Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Spectroscopic study of liquid crystalline *N*-[4-(4-*n*-alkoxybenzoyloxy)2-hydroxybenzylidene]hydroxyanilines

S. Sakagami[a]; T. Koga[a]; M. Nakamizo[a]; A. Takase[a]
[a] Kyushu National Industrial Research Institute, Tosu, Saga 841-0052, Japan,

To cite this Article Sakagami, S. , Koga, T. , Nakamizo, M. and Takase, A.(2001) 'Spectroscopic study of liquid crystalline *N*-[4-(4-*n*-alkoxybenzoyloxy)2-hydroxybenzylidene]hydroxyanilines', Liquid Crystals, 28: 3, 347 — 350

To link to this Article: DOI: 10.1080/02678290010017999

URL: http://dx.doi.org/10.1080/02678290010017999

Liquid Crystals, 2001, Vol. 28, No. 3, 347–350

Spectroscopic study of liquid crystalline *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]hydroxyanilines

S. SAKAGAMI, T. KOGA, M. NAKAMIZO and A. TAKASE*
Kyushu National Industrial Research Institute, Tosu, Saga 841-0052, Japan

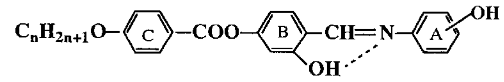
(*Received 4 May 2000; accepted 21 September 2000*)

New homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]hydroxyanilines were synthesized. All 4-hydroxyaniline derivatives exhibited a nematic phase, while 3-hydroxyaniline and 2-hydroxyaniline derivatives exhibited only a nematic phase as the terminal alkoxy group was lengthened. Infrared spectra suggest that the 4-hydroxyaniline derivatives form intermolecular hydrogen bonding of the single bridge type, while the 3-hydroxy and 2-hydroxy derivatives form the polymer type. The Raman band at around 1360 cm^{-1} exhibited large differences in intensity among these derivatives. This can be explained by the effect of intermolecular or hydrogen bonding molecular conformation.

1. Introduction

A number of investigations have been conducted 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. Therefore, almost all rod-like liquid crystals (LCs) reported so far have *para*-substituted terminal groups. Furthermore, it has been indicated that in hydroxyl compounds hydrogen bonding plays an important role in the liquid crystalline behaviour [6]. In fact, Gray has shown that a hydroxyl substituent is unfavourable for mesogen formation because intermolecular hydrogen bonding raises the melting point above the liquid crystalline phase to the isotropic liquid transition temperature [1].

On the other hand, it is well recognized that *N*-salicylideneaniline (SA) and its derivatives are photochromic and/or thermochromic [7–12]. In recent years the study of solid photocromic and thermochromic materials has grown because of their possible application in the optical processing of information. The purpose of this study is to find new mesomorphic compounds having a SA skelton and a terminal hydroxy group. Thus, three homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-4-hydroxyanilines [POH(*n*)], -3-hydroxyanilines MOH(*n*)], and -2-hydroxyanilines [OOH(*n*)] having the following structural formula (**1**) were synthesized and examined for their phase transition behaviour. An intramolecular hydrogen bond is formed between the OH group of ring B and the nitrogen of the Shiff's base [7–12].



OH: *para* POH(*n*)
meta MOH(*n*)
ortho OOH(*n*)

It is of current interest to understand better the relationship between molecular structure and the occurrence of mesophases in LC compounds. Vibrational spectroscopy has been used effectively to study the molecular structures of LCs in various phases [13, 14]; to study the occurrence of the LC phase for the new homologous series, infrared and Raman spectra were measured. The IR bands relating to hydrogen bonding differed in intensity and frequency among members of the three series. The vibrational measurement suggested that hydrogen bonding plays an essential role in the occurrence of the LC phase for these homologous series.

