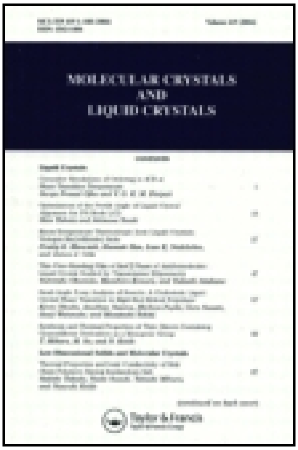

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Liquid Crystalline Properties and Photochromism of 4-Halogeno-N-(4-alkoxysalicylidene) anilines

S. Sakagami [a] , T. Koga [a] & A. Takase [a]

[a] National Institute of Advanced Industrial Science and Technology, Kyushu, Tosu, Saga, Japan

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Liquid Crystalline Properties and Photochromism of 4-Halogeno-N-(4-alkoxysalicylidene) anilines

S. SAKAGAMI, T. KOGA and A. TAKASE

National Institute of Advanced Industrial Science and Technology, Kyushu, Saga, Tosu, Japan

A new homologous series of 4-halogeno-N-(4-alkoxysalicylidene) anilines was synthesized. The phase transitions of these homologues were determined using a differential scanning calorimeter and an ordinary polarizing microscope. It is shown that the homologues exhibit liquid crystalline phases as the terminal alkoxyl chain is increased. A nematic phase is found for only a fluoro-derivative. All the other homologues show a smectic A phase. Furthermore, it is indicated that some members of these homologous series exhibit a photochromic property in the solid state.

Keywords Liquid crystal, smectic A, nematic, photochromism, salicylideneaniline-derivatives

INTRODUCTION

It is well recognized that N-salicylideneaniline (SA) and its derivatives have photochromic and/or thermochromic properties in the crystal and glass state [1–6]. In recent years the study of solid photochromic materials has grown because of their possible application in the optical processing of information. On the other hand, a number of investigations have been undertaken about the relationship between molecular structure and liquid crystallinity [7–11]. Therefore, certain guidelines exist regarding the feature of the molecular structure that favors liquid crystalline formation. The vast majority of compounds exhibiting a liquid crystalline phase may be regarded as a rigid central group (mesogen) and one or two flexible terminal alkyl or alkoxyl chains. Furthermore, SA is one of the good mesogens in liquid crystalline materials because intrahydrogen bonding stabilizes the anil linkage [12].

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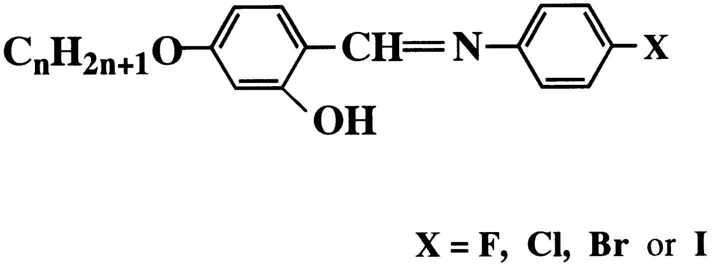
Address correspondence to S. Sakagami, National Institute of Advanced Industrial Science and Technology, Kyushu, Saga, Tosu, 841-0052, Japan. Email: s.sakagami@aist.go.jp



SCHEME 1

The main purpose of this study is to find new mesomorphic compounds having a skeleton of SA. It is well known that the halogen atom is one of the terminal substituents favorable for liquid crystalline formation [7, 10]. Thus, a new homologous series of 4-halogeno-N-(4-alkoxysalicylidene) anilines was synthesized and examined for phase transition behavior and a photochromic property. The members of this homologous series having the following generalized structural formula have been referred to as abbreviations SAFL (*n*), SACL (*n*), SABR (*n*), and SAIO (*n*), respectively. The *n* in parentheses denotes the carbon number of the terminal alkoxyl chain, and the value of *n* ranges from 1 to 8 (see Scheme 1).

