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Metallomesogens Modified by Hydrogen Bonds or by Bridging Groups—New Re-entrant Isotropic Phase

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Two series of tetradental *cis*-enaminoketone Ni(II) complexes with triangular mesogenic core stiffened by external ethylene or methylene units have been synthesized. One of the obtained compounds reveals a unique phase sequence: Iso−Col_h−Iso_{re}. The enormously stable Col_h phase has been detected for metallomesogens having both an external methylene unit and inner hydrogen bonds. Also a new synthetic way to receive 5,6-dialkoxy-7-hydroxyindanone has been presented.

1. Introduction

Up to now only few examples of the re-entrant isotropic phase (Iso_{re}) have been observed. The Iso_{re} phase has been found in the phase sequences Iso−N−Iso_{re}−Cub−Sm C[1] or as an intermediate phase between the columnar and calamitic structures, i.e., Iso−Col_h (D′)−Iso_{re}−N_D−Col_h (D′),[2−4] Iso−Col_h−Iso_{re}−Sm A.[5] However, a bicontinuous cubic phase has been reported more frequently than the Iso_{re} phase as the phase separating columnar and calamitic phases, for example, in the tetracatenar compounds homologous series.[6,7] Also the direct transition between the columnar and the lamellar smectic A phase has been detected.[8−10] The unique mesomorphism with the re-entrant isotropic phase,[5] as the intermediate phase, has been recently found in the materials having a triangular mesogenic core (Table 1), which consist of two *cis*-enaminoketone pseudorings, to which two phenyl rings are joint. Such a mesogenic core is of hybrid shape between rodlike and disklike and can give calamitic as well as discotic molecules. For these compounds the essential factor determining appearance of both lamellar and columnar phases in temperature sequence is the inner hydroxy moieties inserted into the mesogenic core. The hydrogen bonds restrict the aroyl rings' rotation and fill the inner core space.

To examine the influence of the core rigidity in the molecule on the appearance of the re-entrant isotropic phase, two new series of the Ni(II) tetradental complexes in which the core was modified have been synthesized. The inner hydrogen bonds have been replaced by external bridges (ethylene or methylene units), and to fill the inner space of the core the octyloxy or hydroxy groups have been applied. Among obtained substances a new compound exhibiting the re-entrant isotropic phase have been found.

2. Experimental Section

2.1. Structure of the Complexes. Two series of the Ni(II) tetradental complexes containing a triangular core with external ethylene and methylene bridges are presented: series I, tetralone compounds **7**−**12** (Table 2) and **6** (Scheme 2), and series II, indanone compounds **13**−**22** (Table 3). The ethylene (series I) or methylene (series II) unit joins the α-carbon atom of the *cis*-enaminoketone part with the ortho-carbon atom of the aroyl ring and creates an additional ring comprising six or five carbon atoms, respectively. The core changes make the molecular contour broadened. In each of the obtained series the molecular shape has been also modified by the variety of number and position of octyloxy chains substituted at aroyl rings: R_1−R_4 in series I and R_1−R_5 in series II.

2.2. Synthesis. The synthetic procedure to obtain the designed complexes of series I is sketched in Scheme 1. The symmetrical compounds of the series II were obtained in the same manner using as intermediates *3* and *4* the appropriate formyl indanone derivatives. The starting tetralone and indanone derivatives were obtained using different synthetic methods. 6-Octyloxy-1-tetralone (**a**) (NMR data for intermediates labeled with a bold, lower case letter are available in the Supporting Information), 5-octyloxy-1-tetralone (**b**), 4-octyloxy-1-indanone (**c**), 5-octyloxy-1-indanone (**d**), and 4-octyloxyacetophenone (**e**) were prepared by an alkylation reaction[11] by applying commercially available 6-hydroxy-1-tetralone, 5-hydroxy-1-tetralone, 4-hydroxy-1-indanone, 5-hydroxy-1-indanone, and 4-hydroxyacetophenone, respectively.

7-Octyloxy-1-tetralone (**f**), 6,7-dioctyloxy-1-tetralone (**g**), and 6-octyloxy-1-indanone (**h**) were received in a two-step procedure from commercially available substances. In the first step, 7-methoxy-1-tetralone, 6,7-dimethoxy-1-tetralone, and 6-methoxy-1-indanone were demethylated with HBr solution,[12] and

