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# Nickel(II) Complexes of 2,6-Disubstituted Pyridine Bishydrazones as Potential Metallomesogens. Suppression of the Mesogenic Properties Induced by Dimerization

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Ni(II) complexes of hydrazonic ligands derived from 2,6-disubstituted pyridines and alkyl or aryl hydrazides are synthesized and characterized. The coordination geometry depends on the type of R′ substitutents of the ligand. When R′ is alkyl, stable complexes with square planar geometry are obtained with an *E,Z* induced configuration of the hydrazonic arms. These complexes are not mesogenic. For R = aryl two different Ni(II) complexes are formed: the monomeric square planar and a dimeric one with octahedral coordination. In solution the monomer slowly interconverts to the dimer, which is the thermodynamically more stable product. The X-ray structure of the dimer **12a** and its magnetic properties are reported. The mesogenic properties of these Ni(II) derivatives depend on the coordination geometry. The monomeric complex **11b** forms a metastable meso phase. After the clearing point dimerization takes place and the corresponding dimer **12b** does not present liquid crystalline properties.

*Keywords:* Pyridine bishydrazones nickel complexes; metallomesogens; dimerization

## INTRODUCTION

Metallomesogens are an interesting class of functional materials, promising for electronic and electrooptic applications [1]. Among the several possible

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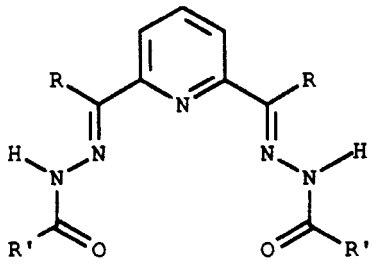
transition metal complexes suitable to exhibit mesomorphic behaviour, little attention has been paid to metal complexes of hydrazonic ligands: only one example is reported in the literature concerning Ni(II) and Cu(II) aroylhydrazone complexes having liquid crystalline properties [2]. Hydrazonic ligands are very versatile as chelating agents and exhibit a wide range of coordination geometries. In particular ligands derived from 2,6-diacetylpyridine present several different coordination possibilities in relation to the type of hydrazide condensed on the pyridine moiety and to the employed reaction conditions [3]. They form particularly stable square planar neutral complexes with a wide range of divalent transition metal ions like nickel and palladium [4].

In this article we report the syntheses and properties of nickel(II) and palladium(II) complexes of hydrazonic ligands with general structure I (Scheme 1), having the R and R′ substituents opportunely chosen in order to impart them mesogenic properties.

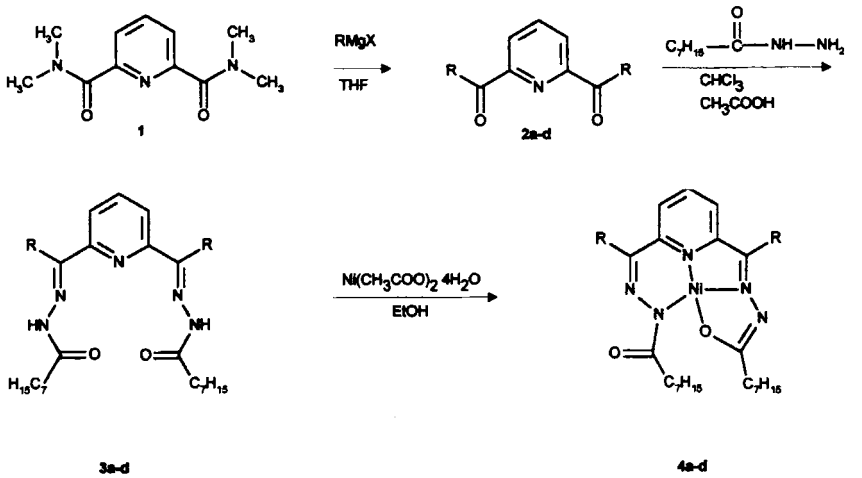


I

SCHEME 1

## RESULTS AND DISCUSSION

Complexes **4a–d**, presenting linear alkyl chains as R and R′ substituents were prepared following the four step procedure outlined in Scheme 2. Reaction of *N, N, N′, N′*-tetraethylpyridin-2,6-dicarboxyamide **1** with an excess of alkyl magnesium bromide gives 2,6-dialcanoylpyridines **2b–d** respectively in 22%, 18% and 8% isolated yields. Condensation of **2a–d** with octanoic hydrazide afforded the corresponding ligands **3a–d**. In solution at room temperature the ligands **3a–d** assume the *E,E* configuration, i.e., both hydrazonic arms are *cis* to the R substituent. Upon heating to 100°C in $C_2D_2Cl_4$ the less symmetrical *E,Z* isomer begins to appear (see the $^1$H-NMR of **3a**, Experimental section). The presence of one arm of the lignd in the *Z* configuration can be detected *via* $^1$H-NMR by the downfield shift observed for the R=$CH_3$ substituent of **3a** in the *Z* configuration with respect to the *E* one, typical of hydrazone derivatives [5].




a R= $CH_3$
b R= $C_5H_{11}$
c R= $C_{12}H_{25}$
d R= $C_{18}H_{37}$

SCHEME 2

The sterically hindered *Z,Z* isomer can not be detected even at higher temperatures.

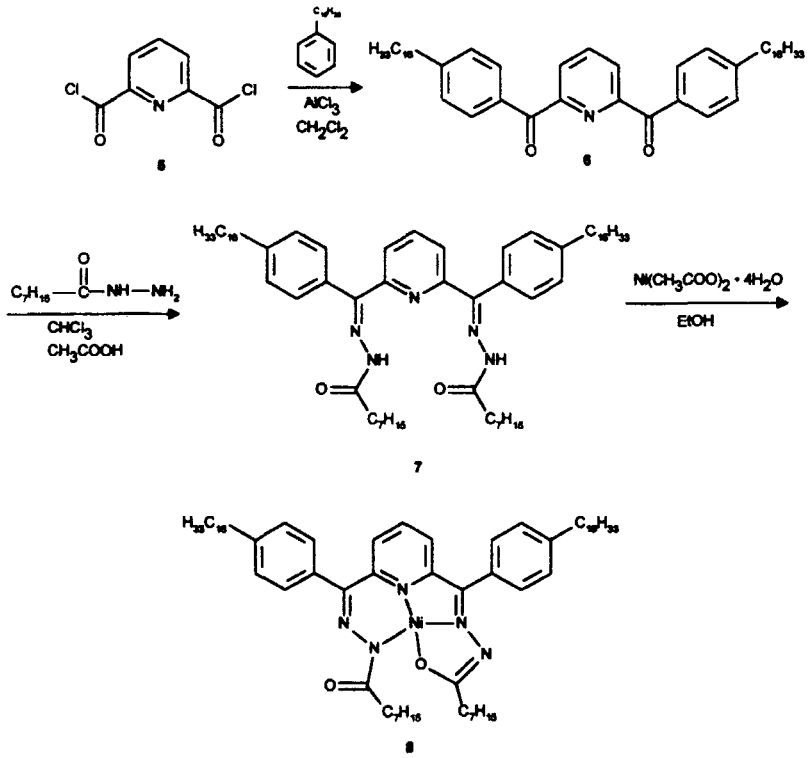
Nickel(II) acetate reacts rapidly with these ligands, giving stable brown-red complexes **4a–d** in excellent yields. The $^1$H-NMR spectra of the complexes show a reduced symmetry reminiscent of the *E,Z* isomer of the ligands: the *meta* protons of the pyridine ring and the $CH_2$ α to C=O in the alkyl chains are not equivalent. In the IR spectra the *ν*(NH) band disappears, while the *ν*(C=O) is nearly at the same value as in the corresponding free ligand, as if at least one of the two carbonylic groups was not coordinated. To explain these data, for this series of complexes we propose a square planar coordination of nickel with the ligand in the *E,Z* configuration so to coordinate the metal atom to the pyridinic, as well as to one of the iminic and one of the hydrazidic nitrogens, and the oxygen of one of the carbonylic groups. It is well known that the ligands, derived from the condensation of 2,6-diacetylpyridine and hydrazides or hydrazines, react with several metal salts normally to form octahedral [3] or bipyramidal pentagonal [4] coordination geometries. To our knowledge, a square planar coordination is suggested only in the palladium(II) complex of 2,6-diacetylpyridine bis(6-chloro-2-pyridyl)hydrazone [6]; also in this compound there is a $^1$H-NMR evidence that the two hydrazonic arms of the ligand assume the *E,Z* configuration.

The thermal behaviour of the ligands **3a–d** and the Ni(II) complexes **4a–d** was analyzed by differential scanning calorimetry (DSC) and optical microscopy

(OM): none of the compounds presents liquid crystalline properties. For the ligands several solid–solid transitions are observed and the clearing temperature decreases with increasing chain length. The Ni(II) complexes behave as normal solids with a solid–solid transition (C-C' 98°C) only for **4d** in the second heating cycle.

Since the presence of four long alkyl chains did not suffice to induce mesogenic properties in **4a–d**, two different approaches were undertaken to change type and distribution of the side chains.

