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Phenyl-cyclohexyl enaminketone ligands and their Cu(II) complexes

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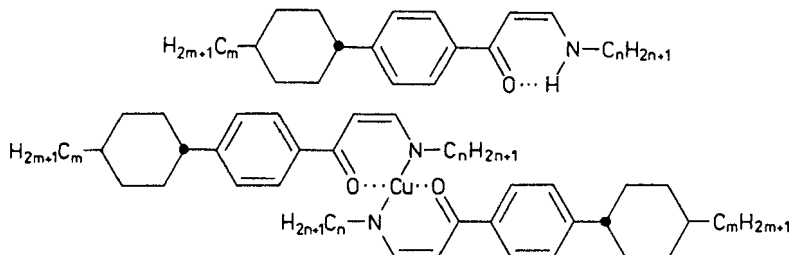
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The liquid crystalline properties of 1-(alkylamino)-3-[(4''-hexyl-*trans*-cyclohexyl)-4'-phenyl]-prop-1-en-3-one-s, from methyl to octadecyl, and their copper(II) complexes have been examined by optical, DSC, X-ray and EPR methods. The compounds are enantiotropic nematogens except those having the shortest and the longest terminal chains. Short chains promote the S_A phase in both ligands and complexes, whereas long chains promote S_C and crystal H phases for the ligands or S_A and S_C phases for the complexes. A partly bilayer smectic A_d phase is observed from ligands terminated with short non-polar substituents. Direct isotropisation from the crystal H phase for some of the compounds, as well as other phase transitions have been studied. The molecular shape of the complexes and the organization of their mesomorphic phases are discussed, based on the refractive indices and X-ray data.

1. Introduction

Mesogenic cores having built-in non-condensed quasi-rings stabilized by intramolecular hydrogen bonds have recently been taken into account in the search for novel liquid crystalline materials [1, 2]. The enaminketones, as compared with other hydrogen-bonded compounds are highly promising materials with respect to their rod-like molecular shape and their ability to yield stable complexes with transition metals. The ligands, as a rule, form mesophases with rather wide temperature ranges and give various types of smectic polymorphism. Their copper(II) complexes, when properly designed, also form thermally stable mesophases [3]. In this work we present the liquid crystalline properties of a homologous series of enaminketone ligands and their complexes:



denoted as m,nLH and m,nL_2Cu , respectively. The compounds belonging to the $6,nLH$ and $6,nL_2Cu$ series have been examined by optical, DSC, X-ray and EPR methods.

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2. Results

2.1. Ligands

The phase diagram for the $6,nLH$ series is presented in figure 1. Most of the ligands are low melting nematogens, except those having the shortest and the longest terminal N -alkyl chains. The short chains promote a partly bilayer smectic A_d phase, whereas long chains favour monolayer smectic C and crystal H phases. The appearance of the

