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Re-entrant Isotropic Phase between Lamellar and Columnar Mesophases

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Received March 19, 2002

Abstract: Tetradental cis-enaminoketone Ni (II) complexes with different molecular shape have been synthesized. Intramolecular hydrogen bonds, which stiffen the mesogenic core and restrict rotation of some molecular parts, have been introduced in these compounds. In the case of molecules with two hydrogen bonds and alkoxy terminal chains filling the inner molecular space, the uncommon phase sequence Iso−D_h−Iso_{re}−SmA (series **III-3**) was detected. For the first time, it was observed that the isotropic re-entrant (Iso_{re}) phase (short-range order) is separating the columnar (D) (high-temperature) and the lamellar (SmA) (low-temperature) phases, both revealing long-range ordered structures.

1. Introduction

The nature of a liquid crystalline phase is distinctly dependent on the shape of its constituent molecules. Rodlike or disklike molecular anisotropy facilitates molecular ordering leading to the lamellar or columnar phase, respectively.[1−3] However, many other substances, which do not follow this general rule, have already been synthesized. In particular, there are compounds which form both types of mesomorphic structure within a single homologue series and a few examples of compounds exhibiting smectic as well as columnar phases as a function of temperature.[4−8] The columnar phase appears more frequently as the higher temperature phase; however, the reverse phase sequence especially with an oblique columnar mesophase (D_{ob}) has also been reported.[9] For some substances, the phase transition between these two types of structures has been found to be direct,[10] but there are also compounds in which the substantial rebuilding of the liquid crystalline structure needs a transitional phase. This is the case of some tetracatenars mesogens where the separating phase is of cubic type.[4,11]

To facilitate both lamellar and columnar phase formation in one substance, the rodlike or disklike mesogenic shapes were modified to obtain molecules with a hybrid shape (between rod- and disklike). The substances with a triangular mesogenic core, formed by two cis-enaminoketone rings, similar to the complexes reported previously,[2,3,12] have been synthesized. In this paper, we describe the case of Ni(II) complexes where lamellar (SmA) as well as columnar hexagonal (D_h) phases were found in the same compound as a function of temperature. The phase separating both liquid crystalline structures is the re-entrant isotropic phase. According to our best knowledge, this is the first time that such a phase sequence has been found in a pure compound. However, it should be noted that the isotropic re-entrant phase has been already reported for a tetracatenar mesogen where the Iso_{re}−Cub phase sequence separates two lamellar phases,[9] and also for truxene derivatives where a columnar phase is surrounded by two isotropic phases.[13,14]

2. Experimental Section

2.1. Structure of the Complexes. To receive the substances exhibiting both lamellar and columnar phases, three main series of complexes, in which the relevant molecular shape can be adjusted, were synthesized (Scheme 1, Table 1).

Alkoxy chains substituted at different positions of aroyl rings allowed for the elongation[3] or broadening[12] of the molecules and enforced the particular conformation. Simultaneously, the hydroxy groups at ortho-positions broadened and stiffened the molecular core. In the first series, the octyloxy chains were attached to the aroyl rings at the fourth positions; in the second series, these chains were substituted at the fourth and fifth positions; and in the third series, alkoxy chains were substituted

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10.1021/ja026234v CCC: $22.00 © 2002 American Chemical Society

Scheme 1. Schematic Structures of the Synthesized Series of Complexes **I**−**III**

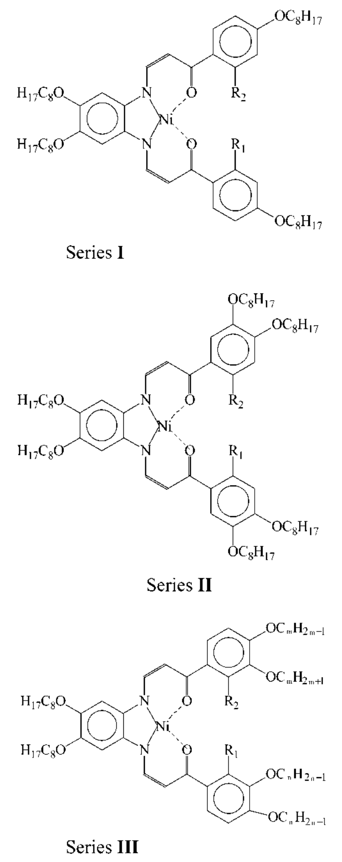


Table 1. Synthesized Series of the Compounds

R_1	R_2	series **I**	series **II**	series **III**
H	H	**I-1**	**II-1** = **III-1**	**II-1** = **III-1**
OH	H	**I-2**		
OH	OH	**I-3**	**II-3**	**III-3a**−**3d**[a]
OCH_3	H	**I-4**		
OCH_3	OCH_3	**I-5**		**III-5**
OCH_3	OH	**I-6**		**III-6**
OC_8H_{17}	OH	**I-7**	**II-7**	**III-7**
OC_8H_{17}	OC_8H_{17}	**I-8**	**II-8**	**III-8**

