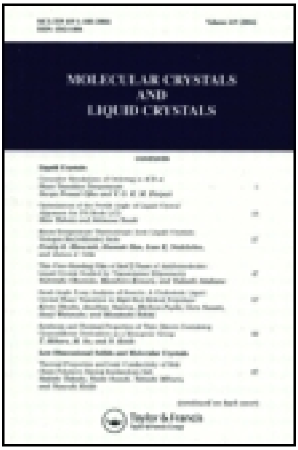

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Hydrogen Bonding and its Role in the Liquid Crystal Formation and Properties

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Hydrogen Bonding and its Role in the Liquid Crystal Formation and Properties

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In this paper the different types of hydrogen bonds are described. The literature, concerning different kinds of mesogenic structures which were built up via intermolecular hydrogen bonds, is discussed. The role of hydrogen bonding in the liquid crystal formation is pointed out and its influence on the thermal and chiral properties of liquid crystals is shown as well.

Keywords: Hydrogen bonding; dimerization; chirality; liquid crystals

INTRODUCTION

In the thirties Linus Pauling underlined that the importance of hydrogen bonding in physiology exceeds that of any other structural property[1]. The most well-known example of hydrogen bonding in the biological world is the interaction of complementary nucleobases stabilizing the double helical structure of DNA.

Hydrogen bonds have the intermediate position between covalent bonds and van-der-Waals interactions. The order of the gap energy of covalent bonds is near 100 kcal/mol, for van-der-Waals interaction this value is near 0.1 kcal/mol, whereas the one of hydrogen bonds ranges between 1 and 10 kcal/mol. This sufficiently weak energy is making very easy the inverse processes under common laboratory conditions. For appearance of H-bond it is necessary to have interaction between two functional groups in the same or different molecules. One of this groups is acting as donor of protons (acidic group), another - as donor of electrons (basic group). The donors of protons are mostly carboxy-, hydroxy-, amino- and amido-groups. The donors of electrons are mostly molecules of oxygen in carbonyl, ethers and hydroxyl groups, nitrogen in amino-group and N-heterocyclic compounds (Fig. 1)

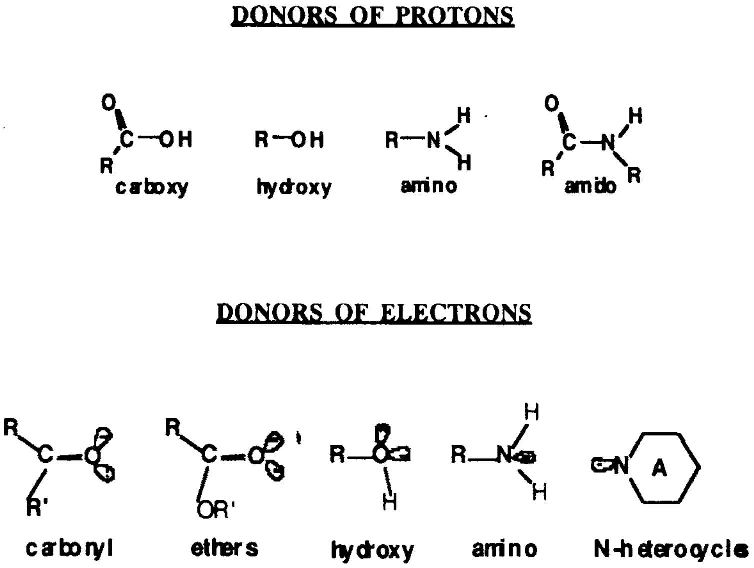


FIGURE 1 Functional groups (donors of protons and donors of electrons) which are forming hydrogen bonds.

The hydrogen bonds are either intermolecular, if the interacting groups belong to different molecules, or intramolecular, when they are in the same molecule. Hydrogen bonds can also play a very important role in the formation of liquid crystalline phases, especially in the field of lyotropic liquid crystals. However, in thermotropic liquid crystals the role of hydrogen bonding has not been greatly appreciated, in particular during the early years of research in this area.

Recently, the hydrogen bonded liquid crystals as well as the hydrogen bonded supramolecular structures have attracted the attention of the scientific community[2-4].

BACKGROUND

The first compounds found to exhibit liquid crystalline behavior due to intermolecular hydrogen bonds were p-n-alkoxybenzoic acids[5-7] . Because of dimerization their molecules are characterized by an appropriately elongated shape and a core rigid enough for the appearance of a mesophase.

