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# On Packing in Smectics: X-Ray Diffraction Study on the Homologous Series 4, 4′-di-n-alkyl-azoxybenzenes

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# ON PACKING IN SMECTICS : X-RAY DIFFRACTION STUDY ON THE HOMOLOGOUS SERIES 4, 4'-DI-N-ALKYL-AZOXYBENZENES

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## ABSTRACT

The smectic layer spacings of the homologous series 4,4'-di-n-alkyl-azoxybenzenes with alkyl chain length from m=6 to m=10 were determined and a mean layer spacing increment of 0.109 nm per methylen group was found.
The results are discussed in relation to two different models :
(I) The diffuse cone model of A. de Vries. Differences between layer spacing and molecular length are attributed to orientational disorder leading to mean tilt angles up to 18° of the molecules.
(II) The second model differentiates between the directions of the rigid aromatic core and that of the alkyl chains. Orthogonality of the rigid core long axis to the smectic layer planes and therefore tilting of the alkyl chains results in coincidence between calculated layer thickness and measured smectic layer spacings.
X-ray film exposures of oriented samples clearly demonstrate the $S_A$-type of the phases and confirm a slight odd-even effect of layer spacing increments.

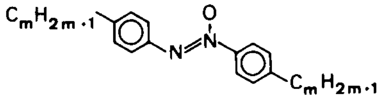
## INTRODUCTION

Attempting to correlate molecular structure and mesomorphic behaviour, homologous series are suitable objects to study distinct parameters, here especially the effect of terminating alkyl chains.

The present series had found our interest mainly beside of two reasons : (i) in this series a change from a clear discontinuous S-N transition (m=10) to a continuous transition (m=6) is found[1] ,[2] and (II) the fact that a variety of different experimental studies on this series exists using e.g. calorimetry[2] [3] , polarization optical microscopy[4] [5] , magnetic susceptibility[6] [2] and dilatometry[7] , requested an investigation of the molecular short range order by small angle X-ray scattering. During the course of this investigation the relations between layer spacing, molecular length, alkyl chain orientation , molecular packing and orientational disorder appeared of particular interest.

## EXPERIMENTAL

The compounds of the homologous series 4,4′-di-alkyl-azoxybenzenes (alkyl chain length from m=6 to m=10)



were synthesized and purified according to the method of van der Veen et al.[8] by R. Lorenz[7] .
The X-ray measurements were performed using a Kratky-Compact-small-angle camera (Anton Paar, Graz, Austria.) A curved linear position sensitive proportional counter (M. Braun, Munich) with an active length of 50 mm and a low flux of a mixture of 75% argon and 25% methane under a pressure of 11 bar served as X-ray detector. Ni-filtered Cu-radiation was used. The samples (thickness 0.5 mm) were placed on a specimen holder consisting of a copper block (20*20*3 $mm^3$ ) with a bore-hole of 2 mm diameter. They were fixed between two teflon foils of 12 µm thickness.
The temperature was controlled by an electronic heating stage (Anton Paar, Graz, Austria) with an absolute accuracy of 0.25 K. The resolution and relative accuracy, however, was ±0.01 K. In order to calibrate the detector, the scattering curve of a cadmium-distearate multilayer ( 35 double layers ) has been recorded at room temperature before each measurement. This calibration sample was prepared on a glass rod of 2 mm diameter using the Blodgett technique[9] . Its diffraction pattern consists of sharp reflections with a first order period of d = (5.03±0.01) nm (Matsuda et al.[10] ).
Preliminary results[11] suffered under an imperfect scattering angle determination in absence of a calibration sample.

The uncertainty of layer spacing determination was estimated to be ±0.03 nm. Control experiments, performed in Kiessig- cameras (R. Seifert, Ahrensburg, FRG) using point-like primary beam geometry and film registration, gave the same layer spacings within experimental error.
Recently scattering patterns of samples, filled in Lindemann capillaries of 1mm diameter and oriented by a magnetic field of ca. 1.1 Tesla (permanent magnet within the collimation path) were recorded using a Kratky PHK (pinhole) camera and film registration. Later on also samples were investigated, oriented off-line(before) in a Bruker magnet (1.6 Tesla) and subsequently placed in the Kiessig-camera.

RESULTS AND DISCUSSION

The X-ray scattering curves of unoriented samples within the smectic state together with a calibration curve are shown in Fig.1.

