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BILAYER PACKING OF THE NEMATOGEN MOLECULES IN THE INDUCED SMECTIC A PHASE

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Abstract A dynamic intermolecular associates in structure of the smectic A phase induced by mixing of two nematogens 4-pentyloxy-4"-cyanobiphenyl (1, high polar), and hexyloxyphenylic ester of nonylbenzoic acid (2, low polar) have been discovered with aid of ^{13}C-NMR spectroscopy. They are connected by means of dipole-dipole interaction between CO- and CN-groups, and dispersion forces between complementary packed aryl fragments. An analysis of the ^{13}C chemical shifts and of the ^{13}C spin-lattice relaxation times, T_1, confirms the bilayer model of the molecular packing for induced SmA phase. By formation of such associates the carbonyl group of 2 continually exchanges a partner because of lateral diffusion. Moreover the aromatic ring of the COOAr group is situated normally to the layer plane between two biphenyl aromatic rings of compound 1. This fact facilitates the co-operative rotation of the aromatic rings of interacting molecules within bilayer.

INTRODUCTION

One of the most striking example of a role of the intermolecular interactions by formation of mesophases is a rise of induced phase state by mixing of two or more mesogens [1, 2]. The induced enantiotropic smectic A phases (SmA) arise usually in the mixtures of two amphyphilic nematogens. The various correlations between a thickness of the interlayer distance, d, and an average length of a mesogen molecule, l, may be observed for such a phase. In dependence on the molecular structure of components and on the mixture composition a formation of the following mesophases is possible: the monolayer SmA (S_A, $d \le l$), partially bilayer SmA (S_{Al}, $l < d < 2l$), and bilayer SmA (S_{A2}, d = 2l). Values of the interlayer distances may be changed both continuously and suddenly [2].

The main goal of the present paper is a development of the model ideas of the supramolecular organization for the induced bilayer SmA phases. The two component system from 4-pentyloxy-4"-cyanobiphenyl (1, high polar) and hexyloxyphenylic ester of nonylbenzoic acid (2, low polar) was the subject of an investigation. The distinctive feature of such a system is the stable existence of the SmA phase within a wide range of temperatures and compositions on the phase chart.

The same systems from related compounds were described earlier in the paper [3]. Using ^1H-, D-NMR spectroscopy, and theoretical models [4-6] it has been shown that these systems might be determined as induced S_{A1}-phase with d = 1.4l.

RESULTS AND DISCUSSION

A study of a mixture of compounds 1 and 2 by dint of the polythermal polarization microscopy showed that such a mixture had a pronounced tendency to super-cooling by the liquid crystal => crystal transition. This one indicates a rise of the molecular mobility in a mixture compared with individual compounds. At equimolar compositions a mixture did not crystallize during a few hours in the liquid nitrogen.

Figure 1a shows the phase chart obtained by heating of samples from the crystal state. The wide regions of the both crystal and mesophase coexistence are well seen. The crystal => liquid crystal transition is accompanied by a solution of crystals in the formed mesophase. Figure 1b shows the phase chart obtained by cooling of samples from the isotropic state. By analysis of these charts three peculiarities have been revealed. Firstly, by cooling the temperature-composition region of the SmA-phase existence becomes wider than by heating. Secondly, the temperature of a transition from mesophase to the isotropic state by the equimolar composition of components rises in comparison with the same temperature for individual nematogens. This fact allows to assume an existence of the equimolar associates in a two-component system.

The third peculiarity is the presence of the well identified SmA-phase at concentrations of compounds 1 in 2 of 1.5-2 %w. It means an exchange of molecular packing for the low polar component at relationship of one molecule of 1 to 50 molecules of 2. This fact is not due to an explanation of the intermolecular associates' stability. Therefore it is correct to suppose the lability of these associates and the rather high frequency of the partner's change within the smectic layer.