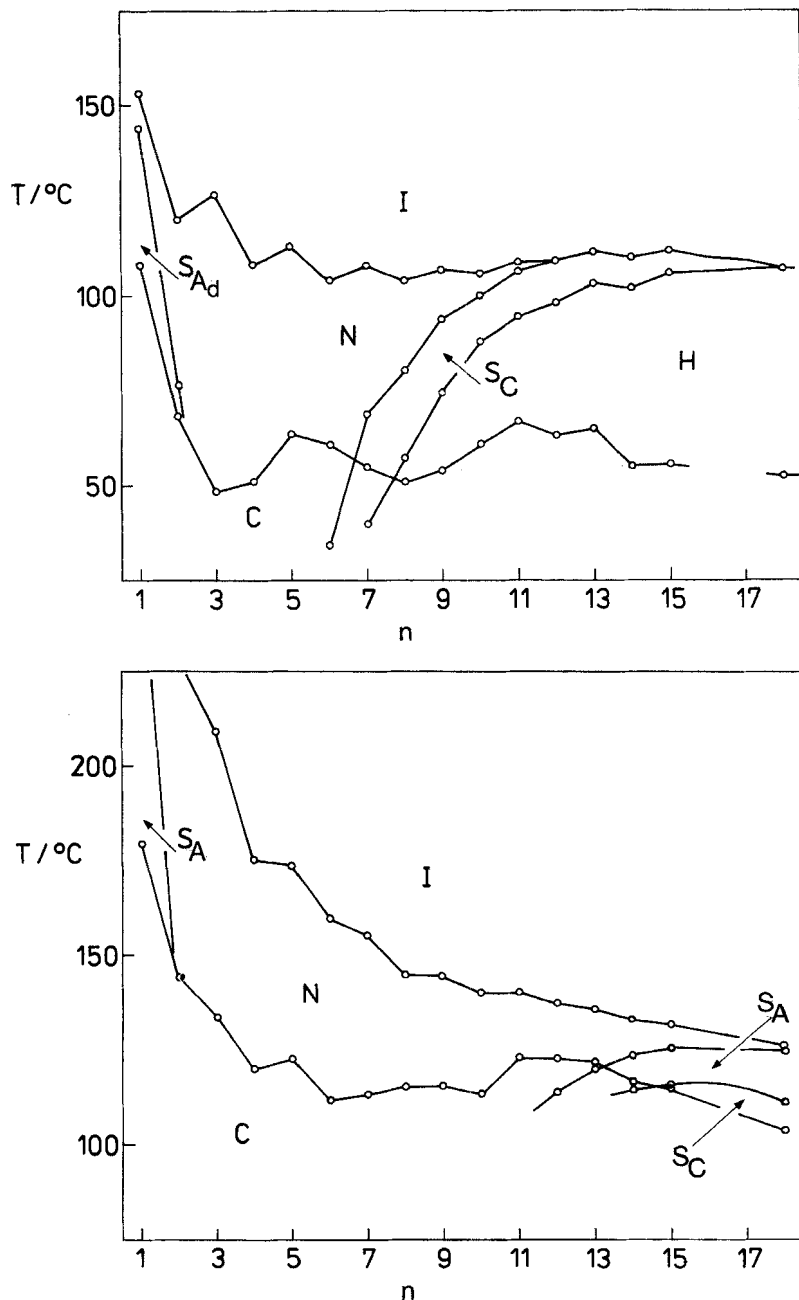


Figure 1. Phase diagrams for the ligands $6,nLH$ (upper) and their copper(II) complexes $6,nL_2Cu$ (lower).

S_{Ad} phase in compounds without terminal nitro or cyano groups is rather exceptional [4]. However, it is possible that in these compounds, the *cis-s-cis* enaminketone rings, if terminated with short alkyl chains, act as strongly polar terminal groups. In fact, the observed d/L ratio, *c.* 1.65, points to interactions between enaminketone groups as a factor which determines the layer thickness.

For compounds having a crystal-crystal H-smectic C-isotropic phase sequence, both mesophases are distinctly tilted. Tilt angles calculated as $\vartheta = \arcsin(d/c)$ are presented in table 1. The smectic layer thickness d and the *c*-parameter of the crystal H unit cell were determined from analysis of X-ray diffraction spectra. As can be seen, no remarkable tilt jumps accompany the S_C -crystal H transitions. A standard calculation procedure, which uses the fully extended molecular length L instead of *c*, gives angles about 8° higher. However, the possibility of shrinkage of the molecular tails must be considered (see below).

A unique phase sequence, crystal-crystal H-isotropic, with a wide, *c.* 80°C mesophase range occurs for the longest homologues. The crystal H phase grows in the form of plates from the isotropic liquid as a natural texture. The shape and size of the plates depend on the cooling rate. Just below the phase transition, they are smooth and rather pale. On cooling, more birefringent cloverleaf-shaped defects usually appear at the plate boundaries. Zig-zag defects, which are characteristic for the crystal H phase [4, 5], were also observed. The number of such defects gradually increases with decreasing temperature. Some of the textures are presented in figure 2.

The molecular arrangement in the crystal H phase was deduced from X-ray data. The strongest high angle diffraction lines were assigned to the (110) and (200) reticular

Table 1. X-ray diffraction data for $6,n\text{LH}$ ligands and $6,n\text{L}_2\text{Cu}$ complexes. All (*hkl*) indices are (001), if not stated otherwise. CPK molecular lengths, L , are given in brackets. Density, γ , is expressed in Mgm^{-3} and ϑ is the tilt angle.

