MOLECULAR NETWORKS FORMING CRYSTALLINE AND LIQUID CRYSTALLINE PHASES BY COMBINED HYDROGEN-BONDING AND IONIC INTERACTIONS

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Received October 20, 2003
Accepted December 8, 2003

Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday.

Molecular recognition of cyclic bisamidinium dication with a series of 4-alkoxybenzoates afforded materials exhibiting lamellar crystalline structures at low temperatures and highly ordered smectic phases at higher temperatures. The liquid crystalline behaviour was investigated by differential scanning calorimetry, polarized optical microscopy and established by X-ray diffraction. Combined hydrogen-bonding and ionic interactions resulted in supramolecular networks which have sufficient stability to maintain their structure at high temperatures following the melting of the long alkyl chains.

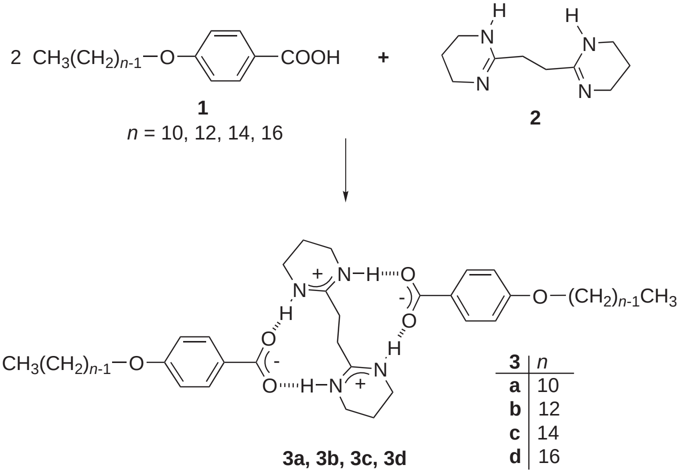
Keywords: Hydrogen bonds; Liquid crystals; Amidinium salts; Amidines; Alkoxybenzoic acids; Self-assembly.

Liquid crystalline formation has been induced by hydrogen-bonding interactions between complementary molecules[1]. In certain cases, however, ionic forces are required to strengthen the rather weak directional hydrogen bonds for enhancing the binding constants of complexes inducing or modifying liquid crystalline properties. For instance, the smectic liquid crystalline character exhibited by long-chain iminodiacetic acids[2], is due to the supramolecular network which is formed through hydrogen-bonding and ionic interactions of their zwitterionic species. Analogously, in a series of alkylbis(2-hydroxyethyl)methylammonium bromides, ionic and hydrogen-bonding interactions act simultaneously[3] leading to the formation of supramolecular structures which exhibit liquid crystalline phases. Two smectic phases were identified, an ordered smectic T phase and a disordered smectic

doi:10.1135/cccc20041161

A phase. Applying the same concepts, smectic liquid crystals were formed based on guanidinium *n*-alkylbenzenesulfonates[4].

Hydrogen-bonding interactions between amidinium and carboxylate derivatives provided bulk crystals[5] or crystalline films at the air-water interface[6]. Additionally, extensive work by Hosseini et al.[7] has established, that cyclic bisamidinium dication forms molecular networks through their recognition with acid anions. Indeed, bisamidinium dication with four weak and directional hydrogen bonds coupled with non-directional but strong electrostatic interactions forms a diversity of molecular networks through its interaction with acid anions. With this background, it could be predicted that the interaction of this dicationic species with amphiphilic-type carboxylates would lead to the formation of liquid crystalline phases in analogy with the long-chain iminodiacetic acids[2] mentioned above. For this purpose, long-chain 4-*n*-alkoxybenzoic acids **1** (*n* = 10, 12, 14, 16) were reacted with bis(cyclic amidine) **2** according to Scheme 1 affording the salts **3** (*n* = 10, 12, 14, 16) as shown in the Scheme. The liquid crystalline character of these compounds was identified by polarizing optical microscopy and differential scanning calorimetry and established by X-ray diffraction.



SCHEME 1

EXPERIMENTAL

Materials

4-Alkoxybenzoic acids **1** with alkyl chains of 10, 12, 14, and 16 carbon atoms were obtained from Aldrich and twice recrystallized from ethanol/benzene mixture (2:1, v/v). 2-[2-(1,4,5,6-Tetrahydro-2-pyrimidinyl)ethyl]-1,4,5,6-tetrahydropyrimidine (**2**) was prepared according to published procedure[8].