Two *p*-alkyl substituted aromatic rings were introduced as R substituents following the synthetic procedure outlined in Scheme 3. The first step is a

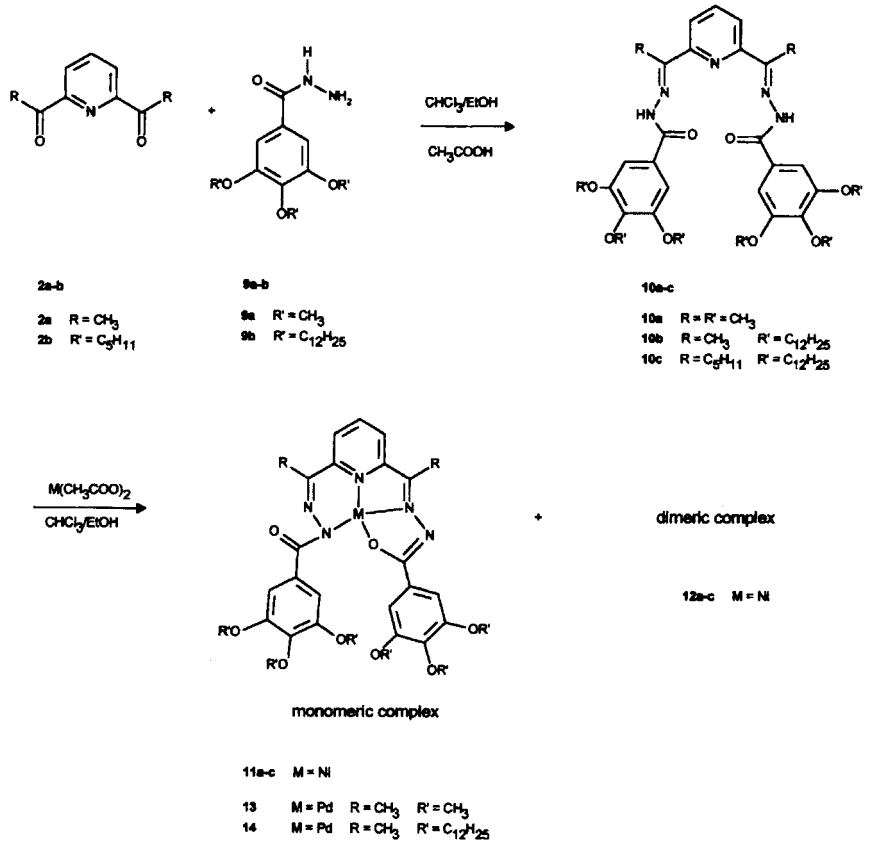


SCHEME 3

Friedel-Craft type acylation starting from 2,6-pyridinedicarbonyl dichloride (**5**) and hexadecylbenzene. The reaction is completely regioselective giving exclusively diketone **6** in 21% isolated yield. Compound **6** was then condensed with octanoic hydrazide to give the bishydrazone **7**. It is interesting to note that **7** is stable in the *E,Z* configuration, as probed by NMR and IR

spectroscopies (see Experimental part). The presence of the aryl groups on the C=N double bonds destabilizes the *E*, *E* isomer with respect to the *E*, *Z* one for steric reasons. The corresponding Ni(II) complex **8** has the same coordination geometry and ligand configuration as **4a**–**d**. Both **7** and **8**, examined *via* DSC and OM, show to be non-mesomorphic.

In the second approach (Scheme 4) a higher number of alkoxy side chains were introduced by condensing 3,4,5-trialkoxybenzoylhydrazides **9a**–**b** with




SCHEME 4

2,6-dialkanoylpyridines **2a**–**b**. In this way hydrazones **10a**–**c** were produced, where **10a** is the model compound and **10b**–**c** present respectively 6 and 8 side chains radiating from the core. All the compounds are in the *E*,*E* configuration in chloroform solution at room temperature.

In this case the reaction of **10a** with Ni(II) acetate led to the formation of the two products **11a** and **12a** which were separated by flash chromatography. The desired monomeric complex **11a** presents the same coordination exhibited by **4a–d**, while the paramagnetic derivative **12a** is the dimeric form of **11a** as shown by X-ray crystallographic analysis. It is important to note that in the IR spectrum of **12a** the $\nu$(C=O) band is absent, because the deprotonated ligand is in the enolic form with both the carbonylic groups coordinated to the metal.

The monomeric units of **12a** are assembled to give a discrete dimeric structure in which the two nickel ions are linked through bridging pyridine nitrogens (see Fig. 1).

Bond distances and angles in the two coordination polyhedra are given in Table I. Both hydrazone ligands act as pentadentate using, beside the pyridine nitrogen, the carbonylic oxygen and the iminic nitrogen of one arm in coordinating one nickel ion and the corresponding two atoms of the other arm in the coordination of the second nickel. Each metal atom has a highly distorted octahedral coordination, the ranges for *trans* and *cis* angles being

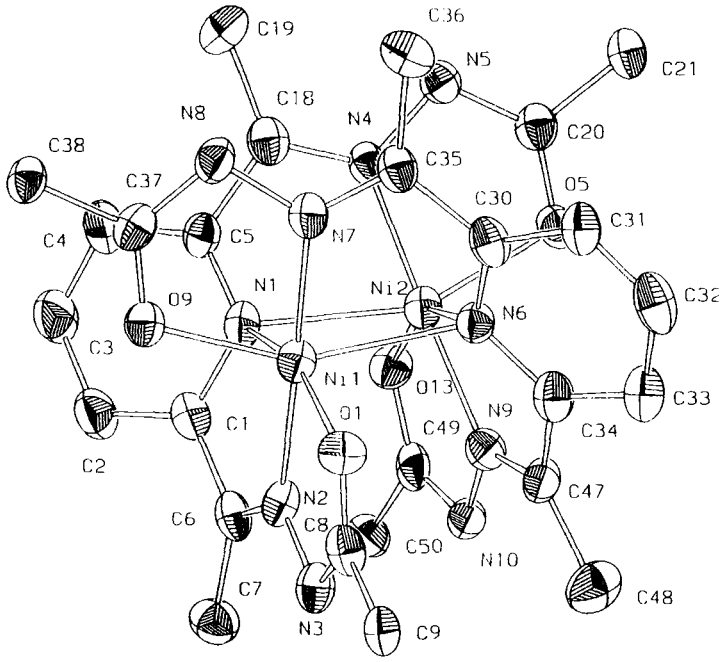



FIGURE 1 ORTEP diagram of compound **12a**; R′ substituents and H atoms are omitted for clarity.

TABLE I Bond distances (Å) and angles (°) in the coordination polyhedra of compound **12a**

| | | | |
|---|---|---|---|
| $Ni_1$-$N_1$ | 2.352(8) | $Ni_2$-$N_1$ | 2.319(11) |
| $Ni_1$-$N_2$ | 1.972(7) | $Ni_2$-$N_4$ | 1.957(7) |
| $Ni_1$-$N_6$ | 2.330(9) | $Ni_2$-$N_6$ | 2.370(7) |
| $Ni_1$-$N_7$ | 1.958(7) | $Ni_2$-$N_9$ | 1.945(8) |
| $Ni_1$-$O_1$ | 1.985(6) | $Ni_2$-$O_5$ | 2.004(7) |
| $Ni_1$-$O_9$ | 2.016(6) | $Ni_2$-$O_{13}$ | 2.032(6) |
| $N_1$-$Ni_1$-$N_6$ | 99.6(3) | $N_4$-$Ni_2$-$O_5$ | 79.4(3) |
| $O_1$-$Ni_1$-$N_2$ | 76.2(3) | $N_1$-$Ni_2$-$O_5$ | 154.3(3) |
| $N_2$-$Ni_1$-$O_9$ | 100.5(3) | $N_1$-$Ni_2$-$N_4$ | 74.9(3) |
| $O_9$-$Ni_1$-$N_7$ | 79.0(3) | $O_5$-$Ni_2$-$O_{13}$ | 105.9(3) |
| $N_7$-$Ni_1$-$N_6$ | 75.2(3) | $O_5$-$Ni_2$-$N_9$ | 98.3(3) |
| $N_6$-$Ni_1$-$O_1$ | 84.7(3) | $O_5$-$Ni_2$-$N_6$ | 84.1(3) |
| $N_2$-$Ni_1$-$O_1$ | 78.9(3) | $N_4$-$Ni_2$-$O_{13}$ | 106.7(3) |
| $O_1$-$Ni_1$-$O_9$ | 104.3(3) | $N_4$-$Ni_2$-$N_9$ | 174.1(3) |
| $N_6$-$Ni_1$-$O_9$ | 154.1(3) | $N_4$-$Ni_2$-$N_6$ | 99.0(3) |
| $O_1$-$Ni_1$-$N_7$ | 106.6(3) | $N_1$-$Ni_2$-$O_{13}$ | 82.2(3) |
| $N_2$-$Ni_1$-$N_7$ | 174.5(3) | $N_1$-$Ni_2$-$N_9$ | 107.3(3) |
| $N_2$-$Ni_1$-$N_6$ | 105.0(3) | $N_1$-$Ni_2$-$N_6$ | 99.4(3) |
| $N_1$-$Ni_1$-$O_9$ | 82.5(3) | $N_9$-$Ni_2$-$O_{13}$ | 79.1(3) |
| $N_1$-$Ni_1$-$O_1$ | 155.0(3) | $N_6$-$Ni_2$-$O_{13}$ | 153.7(3) |
| $N_1$-$Ni_1$-$N_7$ | 98.3(3) | $N_6$-$Ni_2$-$N_9$ | 75.3(3) |

153.7(3)–174.5(3) and 74.9(3)–107.7(3)°, respectively. The intermetallic distance in the $Ni_2N_2$ moiety is 3.015(5) Å. The ligands are both non planar, the two arms being markedly twisted (*ca.* 35°) with respect to the central pyridine ring.

