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A simple molecular model for the interpretation of some properties of smectic C and A phases

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We present a simple geometrical model in which the molecular shape is approximated by a small number of parameters for the dumbbell-like middle group and cylinder-like alkyl end chains. The pair potentials of nearest neighbours are approximated by the sum of anisotropic repulsive terms due to the contact of the different parts of the molecules and attraction due to dispersion forces between different parts of the molecules. Since the number of nearest neighbours at the smectic C/A phase transition is unchanged, the resulting pair potentials are able to describe well the cooperative behaviour of the molecules in the non-ordered layers of the smectic C and A phases. The dependence of the tilt angle on the alkyl chain length and on the temperature and other thermodynamic and structural properties can be interpreted qualitatively very well.

1. Introduction

Ferroelectric liquid crystals derived from chiral smectic C phases are promising media for the construction of optoelectronic displays [1]. In consequence models which are able to describe the properties of smectic C phases are of considerable interest. There are already several models for smectic C and A phases which allow the description with high precision of the temperature and concentration dependence of several properties by means of adjustable parameters [2–4]. The lack of a connection of these parameters with molecular data is an important disadvantage. We propose here a model which allows us to construct qualitative connections between the molecular structure and properties of the liquid crystals.

The structure of liquid crystals results mainly from the interaction between nearest neighbours; long range forces are of minor importance. For molecular attraction isotropic dispersion forces are dominant [5, 6]. Because of the anisotropic geometrical shape of the molecules the repulsion, however, is strongly anisotropic. In order to look for molecular models we consider the strong differences of liquid-crystalline and solid crystalline states. The crystal structures of solid phases are especially sensitive to small changes in the molecular structure. In the liquid phases, however, the details of the molecular shape because of rapid molecular motion are averaged. Consequently the intermolecular interaction may be approximated by a relatively rough model. The widespread complete miscibility between liquid-crystalline phases [7] proves that behaviour. In the solid state, complete miscibility is exceptional. The high melting energy [8] emphasizes the qualitative differences in the state of order. Near the melting point the excitation of intramolecular and intermolecular oscillations is strongly increased, many degrees of freedom are excited and the optimal packing (i.e. the

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position of minimal energy) of single atoms is no longer exactly fixed. Neither the structure of a single molecule in the ground state nor its structure determined from the solid state are sufficient for the characterization of the liquid state. In order to consider all oscillational excitations, molecular models consisting of rigid cores and flexible tails (similar to the models used by Dowell [9] can be used. Molecular statistical methods, for example, those applied by Sanyal *et al.* [5] to the nematogen 4,4′-dimethoxyazoxybenzene, should allow also the calculation of the relatively complicated smectic phases; however, the state of computer techniques at the present does not render this possible. Therefore in our model we have to simplify the molecular geometry drastically in order to consider only the important structurally relevant properties.

The hard rod model [6] of nematic phases shows that by consideration of only the molecular length and breadth it is possible to model the influence of molecular data on the liquid-crystalline state. In special cases, in homogenous rods and discs, the formation of smectic layers can be interpreted as a result of entropy induced ordering [10], but usually it is necessary to consider more sophisticated molecular models. In the model of Sirota [11] the liquid crystal phase sequence is affected by a minimum in the surface free energy. Dershanski and Petrov [12], in their general theory of thermotropic and lyotropic mesophases, describe the molecules in terms of a general multipole which consists of electrical, steric, biphylic and flexible multipoles. We want to avoid their very formal descriptions of the molecular structure and tend to a model which allows the modelling of more individual properties. As we have mentioned, a very detailed reproduction of the molecular structure is not possible and not necessary.

2. Elements of the model

At present many different types of mesogenic molecules are known [13]. Since most of these types do not exhibit smectic C phases we may restrict ourselves to simple rod-like molecules with a hard core and flexible terminal alkyl chains. In our model we consider the existence of regions of different polarizability. Referenced to the same volume unit, the increment of the polarizability of the core is much higher than that of an alkyl chain. This means the attractive core–core dispersion energy (E_{cc}) is much higher than that of the alkyl–alkyl interaction (E_{aa}):

$$E_{cc} \gg E_{aa}.$$

With the usual treatment of the mixed interaction E_{ca} (see, for example, Moelwyn-Hughes [14])

$$E_{ca} = (E_{cc} E_{aa})^{1/2} \tag{1}$$

we find for $E_{cc} \neq E_{aa}$

$$E_{cc} + E_{aa} > 2E_{ca}. \tag{2}$$

In smectic layers each part of the molecule is surrounded by corresponding parts of the neighbouring molecules. Therefore, the sum of the attractive interaction energies is higher than for the lower ordered nematic structures in which the molecules are laterally shifted with respect to each other. Important influences result from packing effects [15]. This may be demonstrated with the aid of figure 1 which defines the molecular parameters: a = distance of belly and indenture of the core, b = maximum lateral molecular radius, c = curvation radius of the belly of the core, d = effective molecular radius, e = lateral molecule radius at the terminal groups, ε = tilt angle, $2x$ = lateral shift of the nearest neighbour molecule.

