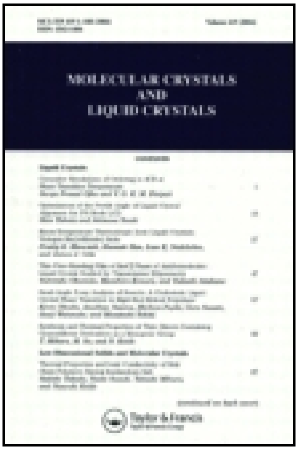

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Induction and Stabilization of Smectic Phases in Amphiphilic Hydrogen-Bond Complexes

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To cite this article: R. V. Talroze , G. A. Shandryuk , S. A. Kuptsov , V. S. Bezborodov & N. A. Platé (1996): Induction and Stabilization of Smectic Phases in Amphiphilic Hydrogen-Bond Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 281:1, 135-144

To link to this article: http://dx.doi.org/10.1080/10587259608042239

Mol. Cryst. Liq. Cryst., 1996, Vol. 281, pp. 135–144
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Induction and Stabilization of Smectic Phases in Amphiphilic Hydrogen-Bond Complexes

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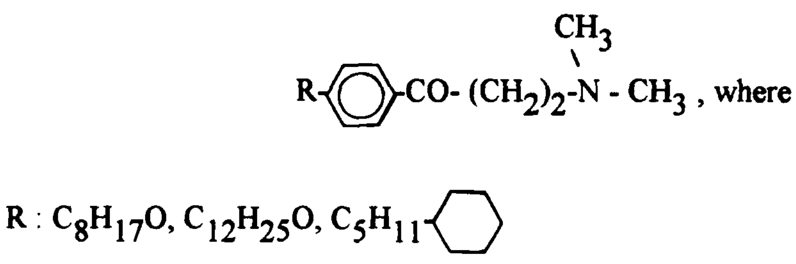
(Received July 25, 1994; in final form February 17, 1995)

Hydrogen-bond complexes of dicarboxylic malonic and glutaric acids with β-*N*-dimethylamino-4-dodecyloxypropiophenone are studied by means of FT-IR spectroscopy, optical microscopy, DSC and X-ray analysis. The formation of a thermotropic SA phase is proved and the model of the layered structure formation is given. The mesomorphic behavior of complexes is discussed in terms of amphiphilic systems.

Keywords: Hydrogen-bond complexes, amphiphilic, phase diagram, sematic phases.

1. INTRODUCTION

The principle of molecular recognition, strongly developed in the last decade by Lehn,[1] Ringsdorf,[2] Frechet and Kato[3] etc. opened the possibility of creating mesogenic-like structures by means of the H-bond interaction between two or more nonmesogenic complementary molecules and inducing liquid crystalline (LC) phases in both low molecular mass and polymer systems. At the same time we have observed in [4] the formation of the smectic-like ordered structures in complexes of polyacrylic acid and β-*N*-dimethylamino-4-alkyloxypropiophenone having the following formula



The type of bonding and the characteristic composition of these complexes are discussed in [5] whereas the description of the structure and the phase behavior is given in [6] in detail.

The main objective of this paper is to answer the question whether the selforganization process observed in [4] results from the ordering effect induced by polymer chains or is related to the formation of the specific mesogenic structure due to the H-bond interaction between acids and tertiary amines under investigation.

To solve this problem we have studied complexes of dicarboxylic malonic (MA) and glutaric (GA) acids

$$HOOC\text{-}CH_2\text{-}COOH \quad HOOC(\text{-}CH_2\text{-})_3COOH$$

with β-N-dimethylamino-4-dodecyloxypropiophenone as well as complexes of different monocarboxylic acids such as benzoic, stearic and methylpropionic acids.

The choice of dicarboxylic acids as model systems was dictated by the following reasons. On the one hand the low molecular mass acid has to be an appropriate model having a structure similar to that in the polyacrylic acid chain between the neighbouring carboxylic groups, and on the other hand, the acid has to provide the preferable formation of a 2:1 complex which is a characteristic one for polyacrylic acid.

GA serves as the best example of a structural model while strong and stable intramolecular H-bonds in MA could contribute in the formation of 2:1 characteristic complex.

That is why both acids were used as model systems in order to understand the role of the acid component structure and reactivity on the selforganization and LC ordering in complexes with the tertiary amines.

