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The Preparation and Measurement of the Temperatures and Heats of Transition of the Liquid Crystal Phases of Two Homologous Series: 2-hydroxy-1,2-bis(4-n-alkyloxyphenyl)-1-(4-ethoxyphenyl)iminoethane and (4-n-decyloxyphenyl)iminoethane

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The Preparation and Measurement of the Temperatures and Heats of Transition of the Liquid Crystal Phases of Two Homologous Series: 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-ethoxyphenyl)iminoethane and (4-*n*-decyloxyphenyl)iminoethane

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Two homologous series A and B, viz, 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-ethoxyphenyl) and 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-*n*-decyloxyphenyl)iminoethanes have been prepared with varying number of carbon atoms in the alkoxy chain.

The transition temperatures and textures of the mesophases were determined with a polarizing microscope equipped with a Mettler FP-5 hot stage. The transition temperatures and transition heats were measured using a Perkin-Elmer DSC-2.

The compounds of the two series with the same number of carbon atoms do not exhibit the same mesophases. Series A exhibits a nematic phase for compounds with n = 1–16 and also a smectic phase for compounds with n = 10, 12 and 16. Series B shows a nematic mesophase for compounds with $n \leq 8$ and either one or two smectic mesophases for compounds with $n \geq 5$.

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1. INTRODUCTION

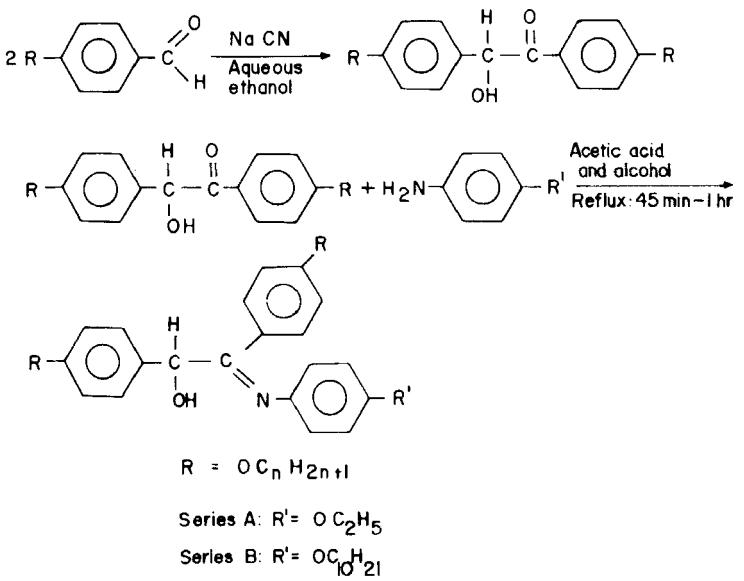
In continuation of our investigation of homologous series of thermotropic liquid crystal compounds, we report here the preparation and liquid crystal properties of 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-ethoxyphenyl) and 2-hydroxy-1,2-bis(4-*n*-decyloxyphenyl)iminoethanes which were synthesized by the condensation of α-hydroxyketones (4-*n*-alkyloxybenzoins) with 4-ethoxyaniline and 4-*n*-decyloxyaniline as outlined in Scheme I. The mesophases were identified using a polarising microscope and the thermal properties studied with a differential scanning calorimeter. The mesophases and some of the physical properties of the 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-propyloxyphenyl)iminoethanes have been reported previously[1] by members of our laboratory.

