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Biphenylbenzoates: Synthesis and Thermodynamic Properties

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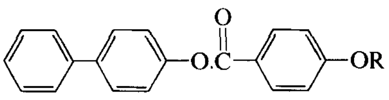
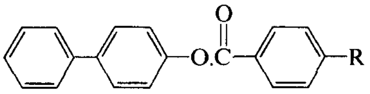
Two homologous series of twelve compounds each of biphenylbenzoates have been synthesised and their mesomorphic properties characterised. Heats of transition for both series of compounds have also been measured using differential scanning calorimetry. In the biphenyl 4-*p*-*n*-alkoxybenzoate series the first few members are monotropic nematic and the higher ones exhibit enantiotropic nematic as well as smectic phases, whereas in the biphenyl 4-*p*-*n*-alkyl benzoate series only the monotropic nematic phase is observed. In both series of compounds the plot of the nematic-isotropic transition temperature against the number of carbon atoms in the alkyl chain exhibit smooth curve relationships.

INTRODUCTION

In continuation of our work[1] on esters containing a biphenyl moiety we present here the properties of the completed series of biphenyl-4-*p*-*n*-alkoxy benzoates (I) in addition to another homologous series, viz., biphenyl 4-*p*-*n*-alkylbenzoates (II).



I



II

where R = C_nH_{2n+1}

It is well known that even small substituents at 4 and 4′ positions of the biphenyl molecule result in materials which show mesophases. Here, we study the effect of having one of these two positions free and suitably substituting the other position. The transition temperatures have been determined by optical as well as by differential scanning calorimetry. The two sets of values agree quite well. The heats of all transitions have also been measured and the thermal stabilities of the two series of compounds have been compared.

RESULTS AND DISCUSSION

The transition temperatures and transition heats for biphenyl 4-*p*-*n*-alkoxy benzoates are summarized in Table I. For compound 5 the transition temperatures reported in our earlier communication[1] have now been corrected. Compound 8 shows a monotropic smectic transition which was not observed earlier.[1] The smectic phase of this and the higher homologues shows a simple fan-shaped texture and is believed to be smectic A. However, no miscibility studies have been carried out to confirm this. Figure 1 shows a plot of the transition temperatures against the number of carbon atoms in the alkoxy chain. The odd-even effect for the nematic-isotropic transition temperatures, $T_{\text{N-I}}$, is evident from this figure. These points lie on two smoothly falling

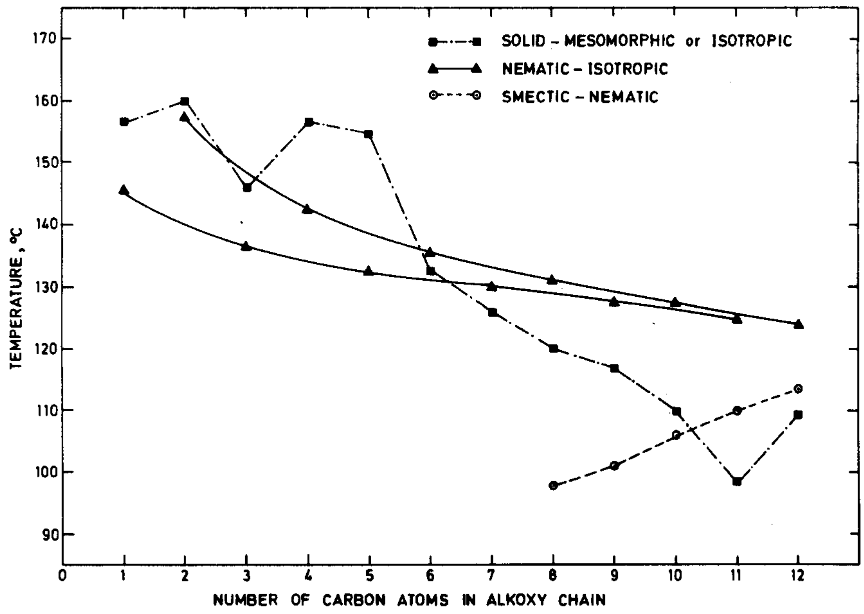


FIGURE 1 Plot of transition temperatures against the number of carbon atoms in the alkoxy chain for biphenyl 4-*p*-*n*-alkoxybenzoates.