EXPERIMENTAL

4-Alkoxy-2-hydroxybenzaldehydes and 4-halogenoanilines were commercially obtained. The substituted benzaldehydes were coupled with the corresponding 4-halogenoanilines by refluxing for about two h in an ethanol solution. The crude product of SAFL (*n*) and SACL (*n*) was purified by successive recrystallization from ethanol. SABR (*n*) and SAIO (*n*) were recrystallized from a mixture of ethanol and benzene by use of activated charcoal. The structure of the products was confirmed, mainly by means of infrared spectroscopy.

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

Ultraviolet photoirradiation was performed by using a Moritex high-pressure mercury lamp (200 W) filtered through a band pass glass filter (transmission maximum, around 365 nm). The irradiation time was 5 min. The absorption spectra in the spectral range of 350–700 nm were obtained with JASCO Ubest spectrometer at room temperature. For UV irradiation and absorption measurements, the polycrystalline film specimen prepared from the melt was held between a pair of quartz plates separated by about 10 μm. The film was allowed to stand overnight in a dry box before measurements.

RESULTS AND DISCUSSION

The phase transition temperatures and photochromism of all the homologues studied here are summarized in Tables 1 through 4. First of all, it should be described that all phase transition temperatures stated above on the basis of the texture change are in good accord with those measured from DSC thermograms. As shown in Table 1, the first three homologues of SAFL (*n*) do not show a liquid crystalline phase. SAFL (4) exhibits both nematic and smectic phases that take place monotropically. Furthermore, it

TABLE 1 The photochromism and the phase transition temperatures of SAFL (*n*) (°C)

n	*Smectic A*	*Nematic*	*Isotropic*	*Photochromism*
1			101	
2			90	○
3			82	○
4	(62)	(63)	77	
5	(68)		70	
6			92	
7	(73)		74	
8	64		76	

The parentheses show the monotropic transitions.

TABLE 2 The photochromism and the phase transition temperatures of SACL (*n*) (°C)

n	*Smectic A*	*Isotropic*	*Photochromism*
1		124	
2		132	○
3	(111)	114	○
4	95	119	○
5	84	122	○
6	77	124	
7	74	123	○
8	67	123	○

TABLE 3 The photochromism and the phase transition temperatures of SABR (*n*) (°C)

n	*Smectic A*	*Isotropic*	*Photochromism*
1		154	○
2		143	○
3	(122)	123	○
4	107	128	○
5	91	129	○
6	80	128	
7	83	131	○
8	73	132	○

TABLE 4 The photochromism and the phase transition temperatures of SAIO (*n*) (°C)

n	*Smectic A*	*Isotropic*	*Photochromism*
1		188	○
2		150	○
3		146	○
4	127	132	○
5	118	131	○
6	114	132	○
7	110	131	○
8	109	133	○

should be stressed that, among all the homologues studied here, the nematic phase is observed only for SAFL (4). This characteristic behavior, that the liquid crystalline phase is observed for homologues with a relatively long terminal alkoxyl chain, is not surprising, because the appearance of the mesomorphic phase is not unusual; it has frequently been observed in other homologous series of liquid crystalline materials [10]. Under polarizing microscopic observation, this smectic phase exhibits a fan-shaped texture or focal conic texture when formed on cooling the nematic phase. In addition, the focal conic or fan textures are easily changed to a pseudoisotropic texture (homeotropic alignment) by cover-slip displacement. These characteristic textures show that this smectic phase can be identified as smectic A [13]. As the end alkoxyl chain is increased, SAFL (8) exhibits the enantiotropic smectic A phase. This finding, that an enantiotropic mesomorphic phase occurs as the terminal alkoxyl chain is increased, is not unusual, because it has been frequently observed for the homologous series of the other liquid-crystalline materials [10]. However, it is unusual that SAFL (6) exhibits no mesomorphic phase, even though unusual phase transitions can rarely be observed for derivatives of SA [14]. This finding is likely to be associated with the different crystal structure of SAFL (6) as compared to that of the other homologues.