Using geometrical arguments we find (here the quantities d_{11}, d_{22}, d_{12} and d_{21} are also defined in figure 1)

$$\tan\varepsilon = x/d, \tag{3}$$

$$d_{11}^2 = d_{22}^2 = d^2 + x^2, \tag{4a}$$

$$d_{12}^2 = d^2 + (a-x)^2, \tag{4b}$$

$$d_{21}^2 = d^2 + (a+x)^2, \tag{4c}$$

$$d = b - c + c^2 - \surd[|x| - a\,\mathrm{int}\,(|x|/a + 1/2)^2]. \tag{5}$$

For special cases we obtain

$$\text{for} \quad -a/2 < x < a/2, \qquad d = b - c + \surd(c^2 - x^2), \tag{6a}$$

$$\text{for} \quad a/2 < x < 3/2a, \qquad d = b - c + \surd[c^2 - (x-a)^2], \tag{6b}$$

$$\text{for} \quad -3/2a < x < -a/2, \quad d = b - c + \surd[c^2 - (x+a)^2]. \tag{6c}$$

In the special case of spheres with $b = c$ we can write

$$d = b^2 - \surd|x| - a\,\mathrm{int}\,(|x|/a + 1/2)^2]. \tag{7}$$

The special case of cylinders with $c = \infty$ yields

$$d = b. \tag{8}$$

We use a van der Waals potential with hard repulsion

$$E^{\mathrm{rep}} = \begin{cases} 0 & \text{for } r \geqslant d \\ \infty & \text{for } r < d \end{cases} \tag{9}$$

and the attractive energy

$$E^{\mathrm{attr}} = A(-2d_{11}^{-6} + d_{12}^{-6} + d_{21}^{-6}). \tag{10}$$

Remarkable differences of the lateral radii of the molecular parts with similar longitudinal extension tend to the formation of intercalated structures with small lateral distances and good space filling. If the bellies and the indentures lie at small distances from one another, the tilted structure yields a good compromise between good space filling and close interaction of neighbouring parts.

Considering smectic A and C phases, we assume rotational symmetry of the molecules around their long axes. This does not mean completely free rotation independent of their neighbours. Several preferred positions of minimum energy during rotation about the long axes are possible, however, in a packing of the molecules in smectic layers with strong disorder of the lateral molecular axes, the latter may be averaged over all lateral directions to describe the lateral area of the molecules.

The mobility of the parts of the molecules controls the temperature dependence of their lateral radii. Rigid parts, for example the cores, have a constant lateral area. The lateral radius of the terminal alkyl chains, however, increases upon raising temperature.

There is a remarkable difference between our model and the zig-zag model of Wulf [16], which contrary to the experimental facts predicts a pronounced order of the lateral molecular axes. In terms of our model the alkyl chains are molten so that only the evaluation of the (temperature dependent) area but not the exact definition of their position is possible. This corresponds to the results of both experiments and theoretical calculations [17].

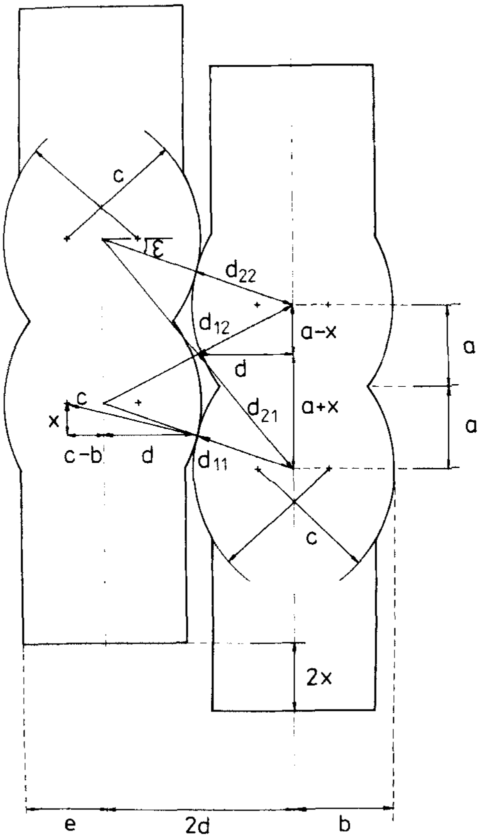


Figure 1. Molecular model of freely rotating molecules with structured surface.