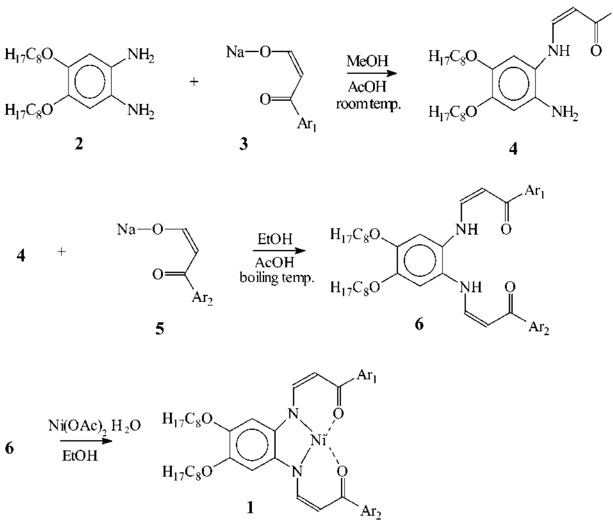
[a] For materials **III-3a**−**3d**, the details are in Table 3.

at the third and fourth positions of the aroyl rings. In each of these series, the substituents R_1 and R_2 at the second positions were modified, and the H, OH, OCH_3, OC_8H_{17} groups were applied.

In all of the compounds, the nickel ion was inserted into the coordination plane to allow NMR structural studies; however, other complexes with transition metals such as Cu(II) or Co(II) could also be synthesized.

2.2. Synthesis. The synthetic procedure to obtain the designed complexes with identical or different aroyl moieties is sketched in Scheme 2. The starting materials are known substances, and their synthesis is a routine. Formyl ketone sodium salts **3** were obtained by the Claisen formylation reaction. 4,5-Dioctyloxy-1,2-phenylenediamine **2** (1 mmol) and the sodium salt of formyl ketone **3** (1 mmol) dissolved in methanol (100 mL), neutralized with acetic acid (to pH about 6), reacted at room temperature selectively. The aroylvinyl group was joint only to one of the amino groups resulting in a crystalline intermediate **4**. Compound **4** was purified by recrystallization from octane (yield ~80%). The remaining amino group of compound **4** reacted further with a formyl ketone derivative **5** (1 mmol) at the boiling point of ethanol (50 mL), giving rise to the tetradentate ligand **6** after 10 min. A metal salt, nickel(II) acetate, dissolved in hot ethanol (15 mL) was added to the boiling mixture. After 5 min of reflux, the mixture was cooled, resulting in the precipitate of compound **1**, which was filtered off. The product **1** was recrystallized from hexane. The complexes having di- or trialkoxy-substituted aroyl rings were recrystallized from 2-propanol. For the symmetrical ligands (Ar_1=Ar_2), the 4,5-dioctyloxy-1,2-phenylenediamine **2** (1 mmol) and the 2-hydroxy substituted formyl ketone, sodium salt **4** (3.3 mmol), were used, and the complexes obtained after 10 min of reflux were chromatographed on silica gel, eluted with hexane/methylene chloride solvents (1:1). To obtain the **III-3d** complex, the same synthetic procedure was applied using 3-methoxy, 4-octyloxy 1,2-phenylenediamine as **2** substrate.

Scheme 2. Synthetic Route to the Tetradental cis-Enaminoketone Complexes



The NMR spectra as well as the results of elemental analyses are presented as Supporting Information.

2.3. Measurements. The mesophase identification was based on microscopic examination of liquid crystalline textures. A Zeiss Jenapol-U polarizing microscope equipped with a Mettler FP82HT hot stage was used. Phase transition temperatures were mainly determined by calorimetric measurements performed with a DSC-7 Perkin-Elmer setup at a scanning rate of 5 K min^{-1}. When heat effects were undetectable or when the phase transitions were monotropic, the temperatures were taken from the microscopic observations. For some compounds, the mesophase structure was studied by X-ray diffraction. The measurements were carried out on powder samples in Lindemann capillaries; the patterns were registered with an Inel CPS 120 curved positional sensitive counter and confirmed with a Gunier setup. The sample temperature was controlled within 0.1 K. Molecular dimensions were estimated by molecular modeling (Hyperchem). NMR spectra were recorded by a Varian Unity Plus spectrometer operating at 500 MHz.

