

Mesomorphic behaviour of *N*-benzoyl-*N'*-aryl thioureas liquid crystalline compounds

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ABSTRACT

A series of *N*-benzoyl-*N'*-aryl thiourea derivatives bearing alkoxy groups in terminal positions have been prepared and investigated for their potential liquid crystals properties. It was found that only the compounds which have only two alkoxy chains show calamitic mesomorphic behaviour, with nematic, smectic A and C phases being displayed. The type and stability of these mesophases are greatly influenced by the alkyl chain length. Successive introduction of additional alkoxy groups on the benzoyl moiety led to a significant decrease of the clearing points and suppression of the mesogenic character. Using of branched alkyl chain, 2-ethyl-hexyl, instead of normal alkyl group, led to the disappearance of mesogenic behaviour together with the lowering of the clearing temperature. The influence of chain length and number of chains is discussed.

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1. Introduction

The *N*-benzoyl thiourea derivatives represent one of the most investigated classes of ligands in the coordination chemistry as they possess very strong donor groups (carbonyl and thioamide) that can bind to various metal ions. It is well known that such compounds, in particular *N,N*-dialkyl-*N'*-benzoyl thioureas, react with transition metals either in monoanionic bidentate form by deprotonation forming neutral homoleptic complexes with *S, O* – coordination or in neutral form only through *S* atom [1].

These derivatives have found many important applications, for example: biological activity [2], solvent extraction of metal ions [3], especially platinum group metals, and, recently, they have been used in the design of liquid crystalline materials [4–6], both in purely organic liquid crystals, simple or connected to a ferrocene moiety, or metal-containing liquid crystals – metallomesogens. Recently, we reported the use of simple *N*-benzoyl thiourea derivatives as co-ligands in luminescent platinum(II) 2-phenylpyridine complexes [7] or in *ortho*-metallated palladium and platinum(II) complexes which show liquid crystals properties [8]. Few examples of *N*-benzoyl-*N'*-aryl thiourea derivatives substituted with terminal alkoxy groups in *para* positions at the both ends of the molecule were reported previously by us [6] and by Seshadri et al. [5]. These compounds were found to exhibit nematic, smectic A and C phases, depending on the alkyl chain length.

In this work we present a systematic study of the influence of the alkyl chain length, number and position of the alkoxy groups as well as branching of alkyl chain on the mesomorphic behaviour of a series of *N*-benzoyl-*N'*-aryl thiourea derivatives with the aim to use further such compounds as ancillary ligands in the organometallic chemistry of platinum(II) and palladium(II) with imine type ligands. This is based on the fact that this class of ligands is very much appealing to be used in the design of metal-containing liquid crystals as they can be easily prepared to provide a large collection in order to tailor the mesogenic or photophysical properties of the metallomesogens.

