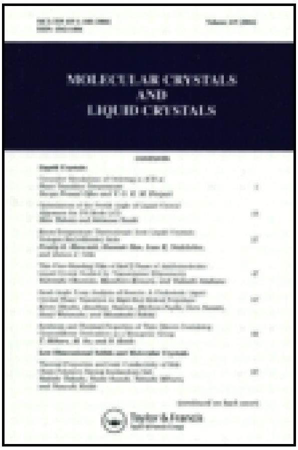

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Low Melting Mesomorphic Homologous Series: 2-Methyl-5-(4′-n-Alkoxybenzoyloxy) Pyridines

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Low Melting Mesomorphic Homologous Series: 2-Methyl-5-(4′-*n*-Alkoxybenzoyloxy)Pyridines

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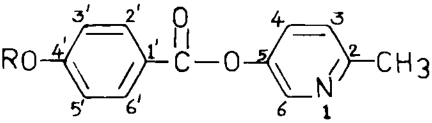
A homologous series of fourteen 2-methyl-5-(4′-*n*-alkoxybenzoyloxy)pyridines was synthesized and the mesomorphic behavior of its members studied. The first six members of the series are non-mesomorphic whereas the remainder exhibit only a smectic phase (either enantiotropic or monotropic). The plot of transition temperatures versus the number of carbon atoms in the alkyl chain shows an ascending tendency. The thermal stability of this series is compared with the related *p*-(*p*′-*n*-alkoxybenzoyloxy) toluenes.

1 INTRODUCTION

The synthesis and investigation of the physical properties of a new homologous series of liquid crystalline compounds are important in studying the relationship between the structure of molecules and the characteristics of the mesomorphic state. Dave and Vora[1] studied the homologous series of *p*-(*p*′-*n*-alkoxybenzoyloxy)toluenes. These esters exhibit both nematic and smectic phases. It was of interest to determine the effect on mesomorphic behavior of replacing a ring carbon atom *ortho* to the methyl group with a nitrogen atom. This structural change gave α-picoline esters (with only smectic properties) having the following general structure:



2 RESULTS AND DISCUSSION

The melting points and transition temperatures of the compounds synthesized are compiled in Table I. Mesomorphism does not begin to appear until the heptyl homolog. Heptyl, octyl, tetradecyl, hexadecyl and octadecyl derivatives show monotropic smectic phases whereas nonyl, decyl and dodecyl derivatives show enantiotropic smectic phases. On cooling the isotropic liquid batonnets separate from it and coalesce together to form a quite clear fan shaped focal conic texture (PLATE 1) in each case indicating that the smectic phase observed in this series is of the S_A type. On moving the coverslip on the slide with the sample in the smectic A phase, the fan texture observed is a focal conic texture but in no case has a schlieren or a homeotropic texture been observed. 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[2] 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 temperature versus the number of carbon atoms in the alkoxy chain Figure 1 shows the usual ascending tendency for the smectic-isotropic transitions.

Table II compares the average thermal stabilities of the present series (A) and the *p*-(*p*'-*n*-alkoxybenzoyloxy) toluene[1] series—the series (B). The thermal stability of series (A) is higher than that of series (B). Dewar *et al.*[3] have suggested that in the case of the pyridine ring, there exists a permanent dipole (Figure 2) in the ring which causes mesophase strengthening effects leading to higher thermal stability.

TABLE I

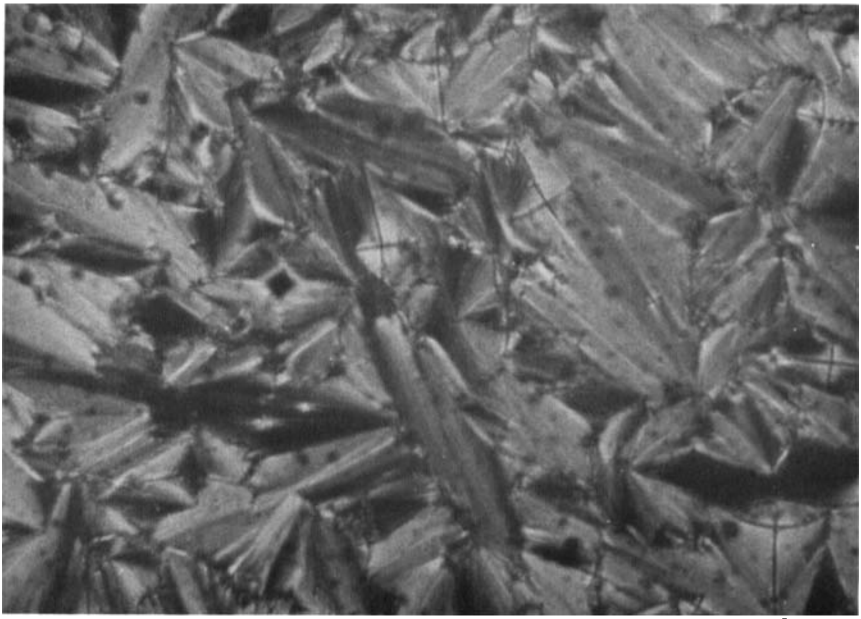
2-Methyl-5-(4'-*n*-alkoxybenzoyloxy)pyridines

