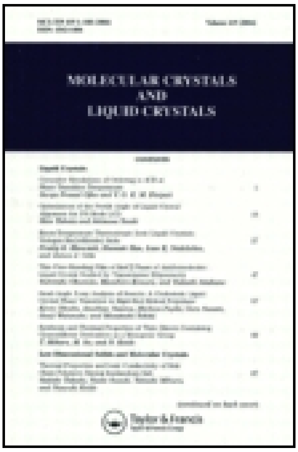

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mesogenic Enaminoketone Ni(II) Complexes of Phenazine and Quinoxaline Derivatives

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Version of record first published: 18 Apr 2012.

To cite this article: Paulina Krzyczkowska , Adam Krówczyński , Joanna Kowalewska , Jerzy Romiszewski , Damian Pociecha & Jadwiga Szydłowska (2012): Mesogenic Enaminoketone Ni(II) Complexes of Phenazine and Quinoxaline Derivatives, Molecular Crystals and Liquid Crystals, 558:1, 93-101

To link to this article: http://dx.doi.org/10.1080/15421406.2011.653714

Mol. Cryst. Liq. Cryst., Vol. 558: pp. 93–101, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.653714

Mesogenic Enaminoketone Ni(II) Complexes of Phenazine and Quinoxaline Derivatives

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The new Ni(II) metallomesogenes were synthesized. Their mesogenic cores are constructed from tetradental enaminoketone unit connected to 1,2:3,4-di(4,5-dioctyloxybenzo)phenazine or 2,3-di(3,4-dioctyloxyphenylo)quinoxaline. The described compounds form columnar hexagonal phase (Col_{hd}) in very broad temperature range. The high stability of the columnar phase results from presence of a permanent dipol moment in enaminoketone moieties created by strong electron withdrawing properties of carbonyl groups.

Keywords Claisen formylation; dipol moment; liquid crystals; metallomesogenes

1. Introduction

Self organization of a substance into liquid crystalline phases depends mainly on its molecular shape anisotropy. A rod-like or disk-like shape, is mainly determined by mesogenic core structure. One of the first molecules that was reported forming columnar phases based on hexasubstituted benzene [1]. The next were constructed, for example, from condensed aromatic ring systems like triphenylenes [2–4] or perylenes [5]. Also metaloorganic cores like porphyrins and phthalocyanines [6] were applied to create compounds showing LC columnar phases. The structure of this types of mesogenic molecules were completed by symmetrical attachment of various chains at the core. Another group of symmetric molecules are dendrimers with fractal structure containing many molecular fragments that induce mesogenity. These can be organized into columnar or calamitic phases in dependance on the number of peripheral paraffinic chains [7]. It is well known that not only discoid cores are essential to generate the columnar phases. There are many examples of substances having the core distorted from the perfect shape [8] like half-discoid [9, 6c], elliptical [10], rectangular [11], triangular [12] and so on. Non perfect shape is compensated by adjusted number of lateral chains attached at proper position [13]. When the number of side chains is too small the compounds with the same mesogenic core can also form lamellar phases [8b, 11, 12]. The circular cross section of columns in D_h phase can be reached by alternating arrangement of molecules. It is the case of half-discs, rectangles or triangules as building blocks [8a, 9a]. Also columnar cylindrical shape can be ashured by

