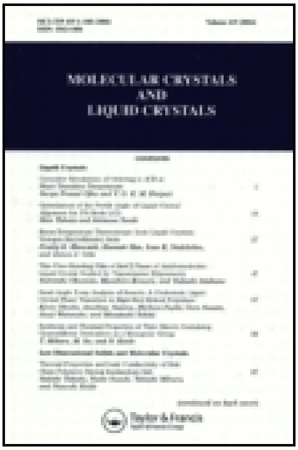

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J. Szabon [a], L. Bata [a] & J. Mink [b]

[a] Central Research Institute for Physics, H-1525, Budapest 114, P.O.B. 49, Hungary

[b] Institute of Isotopes, Budapest

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ALIPHATIC CHAIN CONFORMATIONS IN SMECTIC-A PHASES

J.SZABON, L.BATA AND J.MINK*
Central Research Institute for Physics,
H-1525 Budapest 114, P.O.B. 49. Hungary
*Institute of Isotopes, Budapest

Abstract The nonpolar smectogens, the all-rigid mT and the long-chain 16AOC as well as their mixtures have been studied by FTIR at different temperatures. DSC and X-ray measurements indicated monolayer S_A phases at every concentrations. The calculated molecular length of mT and the measured value of d in S_A phase was equal, otherwise d increased with the 16AOC concentration linearly except $x > 0.8$. While a more liquid-like behaviour of the aliphatic chains were detected in S_A compared to the isotropic phase, a significant decrease of the gauche conformers were found between x=0.3-0.5

INTRODUCTION

Very few information about possible aliphatic packing and conformations in S_A mixtures has been published. In this paper the binary mixtures of mT and 16AOC exhibited smectic induction is studied by FTIR spectroscopy, the components being chosen to have S_A mixtures with polymethylene chain concentrations from zero to maximum. Schematically, the all-rigid

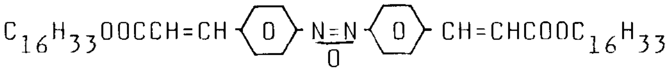
mT (L=2.74 nm)   16AOC (L=5.83 nm)

mT was mixed with 16AOC of flexible segments. By variation of their concentration,

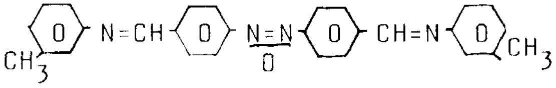
- spectral changes of the vibrations of the polymethylene chain, $(CH_2)_n$, at liquid crystal phase transitions,
- the sign of change due to the build-up of the layer (influence of the temperature), and the
- changes at different layer spacings, d, (influence of the $(CH_2)_n$ concentration)

could be studied.

EXPERIMENTAL



16AOC



mT

The compounds, azoxybenzal-bis-meta-toluidine, mT and bis-hexadecyl azoxycinnamate, 16AOC, as well as their binary phase diagram were made in Halle.[1] The samples for FTIR spectroscopy were made of a thin film of the liquid mixture between KBr windows, the experimental set-up (DIGILAB FTS-20C) was similar as published earlier. The spectra of mT and 16AOC as well as their mixtures of different concentrations were taken at different temperatures. The mixtures exhibited broad smectic A range in middle concentrations, 120-180°C, while at other mole fractions narrow S_A phases existed.

A continuous monolayer $S_A$phase was proved by X-ray measurements. The calculated molecular length of mT and the measured value of the layer distance, d, in S_A phase were equal as well as the measured and calculated d at every concentration of the binary mixtures except $x > 0.8$, where x is the mole fraction of 16AOC. The mixing rule, $d = \Sigma X_i d_i$, was applied for the calculation.[2]

Transitional enthalpies of 0.2-1.5 mg samples were measured by Perkin-Elmer DSC-2 connected to Commodore 2001 for area and error calculations.

RESULTS

The S_A-I transitional enthalpies are illustrated in Fig.1. They varied non-additively in function of XmT in a similar way as in case of earlier results of cyano- or nitro- compounds with an aliphatic end-chain.

The intensities of the CH_2 rocking vibrations of the polymethylene chains changed in the function of the temperature. As an example intensities at four vibrational bands can be compared in different phases in Table I.

