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MESOMORPHIC CHARACTER OF SOME LONG-CHAIN 2,4,6-TRICHLORO-1,3,5-TRIAZINE DERIVATIVES SUSCEPTIBLE TO FACILE FUNCTIONALIZATION

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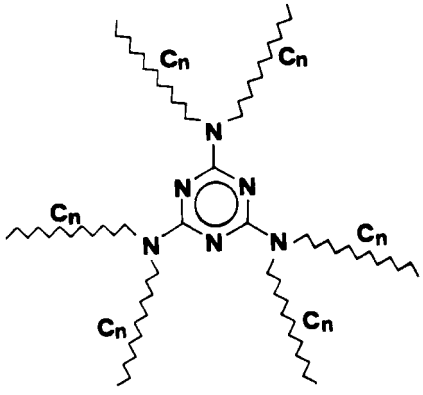
Abstract The interaction of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) with long-chain primary and secondary amines results in the synthesis of disubstituted and trisubstituted derivatives. In this report we investigate the polymorphic and mesomorphic behavior of these compounds and of their hydrochloride salts as well as of the complex resulting by hydrogen bonding interaction of the didodecyl derivative with lauric acid.

INTRODUCTION

In recent years there is a continuing interest in the synthesis of compounds whose thermotropic liquid crystalline character is attributed to their amphiphilicity. The mesomorphic behavior exhibited by amphiphilic molecules is an outcome of the segregation of their hydrophilic and lipophilic sections leading in the formation of smectic[1] and discotic mesophases[2]. Specifically, discotic liquid crystalline phases originate from molecules possessing a distinct disk-like rigid core, which is segregated from the surrounding flexible aliphatic chains. Thus discotic liquid crystals have been prepared with a variety of cores including aromatic[3], macrocyclic[4] or glucopyranose rings[5] and also a metal ion with the interacting moieties of the ligands[6]. The emphasis in modifying discotic mesophases was placed in the use of a suitable core, in a recent paper however the effect of a systematic modification of aliphatic moieties on the mesomorphic properties of the discogens was studied[7].

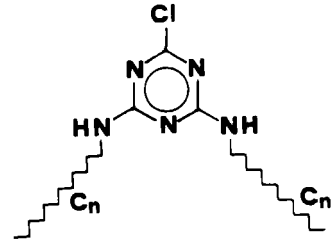
In the present report we investigate, whether the introduction of long aliphatic chains in the triazine moiety (Scheme) may result in the formation of mesophases. In addition the core was protonated with hydrochloric acid in order to enhance its polarity. On the other hand, by interacting N=C-NH group of the core with long-chain organic acids, an accumulation of lipophilic chains is obtained around the enlarged central hydrophilic moiety.

I



n = 12

II



n = 12,16

SCHEME

EXPERIMENTAL

Synthesis of I, IIa and IIb

To 0.01 mole of cyanuric chloride, dissolved in dry methylethylketone, 0.032 of didodecyl amine and 0.033 mole of sodium carbonate were added. The suspension was refluxed for several hours and subsequently the solvent was distilled off and the residue taken in water. The remaining insoluble material was recrystallized from ethyl acetate. Analysis Calcd for I($C_{75}H_{150}N_6$): C, 79.29%; H, 13.31%; N, 7.39%. Found: C, 79.29%; H, 13.49%; N, 7.29%.

IIa and IIb were synthesized in an analogous manner to I except that now an 1:2 molar ratio of cyanuric chloride to primary amine was used. Analysis Calcd for IIa($C_{27}H_{52}N_5Cl$): C, 67.26%; H, 10.87%; N, 14.52%. Found: C, 67.21%; H, 11.01%; N, 14.52%. Analysis Calcd for IIb($C_{35}H_{68}N_5Cl$): C, 70.72%; H, 11.53%; N, 11.78%. Found: C, 70.81%; H, 11.79; N, 11.19%.

Hydrochloride salts of I, IIa and IIb

Hydrochloride salts of I, IIa and IIb were prepared by conducting excess hydrogen chloride in their ethanol dispersion. The salts were now soluble in ethanol and solvent was distilled off. The remaining material was recrystallized from ethyl acetate.

Interaction of IIa with Lauric Acid.

IIa and lauric acid in a molar ratio 1:1 or 1:2 were mixed thoroughly and subsequently shaken in a Vibration Mill MK II for several hours. The mixture was heated at 150 °C for about ten minutes and used for the subsequent experiments.