	$T/^\circ\text{C}$	Mesophase	d/nm	d/L	$\vartheta/^\circ$
6,1LH [2.38]:	115	S_{Ad}	3.98	1.67	
	125	S_{Ad}	3.95	1.66	
	135	S_{Ad}	3.83	1.61	
6,9LH [3.38]:	70	H	2.766 (001), 0.507 (20 $\bar{2}$), 0.485 (20 $\bar{1}$), 0.457 (110), 0.453 (200), 0.417 (201)		28
		Unit cell:	$a = 1.027$, $b = 0.530$, $c = 3.136$, $\beta = 118^\circ$; density: $\gamma = 0.965$		
6,18LH [4.51]:	80	S_C	2.75		28.5
	90	S_C	2.81		26.5
	70	H	4.009 (001), 2.05 (002), 0.473 (20 $\bar{2}$), 0.451 (110), 0.451 (200), 0.433 (201)		18
	Unit cell:	$a = 0.947$, $b = 0.521$, $c = 4.220$, $\beta = 108^\circ$; density: $\gamma = 0.948$ $\beta = 107.5^\circ$			
6,1L ₂ Cu[4.06]:	165	S_A	3.43	0.84	
	130	S_A	3.47	0.86	
	100	S_A	3.57	0.88	
	80	S_A	3.60	0.89	
6,15L ₂ Cu[4.19]:	100	S_C	3.53	0.84	
	120	S_A	3.51	0.84	
6,18L ₂ Cu[4.91]:	105	S_C	3.76	0.77	
	110	S_C	3.78	0.77	
	115	S_A	3.79	0.77	