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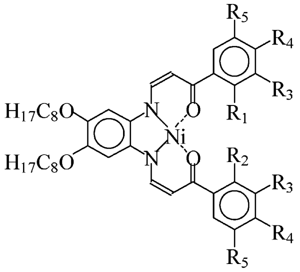
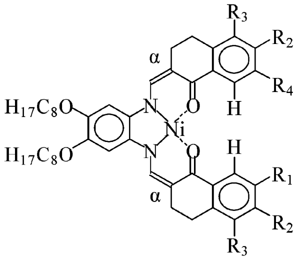
Table 1. Comparative Compounds: Their Melting Points (in °C), Phase Sequences and Phase Transition Temperatures (in °C), and Phase Transition Enthalpy Changes (in parantheses, kJ·mol^{-1})



no.	R_1	R_2	R_3	R_4	R_5	mp	phase sequence and phase transition temp (Δ*H*)
1	OH	H	H	OC_8H_{17}	H	146.7 (33.9)	Sm A−132.6[a]−Iso
2	OH	OH	H	OC_8H_{17}	H	135.3 (36.7)	Sm A−108.5 (4.2)−Iso
3	OH	OH	H	H	OC_8H_{17}	b	Col_h−189.6 (2.1)−Iso
4	OH	OH	OC_8H_{17}	OC_8H_{17}	H	102.2 (45.7)	Sm A−77.7 (1.9)−Iso_{re}−95.0 (2.2)−Col_h−197.5 (2.7)−Iso
5	OH	OH	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	92.2 (18.3)	Sm A−76.2 (3.8)−Iso_{re}−103.2 (1.7)−Col_h−179.3 (3.2)−Iso

[a] Microscopic observation. [b] Below room temperature.

Table 2. Compounds of Series I (Tetralone Derivatives): Their Melting Points (in °C), Phase Sequences, Phase Transition Temperatures (in °C), and Phase Transition Enthalpy Changes (in parantheses, kJ·mol^{-1})



no.	R_1	R_2	R_3	R_4	mp	phase sequence and phase transitions temp (Δ*H*)
7	OC_8H_{17}	H	H	OC_8H_{17}	116.0 (51.0)	−
8	H	OC_8H_{17}	H	H	107.6 (44.4)	−
9	H	H	OC_8H_{17}	H	90.0 (55.6)	−
10	OC_8H_{17}	OC_8H_{17}	H	H	120.0 (52.2)	−
11	OC_8H_{17}	OC_8H_{17}	H	OC_8H_{17}	94.2 (59.8)	Iso_{re}−42.7 (2.2)−Col_h−135.6 (1.8)−Iso
12[a]	OC_8H_{17}	OC_8H_{17}	H	OC_8H_{17}	102.3 (25.0)	Col_h−213 (4.2)−Iso

[a] Cu complex.

in the second step, the obtained 7-hydroxy-1-tetralone, 6,7-dihydroxy-1-tetralone, and 6-hydroxy-1-indanone were alkylated with $C_8H_{17}Br$.[11]

4,7-Dioctyloxy-1-indanone (**i**), 5,6-dioctyloxy-1-indanone (**j**), and 4,5,6-trioctyloxy-1-indanone (**k**) were obtained from 1,4-dioctyloxybenzene, 1,2-dioctyloxybenzene, and 1,2,3-trioctyloxybenzene, respectively, in the reaction with *N*,*N*-dimethylacrylamide/trifluoromethanesulfonic anhydride complex.[13] 1,4-Dioctyloxybenzene, 1,2-dioctyloxybenzene, and 1,2,3-trioctyloxybenzene were prepared by the Williamson reaction from appropriate polyhydroxybenzenes.[14]

Trisubstituted 1-indanones were received in multistep reactions. 3-(3,4,5-Trimethoxyphenyl)propionic acid in the presence of the polyphosphoric acid gives 5,6,7-trimethoxy-1-indanone (mp 120 °C).[15] In comparison to the reported unsuccessful efforts of demethylation with HBr solution,[12] we succeeded to obtain totally demethylated 5,6,7-trihydroxy-1-indanone. 5,6,7-Trimethoxy-1-indanone (1 mmol) with $AlCl_3$ (3.1 mmol) in the presence of dry toluene (100 mL) was heated and stirred under reflux for 30 min and then poured into ice/HCl solution (150 mL). The crude product was filtered from water/toluene and crystallized from water (yield ∼ 80%). The obtained 5,6,7-trihydroxy-1-indanone (1 mmol) was alkylated using $C_8H_{17}Br$ (3 mmol), resulting in 5,6,7-trioctyloxy-1-indanone (**l**), which was purified by recrystallization from cooled hexane (ca. −60 °C) to give a colorless oil at room temperature. 5,6-Dioctyloxy-7-hydroxy-1-indanone (**m**) was prepared by selective dealkylation (1 mmol) using $AlCl_3$ (1 mmol) in dry toluene. The mixture was heated under reflux for 10 min, poured into ice/HCl solution (150 mL), extracted by hexane (2 × 100 mL), evaporated to dryness, and recrystallized from cooled hexane (ca. −60 °C) to give a colorless oil at room temperature (yield ∼ 40%).

Formyl tetralone derivative sodium salts *3* were obtained by the Claisen formylation reaction. To obtain the symmetrical ligands *6*, the 4,5-dioctyloxy-1,2-phenylenediamine *2* (1 mmol in 50 mL of ethanol) and the formyl tetralone sodium salt *3* (3,3 mmol in 50 mL of methanol) were used. The reaction proceeds at room temperature, and the mixture was neutralized with acetic acid (to pH about 6) and then boiled. To the boiling mixture was added a metal salt [nickel(II) acetate] dissolved in hot methanol, and after 5 min of reflux the mixture was cooled, resulting in precipitate of the series I compounds which was filtered off. For the complex **12**, instead of nickel(II) acetate salt, copper(II) acetate was used.

