Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Existence of $S_{A\ 1}$, $S_{A\ d}$, $S_{A\ 2}$ and $S\sim_C$ Smectic Phases in the New Series 4-Alkoxyphenyl-4′- [4″-Cyanobenzyloxy] Benzoates

Nguyen Huu Tinh [a] & C. Destrade [a]
[a] Centre de Recherche Paul Pascal, Domaine Universitaire, 33405, Talence Cédex, France
Version of record first published: 15 Sep 2010.

To cite this article: Nguyen Huu Tinh & C. Destrade (1984): The Existence of $S_{A\ 1}$, $S_{A\ d}$, $S_{A\ 2}$ and $S\sim_C$ Smectic Phases in the New Series 4-Alkoxyphenyl-4′- [4″-Cyanobenzyloxy] Benzoates, Molecular Crystals and Liquid Crystals, 92:9-10, 257-262

To link to this article: http://dx.doi.org/10.1080/01406568408084068

Mol. Cryst. Liq. Cryst. Vol. 92 (Letters), pp. 257-262
0140-6566/84/9209-0257$18.50/0

Printed in the United States of America

THE EXISTENCE OF S_{A_1}, S_{A_d}, S_{A_2} and $S_{\tilde{C}}$ SMECTIC PHASES IN THE NEW SERIES 4-ALKOXYPHENYL-4'- [4"-CYANOBENZYLOXY] BENZOATES.

NGUYEN HUU TINH, C. DESTRADE
Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence Cédex, France

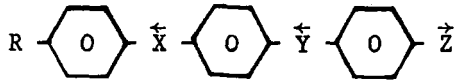
(Received for Publication December 7, 1983)

A homologous series of 4 -alkoxyphenyl-4'-[4"-cyanobenzyloxy] benzoates have been synthesized. Within this series three smectic A phases : S_{A_1}, S_{A_d} and S_{A_2} were identified by mean of small angle X-Ray scattering. Furthermore three derivatives exhibit the novel smectic phase made of ribbons $S_{\tilde{C}}$.

INTRODUCTION

Since the discovery of the three different smectic A phases : S_{A_d}, S_{A_1} and S_{A_2} in a mixture [1] and of the new smectic phase made of ribbons $S_{\tilde{C}}$ [2-4] several new homologous series were recently synthesized [5,6] in order to provide some more examples and to allow systematic structural studies and thermodynamical behaviour of these mesomorphic fluid states.

All these series belong to the same general molecular structure :



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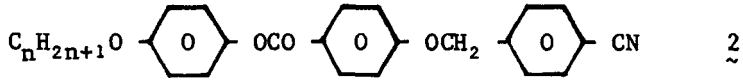
where the longitudinal dipolar moment of the X and Y groups (X and Y = - OCO -, - N = CH -) is antiparallel to that of the Z = - CN or - NO_2 end group. But all through these series one can encounter, at least, two or three of these smectic modifications.

In this paper we report on a new homologous series belonging to the same general architecture :



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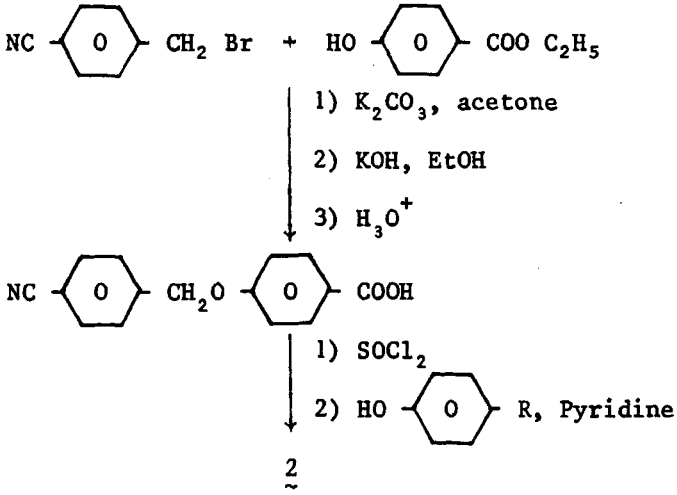
where we have identified the four S_{A_1}, S_{A_d}, S_{A_2} and $S_C^{\sim}$ phases.

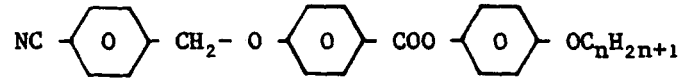
RESULTS AND DISCUSSION

The substances were synthesized according to the scheme below :



They were purified by chromatography on silica gel eluted with benzene and finally recrystallized from ethanol. Phase transitions were studied both by polarizing microscopy (equipped with a Mettler PF5 heating stage) and Differential Scanning Calorimetry (Dupont 990). The transition temperatures and types of mesophases, the structures of which were determined by mean of small angle X-Ray scattering on powder sample [7], are given in Tables I, II and Figure 1.