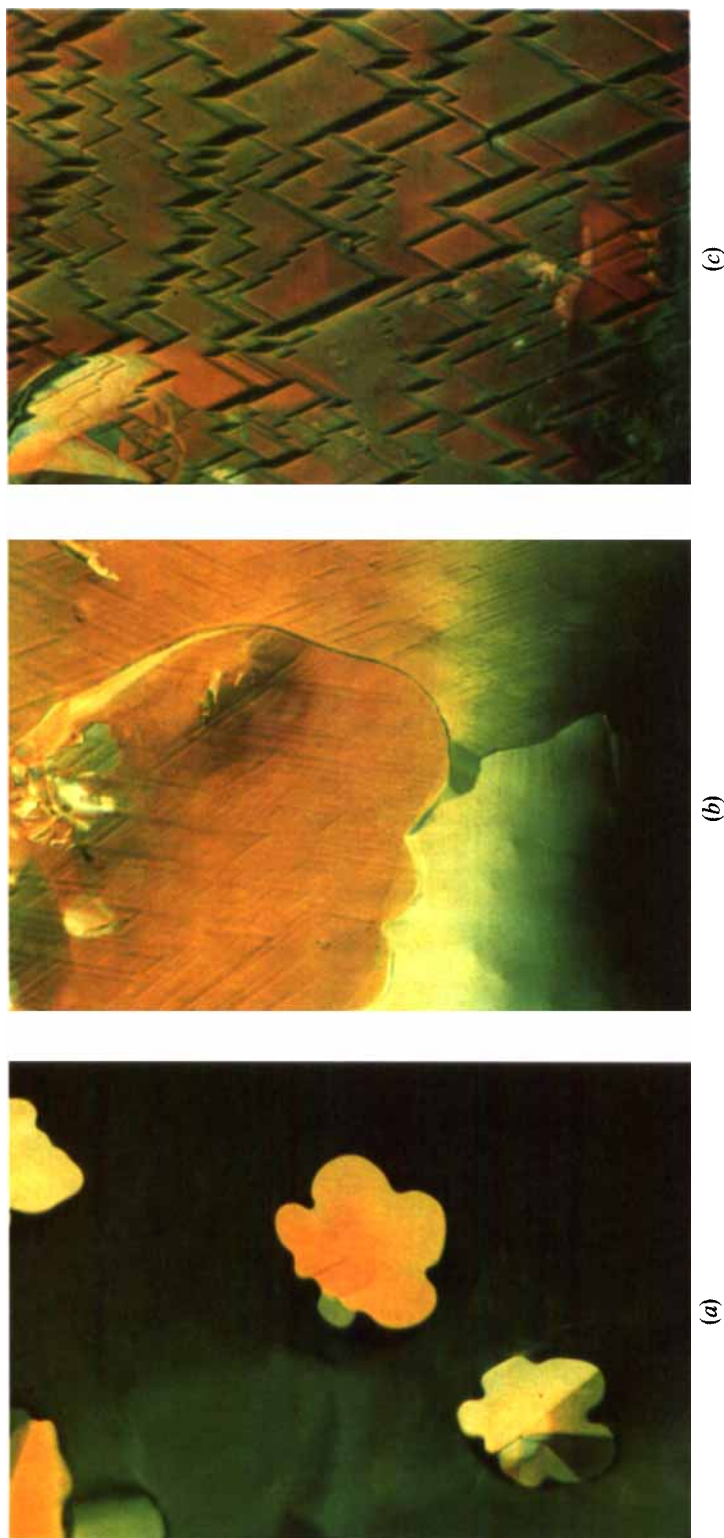


Figure 2. Natural textures of the crystal H phase for the 6,18LH ligand at different temperatures: T_{H} – T is 0-1, 0-5, 25°C for (a), (b) (c), respectively.

Table 2. Phase transition temperatures ($^{\circ}\text{C}$) and, in parentheses, the enthalpies (J g^{-1}) for the ligands of the 6,nLH series.

<i>m</i>	C	H	S_C	S_{Ad}	N	I
1	• 107.8	(65.0)	—	• 144.3	• (3.4)	• (3.7)
2	• 68.4	(83.1)	—	• 76.8	• (0.15)	• (2.05)
3	• 48.3	(40.4)	—	—	—	• (3.15)
4	• 51.2	(59.1)	—	—	—	• (2.5)
5	• 63.6	(46.0)	—	—	—	• (3.05)
6	• 61	(6.1)	—	—	—	• (3.2)
7	• 55.2	(49.5)	• 40	• 35	• (1.2)	• (3.85)
8	• 50.8	(81.1)	• 57.8	• 68.9	• (2.3)	• (3.85)
9	• 54	(4.2)	• 74.6	• 80.3	• (3.4)	• (4.6)
10	• 61.3	(84.5)	• 83.3	• 94.1	• (3.2)	• (5.1)
11	• 66.7	(47.8)	• 94.3	• 100.1	• (2.8)	• (5.5)
12	• 64.1	(44.4)	• 97.8	• 106.6	• (3.2)	• (5.8)
13	• 65	(40.5)	• 103.2	• 109.0	• (16.5)†	• (5.8)
14	• 55	(82.9)	• 102.1	• 111.4	• (18.8)	• (5.8)
15	• 54.2	(75.3)	• 106.1	• 109.8	• (19.1)	• (5.8)
18	• 54.1	(98.4)	• 107.4	• 110.6	• (19.3)	• (5.8)

† Subsequent peaks not resolved.

reflections [5]. The resulting parameters of the unit cell for some of the compounds are given in table 1. It is seen that the tilt angle decreases with increasing length of the terminal substituents. Similar behaviour has been observed for other homologous series [5]. Of interest is the a/b ratio, which differs from the value expected for hexagonal ordering. Deviations, being 12 per cent and 5 per cent for 6,9LH and 6,18LH, respectively, point to a significant influence of the molecular tilt on the herringbone arrangement. In turn, the c parameter is 7 per cent shorter than the molecular lengths obtained from CPK models. This indicates, that for these compounds, the long terminal alkyl chains are partly melted or interdigitized.

Calorimetric data for the phase transitions are presented in table 2. They are typical for calamitic mesogens. The only exception is an extremely high enthalpy of direct isotropization from the crystal phase, $c. 40 \text{ J g}^{-1}$. However, it is still lower than the enthalpy of melting. Also, long terminal chain compounds belonging to related series behave in a similar way, for example the enthalpies of isotropization for 10,15LH and 10,18LH are 38.1 and 40.4 J g^{-1} , respectively. Noteworthy also is the enthalpy of the first order crystal H-S_C transition, which decreases linearly with shortening of the terminal chain. On that basis, the existence of a critical end point on the transition line between tilted smectics and crystal smectics cannot be excluded. Unfortunately, this point, if it exists, is not accessible in the $6,n\text{LH}$ series because of crystallization.