2. EXPERIMENTAL PROCEDURES

2.1. Synthesis

2.1.1. 4-n-Alkoxybenzaldehydes 4-Methoxybenzaldehyde, 4-ethoxybenzaldehyde and 4-ethoxyaniline were purchased from Aldrich Chemical Company and were used after redistillation. 4-*n*-Pro-

SCHEME I



pyloxybenzaldehyde (b.p. 91–92°C/2 mm Hg), 4-*n*-butyloxybenzaldehyde (b.p. 111–112°C/2 mm Hg), 4-*n*-pentyloxybenzaldehyde (b.p. 114–115°C/2 mm Hg), 4-*n*-hexyloxybenzaldehyde,† 4-*n*-heptyloxybenzaldehyde (b.p. 136–137°C/2 mm Hg), 4-*n*-octyloxybenzaldehyde (b.p. 152–153°C/2 mm Hg), 4-*n*-decyloxybenzaldehyde, 4-*n*-undecyloxybenzaldehyde† and 4-*n*-hexadecyloxybenzaldehyde† were prepared from 4-hydroxybenzaldehyde and the corresponding alkylbromides by the method reported by Gray and Jones.[2] The average yields varied between 60–80%. The 4-*n*-decyloxyaniline was prepared according to the method described by Buu-Hoi, *et al.*[3]

2.1.2. Preparation of 4-n-Alkoxybenzoins All the 4-*n*-alkoxybenzoins employed in the present investigation were obtained by the procedure described by Vogel.[4]

In a typical experiment, rectified spirit (20 ml) was taken in a 50 ml round bottom flask to which freshly distilled 4-*n*-alkoxybenzaldehyde (0.1 mole) and a solution of sodium cyanide (1 g, 98%) in 10 ml of water was added. The mixture was gently refluxed for 45 minutes to an hour. The rectified spirit was rotoevaporated and the cooled reaction mixture was poured into ice water (100 ml). The resultant α-hydroxyketone, (4-*n*-alkyloxybenzoin) was extracted with ether (20 × 3 ml). The ether layer was dried and the solvent evaporated in a rotoevaporator. The oil (4-*n*-alkoxybenzoin) was used for the preparation of the 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)1-1(4-*n*-decyloxyphenyl)iminoethanes.

2.1.3. Preparation of 2-hydroxy-1,2-bis(4-n-alkyloxyphenyl)-1-(4-n-decyloxyphenyl)iminoethanes 4-*n*-alkyloxybenzoin (0.01 mole) was dissolved in alcohol (20 ml) and an equimolar quantity of 4-*n*-decyloxyaniline was added followed by one ml of glacial acetic acid. The reaction mixture was refluxed gently on a steam bath for 15–20 minutes and cooled. The precipitate of 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-*n*-decyloxyphenyl)iminoethane was filtered and recrystallised from a mixture of alcohol and acetic acid until the transition temperatures were reproducible (At least 5 times). The 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-ethoxyphenyl)iminoethanes were prepared by the method described above using 4-ethoxyaniline.

The physical properties of these samples are described in Tables I and II.

The CHN analysis of series A and B is reported in Tables III and IV.

†These compounds were used without purification.

TABLE I

Temperatures and enthalpies of transition for the 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-*n*-ethoxyphenyl)iminoethanes

			ΔH	ΔH	ΔS		ΔH	ΔH	ΔS		ΔH	ΔH	ΔS
			cal	kcal	cal		cal	kcal	cal		cal	kcal	cal
n	R	T(°C)	g	mol	mol K	T(°C)	g	mol	mol K	T(°C)	g	mol	mol K
		Crystal–Isotropic (C–I)				Smectic–Nematic (C–N)				Nematic–Isotropic (N–I)			
1	O CH_3	127.4	24.9	9.8	24.4					120.2	0.77	0.30	0.76
2	O CH_2CH_3	146.9	27.7	11.6	27.6					144.5	1.17	0.49	1.17
3	O $(CH_2)_2CH_3$	124.5	23.0	10.3	25.9					123.4	0.76	0.34	0.86
		Crystal–Nematic (C–N)											
4	O $(CH_2)_3CH_3$	103.8	15.6	7.4	19.7					129.2	0.89	0.42	1.04
5	O $(CH_2)_4CH_3$	100.3[b] 102.4[b]								119.1	0.62	0.31	0.79
6	O $(CH_2)_5CH_3$	95.5	21.6	11.5	31.2					121.5	0.81	0.43	1.09
7	O $(CH_2)_6CH_3$	98.3	28.2	15.8	42.6					117.4	0.79	0.41	1.05
8	O $(CH_2)_7CH_3$	97.4	27.0	15.9	42.9					119.1	0.72	0.42	1.07
10	O $(CH_2)_9CH_3$	100.2	28.0	18.0	48.2	92.8	0.11	0.07	0.19	115.3	0.97	0.62	1.60
12	O $(CH_2)_{11}CH_3$	103.1	30.8	21.6	57.4	99.8	0.52	0.36	0.96	112.3	0.94	0.66	1.71
		Crystal–Isotropic (C–I)											
16	O $(CH_2)_{15}CH_3$	105.8	33.4	27.1	71.5	100.0				102.4	2.50[a]	2.30[a]	6.13[a]