Sr. No.	*n*-Alkyl group R	Transition temperatures (°C) Smectic	Isotropic
1	CH_3	—	61.5
2	C_2H_5	—	92.5
3	C_3H_7	—	91.0
4	C_4H_9	—	83.0
5	C_5H_{11}	—	74.5
6	C_6H_{13}	—	72.0
7	C_7H_{15}	(56.0)	64.5
8	C_8H_{17}	(60.5)	67.0
9	C_9H_{19}	58.0	62.5
10	$C_{10}H_{21}$	54.5	65.5
11	$C_{12}H_{25}$	58.5	67.0
12	$C_{14}H_{29}$	(66.5)	69.5
13	$C_{16}H_{33}$	(66.0)	74.5
14	$C_{18}H_{37}$	(65.5)	75.5

Values in the parentheses indicate monotropy.

PLATE 1

Smectic A fan texture of 2-Methyl-5-(4′-*n*-nonyloxy benzoyloxy) pyridine; film between glass slides at 60.5°C; crossed polarizers; magnification X136.



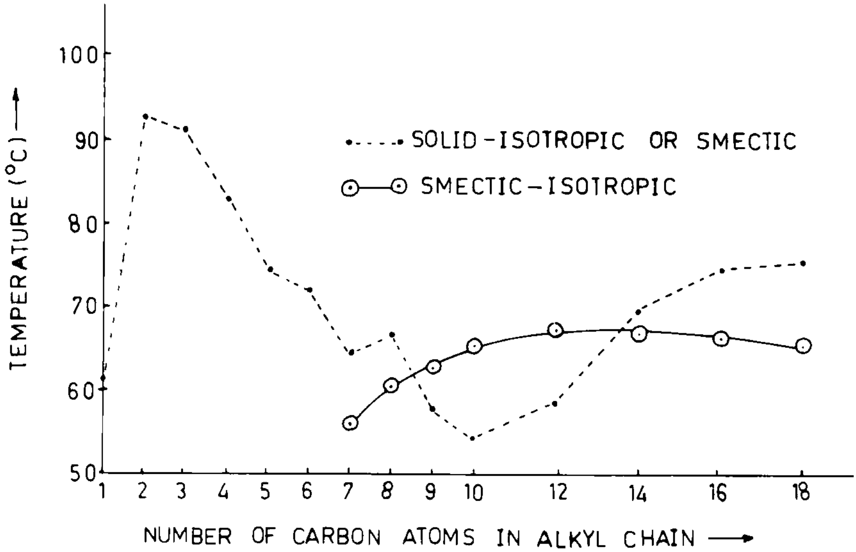


FIGURE 1 2-Methyl-5-(4′-*n*-alkoxybenzoyloxy) pyridines.

TABLE II

Average transition temperatures (°C)

Series	A	B
Smectic-isotropic or nematic (C_9-C_{14})	65.4	52.8
Commencement of smectic phase	C_7	C_9