3. Results and Discussion

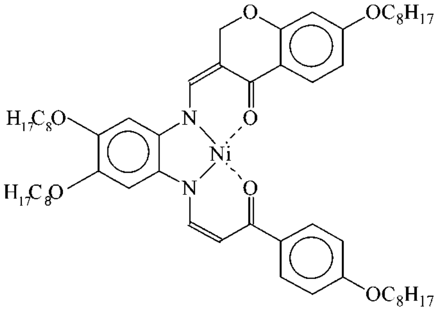
The mesomorphic properties, the phase sequence, phase transition temperatures, and enthalpy changes of the synthesized compounds, are summarized in Tables 2 and 3. Enantiotropic as well as monotropic liquid crystalline phases are observed.

Similar to the complexes described previously,[12] most of the compounds included in series **I** exhibit smectic phases (SmA and SmC). When the aroyl rings of the mesogenic core are substituted at ortho-positions (R_1 and R_2), their rotation around the phenyl−carbonyl bond is substantially biased. The introduction of the hydroxy moieties leads to the formation of intramolecular hydrogen bonds between protons coming from the hydroxy groups and oxygen atoms belonging to the carbonyl groups. These weak bonds totally restrict the aroyl ring's rotation

Table 2. Melting Points, Phase Sequences, Phase Transition Temperatures (in °C), and Phase Transition Enthalpy Changes (in Parantheses, J g^{-1}) for the Synthesized Compounds

complex no.	melting point	phase sequence, phase transition temperatures, and enthalpy changes
I-1	137.2 (37.6)	SmA − 122.2 (micr. obs.) − Iso
I-2	146.7 (35.6)	SmA − 132.6 (micr. obs.) − Iso
I-3	135.3 (37.9)	SmA − 108.5 (4.4) − Iso
I-4	124.5 (50.92)	SmC − 114.4 (0.6) − SmA 117.3 (7.4) − Iso
I-5	124.5 (39.0)	SmA − 81.4 (5.9) − Iso
I-6	139.5 (29.6)	SmC − 118.2 (1.1) − SmA 126.5 (1.5) − Iso
I-7	57.2 (16.6)	
I-8	103.8 (27.2)	SmA − 100.0 (micr. obs.) − Iso
II-1	115.1 (12.0)	
II-3	below room temp	D_h 210.5 (micr. obs.) − Iso
II-7	100.3 (52.0)	D_h − 137.2 (2.1) − Iso
II-8	87.9 (45.5)	
III-3a−3d	see Table 3	
III-5	60.1 (40.1)	
III-6	59.4 (24.6)	
III-7	78.3 (12.7)	
III-8	below room temp	D_h − 68.0 (13.7) − Iso
IV-1	99.5 (20.3)	SmC − 79.9 (4.7) − Iso
V-1	below room temp	D_h − 189.9 (2.2) − Iso

Scheme 3. Structure of Complex **IV-1**



and make the mesogenic core flat and more rigid. The presence of the hydrogen bonds was proved by the proton NMR spectra. The proton signal of the hydrogen bond was found at ca. 12 ppm as a singlet (e.g., in compound **I-3**). Further confirmation of the hydrogen bond was taken from the peak related to the other ortho-substituted proton of the same aroyl ring. This signal is changed and can be seen at 7.49 ppm. For comparison, when the second aroyl ring has not any substituent (e.g., compound **I-2)** or has (e.g., compound **I-6**) an ortho-substituent unable to form the hydrogen bond, the NMR signal of the residual ortho-proton is not influenced and appears at its usual place at ca. 8 ppm. For compound **IV-1**, in which the epoxymethano-bridge stops the aroyl ring rotation (Scheme 3), the nonshifted ortho-substituted proton signal at ca. 8 ppm can also be seen.

The mesophase's stability was found to be slightly better for complex **I-2** with one hydrogen bond than for complexes **I-3** with two hydrogen bonds or compound **I-1** without any. This suggests that the too strong stiffening of the molecular core depresses the calamitic phase formation.