Table 2 shows the phase transition temperatures of SACL (*n*). The first two homologues exhibit no mesomorphic phase. The members with $n \geq 3$ exhibit a smectic A phase, although SACL (3) shows a monotropic smectic A phase. The finding that a monotropic smectic phase is observed for SACL (3), which has a relatively short terminal alkoxyl chain, is not unique, as described previously. Furthermore, it is worthwhile to note that the phase transition temperatures of SACL (*n*) are higher than those of SAFL (*n*) because of strong intermolecular attractive force, which is due to the large and heavy substituent of the chlorine atom compared with that of fluorine.

The phase transition temperatures of SABR (*n*) are shown in Table 3. The phase transitions of this homologous series are quite similar to those of SACL (*n*). The first two homologues show no liquid crystalline phase, and all the higher members exhibit an enantiotropic smectic A phase except for SABR (3), which indicates a monotropic transition.Furthermore, as is expected from comparison between chlorine and bromine atoms, the phase transition temperatures of SABR (*n*) are higher than those of SACL (*n*).

Table 4 shows the phase transition temperatures of SAIO (*n*). In the case of this homologous series the first three homologues exhibit no mesomorphic phase. The members with $n \geq 4$ show an enantiotropic smectic A phase. The finding that there exists no monotropic transition in this series is different from the other three homologous series described previously. In addition, the fact that all the phase transitions are enantiotropic might likely be associated with the very high phase transition temperatures, which are due to the terminal large iodine atom. However, a more detailed discussion is impossible at present.

A photochromic property of each homologue is also given in Tables 1 through 4. The open circles in the Tables indicate that photochromism can be observed for the members with the naked eye, regardless of its photochromic intensity. It should be emphasized that the photochromic property cannot be observed in the liquid crystalline phases, i.e., the photochromism can be found only in the solid phase. Among SAFL (*n*), only SAFL (2) and SAFL (3) show the photochromic property. The other homologues do not indicate a photochromic property. Figure 1 shows the absorption spectra in the visible region of SAFL (3) measured before and after irradiation with ultraviolet light at room temperature. Furthermore, it is worthwhile to note that the photochromic-color sample produced by means of irradiation of ultraviolet light reverts to original color after several minutes if irradiation is discontinued. All homologues studied here are yellow or pale yellow when freshly prepared. At room temperature the color of these homologues exhibiting photochromism deepened to reddish orange by irradiation with

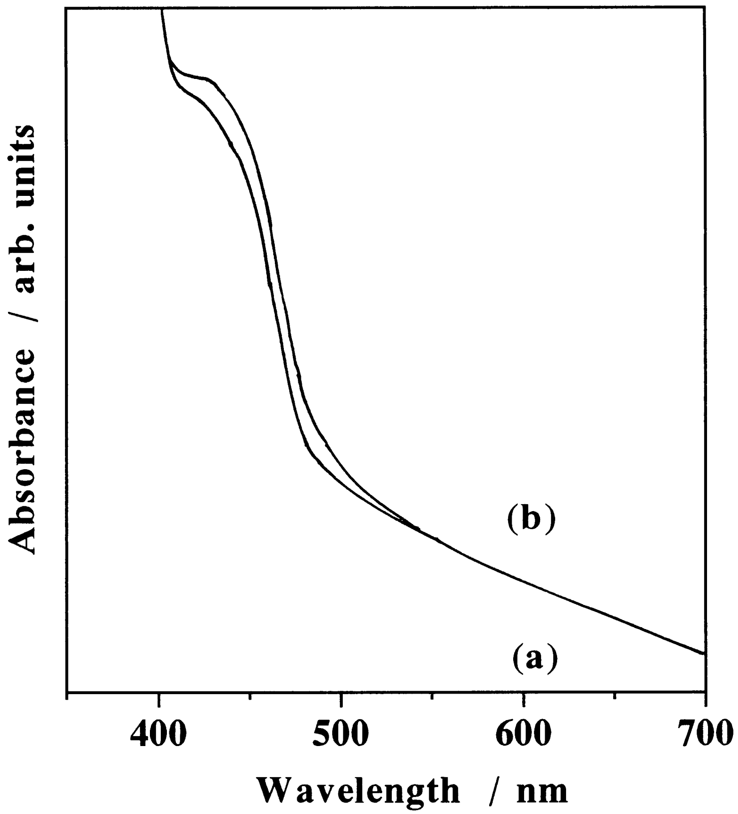


FIGURE 1 Absorption spectra of SAFL (3). Curve (a) before irradiation, curve (b) after irradiation.