[a]Peaks not resolved (estimated).
[b]Two peaks whose size depends on thermal history.

TABLE II

Temperatures and enthalpies of transition for the 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-*n*-decyloxyphenyl)iminoethanes

n	R	T(°C)	ΔH cal/g	ΔH kcal/mol	ΔS cal/mol K	T(°C)	ΔH cal/g	ΔH kcal/mol	ΔS cal/mol K	T(°C)	ΔH cal/g	ΔH kcal/mol	ΔS cal/mol K	T(°C)	ΔH cal/g	ΔH kcal/mol	ΔS cal/mol K
		Crystal–Isotropic (C–I)				Smectic II–Smectic I (S_{II}–S_I)				Smectic I–Nematic (S–N)				Nematic–Isotropic (N–I)			
1	O CH_3	104.4	31.7	16.0	42.4												
		Crystal–Nematic (C–N)															
2	O CH_2CH_3	96.1	29.1	15.5	42.0									113.8	0.77	0.41	1.06
3	O $(CH_2)_3CH_3$	100.4	28.4	15.9	42.6									103.3	0.61	0.34	0.90
4	O $(CH_2)_3CH_3$	97.8	17.2	10.1	27.2									110.6	0.98	0.58	1.51
5	O $(CH_2)_4CH_3$	96.0	16.1	9.9	26.9					94.5	0.90	0.55	1.50	106.8	1.00	0.62	1.63
		Crystal–Smectic I (C–S_I)															
6	O $(CH_2)_5CH_3$	89.0	14.2	9.1	25.2					103.3	0.65	0.42	1.12	110.4	1.36	0.88	2.30
7	O $(CH_2)_6CH_3$	91.7	27.3	18.4	50.4	88.8	0.96	0.65	1.80	107.6	1.13	0.76	2.00	110.3	1.64	1.10	2.87
		Crystal–Smectic II (C–S_{II})															
8	O $(CH_2)_7CH_3$	89.6	18.4	12.9	35.6	92.6	1.03	0.72	1.97	112.0				112.4	4.24[a]	2.99[a]	7.76[a]
		Crystal–Smectic I (C–S_I)												Smectic I–Isotropic (S_I–I)			
10	O $(CH_2)_7CH_3$	103.2	24.6	18.6	49.4									112.7	4.90	3.71	9.62
11	O $(CH_2)_{10}CH_3$	102.5	26.3	20.6	54.9									111.9	5.31	4.16	10.81
		Crystal–Smectic II (C–S_{II})															
12	O $(CH_2)_{11}CH_3$	94.8	22.0	17.8	48.4	98.8	2.37	1.93	5.19					111.8	5.66	4.60	11.96
16	O $(CH_2)_{15}CH_3$	96.6	25.4	23.4	63.3	102.1	3.29	3.04	8.10					108.1	5.60	5.18	13.60

[a]Peaks not resolved (estimated).

