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## MOLECULAR STRUCTURE AND THE OCCURRENCE OF SMECTIC A AND SMECTIC C PHASES (\*)

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**Résumé.** — On étudie les propriétés mésomorphes de divers azobenzènes substitués en para par des chaînes *n*-alkyles ou *n*-alkoxy. Les dialkylazobenzènes non polaires présentent des phases nématiques et smectiques A. Quand on remplace une chaîne alkyl par une chaîne alkoxy (avec création d'un moment dipolaire terminal), il y a augmentation de la tendance à l'apparition d'une phase smectique C. Ces résultats peuvent être interprétés par un modèle dipolaire de la phase smectique C et ne confirment pas l'hypothèse que cette phase résulte principalement d'interactions spatiales entre des molécules en configuration zig-zag. Dans le cas d'un seul moment dipolaire terminal, l'une des deux possibilités de modèle à interaction dipolaire prévoit des couches smectiques ferroélectriques. Cette situation pourrait éventuellement fournir un modèle de la phase smectique F.

**Abstract.** — The mesomorphic properties of various terminally alkyl and/or alkoxy substituted azobenzenes are investigated. The non-polar dialkylazobenzenes have nematic and smectic A phases. For each alkyl group that is replaced by an alkoxy group (thus introducing an outboard dipole moment) the tendency to form a smectic C phase is increased. These results can be rationalized in terms of a dipole model of the smectic C phase, and do not support the idea that this phase occurs mainly because of steric interactions between zig-zag shaped molecules. In the case of only one outboard dipole moment there are two possibilities for a model with dipole interaction, one of which has ferroelectric smectic layers. This situation could possibly provide a model for the smectic F phase.

1. **Introduction** — The various liquid crystalline phases are characterized by long-range orientational ordering [1]. The elongated molecules are, on average, aligned with their long axes parallel to a preferred direction in space. In a nematic liquid crystal the molecules translate freely, and the centres of mass are distributed at random. Therefore the X-ray diffraction pattern contains no sharp reflections. Smectic liquid crystals, on the other hand, have a layered structure: the molecular centres are situated in a series of equidistant planes. In the X-ray diffraction pattern a sharp reflection is observed corresponding to the interplanar distance, which is of the order of the molecular length. In the smectic A and C phases the distribution of the centres of mass within the layers is random. The nematic (N) and the smectic A phase ( $S_A$ ) have the optical properties of a uniaxial crystal; the smectic C phase ( $S_C$ ) is found to be biaxial.

During the last few years much attention has been given to the nature of the intermolecular forces that

lead to the formation of an  $S_A$  phase [2-4] or an  $S_C$  phase [5-8]. A crucial question is whether the interaction between permanent dipole moments is important for the formation of the  $S_C$  phase. It is the purpose of this paper to provide a molecular basis for this discussion by investigating the type of smectic phases occurring in some series of compounds which have been selected because of specific structural differences. Section 2 begins with a review of the various theories for the  $S_C$  phase, with emphasis on the presumptions about the molecular properties of the constituent compounds. Section 3 discusses the smectic phases occurring in various terminally substituted azo- and azoxybenzenes. The *p,p'*-di-*n*-alkylazobenzenes [9] are a suitable starting point for such a comparison because they are non-polar. By substituting alkoxy for alkyl and/or azoxybenzene for azobenzene, dipole moments can be introduced at specific positions while only minor variations of the molecular shape occur. The results are discussed in section 4. It turns out that in these cases the occurrence of an  $S_C$  phase can be understood with the aid of a simple extension of McMillan's dipole model. Steric repulsions are probably not a dominant effect. The extension of the dipole theory of the

(\*) Part of this paper was presented at the « Conférence Européenne sur les Smectiques Thermotropes et leurs Applications », Les Arcs (France), 15-18 December 1975.

$S_C$  phase also provides a possible model for the smectic F phase. In the literature the smectic F phase is reported to occur below an  $S_C$  phase upon cooling of some compounds [10]. It seems to have all the properties of the  $S_C$  phase (liquid layers, biaxiality, etc.) and the ways in which it differs from the  $S_C$  phase have not yet been determined.

**2. Models for the smectic C phase.** — In all models for the smectic C phase it is assumed that the smectic A order is well established : there is orientational ordering of the long molecular axes and positional ordering of the molecules in layers. If  $\theta$  denotes the angle between the long molecular axis and the preferred direction, the molecular orientation can be described by a distribution function  $f(\theta)$ , where

$$f(\theta) d\Omega = f(\theta) 2 \pi \sin \theta d\theta$$

is the probability that the long molecular axis will form an angle between  $\theta$  and  $\theta + d\theta$  with the preferred direction. The average degree of orientational ordering can be described by an order parameter [1]

$$\eta = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle = \int f(\theta) \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) d\Omega . \quad (1)$$

The distribution function  $f(\theta)$  is related to  $V(\theta)$ , the orientation dependent part of the potential, by  $f(\theta) = (1/Z) \exp(-V/kT)$  where  $Z$  is a normalization constant. In Maier and Saupe's theory [11] of the nematic phase  $V(\theta)$  is calculated in a mean-field approximation assuming that it comes from the anisotropic part of the dispersion forces. This leads to a set of self-consistent equations for  $\eta$  and  $V(\theta)$  that can be solved to give  $\eta$  versus temperature, yielding a NI phase transition at  $T_{NI}$ .  $V(\theta)$  can be shown to be approximately proportional to the squared anisotropy of the molecular polarizability [12].

