Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: J. W. Emsley , G. R. Luckhurst , G. N. Shilstone & I. Sage (1984): The Preparation and Properties of the α,ω-bis(4,4′-Cyanobiphenyloxy)Alkanes: Nematogenic Molecules with a Flexible Core, Molecular Crystals and Liquid Crystals, 102:8-9, 223-233

To link to this article: http://dx.doi.org/10.1080/01406568408070532

Mol. Cryst. Liq. Cryst. Vol. 102 (Letters), pp. 223-233
0140-6566/84/1028-0223$20.00/0

Printed in the United States of America

THE PREPARATION AND PROPERTIES OF THE α,ω-BIS(4,4'-CYANOBIPHENYLOXY)ALKANES : NEMATOGENIC MOLECULES WITH A FLEXIBLE CORE

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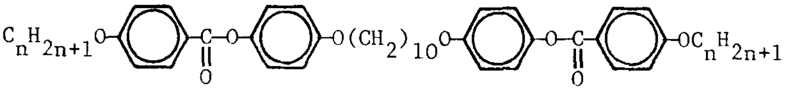
(Received for Publication August 30, 1984)

ABSTRACT

The first twelve members of the homologous series of α,ω-bis(4,4'-cyanobiphenyloxy)alkanes have been synthesised. The compounds are nematogenic, although the mesophases for the first and third members of the series are monotropic. Both the nematic-isotropic transition temperature and the entropy of transition exhibit a pronounced dependence on the length of the flexible core; this is analogous to that found for main chain thermotropic liquid crystal polymers.

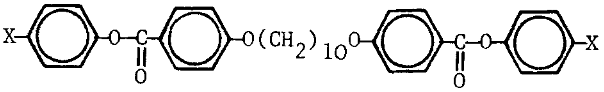
INTRODUCTION

The majority of thermotropic liquid crystals are composed of molecules with a single rigid core attached to which are one or two flexible alkyl chains,[1] as, for example, the 4-n-alkyloxy-4'-cyanobiphenyls. In essence the rigid core enhances the liquid crystal-isotropic transition temperature while the alkyl chains reduce the freezing point. It has been argued therefore that the introduction of a flexible chain linking two rigid groups would result in a reduction of the liquid crystal range or even its destruction. There are however mesogenic materials whose existence does not support this argument.[1] The most notable of these are the thermotropic liquid crystal polymers in which rigid groups and flexible spacers alternate along the main chain, as for example, in the poly α,ω-[4,4'-(2,2'-dimethylazoxyphenyl)] alkanedioates.[2] The discovery of liquid crystalline behaviour for such polymers prompted the synthesis of low molar mass materials with analogous structures. Thus Griffin and Britt[3] have prepared the diesters of 1,10-bis-(4-hydroxyphenyloxy)decane with a series of 4-alkyloxybenzoic



(I)

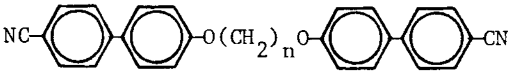
acids (I) and found them to be nematogenic but with higher nematic-isotropic transition temperatures than those for the comparable mesogens containing a rigid core. The nematic-isotropic transition temperatures were observed to alternate with the length of the terminal alkyl chains in a manner reminiscent of nematogens with a single rigid core.[1] However the terminal chains are not essential to the formation of a liquid crystal phase for materials with a flexible core. For example, the 1,10-bis[4-(p-substituted phenyloxycarboxy)-phenyloxy]decanes (II) are observed to be nematogenic for a range of substituents X which includes methyl, chloro, cyano



(II)

and nitro groups.[4] The influence of the substituent on the nematic-isotropic transition temperatures was again found to be in accord with the behaviour of analogous nematogens with a single rigid core.[1]