ultraviolet light. The fact that photochromism is not found for any homologues described above is likely to be associated with the different crystal structure from that of the other photochromic homologues. In the case of SACL (*n*), all members except for SACL (1) and SACL (6) exhibit a photochromic property, as shown in Table 2. Figure 2 shows the absorption spectra in the visible region of SACL (4) measured at room temperature. In addition, among SABR (*n*) all the homologues except for SABR (6) indicate a photochromic property. Figure 3 shows the absorption spectra in the visible region of SABR (7) measured before and after irradiation with ultraviolet light. As described so far, it is curious and not easily understood that some homologues show photochromic behavior while others in the same homologous series do not. This finding is likely to be associated with

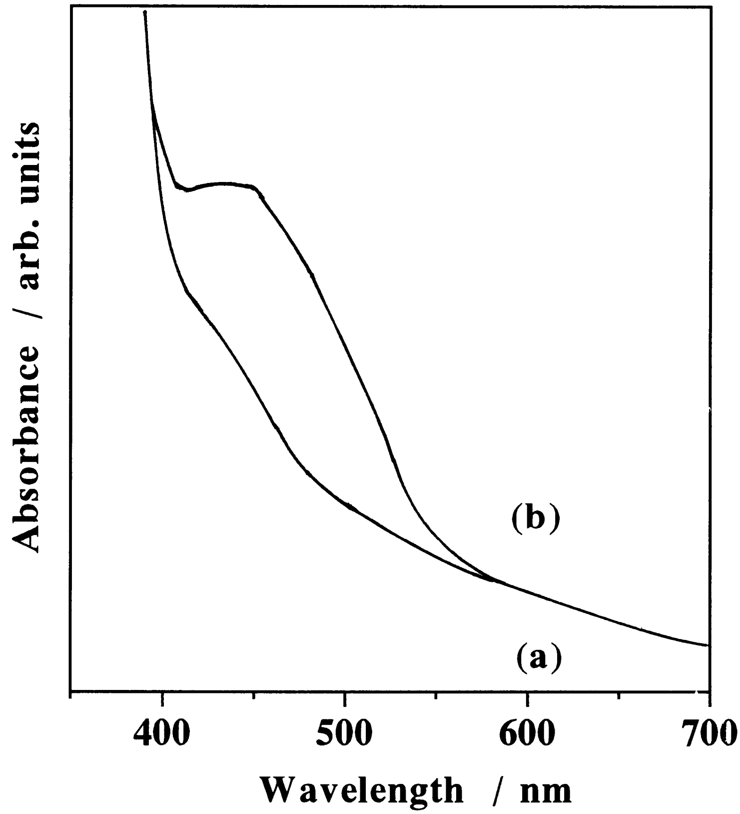


FIGURE 2 Absorption spectra of SACL (4). Curve (a) before irradiation, curve (b) after irradiation.

the complicated differences between them, such as conformational and configurational changes and the different crystalline structure. The photochromic property of SAIO (*n*) is shown in Table 4. It should be noted that in this homologous series all of the homologues indicate a photochromic property. In addition, it should be stated that the photochromic property observed for the five members from SABR (3) to SABR (7) is relatively weak compared with that of the other three homologues. Figure 4 shows the absorption spectra of SAIO (8) measured at room temperature. With regard to this Figure 4 it should be stressed that a clear photochromic change can be observed with the naked eye, although only a slight change is observed in the absorption spectra.

