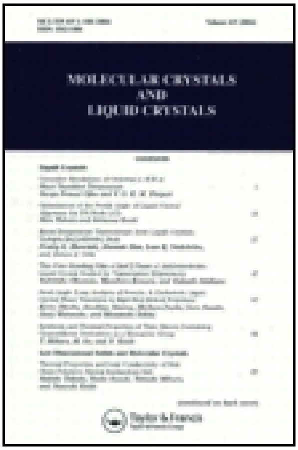

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Properties of the Liquid Crystals Formed by Certain 4-Biphenylyl 4″-n-Alkoxybenzoates.: A Reinvestigation

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Properties of the Liquid Crystals Formed by Certain 4-Biphenylyl 4″-*n*-Alkoxybenzoates.

A Reinvestigation

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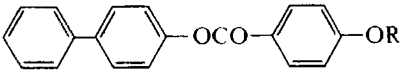
Eleven 4-biphenylyl 4″-*n*-alkoxybenzoates have been prepared and their liquid crystal transition temperatures measured. Comparison of the values obtained with those reported previously reveals one major and some minor differences. The homologous series was studied by differential thermal analysis and the enthalpies of fusion of the various transitions were measured. Smectic mesophases were identified as Smectic A.

INTRODUCTION

The properties of liquid crystals formed by several different types of ester containing the biphenyl group have been investigated by a number of workers.[1]

As part of a wider study, we required information on the properties of the liquid crystals formed by members of the homologous series of 4-biphenylyl 4″-*n*-alkoxybenzoates [(I), where R = *n*-alkyl].



(I)

Ten members (methoxy to *n*-dodecyloxy, but excluding *n*-nonyloxy and *n*-undecyloxy) of this homologous series have been reported by Sadashiva and Subba Rao.[2] These authors state that the series is essentially nematic in character, the N–I transition being monotropic for the early members ($n = 1$ to $n = 5$, where n is the number of carbon atoms in the *n*-alkoxy chain). Only for the *n*-decyloxy and *n*-dodecyloxy compounds was an S–N transition observed, and this transition was monotropic with respect to the solid in the former case.

Sadashiva and Subba Rao comment that "the plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain . . . shows the usual odd–even effect." However, the alternation in the N–I transition temperatures is displayed unusually as a "zig-zag" graph joining points for successive esters rather than in the customary manner showing two smoothly falling curves which tend towards coincidence as *n* increases, the lower curve for esters with an odd value of *n*. When the reported N–I transition temperatures are plotted in this latter fashion, it is immediately apparent (see Figure 1) that the point for the *n*-pentyloxy compound lies approximately 20° below its expected position on the lower curve and that the gradient of this curve is much less than that for the upper curve, so that the two curves rapidly converge as *n* increases.

Transition temperatures were determined by Sadashiva and Subba Rao in open capillary tubes using a polarising microscope in conjunction with a heated stage. The homologous series of esters was not subjected either to differential scanning calorimetry (DSC) or to differential thermal analysis (DTA) in order to confirm that all mesophase transitions had been detected by this optical method, nor was the type of smectic mesophase formed by the *n*-decyloxy and *n*-dodecyloxy compounds identified.

Accordingly, we felt that throughout the homologous series, there was sufficient uncertainty associated with the reported values to warrant re-investigation of the mesophase transition temperatures of the 4-biphenylyl 4″-*n*-alkoxybenzoates.

RESULTS AND DISCUSSION

We prepared the same members of the homologous series of 4-biphenylyl 4″-*n*-alkoxybenzoates as Sadashiva and Subba Rao, except that we also included the *n*-tetradecyloxy compound.

Our results are listed in Table I, together with the corresponding values (in italics) obtained by Sadashiva and Subba Rao. The transition temperatures are shown plotted against the number of atoms, *n*, in the *n*-alkyl chain in Figure I. Also shown, for comparison, are Sadashiva and Subba Rao's values for the N–I transition temperatures of esters with odd values of *n* (broken line curve).

