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SYNTHESIS AND LIQUID CRYSTALLINE PROPERTIES OF 4,4'-DISUBSTITUTED BIPHENYLS (*)

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Summary. — New substances of the type of unsymmetrical substituted biphenyls

\[ R^1 \begin{array}{c} \circ \end{array} - \begin{array}{c} \circ \end{array} - \begin{array}{c} \circ \end{array} - R^2 \] with \( R^1 \) or \( R^2 = n\)-alkyl, \( n\)-alkoxy and \( n\)-alkanoyl were synthesized.

Miscibility measurements in binary systems, texture observation and comparative studies of the trends of the transition temperatures in homologous series yield a classification of the phase types.

In the 4-n-alkyloxy-4'-n-alkanoylbiphenyls the smectic phase types \( A \) and \( E \) in the new variant \( SE, S_E \) and the variant \( SE, S_A \), \( I \) occur. The 4-n-alkyl-4'-n-hexanoylbiphenyls show the polymorphism \( SA, S_B, S_A, I \) and \( SB, S_B, S_A, I \) and \( SB, S_A, I \). In the 4-n-hexyloxy-4'-n-hexylbiphenyl the new variant of polymorphism \( SE, S_R, S_A, I \) exists.

1. Introduction. — 4,4'-disubstituted biphenyls of different types are known and usually possess liquid crystalline properties [1, 2]. Especially in the case of unsymmetrically substituted compounds with simple substituents low melting points are to be expected. Therefore we have synthesized disubstituted biphenyls of the following type:

\[ R^1 \begin{array}{c} \circ \end{array} - \begin{array}{c} \circ \end{array} - \begin{array}{c} \circ \end{array} - R^2 \]

with \( R^1 = n\)-alkyl \( R^2 = n\)-alkoxy
\( R^1 = n\)-alkyl \( R^2 = n\)-alkanoyl
\( R^1 = n\)-alkoxy \( R^2 = n\)-alkanoyl.

The polymorphism of these compounds was investigated and the type of the smectic phases was determined by the miscibility criterion and texture observation [3].

2. Synthesis of materials. — The monoacylation of the biphenyl is a rather simple process; the reduction to the corresponding 4-n-alkylbiphenyls is without any complication.

These hydrocarbons have been acylated in their 4'-position with high yields.

The combination of the \( n\)-alkoxy- and \( n\)-acyl-substituents is hard to achieve. The acylation of the \( n\)-alkoxy-biphenyl was performed under standard conditions with ether cleavage, other procedures of acylation having no success. We found the best method of synthesis to be the acylation of 4-methoxy-biphenyl in a special Friedel-Crafts reaction [4, 5], in which the ether cleavage occurs simultaneously and therefore yields the acylated 4-hydroxybiphenyls. These derivatives were converted into the corresponding ethers by \( n\)-alkyl-bromides, reduction with hydrazine yielding the 4-n-alkoxy-4'-n-alkyl-derivatives.

3. Polymorphism and transition temperatures. — The following tables show the transition temperatures of the new substances. The classification of the smectic modifications has been done according to the miscibility investigations described in section 4. The symbols used are: \( C \) = crystalline solid state; \( S_A, S_B, S_R \) = liquid crystalline states of the types smectic \( A, B, E \) resp.; \( I \) = isotropic liquid state. The temperatures are listed...
in degrees Celsius. The numbers in parentheses are the phase transition temperatures in the metastable state with respect to the crystalline phases. Latin numbers mark the substances used for miscibility investigations in section 4.

### 3.1 4-n-ALKOXY-4'-n-ALKANONYL-BIPHENYLS

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Table I</th>
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<tbody>
<tr>
<td>n</td>
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<tr>
<td>1</td>
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<td>9</td>
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</table>

### 3.2 4-n-ALKYL-4'-n-HEXANOYL-BIPHENYLS

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Table II</th>
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<td>3</td>
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<td>4</td>
</tr>
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<td>5</td>
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</table>

### 3.3 IX. 4-n-HEXYLOXY-4'-n-HEXYL-BIPHENYL

![Chemical structure](image)

<table>
<thead>
<tr>
<th>n</th>
<th>C</th>
<th>S&lt;sub&gt;n&lt;/sub&gt;</th>
<th>S&lt;sub&gt;a&lt;/sub&gt;</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.9</td>
<td>68.0</td>
<td>83.9</td>
<td>I</td>
</tr>
</tbody>
</table>
4. The classification of the smectic phases. — 4.1

MISCIBILITY. — In order to test the behaviour of miscibility in binary systems the following substances were used:

- a) di-n-propyl p-terphenyl-4,4''-dicarboxylate, polymorphism $S_b, S_a$ [6, 7].
- b) n-decyl 4-[4-phenylbenzylideneamino]-cinnamate, polymorphism $S_b, S_a, S_a$ [8].