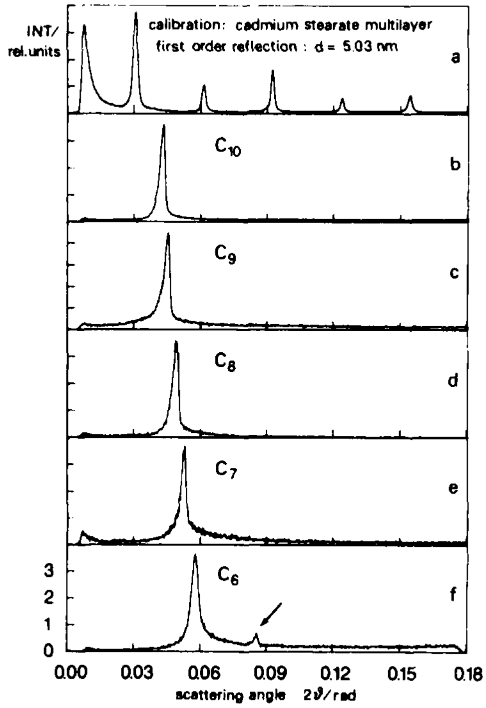


Figure 1 a-f:

X-ray scattering curves of unoriented samples of the di-n-alkyl-azoxybenzenes (m=6-10) in the smectic state (2 K below the transition to the higher temperature phase, which has been the nematic one for m=7,8 and the isotropic one for m = 9, 10. The di-hexyl-azoxybenzene, the first compound in the series which has a smectic phase, was measured at 17.0° C and in this case a re-crystallization could not be prevented. The onset of crystallization is indicated by a little peak, marked by an arrow in Figure 1 f and exposed only 3 - 5 seconds).

The transition temperatures, determined by polarization optical microscopy[7] are collected in table 1.

| m | C | | S | | N | | I |
|---|---|---|---|---|---|---|---|
| 6 | • | 25.9 | (• | 17.0) | • | 53.4 | • |
| 7 | • | 33.9 | • | 53.8 | • | 70.6 | • |
| 8 | • | 39.0 | • | 64.4 | • | 66.5 | • |
| 9 | • | 44.2 | • | 75.7 | - | | • |
| 10 | • | 49.6 | • | 76.0 | - | | • |

TABLE I Transition temperatures [°C] of the compounds under consideration. Temperature in bracketts $(T_m)$ means a monotropic transition at $T_m$, only attainable by cooling; a dot indicates the presence of a phase (C = cryst., S = smectic, N = nematic, I = isotropic liquid) and a dash means the absence of the corresponding phase.

The smectic layer spacings were determined from the diffraction maxima using the Bragg equation $d = \lambda/2\sin\theta$ and are given in table 2 together with calculated molecular lengths and mean tilt angles of the different models.

| m | $d_{exp}$ /nm±0.03/ | l /nm/ | $d_B$ /nm/ | S ±0.03 | $<\theta>_A$ | $<\theta>_B$ | $d^0_{exp}$ /nm/ |
|---|---|---|---|---|---|---|---|
| 6 | 2.67 | 2.78 | 2.65 | 0.89 | 14.0 | 16.1 | - |
| 7 | 2.89 | 3.02 | 2.87 | 0.88 | 14.7 | 16.8 | 2.88 |
| 8 | 3.09 | 3.27 | 3.09 | 0.85 | 16.6 | 17.5 | 3.07 |
| 9 | 3.32 | 3.52 | 3.31 | 0.84 | 16.9 | 18.1 | 3.34 |
| 10 | 3.54 | 3.77 | 3.53 | 0.83 | 17.5 | 18.6 | 3.53 |

TABLE II Comparison of experimental layer spacings and calculated model parameters (see text)

The lengths of the molecules were calculated using atomic bond length and bond angles, given for a very similar compound, the di-heptyl-oxy-azoxybenzene (HOAB), in a crystal structure analysis of Leadbetter and Mazid[12].

The following values were used : C-C (aliph.) = 150.4 ; C-C (arom.) = 138 ; C-N = 144 ;N-N = 126 ; N-O = 128 ; all values in pm. The bond angles were C-C-C (aliph.) = 113° ; C-C-C (arom.) = 120° ; C-N-N = N-N-C = 117.8° and the van der Waals radius of the methyl group was 200 pm. The model length was calculated under the assumption of all trans conformation. Leadbetter and Mazid [12] obtained a value of 326 pm for the length of the di-heptyl-oxy-compound in its fully extended form, comparable to 327 pm, the length of the di-octyl-compound (see columne 2 of table 2).
A plot of the molecular model of the decyl-homologue in its most extended form is seen in Fig. 2.