For the *n*-pentyloxy compound we have established that (i) there is no phase transition at or near the value of 113.5° reported by Sadashiva and Subba Rao, and (ii) the N–I transition occurs at 133.5°, and confirmed that (iii) smectic properties are absent. We conclude that the *n*-pentyloxy com-

TABLE I

Transition temperatures and enthalpies of fusion for 4-biphenylyl 4″-*n*-alkoxybenzoates (I)

Substituent R	Transition temperatures[a,b]			Enthalpy of fusion[c] ΔH (kcal mol^{-1})
	C–I	S_A–N	N–I	
CH_3	155 ; *157*		[148°]; [*145°*]	8.9
C_2H_5	160; *161*		[157]; [*157.5*]	8.1
n-C_3H_7	145; *146*		[139]; [*136*]	
n-C_4H_9	153; *158*		[143]; [*142.5*]	10.6
n-C_5H_{11}	153.5; *144*		[133.5]; [*113.5*]	10.6
	C–N			
n-C_6H_{13}	132.5; *132.5*		136.5; *135.5*	9.4
n-C_7H_{15}	126; *128*		129.5; *130*	9.5
n-C_8H_{17}	119; *120*	[97.5°]	130.5; *131*	9.0
n-$C_{10}H_{21}$	110; *111*	[106.5]; [*106°*]	127; *126.5*	12.7
	C–S_A			
n-$C_{12}H_{25}$	108.5; *110.2*	112; *113.2*	123; *124.5*	14.4
n-$C_{14}H_{29}$	114	116.5	121.5	15.5

[a] Transition temperatures were measured using a Reichert–Kofler hot stage in conjunction with a polarising microscope. The hot stage was calibrated using Analar standards and the precision of measurements thereon is estimated as better than ±0.5°.

[b] Values in italics reported by Sadashiva and Subba Rao[2] and measured by a technique using samples in capillary tubes.

[c] Enthalpies of fusion were measured using Stanton–Redcroft differential thermal analysers, models 670 and 671, with pure indium wire as the standard. The estimated accuracy of the quoted values is 5%. The ΔH values for the S_A–N transitions were in the range 0.3–0.8 kcal mol^{-1} and for the N–I transitions in the range 0.2–0.5 kcal mol^{-1}.

[ ] Monotropic transition.

pound prepared by Sadashiva and Subba Rao was very impure and this conclusion is supported by the higher C–I transition temperature that we obtained for our sample of this compound.

Although the *n*-pentyloxy compound does not have a smectic mesophase, smectic properties occur earlier in the homologous series than Sadashiva and Subba Rao report. Thus, by supercooling our sample of the *n*-octyloxy compound more than 20° below its C–N transition temperature we were able to detect a (monotropic) S–N transition. We therefore prepared the *n*-tetradecyloxy compound in order to establish an accurate gradient for the plot of S–N transition temperatures against *n*. When this latter compound is reached in the homologous series the rising S–N and the falling N–I transition temperature curves are only 5° apart.

The smectic mesophases were shown to be smectic A by observation (using a polarising microscope in conjunction with a heated stage) of the focal conic and fan textures adopted by samples when mounted between a

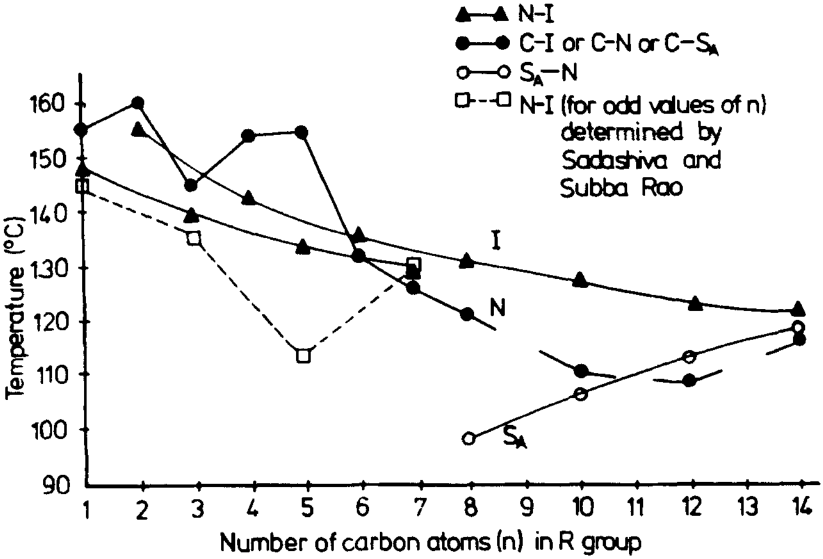


FIGURE 1 Plot of transition temperatures against alkyl chain length (*n*) for 4-biphenylyl 4″-*n*-alkoxybenzoates (I).

