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Trimeric liquid crystals containing lateral alkyl chains

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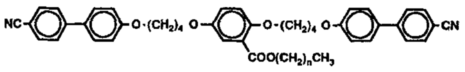
The first twelve members of the *n*-alkyl 2,5-bis-(4′-cyanobiphenyloxybutyloxy)-benzoates have been prepared. The compounds are nematogenic; in addition the first three members exhibit a smectic A phase. The nematic-isotropic transition temperatures decrease with little or no alternation on increasing the number of methylene groups in the lateral chain; this is analogous to the behaviour found in both monomeric and polymeric mesogens possessing lateral alkyl chains.

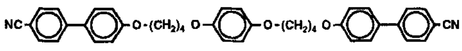
1. Introduction

Dimeric liquid crystals differ from conventional low molar mass mesogens in that they are composed of molecules possessing two semi-rigid anisometric groups joined by a flexible spacer. Recent interest in such materials stems, in part, from the similarity of the dimers to semi-flexible main chain liquid crystal polymers [1]. It appears that there may be a continuum of liquid-crystalline behaviour from dimers to polymers through low molar mass oligomeric structures. In order to investigate this possibility we have prepared mesogens containing three anisometric units linked by flexible spacers,

and describe these as trimers. The trimeric molecular structure has been described for two series of compounds in which cyanobiphenyloxy groups are joined by flexible spacers to either a phenyl or biphenyl unit [2]. These compounds, however, have two main drawbacks. First, they are very insoluble and second, their nematic-isotropic transition temperatures are very high; these problems could preclude determination of their physical properties. In monomeric mesogens the problem of high transition temperatures is usually overcome by attaching terminal alkyl chains to the mesogenic groups. In the case of liquid-crystalline main chain polymers, lowering of the transition temperatures can often be achieved by the introduction of lateral alkyl chains. Therefore, we have prepared a series of trimers possessing a lateral alkyl chain, the *n*-alkyl 2,5-bis-(4′-cyanobiphenyloxybutyloxy)benzoates,



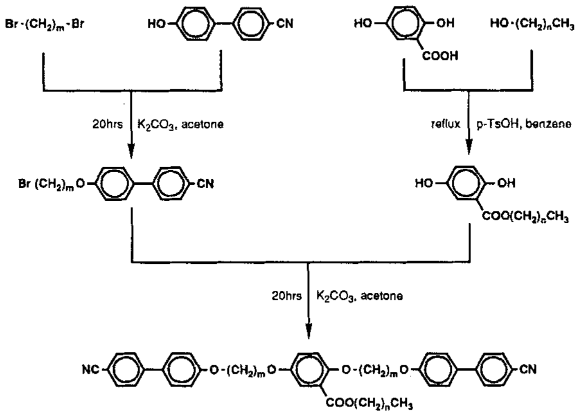
The main reason for choosing this particular series is that the corresponding unsubstituted trimer



is known.

2. Experimental

The synthetic route used to prepare the dimers is shown in the reaction scheme.



The final stage involved the reaction of 1-bromo-4-(4-cyanobiphenyl-4′-oxy)butane with an alkyl 2,5-dihydroxybenzoates using potassium carbonate in dry acetone. This mixture was stirred under reflux overnight and filtered hot; the inorganic residue was washed with acetone. The organic filtrates were combined and the solvents removed. The resulting white solid was recrystallised several times from ethyl acetate. 1-bromo-4-(4-cyanobiphenyl-4′-oxy)butane was prepared by reacting 4-cyanohydroxybiphenyl with a ten-fold excess of 1,4-dibromobutane using potassium carbonate in dry acetone [3]. The alkyl 2,5-dihydroxybenzoates were obtained via the esterification of 2,5-dihydroxybenzoic acid with the corresponding alcohol [4].