2. Experimental

4-*n*-Alkoxybenzoic acids obtained commercially were converted to acid chlorides by treatment with thionyl chloride in benzene solution. After completion of the reaction, the excesses of thionyl chloride and solvent were removed. The acid chlorides were esterified by reaction with 2,4-dihydroxybenzaldehyde (which had been recrystallized from benzene before use) in a mixture of tetrahydrofuran and ether plus triethylamine. After standing overnight, the triethylamine hydrochloride formed was removed by filtration, the solvent mixture

---

*Author for correspondence, e-mail: takase@kniri.go.jp

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010017999

was evaporated, and the solid residue was recrystallized from hexane and benzene. The substituted benzaldehydes thus obtained were finally coupled with a corresponding aniline by heating under reflux in ethanol solution. The crude product was purified by successive recrystallizations from a mixture of ethanol and benzene.

The homologous series having the generalized structural formula shown above are respectively referred to as POH(*n*), MOH(*n*) and OOH(*n*), in which *n* denotes the number of carbons in the terminal alkoxyl group. The liquid crystalline texture and phase transition temperatures were determined by means of a Nikon polarizing microscope equipped with a Mettler FP-52 microfurnace. Checks on the transition temperatures were made using a Shimazu differential scanning calorimeter (DSC). All measurements were carried out under a flow of nitrogen to prevent sample decomposition.

The Raman spectra were obtained with a SPEX 1403 double monochromator equipped with a photon counting system in a back-scattering geometry. 632.8 nm radiation from a helium-neon laser (NEC GLG 7500) was used to excite the Raman spectra to avoid fluorescence in these compounds. IR spectra were measured with a Bio-Rad Digilab FTS-60c/d Fourier transform IR spectrometer. Samples for infrared analysis were prepared in the form of a 10 mm diameter disc by compressing a mixture of specimen and KBr powder.

3. Results and discussion

The phase transition temperatures of POH(*n*) compounds are summarized in the table. In this series all of the homologues exhibit an enantiotropic nematic phase. Although, as mentioned previously, a terminal hydroxyl group is unfavourable for the formation of mesomorphic phases, this finding is understood without difficulty by taking account of the presence of three benzene rings and the rod-like molecular structure.

The phase transition temperatures of MOH(*n*) compounds are shown in the table. It is apparent that enantiotropic mesophorphic phases do not appear in this homologous series, except for MOH(4); only a monotropic nematic phase was observed for relatively higher homologues. From the table, it is also evident that the phase transition temperatures to isotropic liquid of MOH(*n*) compounds are much lower than those of POH(*n*) compounds. It is difficult to explain the unfamiliar behaviour of MOH(4) at this stage.

In general, lateral substituents sterically force apart the interacting molecules, as well as hinder the packing of molecules in a liquid crystalline structure. In addition, a lateral substituent perturbs the molecular ordering in the liquid crystalline phase and causes a significant depression in the clearing point.

The liquid crystalline properties of OOH(*n*) compounds are given in the table. In this homologous series only a monotropic nematic phase is found for higher members than OOH(8). These results indicate that the introduction of a hydroxyl substituent at the *ortho*-position is unfavourable for the occurrence of the mesophases. This characteristic, that the liquid crystalline phase is observed only for homologues with a relatively long alkoxy chain, is not surprising, for the appearance of the mesophase is not unusual; it has frequently been observed as the alkoxy chain length increases in other homologous series of LC materials [4]. As mentioned previously, it is well recognized that a lateral substituent exerts a molecular broadening influence, reducing the lateral intermolecular forces of attraction and thus impeding LC formation.

Figure 1 shows the room temperature IR spectra of POH(4), MOH(4) and OOH(4) in the 400–4000 cm^{-1} region at room temperature. Distinct differences are observed among them around 3500 cm^{-1}. The IR bands in this range can be assigned to the OH stretching

Table. The phase transition temperatures of POH(*n*), MOH(*n*) and OOH(*n*) compounds (°C): parentheses indicate monotropic transitions.