In the last decade there were published many papers, dedicated to the preparation of different liquid crystals via hydrogen bonds. We would like to focus the attention only on few of them.

Associates formed from benzoic acid and pyridine derivatives, which were introduced by Kato[2,8-11], are very promising examples.

Such type of complexes are exhibiting the properties, which were not exhibited by either of the individual components. For instance, the liquid crystalline complex , shown on Fig. 2, was formed by the intermolecular interaction of 4-butyloxybenzoic acid (nematic range 147-160 °C) with *trans*-4-

-[(4-metyloxybenzoyl)oxy]-4'-stilbazole (nematic range 165-213°C). It exhibits a smectic phase (range 136-160°C), which was not exhibited either by butyloxybenzoic acid, or by stilbazole.

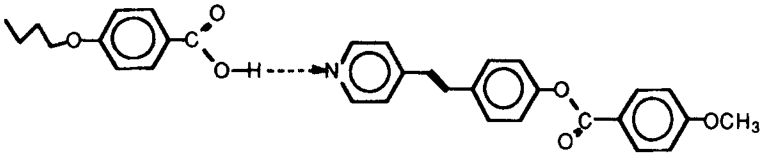


FIGURE 2 Associates formed from benzoic acid and pyridine derivatives.

Very interesting investigation was published by Kresse with coworkers[12]. They synthesized the benzoate's (1) containing different substituents and compared their mesophase behavior with that of the corresponding associates (2), formed by hydrogen bonding (Fig.3).

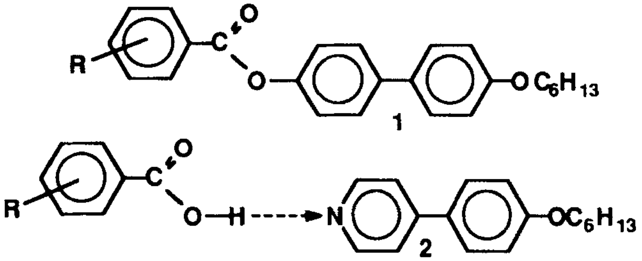


FIGURE 3 Benzoate's (1) with covalent bonds; (2) - corresponding associates, formed by hydrogen bonding.

Almost in all cases the melting point is lower for compounds (**2**) as well as the clearing point (Table I and Table II).

TABLE 1. Phase behavior of the substituted benzoic esters (**1**). Dot and dashes indicate existing and nonexisting phases, respectively.

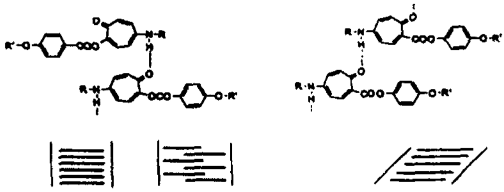
1	R	C		S_E		S_C		S_A		N		I
a	p-$C_7H_{15}NH$	.	171	--		-		--		.	203	.
b	p-$C_6H_{13}O$	.	119	--		(.	115)	--		.	184	.
c	H	.	122	--		-		--		.	135	.
d	p-$ClCH_2$	.	145	--		-		.	202	--		--
e	m-F	.	134	.	135	-		.	149	--		.
f	m-NO_2	.	122	--		-		.	133	.	135	.

TABLE II. Phase behavior of the hydrogen-bonded associates (**2**).

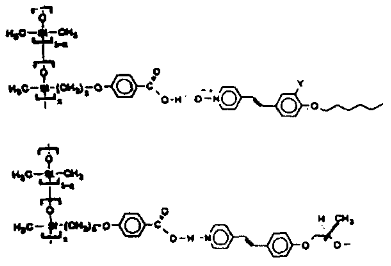
2	R	C		S_C		S_A		N		I
a	p-$C_7H_{15}NH$	.	125	--		--		(.	109)	.
b	p-$C_6H_{13}O$	.	83	(.	74)	.	130	.	134.5	.
c	H	.	63	--		.	103	--		.
d	p-$ClCH_2$	.	234	--		(.	172)			--
e	m-F	.	51	--		.	102.5	-		.
f	m-NO_2	.	61	--		.	73	-		.

The investigated system exhibits a maximum of the stability of the liquid crystalline state for weakly electron-withdrawing substituents. The authors conclude that, by systematically varying the acidity, it should be possible to find optimal mixing partners for any pyridine derivative. Thus, this method provides a simple way to model covalent liquid crystalline compounds by hydrogen-bonded molecules.

