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Liquid crystalline properties and photochromism of 4-alkyl-*N*-(4-alkloxysalicylidene)anilines

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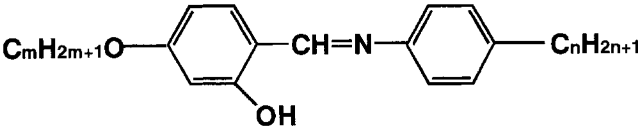
Eight new homologous series of 4-alkyl-*N*-(4-alkloxysalicylidene)anilines were synthesized. The phase transitions of these homologues were determined using differential scanning calorimetry and polarizing optical microscopy. The homologues began to exhibit liquid crystalline phases as the terminal alkyl or alkoxyl chains were lengthened. In addition, some members of these homologues series exhibited photochromism in the solid state.

1. Introduction

A number of investigations have been carried out 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 crystal formation. The vast majority of compounds exhibiting liquid crystalline phases may be regarded as having a rigid molecular central group with one or two flexible terminal alkyl or alkoxyl chains. On the other hand, it is well recognized that *N*-salicylideneaniline (SA) and its derivatives have photochromic properties in the crystal and glass states [6–11]. In addition, much attention has been paid, from fundamental and optical viewpoints, to molecular systems that exhibit photochromism [12, 13].

The main purpose of this study is to find new mesomorphic compounds having the SA skeleton. Another aim is to obtain liquid crystalline compounds with low melting point by changing the length of the terminal alkyl and alkoxyl chains. New homologous series of 4-alkyl-*N*-(4-alkloxysalicylidene)anilines were therefore synthesized, and their phase transition behaviour examined. The members of these homologous series, having the generalized structural formula depicted below, are referred to as *m*-SA-*n* in which *m* and *n* denote the carbon number of the terminal alkoxyl and alkyl groups, respectively.



2. Experimental

4-Alkoxy-2-hydroxybenzaldehydes and 4-alkylanilines were obtained commercially. The substituted benzaldehyde was coupled with the required 4-alkylaniline by heating under reflux for about 1 hour in ethanol solution. The crude products were purified by repeated crystallization from ethanol. The structure of the products was confirmed mainly by means of infrared spectroscopy.

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. Transition temperatures were measured 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 using a Moritex high pressure mercury lamp (200 W) with a band pass glass filter (transmission maximum around 365 nm). The absorption spectra in the range 250–700 nm were obtained with a JASCO Ubest spectrometer at room temperature. For UV irradiation and absorption measurement, 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.

3. Results and discussion

The phase transition temperatures and photochromism of all the homologues studied here are summarized in tables 1 to 8. First, it should be mentioned that all the phase transition temperatures quoted on the basis of texture change are in good accord with those measured by DSC, except for one smectic to smectic transition which is described later in detail. As shown in table 1, all the 1-SA-*n* series exhibit a nematic phase, except for the first member. This finding, that the enantiotropic nematic phase is observed only for homologues with a

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Table 1. Photochromism and phase transition temperatures (°C) of 1-SA-*n* compounds.

n	Nematic	Isotropic	Photochromism
1		93	○
2	(48)[a]	58	
3	57	74	○
4	43	64	○
5	74	79	○
6	61	69	○
7	42	78	○
8	44	74	○

[a] Parenthesis indicate a monotropic transition.

Table 2. Photochromism and phase transition temperatures (°C) of 2-SA-*n* compounds.

n	Smectic C	Nematic	Isotropic	Photochromism
1		(87)[a]	99	○
2		66	70	○
3		67	94	○
4		63	85	
5		73	97	○
6		53	88	○
7		45	96	○
8	36	57	91	○

[a] Parenthesis indicate a monotropic transition.

Table 3. Photochromism and phase transition temperatures (°C) of 3-SA-*n* compounds.

n	Smectic C	Smectic A	Nematic	Isotropic	Photochromism
1				80	○
2			(47)[a]	49	
3			(75)[a]	76	○
4			52	69	○
5			49	82	○
6	32		46	76	
7	46	57	63	84	○
8	28	41	69	79	○

[a] Parenthesis indicate monotropic transitions.

Table 4. Photochromism and phase transition temperatures (°C) of 4-SA-*n* compounds.

n	Smectic C	Smectic A	Nematic	Isotropic	Photochromism
1			74	83	
2			57	69	○
3			47	90	○
4	34		36	83	○
5	36		51	94	○
6	34		64	89	○
7	38		75	95	○
8	35	70	83	91	

Table 5. Photochromism and phase transition temperatures (°C) of 5-SA-*n* compounds.

n	Smectic C	Smectic A	Nematic	Isotropic	Photochromism
1			(75)[a]	76	○
2			60	64	○
3	(32)[a]		33	85	○
4	24		48	79	○
5	39		61	89	○
6	35		72	85	○
7	34		80	91	○
8	39	76	84	87	

[a] Parenthesis indicate monotropic transitions.

