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The preparation and properties of low molar mass liquid crystals possessing lateral alkyl chains

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The preparation and properties of low molar mass liquid crystals possessing lateral alkyl chains

by C. T. IMRIE and L. TAYLOR

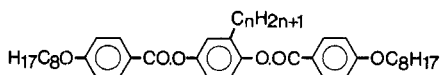
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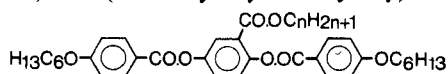
The first twelve members of three new mesogenic homologous series have been characterized, each of which are composed of molecules possessing lateral alkyl chains. The *n*-alkyl 2,5-bis-(4-*n*-hexyloxy-benzoyloxy)-benzoates are purely nematic whereas both nematic and smectic behaviour is observed for the 4-cyano-4'-biphenyl 3'-*n*-alkyloxybenzoates and the 4-cyano-4'-biphenyl 3'',4''-*n*-alkyloxybenzoates. The transitional properties of these series are similar to those of the analogous conventional mesogens and hence, can be rationalized without making any special assumptions concerning the conformational distribution of the lateral alkyl chain.

1. Introduction

For many years it was believed that a lateral substituent on the rigid core of a liquid crystal depresses the nematic-isotropic transition temperature according to the size of the substituent irrespective of its other properties such as polarizability and polarity [1]. Hence, it was assumed that only relatively small lateral substituents may be incorporated into a mesogenic structure without the destruction of liquid-crystalline behaviour. It was particularly exciting, therefore, when Weissflog and Demus [2] showed that the 1,4-bis-(4-*n*-octyloxybenzoyloxy)-2-*n*-alkylbenzenes,



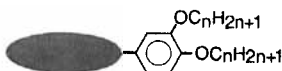
are enantiotropic nematogens even with lateral alkyl chains containing up to sixteen carbon atoms. They proceeded to synthesize several closely related series [2, 3] and confirmed that long lateral alkyl chains do not necessarily destroy mesogenic behaviour in low molar mass compounds. In addition, the Halle group has determined certain physical properties of these novel compounds such as their density and viscosity [4] as well as performing X-ray diffraction studies [4, 5]. In order to investigate the transitional properties of these interesting compounds further, we have synthesized the *n*-alkyl 2,5-bis-(4-*n*-hexyloxy-benzoyloxy)-benzoates,



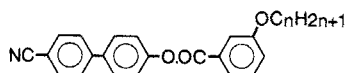
with $n = 1-12$. The pentyl homologue of this series has already been prepared by Weissflog and Demus [3] and the two sets of transition temperatures are in excellent agreement.

More recently, Tinh *et al.* [6] and Weissflog *et al.* [7] have reported the transition temperatures of the so-called polar forked mesogens in which the terminal and lateral

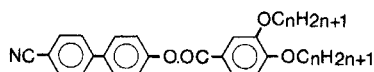
alkyl chains are attached to the same phenyl ring,



The observation of liquid-crystalline behaviour in forked compounds has been thought to imply that the meta-alkoxy chain is, to some extent, adopting conformations in which it lies parallel to the major axis of the rest of the molecule [7]. It should be noted, however, that on average this condition is rarely, if ever, achieved by a terminal alkyl chain [8]. In an attempt to resolve this apparent contradiction we have synthesized the 4-cyano-4'-biphenyl 3'-*n*-alkoxybenzoates,



with $n = 1-12$; surprisingly, mesogenic behaviour is observed for all twelve homologues. The mnemonic 3-*n* is used to describe this series in which n represents the number of carbon atoms in the alkoxy chain attached to the meta (3) position. We then proceeded to prepare the analogous forked compounds, the 4-cyano-4'-biphenyl 3',4''-di-*n*-alkoxybenzoates,



with $n = 1-12$; all twelve homologues also show mesogenic behaviour. By analogy, we use the mnemonic 3,4-*n* to denote members of this series.

