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# On the Mesomorphic Properties of New Aryl Esters of Carbocyclic and Heterocyclic Acids

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# ON THE MESOMORPHIC PROPERTIES OF NEW ARYL ESTERS OF CARBOCYCLIC AND HETEROCYCLIC ACIDS

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Abstracts This paper presents a number of laterally substituted liquid crystalline compounds which have been synthesized by systematically varying both the position and the type of the lateral substituent.

## INTRODUCTION

We recently reported our results and liquid crystalline properties of some strong polar laterally substituted liquid crystals [1-4].

In an attempt to synthesize weakly polar liquid crystals of low smectic tendencies and, at the same time, having the high clearing point (T n-i) (i.e., with a wide temperature range), some new series of laterally substituted liquid crystalline compounds ( **I** - **VI** ) have been synthesized:

## SYNTHESIS AND DISCUSSION

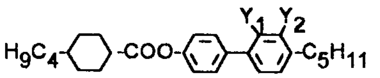
The mesomorphic esters (**I-VI**) were prepared by the interaction of chlorides of 4-alkylbenzoic, *trans*-4-alkylcyclohexanecarboxylic, 4-alkylbiphenyl-4-carboxylic, 4-(*trans*-4-alkylcyclohexyl)benzoic, 4-(1-alkylbicyclo[2,2,2]octyl-4)benzoic, 4-(5-alkyl-1,3,2-dioxaboranyl-2)-2-fluorobenzoic [1] acids with 4-(6-alkylcyclohex-2-enonoyl-3)phenols (**VII**), 4-(6-alkylcyclohexanonoyl-3)phenols (**VIII**), 4-(1-alkyl-2-$Y_2$-cyclohex-1-enyl-4)phenols (**IX**), 4-hydroxy-2-$Y_1$-3-$Y_2$-5-$Y_3$ -4-alkylbiphenyls (**X**) .The phenols (**VII** - **X**) were obtained by the dealkylation of the corresponding alkoxyderivatives [5, 6] with aluminum bromide or chloride and boron tribromide or by boiling of them in the mixture of acetic and hydriodic or hydrobromic acids, or by heating with pyridine hydrochloride.

It was found that the phenols (**VII - X**) are formed with the highest yield (70- 80%) during refluxing of the corresponding alkoxyderivatives in the mixture of acetic and hydriodic acids or heating with pyridine hydrochloride.

The phase transition temperatures of some cyclohexenones and cyclohaxenones (**I, II**) are collated in table 1.The dependence of the transition temperatures of some reference liquid crystals and new esters series (**III - VI**) on the type and position of lateral substituents can be defined by comparising the corresponding values presented in tables 2,3.

As can be seen from table 3, the introduction of lateral methyl substituent into the rigid core of the 4-alkylbiphenyl esters of 4-alkylbenzoic acids sufficiently reduces the melting points, smectic and nematic thermostabilities (**IV a,b,q**).

The influence of the position of methyl substituent on the clearing points and nematic ranges of the corresponding laterally substituted 4-pentylbiphenyl esters of *trans*-4-butylcyclohexanecarboxylic acid and laterally unsubstituted analogue can be expressed by the following orders of increasing T n-i and ΔT (table 3):



T n-i : $Y_1$=$CH_3$, $Y_2$=H < $Y_1$=H, $Y_2$=$CH_3$ < $Y_1$=H, $Y_2$=H
ΔT: $Y_1$=$CH_3$, $Y_2$=H < $Y_1$=H, $Y_2$=H < $Y_1$=H, $Y_2$=$CH_3$

The same effects have been found for other liquid crystalline derivatives [ 7-9].

The introduction of the second lateral alkyl substituent ($CH_3$ or $C_8H_{17}$) into the rigid core of the 3-methyl-4-alkylbiphenyl esters of *trans*-4-alkylcyclohexanecarboxylic acids leads to the disappearance of the mesophase for the 3,5-dimethyl-4-alkylbiphenyl and 3-methyl-5-octyl-4-alkylbiphenylesters of *trans*-4-alkyl-cyclohexanecarboxylic acids (**IV f,k**).The increasing the size of the lateral substituent ($CH_3$ → $C_2H_5$, or $CH_3$ → $OCH_3$, or $CH_3$ → Cl) in 3-methyl-4-pentylbiphenylester of *trans*-4-butylcyclohexanecarboxylic acid (**IV h**) sufficiently lowers the clearing point and introduces the smectic phase in the second case (**IV j, p**).