TABLE I : Transition temperatures(°C) of compounds 2



n	K	S_{A_2}	$S_C^{\sim}$	S_{A_1}	S_{A_d}	N	I
5	. 135	-	-	(. 111)	-	. 174	.
6	. 115	-	-	. 116	-	. 173	.
7	. 106	-	-	. 118.5	-	. 168	.
8	. 114.5	-	(. 110.5)	. 122	-	. 167	.
9	. 116	(. 114.5)	. 122.5	. 123.7	-	. 163	.
10	. 102	. 124	. 125	-	. 141	. 162	.
11	. 106	. 127	-	-	. 155	. 160	.
12	. 104	-	-	-	. 158	-	.

K : crystal phase ; S_{A_2} bilayered smectic A phase ; $S_{\tilde{C}}$: smectic phase made of ribbons ; S_{A_1} : monolayered smectic A phase ; S_{A_d} partially bilayered smectic A phase ; N : nematic phase ; I : isotropic phase ; ( ) : monotropic transition ; . : the phase exists ; - : the phase is not observed.

TABLE II. Transition enthalpies and entropies of compounds $\underset{\sim}{2}$

(ΔH in cal. g^{-1} and ΔS in cal. g^{-1} K^{-1})

n		K	S_{A_2}	$S_{\tilde{C}}$	S_{A_1}	S_{A_d}	N	I
6	ΔH	. 16.6	-	-	. 47×10^{-3}	-	. 872×10^{-3}	.
	ΔS	*0.043*			*0.12×10^{-3}*		*1.96×10^{-3}*	
7	ΔH	. 19	-	-	. 43×10^{-3}		. 873×10^{-3}	.
	ΔS	*0.051*			*0.11×10^{-3}*		*1.98×10^{-3}*	
8	ΔH	. 16.33	-	($.15\times10^{-3}$).	51×10^{-3}		. 840×10^{-3}	.
	ΔS	*0.042*		*(0.04×10^{-3})*	*0.13×10^{-3}*		*1.91×10^{-3}*	
9	ΔH	. 18.32	($.58\times10^{-3}$)	. 27×10^{-3}	. 77×10^{-3}		. 836×10^{-3}	.
	ΔS	*0.046(0.15×10^{-3})*		*0.07×10^{-3}*	*. 0.19×10^{-3}*		*1.92×10^{-3}*	
10	ΔH	. 16.85	. 54×10^{-3}	$.108\times10^{-3}$	-	. 20×10^{-3}	$.1090\times10^{-3}$	.
	ΔS	*0.044*	*0.14×10^{-3}*	*0.27×10^{-3}*		*0.05×10^{-3}*	*2.51×10^{-3}*	
11	ΔH	. 20.8	$.360\times10^{-3}$	-	-	. 50×10^{-3}	. 966×10^{-3}	.
	ΔS	*0.055*	*0.91×10^{-3}*			*0.12×10^{-3}*	*2.24×10^{-3}*	
12	ΔH	. 20.9	-	-	-	$.1513\times10^{-3}$		
	ΔS	*0.053*				*3.54×10^{-3}*		

The three first compounds (n = 5,6,7) give S_A and N phases. This S_A phase is monolayered smectique A phase (S_{A_1}) which still exists until n = 9. We must point out that the T_{NA}/T_{NI} ratio calculated for these compounds are equal or superior to the Mc Millan's number [8] ($\simeq$ 0.87) with the exception of S_{A_1} phase of the derivative n = 5 because it is very metastable (T_{NA}, T_{NI} are respectively the temperature in Kelvin of the S_A - N transition and the N - I transition) whereas in the series which present the reentrant nematic phase, this ratio largely inferior to 0.87 (for example 0.70 for 4-alkoxybenzoyloxy-4'-cyanotolanes series [9]).