TABLE I

Transition temperatures and transition heats for biphenyl-4-*p*-*n*-alkoxybenzoates. I.

Compound number	R = *n*-alkyl group	Transition	Transition temperature °C	Transition heat ΔH, kcal/mole
1	Methyl	K → I	156.5	8.50
		N → I	(145.3)	0.137
2	Ethyl	K → I	160	7.56
		N → I	(157.5)	0.160
3	Propyl	K → I	146	7.66
		N → I	(136.2)	0.137
4	Butyl	K → I	156.5	10.05
		N → I	(142.4)	0.160
5	Pentyl	K → I	154.5	10.17
		N → I	(132.3)	0.137
6	Hexyl	K → N	132.5	9.24
		N → I	135.3	0.171
7	Heptyl	K → N	126	9.35
		N → I	130	0.130
8	Octyl	K → N	120	8.81
		N → I	130.8	0.204
		S → N	(98)	
9	Nonyl	S → N	117.1	12.52
		N → I	127.5	0.178
		S → N	(101)	0.223
10	Decyl	K → N	110	11.24
		N → I	127	0.190
		S → N	(106)	0.213
11	Undecyl	K → S	98.5	12.72
		S → N	109.5	0.336
		N → I	125	0.221
12	Dodecyl	K → S	109.7	12.86
		S → N	113.2	0.466
		N → I	124	0.302

K = Crystal, N = Nematic, S = Smectic, I = Isotropic liquid. Temperatures in parentheses indicate monotropic transitions.

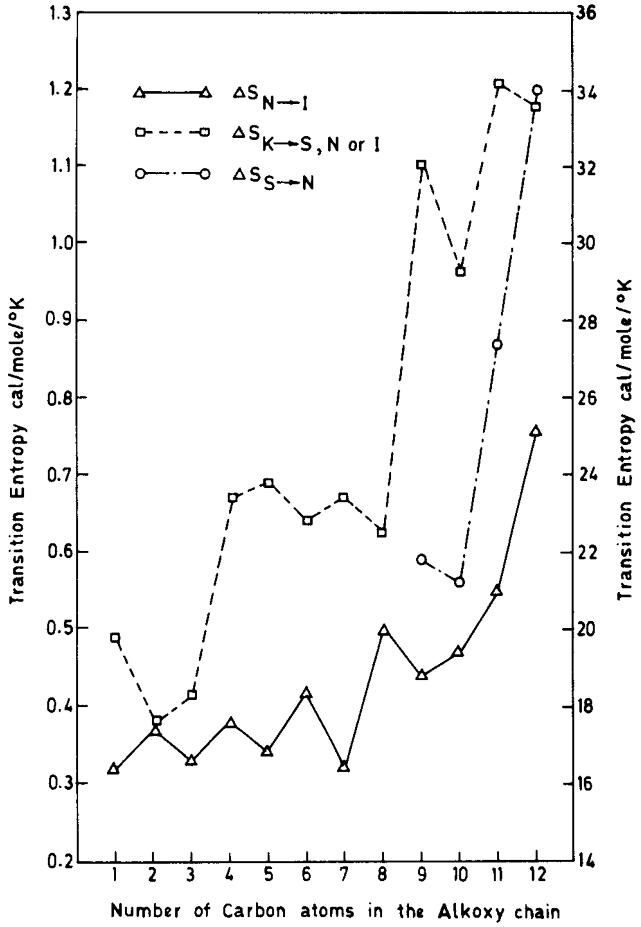


FIGURE 2 Transition entropies for biphenyl 4-*p*-*n*-alkoxybenzoates.

curves, the curve for the even homologues lying above that for the odd ones. The curve for the smectic-nematic transition points shows the usual upward trend. The transition heats for compounds exhibiting a monotropic phase was obtained by reheating of these supercooled mesophases. Figure 2 shows the relationship between the ΔS values (obtained from ΔH) and the alkoxy chain length for the various transitions. Enthalpy values showed similar trends. There is an alternation in the ΔS values for the nematic-isotropic transition between successive homologues up to C_9 after which there is a sharp increase. Beyond C_8 the compounds show a smectic phase also, and hence the increase in $\Delta S_{\text{N-I}}$ beyond C_8 may be due to the onset of smectic-like short range order in the nematic phase. For the smectic-nematic transi-

TABLE II

Transition temperatures and transition heats for biphenyl 4-*p*-*n*-alkylbenzoates. II.

