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Nitrophenyl Liquid Crystals with Intramolecular Hydrogen-Bonding in the Mesogenic Core

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Nitrophenyl Liquid Crystals with Intramolecular Hydrogen-Bonding in the Mesogenic Core

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A liquid crystalline homologous series of 4-nitrophenyl-4′-alkoxyphenyl diazene and their 2′-hydroxy analogs were synthesized, and their mesogenic properties were studied. The formation of intramolecular hydrogen bonding in the 2′-hydroxy analog series increased the rigidity of the mesogenic core and enhances the ranges of the liquid crystalline phases.

Keywords: Liquid crystals, nitro, diazene compounds, hydrogen-bond.

INTRODUCTION

Most rod-like liquid crystals have a rigid core composed of aromatic and/or aliphatic rings and one or two flexible terminal alkyl/alkoxy chains.[1,2] Different molecules may produce a rigid core by forming intermolecular hydrogen bonds between two geometrically matched nonmesogenic components.[3] Another approach to the synthesis of new liquid crystalline materials is to design rigid molecular cores containing quasi-rings stabilized by intramolecular hydrogen bonding. Some examples are the chemical stabilization of imine linkage of Schiff bases,[4,5] the increase in the mesomorphic range of azo compounds,[6,7] and the formation of a *cis-s-cis* quasi-ring form of the enaminoketone group.[8] In this paper, we wish to report the mesogenic properties of two homologous series: 4-nitrophenyl-4′-alkoxyphenyl diazenes and their derivatives, 4-nitrophenyl-4′-alkoxy-2′-hydroxyphenyl diazenes, which have a lateral hydroxysubstituent.

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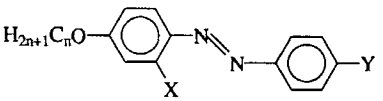


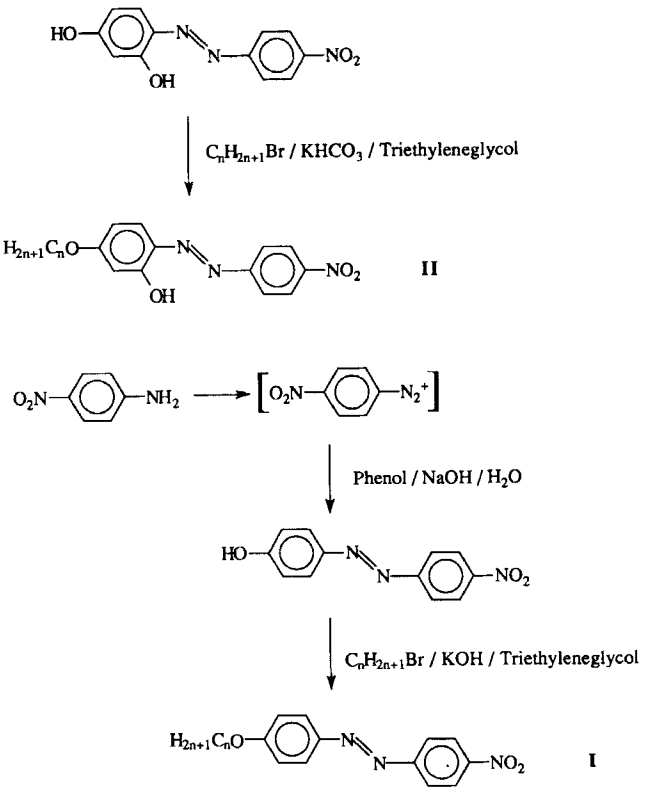
(n = 4-12, X = H or OH, Y = NO_2)

Although the nitro group is not as good as a mesogenic unit as the cyano group, liquid crystals containing the nitrophenyl unit has attracted some attention in recent years because of the potential application as nonlinear optics materials.[9-12] It has been shown that the second-order molecular hyperpolarizability of the 4-nitrophenyl-4′-phenyl diazene moiety is comparable to that of the 4-nitro-*trans*-stilbene unit.[13] Substitution by a hydroxy group in the second ring of nitrophenyl diazene liquid crystals can have two effects: a change in the mesogenic property of the rigid core and an increase in conjugation. Therefore, a study of these compounds is significant for the design of new liquid crystals and liquid crystal polymers suitable for second harmonic generation.

