X-RAY STUDIES ON LIQUID-CRYSTALLINE PHASES OF 2-[4-n-ALKYLPHENYL]-5-[4-n-ALKYLOXYPHENYL]--PYRIMIDINES*

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The results of X-ray investigations of the homologous series of the 2-[4-n-alkylphenyl]--5-[4-n-alkyloxyphenyl]-pyrimidines with 4, 6, 7, 8, 9, 10 respectively, C-atoms in the alkyl chains are represented. The structure of the S_G-modifications can be described with a monoclinic unit cell. The lattice parameters are investigated as a function of the temperature and the chain length. The temperature dependence of the layer thickness shows a characteristic behaviour in the homologs and is discussed in connection with the polymorphism of the investigated substances.

1. Introduction

The investigation of 2-[4-n-pentylphenyl]-5-[4-n-pentyloxyphenyl]-pyrimidine by microscopy, differential scanning calorimetry, dilatometric and X-ray measurements led to the new smectic phase types S_F and S_G [1]. Now the existence of the S_F and S_G phases was proved in the homologs of this substance by their miscibility relations [2]. Smectic G phases are also known in compounds of other chemical nature [3].

In this paper further structure parameters for the smectic modifications of the alkyl-phenyl-alkyloxyphenyl-pyrimidines

$$C_n H_{2n+1} - \langle\bigcirc\rangle - \langle\!\!{}^{N-}_{N=}\!\!\rangle - \langle\bigcirc\rangle - OC_n H_{2n+1}$$
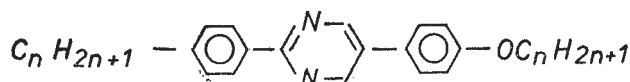
with $n = 4, 6, 7, 8, 9, 10$ are given, obtained by X-ray studies of non oriented samples. Special emphasis is laid on the structures of the smectic G modifications and the temperature dependence of the layer thickness in connection with polymorphism in this series.

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2. Experimental

The substances and their polymorphism schemes containing the transition temperatures are listed in Table I. They were investigated using a Guinier camera and the CuK_α--radiation. The camera has a radius $r = 57.7$. mm and is equipped with a heating stage. The samples were molten on a Al-foil. A movement of the sample during the exposition

TABLE I

$$C_nH_{2n+1}-\langle\bigcirc\rangle-\langle\!\!\!\!\overset{N}{\underset{N}{\bigcirc}}\!\!\!\!\rangle-\langle\bigcirc\rangle-O-C_nH_{2n+1}$$
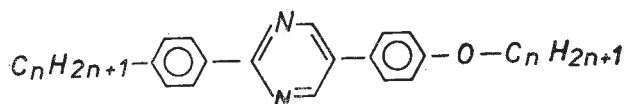
n	cr.		S_G		S_F		S_C		S_A		is
4	·	90.5	·	113.7	·	—	—	120.8	·	214	·
6	·	64.8	·	98.2	·	116.4	·	152	·	210.5	·
7	·	80.5	·	84.5	·	124.7	·	171.8	·	200.0	·
8	·	76.5	·	89	·	129	·	1770.0	·	195.2	·
9	·	88.5	·	93	·	130.6	·	180.2	·	188.0	·
10	·	86.0	·	117.6	·	132.8	·	179.4	·	183.5	·

was possible. To get a precise layer-thickness the measurements of the Bragg angles θ of the inner ring must be done very exactly. Therefore we used a counter-tube-goniometer in the Bragg-Brentano geometry which was equipped with a special heating stage [4].

The relative error is about $\Delta d = \pm 0.1$ Å and is related to the measurements of the temperature dependence of d in one and the same sample.

However, the absolute error, due to several experimental conditions, is about $\Delta d = \pm 0.4$ Å.

