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Mesomorphic Behaviour of Biphenyl Esters I: Biphenyl-4-Trans-p-n-Alkoxycinnamates

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INTRODUCTION

Many mesomorphic compounds undergo decomposition on repeated heating. In the search for compounds which are appreciably stable to heating cycles and which display mesophases over a wide range of temperatures, we have prepared some biphenyl-4-*trans-p*-n-alkoxycinnamates and have investigated their mesomorphic properties. Table 1 shows the transition temperatures for the compounds prepared in this work.

RESULTS AND DISCUSSION

Biphenyl-4-*trans*-cinnamate is non-mesomorphic while the biphenyl-4-*trans-p-n*-alkoxycinnamates are mesomorphic. The methyl to hexyl derivatives are only nematic; heptyl to tetradecyl derivatives are both smectic and nematic while hexadecyl and octadecyl derivatives are purely smectic. The smectic phase originates at the heptyl homologue as a monotropic mesophase and becomes enantio-

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TABLE I

Biphenyl-4-*trans*-*p*-*n*-alkoxycinnamates: $RO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2{\cdot}C_{12}H_9$

R=	Transition temperatures (°C)		
	Solid-smectic	Solid-nematic or smectic-nematic	Nematic-isotropic or smectic-isotropic
Methyl	–	188.0	211.5
Ethyl	–	169.0	215.5
Propyl	–	163.0	199.5
Butyl	–	154.0	197.5
Pentyl	–	146.5	187.5
Hexyl	–	141.5	186.5
Heptyl	(127.5)[a]	137.5	179.0
Octyl	134.0	141.0	178.0
Nonyl	130.0	147.0	173.0
Decyl	126.0	151.0	170.0
Dodecyl	125.0	156.0	165.5
Tetradecyl	122.0	156.0	159.0
Hexadecyl	118.5	–	157.5
Octadecyl	114.0	–	153.5

[a] Value in parentheses indicates monotropy.

tropic for the succeeding homologues. The nematic phase is enantiotropic throughout. A plot of the transition temperatures versus the number of carbon atoms in the alkoxy chain is given in Fig. 1. The behaviour is analogous to other homologous series exhibiting nematic and smectic mesophases.

Table 2 summarizes the average thermal stabilities for (1) biphenyl-4-*trans*-*p*-n-alkoxycinnamates-A, (2) *trans*-*p*-n-alkoxycinnamic acids-B[1] and (3) 4-*p*-*n*-alkoxybenzylideneaminobiphenyls-C[2].

The average nematic thermal stability of series A is higher than that of series B or C. In comparision to series B, series A has a biphenyl nucleus and an ester linkage which could contribute appreciably to the polarizability of the molecules in the direction of molecular axis, thereby enhancing terminal cohesions. This would give higher nematic-isotropic transition temperatures than series B. Likewise molecules of series A are longer than those of series C due to different linking middle groups. The polarizability of $\text{-CH=CH-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-O-}$ is more than that of -CH=N- and hence series A has higher thermal stability for the nematic phase than series C.

Smectic thermal stabilities of series A, B and C are almost the same. The molecules of series A contain a -COO group and the biphenyl ring; these will

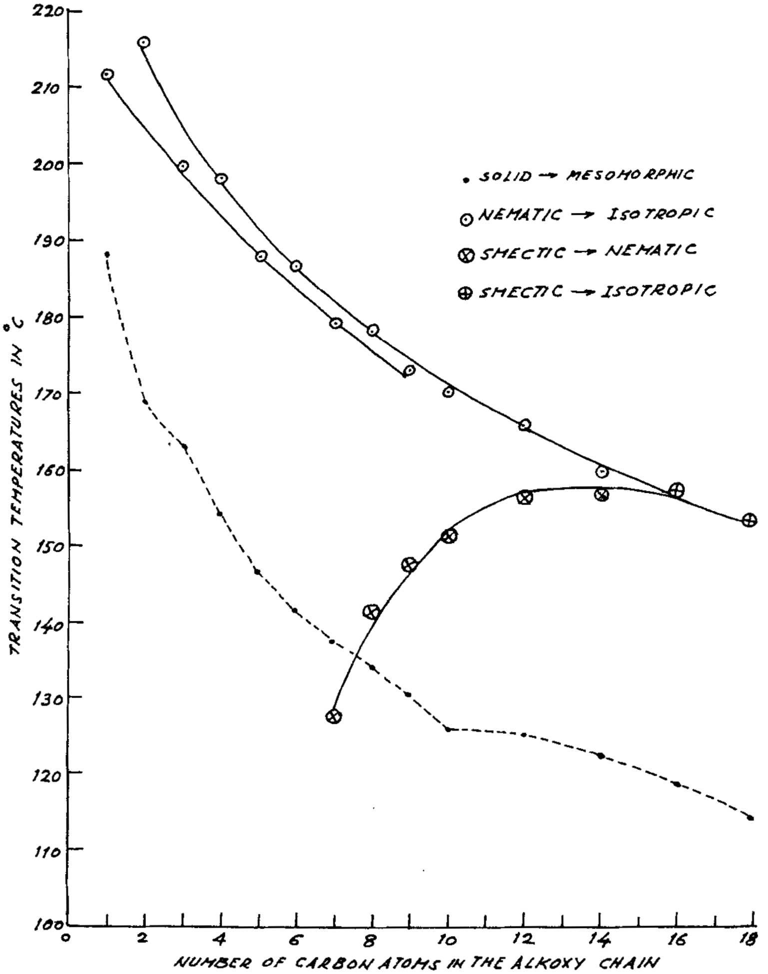
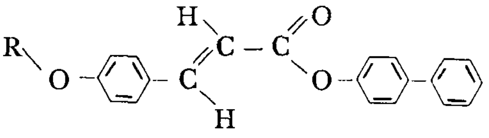


