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Mesomorphic Homologous Series I. 2-Methyl-5-(4′-n-Alkoxycinnamoyloxy)pyridines II. 4-(4′-n-Alkoxycinnamoyloxy)toluenes

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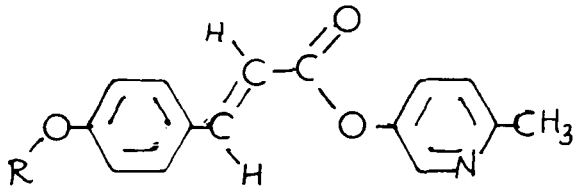
Two homologous series of mesomorphic esters containing pyridine ring and aromatic nucleus have been synthesized and mesomorphic behaviour of their members studied. In series I, the first two and seventh members are non-mesomorphic. The propyl to hexyl derivatives show nematic phase (either monotropic or enantiotropic). The smectic phase commences from the amyl derivative as monotropic and continues till the last member studied. In series II, methyl to dodecyl derivatives exhibit nematic phase (either monotropic or enantiotropic) except the ethyl homolog which is non-mesomorphic. The smectic phase commences from the octyl derivative as enantiotropic and continues till the octadecyl derivative. Plots of transition temperatures against the number of carbon atoms in alkyl chain in series I and II behave in a normal manner. The thermal stability of the series I is compared with that of series II.

I. INTRODUCTION

A few workers have reported mesomorphic nitrogen heterocycles in the recent past.[1–3] The synthesis and investigation of physical properties of a new homologous series of liquid crystalline compounds are important in studying the relationship between the structures of molecules and the characteristics of the mesomorphic state. We report here the synthesis and study of mesomorphic behaviour of the two series viz. 2-methyl-5-(4′-n-alkoxy-cinnamoyloxy)pyridines (I) and 4-(4′-n-alkoxycinnamoyloxy)toluenes (II). It was of interest to determine the effect of replacing a ring carbon atom ortho to the methyl group with a nitrogen atom on mesomorphic behaviour.



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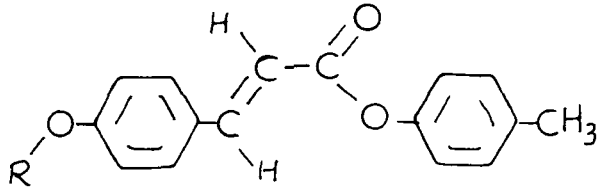

II

II. EXPERIMENTAL

Melting points and transition temperatures were determined using a Leitz Ortholux polarizing microscope equipped with a heating stage. In the neighborhood of each phase transition the temperature was raised at the rate of 0.5°C per minute.

Preparation of compounds:

1. 4-n-Alkoxybenzaldehydes were prepared according to the method of Vyas and Shah.[4]

2. 4-n-Alkoxycinnamic acids and 4-n-alkoxycinnamoyl chlorides were prepared as described by Gray and Jones.[5]

3. 2-Methyl-5-(4′-n-alkoxycinnamoyloxy)pyridines.

A solution of equimolar amounts of 4-n-alkoxy-cinnamoyl chloride (0.005 mol) and 3-hydroxy-6-methyl-pyridine (0.005 mol) (Aldrich Chemicals, USA) in dry pyridine (5–7 ml) was heated on a water bath for an hour and left overnight. The reaction mixture was poured into cold water, the product was washed with 50 ml 10% NaOH followed by water, crystallized from petroleum ether (yield 55–60%). The analytical data of the compounds are given in Table I. The structure of the methyl derivative was confirmed by NMR spectrum. NMR ($CDCl_3$) δ 2.6(s, 3H, CH_3 at C_2), 3.85(s, 3H, CH_3 at C_4), 6.4–6.6(d, J = 9Hz, 18Hz, 1H, of $=CH.\overset{\overset{O}{\|}}{C}.O$), 6.9–7.0(d), J = 9Hz, 1H at C_3), 7.2–7.4(m, 4H, C_2', C_3', C_5' and C_6'), 7.5–7.6(d, J = 9Hz,