The introduction of the additional 1,4-phenylene group into molecular structure of the 2-methyl-4-alkylbiphenyl and 3-methyl-4-alkylbiphenyl esters of *trans*-4-alkylcyclohexanecarboxylic acids causes the appearance of the smectic phase and sufficiently increases the nematic thermostability of the 2-methyl-4-alkylbiphenyl and 3-methyl-4-alkylbiphenyl esters of 4-(*trans*-4-alkylcyclohexyl)benzoic acids (**IV m,n;** table 3).

The substitution of the trans-1,4-cyclohexylene group by the 1,4-bicyclo-[2,2,2]-octylene group in the 3-methyl-4-alkylbiphenyl esters of 4-(*trans*-4-alkylcyclohexyl)benzoic acids leads to increasing nematic thermostability of the 3-methyl-4-alkylbiphenyl esters of 4-( 4-alkyl{2,2,2]bicyclooctanyl-1)benzoic acids (**VI**).

The presented results on the mesomorphic properties of laterally substituted esters and the results received for other liquid crystalline derivatives [1-11] reveal that the lateral alkyl, alkoxy or halogeno substitution sufficiently reduces the smectic tendency and nematic thermostability. These can be explained in terms of weakening intermolecular interactions due to the broadering the molecules.

As can be seen from table 4, new laterally substituted esters can be used as the components of liquid crystalline materials, which are characterized by the low threshold and saturation voltages of the twist-effect and steep voltage-contrast characteristics.

## CONCLUSIONS

The new three and four-ring laterally substituted esters exhibit low smectic tendencies and moderate clearing points. These make possible to consider them as the promising components for wide temperature range liquid crystalline materials for display applications.

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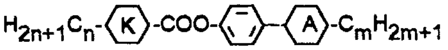
TABLE 1

Yields and transition temperatures of esters (**I, II**)



| N | n | K | A | m | Yield /% | Transition temperatures, °C | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | | S | | N | | I |
| **Ia** | 7 | - | CE | 3 | 57 | ● | | - | | ● | 110 | ● |
| **Ib** | 3 | B | CE | 3 | 53 | ● | 88 | ● | 142 | ● | 176 | ● |
| **Ic** | 3 | B | CE | 5 | 68 | ● | 91 | ● | | - | 171 | ● |
| **Id** | 4 | B | CE | 5 | 60 | ● | 118 | ● | | - | 194 | ● |
| **Ie** | 4 | C | CE | 5 | 59 | ● | 106 | ● | | - | 184 | ● |
| **IIa** | 3 | B | CA | 5 | 49 | ● | 84 | ● | | - | 136 | ● |
| **IIb** | 4 | B | C | 5 | - | ● | 67 | ● | 149 | ● | 154 | ● |

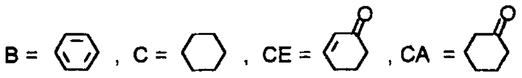
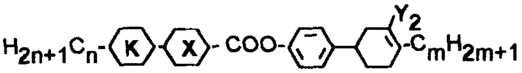


TABLE 2

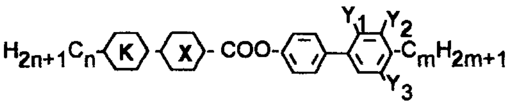
Yields and transition temperatures of esters (III)



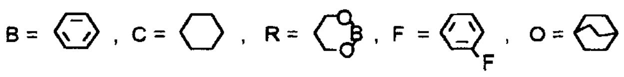
| N | n | K | X | $Y_2$ | m | Yield /% | Transition temperatures, °C | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | | S | | N | | I |
| IIIa | 4 | - | C | H | 5 | 36 | • | 81 | • | 113 | • | 122 | • |
| IIIb | 4 | - | C | $CH_3$ | 3 | 47 | • | 23 | - | | • | 91 | • |
| IIIc | 4 | - | C | $CH_3$ | 5 | 34 | • | 28 | - | | • | 108 | • |
| IIId | 5 | B | B | $CH_3$ | 5 | 40 | • | 78 | • | 163 | • | 228 | • |
| [illegible] | 5 | B | B | $C_2H_5$ | 5 | 33 | • | 77 | • | 162 | • | 214 | • |
| IIIf | 5 | C | B | $CH_3$ | 5 | 45 | • | 83 | • | 126 | • | 197 | • |

