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Conjugated Schiff's Bases-Synthesis and Preliminary Characterization of 4-(Alkoxycinnamylidene)-4′-Nitroanilines

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Conjugated Schiff's bases (—CH=CH—CH=N—) of 4-(alkoxycinnamylidene)-4′-nitroanilines (AN) were successfully synthesized by the Wittig reaction. Most of the homologues series exhibit lower clearing temperatures than those reported for the 4-(nitrocinnamylidene)-4′-alkoxyanilines (NA). A plausible reason may be due to the higher extent of non-coplanarity in the AN system than in the NA system. Comparison of the conjugated Schiff's bases with the simple Schiff's bases suggests that the addition of one more double bond increases the phase transition temperatures and stabilities of the mesophases. It seems that the increase of molecular length contributes to these effects.

Keywords: conjugated Schiff's bases, 4-(alkoxycinnamylidene)-4′-nitroanilines, mesophase stability, molecular length

INTRODUCTION

Conjugated Schiff's bases with the structural unit of Ph—(CH=CH)*n*—CH=N—Ph were first studied by Vorländer back in 1929.[1] The condensation of 5-phenyl-pentadi-2,4-enal or 7-phenyl-heptatri-2,4,6-enal with different *p*-substituted anilines were reported to give simple organic or monotropic materials. The failure of them to exhibit mesophases is due to the absence of suitable terminal tails at the end of the molecules, as was further demonstrated.[2] By incorporation of nitro and alkoxy groups at the para position of the terminal benzene rings, the 4-(nitrocinnamylidene)-4′-alkoxyanilines molecules (NA-Cn system in Figure 1, *n* represents the number of carbons in the alkoxy terminals) exhibit either a nematic or smectic phase at certain temperatures. The introduction of terminal groups should increase the polarities, the molecular length, and the intermolecular attractive forces between neighboring groups of the corresponding molecules; which in turn, stabilize the individual mesophases[3–5] at elevated temperatures.

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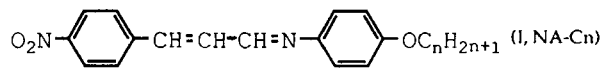
4-(Nitrocinnamylidene)-4′-alkoxyanilines (NA-Cn) are interesting due to the inherent long-chain conjugation and high polarity, the general characteristics for organic compounds to be nonlinear optical materials.[6,7] In respect of polarity, a system with the electron-withdrawing substituents on the N-phenyl and electron-donating substituents on the C-phenyl rings should possess higher polarity than in the NA system since the azomethine (—CN═N—) is basically an electron-accepting group. In this study, we report for the first time the synthesis procedures for 4-(alkoxycinnamylidene)-4′-nitroanilines (AN-Cn system in Figure 1, *n* represents the number of carbons in the alkoxy terminals) and the preliminary characterization of their liquid crystalline properties.

RESULTS AND DISCUSSION

An initial attempt to react the 4-alkoxybenzaldehydes with acetaldehyde in alkaline solution (NaOH/ethanol) did not yield 4-alkoxycinnamaldehydes, the desired precursor for the final conjugated Schiff's base. Therefore, another synthetic approach utilizing the Wittig reaction[8] was performed (2nd step in Scheme I).Condensation of 4-alkoxybenzaldehydes with 1,3-dioxan-2-ylmethyltriphenylphosphonium salt and the subsequent hydrolysis resulted in the desired products, 4-alkoxycinnamaldehydes. Reaction of these aldehydes with *p*-nitroaniline gave the final products, 4-(alkoxycinnamylidene)-4′-nitroanilines (AN-Cn, *n* represents the number of carbons in the alkoxy terminals). Altogether, six monomeric liquid crystals in AN-Cn series (n = 1, 3, 4, 6, 8 and 12) were prepared.

The phase transition temperatures of the AN-Cn and 4-(nitroanilidene)-4′-alkoxycinnamylidene (NA-Cn) series[2] are summarized in Table I. The homologue, AN-C1, shows monotropic behavior due to the short methoxy terminal chain. At the homologue AN-C6, smectic phases begin to occur. With increasing alkoxy chain lengths, smectic phases become the dominating phase until the complete disappearance of the nematic mesophase at AN-C12. Selected DSC thermograms for homologues of AN-C3 and AN-C4 are given in Figure 2. The narrow nematic ranges for AN-C3 and AN-C4 (11 and 10°C as observed from optical microscopy) resulted in broad endotherms corresponding to the inseparable crystal to nematic ($k \dashrightarrow n$) and nematic to isotropic ($n \dashrightarrow i$) transitions as shown in their DSC thermograms. This is different from the NA-Cn series (see Table I), where we generally observed wider mesophase ranges. Also, homologues of the NA-Cn series generally (except the higher homologues of AN-C12 and NA-C12) possess higher clearing temperatures than those in the AN-Cn series. This result does not coincide



