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Study on Differential Scanning Calorimetry (DSC) of 4-(4′ -n-Alkoxycinnamoyloxy) Ethoxybenzenes (A) and 4-(4′ -n-Alkoxycinnamoyloxy)-n-Propoxybenzenes (B)

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Study on Differential Scanning Calorimetry (DSC) of 4-(4′-n-Alkoxycinnamoyloxy) Ethoxybenzenes (A) and 4-(4′-n-Alkoxycinnamoyloxy)-n-Propoxybenzenes (B)

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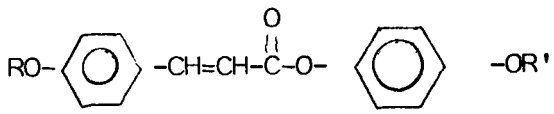
Two homologous series (A) and (B), with the following structure, were synthesized by reacting 4-n-



$R' = C_2H_5$ (Series A), C_3H_7 (Series B)

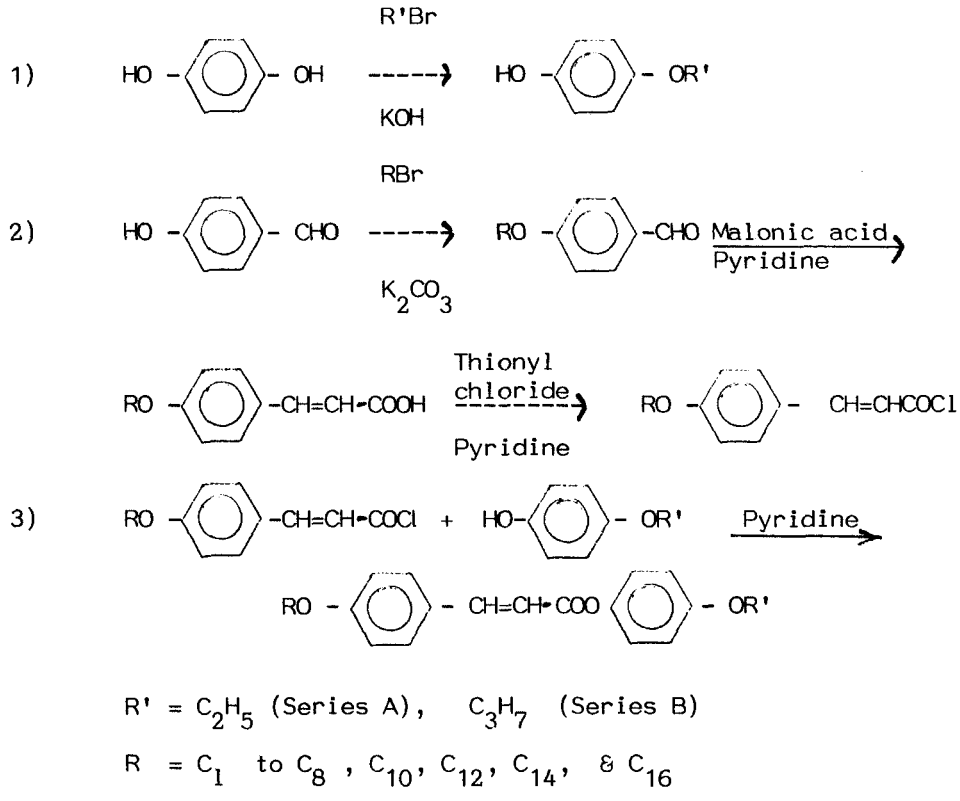
$R = C_1$ to C_8, C_{10}, C_{12}, C_{14} & C_{16}

alkoxycinnamoyl chlorides with 4-ethoxyphenol and 4-n-propoxyphenol, respectively. It was envisaged that the esters from esterification of 4-n-alkoxy cinnamic acids with 4-substituted phenols would have relatively lower transition enthalpies than the analogous phenylbenzoates. This is reflected in the mesogenic behaviour of both these series. The solid-mesogenic and mesogenic—isotropic transitions are lowered considerably. Both series exhibit nematic behaviour at short chain lengths and both smectic and nematic phases at longer chain lengths. DSC studies not only confirmed the results observed under polarising microscope but also revealed additional phase transitions in the solid phase. Entropies and enthalpies are also provided. Enthalpy values of structurally similar compounds reveal that the values for these series are comparable. The enthalpies of various types of phase transitions also fall in the range of reported values for these transitions.