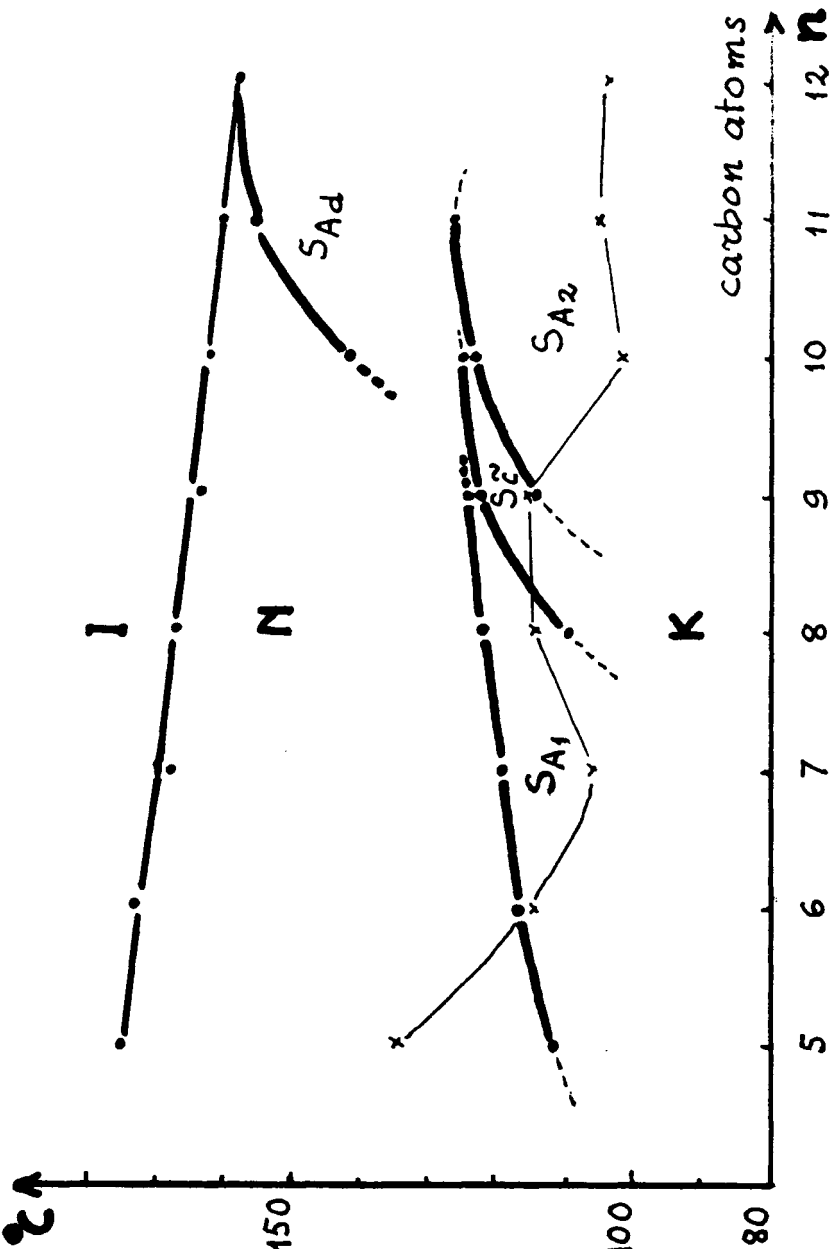


Fig. 1. Plot of transition temperatures against n

n	5	6	7	8	9	10	11	12
T_{NA}/T_{NI}	0.86	0.87	0.89	0.90	0.91	0.95	0.99	-

From the derivative n = 10, the partially bilayered S_A phase (S_{A_d}) appears while the S_{A_1} disappears. The reentrant nematic phase was also obtained with the mixture between n = 9 and n = 10 derivatives. The novel smectic phase made of ribbons $S_{\tilde{C}}$ is present in the three derivatives n = 8 → 10. This phase is very difficult to observe under the microscope while the higher temperature smectic phase is a S_{A_1} one (n = 8 and 9) whereas it appears highly birefringent when it originates from a S_{A_d} phase (n = 10). This behaviour may be correlated with the corresponding entropies of the S_{A_1} - $S_{\tilde{C}}$ transition (18 and 33 $mcal.g^{-1} K^{-1}$ respectively in the n = 8 and 9 derivatives) and the S_{A_d} - $S_{\tilde{C}}$ transition ($61\ mcal.g^{-1} K^{-1}$ in the derivative n = 10).

The three smectic A phases (S_{A_d}, S_{A_1} and S_{A_2}) have the same textures (focal conic or homeotropic textures) while the $S_{\tilde{C}}$ phase presents a texture formed by polydomains (ressembling typical textures of hexagonal columnar phase) in the precedent homeotropic domain and a mosaic texture.

We must point out that the derivative n = 11 exhibits a direct transition S_{A_d} - S_{A_2} providing a new example of observable S_{A_d} - S_{A_2} phase transition, as a matter of fact clear textural change are observed under microscope correlatively the entropy change ($0.91\ mcal.g^{-1} K^{-1}$) and the layer spacing are strongly enhanced at this transition.

CONCLUSION

We have described several 4-alkoxyphenyl-4'(4"-cyanobenzyloxy) benzoates which provide, for the first time, the S_{A_1}, S_{A_d}, S_{A_2} and $S_{\tilde{C}}$ fluid smectic phases in the same series.

Let us underline the T_{NA_1}/T_{NI} ratio is superior to Mc Millan parameter as opposed to previous results. Furthermore we give evidence of S_{A_d} - S_{A_2} transition directly observable under microscope. At last we must point out that these new mesogenic materials are chemically stable and the different

interesting smectic phases are available at rather low temperature, so that we stress that they could raise to some more physical investigations.

ACKNOWLEDGEMENTS

The authors are indebted to Drs F. Hardouin and G. Sigaud for the interest they manifest to this work.

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