Changes of the vibrational band peak heights (in arbitrary unit)of the polymethylene chains at 735 cm^{-1} and 722 cm^{-1} in the mixture of x=o.5 in different phases as solid, S_A and isotropic liquid are illustrated in Fig.2b. Redistribution of CH_2r band in 750-720 cm^{-1} were rather general in other concentrations as well, but the strong increase of $I(CH_2)_{n\geqslant 6}$ in S_A phase was exceptional compared to, for

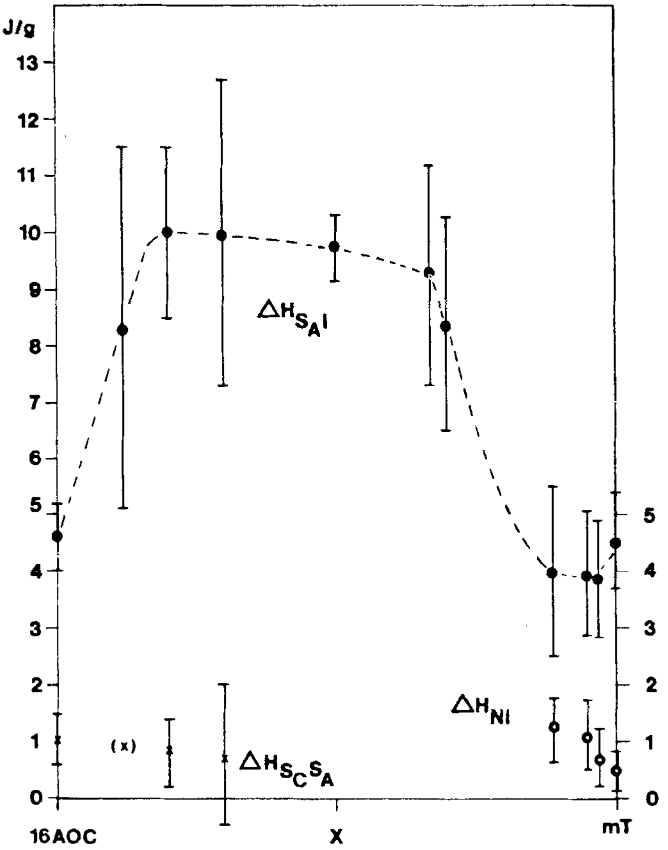


FIGURE 1. Transitional enthalpies as a function of the concentration

example, the case of x=0.8.

The CH_2 stretching vibrations at $2925 \pm 10\ cm^{-1}$ and $2860 \pm 10\ cm^{-1}$ ruled the spectra in mixtures of each concentrations if $X_{16AOC} \neq 0$. The ratio, α, of their intensities

$$\alpha = \frac{\text{intensity of the asymmetric stretch}}{\text{intensity of the symmetric stretch}}$$

as a function of the temperature is illustrated in Fig.2a. It shows a decrease of this ratio in S_A phase, compared both to solid as well as to isotropic phases at phase transition temperatures.

TABLE I CH_2 rocking vibrational intensities of the mT - 16AOC mixture, x=0.50, at different temperatures (arb.units)

T(^{0}C)	Intensities				Phases
	750-740	740-730	730-725 cm^{-1}	722 cm^{-1}	
200	2.0	2.2	3.4	2.4	isotropic
190	2.0	2.2	3.5	1.8	isotropic
180	1.5	2.2	3.6	3.0	(is --- S_A)
160	0.7	0.5	3.3	3.8	Smectic-A
130	1.0	0	2.5	3.7	Smectic-A
115	1.2	2.0	3.4	2.0	(melting)
95	0.7	0.2	3.7	2.2	Solid
75	1.5	0	4.4	4.0	Solid
30	1	0	4.3	5.4	Solid
assignements: (see text)	$(CH_2)_2r$	$(CH_2)_3r$	$(CH_2)_4r$	$(CH_2)_{n\geq 6}r$	(Ref.3.)

Finally, intensities of the polymethylene CH_2 asymmetric stretching vibrations in S_A phases of different layer spacings can be compared if an independent vibrational band, as the C = O st band at 1720 cm^{-1} was used as inner reference. (This band

