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Liquid crystalline properties of 4-isopropyl- and 4-isopropoxy-*N*-(4-*n*-alkoxysalicylidene)anilines

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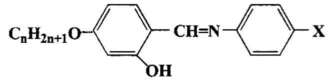
New homologous series of 4-isopropyl- and 4-isopropoxy-*N*-(4-*n*-alkoxysalicylidene)anilines were synthesized. The phase transitions of these homologues were determined by differential scanning calorimetry and polarizing optical microscopy. No enantiotropic liquid crystalline phases were observed for homologues having a terminal isopropyl group; as the terminal alkoxyl chain is lengthened, smectic C and nematic phases occur monotropically. The members with an isopropoxy substituent exhibit an enantiotropic nematic phase as the terminal alkoxyl chain is lengthened; the octyloxy member exhibits a monotropic smectic C phase as well as an enantiotropic nematic state.

1. Introduction

Many investigations have been undertaken concerning the relationship between molecular structure and liquid crystallinity [1–5]. These have resulted in certain guidelines regarding the features of molecular structure that favour liquid crystalline formation. The vast majority of compounds exhibiting a liquid crystalline phase may be regarded as consisting of a rigid central group and one or two flexible terminal alkyl or alkoxyl chains. Almost all rod-like liquid crystals reported so far have a *para*-substituted terminal group. Furthermore, the terminal alkyl and/or alkoxyl chains are predominantly straight chain type. On the other hand, it is well recognized that *N*-salicylideneaniline (SA) is a good mesogen in liquid crystalline materials because the anil linkage is stabilized by intrahydrogen bonding [6].

The purpose of this study is to find new mesomorphic compounds which have an SA skeleton and a terminal branched group. Thus, two new homologous series of 4-isopropyl- and 4-isopropoxy-*N*-(4-*n*-alkoxysalicylidene)anilines were synthesized, and examined for phase transition behaviour. The members of these homologous series having the following generalized structural formula are referred to as ISO (*n*) and PRO (*n*), respectively. The *n* in parentheses denotes the carbon number of the terminal alkoxyl chain; the value of *n* ranges from 1 to 8.



$X = CH(CH_3)_2$ or
$OCH(CH_3)_2$

2. Experimental

2.1. *Materials*

4-*n*-Alkoxy-2-hydroxybenzaldehydes, and 4-isopropyl- and 4-isopropoxyanilines were obtained commercially. The substituted benzaldehyde was coupled with the corresponding aniline derivative by heating under reflux for about two hours in ethanol solution. The crude ISO (*n*) or PRO (*n*) product was purified by recrystallization from ethanol. The structure of the products was confirmed mainly by infrared spectroscopy and Raman scattering.

2.2. *Measurements*

The liquid crystalline textures and phase transition temperatures were determined by means of a Nikon polarizing microscope equipped with a Mettler FP-52 microfurnace for sample temperature control. Checks on the transition temperatures were made with a Shimazu differential scanning calorimeter (DSC). All measurements were carried out under a flow of nitrogen gas to prevent decomposition.

3. Results and discussion

The phase transition temperatures of all the homologues studied here are summarized in tables 1 and 2. First, it should be mentioned that all of the phase transition temperatures evaluated on the basis of texture change is in good accord with those measured by DSC.

The phase transition temperatures in the case of ISO (*n*) are compiled in table 1. In this series, enantiotropic liquid crystalline phases are not observed. As the terminal alkoxyl chain is increased, monotropic nematic

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Table 1. The phase transition temperatures of ISO (*n*) (°C): parentheses indicate the monotropic transitions.

n	Smectic C	Nematic	Isotropic
1			79
2			84
3			75
4			68
5			66
6			75
7	(39)	(48)	64
8	(43)	(54)	55

Table 2. The phase transition temperatures of PRO (*n*) (°C): parentheses indicate the monotropic transitions.

n	Smectic C	Nematic	Isotropic
1			90
2			108
3			86
4		(67)	85
5		(60)	72
6		(69)	76
7		53	68
8	(39)	54	74

and smectic phases appear in ISO (7) and ISO (8). This finding that enantiotropic mesomorphic phases are not observed for ISO (*n*) is easily understood by taking account of the terminal branched and bulky isopropyl substituent. Under polarizing microscopy, the smectic phase exhibits a broken fan-shaped texture or a broken focal-conic texture on cooling from the nematic phase. Furthermore, no pseudo-isotropic texture (homeotropic alignment) is seen on displacing the cover-slip. These characteristic textures identify the smectic phase as smectic C [7].

Table 2 shows the phase transition temperatures of PRO (*n*). The first three homologues exhibit no mesomorphic phase. The members with $n \geqq 4$ show a nematic phase although PRO (4) to PRO (6) exhibit a monotropic nematic state. The homologues with $n \geqq 7$ exhibit an enantiotropic nematic phase. This finding that an enantiotropic mesomorphic phase occurs as the terminal alkoxy chain is increased is not unusual, because it has been frequently observed in the homologous series of the other liquid crystalline materials [4]. The octyloxy derivative exhibits a monotropic smectic C phase as well as the nematic phase. From comparison between tables 1 and 2, it is evident that the isopropoxy substituent is more favourable for liquid crystalline formation. This is a general observation explained as follows: (a) the alkoxyl chain is longer than the alkyl substituent due to presence of an oxygen atom, (b) the alkoxyl group has a stronger dipole moment than the alkyl substituent, favouring a liquid crystalline molecular arrangement owing to intermolecular attractive forces. These factors hold for the difference between isopropyl and isopropoxy groups. In addition, it should be emphasized that even compounds having branched terminal alkyl or alkoxyl chains exhibit a liquid crystalline phase if another terminal alkoxy chain is appropriately lengthened.

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