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SYNTHESIS AND MESOMORPHIC PROPERTIES OF p-(p'-n-ALKOXYCINNAMOYLOXY) BENZYLIDENE- p"-HALOGEN SUBSTITUTED ANILINE

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SUMMARY

Synthesis and properties of a new homologous series p-(p'-n-alkoxycinnamoyloxy) benzylidene-p" - fluoroaniline with fluoro terminal groups are described. They exhibit mesomorphic behaviour over a wide range of temperatures. The mesomorphic behaviour has been studied and compared with other homologues series having terminal or lateral halogen groups which also exhibit mesomorphism.

INTRODUCTION

A large number of homologous series with terminal or lateral chloro- and bromo- groups which exhibit mesomorphic characteristics have been reported though a few data are available in the literature on the synthesis of series containing the fluoro group. The fluoro group is very small in size and also it is highly polar and these characteristics may alter the mesomorphic characteristics to a great extent. With this in view, the series p-(p'-alkoxycinnamoyloxy) benzylidene-p"- fluoro aniline have been synthesised and mesomorphic properties studied.

EXPERIMENTAL

Chemicals

All the chemicals used were Fluka A.R. Grade unless otherwise specified.

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Apparatus

Infrared spectra were recorded in the 2-15 μ region on a Perkin-Elmer Model 1420 ratio recording Spectrophotometer equipped with sodium chloride optics and calibrated by standard methods.

The mesomorphic characteristics were studied on a Leitz-Laborlux-12 Polarising microscope fitted with a heating arrangement.

Synthesis

Trans-p-n- alkoxycinnamic acids

These acids were synthesised by the method of Gray and Jones [1]. Into a 500 ml round bottom flask equipped with a condenser, 0.02 mol of p-n-alkoxy benzaldehyde, 0.04 mol of malonic acid, 8 ml of pyridine were transferred and 3 drops of piperidine were added. The contents were refluxed on a steam bath for 3 hrs. The mixture was poured in a beaker containing crushed ice (25 g) and conc. hydrochloric acid (25 ml). The solid mass thus obtained was filtered, washed with diluted hydrochloric acid and finally with distilled water and recrystallised from acetic acid. The m.p. of these acids were in agreement with those reported in the literature [1].

Acid Chlorides

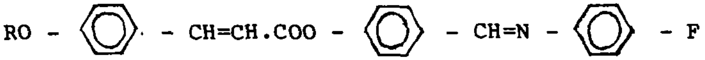
These were prepared by the action of thionyl chloride on the corresponding alkoxycinnamic acids. The boiling points and yields of the acid chlorides, thus produced were in agreement with the values given in the literature [2].

p-(p'-n-alkoxycinnamoyloxy) benzylidene -p"-fluoroaniline

The respective acid chlorides were reacted with p-hydroxybenzaldehyde to obtain p-(p'-n-alkoxycinnamoyloxy) benzaldehyde. Into a 50 ml round bottom flask fitted with a Leibig condenser were transferred 0.01 mol of p-(p'-n-alkoxycinnamoyloxy) benzaldehyde and p-fluoroaniline along with 20 ml of ethyl alcohol and a few drops of acetic acid. The contents were refluxed for 5 hrs. and cooled to room temperature. The product thus obtained was filtered and recrystallised from ethyl alcohol to give fine white needles.

TABLE 1

Physico-chemical properties of the substituents p-(p'-n-Alkoxycinnamoyloxy) benzylidene -p"-fluoroaniline