There are a few examples of dimeric complexes with a bridging pyridine [7]. Worthy of note in particular is the nickel complex of 2,6-diacetylpyridine bis(1′-phthalazinylhydrazone), where the ligand behaves as pentadentate with the phthalazine nitrogen replacing the carbonylic oxygen of **10a** [8].

Magnetic susceptibility data, obtained on a powder sample of **12a**, are reported in Figure 2 in the form of $\chi_m$ and $\chi_m T$ versus the temperature T. The room temperature value of $\chi_m T$ (1.97 emu K/mol) is lower than that expected for two uncorrelated S = 1 nickel(II) spins ($\chi_m T \approx 2.24$ emu K/mol with g = 2.2) and it decreases upon lowering the temperature, indicating the presence of an antiferromagnetic coupling; the ground state is diamagnetic, since $\chi_m T$ does not meaningfully differ from zero at the lower temperature that was reached (11.5 K). $\chi_m$ passes through a broad maximum at $T \approx 85$ K. No signal is present in the EPR powder spectra in the observed range of temperature and this result agrees with the susceptibility data, since at low temperature only the S = 0 ground state is populated, while at higher temperature nickel(II) ions in a tetragonal environment are EPR silent [9]. The Heisenberg exchange H amiltonian for a dimer, $H = JS_1S_2$, was used in

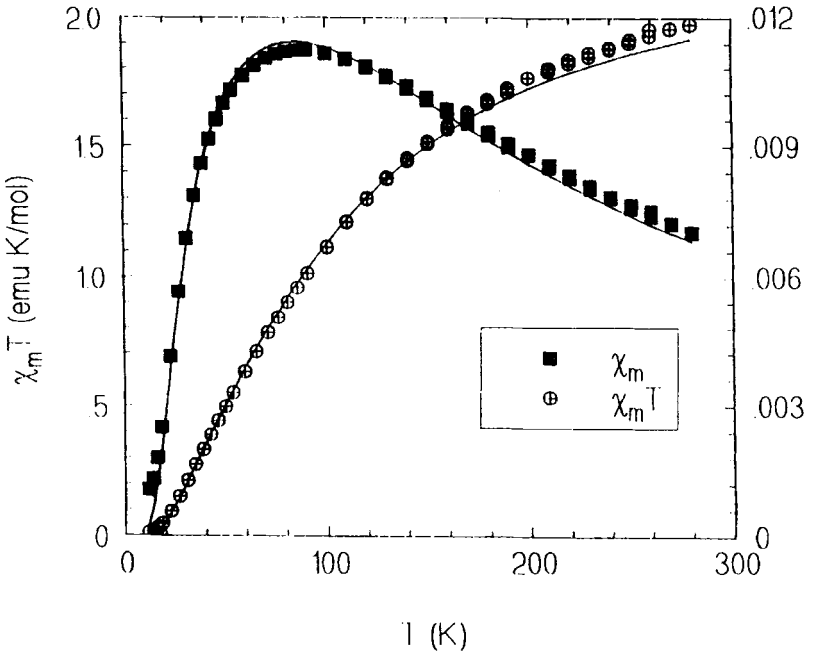



FIGURE 2 Plots of $\chi_m$ and $\chi_m$ T versus T for the compound **12a**. The solid lines represent the best fit.

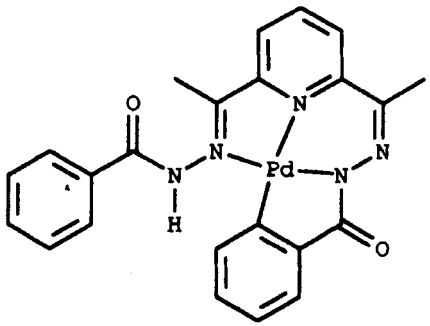
the interpretation of the magnetic data. The least squares fitting of the $\chi_m$ vs T curve yields $J = 57.7$ cm$^{-1}$ and $g = 2.197$ ($R = 8.9 \cdot 10^{-4}$, where $R = \Sigma(\chi_m^{exp} - \chi_m^{calc})^2/\Sigma(\chi_m^{exp})^2$), in accordance with the value of J found in the already quoted nickel complex of the ligand 2,6-diacetylpiridine bis(1'-phthalazinyl-hydrazone)($J = 65.4$): the pyridine nitrogens clearly provide a very efficient superexchange interaction between the two metal ions [8, 10].

The unusual equilibrium between the two forms led us to investigate the relative stability of the two complexes. **11a** is stable in acidic solution, while it is completely converted into **12a** in organic solvents within few hours. It is possible to transform **12a** into **11a** by refluxing the former in ethanol/glacial acetic acid.

The same complexing behaviour is observed in the other members of this series, **10b** and **10c**. In this case evidence for the formation of the dimeric complex comes from their paramagnetism, from the presence of the dimeric peak as molecular ion in the mass spectra and from the absence of the free $\nu$(C=O) band in the IR spectra. The type of coordination observed in the nickel complexes is dictated by the bulkiness of R' substituents (Scheme 1, general structure I). When R' is an alkyl group (**4a–d**, **8**) the square planar

monomeric complexes are indefinitely stable both in solution and in solid state. The presence of bulkier aryl substituents destabilizes the square planar coordination, forcing the dimerization and the octahedral coordination around the metal atom. On the contrary variation of the R groups from alkyl to aryl (**4a–d** *versus* **8**) does not change the coordination geometry around the nickel.

To bypass the formation of the dimeric compounds, the palladium(II) complexes **13** and **14** of the ligands **10a** and **10b** were also synthesised. They present the same *E,Z* configuration of the ligand observed in the corresponding nickel(II) derivatives. The formation of palladacycle isomers (Scheme 5),




SCHEME 5

observed with a similar ligand [11], is excluded due to the absence of the two amidic protons both in the $^1$H-NMR and IR spectra.

The thermal properties of **11b–c** and **14** were studied using DSC and OM. The monomeric palladium complex **14** presents a melting point of 121°C, temperature at which decomposition takes palce preventing the possible formation of a mesophase.

The Ni complex **11b** exhibits an unusual thermal history effect. The freshly prepared samples of **11b** present a mesomorphic phase already at room temperature, showing a dark red coloured *schlieren* texture reminescent of a smetic phase [12]. Upon cooling from the isotropic phase a solid phase is formed, which, upon further heating, directly melts to isotropic liquid at 145–148°C. Subsequent cooling-heating cycles do not change this situation. $^1$H-NMR and mass analyses of the resulting solid prove the complete conversion of **11b** in its dimeric form **12b**. The partial conversion of **11b** in **12b** is observed *via* OM, leaving a virgin sample of **11b** to stand days between two glass slides at room temperature.

In the case of **11c** the presence of two additional peripheral alkyl changes the mesomorphic properties and the thermal stability of the monomeric form. At

room temperature **11c** is an indefinitely stable isotropic liquid; interconversion of **11c** to the dimer **12c** requires heating to 200°C for several minutes. Once formed the dimeric **12c** is stable and behaves as a normal solid with a sharp melting point at 115°C.

## CONCLUSIONS

The rich coordination chemistry of 2,6-disubstituted pyridine bishydrazones has been investigated with the aim to generate metallomesogens. Stable square planar complexes of Ni(II) having four long alkyl chains as R and R′ substituents do not present mesogenic properties. By increasing the number of the side chains from four to six in the ligands, two different, monomeric and dimeric, nickel(II) complexes are formed. The monomeric square planar **11b** present a mesomorphic phase at room temperature, but it turns itself into the non mesogenic octahedral dimer **12b** upon entering the isotropic liquid phase. Steric hindrance forces the formation of the dimer when the R′ groups are aryl derivatives. The interconversion of the monomer into the dimer is relatively fast when the monomer is either in solution or in the isotropic liquid phase. The introduction of two additional alkyl chains as in **11c** makes the monomer form indefinitey stable at room temperature.

## EXPERIMENTAL

ACS Grade reagents were used without further purification, all other solvents were dried over 3 Å molecular sieves. THF was distilled under nitrogen from sodium benzophenone ketyl. $^1$H-NMR spectra were recorded on Bruker AC100, CXP200, AC300 and AMX400 spectrometers. Chemical shifts are given in parts per million ($\delta_{TMS} = 0$) using the solvent peak referred to TMS (7.25 ppm for chloroform) as internal reference. The FTIR spectra were re corded using a Nicolet SPC spectrometers. Melting points were found using a Electrothermal melting-point apparatus. Thin-layer chromatography (TLC) was carried out using Kieselgel 60 $F_{254}$ (Merck) and flash chromatography was performed by using silica gel 60 (Merck 230–400 mesh), while the preparative chromatography was performed by using silica gel 60 (Merck 70–230 mesh). All new ligands and complexes gave satisfactory elemental analyses. Optical microscopy was performed using a Leitz-Wetzlar polarizing microscope, equipped with a Mettler FP 82 hot stage. Thin samples were observed between two untreated cover slips of ordinary glass. DSC measurements were made with a Perkin-Elmer DSC 7

thermal analyser. Reproducible traces were obtained for all compounds during the second and subsequent heating-cooling cycles (scanning rate 10°C $min^{-1}$). Mass spectra were recorded on a Finnigan/MAT SSQ 710 spectrometer, using EI and CI technique. Magnetic susceptibility measurements have been performed on a powdered sample in the temperature range 11.5–280 K, with an applied field of 1 T, by using a Métronique Ingéniérie MS03 SQUID magnetometer. The diamagnetic contribution to the susceptibility has been estimated through the Pascal's constants. EPR spectra were recorded with a VARIAN E9 spectrometer operating at the X-band frequency, equipped with an Oxford Instrument ESR9 continuous-flow cryostat.