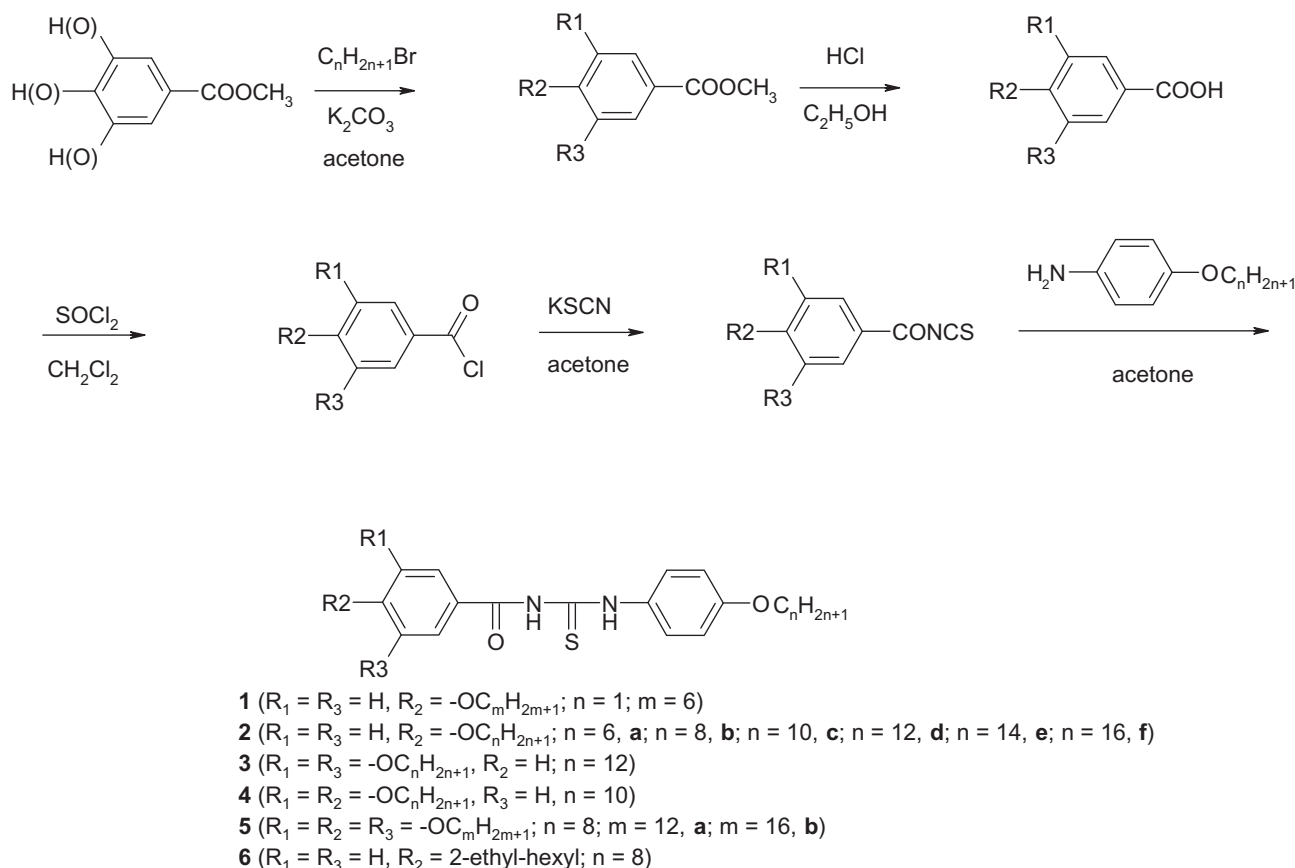
2. Results and discussion

The availability of a large number of carboxylic acids derivatives through the *O*-alkylation reaction with different alkyl bromides of the corresponding starting material (methyl 4-hydroxybenzoate, methyl 3,5-hydroxybenzoate or ethyl gallate) prompted us to synthesize a series of BTU derivatives in which the benzoyl fragment contains different number of alkoxy groups while keeping only one alkoxy group on the thioureaic fragment. Such approach, the increase of the number of alkoxy groups at the periphery of the molecule, proved to be very successful in the design of polycatenar materials that can display both rod or disk-like behaviour, in particular the tetracatenar mesogens, where the number and position of alkoxy groups has a great influence on the mesogenic behaviour [9].

The synthetic procedure used to prepare the BTU compounds is depicted in Scheme 1. These *N*-benzoyl-*N'*-aryl thiourea deriva-

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Scheme 1. Preparation of *N*-benzoyl-*N'*-aryl thiourea derivatives (BTU).

tives were obtained in good yields as white or off-white microcrystalline solid products, which are stable under normal conditions. These compounds were characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy while their liquid crystalline properties were investigated by DSC and polarizing optical microscopy.

The acid chlorides were prepared from the corresponding carboxylic acid and thionyl chloride and were used in the next step without further purification. The entire procedure is similar to the one used for the synthesis of simple *N*-benzoyl thiourea compounds and comprises the reaction between acid chloride and KSCN in dry acetone to form the corresponding isothiocyanate derivatives that further reacts with different anilines to give the final BTU products [10]. The formation of these products can be easily monitored by the ^1H NMR spectra where two singlets, one in the range 12.48–12.37 ppm and a second one in the range 9.02–8.98 ppm, which can be assigned to the two NH groups, can be seen. The first one was assigned to the NH proton located between the thiocarbonyl group and benzene ring while the second one was assigned to the NH proton located between the carbonyl and thiocarbonyl groups. This assignment is also based on the fact that when these type of ligands bind to metal ions in monoanionic bidentate form, the latter signal disappears in the corresponding ^1H NMR spectra of metal complexes. The other signals assigned to aromatic protons show the normal splitting pattern corresponding to 1,4-, 1,3,4-, 1,3,4,5-substitution of the aromatic ring. The IR spectra show the expected absorption bands attributed to $\nu_{\text{N-H}}$ in the range 3200–3400 cm^{-1} and to $\nu_{\text{C=O}}$ at ~ 1670 cm^{-1} . Three other strong absorption bands can be found in the regions 1500–1510 cm^{-1} , 1240–1250 cm^{-1} and 1145–1155 cm^{-1} which were assigned to a combination of $\nu_{\text{C-N}}$ and ν_{phenyl} stretching frequencies [11].

3. Thermal behaviour

The new compounds were investigated for their potential liquid crystalline properties by a combination of hot stage polarizing optical microscopy and differential scanning calorimetry (DSC). The transition temperatures and the corresponding enthalpies are presented in Table 1. The assignment of the mesophases was made based on their optical texture and several examples are presented in Figs. 4–7 [12].

The nematic phase was evidenced based on its marbled or threaded texture which flashed when subjected to exterior mechanical stress applied on the cover slip. An example of such a texture can be seen in Fig. 4. The smectic A phase could be detected based on the typical focal-conic texture displayed (Fig. 7) accompanied by black homeotropic regions that, indeed confirm the identity of this mesophase. Compounds **2b** and **2c** also showed a smectic C phase that was separated from a previous SmA phase. This transition could not be evaluated from the DSC trace but from polarizing optical microscopy observations when the previous texture of SmA phase transforms into a broken focal-conic texture typical for SmC phase (Fig. 7). The SmC phase that was isolated straight from the isotropic state (compounds **2d–f**) could be detected by the typical appearance of the broken focal-conic texture and accompanied sometimes by gray regions of Schlieren textures (Figs. 5 and 6).

Now, if we consider the first group of compounds, **1** and **2a–f**, bearing only two alkoxy groups in terminal position, it is very clear that the mesomorphic behaviour is dominated by the alkyl chain length. The nematic phase is displayed only by the compounds having short alkyl chains (methoxy or hexyl) and this phase is strongly destabilized as it has only a monotropic character.

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