slide and a cover slip and allowed to cool slowly from the isotropic liquid. This assignment was confirmed by miscibility studies on mixtures of the smectic compounds prepared in this work and compounds with known S_A mesophases.

Discounting the value for the *n*-pentyloxy compound, the two sets of N–I transition temperatures are in quite close agreement, although the results for esters with an even value of *n* correspond much better than those for esters with an odd value of *n*.

For esters with an even value of *n* the two sets of N–I values show the type of scatter to be expected when a series of compounds is prepared and the transition temperatures of its members are determined by two independent groups of workers. Our values are slightly higher than Sadashiva and Subba Rao's in three instances and slightly lower for the other three compounds −1.5° lower (the largest difference between the two sets of results for esters with an even value of *n*) for the *n*-dodecyloxy compound. This scatter is such that essentially the same smooth curve may be drawn for the two sets of results when the N–I transition temperatures for the even members of the series are plotted against *n* (Figure I).

However, this is not the case for esters with an odd value of *n*. The very large discrepancy in the N–I values for the *n*-pentyloxy compound has already been discussed. The N–I values quoted by Sadashiva and Subba Rao for the remaining esters with an odd value of *n*, namely, the methoxy, *n*-propoxy, and *n*-pentyloxy compounds are, respectively, 3° lower, 3° lower, and 0.5° higher than those obtained in the present work. In conjunction with the value for the pure sample of the *n*-pentyloxy compound our values give rise to a steeper, more acceptable plot of *n* against the N–I transition temperatures for esters with an odd value of *n* than do the values quoted by Sadashiva and Subba Rao.

With the exception of the impure *n*-pentyloxy compound, all the C–I, C–N, or C–S_A transition temperatures quoted by Sadashiva and Subba Rao are slightly higher than those determined in the present work; in one instance (the *n*-butoxy compound) 5° higher. This general trend is probably a function of the different methods used for the determination of transition temperatures involving the solid phase. The existence of all the transitions was confirmed by DTA and the enthalpies of fusion at the various transitions were also determined by this technique.

In order for a "three-ring" ester of the type studied in the present work to be suitable for use (in mixtures with compounds of positive dielectric anisotropy) in electro-optical displays of the twisted nematic types, a low C–N value (preferably $< 100°$) and a low enthalpy of fusion (ideally < 6 kcal mol^{-1}) are normally required. In each instance, the enthalpies of fusion of the 4-biphenylyl 4″-*n*-alkoxybenzoates are in excess of 6 kcal mol^{-1}, and the values are unexpectedly high, higher than, for example, those for the corresponding dimeric 4-*n*-alkoxybenzoic acids[3] and the 4″-*n*-alkoxyphenyl 4′-cyanobiphenyl-4-carboxylates.[1] As *n* increases, the enthalpies of fusion show an odd–even alternation in the opposite sense to that observed for the N–I transition temperatures.

EXPERIMENTAL

4-n-Alkoxyacetophenones

These were prepared[4] by alkylation of 4-hydroxyacetophenone with the appropriate alkyl bromide in cyclohexanone in the presence of anhydrous potassium carbonate. The ethers were purified by vacuum distillation through a short column except for the 4-*n*-dodecyloxy- and -tetradecyloxy-acetophenone which were purified by recrystallisation from methanol. Yields varied in the range 80–90%. The b.p.s of the 4-*n*-butoxy-;[5] -pentyloxy-, -hexyloxy-, and -octyloxy-;[6] and -heptyloxy- and -decyloxy-acetophenone[7] were in good agreement with values reported in the literature. The 4-*n*-dodecyloxyacetophenone melted at 48–49° (lit.,[8] 50°) and 4-*n-tetradecyloxyacetophenone* had m.p. 58–59°. (Found: C, 79.2; H, 10.6. $C_{22}H_{36}O_2$ requires C, 79.5; H, 10.9%).