The complex **6** with an unsymmetrical ligand was obtained in the subsequent way: 4,5-dioctyloxy-1,2-phenylenediamine

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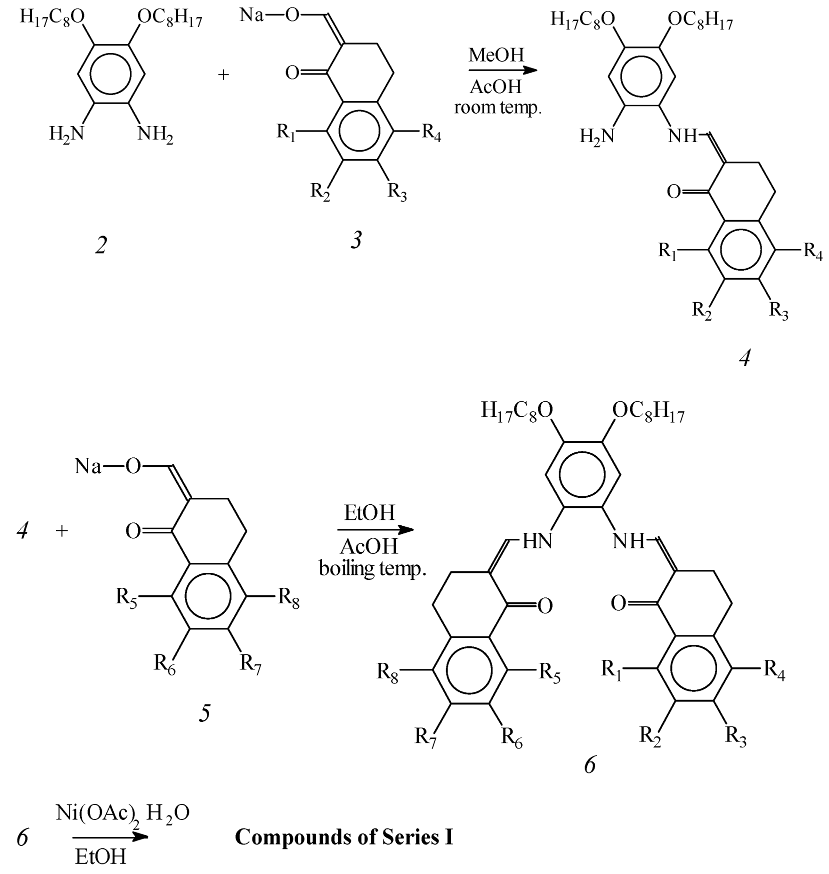
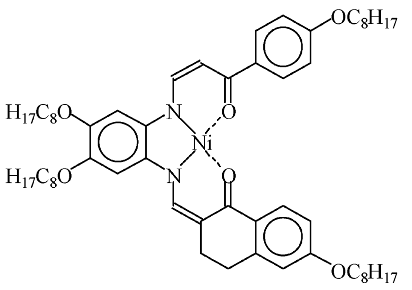
Scheme 1. Synthetic Route to the Series I



Scheme 2. Structure of the Complex 6



m.p. 114.8 °C (43.2 kJ·mol^{-1})
Sm C – 88.2 °C (7.1 kJ·mol^{-1}) – Iso

2 (1 mmol) and the sodium salt of formyl 6-octyloxy-1-tetralone (**a**) (1 mmol) dissolved in methanol (50 mL) and neutralized with acetic acid (to pH about 6) reacted at room temperature selectively. The aroylvinyl group was joined only to one of the amino groups, resulting in a crystalline intermediate *4*. The compound *4* was purified by recrystallization from octane (yield ~ 70%). The remaining amino group of compound *4* reacted further with the sodium salt of formyl 4-octyloxyacetophenone (**e**) (1 mmol) at the boiling point of ethanol (50 mL), giving rise to the tetradentate ligand after 10 min. A 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 **6**, which was filtered off.

The complex **21** was obtained in similar way. 4,5-Dioctyloxy-1,2-phenylenediamine *2* (1 mmol) and the sodium salt of formyl 5,6-dioctyloxy-1-indanone (**j**) (1 mmol) dissolved in methanol (50 mL) and neutralized with acetic acid (to pH about 6) reacted at room temperature selectively. Only one of the amino groups reacted with the aroylvinyl group, giving a crystalline intermediate analogous to intermediate *4*. After recrystallization from octane (yield ~ 70%) the remaining amino group reacted further with the sodium salt of formyl 5,6-dioctyloxy-7-hydroxy-1-indanone (**m**) (1 mmol) at the boiling point of ethanol (50 mL), resulting in the tetradentate ligand after 10 min. To the boiling mixture nickel(II) acetate dissolved in hot ethanol (15 mL) was added, and after 5 min of reflux the mixture was cooled and the precipitate of compound **21** was filtered off.

