

Synthesis, characterization and mesomorphic investigations of ester-substituted aroylhydrazones possessing a lateral hydroxyl group



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ABSTRACT

The synthesis, characterization and investigation of a new liquid crystalline series of ester containing aroylhydrazones with a lateral hydroxyl group, N-[4-(4'-alkoxy)benzoyloxy-2-hydroxy-benzylidene]-N'-[4'-alkoxybenzoyl]hydrazine (C_{m,n}LH), with the same or different peripheral alkoxy chains, and some of their nickel(II) and copper(II) complexes are described. All the ligands, except those with no terminal chains on either end of the molecule, exhibit an enantiotropic SmC mesophase, as evidenced by polarizing optical microscopy and differential scanning calorimetric studies. It has been found that addition of a lateral hydroxyl group along with ester-substitution to the aroylhydrazone core increases the mesomorphic as well as thermal stability of the ligands. Also, the coordination of Ni²⁺ and Cu²⁺ with the aroylhydrazone core inhibits the mesomorphic potential of the ligands. A temperature dependent Raman study of one of the members, C_{12,12}LH (*m* = *n* = 12) has been made to identify phase transitions and to understand the molecular rearrangement as a result of changes in intermolecular interactions at the phase transition. DFT calculations have been performed to obtain the stable electronic structure of the ligand (C_{6,6}LH) and its nickel(II) complex.

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1. Introduction

N-alkylidene- and N-benzylidene aroylhydrazone derivatives and their metal complexes are known to exhibit a wide spectrum of properties, such as redox activity, magnetism, luminescence, biological activities and supramolecular order etc. There are a large number of reports which describe the above aspects and their metal complexes [1–3], but in contrast to that, reports on liquid crystalline aroylhydrazones and their metal complexes are very few. This is largely attributed to the extensive hydrogen bonding between amide linkage in these types of ligands and their high melting point metal complexes [4,5].

In order to obtain mesogenic aroylhydrazone derivatives, the commonly used approach is reduction of hydrogen bonding between neighbouring layers. This can be achieved by coordination of the aroylhydrazone derivatives with the metal ions, through the oxygen and nitrogen donor ligand (–C(=O)=N–N=CH–), so that the amidic bond (–C(=O)–NH–) cannot be available for intermolecular

hydrogen bonding (Fig. 1a) [4a,b] or using a polycatenar substitution pattern of the alkoxy chains attached to aromatic core (Fig. 1b) [5a,b], or even both approaches in a single molecule (Fig. 1c) [4c].

Recently, we have reported for the first time a new series of calamitic mesogenic aroylhydrazones with ester substitution at the benzylidene moiety, which are found to exhibit the SmC mesophase [6]. This observation was very important due to fact that structurally similar simple alkoxy non-substituted benzylidenehydrazine derivatives are not mesogenic in nature [4b]. However, until now mesogenic aroylhydrazones bearing a lateral group have not been reported. In view of the fact that lateral group substitution enhances the mesogenic properties of compounds significantly [7], it would be interesting to investigate the mesomorphic properties of *o*-hydroxy group containing aroylhydrazones. In the present work a new series of ester containing *o*-hydroxy-benzylidenehydrazine derivatives with the same or different peripheral chain lengths have been synthesized. The effect of a lateral hydroxyl group on the mesomorphic properties of these new derivatives is clearly distinguishable from the ester containing aroylhydrazones without a lateral group, as all the former materials exhibit very high mesomorphic stability of the smectic C phase.

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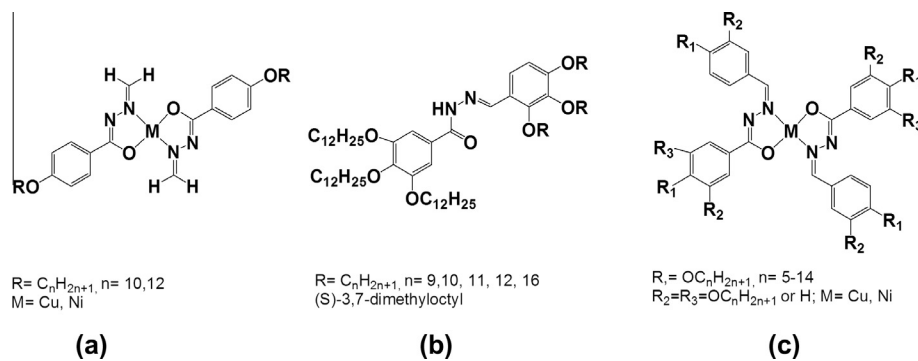


Fig. 1.

The nickel(II) and copper(II) complexes are found to be non-mesogenic in nature.

Raman spectra, having a molecular origin, have great potential for studying the mesogenic behavior of liquid crystals because the molecular changes during phase transitions are associated with a linewidth change, peak shift and intensity change of the Raman marker bands. At a mesogenic transition, new Raman bands may appear or some bands in the crystal phase may disappear. The precise study of linewidth changes may give information about the dynamical processes causing the transition and the peak shifts, together with intensity variation, may give information about the static processes [8]. A temperature dependent Raman spectroscopic investigation has also been carried out to identify and understand the molecular changes at phase transitions.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic route for the preparation of the ester containing *o*-hydroxy benzylidene-hydrazine derivatives N-[4-(4'-alkoxy)benzoyloxy-2-hydroxy-benzylidene]-N'-(4'-alkoxybenzoyl)hydrazine ($C_{m,n}$ LH) (**1a–q**) and their nickel(II) and copper(II) complexes (**2a–d**) is outlined in Scheme 1. The synthetic procedure was similar to that of an earlier report on ester containing aroylhydrazine derivatives [6]. The binuclear nickel(II) and copper(II) complexes (**2a–d**) studied were prepared by the reaction of the ligand with metal acetates in ethanol, by refluxing for 2 h.

