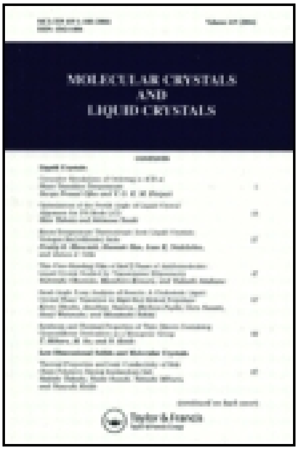

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# New Heterocyclic Analogs of BCH- and CBC-Compounds

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# New Heterocyclic Analogs of BCH- and CBC-Compounds

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A series of new liquid crystalline compounds with BCH- and CBC- structures was synthesized. They differ from the known carbocyclic analogs by the 1,2,4-oxadiazole fragment placed in various positions of the long mesomorphic molecule. The cross-coupling reaction of the aromatic boric acids and bromides is a new way for mesogenic heterocycles design. The transition temperatures of these new liquid crystals are lower as compared with carbocyclic BCH- and CBC- analogs and significantly depend on the position of the nonlinear heterocyclic unit in the molecular chain.

*Keywords:* 1,2,4-oxadiazole; cross-coupling; biphenylcyclohexane (BCH); dicyclohexylbiphenyl (CBC)

## INTRODUCTION

The cross-coupling reaction of aromatic halogenides, arylmagnesium halogenides and arylboric acids with Pd complexes as catalists is widely used in organic synthesis for designing different types of molecules containing biphenyl fragment.

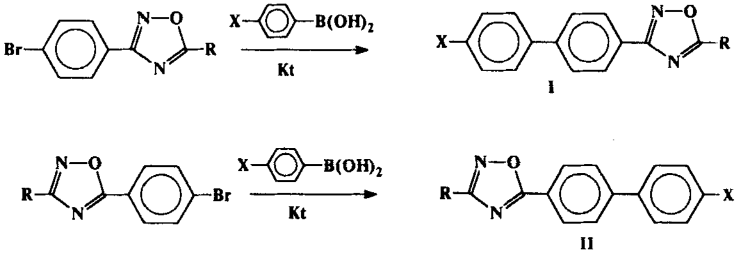
In the present time this method is also applied to the synthesis of a large number of mono- and bi-cyclohexylbiphenyl liquid crystalline compounds[1]. However, there are few examples of application of the cross-coupling reaction to the synthesis of heterocyclic mesogens[2]. In the present work the cross-coupling reaction is used for obtaining the mesomorphic 1,2,4-oxadiazoles.

The last ones contain biphenyl- and cyclohexane- fragments and differ from the known BCH- and CBC- compounds by the asymmetric heterocyclic unit, placed in different parts of the long mesomorphic molecule.

## EXPERIMENT

The synthesis of cyclohexyl containing oxadiazoles was fulfilled starting from arylbromides and arylboric acids, according to the common Scheme 1. The palladium complex $PdCl_2{\cdot}(PPh_3)_2$ was used as a catalist.

SCHEME 1



where R, X = Alk, Cyclohexyl (Cy), Ar and X = F.

3,5-Disubstituted 1,2,4-oxadiazoles, containing cyclohexyl fragment (III), correspondent with respect to the structures (I, II) given in the Scheme 1 were synthesized by the method of direct heterocyclic formation described in our previous work[3]. Here we report the cross-coupling reaction for obtaining the compounds I-IV.

### General procedure of cross-coupling reaction

The mixture of arylboric acid (0.095 mol) in 90 ml of DMF and 50 ml of 2M water solution of $Na_2CO_3$ was stirred with further addition of water till complete solubilization of arylboric acid. 1% of the catalist $PdCl_2 \cdot (PPh_3)_2$ was added. A solution of corresponding arylbromide (0.095 mol) in 30 ml DMF was added at room temperature and the mixture was refluxed 3-4 hours, then it was extracted by benzene or chlorophorm, followed by chromatography on $SiO_2$ and crystallization.