![Diagram 1](image1)

**Fig. 1.**

![Diagram 2](image2)

**Fig. 2.**

![Diagram 3](image3)

**Fig. 3.**

![Diagram 4](image4)

**Fig. 4.**
c) 4-[4-n-dodecyloxybenzylidene-amino]-azobenzene, polymorphism S₄, S₅ [9].

The diagrams of state (temperature-concentration diagrams) have been investigated by means of microscopic observation in polarized light with samples of known concentration. In the preparations the substances were mounted between a glass slide and a cover slip.

In some cases the temperature of the beginning of the melting or crystallisation is not exactly observable. In the diagrams this is indicated by lines which show the probable region of the start of melting or crystallisation.

According to the miscibility rule (uninterrupted miscibility shown in Fig. 1-6) the smectic phases of the compounds I, II, III, IV and V are classified as phases E and A.

In the diagrams of the figure 7 and figure 8 the classification of the compounds VI and VII is shown.

The diagram of figure 9 is more complicated. According to the different variants of polymorphism of the compounds (S₅ or else S₄, S₅) the miscibility gap expected between the B- and E-phase regions can be
observed. The appearence of an intermediate nematic phase is remarkable.

In figure 10 the polymorphism $S_A$, $S_B$ of the component VIII is demonstrated. In figure 11 the classification of the smectic high-temperature modification of the component IX as a $B$-phase is to be seen. This is also verified by figure 12 together with the classification of the smectic low-temperature modification of the component IX as an $E$-phase.

4.2 POLYMORPHISM IN THE HOMOLOGOUS SERIES. — The classification of the phase types of the substances I-VII by the investigation of miscibility is representa-
tive for the homologous series of the 4-n-alkoxy-4'-n-alkanoylbiphenyls with \( n = 2, n = 3, n = 4, n = 9 \) and \( n = 10 \) (Table I).

With respect to the regular trends of the transition temperatures in all series of Table I the classification of the smectic modifications as types \( S_E \) and \( S_A \) is justified.

The dependence of transition temperature on chain length of the alkanoyl residue in the homologous series of the 4-n-butyloxy-4'-n-alkanoylbiphenyl is given in figure 13.

The same trend of the transition temperatures can be observed with little variation in all homologous series of Table I.

The \( S_A^{-1} \) and \( S_E^{-1}S_A \) transition temperatures decrease with increasing chain length, the latter more strongly. In members with long chains the transition \( S_E^{-1}S_A \) cannot be observed since the temperatures of these transitions fall below the melting points. The first members of the series show only E-modifications. Therefore transitions from \( S_E \) to 1 can be observed.

The polymorphism \( S_E, S_A \) found in substance IX should be representative for the other members of the homologous series of the 4-n-alkyl-4'-n-alkanoylbiphenyls investigated so far (Table II).

Until now substance IX is the only investigated example of the 4-n-alkoxy-4'-n-alkyl-biphenyls and shows the new variant of polymorphism \( S_E, S_B \) (Fig. 11, Fig. 12).

4.3 TEXTURES. — All investigated A-modifications yield the well-known fan-shaped textures. The stable textures of the E-modifications and of the B-modifications are mosaic-textures.

The smectic E- and B-modifications which have developed from the A-modifications mostly show para-morphic fan-shaped textures, sometimes with concentric arcs as described in references [3] and [7].

Because of the similarity or identity of the textures of the E- and B-phases the transition \( S_E^{-1}S_B \) must be carefully observed. Within the domains new orientations become observable.

The texture observations of the members of the homologous series not investigated by miscibility investigations confirm the classification deduced from transition-temperature trends in the above mentioned homologous series.

References