TABLE III

CHN Analysis of 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-ethoxyphenyl)iminoethane

R	Mol. Formula	Analysis %					
		Calculated			Found		
		C	H	N	C	H	N
OCH_3	$C_{24}H_{25}NO_4$	73.67	6.39	3.58	73.44	6.50	3.41
OC_2H_5	$C_{26}H_{29}NO_4$	74.48	6.92	3.34	74.31	6.98	3.49
OC_3H_7	$C_{28}H_{33}NO_4$	75.18	7.38	3.13	75.51	7.27	2.95
OC_4H_9	$C_{30}H_{37}NO_4$	75.80	7.78	2.94	75.37	7.53	2.82
OC_5H_{11}	$C_{32}H_{41}NO_4$	76.36	8.15	2.78	76.45	8.28	2.80
OC_6H_{13}	$C_{34}H_{45}NO_4$	76.86	8.47	2.64	76.95	8.33	2.48
OC_7H_{15}	$C_{36}H_{49}NO_4$	77.29	8.76	2.50	77.15	8.61	2.76
OC_8H_{17}	$C_{38}H_{53}NO_4$	77.70	9.02	2.38	77.83	9.29	2.23
$OC_{10}H_{21}$	$C_{42}H_{61}NO_4$	78.40	9.48	2.18	78.61	9.71	2.31
$OC_{12}H_{25}$	$C_{46}H_{69}NO_4$	78.98	9.86	2.00	79.19	10.03	1.91
$OC_{16}H_{33}$	$C_{54}H_{85}NO_4$	89.92	10.92	1.72	79.73	10.61	1.49

2.2. Microscopic Observation

The transition temperatures and textures of the mesophases were determined using a Leitz Ortholux polarizing microscope equipped with a Mettler FP-5 hot stage. The smectic phase of series A generally showed a fan texture or in drops without a cover slip, a homeotropic

TABLE IV

CHN Analysis of 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-*n*-decyloxyphenyl)iminoethane

R	Mol. Formula	Analysis %					
		Calculated			Found		
		C	H	N	C	H	N
OCH_3	$C_{32}H_{41}NO_4$	76.36	8.15	2.78	76.63	7.82	2.59
OC_2H_5	$C_{34}H_{45}NO_4$	76.86	8.47	2.64	76.54	8.11	2.35
OC_3H_7	$C_{36}H_{49}NO_4$	77.29	8.76	2.50	77.57	8.58	2.73
OC_4H_9	$C_{38}H_{53}NO_4$	78.69	9.02	2.38	78.43	9.39	2.11
OC_5H_{11}	$C_{40}H_{57}NO_4$	78.06	9.26	2.27	78.49	9.57	2.03
OC_6H_{13}	$C_{42}H_{61}NO_4$	78.40	9.48	2.18	78.18	9.25	2.13
OC_7H_{15}	$C_{44}H_{65}NO_4$	78.70	9.68	2.08	79.07	9.61	2.34
OC_8H_{17}	$C_{46}H_{69}NO_4$	78.98	9.86	2.00	79.31	9.53	1.71
$OC_{10}H_{21}$	$C_{50}H_{73}NO_4$	79.48	10.19	1.85	79.45	10.07	1.49
$OC_{11}H_{23}$	$C_{52}H_{81}NO_4$	79.71	10.34	1.79	79.78	9.95	1.93
$OC_{12}H_{25}$	$C_{54}H_{85}NO_4$	79.92	10.47	1.72	80.26	10.41	1.38
$OC_{16}H_{33}$	$C_{62}H_{101}NO_4$	80.62	10.94	1.52	80.44	11.14	1.40

texture. The homeotropic texture was examined using convergent light and the phase is uniaxial positive which indicates that the phase can probably be classified as smectic A. The two smectic phases of series B both show schlieren textures or a mixture of schlieren with a fan texture. Generally it is difficult to see the transition optically and there appears to be a decrease in the interference colors when the transition from smectic I to smectic II occurs. The transition temperatures agree to within ± 1.0°C with those determined from the DSC. The transition temperatures reported in the tables are those determined with the DSC.