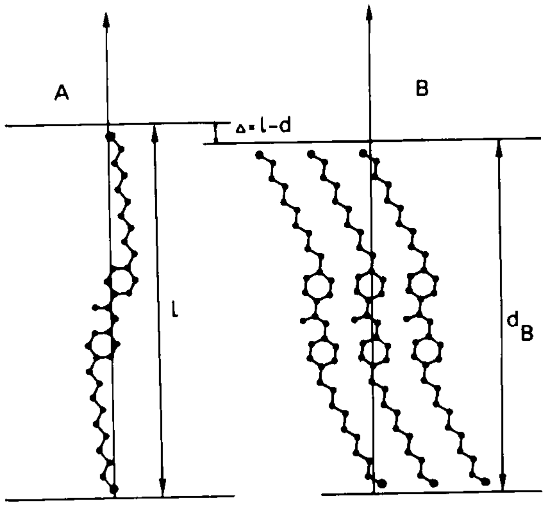


Figure 2

Comparison of molecular length l (fully stretched, A) to layer thickness of molecules packed with their rigid parts orthogonally to the layer planes (B), tilt azimutally averaged to allow uniaxial symmetry.

The discussion of the results and the comparison of the measured smectic layer spacings with molecular lengths are done on the basis of two different assumptions (models) :

Model A ( diffuse cone model of A. de Vries )

Starting from the molecule in its most extended form, seen in Fig. 2 A, there results small differences between molecular length and measured layer spacings, which can formally be attributed to tilt angles of the molecules against the layer normal, caused by orientational disorder as has been outlined in the diffuse cone model of A. de Vries[13] . For an orientational order parameter S = 0.8 e.g., one obtains an averaged value of $\langle\cos\Theta\rangle$ of 0.927 and an averaged tilt angle of 19° , whereas the director remains in an orthogonal direction to the layer planes.

Comparing the values of the calculated molecular length l and observed smectic layer spacings d, listed in table 2, we get mean values of $\langle\cos\theta\rangle = d/l$ between 0.94 and 0.96 and subsequently orientational order parameter values S between 0.8 and 0.9, seen in column 5 of table 2.
Averaged values of the tilt angle $\theta$ of the molecules are given in the next columne. It results a continuous decrease of the orientational order parameter S with increasing alkyl chain length, caused by an increasing difference l-d from 0.11 nm (m=6) to 0.23 nm (m=10).
Alternatively, this increasing l-d difference can also easily be explained as an effect of alkyl chain length, which will be shown in the following :

Model B (rigid parts orthogonally packed)

This model differentiates between the direction of the alkyl chains and that of the rigid aromatic core. Parallel orientation of the rigid core long axis to the normal of the smectic layer planes is proposed as mean packing of the molecules in this model. Mainly two reasons are responsible for this choice :
(i) The "odd-even" effect of the transition temperatures and the transition entropies, particularly exposed for the lower homologues of this series.
(ii) The experimentally determined layer spacing increment $\Delta d$.
As has been reviewed by Kelker and Hatz[14] , several attempts has been made to explain the alternation of the nematic to isotropic transition temperatures and entropies, clearly pronounced for the lower members of a homologous series. Especially Marcelja[15] has to be mentioned who could explain the even-odd effect by detailed calculations of the interaction energy, the contributions of the rigid aromatic core and the alkyl chains separately. Lengthening the chain from an even to an odd number of C-atoms gives a higher contribution to the molecular polarizability than a lengthening from an odd to an even number, because in the first case the chain segments are more collinear to the long axis of the rigid aromatic core, the part of the highest polarizability ( see Fig. 2 B ).
Secondly, X-ray measurements of the layer spacing increment per methylenic group, $\Delta d$, for homologous series indicate also a different orientation of the terminating alkyl chains and the smectic layer normales. For the present series a mean $\Delta d$ of 0.109 nm was found, ranging from 0.100 to 0.150 nm. This would imply a mean tilt angle of the chains of $\theta_p = 29^\circ \pm 5^\circ$ . This value can be compared with that of three other series with alkyl chains symmetrical on both sides of the aromatic core : p-n-alkoxybenzoic acids (Blumstein and Patel[16] ), $\theta_p = 28 \pm 5^\circ$ ; p-n-alkoxycinnamic acids (Bryan et al.[17] ) $\theta_p = 30^\circ$ ; (both $S_C$ -phases) ; terephthal-bis-(4n)-alkylanilines (Kumar[18] ) $\theta_p$ between 30° and 35° (estimated); ($S_A$-phase).