*N, N, N', N'* Tetraethylpyridine-2,6-dicarboxyamide (**1**) was synthesized following a literature method [13], while 2,6-diacetylpyridine (**2a**) is commercially available.

*X-ray Analysis*-Diffraction measurements were made at room temperature on a Siemens AED single crystal diffractometer with niobium-filtered Mo-K$\alpha$ radiation ($\lambda = 0.71069$ Å). Intensities in the range $6 < 2\theta < 56°$ were measured in the $\theta$–$2\theta$ scan mode for one hemisphere of data. The 6009 unique reflections obeying the condition $I > 3.5\ \sigma(I)$ were retained out of a total of 14179 measured reflections. The check of the standard reflections showed no deterioration during data collection. Intensity data were corrected for Lorentz and polarization factors as well as for absorption effects.

The structure was solved by a combination of Patterson and Fourier techniques and refined by least-squares procedures using anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms which were all placed at calculated positions. The final R is 0.079 for 906 variables. Calculations were carried out on a Gould 6040 and a Encore91 using the programs SHELX76 [14], SHELX86 [15], PARST [16], and ORTEP [17]. Fractional atomic coordinates for non-hydrogen atoms are listed in Table II.

**2,6-Dihexanoylpyridine 2b**

A solution of pentylmagnesium bromide 2.0M (4 ml, 3.9 mmol), was added dropwise under argon to a solution of *N, N, N', N'*-tetraethylpyridine-2,6-dicarboxyamide **1** (484 mg, 1.75 mmol) in dry THF (20 ml) cooled to −70°C. The reaction mixture was stirred for 2 hours at room temperature, then quenched with 20 ml of 0.1 N hydrochloric acid. The resulting solution was extracted with dichloromethane, washed to neutrality with water, dried over sodium sulphate and the solvent removed in vacuo to give a red oil. After purification by flash chromatography using *n*-hexane, followed by *n*-hexane/ethyl acetate 9/1 as eluants, 216 mg of **2b** as colourless oil were obtained (22% yield).

TABLE II Atomic coordinates ($x\ 10^4$) and equivalent isotropic displacement parameters ($Å^2 x10^4$) (one third trace of the diagonalized matrix), with e.s.d's in parentheses

| *Atom* | *X/a* | *Y/b* | *Z/c* | *Ueq* |
|---|---|---|---|---|
| $Ni_1$ | 2568.1(7) | 673.7(9) | 335.7(9) | 477(6) |
| $Ni_2$ | 2660.9(7) | 2928.4(9) | 1455.4(9) | 465(6) |
| $N_1$ | 2178(5) | 1797(6) | 1841(6) | 527(43) |
| $N_2$ | 1230(5) | 766(5) | −239(6) | 480(39) |
| $N_3$ | 842(5) | 301(6) | −1330(6) | 531(42) |
| $N_4$ | 3675(4) | 2935(5) | 2672(6) | 457(38) |
| $N_5$ | 4472(5) | 3459(6) | 2963(6) | 495(39) |
| $N_6$ | 3222(5) | 1802(5) | 73(5) | 448(37) |
| $N_7$ | 3891(5) | 682(5) | 1040(6) | 490(39) |
| $N_8$ | 4145(5) | 216(6) | 1686(6) | 550(44) |
| $N_9$ | 1737(5) | 2859(6) | 161(6) | 494(40) |
| $N_{10}$ | 896(5) | 3251(6) | 240(6) | 500(41) |
| $O_1$ | 2326(4) | −201(5) | −1206(5) | 542(33) |
| $O_2$ | −727(5) | −1184(6) | −5334(6) | 897(47) |
| $O_3$ | 369(6) | −2472(6) | −6158(6) | 844(45) |
| $O_4$ | 2052(6) | −2716(6) | −4937(6) | 945(50) |
| $O_5$ | 3556(4) | 3920(4) | 1670(5) | 518(33) |
| $O_6$ | 5469(5) | 6318(7) | 1648(7) | 1027(63) |
| $O_7$ | 6914(5) | 6848(6) | 3425(7) | 925(53) |
| $O_8$ | 7223(5) | 5928(6) | 4616(6) | 867(47) |
| $O_9$ | 2604(4) | −284(4) | 928(5) | 538(34) |
| $O_{10}$ | 5302(5) | −1289(6) | 4267(6) | 813(48) |
| $O_{11}$ | 3858(5) | −2191(6) | 4091(6) | 820(49) |
| $O_{12}$ | 2181(5) | −2105(6) | 2832(7) | 891(55) |
| $O_{13}$ | 1673(4) | 3745(4) | 2033(5) | 511(33) |
| $O_{14}$ | −2285(5) | 4472(6) | 194(7) | 935(55) |
| $O_{15}$ | −2520(5) | 4219(7) | 1737(8) | 1079(67) |
| $O_{16}$ | −1096(6) | 3908(7) | 3189(7) | 967(60) |
| $C_1$ | 1284(6) | 1506(7) | 1510(7) | 530(51) |
| $C_2$ | 902(7) | 1461(8) | 2210(8) | 680(61) |
| $C_3$ | 1480(8) | 1675(9) | 3216(9) | 784(69) |
| $C_4$ | 2385(7) | 1916(7) | 3531(8) | 624(55) |
| $C_5$ | 2701(6) | 2021(6) | 2825(7) | 460(45) |
| $C_6$ | 745(6) | 1158(6) | 367(7) | 480(48) |
| $C_7$ | −269(6) | 1226(8) | 6(8) | 646(57) |
| $C_8$ | 1487(7) | −167(6) | −1736(7) | 518(50) |
| $C_9$ | 1187(6) | −733(7) | −2896(7) | 540(52) |
| $C_{10}$ | 340(6) | −635(7) | −3538(8) | 568(54) |
| $C_{11}$ | 80(7) | −1231(9) | −4635(8) | 656(61) |
| $C_{12}$ | 652(8) | −1949(8) | −5087(8) | 630(58) |
| $C_{13}$ | 1530(8) | −2027(8) | −4431(9) | 663(61) |
| $C_{14}$ | 1789(7) | −1449(8) | −3347(9) | 661(60) |
| $C_{15}$ | −1284(8) | −362(12) | −4996(11) | 983(93) |

MS($CI^+$, m/e): 275 ($M^+$, 100); $^1$H-NMR ($CDCl_3$, 100 MHz): $\delta$ 0.87 (bt, 6 H, $CH_3$), 1.35 [m, 8 H, $(CH_2)_2$], 1.69 (m, 4 H, CO-$CH_2$-$CH_2$), 3.21 (t, 4 H, CO-$CH_2$, J = 7.3 Hz), 8.11 (m, 3 H, Ar-H); FTIR ($cm^{-1}$, KBr): 2932 ($\nu$ aromatic CH), 2861 ($\nu$ aliphatic CH), 1699 ($\nu$ C=O), 1467 ($\delta$ $CH_2$), 1358 ($\delta$ $CH_3$).

TABLE II (Continued)