2.3. Thermal Analysis

The thermal properties of the two series were studied using a Perkin-Elmer DSC-2. The temperature scale of the calorimeter was calibrated using indium, tin and lead as standards (supplied by the manufacturer). A scanning rate of 2.5°C/min was used in the determination of heats of transition except when slower rates were necessary to resolve two transitions with a small temperature separation. The temperatures shown in the tables on the following pages were taken directly from the calorimeter data after correcting for scanning rate.

The determination of the base line for calculation of enthalpies of transition was done by the method of Guttmann and Flynn.[5]

The reproducibility in the transition temperatures was ± 0.1°C and the transition heats were reproducible to within $\pm 2\%$ for $4.0 \leq H \leq 25$ cal/g and within $\pm 5\%$ for $H \leq 1.0$ cal/g.

3. RESULTS AND DISCUSSIONS

The temperatures of transition and transition enthalpies are presented in Tables I and II for series A and B respectively. The Figures 1–4 are plots of temperature of transition and transition enthalpy against the number of carbon atoms in the alkoxy chain of each series under consideration.

From the graphs, it is evident that both series A and B exhibit an even-odd effect which is more pronounced at the nematic–isotropic transition. The compounds containing an even number of carbon atoms in the alkoxy chain have higher transition temperatures; series A presents a greater regularity in the transition temperature and enthalpies.