TABLE I

Compound	Molecular formula	:: % Required			% Found		
		C	H	N	C	H	N
1	$C_{16}H_{15}O_3N$	71.37	5.57	5.20	71.80	5.70	4.81
2	$C_{17}H_{17}O_3N$	72.07	6.00	4.94	72.52	6.08	4.76
3	$C_{18}H_{19}O_3N$	72.73	6.39	4.71	73.18	5.95	4.46
4	$C_{19}H_{21}O_3N$	73.30	6.75	4.50	73.28	6.79	4.12
5	$C_{20}H_{23}O_3N$	73.84	7.07	4.30	73.36	7.44	4.10
6	$C_{21}H_{25}O_3N$	74.33	7.37	4.13	74.50	7.45	3.77
7	$C_{22}H_{27}O_3N$	74.78	7.64	3.96	75.23	7.45	3.75
8	$C_{23}H_{29}O_3N$	75.20	7.90	3.81	75.65	8.01	3.80
9	$C_{24}H_{31}O_3N$	75.60	8.13	3.67	75.68	7.71	3.42
10	$C_{25}H_{33}O_3N$	75.95	8.35	3.54	75.63	8.14	4.00
11	$C_{27}H_{37}O_3N$	76.60	8.74	3.31	76.28	8.48	3.29
12	$C_{29}H_{41}O_3N$	77.16	9.08	3.10	77.62	8.82	3.12
13	$C_{31}H_{45}O_3N$	77.66	9.39	2.92	77.57	9.43	2.89
14	$C_{33}H_{49}O_3N$	78.11	9.66	2.76	78.05	9.30	2.61
15	$C_{17}H_{16}O_3$	76.12	5.97	-	76.49	6.04	-
16	$C_{18}H_{18}O_3$	76.61	6.39	-	77.00	6.53	-
17	$C_{19}H_{20}O_3$	77.02	6.75	-	77.07	6.83	-
18	$C_{20}H_{22}O_3$	77.41	7.09	-	77.69	7.31	-
19	$C_{21}H_{24}O_3$	77.78	7.40	-	78.20	7.10	-
20	$C_{22}H_{26}O_3$	77.94	7.68	-	78.40	8.02	-
21	$C_{23}H_{28}O_3$	78.41	7.95	-	78.82	7.75	-
22	$C_{24}H_{30}O_3$	78.68	8.19	-	79.02	8.64	-
23	$C_{25}H_{32}O_3$	78.94	8.42	-	79.32	8.59	-
24	$C_{26}H_{34}O_3$	79.20	8.63	-	79.57	8.43	-
25	$C_{28}H_{38}O_3$	79.62	9.00	-	80.04	9.10	-
26	$C_{30}H_{42}O_3$	80.00	9.33	-	80.28	9.27	-
27	$C_{32}H_{46}O_3$	80.34	9.62	-	80.11	9.59	-
28	$C_{34}H_{50}O_3$	80.63	9.88	-	80.41	9.87	-

1H at C_4), 7.79–7.92(d, J = 18Hz), 1H of =CH.Ph), 8.4(s, 1H at C_6').

4. 4-(4′-n-Alkoxycinnamoyloxy)toluenes.

4-n-Alkoxycinnamoyl chlorides and p-cresol in equimolar quantity (0.005 mol) were mixed and heated on a water bath for about half an hour. The reaction mixture was then poured into ice-cold water, washed with 10% NaOH (50 ml), followed by H_2O. The products were crystallised from ethanol (Yield 75–78%). The analytical data of the compounds are given in Table I. The structure of the butyl derivative was confirmed by NMR spectrum. NMR ($CDCl_3$) δ 1.0 (t, 3H, CH_3 at C_4'), 1.4–1.9 (m, 4H, —$(CH_2)_2$— at C_4'), 2.35 (s, 3H, CH_3 at C_1), 4.0 (t, 2H, OCH_2— at C_4'), 6.45–6.55(d, J = 18Hz, 1H of =CH.C(=O).O), 6.8–7.6 (m, 8H, aromatic protons) 7.75–7.9 (d, J = 18Hz, 1H, =CH.Ph).