	POH(*n*)		MOH(*n*)		OOH(*n*)	
n	Nematic	Isotropic	Nematic	Isotropic	Nematic	Isotropic
1	246	284		204		211
2	218	279		187		232
3	198	265	(156)	170		230
4	182	258	159	166		212
5	166	246	(144)	156		196
6	155	238	(135)	165		189
7	153	231	(142)	175		178
8	150	228	(146)	157	(156)	171
9					(154)	165
10					(155)	163

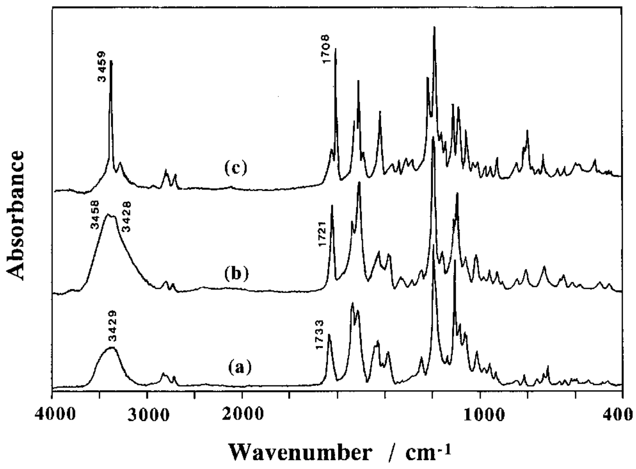


Figure 1. IR spectra of (*a*) OOH(4), (*b*) MOH(4) and (*c*) POH(4) at room temperature.

vibrational mode. A sharp band at 3459 cm^{-1} was observed in POH(4). Such a band has been ascribed to intermolecular hydrogen bonding for single-bridge compounds [15]. POH(4) is therefore considered to form dimeric associations due to hydrogen bonding through the hydroxyl (OH) group of ring A (formula 1). A broad band was observed at about 3450 cm^{-1} in MOH(4) and at about 3430 cm^{-1} in OOH(4). Such a broad band is observed when the intermolecular association attributed to hydrogen bonding is polymeric [15]. In this case, the intermolecular hydrogen bond should be considered to form between the OH group of ring A and the ester carbonyl (C=O) group. This results in a wavenumber shift of the C=O stretching vibration. In general, the C=O stretching vibrational band has been observed around 1700 cm^{-1} [16, 17]: in POH(4), the C=O stretching vibration was observed at 1708 cm^{-1}. On the other hand, it was observed at 1733 cm^{-1} and 1721 cm^{-1} in OOH(4) and MOH(4), respectively. Thus, OOH(4) and MOH(4) are considered to form a polymeric association through the intermolecular hydrogen bond. All homologues exhibited spectra similar to their respective series member described above.

The IR spectroscopic study suggests that hydrogen bonding between the hydroxyl group and the carbonyl group, restricting free motion of the molecules, is probably the reason for the decrease in phase stability in MOH(*n*) and OOH(*n*) compounds. Hydrogen bonding also reduces the clearing point by broadening the molecular structure [1]. The clearing points of MOH(*n*) and OOH(*n*) compounds are considerably lower than for POH(*n*) compounds of corresponding alkoxy chain lengths, as shown in the table.

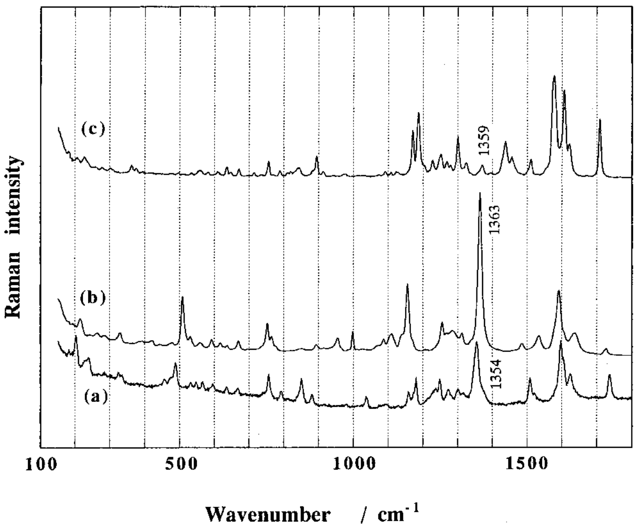


Figure 2. Raman spectra of (*a*) OOH(4), (*b*) MOH(4) and (*c*) POH(4) at room temperature.

