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Some Comments on the Effect of a Lateral Substituent on the Reentrant Nematic Phase

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SOME COMMENTS ON THE EFFECT OF A LATERAL
SUBSTITUENT ON THE REENTRANT NEMATIC PHASE

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A comparative study is made of the role of the lateral substituent on the reentrant nematic phase of some phenyl benzoyloxybenzoates and cinnamoyloxybenzoates. The lateral substituent, depending on its location, seems to have varying degrees of influence on the reentrant nematic phase.

INTRODUCTION

The reentrant phenomenon has been observed in a large number of compounds belonging to different homologous series.¹⁻⁷ In general, these compounds have (i) a -CN end group, (ii) at least three phenyl rings in the core and (iii) an electronic distribution such that the maximum electronic density is located on the terminal cyano group. However, exceptions to these rules have been found. For example, a compound with a -NO₂ end group,⁸ a compound with only two benzene rings¹ have also been found to exhibit reentrant phases. Further, the introduction of bridging groups like -CH=CH-, -N=N-,⁹ etc. in conjugation with the cyanophenyl group appears to favor the formation of the reentrant phase.

In the present communication, we examine the effect of a lateral substituent on the reentrant phase transition

of a few representative compounds.

EXPERIMENTAL

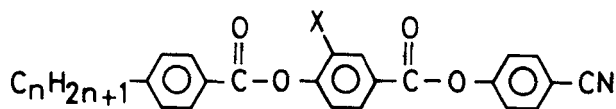
The compounds were synthesized by standard methods. The new compounds had satisfactory spectral (infrared and proton magnetic resonance spectra) and analytical data. The transition temperatures were determined on a Mettler hot stage (Model FP52) as well as from thermograms taken on a differential scanning calorimeter (Perkin-Elmer Model DSC-2).

RESULTS

It is well known that molecules with three benzene rings and a cyano terminal group constitutes an optimal requirement for the formation of reentrant nematic (N_R) phase. Hence we have synthesized molecules with this basic skeleton and also introduced a lateral group into some of these compounds to examine its influence.

The phase transition temperatures of the series alkyl benzoyloxybenzoates are given in table 1. Compound 1 shows a smectic A (S_A) phase which has a range of about 101° and a short range of nematic phase. No reentrant phase is observed on cooling. However, the introduction of a methyl group in the 3' position of this molecule (compound 3) has an interesting effect. This group increases the breadth of the molecule to a small extent and decreases the lateral intermolecular attractions. As expected, the N-I transition temperature is lowered considerably. However, the nematic phase range is increased and a metastable N_R phase is observed. Compound 2 exhibits only a S_A phase, the smectic range being about 106° . On

TABLE 1

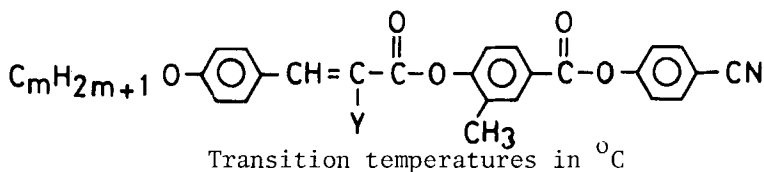
Transition temperatures in $^{\circ}\text{C}$

No.	n	X	K	N_R	S_A	N	I
1	11	H	. 95	*	. 196.5	. 200.5	.
2	12	H	. 91	*	.	197.5	.
3	11	CH_3	. 103	(. 78.5)	. 127	. 152.5	.
4	12	CH_3	. 102	(. 59.8)	. 138.5	. 148	.

* There is a solid-solid transition at 90.5°C and 81.5°C for compounds 1 and 2 respectively. Temperatures in parentheses indicate monotropic transitions.

introducing a methyl group in the 3' position (compound 4), a dramatic change in the phase sequence occurs and three transitions take place. A nematic phase, a S_A phase and a metastable N_R phase are observed. These two examples clearly indicate that even small changes in the molecular structure can have a profound effect on the formation of the reentrant nematic phase.

The transition temperatures of 4-cyanophenyl-3'-substituted-4'-(*trans*-4''-n-alkoxy- α -methylcinnamoyloxy) benzoates are given in table 2. All the three compounds already have a lateral methyl group. Compound 5 ($\text{Y}=\text{H}$) exhibits an enantiotropic N_R phase, a S_A phase and a nematic phase. The introduction of a methyl group into the 3' position of this molecule (compound 6), certainly enhances the lateral dimensions considerably. In spite of this, the N_R phase is still enantiotropic, although all the transition points are lowered. When a bulky group

TABLE 2^{*}

No.	m	Y	K	N _R	S _A	N	I
5	11	H	. 102.4	. 107	. 153.2	. 193.6	.
6	11	CH ₃	. 80.8	. 93	. 122.5	. 169.8	.
7	11	OCH ₃	. 82.9 (.	48)	. 123	. 139.8	.

Temperatures in parentheses indicate monotropic transitions.

* Reference 7.

such as a methoxy substituent is introduced (compound 7), the lateral intermolecular attractive forces are significantly reduced, but still the N_R phase appears, though as a metastable phase.

In conclusion, these results indicate that a lateral substituent, depending on its location, can have different effects on the reentrant behaviour.

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