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Variability of the Smectic a Layer Spacing and Dielectric Properties in the Homologous Series of 4-Isothiocyanatophenyl 4-(Trans-4-Alkylcyclohexyl) Benzoates

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VARIABILITY OF THE SMECTIC A LAYER SPACING AND DIELECTRIC PROPERTIES IN THE HOMOLOGOUS SERIES OF 4-ISOTHIOCYANATOPHENYL 4- (TRANS-4-ALKYLCYCLOHEXYL) BENZOATES

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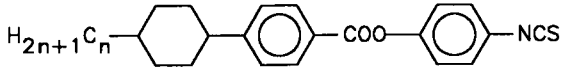
Abstract The homologous series of 4-isothiocyanatophenyl 4-(trans-4-alkylcyclohexyl)benzoates (with n-alkyl chain from ethyl to dodecyl) were synthesized and their phase transition temperatures and enthalpies, smectic layer spacing and dielectric permittivity were measured. It was observed that the smectic A_1 layer spacing is expanding from $d/l \sim 1$ to $d/l \sim 1.1$ when the alkyl chain increases from butyl to dodecyl. It was proposed to term the smectic A_1 with $d/l > 1$ as the enhanced smectic A_1 (A_{1e}).

INTRODUCTION

The compounds of the formula:



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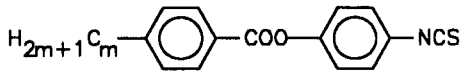
have been investigated for some years mainly as the mixture components giving systems with an abnormal behavior of the smectic A phase stability.[1-4] These compounds seemed to be the classical monolayer smectic A with molecules randomly distributed

up and down within the layers.[5] Assuming that this distribution is valid for all members of the homologous series 1, it is difficult to explain some of the experimental results. It was observed that the smectic A phase of compound 1, n=10, is not miscible with the smectic A_1 phase of the compounds 2 or 3, or 4 (a nematic gap appears)



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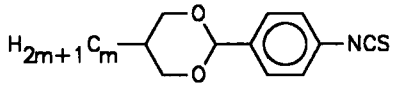

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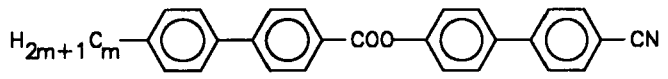

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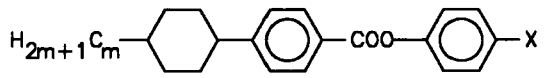

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or its stability in these mixtures is depressed when m<8.[3,4] On the other hand, this phase is miscible with the smectic A phase of compounds 4 for m>7, when they exist as the smectic A_d. The same behaviour but with stronger induction of the smectic A phase is observed for compound 1, n=12 (see Figure 1). These compounds are also miscible with the classical smectic A_d (for example with the A phase of compounds 5) wherein X= -CN, $-NO_2$ and -CHO.

To know better the structure of the smectic layers of compounds 1 we have investigated members of homologous series 1 from n=4 to n=12 by X-ray and dielectric methods.