**TABLE 3**

Yields and transition temperatures of esters (**IV**, **V**, **VI** )



| N | n | K | X | $Y_1$ | $Y_2$ | $Y_3$ | m | Δε* | Yield /% | Transition C | | S | | temperatures, °C N | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **IVa** | 4 | - | B | - | $CH_3$ | - | 5 | - | 43 | • | 46 | - | | • | 106 | • |
| **IVb** | 4 | - | B | $CH_3$ | - | - | 5 | - | 42 | • | 25 | - | | • | 69 | • |
| **IVc** | 4 | - | C | - | - | - | 5 | - | 36 | • | 123 | • | 136 | • | 184 | • |
| **IVd** | 4 | - | C | - | $CH_3$ | - | 0 | - | 41 | • | 65 | - | | • | 76 | • |
| **IVe** | 4 | - | C | - | $CH_3$ | - | 3 | 0.23 | 49 | • | 69 | - | | • | 116 | • |
| **IVf** | 4 | - | C | - | $CH_3$ | $CH_3$ | 3 | - | 62 | • | | - | | - | 79 | • |
| **IVg** | 4 | - | C | - | $CH_3$ | - | 4 | - | 50 | • | 61 | - | | • | 121 | • |
| **IVh** | 4 | - | C | - | $CH_3$ | - | 5 | - | 52 | • | 44 | - | | • | 128 | • |
| **IVi** | 4 | - | C | $CH_3$ | - | - | 5 | - | 42 | • | 68 | - | | • | 82 | • |
| **IVj** | 4 | - | C | - | $C_2H_5$ | - | 5 | - | 38 | • | 47 | - | | • | 67 | • |
| **IVk** | 4 | - | C | - | $CH_3$ | $C_8H_{17}$ | 0 | - | 34 | • | | - | | - | 49 | • |
| **IVl** | 6 | - | C | - | $CH_3$ | - | 5 | - | 47 | • | 54 | • | 84 | • | 123 | • |
| **IVm** | 5 | C | B | - | $CH_3$ | - | 5 | - | 56 | • | 91 | • | 170 | • | 220 | • |
| **IVn** | 5 | C | B | $CH_3$ | - | - | 5 | - | 60 | • | 85 | • | 96 | • | 205 | • |
| **IVo** | 4 | - | C | - | Cl | - | 5 | - | ·57 | • | 54 | • | 110 | • | 129 | • |
| **IVp** | 4 | - | C | - | $OCH_3$ | - | 5 | - | 61 | • | 48 | • | 74 | • | 94 | • |
| **IVq** | 4 | - | B | - | - | - | 5 | - | | • | 88 | • | 98 | • | 171 | • |
| **Va** | 4 | R | F | - | $CH_3$ | - | 5 | 4.01 | 52 | • | 73 | - | | • | 184 | • |
| **Vb** | 5 | R | F | - | $CH_3$ | - | 5 | - | 52 | • | 72 | - | | • | 189 | • |
| **Vc** | 5 | R | F | $CH_3$ | - | - | 5 | - | 51 | • | 68 | - | | • | 166 | • |
| **Vd** | 5 | R | F | - | $C_2H_5$ | - | 5 | - | 54 | • | 52 | • | 66 | • | 138 | • |
| **VI** | 4 | O | B | - | $CH_3$ | - | 5 | - | 47 | • | 104 | • | 140 | • | 249 | • |



*T = T n-i - 50°C

TABLE 4

Electrooptic parameters of the liquid crystalline mixtures *

| Compounds in mixture | Treshold voltage V | Saturation voltage V | ΔU/V |
|---|---|---|---|
| **IIb** | 1.52 | 2.51 | 0.189 |
| **IIIa** | 1.48 | 2.19 | 0.202 |
| **IVc** | 1.50 | 2.09 | 0.174 |
| **IVh** | 1.49 | 2.06 | 0.190 |
| **IVo** | 1.41 | 1.96 | 0.188 |

* The mixtures were composed of 58 per cent 4-pentyl-4-cyanobiphenyl, 32 per cent 4-cyano-4-biphenyl ester of *trans*-4-propylcyclohex-2-encarboxylic acid and 10 per cent of the compounds indicated in the first column of the table