Further modification of the R_1 and R_2 moieties by using the alkoxy groups of various length reveals their destructive influence on rodlike structures. The presence of two methoxy groups (compound **I-5**) seems to disturb the mesophase formation more than the presence of one methoxy group (compound **I-4)**. The isotropization temperature is higher in the latter complex **I-4** than in the former compound **I-5**. Comparing complex **I-5** to compound **I-8**,[12] the liquid crystalline stability was found to be enhanced for the complex with the longer terminal chains, the clearing point being higher for compound **I-8**. It can be supposed that both ortho-substituted octyloxy chains are directed along the molecular symmetry axis and can stabilize the calamitic phases. As for the compounds containing different R_1 and R_2 groups, complex **I-6** having the hydroxy and methoxy substituents exhibits SmA and SmC phases, whereas complex **I-7** having the hydroxy and octyloxy groups does not reveal any liquid crystalline property. The mesophase creation probably results from two competitive tendencies: stiffening of the molecular core by the hydrogen bond, which depresses the calamitic phases, and elongation of two ortho-substituents promoting these mesophases.

Broadening the molecular structure (series **II**) by introducing octyloxy chains at the fourth and fifth positions of the aroyl rings destroys the lamellar phases definitely for compound **II-1**. Two hydroxy groups, forming the hydrogen bonds, inserted as R_1 and R_2 drastically change the mesomorphic properties that lead to the conversion of the lamellar into the columnar phase. Complex **II-3** exhibits the columnar hexagonal phase stable over a wide temperature range (more than 190 K) with the melting point below room temperature. The isotropization enthalpy was difficult to measure because of decomposition of complex **II-3** above 200 °C. Two inner hydrogen bonds appear to be essential in the columnar phase formation because of stiffening and broadening of the molecular core. In compound **II-7**, the hydrogen bond and the long octyloxy chains at the R_1 and R_2 positions, respectively, biased the rotation of both molecular parts. However, this molecular core is less rigid than that in compound **II-3**, resulting in the formation of the columnar hexagonal phase, which is stable in a narrower temperature range.

No mesophase was found for compound **II-8** having both ortho-octyloxy (R_1 and R_2) substituted aroyl rings. Complex **II-8** has an external molecular shape similar to that of complex **I-8**.[12] These two molecules, in their most probable conforma-

Table 3. Melting Points, Phase Sequences, Phase Transition Temperatures (in °C), and Phase Transition Enthalpy Changes (in Parantheses, J g^{-1}) for Compounds **III-3a−3d**

complex no.	group **III-3**	melting point	phase sequence, phase transition temperatures, and enthalpy changes
III-3a	$n, m = 8$	102.2 (37.3)	SmA − 77.7 (1.6) − Iso_{re} − 95.0 (1.8) − D_h − 197.5 (2.2) − Iso
III-3b	$n, m = 10$	93.3 (29.2)	SmA − 76.2 (2.9) − Iso_{re} − 103.2 (1.3) − D_h − 164.2 (1.1) − Iso
III-3c mixture	0.25 of **III-3a**, 0.25 of **III-3b**, 0.5 of $n = 8$, $m = 10$	92.2 (28.2)	SmA − 76.5 (2.8) − Iso_{re} − 101.3 (1.4) − D_h − 179.3 (0.5) − Iso
III-3d	$n = 8$	98.1 (13.7)	SmA 104.1 (2.4) − Iso

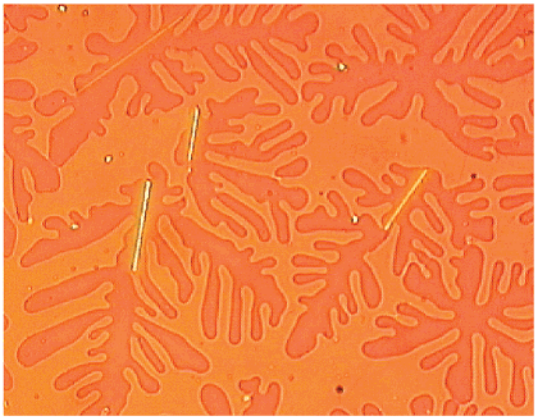


Figure 1. The D_h phase of compound **III-3b** growing from the Iso phase at 161 °C observed without polarizers.

tions, differ in filling the inner molecular space between the para-substituted octyloxy chains. In compound **I-8**, this space, remained free, promotes the smectic A phase formation.

It is worth noticing that complex **V-1** having two hydroxy groups at R_1 and R_2 positions, forming inner hydrogen bonds and bearing only two octyloxy chains, joint at the fifth positions, without any alkoxy chains at the para-positions (Scheme 1), exhibits the enantiotropic columnar D_h phase. The temperature range of this D_h phase is slightly narrower than that of the broadest one found in the D_h phase for complex **II-3**.