2. EXPERIMENTAL

β-N-Dimethylamino-4-dodecyloxypropiophenone is synthesized as described in [7]. Mono- and dicarboxylic acids used are crystallized twice from ethanol. Samples are prepared by mixing acid and amine solutions in ethanol followed by the evaporation of the solvent.

Mettler DSC (TA 4000) is used to investigate the thermal behaviour of complexes and initial components.

X-ray measurements are performed using Rotaflex RU-200 "Rigaku Dmax-RC" instrument (Ni-filtered Cu_K radiation, transmission mode).

Optical microscope POLAM L-312 equipped with the heating state RNMK-05 (Boetius) is used for optical texture observations.

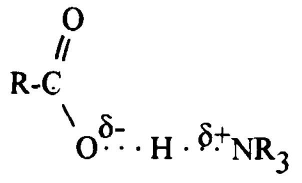
FT-IR-spectra are performed with FT-IR spectrometer IFS-113v (Bruker).

3. RESULTS AND DISCUSSION

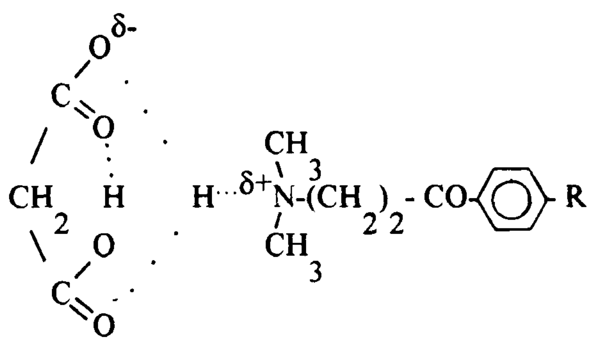
Products of the reaction between different mono- and dicarboxylic acids and β-N-dimethylamino-4-dodecyloxypropiophenone are soluble in ethanol. After the solvent evaporation one obtains crystalline samples manifesting the main spectral features of the complex formation (Fig. 1): bands corresponding to the initial amine (ν(CH) in CH_3 at nitrogen atom at 2820 cm^{-1}, ν(CN) = 1201 cm^{-1}) and acids ν(OH) at

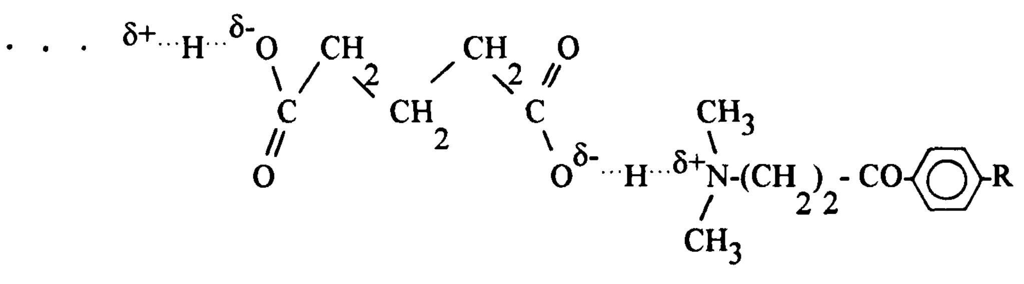
3600–2400 cm^{-1} disappear. Two new weak broad absorption bands at 2450 and 1900 cm^{-1} appear.

The analysis of FT-IR spectra given in [5] indicates the formation of H-bond complexes with the strong proton polarization when the partial charge transfer takes place:



At the same time FT-IR data show that the initial equimolar ratio of components in ethanol solutions of dicarboxylic acids and amine results in the formation of the solid complex having 2:1 composition (number of carboxylic groups: number of amine molecules) for MA systems whereas GA is able to form both 2:1 and 1:1 complexes:





The reason for the difference in the complex composition for MA and GA is discussed in [5]. "Independent" behavior of carboxylic groups in GA permits the binding of amine molecules from both sides of the molecule whereas the strong intramolecular H-bond is responsible for the limited binding of amine molecules by MA.