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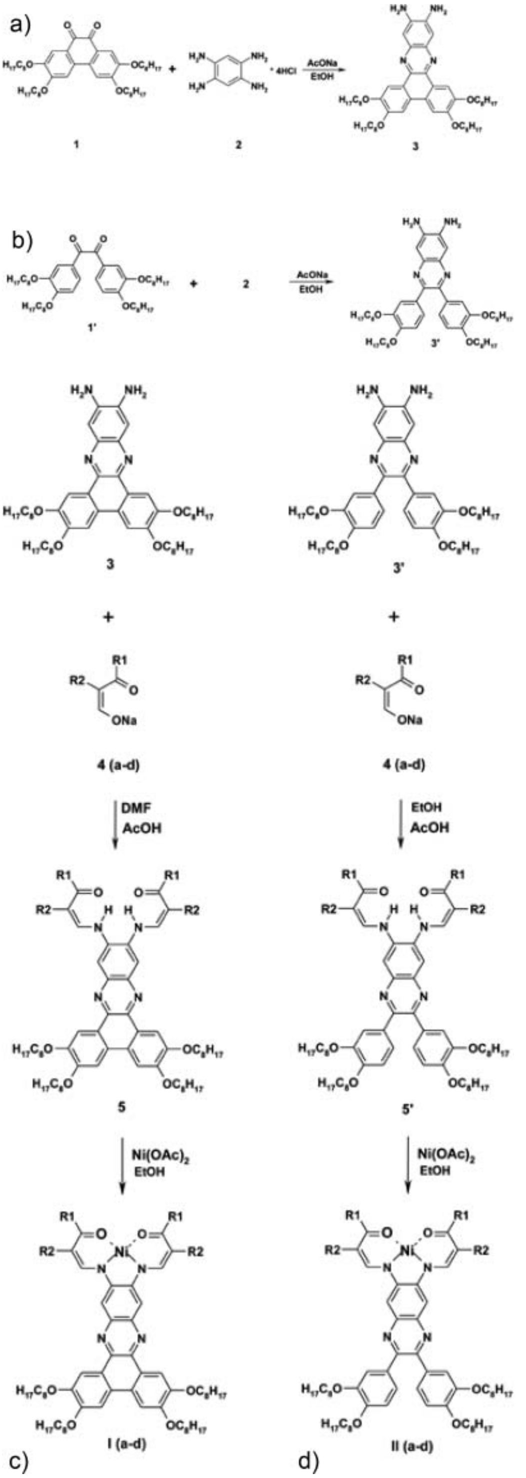
*Address correspondence to P. Krzyczkowska, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland. E-mail: pkrzyczkowska@chem.uw.edu.pl molecular tilt to the columnar axis. It is the way when the longest molecular dimension is effectively shortened in projection [3, 10]. Substances exhibiting LC columnar phases and having the most disadvantageous shape of mesogenic centres are polycatenars. These are constructed from a long chain of aromatic rings [4, 14]. To fill the columnar diameter with calamitic molecules the one columnar slice is occupied by a few mesogenic cores [15]. Similar as previously the circular cross section of the columns can be achieved due to molecular tilt [16]. Despite the intermolcecular dispersion forces that induce LC phase organization the molecular self-assambling can be strengthened by additional interaction like metal-metal [8a, 9a] or hydrogen bonds [7] directed along the columnar axis. Another important factor stabilizing columnar phases is intermolecular dipol-dipol interaction [17]. Thanks to this forces even half disc molecules or bend core policatenares can create columnar phases [9b, 18]. A permanent dipol moment can be introduced into molecules as an electron shifting moiety like carbonyl, cyano, chloride or other group. As it was reported by Foster, Lavigueur, and Ichihara for compounds with triphenylene or dibenzophenazine cores, substitution of electron-withdrawing fragments increase temperature range of LC phases [19]. Their higher stability results from antiferroelectric interaction appearing between neighboring molecules that stabilize columnar stack. The intermolecular forces can even result in creation of molecular dimers that broaden the columnar diameter and give larger lattice parameters [20].

In described here newly synthesized compounds the polarizing moiety was inserted into molecular core and tetradental enaminoketone chelating center was applied as an electron withdrawing group. The Ni(II) metallic center was connected to dibenzophenazine or diphenyloquinixaline units. The nickel complexes of **Series I** were constructed from 1,2:3,4-di(4,5-dioctyloxybenzo)-7,8-diaminophenazine moiety expanded by two acylvinyl groups which give chelating plane (Scheme 1a, **I a–d**). To acylvinyl fragments alkyl chains R_1 and R_2 were attached at carbonyl and vinyl carbons, respectively. The diaminophenazine unit with enaminoketone rings constitute a condensed polycyclic aromatic system. In the next series of complexes, to make core structure more loose and flexible, the bond between phenyl groups in the phenatrene moiety was broken. In **Series II** the benzophenazine moiety was replaced by 2,3-di(3,4-dioctyloxyphenylo)-6,7-diaminoquinoxaline group (Scheme 1b, **II a–d**). The both series of the described complexes exhibit liquid crystalline hexagonal columnar disordered phase (Col_{hd}).

