January, 1980] © *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **53**, *265—266 (1980)* 265

Liquid Crystalline Properties of *N*-(4-Alkoxybenzylidene)-4-halogenoanilines

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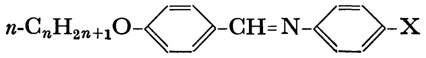
(Received July 3, 1979)

Synopsis. *N*-(4-Alkoxybenzylidene)-4-halogenoanilines have been synthesized, and the phase transitions determined using a differential scanning calorimeter and a polarizing microscope. Smectic and nematic phases have been observed for fluoro and chloro derivatives whereas bromo and iodo derivatives exhibit only a smectic phase.

A number of investigations have been conducted on the relationship between molecular structure and liquid crystallinity.[1–4] The vast majority of compounds exhibiting a liquid crystalline phase may be regarded as consisting of a rigid central group and a flexible end group.[4] In order to understand the relationship between liquid crystallinity and terminal substituents, the homologous series of *N*-(4-alkoxybenzylidene)-4-halogenoanilines has been synthesized. The members of this homologous series having the generallized structural formula have been given the



abbreviation n-O–X, in which the value of n ranges from 1 to 8 and X denotes a halogen atom.

Experimental

Materials. The *N*-(4-alkoxybenzylidene)-4-halogenoanilines were prepared by condensing 4-halogenoaniline with an equimolar amount of 4-alkoxybenzaldehyde in absolute ethanol. The reaction mixture was refluxed for one hour after which the product was collected as a solid crystalline precipitate. The product was recrystallized two or three times from ethanol and benzene.

Measurements. The liquid crystalline texture and the transition temperatures were determined by a Nikon polarizing microscope equipped with a Mettler FP 52 microfurnace and control unit. Checks on the transition temperatures and the measurement of enthalpies of transitions were made using a Rigaku differential scanning calorimeter.

Results and Discussion

The transition temperatures and the heats of transition in the case of the homologous series n-O–F are given in Table 1. In this series the only methoxy member shows no mesomorphic property, all the other higher members exhibiting a smectic II phase. The pentyloxy and hexyloxy members of this series show an enantiotropic smectic II phase although the smectic II phases of the other members occur monotropically. With increasing alkoxyl chain another feature is found on the appearance of the smectic phase, *i.e.*, a smectic I phase is enantiotropically observed for the hexyloxy to octyloxy members. On cooling the nematic state of the hexyloxy member, focal conic or fan texture may be observed for the smectic I phase. In addition, the focal conic or fan textures are easily changed to a pseudo-isotropic texture (homeotropic alignment) by cover slip displacement. The characteristic behavior of the textures indicates that the smectic I phase can be identified as smectic A.[5] In the phase transition from smectic I to smectic II transition bars are temporarily formed. On further cooling the transition bars disappear, and mosaic or fan-shaped textures similar to those observed for the smectic I phase are found. It should be emphasized that on cooling the smectic I phase with homeotropic alignment, the homeotropic alignment is also maintained in the smectic II phase. From these characteristic changes in microscopic textures, it follows that the smectic II phase can be classified as smectic B.[5] Smectic polymorphism is not unusual, and has been frequently observed as the alkoxyl chain length increases in other homologous series of liquid crystalline materials.[4]

TABLE 1. THERMODYNAMIC DATA FOR THE HOMOLOGOUS SERIES, n-O–F

n	Smectic B(II)	Smectic A(I)	Nematic	Isotropic
1				63.0 4800
2	(56.0) (1800)		(62.5) (140)	72.2 4900
3	(55.0) (1800)			62.1 5400
4	(58.0) (1700)		(59.6) (130)	64.5 6300
5	51.5 3800			57.4 1900
6	52.3 5200	55.0 640	59.3 770	61.1 150
7	(56.4) (640)	57.0 7200		61.6 1100
8	(54.3) (590)	60.0 7700		63.6 1000

The upper value indicates the transition temperature (°C) and the lower value the heat of transition (cal/mol). 1 cal=4.184 J. The parentheses show the monotropic transition.

Furthermore, it should be noted that a nematic phase occurs only for ethoxy, butoxy, and hexyloxy members. That the nematic phase can only be observed for homologues with even numbers of carbon atoms in alkoxyl chain is not surprising, and can be explained by considering the chain-order parameter of the end alkoxyl group with respect to the molecular axis.[6]

The phase transition temperatures of the homologous series n-O–Cl are given in Table 2. In this series the appearance of liquid crystalline phases is similar to that observed for n-O–F as stated above. As the length of the alkoxyl chain is increased, two smectic phases, *i.e.*, smectic A and B phases are found. It should be emphasized however that the nematic phase is monotropically observed for only ethoxy member. This indicates that increasing the ionic radius of the terminal substituent tends to destroy the parallel orientation of the molecules. This observation is more

Table 2. Thermodynamic data for the homologous series, *n*-O-Cl

n	Smectic B	Smectic A	Nematic	Isotropic
1				90.2 8300
2			(85.0) (151)	94.0 6500
3	(81.5) (1900)			82.0[a]
4	83.5 5000	88.6 900		89.4 1200
5	58.5 4400	90.7 840		92.8 1300
6	56.5 5200	88.7 750		96.3 1300
7	59.4 6500	89.4 770		97.5 1300
8	61.0 6100	87.7 740		98.5 1300

a) The heat of transition could not be determined due to complex crystal-to-crystal transitions.

Table 3. Thermodynamic data for the homologous series, *n*-O-Br

n	Smectic B	Smectic A	Isotropic
1			115.0 5000
2			103.1 4100
3	(92.2) (2200)		94.1 4500
4	78.5 4500		99.1 2300
5	71.9 5100	100.5 850	103.2 1500
6	72.1 5100	100.4 830	103.3 1400
7	64.5 6600	100.7 870	103.8 1600
8	65.4 6100	100.1 860	104.9 1600

Table 4. Thermodynamic data for the homologous series, *n*-O-I

n	Smectic B	Isotropic
1		149.5 6800
2		132.8 5100
3		117.0 4300
4	78.0 3000	111.4 2600
5	72.7 4300	108.5 2500
6	85.7 5400	110.3 2600
7	80.1 6300	110.7 2600
8	79.0 6500	110.8 2700

readily demonstrated in Tables 3 and 4 which show the phase transition temperatures for *n*-O–Br and *n*-O–I, respectively. In both homologous series the nematic phase is no longer found. In the homologous series, *n*-O–I, the smectic B phase alone is observed while in the series *n*-O–Br both the smectic A and B phases are exhibited depending on the length of the alkoxyl chain.⁷⁾

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7) Vora has recently studied the phase transitions of the series *n*-O–Br. There is an essential discrepancy between his and the present data besides the slight difference in transition temperatures. According to Vora the smectic B phase may be observed only for the hexyloxy member which is in contrast with the results reported here. This discrepancy could be ascribed to the fact that the authors determined the phase transitions from both the DSC measurements and microscopic observations while Vora employed only an optical microscope to identify the smectic phases. R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **44**, 83 (1978).