In practice the elongated molecules often possess a skeleton of  $\sigma$  electrons and additionally a central core of delocalized  $\pi$  electrons. Consequently the polarizability is to a large extent concentrated in the central part of the molecule, and therefore the molecules will prefer to have their central parts close together. This effect becomes more pronounced if the skeleton of  $\sigma$  electrons is extended. Thus in a homologous series the tendency to form smectic phases increases with increasing length of the molecules. This is generally accepted to be the origin of the occurrence of smectic phases, although some curious exceptions have been noted in the case of strongly asymmetrically substituted molecules [13]. McMillan has made these ideas more quantitative in a model that ignores the polarizability of the end groups, and takes a Gaussian distribution for the interaction between the central parts of the molecules [3]. The model predicts a  $NS_A$  phase transition that may be second-order, depending on the

ratio between the length of the central aromatic core and the total length of the molecule. These predictions are at least qualitatively in agreement with experimental results.

For the  $S_C$  phase the literature contains various models on which there is as yet no general agreement. McMillan [5] assumes that a primary role is played by interactions between *transverse* permanent dipole moments. Unlike the situation in the N and the  $S_A$  phase, the rotation around the long molecular axis cannot then be completely free for the functional groups with which the dipoles are connected. Let us assume that the  $S_A$  order is well established, and that the molecules can be represented by cylinders with two outboard dipole moments  $\mu$  at a distance  $d/2$  from the centre [5] (see Fig. 1a). Now we consider the interaction between the dipole moments of the molecules in a smectic plane. The preferred direction is taken along the  $z$ -axis, while the angle between the  $x$ -axis and one of the dipoles is denoted by  $\varphi$ . Then the single particle potential can be written as

$$V_1(\varphi) = - 2 \mu E \cos \varphi , \quad (2)$$

where  $E$  is the field at the position of a dipole due to the dipoles of the other molecules. This field depends on  $g(r)$ , the two-particle correlation function, which is simply assumed to be

$$g(r) = \begin{cases} 0 & \text{for } r < D , \\ n_2 & \text{for } r \geq D , \end{cases} \quad (3)$$

$$\pi D^2 n_2 = 1 ,$$

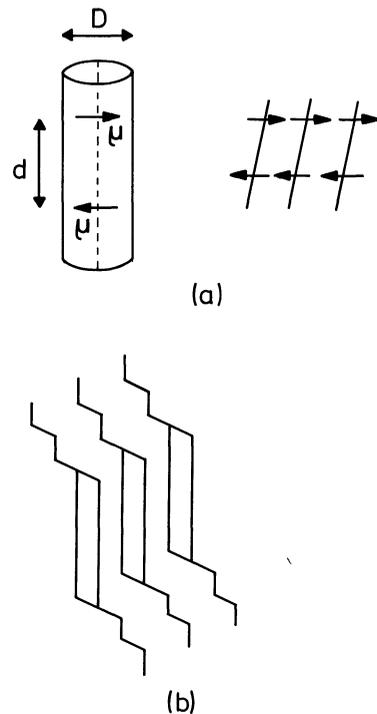


FIG. 1. — Schematic representation of the dipole model (a) and of the steric model (b) of the  $S_C$  phase.

where  $n_2$  is the particle density in the smectic plane. Neglecting the interactions between dipoles at different levels, we can then calculate  $E$  and find that it is a function of  $\bar{\mu} \equiv \mu\beta$ , the average value of the upper or lower dipole moment. In turn  $\mu\beta$  is calculated self-consistently using the potential of equation (2). As a result a second-order phase transition  $S_A S_C$  is predicted at [5]

$$T_{CA} = \frac{\mu^2(\pi n_2)^{3/2}}{k\varepsilon_\infty} \quad (4)$$

where  $k$  is Boltzmann's constant and  $\varepsilon_\infty$  the high-frequency dielectric permittivity. In this model the  $S_C$  phase is predicted to be biaxial provided the constituent molecules are biaxial [5]. If the outboard dipoles are not exactly perpendicular to the long molecular axis, but have a component  $\delta$  along this axis, there is a torque  $3kT_{CA}\delta\beta$  to tilt the molecule over in the  $x$  direction. There will be a restoring torque  $-K\psi$ , where  $\psi$  is the tilt angle and  $K$  is an elastic constant. Equating the two torques and using the explicit result for  $\beta$  [5] a tilt angle is found given by