3. The patterns of the S_G-modifications

The X-ray diagrams (Fig. 1) are of the same kind as described earlier [1]. They exhibit the characteristics also found in other smectic modifications: there exists an inner ring at Bragg angles of about 1–2° and in many cases its second order, corresponding to the thickness of the smectic layers. Further there are several outer rings at Bragg-angles from 8–12° indicating a higher degree of order within the smectic layers. Especially, two strong outer reflexes are found, surrounded by several weaker ones. All outer reflexes approach each other with increasing C-number n within the homologous series. The identification of the rings of the homolog $n = 10$ was possible only by a comparing observation with all members of the series (Fig. 2). A microdensitometer trace (Fig. 3) shows that a very high background is found on the pattern in an angle range from 8°–12°.
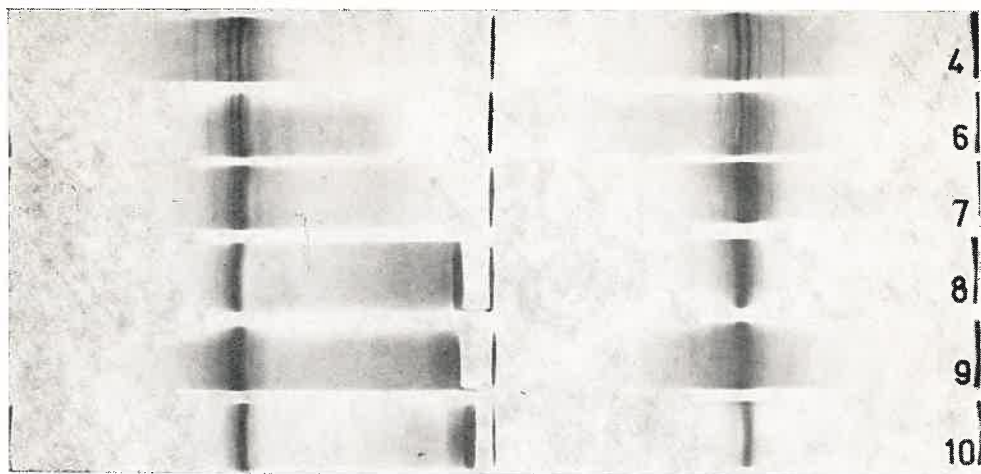
Fig. 1. X-ray patterns of S_G modifications. Numbers indicate the homologs

Preliminary investigations of oriented samples and the differences between the d-values and the molecular lengths pointed to a tilted arrangement of the molecules within the smectic layers in the G-phase. Therefore the tilt angles were determined in two ways: first by comparison of the layer thickness and the length of the molecules and second on
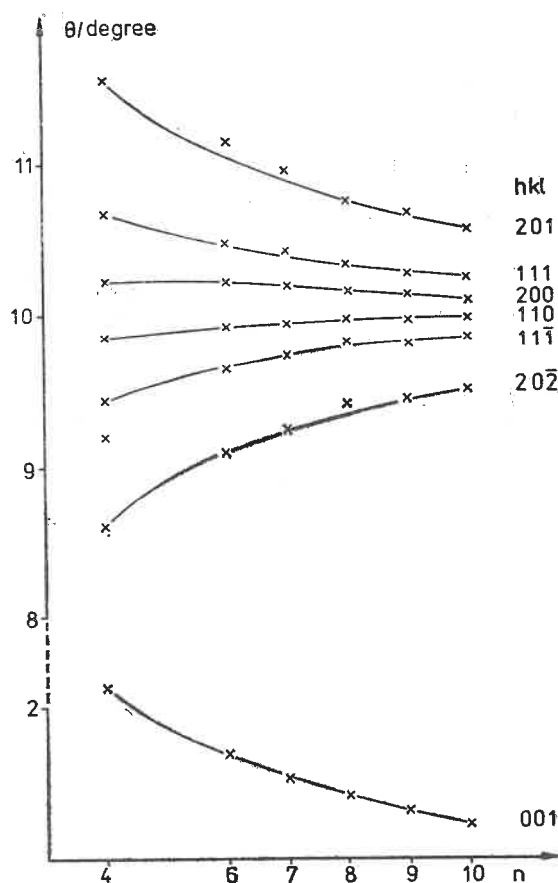

Fig. 2. The Bragg-angles of the outer rings as a function of the C-number

the base of the X-ray patterns. The length of the molecules was obtained as well with the aid of Stuart-Briegleb-models as by calculation of the most stretched molecular form.