3. Packing in the volume

If the parameters for the molecular model are chosen so that the indentures of a molecule and the bellies of the neighbour can come together without steric hindrance, by use of equation (10) the pair potential scheme given in figure 2 results. The minimum of the potential, and with that the stable position of parallel oriented neighbouring molecules, is obtained through a shift by *a* along the longitudinal direction. Looking to all layer structures which enable a realization of this optimal pair position, only a few possibilities can be found. Rectangular structures with alternating shift (figures 3 (*a*), (*b*)) and with uniform tilt (figures 3 (*c*), (*d*)) are equivalent from the standpoint of the energy. In one direction in the layer plane there is a maximal shift, and in the corresponding perpendicular direction there is zero shift. In order to obtain efficient space filling, in the structure *a*, *b* the gaps at the surface of the layers must be filled by the molecules which jut out of the neighbouring layer. Therefore in these cases strong correlations between the layers are obtained; this means structures with three dimensional order (i.e. solid smectics, or crystalline solid phases). Only structure *c*, *d*, the model of the smectic C phase, fulfils the conditions of high packing fraction, maximal intercalation of the neighbours and minimal correlation between the layers.

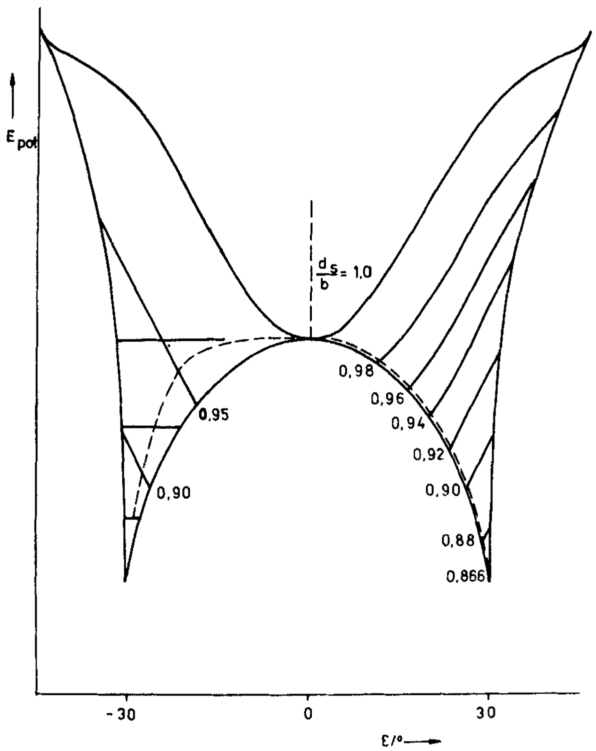
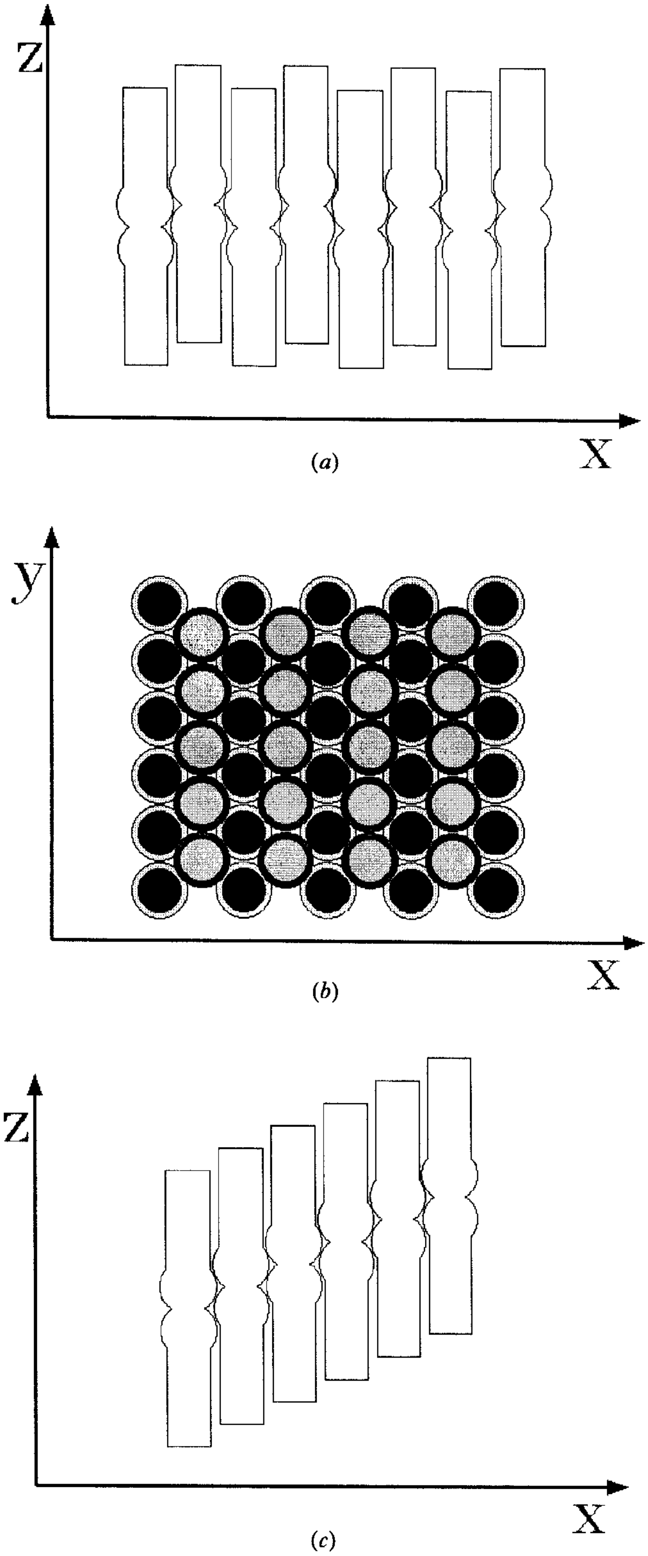


