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Liquid Crystals

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Liquid crystalline properties and photochromism of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-methoxy and -ethoxy anilines

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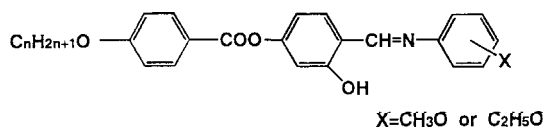
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New homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-methoxy and -ethoxyanilines were synthesized. The phase transitions of these homologues were determined using differential scanning calorimetry and an polarizing microscopy. *para*-substituted homologues exhibit a nematic phase, while *ortho*-substituted members do show no mesomorphic phase. In addition, some members of these homologous series exhibit a photochromic property in the solid state.

1. Introduction

A number of investigations have been carried out on the relationship between molecular structure and liquid crystallinity [1–5]. 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 alkoxy chains. On the other hand, it is well known that *N*-salicylideneaniline (SA) and its derivatives have photochromic and/or thermo-chromic properties in the crystalline and glassy states [6–11]. Moreover, much attention has been paid from fundamental and optical points of view to molecular systems that exhibit photochromisms [12, 13].

The aim of this study was to find a new mesomorphic compound having the SA skeleton. Thus, new homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-methoxy and -ethoxyanilines were synthesized, and examined for phase transition behaviour. The members of these homologous series having the generalized structural formula shown below are referred to as *n*-OMA, *n*-MMA, *n*-PMA for homologues having a methoxy substituent, and *n*-OEA, *n*-MEA, *n*-PEA for the members having an ethoxy group; *n* denotes the number of carbon atoms in the alkoxy end group; O, M, P denote *ortho*, *meta*, *para*, respectively.



2. Experimental

4-*n*-Heptyloxy-, 4-*n*-hexyloxy-, 4-*n*-butoxy-, 4-ethoxy- and 4-methoxybenzoyl chlorides were obtained commercially. The other acid chlorides were synthesized from commercial 4-*n*-alkoxybenzoic acids. The 4-*n*-alkoxybenzoic acids were converted to acid chlorides by treatment with thionyl chloride in benzene solution as solvent. After completion of the reaction, excess thionyl chloride and the solvent were removed by evaporation. These acid chlorides and 2,4-dihydroxybenzaldehyde (recrystallized from benzene prior to use) were esterified by stirring the mixture with an equimolar amount of triethylamine. After standing overnight, the solid triethylamine hydrochloride formed was removed by filtration. The solvent was evaporated, and the solid residue purified by recrystallization from a mixture of hexane and benzene. Finally, the substituted benzaldehydes thus obtained were coupled with a corresponding aniline by heating under reflux in ethanol solution. The crude products were purified by successive recrystallization from a mixture of ethanol and benzene. The molecular structure of the compounds thus purified were confirmed by 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 using a Shimadzu differential scanning calorimeter (DSC). All measurements were carried out under a flow of nitrogen gas to prevent decomposition of the sample.

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UV irradiation was performed 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 250–700 nm were obtained with a JASCO Ubest-35 spectrometer at room temperature. For UV irradiation and absorption measurement, the polycrystalline film prepared from the melt was held between a pair of quartz plates separated by about 10 μm . The sample 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 6.

3.1. Phase transitions

All of phase-transition temperatures given in the tables, on the texture change, are in good accord with those measured by DSC. As shown in tables 1 and 4, *n*-PMA and *n*-PEA exhibit an enantiotropic nematic phase. This is easily understood by taking account of the three benzene rings and the resulting rod-like molecular structure. Table 2 indicates that *n*-MMA compounds have a nematic phase for *n* greater than 2. The finding that the nematic phase of *n*-MMA are monotropically observed except for 6-MMA is explained by the long

Table 1. Photochromism (indicated by \odot) and phase transition temperatures ($^{\circ}\text{C}$) of *n*-PMA compounds

<i>n</i>	Nematic	Isotropic	Photochromism
1	187	299	
2	155	308	
3	138	293	
4	112	288	
5	109	278	
6	110	266	
7	105	260	
8	100	253	\odot

Table 2. Photochromism (indicated by \odot) and phase transition temperatures ($^{\circ}\text{C}$) of *n*-MMA compounds

<i>n</i>	Nematic	Isotropic	Photochromism
1		117	\odot
2	(91) ^a	113	\odot
3	(60)	112	\odot
4	(61)	95	\odot
5	(76)	77	\odot
6	82	86	\odot
7	(77)	85	\odot
8	(86)	103	\odot

^a The parentheses show monotropic transitions.