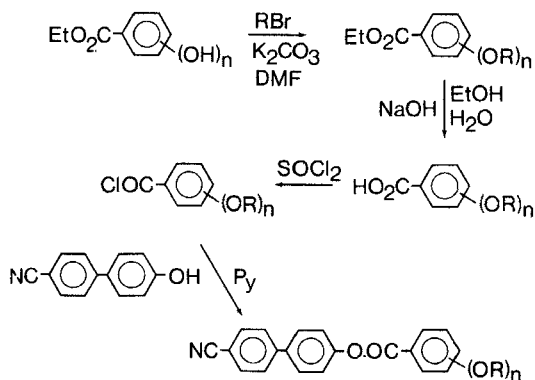
2. Experimental

2.1. *n*-Alkyl 2,5-bis-(4-*n*-hexyloxy-benzoyloxy)-benzoates

This homologous series was synthesized in two steps; first, 2,5-dihydroxybenzoic acid was esterified using an *n*-alcohol [9] and then this ester was reacted with 4-*n*-hexyloxybenzoyl chloride in pyridine to yield the final products which were recrystallized twice from absolute ethanol.

2.2. 3-*n* and 3,4-*n* series

The 3-*n* and 3,4-*n* homologous series were prepared using essentially the same reaction scheme consisting of four steps;



The preparation of ethyl 3-methoxybenzoate and ethyl 3,4-dimethoxybenzoate used methyl iodide. The final products were recrystallized twice from an ethanol/chloroform mixture.

2.3. Characterization

The structures of all the products were verified using $^1\text{H N.M.R.}$ and I.R. spectroscopy. Their high purity was demonstrated using thin layer chromatography. The transitional properties of these compounds were determined using a Perkin-Elmer DSC-2C differential scanning calorimeter as well as a Nikon polarising microscope equipped with a Linkam hot stage. This was also employed to investigate the optical textures of the liquid-crystalline phases. Selected examples of the smectic phases were studied further by X-ray diffraction with a Guinier camera fitted with a bent quartz monochromator using $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15405 \text{ nm}$).

3. Results and discussion

3.1. *n*-Alkyl 2,5-bis-(4-*n*-hexyloxy-benzoyloxy)-benzoates

The transitional properties of this homologous series are given in table 1; all the members are enantiotropic nematogens with the sole exception of the third member which is monotropic. The nematic phases were assigned from their schlieren optical texture, combined with the high mobility of the phase which flashed when subjected to mechanical stress. Figure 1 shows the dependence of the transition temperatures on the number of carbon atoms, n , in the lateral alkyl chain. The melting points show no regular dependence on n . In contrast, the nematic–isotropic transition temperatures decrease with increasing n with little or no alternation. This apparent absence of an odd–even effect coupled with a convergence of T_{NI} on increasing n has been interpreted by Weissflog and Demus [2] as implying that the lateral chain adopts conformations in which it lies parallel to the molecular axis so keeping the molecular breadth constant over a range of chain lengths. Figure 2, however, shows the dependence of the nematic–isotropic transition temperatures on the length of the terminal chains for the parent compound, 1,4-bis-(4-*n*-alkyloxybenzoyloxy)benzene [10]; if a single chain is increased in length a small odd–even effect in T_{NI} is observed whereas if both chains are varied there is little or no alternation in T_{NI} . Indeed, the similarities

Table 1. The transition temperatures and entropies of transition for the *n*-alkyl-2,5-bis-(4-*n*-hexyloxy-benzoyloxy)-benzoates.

n	$T_{\text{CN}}/^\circ\text{C}$ $\dagger T_{\text{CI}}/^\circ\text{C}$	$T_{\text{NI}}/^\circ\text{C}$	$\Delta S_{\text{C-}}/R$	$\Delta S_{\text{NI}}/R$
1	98.5	135	10.9	0.67
2	85.5	124.5	11.9	0.75
3	$\dagger 111.5$	(106.5)	9.84	0.68
4	100.5	104.5	9.25	0.64
5	67.5	101	8.18	0.60
6	75	101	12.1	0.60
7	70.5	97.5	12.9	0.58
8	70.5	94.5	12.1	0.63
9	58.5	90.5	12.5	0.57
10	63	89	15.9	0.62
11	67	87.5	13.2	0.62
12	70	86.5	20.1	0.65

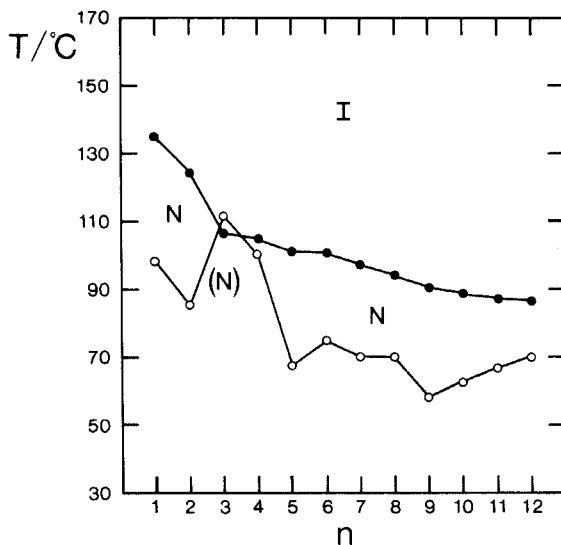


Figure 1. The dependence of the transition temperatures on the number of carbon atoms, n , in the lateral alkyl chain for the n -alkyl 2,5-bis-(4- n -hexyloxy-benzoyloxy)-benzoates. The melting point is denoted by \circ while \bullet indicates the nematic-isotropic transition.