Experimental

Measurements

The mesophase identification was based on microscopic examination of liquid crystalline texture. A Zeiss Imager A2m polarizing microscope equipped with a Linkam hot stage was used. The microscopic identification was confirmed by the X-ray studies, performed with Bruker diffractometer D8 GADDS (CuK_α radiation, Vantec 2000 area detector) equipped with temperature hot stage. The X-ray diffraction patterns were obtained for partially oriented samples. The detected diffraction signals were indexed with Miller indices of two dimensional hexagonal lattice. The spacing ratio of the first three visible sharp peaks ((100): (110): (200)) fulfilled the known relation $1 : 1/\sqrt{3} : 1/2$. Phase transition temperatures and enthalpy changes were determined by calorimetric measurements performed with a TA DSC Q200 set-up, in inertnitrogen atmosphere. The molecular dimensions were estimated with HyperChem software package.



Scheme 1. Synthetic route to the complexes of.

Synthesis

The synthetic procedure leading to the complexes of Series I and II is sketched in Scheme 1.

It starts from preparation 2,3,6,7-tetraoctyloxyphenantrene-9,10-dione, **1** and 3,3′,4,4′-tetraoctyloxydibenzoyl, **1**′ that was described many times previously [12].

The derivatives of diamines, **3** or **3**′ were received in the condensation reaction of **1** or **1**′ with 1,2,4,5-benzenetetramine tetrahydrochloride, **2**. In compounds **3** and **3**′ two amino groups were substituted by various formyl ketone sodium salts that determines the structure of final complexes. To the obtained ligands **5** or **5**′ without their purification nickel acetate solution was added. It gave the designed final Ni(II) complexes **I a–d** and **II a–d**.

1,2:3,4-di(4,5-octyloxybenzo)-7,8-diaminophenazine (3). 2,3,6.7-tetraoctyloxy-phenantrene-9,10-dione, **1** (3.6 g, 1.2 mmol) and anhydrate sodium acetate were dissolved in warm ethanol (100 ml). To this solution 1,2,4,5-benzenetetramine tetrahydrochloride, **2** (2.8 g, 3.8 mmol) dissolved in water-ethanol solvent was added and the reaction mixture was refluxed for several hours in inert atmosphere. After that to the reaction mixture water (500 ml) was poured and contents was alkalized with sodium carbonate. The precipitate was filtrated under reduced pressure, washed with water and purified in crystallization from toluene to give dark orange crystals of **3** (4 g). Yield: 70%.

Elemental Analysis for **3** $C_{52}H_{78}N_4O_4$ (823.20 g/mol); Calculated: C, 75.87; H, 9.55; N, 6.81%; Found: C, 75.94; H, 9.76; N, 6.94%; **^{1}H NMR** –(500 MHz, $CDCl_3$): $\delta = 0.84 - 2.20$ (60H, m); 4.27 (4H, t, $J = 6.6$ Hz); 4.34 (4H, t, $J = 6.6$ Hz);7.43 (H, s); 7.76 (H, s); 8.71 (H, s).

2,3-di(3,4-dioctyloxyphenylo)-6,7-diaminoquinoxaline (3′). 3,3′,4.4′-tetraoctyloxy dibenzoil, **1** (3.6 g, 1.2 mmol) and anhydrate sodium acetate were dissolved in warm ethanol (100 ml). To this solution 1,2,4,5-benzenetetramine tetrahydrochloride, **2** (2.8 g, 3.8 mmol) dissolved in water-ethanol solvent was added and the reaction mixture was refluxed for several hours in inert atmosphere. After that water (500 ml) was poured to the reaction mixture and it was alkalized with sodium carbonate. The crude product **3**′ was extracted with hexane and the solvent was evaporated to give amorphous residue (4 g). The diamine derivative, **3**′ was used in the next reaction step without purification. Yield: 70%.