Figure 2. The pair potential between attaching molecules versus the tilt angle ε for different ratios between the radii of the end and middle groups. Arbitrary energy units are used.

4. Oscillation excitations and phase transitions

We only consider two of the dominating intramolecular and intermolecular degrees of freedom. The lateral vibration of the terminal alkyl chains in the volume available (libration), and the longitudinal oscillation of the whole molecule in the environment of its neighbours (for comparison see for example Druon and Wacrenier [18]). The first effect increases the lateral radius of the terminal groups *e* with increasing temperature. At low temperatures the alkyl chains tend to the all-trans conformation; in this case *e* and also the temperature independent radius of the core *b* can be calculated from space filling models (see § 5). The packing is favourable for the existence of the smectic C phase. With increasing temperature the lateral area of the terminal groups, and with that the distances between neighbouring molecules, increase. The longitudinal shift allowing optimal interaction between the middle groups decreases; that means the tilt angle also decreases. At the temperature of the S_C–S_A transition the radius of the terminal groups is equal to that of the core. Therefore, molecular intercalation is no longer possible and the orthogonal structure of the smectic A phase is obtained.

Also the longitudinal oscillation of the whole molecule in the field of all neighbouring interactions with increasing temperature leads to the S_C–S_A transition. The longitudinal oscillation of a single molecule cannot explain a phase transition during which the environment is changed. We can interpret the transition as being caused by changes in the pair potential since the number of nearest neighbours during the transition is nearly unchanged. The pair potential (see figure 2) is very unsymmetrical with respect to the minima: on tending to high values of the shift it is very steep,



(a)

(b)

(c)

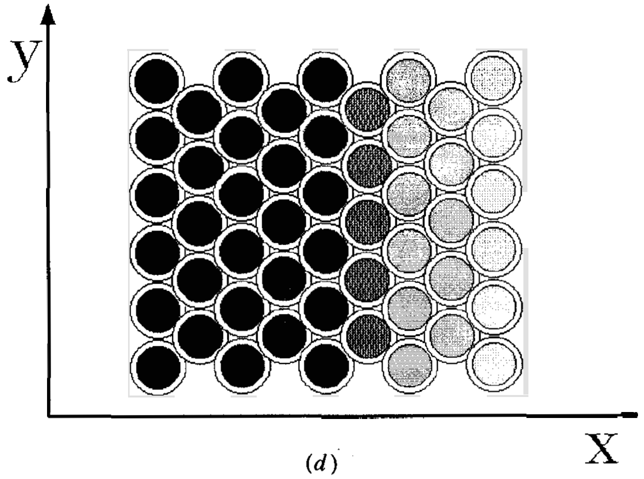
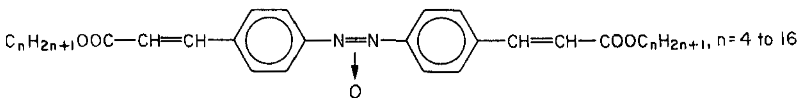


Figure 3. Possible structures with optimal packing density within the layers. (*a*, *b*) Alternating shift, (*c*, *d*) tilted structure.

while the maximum in the middle is relatively flat. By supplying energy to the system the medium value of the shift, and with that the tilt angle ε, are diminished (see figure 2 dotted lines). Both excitations of oscillations lead to the same effect: with increasing temperature the tilt angle is diminished and the S_C–S_A transition is promoted.

5. Application of the model

We now apply the model to a homologous series for which many thermodynamic and structural data are known namely the di-*n*-alkyl 4,4′-azoxycinnamates



The series contains benzene rings in the core and terminal alkyl chains which are characteristic groups for many mesomorphic compounds with the S_C–S_A polymorphism. Using the increment system of Subramhanyam *et al.* [19] as well as Prasad [20] we have calculated the parameters for the core:

Longitudinal length	20·3 Å
Longitudinal polarizability	$71{\cdot}8\times10^{-24}\,\mathrm{cm}^3$,
Polarizability anisotropy	$51{\cdot}5\times10^{-24}\,\mathrm{cm}^3$.