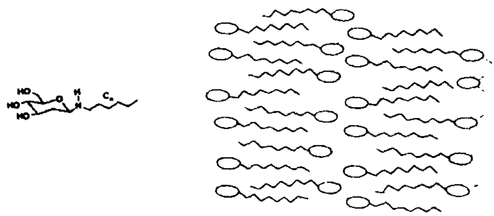
A detailed review was published by Paleos and Tsiourvas[2]. In this review the authors described not only hydrogen-bonded liquid crystals from rigid-rod monomeric molecules, but also hydrogen-bonded liquid crystals formed from polymeric mesogens as well as from amphiphilic carbohydrates (Fig.4).



Hydrogen-bonded liquid crystals from rigid-rod monomeric molecules



Hydrogen-bonded liquid crystals formed from polymeric mesogens



Hydrogen-bonded liquid crystals formed from amphiphilic carbohydrates

FIGURE 4 Thermotropic liquid crystals formed by intermolecular hydrogen bonding interactions.

The intramolecular hydrogen bonds leads to the thermal stabilization of the mesophase. As a typical example, it is possible to quote the liquid crystalline enaminoketones[13], recently synthesized, and the well known o-hydroxy-benzylidene-anilines (Fig.5).

It was shown with help of IR-spectroscopy that hydrogen bonds in o-hydroxy-benzylidene-anilines are intramolecular[14].

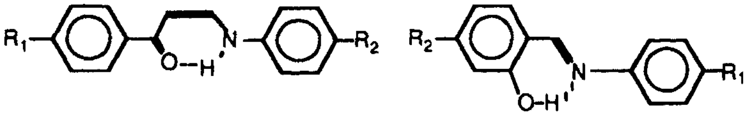


FIGURE 5 Intramolecular hydrogen bonds: enaminoketone and o-hydroxy-benzylidene-anyline.

Interesting results were published by Soto Bustamante *et al.*[15]. These authors found the evidence of antiferroelectric properties after application of DC electric field to the mixtures of both achiral polymer and monomer containing the o-hydroxy-benzylideneamino groups (Fig.6).

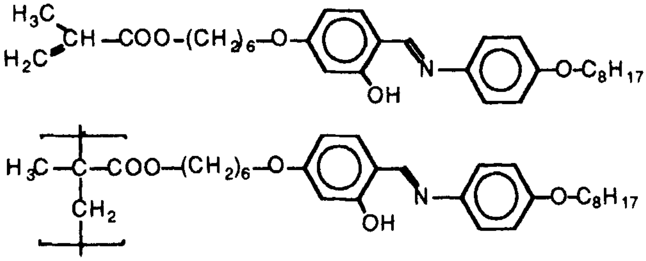


FIGURE 6 Antiferroelectric properties in the mixtures of both achiral polymer and monomer (15-75% of monomer)

The individual substances do not exhibit such a behavior. The mixtures are exhibiting antiferroelectric properties only in the case, when the variation of monomer percentage is from 15 to 75 %. It was given the explanation that at certain conditions it occurs the transition from intramolecular- into intermolecular hydrogen bonds. This phenomenon is very promising for practical applications.

The field of our interest is the set of carboxylic acids. The formation of liquid crystalline phases through dimerization of certain carboxylic acids can be considered as the starting point for the formation of a mesophase by hydrogen bonding between similar- or dissimilar molecules. It is necessary to mention that dimers can be of two types: - closed (with two hydrogen bonds), and open - with only one hydrogen bond.

Among liquid crystals formed by similar carboxylic acids the most known are alkoxybenzoic acids: HOBA (4-heptyloxybenzoic acid), OOBA (4-octyloxybenzoic acid), and NOBA (4-nonyloxybenzoic acid). There are many articles, dedicated to these acids and especially to the investigation of the dimerization processes[16-18] and the interaction of the acids with the surface[19-22]. The investigations of dimerization processes mostly were made by far IR or IR technique[16-18, 23].

For what is concerning liquid crystals formed via hydrogen bonds by dissimilar molecules, Kresse demonstrated by dielectric investigations[24] the existence of mixed dimers formed from 4-substituted benzoic acids. It was also shown the appearance of mixed dimers for 4-*trans*-butyl- and 4-*trans*-hexylcylohexanecarboxylic acids[25] (Fig.7).