Synthesis of Bis(cyclic amidinium) Dialkoxybenzoates

The bis(cyclic amidinium) derivatives 2-[2-(1,4,5,6-tetrahydropyrimidin-3-ium-2-yl)ethyl]-1,4,5,6-tetrahydropyrimidin-3-ium di(4-alkoxybenzoates) with alkyl chains of 10 (**3a**), 12 (**3b**), 14 (**3c**) and 16 (**3d**) carbon atoms were prepared by reacting 1 mmol of bis(cyclic amidine) **2** dissolved in ethanol with 2 mmol of 4-*n*-alkoxybenzoic acid **1** dissolved in the same solvent. For dissolving the higher members of the acids, slight heating was required. The precipitated salts were filtered off and recrystallized twice from ethyl acetate. The resulting materials were exhaustively dried under vacuum over phosphorous pentoxide and their purity was established by elemental analysis and ^{1}H NMR. ^{1}H NMR (Brucker 500 MHz, $CDCl_3$): 0.86 (t, 6 H, CH_3); 1.2–1.4 (m, 4 *n*H, $CH_2(C\mathbf{H}_2)_nCH_3$); 1.45 (m, 4 H, $OCH_2CH_2C\mathbf{H}_2$); 1.76 (m, 4 H, $OCH_2C\mathbf{H}_2CH_2$); 1.91 (m, 4 H, $CH_2C\mathbf{H}_2CH_2$); 3.23 (t, 4 H, $NCC\mathbf{H}_2$); 3.44 (t, 8 H, NCH_2); 3.98 (t, 4 H, OCH_2); 6.87 and 7.98 (2d, 8 H, arom.); 11.95 (s, 4 H, NH). Elemental analyses: **3a**, for $C_{44}H_{70}N_4O_6$ calculated: 70.36% C, 9.39% H, 7.46% N; found: 70.16% C, 9.45% H, 7.39% N. **3b**, for $C_{48}H_{78}N_4O_6$ calculated: 71.43% C, 9.74% H, 6.94% N; found: 71.46% C, 9.83% H, 6.97% N. **3c**, for $C_{52}H_{86}N_4O_6$ calculated: 72.35% C, 10.04% H, 6.49% N; found: 72.18% C, 10.04% H, 6.47% N. **3d**, for $C_{56}H_{94}N_4O_6$ calculated: 73.16% C, 10.31% H, 6.09% N; found: 73.05% C, 10.22% H, 6.01% N.

Liquid Crystalline Characterization

Liquid crystal textures were observed using a Leitz–Wetzlar polarizing microscope equipped with a Linkam hot-stage. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-10 calorimeter (TA Instruments) at heating/cooling rates of 10 °C min^{-1}. Thermal stability was assessed by thermogravimetry employing a TGA 2050 analyzer (TA Instruments) at a heating rate of 10 °C min^{-1}. Liquid crystalline phases were investigated by X-ray diffraction using CuKα radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powder samples were sealed in Lindemann capillaries and heated employing an INSTEC hot-stage.

RESULTS AND DISCUSSION

The salts were thermally stable up to about 170 °C, as studied by thermogravimetry. Decomposition was observed following their clearing temperatures, with the exception of the C16 derivative, which starts decomposing at 160 °C, i.e. before its transition to the isotropic melt. On heating, the salts exhibited three sharp endothermic peaks (Table I). The first peak corresponds to a crystal–crystal transition, which is not observed on cooling or during the second heating run indicating that the second crystal phase is more stable, at least under the experimental conditions employed. The second transition corresponds to the melting of the aliphatic chains (see also X-ray results) leading to the formation of an ordered smectic phase as implied from the mosaic textures observed under the polarizing microscope (Fig. 1). It is interesting to note that this transition is observed at temperatures which decrease with *n* suggesting that the crystal stability is mainly controlled by the packing of the ionic part of the compounds. The third endothermic transition leading to the isotropic phase is almost independent of the chain length (with the exception of compound C16 which simultaneously decomposes). The rather high transition enthalpy involved is another indication that the mesophase is highly ordered. On cooling, the reverse phase transition was observed with a hysteresis of about 5 °C while the transition from the smectic to crystalline phase was observed with a hysteresis of about 15 °C showing the significance of nucleation.