Elemental Analysis for **3**′ $C_{52}H_{78}N_4O_4$ (823.20 g/mol); Calculated: C, 75.68; H, 9.77; N, 6.79%; Found: C, 75.75; H, 9.82; N, 6.87%; **^{1}H NMR** –(500 MHz, $CDCl_3$): $\delta =$ 0.85–1.84 (60H, m); 3.79 (2H, t, $J = 6.5$ Hz); 3.95-4.00 (8H, m);6.81 (2H, d, $J = 8.4$ Hz); 6.97 (2H, d, $J = 1.9$ Hz); 7.04 (2H, dd, $J = 1.9$ and 8.4 Hz); 7.28 (2H, s).

Ligand (5). 1,2:3,4-di(4,5-octyloxybenzo)-7,8-diaminophenazine, **3** (0.2 g, 0.25 mmol) was dissolved in DMF on heating. To the warm solution of an appropriate formyl ketone sodium salt **4 a–d** (1 mmol) dissolved in DMF was added. Then the solution was acidified with acetic acid (to pH = 6). The mixture was stirred and heated at 80°C for 15 min. After cooling the residue was isolated by filtration under reduced pressure and washed with ethanol. The crude product **5** was used to the next step.

Ligand (5′). 2,3-di(3,4-dioctyloxyphenylo)-6,7-diaminoquinoxaline, **3**′ (0.2 g, 0.25 mmol) was dissolved in ethanol on heating. To the warm solution of an appropriate formyl ketone sodium salt **4 a–d** (1 mmol) dissolved in ethanol was added. Then the solution was acidified with acetic acid (to pH = 6). The mixture was boiled and stirred for 15 min. After cooling the residue was isolated by filtration under reduced pressure and washed with cold ethanol. The crude product **5**′ was used to the next step.

Ni(II) complexes I a–d and II a–d. The crude ligands **5** or **5**′ were dissolved in isopropanol or ethanol, respectively. Then a small excess of nickel acetate (0.2 g) dissolved in methanol was added and the mixture was boiled under stirring for 10 min. After cooling the precipitate was filtered under reduced pressure, washed with ethanol and purified by preparative thin layer chromatography (silicagel, hexane/methylene chloride 1:2).

Elemental Analysis for **I a** $C_{84}H_{136}N_4NiO_6$ (1356.69 g/mol); Calculated: C, 74.36; H, 9.55; N, 4.13%; Found: C, 74.46; H, 9.68; N, 4.21%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.88$–2.02 (108 H, m); 2.40 (4H, t, $J = 7.7$ Hz); 2.48 (4H, t, $J = 7.6$ Hz); 4.26 (4H, t, $J = 6.6$ Hz); 4.34 (4H, t, $J = 6.6$ Hz); 7.66 (2H, s); 7.73 (2H, s); 8.13 (2H, s); 8.73 (2H, s).

Elemental Analysis for **I b** $C_{72}H_{112}N_4NiO_6$ (1188.37 g/mol); Calculated: C, 72.77; H, 9.50; N, 4.71%; Found: C, 72.85; H, 9.63; N, 4.81%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.88$–2.00 (86H, m); 2.43 (4H, t, $J = 7.8$ Hz); 4.24 (4H, t, $J = 6.6$ Hz); 4.28 (4H, t, $J = 6.6$ Hz); 5.55 and 7.52 (4H, AB, $J = 6.7$ Hz); 7.64 (2H, s), 7.92 (2H, s); 8.56 (2H, s).