Complexes of monocarboxylic acids with the amine are crystalline substances with melting points given in the Table 1. The melting of the crystalline 2:1 complexes of both MA and GA proceeds in several steps: DSC curves (Fig. 2) show endothermic peaks indicating high enthalpies of melting (42 and 48 kJ/mole). At the same time one can see

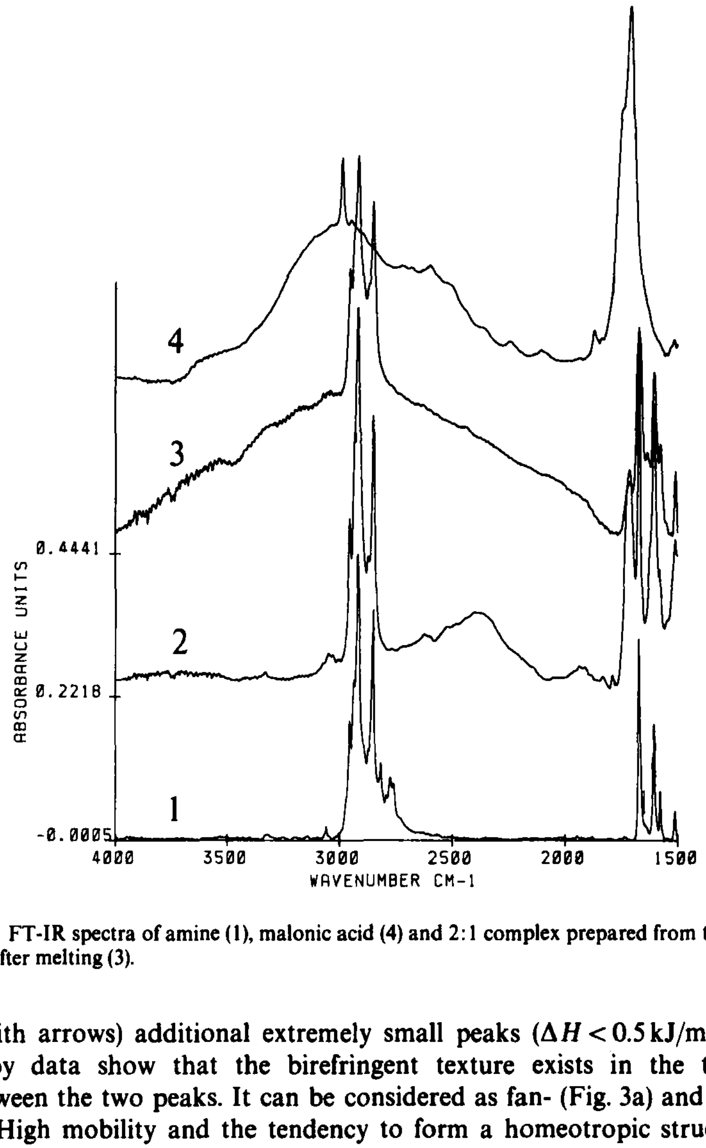


FIGURE 1 FT-IR spectra of amine (1), malonic acid (4) and 2:1 complex prepared from the solution (2) and cooled after melting (3).

(shown with arrows) additional extremely small peaks ($\Delta H < 0.5$ kJ/mol). Optical microscopy data show that the birefringent texture exists in the temperature range between the two peaks. It can be considered as fan- (Fig. 3a) and oiled strips (Fig. 3b). High mobility and the tendency to form a homeotropic structure under shearing indicate the formation of the smectic-like structure which melts with the low enthalpy.

X-ray scattering measurements strictly confirm the conclusion given above. In Figures 4and 5 X-ray diffraction patterns for 2:1 complexes of both MA and GA acids are shown. At room temperature X-ray diagrams present a great number of small- and wide-angle reflections indicating the crystallinity of complexes. Most of the reflections disappear at melting points corresponding to first peaks at DSC curves (Fig. 2). Above the melting points both complexes are characterized by a small angle maximum and diffuse halo at wide angles. The latter is preserved above the second transition temperature when the small angle maximum disappears.