RESULTS AND DISCUSSION

Series I. 2-Methyl-5-(4'-n-alkoxycinnamoyloxy)pyridines

The melting points and transition temperatures of the compounds synthesized are compiled in Table II. The first two members are non-mesomorphic. The propyl derivative exhibits monotropic nematic while the butyl derivative exhibits enantiotropic nematic. The smectic phase begins with the amyl derivative as monotropic phase and continues till the last member studied. On cooling the isotropic liquid batonnets separate from it and coalesce together to form a quite clear fan shaped focal conic textures in each case indicating that the smectic phase observed in this series is of the S_A type. The smectogenic tendencies of the compounds of this series compared to those of the benzene analogs can be attributed to the presence of a heterocyclic nitrogen atom. Oh[6] has suggested that the presence of the nitrogen atom in heterocyclic liquid crystalline Schiff bases is credited with enhancing smectogenic properties. A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain (Figure 1) shows the usual odd-even effect.

Table III compares the average thermal stabilities of the series (I) and the series II.

TABLE II

Transition temperatures of 2-Methyl-5-(4'-n-alkoxycinnamoyloxy)-pyridines (I)

Alkyl group	Transition temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	-	126.5
Ethyl	-	-	138.0
Propyl	-	(92.5)	105.5
Butyl	-	98.5	106.0
Amyl	(88.5)	98.0	103.0
Hexyl	(97.0)	103.0	107.5
Heptyl	-	-	116.5
Octyl	107.0	-	108.5
Nonyl	109.5	-	110.5
Decyl	97.5	-	112.5
Dodecyl	86.0	-	113.5
Tetradecyl	91.5	-	112.0
Hexadecyl	94.5	-	110.0
Octadecyl	96.5	-	108.0

Values in parentheses indicate monotropy.

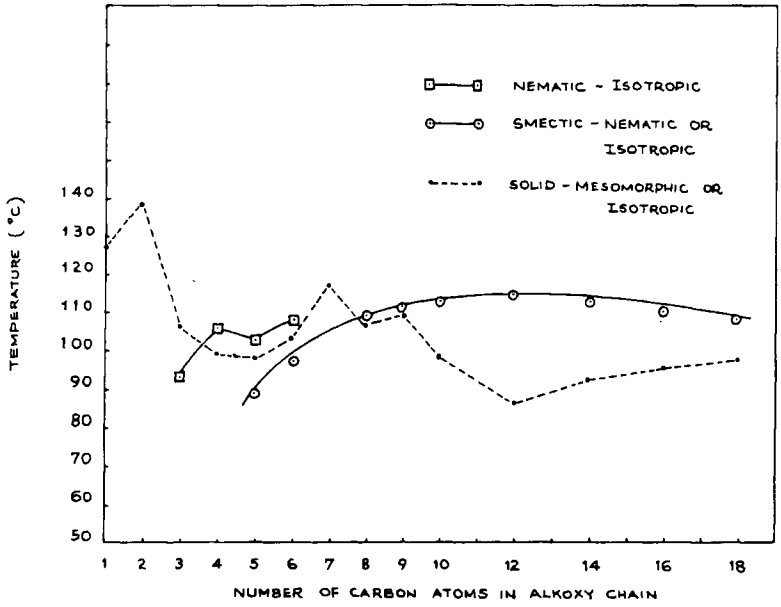

FIGURE 1 2-Methyl-5-(4′-n-alkoxy cinnamoyloxy)pyridines

Series II. 4-(4′-n-alkoxycinnamoyloxy)toluenes

The melting points and transition temperatures of the compounds synthesized are compiled in Table IV. The first seven members exhibit monotropic nematic phase except the ethyl homolog which is non-mesomorphic and hexyl derivative which shows enantiotropic nematic phase. The smectic phase commences with the octyl derivative as the enantiotropic phase. The octyl, nonyl, decyl and dodecyl derivatives exhibit both smectic and nematic as enantiotropic phase. Whereas the tetradecyl, hexadecyl and octadecyl derivatives exhibit only enantiotropic smectic phase. The heptyl, octyl, nonyl, hexadecyl and octadecyl derivatives adopt homeotropic textures while heating and

TABLE III

Average transition temperatures (°C)