All the synthesized complexes were chromatographed on silica gel, eluted with hexane/methylene chloride solvents (1:1), (yield ~ 50%). The synthesized compounds were resistant to the moisture and air, except **21** and **22**.

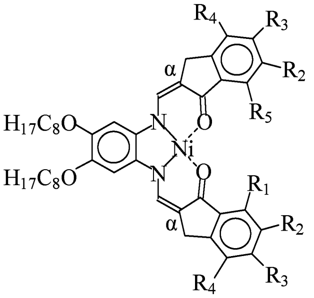
The elemental analyses (C, H, and N) for the obtained complexes were satisfactory. The ^{1}H NMR and ^{13}C NMR spectra (in $CDCl_3$) are consistent with assumed structure without any sign of additives or impurities. The mass spectra obtained for **21** and **22** are consistent with the assumed molecular structure.

2.3. Experimental Conditions. 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 determined by calorimetric measurements performed with a DSC-7 Perkin-Elmer setup. When the phase transition temperatures were close to the sample decomposition temperatures, heat effects were undetectable and the temperatures were taken from microscopic observation. In X-ray studies, a DRON diffractometer was used. EPR investigations were performed in the X-band on a Bruker spectrometer ELEXYS-500 equipped with a nitrogen flow heater. NMR spectra were recorded by a Varian Unity Plus spectrometer operating at 500 MHz. Mass spectra were taken from a Mariner PerSeptive Biosystem mass spectrometer (electron spray mode).

3. Results and Discussion

The mesomorphic properties of the new synthesized compounds—the phase sequence, phase transition tem-

Table 3. Compounds of Series II (Indanone Derivatives): Their Melting Points (in °C), Phase Sequences, Phase Transition Temperatures (in °C), and Phase Transition Enthalpy Changes (in parantheses, kJ·mol^{-1})



no.	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	mp	phase sequence and phase transitions temp (ΔH)
13	H	OC_8H_{17}	H	H	H	184.5 (26.7)	–
14	H	H	OC_8H_{17}	H	H	113.9 (4.6)	–
15	H	H	H	OC_8H_{17}	H	110.2 (2.7)	–
16	H	OC_8H_{17}	OC_8H_{17}	H	H	124.2 (9.5)	–
17	OC_8H_{17}	H	H	OC_8H_{17}	OC_8H_{17}	139.8 (11.3)	–
18	H	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	H	106.7 (5.7)	Col$_h$–186.8 (1.2)–Iso
19	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	H	H	121.7 (1.5)	Col$_h$–288[a,b]
20	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	H	OC_8H_{17}	223.5 (20.5)	Col$_h$–222.1 (9.6)–Iso
21	OH	OC_8H_{17}	OC_8H_{17}	H	H	123.7 (22.7)	Col$_h$–360[a,b]
22	OH	OC_8H_{17}	OC_8H_{17}	H	OH	c	Col$_h$–360[a,b]

[a] Microscopic observation. [b] Decomposition of complex. [c] Below room temperature.

peratures, and enthalpy changes—are summarized in Tables 2 and 3. The obtained compounds show enantiotropic as well as monotropic columnar liquid crystalline phases and for compound **6** also a lamellar phase appears.

The rotation restriction imposed on one of the aroyl rings by the ethylene unit (compound **6**, Scheme 2) disturbs liquid crystalline phases: only monotropic smectic C appears. For comparison, compound **1**, having a mesogenic core stiffened by one inner hydrogen bond, reveals the more stable smectic A phase (Table 1).

In series I the core is stiffened and broadened by two external six-membered rings. The compounds with one octyloxy substituent at each aroyl ring (**7**–**9**) do not reveal any mesophases (Table 2), although the analogous substances **2** and **3**, having inner hydrogen bonds and being related to the complexes **7** and **8**, showed smectic A and columnar Col$_h$ phases, respectively (Table 1). The melting point of the compounds **7**–**9** decreases when the alkoxy chains are shifted outward from the core symmetry axis.

For complex **11**, having two octyloxy terminal chains at each aroyl rings, at positions R$_1$, R$_2$, and R$_4$, the exotic Iso–Col$_h$–Iso$_{re}$ phase sequence has been found (Table 2). In this case, the configuration of the octyloxy chains is the same as for the Ni(II) complex **4**, which exhibits the Iso–Col$_h$–Iso$_{re}$–Sm A phase sequence. However, for the substance **11**, the smectic A phase below the Iso$_{re}$ phase does not appear. This discrepancy in polymorphism can be explained by broadening of the molecular core and differences in the mass distribution in the molecule; in molecule **11** there is empty space in the molecular center.