TABLE 1

Temperatures of phase transitions for complexes of *β*-*N*-dimethylamino-4-dodecyloxypropiophenone with carboxylic acids

Acid	Complex composition (COOH-group: amine)	Tm,°C	Tc,°C
Stearic	1:1	53	–
Methylpropionic	1:1	42	–
Benzoic	1:1	57	–
	2:1	42	–
Glutaric	1:1	50	51
	2:1	56	67
Malonic	2:1	82	110

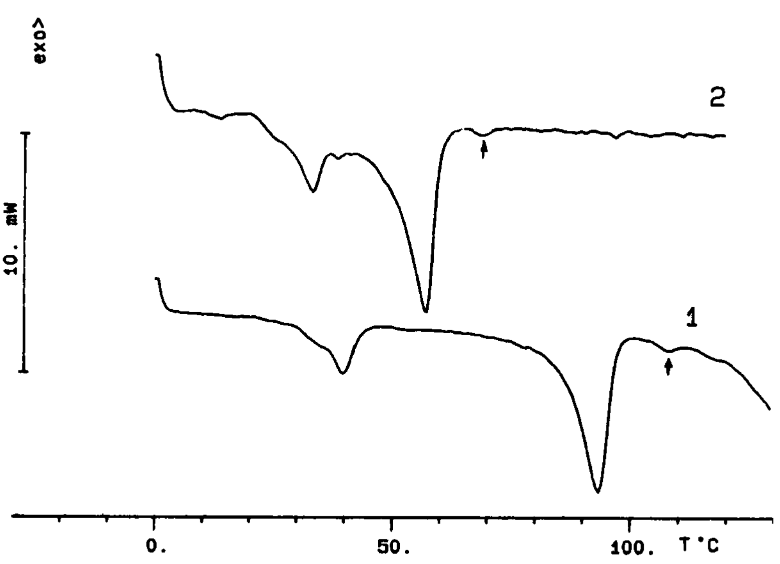


FIGURE 2 DSC curves for 2:1 complexes of MA (1) and GA (2).

The set of experimental data leads to the conclusion that complexes of MA and GA with the amine studied form liquid crystalline phases within certain temperature ranges. In Figure 6the whole phase diagram for GA-amine system is given. One can see that the smectic phase appears at the point corresponding to 1:1 complex composition when there is no free amine in the system. The 2:1 complex has the highest temperature for smectic↔isotropic transition as well as the highest melting point. Nevertheless the whole range of the smectic phase is broadened to the left side of the phase diagram where excess GA exists. It shows that the presence of the excess acid is necessary to stabilize the smectic phase which provides the formation of the ordered LC structure interacting with 2:1 complex due to the presence of free carboxylic groups in acid molecules.