For the compounds substituted at the second, third, and fourth positions (**III-3** series), the mesophases appear only in the complexes having two hydrogen bonds (**III-3** subgroup described separately) or when all of the substituents are the octyloxy chains (compound **III-8**).[12] The contour of the latter compound **III-8** is the closest to a circular shape, so the columnar hexagonal phase, stable at room temperature, is formed. For complexes **III-5**, **III-6**, and **III-7** with mixed hydroxy and alkoxy ortho-substituents, the aroyl ring's rotation is biased. However, the stiffening of the core is too weak and the molecular shape is not disklike enough to promote columnar phases.

From the point of view of the mesomorphic behavior, the complexes from the subgroup **III-3** appear to be the most interesting and are described below.

3.1. Isotropic Re-entrant Phase Separating Lamellar and Columnar Phases. In subgroup **III-3**, two hydrogen bonds enforce the molecular conformation in which the meta-substituents always fill the inner space between the para-substituted octyloxy chains, as was similarly found for the **II-8** compound. Stiffening of the molecular core by the hydrogen bonds is essential and leads to an exotic polymorphism. Homologous complexes with either octyloxy or decyloxy terminal chains were synthesized. The compounds **III-3a**, **III-3b**, and the mixture **III-3c** exhibit an uncommon phase sequence: Iso−D_h−Iso_{re}−SmA. The phases were identified because of characteristic optical textures (Figure 1).

On cooling, at the transition temperature between the D_h and Iso_{re} phases, a black isotropic texture appeared against the background of the birefringent texture of the hexagonal columnar phase (Figure 2).

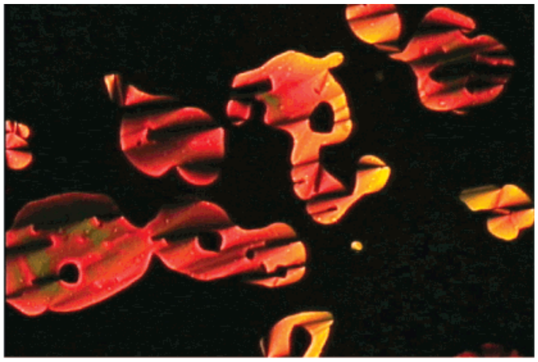


Figure 2. Texture at the D_h−Iso_{re} phase transition of compound **III-3b**.

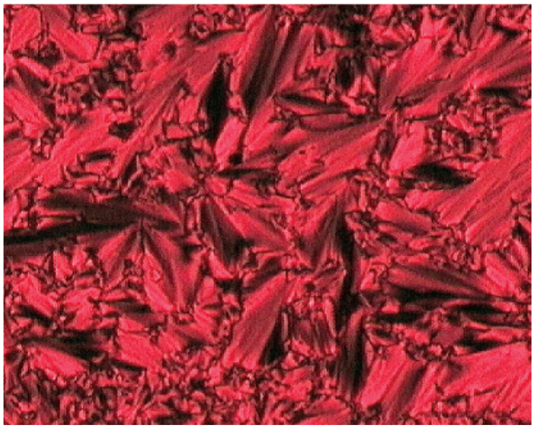
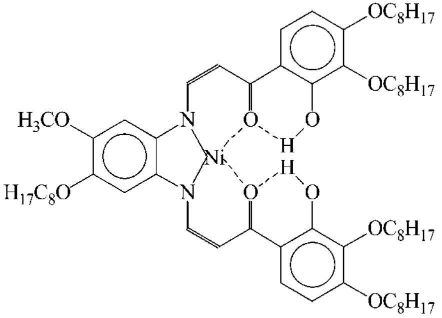


Figure 3. Fanlike texture of SmA phase of compound **III-3c**.

Scheme 4. Structure of Complex **III-3d**



The viscosity of the isotropic re-entrant phase was substantially lower than that of the D_h phase, and the isotropic droplets were identical to the liquid ones formed at the upper D_h−Iso clearing point. The smectic A phase is monotropic and is difficult to determine immediately in compounds **III-3a**, **III-3b**. To lower the recrystallization temperature, the mixture **III-3c** exhibiting the same phase sequence was prepared, and the presence of the monotropic smectic A, being the lowest temperature phase, was confirmed (Figure 3).

Further attempts to reduce the recrystallization temperature by symmetry breaking of the synthesized compounds were not fully successful. By replacing one octyloxy chain at the diamniophenyl molecular part by the methyloxy moiety, we found that the corresponding compound **III-3d** exhibits only a smectic A phase (Scheme 4).

A planar focal-conic texture of complex **III-3d** is identical to the texture of the smectic A phase of the **III-3c** mixture. The nature of the phase is also confirmed by a contact sample preparation between the two smectic A phases formed by substances **III-3a** and **III-3d**, showing a complete miscibility.