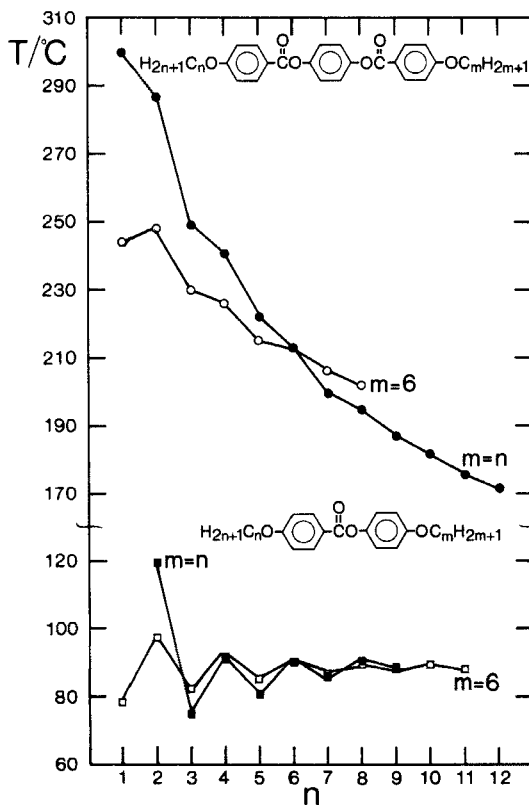


Figure 2. The dependence of the nematic-isotropic transition temperature on the number of carbon atoms, n , in the terminal alkyl chains for the 1,4-bis-(4- n -alkyloxybenzoyl)-benzenes [10] and the 4'- n -alkyloxyphenyl 4- n -alkyloxybenzoates [10].

between the curves shown in figures 1 and 2 are striking. It appears, therefore, that the laterally substituted compounds are behaving similarly to conventional mesogens possessing only terminal alkyl chains.

The effect of increasing the length of a terminal alkyl chain is two-fold; first, the anisotropic properties of the molecule are increased resulting in an increased T_{NI} ; second, the dilution of the cores is increased resulting in a decrease in the T_{NI} . Thus, the overall effect of increasing the length of a terminal alkyl chain depends essentially on the interaction strength parameter of the core. If the core is, for example, a two ring unit then the increase in molecular anisotropy dominates resulting in an odd-even effect being observed. If, however, the core is large, for example a three ring system, then the dilution effect dominates and so the transition temperatures simply fall with increasing chain length with little or no alternation. This differing behaviour is clearly shown in figure 2 which compares the nematic-isotropic transition temperatures of a three ring system, the 1,4-bis-(4-*n*-alkoxybenzoyloxy)-benzenes [10], with those of the analogous two ring system, the 4'-*n*-alkoxyphenyl-4-*n*-alkoxybenzoates [10]; the two ring system shows a far more pronounced odd-even effect than the three ring system. The behaviour of the laterally substituted series is easily understood within this framework although, of course, there is a possibility that the nematic field may force the lateral chain into conformations in which it tends to lie parallel to the molecular long axis. We stress, however, that to understand our results it is not necessary to make such an assumption.

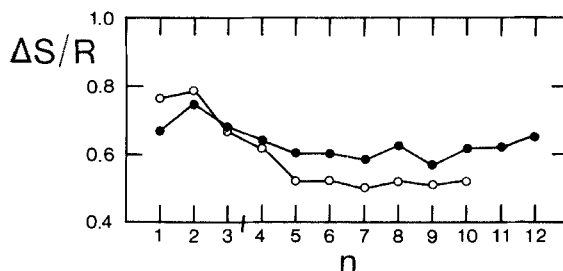


Figure 3. The dependence of the entropy change at the nematic-isotropic transition on the number of carbon atoms, n , in the lateral alkyl chain for the n -alkyl 2,5-bis-(4- n -hexyloxybenzoyloxy)-benzoates denoted by closed circles. Also shown are the nematic-isotropic entropy changes for the 1,4-bis-(4- n -octyloxybenzoyloxy)-2- n -alkylbenzenes [8] indicated by open circles where $(n + 2)$ now represents the number of carbon atoms in the lateral alkyl chain.

