# New Compound with Potential Liquid Crystal Properties.
# III. Synthesis, Characterization and Mesomorphic ordering of
# N,n'-bis-[4-(4'-octyloxy-benzoic)-ester-benzyliden-n-propyl]-piperazine

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**Abstract:** The synthesis of Schiff base - N,N'-bis-[4-(4'-octyloxy-benzoic)-ester-benzyliden-n-propyl]-piperazine **(4)** in a multistep process is repported. The last step involves the condensation of 4-octyloxy-benzoic acid 4-formyl-phenyl ester aldehyde **(3)** with 1,4-bis(3-aminopropyl)piperazine. The intermediates as well as the product were characterized by elemental analysis, melting point and IR, ^{1}H and ^{13}C-NMR spectroscopies. The potential mesogenic property of **(4)** has been checked with a polarising microscope equipped with a heating stage.

**Keywords:**  Schiff base, liquid crystals, spectral properties

## 1. Introduction

The most studied and applied liquid crystals are pure organic compounds. In the last decades, the introduction of a metal ion lead to a new class of liquid crystals: metallomesogens. The metal  complexes which contain organic mesogens as ligands may retain these  properties. Also, the introduction of a metal ion in an organic compound which does not exhibit liquid crystal properties lead to a new complex with liquid crystal properties [1-3]. Most of the metallomesogens are thermotropics. According to the shape of the molecules, thermotropic crystals are classified in two main groups, calamitic (rod-like) and discotic (disc-like) or columnar. The molecular requirements of liquid crystals have been summarised [4] as *i)* stucturally anisotropy, *ii)* the presence of a permanent dipole and *iii*) a high anisotropy of polarisability. The liquid crystal phases are characterized by anisotropy of the phisical properties like refractive indices (which leads to birefringence), dielectric permittivity and magnetic susceptibilities. Further definition and basic principles of the liquid crystals including metallomesogenes can be found in  some representative works [4-9]. Geometric and structural criteria of the mesomorphism of metallomesogenes has been studied [10] and principles to design metallomesogens with specific ligands have been pointed out [11,12]. Among the ligands, Schiff bases offer the posibility of controlling alignment and orientation of metal complexes in their mesophases and of generating liquid crystalline materials of unconventional structures and properties. To the complex cores, alkyl- or alkyl-substituted phenyl groups are attached and the nature and the length of the tails allow the tuning the phase properties. In this frame, Schiff bases containing saturate cyclic systems as cyclohexane [13,14], 1,3-dioxane [15], or piperazine [16,17] are well known as mesogens. With the

aim to obtain metallomesogens, we designed and futher, obtained the Schiff base **(4)**. It contains benzenic rings as rigide fragments, -CH=N- and -COO- as linkage units and $C_nH_{2n+1}O$- terminal substituents. Thanks to these structural features, nematic properties can be expected. Additionally, the Schiff base **(4)** can be regarded as an appropriate ligand for metallomesogens.

## 2. Experimental section

*All the reagents and solvents* were purchased from Merck, Aldrich, Avocado, Fluka and Lancaster Synthesis and used without further purification, except 2-butanone and dichloromethane. 2-Butanone was dried by distillation under nitrogen and the 79°C ÷80°C fraction was collected. Dichloromethane (DCM) was dried over molecular sieves for a week.

*Thermomicroscopy* was realised under polarised light, using an Olympus BH-2 polarising microscope with Mettler FP52 hot stage linked to an FP5 temperature control unit. The accuracy of measurements is ± 1°C.
The thin layer chromatography (TLC): Merck 60 F254 plates were used. Detection was by UV fluorescence (254 nm).
*Column Chromatography:* Flash or gravity column chromatography was carried out using Merck Kieselgel C60 230-240 mesh silica gel.
The elemental analysis was made with a Perkin-Elmer 2400 analyzer.
*Spectroscopic Techniques*
1. Nuclear Magnetic Resonance Spectroscopy (NMR): Analysis was carried out using a JEOL Lamda 400 FT NMR (400 MHz) spectrometer.
2. Infra Red Spectroscopy (IR): Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR

spectrophotometer, as KBr pellet, in the 400-4000 cm$^{-1}$ range.