Clearing entropies for the ligands and the complexes are presented in figure 3. The Landau-de Gennes phenomenological theory [6] relates the entropy of isotropization from the nematic phase, $\Delta S = (1/2)aQ_{\text{NI}}^2$, to the discontinuity of the order parameter, Q_{NI} , as well as to the amplitude, a , of the component $(1/2)a(T - T^*)Q^2$ contributing to the free energy of the system. The parameters involved can be determined independently from an analysis of precritical phenomena in the nematic and the isotropic phase,

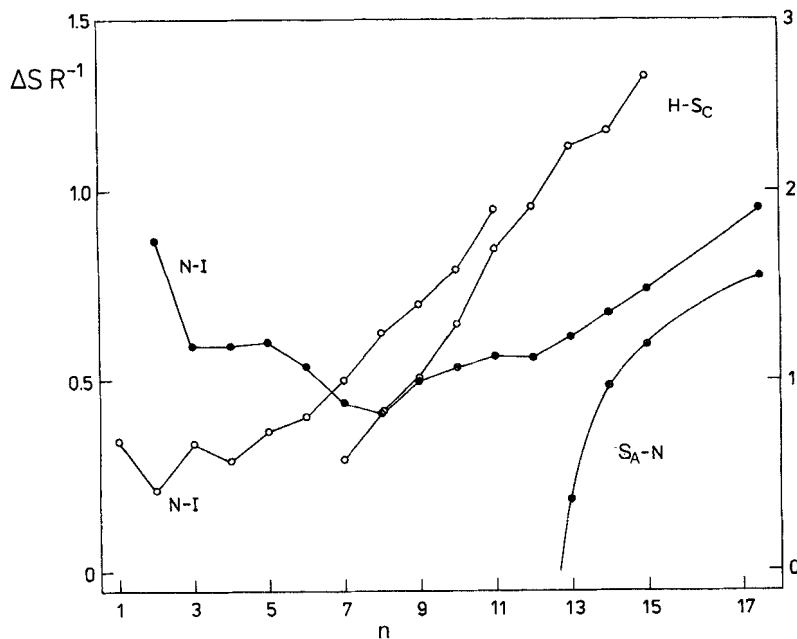


Figure 3. Entropies of phase transitions for the ligands $6,n\text{LH}$ (\circ) and their copper(II) complexes $6,n\text{L}_2\text{Cu}$ (\bullet). Data for the crystal H-S_C phase transition constitute the right-hand scale.

Table 3. Phase transition temperatures ($^{\circ}\text{C}$) and, in parentheses, the enthalpies (J g^{-1}) for the complexes of the $6, \mu\text{L}_2\text{Cu}$ series.

m	C	S_{C}	S_{A}	N	I
1	●	179.5 (39.2)	—	270 (dec.)	●
2	●	144.0 (38.3)	—	—	●
3	●	133.4 (33.7)	—	—	●
4	●	120.1 (27.7)	—	—	●
5	●	122.6 (34.5)	—	—	●
6	●	112.1 (37.3)	—	—	●
7	●	113.6 (38.2)	—	—	●
8	●	115.6 (49.6)†	—	—	●
9	●	115.5 (50.5)	—	—	●
10	●	113.4 (43.5)	—	—	●
11	●	122.5 (51.2)	—	—	●
12	●	122.5 (45.6)	—	—	●
13	●	122.2 (46.5)	—	—	●
14	●	116.4 (42.1)	●	114 120.2 (0.4)	●
15	●	114.8 (43.7)†	●	123.5 (1.4)	●
18	●	103.6 (32.5)	●	126.1 (1.8) 125.3 (2.0)	●
			●	235 (4.9) 209.2 (3.05) 175.2 (2.75) 173.7 (2.7) 160.0 (2.25) 155.5 (1.8) 145.2 (1.6) 145.2 (1.85) 140.3 (1.9) 140.4 (1.95) 137.5 (1.85) 136.0 (2.0) 132.9 (2.2) 131.6 (2.25) 125.8 (2.6)	●

