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NEW "ROD-LIKE" COMPOUND WITH A POLAR CYANO HEAD GROUP GIVING AN ORTHOGONAL SMECTIC B PHASE

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ABSTRACT

"Rod like" molecules with a cyano head group seldom exhibit a polymorphism with more than a nematic and a smectic A phase. The compound here reported presents a low temperature ordered mesophase which is shown to be of orthogonal smectic B type by the way of miscibility observations in agreement with a recent X-ray characterization. This preliminary structural study also suggests some stimulating remarks about possible incommensurate periodicities in the three mesophases.

INTRODUCTION

No mesogenic compound with two phenyl rings and a cyano end group (such as cyanobiphenyls for example) is now reported to exhibit more than a nematic and a smectic A phases*. To our knowledge two compounds with three phenyl rings in the rigid core and a cyano end group so far present a **N-S_A**-ordered smectic sequence^{2,3}. This small number has been still reduced since one of two was proved⁴ to afford a reentrant nematic instead of the ordered smectic phase.

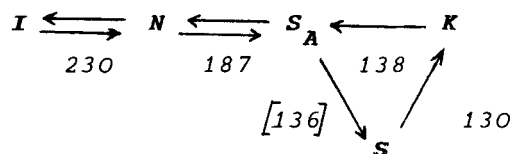
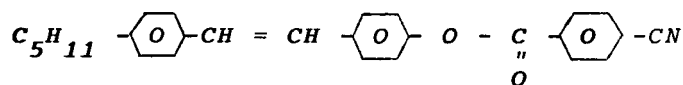
* Ordered smectic phases were described in cyano derivatives of p-alkyl cyanocyclohexylcyclohexane¹.

Indeed, this type of compounds exhibits some unusual behaviours : many of them give nematic and smectic A reentrant phases ^{5,6,7,8,9} or smectic A phases with original structural features ^{10,11}.

Proceeding with our systematic study of such molecules we describe in this paper the main characteristics of a new cyano derivative which induces an ordered smectic phase of B type.

EXPERIMENTAL RESULTS

The compound we are interested in, is the 4-cyano-benzoyloxy-4'-pentylstilbene which presents a polymorphism with a nematic, a smectic A and a lower temperature smectic phase slightly monotropic. The temperature of the different transitions are given below together with the chemical formula :



The enthalpy of the S_A -S transition is of same order of magnitude than for S_A - S_B ones : $\Delta H \sim 660$ cal mole⁻¹. This is connected with a sharp discontinuity in the thermal variation of the magnetic susceptibility (**FIGURE 1**). The decrease of this quantity corresponds in fact to an increase of the diamagnetic anisotropy $\Delta\chi$ and consequently indicates a better orientational order. This can be compared to the behaviour of $\Delta\chi$ for well known S_A - orthogonal S_B transitions¹².

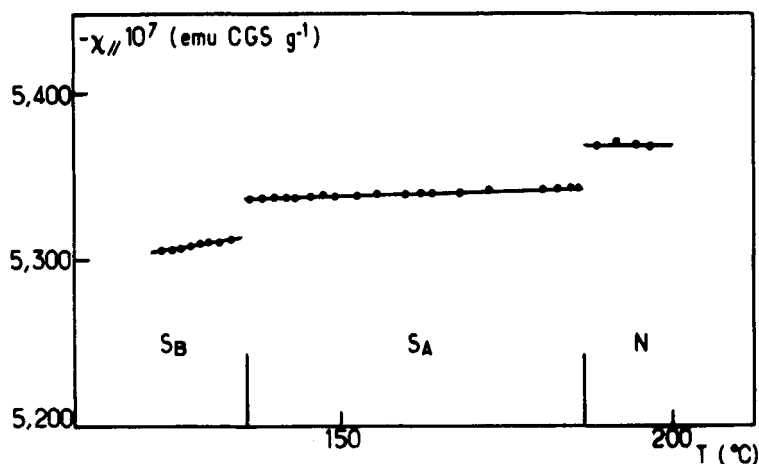


FIGURE 1 - Thermal variation of the diamagnetic susceptibility in the nematic, smectic A and smectic B phases.

The microscopic texture of the phase, clearly fan-shaped in the S_A phase, remains almost unchanged through the transition but it appears a tendency to organize to a mosaic texture. No transitional texture such as stripes is observable. Then we have performed a contact method between this compound and the 4 - heptyloxy benzoyloxy-4' bromostilbene¹³ which exhibits nematic, smectic A and smectic B phases. The resulting binary diagram is reported in **FIGURE 2**. This shows the isomorphism between the S_B phase of the bromo compound and the ordered smectic of the cyano compound. Moreover we detect in the central part of the diagram a domain of stability of an additional smectic phase, may be of E type, which could indicate virtual phases at low temperature in the pure compounds (the complete polymorphism of the octylcyano_terphenyl mentions also the existence of a S_E phase²).