Elemental Analysis for **Ic** $C_{76}H_{120}N_4NiO_6$ (1244.48 g/mol); Calculated: C, 73.35; H, 9.72; N, 4.50%; Found: C, 73.56; H, 9.84; N, 4.62%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.88$–2.00 (94H, m); 2.43 (4H, t, $J = 7.8$ Hz); 4.24 (4H, t, $J = 6.6$ Hz); 4.28 (4H, t, $J = 6.6$ Hz); 5.55 and 7.52 (4H, AB, $J = 6.7$ Hz); 7.64 (2H, s), 7.92 (2H, s); 8.56 (2H, s).

Elemental Analysis for **Id** $C_{66}H_{100}N_4NiO_6$ (1104.21 g/mol); Calculated: C, 71.66; H, 9.13; N, 5.07%; Found: C, 71.75; H, 9.24; N, 5.15%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.88$–0.93 (12H, m); 1.23 (18H, s); 1.28-2.10 (48H, m); 4.26 (4H, t, $J = 6.6$ Hz); 4.32 (4H, t, $J = 6.6$ Hz); 5.75 and 7.75(4H, AB, $J = 6.8$ Hz), 7.70 (2H, s); 8.09 (2H, s); 8.69 (2H, s).

Elemental Analysis for **IIa** $C_{84}H_{138}N_4NiO_6$ (1358.71 g/mol); Calculated: C, 74.26; H, 10.24; N, 4.12%; Found: C, 74.45; H, 10.37; N, 4.19%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.86$–1.86 (108 H, m); 2.35 (4H, t, $J = 7.6$ Hz); 2.48 (4H, t, $J = 7.6$ Hz); 3.80 (4H, t, $J = 6.6$ Hz); 3.99 (4H, t, $J = 6.6$ Hz); 6.82 (2H, d, $J = 8.3$ Hz), 7.00 (2H, d, $J = 2.1$ Hz); 7.08 (2H, dd, $J = 2.1$ and 8.3); 7.58 (2H, s); 8.00 (2H, s).

Elemental Analysis for **IIb** $C_{72}H_{114}N_4NiO_6$ (1190.39 g/mol); Calculated: C, 72.65; H, 9.65; N, 4.70%; Found: C, 72.77; H, 9.81; N, 4.86%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.86$–1.87 (86H, m); 2.43 (4H, t, $J = 7.8$ Hz); 3.80 (4H, t, $J = 6.6$ Hz); 3.99 (4H, t, $J = 6.6$ Hz); 5.60 and 7.54 (4H, AB, $J = 6.8$ Hz); 6.82 (2H, d, $J = 8.3$), 7.01 (2H, d, $J = 2.1$); 7.06 (2H, dd, $J = 2.1$ and 8.3 Hz); 7.98 (2H, s).

Elemental Analysis for **IIc** $C_{76}H_{122}N_4NiO_6$ (1246.49 g/mol); Calculated: C, 73.23; H, 9.86; N, 4.49%; Found: C, 73.36; H, 9.94; N, 4.57%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.86$–1.86 (94H, m); 2.43 (4H, t, $J = 7.8$ Hz); 3.80 (4H, t, $J = 6.6$ Hz); 3.99 (4H, t, $J = 6.6$ Hz); 5.60 and 7.54 (4H, AB, d, $J = 6.8$ Hz);.6.82 (2H, d, $J = 8.3$ Hz), 7.01 (2H, d, $J = 2.1$ Hz); 7.06 (2H, dd, $J = 2.1$ and 8.3 Hz); 7.98 (2H, s).

Elemental Analysis for **IId** $C_{66}H_{102}N_4NiO_6$ (1106.23 g/mol); Calculated: C, 71.66; H, 9.29; N, 5.06%; Found: C, 71.74; H, 9.35; N, 5.13%.

^{1}H NMR –(500 MHz, $CDCl_3$): $\delta = 0.86$–0.92 (12H, m); 1.22 (18H, s); 1.24–2.10 (48H, m); 3.80 (4H, t, $J = 6.6$ Hz); 3.99 (4H, t, $J = 6.6$ Hz); 5.75 and 7.62 (4H, AB, $J = 7.0$ Hz), 6.82 (2H, d, $J = 8.3$ Hz); 7.00 (2H, d, $J = 2.1$); 7.06 (2H, dd, $J = 2.1$ and 8.3 Hz); 7.99 (2H, s)

Results and Discusion

The phase sequence, phase transition temperatures and enthalpy changes for the studied compounds of series **I** and **II** are gathered in Table 1.