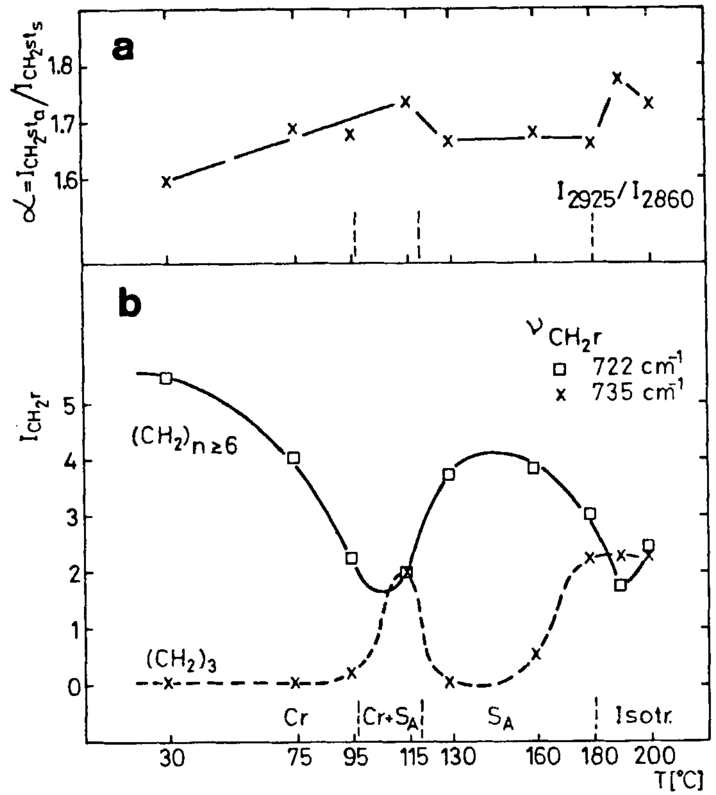


FIGURE 2.a. Ratio of intensities (see text).
b. Vibrational intensities at two band frequencies as a function of the temperature in the mT-16AOC mixture at x=0.50.

showed no shift and their intensities changed linearly with x)

Fig.3 shows the change of the intensity ratio

$$\beta = \alpha_{S_A} / \alpha_{isotropic}$$

(where $\alpha = I_{2925}/I_{1720}$)

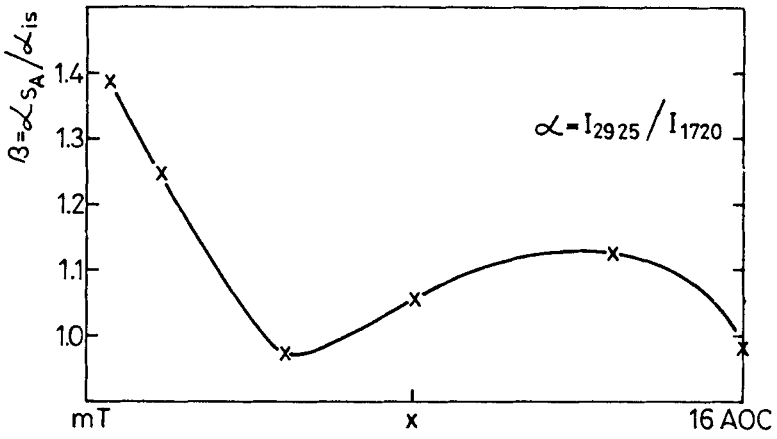


FIGURE 3. Influence of the concentration on β (see text)

during phase transition S_A-I at different concentrations. A minimum and two maxima can be seen on the curve, the minimum belongs to the x=0.3-0.5 concentration range.

CONCLUSION

Shortening of the layer distance d of S_A phase of 16AOC compared to the molecular length L_{16AOC} is a consequence of conformational changes of the long aliphatic chains which were non-all-trans. This is true in the range x=0.5-1 for 16AOC as well. On the other hand no d-shortening could be detected if the molecule had no flexible segment as in the case of mT.

The broad maximum of the S_A-I transitional enthalpies around $x_{16AOC}\sim 0.8$ in Fig.1 gave evidence for loose, non-localised outer-sphere-type two dimensional intermolecular interaction (2D-solvation) at a molecular ratio of 6:1 at which the first complete 2D-solvation shell could be built around the all-core mT component. The broadening of the maximum towards x_{16AOC}= 0.5-0.3 can be compared to the minimum in $\beta = \alpha_{S_A} / \alpha_{is}$ curve around the same range of x in Fig.3. It indicates increased proportion of co-vibrating all- trans sequences as well as greater van der Waals interactions in S_A phase, compared to the isotropic liquid which is more liquid-like. The redistribution of CH_2 rocking band intensities in different phases support this conclusion. (Fig.2b.). It has been noted that the band at 722 cm^{-1} requires the presence of at least six trans-linked methylene groups[4]. In the liquid state the long aliphatic chains exist predominantly in conformation sets and each section will then contribute a set of bands to the vibrational pattern determined by its chain length. As Fig.2.b. illustrates, the length of the co-vibrating all-trans sequences are increased in S_A (if x=0.5). On the other hand, shorter sequences were proved at x=0.1 and x=0.8, indicating an increase of gauche conformation.

This is probably due to an increase of steric stress either if d is too low compared to L_{16AOC} (x=0.1-0.2) or by increasing the number of vacancies by increasing the concentration of the small rigid mT in the "thick" mixed layer, around x=0.8. By detecting the change of the CH_2 stretching vibrations compared to an inner reference or the redistribution of CH_2 rocking it is possible to follow the change in the population of gauche conformers

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