Figure 3 shows the dependence of the entropies associated with the nematic-isotropic transition on the number of carbon atoms, n , in the lateral alkyl chain; the entropies fall initially, pass through a minima and then appear to rise again as n is increased. It is interesting to note that similar behaviour was reported by Demus *et al.* [4] for the entropies of transition of the 1,4-bis-(4- n -octyloxybenzoyloxy)-2- n -alkylbenzenes and these are also shown in figure 3. This similarity suggests that the nature of the link between the lateral alkyl chain and the core is not important in determining the value of the entropy change at the nematic-isotropic transition. The fall in $\Delta S_{\text{NI}}/R$ with increasing n , shown in figure 3, is surprising since quite the opposite behaviour is observed if the length of a terminal alkyl chain is increased [11]. In the case of a terminal chain, the increase in $\Delta S_{\text{NI}}/R$ arises from the increased conformational entropy. These results suggest, therefore, that the conformational

entropy contribution to $\Delta S_{NI}/R$ for a lateral alkyl chain is essentially independent of the length of the chain.

3.2. 3-*n* series

The transitional properties of the 3-*n* series are given in table 2; all the members of this series are monotropic with the sole exception of 3-11 which exhibits an enantiotropic smectic A phase. The first four homologues are purely nematic; the fifth, sixth and seventh members exhibit both nematic and smectic A phases while the remaining homologues show only smectic A behaviour. The nematic phases were assigned using the same arguments as for the *n*-alkyl 2,5-bis-(4-*n*-hexyloxy-benzoyloxy)-benzoates. On cooling the nematic phases of the fifth, sixth and seventh members, the nematic schlieren texture changed to give regions of homeotropic and focal-conic fan texture. We, therefore, assign the lower temperature phase as a smectic A. On cooling the isotropic liquid for the higher homologues regions of focal-conic fan and homeotropic texture developed; we assign this phase as a smectic A, a result which is confirmed by X-ray diffraction experiments for 3-11. The periodicity in the smectic A phase of 3-11 was found from these experiments to be 39.5 Å ($T = 72^\circ\text{C}$); the estimated all-trans molecular length of 3-11 is 33 Å. We conclude, therefore, that the molecules in the smectic A phase are interdigitated.

Table 2. The transition temperatures of the 4-cyano-4'-biphenyl 3'-*n*-alkyloxybenzoates. Monotropic transitions are marked in parentheses.

<i>n</i>	$T/^\circ\text{C}$		
	C-I †C-S _A	S _A -N	N-I *S _A -I
1	155.5	—	(132)
2	127.5	—	(93.5)
3	154	—	(81)
4	111	—	(67)
5	98.5	(38)	(65.5)
6	80	(53.5)	(61.5)
7	78.5	(62.5)	(63.5)
8	86.5	—	*(65.5)
9	77	—	*(70.5)
10	88.5	—	*(73.5)
11	†69.5	—	*76
12	84.5	—	*(78.5)

Figure 4 shows the dependence of the transition temperatures on the length of the alkyloxy chain for the 3-*n* series; the nematic-isotropic transition temperature curve falls with increasing chain length with little or no alternation and is intersected by the smectic A-isotropic transition temperature curve which rises with increasing chain length. The nematic-isotropic transition temperature of the core, 4-cyano-4'-biphenyl benzoate is 197.5°C [12]; the introduction of a 3-methoxy substituent has, therefore, decreased the nematic thermal stability by 68°C. This reduction seems disproportionately large when compared simply to the decrease in the length to breadth ratio of the molecule. The dependence of the clearing point on *n* for the 3-*n* series will be discussed together with the results for the 3,4-*n* series and also those of the para-substituted analogues, the 4-cyano-4'-biphenyl 4-alkyloxybenzoates.