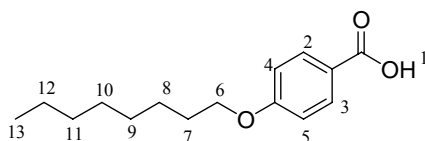**Synthesis of 4-octyloxy-benzoic acid methyl ester (1)** [18]
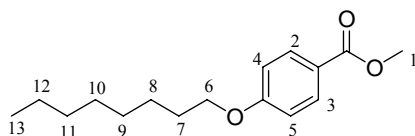


1-Bromooctane (683 ml, 0.4 mol) was added to a suspension of 4-hydroxy-benzoic acid methyl ester (50 g, 0.3 moli), K$_2$CO$_3$ (171.5 g, 1.2 mol) and powdered 4Å molecular sieves (18 g) in dry butanone (500 ml) under reflux. The reaction mixture was refluxed for 17 h, cooled to room temperature and the solid rezidue removoued by filtration. The solvent (butanone) was distilled off and the residue recrystallized three times from methanol resuilting in white crystals. The purity of the product was verified by TLC (silica gel; DCM) when Rf = 0.65. Yield η = 60 % (50 g).
Anal: calcd for C$_{16}$H$_{24}$O$_3$ (264.36) C 72.69 %, H 9.15 %; found C 72.71 %, H 9.37 %;
**$^1$H-NMR** 400 MHz, CDCl$_3$/δ [ppm]: 7.90 (m, 2H, H$^{2,3}$); 6.82 (m, 2H, H$^{4,5}$); 3.93 (t, 2H, H$^6$); 3.81 (s, 3H, H$^1$); 1.72 (m, 2H, H$^7$); 1.20-1.42 (m, 10H, H$^{8-12}$); 0.81 (t, 3H, H$^{13}$).

**Synthesis of 4-octyloxy-benzoic acid (2)**



KOH (25 g, 0.44 mol) disolved in water (50 ml) was added to a solution of 4-octyloxy-benzoic acid methyl ester **(1)** (50 g, 0.19 mol) dissolved in methanol (230 ml). The mixture was refluxed for 14 h and then was stirred for other 48 h. Saturated aqueous NaCl (400 ml) was added. After acidification with concentrated HCl until pH = 2, a mixture of diethyl ether and hexane (150 ml/150 ml) was added. After phase separation the aqueous layer was extracted with DCM (6 × 250 ml). The organic phase was dried over MgSO$_4$ and the solvents were distilled off. Recrystallization from chloroform/n-heptane (75 ml/ 330 ml) resulted in white crystals of product. Yield: 73 % (33 g).
Anal: calcd for C$_{15}$H$_{22}$O$_3$ (250.33) C 71.97 %, H 8.86 %; found C 80.21 %, H 8.75 %;
**$^1$H-NMR** 400 MHz, CDCl$_3$/δ [ppm]: 8.05 (m, 2H, H$^{2,3}$); 6.92 (m, 2H, H$^{4,5}$); 4.01 (t, 2H, H$^6$); 1.80 (m, 2H, H$^7$); 1.28-1.45 (m, 10H, H$^{8-12}$); 0.86 (t, 3H, H$^{13}$);
**$^{13}$C-NMR** 400 MHz, CDCl$_3$/δ [ppm]: 172, 164, 132, 121, 114, 78, 77, 76, 68, 32, , 29(3), 26, 23, 14;
**IR** (KBr pellet) ν$_{max}$ [cm$^{-1}$]: 3436, 2950, 2927, 2870, 2851, 2673, 2559, 1690, 1607, 1578, 1515, 1464, 1428, 1389, 1330, 1316, 1296, 1256, 1207, 1171, 1147, 1130, 1122,

1109, 1067, 1018, 998, 959, 933, 910, 897, 848, 813, 771, 753, 724, 692, 647, 630, 551, 508, 476, 450.