Compounds having a similar structure with Y = CN or n-C_4H_9 were synthesized some years ago.[6,7] A comparison of the results of these earlier work with those of ours will be discussed later.

EXPERIMENTAL

The compounds were prepared according to the scheme shown below.



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To obtain 4-nitrophenyl-4′-hydroxphenyl diazene, a mixture of sodium nitrite (7.0 g, 0.1 mole) and sodium tetrafluoroborate (11.0 g, 0.1 mole) in water (20 mL) was added slowly to a solution of *p*-nitroaniline (13.8 g, 0.1 mole) in aqueous hydrochloric acid (0.2 mole). The mixture was cooled and stirred in an ice bath. After 30 minutes, phenol (14.1 g, 0.15 mole) and sodium hydroxide (6.0 g, 0.15 mole) were subsequently added to the above mixture. After 15 minutes, the purple solid was filtered off and recrystallized from ethanol (95%). Yield 16.4 g (67%).

4-Nitrophenyl-4′-alkoxyphenyl diazenes (**I**) were synthesized by reacting the alkylbromide with 4-nitrophenyl-4′-hydroxyphenyl diazene. As an example, 1-bromooctane (1.9 g, 0.01 mol), potassium hydroxide (1 gm) and 4-nitrophenyl-4′-hydroxyphenyl diazene (2.4 g, 0.01 mol) were added into triethyleneglycol (30 mL).[14] The mixture was heated for 2 hours at 80°C. After cooling to room temperature, the resultant solution was extracted with diethyl ether (2 × 70 mL) and the ether was washed with water (2 × 20 mL). After evaporating the solvent, the crude product was recrystallized from ethanol (95%). Yield 2.2 g (63%). The NMR spectrum is consistent with the molecular structure. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 3H), 1.31 (m, 8H), 1.50 (m, 2H), 1.81 (m, 2H), 4.04 (t, J = 6.6 Hz, 2H), 7.01 (AB, J = 8.9 Hz, 2H), 7.94 (AB, J = 8.9 Hz, 2H), 7.96 (AB, J = 9.0 Hz, 2H), 8.34 (AB, J = 9.0 Hz, 2H).

For the homologous series **II**, 4-nitrophenyl-4′-hydroxy-2′-hydroxphenyl diazene, which is commercially available, was selectively alkylated with the corresponding alkylbromides in triethyleneglycol. For example, 1-bromoundecane (2.4 g, 0.01 mole), potassium hydrogen carbonate (1.0 g, 0.01 mole), and 4-nitrophenyl-4′-hydroxy-2′-hydroxphenyl diazene (2.6 g, 0.01 mole) were added into triethyleneglycol (30 mL).[14] The mixture was heated for 4 hours at 80°C. After cooling to room temperature, the resultant solution was extracted with diethyl ether (2 × 70 mL) and the ether was washed with water (2 × 20 mL). After evaporating the solvent, the crude product was recrystallized from ethanol (95%). Yield 0.6 g (15%). The NMR spectrum and elemental analysis are consistent with the molecular structure. ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, J = 7.0 Hz, 3H), 1.41 (m, 16H), 1.80 (m, 2H), 4.02 (t, J = 6.6 Hz, 2H), 6.36 (d, J = 2.4 Hz, 1H), 6.60 (dd, J = 9.1, 2.4 Hz, 1H), 7.66 (d, J = 9.1, Hz, 1H), 7.85 (AB, J = 9.1 Hz, 2H), 8.32 (AB, J = 9.1 Hz, 2H), 14.10 (s, 1H). Anal. Calcd for $C_{23}H_{31}N_3O_4$: C 66.80, H 7.56, N 10.16; Found: C 67.0, H 7.42, N 10.11.

The purity of the compounds were monitored by thin layer chromatography (TLC). The phase transitions were observed by using Olympus BHT polarizing microscope fitted with PR 600 heating stage, and by using Perkin-Elmer DSC-2. NMR spectra were recorded on a Varian XL-30 NMR spectrometer.