The analogous data for an alkyl chain of comparable length $-C_{13}H_{27}$ are

Length in all-trans conformation	20·2 Å,
Longitudinal polarizability	$30{\cdot}8\times10^{-24}\,\mathrm{cm}^3$,
Polarizability anisotropy	$10{\cdot}2\times10^{-24}\,\mathrm{cm}^3$.

From these data it is clear that the average of the interaction core–core and alkyl–alkyl is larger than the mixed interaction core–alkyl. Also the lateral area is in good agreement with the model:

Alkyl $e=2{\cdot}39\,\text{Å}$, $\pi e^2=18\,\text{Å}^2$,
Benzene $b=2{\cdot}65\,\text{Å}$, $\pi b^2=22\,\text{Å}^2$.

The difference of 18 per cent is so small that there is still no tendency for the formation of three dimensional (intercalated) structures. Indeed there are favourable conditions for a good interaction and good space filling in simple smectic layers. It is not so easy to decide the part of the molecule which is responsible for the sterically induced longitudinal shift and which, therefore, determines the tilt angle of the S_C phase at low temperatures. For $x=a/2$ we obtain by use of equations (3) and (6*a*)

$$\tan \varepsilon_0 = \frac{1}{2(b/a - c/a) + \sqrt{[4(c/a)^2 - 1]}},$$
$$c:a:b = 2:3:4.$$

The oxygen of the azoxy group as well as the oxygen of the ester group jut out slightly from the surface of the molecule. From the lateral area of these groups and the longitudinal distance of belly and indenture of the molecules a tilt angle of about 20–25° (experimental values 20–25° [22]) for the S_C phase at low temperatures can be estimated.

6. Comparison with experiment

Now we summarize the results of the model and give a comparison with experimental data.

With decreasing temperature the tilt angle tends to a limiting value ε_0 which depends on the geometrical parameters of the core and so is nearly constant within a homologous series (see figure 4).

With increasing temperature short molecules are excited to intermolecular longitudinal vibrations which, because of the asymmetry of the pair potential, leads to a decrease of the tilt angle. That means there is a continuous S_C–S_A transition extending over a large temperature interval with a half width of 30 K for the hexyl homologue (figure 5).

In compounds with long alkyl chains the increasing repulsion of the terminal chains is the additional second reason for the S_C–S_A transition. The transition becomes sharper and its temperature interval diminishes with increasing chain length (see figure 5). The influence of the distance from the clearing point on the sharpness of the S_C–S_A transition has also been discussed by Lien and Huang [23].

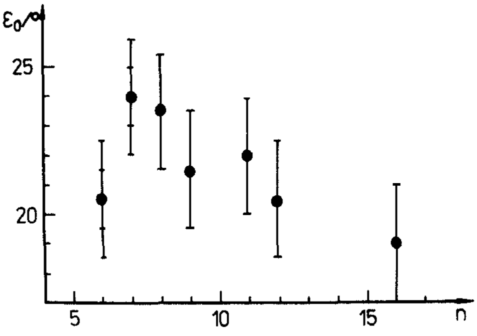


Figure 4. Extrapolated tilt angle ε_0 in the smectic C phase versus chain length. The data from [22] are used.

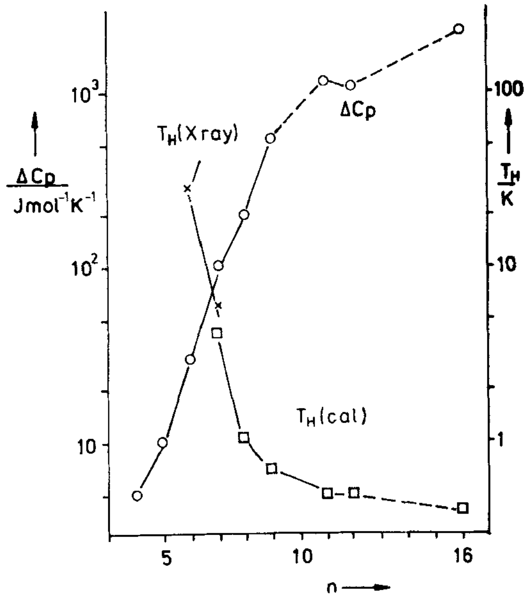


Figure 5. Peak heights ΔC_p and half widths T_H of the transitions smectic C–smectic A versus chain length *n*; di-*n*-alkyl 4,4′-azoxycinnamates [21].