RO - C_6H_4 - CH=CH.COO - C_6H_4 - CH=N - C_6H_4 - F

Compound No.	n-alkyl group	Molecular formula	M.P. °C	Elemental* analysis			IR spectral data cm^{-1}		
				C	H	N	C=O	C=N-	-F
I	Methyl	$C_{23}H_{18}O_3NF$	285	73.60 (73.80	5.012 4.80	3.359 3.73)	1740	1580	1200
II	Ethyl	$C_{24}H_{20}O_3NF$	272	73.82 (74.02	5.181 5.14	3.621 3.59)	1730	1560	1190
III	Propyl	$C_{25}H_{22}O_3NF$	265	74.67 (74.44	5.249 5.45	2.994 3.47)	1760	1550	1185
IV	Butyl	$C_{26}H_{24}O_3NF$	250	74.91 (74.82	5.513 5.75	3.112 3.35)	1760	1560	1175
V	Amyl	$C_{22}H_{26}O_3NF$	227	74.98 (75.17	5.791 6.03	3.015 3.24)	1748	1570	1180
VI	Hexyl	$C_{28}H_{28}O_3NF$	222	75.22 (75.56	5.837 6.29	2.912 3.14)	1720	1575	1185
VII	Heptyl	$C_{29}H_{30}O_3NF$	215	75.62 (75.81	6.022 6.53	2.891 3.05)	1730	1590	1190
VIII	Octyl	$C_{30}H_{32}O_3NF$	215	76.325 (76.10	6.821 6.76	2.440 2.96)	1758	1595	1190
IX	Decyl	$C_{32}H_{36}O_3NF$	198	76.71 (76.64	7.257 7.18	3.011 2.79)	1745	1580	1180
X	Dodecyl	$C_{34}H_{40}O_3NF$	185	76.78 (77.12	7.115 7.56	2.025 2.64)	1755	1580	1178
XI	Tetradecyl	$C_{36}H_{44}O_3NF$	170	77.02 (77.55	7.613 7.89	2.031 2.51)	1740	1600	1170
XII	Hexadecyl	$C_{38}H_{48}O_3NF$	160	77.43 (77.95	7.981 8.20	1.981 2.39)	1740	1580	1180

* The theoretical values are given in parentheses.

All the compounds viz. methyl to octyl, decyl, dodecyl, tetradecyl and hexadecyl, belonging to this series were synthesized by following the above procedure.

RESULTS AND DISCUSSION

The physico - chemical properties of the newly synthesised p(p'-n-alkoxycinnamoyloxy) benzylidene-p"-fluoroanilines are given in Table 1 and the transition temperatures recorded are shown in Table 2.

TABLE 2

(Transition temperatures of p-(p'-n-Alkoxycinnamoyloxy) benzylidene-p"-fluoroaniline

Compound No.	n-Alkyl group.	Transition temperatures °C Smectic	Nematic	Isotropic
I	Methyl	-	147.0	285.0
II	Ethyl	-	140.0	272.0
III	Propyl	-	135.0	265.0
IV	Butyl	-	128.0	250.0
V	Amyl	110.0	152.0	227.0
VI	Hexyl	111.0	168.0	222.0
VII	Heptyl	105.0	180.0	215.0
VIII	Octyl	100.0	187.0	215.0
IX	Decyl	85.0	194.0	198.0
X	Dodecyl	73.0	-	185.0
XI	Tetradecyl	76.0	-	170.0
XII	Hexadecyl	73.0	-	160.0

In the infrared absorption spectra characteristic bands associated with functional groups viz carbonyl (C=0) of the ester group, 1740 ± 20 cm^{-1}, -C=N of the HC=N 1680 ± 30 cm^{-1} and fluoro substitution 1200 ± 15 cm^{-1} have been assigned.

As the molecules of the series p-(p'-n-alkoxycinnamoyloxy) benzylidene-p"-fluoroaniline are elongated, rod shaped, having three benzene rings supported by rigid bridges the molecule is structurally suitable for exhibiting mesomorphism over wide ranges of temperatures [3]. All the compounds studied show mesomorphism and some of them even exhibit polymesomorphism.

The first four members (4 carbon atoms, compound I-IV) exhibit only a nematic mesophase but compound V shows a nematic and smectic mesophase and compounds VI - X show both smectic and nematic mesophases making them polymesomorphic. After the tenth member (10 carbon atom) viz. compounds XI the nematic mesophase disappears and only the smectic mesophase is exhibited up to the highest homologue studied. The plot of number of carbon atoms in the alkyl chain versus transition temperature is shown in Fig. 1.

