

# Smectic behavior and molecular structure: On the mesomorphism of a series of hydrocarbons

W. H. de Jeu

Solid State Physics Laboratory, Melkweg 1, 9718 EP Groningen, The Netherlands

R. Eidenschink

E. Merck, P.O. Box 4119, 6100 Darmstadt 1, West Germany

(Received 6 October 1982; accepted 16 December 1982)

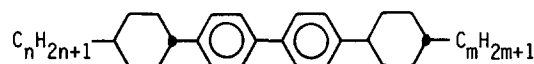
The polymorphism is discussed of a series of hydrocarbons that show, besides a smectic-A phase, a strong tendency towards the formation of smectic-B. The powder x-ray diffraction patterns show at large Bragg angles an unusual double reflection with a very small separation, which indicates a 3D hexagonal closed packing. It is shown that, quite generally, nonpolar molecules form orthogonal smectic phases. The implications are discussed for the relationship between molecular structure and smectic behavior.

## I. INTRODUCTION

Liquid crystals are characterized by long-range orientational order of the long molecular axis of the elongated molecules.<sup>1</sup> Thus a preferred direction is defined in space, which can be labeled by a unit vector  $n$ , the director. The nematic phase is truly a liquid: the centers of the molecules translate freely. The common feature of the various types of smectic phase is a periodic density modulation (density wave) along a certain direction (say the  $z$  axis), leading to what is called in a loose way a layer structure.<sup>2</sup> If the director is also along the  $z$  axis we speak of orthogonal phases, otherwise of tilted phases. The tilt angle is defined as the angle between  $n$  and the  $z$  axis. Depending on the arrangement within the layers various types of smectic phase can be distinguished.<sup>3</sup> This is summarized in Table I. The two lowest rows refer in fact to crystalline phases with 3D positional order. The distinction between crystalline  $B$  and hexatic  $B$  is relatively recent.<sup>4</sup> The latter type of phase has only limited 2D positional order in addition to 3D bond orientational order. The main difference between  $S_F$  and  $S_I$  is in the direction of the tilt: towards an edge of the hexagon in  $S_F$  and towards an apex in  $S_I$ .<sup>5</sup>

The key question for the synthesis of liquid crystalline materials is the relation between molecular structure and the type of mesophase.<sup>6</sup> As far as the smectic phases are concerned, it is only for the  $S_A$  and the  $S_C$  phase that models have been proposed that are able to account for at least part of the experimental material. According to these models the density wave is due to the existence of distinct polarizable parts within the molecules,<sup>7</sup> and the tilt is related to additional interactions in which permanent dipoles take part.<sup>8</sup> Of course, this does not exclude any influence of permanent dipoles on the occurrence of orthogonal smectics, but these seem to be more a complicating factor in that case than an essential requirement. If the above-mentioned model results can be generalized, one would expect only orthogonal phases for nonpolar molecules. This is the question to which the present paper is addressed.

In the following two sections the mesomorphic behavior of  $p$ -substituted cyclohexyl-biphenyl-cyclohexanes (CBC) [alternatively named as bis(4-*trans*-4-alkylcyclohexyl)-bisphenyls], will be explored,



and indicated as  $CBC_{nm}$ . This series is interesting because in these nonpolar compounds, up to three smectic phases can occur, apart from a nematic phase. In the final section, these results will be compared with those for other nonpolar compounds, and the relation with the structures indicated in Table I will be considered.

## II. EXPERIMENTAL METHODS

The compounds were synthesized at the laboratories of E. Merck (Darmstadt, FRG). The transition temperatures were determined using optical microscopy with a Leitz-orthoplan-pol equipped with a Mettler FP52 heating stage. The transition heats were obtained by differential scanning calorimetry using a Perkin-Elmer DSC-1B at heating rates of the order of  $2\text{ Kmin}^{-1}$ . Calibration was performed using the known heats of transition of tin, indium, and *trans*-azobenzene.

X-ray photographs were made from nonoriented samples in Lindeman glass tubes ( $\phi = 0.3\text{ mm}$ ) with a Guinier-Simon camera (Enraf-Nonius) using  $\text{CoK}_{\alpha 1}$

TABLE I. Summary of the structural characteristics of the various smectic phases.