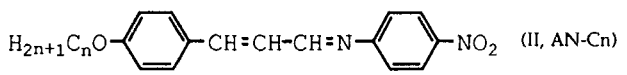
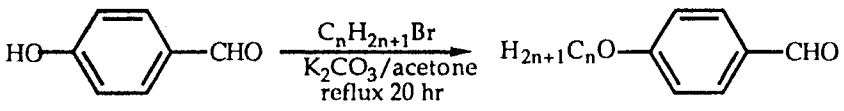
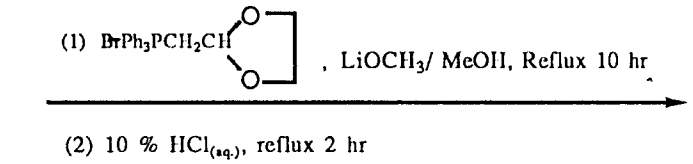
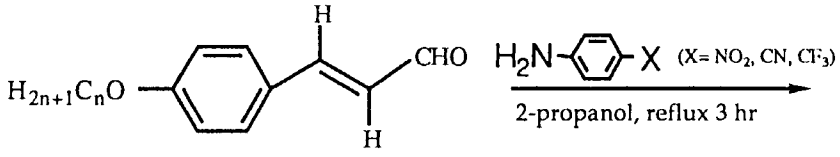


FIGURE 1 Chemical structures of conjugated Schiff's bases, NA-Cn and An-Cn series.

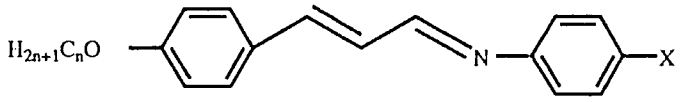


(4-hydroxybenzaldehyde) (4-alkoxybenzaldehyde)





(4-alkoxycinnamaldehyde)



(n=1,3,4,6,8,12) {4-(alkoxycinnamylidene)-4'-X-aniline)}

(X= NO_2, CN and CF_3)

SCHEME I Syntheses of conjugated Schiff's bases, AN-Cn.

with our expectation that the increasing polarity should consequently increase the clearing temperatures of the corresponding AN homologues.

Previous investigations on various Schiff's[9] and conjugated Schiff's bases[10] revealed that the nitrogen lone pair electrons of the axomethine moiety is conjugated to the terminal N-phenyl ring and these molecules are noncoplanar in different media. From the ultraviolet absorption spectra data this conjugation can be enhanced by the introduction of an electron-withdrawing nitro group on the N-phenyl ring of 1-phenyl-4-nitrophenyl-1-aza-1,3-butadiene.[10] As predicted by theoretical calculations and confirmed by experimental data, the azomethine molecule exists as a stable non-planar conformation.[11] In our opinion, the extent of non-coplanarity is enhanced in the AN-Cn system by the introduction of a nitro substituent on the N-phenyl ring and probably contributes to the less stable mesophases of this system as compared to the NA-Cn system. This may account for the lower clearing temperatures of the AN-Cn system than the NA-Cn system.

TABLE I

Summarized results from optical microscopy

AN-Cn	Transition	Temperature[a] (°C)	NA-Cn	Transition	Temperature[b] (°C)
AN-C1	k --> i	138	NA-C1	k --> n	166
	n --> i	(128)[c]		n --> i	171
AN-C3	k --> n	112	NA-C3	k --> n	106
	n --> i	133		n --> i	142
AN-C4	k --> n	120	NA-C4	k --> n	102
	n --> i	130		n --> i	141
AN-C6	k --> s	54	NA-C6	k --> n	90
	s --> n	98		n --> i	135
	n --> i	127			
AN-C8	k --> s	46	NA-C8	k --> n	115
	s --> n	128		n --> i	138
	n --> i	129			
AN-C12	k --> s	63	NA-C12	k --> s	64
	s --> i	139		s --> i	118

a Transition temperature of AN-Cn measured from hot-stage polarizing optical microscopy

b Transition temperature of AN-Cn measured from hot-stage polarizing optical microscopy, data was adapted from Ref. 2