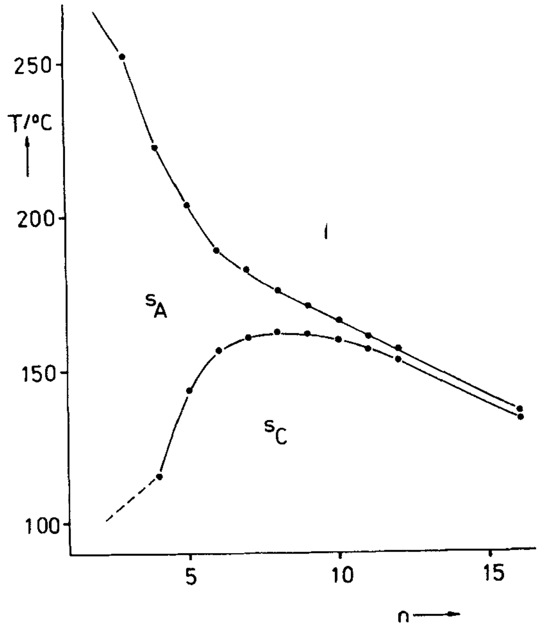


Figure 6. Transition temperatures S_S–S_A and S_A–I for the di-*n*-alkyl 4,4′-azoxycinnamates versus alkyl chain length *n* [21].

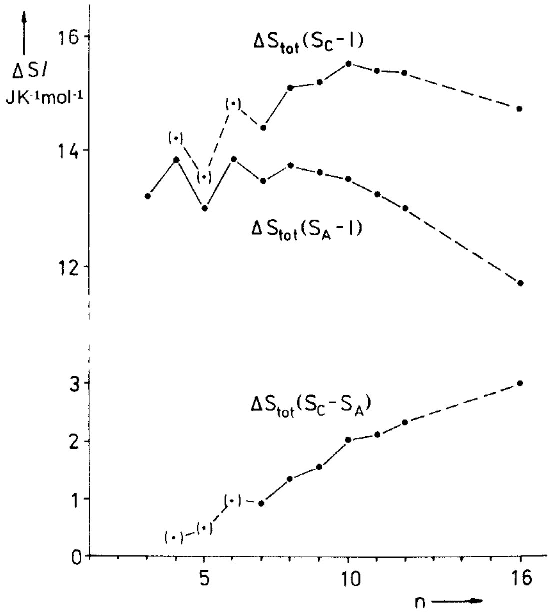


Figure 7. Total entropies of the transitions S_C–S_A, S_A–I and the sums S_C–I versus alkyl chain length *n*; di-*n*-alkyl 4,4′-azoxycinnamates [21].

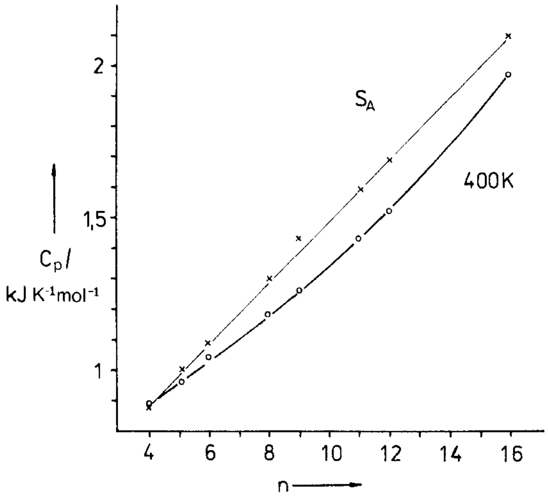


Figure 8. Molar heat capacities C_p of the di-*n*-alkyl 4,4′-azoxycinnamates at 400 K (○) as well as at the corresponding state above the transition S_C–S_A (×) versus alkyl chain length *n* [21].

The main reason for the stability of the smectic layers is the interaction (intercalation and the relatively strong attraction) of the cores of neighbouring molecules. The molten terminal chains do not affect the formation of the structure. The transition temperature, as a measure of the stability of the smectic phase, decreases with increasing chain length (see figure 6).

The terminal chains are more flexible than the core. Therefore, the heat capacity C_p increases on elongation of the chains more than the molecular mass. Increasing the molecule length by a factor of 2, at constant temperature C_p increases by a factor 2·2 (see figure 8). At a temperature just above the S_C–S_A transition the alkyl chains of all homologues are in a comparable molten situation, and C_p increases linearly along the series.

Short terminal chains are stiff and possess a smaller area than the core. In the tilted structure the possibilities for a dense packing are better, therefore the S_C phase is stabilized and the transition temperature increases with growing chain length (see figure 6 left side).

Long alkyl chains are flexible. They are therefore able to fill favourably the available volume; however, because of their molten state the repulsion is predominant and the S_C–S_A transition temperature decreases along the series (see figure 6, right side).