| *Atom* | *X/a* | *Y/b* | *Z/c* | *Ueq* |
|---|---|---|---|---|
| $C_{16}$ | 305(10) | −3549(9) | −6601(10) | 1003(79) |
| $C_{17}$ | 2980(8) | −2705(12) | −4311(10) | 1112(93) |
| $C_{18}$ | 3627(6) | 2455(7) | 3168(7) | 540(51) |
| $C_{19}$ | 4398(7) | 2402(9) | 4059(8) | 744(64) |
| $C_{20}$ | 4310(6) | 3957(7) | 2390(7) | 523(50) |
| $C_{21}$ | 5055(6) | 4649(7) | 2641(7) | 503(49) |
| $C_{22}$ | 4921(7) | 5085(8) | 1969(9) | 693(65) |
| $C_{23}$ | 5561(8) | 5834(8) | 2239(9) | 703(66) |
| $C_{24}$ | 6338(7) | 6073(8) | 3141(9) | 683(64) |
| $C_{25}$ | 6469(7) | 5614(8) | 3774(8) | 664(59) |
| $C_{26}$ | 5835(6) | 4890(7) | 3529(8) | 603(55) |
| $C_{27}$ | 4606(10) | 6252(13) | 896(13) | 1241(125) |
| $C_{28}$ | 7778(7) | 6581(10) | 3286(12) | 966(89) |
| $C_{29}$ | 7480(9) | 5412(10) | 5266(11) | 1038(84) |
| $C_{30}$ | 4091(6) | 1561(7) | 216(7) | 546(51) |
| $C_{31}$ | 4594(7) | 1602(8) | −379(8) | 626(59) |
| $C_{32}$ | 4165(8) | 1855(8) | −1152(9) | 717(67) |
| $C_{33}$ | 3232(7) | 2092(7) | −1367(8) | 644(60) |
| $C_{34}$ | 2801(7) | 2099(7) | −686(7) | 554(51) |
| $C_{35}$ | 4506(6) | 1118(7) | 963(7) | 504(49) |
| $C_{36}$ | 5507(6) | 1159(8) | 1535(8) | 675(58) |
| $C_{37}$ | 3400(6) | −247(7) | 1561(7) | 520(50) |
| $C_{38}$ | 3541(6) | −759(7) | 2242(7) | 522(51) |
| $C_{39}$ | 4391(6) | −746(7) | 2927(8) | 562(53) |
| $C_{40}$ | 4495(7) | −1261(7) | 3546(8) | 620(57) |
| $C_{41}$ | 3733(7) | −1729(8) | 3461(8) | 680(63) |
| $C_{42}$ | 2866(7) | −1691(8) | 2783(9) | 696(64) |
| $C_{43}$ | 2769(6) | −1214(8) | 2158(8) | 624(59) |
| $C_{44}$ | 6106(7) | −821(9) | 4390(10) | 774(73) |
| $C_{45}$ | 3674(11) | −3253(11) | 3514(11) | 1090(97) |
| $C_{46}$ | 1278(8) | −1994(11) | 2250(11) | 988(93) |
| $C_{47}$ | 1877(6) | 2469(7) | −744(7) | 521(52) |
| $C_{48}$ | 1192(7) | 2446(10) | −1739(8) | 808(72) |
| $C_{49}$ | 948(6) | 3650(6) | 1256(8) | 500(52) |
| $C_{50}$ | 51(6) | 3909(7) | 1423(8) | 532(51) |
| $C_{51}$ | −664(6) | 4128(8) | 714(8) | 628(60) |
| $C_{52}$ | −1517(7) | 4250(8) | 821(9) | 701(66) |
| $C_{53}$ | −1661(7) | 4126(9) | 1643(10) | 809(77) |
| $C_{54}$ | −935(7) | 3972(8) | 2347(9) | 675(63) |
| $C_{55}$ | −54(7) | 3854(7) | 2283(9) | 648(59) |
| $C_{56}$ | −2146(8) | 4673(11) | −601(11) | 959(91) |
| $C_{57}$ | −2975(9) | 3281(12) | 1372(13) | 1174(119) |
| $C_{58}$ | −428(11) | 3662(12) | 3866(12) | 1104(109) |

Following the same procedure, using respectively dodecylmagnesium bromide and octadecylmagnesium bromide, compounds **2c** and **2d** were obtained respectively in 18% and 8% yield.

**2,6-Ditridecanoylpyridine 2c:** white solid, mp 40–41°C; MS ($CI^+$, m/e): 472 ($MH^+$, 100); $^1$H-NMR($CDCl_3$, 100 MHz): $\delta$ 0.85 (t, 6 H, $CH_3$) 1.24 [bs 36 H, $(CH_2)_9$], 1.75 (m, 4 H, $COCH_2$-$CH_2$), 3.23 (t, 4 H, CO-$CH_2$, J = 7.1 Hz), 8.14

(m, 3 H, Ar-H); FTIR ($cm^{-1}$, KBr): 2919 ($\nu$ aromatic CH), 2850 ($\nu$ aliphatic CH), 1698 ($\nu$ C=O), 1464 ($\delta$ $CH_2$).

**2,6-Dinonadecanoylpyridine 2d:** white solid, mp 71°C; MS($CI^+$, m/e): 639 ($M^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ 0.86 (t, 6 H, $CH_3$), 1.24 [bs, 60 H, $(CH_2)_{15}$], 1.76 (m, 4 H, CO-$CH_2$-$CH_2$), 3.24 (t, 4 H, CO-$CH_2$, J = 7.4 Hz), 7.96 (t, 1 H, $H_p$, J = 7.8 Hz), 8.17 (d, 2 H, $H_m$, J = 7.8 Hz); FTIR ($cm^{-1}$, KBr): 2917 ($\nu$ aromatic CH), 2849 ($\nu$ aliphatic CH), 1699 ($\nu$ C=O), 1466 ($\delta$ $CH_2$).

**2,6-Diacetylpyridine bis(octanoylhydrazone) 3a** was prepared following the procedure reported in reference 4. Mp 225°C; MS ($CI^+$, m/e): 444 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz, *E,E* isomer); $\delta$ 0.87 [t, 6 H, $(CH_2)_n$-$CH_3$], 1.25–1.40 [m, 16 H, $(CH_2)_4$], 1.73 (m, 4H, CO-$CH_2$-$CH_2$), 2.37 (s, 6H, CN-$CH_3$), 2.79 (t, 4H, CO-$CH_2$, J = 7.6 Hz), 7.73 (t, 1 H, $H_p$, J = 7.8 Hz), 8.02 (d, 2 H, $H_m$, J = 7.8 Hz), 8.57 (s, 2 H, NH); FTIR ($cm^{-1}$, KBr): 3200 ($\nu$ NH), 2954 ($\nu$ aromatic CH), 2853 ($\nu$ aliphatic CH), 1672 ($\nu$ C=0), 1568.

$^1$H-NMR [$C_2D_2Cl_4$, 400 MHz, 100°C, E, E + E, Z($\cong$15%)]: $\delta$ 0.87 [t, 6 H, $(CH_2)_n$-$CH_3$], 1.25–1.40 [m, 16 H, $(CH_2)_4$], 1.73 (m, 4 H, CO-$CH_2$-$CH_2$), 2.40 (s, CN-$CH_3^E$), 2.45 (s, CN-$CH_3^Z$), 2.76 (bt, 4 H, CO-$CH_2$), 7.52 (d, $H_m^{E,Z}$ meta, J = 8.0 Hz), 7.76 (t, $H_p^{E,E}$, J = 7.8 Hz), 7.91 (t, $H_p^{E,Z}$, J = 8.0 Hz), 8.05 (d, $H_m^{E,E}$, J = 7.8 Hz), 8.10 (d, $H_m^{E,Z}$, J = 8.0 Hz), 8.40 (bs, $NH^{E,E}$), 8.47 (bs, $NH^{E,Z}$), 8.99 (bs, $NH^{E,Z}$).

**2,6-Dihexanoylpyridine bis(octanoylhydrazone)3b**

A solution of octanoic hydrazide (221 mg, 1.4 mmol) and **2b** (165 mg, 0.6 mmol) in chloroform (30 ml) was heated under reflux for 72 hours. After cooling the mixture to room temperature, the white precipitate formed was filtered off and crystallized from ethanol to give **3b** (166 mg, 50% yield).

Mp 155°C; MS ($CI^+$, m/e): 556 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz, *E,E* isomer): $\delta$ 0.87 (m, 12 H, $CH_3$), 1.24–1.45 [m, 24 H, $(CH_2)_n$], 1.54 (m, 4 H, CN-$CH_2$-$CH_2$), 1.74 (m, 4 H, CO-$CH_2$-$CH_2$), 2.79 (t, 4 H, CO-$CH_2$, J = 7.6 Hz), 2.87 (pseudo t, 4 H, CO-$CH_2$), 7.72 (t, 1 H, $H_p$, J = 7.9 Hz), 7.99 (d, 2 H, $H_m$, J = 7.9 Hz), 8.81 (s, 2 H, NH); FTIR ($cm^{-1}$, KBr): 3190 ($\nu$ NH), 2926 ($\nu$ aromatic CH), 2850 ($\nu$ aliphatic CH), 1675 ($\nu$ C=O), 1569, 1434.

Following the same procedure, using respectively 2,6-ditridecanoylpyridine **2c** and 2,6-dinonadecanoylpyridine **2d** compounds **3c** and **3d** were obtained in 26% and 13% yield respectively.

**2,6-Ditridecanoylpyridine bis(octanoylhydrazone) 3c:** white solid, mp 145°C; MS ($CI^+$, m/e): 752 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz, *E, E* isomer): $\delta$

0.86 (m, 12 H, $CH_3$), 1.20–1.42 [m, 52 H, $(CH_2)_n$], 1.53 (m, 4 H, CN-$CH_2$-$CH_2$), 1.73 (m, 4 H, CO-$CH_2$-$CH_2$), 2.78 (t, 4 H, CO-$CH_2$, J = 7.7 Hz), 2.88 (pseudo t, 4 H, CN-$CH_2$), 7.71 (t, 1 H, $H_p$, J = 7.9 Hz), 7.99 (d, 2 H, $H_m$, J = 7.9 Hz), 8.84 (s, 2 H, NH); FTIR ($cm^{-1}$, KBr): 3188 (ν NH), 2923 (ν aromatic CH), 2850 (ν aliphatic CH), 1673 (ν C=O), 1568, 1433, 1386, 1098.

**2,6-Dinonadecanoylpyridine bis(octanoylhydrazone) 3d:** white solid, mp 120–121°C; MS ($CI^+$, m/e): 920 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz, *E,E* isomer): δ 0.86 (m, 12 H, $CH_3$), 1.20–1.42 [m, 76 H, $(CH_2)_n$], 1.55 (m, 4 H, CN-$CH_2$-$CH_2$), 1.74 (m, 4 H, CO-$CH_2$-$CH_2$), 2.79 (t, 4 H, CO-$CH_2$, J = 7.6 Hz), 2.86 (pseudo t, 4 H, CN-$CH_2$), 7.72 (t, 1 H, $H_p$, J = 7.7 Hz), 7.99 (t, 2 H, $H_m$, J = 7.7 Hz), 8.60 (s, 2 H, NH); FTIR ($cm^{-1}$, KBr): 3180 (ν NH), 2922 (ν aromatic CH), 2849 (ν aliphatic CH), 1674 (ν C=O), 1568, 1465, 1433, 1387.