The transition temperatures of liquid crystals (LC) I-IV were measured using a Mettler FP-51 apparatus: they are reported in Table 1.

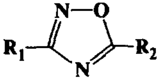
## RESULTS AND DISCUSSION

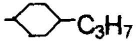
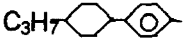
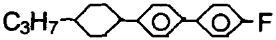
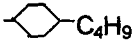
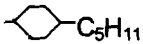
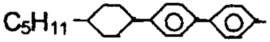
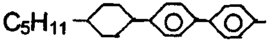
The introduction of a supplementary heterocyclic unit into the BCH- or CBC-structures leads to the following consequences:

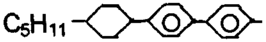
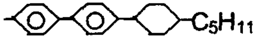
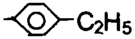
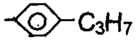
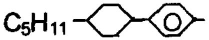
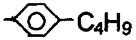
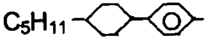
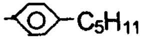
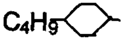
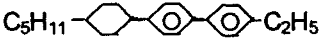
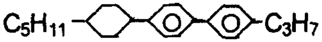
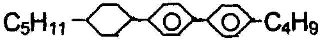
i. In the series of BCH-analogs: the increase of the clearing points and the enlargement of the mesomorphic interval, as compared with the corresponding carbocycles IV a-d (compare substances Ia, IIIa-b with IVa and Ib, IIa, IIIc-h with IVb-d). In the more symmetric structures (III) the tendency to rising of clearing points is less defined. It is necessary to note that some of new heterocyclic mesogens exhibit the thermal destruction before reaching the isotropic transition. As a rule, the series of CBC- heteroanalogs (Ig, h, IIb, IIIi, j) are characterized by lower mesophase thermostability as well as by lower chemical stability with respect to the correspondent carboxylic compounds IVe-g.

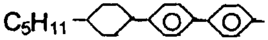
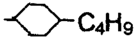
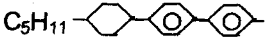
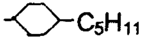
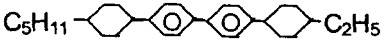
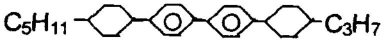
ii. The change of the type of mesophase, depending on the heterocycle position with respect to the biphenyl system. The more symmetrical shape of the molecule (when the oxadiazole fragment is in the centre of the molecular chain) results in the appearance of the nematic phase more likely than in the case when the heterocyclic unit has the ended position (compare in the BCH series the compounds I a-c, II a and III d-f with I d,e and also I g,h III i with II b - in the series of CBC analogs).

TABLE 1 Phase transition temperatures of oxadiazoles with BCH- and CBC-structures (I-IV)



| NN | $R_1$ | $R_2$ | Transition temperatures (°C) |
|---|---|---|---|
| Ia[a] |  |  | C 102 N 199,5 I |
| IIIa |  |  | C 90 N 210 I |
| IIIb |  |  | C 75 S 100 N 200 I |
| IVa[b] |  | | C 99 N 160 I |
| Ib |  |  | C 141 S 153 N 245 I |
| Ic |  |  | C 61.4 S 144.5 N >250 decomp.I |
| Id |  | $-C_2H_5$ | C 100 S 155 N 212 I |
| Ie |  | $-C_3H_7$ | C 78 $S_I$ 148 $S_2$ 210 N >230 decomp. |

| NN | $R_1$ | $R_2$ | Transition temperatures (°C) |
|---|---|---|---|
| If |  | $-C_4H_9$ | C 106,5 $S_B$ 157 $S_A$ 212 N 216 I |
| IIa | $C_3H_7$ |  | C 75 $S_Q$ 155 $S_B$ 187 $S_A$ 239 I |
| IIIc |  |  | C 70 N 183 I |
| IIId[a)] |  |  | C 48 N 187 I |
| IIIe |  |  | C 65 N 190 I |
| IIIf[c)] |  |  | C 62 N 190 I |
| IIIg[a)] |  |  | C 53 S 98 N 193 I |
| IIIh |  |  | C 80 S 180 N 185 I |
| IVb[d)] |  | | C 34 S 146 N 164 I |
| IVc[d)] |  | | C 14 S 158 I |
| IVd[d)] |  | | C 20 S 160 N 170,5 I |