Structure of layers	Orthogonal	Tilted <sup>a</sup>	
		$a > b$	$a < b$
Liquid	A	C	
Bond orientational order	hexatic B	F	I
(Pseudo)-hexagonal packing	B	G	G'
Herringbone packing	E	H	H'

<sup>a</sup> $b$  is the unique axis of the monoclinic cell.

radiation ( $\lambda = 1.78892 \text{ \AA}$ ). The temperature was varied at rates of the order of  $1\text{--}5 \text{ K h}^{-1}$ .

### III. RESULTS

Table II gives the results for the transition temperatures and enthalpies. The classification of the first smectic phase as  $S_A$  is immediately evident from the occurrence of both homeotropic and focalconic textures. The second smectic phase takes the form of homeotropic or mosaiclike textures, which makes a classification as  $S_B$  or  $S_E$  probable,<sup>9</sup> provided that no new orthogonal phase is involved. The third smectic phase of CBC53 is biaxial, which is evident from the disruption of the homeotropic texture of the second smectic phase upon further cooling.

A more detailed microscopic study was made of CBC50. Because no  $S_A$  phase exists in this compound, the textures of the other orthogonal phase are much more meaningful, paramorphism being absent. The clear and well-defined mosaics strongly suggest  $S_B$ . This is confirmed by the complete miscibility with the known  $S_B$  phase of *p*-pentyl-*p'*-hexyloxybiphenyl.<sup>10</sup> A miscibility study with a known  $S_E$  phase leads to the injection of  $S_A$  behavior.

The results from x-ray diagrams of the second smectic phase are given in Table III. Several orders (at low temperatures, up to 5) of the layer spacing can usually be observed. A comparison with the length of the stretched molecule  $l$ , as measured from space-filling molecular models, confirms the orthogonality. At higher Bragg angles there is one intense Bragg reflection, classified as 110/200 (orthorhombic indexing).<sup>3</sup> However, under conditions of very high resolution, a weaker second Bragg peak is observed very close to the first one in some cases. In  $d$  spacings, the difference is only of the order of a few hundredths of an angstrom. By changing the setting of the Guinier

TABLE II. Phase transitions in the series CBC $n$ m indicated as transition temperature/ $^{\circ}\text{C}$  and transition enthalpy/ $\text{kJ mol}^{-1}$  between parenthesis.

Compound	Transition to	Transition to			
		$S_B$	$S_A$	$N$	$I$
CBC50	...	68	...	184	192
		(12)		(10)	(0.7)
CBC51	...	112	206	210	283
		(9.2)	(5.5)	(~0)	(0.8)
CBC53	54 <sup>a</sup>	58	232	251	311
	(5.1)	(1.4)	(6.1)	(0.5)	(1.1)
CBC55	45 <sup>b,c</sup>	55	247	275	305
	(17)	(10)	(4.1)	(2.9)	(1.3)
CBC33	127 <sup>b,d</sup>	155	210	220	325
	(0.1)	(12)	(5.2)	(~0)	(1.2)

<sup>a</sup> $S_H$  phase; another crystalline form melts directly into the  $S_B$  phase at  $61 \text{ }^{\circ}\text{C}$  ( $8.1 \text{ kJ mol}^{-1}$ ).

<sup>b</sup>Solid–solid transition.

<sup>c</sup>There are at least two other crystalline forms that all show transitions around  $43\text{--}45 \text{ }^{\circ}\text{C}$ .

<sup>d</sup>There are additional solid–solid transitions at  $13 \text{ }^{\circ}\text{C}$  ( $3 \text{ kJ mol}^{-1}$ ) and  $108 \text{ }^{\circ}\text{C}$  ( $1.0 \text{ kJ mol}^{-1}$ ).

TABLE III. X-ray reflections of the CBC series around  $175 \text{ }^{\circ}\text{C}$ .

Compound	$l/\text{\AA}$	$d_{hkl}/\text{\AA}$			
		002	004	200/110	201/111
CBC50	25	25.0	12.5	4.80	4.77
CBC51	26	26.4	13.2	4.79	4.76
CBC53	28	28.0	14.0	4.80	...
CBC55	31	30.0	15.1	4.80	...
CBC33	26	26.5	13.2	4.78	4.76

camera, and by comparing with peaks at similar Bragg angles in the crystalline phase, we made sure that the second peak is not due to an admixture of the  $K_{\alpha 2}$  line. Furthermore, the second peak was usually more intense when the temperature was decreased, which makes any type of experimental error very unlikely. The additional peak can be indexed as  $11\frac{1}{2}$  or  $20\frac{1}{2}$ , which means that the  $c$  vector of the unit cell, and thus all  $l$  values of indices  $hkl$ , have to be doubled.