Table 4. Crystallographic Distances (in Å) Obtained from X-ray Diffraction Signals for Complexes **III-3b** and **III-3d** and (in Parentheses) Values Calculated from the Hexagonal Crystallographic Cell ξ − Correlation Length (in Å)

complex no.	phase	low angle			high angle		cell dimensions
III-3b	Iso	24.9			3.4	4.6	
		$\xi = 100$			$\xi = 6.0$	$\xi = 3.1$	
	D_h	(200) = (110)	(020) = (310)	(400) = (220)	(001)		$a = 49.4$
		24.7	14.3	12.3	3.4	4.6	$b = 28.5$
							$c = 3.4$
		$\xi = 190^a$			$\xi = 9.5$	$\xi = 3.3$	
	Iso_{re}	26.2			3.4	4.3	
		$\xi = 35$			$\xi = 7.3$	$\xi = 3.5$	
III-3d	SmA	(001)				4.4	
		27.4					
		$\xi = 163$				$\xi = 2.6$	

[a] Limit of the diffractometer resolution.

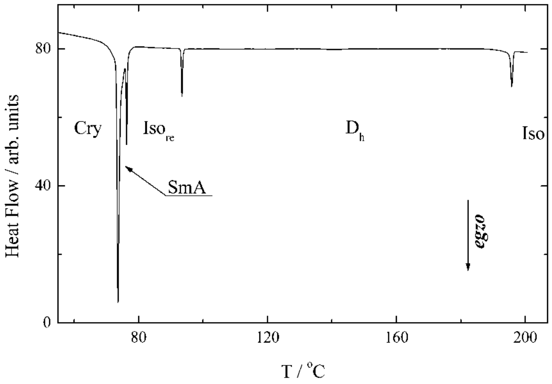


Figure 4. DSC thermograph of compound **III-3a**.

The DSC thermograms for all of the compounds of this subgroup **III-3** confirm the phase transition temperatures detected under microscope (Figure 4).

The enthalpy changes at the D_h−Iso_{re} transition on cooling are exothermic. At the Iso_{re}−SmA transition, the values of the enthalpy changes are rather small (1−3 J/g) in comparison to the common Iso−SmA transition (usually 10−30 J/g). Moreover, for the **III-3d** compound, exhibiting only the smectic A phase, the transition enthalpy at the isotropization point is also relatively small and similar to that of the Iso_{re}−SmA transition.

Crystallographic distances measured in the X-ray studies are collected in Table 4. The diffractogram of the **III-3b** compound (Figure 5a) confirms the nature of the columnar hexagonal phase. In the small angle region, the most intensive signal is assigned to (200) = (110) = (1-10) crystallographic indices related to the centered planar rectangular cell, describing hexagonal lattice. Also, (020) = (310) and (400) = (220) reflections are visible. The intercolumnar distance calculated form the X-ray data (b = 28.5, Table 4) is smaller than the largest measured molecular dimension (35 Å) for the most extended conformation, which could suggest that about six carbon atoms of the terminal chains interdigitate in the D_h phase. In the wide-angle region, two diffused signals are observed − one being related to the distance between the molecular disks, and the other one to the liquidlike order of the alkoxy chains. Assuming that in the single crystallographic cell there are two molecules, we found the density of the D_h phase calculated from received cell dimensions (see Table 4) to be ca. 0.88 g/cm^3. It seems to be a very low value; however, the mesogens of similar structure, described before, also have very low density in the D_h phase.[2,12]

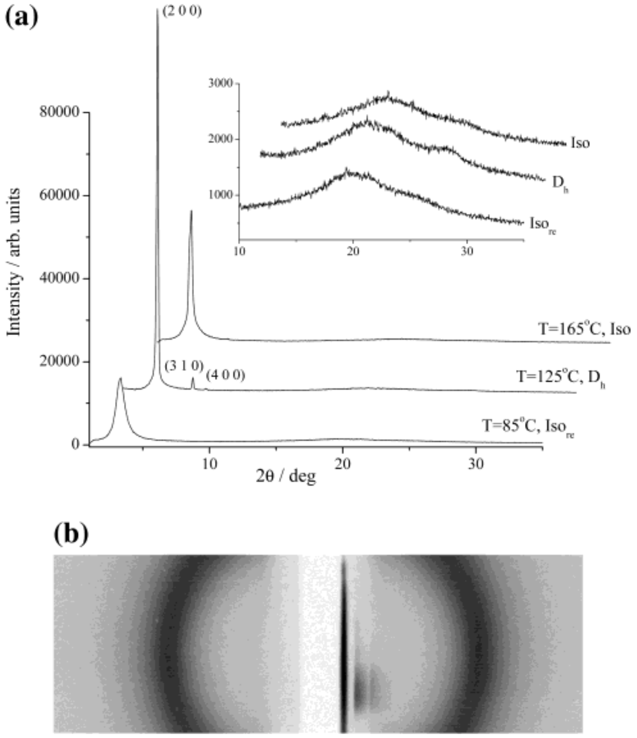


Figure 5. (a) X-ray diffraction pattern of compound **III-3b**; in the inset is the enlarged high angle region. (b) Diffused low angle signal recorded in Iso_{re} phase showing liquidlike molecular ordering.

