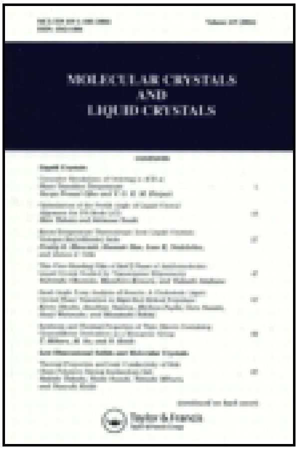

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Liquid Crystalline Properties and Photochromism of 4-Cyano- and 4-Nitro-N-(4-Alkoxysalicylidene) Anilines

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LIQUID CRYSTALLINE PROPERTIES AND PHOTOCHROMISM OF 4-CYANO- AND 4-NITRO-N-(4-ALKOXYSALICYLIDENE) ANILINES

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Two new homologous series of 4-cyano- and 4-nitro-N-(4-alkoxysalicylidene) anilines were synthesized. The phase transitions of these homologues were determined by using a differential scanning calorimeter and an ordinary polarizing microscope. It is shown that all the homologues having a terminal cyano group exhibit a nematic phase. The members with a nitro substituent exhibit a mesomorphic phase as the terminal alkoxyl chain is increased. The homologues of these two homologous series having an alkoxyl chain longer than heptyloxy 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-cyanoderivatives; salicylideneaniline-nitroderivatives

INTRODUCTION

It is well recognized that N-2-hydroxybenzylideneaniline, i.e., N-salicylideneaniline (**SA**) and its derivatives exhibit photochromic and/or thermochromic properties in the crystal and glass state [1–7]. In addition, a number of investigations have been undertaken about the relationship between molecular structure and liquid crystallinity [8–12]. Therefore, certain guides exist with respect to the characteristic feature of the molecular structure that favors liquid crystalline formation. The vast majority of rodlike compounds exhibiting a liquid crystalline phase may be

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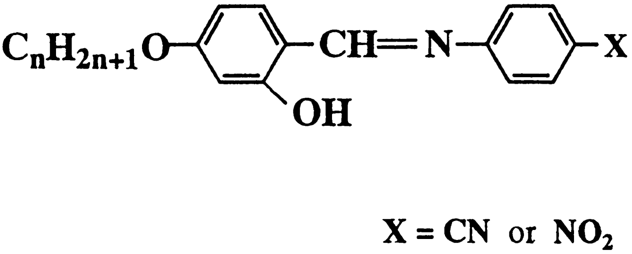
regarded as a rigid central group (mesogen) and one or two flexible terminal alkyl or alkoxyl chains. Furthermore, **SA** is one of the good mesogens in liquid crystalline materials because the anil linkage is stabilized by intramolecular hydrogen bonding [13].

The main purpose of this study is to find new mesomorphic compounds with a mesogen of **SA** and a terminal group having a large dipole moment. Thus, new homologous series of 4-cyano- and 4-nitro-N-(4-alkoxysalicylidene) anilines were synthesized and examined for liquid-crystalline phase transition behavior and a photochromic property. The members of these homologous series, that have the generalized structural formula shown below have been referred to by the abbreviations **SACN**(*n*) and **SANO**(*n*), respectively. The *n* in the parentheses denotes the carbon number of the terminal alkoxyl chain, and the value of *n* ranges from 1 to 8.



EXPERIMENTAL

4-Alkoxy-2-hydroxybenzaldehydes and 4-cyano- and 4-nitroanilines were commercially obtained. The substituted benzaldehydes were coupled with the 4-cyanoaniline and 4-nitroaniline by refluxing for several hours in an ethanol solution. The crude product of **SACN**(*n*) was purified by repeated recrystallization from ethanol. **SANO**(*n*) was recrystallized from a mixture of ethanol and benzene. The structure of the products was confirmed mainly by means of infrared spectroscopy and Raman scattering.