Although the calculation of the tilt angles in the first way is somewhat doubtful (because of the assumption of the most stretched molecular form) the values determined in these two ways agree well. This supports further the assumed form of the molecules in the S_G phase.

The tilt angles as a function of the number of the C-atoms in the alkyl chains are given in figure 4. It can be seen, that the tilt angles decrease with increasing molecular-length within the homologous series.
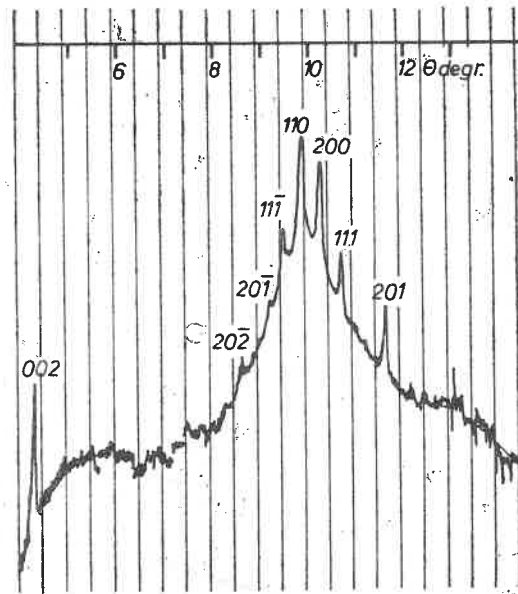
Fig. 3. Microdensiometer trace of the S_G modification of substance $n = 4$
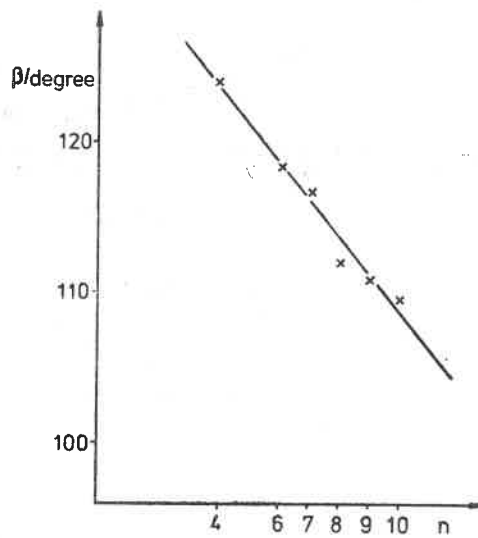

Fig. 4. The calculated tilt angles as a function of the C-number

The diagrams were evaluated on the base of a monoclinic cell. The tilt angle given in figure 4 is used in order to determine the c-parameter in connection with the d-value of the inner ring. The indexing of the outer reflections was made on the assumption, that the two strongest rings are the 110 and the 200 reflex, respectively, and that the unit cell is centred. These two assumptions could be made on the base of the knowledge of other smectic phases and of the steric packing of such organic molecules.

In this way we obtained the *hkl* indices of all reflections. Table II shows the very good agreement between the calculated and measured Bragg-angles. Table III gives a summary of the calculated lattice constants of the investigated substances. The very good agreement