RESULTS AND DISCUSSION

Members of the homologous series **I** with $n \geq 7$ and those of **II** with $n \geq 4$ exhibit enantiotropic liquid crystalline phases. The transition temperatures are listed in Tables I and II, respectively, and plotted against the carbon number n in the alkoxy chain in Figure 1. Both homologous series have a strong tendency to form the smectic A phase. The melting points and the clearing points of **I** are lower than those of **II**. In addition, compounds in series **II** have wider smectic A ranges than those in series **I**. For n = 12, the hydroxy substitution increases the melting point

TABLE I

Transition temperatures of series **I**

n	Transition Temp./°C
4	$K \underset{101.4}{\overset{111.3}{\rightleftharpoons}} I$
5	$K \underset{83.6}{\overset{99.6}{\rightleftharpoons}} N \underset{93.5}{\overset{}{\rightleftharpoons}} I$
6	$K \underset{91.9}{\overset{98.9}{\rightleftharpoons}} N \underset{98.7}{\overset{}{\rightleftharpoons}} I$
7	$K \underset{67.5}{\overset{77.9}{\rightleftharpoons}} S_A \underset{94.0}{\overset{94.1}{\rightleftharpoons}} N \underset{96.6}{\overset{96.7}{\rightleftharpoons}} I$
8	$K \underset{75.3}{\overset{86.4}{\rightleftharpoons}} S_A \underset{98.5}{\overset{98.7}{\rightleftharpoons}} N \underset{99.2}{\overset{99.2}{\rightleftharpoons}} I$
9	$K \underset{62.2}{\overset{79.1}{\rightleftharpoons}} S_A \underset{99.0}{\overset{99.1}{\rightleftharpoons}} I$
10	$K \underset{82.4}{\overset{89.4}{\rightleftharpoons}} S_A \underset{100.5}{\overset{100.3}{\rightleftharpoons}} I$
11	$K \underset{63.6}{\overset{78.9}{\rightleftharpoons}} S_A \underset{99.8}{\overset{99.9}{\rightleftharpoons}} I$
12	$K \underset{73.8}{\overset{81.8}{\rightleftharpoons}} S_A \underset{101.1}{\overset{101.0}{\rightleftharpoons}} I$

K: Crystal, S_A: Smectic A, N: Nematic, I: Isotropic

by only 9°C, but raises the clearing point by 37°C (Tables I and II). The transition temperatures from crystal to smectic A show the normal odd-even effect for series **I**, but decreases monotonically with n for series **II**. The clearing temperatures of series **I** increase slightly with increasing n, but those of series **II** do not change regularly with n.

Compared with the cyano analogs,[6] compounds in series **II** have higher clearing points and a greater tendency to form layered smectic phase. It was suggested that the cyano group causes a polarization of the aromatic ring, and the resulting charge distribution leads to a head-to-tail arrangement of the molecules with opposing charges at minimal separation.[5] This kind of molecular association would favor the formation of nematic phase and it is probably true for the nitro group also. However, due to the lateral dipole of the nitro group, the dipolar interaction among neighboring molecules would be stronger than that of cyano group. This may explain the enhanced clearing point and the presence of smectic A phase for compounds in series **II**. Moreover, compared with the compounds in series **I**, the n-butyl analogs[7] have lower clearing points and exhibit only the nematic phase. These differences can also be explained by increased molecular association caused by the nitro group.

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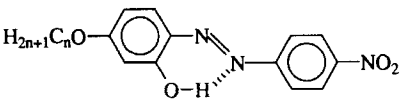
TABLE II

Transition temperatures of series **II**

n	Transition Temp./°C
4	$K \underset{133.4}{\overset{139.4}{\rightleftharpoons}} N \underset{137.6}{\overset{}{\rightleftharpoons}} I$
5	$K \underset{118.7}{\overset{120.5}{\rightleftharpoons}} S_A \underset{128.0}{\overset{126.8}{\rightleftharpoons}} N \underset{138.7}{\overset{138.6}{\rightleftharpoons}} I$
6	$K \underset{115.5}{\overset{119.9}{\rightleftharpoons}} S_A \underset{137.8}{\overset{137.1}{\rightleftharpoons}} N \underset{142.1}{\overset{141.5}{\rightleftharpoons}} I$
7	$K \underset{108.5}{\overset{114.5}{\rightleftharpoons}} S_A \underset{140.3}{\overset{140.5}{\rightleftharpoons}} I$
8	$K \underset{97.1}{\overset{99.0}{\rightleftharpoons}} S_A \underset{138.9}{\overset{138.6}{\rightleftharpoons}} I$
9	$K \underset{92.5}{\overset{95.5}{\rightleftharpoons}} S_A \underset{139.5}{\overset{139.5}{\rightleftharpoons}} I$
10	$K \underset{90.5}{\overset{94.1}{\rightleftharpoons}} S_A \underset{139.1}{\overset{139.2}{\rightleftharpoons}} I$
11	$K \underset{88.2}{\overset{91.4}{\rightleftharpoons}} S_A \underset{137.3}{\overset{137.2}{\rightleftharpoons}} I$
12	$K \underset{88.2}{\overset{90.4}{\rightleftharpoons}} S_A \underset{137.5}{\overset{137.9}{\rightleftharpoons}} I$