The conditions for the existence of the phases are

$e<d_{\min}$	the S_C phase is stabilized with increasing chain length;
$d_{\min}<e<b$	transition region, the S_C phase is destabilized with increasing chain length;
$e=b$	the S_A phase is stable;
$e>b$	the isotropic phase is stable.

In most series the phase sequence S_C–S_A–I occurs. With increasing molecular length the order parameter grows, and therefore the validity of the condition $e=b$ for the existence of S_A becomes stronger and the existence region of the S_A phase shrinks.

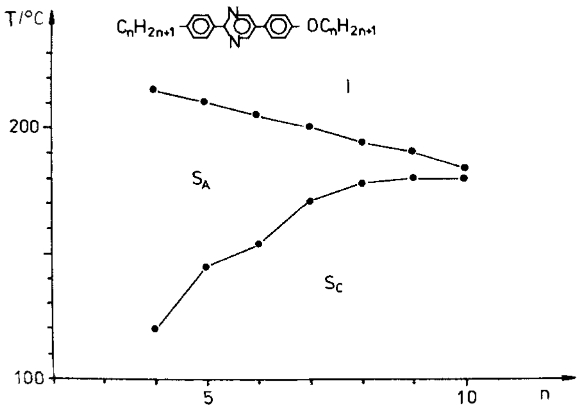
At the S_C–S_A transition the terminal chains absorb energy in such amount that their lateral radius grows up to the value of the core and the lateral distance of the molecules increases. Therefore the total transition entropy $\Delta S_C S_A$ as well as the jump in the molar heat capacity $\Delta C_p S_C S_A$ grows along the series (see figure 7 resp. 5).

The terminal alkyl chains at lower temperatures in the S_C phase as well as at high temperatures in the isotropic state lie at a characteristic equilibrium distance; only in the S_A phase is the structure in the region of the terminal chains looser. Therefore, the total entropy change $\Delta S_C I$ is a measure of the change of the interaction of the middle groups and is nearly independent of the chain length (see figure 7).

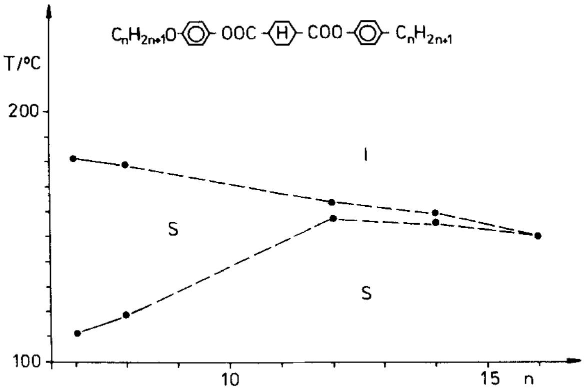
The tilt angle as well as the irregular part in C_p may be considered as order parameters for the S_C–S_A transition which is an order–disorder transition in which structural and thermodynamic effects are closely coupled [22].

7. Conclusions

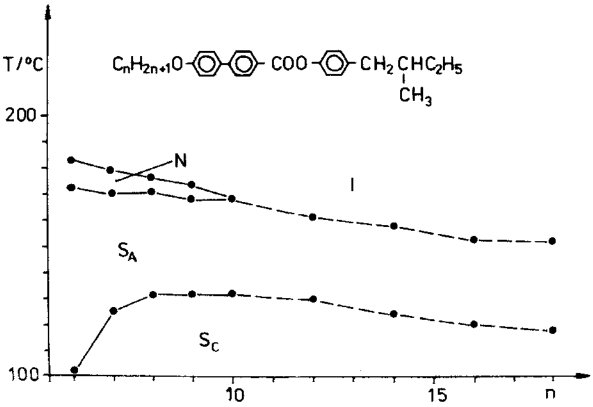
The model presented here contains only a few substance specific parameters, and therefore should be applicable to the S_C and S_A phases of similar molecules. Indeed all homologous series with the S_C–S_A–I polymorphism in temperature regions above 100°C show the same behaviour. In the series the clearing temperatures decrease, the S_C–S_A transition temperatures first increase and above a maximum decrease (see figure 9, and also [24, 25]). As far as structural and thermodynamic properties of these