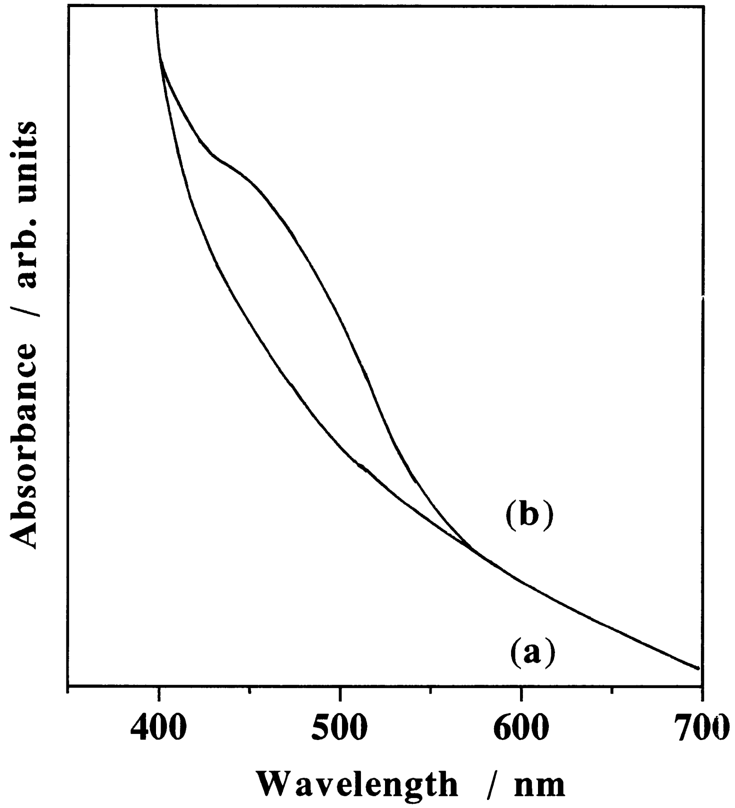


FIGURE 3 Absorption spectra of SABR (5). Curve (a) before irradiation, curve (b) after irradiation.

In addition, it is interesting to note that Table 5 shows the photochromic property as well as the phase transition temperatures of N-(4-alkoxy-2-hydroxybenzylidene) anilines (AHBA (*n*)), which have no substituent of a halogen atom. It is easily understood that no mesomorphic phase is found in this homologous series because no terminal substituent exists. Among these homologues, four members exhibit the photochromic property (shown in Table 5). These findings indicate that the photochromic property is delicately dependent upon the terminal substituent. Figure 5 indicates the absorption spectra in the visible region of AHBA (1).

It has been indicated that photochromic salicylideneaniline exists in enol form in the crystalline state, and that the photochromic change occurs through a hydrogen transfer to the imine nitrogen atom followed by

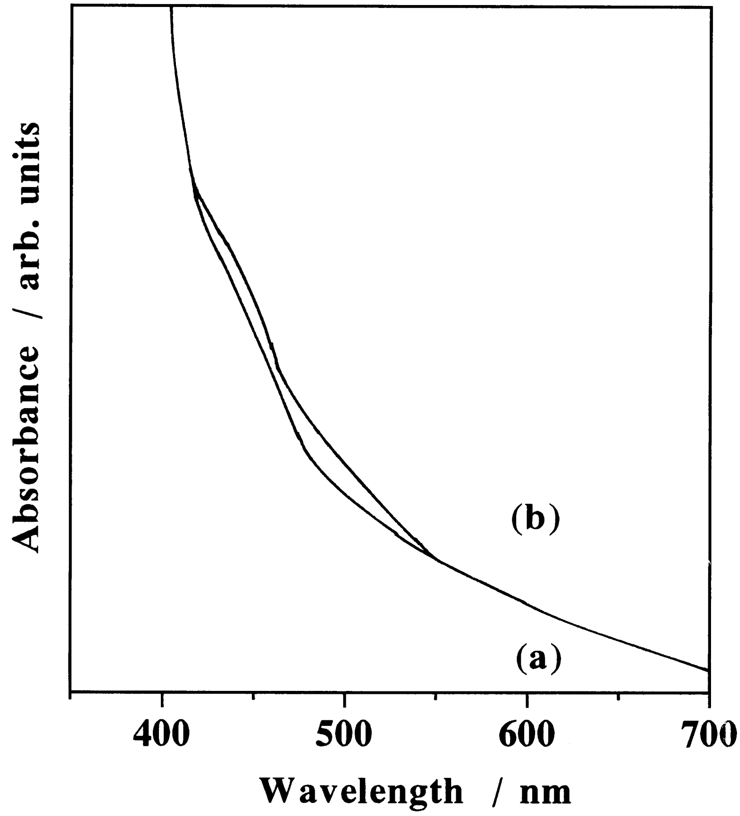


FIGURE 4 Absorption spectra of SAIO (8). Curve (a) before irradiation, curve (b) after irradiation.