Powder X-ray diffraction established that the two crystalline phases observed have a lamellar structure (Fig. 2), since in the small-angle region more than four equidistant small-angle reflections were observed. In addition, several sharp reflections were observed in the wide-angle region indicating a crystalline structure. The lamellar periods *d* vary linearly with the number of carbon atoms in the aliphatic chains, *n*, following the equations

TABLE I
Phase transition temperatures (onset, °C) and enthalpies (kJ mol^{-1}). T_k corresponds to a crystal–crystal transition, T_s to a crystal-ordered smectic transition and T_i to an ordered smectic–isotropic transition

n	T_k	ΔH_k	T_s	ΔH_s	T_i	ΔH_i
10	114.4	31.2	149.7	42.4	171.7	25.5
12	116.3	37.7	143.4	54.2	176.1	31.5
14	123.4	47.4	139.0	63.2	176.7	32.0
16	124.8	63.9	133.6	38.1	164.2[a]	–

[a] Decomposition is simultaneously observed. The accuracy of enthalpy values is better than 0.15 kJ mol^{-1}.

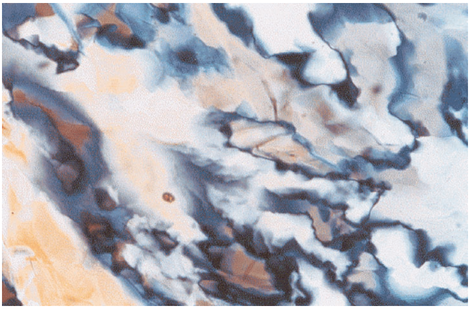


FIG. 1
The mosaic texture obtained on cooling the isotropic melt of the C10 derivative

d(Å) = 14.84(13) + 1.07(1) n for the first crystal phase and d(Å) = 14.40(19) + 1.26(1) n for the second crystalline phase (Fig. 3). It becomes evident that the thickness of the polar sublayers, deduced from the Y-intercept of the straight line, is only slightly different in the two phases. However, in the low-temperature crystal phase, the slope of the d vs n line, representing the length of an ethylene group (2.14 Å per ethylene unit), is less than that of a fully extended paraffin chain (2.54 Å). This suggests that the alkyl chains are interdigitated and tilted with respect to the layer normal by ca. 32° (cos 32 = 2.14/2.54). On the other hand, the slope of the line determined for the second crystalline phase perfectly agrees with the known distance of

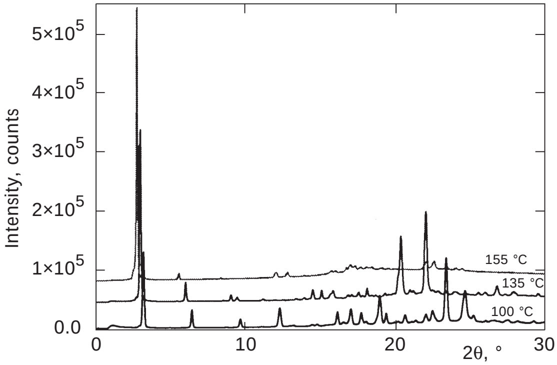


FIG. 2
X-ray powder diffraction patterns of the C12 derivative in the two crystalline phases (100, 135 °C) and in the smectic phase (155 °C)

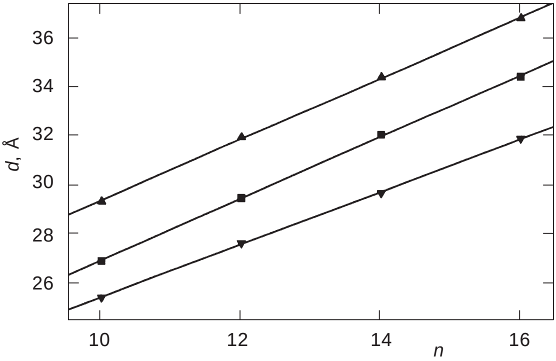


FIG. 3
Lamellar periods of the two crystalline phases and the smectic phase as a function of the number of carbon atoms in the aliphatic chains. T (°C): ▼ 20, ■ 130, ▲ 155

an ethylene group in an all-trans aliphatic chain. It is evident therefore that in this phase the alkyl chains are interdigitated and normal to the lamellae.