The liquid crystalline texture 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 by using a Shimadzu 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 20 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 are summarized in Tables 1 and 2. First of all, it should be stressed that all of the phase transition temperatures stated above on the basis of

TABLE 1 The Photochromism and the Phase Transition Temperatures of **SACN**(n) (°C)

n	Smectic A	Nematic	Isotropic	Photochromism
1		140	149	○
2		(149)	154	
3		118	125	○
4		89	130	○
5		76	120	
6		84	125	
7	80	91	121	
8	83	112	122	

The parentheses show the monotropic transition.

The open circles indicate that the photochromic property is observed for the member.

TABLE 2 The Photochromism and the Phase Transition Temperatures of **SANO**(n) (°C)

n	Smectic A	Nematic	Isotropic	Photochromism
1			153	
2			157	○
3			152	
4			117	
5			114	
6		101	109	
7	78	103	111	
8	88		110	

The open circle indicates that the photochromic property is observed for the member.

the texture change are in good accord with those measured from DSC thermograms. As shown in Table 1, all of the homologues of **SACN**(n) exhibit a nematic phase, although **SACN**(2) shows the monotropic nematic phase. This finding that only **SACN**(2) exhibits the monotropic nematic phase is not usual, taking into account the fact that all the other homologues, including **SACN**(1), indicate the enantiotropic nematic phase. This result is likely to be associated with the different crystalline structure of **SACN**(2) compared to the other members. However, a more detailed understanding is not available at present. As the terminal alkoxyl chain length is further increased, a smectic phase, as well as the nematic phase, appears, i.e., **SACN**(7) and **SACN**(8) show the smectic phase. Under polarizing microscopic observation, this smectic phase exhibits a fan-shaped texture or a focal conic texture when formed on cooling the nematic phase. In addition, the focal conic or the fan texture is easily changed to a pseudo-isotropic texture (homeotropic alignment) by cover-slip displacement. These characteristic textures show that this smectic phase can be identified as a smectic A [14].

Table 2 shows the phase transition temperatures of **SANO**(n). In this homologous series the first five homologues exhibit no mesomorphic phase. The members with $n \geq 6$ exhibit a liquid crystalline phase. **SANO**(6) exhibits only the enantiotropic nematic phase while **SANO**(7) shows both the nematic and the smectic A phases. As the end alkoxyl chain is further lengthened, **SANO**(8) exhibits only the smectic A phase. This characteristic behavior, that the smectic phase is observed for homologues with a relatively long terminal alkoxyl chain, is not surprising since the appearance of the smectic phase is not unusual; it has frequently been observed in other homologous series of liquid crystalline materials [8,11].

It is evident from comparison between Table 1 and Table 2 that the cyano substituent is much more favourable for the liquid crystalline formation than the nitro group. This tendency is easily understood by taking account of the nonlinear structure of the nitro substituent, and it is, in general, observed for the other liquid crystalline homologous series [8,11]. Considering the finding that all the members having a cyano substituent exhibit a mesomorphic phase, it is interesting to synthesize the homologous series having a cyano substituent at *ortho* and *meta* positions (hereafter abbreviated as *o*-**SACN**(n) and *m*-**SACN**(n), respectively). The phase transition temperatures of *o*-**SACN**(n) and *m*-**SACN**(n) are compiled in Tables 3 and 4, respectively. It should be emphasized that neither *o*-**SACN**(n) nor *m*-**SACN**(n) exhibits a liquid crystalline phase. This finding can be understood without difficulty by taking their molecular structures into account. In general, lateral substituents sterically force the interacting molecules apart as well as hinder the packing of molecules in a liquid crystalline structure, and cause a significant depression in the

TABLE 3 The Photochromism and the Phase Transition Temperatures of *o*-**SACN**(*n*) (°C)

n	Isotropic	Photochromism
1	154	○
2	106	○
3	86	
4	103	
5	70	○
6	57	
7	80	
8	63	○

The open circles indicate that the photochromic property is observed for the member.

clearing point. Furthermore, it is well recognized that the lateral substituents enforce a full molecular-broadening influence and thus reduce the lateral intermolecular force of attraction [8]. This force—responsible for maintaining order in the liquid crystalline phases—is, the dispersion force which will decrease rapidly with increasing separation of the long molecular axes. Thus, mesomorphic thermal stability decreases regularly as the broadening effect or size of the lateral substituent increases. In brief, introduction of the lateral substituents is unfavorable for the liquid crystalline formation. Considering these characteristics, the finding about the behavior of *o*-**SACN**(*n*) and *m*-**SACN**(*n*) in which a fairly bulky cyano-substituent is introduced at *ortho* or *meta* positions is reasonably understood.