TABLE 5 The photochromism and the phase transition temperatures of AHBA (*n*) (°C)

n	*Isotropic*	*Photochromism*
1	62	○
2	75	
3	61	
4	69	○
5	62	○
6	63	
7	52	○
8	54	

geometrical molecular rearrangement [1, 15]. Potashnik and Ottolenghi have suggested that the molecular rearrangement is the cis-trans isomerization due to rotation about the bond, including the benzene ring [4].

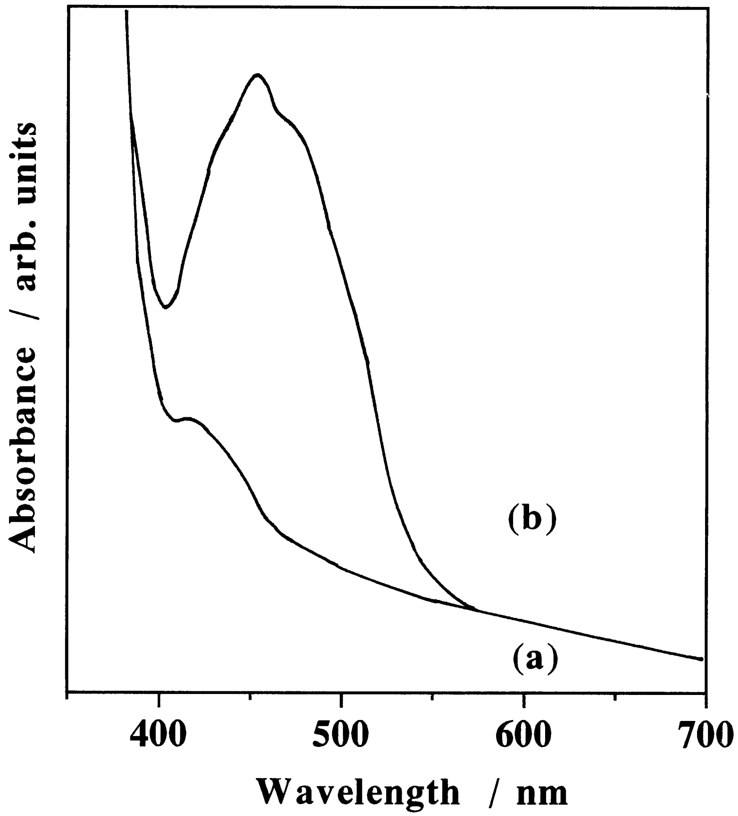


FIGURE 5 Absorption spectra of AHBA (1). Curve (a) before irradiation, curve (b) after irradiation.

From the comparisons among Tables 1 to 5, it is evident that a larger terminal halogen atom is much more favorable for the appearance of photochromism than small hydrogen or fluorine atoms. In other words, the proton transfer and molecular rearrangement are easy for the homologues with large and heavy terminal substituents. Recently, it has been shown by means of X-ray diffraction analysis that an interconversion between the enol and transketo form is responsible for the color change [16]. The finding that no photochromism is observed for any members studied here suggests that in the case of these homologues it is difficult for the transketo molecular isomerization to occur. Finally, it must be pointed out that there is no definite correlation between the length of the terminal alkoxyl chain and the photochromism.

CONCLUSION

The experimental results on the new liquid crystalline homologous series of 4-halogeno-N-(4-alkoxysalicylidene) anilines reveal the following salient features:

1. A Relatively low members of every halogeno-derivative exhibit no mesomorphic phase.
2. The smectic A phase appears as the terminal alkoxyl chain is increased.
3. The nematic phase is observed for only one homologue of the fluoro-derivatives.
4. All the members of the iodo-derivatives exhibit a photochromic property, while no homologues of the other three, halogeno-derivatives show photochromism.

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