Keywords: DSC, esters, enthalpy, entropy

INTRODUCTION

It was planned to synthesize new mesogens having an ester linkage with the variation of substituents at the ends of molecules to evaluate the effect of these changes on the mesomorphic properties as well as to provide relatively stable molecules with moderate transition temperatures. With this in mind, two homologous series were synthesized by the following route:



EXPERIMENTAL

The following starting materials were prepared using previously reported procedures:

4-n-alkoxyphenols,[1,2] 4-n-alkoxybenzaldehydes[3] and trans 4-n-alkoxycinnamic acids. Melting points and transition temperatures agreed with the literature values. trans-4-n-Alkoxycinnamoyl chlorides were prepared using thionyl chloride[5] and used without purification. The esters were prepared by esterification of the acid chlorides with the respective 4-n-alkoxyphenols in pyridine[6] in yields of 65% and purified by recrystallization from absolute ethanol. The compounds were characterized by elemental analysis (Table I). The transition temperatures are recorded in Table II.

TABLE I

Elemental analysis

n-Alkyl Group	Molecular Formula	% Required		% Found	
		C	H	C	H
1	2	3	4	5	6
		SERIES (A)			
Methyl	$C_{18}H_{18}O_4$	72.48	6.04	72.78	6.20
Ethyl	$C_{19}H_{20}O_4$	73.08	6.41	72.83	6.66
Propyl	$C_{20}H_{22}O_4$	73.62	6.75	73.98	6.47
Butyl	$C_{21}H_{24}O_4$	74.12	7.06	74.36	7.22
Pentyl	$C_{22}H_{26}O_4$	74.58	7.34	74.78	7.18
Hexyl	$C_{23}H_{28}O_4$	75.00	7.61	75.23	7.45
Heptyl	$C_{24}H_{30}O_4$	75.39	7.85	75.16	7.95
Octyl	$C_{25}H_{32}O_4$	75.76	8.08	75.85	8.48
Decyl	$C_{27}H_{36}O_4$	76.42	8.49	76.36	8.52
Dodecyl	$C_{29}H_{40}O_4$	76.99	8.85	77.23	8.97
Tetradecyl	$C_{31}H_{44}O_4$	77.50	9.17	77.32	9.35
Hexadecyl	$C_{33}H_{48}O_4$	77.95	9.45	77.85	9.49
		SERIES (B)			
Methyl	$C_{19}H_{20}O_4$	73.08	6.41	72.95	6.65
Ethyl	$C_{20}H_{22}O_4$	73.62	6.75	73.36	6.58
Propyl	$C_{21}H_{24}O_4$	74.12	7.06	74.03	7.36
Butyl	$C_{22}H_{26}O_4$	74.58	7.34	74.38	7.64
Pentyl	$C_{23}H_{28}O_4$	75.00	7.61	74.86	7.75
Hexyl	$C_{24}H_{30}O_4$	75.39	7.85	75.56	7.75
Heptyl	$C_{25}H_{32}O_4$	75.76	8.08	75.65	7.95
Octyl	$C_{26}H_{34}O_4$	76.10	8.29	75.80	8.58
Decyl	$C_{28}H_{38}O_4$	76.71	8.68	76.90	8.75
Dodecyl	$C_{30}H_{42}O_4$	77.25	9.01	76.80	9.36
Tetradecyl	$C_{32}H_{46}O_4$	77.73	9.31	77.31	9.16
Hexadecyl	$C_{34}H_{50}O_4$	78.16	9.58	78.39	9.39

The transition temperatures were determined by using a Laborlux 12 POL Polarising microscope. The calorimetric studies were carried out by using DU Pont 910 Differential Scanning Calorimeter.

RESULTS AND DISCUSSIONS

Both series (A) and (B) exhibited nematogenic phases. The calorimetric study indicated solid—solid transitions (Table III) in many of the homologues of both these series. The enthalpy changes of these solid modifications were small in magnitude.

The changes in entropies were calculated from the enthalpy changes obtained during phase transitions. The plots of ΔS versus the number of carbon atoms in the alkyl chain exhibit the odd-even effect up to the fourth member of the series (A) (Figure 1). In the case of series (B), the odd-even effect could not be observed as only a few lower members were studied for calorimetry. The entropy changes

TABLE II

Transition temperatures (optical and DSC method)