4-n-Alkoxybenzoic acids

Hypobromite oxidation[9] in dioxan solution of the appropriate 4-*n*-alkoxyacetophenone afforded the 4-*n*-alkoxybenzoic acids, which were purified by recrystallisation from benzene or acetone. C–S_C, S_C–N, S_C–I, and N–I transition temperatures corresponded very closely with those recorded in the literature.[10] The yields of the pure acids varied from 60 to 85%.

4-Biphenylyl 4″-n-alkoxybenzoates

The esters were prepared by two methods.

i) The 4-*n*-alkoxybenzoic acid (0.01 mol) was converted into the acid chloride using thionyl chloride. 4-Hydroxybiphenyl (0.01 mol) in dry pyridine (15 ml) was added to the acid chloride, and the mixture was heated under reflux for 3 h. After cooling, the reaction mixture was treated with 5% aqueous sulphuric acid (35 ml), water (150 ml) was added, and the precipitated crude ester was filtered off and dried.

ii) The 4-*n*-alkoxybenzoic acid (0.005 mol) and 4-hydroxybiphenyl (0.0075 mol) were dissolved in dry toluene (50 ml). Boric acid (0.03 g) and concentrated sulphuric acid (3 drops) were added and the mixture was heated under reflux in a Dean and Stark apparatus for 24 h.[11] The toluene was then removed.

In either case, the crude ester was purified as follows. The ester, dissolved in chloroform, was freed from unchanged starting materials by column

TABLE II

Elemental analyses for 4-biphenylyl 4″-*n*-alkoxybenzoates (I)

Substituent *R*	Found (%)		Molecular formula	Calculated or required (%)	
	C	H		C	H
CH_3	79.0	5.4	$C_{20}H_{16}O_3$	79.0	5.3
C_2H_5	79.3	5.7	$C_{21}H_{18}O_3$	79.2	5.7
n-C_3H_7	79.3	6.0	$C_{22}H_{20}O_3$	79.5	6.0
n-C_4H_9	79.7	6.3	$C_{23}H_{22}O_3$	79.8	6.4
n-C_5H_{11}	79.9	6.9	$C_{24}H_{24}O_3$	80.0	6.8
n-C_6H_{13}	80.0	6.9	$C_{25}H_{26}O_3$	80.2	7.0
n-C_7H_{15}	80.2	7.1	$C_{26}H_{28}O_3$	80.4	7.2
n-C_8H_{17}	80.7	7.3	$C_{27}H_{30}O_3$	80.6	7.5
n-$C_{10}H_{21}$	80.7	7.7	$C_{29}H_{34}O_3$	80.9	7.9
n-$C_{12}H_{25}$	81.2	8.3	$C_{31}H_{38}O_3$	81.2	8.3
n-$C_{14}H_{29}$	81.4	8.5	$C_{33}H_{42}O_3$	81.5	8.6

chromatography on alumina, eluting with chloroform. After removal of the chloroform, the esters were recrystallised (and decolourised with charcoal, when necessary) from acetone until the mesophase transition temperatures remained constant following successive recrystallisations. The average final yield (several esterifications) was 69% by method (i) and 74% by method (ii). Analytical results for the esters are given in Table II.

The following data for 4-biphenylyl 4″-*n*-pentyloxybenzoate are representative of the series as a whole.

ν_{max} (KBr) 1732, 1605, 1580, 1518, 1510, 760 cm^{-1}; δ 1.0 (s, 3H, CH_3), 1.1–2.0 (m, 4H), 4.09 (t, J6.0 Hz, 2H, OCH_2), 7.04 (δ, J9.0 Hz, 2H), 7.55 (m, 9H), 8.3 (d, J9.0 Hz, 2H); m/e 360 (M^+, 19.8%), 192 (acylium ion, 68.5), 170 (15.2), 121 (100).

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