$$\psi = \frac{3kT_{CA}\delta}{K} [2(1 - T/T_{CA})]^{1/2}. \quad (5)$$

Although the physical properties of McMillan's model agree well with those of the  $S_C$  phase, there is considerable disagreement on the question of whether there is in reality no free rotation of the molecules around their long axis [14, 15]. It should be emphasized, however, that the model still permits rotation of parts of the molecule not connected with the dipole moments. Hence techniques that probe the movement of, for example, the phenyl rings are of limited value in testing the model. In fact the model requires that the various parts of the molecule differ in their freedom of rotation. The molecules will often possess a third central dipole moment which is still assumed to be randomly distributed. If this is not the case additional phase transitions are predicted, leading to other phases that are two-dimensional ferroelectrics within the smectic layers.

Wulf [6] has given a model of the  $S_C$  phase in which the repulsive, or steric, forces play a dominant role. The characteristic order is assumed to be mainly a result of the effect of the molecular shape on the packing problem for the liquid. In the case of the  $S_C$  phase the relevant factor is the zig-zag gross shape of the molecules, thought to be a result of end chains that are symmetrically attached to the molecules, and are not collinear with the central body of the molecules (see Fig. 1*b*). The model calculation starts by writing down an effective interaction between the molecules that simulates, at least qualitatively, the effect of the molecular zig-zag shape. This interaction is then used in a mean field calculation, assuming that the  $S_A$  order is well established. Let  $\mathbf{u}^1 \cdot \mathbf{u}^2$  and  $\mathbf{u}^3$  be unit vectors in a

molecule-fixed coordinate system,  $u^3$  being along the long molecular axis. The zig-zag interaction between a pair of molecules 1 and 2 is taken to be [6]

$$V_{12} = -A_1(r_{12}) [\mathbf{u}^3(1) \cdot \mathbf{u}^3(2)] [\mathbf{u}^2(1) \cdot \mathbf{u}^2(2)] \\ - A_2(r_{12})/r_2^2 [\mathbf{u}^3(1) \cdot \mathbf{r}_{12} \mathbf{u}^2(1) \cdot \mathbf{r}_{12} \\ + \mathbf{u}^3(2) \cdot \mathbf{r}_{12} \mathbf{u}^2(2) \cdot \mathbf{r}_{12}]. \quad (6)$$

The first term accounts for the fact that the molecules interfere less with one another if their long and short axes align together. Consequently, the resulting  $S_C$  phase will be biaxial if the constituent molecules are biaxial. In this model there is no completely free rotation of the molecules around their  $\mathbf{u}^3$  axis in the  $S_C$  phase. The second term in equation (6) represents the additional tendency of the molecules to tilt over with respect to the intermolecular vector  $\mathbf{r}_{12}$ ;  $r_2$  is the range of  $A_2(r_{12})$ . We must require that  $0 < A_2(r) \ll A_1(r)$  in order to ensure that the molecules do not tilt when the long and short axes are not yet aligned. We shall not discuss the details of the model. A second-order phase transition  $S_A S_C$  is predicted with a tilt angle  $\psi$  growing continuously from zero at the transition, and always remaining smaller than  $\pi/4$  [6]. In order to distinguish between McMillan's dipole model and Wulf's steric model it will be necessary to investigate in detail the type of molecules that give an  $S_C$  phase. Both models are incompatible with completely free rotation around the long molecular axis.

Finally Priest [7] has given a model of the  $S_A S_C$  phase transition assuming that there is an effective molecular second-rank tensor which is responsible for the orientational phenomena in the smectic phase. Denoting an element of this tensor by  $q_{ij}$ , the average of  $q_{ij}$  over molecules in the vicinity of a point  $\mathbf{r}$  can be introduced :

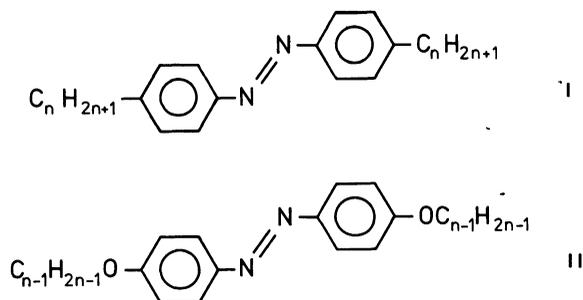
$$Q_{ij}(\mathbf{r}) = \langle q_{ij} \rangle. \quad (7)$$