The compounds of series A with 1, 2, 3 and 16 carbon atoms in

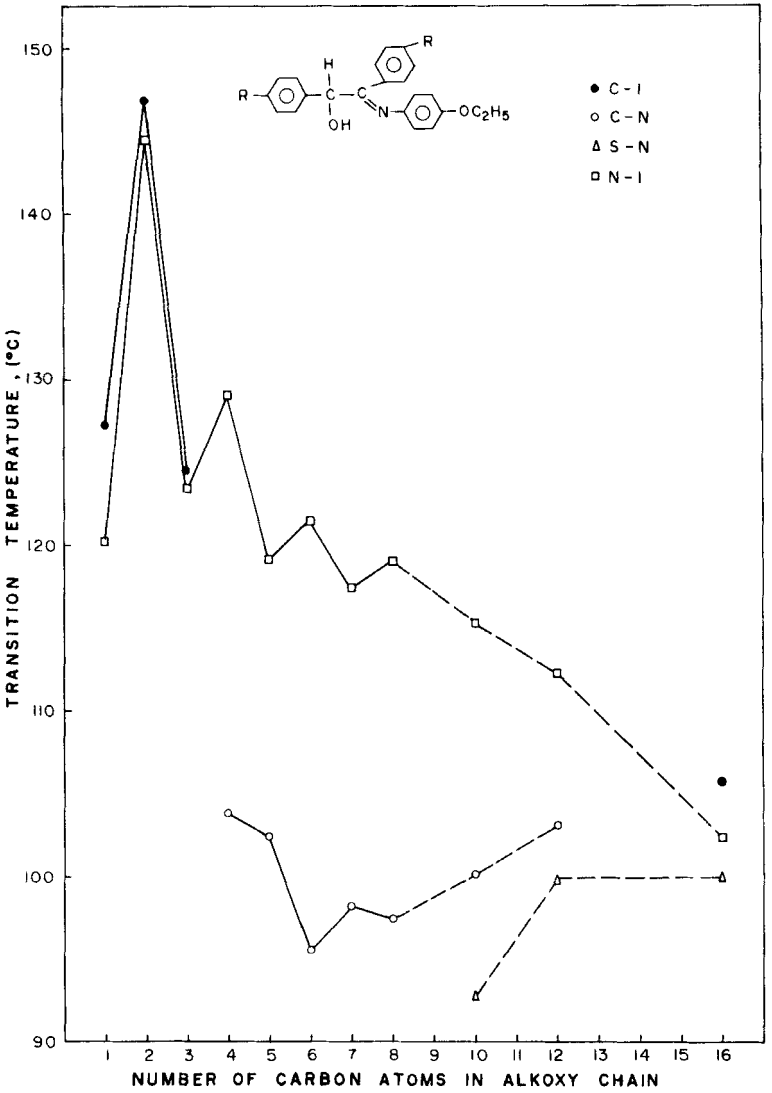


FIGURE 1 Transition temperatures for the mesophases of series A viz. 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-ethoxyphenyl)iminoethanes.

the alkoxy side chain show a monotropic nematic phase. The compounds with 10, 12 and 16 carbon atoms in the alkoxy chain have a monotropic smectic phase. The nematic–isotropic and smectic–Nematic peaks with the DSC for the compound with 16 carbon atoms in the alkoxy chain were not resolved, even with the slowest scanning

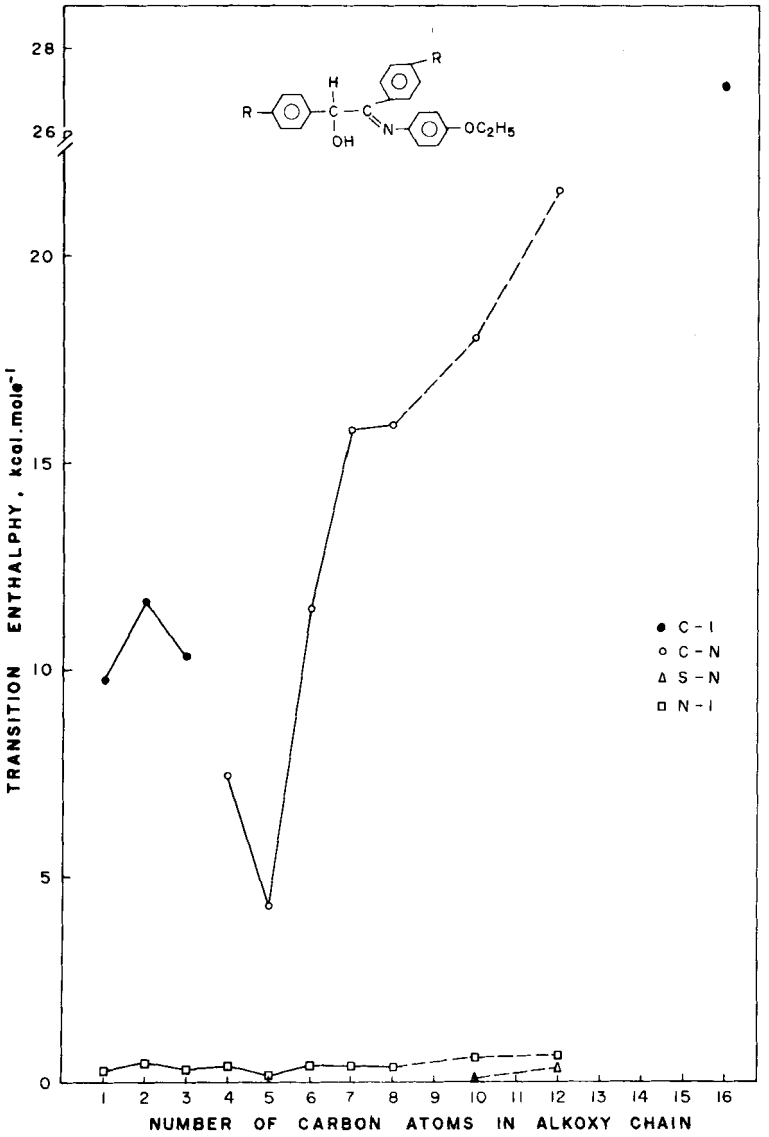


FIGURE 2 Enthalpies of transition of series A viz. 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-ethoxyphenyl)iminoethanes.