In the diffractogram of the low-temperature re-entrant isotropic phase, two signals in the wide-angle region as well as a rather broad peak of low intensity in the small angle region are visible, suggesting that some short-range order remains from the D_h phase structure. The low angle signal is slightly shifted toward longer distances when compared to the (200) reflection of the D_h phase. The shape of the low angle peak, obtained in the Guinier camera, is smooth (Figure 5b), thus excluding any ordered phases, for example, the cubic phases. This confirms that the low-temperature phase is undoubtedly a re-entrant isotropic phase. On the contrary, the X-ray spectra of the known cubic phases reveal crystallographic distances, characterized by a series of sharp peaks in the small angle region.[5,15,16]

The X-ray spectra of the upper temperature isotropic phase, just above the clearing point, also show broad signals at positions

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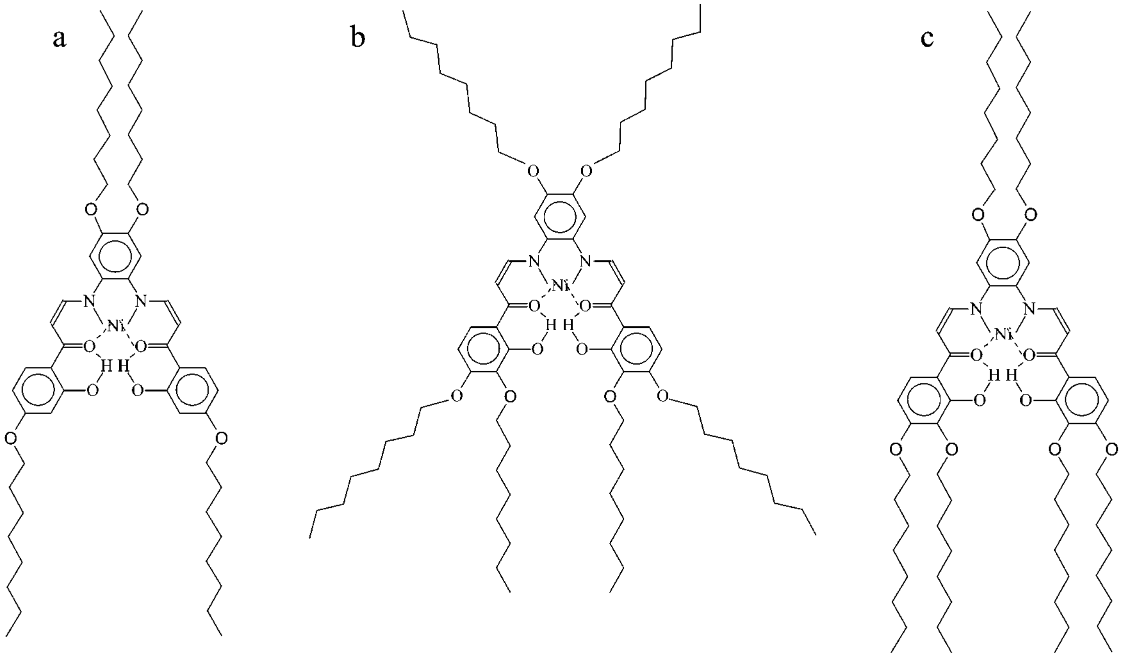
Scheme 5. Possible Conformation of the Alkoxy Chains (a) for Complex **I-3**, (b and c) for Compound **III-3a**



similar to those in the D_h phase, pointing to the presence of columnar-like fluctuations. However, the low angle peak is somewhat more intense and narrower as compared to the related signal in the Iso_{re} phase. The data (for the **III-3b** complex) of the low angle peaks fitted to the Lorentzian line shape $S(q) \approx [1 + \xi^2(q - q_o)^2]^{-1}$ ($q = 2\pi/d$) indicate a transverse correlation length ξ that changes substantially for successive phases (Table 4). For the re-entrant Iso_{re} phase, the ξ value seems to be constant in the whole phase temperature range. In the Iso phase, close to the clearing point, this correlation length is much higher than that for the Iso_{re} phase, but drastically falls with increasing temperature. The longitudinal correlation length taken from the wide-angle signals, related to the intracolumnar molecular order (signal (001)), is the highest for the D_h phase. In both isotropic phases, these peaks are much weaker and give similar ξ values. The correlation length related to the distance between alkyl chains remains almost unchanged in three phases.