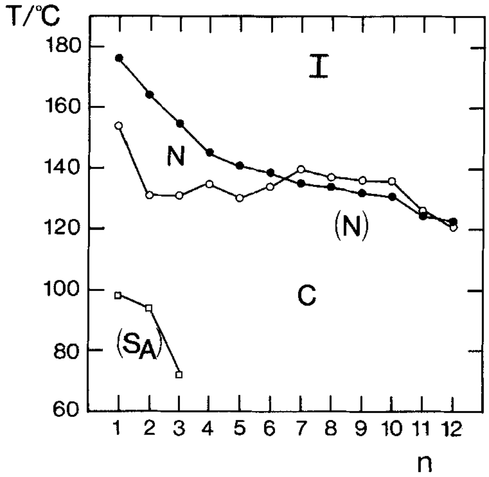
3. Characterization

The structures of the products were characterized using ^{1}H-N.M.R. and I.R. spectroscopy. The thermal behaviour of the trimers was investigated using a Perkin-Elmer DSC-2 differential scanning calorimeter as well as a Nikon polarising microscope equipped with a Linkam hot stage; this was also employed to study the optical textures of the mesophases exhibited by these compounds. It should be noted that these compounds have small but definite biphasic regions, the origin of which is unclear. This has also been noted for dimeric mesogens [5].

4. Results and discussion

The transitional properties of the trimers are given in the table; all twelve members show nematic behaviour. In addition, the first three homologues also have a smectic A phase; it is interesting to note that the unsubstituted trimer is solely nematic. The nematic phases were identified on the basis of the schlieren optical texture when viewed under the polarizing microscope. On cooling the first three members, the schlieren texture changes to give regions of homeotropic and focal-conic fan texture. In consequence, this new phase is assigned as a smectic A.

The figure shows the dependence of the transition temperatures on the number of methylene groups, *n*, in the lateral alkyl chain. The melting points do not show a regular dependence on *n*. In contrast, the nematic–isotropic transition temperatures decrease with increasing *n* with little or no alternation; this behaviour has also been



The dependence of the transition temperatures on the number of methylene units, *n*, in the lateral alkyl chain for the *n*-alkyl 2,5-bis-(4′-cyanobiphenyloxybutyloxy)benzoates; ○ indicates the melting transition, ● the nematic–isotropic transition and □ the smectic A-nematic transition.

The transitional properties of the *n*-alkyl 2,5-bis-(4′-cyanobiphenyloxybutyloxy)benzoates.

n	†T_{CI}/°C T_{CN}/°C	T_{S_AN}/°C	T_{NI}/°C	$\Delta S_{C-}/R$	$\Delta S_{NI}/R$
1	154	(98)	176	7·87	2·07
2	131	(94)	164	24·7	2·44
3	131	(72)	155	15·7	2·21
4	135	–	145	15·7	2·10
5	130	–	141	13·2	2·06
6	134	–	139	14·1	2·16
7	†140	–	(135)	18·1	2·00
8	†137	–	(134)	16·3	2·01
9	†136	–	(132)	17·0	2·05
10	†136	–	(131)	20·9	2·20
11	†126	–	(125)	21·4	2·13
12	121	–	122	21·8	2·66

observed in both monomeric [6, 7] and polymeric [8] liquid crystals. This observation has often been thought to imply that the lateral chain adopts conformations in which it lies parallel to the molecular long axis. We have recently suggested [7], however, that such an assumption is not necessary to describe the behaviour of mesogens possessing lateral alkyl chains and that the decrease in the nematic–isotropic transition temperatures may be rationalized by proposing that the role of the lateral alkyl chain is simply one of diluting the interactions between the anisometric semi-rigid units. We accept, of course, that it may be possible for the nematic field to force the chain into conformations in which it aligns parallel to the long molecular axis but we stress that to understand the dependence of the nematic–isotropic transition temperatures in these compounds such an assumption is unnecessary.

The entropy changes associated with the nematic–isotropic transition, $\Delta S_{NI}/R$, for these trimers are essentially independent of the length of the lateral chain and are significantly lower than the value of 3·1 measured for the unsubstituted trimer [2].

Increasing the length of a terminal alkyl chain in both monomeric [9] and dimeric [10] mesogens increases $\Delta S_{NI}/R$; this is thought to reflect an increase in the conformational entropy arising from the alkyl chain. These results suggest, therefore, that for mesogens possessing lateral alkyl chains the conformational entropy contribution to $\Delta S_{NI}/R$ is essentially independent of the length of the chain. This also appears to be the case for monomeric mesogens possessing a lateral alkyl chain [7].

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