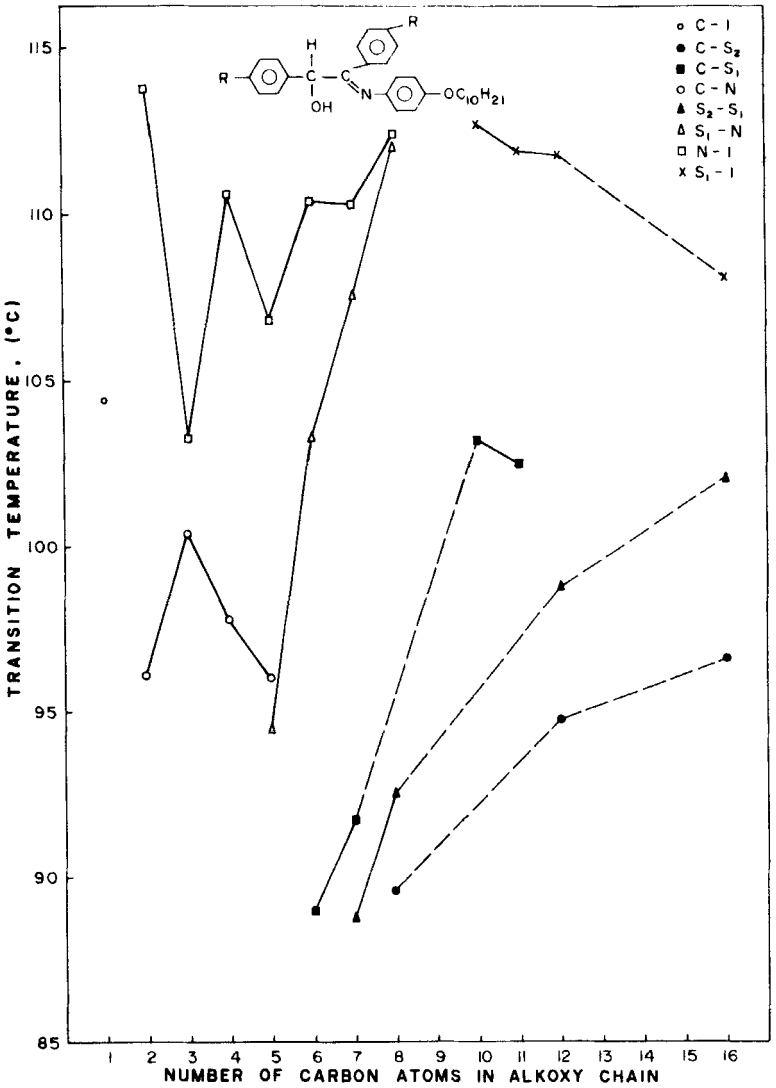


FIGURE 3 Transition temperatures for the mesophases of series B viz. 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1(4-*n*-decyloxyphenyl)iminoethanes.

rate possible. 2-Hydroxy-1,2-bis(4-*n*-pentyloxyphenyl)-1-(4-ethoxyphenyl)iminoethane at the melting point showed two peaks with a very small temperature difference between them. This compound also exhibited an anamolous behaviour in that the sample on first heating gave two peaks, the first one being larger than the second but on