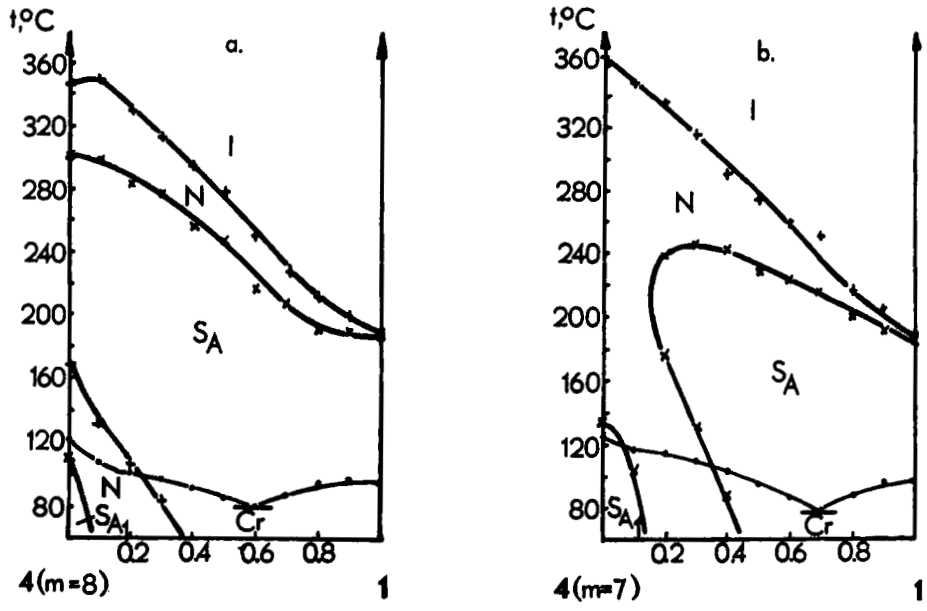


FIGURE 1 Phase diagrams for the mixtures of compound 1, n=12, and compound 4, m=8 (full miscibility of smectic A phases)-(a) and compound 4, m=7, (a nematic gap and a nematic reentrant phase appears)-(b)

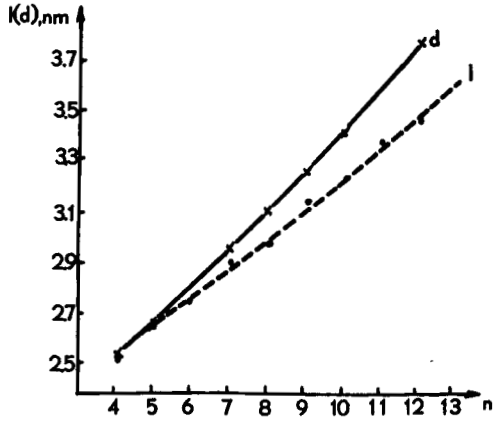


FIGURE 2 The comparison of the experimental values of the layer spacing (d) (continous line) and the calculated lenght of molecules (l) in the most stretched all-trans configuration (dashed lines) in the homologous series of compounds 1.

EXPERIMENTAL PART

The synthesis of esters 1 was carried out according to the method described previously.[6] The smectic layer spacings were calculated from the X-ray patterns of freestanding film samples,[7] and the dielectric measurements were carried out with the Wayne-Kerr B330 bridge at 1.5 kHz. The condenser used was described previously in Ref. 8.

RESULTS AND DISCUSSION

In Table I we present the values of the phase transition temperatures and enthalpies, the experimental data of the smectic layer spacing (d) (at 100°C) and the calculated length of molecules (l) for the most stretched all trans-configuration of the compounds 1. The smectic A phase is observed for the compounds with $n \geq 4$ and its thermal stability strongly increases with increasing n, so for $n=12$ the nematic phase exists only in the narrow temperature range. The layer spacing is enhancing when the alkyl length is increasing. The ratio d/l changes from about 1.0 to 1.09 in the homologous series 1, when n changes from 4 to 12. The deviation in the dependence of d(n) and l(n) is presented in Figure 2. The smectic layer spacings are also expending with increasing temperatures (Table II). Therefore the ratio d/l at the temperatures of the same distance from the S_A-N phase transition should be a little bit higher than at the temperature 100°C.

The observed enhancement of the smectic layer spacing with increasing the alkyl chain lenght suggests that the internal structure of the smectic layers changes and this happens in a continuous way. The accuracy of the molecular length calculations is about 0.1 nm, what is much smaller then the difference d-l observed for large n. Our results are in a good agreement with those obtained by Gramsbergen and de Jeu.[5] Taking into account disordering in the tilt of the molecule and the effect of conformational disordering of the terminal chains which involve shortening the smectic layer,[9] the observed relation $d/l > 1$ for long alkyls is beyond doubt. We suppose that the enhancement of the smectic layers is involved by the molecular dimerization.