One can expand the orientational interaction energy between two molecules in a series bilinear in  $\mathbf{Q}$ . With appropriate values for the expansion coefficients a second-order phase transition  $S_A S_C$  can be obtained. The tilt angle varies as  $(T_{CA} - T)^{1/2}$  as in the other models, while a small biaxiality is induced [7]. Contrary to the previous models, the biaxiality is due to the symmetry of the  $S_C$  phase rather than the  $S_C$  tilt being the result of a tendency to form a biaxial phase. Note that in equation (7)  $Q_{ij}$  may be uniaxial even if  $q_{ij}$  is biaxial. However, if  $q_{ij}$  is also uniaxial, free rotation around the long molecular axis is not forbidden in the  $S_C$  phase. Priest did not give suggestions for the specific tensor  $q_{ij}$  to be considered. However, this point was recently taken up by Cabib and Benguigui [8], who treated the molecules as axially symmetric objects in both the  $S_A$  and the  $S_C$  phase, and considered the interaction between the components of the dipole moments *parallel* to the long molecular axis. Hence their model is complementary to McMillan's dipole model. In fact they suppose that each molecule

has two opposite dipoles along the long axis. The  $S_C$  phase is induced because the molecules tend to slide along each other due to the electrostatic interaction, thus increasing the distance between the molecular centres.

A well-known case of an  $S_A S_C$  phase transition is found in terephthal-*bis*-butylaniline [16] (TBBA), where the tilt angle indeed grows with decreasing temperature from zero at  $T_{CA}$ , as predicted by all the models given above. There are hardly any other compounds for which this point has been investigated. In some other cases the  $S_C$  phase is observed directly below a N phase. Usually a large tilt angle is then observed (say  $45^\circ$ ), independent of temperature [17]. Formally a  $NS_C$  phase transition may be described by combining models for the  $NS_A$  and the  $S_A S_C$  phase transitions in a situation where  $T_{AN} < T_{CA}$ . It is clear that the tilt angle cannot then be zero at the  $NS_C$  phase transition, and may be approximately independent of temperature if the curve of  $\psi$  versus  $T/T_{CA}$  saturates with decreasing temperature. The maximum value of the tilt angle in Wulf's and in Priest's model ( $45^\circ$  and  $49.1^\circ$ , respectively) is of the right order of magnitude. In McMillan's model the maximum tilt angle depends on the details of the molecules.

### 3. Smectic phases of alkyl- and alkoxy-substituted azobenzenes. — First we shall discuss the nature of the mesophases found in the compounds of the series



The transition temperatures were determined with a Leitz Orthoplan polarizing microscope equipped with a Mettler FP52 heating stage. Heats of transition were recorded by means of differential scanning calorimetry with a Perkin-Elmer DSC 1B. The results for series I and some of the higher members of series II are given in tables I and II and displayed in figure 2. The compounds of series I have also been discussed in reference [9], but without explicit reference to the smectic phases. The transition temperatures given

TABLE I

*Phase transitions of series I (K stands for crystalline; monotropic transitions are placed between parentheses)*

$n$		$t$ ( $^\circ\text{C}$ )	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )
3	KN	81.1-81.5	22.3	63
	(NI)	30.0-30.7	— <sup>(a)</sup>	—
4	KN	28.3-29.1	33	110
	(NI)	$\sim -5$	— <sup>(a)</sup>	—
5	KN	48.5-49.1	34	105
	(NI)	41.8-42.2	0.86	2.74
6	KN	36.7-37.2	25.5	82
	(NI)	23.9-24.3	0.55	1.85
7	KN	39.6-40.0	24.4	78
	NI	47.0-47.3	1.10	3.4
	( $S_A$ N)	21.0-21.4	— <sup>(a)</sup>	—
8	KN	47.5-47.9	39	121
	(NI)	41.5-41.8	1.16	3.7
	( $S_A$ N)	35.2-36.4	1.35	4.4
9	$KS_B$	36.8-37.0	35	111
	$S_B S_A$	40.3-40.5	1.30	4.1
	$S_A$ I	51.5-53.2	5.0	15.5
10	$KS_B$	41.5-42.3	49	156
	$S_B S_A$	44.3-44.6	1.9	6.1
	$S_A$ I	52.3-53.7	6.6	20.2

<sup>(a)</sup> Due to crystallization no quantitative measurement was possible.

TABLE II

*Phase transitions of series II*

$n$		$t$ ( $^\circ\text{C}$ )		$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )
		this work	Ref. [18]		
7	KN	101.5-102.2	102	39	104
	NI	114.1-114.7	114	1.51	3.9
8	KN	101.0-101.3	102 <sup>(a)</sup>	42	113
	NI	108.8-109.1	109	1.51	3.9
9	KN	98.8- 99.2	98	40	109
	NI	112.0-112.3	112	2.17	5.6
	( $S_C$ N)	95.2- 95.6	—	1.83	5.0
10	KN	104.1-104.5	103	55	145
	NI	108.6-108.8	107	2.67	7.0
	( $S_C$ N)	101.5-101.7	99	2.32	6.2

<sup>(a)</sup> Gabler, ref. [18], gives for this compound a monotropic SN transition at  $97^\circ\text{C}$ . We could not reproduce this result, although the N phase could be supercooled down to  $94^\circ\text{C}$ . In some cases we observed a metastable crystalline phase in the region  $95^\circ$ - $100^\circ$ , which could probably be mistaken for a smectic phase. This idea is in agreement with the fact that Gabler did not observe a smectic phase for  $n=9$ .