Methods

DSC studies were performed with a Perkin Elmer DSC-7 coupled with a TAC 7/DX controller at a heating-cooling rate of 10 °C/min. Optical microscopy was performed with a Reichert polarizing microscope equipped with a Linkam THMS 600 hot-stage and a TMS 91 temperature controller. Diffuse reflectance infra-red Fourier transform (DRIFT) spectra were obtained with a Bomem Michelson 100 FT-IR spectrometer at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

The objective of this work was to use triazine moiety as a core for the synthesis of non-hydrolyzable discogens. Among the long-chain primary and secondary amines that were allowed to react with cyanuric chloride only didodecyl amine afforded the trisubstituted derivative (I) under, at least, the experimental conditions employed. This may be attributed to the different mechanisms by which cyanuric chloride reacts with primary and secondary long chain amines. It seems that the nature of the amine affects the rate and the products of the reaction. According to a relevant report dealing with the reactivity of triazine derivatives[8] with simple secondary or primary amines, the elimination of Cl^- is the rate determining step while for sterically hindered primary amines the nucleophilic attack on cyanuric chloride is the rate determining step. Obviously didodecyl amine effectively replaces the chloride affording trisubstituted product while this is not the case with long-chain primary amines.

Optical microscopy and DSC studies showed that symmetrical compound I does not exhibit liquid crystalline character. The accumulation of six long aliphatic chains around a relatively small core does not apparently seem to induce liquid crystallinity. Reaction of I with hydrogen chloride affords the corresponding salt whose DSC traces are shown in Fig. 1. The thermograms of I are typical of a crystalline solid whereas those of the hydrochloride salt resemble the behavior of liquid crystalline materials. In all experiments however substantial supercooling was observed.

Optical microscopy also showed that I is a crystalline material while its salt exhibits on heating a mostly homeomorphic texture which after its complete isotropization it significantly supercools to a texture shown in Fig. 2.

Disubstituted derivatives IIa and IIb were crystalline solids. The behavior of the hydrochloride salt of IIa was drastically different. Thus a non-conventional first heating run was followed by thermograms resembling those of liquid crystalline compounds, Fig. 3. On cooling from 210 °C oil streaks were observed. The DSC trace of the hydrochloride salt of IIb, following its first heating-cooling run, is that of a polymorphic crystalline solid.

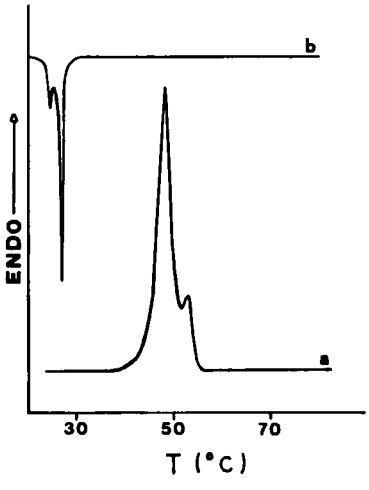


FIGURE 1 DSC traces of I.HCl salt (second heating (a) - cooling (b) run)

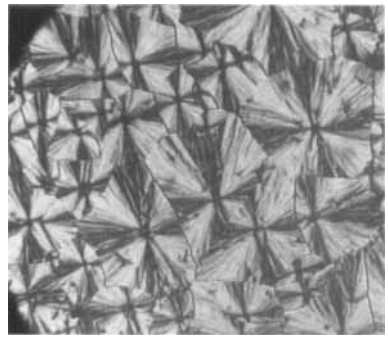


FIGURE 2 Optical texture of I.HCl salt (observed on cooling)

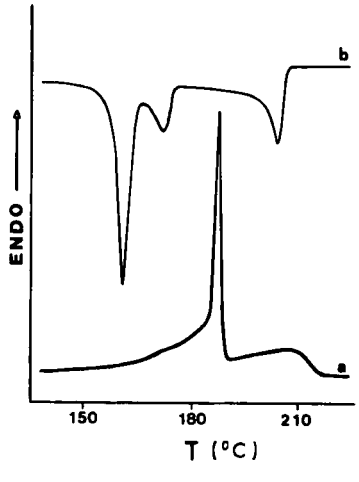


FIGURE 3 DSC trace of IIa.HCl salt (second heating (a) - cooling (b) run).

The transition temperatures observed for these materials and also the enthalpies involved are summarized in Table I.