Compound number	R = *n*-alkyl group	Transition	Transition temperature °C	Transition heat ΔH, kcal/mole
13	Methyl	K → I	155.5	7.71
14	Ethyl	K → I	153	8.18
15	Propyl	K → I N → I	114.2 (108.5)	6.75 0.126
16	Butyl	K → I	133.4	8.32
17	Pentyl	K → I N → I	137.5 (106.5)	11.62 0.143
18	Hexyl	K → I N → I	130.3 (97.4)	8.56 0.111
19	Heptyl	K → I N → I	120.3 (102.5)	8.50 0.140
20	Octyl	K → I N → I	112.6 (96.3)	8.35 0.111
21	Nonyl	K → I N → I	105.5 (99.2)	9.77 0.154
22	Decyl	K → I N → I	106 (96)	11.92 0.232
23	Undecyl	K → I N → I	105.5 (96.5)	9.60 0.219
24	Dodecyl	K → I N → I	103 (94)	9.66 0.202

K = Crystal, N = Nematic, I = Isotropic liquid. Temperatures in parentheses indicate monotropic transitions.

tion there is a small initial decrease followed by a continuous increase as the series is ascended. The dielectric properties of biphenyl 4-*p*-*n*-alkoxy benzoates have already been reported by Ratna and Shashidhar;[2] the mesophases exhibit a weak positive dielectric anisotropy.

The transition temperatures and transition heats for the biphenyl 4-*p*-*n*-alkylbenzoates are given in Table II. It is seen that only nine of the twelve compounds have mesomorphic properties all of them showing the monotropic nematic phase. Figure 3 is a plot of the transition temperatures versus the number of carbon atoms in the alkyl chain. There is a general decrease

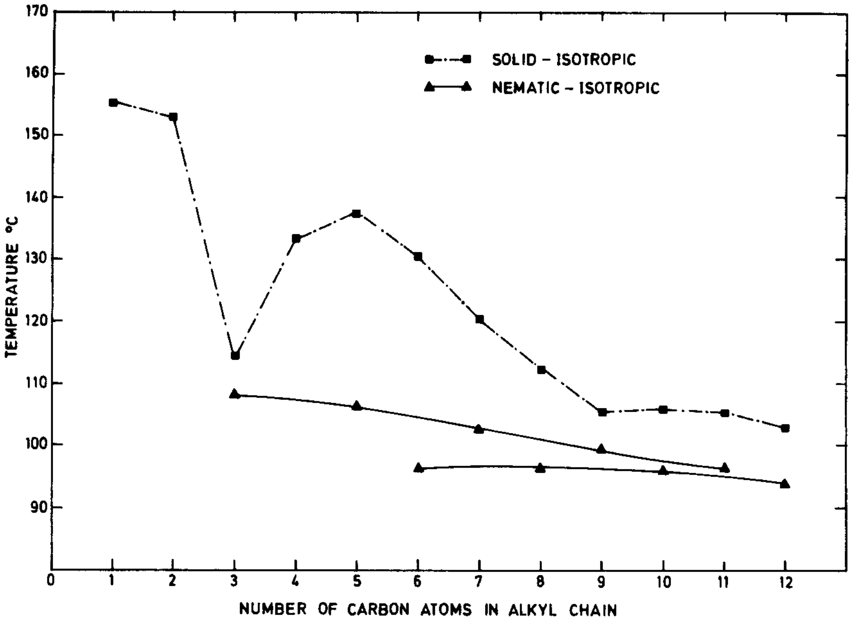


FIGURE 3 Plot of transition temperatures against the number of carbon atoms in the alkyl chain for biphenyl 4-*p*-*n*-alkylbenzoates.