| NN | $R_1$ | $R_2$ | Transition temperatures (°C) |
|---|---|---|---|
| Ig |  |  | C 78 $S_1$(C?) 107 $S_2$ 209 N 282 I |
| Ih |  |  | C 51 $S_1$ 101 $S_2$ 171.5 N 274 I |
| IIIi |  |  | C 113-114 N 265 I |
| IIIj |  |  | C 111-113 N 285 I |
| IVe$^{e)}$ |  | | C 90 $S_B$ 215 $S_A$ 227 N 259 I |
| IVf$^{*e)}$ |  | | C 58 $S_B$ 232 $S_A$ 251 N 311 |
| IVg$^{*e)}$ |  | | C 55 $S_B$ 247 $S_A$ 275 N 305 I |

a) has been cited in our previous work [3]
b) has been cited in the patent [4]
c) has been published [5] in our previous work
d) has been published [6]
e) has been published [7]

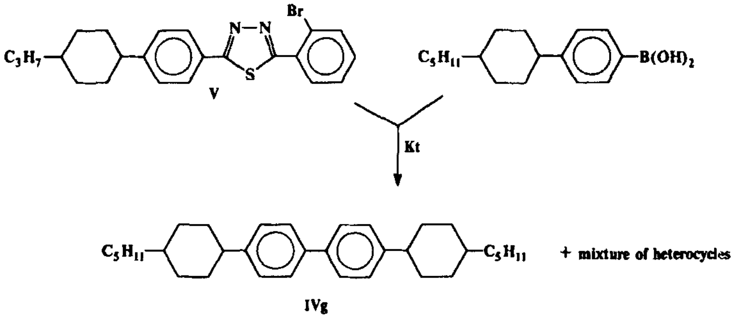
iii. As it was indicated also in the refs.[3,5] the phenylcyclohexane fragment in the diazolic part of the molecule leads to the predominancy of the nematic phase. On the contrary, the phenylcyclohexane system in the oxazolic part plays a smectogenic role (compare III d-f and III g. This tendency is more pronounced in the case of biphenyl substituent in the oxazolic part (compounds III h and I d-f as compared with II a, and I g,h as compared with II b).

It is interesting the fact that, as a rule, in the homologous series of the new 1,2,4-oxadiazoles there is an essential depression of the melting points, when Alk=$C_3H_7$.

As a conclusion, the use of the asymmetrical 1,2,4-oxadiazolic cycle results in a wide variety of the mesomorphic behavior, according to the different position of the heterocyclic unit in the molecule.

It is known, that in the cross-coupling reactions also dimers of the type IV are obtained, together with the usual products of the classic cross-interaction. This is due to the self-interaction of the arylboric acid radicals[8]. By obtaining new oxadiazoles of the types I, II according to the present method, the amount of these products IV considerably increases, especially when the arylbromide contains a Hal-substituent in o-position (to 50% weight). For example, by the cross-coupling reaction of thiadiazolic bromide (V) with amylcyclohexyl phenylboric acid, the carbonic compound IV g was obtained, and purified by chromatography on $SiO_2$ (see Scheme 2).

SCHEME 2



Accordingly to NMR data, the heterocyclic mesomorphic product of this reaction really is a mixture which could contain as a classic cross-coupling products both products of coupling of starting bromide (V) by the type of Vurtz reaction. Some nonlinear products with 2,2'-disubstituted biphenyl system could be formed hereby[8]. This interesting fact will be a subject of our further investigations, devoted to the applications of cross-coupling reaction to the new oxa(thia)diazolic synthesis.

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