



Synthesis and Mesomorphic Properties of 4-(Methylthio)benzylidene-4'-*n*-alkanoyloxyanilines

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A homologous series of Schiff base esters, 4-(methylthio)benzylidene-4'-*n*-alkanoyloxyanilines possessing even number of carbon atoms at the alkanoyloxy chain ($C_{n-1}H_{2n-1}COO-$, $n = 2$ to 18) was synthesized. The structure of the 4-(methylthio)benzylidene-4'-*n*-alkanoyloxyanilines was confirmed by elemental analysis and spectroscopic techniques including FT-IR, ¹H and ¹³C NMR and EI-MS. Mesomorphic properties were evaluated by differential scanning calorimetry and polarizing optical microscopy techniques. Whilst *n*-butanoyloxy to *n*-octanoyloxy derivatives exhibited monotropic nematic phase, *n*-ethanoyloxy and *n*-decanoyloxy to *n*-octadecanoyloxy derivatives were non-mesogenic compounds. The mesomorphic properties of the present series were compared with other structurally related series to establish the chemical structure-mesomorphic property relationship.

Key Words: Thermotropic liquid crystal, Schiff base, Nematic, 4-(Methylthio)benzylidene-4'-*n*-alkanoyloxyanilines.

INTRODUCTION

The fourth phase of matter-liquid crystal was first reported by Otto Lehman, a physicist in 1889 after he investigated the double-melting points phenomenon of molten cholesteryl benzoate^{1,2}. After 120 years of studies, liquid crystals had become the essential advanced materials in our daily life. Its applications were developed in various areas such as advanced technological devices, prototypical self-organizing molecular materials and smart biological and pharmacological uses³.

A minor change in chemical structure will result a great effect on the mesomorphic property. Therefore, in order to modify or synthesis a new mesogen with desirable property and application, it is elemental to understand chemical structure-mesomorphic property relationships⁴. An earlier report has shown that low-mass molecules compounds containing two unsaturated rings with one or multiple terminal substituents are capable of exhibiting mesomorphic properties^{5,6}. Discovery of 4-methoxybenzylidene-4'-butylaniline (MBBA) and its application of nematic phase at room temperature in displays sparked a renewed interest of researcher on Schiff bases⁷⁻¹².

In our previous studies¹³⁻¹⁸, the results revealed that imine and ester are useful linking units for generating mesomorphism

in two and three aromatic rings thermotropic liquid crystals. In order to accomplish the research of Schiff base ester mesogens, we report another homologous series of Schiff base ester, 4-(methylthio)benzylidene-4'-*n*-alkanoyloxyanilines possessing even number of carbon atoms at alkanoyloxy chain ($C_{n-1}H_{2n-1}COO-$, $n = 2, 4, 6, 8, 10, 12, 14, 16, 18$).

EXPERIMENTAL

4-Aminophenol, 4-dimethylaminopyridine (DMAP) and fatty acids ($C_nH_{2n-1}COOH$ where $n = 2, 4, 6, 8, 10, 12, 14, 16, 18$) were purchased from Merck (Germany). Dicyclohexyl-carboiimide (DCC) and 4-(methylthio) benzaldehyde were purchased from Acros Organics (USA). All solvents and reagents were purchased commercially and used without any further purification.

FT-IR spectra were recorded using a Perkin-Elmer System 2000 FT-IR Spectrometer via KBr disc procedure. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ using Bruker Avance 400 MHz Spectrometer with TMS as the internal standard. EI-MS (70 eV) were measured with a Mass Spectrometer Finnigan MAT95XL-T. Microanalyses were carried out on Perkin Elmer 2400 LS Series CHNS/O analyzer.

Liquid crystal study: Phase-transition temperatures and enthalpy changes were measured using Differential Scanning Calorimeter Mettler Toledo DSC823^c at heating and cooling rates of 10 °C min⁻¹ and -10 °C min⁻¹, respectively. Polarizing optical microscope (Carl Zeiss) equipped with Linkam heating stage was used for temperature dependent studies on liquid crystal textures. Video camera (Video Master coomo20P) installed on the polarizing optical microscope was coupled with video capture card (Video Master coomo600), allowing real-time video capturing and image saving. Textures exhibited by the samples were observed using polarized light with crossed polarizers. Samples were sandwiched between glass slide and cover slip as thin films. Mesophase identification was made by comparing the observed textures with literature^{19,20}.