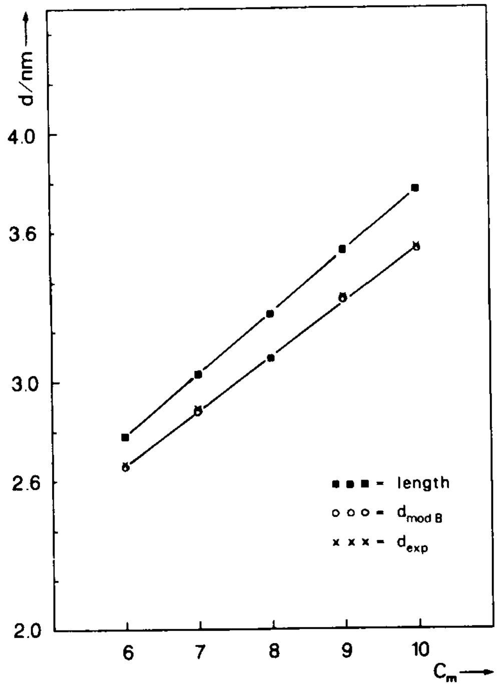
Therefore, a line connecting the para-positions of the phenyl rings, is chosen as long axis of the rigid part of the molecule, seen in Fig. 2 B. Assuming now orthogonality of this rigid middle part to the smectic layer planes, the layer spacing of model B is calculated by :

$$d = d_a + 2\, d_p \cos\Theta_p \qquad (1)$$

where $d_a$ is the thickness of the rigid aromatic part and the second term is the contribution of the alkyl chains, projected onto the layer normal.
The results are also listed in table 2. It turns out that the calculated layer spacings of model B agree with the experimentally determined long spacings within the experimental error of ±0.03 nm, as is demonstrated in the graph of Fig. 3.

FIGURE 3

Comparison of molecular length, exp. layer spacing and calculated layer spacing of model B (Fig. 2B) as function of alkyl chain length



We see that both models are suitable to describe the experimental facts. The increasing difference l-d with raising m is in the diffuse cone model explained by a decreasing orientational order parameter S. The second model (RPOP = rigid parts orthogonally packed) seems to be more convenient in explaining this difference simply by an increase of the length of the projected alkyl chains. Furthermore, a comparison of the mean tilt angles

of the molecules in both models, columne 6 and 7 in table 2, shows that the mean orientation of the molecules agrees in both models, but model B has the advantage that no definite choice of the orientational order parameter S is needed. Especially the constancy of the smectic layer spacing d in the immediate neighbourhood of a smectic to nematic phase transition, as has been shown e.g. in high resolution X-ray investigations by Ocko et al.[19] , can be more easily explained on the base of model B, because at least in the neighborhood of a phase transition a change of the orientational disorder should be expected.
Taking in mind the fluid state of the chains, one may argue that that the configuration of model B is too well ordered. However, all types of disorder - longitudinal disorder, conformational disorder, orientational disorder and director fluctuations - are allowed in model B under one condition : the mean value of the layer spacing must remain constant and equal to $d_B$.
Finally, a diffraction pattern of an oriented sample is presented in Fig.4, which clearly demonstrates the $S_A$-phase character: a right angle between the inner reflection, occuring from the layering, and the outer reflection caused by the lateral short range order of the molecules within the layers. The layer spacings of a series of oriented specimens are given in columne 8 of table 2.

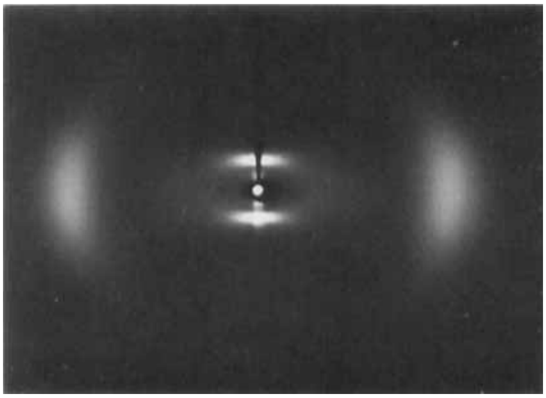


Figure 4

X-ray diffraction pattern of di-heptyl-azoxybenzene (magnetic field of ca. 1.1 Tesla; the inner reflection is strongly overexposed; $I_\perp/I_\parallel \approx 0.01$)

CONCLUSIONS

Alternatively to the interpretation of smectic layer spacings in terms of the diffuse cone model of A. de Vries, a model is presented, consisting of orthogonally packed rigid aromatic parts and therefore tilted alkyl chains. It leads, in a straight-forward manner, to an agreement between model layer spacing and experimentally determined values of this spacing.

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