TABLE 4 The Photochromism and the Phase Transition Temperatures of *m*-**SACN**(*n*) (°C)

n	Isotropic	Photochromism
1	136	
2	109	
3	82	
4	80	
5	70	
6	69	
7	71	
8	62	○

The open circle indicates that the photochromic property is observed for the member.

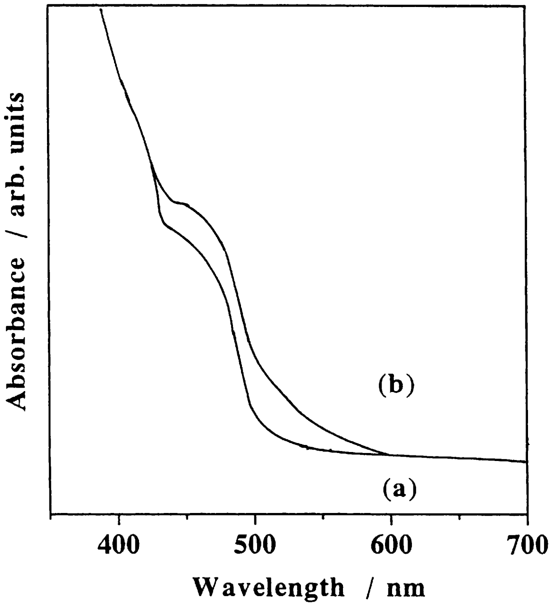


FIGURE 1 Absorption spectra of **SACN**(1): curve (a) before irradiation, (b) after irradiation.

Photochromic property of each homologue of **SACN**(*n*) and **SANO**(*n*) is also given in Tables 1 and 2, respectively. The open circles in the Tables show that photochromism can be observed for the members with the naked eye, regardless of its intensity of photocoloration. Among **SACN**(*n*), only **SACN**(1), **SACN**(3), and **SACN**(4) show relatively strong photochromic property. The other homologues do not indicate a photochromic property. Figure 1 shows the absorption spectra in the visible region of **SACN**(1) measured before and after irradiation with ultraviolet light at room temperature. In addition, it should be described that this homologue **SACN**(1) exhibits the strongest photochromic property of all the members studied here. 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 of ultraviolet light. In the case of **SANO**(*n*) only one homologue, i.e., **SANO**(2), exhibited a weak photochromic property, as shown in Table 2. Figure 2 shows the absorption spectra in the visible region of **SANO** (2) measured at room temperature.

The photochromism of *o*-**SACN**(*n*) and *m*-**SACN**(*n*) is also shown in Tables 3 and 4, respectively. Among *o*-**SACN**(*n*), four homologues exhibit a

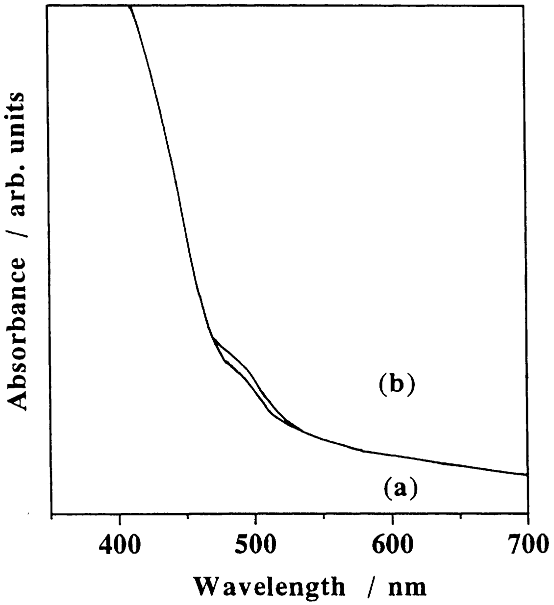


FIGURE 2 Absorption spectra of **SANO**(2): curve (a) before irradiation, (b) after irradiation.