The identification of the Iso$_{re}$ phase was done in analogy to that for **4**. In microscopic observation of the compound **11**, on fast and slow cooling, the re-entrant isotropic phase appears as black isotropic droplets against the background of the birefringent texture of the Col$_h$ phase (Figure 1). The isotropic droplets are identical to the liquid ones formed at the clearing point. Moreover, the re-entrant isotropic phase is visibly more fluid and so less viscous then the columnar hexagonal phase. The low viscosity excludes any known optically isotropic cubic phases, which are highly viscous. For compound **11**, the re-entrant isotropic phase is monotropic.

The DSC thermogram confirms the phase transition temperatures detected in texture studies (Figure 2). The enthalpy change at the Col$_h$–Iso$_{re}$ transition is exothermic and its value is on the same order as reported before (i.e. ~2 kJ·mol^{-1}).

The X-ray diffractogram of compound **11** in the Col$_h$ phase (at 120 °C) shows three sharp signals in the low-angle region and two diffused signals in high-angle range. The sharp signals reflect the hexagonal crystallographic lattice, which can be described by indices (010) = (100) = 22.9 Å, (110) = 13.4 Å, and (020) = (200) = 11.7 Å related to the primitive cell. As for the diffused signals, the sharper one at 3.8 Å is assigned to the (001) crystallographic index and connected with the core–core distance in the column, and the broader one at 4.45 Å is related to the distance between aliphatic chains. It gives the dimensions of the single hexagonal crystallographic cell $a_{hex} = 22.9$ Å and $c = 3.8$ Å. The density of the Col$_h$ phase calculated from crystallographic parameters is equal to ca. 0.85 g·cm^{-3}, which is rather low. This Col$_h$ phase density is on the same order as for the mesogenes having similar structure reported before.[5,16] Because of fast recrystallization of the sample, the attempts to register the X-ray spectra of the Iso$_{re}$ phase were not successful.

For comparison, we also synthesized copper(II) complex **12**, whose structure is similar to that of the Ni(II) compound **11**. Because the copper(II) ion is a little larger, i.e., its coordination plane is ca. 10% wider then

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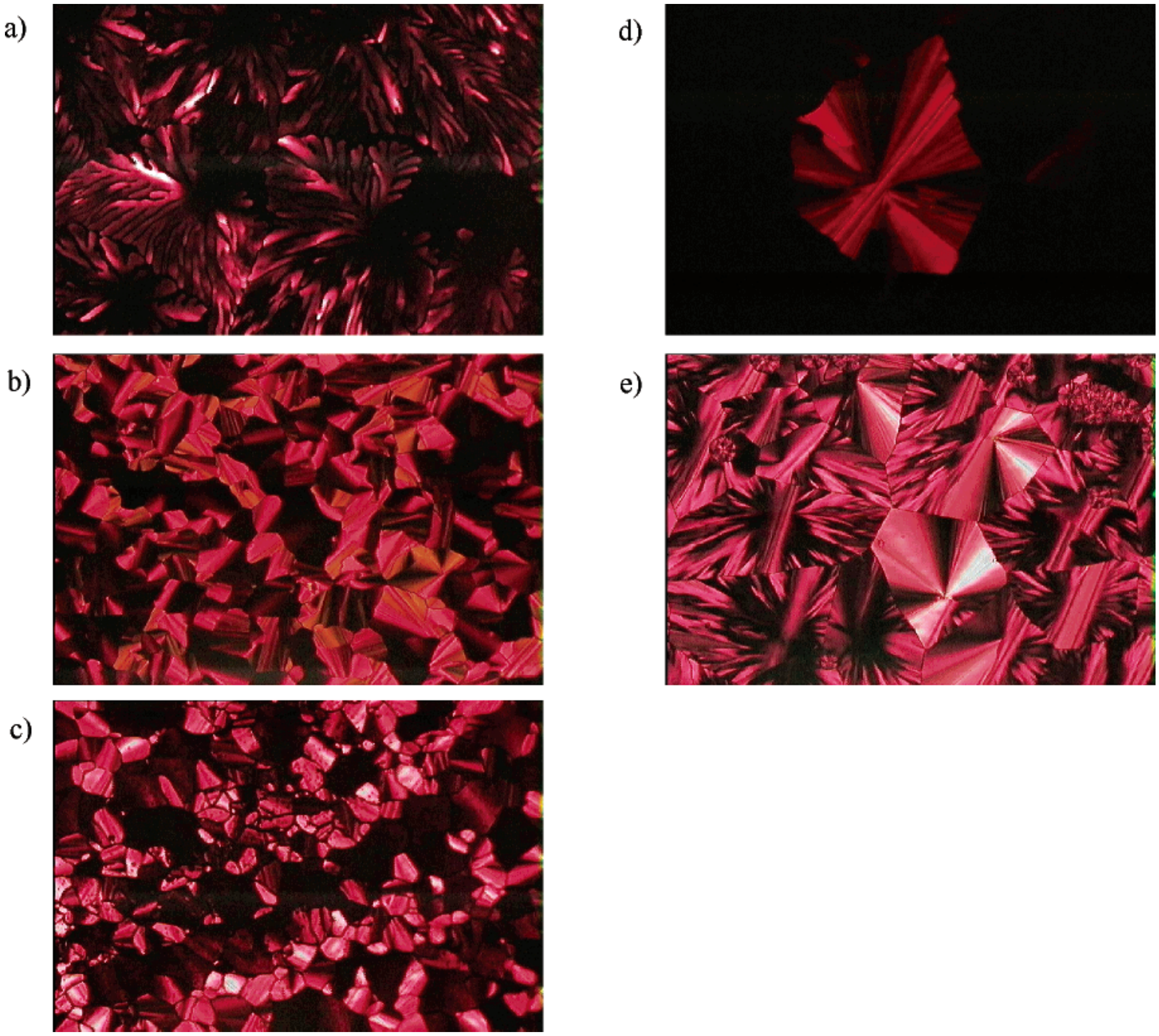