**[2, 6-Diacetylpyridine bis(octanoylhydrazonato)] nickel(II) 4a**

A mixture of nickel (II) acetate tetrahydrate (38 mg, 0.15 mmol) and **3a** (68 mg, 0.15 mmol) was heated for 3 hours in boiling ethanol (30 ml). Addition of water (30 ml) to the cooled solution caused the formation of a red solid, which, collected by filtration, gave 49 mg of pure **4a** as red solid (59% yield).

Mp 107°C; MS ($CI^-$, m/e): 499 ($M^-$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): δ 0.86 [bt, 6 H, $(CH_2)_n$-$CH_3$], 1.26 – 1.34 [m, 16 H, $(CH_2)_4$], 1.65 (m, 4 H, CO-$CH_2$-$CH_2$), 2.34 (s, 3 H, CH-$CH_3^Z$), 2.37 (t, 2 H, CO-$CH_2$, J = 7.7 Hz), 2.56 (s, 3 H, CN-$CH_3^E$), 2.88 (t, 2 H, CO-$CH_2$, J = 7.7 Hz), 7.31 (d, 1 H, $H_m^Z$, J = 7.4 Hz), 7.74 (d, 1 H, $H_m^E$, J = 8.1 Hz), 8.03 (bt, 1 H, $H_p$); FTIR ($cm^{-1}$, KBr): 2925 (ν aromatic CH), 1686 (ν C=O), 1600 (ν coordinated C=O), 1515, 1396, 1151, 1094 (ν C-O).

**[2,6-Dihexanoylpyridine bis(octanoylhydrazonato)] nickel (II) 4b**

A mixture of nickel (II) acetate tetrahydrate (27 mg, 0.11 mmol) and **3b** (0.1 mmol) was heated for 3 hours in boiling ethanol (20 ml). Addition of water (20 ml) to the cooled solution caused the formation of a red solid, which was collected by filtration and purified by flash chromatography (dichloromethane/ethyl acetate 4/1 as eluant) to give 49 mg of pure **4b** as red solid (80% yield).

Mp 153°C; MS ($CI^-$, m/e): 611 ($M^-$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): δ 0.86 (m, 12 H, $CH_3$), 1.24 – 1.36 [m, 24 H, $(CH_2)_n$], 1.65 (m, 8 H, CO-$CH_2$-$CH_2$ + CN-$CH_2$-$CH_2$), 2.37 (t, 2 H, CO-$CH_2$, J = 7.9 Hz), 2.78 (t, 2 H, CO-$CH_2$, J = 7.9 Hz), 2.90 (m, 4 H, CN-$CH_2$), 7.26 (d, 1 H, $H_m^Z$, J = 7.6 Hz), 7.75 (d, 1 H, $H_m^E$, J = 8.3 Hz), 8.00 (bt, 1 H, $H_p$); FTIR ($cm^{-1}$, KBr): 2924 (ν aromatic CH), 2855 (ν aliphatic CH), 1670 (ν C=O), 1600 (ν coordinated C=O), 1506, 1395, 1351, 1262, 1178, 1159, 1095 (ν C-O).

Following the same procedure of **4a**, using respectively **3c** and **3d**, compounds **4c** and **4d** were obtained in 85% and 87% yield respectively.

**[2,6-Ditridecanoylpyridine bis(octanoylhydrazonato)] nickel (II) 4c**: red solid, mp 123°C; MS ($EI^+$, m/e): 807 ($M^+$, 20), 665 (100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ 0.86 (m, 12 H, $CH_3$), 1.24 [m, 52 H, $(CH_2)_n$], 1.65 (m, 8 H, $CO\text{-}CH_2\text{-}CH_2 + CN\text{-}CH_2\text{-}CH_2$), 2.38 (t, 2 H, $CO\text{-}CH_2$, J = 7.7 Hz), 2.79 (t, 2 H, $CO\text{-}CH_2$, J = 7.7 Hz), 2.90 (m, 4 H, $CN\text{-}CH_2$), 7.26 (d, 1 H, $H_m^Z$, J = 7.6 Hz), 7.75 (d, 1 H, $H_m^E$, J = 8.3 Hz), 7.99 (bt, 1 H, $H_p$); FTIR ($cm^{-1}$, KBr): 2922 ($\nu$ aromatic CH), 2851 ($\nu$ aliphatic CH), 1670 ($\nu$ C=O), 1600 ($\nu$ co-ordinated C=O), 1506, 1468, 1394, 1159, 1095 ($\nu$ C-O).

**[2,6-Dinonadecanoylpyridine bis(octanoylhydrazonato)] nickel (II) 4d:** red solid, mp 107°C; MS ($CI^+$, m/e): 976 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ 0.88 (m, 12 H, $CH_3$), 1.25 [bs, 76 H, $(CH_2)_n$], 1.68 (m, 8 H, $CO\text{-}CH_2\text{-}CH_2 + CN\text{-}CH_2\text{-}CH_2$), 2.39 (t, 2 H, $CO\text{-}CH_2$, J = 7.7 Hz), 2.80 (t, 2H, $CO\text{-}CH_3$, J = 7.7 Hz) 2.91 (m, 4 H, $CN\text{-}CH_2$), 7.25 (d, 1 H, $H_m^Z$, J = 7.6 Hz), 7.76 (d, 1 H, $H_m^E$, J = 8.3 Hz), 8.00 (bt, 1 H, $H_p$); FTIR ($cm^{-1}$, KBr): 2921 ($\nu$ aromatic CH), 2850 ($\nu$ aliphatic CH), 1669 ($\nu$ C=O), 1600 ($\nu$ co-ordinated C=O), 1469, 1396, 1261, 1158, 1099 ($\nu$ C-O).

**2,6-(4,4′-Dihexadecyl)dibenzoylpyridine 6**

A suspension of $AlCl_3$ (688 mg, 5.1 mmol) and 2,6-pyridinedicarbonyl dichloride **5** (500 mg, 2.5 mmol) in dry dichloromethane (30 ml), was stirred for 15 min. To this suspension hexadecylbenzene (1.776 g, 6.8 mmol), dissolved in 10 ml of dry dichloromethane, was added dropwise. The reaction mixture was heated under reflux for 2 hours and then treated with a saturated solution of oxalic acid (30 ml) and sodium carbonate. The organic phase was dried over sodium sulphate, evaporated in vacuo and the crude solid purified by flash chromatography using *n*-hexane/ethyl acetate 9/1 as eluant followed by crystallization from *n*-hexane to give **6** as a white solid (379 mg, 21% yield).

Mp 79–80°C; MS ($CI^+$, m/e): 736 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ 0.86 (t, 6 H, $CH_3$), 1.24 [bs, 53 H, $(CH_2)_{13}$], 1.60 (m, 4 H, $Ar\text{-}CH_2\text{-}CH_2$), 2.64 (t, 4 H, $Ar\text{-}CH_2$, J = 7.2 Hz), 7.20 (d, 4 H, $H_o$ to the alkyl chains, J = 8.1 Hz), 8.09 (m, 5 H, Ar-H), 8.22 (d, 2 H, $H_m$ to N, J = 7.8 Hz); IR ($cm^{-1}$, KBr): 2920 ($\nu$ aromatic CH), 2850 ($\nu$ aliphatic CH), 1670 ($\nu$ C=O), 1465, 1325.

**2,6-(4,4′-Dihexadecyl)dibenzoylpyridine bis(octanoylhydrazone) 7**

This ligand was synthesized using a procedure similar to that used for **3**. After the usual work-up, the crude product was purified by flash chromatography using *n*-hexane/ethyl acetate 17/3 as eluant to give pure **7** as a yellow solid (85 mg, 60%).

Mp 57°C; MS ($CI^+$, m/e): 1016 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz, isomer *E,Z*): $\delta$ 0.86 (m, 12 H, $CH_3$), 1.24 – 1.45 [m, 68 H, $(CH_2)_n$], 1.63 (m, 6 H,

Ar-$CH_2$-$CH_2$ + CO-$CH_2$-$CH_2$), 1.75 (m, 2 H, CO-$CH_2$-$CH_2$), 2.65 (m, 6 H, Ar-$CH_2$ + $CH_2^Z$), 2.89 (t, 2 H, $CH_2^E$, J = 7.6 Hz), 7.17 (d, 2 H, Ar-H, J = 8.0 Hz), 7.22 (d, 2 H, Ar-H, J = 8.0 Hz), 7.26 (d, 1 H, $H_m^Z$), 7.39 (pseudo t, 4 H, Ar-H, J = 8.0 Hz), 7.79 (pseudo t, 1 H, Ar-H, J = 8.0 Hz), 7.95 (d, 1 H, $H_m^E$, J = 7.9 Hz), 8.64 (s, 1 H, $NH^E$), 8.69 (s, 1 H, $NH^Z$); FTIR ($cm^{-1}$, KBr, *E*,*Z* isomer): 3194 e 3100 (*v* NH), 2920 (*v* aromatic CH), 2850 (*v* aliphatic CH), 1685 and 1668 (*v* C=O), 1566, 1468, 1437, 1390.