Table 3. Photochromism (indicated by \odot) and phase transition temperatures ($^{\circ}\text{C}$) of *n*-OMA compounds

<i>n</i>	Nematic	Isotropic	Photochromism
1		150	
2		131	
3		96	
4		117	
5		115	
6		99	
7		87	
8		84	

Table 4. Photochromism (indicated by \odot) and phase transition temperatures ($^{\circ}\text{C}$) of *n*-PEA compounds

<i>n</i>	Nematic	Isotropic	Photochromism
1	137	304	\odot
2	162	305	\odot
3	133	297	
4	117	288	
5	116	280	\odot
6	111	272	
7	105	253	
8	122	246	

Table 5. Photochromism (indicated by \odot) and phase transition temperatures ($^{\circ}\text{C}$) of *n*-MEA compounds

<i>n</i>	Nematic	Isotropic	Photochromism
1		127	\odot
2		122	\odot
3		110	
4		84	\odot
5		90	\odot
6		87	\odot
7		86	\odot
8		84	\odot

Table 6. Photochromism (indicated by \odot) and phase transition temperatures ($^{\circ}\text{C}$) of *n*-OEA compounds

<i>n</i>	Nematic	Isotropic	Photochromism
1		121	
2		132	
3		96	
4		123	
5		125	
6		115	
7		100	
8		95	

molecular axes being forced apart by the lateral substituent, reducing intermolecular forces of attraction and thus lowering liquid crystalline thermal stability. The unusual behaviour of 6-MMA suggests that its

crystalline structure is different from that of the other members. However, a more detailed understanding is not available at present.

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 clearing point. As mentioned previously, it is well recognized that a lateral substituent results in molecular broadening, and thus reduces the lateral intermolecular force of attraction [1]. The force responsible for maintaining order in the liquid crystalline phases is a 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 substituent increases. In brief, the introduction of lateral substituents is unfavourable for liquid crystal formation; the absence of mesomorphic phases in *n*-OMA, *n*-MEA and *n*-OEA compounds is therefore understandable. In addition, the finding that an enantiotropic nematic phase is not found in *n*-MMA compounds except for 6-MMA, as shown in table 2, may also be understood by this deviation of molecular structure from a rod-like shape.

3.2. Photochromism

The occurrence of photochromism for each homologue is given in tables 1–6. The open circles in the tables show that definite photochromism is observed for the member. In the case of *n*-OMA, no members exhibit a photochromism. As shown in table 2, all *n*-MMA members show photochromism. Table 1 indicates that the photochromism is also found for *n*-PMA as the terminal alkoxy group is lengthened. 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 red–orange under UV irradiation.

Figure 1 shows the absorption spectra of 3-MMA in the visible region, measured before and after irradiation with the UV light at room temperature. The absence of photochromism for any members described above is likely to be associated with a different crystal structure from that of the photochromic homologues. It has been indicated that the photochromic change occurs through a hydrogen transfer followed by a geometrical molecular rearrangement [6, 14]. Potashnik and Ottolenghi have suggested that the molecular rearrangement is the keto-*trans* isomerization caused by rotation about the bond including the central benzene ring [15]. Where photochromism is not observed for any members of a series, it seems to be difficult for the keto-*trans* molecular isomerization to occur. Figure 2 indicates the absorption spectra of 2-PEA before and after UV irradiation.

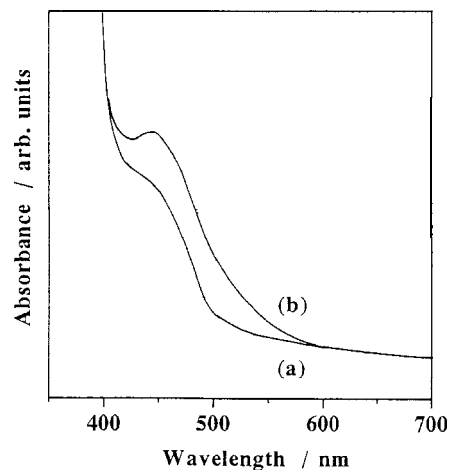


Figure 1. Absorption spectra of 3-MMA. (a) Before irradiation; (b) after irradiation.

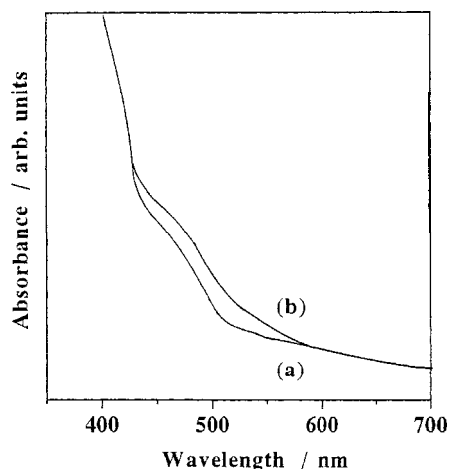


Figure 2. Absorption spectra of 2-PEA. (a) Before irradiation; (b) after irradiation.

Finally, it is observed that all the *n*-MMA and *n*-MEA members, except for 3-MEA, show photochromism, indicating that *meta*-substituted homologues are favourable for the occurrence of photochromism. It has to be stated that there is no definite correlation between photochromism and the length of the terminal alkoxy chain.

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