† Subsequent polymorphic transition peaks not resolved.

respectively. For some of the compounds, we have determined Q_{NI} from the refractive indices (see §2.2.). Then, from the entropy data we obtained amplitude values of $a=9.2\text{ R}$ and 5.8 R for 6,7LH and 6,7L₂Cu, respectively. For free energy density, the amplitude for the ligand is $0.22 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$, which is a typical value for polar nematogens. Also the optical polarizability is typical for three-ring cyclohexyl derivatives, being for example $58.5 \times 10^{-40} \text{ m}^2 \text{ J}^{-1} \text{ C}^2$ for the compound 6,7LH.

2.2. Complexes

For the 6, n L₂Cu complexes, the clearing temperature decreases with increased length of the N -alkyl substituent, whereas the melting temperature varies non-monotonically, having minima at 100–110°C. Such behaviour is similar to that observed for the 2, n L₂Cu series [3]. As a result, a uniaxial nematic phase of low viscosity is formed over a wide temperature range (for example *c.* 75°C for 6,3L₂Cu). For compounds terminated by either very short or long N -alkyl substituents, smectic phases are formed. The topology of the phase diagram is similar to that observed for the ligands. However, in the case of the complexes, layers thinner than the length of the fully extended molecules are formed in the S_A phase for both short and long homologues (see table 3). A similar topology of the phase diagram, with a distinct nematic gap between short and long chain smectics, was reported previously for some book-shaped orthopalladated azine complexes [7].

Inspecting the clearing entropies (see figure 3), we can see that short chain terminated complexes give more pronounced thermal changes than the parent ligands. Therefore, either their free energy is more influenced by the ordering, (higher a factor), or they are more ordered (higher Q_{NI} factor). A value of $a=0.065 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$ for 6,7L₂Cu, found from analysis of the transition entropy and the refractive index, is one quarter of that for 6,7LH. Therefore, the stronger ordering of metallo-organic mesophases is probably responsible for their higher clearing entropies. A comparison of the amplitudes a for different complexes is not possible because of a lack of relevant literature data.

An insight into the molecular geometry of the complexes is possible by examining some tensor properties of the compounds and comparing them to the relevant properties of the parent ligands. For this purpose we measured extraordinary and ordinary refractive indices, n_{\parallel} and n_{\perp} , for 6,7L₂Cu and 6,7LH in their nematic phases. Data now presented in figure 4 were analysed by assuming a simplified pretransitional behaviour of the nematic ordering, $Q = Q^{**} + A_0 t^{\beta}$, and applying Vuks equations for refractive indices [8]

$$N\alpha = 3\varepsilon_0(\bar{n}^2 - 1)/(\bar{n}^2 + 2), \quad (1a)$$

$$NQ\Delta\alpha = 3\varepsilon_0(n_{\parallel}^2 - n_{\perp}^2)/(\bar{n}^2 + 2), \quad (1b)$$

where

$$Q = (1 - T/T^{**})^{\beta}. \quad (2)$$

Here N is the volume number of molecules, $\bar{n}^2 = (n_{\parallel}^2 + 2n_{\perp}^2)/3$, and $\alpha = (\alpha_1 + \alpha_2 + \alpha_3)/3$ and $\Delta\alpha = (2\alpha_1 - \alpha_2 - \alpha_3)/2$ are the mean molecular polarizability and the anisotropy, respectively. The resulting relative anisotropy of a hypothetical, perfectly ordered phase, the thermal coefficient of density and some critical parameters for the nematic–isotropic phase transition are given in table 4. It is seen that the normalized anisotropies of the ligand and the complex are different and their ratio

$$\Delta = (\Delta\alpha/\alpha)_{\text{LH}}/(\Delta\alpha/\alpha)_{\text{L}_2\text{Cu}}, \quad (3)$$