photochromic property. Figure 3 shows the absorption spectra in the visible region of *o*-**SACN**(1) measured at room temperature. In the case of *m*-**SACN**(*n*) only one member, i.e., *m*-**SACN**(8), exhibits relatively strong photochromism. Figure 4 indicates the absorption spectra in the visible region of *m*-**SACN**(8). The fact that neither *o*-**SACN**(*n*) nor *m*-**SACN**(*n*) exhibits the liquid crystalline phase while some members show the photochromic property indicates that there exists no definite correlation between the photochromic property and the liquid crystallinity. In addition, it is evident that a photochromic property does not depend on the length of terminal alkoxyl chain (see Tables 1 to 4). In other words, it is curious and cannot be understood easily that some homologues show photochromic behavior while the others in the same homologous series do not. These results are likely to be associated with the complicated difference such as the conformational and configurational changes as well as the different crystalline structure.

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 a geometrical molecular rearrangement [1,15]. Potashnik and Ottolenghi

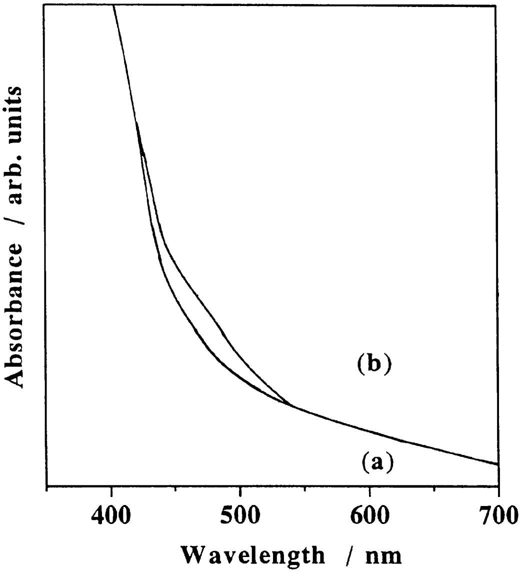


FIGURE 3 Absorption spectra of *o*-**SACN**(1): curve (a) before irradiation, (b) after irradiation.

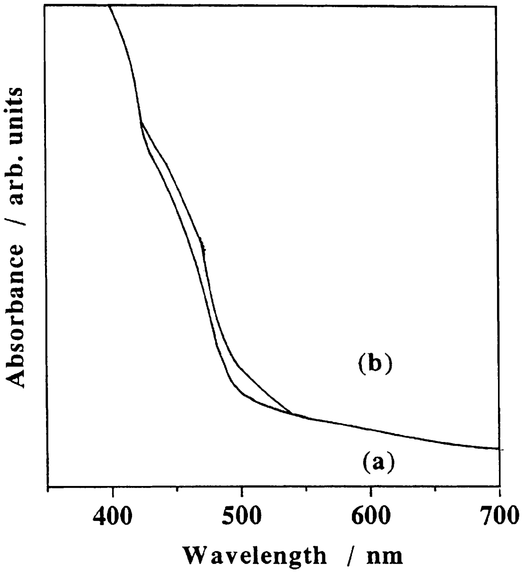


FIGURE 4 Absorption spectra of *m*-**SACN**(8): curve (a) before irradiation, (b) after irradiation.

have suggested that the molecular rearrangement is the ***cis-trans*** isomerization due to rotation about the bond including the benzene ring [4]. It has also been suggested by means of Raman spectra that the photochromic behavior can be explained by a change in the twist angle of the aniline ring to the salicylidene part of the molecule [16]. Recently, it has been shown by use of X-ray diffraction analysis that an interconversion between the enol and trans-keto form is responsible for the color change [17]. 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 trans-keto molecular isomerization to occur owing to the difficulty of rotation of the aniline ring.

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