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Smectic Polymorphism in Copper Complexes of Salicylaldimine Derivatives Carrying Polar Carbonyl Groups

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SMECTIC POLYMORPHISM IN COPPER COMPLEXES OF SALICYLALDIMINE DERIVATIVES CARRYING POLAR CARBONYL GROUPS

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Abstract New series of copper-salicylaldimine mesogens carrying 4-alkanoyloxy substituents of varied size on the *N*-phenyl group have been prepared and characterized for their liquid crystalline behaviors. These complexes are commonly smectogenic, and a tilted smectic C phase is enhanced as the alkanoyl group is elongated. Similar tendency has been observed with the ligands, but an orthogonal smectic A phase is not as stable (relative to the smectic C phase) as in the complexes. These behaviors have been interpreted to result from the dipolar interactions as a secondary effect between the carbonyl groups. Their mobility is more restricted in derivatives with longer alkanoyl chains, which would enhance the tilted phase. The relative stability of orthogonal and tilted smectics may be related to the difference in topological arrangement of the polar groups between the complex and its ligand, which have similar smectic layer distances.

INTRODUCTION

Metallomesophase materials or thermotropic liquid crystals containing transition metal atoms can be viewed as an organic-inorganic hybrid system with unique assembling characteristics. They are fluid, and still anisotropic in their properties. Polarized mesophases of low symmetries are particularly of current interest and more recently the issue of dipolar ordering process has aroused a lot of discussion as new varieties of mesophase types such as antiferroelectrics¹ in chiral mesogens have been disclosed. The effect of dipolar interactions has not been attentively investigated with metallomesogens so far, but assessment of this effect should be of fundamental importance, since coordinate bonds are more or less polar inherently and transition

metal sites are often susceptible to intermolecular bonding interactions with polar groups.

As a part of our systematic study of structure-property relationship in the copper-salicylaldehyde mesogens,²⁻⁴ new homologous series of complexes (**1**, Figure 1) carrying 4-alkanoyloxy substituents of varied size on the *N*-phenyl group have been prepared, and their liquid crystalline behaviors have been characterized, together with those of the ligands (**2**). The complexes are approximated to be of centrosymmetric, bis-chelate type, which would lead to cancellation of the dipole moments associated with the coordinate bonds and those in the bis(salicylidene) part of the molecule but not those of mobile carbonyl groups. The mobility is varied among the series **a**, **b**, and **c**, by attached methyl, *n*-nonyl, and *n*-heptadecyl chains, respectively. Each of the homologous series covers roughly the whole range of alkoxy chain length available ($2 \leq n \leq 18$), and this is comparable to the length of alkanoyloxy chains spanning over the series **a** to **c** ($2 \leq m \leq 18$).

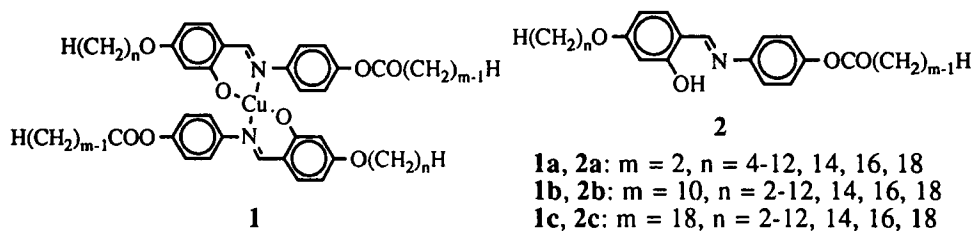


FIGURE 1 Structure of the compounds studied.

RESULTS AND DISCUSSION

Mesomorphic Properties of the Complexes

All of the present copper complexes except for **1a** ($n=4$) and **1a** ($n=5$) proved to be smectogenic. Figure 2 summarizes the mesomorphic properties by means of phase pattern diagrams for the series **1a-c**, leaving aside details of each homologue. Areas labeled by K, SmC, SmA, N, and I are temperature ranges where crystalline, smectic C, smectic A, nematic, and isotropic liquid phases, respectively, are thermodynamically stable. It can be seen that the metallomesophase in series **1a** carrying throughout a small acetoxyl substituent in 4-position of the *N*-phenyl moiety is exclusively SmA. On extending this "inner" alkanoyl group up to decanoyl chain, higher part of the series **1b** displays the SmC phase but the phase tends to give way to SmA as the alkoxy chains are shortened. The last series **1c** shows a similar phase pattern, although the mesophase upper boundary is much lowered. Crystalline phase is relatively stabilized for higher

homologues, and as a consequence the smectic region is gradually narrowed with increasing n .