K: Crystal, S_A: Smectic A, N: Nematic, I: Isotropic

In general, a lateral substituent can perturb the ordering of liquid crystalline phases and cause a significant depression in the clearing point of rod-like thermotropic liquid crystals. In addition, lateral substitutents sterically force the interacting molecules apart as well as hinder the packing of the molecules in a layered structure, thus suppressing smectic order and favoring the nematic phase.[16,17] However, this is not the case for series **II**: the members with the lateral hydroxyl group exhibit higher melting and clearing temperatures than those without the lateral substituent in series **I**, and smectic A phase persists for the homologous with $n \geqslant 6$. The reason for this is most likely due to intramolecular hydrogen bonding between the lateral hydroxyl group and the azo link. Indeed, the intramolecular hydrogen bonding has been used to explain the increased clearing points of 4-butylphenyl-4′-alkoxy-2′-hydroxyphenyl diazene[6] compared with the corresponding compounds without the 2′-hydroxy group.[7]



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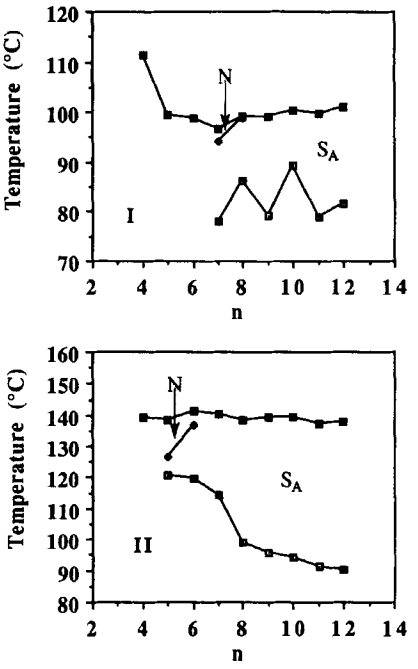

FIGURE 1 Phase behavior for the homologous series **I** and **II**. *n* is the number of carbons in the alkoxy chain. The transition temperatures (heating) were obtained by polarizing microscopy.

In $CDCl_3$ solutions, the hydroxy proton in **II** is found to have $\delta = 14.10$ ppm, shifted to a much lower field compared with phenol, $\delta = 6.11$ ppm. This strongly indicates the formation of intramolecular hydrogen bonding. A similar type of intramolecular hydrogen bonding has been found to exist for certain Schiff bases.[18–20] Such a hydrogen bonding will lead to a restriction in certain internal rotations of the molecule, creating an effectively bulkier rigid core. This would also favor the coplanarity of the molecule and raises the barrier for the *trans* $\rightleftharpoons$ *cis* equilibrium. These effects obviously enhance the phase transition temperatures.

For Schiff base analogs containing two aromatic rings, the nematic range is usually retained or depressed by the introduction of the lateral hydroxyl group.[4,5] The peculiarity of the series presented in this work consists in the considerable increase of the smectic range with the introduction of the lateral hydroxyl group. This can be explained by the introduction of a lateral dipole which may force the central parts of different molecules to lie side by side, enforcing the layer arrangement characteristics of smectic phases. This may also explain the disappearance of the odd-even effect usually present for liquid crystals with two aromatic rings. In fact, this effect is observed when the increase of the molecular anisotropy induced by the increasing carbon number in the terminal alkyl/alkoxy chain is predominant.[21] In our series the lateral dipole-dipole interaction dominates the increase of the molecular anisotropy.

In conclusion, we wish to point out that it is possible to create mesogenic molecular cores of pronounced rigidity through stabilization by intramolecular hydro-

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gen bonding. The compounds **I**, **II** and their derivatives may be good candidates for nonlinear optics materials, and the series **II** may be useful in the synthesis of organometallic mesogens which are attracting increasing interest in recent years for their colors and paramagnetism.[22,23]

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