The N-I transitions show a steep descending tendency, a characteristic of a high melting series. [5]. These transitions also exhibit the usual alternation for odd and even members of the homologous series.

S-N transitions show an initial rising tendency and these transitions do not exhibit any alternation for odd and even members.

Information about the effects of terminal substituent on mesomorphic properties can be obtained by studying a range of mesogenic homologous series differing only in the nature of their terminal substituents.

The present series A p (p'-n-alkoxycinnamoyloxy) benzylidene-p"-fluoroaniline may be compared with-

Series B p-(p'-n-alkoxycinnamoyloxy) benzylidene-p"-chloroaniline [4].
Series C p-(p'-n-alkoxycinnamoyloxy) benzylidene-p"-bromoaniline [4].
Series D p-(p'-n-alkoxycinnamoyloxy) benzylidene-anilines [4].

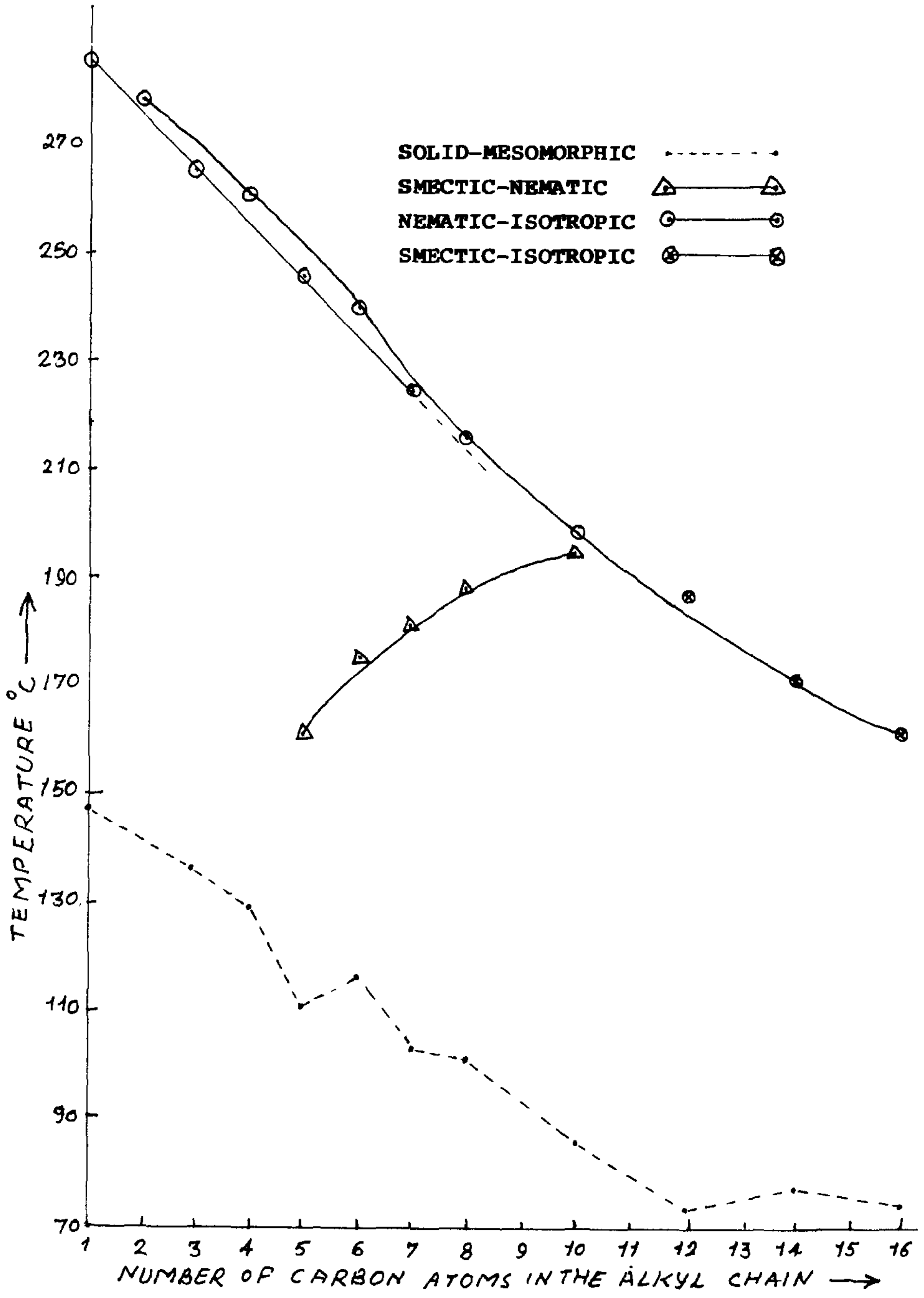
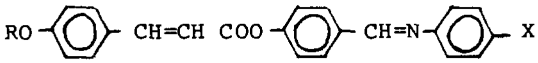