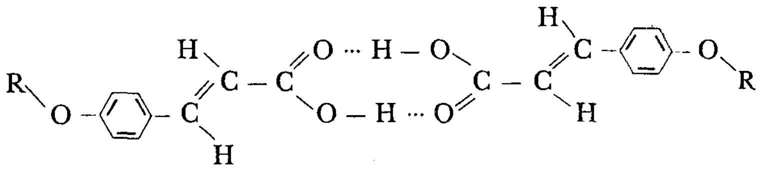
FIGURE 1 Biphenyl-4-*trans*-*p*-*n*-alkoxycinnamates.

bring about a reduction in lateral cohesive forces due to the transfer of conjugation from one end of the molecule to the other which is not possible in the acid dimer series B^3. Because of this effect though, nematic thermal stability of series A is higher as noted above the smectic thermal stability is not increased and it coincides with that of series B. In the case of series A and C, no doubt conjugation exists but the presence of the trans $\text{-CH=CH-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-O-}$ group in series A will contribute to the increase in the breadth of the molecules.

TABLE II

Average transition temperatures in (°C)	A	B	C
Nematic-isotropic $C_1 - C_{10}$	189.8	181.2	169.2
Smectic-nematic or isotropic $C_9 - C_{18}$	152.8	153.6	153.0
Commencement of the smectic phase in the series.	heptyl derivative	nonyl derivative	pentyl derivative


A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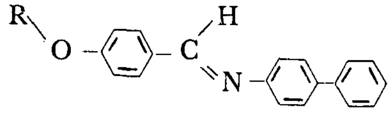
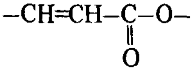

C

This will affect the smectic thermal stability of series A and thus it coincides with the smectic thermal stability of series C as molecular breadth has a more pronounced effect on the smectic mesophase than on the nematic mesophase[2, 4].

It is rather difficult to postulate the exact commencement of the smectic mesophase in a homologous series as it depends on a number of factors like polarizability, length to breadth ratio and geometry of the molecules.

The smectic mesophase in series C commences at the pentyl derivative which is earlier than that in the series A. The difference between the two series is in the middle group. Series A has the *trans*  $-CH{=}CH-\underset{\underset{O}{\|}}{C}-O-$ group which, due to its *trans* configuration, would increase the breadth of the molecule compared to the -CH=N- middle group in the other series. This increase in the breadth seems to be responsible for the late commencement of the smectic mesophase in series A.

Experimental

Preliminary measurements were made by the optical method of Dave and Dewar[5]. Precise measurements were made by the Leitz Ortholux polarizing microscope equipped with a heating stage. The slides were prepared by heating the substance on the slide up to its mesomorphic temperature and putting the cover slip over it and cooling. The slides were then heated in the slot of the heating block of the microscope and the temperatures were noted. The temperature was raised gradually and within the critical region of the transition temperature, the heating was regulated at three degrees per minute.

Preparation of Compounds

1.) *p-n*-alkoxybenzaldehydes and *trans-p-n*-alkoxycinnamic acids were prepared by the method of Gray[1]. Boiling points and the transition temperatures compare well with the literature.

2.) *Trans-p-n*-alkoxycinnamoyl chlorides[6]
Trans-p-n-alkoxycinnamoyl chlorides were prepared by treating the corresponding *trans-p-n*-alkoxycinnamic acids with thionyl chloride (25% excess) and heating on a water-bath till evolution of hydrochloric acid gas ceases. Excess thionyl chloride was distilled off.

3.) Biphenyl-4-*trans-p-n*-alkoxycinnamates
Equimolecular quantities of the *trans-p-n*-alkoxycinnamoyl chlorides and 4-hydroxybiphenyl were dissolved in pyridine, heated to boiling and allowed to stand at room temperature for six hours. The solid mass separated which was filtered and washed with alcohol to remove pyridine. The esters were first crystallized from chloroform-alcohol mixture (1:2). Finally they were recrystallized from acetic acid. Microanalytical data were satisfactory for carbon and hydrogen analysis.

Acknowledgement

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