No. of Carbon Atom in n-alkyl Chain	$K_1 - K_2$ °C	K – S °C	K – N or S – N °C	N – I or S – I °C
1	2	3	4	5
		SERIES (A)		
C_1	—	—	131 [125]	150 [142]
C_2	—	—	145 [138]	161 [150]
C_3	— [70]	—	126 [125]	145 [145]
C_4	—	—	111 [103]	150 [136]
C_5	—	—	97 [95]	131 [123]
C_6	[62,73]	—	88 [87]	140 [129]
C_7	—	(72) [–]	88 [85]	136 [126]
C_8	—	(92) [–]	99 [94]	133.5 [125]
C_{10}	—	80 [75]	104 [98]	126 [118]
C_{12}	—	86 [78]	109 [102]	122 [114]
C_{14}	—	86 [82]	109.5 [100]	116.5 [106]
C_{16}	— [68] — [70]	90 [85]	108 [102]	113 [105]
		SERIES (B)		
C_1	—	—	(126) [–]	127 [127]
C_2	—[120]	—	125 [124]	144 [144]
C_3	— [86]	—	(127) [–]	128 [126]
C_4	—	—	110 [112]	137 [137]
C_5	—	—	102 [102]	124 [124]
C_6	— [85]	—	98 [97]	130 [126]
C_7	—	(92) [–]	94 [–]	127 [–]
C_8	—	99 [–]	101.5 [–]	124 [–]
C_{10}	—	78.5 [81]	102 [104]	116 [119]
C_{12}	—	85 [–]	102 [–]	111 [–]
C_{14}	—	86 [–]	— [–]	107 [–]
C_{16}	— [80]	88 [88]	— [–]	104 [104]

K, Solid; S, smectic; N, nematic; I, Isotropic; ( ), Monotropic; [ ], DSC Method.

when plotted against the number of carbon atoms exhibit rising tendency as the chain length increases.

A comparison of enthalpy changes (Table IV) indicate that the present series have lower enthalpy values for all the transitions compared to those for the analogous phenyl benzoates. In the case of stilbenes, the enthalpy values of the cinnamates for solid-mesogenic (K—N) transition is lower whereas it is almost the same for nematic-isotropic (N—I) transitions. The comparison indicates that cinnamates are less ordered compared to the benzoates. This can be attributed to the trans conformation of the cinnamates.

The texture of the smectic phases observed was focal conic-fan shaped suggesting that these are smectic phases except the seventh, eight & tenth homologues of the series (B) which exhibited homeotropic textures.

The present study has provided a host of new mesogens. Calorimetric data was also obtained for these mesogens.

TABLE III

Enthalpy and entropy

No. of Carbon Atom in n-alkyl Chain	Phase	Enthalpy ΔH Kcal/mole	Entropy ΔS Cal/mole/°K	Total ΔS Cal/mole/°K
1	2	3	4	5
		SERIES (A)		
C_1	N	5.38	13.51	
	I	0.17	0.41	13.92
C_2	N	6.48	15.76	
	I	0.26	0.61	16.37
C_3	K	0.18	0.52	
	N	5.80	14.56	
	I	0.24	0.57	15.65
C_4	N	6.75	17.95	
	I	0.36	0.88	18.83
C_5	K_1	0.089	0.26	
	K_2	0.29	0.84	
	N	6.05	16.44	
	I	0.30	0.76	18.30
C_6	N	8.17	22.69	
	I	0.28	0.69	23.38
C_7	N	9.20	25.69	
	I	0.24	0.60	26.29
C_8	N	6.17	16.82	
	I	0.28	0.70	17.52
C_{10}	S	6.52	18.74	
	N	0.14	0.37	
	I	0.36	0.91	20.02
C_{12}	S	5.56	15.83	
	N	0.24	0.63	
	I	0.47	1.22	17.68
C_{14}	K	0.33	0.98	
	S	7.55	21.27	
	N	0.57	1.53	
	I	0.60	1.69	25.47
C_{16}	K	0.20	0.61	
	S	7.72	21.27	
	N	0.69	1.84	
	I	0.53	1.39	25.11
		SERIES (B)		
C_1	I	4.33	10.83	10.83
C_2	K	0.51	1.30	
	N	2.87	7.22	
	I	0.11	0.27	8.79
C_3	I	3.73	9.35	9.35
C_4	N	3.11	8.08	
	I	0.13	0.32	8.40
C_5	N	6.27	16.72	
	I	0.16	0.39	17.11
C_6	K	1.20	3.38	
	N	6.05	16.36	
	I	0.19	0.46	20.20
C_{10}	S	5.15	14.55	
	N	0.10	0.27	
	I	0.22	0.57	15.39
C_{16}	K	0.52	1.46	
	S	5.23	14.48	
	I	1.06	2.80	18.74