TABLE III

2-Methyl-5-(4′-*n*-alkoxybenzoyloxy)pyridines

n-Alkyl group	Molecular formula	% Required			% Found		
		C	H	N	C	H	N
Methyl	$C_{14}H_{13}O_3N$	69.12	5.39	5.76	68.70	5.38	5.99
Ethyl	$C_{15}H_{15}O_3N$	70.01	5.88	5.44	70.48	6.01	5.84
Propyl	$C_{16}H_{17}O_3N$	71.29	6.27	5.17	70.85	6.26	5.16
Butyl	$C_{17}H_{19}O_3N$	71.58	6.67	4.91	71.94	6.80	4.88
Pentyl	$C_{18}H_{21}O_3N$	72.24	7.02	4.68	71.83	7.23	4.78
Hexyl	$C_{19}H_{23}O_3N$	72.82	7.40	4.47	73.19	7.10	4.88
Heptyl	$C_{20}H_{25}O_3N$	73.36	7.70	4.28	73.79	7.47	4.73
Octyl	$C_{21}H_{27}O_3N$	73.87	7.79	4.10	73.72	7.71	4.49
Nonyl	$C_{22}H_{29}O_3N$	74.33	8.22	3.94	74.59	7.95	4.02
Decyl	$C_{23}H_{31}O_3N$	74.76	8.46	3.79	74.96	8.05	3.93
Dodecyl	$C_{25}H_{35}O_3N$	75.56	8.82	3.53	75.54	9.16	3.85
Tetradecyl	$C_{27}H_{39}O_3N$	76.19	9.24	3.29	76.52	8.82	3.72
Hexadecyl	$C_{29}H_{43}O_3N$	76.78	9.55	3.09	77.03	9.09	3.57
Octadecyl	$C_{31}H_{47}O_3N$	77.34	9.77	2.91	76.93	9.47	3.07

The smectic phase in series (B) commences at the nonyl derivative whereas in the present series (A), the smectic phase begins with the shorter chain heptyl homolog. Konstantinov *et al.*,[4] 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 ether 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

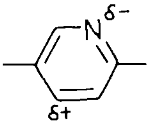


FIGURE 2 Permanent dipole in pyridine ring.

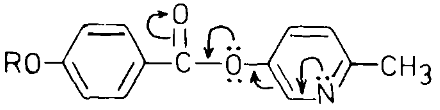


FIGURE 3

dipole-dipole and dispersion types. This additional contribution to the energy of interaction between molecules predominates in the lateral direction and favors 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 present series as represented in Figure 3 can explain the early commencement of the smectic phase.

3 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. *p-n*-Alkoxybenzoic acids and *p-n*-alkoxybenzoyl chlorides were prepared as described by Dave and Vora.[5]

2. A solution of equimolar amounts of *p-n*-alkoxybenzoyl chloride (0.005 mole) and 3-hydroxy-6-methylpyridine (0.005 mole) (Aldrich chemicals, USA) in pyridine (5–7 ml) was heated on a water bath for an hour and left overnight. The solidified reaction product was then stirred with 3–4 portions of petroleum ether (20 ml) and the supernatent solution was decanted each time. Petroleum ether and pyridine were removed from the decanted solution under reduced pressure and the residue was crystallized from dil. ethanol or ethanol (yield 50–60%). The analytical data of the compounds are given in Table III. The structure of the hexyl derivative, 2-methyl-5-(4′-*n*-hexyloxybenzoyloxy)pyridine is also confirmed by nmr spectra. NMR ($CDCl_3$) δ 0.90 (t, 3H, terminal CH_3 group of hexyloxy chain), 1.3-2.0(m, 8H, $-(CH_2)_4-$ of hexyloxy chain), 2.58 (s, 3H, CH_3 at C_2), 4.02 (t, 2H, $-CH_2$-0- of hexyloxy chain), 6.98 (d, J = 9Hz, 2H, C_3' and C_5' proton), 7.2 (d, J = 9Hz, 1H, C_3 proton), 7.49 (dd, $J_{(4,6)}$ = 1.8Hz and $J_{(4,3)}$ = 9Hz, 1H, C_4 proton), 8.15 (d, J = 9Hz, 2H, C_2' and C_6' proton), 8.41 (d, $J_{(6,4)}$ = 1.8Hz, 1H, C_6 proton).

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References

1. J. S. Dave and R. A. Vora, *Pramana, Suppl. No. 1* p. 447 (1975).
2. C. S. Oh, *Mol. Cryst. Liq., Cryst.*, **19,** 95 (1972).
3. M. J. S. Dewar, A. Griffin and R. M. Riddle in *Liquid Crystals and Ordered Fluids* **2** (Plenum Press, New York) 1974, p. 733
4. I. I. Konstantinov, Y. B. Amerik, B. A. Krentsel and E. V. Polunin, *Mol. Cryst. Liq. Cryst.*, **29,** 1 (1974).
5. J. S. Dave and R. A. Vora in *Liquid Crystals and Ordered Fluids* (Plenum Press, New York) 1970, p. 477.