**Synthesis of 4-octyloxy-benzoic acid 4-formyl-phenyl ester (3)** [19]
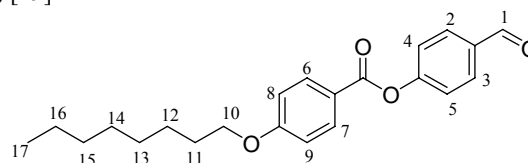


At a mixture of 4-octyloxy-benzoic acid (3 g, 12 mmol) and 4-hydroxy-benzaldehyde (1.5 g, 12 mmol) in dry DCM (50 ml) was added N,N-diciclohexilcarbodiimida (2.97 g, 14.4 mmol) and N,N-dimetilaminopiridina (0.08 g). The reaction mixture was stirred for 7 h at room temperature and then the precipitate was filtered and the solvent from filtrate distilled off. The residue was purified by column chromatography (silica gel; DCM) when Rf = 0.51. The product was obtained as a white solid. Yield: η = 90.28 % (3.84 g); mp = 103 °C;
Anal: calcd for C$_{22}$H$_{26}$O$_4$ (354.44) C 74.55 %, H 7.39 %; found C 74.31 %, H 7.55 %;
**$^1$H-NMR** 400 MHz, CDCl$_3$/δ [ppm]: 10.01 (s, 1H, H$^1$); 8.13 (m, 2H, H$^{2,3}$) J = 8.98; 7.96 (m, 2H, H$^{6,7}$), J = 8.61; 7.39 (m, 2H, H$^{8,9}$), J = 8.61; 6.98 (m, 2H, H$^{4,5}$), J = 8.98; 4.04 (t, 2H, H$^{10}$); 1.82 (q, 2H, H$^{11}$); 1.24-1.52 (m, 10H, H$^{12-16}$); 0.89 (t, 3H, H$^{17}$);
**IR** (KBr pellet) ν$_{max}$ [cm$^{-1}$]: 2954, 2931, 2911, 2846, 2824, 1733, 1700, 1605, 1577, 1511, 1468, 1421, 1388, 1269, 1215, 1168, 1099, 1070, 1057, 1009, 995, 956, 912, 881, 844, 813, 795, 759, 719, 690, 663, 628, 512.

**Synthesis of N,N'-bis-[4-(4'-octyloxy-benzoic)-ester-benzyliden-n-propyl]-piperazine (4)**
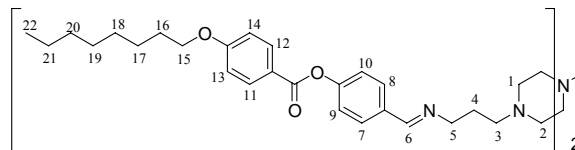


Aldehyde **(3)** (5 mmol, 1.77 g) dissolved in dry methanol (15 ml) was treated with 1,4-bis(3-amino-propyl)-piperazine (2.5 mmol, 0.51 ml) and further with 2-3 drops of glacial acetic. The mixture was refluxed for 1 h and then cooled slowly to room temperature. The precipitate was filtered off and purified by recrystallization from ethanol. A slightly yellow solid was obtained (η = 92 %); mp = 133-134 °C;
Anal: calcd for C$_{57}$H$_{72}$N$_4$O$_6$ (873.17) C 74.27 %, H 8.31 %, N 6.42 %; found C 74.21 %, H 8.32 %, N 6.51 %;
**$^1$H-NMR** 400 MHz, CDCl$_3$/δ [ppm]: 8.22 (s, 1H, H$^6$); 8.06 (dd, 2H, H$^{11,12}$), J = 8.98; 7.70 (dd, 2H, H$^{7,8}$), J = 8.61; 7.18 (dd, 2H, H$^{9,10}$), J = 8.61; 6.89 (dd, 2H, H$^{13,14}$), J = 8.98; 3.95 (t, 2H, H$^{15}$); 3.58 (t, 2H, H$^5$); 2.49 (m, 4H, H$^{1,2}$); 2.40

(t, 2H, H$^3$); 1.85 (q, 2H, H$^4$); 1.75 (q, 2H, H$^{16}$); 1.18-1.45 (m, 10H, H$^{17-21}$); 0.82 (t, 3H, H$^{22}$);

**$^{13}$C-NMR** 400 MHz, CDCl$_3$/δ [ppm]: 164, 163, 160, 152, 133, 132, 129, 122, 121, 114, 77, 76, 68, 59, 56, 53, 31, 29(2), 25, 22, 14;

**IR** (KBr pellet) ν$_{max}$ [cm$^{-1}$]: 2941, 2923, 2869, 2853, 2807, 2775, 1734, 1646, 1604, 1579, 1510, 1467, 1444, 1418, 1395, 1379, 1353, 1314, 1254, 1221, 1192, 1163, 1065, 1017, 1007, 997, 967, 940, 874, 844, 822, 804, 761, 722, 691, 662, 631, 529, 508.

# 3. Results and discusions

*Results and discussions synthesis*

The synthesis of N,N'-bis-[4-(4'-octyloxy-benzoic)-ester-benzyliden-n-propyl] piperazine **(4)** shown in the Scheme A involves several steps in which intermediate products are separated. The purity and the identity of the three intermediates (**(1)**, **(2)** and **(3)**) are proved by TLC, elemental analysis and NMR and IR techniques. The first step involves the alkylation of the 4-hidroxy-benzoic acid methyl ester in basic medium according to a typical Williamson process resulting in **(1)**. The $^1$H-NMR spectrum proves the presence of the C$_8$ tail. Thus, a complex system of signals can be observed at higher field with small difference of chemical shift values (0.81, 1.20 ÷ 1.42, 1.72 and 3.93 ppm).