in the $T_{N\text{-}I}$ on ascending the series, the points lying on two smoothly falling curves. Compounds 13, 14 and 16 do not supercool sufficiently to show the mesophase. They tend to crystallize about 10°C below their melting points, whereas from Figure 3 it may be estimated that they would have to supercool about 30°C in order to exhibit a mesophase. As mentioned earlier the heats of nematic-isotropic transition were obtained by reheating these supercooled mesophases. These heats are typically in the range of 0.1 to 0.25 Kcal/mole. The effect of alkyl chain length on the solid to isotropic liquid transition entropy and the mesophase transition entropies for the biphenyl 4-*p*-*n*-alkyl benzoates are shown in Figure 4. There is an odd-even alternation for the nematic to isotropic transition up to C_8 followed by a sharp rise up to C_{10} and then a decrease for C_{11} and C_{12}. The reason for this behaviour is not understood at present.

A comparison of the two series of compounds, i.e., alkyl versus alkoxy reveals that alkoxy substitution favours the thermal stabilization of all phases. This is possibly due to the oxygen atom adjacent to the phenyl ring undergoing an electronic interaction with it, which in turn stabilizes the mesophases. The smectic properties observed in the alkoxy series may also be explained in terms of strong dipole moments operating across the major axis of the molecules which enhance the lateral attractive forces.

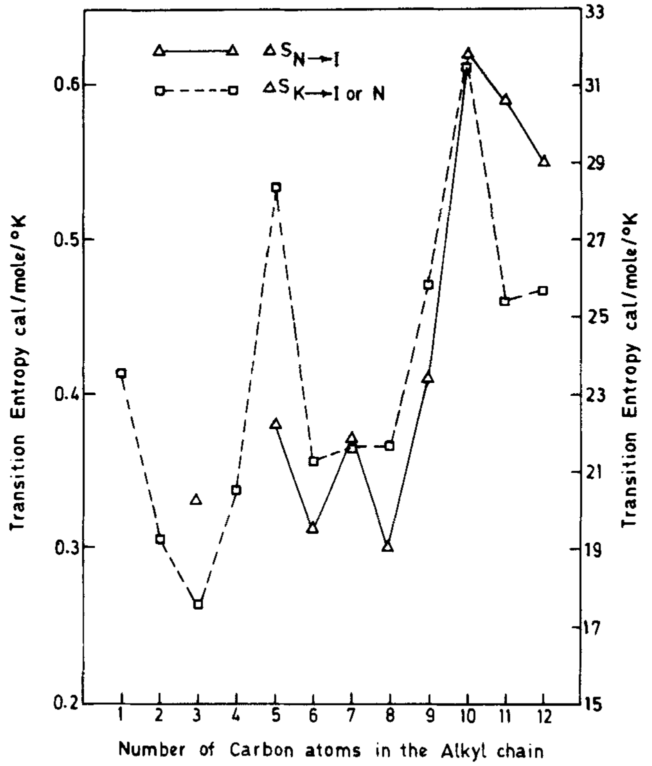


FIGURE 4 Transition entropies for biphenyl 4-*p*-*n*-alkylbenzoates.

EXPERIMENTAL

The melting points and transition temperatures were determined in open capillary tubes using a microscope (Franz Kuztner Nacht KG, Dresden, Model HMK 70/3171) provided with a heating stage. A heating rate of 5°/min was used initially and reduced to 1°/min close to the expected transition temperature. The mesophase textures were observed in thin films by sandwiching samples between a glass slide and cover slip, under a polarizing microscope. The heats of transition were measured using a Perkin-Elmer differential scanning calorimeter, Model DSC-2, with pure Indium as the calibration standard with a heating rate of 5°/min. The transition temperatures obtained by this method agreed to within 0.5° of those obtained from microscopic observation. All the compounds had satisfactory ir and pmr spectra and elemental analyses. The purity of the materials was also checked by thin layer chromatography.

p-n-Alkylbenzoic acids Commercial p-toluic acid was recrystallized from dilute ethyl alcohol to constant melting point and used. p-Ethyl to p-n-dodecylbenzoic acids were prepared according to the procedure of Weygand and Gabler.[3]

p-n-Alkoxybenzoic acids These were prepared according to the method of Lauer *et al.*[4] and used.

The esters were prepared as described previously.[1] The yield of the products ranged from 70 to 80%.

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