de Investigación Científica y Técnica (SAB 95–0131) and the Comisión Interministerial de Ciencia y Tecnología (project MAT 93–0329) is gratefully acknowledged.

References

1 (*a*) C. Piechocki and J. Simon, *New. J. Chem.*, 1985, **3**, 159; (*b*) H. Groothues, F. Kremer, P. G. Schouten and J. W. Warman, *Adv. Mater.*, 1995, **7**, 283; (*c*) F. Lelj, G. Morelli, G. Riccardi, A. Roviello and A. Sirigu, *Liq. Cryst.*, 1992, **12**, 941; (*d*) D. W. Bruce, in *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992; (*e*) N. V. Usol'tseva and V. V. Bykova, *Mol. Cryst. Liq. Cryst.*, 1992, **215**, 89; (*g*) N. B. McKeown and J. Painter, *J. Mater. Chem.*, 1994, **4**, 1153; (*f*) N. Usol'tseva and K. Praefcke, oral presentation at the *International Symposium on Liquid Crystals and Supramolecular Order, January 3–5, 1996, Bangalore, India*, to be published in *Mol. Cryst. Liq. Cryst.*, 1996.

2 (*a*) K. Praefcke, D. Singer and B. Gündogan, *Mol. Cryst. Liq. Cryst.*, 1992, **223**, 181; (*b*) K. Praefcke, B. Bilgin, J. Pickardt and M. Borowski, *Chem. Ber.*, 1994, **127**, 1543; (*c*) N. Usol'tseva, K. Praefcke, D. Singer and B. Gündogan, *Liq. Cryst.*, 1994, **16**, 601; (*d*) K. Praefcke, B. Bilgin, N. Usol'tseva, B. Heinrich and D. Guillon, *J. Mater. Chem.*, 1995, **5**, 2257.

3 P. Espinet, M. A. Estruelas, L. A. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.*, 1992, **117**, 215.

4 (*a*) D. W. Bruce, D. A. Dunmur, P. M. Maitlis, J. M. Watkins and G. J. Tiddy, *Liq. Cryst.*, 1992, **11**, 127; (*b*) D. W. Bruce, J. D. Holbray and G. J. Tiddy, *9th Ann. Conf. British Liq. Cryst. Soc.*, University of Hull, Hull, 1994, poster 49.

5 D. W. Bruce, M. A. Wali and Q. M. Wang, *J. Chem. Soc., Chem. Commun.*, 1994, 2089.

6 H. T. Nguen, C. Destrade and J. Malthète, *Liq. Cryst.*, 1990, **8**, 797.

7 (*a*) M. J. Baena, P. Espinet, M. B. Ros and J. L. Serrano, *J. Mater.*

Chem., 1996, **6**, 1291; (*b*) N. J. Thompson, J. L. Serrano, M. J. Baena and P. Espinet, *Chem. Eur. J*., 1996, **2**, 186; (*c*) M. J. Baena, J. Buey, P. Espinet, H-S. Kitzerow and G. Heppke, *Angew. Chem., Int. Ed. Engl*., 1993, **32**, 1201.

8 (*a*) C. Casagrande, M. Veyssie and H. Finkelman, *J. Phys. Lett*., 1980, **43**, 671; (*b*) P. Ekwall, in *Advances in Liquid Crystals*, ed. G. Brown, Academic Press, New York, San Francisco, London, 1975, vol. 1, p. 1.

9 H. Kelker, *Handbook of Liquid Crystals*, ed H. Kelker and R. Hatz, Weinheim, Deerfield, Verlag Chemie, 1980, p.14.

10 (*a*) K. Radley and A. Saupe, *Mol. Phys*., 1978, **35**, 1405; (*b*) L. J. Yu and A. Saupe, *J. Am. Chem. Soc*., 1980, **102**, 4879; (*c*) T. M. H. DoAido, M. R. Alcantara, O. Felippe, Jr., A. M. J. Pereira and J. A. Vanin, *Mol. Cryst. Liq. Cryst*., 1993, **226**, 195; (*d*) K. Radley and H. Cattey, *Liq. Cryst*., 1992, **12**, 875; (*e*) *Mol. Cryst. Liq. Cryst*., 1993, **226**, 195; (*f*) M. R. Alcántara and J. A. Vanin, *Liq. Cryst*., 1995, **18**, 207; (*g*) N. Usol'tseva, K. Praefcke, D. Singer and B. Gündogan, *Liq. Cryst*., 1994, **16**, 617.

Paper 6/05361K; *Received* 31*st July*, 1996