In our work we had as tasks:

1) to investigate the possibility of the formation of mixed dimers between *cis*- and *trans*- isomer of 4-alkylcyclohexanecarboxylic acids;

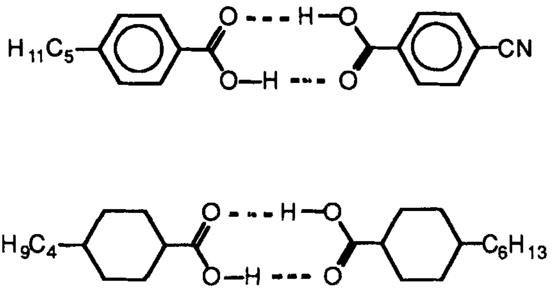


FIGURE 7 Dimers, formed by dissimilar molecules.

2) to have information about the dependence of the dimerisation process on the temperature change and its speed.

The substituents in cyclohexane ring can have axial (a) or equatorial (e) position[26]. The last one is energetically more favored. *trans*-1,4-Disubstituted cyclohexanes can exist as e,e- or a,a- conformers, and *cis*-isomers can be either e,a- or a,e-ones (see Fig. 8).

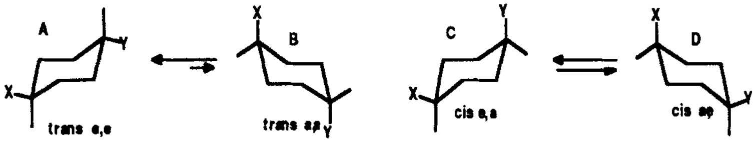


FIGURE 8 Conformational equilibria for 1,4-disubstituted cyclohexanes.

The *trans*-e,e structure is thermodynamically more stable than *cis*-e,a or -a,e and much more stable than *trans*-a,a because it has no any shielded conformation.

So, the equilibrium between the A,B and C,D forms, which appears due to inversion of the cycle will be shifted to the form A, and in the second pair - to the conformer which has in e-position more volumetric substituent. Note, that it is impossible to make conversion like A ⇔ C and B ⇔ D only through inversion of the cycle. Hence for 4-butyl-cyclohexanecarboxylic acids in both cases (*trans*- and *cis*-) the carboxylic group will be in the e-position.

EXPERIMENT

Several mixtures of 4-butylcyclohexanecarboxylic acid with different *cis-trans*-ratio were prepared. The mixtures were obtained, following the common procedure: the substance containing pure *trans*-isomer (melting point C → N = 37.1 °C; clearing point N → I = 91.6 °C) was mixed with defined amount of the mixture, containing *cis*- and *trans*-isomer with the ratio *cis*/*trans* = 48.9/51.1 (liquid at room temperature), in order to have the requested concentration of *cis*-isomer in the mixture. The concentration of *cis*- and *trans*-isomer was controlled with help of GLC (Gas Liquid Chromatography). After mixing, the samples where heated till reaching the isotropic liquid condition, and immediately cooled to room temperature. There were made samples, which had: 0, 2, 4, 5, 6, 8, 10, 12 and 20 % of *cis*-isomer.

In the experiment, conventional sandwich cells were used. The cells were inserted in a Mettler FP-52 hot stage. The textures were investigated with polarizing microscope (Zeiss).

RESULTS AND DISCUSSION

The results of the microscopy observations are shown in the Tables III and IV. With a small percentage of *cis*-isomer (to 5%), there was only the decreasing of the melting and clearing points, what is well known. When the presence of *cis*-isomer was 5% and higher, the mixtures behaved as multiphase materials, and the separation of phases was observed.

TABLE III Transition temperatures on heating of the mixtures, containing 0, 2 and 4% of *cis*-isomer

Percentage of *cis*-isomer (%)	Melting point (°C) (C → N)	Clearing point (°C) (N → I)
0	37.1	91.6
2	35.2-36.1	85.1-86.9
4	31.2-34.1	79.9-81.0

As a consequence, the transition temperatures were spread over large ranges (melting- and clearing interval, respectively).

A big hysteresis between temperatures on heating and on cooling was present.