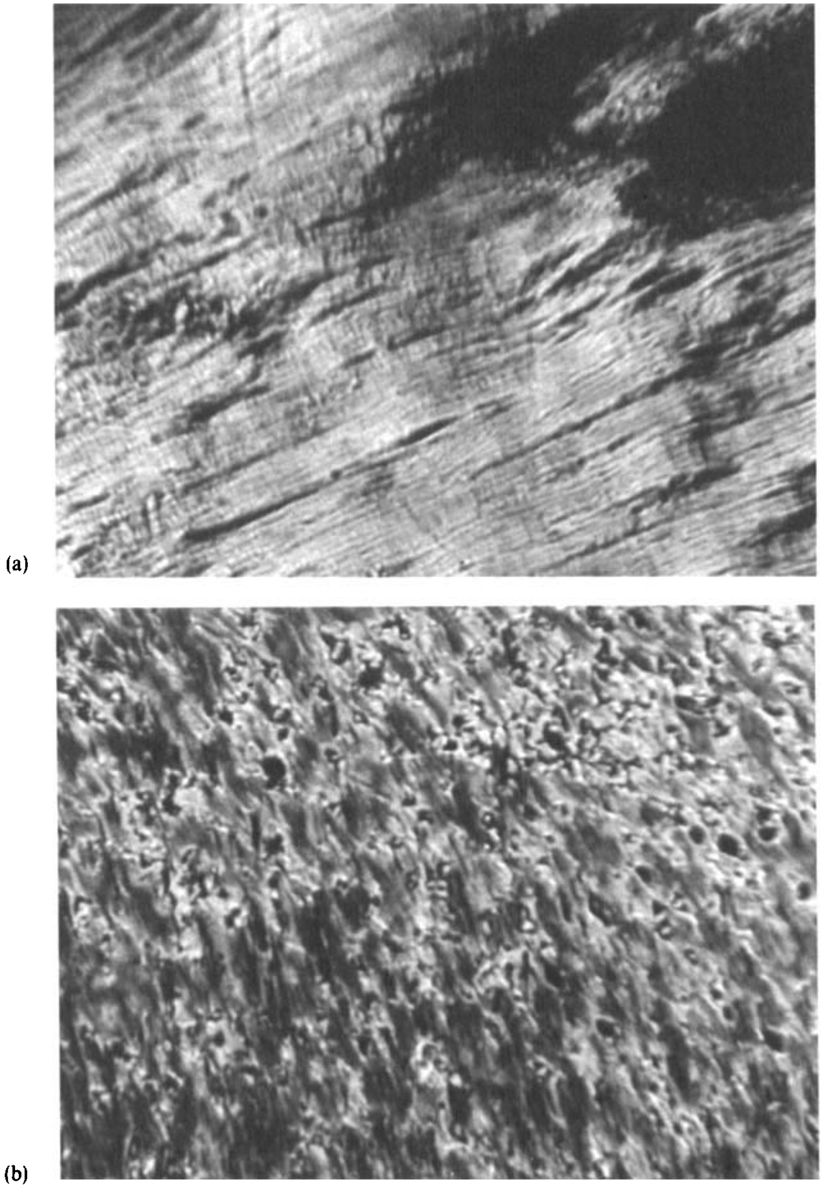


FIGURE 3 Optical textures of 2:1 complexes of MA (a) and GA (b) at 100 and 52°C.

Similar behavior is found for MA-amine complexes saturated with the excess acid but the phase diagram for this system is much more complicated because the phase transitions are irreversible after the cooling of preliminary heated MA-amine complexes above the clearing point. The reasons for it is the thermal instability of the malonic acid which is known to decompose during heating to the melting point at

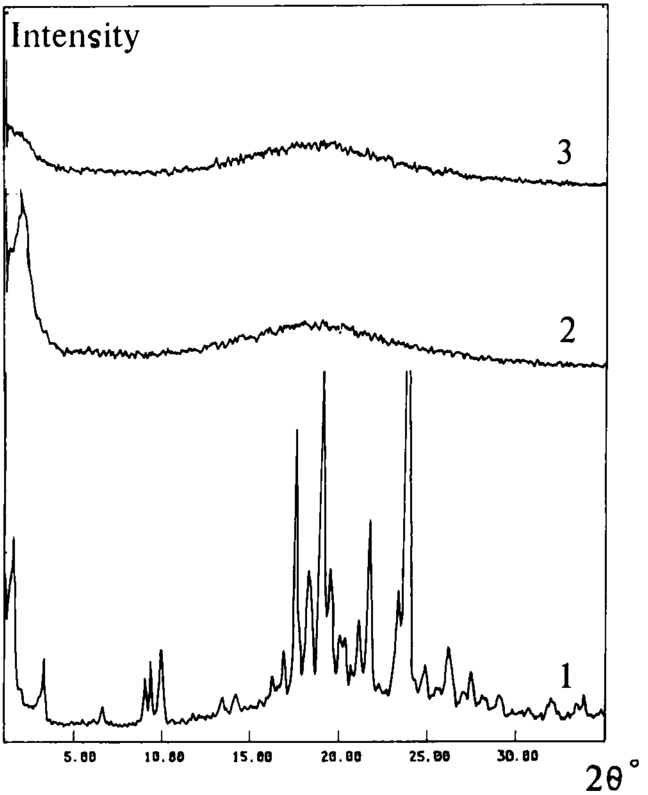


FIGURE 4 X-ray diffraction patterns of 2:1 complexes of MA at 20 (1), 100 (2) and 115°C (3).

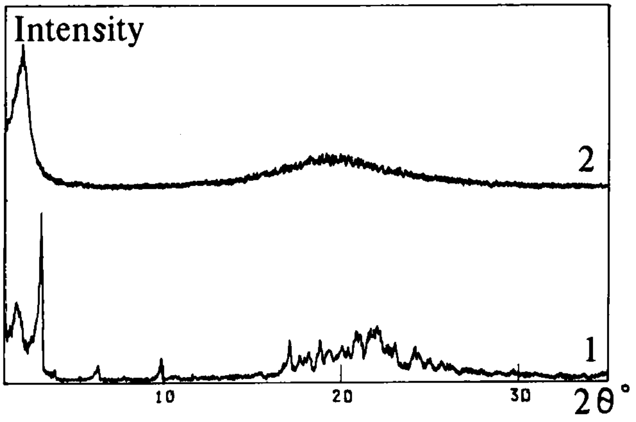


FIGURE 5 X-ray diffraction pattersn of 2:1 complexes of GA at 18 (1) and 60°C (2).