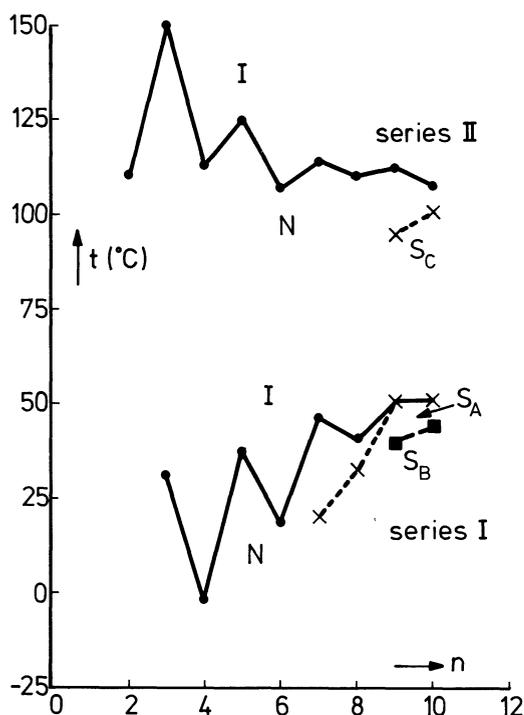


FIG. 2. — Transition temperatures versus chain length for series I and II (for series II,  $n \leq 6$ , from reference [18]).

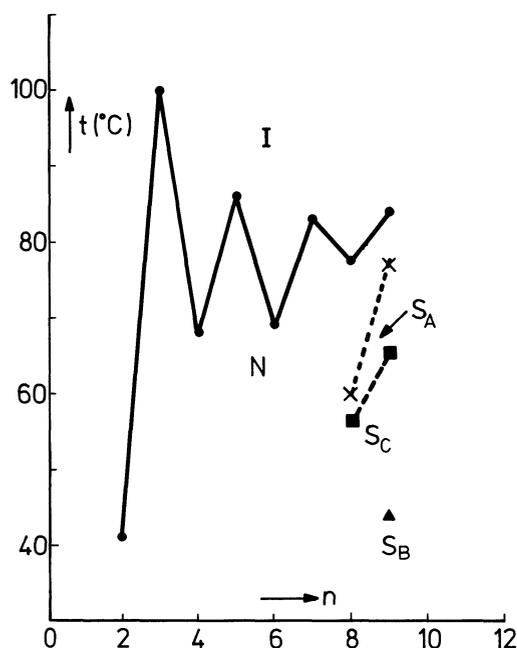


FIG. 3. — Transition temperatures versus chain length for series III (for  $n \leq 5$  from reference [24]).

here should be considered as more accurate. For the higher members of series I,  $S_A$  phases occur in addition to the N phases. This is easily established from the simple focal-conic or homeotropic textures and the occurrence of one sharp X-ray reflection at small Bragg angle in a powdered sample [19]. For  $n = 9$  and  $n = 10$  an additional  $S_B$  phase is found. The textures of this phase are either blurred focal-conic or homeotropic, the latter again indicating uniaxiality. In the powder X-ray diffraction pattern two sharp reflections are observed (one at small, the other at large Bragg angle). This classification of the  $S_B$  phase of (I,  $n = 9$ ) has been confirmed from its complete miscibility with the known  $S_B$  phase of N-(*p*-*n*-pentylbenzylidene)-*p'*-*n*-hexylaniline [20].

For the higher members of series II,  $S_C$  phases are observed below the N phases. Under the polarizing microscope either broken focal-conic textures or schlieren textures are observed. The absence of interference colours in the schlieren textures indicates a relatively large tilt angle directly below the  $NS_C$  transition. The classification of the  $S_C$  phase of (II,  $n = 10$ ) has been confirmed from its complete miscibility with the known  $S_C$  phase of *p,p'*-di-*n*-heptyloxyazoxybenzene [21].

It is interesting to compare these results with those for the correspondingly substituted azoxybenzenes. The mesophases of the *p,p'*-di-*n*-alkylazoxybenzenes are described in reference [22]. The smectic phases of the higher homologues of this series are all  $S_A$  (simple focal-conic or homeotropic textures, complete misci-

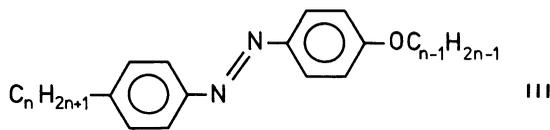
bility with the  $S_A$  phase of series I). The mesophases of the *p,p'*-di-*n*-alkoxyazoxybenzenes are described in references [18] and [23]. The smectic phases of the higher members of this series are well known to be of the  $S_C$  type [21]. Hence we conclude that replacement of the azo linkage by an azoxy linkage, thus introducing a central dipole moment, does not have any influence on the type of smectic phases that occur in these systems.