The synthetic route of 4-(methylthio)benzylidene-4'-*n*-alkanoyloxyanilines, nMTBAA is illustrated in Fig. 1.

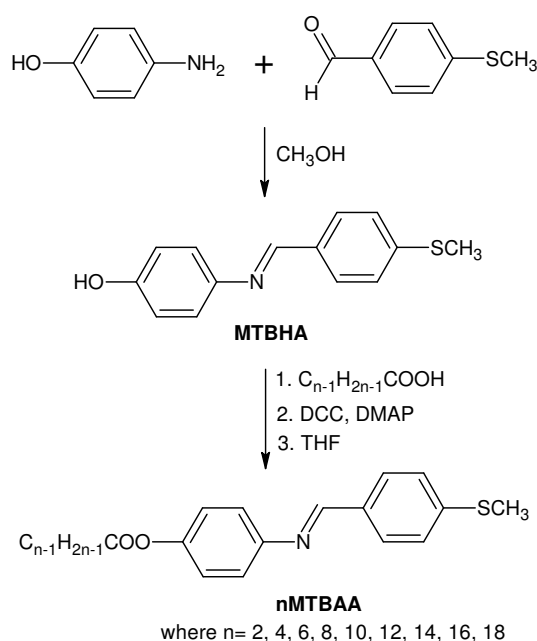


Fig. 1. Synthetic route towards title compound

Synthesis of 4-(methylthio)benzylidene-4'-hydroxyaniline (MTBHA): MTBHA was prepared according to a previously described method²¹. 4-Aminophenol (0.5457 g, 5 mmol) and 4-(methylthio)benzaldehyde (0.7611 g, 5 mmol) were reacted at room temperature for 1 h in appropriate amount of methanol. Precipitate formed was separated by suction filtration and washed several times with deionized water.

Synthesis of 4-(methylthio)benzylidene-4'-*n*-alkanoyloxyaniline (nMTBAA): nMTBAA were synthesized *via* one pot esterification method²². MTBHA (0.2433 g, 1 mmol), 1.3 mmol of fatty acids ($C_nH_{2n-1}COOH$, $n = 2, 4, 6, 8, 10, 12, 14, 16, 18$), DMAP (0.0244 g, 0.2 mmol) and DCC (0.2063 g, 1 mmol) were stirred at room temperature for 6 h in appropriate amount of THF. Then, the solvent was removed by evaporation. Product obtained was recrystallized several times with hexane and methanol whereupon pure compound was isolated. Percentage yields and analytical data of nMTBAA are tabulated in Table-1. IR, NMR (¹H and ¹³C) and mass spectral data of representative compound, 18MTBAA, are summarized as follows.

TABLE 1					
PERCENTAGE YIELDS AND ANALYTICAL DATA OF nMTBAA					
Compound	Yield (%)	% Experimental (Theoretical)			
		Formula	C	H	N
2MTBAA	38	C ₁₆ H ₁₅ NO ₂ S	67.45 (67.34)	5.22 (5.30)	4.88 (4.91)
4MTBAA	50	C ₁₇ H ₁₇ NO ₂ S	68.09 (68.20)	5.79 (5.72)	4.73 (4.68)
6MTBAA	44	C ₁₈ H ₁₉ NO ₂ S	69.09 (68.98)	6.09 (6.11)	4.40 (4.47)
8MTBAA	44	C ₁₉ H ₂₁ NO ₂ S	69.78 (69.69)	6.33 (6.46)	4.26 (4.28)
10MTBAA	48	C ₂₀ H ₂₃ NO ₂ S	70.43 (70.35)	6.71 (6.79)	4.12 (4.10)
12MTBAA	45	C ₂₁ H ₂₅ NO ₂ S	70.86 (70.95)	7.18 (7.09)	3.97 (3.94)
14MTBAA	53	C ₂₂ H ₂₇ NO ₂ S	71.68 (71.51)	7.41 (7.36)	3.74 (3.79)
16MTBAA	64	C ₂₄ H ₃₁ NO ₂ S	72.41 (72.50)	7.91 (7.86)	3.50 (3.52)
18MTBAA	72	C ₂₆ H ₃₅ NO ₂ S	73.48 (73.37)	8.32 (8.29)	3.21 (3.29)