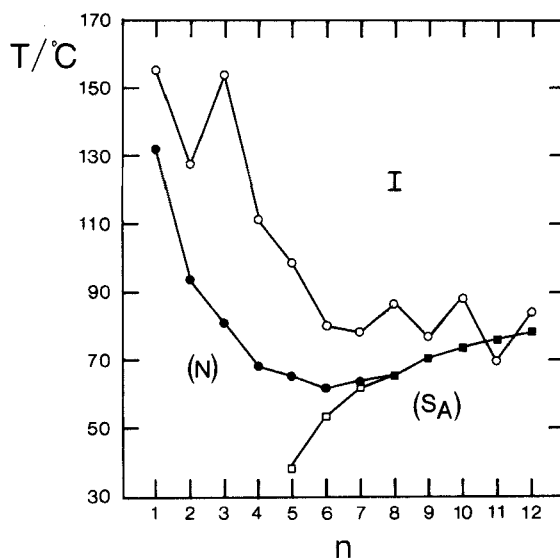


Figure 4. The dependence of the transition temperatures on the number of carbon atoms, n , in the lateral alkyloxy chain for the $3-n$ series. The melting point is denoted by \circ , \bullet indicates the nematic-isotropic transition, \square the smectic A-nematic transition and \blacksquare the smectic A-isotropic transition. Monotropic phases are marked in parentheses.

3.3. 3,4- n series

The transitional properties of the 3,4- n series are given in table 3; the phase assignments were made using the same arguments as for the $3-n$ series. The early

Table 3. The transition temperatures and entropies of transition for the 4-cyano-4'-biphenyl-3'',4''-di- n -alkyloxybenzoates. Monotropic transitions are marked in parentheses.

n	$T/^\circ\text{C}$				
	$\dagger\text{C-I}$ $^*\text{C-N}$ C-S_A	$^*\text{S}_A\text{-N}$ $\text{S}_C\text{-S}_A$	$\ddagger\text{N-I}$ $\text{S}_A\text{-I}$	ΔS_{C-}	$\ddagger\Delta S_{N-I}$ ΔS_{S-I}
1	*187.5	—	\ddagger 191	9.33	\ddagger 0.22
2	\dagger 171	—	\ddagger (167)	13.9	\ddagger 0.20
3	\dagger 163	—	\ddagger (141.5)	11.8	—
4	\dagger 154	*(138)	\ddagger (143)	13.0	\ddagger 0.43
5	\dagger 143.5	—	(142.5)	12.7	1.25
6	138.5	—	147	12.7	1.47
7	133.5	—	145.5	12.7	1.57
8	131	—	146	14.6	1.79
9	130.5	—	144	15.5	1.76
10	130.5	(115)	143	15.9	1.87
11	128.5	(118)	139.5	16.3	1.84
12	130	(113)	142.5	17.3	2.15

members of this series are solely nematogens; 3,4-4 exhibits both nematic and smectic A phases while the remaining homologues are purely smectic. On cooling the smectic A phases of 3,4-10, 3,4-11 and 3,4-12, the regions of focal-conic fan texture become broken and somewhat sanded while a schlieren texture develops from the areas of

Table 4. The smectic A layer spacing, d , and the ratio of the layer spacing to the estimated all-trans molecular length, d/l , for members of the 3,4- n series.

n	T/T_{SI}	$d/\text{\AA}$	d/l
6	0.98	34.4	1.25
7	0.98	36.0	1.25
8	0.97	37.7	1.26
9	0.97	39.5	1.27
10	0.97	40.3	1.24
11	0.97	42.1	1.25
12	0.98	41.0	1.18

homeotropic alignment. In consequence, this new phase is assigned as a smectic C. The layer spacings or periodicities of the smectic A phases exhibited by several members of the 3,4- n series, measured using X-ray diffraction, are given in table 4. The ratio of the layer spacing to the estimated all-trans molecular length is almost constant and approximately equal to 1.25, although the ratio for 3,4-12 appears to be slightly smaller. These results are in excellent agreement with Weissflog *et al.* [7] who measured the d/l ratio to be 1.25 for two members of the structurally very similar 4-(3,4-di-alkyloxybenzylidene-amino)-4'-cyanobiphenyl series. These measurements suggest that the smectic A phase is of the S_{Ad} type in which the cyanobiphenyl groups are interdigitated.