The X-ray diffraction patterns of the smectic phase contain, in the wide-angle region, a diffuse band characteristic of the liquid-like conformation of the alkyl chains and a number of rather sharp reflections indicative of long-range ordering of the ionic species within the smectic layers. In the small-angle region five equidistant and sharp reflections consistent with the lamellar arrangement of the molecules are observed. The smectic periods measured, like the lamellar periods of the crystal phases, increase linearly with the number of carbon atoms in the alkyl chains (Fig. 3) following the equation $d(\text{Å}) = 16.95(23) + 1.25(2)\,n$. The slope of the straight line is equal to that of the higher-temperature range crystalline phase indicating that the alkyl chains are still interdigitated and, although in a disordered conformation, rather stretched. However, the thickness of the polar sublayers is approximately 2.5 Å larger than in the crystalline phases suggesting either a rearrangement of the polar groups inside the layers or changes in the hydrogen-bonding pattern of the polar head groups.

For a better understanding of the arrangement of the polar groups in the mesophase, the surface covered by each molecule in the layers, S, can be calculated utilizing the linear dependence of the smectic periods d on the number of aliphatic carbon atoms. Assuming additivity of the partial volumes of the polar and aliphatic parts of the molecule ($V = V_p + 2n\,V_{CH2}$), the measured slope of the straight line can be taken equal to $2V_{CH2}/S$. From the known volume of one methylene group[9] (V_{CH2} = 29.1 Å^3), the molecular area obtained is 46.5(8) Å^2.

The length of the dinuclear molecular complex estimated using Hyperchem software is about 22 Å, in good agreement with the data reported for the complex of bis(cyclic amidine) with 4-methylbenzoic acid[10]. Apparently, this length is considerably higher than the obtained thickness of the polar sublayer by about 5 Å. This can only be rationalized by assuming that the complex is tilted with respect to the lamellar plane by 39.4° (cos 39.4 = 17/22). On the other hand, assuming that the density of the polar part is equal to the density (1.277 g cm^{-3}) of the bis(cyclic amidine)–methylbenzoic acid complex determined crystallographically[10], the molecular volume of the polar part can be easily approximated (609 Å^3). The cross-sectional area of the complex can be deduced from the known thickness of the polar sublayer (17 Å). The value obtained, 35.8 Å^2, is consistent with the above estimated area covered by two alkyl chains, 46.5 Å^2, if the complex is tilted by 39.6° (cos 39.6 = 35.8/46.5). Both estimations of the tilt angle of the complex are in perfect agreement. It is thus evident that the complex is tilted away from the layer normal allowing the carboxylate groups to be positioned properly along the surface of the lipophilic layer and permitting close packing of the interdigitated alkyl chains (Fig. 4). Summarizing, based on the X-ray analysis and on the optical textures observed, this high-temperature structure can be assigned as that of a smectic H phase[11].

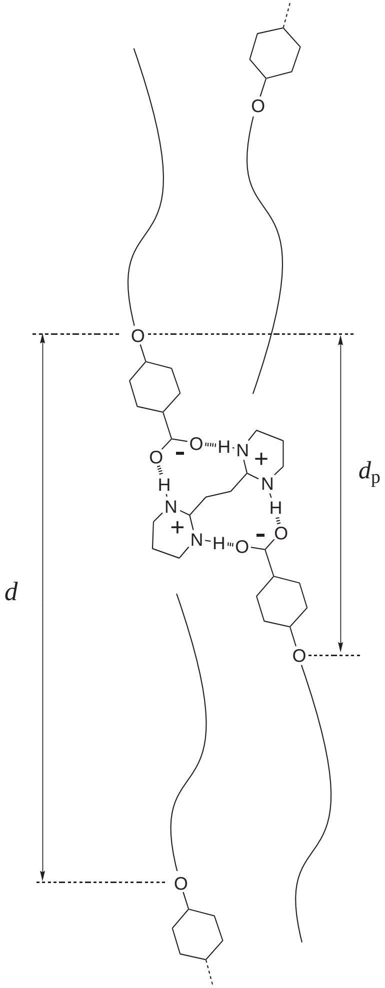


FIG. 4
Schematic view of the proposed molecular arrangement in the ordered smectic phases. The polar core is tilted in order to allow the close packing of the molecular tectons and to ensure positive and negative group alternation minimizing Coulombic repulsions

CONCLUDING REMARKS

Supramolecular networks were formed by a combination of ionic interactions with a dihapto mode of H-bonding between a bisamidinium dication and 4-alkoxybenzoates. At low temperatures, in the crystalline phase, they exhibited lamellar structures while at higher temperatures they were transformed to highly ordered smectic H phases. The strength of the combined intermolecular interactions is sufficient as to maintain the supramolecular architecture even after the melting of the alkyl chains.

This work has been performed within the framework of COST ACTION D11, "Supramolecular Chemistry".

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