**[2,6-(4,4′-Dihexadecyl)dibenzoylpyridine bis(octanoylhydrazonato)] nickel (II) 8**

Treatment of **7** (101 mg, 0.1 mmol) with nickel acetate tetrahydrate (30 mg, 0.12 mmol) in absolute ethanol (15 ml), under reflux for 3 hours, followed by crystallization from the crude at −20°C gave pure **8** as a red solid (22 mg, 20%). Mp 76–77°C; MS ($CI^-$, m/e): 1071 ($M^-$, 70), 414 (80), 303 (100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ 0.87 (m, 12 H, $CH_3$), 1.26 [bs, 68 H, $(CH_2)_n$], 1.67 (m, 8 H, Ar-$CH_2$-$CH_2$ + CO-$CH_2$-$CH_2$), 2.40 (pseudo t, 2 H, CO-$CH_2$), 2.66 (m, 4 H, Ar-$CH_2$), 2.97 (pseudo t, 2 H, CO-$CH_2$), 7.21 (d, 1 H, $H_m^Z$ to N, J = 8.2 Hz), 7.24 (d, 2 H, Ar-H, J = 8.0 Hz), 7.32 (d, 2 H, Ar-H, J = 8.0 Hz), 7.36 (d, 2 H, Ar-H, J = 7.9 Hz), 7.46 (d, 2 H, Ar-H, J = 7.9 Hz), 7.64 (d, 1 H, $H_m^E$ to N, J = 8.3 Hz), 7.80 (pseudo t, 1 H, $H_p$, J = 4.0 Hz); FTIR ($cm^{-1}$, KBr): 2919 (*v* aromatic CH), 2851 (*v* aliphatic CH), 1685 (*v* C=O), 1600 (*v* co-ordinated C=O), 1495, 1469, 1385, 1096 (*v* C-O).

**3,4,5-Trimethoxybenzoylhydrazide 9a**

Dry hydrazine (1.38 ml, 44 mmol) was added to a solution of methyl 3,4,5-trimethoxybenzoate in ethanol (10 ml) and the reaction mixture was heated at 50°C for 60 hours. On cooling the solution at 5°C for several hours **9a** precipitated as white solid and was collected by filtration (750 mg, 75%).
MS ($CI^+$, m/e): 227 ($MH^+$, 100). $^1$H-NMR ($CDCl_3$, 100 MHz): $\delta$ 3.88 (s, 9 H, $OCH_3$), 4.12 (bs, 2 H, $NH_2$), 6.96 (s, 2 H, Ar-H), 7.50 (bs, 1 H, NH). FTIR ($cm^{-1}$, KBr): 3292 (*v* NH), 3197 (*v* aromatic CH), 2971 − 2840 (*v* aliphatic CH), 1614 (*v* C=O), 1584 (*v* C=N), 1129, 991.

**3,4,5-Tridodecyloxybenzoylhydrazide 9b**

A stirred solution of methyl 3,4,5-tridodecyloxybenzoate [18] (206 mg, 0.3 mmol), dry hydrazine (94 ml, 3 mmol) and ethanol (4 ml) in a Schlenk tube was heated at 160°C for 60 hours. On cooling the white solid hydrazide **9b** precipitated from the solution (124 mg, 60%).
Mp 70–71°C; MS ($CI^+$, m/e): 689 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ 0.86 (t, 9 H, $CH_3$), 1.26 [m, 48 H, $(CH_2)_8$], 1.44 (m, 6 H, O-$CH_2$-$CH_2$-$CH_2$), 1.75 (m, 6 H, O-$CH_2$-$CH_2$), 3.96 (m, 6 H, O-$CH_2$), 4.0 (bs, 2 H, $NH_2$), 6.92 (s,

2 H, Ar-H), 7.51 (bs, 1 H, NH). FTIR ($cm^{-1}$, KBr): 3240 ($\nu$ NH), 2920–2840 ($\nu$ aliphatic CH), 1710 ($\nu$ C=O), 1582 ($\nu$ C=N), 1120.

**2,6-Diacetylpyridine bis(3,4,5-trimethoxybenzoylhydrazone) 10a**

A mixture of 2,6-diacetylpyridine **2a** (720 mg, 4.42 mmol), **9a** and a few drops of glacial acetic acid in chloroform/ethanol 1/1 (120 ml) was heated under reflux. After 60 hours the reaction was stopped and the solvent evaporated under vacuo. Crystallization of the crude from ethanol/toluene 7/3 gave pure **10a** as a white solid (1.8 g, 70%).

Mp 216–218°C; MS ($CI^-$, m/e): 579 ($M^-$, 60); $^1$H-NMR ($CDCl_3$, 100 MHz, *E,E* isomer): $\delta$ 2.48 (s, 6 H, CN-$CH_3$), 3.89 (s, 18 H, $OCH_3$), 7.13 (bs, 4 H, Ar-H), 7.69 (bt, 1 H, $H_p$), 8.21 (bd, 2 H, 2 $H_m$), 9.03 (s, 2 H, NH); FTIR ($cm^{-1}$, KBr): 3340 ($\nu$ NH), 3000 ($\nu$ aromatic CH), 2940, 2836 ($\nu$ aliphatic CH), 1687 ($\nu$ C=O), 1588 ($\nu$ C=N), 1495, 1447, 1332, 1218, 1125.

**2,6-Diacetylpyridine bis(3,4,5-tridodecyloxybenzoylhydrazone) 10b**

To a solution of 2,6-diacetylpyridine **2a** (8 mg, 0.05 mmol) in chloroform/ethanol 1/1 (4 ml), **9b**, (70 mg, 0.1 mmol) and a few drops of glacial acetic acid were added. The reaction mixture was heated under reflux for 12 hours, cooled to room temperature, diluted with water and extracted with dichloromethane. The organic phase was evaporated and the remaining crude treated with boiling ethanol. After keeping the resulting solution at room temperature for 72 hours **10b** (52 mg, 70%) was obtained as a white solid.

Mp 102–104°C; MS ($CI^-$, m/e): 1504 ($M^-$, 100); $^1$H-NMR ($CDCl_3$, 100 MHz, *E,E* isomer): $\delta$ 0.85 (t, 18 H, $CH_3$), 1.25 [m, 108 H, $(CH_2)_9$], 1.74 (m, 12 H, O-$CH_2$-$CH_2$), 2.49 (s, 6 H, CN-$CH_3$), 4.01 (t, 12 H, O-$CH_2$, J = 6.0 Hz), 7.12 (bs, 4 H, Ar-H), 7.68 (bt, 1 H, $H_p$), 8.16 (bd, 2 H, $H_m$), 8.94 (bs, 2 H, NH); FTIR ($cm^{-1}$, KBr): 3211 ($\nu$ NH), 2921, 2852 ($\nu$ aliphatic CH), 1646 ($\nu$ C=O), 1581 ($\nu$ C=N), 1334, 1218, 1116.

**2,6-Dihexanoylpyridine bis(3,4,5-tridodecyloxybenzoylhydrazone) 10c**

This ligand was synthesized using a similar method to that used for **10b**. Treatment of **2b** (90 mg, 0.33 mmol) with **9b** (472 mg, 0.68 mmol) in chloroform/ethanol 1/1 (10 ml), under reflux and with the usual procedure followed by crystallization from ethanol and *n*-hexane, gave the ligand **10c** as white solid (183 mg, 34%).

Mp 129–131°C, MS ($CI^+$, m/e): 1617 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 200 MHz, *E,E* isomer): $\delta$ 0.85 (bt, 24 H, $CH_3$), 1.25 [bs, 120 H, $(CH_2)_n$], 1.80 (m, 12 H, O-$CH_2$-$CH_2$), 3.02 (bt, 4 H, CN-$CH_2$), 4.02 (m, 12 H, O-$CH_2$), 7.08 (bs, 4 H, Ar-H), 7.68 (bt, 1 H, $H_p$), 8.16 (bd, 2 H, $H_m$), 9.25 (bs, 2 H, NH); FTIR ($cm^{-1}$,

KBr): 3210 ($\nu$ NH), 2921, 2851 ($\nu$ aliphatic CH), 1649 ($\nu$ C=O), 1586 ($\nu$ C=N), 1337, 1219, 1123.

**[2,6-Diacetylpyridine bis(3,4,5-trimethoxybenzoylhydrazonato)nickel (II)] 11a; bis[2,6-diacetylpyridine bis(3,4,5-trimethoxybenzoylhydrazonato) nickel(II)] 12a**

Nickel (II) acetate tetrahydrate (128 mg, 0.51 mmol) was added to an ethanolic solution (250 ml) of **10a** (300 mg, 0.51 mmol). After heating the mixture under reflux for 1 hour, the solvent was evaporated and the remaining red solid was purified by flash chromatography using chloroform/ethanol 19/1 as eluant (TLC $R_f = 0.5$ for **11a** and 0.8 for **12a**), to give the monomeric **11a** and dimeric **12a** complexes. While **11a** spontaneously dimerizes to **12a** in organic solution, it was possible to regenerate **11a** by treating **12a** with glacial acetic acid in ethanol at 60°C for 1 hour.