Figure 5 shows the dependence of the transition temperatures on the number of carbon atoms in the alkyloxy chains for the 3,4- n series. The melting points show a decreasing trend for the early members but then appear to converge to a given value with increasing chain length. The clearing points also decrease for the first three members and then increase slightly before decreasing gradually with increasing chain length. The clearing points do appear to show a small odd-even effect. The 3,4- n

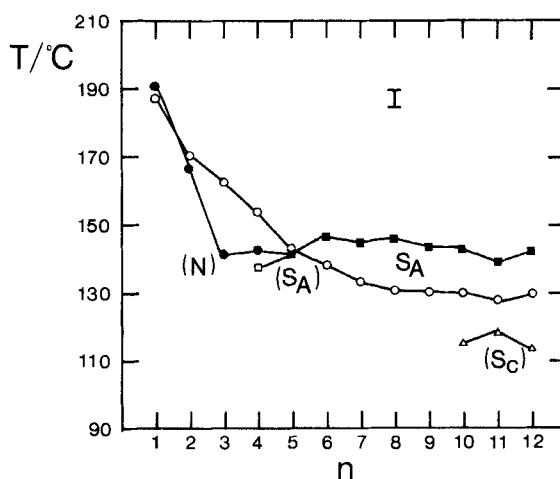


Figure 5. The dependence of the transition temperatures on the number of carbon atoms, n , in the alkyloxy chains for the 3,4- n series. The melting point is denoted by \circ , \bullet indicates the nematic-isotropic transition, \square the smectic A-nematic transition, \triangle the smectic C-smectic A transition and \blacksquare the smectic A-isotropic transition. Monotropic phases are marked in parentheses.

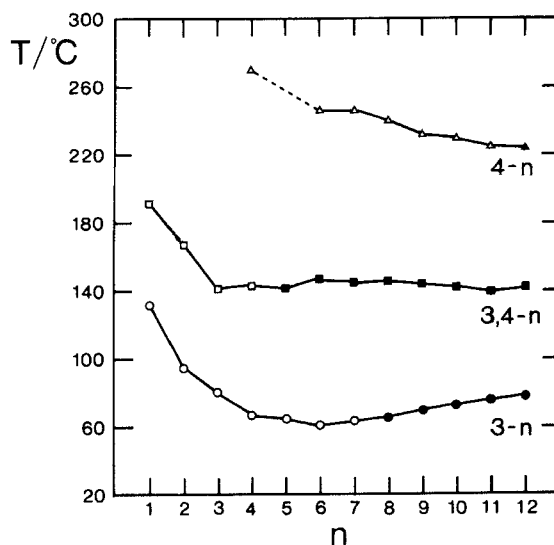


Figure 6. The dependence of the transition temperatures on the number of carbon atoms, n , in the alkyloxy chains for the 3- n series denoted by circles, the 3,4- n series represented by squares and the 4- n [12] indicated by triangles. Open symbols represent nematic-isotropic transitions while filled symbols denote smectic A-isotropic transitions.

compounds represent only the fourth series of forked mesogens to be reported and provide the only example for which as many as twelve homologues have been characterized; the dependence of the clearing temperatures on the length of the alkyl chains is very similar for all four series [6, 7].

The observation of liquid-crystalline behaviour in compounds of this general molecular structure has been thought to imply that the meta-alkyloxy chain is to some extent adopting conformations in which it lies almost parallel to the molecular long axis [6, 7]. The properties of the 3- n and 3,4- n series may, however, be understood without making such an assumption. Figure 6 compares the clearing temperatures of the 3- n and 3,4- n series with those of the 4-cyano-4'-biphenyl 4''- n -alkyloxybenzoates [12] which using our terminology may be referred to as the 4- n series; the clearing temperatures of the 4- n series are dramatically reduced by the introduction of a meta-alkyloxy chain and even more so by moving the para-chain into the meta position. It is interesting to note that the relative stability of the smectic A phase is increased on going from the 4- n series to either the 3- n or 3,4- n series. The dependence of the clearing points on n for the three series are essentially very similar and presumably reflects that the dominant role of the alkyloxy chains is simply one of diluting core-core interactions.

4. Conclusions

We have described three different types of mesogenic series each of which are composed of molecules having lateral alkyl chains. The transitional properties of these compounds are consistent with the model proposed by Weissflog and Demus [2] which confines the lateral alkyl chain to special conformations in which it tends to lie parallel to the major axis of the core. We have suggested, however, that such assumptions are not required and that the properties of laterally substituted compounds may

be similar to those of conventional mesogens. In order to investigate this possibility further, we plan an experimental investigation of the order parameter profile along the lateral chain using deuterium N.M.R. spectroscopy.

We wish to thank the Royal Commission for the Exhibition of 1851 for the award of a postdoctoral fellowship to Dr. C. T. Imrie and the Science and Engineering Research Council for a research studentship for Miss L. Taylor as well as for grants towards the cost of equipment used in this investigation.

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