TABLE III

Phase transitions of series III

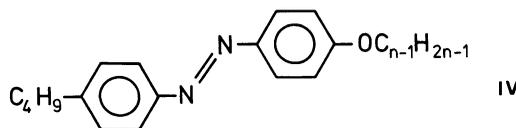
$n$		$t$ (°C)	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (JK <sup>-1</sup> mol <sup>-1</sup> )
6	KN	39.4-39.9	10.5	34
	NI	68.8-69.2	0.67	1.94
7	KK	~ 37	8.1	26
	KN	49.9-50.1	20.6	64
	NI	82.8-83.1	1.32	3.7
8	$KS_C$	53.0-53.2	43	133
	$S_C S_A$	56.1-56.6	0.05	0.15
	$S_A N$	59.9-60.2	0.37	1.10
	NI	77.2-77.5	1.31	3.7
9	$KS_C$	46.5-46.7	3.6	111
	$S_C S_A$	65.5-65.8	< 0.05	< 0.1
	$S_A N$	77.2-77.4	0.91	2.6
	NI	84.0-84.2	2.16	6.0
	( $S_B S_C$ )	~ 44	0.17	0.6

Next we consider the mesophases occurring in the series



Although a strong dipole is found in this series only at one end, the molecular shape is still approximately symmetric. The results for some of the higher members of this series are given in table III and figure 3. For  $n = 8$  and  $n = 9$ , on cooling from the N phase, an  $S_A$  phase is first observed, then an  $S_C$  phase. The enthalpy of the  $S_A S_C$  transition is very small. The transition is best observed on cooling a homeotropic  $S_A$  texture. At the  $S_A S_C$  transition a schlieren texture appears with interference colours indicating a tilt angle that grows continuously from zero. This is confirmed by conoscopic measurements where the maltese cross observed in a homeotropic  $S_A$  sample moves off-centre when the  $S_A S_C$  transition is passed. For  $n = 9$  one observes on cooling a transition to a third smectic phase that was classified as  $S_B$ .

In order to investigate whether the asymmetric shape of the molecules affects certain mesophases, we finally consider the series



The various phases of some of the higher members of the series are indicated in table IV and figure 4. The results are very similar to those found for series III.

TABLE IV

Phase transitions of series IV

$n$		$t$ (°C)	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (JK <sup>-1</sup> mol <sup>-1</sup> )
8	KN	53.4-53.7	25.5	78
	NI	69.9-70.2	0.73	2.1
	( $S_C$ N)	39.7-40.3	1.37	4.4
9	$KS_A$	55.0-55.2	34	102
	$S_A$ N	57.5-57.6	1.15	3.5
	NI	74.9-75.2	1.14	3.3
	( $S_C S_A$ )	54.0-54.2	0.04	0.1
	( $S_B S_C$ )	~ 35	0.2	0.6
10	$KS_A$	62.0-62.1	35	104
	$S_A$ N	63.6-63.8	1.65	4.9
	NI	73.0-73.2	1.06	3.1
	( $S_C S_A$ )	58.6-58.9	< 0.04	< 0.1
11	$KS_C$	53.9-54.4	24.3	74
	$S_C S_A$	60.0-61.5	0.03	0.1
	$S_A$ N	69.0-69.4	2.27	6.6
	NI	75.5-75.8	1.46	4.2
	( $S_B S_C$ )	49.8-50.3	1.3	4.1

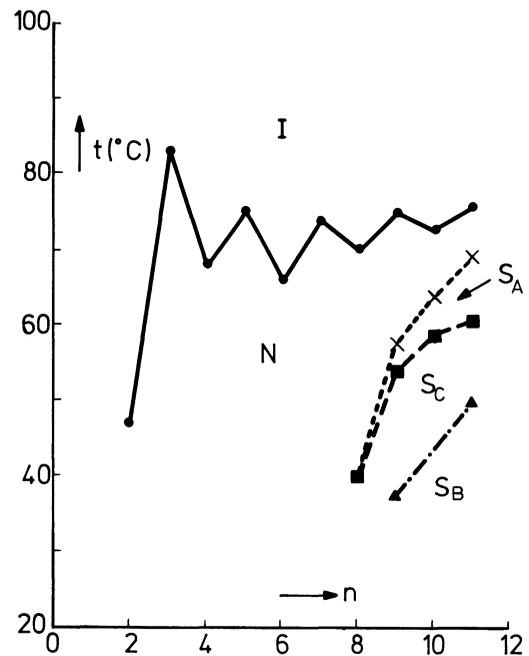


FIG. 4. — Transition temperatures versus chain length for series IV (for  $n \leq 7$  from reference [24]).