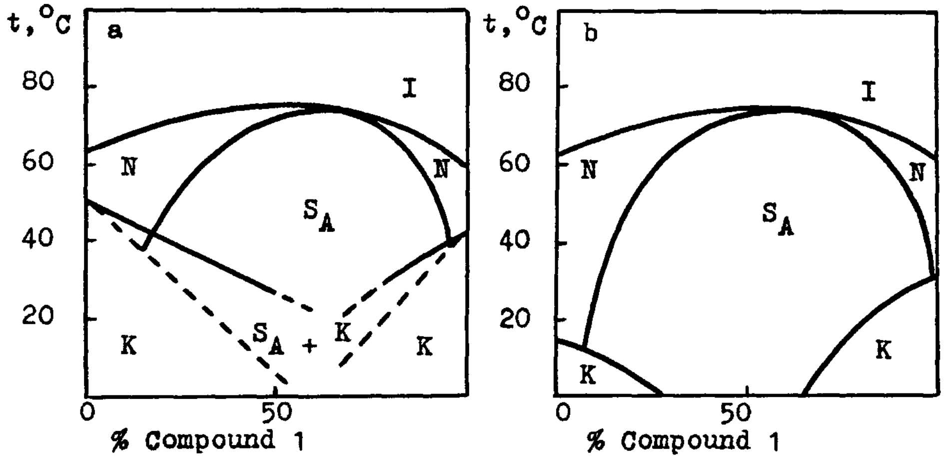


FIGURE 1 The phase charts for a mixture of 4-pentyloxy-4"-cyanobiphenyl (1) and hexyloxyphenylic ester of nonylbenzoic acid (2) obtained by heating of system from the crystal state (a), and by cooling of system from the isotropic state (b). Designations: I - isotropic, N - nematic, S_A - smectic, C - crystal states.

The data about a character of molecular packing in SmA mesophase and molecular mobility have been obtained using an analysis of the chemical shifts in ^{13}C-NMR spectra and the spin-lattice relaxation times, T_1, of ^{13}C nuclei of mesogen molecules. For that purpose the spectra of compounds 1, 2 and their mixture of 1.3:1 (mole/mole) at 333 K have been obtained.

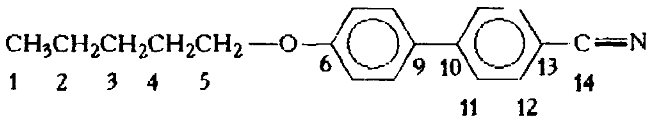
The values of the ^{13}C chemical shifts of signals in spectra of pure compounds and their mixture have been given in Table 1. An assignment of signals in spectra was carried out using the literature data [7] and the calculations by Lindeman and Adams [8].

TABLE 1 ^{13}C-NMR chemical shifts (relative to TMS), δ, ppm, and spin-lattice relaxation times, NT$_1$*, s, for 4-pentyloxy-4"-cyano-biphenyl (1), hexyloxyphenylic ester of nonyl-benzoic acid (2), and their mixture at 333 K.

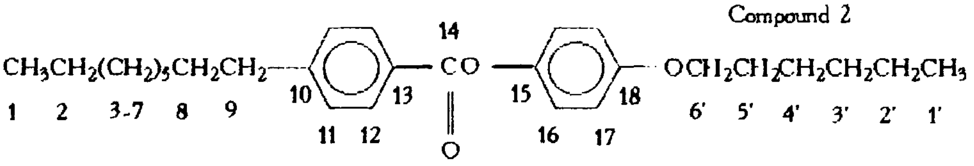
Compound 1					Compound 2				
Carbon	Pure		Molar mixture of 1:2 = 1.3:1		Carbon	Pure		Molar mixture of 1:2 = 1.3:1	
	δ,ppm	T$_1$, s	δ,ppm	T$_1$, s		δ,ppm	T$_1$, s	δ,ppm	T$_1$, s
1	14.12	3.71	14.18	3.94	1,1'	14.28	3.49	14.18	3.94
2	29.37	0.56	29.44	0.64	2,2'	23.01	1.37	22.82	1.78
3	28.41	1.05	28.49	1.22	3-7	29.91	0.55	29.84	0.68
4	22.77	1.40	22.82	1.78	8	31.28	0.44	31.12	0.48
5	68.43	0.38	68.39	0.40	9	36.38	0.30	36.31	0.31
6	160.18	2.48	160.17	2.77	3'	32.40	1.05	32.28	1.33
7	115.39	0.38	115.39	0.48	4'	26.16	0.76	26.06	0.88
8	126.71	0.42	126.73	0.53	5'	32.17	0.96	32.08	1.14
9	130.70	2.28	130.85	2.61	6'	68.58	0.38	68.71	0.40
10	144.58	2.11	144.62	2.56	10	145.08	2.30	144.96	2.66
11	128.18	0.38	128.19	0.46	11	128.58	0.35	128.60	0.41
12	132.60	0.42	132.48	0.52	12	130.34	0.35	130.26	0.40
13	110.38	2.07	110.50	2.47	13	127.91	2.29	127.72	1.88
14	118.88	0.61	118.63	0.71	14	164.55	3.52	164.89	4.99
					15	148.74	1.61	148.94	1.94
					16	122.55	0.44	122.54	0.50
					17	115.04	0.42	115.11	0.49
					18	157.04	2.50	157.03	2.53