Table 1. Structure of Ni(II) complexes of Series I and II, phase transition temperatures and their thermal effects

	R1	R2	Phase sequence, (enthalpy changes)
Ia	C_7H_{15}	C_6H_{13}	Cr 117.1 (34.0) Col_{hd} 171.9 (0.7) I
Ib	C_7H_{15}	H	Cr 65.1 (33.6) Col_{hd} 265.5 (1.7) I
Ic	C_9H_{19}	H	Cr 78.1(30.7) Col_{hd} 260.0* I
Id	$C(CH_3)_3$	H	Cr 106.2 (35.6) Col_{hd} 253.3 (4.9) I
IIa	C_7H_{15}	C_6H_{13}	Cr 75.7 (50.3) Col_{hd} 87.8 (2.4) I
IIb	C_7H_{15}	H	m.p. below r.t. Col_h 109.0 (5.1) I
IIc	C_9H_{19}	H	Cr 73.5 (33.7) Col_h 112.4 (5.2) I
IId	$C(CH_3)_3$	H	Cr 82.8 (5.9) I

- Taken from microscopy.

Figure 1 shows, as an example, a microscopic texture obtained for the compound **Ia** near clearing temperature. Beside the dark isotropic phase, the dendrite-like dark domains were detected confirming formation of hexagonal columnar phase that have columns alignment homeotropic to the glass plate. Similar dendritic textures were observed for other complexes.

All the complexes of **Series I** having condensed polycyclic aromatic rings form liquid crystalline columnar hexagonal disordered phase (Col_{hd}). The temperature range of liquid crystallinity is very broad and, in the case of complex **Ib**, with heptyl chains in positions R_1, reaches 200°C. However, substitution of longer terminal chains *e.i.* nonyl chains makes the liquid crystalline properties slightly weaker. Broadening the molecules due to attachment of hexyl side chains at vinyl carbons (R_2, compound **Ia**) raises the melting point and makes lower the clearing points, respectively. Less condensed aromatic rings system of diaminoquinoxaline in **Series II** does not give so rigid mesogenic core as it is for diaminophenazine derivatives of **Series I**. The compounds **IIa–IIc** show less stable hexagonal columnar phase and have much lower clearing points. The complex **IId** with the bulky tertbutyl substituents does not form any LC phase.

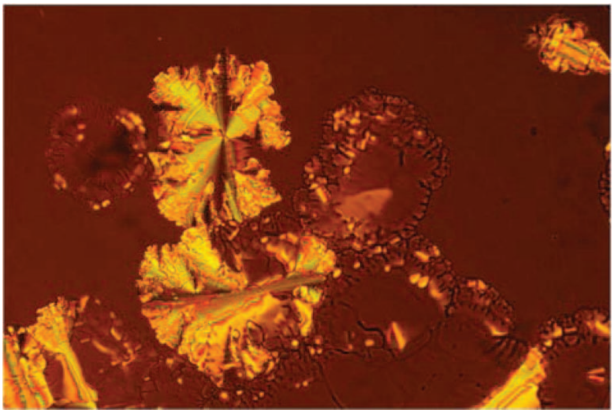


Figure 1. Microscopic texture of **Ia** complex at 172°C at crossed polarizers.

Figure 2. X-ray pattern for partially oriented sample of **IIb** complex at room temperature.