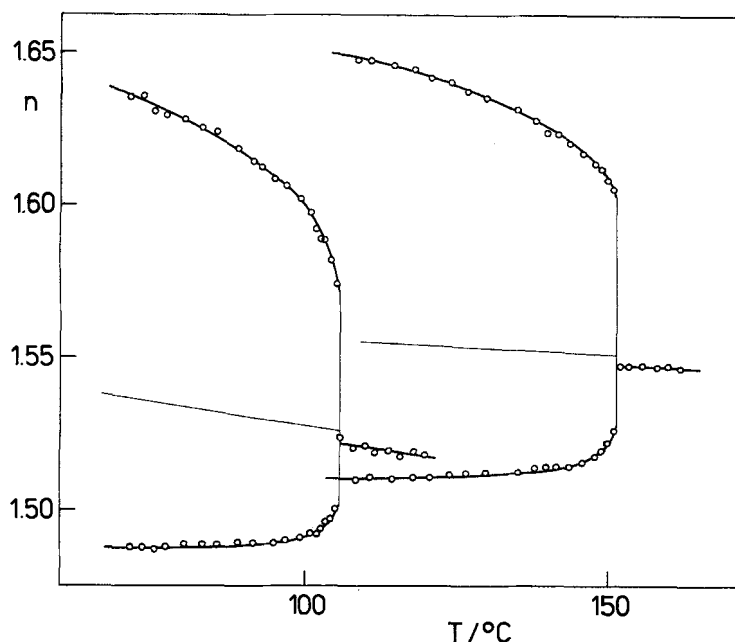


Figure 4. Refractive indices, $\lambda = 623$ nm, for the 6,7L₂Cu complex (right) and the parent ligand 6,7LH (left).

Table 4. Parameters for the nematic phase of 6,7LH and 6,7L₂Cu as derived from the analysis of refractive indices (see equations (1) and (2)).

	6,7LH	6,7L ₂ Cu
$10^{40} \alpha$	58.5 ± 0.5	$135 \pm 5 \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$
$A\alpha/\alpha$	0.510	0.438 ± 0.004
$Q(T_{NI})$	0.33	0.39 ± 0.01
$d\gamma/dT$	-0.61	$-0.24 \pm 0.03 \text{ kg m}^{-3} \text{ K}^{-1}$
$T^{**} - T_{NI}$	0.6	$1.1 \pm 0.1 \text{ K}$
β	0.170	0.157 ± 0.005

amounting to 1.164 ± 0.02 , is remarkably different from unity. Therefore, a collinearity of the ligands within individual molecules of the complex or within molecular clusters must be excluded.

The angle γ between the ligand axes can be roughly estimated by assuming their coplanarity. Neglecting a contribution of the central copper atom to the anisotropy of the polarizability, we get

$$\sin^2 \gamma = \frac{2}{3} [1 - (1 + A)/\Delta], \quad (4)$$

where $A = \alpha_{\text{Cu}}/2\alpha_{\text{LH}}$ is the polarizability excess resulting from complexation of the copper ion. The determined angle γ is $35 \pm 5^\circ$. This value indicates that the coordination type of an isolated molecule is intermediate between planar and tetrahedral. An alternative explanation assumes the existence of short range angular intermolecular correlations in the nematic phase.

The geometrical parameters characterizing a distorted chelate core can, in principle, be determined from analysis of the EPR g -tensor [9]. For m,nL_2Cu complexes in both the nematic and isotropic phases, only one broad, almost symmetrical EPR line is observed. Thus we had to desist from a numerical analysis of the spectra [10]. A small increase in line anisotropy is observed during the transition into the smectic A and C phases. The line is located at about $g=2.09$, which corresponds to the isotropic g -value for the copper(II) ion. The broadening of the line shape can be attributed to the presence of a variety of locally ordered structures, resulting in a wide distribution of the g -factor, divalent copper pair formation, etc. Similar spectra were reported for some copper complexes of polymeric salicylaldimines [11].

X-ray data for the smectic phase reveal an anomalous layer thickness, distinctly less than the length of the fully extended molecules. A value of d/L of about 0.8 is typical for long homologues. Such a shortening of the interlayer distance in the orthogonal S_A phase has been observed also for copper complexes based on salicylaldimine ligands [12]. However, a remarkable temperature $d(T)$ dependence observed for $6,1L_2Cu$ seems to be a new feature. The longitudinal dimension of this rod-like complex is defined by the length of its rigid core, together with two pendant hexyl substituents. The magnitude of the layer compression corresponds to permeation of the layers to a length of two C–C bonds or, less likely, to a complete melting of the alkyl chains. A possible deformation of the planar chelate core could also be considered as a factor influencing the layer thickness.