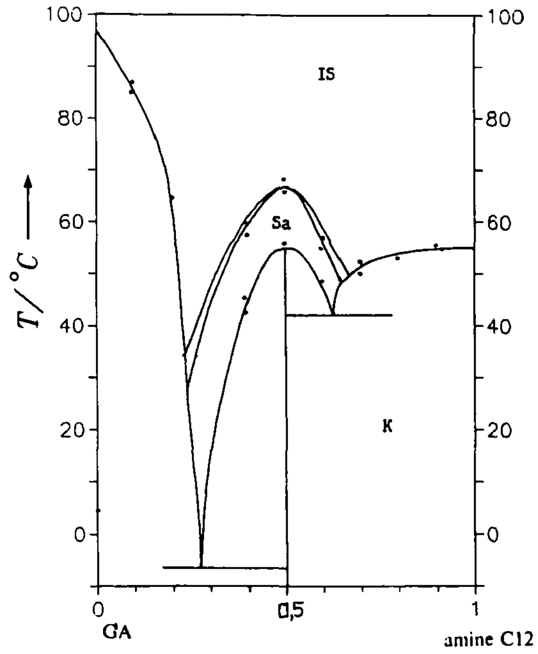


FIGURE 6 Phase diagram for GA-amine complex system.

140°C. If one compares IR-spectra for complexes prepared from the solution at the room temperature (Fig. 1) and cooled after heating the clearing point (Fig. 1) one can observe a strong decrease of the intensity of ν(CO) at 1720 cm^{-1} indicating the decrease of the acid component in the complex after heating. It means that the partial decomposition of H-bonded malonic acid in complexes proceeds at a lower temperature when smectic↔isotropic phase transition takes place.

TABLE 2

Interplanar spacings **d** of complexes of dicarboxylic acids with β-*N*-dimethyl-4-dodecyloxypyropiophenone (AM)

Complex	Model	Calculated* d, Å	Experimental d ± 1, Å
MA-AM			
2:1	a	30–33	
	b	53–58	42
	c	40–44	(at 100°C)
GA-AM			
2:1	a	32–35	
	b	55–60	44
	c	41–46	(at 60°C)
1:1	d	41–46	43 (at 48°C)

* Different models given in Figure 7 (a, b, c, d) are used for calculations.

Regarding the structure of the smectic layer it is necessary to analyze the value of the interplanar spacing **d** corresponding to the small angle X-ray reflection for both complexes of different composition.

As is seen from the data given in Table 2 one can conclude that **d** value practically does not depend on the acid structure as well as on the complex composition and is equal to 42–44 Å. In Figure 7 three main types of the layered structure for complexes of