In contrast T_{NI} for the liquid crystal polymers exhibits a pronounced variation with the length of the flexible spacer[2] which is quite unlike that found for the corresponding materials with a single rigid core.[1] In addition the entropy change at the nematic-isotropic transition also alternates dramatically with the number of methylene groups in the flexible spacer.[2] This behaviour differs considerably from the variation observed for materials with a rigid core where the alternation is much less and is rapidly attenuated with the length of the terminal alkyl chain. It is of considerable interest to know if such marked alternation in mesogenic properties is exhibited by materials with just two rigid groups terminal to a flexible core. In fact many years ago Vorlander[5] reported the transition temperatures for just such compounds, the α,ω-bis(4-alkyloxyphenyl-4'-azophenyl)-alkane dioates, and found that the T_{NI} do alternate strongly with the length of the flexible core, although this important observation appears to have been overlooked. We wish to investigate the dependence of T_{NI} and other properties of nematogens formed by compounds with two rigid groups linked by a flexible chain in greater depth, and so we have synthesised the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes (III).



(III)

This particular series was chosen primarily for the relative simplicity of their molecular structure which makes them good candidates for theoretical investigations but also because the analogous 4-n-alkyloxy-4'-cyanobiphenyls have been well studied. Our first requirement is that these materials are mesogenic; in fact all of the members of the series which we synthesised are nematogenic, although those with one and three methylene groups in the flexible core are monotropic. This allowed us to proceed to our more important objective, namely to investigate the dependence of the nematic-isotropic transition temperature and entropy of transition on the length of the linking n-alkane. Subsequently we learnt of a similar investigation by Buglione, Roviello and Sirigu who had employed terminal rigid groups with greater structural complexity namely α-methylstilbene and acetophenoneazine; in addition alkyl chains were attached through ester linkages to each end of the molecule.[6] Nonetheless the behaviour of these nematogenic materials changes with the length of the central alkyl chain in a way which is comparable to that for the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes which we have prepared.

EXPERIMENTAL

Bis(4,4'-cyanobiphenyloxy)methane. 4-hydroxy-4'-cyanobiphenyl (1.0g), potassium hydroxide (0.43g) and potassium iodide (0.25g) were dissolved in dry dimethylformamide (20ml). Anhydrous potassium carbonate (1.0g) and dichloromethane (0.21g) in dimethylformamide (5ml) were added and the reaction mixture refluxed with stirring for 18h. More dichloromethane (0.05g) was then added and the mixture was refluxed for a further 12h; this step was repeated. After cooling the mixture was shaken thoroughly with water (100ml) and the cream solid filtered off, washed with water (3 x 25ml) and dried. The solid was passed through silica gel (40g) using dichloromethane as eluent. After evaporation of the solvent and crystallization from methanol the product was obtained as a white solid (yield 30%).

1,2-bis(4,4'-cyanobiphenyloxy)ethane. 4-hydroxy-4'-cyanobiphenyl (1.5g) and potassium hydroxide (0.4g) were dissolved in ethanol (25ml). Potassium iodide (0.2g) and 1,2-dibromoethane (0.48g) were added and the mixture refluxed for 72h. After cooling, the mixture was shaken thoroughly with water (100ml) and the off-white solid filtered off, washed with water (3 x 25ml), isopropanol (3 x 10ml) and dried. The solid was dissolved in the minimum amount of boiling ethyl acetate ($\sim$ 200ml g^{-1}) and the hot solution was filtered; a small amount of decolourising charcoal was added a few minutes before filtration if the solution appeared particularly yellow. The filtrate was allowed to stand at room temperature overnight when the product crystallized as a white solid (yield 40%).

α,ω-bis(4,4'-cyanobiphenyloxy)alkanes. All other members of the series were prepared in the following way. 4-hydroxy-4'-cyanobiphenyl (1.0g) was dissolved in cyclohexanone (25ml) and anhydrous potassium carbonate (3.5g) was added. The α,ω-dibromoalkane (0.0025 moles) was added and the mixture stirred under reflux for 18h. After cooling the mixture was shaken thoroughly with water (100 ml) and the off-white solid filtered off, washed with water (3 x 25ml) and dried. The solid was purified in the same way as 1,2-bis-(4,4'-cyanobiphenyloxy)ethane but in most cases a greater solubility in boiling ethyl acetate was found. Usually a single recrystallization was sufficient for a purity greater than 98% (yields 70 - 90%).