It may be convenient to recall here an empirically found tendency in mesomorphic behavior of polar organic mesogens. Walba et al. have pointed out, based on a survey of about 300 compounds, that tilted phases tend to occur when the tails are of about equal length and of intermediate length (about seven carbons), and at least one tail is an alkoxy grouping.⁵ Attention is called to the fact that almost all of the present mesomorphic complexes carry tails of equal length of more than seven carbons, regardless of whether the alkoxy group is longer (as in **1a**), the alkanoyloxy is longer (**1c**), or it changes over across the series (**1b**), and yet SmA phase is quite stable (relative to SmC).

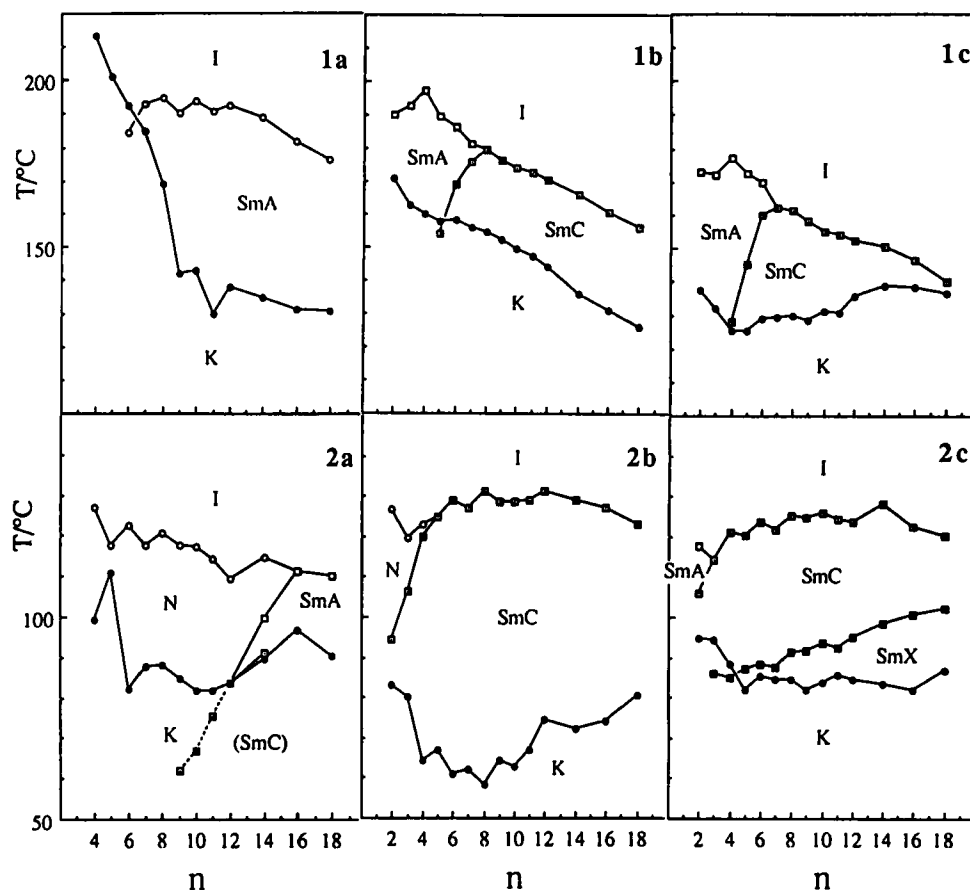


FIGURE 2 Mesomorphic phase pattern diagrams for the compounds **1** and **2**.

Mesomorphic Property of the Ligands

In search for a rationale of this exceptional behavior, the ligand series **2a-c** have also been investigated as reference organics. The series **2a** having a rather unbalanced tail composition of a small acetoxy group and a longer alkoxy chain is indeed mostly nematogenic with SmA phase being exhibited by the three highest homologues. It should be noted that higher homologues ($n=9-14$) shows a part of SmC phase boundary. If the acetyl group is substituted by decanoyl group, the series **2b** changes to largely smectogenic and the mesophase pattern is dominated by SmC. The effect of promoting smectic phase by the alkyl chain elongation is obvious here, but the lack of SmA region is also noted. Further elongation of the alkanoyl tail as in **2c** brings about little change on the stability of the SmC phase but a more ordered smectic phase (SmX) emerges and the remaining N region is finally replaced by SmA. The SmX phase is presumed to be of hexatic type from X-ray diffraction patterns, and the series **2b** appears to have the same phase in metastable state (not plotted in Figure 2).

Thus the mesomorphic tendency of organic ligands basically follow the above empirical rule for the emergence of SmC phase with regard to a certain length of the tail. A modification as to the point of two tails of comparable size would be that, if alkanoyl tail is employed and it is sufficiently long as in **2b** and **2c**, the other can be as short as two carbons. Anyhow strong preference for SmC is evident in these series.