Note, however, that for (IV,  $n = 8$ ) there is no  $S_A$  phase; the  $S_C$  phase goes directly over into the N phase. For  $n = 9$  an intermediate  $S_A$  phase appears. The temperature range in which the  $S_A$  phase is stable increases with increasing chain length. All the mesophases of series IV have textures similar to those of the corresponding mesophases of series III, with which they are also completely miscible. From the shift of the conoscopic cross observed in homeotropic samples the tilt angle has been calculated for (IV,  $n = 11$ ) in the vicinity of  $T_{CA}$ ; the results are given in figure 5. The numerical aperture of the conoscope was only 0.33 as determined by the condenser, corresponding to an angular field of view of about 40° in air. The absolute value of the tilt angle depends on the value of the maximum index of refrac-

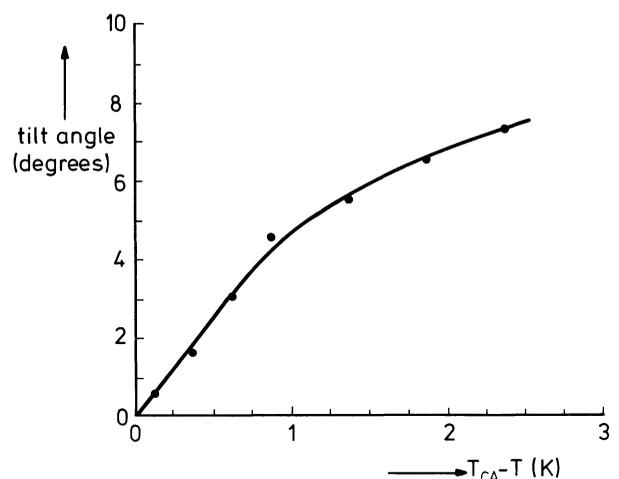


FIG. 5. — Tilt angle versus relative temperature in the  $S_C$  phase of compound (IV,  $n = 11$ ).

tion, which was assumed to be 1.7. The variation of tilt with temperature around  $T_{CA}$ , as given in figure 5, is very similar to that found in the well-known case of TBBA.

In general the transition  $S_C S_B$  is only visible if the  $S_C$  phase is in a schlieren texture. With decreasing temperature a new schlieren texture then appears at the transition, which is brighter and has fewer singularities. In order to study this third smectic phase in more detail we made a mixture of 50 per cent (by weight) of (III,  $n = 9$ ) and (IV,  $n = 11$ ). The transitions of this mixture are approximately  $K30S_B49S_C61S_A73N80$ , and the  $S_B$  phase supercools easily down to room temperature. The  $S_B$  phase in this mixture also occurs as a blurred focal-conic texture that gradually tends to change into a mosaic texture. The powder X-ray diffraction pattern contains two sharp reflections without any additional structure. Hence we conclude that the classification of this phase as an  $S_B$  phase is correct. The occurrence of schlieren textures and the absence of homeotropic textures indicates that this  $S_B$  phase is probably biaxial.

**4. Discussion.** — We shall first discuss the results for series I and II. The replacement of a  $CH_2$  group by an oxygen atom has the effect of introducing a dipole moment of about 1.3 D, at an angle of about  $72^\circ$  with the  $p,p'$  axis of the adjacent aromatic ring [25], giving a dipole component of about 0.4 D along the  $p,p'$  axis. In the case of an alkyl group there is a dipole moment of 0.4 D along this  $p,p'$  axis. Hence the dipole components along the long molecular axis are very similar for the compounds of series I and II. As  $S_A$  phases occur in one series and  $S_C$  phases in the other, the model of Cabib and Benguigui cannot be expected to apply to these systems. Furthermore the molecules of series I and II have a very similar molecular shape. An oxygen atom is somewhat smaller than a  $CH_2$  group [26], which may make the molecules of series II about  $0.5 \text{ \AA}$  shorter than the corresponding ones of series I. Moreover the  $C_{ar} CC$  angle of  $108^\circ$  (tetrahedral value) is replaced by a  $C_{ar} OC$  angle of  $120^\circ$  which may lead to a slightly more pronounced zig-zag shape for series I. This difference between the series is reinforced by the fact that the mesophases of series I occur at lower temperatures, thus decreasing the flexibility of the end chains in series I as compared with series II. This flexibility can be expected to counteract the zig-zag form. Hence if these differences are important at all, it leads to a more pronounced zig-zag form for the molecules of series I than for series II. As the  $S_A$  phases occur in series I and the  $S_C$  phases in series II it is unlikely that this difference is due to a change in the repulsions between the zig-zag shaped molecules. On the other hand when going from series I to series II two outboard dipole moments are introduced. Hence the results are at least qualitatively consistent with McMillan's dipole model of the  $S_C$  phase. The fact

that an additional *central* dipole moment has no influence on the type of smectic phases (substitution azo-azoxy) requires that the central aromatic cores of the molecules still rotate relatively freely in these systems. It is only for the dipoles on the oxygen atoms that this rotation is not allowed. The tendency to form an  $S_C$  phase is strong for series II; there is no  $S_A$  phase intermediate between the N and the  $S_C$  phase. As soon as the layered structure is established the phase takes the form of an  $S_C$  phase with a relatively large tilt angle.