18MTBAA: IR (KBr, ν_{max} , cm⁻¹) 2954, 2917, 2849 (C-H aliphatic), 1748 (C=O ester), 1622 (C=N), 1213, 1089 (C-O ester). ¹H NMR (300 MHz, CDCl₃): δ /ppm 0.9 (t, 3H, CH₃), 1.3-1.4 (m, 28H, CH₃-(CH₂)₁₄), 1.8 (m, 2H, -CH₂-CH₂-COO-), 2.6 (s, 3H, CH₃S-), 2.6 (t, 2H, -CH₂-COO-), 7.1 (d, 2H, Ar-H), 7.2 (d, 1H, Ar-H), 7.3 (d, 1H, Ar-H), 7.8 (d, 1H, Ar-H), 8.4 (s, 1H, -CH=N-). ¹³C NMR (100 MHz, CDCl₃): δ /ppm 171.41 (-C=N-), 159.66, 149.60, 148.83, 143.34, 132.80, 129.10, 125.74, 122.17, 121.72 for aromatic carbons, 34.42 (-COO-CH₂-), 31.92 (-COO-CH₂-CH₂-), 29.69, 29.65, 29.60, 29.46, 29.35, 29.26, 29.12 for methylene carbons [- (CH₂)₁₃CH₂CH₂CH₃], 24.97 (-CH₂CH₂CH₃), 22.68 (-CH₂CH₃), 15.11 (-SCH₃), 14.10 (-CH₃). EI-MS m/z (rel. int. %): 509(5) (M)⁺, 243(100).

RESULTS AND DISCUSSION

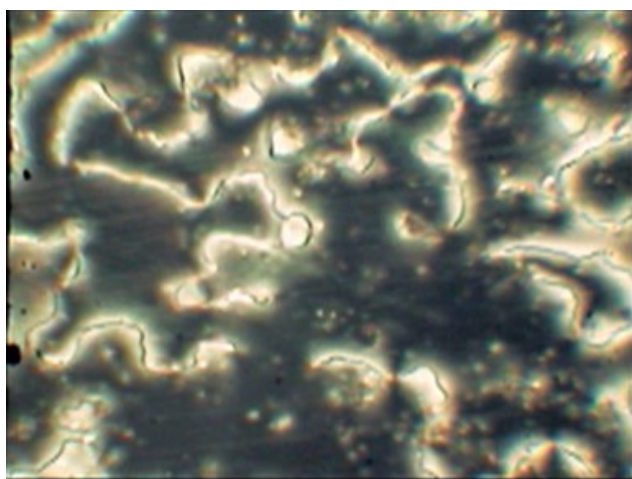
Structural identification of nMTBAA was carried out by employing a combination of elemental analysis and spectroscopic techniques (FT-IR, ¹H and ¹³C NMR and EI-MS). Percentages of C, H and N from the elemental analysis conform with composition of nMTBAA as presented in Table-1. Molecular ion peak at m/z 509 suggested molecular formula of C₃₂H₄₇NO₂S, which supported the proposed structure of 18MTBAA.

FTIR, ¹H NMR and ¹³C NMR Spectral Studies: Based on FT-IR spectrum of 18MTBAA, absorption peak at 2954, 2917, 2849 cm⁻¹ can be assigned to aliphatic (CH₃ and CH₂) group. Three absorption peaks due to the ester group were observed at 1748, 1213, 1089 cm⁻¹. Relative intensity of absorption bands of aliphatic group increased upon ascending the series due to the increasing number of carbons in the alkanoyloxy chain. Absorption peak of imine (C=N) group was observed at 1622 cm⁻¹.

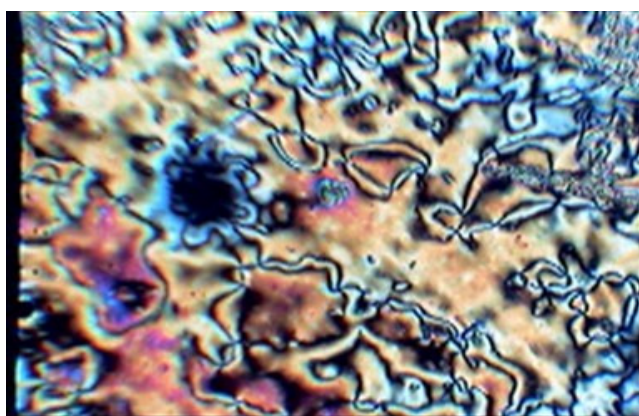
A triplet signal at $\delta = 0.9$ ppm is assigned to methyl protons (CH₃CH₂-), two multiplet signals between $\delta = 1.3$ -1.4 and 1.8 ppm are attributed to methylene protons [CH₃-(CH₂)₁₃] and (-CH₂-CH₂-COO-), respectively. Methylthio group showed a singlet signal at $\delta = 2.6$ ppm. Eight aromatic protons (Ar-H)