Table 6. Photochromism and phase transition temperatures (°C) of 6-SA-*n* compounds.

n	Smectic C	Smectic A	Nematic	Isotropic	Photochromism
1			66	85	
2			68	75	○
3	(42)[a]		51	92	
4	43		56	86	○
5	49		72	96	
6	38		80	92	○
7	45		89	96	○
8	37	90	94	95	○

[a] Parenthesis indicate a monotropic transition.

Table 7. Photochromism and phase transition temperatures (°C) of 7-SA-*n* compounds.

n	Smectic C	Smectic A	Nematic	Isotropic	Photochromism
1			63	82	○
2			55	74	○
3	(50)[a]		54	89	○
4	47		64	86	○
5	53		79	96	○
6	33		85	92	○
7	43	94	95	97	○
8	34	89		95	

[a] Parenthesis indicate a monotropic transition.

relatively long alkoxyl chain, is not unusual, for the appearance of the mesomorphic phase has frequently been observed as the alkoxyl chain length increases in other homologous series of liquid crystalline materials [4]. There are previous reports concerning the photochromic properties or phase transition temperatures of some 1-SA-*n* compounds [14, 15].

All members of the 2-SA-*n* series show a nematic phase although 2-SA-1 exhibits a monotropic nematic

Table 8. Photochromism and phase transition temperatures (°C) of 8-SA-*n* compounds.

n	Smectic C	Smectic A	Nematic	Isotropic	Photochromism
1			67	85	
2			44	78	
3	(56)[a]		57	93	○
4	36		68	88	
5	47	85	86	97	○
6	33	88	89	94	
7	36	96	97	98	○
8	35	98		99	

[a] Parenthesis indicate a monotropic transition.

phase (see table 2). Furthermore, it should be stressed that 2-SA-8 exhibits a smectic phase (smectic I) as well as a nematic phase. This characteristic behaviour, that the smectic phase is observed only for homologues with a relatively long terminal alkyl chain, is not surprising; it has frequently been observed in other homologous series of liquid crystalline compounds [1, 4]. Under polarizing optical microscopy (POM), this smectic phase exhibits broken fan-shaped or smectic schlieren textures when formed on cooling from the nematic phase. In addition, no pseudo-isotropic texture (homeotropic alignment) is observed on cover-slip displacement. From these characteristic textures, it seems likely that the smectic I phase can be identified as smectic C [16]. In the case of 3-SA-*n*, another smectic (smectic II) phase, besides the smectic I phase, appears as the terminal alkyl chain is increased, as shown in table 3.

The phase transition from smectic I to smectic II can be confirmed without difficulty by a mircroscopic texture change. On heating the smectic I phase showing a smectic schlieren texture, a homeotropic alignment is attained at the phase transition to the smectic II phase. On the other hand, on cooling the nematic state, focal-conic or fan-shaped textures are observed for the smectic II phase. It should be emphasized that the phase transition of the smectic I to the smectic II could not be detected by DSC due to the very small enthalpy change. Among the several smectic modifications, only the smectic C–smectic A transition is a second order transition. Both the DSC studies and the characteristic behaviour of the textures indicate that the smectic II phase can be identified as smectic A.

The liquid crystal behaviour versus terminal alkyl chain length of the 4-SA-*n*, 5-SA-*n*, and 6-SA-*n* series is quite similar to that of 3-SA-*n* (tables 4, 5, 6). In other words, two smectic phases as well as the nematic phase are observed as the terminal alkyl chain length is increased. In the case of series 7-SA-*n* and 8-SA-*n*, the relationship between liquid crystalline behaviour and terminal alkyl chain length is apparently different from that of the lower homologous series, as shown in tables 7 and 8, e.g. 7-SA-8 and 8-SA-8 do not exhibit the nematic phase. This finding that the nematic phase disappears for homologues having a fairly long alkyl chain is one of the common features in liquid crystalline homologous series [1, 4]. Furthermore, it is worthwhile to point out that 5-SA-4 melts at 24°C as shown in table 5, and thus may be regarded as a room temperature nematic liquid crystal.