An interesting test on the dipole model of the  $S_C$  phase is provided by the results for series III, where a weak tendency to form an  $S_C$  phase is found ( $S_A$  phase intermediate between N and  $S_C$  phase, tilt angle growing with decreasing temperature from zero at the  $S_A S_C$  transition). In this series a strong dipole is available only at one side of the molecules, while the shape of the molecules of series I or II is retained. Assuming that there is no preference for the asymmetric molecules to be with the polar side up or down, McMillan's model can still be applied (see Fig. 6a). However, as the average distances between the dipoles has been increased,  $T_{CA}$  is reduced by a factor  $2\sqrt{2}$ . This decrease of  $T_{CA}$  is less pronounced if the induced dipole moments due to the transverse polarizabilities are taken into account. If, for simplicity, the transverse polarizability of the molecule is assumed to be represented by two point polarizabilities  $\alpha$  at positions  $\pm d/2$ , equation (4) must be replaced by

$$T_{CA} = \frac{\mu^2}{k[\epsilon_\infty/(\pi n_2')^{3/2} - \alpha]} \quad (8)$$

where  $n_2' = n_2/2$ . Using  $\epsilon_\infty \approx 2.5$  (Ref. [27]) and  $n_2 \approx 4 \times 10^{14}$  (Ref. [5]) we find

$$\epsilon_\infty/(\pi n_2')^{3/2} \approx 5 \times 10^{-23} \text{ cm}^3,$$

while  $\alpha$  can be expected to be of the order of  $1 \times 10^{-23} \text{ cm}^3$  [27]. Hence the effect of the inclusion of  $\alpha$  is an increase of  $T_{CA}$  by about 50%.

In the case of one end dipole only, we must also consider the alternative situation of a phase that is a

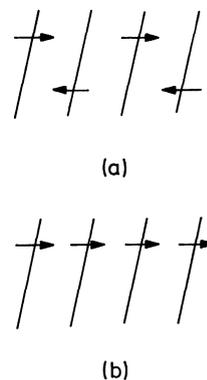


FIG. 6. — The two possibilities for dipole interaction in the case of one outboard dipole moment only; in situation (b) the smectic layers are two-dimensional ferroelectrics.

two-dimensional ferroelectric within the smectic layers (see Fig. 6b). In the context of the present simple models it is not useful to compare the relative stability of the  $S_C$  phases depicted in figure 6a and figure 6b, which in general will depend on the ratio between the asymmetric dipole potential and the symmetric part of the total intermolecular potential. We suggest that figure 6b provides a possible model for the  $S_F$  phase. Like the  $S_F$  phase the model has the physical properties of the  $S_C$  phase. In addition it will be ferroelectric or anti-ferroelectric, depending on the sign of the interplanar interaction. The compounds studied here do not possess such an additional phase. These ideas would have to be tested on compounds showing an  $S_C$  and an  $S_F$  phase [10], which are unfortunately not easily available.

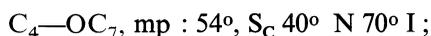
Finally we come to the effect which the symmetry of the shape of the molecules has on the formation of smectic phases. When comparing series IV with series III we first consider some *isometric* compounds that have the same number of  $CH_2$  groups but a different shape.

Compare for example :

— series III :



— series IV :



or alternatively

— series III :



— series IV :



We see that in compounds of the same length the tendency to form a smectic phase is greater in the case of a less symmetric shape. This conclusion was also arrived at by Malthète *et al.*, who studied several isometric series in detail [28]. An explanation for this effect has not yet been given. From tables III and IV we

see that there is no difference between the type of smectic phases that occur in series III and IV. In particular the suggestion that  $S_C$  phases are preferentially found in symmetrically substituted compounds [28, 29] is not confirmed, although the results for series IV with increasing  $n$  indicate that if the deviation from symmetry increases, the tendency to form a smectic phase of some other type increases more strongly than the tendency to form an  $S_C$  phase.

**5. Conclusion.** — We have shown that alkyl and/or alkoxy substituted azobenzenes may show, besides the N phase,  $S_A$  or  $S_C$  phases or both, depending on the end substituents. The results, summarized in table V, suggest that the repulsions between the zig-zag shaped molecules do not play a dominant role in the formation of the  $S_C$  phase. The results are at least qualitatively in agreement with McMillan's dipole model of the  $S_C$  phase, provided the asymmetric molecules of series III and IV have no preference for being up or down. Otherwise the model gives a ferroelectric or anti-ferroelectric phase that could possibly be identified with the  $S_F$  phase.

TABLE V

Summary of the results

Series	Substituents	Number of outboard dipoles	Smectic phases	Tilt angle
I	di-alkyl	none	$S_A$ only	none
II	di-alkoxy	two	$S_C$ only	large
III, IV	alkyl-alkoxy	one	$S_A$ and $S_C$	$\psi = \psi(T)$ , $\psi = 0$ at $T_{CA}$

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