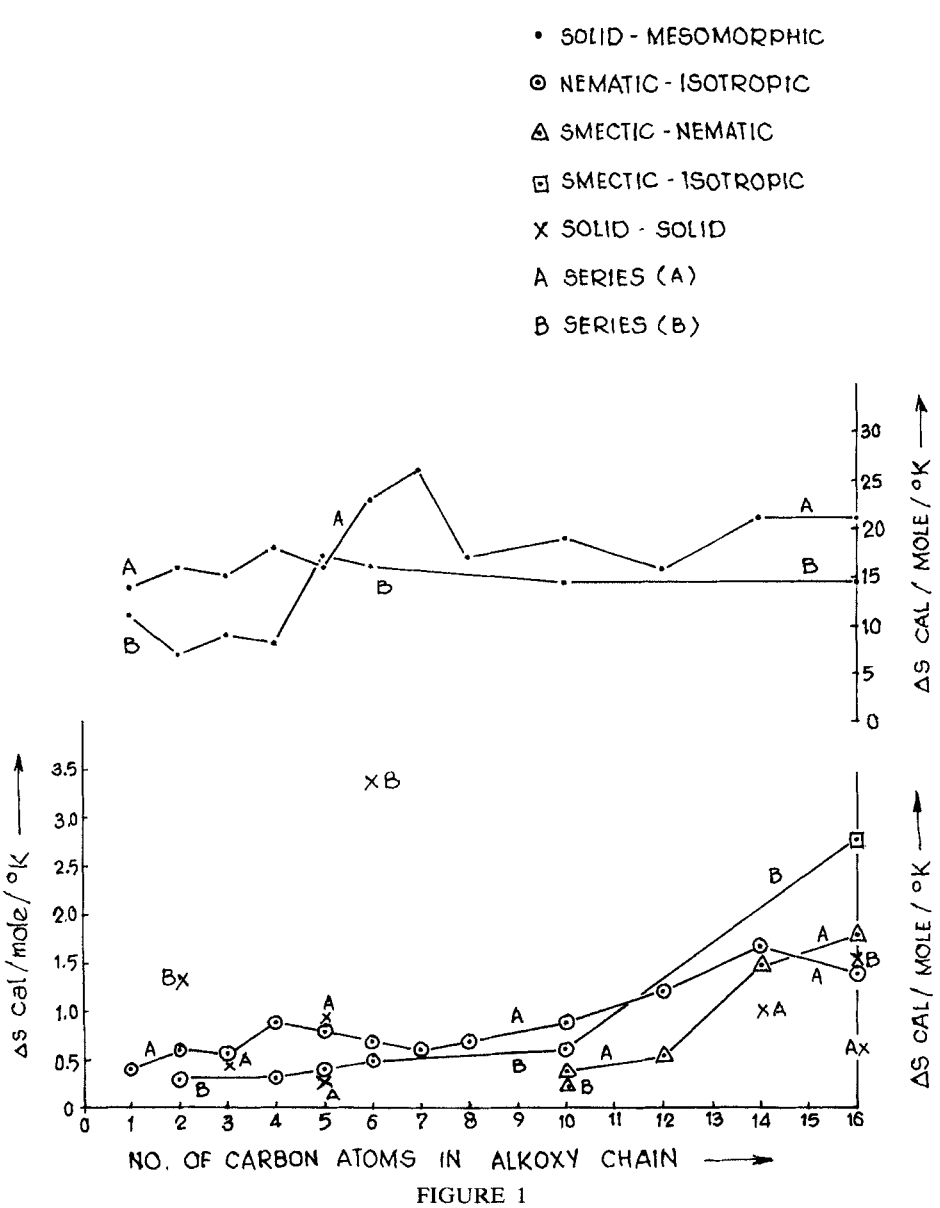


FIGURE 1

Acknowledgment

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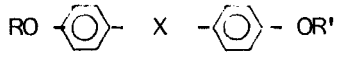
TABLE IV



R	R′	X	ΔH (Kcal/mole) K – N	ΔH (Kcal/mole) N – I
C_8H_{17}	C_2H_5	—COO—[7]	8.36	0.33
C_8H_{17}	C_2H_5	—CH=CH—COO—	6.17	0.28
C_6H_{13}	C_4H_9	—COO—[7]	8.36	0.32
C_6H_{13}	C_4H_9	—CH=CH—COO—	3.41	0.16
CH_3	C_4H_9	—CH=CH—[8]	9.48	0.18
CH_3	C_4H_9	—CH=CH—COO—	6.67	0.19

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