Figure 1. The texture of the $\mathrm{Col_h}$ phase of compound **11**: (a) growing from the Iso phase (135 °C), (b) on cooling (100 °C), (c) at the $\mathrm{Col_h}$–$\mathrm{Iso_{re}}$ phase transition (43 °C), (d) growing from the $\mathrm{Iso_{re}}$ phase (43 °C), and (e) on second heating (60 °C).

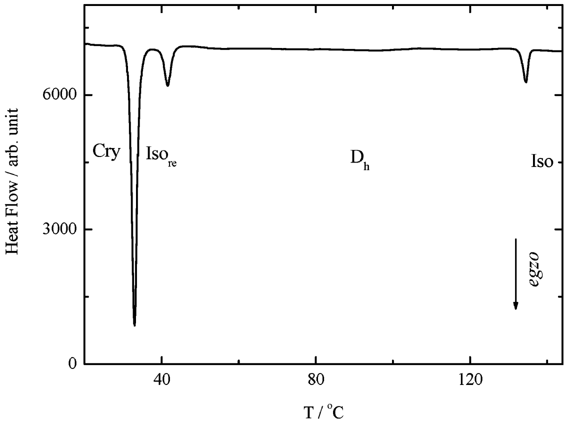

Figure 2. DSC thermograph of compound **11**.

that of the nickel (II) ion, the width of the **12** molecules is slightly broader.[17,18] This effect can stabilize the columnar hexagonal phase in a wide temperature range (more then 110 K) and prevent the appearance of the re-entrant isotropic phase.

To study the behavior of molecules in liquid crystalline phases, we used the EPR spin probe method.[19] The compound **11** forming re-entrant isotropic phase was doped by the related paramagnetic copper(II) complex **12**. The copper ions in the dopant had natural isotope composition. The shape of the copper complex was well adjusted to be built into phases formed by the matrix molecules (**11**). In the EPR glassy state spectrum of copper(II) ion (Figure 3), the characteristic signals for z molecular axis, which is perpendicular to the coordination plane (inset in Figure 3), can be seen. The magnetic parameters for this direction are $g_{zz} = 2.190$ and $A_{zz} = 19.4$ mT. The signals related to other the axes x and y are hard to be separated, because of the complicated superhyperfine structure coming from the nitrogen and hydrogen atoms situated in the vicinity of the copper ion. At higher temperature, in the $\mathrm{Col_h}$ phase the main features of the EPR spectrum remain almost unchanged: the signals are slightly blurred but their sharp superhyperfine structure is preserved. The magnetic g_{zz} and A_{zz} parameters are slightly lower. Moreover, the EPR spectrum taken in the isotropic phase, even at very high temperature, is still glassy-

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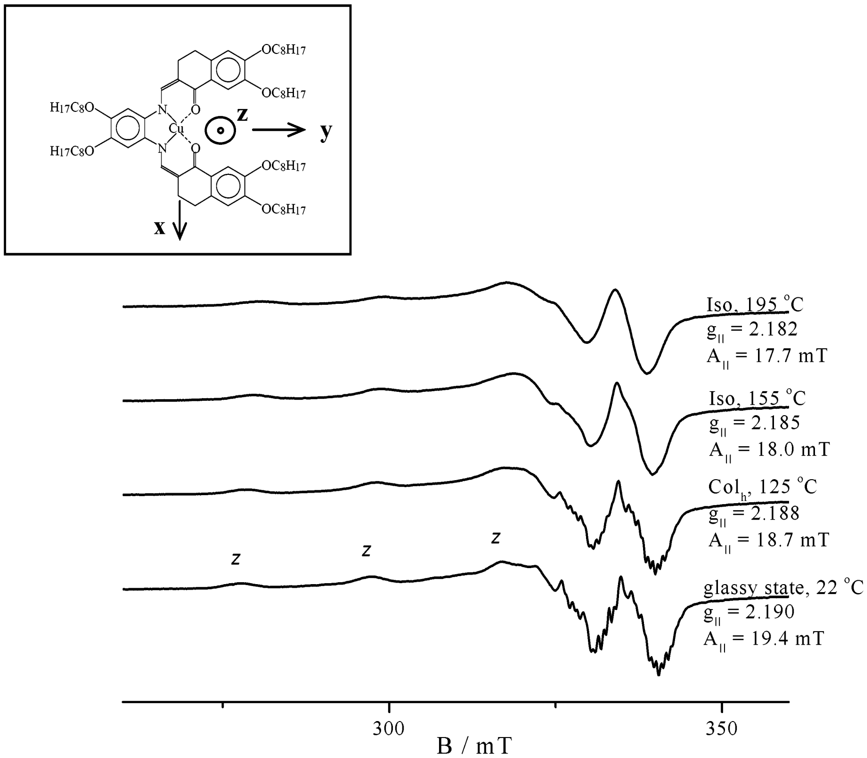