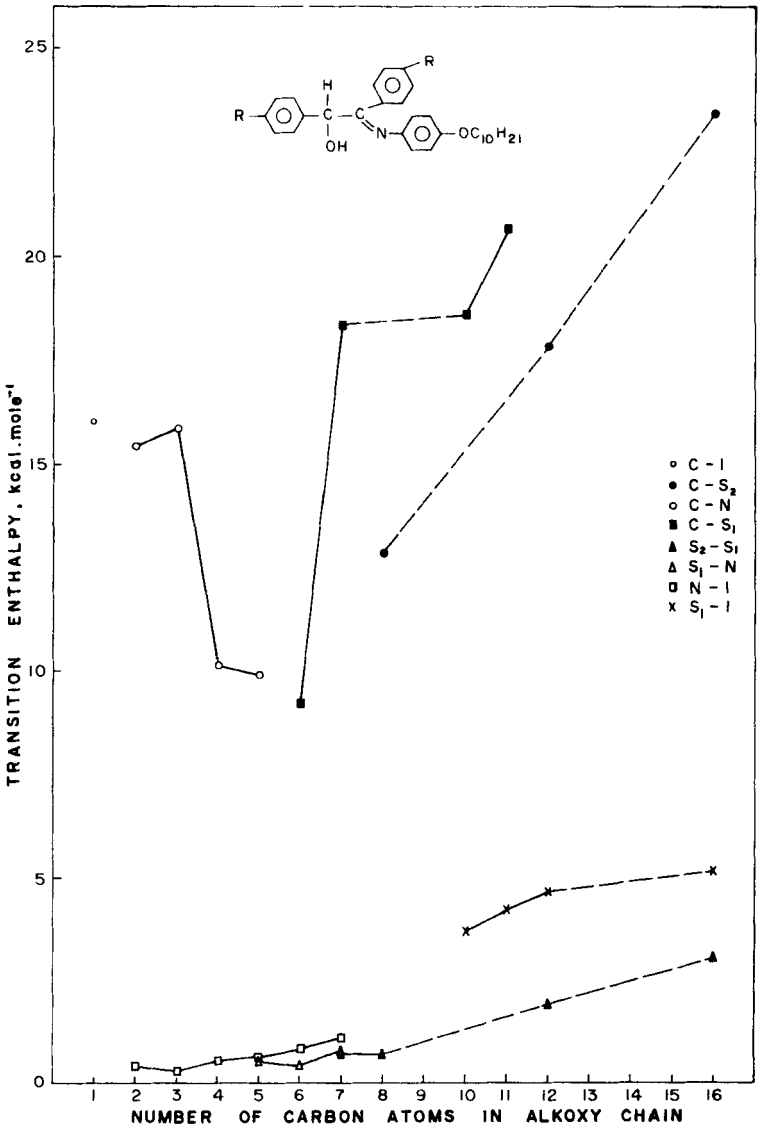


FIGURE 4 Enthalpies of transition of series B viz. 2-hydroxy-1,2-bis(4-*n*-alkyloxyphenyl)-1-(4-*n*-decyloxyphenyl)iminoethanes.

subsequent cooling and heating, the sizes of the two peaks were almost equal. This anamolous behaviour persisted after repeated crystallizations and even after the compound was reprepared and purified. Observation with the polarizing microscope shows that both peaks

correspond to melting behaviour. At a temperature of 100.3°C a part of the crystals transform to the nematic but there remains a large number of crystallites floating in this nematic phase and there is little flowing of the phase. At the temperature of 102.4°C the remaining crystallites transform to the nematic phase and the nematic phase flows. Since the compound has an assymetric carbon atom this could indicate that the two possible crystalline forms have different melting points but it is not clear why this behaviour only occurs in the compound with 5 carbon atoms in the alkoxy chain.

In series B, compounds containing 5 and 6 carbon atoms in the alkoxy chain showed one smectic phase (smectic I); for compounds with 7, 8, 12 and 16 carbon atoms we observed two smectic phases (smectic I and smectic II), smectic II being monotropic for 7 carbon atoms. A nematic phase was observed for compounds with 2, 3, 4, 5, 6, 7 and 8 carbon atoms. For the compound with 8 carbon atoms in the alkoxy chain the smectic I–nematic and nematic–isotropic transitions were separated by a very small temperature difference and we could not resolve the peaks even with the slowest heating rate possible.

Acknowledgments

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