Series	I	II
Smectic-isotropic or nematic (C_8 – C_{18})	110.7	94.9
Commencement of smectic phase	C_5	C_8

TABLE IV

Transition temperatures of 4-(4′-n-alkoxy-cinnamoyloxy)toluenes (II)

Alkyl group	Transition temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	(97.5)	104.5
Ethyl	-	-	165.5
Propyl	-	(99.5)	104.5
Butyl	-	(110.0)	125.5
Amyl	-	(102.5)	106.0
Hexyl	-	97.5	106.5
Heptyl	-	(101.0)	107.5
Octyl	82.5	101.0	104.0
Nonyl	82.0	88.0	101.0
Decyl	72.0	93.5	103.0
Dodecyl	69.0	97.0	101.0
Tetradecyl	67.5	-	199.5
Hexadecyl	73.0	-	83.5
Octadecyl	92.0	-	101.0

Values in parentheses indicate monotropy.

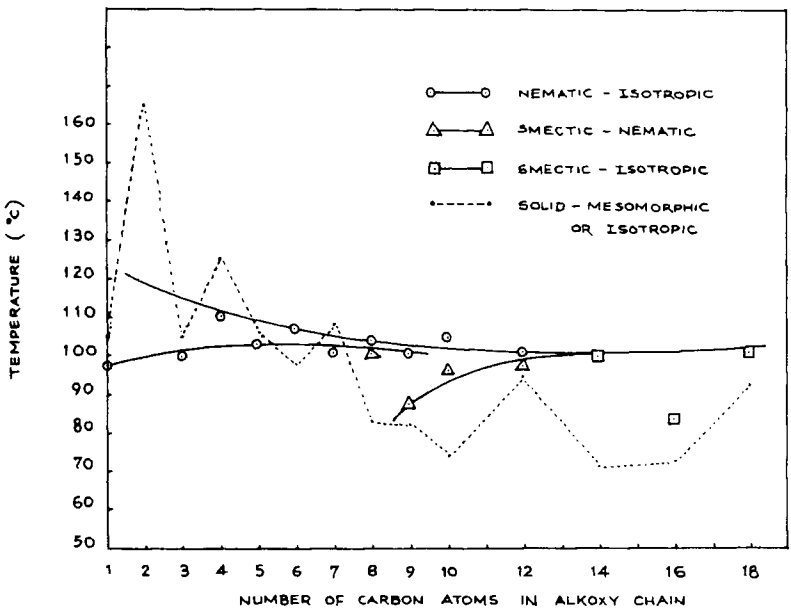

FIGURE 2 4-(4′-n-Alkoxycinnamoyloxy)toluenes

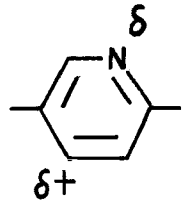

FIGURE 3

cooling the isotropic liquid. A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain is shown in Figure 2.

The thermal stability of series (I) is higher than that of series (II). Dewar et al.[7] have suggested that in the case of pyridine ring, there exists a permanent dipole (Figure 3) in the ring which causes mesophase strengthening effect leading to higher thermal stability. The smectic phase in series II commences at the octyl derivative whereas in the series (I) the smectic phase begins with the shorter chain amyl homolog. Konstantinov et al.[8] in their study of p-acylphenyl esters of p-n-alkoxybenzoic acids, have proposed that conjugation between the chain carbonyl group and the unshared electron pair of the other oxygen atom via the π benzene ring system can enhance the primary formation of a smectic mesophase so that a smectic phase will occur in a lower homolog. According to them, such conjugation leads to an increase in polarizability of this particular part of the molecule and to an increase in the dipole moment of the carbonyl due to the growth of a partial negative charge on its oxygen. As a result, there is an increase in the energy of the intermolecular interactions of the dipole-dipole and dispersion types. The additional contribution to the energy of interaction between molecules predominates in the lateral direction and favours formation of a smectic mesophase starting with a lower homolog.

A similar conjugation between the carbonyl group and the unshared electron pair of the heterocyclic nitrogen atom in the series I can explain the early commencement of smectic phase.

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