The Effect of Dipolar Interactions

In interpreting the above observation regarding to the orthogonal vs tilted smectic ordering, the effect of dipolar interactions is highlighted with reservation of primary importance to the van der Waals interaction involving long hydrocarbon chains. The complex molecules are viewed for this purpose as carrying two pairs of tails, one "nonpolar" alkyl and the other "polar" alkanoyl group pair, and they are schematically drawn in Figure 3, where decyl homologue represents each series of **1a-c** and the alkanoyl group is tagged by an arrow at its link.

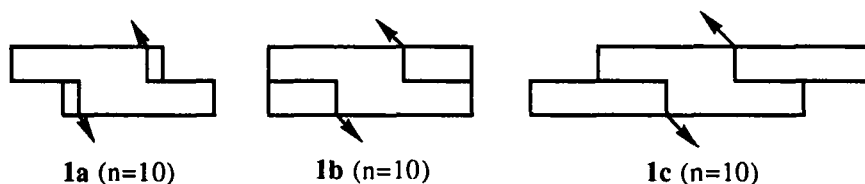


FIGURE 3 Schematic drawings for decyl homologues of the complexes.

It is important to note that the unbalancing molecular shape factor is in lateral position; two pairs of tails are of unequal length for a majority of the complexes while

keeping the longitudinal symmetry. Thus the acetyl groups in **1a** would rotate freely and the associated dipole moments would be averaged to make little contribution to the intermolecular force. In this case the phase pattern is purely of SmA. Mixed SmA/SmC type occurs with extended tails as in **1b** and **1c** where restricted motion of the carbonyl groups would lead to intralayer dipolar repulsion, forming tilted lamellar structure. But the tilted smectic polymorph is stabilized only if the nonpolar pair matches a certain proportion of the length of the polar pair. Extension of the polar pair as in **1c** would reinforce the dipolar effect, but at a greater cost of the layer stability. Additional structural factor is apparent in Figure 3; the molecular long axis will shift from a direction defined by the rigid, nonpolar fragment to one along the polar part of the molecule as going from the complex **1a** to **1c**. This will affect the size of outboard component of net dipole moment, as indicated symbolically by arrows of growing size.

Among the homologues with virtually four tails in shape, **1a** ($n=2$), **1b** ($n=10$), and **1c** ($n=18$), the last two are located deep in the SmC region of the phase pattern diagrams. The number of carbon atoms in the alkoxy group at which the SmA phase disappears is either $n>18$, 8, and 7 for the series **1a**, **1b**, and **1c**, respectively. Fully symmetrical complexes thus come in accord with Walba's rule. In retrospect, the exceptional cases of lower homologues must involve rotational dynamics about the molecular long axis quite unlike those of pure organics.

Topological role of the metal center in connecting the ligands with unequal tails may also be extracted. Imagine that the entities in Figure 3 are split lengthwise and laid along, then the dipoles will line up either nearer the layer interface for **2a** or towards the middle of a layer for **2c**. The weakness in positional ordering in **2a** (relative to **1a**) and in SmC tendency in **1c** (relative to **2c**) may owe some to this spatial factor. Preliminary X-ray diffraction studies have revealed that the layer distances are similar between the ligands and the complexes, suggesting a fully interdigitated layer packing in the latter. Tuning of the dipole distribution along the one-dimensional lattice may be related the relative stability of orthogonal and tilted arrangements of the molecules.

In summary, the present work has demonstrated that the use of large alkanoyl groups in copper-salicylalimine mesogens promotes SmC phase. The problem as to how is being resolved by studying phase behaviors comparatively over a wide range of homologous series including the ligands. An interplay between the positional ordering process and the dipolar interactions has been hinted, and it should be useful to clarify this point in designing materials in which dipolar ordering occurs. Our structural study on the smectic phases will provide relevant information when it is completed.

EXPERIMENTAL

Synthesis

The ligands were prepared using conventional procedures in three steps of alkylation of 2,4-dihydroxybenzaldehyde (in 4-position), condensation with *p*-aminophenol, and DCC esterification using *n*-alkanoic acid. Metallation reaction and purification conditions were similar to those reported for analogous compounds.² Lower homologues of **1a** and **1b** were relatively prone to decomposition when heated in solution and received only one or two recrystallizations for maximum purity attainable.

Physical Measurements

Optical and DSC characterizations of the mesomorphic properties were conducted as previously reported.² Phase transition temperatures plotted in Figure 2 are those determined by the DSC analysis, except for those of mesomorphic transformations between smectic polymorphs. Compounds with longer alkyl groups showed solid state polymorphism more frequently, but we did not look further into this phenomenon for the present study. Plotted melting points are the highest observed for multiply melting samples.

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