The photochromism of each homologue is indicated in tables 1 to 8. The open circles in the tables indicate that photochromism can be observed for these members with the naked eye, regardless of photochromic intensity. All members of series 1-SA-*n* except for 1-SA-2 show photochromism. Photochromism is also found for each member of series 2-SA-*n* except for 2-SA-3. Figure 1 shows the absorption spectra in the visible region for 2-SA-6, measured before and after irradiation with UV light at room temperature. All the homologues studied here are yellow or pale yellow when freshly prepared. At room temperature the colour of the homologues exhibiting photochromism deepened to reddish orange on irradiation with UV light. The absence of photochromism in any members described above is likely to be associated with a crystal structure differing from that of the photochromic homologues. However, a more

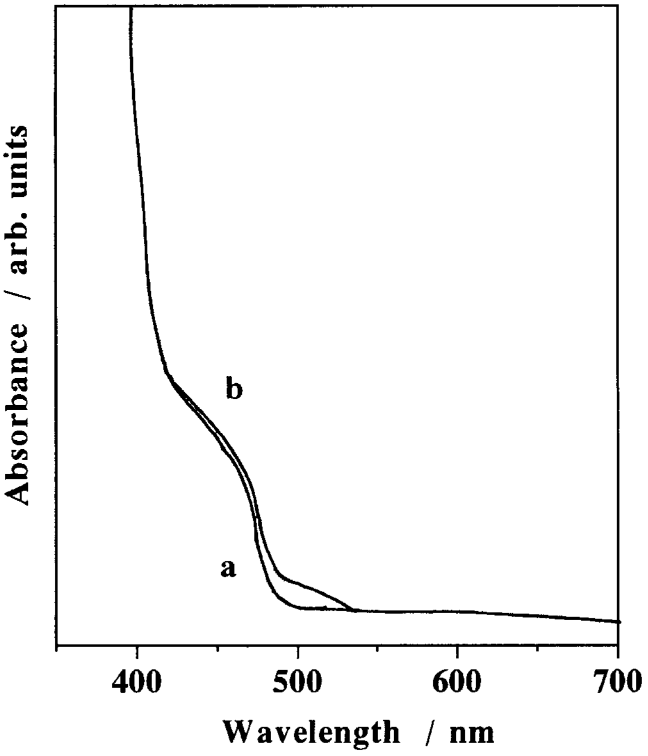

Figure 1. Absorption spectra of 2-SA-6: curve a before irradiation, curve b after irradiation.

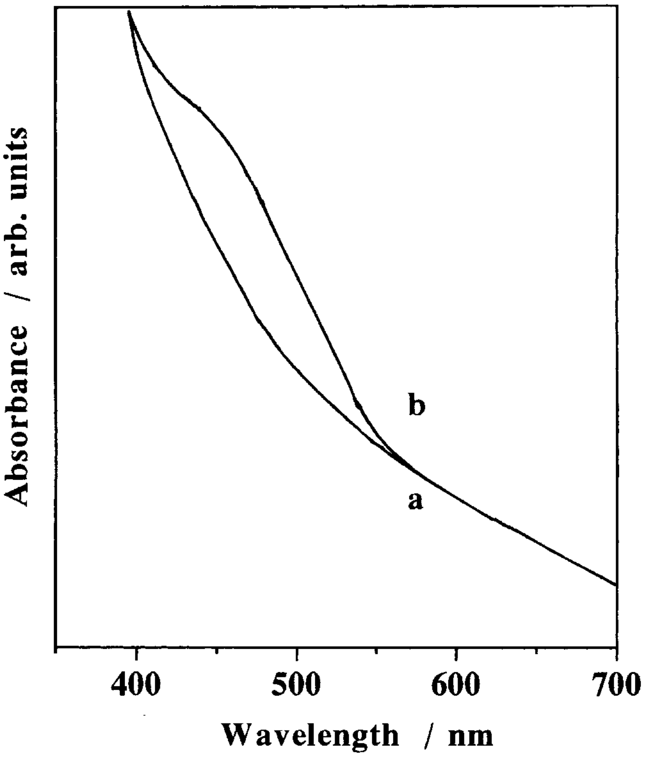

Figure 2. Absorption spectra of 3-SA-3: curve a before irradiation, curve b after irradiation.

detailed understanding is not available at present. Figure 2 shows the absorption spectra of 3-SA-3 which exhibit relatively strong photochromisms among all the compounds studied here.

It has previously been indicated that photochromic salicylideneanilines exist in the enol form in the crystal phase, and that the photochromic change occurs through a hydrogen transfer to the imine nitrogen atom followed by a geometrical molecular rearrangement [6, 17]. Potashnik and Ottolenghi have suggested that the molecular rearrangement is *cis–trans*-isomerization due to rotation about the bond including the benzene ring [18]. Recently, it has been indicated by X-ray diffraction analysis that an interconversion between the enol and *trans*-keto forms is responsible for the colour changes [19]. Where no photochromism is observed for a series member, it appears difficult for the *trans*-keto molecular isomerization to occur. It should be noted that there is no definite correlation between the length of the terminal alkyl or alkoxyl chains and photochromism.

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