Figure 2 shows Raman spectra of the same compounds in the 150–1800 cm^{-1} range at room temperature. The overall contours of the Raman spectra differ among the homologues. This can be explained by the molecular structure and molecular packing. It is difficult to identify the origin of all bands for the homologues, and the differences between the spectra cannot be exactly explained at this stage. However, the bands at about 1360 cm^{-1} are particularly interesting, for they exhibit significant differences in intensity among the homologues. The band is strong in MOH(*n*) and OOH(*n*) compounds, while it is weak in POH(*n*) compounds. The band has been ascribed to the coupling mode between the in-plane CCH deformational vibration and the ring-N stretching vibration [18]. MOH(4) and OOH(4) are considered to form intermolecular polymeric associations through hydrogen bonding, as mentioned above; in this case, lateral intermolecular interaction takes place. This interaction must cause a conformation change of the molecule, and thus change the band intensity. It is difficult to explain exactly the molecular structure of these compounds from the Raman spectroscopic study alone.

Some of these compounds exhibited photochromism in the solid phase. Their photochromic properties will be reported elsewhere.

A part of this study was supported by the scientific research fund from the cooperative program between Kyushu National Industrial Research Institute and Saga Graduate School.

References

[1] Gray, G. W., 1962, *Molecular Structure and Properties of Liquid Crystals* (New York: Academic Press).
[2] Brown, G. H., Doane, J. W., and Neff, V. D., 1971, *A Review of the Structure and Physical Properties Liquid Crystals* (Cleveland: Chemical Rubber Co.).

[3] Gray, G. W., 1974, in *Liquid Crystals and Plastic Crystals*, Vol. 1, edited by G. W. Gray and P. A. Winsor (Chichester: Ellis Horwood), p. 103.

[4] Demus, D., Demus, H., and Zaschke, H., 1974, *Fluessige Kristalle in Tabellen* (Leipzig: Verlag).

[5] Demus, D., 1988, *Mol. Cryst. liq. Cryst.*, **165,** 45.

[6] Sakurai, Y., Tamatani, A., Kusabayashi, K., and Takenaka, S., 1992, *Mol. Cryst. liq. Cryst.*, **213,** 163.

[7] Cohen, M. D., and Schmidt, G. M., 1962, *J. phys. Chem.*, **66,** 2442.

[8] Ottolenghi, M., and McClure, D. S., 1967, *J. chem. Phys.*, **46,** 4620.

[9] Richey, W. F., and Becker, R. S., 1968, *J. chem. Phys.*, **49,** 2092.

[10] Potashnik, R., and Ottolenghi, M., 1969, *J. chem. Phys.*, **51,** 3671.

[11] Nakagaki, R., Kobayashi, T., Nakamura, J., and Nagakura, S., 1977, *Bull. chem. Soc. Jpn.*, **50,** 1909.

[12] Hadjoudis, E., and Mavridis, I. M., 1990, *Mol. Cryst. liq. Cryst.*, **186,** 31.

[13] Bulkin, B. J., 1979, in *Liquid Crystals*, edited by F. D. Saeva (New York: Marcel Dekker), p. 365.

[14] Fontana, M. P., and Bani, S., 1976, *Phys. Rev. A*, **14,** 1555.

[15] Bellamy, L. J., 1958, *The Infra-red Spectra of Complex Molecules* (John Wiley), Chap. 6.

[16] Bellamy, L. J., 1958, *The Infra-red Spectra of Complex Molecules* (John Wiley), Chap. 10.

[17] Ghanem, A., and Noël, C., 1987, *Mol. Cryst. liq. Cryst.*, **150b,** 447.

[18] Vergoten, G., 1976, *J. mol. Struct.*, **30,** 347.