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DEPENDENCE OF LIQUID CRYSTALLINE PROPERTIES OF ESTERS ON THE CENTRAL $(CH_2)_n$ BRIDGE

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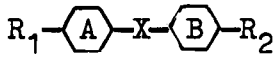
Abstract Effects of the central polymethylene group $(CH_2)_n$ on the liquid crystalline properties displayed by cyanobiphenyl esters of ω-phenyl and cyclohexylalkanic acids were studied.

INTRODUCTION

The linear structure of a molecule in the liquid crystalline compound:



where A and B are alicyclic, aromatic, or heteroaromatic fragments,

is mostly provided by the central bridge group X. Proceeding from geometrical considerations, this group should be composed of even-numbered links. The requirement is met with a simple C-C bond, ethane, ethylene, acetylene fragments, $-CH_2O-$, -COO- and other groups that enter into the structure of classical mesogens.

The purpose of the present investigation is to study the mesomorphic behavior of compounds with the central link $-(CH_2)_nCOO-$ depending on the length of a polymethylene chain (value "n") using as an example 4-cyanodiphenyl esters of ω-(4-alkylphenyl)- and

ω-(4-trans-alkylcyclohexyl)alkanic acids:

Alk-⟨A⟩-$(CH_2)_n$COO-⟨O⟩-⟨O⟩-CN

A=C_6H_4, n=0(I), 1(II), 2(III), 3(IV), 4(V);

A=C_6H_{11}, n=0(VI), 1(VII), 2(VIII), 5(IX), 6(X).

RESULTS AND DISCUSSION

It is well known that the compounds with the above formula where n=0 (benzoates (I)[1] and cyclohexanoates (VI)[2]) are mesogenes with wide temperature ranges, cyclohexanecarboxylic acid esters showing a wider temperature range of a mesophase. When transited to phenylacetic acid esters (II), the mesomorphic properties disappear (Table I), i.e. the geometry of a molecule is nonlinear just in the first odd-numbered homologue (n=1).

TABLE I Phase transition temperatures for compounds I-V (°C)

Index	n	Alk	T_{C-S}	T_{C-N} S-N	T_{C-I} S-I N-I	Mesophase range
Ia*	0	C_3H_7	-	114	259	145
Ib	0	C_4H_9	-	110	242	132
Ic	0	C_6H_{13}	-	91	230	139
Id	0	C_7H_{15}	-	92	224	132
II	1	C_4H_9	-	-	78-80	-
III	2	C_3H_7	-	87	115	28
IV	3	C_7H_{15}	-	55	69	14
V	4	C_7H_{15}	67	-	105	38

* Data given in ref. 1

A further increase in the polymethylene chain no longer shows such a profound change in the parameters of

even- and odd-numbered homoloques. Yet compound IV (n=3) exhibits mesomorphism, though in a narrower temperature range than the neighbouring even-numbered homologue III (n=2) and V (n=4). These properties are accountable for by a loose packing both in the solid crystal and mesophase of molecules with odd conformation of the central $(CH_2)_n$ link. This is evidenced by the fact that the examined aromatic compounds with n=3 are nematic liquid crystals and those with n=4 are purely smectic.

The similar relationship of mesomorphic parameters to "n" was seen for the homologous esters (VI-X) (Table II) containing a saturated 6-membered ring (fragment A) with the difference that the flexible cyclohexane fragment enables the molecules even with an odd "n" to better adjust to each other and to be packed in the mesophase. So the transitions of odd homologues to

TABLE II Phase transition temperatures for compounds VI-XI (°C)

Index	Central link n	Alk	T_{C-S}	T_{C-N} S-N	T_{S-I} N-I	Mesophase range
VIa*	0	C_4H_9	-	80	242	162
VIb	0	C_6H_{13}	84	142	227	143
VIIa	1	C_4H_9	55	-	60.5	5.5
VIIb	1	C_5H_{11}	65	-	69.5	4.5
VIII	2	C_4H_9	71_A	124	174	104
IX	5	C_4H_9	80_A	-	109	29
X	6	C_4H_9	71_A	-	136.5	65.5
XI	$-(CH_2)_3\overset{CH_3}{\overset{\vert}{C}}H(CH_2)_2-$	C_4H_9	65_A	-	88	23

* Data given in ref. 2

even ones are not so profound as in the aromatic series. There is a clearly distinct tendency for smectic phase formation as compared to aromatic analogues (compounds III and VIII) with increasing "n". The compounds with n=5 or n=6 show solely smectic properties, the even-numbered homologue (X) displaying them in a wider temperature range.

Thus the aromatic and cyclohexane derivative series vividly demonstrate that the presence of the central fragment with an even $(CH_2)_n$ chain number markedly improves mesomorphic properties.

Introduction of a lateral methyl group into the central $(CH_2)_n$ chain produces a decrease in geometrical anisotropy (ester XI). However, in this case no depression of the smectic phase occurs, as is frequently the case when the similar lateral substituent is introduced, there is a depressed clearing temperature as compared to the unsubstituted analogue (X) at 50°C.

EXPERIMENTAL

The esters II to XI were prepared by conventional acylation of 4-hydroxy-4'-cyanodiphenyl with chloric anhydrates of the respective acids. Phenylacetic acids were synthesized from the appropriate acetophenones using thiomorpholids[3], cyclohexylacetic acids were produced by hydrogenation of the former. Phenylpropionic acid was prepared via hydrogenation of the appropiate n-alkylcinnamic acid, phenylbutyric and phenylvaleric acids were obtained via acetylation of alkylbenzenes with glutaric anhydrides[4], followed by reduction of ketoacids by the Kishner-Wolff method. Hydrogenation of the appropriate aromatic acid[5] gave rise to cyclohexylpropionic acid. Cyclohexylcaproic and cyclohexyl-

enanthic acids, as well as acid with a lateral methyl substituent were prepared by chloric anhydride acylation of trans-4-n-butylcyclohexanecarboxylic acid, enamines of cyclopentanone, cyclohexanone and 4-methylcyclohexanone, by alkaline decomposition of the resultant β-diketones and by reduction of ketoacids by the Kishner-Wolff method[6].

All the novel liquid crystalline compounds have positive evidence of elementary analysis. Their phase transition temperatures were determined by a Mettler FP-5 device with a MIN-8 polarizing microscope.

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