**11a:** Red solid, Mp 260–262°C; MS ($CI^-$, m/e): 636 ($M^-$, 100); $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 2.46 (s, 3 H, CN-$CH_3^Z$), 2.59 (s, 3 H, CN-$CH_3^E$), 3.73 (s, 3 H, $OCH_3^Z$), 3.77 (s, 6 H, $OCH_3^Z$), 3.81 (s, 3 H, $OCH_3^E$), 3.87 (s, 6 H, $OCH_3^E$), 6.88 (s, 2 H, Ar-$H^Z$), 7.41 (d, 1 H, $H_m^Z$, J = 9.0 Hz), 7.59 (s, 2 H, Ar-$H^E$), 7.70 (d, 1 H, $H_m^E$, J = 9.0 Hz), 7.96 (pseudo t, 1 H, $H_p$, J = 9.0 Hz); FTIR ($cm^{-1}$, KBr): 2995 ($\nu$ aromatic CH), 2937, 2834 ($\nu$ aliphatic CH), 1653 ($\nu$ C=O), 1586 ($\nu$ C=N), 1382, 1125.

**12a:** Dark red solid, Mp > 320°C; MS ($CI^-$, m/e): 1272 ($M^-$, 40); FTIR ($cm^{-1}$, KBr): 2995 ($\nu$ aromatic CH), 2937, 2834 ($\nu$ aliphatic CH), 1589 ($\nu$ C=N), 1552, 1368, 1121.

**Crystal data for 12a:** $C_{58}H_{62}N_{10}O_{16}Ni_2$, M = 1272.61, triclinic, space group P-1, a = 15.548 (4), b = 15.145 (3), c = 15.098 (4) Å, $\alpha = 117.86$ (4), $\beta = 110.34$ (4), $\gamma = 83.31$ (5)°, V = 2943 (2) Å$^3$, $D_m = 1.44$, $D_c = 1.436$ g cm$^{-3}$, $\mu$ (Mo–K$\alpha$) = 7.18 cm$^{-1}$.

**[2,6-Diacetylpyridine bis(3,4,5-trimethoxybenzoylhydrazonato)] palladium (II) 13**

To a refluxing solution of **10a** (500 mg, 0.86 mmol) in ethanol/chloroform 1/1 (50 ml) palladium(II) acetate (281 mg, 0.86 mmol) in ethanol (10 ml) was added. After heating under reflux the mixture for further 30 min and cooling at room temperature, the orange-yellow complex **12** was formed (510 mg, 86%).

MS ($CI^+$, m/e): 685 ($MH^+$, 100); $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 2.58 (s, 3 H, CN-$CH_3^Z$), 2.60 (s, 3 H, CN-$CH_3^E$), 3.85 (s, 3 H, $OCH_3^Z$), 3.86 (s, 6 H, $OCH_3^Z$), 3.89 (s, 3 H, $OCH_3^E$), 3.90 (s, 6 H, $OCH_3^E$), 7.12 (s, 2 H, Ar-$H^Z$), 7.39 (s, 2 H, Ar-$H^E$), 7.50 (dd, 1 H, $H_m^Z$, $J_1 = 9.0$ Hz, $J_2 = 0.9$ Hz), 7.93 (dd, 1 H, $H_m^E$, $J_1 = 9.0$ Hz, $J_2 = 0.9$ Hz), 8.12 (pseudo t, 1 H, $H_p$, J = 8.9 Hz); FTIR ($cm^{-1}$, KBr): 2924, 2855 ($\nu$ aliphatic CH), 1648 ($\nu$ C=O), 1587 ($\nu$ C=N), 1370, 1333, 1127.

**[2,6-Diacetylpyridine bis(3,4,5-tridodecyloxybenzoylhydrazonato)]nickel(II) 11b; bis[2,6-Diacetylpyridine bis(3,4,5-tridodecyloxybenzoylhydrazonato)] nickel(II) 12b.**

**11** and **12b** were prepared using a similar method to that used for **11** and **12a. 10b** (50 mg, 0.03 mmol) was heated under reflux with nickel(II) acetate tetrahydrate (8 mg, 0.03 mmol) in ethanol (20 ml) for 30 min. After keeping the reaction mixture at room temperature for 24 hours the paramagnetic dimeric complex **12b** was separated as a red solid; removing the solvent under vacuo from the remaining solution the diamagnetic monomeric complex **11b** was obtained as red oil. **11b**: no traces of solvent are observed by $^1$H-NMR or elemental analysis (found: C, 73.00, H 10.50, N 4.78 calc. for $C_{95}H_{162}N_5NiO_8$: C, 73.12, H 10.47, N 4.69).

**11b**: MS ($CI^-$, m/e): 1560 ($M^-$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ 0.87 (t, 18 H, $CH_3$), 1.25 [m, 96 H, $(CH_2)_8$], 1.42 (m, 12 H, O-$CH_2$-$CH_2$-$CH_2$), 1.60 – 1.77 (m, 12 H, O-$CH_2$-$CH_2$), 2.48 (s, 3 H, CN-$CH_3^Z$), 2.63 (s, 3 H, CN-$CH_3^E$), 3.80 (t, 2 H, O-$CH_2^Z$, J = 6.8 Hz), 3.87 (t, 4 H, O-$CH_2^Z$, J = 6.8 Hz), 3.92 (t, 2 H, O-$CH_2^E$, J = 6.8 Hz), 3.99 (t, 4 H, O-$CH_2^E$, J = 6.8 Hz), 6.89 (s, 2 H, Ar-$H^Z$), 7.42 (d, 1 H, $H_m^Z$, J = 7.6 Hz), 7.57 (s, 2 H, Ar-$H^E$), 7.78 (d, 1 H, $H_m^E$, J = 7.4 Hz), 8.02 (pseudo t, 1 H, $H_p$, J = 7.6 Hz); FTIR ($cm^{-1}$, KBr): 2915, 2851 ($\nu$ aliphatic CH), 1669 ($\nu$ C=O), 1577 ($\nu$ C=N), 1469, 1378, 1106.

**12b**: Mp. 145–148°C; MS ($CI^-$, m/e): 3120 ($M^-$, 100).

**[2,6-Diacetylpyridine bis(3,4,5-tridodecyloxybenzoylhydrazonato)] palladium (II) 14**

**10b** (500 mg, 0.33 mmol) in ethanol (50 ml) and palladium (II) acetate (74 mg, 0.33 mmol) in chloroform (10 ml) were mixed. After heating the mixture under reflux for 30 minutes the formation of an orange solid was observed. On cooling the solution at room temperature complete precipitation of the solid was obtained and the filtration gave complex **14** in pure form (298 mg, 56%). Mp 120–122°C (dec.); MS ($CI^-$, m/e): 1609 ($M^-$, 100); $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 0.87 (t, 18 H, $CH_3$), 1.26 [m, 96 H, $(CH_2)_8$], 1.45 (m, 12 H, O-$CH_2$-$CH_2$-$CH_2$), 1.77 (m, 12 H, O-$CH_2$-$CH_2$), 2.55 (s, 3 H, CN-$CH_3^Z$), 2.57 (s, 3 H, CN-$CH_3^E$), 3.98 (m, 12 H, O-$CH_2$), 7.06 (s, 2 H, Ar-$H^Z$), 7.34 (s, 2 H, Ar-$H^E$), 7.49 (d, 1 H, $H_m^Z$, J = 10.0 Hz), 7.98 (d, 1 H, $H_m^E$, J = 10.0 Hz), 8.09 (pseudo t, 1 H, $H_p$, J = 10.0 Hz); FTIR ($cm^{-1}$, KBr): 2921, 2852 ($\nu$ aliphatic CH), 1653 ($\nu$ C=O), 1591 and 1558 ($\nu$ C=N), 1414, 1375, 1118.

**[2,6-Dihexanoylpyridine bis(3,4,5-tridodecyloxybenzoylhydrazonato)] nickel (II) 11c;**
**bis[2,6-Dihexanoylpyridine bis(3,4,5-tridodecyloxybenzoylhydrazonato)] nickel (II) 12c**

These complexes were synthesized using a preparation similar to that used for **11** and **12b**. Reaction of **10c** (190 mg, 0.12 mmol) with nickel (II) acetate

tetrahydrate (30 mg, 0.12 mmol) in ethanol (20 ml), after the usual work up gave the monomeric complex **11c** as a red oil and the dimeric complex **12c** as a red solid by separation with flash chromatography (eluant: dichloromethane/ethyl acetate 19/1).

**11c**: MS ($CI^+$, m/e): 1674 ($M^-$, 100); $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ (m, 24 H, $CH_3$), 1.20 – 1.48 [m, 120 H, $(CH_2)_n$], 1.60–1.77 (m, 12 H, O-$CH_2$-$CH_2$), 2.92 (bt, 4 H, CN-$CH_2$), 3.85 (t, 2 H, O-$CH^Z_2$, J = 6.8 Hz), 3.90 (t, 4 H, O-$CH^Z_2$, J = 6.8 Hz), 3.92 (t, 2 H, O-$CH^E_2$, J = 6.8 Hz), 3.99 (t, 4 H, O-$CH^E_2$, J = 6.8 Hz), 7.03 (s, 2H, Ar-$H^Z$), 7.36 (d, 1 H, $H^Z_m$, J = 7.5 Hz), 7.43 (s, 2 H, Ar-$H^E$), 7.82 (d, 1 H, $H^E_m$, J = 8.3 Hz), 8.05 (pseudo t, 1 H, $H_p$, J = 7.8 Hz); FTIR ($cm^{-1}$, KBr): 2923, 2853 ($\nu$ aliphatic CH), 1653 ($\nu$ C=O), 1584 ($\nu$ C=N), 1467, 1367, 1115.

**12c**: Mp. 115°C; MS ($CI^+$, m/e): 3349 ($MH^+$, 100).

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