Characterization. All of the compounds were characterized using NMR and IR spectroscopy; in addition an elemental analysis for 1,2-bis(4,4'-cyanobiphenyloxy)ethane gave results in complete accord with the anticipated structure. The mesophase formed by these materials was found to be turbid and mobile, while under a polarising microscope they exhibit a schlieren texture. We therefore identify these compounds as nematogens. The nematic-isotropic transition temperatures and the melting points were determined using an Electrothermal melting point apparatus as well as a polarising microscope equipped with a Mettler FP-2 hot stage. The enthalpy and hence entropy changes at the transitions were measured using a Perkin Elmer DSC-2 differential scanning calorimeter which had been calibrated with indium as a standard.

RESULTS AND DISCUSSION

The results of our measurements for the first twelve members of the homologous series of α,ω-bis(4,4'-cyanobiphenyloxy)alkanes are listed in the table. The transition temperatures and entropies of transition are plotted against the number of methylene groups in the central n-alkane in figures 1 and 2 respectively.

TABLE The transition temperatures, enthalpies and entropies of transition for the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes; n is the number of methylene groups in the flexible core.†

n	$T_{CN}/^{o}C$	$T_{NI}/^{o}C$	$\Delta H_{CN}/$ kJ mol^{-1}	$\Delta H_{NI}/$ kJ mol^{-1}	$\Delta S_{CN}/R$	$\Delta S_{NI}/R$
	$^{*}T_{CI}/^{o}C$		$^{*}\Delta H_{CI}/$ kJ mol^{-1}		$^{*}\Delta S_{CI}/R$	
1	144*	(124)	33.7*	-	9.7*	-
2	205	265	37.4	7.91	9.4	1.77
3	185*	(170)	45.5*	1.99	12.0*	0.54
4	209	250	41.7	8.47	10.4	1.95
5	137	186	30.2	2.53	8.8	0.66
6	187	221	47.6	8.17	12.4	1.98
7	137	181	51.9	2.95	15.3	0.78
8	175	201	56.5	7.92	15.2	2.01
9	133	172	47.1	3.46	13.9	0.94
10	164	184	54.0	8.12	14.9	2.14
11	123	164	52.0	4.63	15.8	1.27
12	152	169	66.7	7.06	19.0	1.92

†The uncertainties in (a) the melting points are ± 2^{o}C, (b) the nematic-isotropic transition temperatures are ±1^{o}C, (c) the enthalpies and hence the entropies of transition are ± 5%.

( ) indicates a monotropic transition.

We begin our discussion with the nematic-isotropic transition temperature which is found to depend critically on the length of the flexible core as we can see from the results shown in figure 1. The values for the members of the homologous series with an even number of methylene groups lie on a smooth curve which falls as the length of the linking chain increases. The values for the odd members of the series also lie on a smooth curve but this rises and passes through a maximum before falling with increasing chain length. Together these trends produce a dramatic alternation in T_{NI} which is attenuated as the number of methylene groups in the flexible core increases. This odd-even effect is frequently observed for nematogens with a rigid core and terminal chains;[1] however the alternation found for these new materials with a flexible core is considerably greater than that exhibited by nematogens with a rigid core and terminal chains. As an example of this profound difference we show, in figure 1, the nematic-isotropic and smectic A-isotropic transition temperatures for the 4-n-alkyloxy-4'-cyanobiphenyls as a function of the number of carbon atoms in the chain.[1]

The melting points of the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes also exhibit a pronounced odd-even effect, as the results in figure 1 show. This strong alternation in the melting points is not found for nematogens, such as the 4-n-alkyloxy-4'-cyanobiphenyls, with a rigid core, for here the dependence on the number of methylene groups in the alkyl chain is quite haphazard. This difference in behaviour may indicate that the change in the conformational statistical weights for the alkyl chain on melting is small for compounds with a flexible core unlike the variations for those with terminal chains.