T/°C
C_nH_{2n+1}
OC_nH_{2n+1}
N
N
I
S_A
S_C
200
100
5
10
n

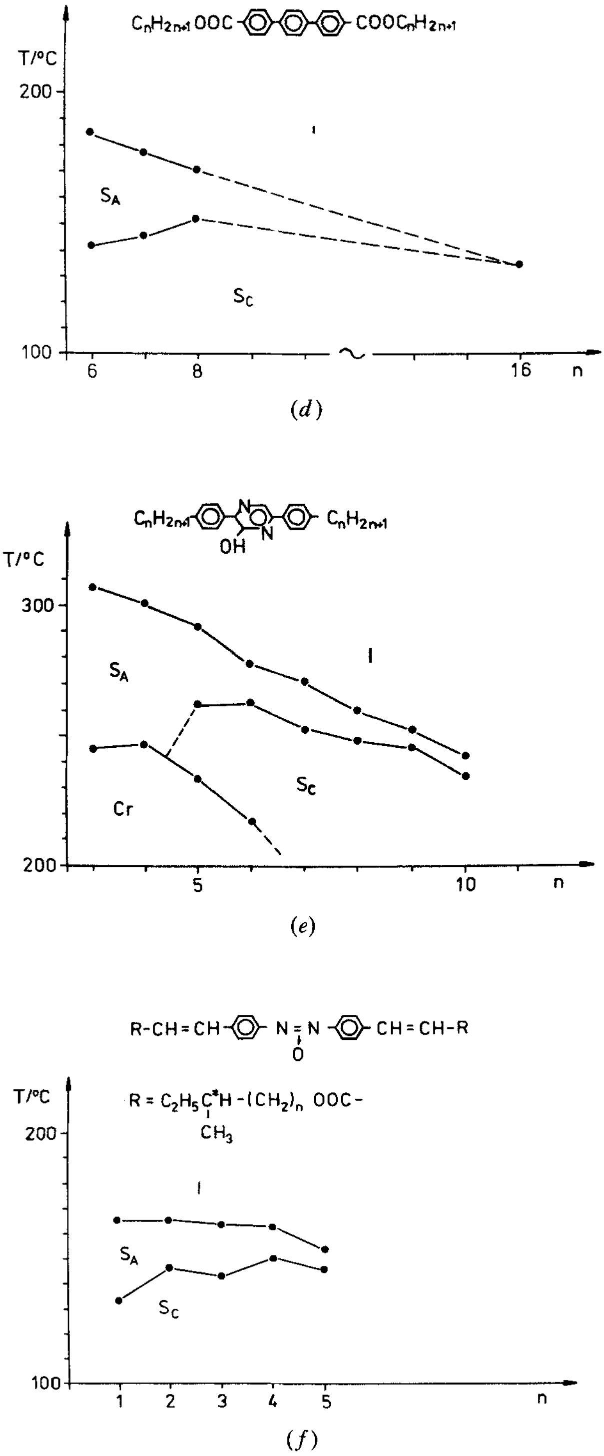
(*a*)


$C_nH_{2n+1}O$
OOC
H
COO
C_nH_{2n+1}
T/°C
200
100
I
S
S
10
15
n

(*b*)


T/°C
$C_nH_{2n+1}O$
COO
$CH_2CHC_2H_5$
CH_3
200
100
N
I
S_A
S_C
10
15
n

(*c*)



(*d*)

(*e*)

(*f*)

Figure 9. Transition temperatures [24, 25] along the homologous series with S_C–S_A transitions above 100°C.

series are known, they show agreement with the trends explained previously, for example the decrease of the breadth of the peaks in the C_p and ε curves in the series of substituted phenylpyrimidines [26, 27] and terephthalylidene-bis-(4-*n*-alkylanilines) [28]. Also, mixtures exhibit the expected behaviour. If the cores of the components are not suitable, the S_C phases at equimolar concentrations are destabilized and induced S_A phases appear [29]. Since achiral and chiral phases are very similar from the thermodynamic standpoint, the model should be applicable also to C* phases.

The model presented explains the properties of compounds in which the smectic potential is governed by the competition of the core–core attraction and the repulsion between the molten terminal chains, whereby the radius of the latter at low temperatures is somewhat smaller than that of the cores. In compounds with cores having smaller attraction (small polarizability) smectic phases can be formed only at low temperatures where the repulsion of the terminal alkyl groups is very small. The clearing temperatures in these cases increase with elongation of the alkyl chains. The favourable packings of the cores and those of the stiff terminal chains may compete with one another, and in favourable cases smectic phases with higher order (for example B, E, G, H,...) may occur. The bi-swallow-tailed compounds [30] are a special case in which our model has to be modified. The area of the terminal groups is larger than that of the cores. The S_C phases in these compounds are stabilized also by intercalation of bellies and indentures. With increasing temperature the vibrations of the terminal chains enhance the lateral distances between the neighbouring molecules without change of the tilt angle. Therefore the destruction of the smectic layers leads immediately to the nematic as well as the isotropic phase, and S_A phases are lacking. However, by inserting small molecules into the indentures of the bi-swallow-tailed molecules, smectic A phases may be induced (i.e. the so-called filled A phases [31, 32]).

The proposed model allows the design of smectic C and C* compounds. If compounds with S_C phases at low temperatures are desired the main problem is to avoid high ordered smectic phases which with respect to dense packing may be more favourable than the low order smectic structures considered here.

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