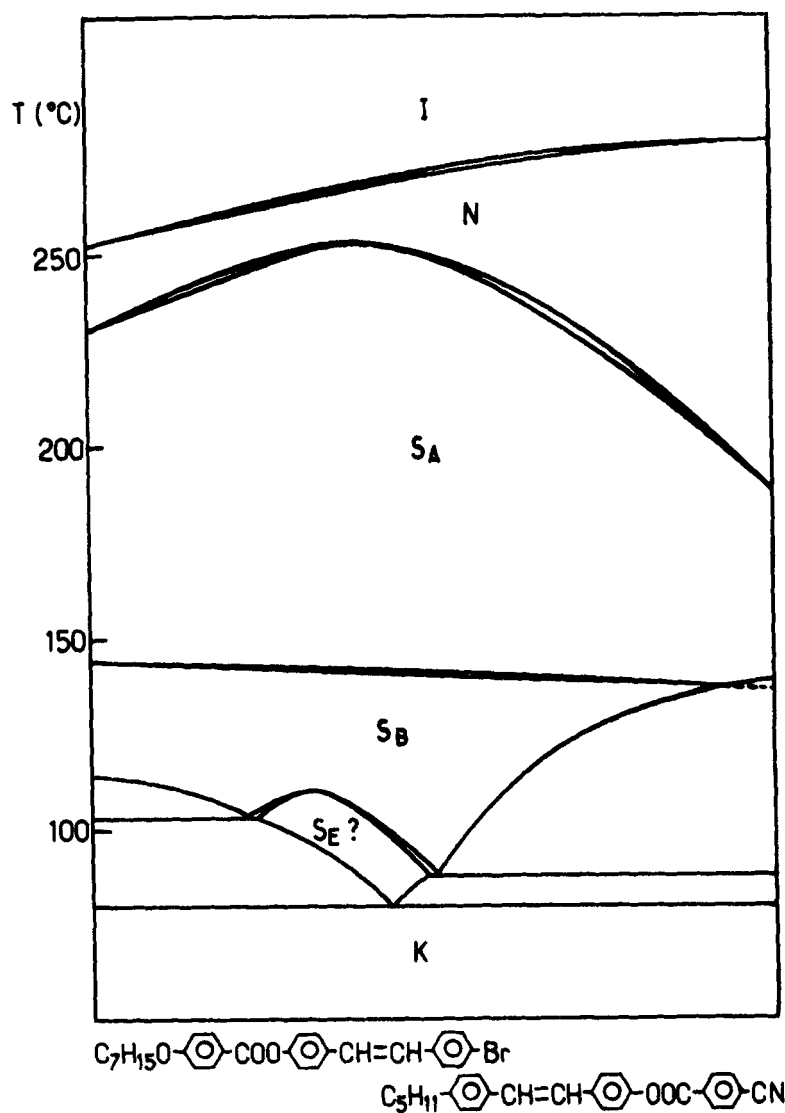


FIGURE II - Isobaric binary diagram (contact method) between the above compounds.

At the same time these observations have been supported by X-ray experiments in a magnetic field. Indeed, preliminary results seem to confirm the orthogonal S_B nature of this ordered smectic state but an imperfect orientation due to a too weak magnetic field (0.3T) requires more experiments on powder samples with a GUINIER camera. Nevertheless the magnet is sufficient to form well aligned domains of the nematic phase and also of the smectic A phase by slow cooling in the field. The diffraction patterns obtained from both of these phases can be compared to these got from a quite similar cyano derivative already described in a recent paper¹¹. For this latter compound, in which only the stilbene linkage is replaced by a benzoate group, for the first time two commensurate diffuse scatterings are observable in the nematic state which then give two Bragg reflection orders of same intensity in S_A phase. By comparison the new "stilbene" compound presents also at small angles two unusual diffuse scatterings in the nematic phase but in this case they seem to be incommensurate and their respective intensities appear different ! Moreover, in contrast with the "benzoate" compound for which the layer spacing d is very close to two molecular lengths l , here $d \simeq l$ in S_A and S_B phases, while the second diffuse scattering at smaller angles remains unchanged in these smectic phases. The detailed X-ray results will be published elsewhere¹⁴. A tentative explanation of these original periodicities with respect to the molecular packing and to the polarity will be also soon proposed.

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