TABLE I Transition temperatures (in °C) and enthalpies (in parenthesis, kJ/mol) for compounds I, IIa and IIb and their salts (K: Crystalline, M: Mesomorphic, I: Isotropic).

Compound	T, K-K_I	T, K-M	T, K-I	T, M-I
I			49.8 (140.0)	
IIa			153.8 (51.2)	
IIb	60		126.3 (18.5)	
I salt		45.5 (97.6)		52.1 (46.5)
IIa salt		185.4 (17.3)		191.7 (5.3)
IIb salt		75.1 (20.2)		88.8 (51.6)

It may be concluded therefore that the enhancement of the polarity of the core in triazine derivatives may induce the formation of mesomorphic phases. The mesomorphic behavior of disubstituted salt derivative may be attributed to the formation of a molecular structure reminiscent of common surfactants. The difference lies on the head group which in this case is a protonated triazine moiety instead of the simple polar groups of typical surfactants.

In a final endeavor to induce liquid crystallinity in long-chain functionalized triazines, advantage was taken of the existence in the core of the recognizable N=C-NH moiety. This donor-acceptor system can be recognized by the complementary carboxylic acids. As an example, IIa interacted with lauric acid in 1:1 molar ratio through hydrogen bonding, Fig 4. It is rather certain that steric hindrance would inhibit attainment of equilibrium towards the production of the complex and this is the reason that recognition was performed in the isotropic melt under isothermal conditions. In another mode to achieve molecular recognition, cocrystallization was attempted by dissolving the compounds in chloroform and allowing the solvent to evaporate slowly. This later method has not proved effective in inducing the recognition between the molecules as evidenced by DSC and IR spectra.

Following the first run and isothermal heating the product resulting from recognition behaves as a compound in its own merit, not as a mixture of the individual materials and its DSC thermograph is shown in Fig. 5.

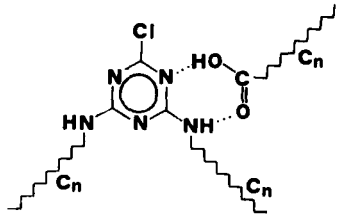


FIGURE 4 Hydrogen bonding interaction of IIa with lauric acid

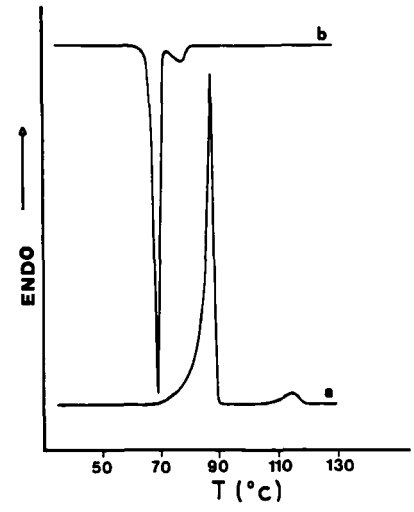


FIGURE 5 Thermograph of hydrogen bonded complex of IIa with lauric acid

The hydrogen bonding of complexes obtained with melt cocrystallization is confirmed by DRIFT spectroscopy. Thus the spectrum of complex after cooling from 150 °C exhibits a broad band centered at 2450 cm^{-1} indicating strong hydrogen bonding of the A-H···B type between the OH and N atom of the aromatic ring[9,10] which has replaced the broad ν(OH) band of the carboxylic group[11] at 2600 - 3000 cm^{-1}. In addition the ν(C=O) stretching mode of the carboxylic dimer that appears at about 1700 cm^{-1} becomes less intense and shifts to 1715 cm^{-1}. On the other hand, the peaks at 1625, 1580 and 1400 cm^{-1} attributed to $COO^{-}\cdots NH_2^{+}$ modes[9a,12] together with a considerable decrease of the intensity of the coupled δ(OH) and ν(C-O) vibration bands[11] at 1420 and 1300 cm^{-1} and finally of the deformation γ(OH) band at 930 cm^{-1} indicate that partial protonation has occurred. The partial protonation is also supported by the lowering of the intensity of the NH deformation band[11] at 1636 cm^{-1}.

It is therefore clear that lauric acid protonates the basic secondary amine group and forms hydrogen bonds with the less basic heterocyclic nitrogen.

CONCLUDING REMARKS

Cyanuric chloride has proved a useful starting compound for the synthesis of a series of compounds which on further interaction with acids afford materials exhibiting mesomorphic textures. Further work is planned on the synthesis of other cyanuric chloride based compounds including characterization by X-ray diffraction.

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