* N is the protonation degree of a carbon atom.

Compound 1



Compound 2



The selective alterations of the ^{13}C chemical shifts observed by transition from nematic phase of the pure compounds 1 and 2 to the SmA mesophase indicate a formation of their intermolecular associates. The considerable shielding of the CN-groups' carbon nuclei and C12 of the biphenyl fragment, and deshielding of the CO-group and the nearest to it C13 and C15 nuclei prove the stabilization of such associates during the dipole-dipole interaction between nitric group of the compound 1 and carbonyl group of the compound 2. As far as the signals from CO- and CN-groups in the ^{13}C-NMR spectrum of the SmA phase remain as singlets, one can conclude, that associates are dynamic and have a high frequency of the partner exchange. On the contrary, in case of low in the NMR time scale and reversed formation and destruction of associates it should be expected the separate signals from free and associated molecules by a distinction of the molar compositions of compounds 1 and 2.

The opposite signs of the ^{13}C shielding alteration for amyl and hexyl chains of the compounds 1 and 2 testify to the dispersion intermolecular interaction of these fragments. The dispersion strengths exercise the orientating influence on the nematic molecules, promoting an approach of polar groups and their interaction. In this way a model of the intermolecular associate may be represented as a layer of regulated molecules the main axes of which are oriented normally to the common place where their dipole-dipole interaction occurs. The relative fixation of a spatial situation of nematic molecules having CO- and CN-groups leads to formation of the SmA layers.

The most substantiated hypothetical model of molecular packing in the induced smectic phase was described in the paper [9]. The showed on Figure 2 molecular orientation within the framework of this model is more likely for the mixture having the equimolar component composition. By such an orientation the electropositive end of a molecular dipole for one molecule can interact with the electronegative end for another. By interaction an alkyl chain of the more long molecule in one layer must get into the cavity formed by the short molecule situated in the neighbouring layer. The such layers can glide easy relatively one another as in a soap. The above mentioned analysis of the chemical shifts for ^{13}C nuclei in the spectra of nematics and induced SmA phase confirms the described principal model.

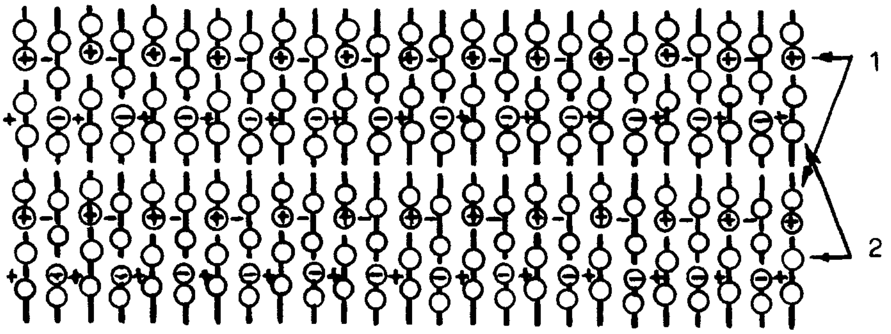


FIGURE 2 Bilayer molecular packing in the induced SmA phase: 1 - 4-pentyloxy-4"-cyanobiphenyl; 2 - hexyloxyphenylic ester of nonylbenzoic acid.