The X-ray studies confirmed hexagonal structure of the detected liquid crystalline phase (Figs. 2 and 3). The X-ray diffraction signals of all compounds well matched to the $\mathrm{Col_{hd}}$ phase structure; unit cell parameter, *a,* is presented in Table 2 for all compounds. The quinoxaline derivatives (**Series II**) have larger intercolumnar distances and form narrower liquid crystalline phases than it is observed for the phenazine derivatives (**Series I**). This can be related to more flexible mesogenic core of molecules of **Series II** and more free molecular motions. In both series, compounds having the largest number of attached chains (**Ia** and **IIa**) exhibit highest density. One of the reasons can be related to the effective size of molecular discs and the dimensions of the created LC columns that do not depend on the side chains R_2. The discussed molecules are elongated and when they form the columns in LC phase the following molecules are probably aligned more or less perpendicular to one another. In this arrangement the circular cross section of the column is formed by two or more molecules and its dimension is mainly determined by the molecular length. So

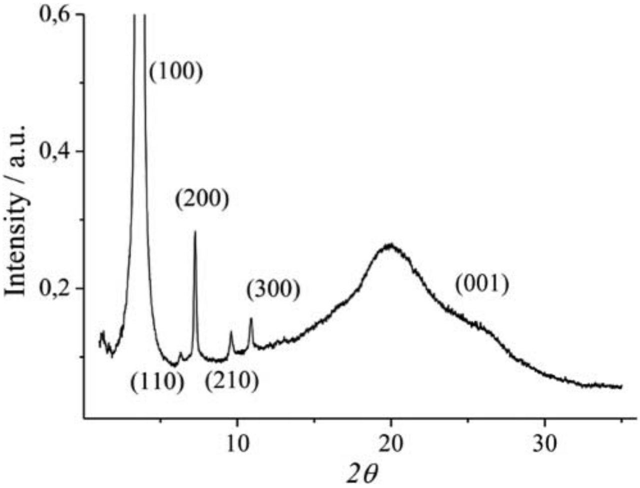


Figure 3. Intensity distribution of X-ray diffraction signals of (**IIb**) complex at room temperature. Signal indexed as (001) reflects distance between mesogenic cores of neighboring molecules along the column, while the strong diffused signal, centered at ~20 deg. reflects mean distance between aliphatic chains.

Table 2. Hexagonal lattice parameters (in Å) taken from X-ray measurements performed at given temperature (°C) and calculated density, ρ (g·cm^{-3}) for Col$_{hd}$ phase of compounds of **Series I** and **II**

	T	*a*	Chains	Disc distance (001)	ρ
Ia	170	24.9	4.6	3.6	1.18
Ib	100	25.75	4.55	3.5	1.00
Ic	200	26.6	4.7	3.5	0.98
Id	245	24.3	4.7	3.5	1.05
IIa	80	26.1	4.5	3.5	1.11
IIb	100	27.2	4.5	3.5	0.90
IIc	100	28.3	4.6	3.5	0.87

the presence of side chains R$_2$ in the complexes **Ia** and **IIa** only increase the molecular weight. This growth is about several percent that contributes to the phase density growth. However, the value of the lattice parameter *a* of the complexes **Ia** and **IIa** which was found smaller than for related complexes **Ib** and **IIb** is hard to explain. The size of the molecules when modelled in the most extended conformation is equal for all the complexes **Ia**, **Ib**, **IIa** and **IIb,** being ~33 Å. Comparison of this value to the *a* distances taken from X-ray measurements shows that molecular chains of neighbouring molecules interdigitate by 3–4 carbon atoms.

It is worth noticing that semiproduct **1** exhibit also LC properties with a phase sequence Cr 83.6 (80.0) Col$_{hd}$ 92.7 (3.4) I.

Conclusions

Two series of LC Ni(II) complexes with new structure of mesogenic cores were synthesized and studied. The phenazine and quinoxaline cores were extended by dienaminoketone moiety forming chelating plane. The oxygen atoms in the carbonyl groups of enaminoketones withdraw electrons from the conjugated π bond system of the molecular core and create strongly non-uniform electron distribution resulting in permanent dipol moment. The dipol-dipol interaction between molecules promote Col$_{hd}$ phase with very high clearing temperature especially in the case of rigid phenazine mesogenic core.

Acknowledgment

This work was supported by FNP Program TEAM/2010-5/4.

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