FIG. 1 p-(p'-n-alkoxycinnamoyloxy) benzilidene-p"-fluoraniline.

The molecular structure of all the series is :



where X=F, Cl, Br and H in the series A, B, C and D respectively.

All the four series are of high melting points. The N-I transition of all these series show a decreasing tendency however, the initial slopes of these transitions show a gradation. The decreasing tendency is much steeper in the terminal fluoro series, less steep with chloro and bromo groups and least steep in the -H terminal groups series. For the most sterically affected system in which the residual lateral attractions are weakest, the percentage increase in these lateral forces will be greatest with the increase in alkyl chain length and the transition curve will level off rapidly [5]. The size of the terminal substituent increases from F to Br with a more pronounced steric effect at bromo [5], and though the size of H-group is almost comparable with F-group. It is less polar than the halogens.

The homologues of the present series do not show decomposition even after 250°C but the first four members of series B and C undergo decomposition after 200°C. As the fluoro group is strongly polar, the cohesive forces of the molecule of this series are strong enough to resist thermal vibrations and maintain a parallel alignment thus exhibiting mesophasae at high temperatures whereas in series B and C these cohesive forces are not strong enough to resist thermal vibrations at high temperatures and ultimately break down without passing through a smooth isotopic transition and show decomposition [5].

Comparing the thermal stabilities of smectic and nematic mesophase of present series A with series B, C and D, substitution of the H- group increase the smectic and nematic thermal stabilities (Table 3).

TABLE 3

Thermal Stabilities

	A (X = F)	B (X = Cl)	C (X = Br)	D (X = H)
Average Nematic-Isotropic transition	226.0°C	266.0°C	266.0°C	195.0°C
Increase in nematic thermal stability from unsubstituted compound	31.0°C	71.0°C	71.2°C	-
Average Smectic-Nematic or Smectic-Isotropic transitions	170.0°C	232.2°C	232.5°C	168.2°C
Increase in smectic thermal stability from unsubstituted compound	1.8°C	64.0°C	64.0°C	-

The average smectic and nematic thermal stabilities are highest and very similar in the case of series B and C having Cl- and Br- terminal groups. Here again, the size of the terminal substituent affects mesomorphic characteristics as the fluoro group though strongly polar is very small in size and therefore, does not contribute much towards the axial polarizability reducing its smectic and nematic thermal stabilities.

In spite of this the average nematic mesophase of the present series is more stable thermally than for series D by 37.0°C.

The increase in average smectic thermal stability relative to the series D only at 7.8°C is much smaller. This suggests that the residual lateral attractions in the nematic mesophase exert a less dominant effect than the lateral attractions in the smectic mesophase and suggests that the increase in nematic thermal stability on passing from X=H to X=F is explained by increased residual terminal attractions (due to increased dipole moment of terminal substituent F) between the molecules.

It can be concluded that the fluoro group although small in size, affects the mesomorphic characteristics.

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