c Monotropic behavior was observed

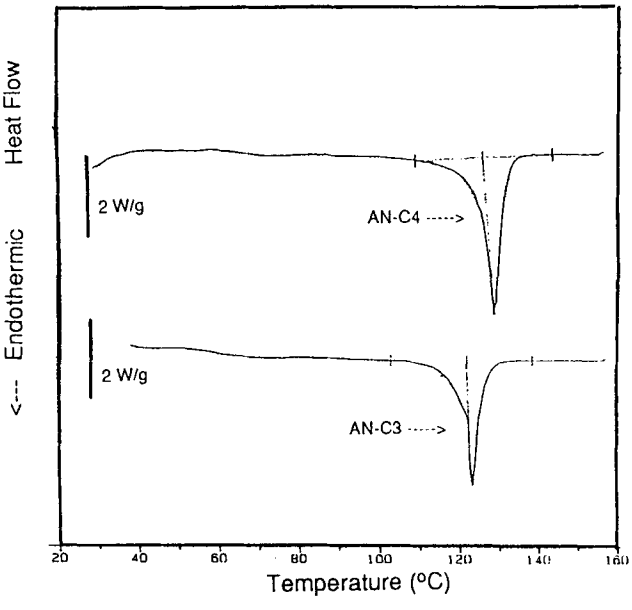
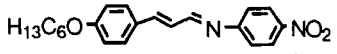
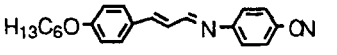
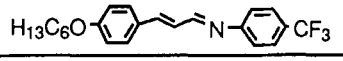
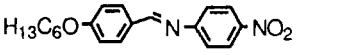
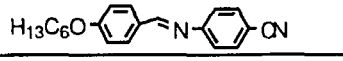
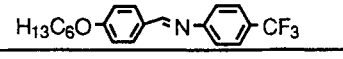


FIGURE 2 Selected DSC thermograms of AN-C3 and AN-C4.

TABLE II

Phase transition temperatures for some simple Schiff's and conjugated Schiff's bases

Compounds	Transition	Temperature (°C)[a]
	k -----> s s -----> n n -----> i	79 100 130
	k -----> n n -----> i	109 150
	k -----> s s -----> i	87 102
	k -----> i n -----> i	86 (81)[b]
	k -----> n n -----> i	49 95
	K -----> i	85

[a]Transition temperatures are measured by hot-stage polarizing optical microscopy.
[b]Monotropic transition.

Several other conjugated Schiff's and simple Schiff's bases were synthesized for comparison and their phase transition temperatures from optical microscopy are summarized in Table II. Different substitutions on the N-phenyl ring of conjugated Schiff's bases cause some variations of the $n \longrightarrow i$ temperatures. The high phase transition temperature for cyano-substituted compounds is due to the known dimer structure originated from the association of the cyano terminals.[12-15] The destruction of the dimer structure results in the lowering of the transition temperatures and the appearance of a smectic phase as observed in samples of the nitro- and trifluoromethyl-substituted AN compounds. The effect of molecular length can be easily demonstrated by the comparison of conjugated Schiff's bases with the simple Schiff's bases. Generally, more stable mesophases and higher phase transition temperatures are observed for conjugated Schiff's bases than those of simple Schiff's bases. In the case of the trifluoromethyl-substituted compounds, extension of the molecular length by one double bond results in the formation of mesophases. The unstable monotropic mesophase observed in the nitro-substituted Schiff's base changes to stable mesophases in the nitro-subsituted conjugated Schiff's base, AN-C6.

CONCLUSION

Conjugated Schiff's bases with different alkoxy terminals (AN-Cn) on the C-phenyl ring were successfully synthesized by the Wittig reaction. Most of the homologues

series exhibit lower clearing temperatures than those in the NA-Cn system. A plausible reason may be due to the higher extent of non-coplanarity in the AN system than in the NA system.

A comparison of the transition temperatures for the conjugated Schiff's bases with those for the corresponding Schiff's bases suggests that the addition of one more double bond increases the transition temperatures and stabilities of the mesophases. It seems that the increased molecular length of NA-C6 contributes to these effects.

EXPERIMENTAL

Materials and Instrumentation

Chemical purifications and instrumentation. Dichloromethane was purified by distillation of its mixture with calcium hydride. Methanol was purified by distillation after treatment with magnesium and iodine. N,N-dimethylformamide was vacuum distilled after dehydration with barium oxide. Tetrahydrofuran and diethyl ether were simply treated with sodium before use.

NMR spectra were recorded with a VXR-300 FT-NMR model. Deuterium-chloroform ($CDCl_3$) with tetramethylsilane as an internal standard were used for NMR spectral measurements for all samples. Textures of liquid crystals and phase transition temperatures were observed with a Nikon E-100-instrument model. Phase transition temperatures were also detected with a Du-Pont DSC-910 model (with heating rate = 10°C/min).