The spin-lattice relaxation times for ^{13}C nuclei have been measured for an appreciation of mobility for the nematogenic molecules in the induced SmA structure. The T_1 values for the all ^{13}C nuclei increase by transition from the nematic phases for the compounds 1 and 2 to SmA phase at 333 K (Table 1). This result seems a little strange, but it might be explained nevertheless easily: the lateral diffusion rate for molecules in SmA phase is essentially higher than in nematic phase. The molecular packing regulation in layers causes the co-operative lateral motions of molecules similar to discovered in the bilayer structures of the phospholipid membranes [10]. The such co-operative lateral motions in layers would prompt the similar increase of T_1-values. However, the ratios of the spin-lattice relaxation times for ^{13}C nuclei of the several fragments of molecules 1 and 2 by transition from nematic phase to SmA phase increase selectively as it is seen from Table 1.

A selectivity of T_1's alteration may be explained of the two reasons [11]. Firstly, the segmental mobility of molecules is determined by a structure of the formed associates. Secondly, a regions of the co-operative molecular rotation may exist in the associate itself.

Really, the most increase of the segmental mobility by transition from nematic mesophase to SmA is observed for carbonyl (at 1.42 times) and methylene fragments C2-C7, C2'-C3' (at 1.23-1.30 times) of compound 2, and also for C4 and protonated carbon atoms of biphenyl fragment (at 1.24-1.27 times) of compound 1. Moreover the segmental mobility of the terminal methyl groups and α-methylen fragments respect to the ester oxygen atom and to the phenyl ring does not change. A mobility of the other fragments increases only a few.

As it can be seen from Table 1 the segmental mobility of the protonated carbon atoms in aromatic rings for the both mesogens is low (T_1 = 0.35-0.44 s). It may be explained during the steric hindrance to the translational and rotatory movement of neighbouring molecules by their compact packing.

The considered exchanges of the segmental mobility may be understood on an assumption that by induction of the SmA mesophase

1) carbonyl group of the compound 2 is forced regular to change a partner in the intermolecular associate because of the intensive lateral diffusion,
2) above mentioned parts of the alkyl chains by their lamellar packing form regions having a low local viscosity,
3) aromatic ring of COOAr is situated in the structure of bilayer SmA phase practically between two aromatic rings of the biphenyl. This one facilitates the co-operative rotation of aromatic rings for interacting molecules.

Hence a comparison of results for the segmental mobility of nematic and SmA mesophases corroborates also the bilayer model of molecular packing for the induced SmA mesophase shown on the Figure 2.

EXPERIMENTAL

$^{13}C\{^1H\}$ NMR spectra were obtained in the Fourier-transform mode with a strobe-mode decoupling of the spin-spin interaction with protons using a Bruker AM-250 spectrometer at a working frequency of 62.896 MHz. The 90°-pulse width was 16 μs, the acquisition time, 1.05 s, number of scans,

400. Stabilization was carried out on deuterium nuclei of etylenglycol-d_6. The temperature in the spectrometer probehead was preset and maintained constant with an accuracy of ±0.5 K.

The samples have been put into the 5-mm tube which was fixed coaxially inside of the 10-mm tube. Ethylenglycol-d_6 used as an external reference has been situated in the clearance between tubes. Chemical shifts were recalculated to the TMS-scale with an appreciation of the difference of magnetic susceptibilities for both a reference and a sample having an absolute error of ±0.01 ppm.

Measurements of spin-lattice relaxation times, T_1, of ^{13}C nuclei was conducted by the inversion-recovery method using the pulse sequence $T-180^o-\tau-90^o$ [11]. The relative error did not exceed 5%.

By use of the polythermal polarization microscopy the temperature was determined with error of ±0.5°, and changed with a velocity of 0.1-0.2 deg/min. An identification of mesophases was carried out using the methods described in monograph [12].

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