TABLE IV Transition temperature intervals on heating of the mixtures containing 5, 6, 8, 10, 12 and 20% of *cis*-isomer

Percentage of *cis*-isomer (%)	Melting interval (C→N) (°C)	Clearing interval (N→I) (°C)
5*	29.0-32.6	74.5-78.1
6*	23.0-27.9	67.5-71.1
8*	20.0-22.1	56.8-61.6
10	19.2-21.7	50.3-57.1
12	17.6-20.0	38.5-46.8
20**	12.0-15.3	18.9-20.0

* for the sample at room temperature there is a mixture of crystals + isotropic liquid

** isotropic liquid is also present in the nematic range

The most interesting behavior was exhibited by mixtures with 8-12% of *cis*-isomer. On cooling from isotropic phase with rate no more than 1°C/min within the "clearing interval" it was observed the coexistence of stable nematic domains with isotropic liquid. The concentration of this domains was strictly dependent on the temperature.

We also tried to investigate the mixture, containing 12% of *cis*-isomer with help of NMR[26], with the aim of obtaining the prove of the existence of open dimers and of mixed *cis-trans* dimers. We got evidence of the presence of open dimers of *trans*-isomer, but up to now we didn't succeed to have any information about mixed dimers.

The proton-NMR investigation of pure *trans*-4-butylcyclohexane carboxylic acid at various temperatures, approaching on cooling the clearing point, showed[27], as expected, the increasing of the amount of closed dimers. Just below the clearing point, in a range of a couple degrees only, the presence of open dimers ($\nu_{2'}$) was detected. On the contrary, down into the nematic phase, only closed dimers (ν_1) were present. One degree below the clearing point it appears the small peak ($\nu_{2''}$), which probably is related to the formation of oligomers (Fig. 9). The existence of oligomers was proved by Volod'ko and Posledovich for the homologous series of p-alkoxybenzoic acids[28]. The presence of oligomeric molecules can explain the chirality which characterizes the macroscopic domain texture of some carboxylic acids having in the monomeric molecule no any chiral group. We found the chiral domains in *trans*-4-hexylcyclohexanecarboxylic acid[29] (see Fig. 10) and also in 4'-alkyl- and alkyloxy-biphenylcarboxylic acids[30].

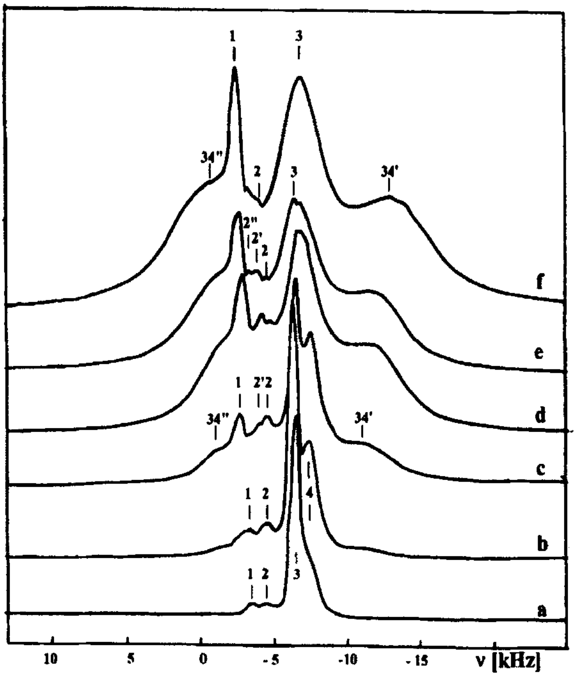


FIGURE 9 Proton-NMR data from *trans*-4-butylcyclohexane carboxylic acid passing on cooling the clearing point (T=368.3K - 368.2K): a) 372K, b) 370K, c) 369K d) 368K, e) 367K, f) 362K. Indicating numbers (1, 2, 2', etc.) refer to peak frequencies (ν_1, ν_2, $\nu_{2'}$, etc., respectively)

The chirality was found in all cases mostly on cooling by means of optical microscopy, and the appearance of chiral domains was strictly dependent on the speed of cooling.