appeared as four doublets at $\delta = 7.1, 7.2, 7.3$ and 7.8 ppm. Azomethine proton ($-\text{CH}=\text{N}-$) appeared as singlet peak at $\delta = 8.4$ ppm. It suggested presence of 28 carbons. Signal at $\delta = 171.41$ ppm is attributed the imine carbon ($-\text{C}=\text{N}-$). It is the most deshielded signal among others because it is double bonded to nitrogen which is a high electronegative element. Aromatic carbons were observed within the chemical shift range of $\delta = 115.24-161.96$ ppm. Carbon resonances between $\delta = 14.10-34.42$ ppm were indicative of methyl and methylene carbons of methylthio and alkanoyloxy chain.

Phase-transition behaviour and liquid crystallinity of *n*MTBAA: Under polarized optical microscope, *n*-butanoyloxy to *n*-octanoyloxy derivatives exhibited nematic phase while *n*-ethanoyloxy and *n*-decanoyloxy to *n*-octadecanoyloxy derivatives did not display liquid crystal phase. Optical photomicrographs of 4MTBAA and 6MTBAA are illustrated in Fig. 2. 4MTBAA exhibited homogenous *schlieren* texture with surface disclination lines of nematic phase while 6MTBAA exhibited homogenous *schlieren* texture under planar anchoring condition of nematic phase¹⁹.



(a)



(b)

Fig. 2. (a) Optical photomicrograph of 4MTBAA exhibiting homogenous schlieren texture with surface disclination lines of nematic phase; (b) optical photomicrograph of 6MTBAA displaying homogenous schlieren texture under planar anchoring condition of nematic phase.

Phase transition temperatures and enthalpy changes upon heating and cooling scans obtained from DSC measurements are summarized in Table-2. Plots of phase transition temperatures

TABLE 2
PHASE TRANSITION TEMPERATURES AND ENTHALPY CHANGES OF *n*MTBAA UPON HEATING AND COOLING SCANS

Compound	Phase transition temperature, °C (enthalpy change, J g ⁻¹)	Heating Cooling
2MTBAA	Cr 92.5 (85.2) I I 52.1 (85.2) Cr	
4MTBAA	Cr 99.3 (86.3) I I 92.5 (1.2) N 78.1 (81.4) Cr	
6MTBAA	Cr 100.6 (98.5) I I 92.8 (2.8) N 75.9 (88.2) Cr	
8MTBAA	Cr 100.6 (100.2) I I 93.1 (2.4) N 82.7 (93.0) Cr	
10MTBAA	Cr 97.5 (70.2) I I 76.1 (75.8) Cr	
12MTBAA	Cr 105.3 (113.5) I I 91.9 (113.8) Cr	
14MTBAA	Cr 108.7 (121.5) I I 95.7 (124.2) Cr	
16MTBAA	Cr 109.0 (115.5) I I 97.2 (113.2) Cr	
18MTBAA	Cr 109.0 (181.1) I I 102.0 (181.1) Cr	

Note: Cr= crystal; N= nematic; I= isotropic.

against number of carbon atoms (*n*) in alkanoyloxy chain upon heating and cooling scans are shown in Figs. 3 and 4, respectively. Based on the plot, it can be deduced that mesophase properties were greatly influenced by length of alkanoyloxy chains. Crystal-isotropic transition (melting) temperatures exhibited ascending trend as length of alkanoyloxy chain increased from *n*-ethanoyloxy to *n*-octadecanoyloxy except *n*-decanoyloxy derivatives. Same phenomenon was observed on isotropic-crystal transition (freezing) temperatures.