TABLE I Temperatures (°C) (upper line) and enthalpies (kcal/mol) (lower line) of phase transitions, smectic layer spacing d (nm) and length of molecules l (nm) in the most stretched all trans-configuration in the homologous series of the compounds of the formula 1; μ is calculated dipole moment of the molecule (in D), and α is the angle between long molecular axis and the terminal NCS group(°).

n	Cr_1	Cr	S_A	N	I	l	d	d/l	μ	α
2		• 143 7.70		• 220 0.19	•					
4		• 109 6.20	• 124.5 0	• 239 0.22	•	2.50	2.52	1.008	4.61	8.7
5	• 66.5 0.19	• 117 5.30	• 129 0	• 235 0.30	•	2.66	2.65	0.996	4.51	9.6
6	• 48.3 3.01	• 104 5.94	• 146.5 0.05	• 225 0.48	•	2.74	2.81	1.026	4.61	7.7
7		• 109.5 6.84	• 155.5 0.03	• 222 0.30	•	2.89 2.96	2.95 2.98	1.021 1.006+	4.57	7.1
8	• 67.3 4.05	• 99 5.70	• 170.5 0.04	• 214 0.26	•	2.79	3.10	1.043	4.55	6.4
9		• 100.5 8.60	• 177.5 0.03	• 211 0.42	•	3.13	3.25	1.038	4.57	5.7
10	• 84.0 3.70	• 95.5 7.74	• 180 0.10	• 200 0.17	•	3.22	3.40	1.056	4.56	
12		• 90.5 12.70	• 182 0.21	• 188 0.31	•	3.45	3.76	1.089	4.55	

+ According to Ref 5.

It means that the internal structure of layers leads to the transformation into an A_d like structure. For classical A_d smectic the ratio d/l is about 1.4. In case of compounds 1 the maximal value of the ratio d/l is about 1.09 (n=12). We propose to term such a smectic A "the enhanced monolayer smectic A" (A_{1e}) to distinguish it from the classical A_d smectic and to stress that it is formed by a progressive expansion of the monolayer spacing. Such behaviour is not only characteristic for homologous series of compounds

TABLE II The influence of temperature on the smectic A layer spacing of compounds 1

Temperature (°C)	d (nm)
	n=6
100	28.09
120	28.06
	n=10
100	34.05
120	34.27
140	34.82
	n=12
100	37.57
120	37.85
135	38.32
160	38.77

with -NCS terminal group, but it seems to be typical also for analogous compounds with terminal group -Cl, -F, -Br and -$COCH_3$. In our previous paper[10], we reported the values of the layer smectic spacing for 4-fluor, 4-chlor, 4-brom, 4-acetylphenyl 4-trans-decylcyclohexyl benzoates: the value of d was a little higher than l (d-l$\approx$0.1 nm). We believed then, that it was due to the experimental errors. Now, taking into account the present results, it is possible that in the mentioned compounds we are dealing with the enhancement of the smectic layers.

It was mentioned in Ref 9, that smectic A_1 may be classified into the group wherein d<l and in some cases into the group wherein d$\sim$l. The results obtained by us show that, for the compounds belonging to the same homologous series, the ratio of d/l is not fixed but it smoothly evoluates to the higher values for longer alkyl chains. The dielectric studies (Figure 3) confirm that the situation of molecules in the smectic A layer of compounds 1 is changing with the alkyl length. The dielectric properties of members with the short alkyl tail (n=5) are quite different from the properties of members with the long alkyl tail (n=10). It can be especially seen in the temperature dependence of $\varepsilon_\perp$ and $\bar{\varepsilon}$, (see Figure 3b and 3d). For compound 1, n=5, $\varepsilon_\perp$ does not change with the temperature. Its value is the same in the nematic and smectic A phases