The entropy change at the nematic-isotropic transition shows a pronounced variation with the length of the flexible core (cf. figure 2). Indeed for the early members of the homologous series $\Delta S_{NI}/R$ for those with an even number of methylene groups is almost four times as great as for the odd members. There is however a slight diminution of this difference as the flexible core increases in length. The large variation in $\Delta S_{NI}/R$ for the odd and even members almost certainly implies an equally dramatic difference in the orientational order at the nematic-isotropic transition.^{2} Such a large difference could have important implications

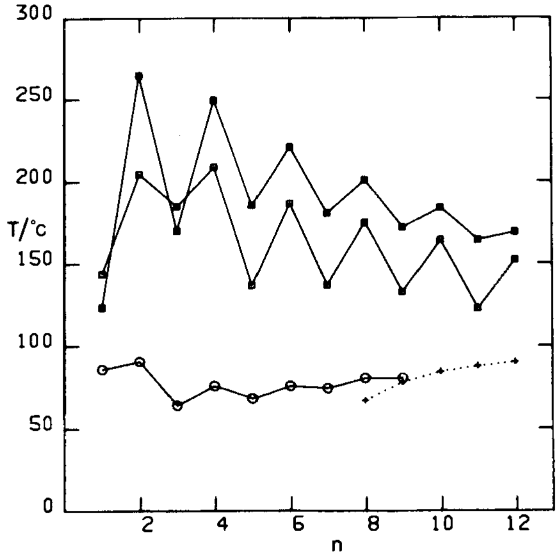


FIGURE 1. The dependence of the transition temperatures for the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes on the number of methylene groups in the flexible core; □ indicates C-N or C-I while ■ denotes N-I transition. The nematic-isotropic (O) or smectic A-isotropic (+) transition temperatures for the 4-n-alkyloxy-4'-cyanobiphenyls are also shown where n now gives the number of carbon atoms in the alkyloxy chain.

for the applications of these new materials. We are investigating therefore the orientational order in the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes with the aid of deuterium NMR spectroscopy.

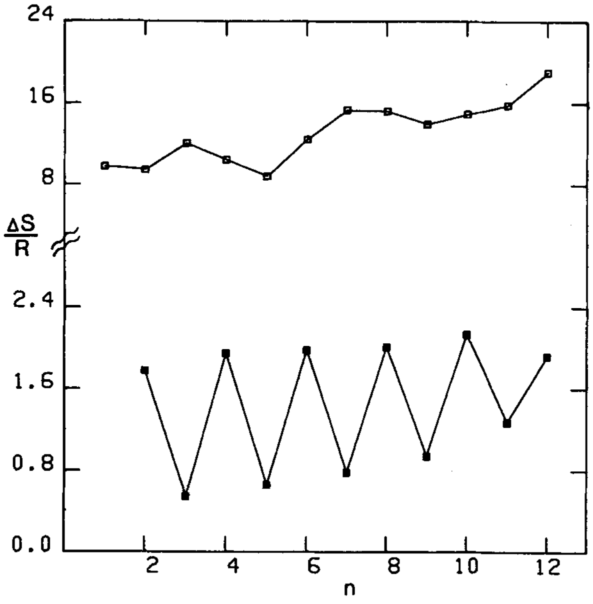


FIGURE 2. The entropy of melting (■) and the entropy change (□) at the nematic-isotropic transition for the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes as a function of the number of methylene groups in the flexible core.

In contrast, the entropy of melting $\Delta S_{CN}/R$ shows only minor variations with the length of the flexible core (cf. figure 2). This behaviour is consistent with our view that the conformational distribution of the linking alkyl chain does not change significantly when the solid melts.

Finally, we note the strong similarity between the dramatic alternations in the nematic-isotropic transition temperature and the entropy of transition with the length of the flexible core observed for these new materials and those found for main chain liquid crystal polymers.[2] This similarity suggests that the polymeric character is not dominant in determining the variation of the liquid crystal properties with the length of the flexible spacer. In consequence we should be able to understand these variations by constructing a theory for the far simpler model systems which we have synthesised. Such a theoretical development is under way.

ACKNOWLEDGEMENT

We are grateful to the Science and Engineering Research Council for the award of a CASE Studentship to Mr. G. N. Shilstone.

A preliminary account of this work was presented at the ESF Sixth Polymer Workshop on Liquid Crystal Polymer Systems 12th - 14th September 1983, Lyngby, Denmark.

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