The X-ray diffractogram of the **III-3d** compound, forming only the smectic A phase, reveals one low angle signal (Table 4). The smectic layer thickness (27.4 Å) is slightly shorter than the molecular length (32 Å) measured by molecular modeling, because of the interdigitation of the terminal alkoxy chains.

Assuming that the in-plane disordered SmA phase has a local hexagonal molecular arrangement and the phase density is similar to that of the columnar phase (0.88 g/cm^3), we calculated the molecular area (in the plane perpendicular to the director) to be 77 Å^2 for the single layer arrangement. It gives an averaged 8−9 Å intermolecular distance, which is much smaller than the molecular width (11 Å), being expected in the SmA phase from molecular modeling (Scheme 5a). However, because of the triangular core shape and possible alternating molecular arrangement in one layer, the molecules could be packed with a shorter averaged molecular distance than that estimated from molecular dimensions.[17]

4. Conclusions

We have synthesized the lath-like tetradental cis-enaminoketone Ni(II) complexes. Some of them (compounds **III-3a−c**) exhibit the Iso−D_h−Iso_{re}−SmA phase sequence, which has never been observed before. The isotropic re-entrant phase separates the columnar and lamellar phases. The described compounds have an intermediate molecular shape between the rod- and disklike ones, which is probably necessary for the appearance of this unique phase sequence. However, the important factor in the molecular structure is the presence of two intramolecular hydrogen bonds that stiffen the molecular core. These bonds restrict the aroyl ring's rotation and limit the number of available molecular conformations.

In subgroup **III-3**, containing the hydrogen bonds, the meta-alkoxy-substituents at aroyl rings always fill the inner space between the para-substituted chains so the molecular width depends exclusively on the external para-chains. At higher temperature, almost all terminal-chain conformations are available, and thus the chains broaden the molecular shape effectively. Moreover, the para-chains are pushed away by the inner meta-substituents (Scheme 5b). In the case of the most spread-out structure, the length to width (L/W) ratio was estimated to be 1.1, which is inherent to the D_h phase. In the lower temperature, the carbon atoms of the alkoxy-chains are expected to be in all trans-conformations. For this low-energy system, the molecules tend to form parallel alignment of the terminal chains that result in the elongated molecular structure (Scheme 5c). The measured L/W ratio is 2.9, which is identical to that of compound **I-3** (Scheme 5a), having the same external molecular shape and revealing only the smectic A phase.

It can be supposed that the same molecules forming lamellar or columnar phases differ in their conformations. These structural differences give the various length to width (L/W) ratios which seem to be crucial for the molecular microsegregation into proper liquid crystalline phases in which the molecules rotate around one of their axes. In the hexagonal

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(17) Krówczyński, A.; Górecka, E.; Pociecha, D.; Szydłowska, J.; Przedmojski, J. *Liq. Cryst.* **1996**, *20*, 607.

columnar phase, molecules rotate around the short axis perpendicular to the flat core and, in the smectic A phase, around the long axis placed in the core plane. However, in some temperature range in which the molecular shape is not distinctively elongated or flat, the molecules do not have any single axis to rotate exclusively around. It seems that the rotation around neither the short nor the long axis is prevailing enough to dominate and form a liquid crystalline phase. Thus, effectively the molecular movement appears to be isotropic, and the reentrant isotropic phase emerges as the intermediate phase between lamellar and columnar phases. The presence of both lamellar and columnar phases fluctuations is probably responsible for the shorter correlation length measured in the $\mathrm{Iso_{re}}$ than in Iso phase. In the latter, the $\mathrm{D_h}$ phase fluctuations may only appear. Moreover, in the re-entrant isotropic phase, the molecular rotation can be supposed to take place only around two axes without movement around the third, medium axis.

It is also worth emphasizing that in our compounds the intramolecular hydrogen bonds promote the columnar and depress the calamitic phases. In the presence of the hydrogen bond, the columnar phase appears for the substance **V-1** containing only one pair of meta-substituents, whereas for the compounds lacking the hydrogen bonds, as many as six external octyloxy substituents (complex **III-8**) are necessary to create the columnar phase.

Acknowledgment. The work was supported by KBN Grant No. 3T09A 046 15.

Supporting Information Available: Spectral and elemental analyses (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA026234V