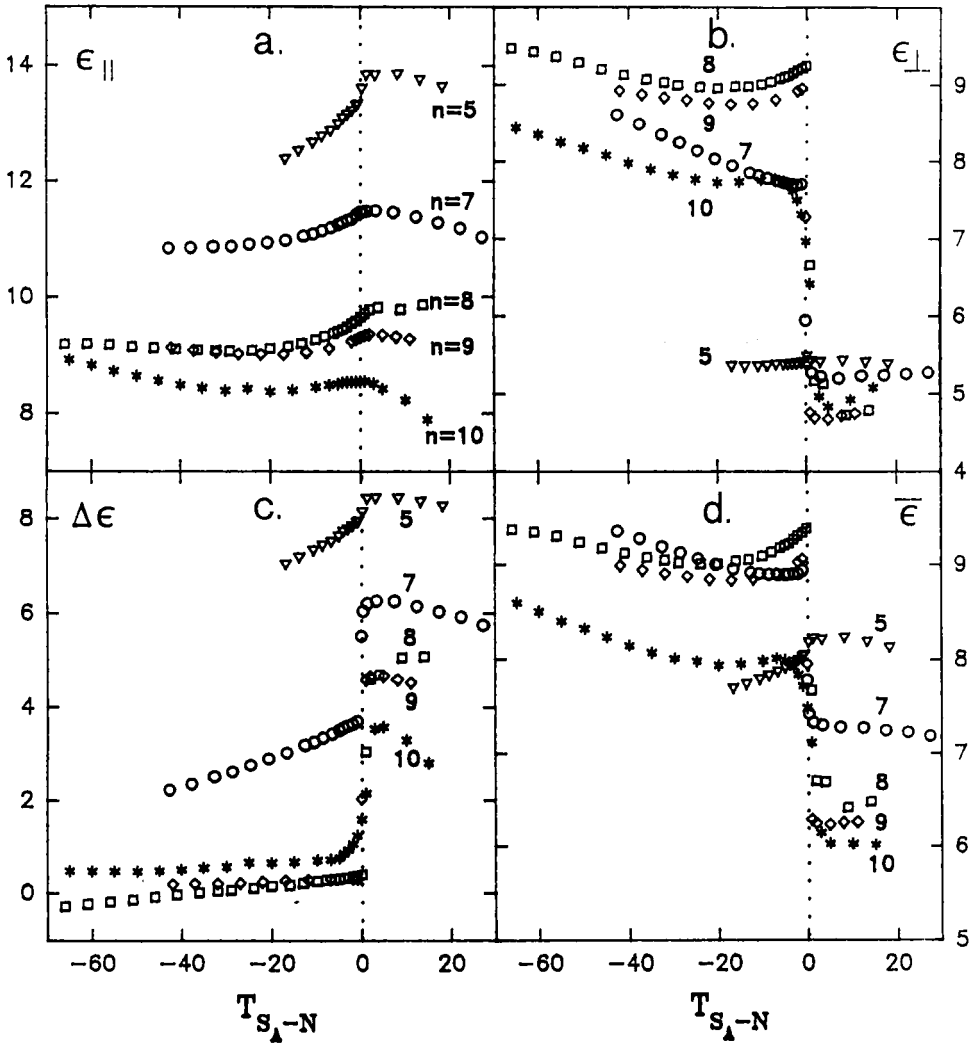
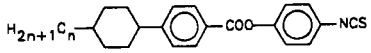


FIGURE 3 Static dielectric permittivities for



and $\bar{\varepsilon}$ is smaller in the smectic phase than in the nematic one. For the higher members of compounds 1, $\varepsilon_\perp$ is greatly increasing when the phase transition from the nematic to the smectic A phase occurs ($\varepsilon_\perp$ and $\bar{\varepsilon}$ take maximal values for n=8).

The increase of $\varepsilon_\perp$ is the most spectacular behavior observed for the compounds 1 and we interpret it as follow:

- The increase of the alkyl chain from n=5 to n=8 strongly disturbs the rotation of molecules along the long axis (steric repulsive forces are increasing effectively) and the dipoles in the space are oriented in such a way that their perpendicular components are parallel to each other and involve the order similar to the ferroelectric one.
- For $n \geq 9$, when the dimerization is more effective, $\varepsilon_\perp$ is less increasing because repulsion forces are decreasing and the rotation again becomes more allowed. MNDO calculations show that the angle α between direction of dipole moment of terminal -NCS group and the long molecular axis is diminished. Probably it may have also some influence for ordering molecules in the layer.

This dielectric studies confirm that the short molecules of compounds 1 in smectic A layer prefer parallel ordering (higher values of $\varepsilon_\parallel$ and $\Delta\varepsilon$) when for longer alkyl chains an antiparallel order is favorable. The dimerization of the molecules of compounds 1 diminishes the steric repulsive forces between long alkyl chains. This is why for homologous members with longer alkyl chains the equilibrium between monomers and dimers is moved to the state in which there are more dimers. Such an explanation is also in concordance with the results of the theoretical calculations made by Madhusudana[11] and Longa.[12]

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