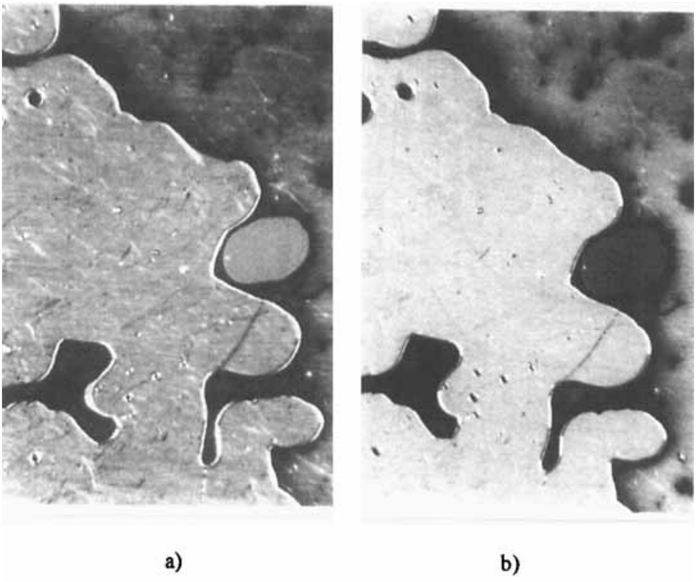


FIGURE 10 *trans*-4-Hexylcyclohexanecarboxylic acid in a 12μm-thick cell under crossed polarizers, on cooling from the isotropic- into the nematic phase (-0.2°C/min), at ≈1°C below the clearing point. The yellow region in the left and in the centre part of the picture - a), shaded yellow; b), bright yellow - is the main area with unidirectional planar alignment; above at the right, the dark yellow region is relevant to the part, where the nucleation of the nematic phase started from one of the two cell surfaces. The blue domain - a), bright blue; b), dark blue - is a spontaneous twisted chiral domain. In a) the sample is rotated by 5° with respect to b). See Color Plate II at the back of this issue.

We would like to underline, that it is enough to have a trimer in order to provide microscopic chirality either right or left handed (Fig.11). Such chiral oligomers can play the role of chiral dopants.

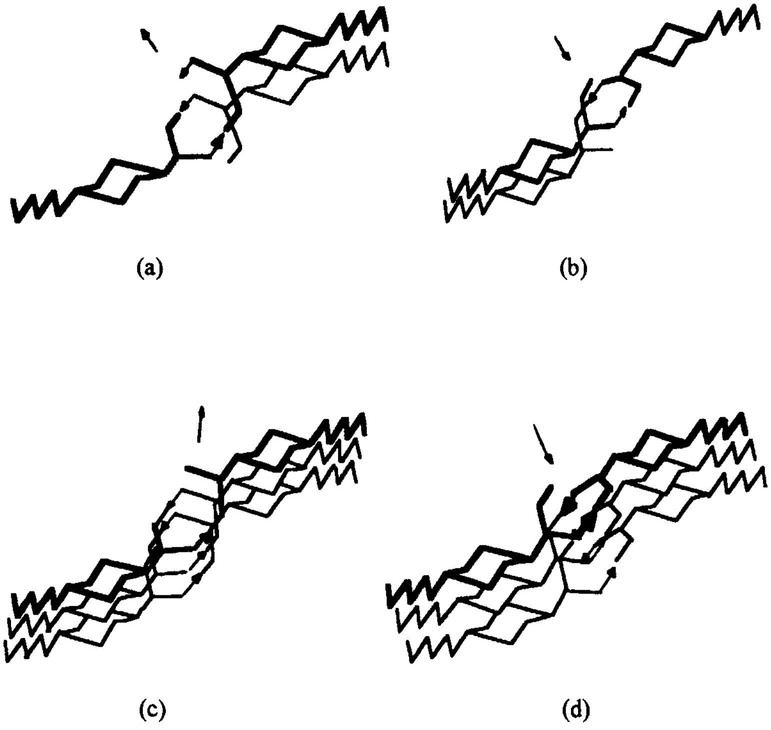


FIGURE 11 The formation of oligomers. It is enough a trimer to provide microscopic chirality either left- or right-handed -(a), (b).
Also tetramers and other oligomers can be present, for instance hexamers -(c), (d).

We think that this explanation has right to exist, because also in biological cells the achiral molecules are forming chiral polymeric chains via hydrogen bonding[3]. In other context, spontaneous twisted structures were found in the nematic phase of mesogens exhibiting smectic phase: such textures were explained as due to short range smectic ordering, providing cybotactic clusters[31,32].

CONCLUSION

The hydrogen bonding in mesogenic systems is being intensively investigated: its interest from both fundamental and applied point of view renders the hydrogen bonding one of the major subjects in the field of mesogenic compounds.

Acknowledgments

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