<table>
<tr><td colspan="3" align="center">TABLE II</td><td colspan="6" align="center">TABLE III</td></tr>
<tr><td>*hkl*</td><td>θ_{meas}</td><td>θ_{calc}</td><td>Substance</td><td>$a/\text{Å}$</td><td>$b/\text{Å}$</td><td>$c/\text{Å}$</td><td>β/dgr</td><td>ml/Å</td></tr>
<tr><td>201</td><td>11.57</td><td>11.58</td><td>4-pyrim.</td><td>10.46</td><td>5.26</td><td>25.0</td><td>124.0</td><td>25.1</td></tr>
<tr><td>111</td><td>10.68</td><td>10.68</td><td>6-pyrim.</td><td>9.90</td><td>5.22</td><td>29.5</td><td>118.4</td><td>29.5</td></tr>
<tr><td>200</td><td>10.23</td><td></td><td>7-pyrim.</td><td>9.62</td><td>5.18</td><td>32.1</td><td>116.7</td><td>31.6</td></tr>
<tr><td>110</td><td>9.85</td><td></td><td>8-pyrim.</td><td>9.52</td><td>5.17</td><td>33.7</td><td>112.0</td><td>33.8</td></tr>
<tr><td>111</td><td>9.46</td><td>9.46</td><td>9-pyrim.</td><td>9.40</td><td>5.17</td><td>35.8</td><td>110.8</td><td>35.9</td></tr>
<tr><td>201</td><td>9.20</td><td>9.20</td><td>10-pyrim.</td><td>9.26</td><td>5.16</td><td>38.0</td><td>109.5</td><td>38.0</td></tr>
<tr><td>202</td><td>8.61</td><td>8.56</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>002</td><td>4.25</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>001</td><td>2.13</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

between the measured and calculated values in Table II proves the assumption of a monoclinic cell. Further this indicates, that one molecule is positioned in the centre of the C-face. The extinction rule $(h0l)$ $h = 2n+1$ suggests a C-face centred cell which could be explained by a rotational disorder as in the phase V of TBBA [5]. But the packing type of the molecules in the C-face cannot be decided with certainty because of the small numbers of the interferences. The structure of the S_G-modifications of the alkyl-phenyl-alkyloxy-phenyl-pyrimidines agrees with those structures, which were proposed for the phase V of TBBA [5] and the smectic phase of BBEA [6]. These both phases in the mean time were classified as phases of the type smectic G [7].

4. The patterns of the other phases

The X-ray patterns of the S_F modifications contain only one outer ring besides the inner ring. This proves that the high order of the S_G phases is partly destroyed. The S_F modifications have a tilted structure. This can be concluded by the difference of the molecule length and the layer thickness (similar to S_G) and by preliminary investigations of oriented sample. It also corresponds with the observed textures [2]. The tilt angle calculated by the difference of the molecular lengths and the layer thicknesses is about 25°–30° depending on the substance and is similar to the tilt angle of the corresponding S_G phase.

The X-ray patterns of the S_C and S_A phases have the well known picture: an inner sharp ring and a very diffuse outer interference.

5. The temperature dependence of the layer thickness

The temperature dependence of the layer thickness (d-values) within the homologous series (Fig. 5) shows some interesting facts, concerning the arrangement of the molecules within the smectic layers.

In the S_G modification the d-values of all investigated members of the series are nearly independent of the temperature. The d-values allowed to estimate the tilt angles.
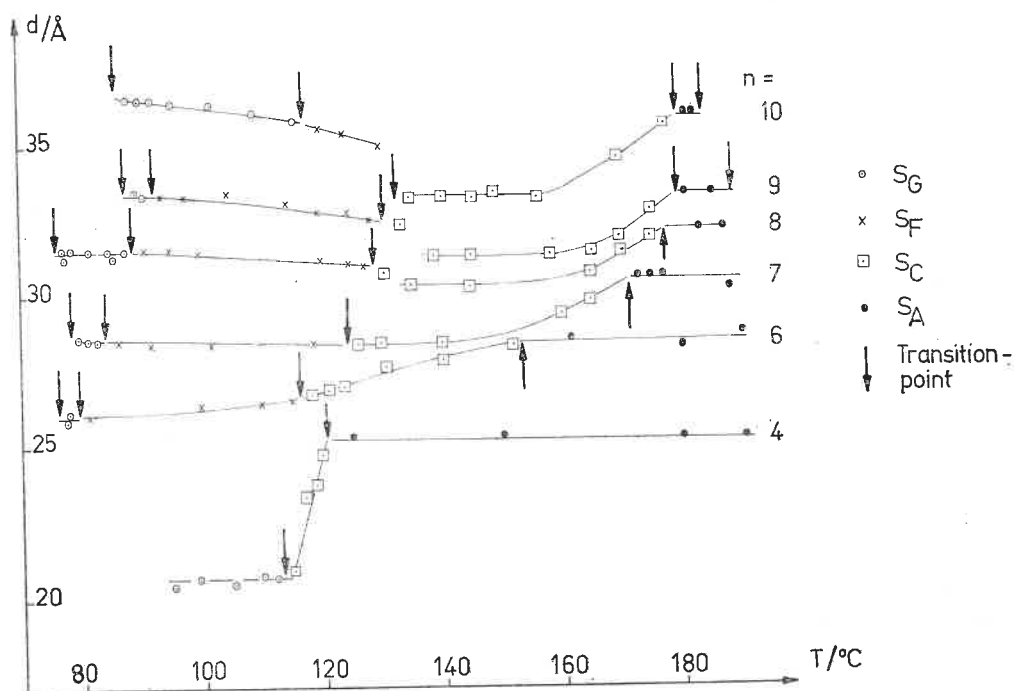