Figure 3. EPR spectra of the probe **12** (in the inset) dispersed in the host matrix **11**.

state-like. The *z* direction signals are visible, being caused by the strongly restricted molecular movement. Slow molecular motions are due to the high viscosity of the Col$_h$ and isotropic phases, which does not allow the molecules to rotate at a frequency that is high enough for averaging of the magnetic parameters in EPR measurements. Thus, under these conditions the position of EPR signals cannot reflect the matrix molecules rotation.

In the complexes of series II the introduced external methylene group allowed formation of a rigid five-membered ring. As usual, the five-carbon rings impose a stretching tension on the molecule, leading to a larger distance between the two aroyl rings. Compounds with a monooctyloxy substituent at each aroyl ring (**13**−**15**) behave similarly as related series I compounds (**7**−**9**); i.e., they do not exhibit mesophases and show the same dependence of the melting point temperatures upon changing the position of the terminal chains.

Substituting at each aroyl ring two chains at positions R$_2$, R$_3$ (**16**) does not lead to liquid crystalline mesophases, contrary to what could be expected from the structural similarity to compound **11**, which exhibits the Iso$_{re}$ phase. Thus, even small changes in the molecular structure can result in total destruction of mesophases.

Further modification of the molecule by substituting at each aroyl rings two chains at inner ortho- and outer meta-positions also does not lead to appearance of the liquid crystalline mesophases (**17**). The lack of mesomorphic properties is due to steric hindrances and disturbance of the flat disklike molecular shape caused by the too long inner chains.

Broadening the molecular contour by increasing the number of the octyloxy chains at outer positions of aroyl rings in compound **18** gives, as expected, the Col$_h$ phase with a broad temperature range. In the molecule **19**, applying octyloxy chains at the inner ortho-position of one of the aroyl rings fills the inner molecular space and results in the Col$_h$ phase in the temperature range ~170 K. However, additional filling of the inner space by two octyloxy chains at ortho-positions of both aroyl rings (**20**) does not improve the stability of the Col$_h$ phase. It plausibly comes from disturbances of the molecular plane caused by the long inner alkoxy chains.

Applying both kinds of stiffening units—external methylene and one or two inner hydroxy groups (**21**, **22**, respectively)—results in an extremely stable Col$_h$ phase. The isotropization temperature is difficult to determine because of the compounds decomposition at about 360 °C. The hydroxy moieties strongly promote the columnar phase due to the intra- as well as intermolecular bonds. Moreover, similarly as for compounds **19** and **20** with inner octyloxy chains, the hydroxy groups also fill the inner core space, which stabilizes the columnar hexagonal phase. The NMR studies[20] confirmed the increase in the aroyl arms distance for compounds **21** and **22** in comparison to the substances with or without any ethylene external bridges. In the ^{1}H NMR spectra the proton signals from hydroxy groups are shifted toward higher magnetic field, i.e., from about 11 to 8 ppm. This points to a weaker hydrogen bond with the carbonyl oxygen atom and the larger distance between oxygen atoms of carbonyl and hydroxy groups.

4. Conclusions

Two series of the tetradental *cis*-enaminoketone Ni(II) complexes with the core modified by external units have been synthesized and examined in order to obtain compounds having both lamellar and columnar

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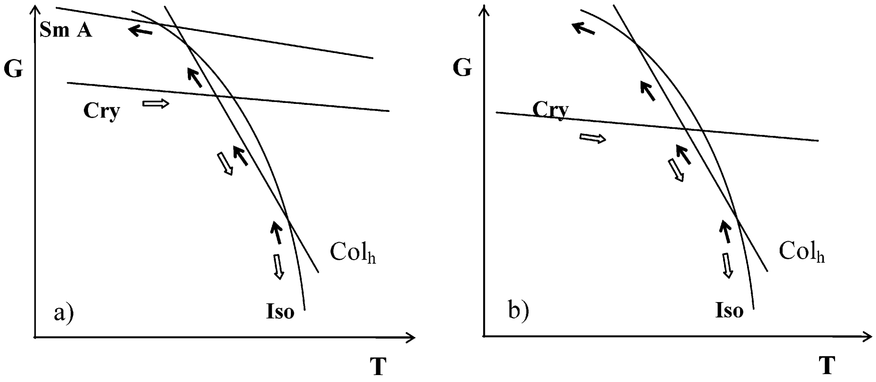