Out of nine members, only three members (*n* = 4, 6, 8) exhibited mesophase. This trend is rather rare but yet interesting to study. Additional peak of low enthalpy change were observed on *n*-butanoyloxy to *n*-octanoyloxy derivatives upon cooling scan indicated the exhibition of monotropic phase. In monotropic mesogens, the melting points were always equal to or higher than the clearing points, hence exhibiting supercooling properties²³. Nematic phase range increased from *n*-butanoyloxy to

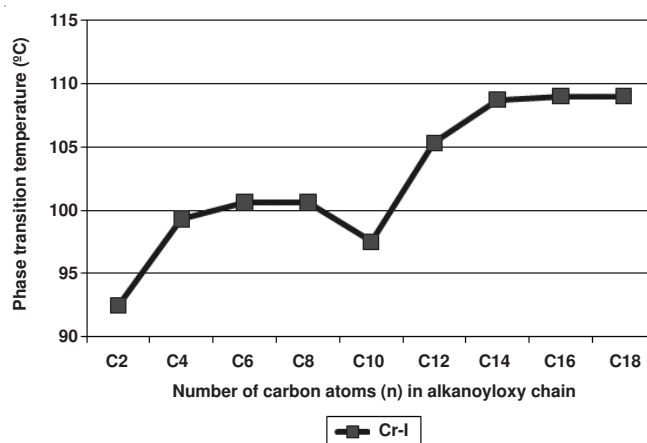


Fig. 3. Plot of phase transition temperature against number of carbon atoms (*n*) in alkanoyloxy chain of *n*MTBAA during heating scan

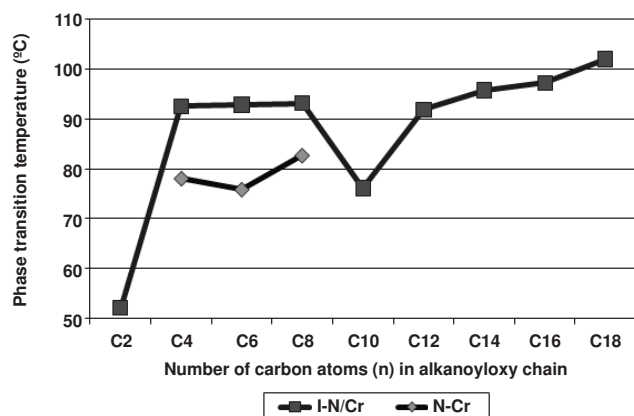


Fig. 4. Plot of phase transition temperature against number of carbon atoms (n) in alkanoyloxy chain of nMTBAA during cooling scan.

n-hexanoyloxy derivatives but decreased from *n*-hexanoyloxy to *n*-octanoyloxy derivatives. This indicated that 6MTBAA having the optimum balance of rigidity and flexibility which contributed to its highest thermal stability than 4MTBAA and 8MTBAA.

2MTBAA is not mesogenic due to incorporation of rigid core system with short alkanoyloxy chain, resulting in high melting point, thus suppressing liquid crystals phase. However, high flexibility of long alkanoyloxy chain in nMTBAA ($n = 10, 12, 14, 16, 18$) also depressed formation of liquid crystals phase²⁴.

Chemical structure-mesomorphic property relationship:

In order to establish chemical structure-mesomorphic property relationship, 12MTBAA was compared with structurally related compounds A¹⁷ and B¹⁸ (Table-3). Different terminal substituents

can influence exhibition of liquid crystals phase. Present compound with terminal methylthio substituent (12MTBAA) is not liquid crystal. When methylthio replaced with chloro group as in compound A, it displayed SmA and SmB phases. By having dimethylamino as terminal group in compound B, it changed to nematic and SmA phases. This comparison served as an evidence to reveal that terminal methylthio substituent not favourable to exhibit liquid crystal phase and less likely to form mesogen.

Conclusion

In this paper, we report a homologues series of 4-(methylthio)-benzylidene-4'-*n*-alkanoyloxyanilines. Whilst *n*-butanoyloxy to *n*-octanoyloxy derivatives exhibited monotropic nematic phase, the rest members were not mesogenic. Comparison of present series with other structurally related compounds revealed that terminal methylthio substituent not favourable to exhibit mesophase.

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TABLE -3 MOLECULAR STRUCTURE, PHASE TRANSITION TEMPERATURE AND MESOPHASE RANGE OF 12MTBAA, COMPOUND A AND B UPON HEATING SCAN.				
			2MTBAA	
			Compound A ¹⁷	
			Compound B ¹⁸	
Compound	Transition temperatures (°C)	Mesophase range (°C)		
		SmB	SmA	N
2MTBAA	Cr 105.3 I	-	-	-
A	Cr (SmB 79.9)* 94.6 SmA 101.3 I	-	20.4	-
B	Cr (SmA 91.5 N 93.2)* 104.8 I	-	-	-

Note: Cr = crystal; SmB = smectic B; SmA = smectic A; N= nematic; I= isotropic, (*) = monotropic value