Recently, the possibility of the existence of a ferromagnetic order in chiral mesogenic phases composed of paramagnetic molecules has been suggested [13]. In view of the presence of the smectic C phase in the m,nL_2Cu series, we tried to modify the compounds by introducing chiral centres into the molecules as close as possible to the chelate core. Using in the synthesis procedure some 2-aminoalkanes, $H_2N-CH(CH_3)-C_{n-1}H_{2n-1}$, instead of 1-aminoalkanes, $H_2N-CH_2-C_{n-1}H_{2n-1}$, we synthesized complexes having two chiral atoms attached directly to the core. However, the nematic phase appeared to be monotropic and the strong depression of the clearing temperature was discouraging. Thus, for example, $10,10L_2Cu$ (mp $111^\circ C$) and its chiral analogue (mp $80^\circ C$) clear at $132^\circ C$ and $33^\circ C$, respectively. Complexes having chiral centres separated from the mesogenic core and exhibiting enantiomorphic mesophases will be described elsewhere.

3. Discussion

For the presence of a stable, hydrogen-bonded quasi-ring built into a mesogenic core, enaminketone ligands behave like rigid molecules and form conventional mesophases. The ratio of the terminal chain length to the core length controls the presence of partly bilayer smectic A_d (in the case of short substituents), monolayer smectic C and crystal H phases (in the case of long chains) or the nematic phase (in intermediate cases). The properties of the nematic phase are typical for polar nematogens, although none of the terminal substituents is distinctly polar.

Copper complexes of enaminketones reveal a similar topology of the phase diagram, although the smectic phases are less ordered than those formed by free, long tailed ligands. Based on the mesomorphic properties and qualitative studies of refractive indices, it was previously suggested that, in the nematic phase, the complexes are planar rather than tetrahedral [3]. Analysis performed in this work gives some evidence that the axes of the ligands are not strictly collinear. This may result either

from a distorted planarity of the chelate core, or from remarkable angular correlations between neighbouring molecules. The first possibility would be consistent with the well-known plasticity of four-coordinated copper complexes [9, 14]. However, the EPR data suggest, that the second possibility must be also taken into account. The same factors (molecular distortion or molecular interactions) could be responsible for the compression of the smectic layers because of the reduced length arising from V-shaped molecules or X-shaped clusters.

Recent X-ray [15] and EXAFS [16] studies of some salicylaldehyde liquid crystalline copper complexes provide data indicating the presence of copper-copper correlations at distances corresponding to both molecular width and thickness. Thus, the smectic phases of metallomesogens may be composed of small statistical clusters of individual molecules. Cluster geometry is defined by intermolecular interactions between chelate cores, which favour a momentary stacking ordering, and steric repulsions between lateral substituents, which lead to a mutual twisting of interacting molecules. A loose structure of X-shaped clusters, or alternatively, non-planar complex molecules promotes interdigitization of smectic layers. To choose between these two concepts and to get a more complete understanding of the properties of the mesomorphic complexes, further studies are necessary.

4. Experimental

Compounds were synthesized analogously to the 2_nLH and 2_nL_2Cu series [3]. Microscopic observations (ortho- and cono-sopic) were performed using a Jenapol-U polarizing microscope and a Mettler HP82 hot stage. DSC thermograms were obtained using a Perkin-Elmer DSC7, at a scan rate of $5^\circ C \text{ min}^{-1}$. To resolve the signals corresponding to those phase transitions occurring over a narrow temperature range, the scan rate was reduced to $0.2-1^\circ C \text{ min}^{-1}$. Refractive indices were measured goniometrically using He-Ne light. EPR spectra were recorded using an X-band Radiopan spectrometer. X-ray diffractograms of powder samples were recorded using a Guinier camera and $Cu-K_\alpha$ radiation.

Note added in proof.—Careful analysis of EPR spectra of phenylazophenyl-enaminketone $Cu(II)$ complexes confirms planarity of the chelate core in diluted solutions as well as in the S_C mesophase [17].

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