Figure 4. Schematic diagram of free energy vs temperature ($G-T$): (a) for **5** and (b) for **11** complex, on heating and cooling.

mesophases. In the series with the ethylene bridge, a compound revealing the re-entrant isotropic phase below the columnar hexagonal phase has been synthesized. For this compound, the positions of the octyloxy chains at the aroyl rings are the same as for the substance with inner hydrogen bonds and having Iso$-$Col$_h$$-Iso_{re}$$-$Sm A phases. Only for this particular terminal chain configuration, i.e., at para- and inner meta-positions, the investigated materials show the unique mesomorphism with the re-entrant isotropic phase. For both compounds, in the high-temperature Col$_h$ phase, the terminal chains are melted and distributed uniformly around the molecular core. At lower temperature, when the Sm A can be created, the terminal chains are in their *trans*-conformation, so they are aligned parallel to one another and give the rodlike molecular shape. For intermediate temperatures, the re-entrant isotropic phase emerges as a result of competition between the disklike and elongated molecular configurations.

The appearance of the Iso$-$Col$_h$$-Iso_{re}$$-$Sm A mesomorphism, in which the less ordered re-entrant isotropic phase (Iso$_{re}$) is created below the higher ordered Col$_h$ phase, could be explained by considering a schematic free energy (G)$-$temperature diagram.[6,21] The isotropic phase can be formed at two temperature regions if the lines of free enthalpy for isotropic and columnar phases have two crossing points, i.e., the free enthalpy of one of the phases is not a linear function of temperature. For the well-documented re-entrant nematic phase, which is situated below the smectic A phase, the nonlinearity of the free enthalpy function is assigned to the more ordered smectic phase.[22] This complicated behavior results from some differences in the smectic phase structure upon temperature change. However, in our case, we have no evidence of any structural reorganization for the Col$_h$ phase. Also between two isotropic phases—the high temperature and re-entrant—any substantial changes are not supposed; only the molecular conformations of the terminal chains in the ordinary isotropic phase could be different from those of the re-entrant isotropic phase. So not having a clear suggestion, we assumed that the bent line of free enthalpy is the line of the isotropic phase (Figure 4). On heating the substances, the minimized value of free enthalpy is observed when the phase sequence is Cry$-$Iso$_{re}$$-Col_h$$-$Iso for the first diagram (Figure 4a, for **5** complex) and Cry$-$Col$_h$$-$Iso for the second one (Figure 4b, for **11** complex). On cooling, the low-temperature noncrystalline phases becomes supercooled and Iso$-$Col$_h$$-Iso_{re}$$-$Sm A (Figure 4a) or Iso$-Col_h$$-Iso_{re}$ (Figure 4b) phases can be seen.

For synthesized compounds, the enthalpy changes at transitions points Col$_h$$-Iso_{re}$ and Iso$_{re}$$-$Sm A are on the order of 1$-$3 kJ·mol^{-1}. The measured enthalpy values are rather high in comparison to the other reported compounds exhibiting the Iso$_{re}$ phase. The enthalpy change at similar Col$_h$$-Iso_{re}$ phase transition in the truxene derivative was below the detection limit.[2,3] Also low-temperature transition enthalpy values between Iso$_{re}$ and columnar nematic (N$_D$) phase for the truxene derivative[2,3] or the polycatenar compound[1] were undetected or very small. This could suggest that the higher enthalpy changes in our complexes, similarly as for the compound having a nematic re-entrant phase,[23] can be related to the broader temperature range of the Iso$_{re}$ phase and smaller fluctuations coming from neighboring phases.

For the indanone series, the methylene unit introduces stretching tension, which enlarges the molecular width. This disturbs the molecular shape, and the compound with the adjusted configuration of the alkoxy chains, which leads to the Iso$_{re}$ phase, does not give any liquid crystalline phases. However, in this series some compounds reveal an especially stable Col$_h$ phase (more then 360 K) when the number of octyloxy chains increases and when the hydroxy groups are attached to the molecular center.[7,24] The hydroxy groups can create the intermolecular hydrogen bonds along the columns. This interaction supports microsegregation of incompatible molecular parts of different polar properties. The large polarized center is surrounded by the polarizable phenyl rings and then by the incompatible peripheral aliphatic chains. So, similarly as in lyotropic phases,[25,26] in the termotropic columnar phase the onionlike columns built from polarized and polarizable parts are surrounded by an apolar environment of terminal chains. Thus, in the phase structure the segregation of different molec-

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ular fragments promotes a very stable $\mathrm{Col_h}$ columnar phase.

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Supporting Information Available: Spectral Data for **6**−**22** and intermediates **a**−**m**. This material is available free of charge via the Internet at http://pubs.acs.org.

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