The second step refers to the deprotection of the carboxylic group resulting in the intermediate **(2)**. The success of this step was proved by the $^1$H- and $^{13}$C-NMR spectra. Thus, the signal at 3.81 ppm in the $^1$H-NMR spectrum of **(1)**, assigned to the three methyl protons, disappeared in the spectrum of **(2)**. Also, the IR spectrum shows a strong C=O stretching absorption at 1690 cm$^{-1}$ and a broad OH stretch absorption at 3436 cm$^{-1}$ characteristic of carboxylic group as dimmers [20].

The third step in Scheme A refers to the esterification of the acid **(2)** in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino) pyridine (DMAP). This approach takes the advantage of DCC to bind water and further, the formation of easy-removable product, dicyclohexylurea. Additionally, it is an one-pot reaction which occurs in mild conditions thus preserving the alkoxy and carbonyl groups. However, the formation of N-acylureas as undesired products is possible thereby reducing the yields. The success of esterification reaction and the purity of compound **(3)** were confirmed by $^1$H-NMR and IR spectra. Indeed the two groups of signals at 10.01 ppm, and 8.13 and 6.98 ppm and the values of the peak's integration in the $^1$H-NMR spectrum, support the presence of the aldehydic group proton and those of the new attached benzene ring, respectively. Concerning the IR spectrum, it can be noticed the disappearance of the band at 3436 cm$^{-1}$ and the presence of a new band at 1700 cm$^{-1}$ associated to the new carbonylic group in **(3)**.
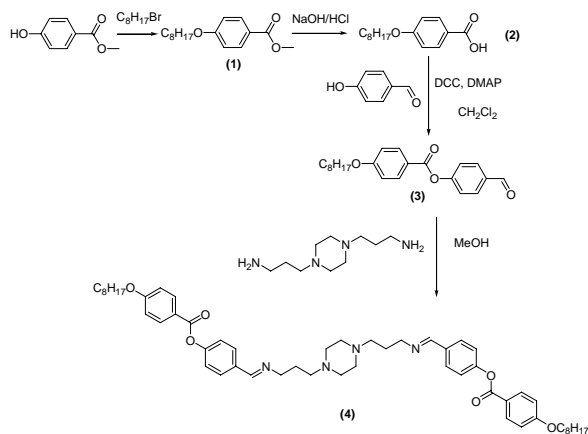


**Scheme A**

The last step refers to the Schiff condensation resulting in the new base N,N'-bis-[4-(4'-octyloxy-benzoic)-ester-benzyliden-n-propyl]piperazine **(4)**. The reaction occurs according to method described in the literature [21], into absolute methanol and in the catalytic amount of glacial acid acetic. The new band which appears at 1646 cm$^{-1}$ in the IR spectrum of **(4)** compared to that of **(3)**, is attributed to the new formed C=N bond [20]. Also, the IR spectrum of compound **(4)** does not contain the characteristic bands of the reactants, namely that at 3360 and 3280 cm$^{-1}$ in the spectrum of 1,4-bis-(3-aminopropyl) piperazine and that of the corresponding aldehyde at 1700 cm$^{-1}$. The identity of the Schiff base was proved by $^1$H- and $^{13}$C-NMR. Thus, the signal at 10.01 ppm in the $^1$H-NMR spectrum of **(3)**, was shifted in the spectrum of **(4)** at 8.22 ppm, due to the formation of azomethinic bond. In addition, new signals at 3.58, 2.49, 2.40 and 1.85 ppm appear in the spectrum of **(4)**, which are attributed to protons belonging to the bis–(n-propyl)piperazine fragment. The peaks attributable to the solvent, in the $^{13}$C-NMR spectrum, can be noticed as a triplet at at δ 77 ppm. Assuming this signal as reference [22], the peaks to the left side at 53, 56 and 59 ppm are attributed to the saturated carbons bonded to the nitrogen atoms.

*Mesomorphic ordering*

The potential mesogenic properties of **(4)** have been checked with a polarising microscope equipped with a heating stage and a single melting point has been noticed at 133 – 134 ºC. Although the new Schiff base **(4)** contains the characteristic structural features, it does not show any mesogenic properties. This behaviour may be explained by the flexibility of molecule. However this disadvantage can be overtake when **(4)** is included in an appropiate metal complex.

## 4. Conclusions

The new Schiff base was obtained with a good yield (92%) and a high purity.

The study of the mesomorphic ordering of Schiff base showed the flexibility of the molecule given by aminic component does not promote liquid crystal properties for this compound **(4)**, but through the introduction of a metal ion in an organic compound forms new bonds metal-ligand, which decrease de flexibility of the molecule and thereby can lead to a complex with liquid crystal properties.

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