Fig. 5. Layer thickness of the investigated substances as a function of the temperature

The obtained results (Section 3) confirm the assumption of completely stretched chains within the S_G phases.

In the case of the homolog $n = 4$ the layer is enlarged drastically within the S_C phase and the value increase to the molecular length at the S_C–S_A-transition. It can be explained by the usual interpretation of the tilted and orthogonal arrangement of the molecules in the S_C and S_A phase, respectively.

On the other hand in the case of the homolog $n = 10$ the transition S_F/S_C is connected with a sudden decrease of the layer thickness. Within the existence range of the S_C phase an increase of the d-values is observable. But the d-values of the S_A phase do not reach the molecular length. The d-values of the S_A phase agree with those of the S_G and the S_F modifications. This agreement with the d-values of the tilted S_G phase could be explained by a tilted arrangement of the molecules in the S_A modification also. It could lead to a new

structure type of the S_A phase already postulated in some other papers [8, 9]. However, the results given in figure 6 lead to another conclusion. In Fig. 6 besides the calculated molecular length the d-values of the S_G and S_A modifications are presented. It can be seen that the difference between the d-values of the S_A modification and the molecular length increases continuously with increasing chain length. We see the reason for the in-
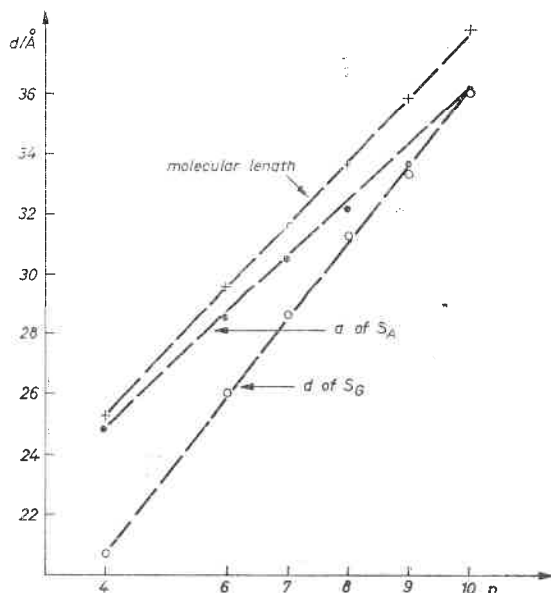

Fig. 6. Molecular length and layer thickness as a function of the C-number

creasing difference in an increase of the mobility of the alkyl chains. This leads to an apparent shortening of the molecules as well as to a possibility of an interpenetration of the molecules of the adjacent layers. The disorder is dependent of the chain length and takes place at the S_F–S_C-transition indicated by the jump to deeper values. This assumption is supported by calorimetric measurements demonstrating high values of the heat of transition at the S_F–S_C-transition, especially at the substances $n = 8$, 9 and 10.

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