Synthesis

4-Alkoxybenzaldehyde. A mixture of 4-hydroxybenzaldehyde (0.08 mol), bromoalkane (0.10 mol), and potassium carbonate (0.21 mol) in 10 mL of dry acetone were refluxed for 36–48 hrs (the reaction time was confirmed by the TLC analysis). The reaction mixture was cooled, filtered and the acetone removed from the filtrate. The remaining material was washed with distilled water and extracted with benzene three times. The combined benzene layer was further washed with saturated aq. NaCl, dried over magnesium sulfate, filtered and the solvent removed from the filtrate. This material (80–85%) was purified by column chromatography (1:5 = ethyl acetate: hexane as eluting solvent). ^{1}H NMR of 4-hexyloxybenzaldehyde: $\delta(CDCl_3$, 300 MHz), 0.88–1.86(11H, m, C_5H_{11}), 3.92–4.05(2H, *t*, J = 6.0 Hz, OCH_2), 6.87–6.97(2H, *d*, J = 8.9 Hz, aromatic H), 7.74–7.84(2H, *d*, J = 8.9 Hz, aromatic H), 9.85(1H, s, CHO).

4-Alkoxycinnamaldehydes. A mixture of lithium (0.31 g) in anhydrous methanol (50 mL) was stirred for 1–2 hrs to prepare lithium methoxide solution. To the nitrogen blanketed mixture of 4-alkoxybenzaldehyde (10 mmol), 1,3-dioxan-2-ylmethyltriphenylphosphonium salt[8] (16 mmol), and anhydrous DMF (50 mL), lithium methoxide solution (50 mL) was slowly added dropwise and the mixture refluxed for 5–8 hrs (TLC was used to detect the completeness of reaction). The

resulting mixture was washed with 600 mL of water and extracted with ether three times. The organic ether layer was further washed with saturated aq. NaCl solution, dried over magnesium sulfate, filtered and the solvent removed from the filtrate to give the crude product. Hydrolysis was performed by stirring the crude product in a mixture of 50 mL of tetrahydrofuran and 50 mL of 10% aq. HCl solution for 2–3 hrs. The resulting solution was diluted with 500 mL of water and extracted with ether three times. The combined ether layer was neutralized with saturated aq. $NaHCO_3$ solution and washed with saturated aq. NaCl solution. The resulting solution was dried over magnesium sulfate, filtered and the solvent removed from the filtrate. The crude product was purified by column chromatography (1:5 = ethyl acetate:hexane). Approximately a 50% yield was obtained. ^{1}H NMR of 4-hexyloxycinnamaldehyde: δ($CDCl_3$, 300 MHz), 0.91–1.81(11H, *m*, C_5H_{11}), 3.96–4.01(2H, *t*, J = 6.6 Hz, OCH_2), 6.55–6.63(1H, *dd*, J = 7.8, 15.9 Hz, olefinic H), 6.91–6.93(2H, *d*, J = 8.7 Hz, aromatic H), 7.74—7.43(1H, *d*, J = 15.9 Hz, olefinic H), 7.48–7.51(2H, *d*, J = 8.7 Hz, aromatic H), 9.62–9.64(1H, *d*, J = 7.8 Hz, CHO).

4'-(Alkoxycinnamylidene)-4-nitroanilines. A mixture of 4-alkoxycinnamaldehyde (6.17 mmol), and *p*-nitroaniline (7 mmol) was dissolved in 50 mL of isopropanol and refluxed for 2–3 hrs under a nitrogen atmosphere. The yellow precipitate formed after cooling overnight was removed by filtration and recrystallized from isopropanol. ^{1}H NMR of 4-(hexyloxycinnamylidene)-4'-nitroanilin: δ($CDCl_3$, 300 MHz), 0.92–1.81(11H, *m*, C_5H_{11}), 3.98–4.03(2H, *t*, J = 6.3 Hz, OCH_2), 6.92–7.95(2H, *d*, J = 8.7 Hz, aromatic H), 6.94–7.02(1H, *m*, olefinic H), 7.19–7.22(2H, *d*, J = 8.7 Hz, aromatic H), 7.23(1H, *m*, olefinic H), 7.49–7.52(2H, *d*, J = 8.7 Hz, aromatic H), 8.18–8.21(1H, *d*, J = 9.0 Hz, CH=N), 8.24–8.26(2H, *d*, J = 8.7 Hz, aromatic H).

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