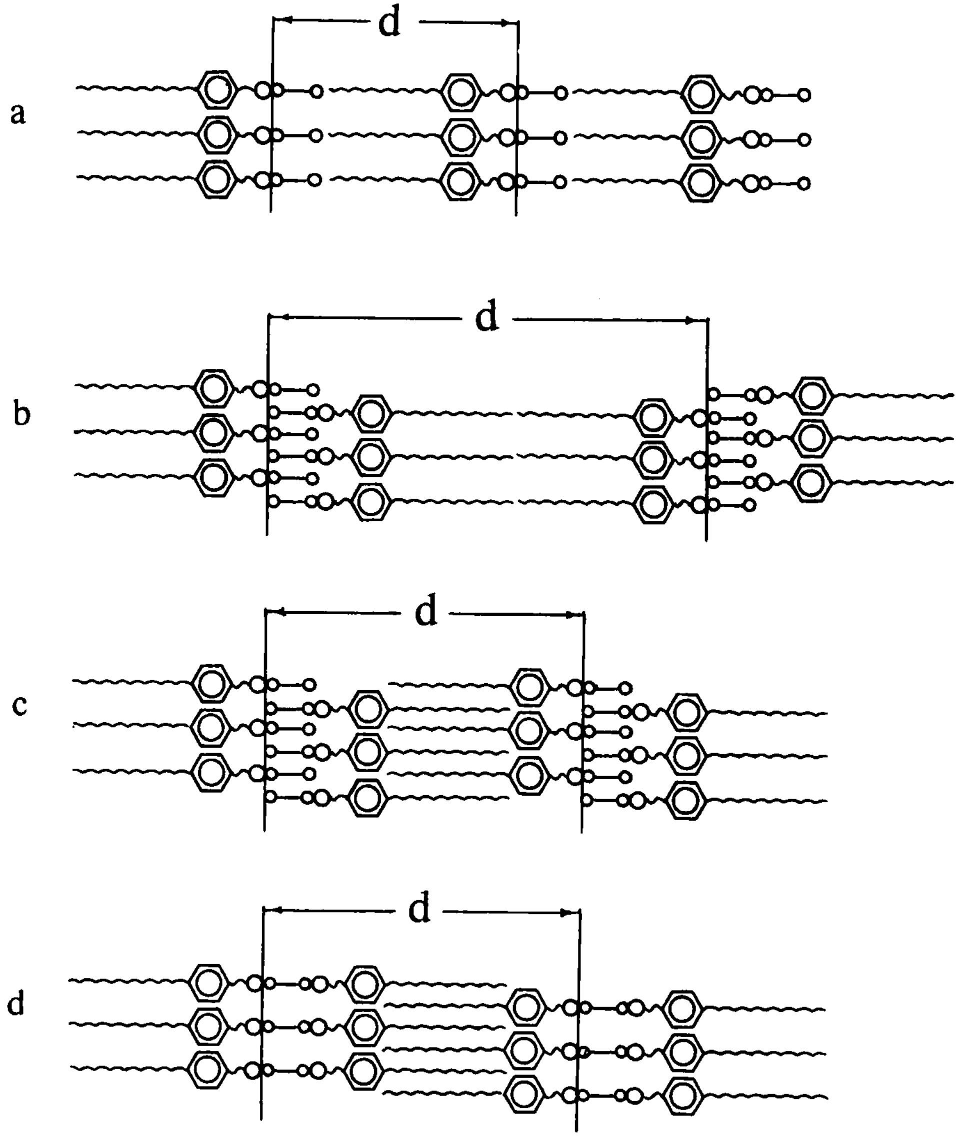


FIGURE 7 Models of smectic layer ordering in dicarboxylic acid: amine complexes.

dicarboxylic acids are given. Taking into account the length of the amine molecule (23.5–26.5 Å) and the size of dicarboxylic acids molecules equal to 8–10 Å (GA) and 7–9 Å (MA) as well as calculated values for the interplanar distance *d* shown in Figure 7 one can conclude that one layered structure (a) as well as double layered structure (b) are not realized. The most realistic model corresponds to a double layered ordering with percolated aliphatic tails and acid residues (c). It shows also that both 2:1 (c) and 1:1 complexes (d) of GA have to form an identical layered structure with the same interplanar distance. This model permits one to suppose that in complexes containing an excess acid its molecules are displaced between complex molecules within the domains enriched by acid residues. In this case the layered structure with the similar interplanar distance has to be preserved.

To explain the reasons for the mesomorphic behavior of complexes investigated one has to conclude that typical mesogenic cores as well as essentially high geometrical shape anisotropy cannot be responsible for the creation of the LC ordering in these systems. On the other hand, the amphiphilic structure inducing micro segregation processes has to be taken into consideration. One can compare the layered structure of complexes with lamellar phases in water solutions of amphiphylic molecules and in particular in solutions of *β*-*N*-dimethylamino-4-dodecycloxypropiophenone hydrochloride [4]. In our case H-bond complexes represent micro heterogeneous systems with the layered structure resulting from the arrangement of amine residues. The latter are strongly found with dicarboxylic acid microphase which performs as an aqueous interlayer. Such complexes could be considered as a particular group of liquid crystals which is displaced at the boundary between the thermotropic and lyotropic systems. The main regularities of LC behavior for these complexes as a function of amine and carboxylic acid structures will be studied further in details.

Acknowledgments

Authors express gratitude to Dr. T. L. Lebedeva, Prof. Dr. G. Pelzl and Dr. J. Lindau for useful discussions. The research described in this publication was made possible in part by Grant No M-000R from the International Science Foundation and in part by Russian Foundation for Fundamental Research (Grant No 94-03-09535).

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