All the complexes and free ligands were characterized by elemental analyses and standard spectroscopic techniques. The absorption bands appearing at 3389, 3209, (2926, 2857), 1725, 1651, 1579, (1608, 1510, 1471) and (1535, 1284, 1257) cm^{-1} in the FT-IR spectrum of N-[4-(4'-decyloxy)benzoyloxy-2-hydroxy-benzylidene]-N'-(4'-decyloxy benzoyl)hydrazine, ($C_{10,10}$ LH) are attributed to $\nu(O-H)$, $\nu(N-H)$, $\nu(\text{aliphatic C-H})$, $\nu(C=O, \text{ester})$, $\nu(C=O, \text{amide-I})$, $\nu(N-H, \text{amide-II, Ph})$, $\nu(Ph)$ and $\nu(OPh)$ modes, respectively. The occurrence of characteristic N–H stretching vibration (ν_{N-H}) band at 3209 cm^{-1} and the absorption band of amide-I ($\nu_{C=O}$) at 1651 cm^{-1} clearly reveal that there is an interaction of the N–H group with that of the C=O groups through intermolecular H-bonds ($C=O \cdots H-N$) [9] (Fig. 2). The 1H NMR spectrum of N-[4-(4'-decyloxy)benzoyloxy-2-hydroxy-benzylidene]-N'-(4'-decyloxybenzoyl)hydrazine ($C_{10,10}$ LH) in DMSO- d_6 exhibits peaks at δ 11.85 (s), 11.41 (s), 8.52 (s), 8.09–6.77, 4.03, 1.78–1.28 and 0.88, which are attributed to –OH, –NH, –CH=N, aryl rings, –OCH₂, –(CH₂)₈ and –CH₃ protons, respectively.

Aroylhydrazones of 2-hydroxybenzaldehyde derivatives generally exist in the keto form (Fig. 3-I) in the solid state. However in solution and in the presence of some metal ions, the ligands may

exist in an equilibrium with the tautomeric enol form (Fig. 3-II). The enol form contains two dissociable protons at the amide and phenol functionalities. In the deprotonated form these ligands provide a phenolate-O, an imine-N and a deprotonated amide-O as metal-coordinating centres, and therefore act as tridentate dianionic ligands (Fig. 3-III). These tridentate Schiff bases are very effective in producing binuclear species of metal ions, such as copper(II), which prefers a square-planar or square-pyramidal geometry, or nickel(II), which prefers a square-planar geometry only [10–14]. In the dicopper(II) complex with a dianionic ligand (Fig. 3-III), either the phenolate-O or the deprotonated amide-O can bridge the metal ions. In such a situation, it has been observed earlier that the most negatively charged centre acts as the bridging atom [15–16]. A number of binuclear complexes of tridentate Schiff bases of this type have been reported, with or without X-ray crystallographic studies. Due to the insolubility of the metal complexes in polar and non-polar solvents, single crystals of the complexes could not be grown. All standard spectroscopic analyses of these complexes in the solid state, such as IR, UV–Vis, ESR and elemental analysis (CHN) data, are fully consistent their binuclear nature, as reported earlier.

The absorption bands at (2926, 2857), 1725, 1604, (1604, 1509, 1469) and (1556, 1284, 1256) cm^{-1} in the IR spectrum of the copper(II) complex of N-[4-(4'-decyloxy)benzoyloxy-2-hydroxy-benzylidene]-N'-(4'-decyloxybenzoyl)hydrazine ($C_{10,10}$ LH) are attributed to the $\nu(\text{aliphatic C-H})$, $\nu(C=O, \text{ester})$, $\nu(C=N=N=C-)$, $\nu(Ph)$ and $\nu(OPh)$ modes, respectively. Disappearance of absorptions bands due to the $\nu(N-H)$, amide I [$\nu(C=O)$] and amide II [$\delta(N-H)$] bands and the appearance of an intense band at 1604 cm^{-1} due to an asymmetric vibration of the conjugated $C=N=N=C-$ residue [9,17–18] (Fig. 2c) indicate enolisation of the ligand during metal complexation. The spectra also suggest deprotonation of both phenolic and enolimide groups, and therefore the ligand acts as an ONO tridentate dianion (Fig. 3-III). The bands at 1535, 1284 and 1254 cm^{-1} in the free ligand are due to phenyl-OH and alkoxy phenyl-oxygen ($Ph-O-C_{10}H_{21}$). In the complex two new phenolic $\nu(C-O)$ stretching bands appear at 1556 and 1304 cm^{-1} , indicating phenoxide bridging, resulting in the dimeric structure [19–20]. The shift of the bands towards higher frequency is consistent with an increase in the C–O bond strength because of extended delocalization of the π -system of the azine moiety [21]. The unaltered phenolic $\nu(C-O)$ bands are due to the presence of the alkoxy phenyl-oxygen atom, which remains as such in the complex. The coordination of the azomethine nitrogen to the Cu(II) ion is indicated by the shifting of the bands due to the $\nu(C=N)$ and $\nu(N-N)$ stretching vibrations [22]. The spectra of the complexes exhibit a downward shift of $\nu(C=N)$ from 1621 cm^{-1} for the ligands to 1604 cm^{-1} (merged with the $C=N=N=C-$ band) and an upward shift of $\nu(N-N)$ from 1058 to 1070 cm^{-1} . The changes are indicative of the coordination of the azomethine nitrogen to the copper(II) ion

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