Finally, in Table IV, we show that the third, tilted phase of CBC53 can be classified on the basis of a monoclinic lattice. In fact, two least-square fits to the observed reflections were made. In fit (I), all parameters were left free, leading to a value of  $c \approx 26 \text{ \AA}$ , somewhat smaller than the  $d$  spacing in the  $S_B$  phase. If  $c$  is kept fixed at the  $d$  spacing of the  $S_B$  phase, a somewhat less perfect fit (II) is obtained. A monoclinic lattice leaves (again assuming that no new phase is involved) the possibility of an  $S_C$  or  $S_H$  phase. The  $S_C$  phase is C-face-centered, which leads to specific extinction conditions: reflections with  $h+k=2n+1$  ( $n$  is integer) should be absent. From the occurrence of the 010 reflection we conclude that an  $S_H$  phase (monoclinic  $P$ ) is most plausible.

### IV. DISCUSSION

The nematogeneity of hydrocarbons, including the present CBC series has been discussed in some detail elsewhere.<sup>11</sup> Here we note only the relatively low value of  $T_{NI}$  of CBC50 as compared with the others. This is most probably related to the fact that a monosubstituted

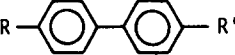
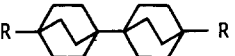
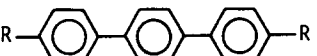
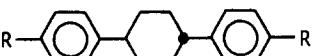
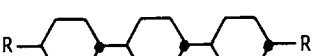


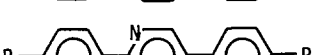
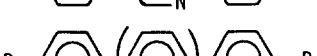
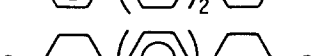
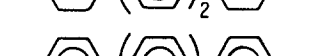

TABLE IV. Observed and calculated Bragg reflections for the third smectic phase of CBC53.

$hkl$	$d_{hkl}/\text{\AA}$		
	Observed	Calculated <sup>a</sup>	Calculated <sup>b</sup>
001	21.0	21.00	21.65
002	10.5	10.50	10.82
010	5.58	5.579	5.582
201	5.18	5.180	5.205
110	4.77	4.770	4.768
200	4.60	4.600	4.586

<sup>a</sup> $a = 11.4 \text{ \AA}$ ,  $b = 5.58 \text{ \AA}$ ,  $c = 26.1 \text{ \AA}$ ,  $\beta = 126.3^{\circ}$ .

<sup>b</sup> $a = 11.9 \text{ \AA}$ ,  $b = 5.58 \text{ \AA}$ ,  $c = 28.0 \text{ \AA}$  (fixed),  $\beta = 129.4^{\circ}$ .

TABLE V. Types of smectic phases observed with nonpolar molecules (R, R' is alkyl); a question mark indicates that the assignment is preliminary.

No.	Type of compound	Phases	Ref.
1.		$S_B, S_E$	13
2.		$S_B$	14
3.		$S_A, S_B, S_F(?), S_G(?)$	15
4.		$S_B$	16
5.		$S_B(?)$	16
6.		$S_B$	17
7.		$S_B, S_E$	16
8.		$S_A, S_C$	18
9.		$S_A$	19
10.		$S_A, S_B, S_H$	
11.		$S_A$	20
12.		$S_A, S_B$	21

cyclohexane ring is present in CBC50. In that case there will be, at the relatively elevated temperatures around  $T_{NI}$ , an appreciable amount of the conformer having the biphenyl substituted in the axial position.<sup>12</sup> This leads to a molecular shape that is effectively less elongated, and thus to a lower  $T_{NI}$ . Similar effects could play a role in explaining the difference in  $T_{NI}$  of the isometric compounds CBC33 and CBC51. In addition, in CBC51 there is an increased possibility of *gauche-trans* kinks of the pentyl chain.

The tendency to form an  $S_A$  phase decreases with both decreasing alkyl chain length and increasing asymmetry of the molecules until, for CBC50, no  $S_A$  phase is observed at all. This is very similar to the results for many homologous series, provided the compounds have an approximately symmetric central part.

The tendency of the CBC series to form  $S_B$  phases is very pronounced. This seems to be true for nonpolar compounds generally, as shown in Table V, where results have been compiled from various literature sources. Many of the substances synthesized in Halle

(DDR) have been summarized in Ref. 22. There is a remarkable tendency for nonpolar compounds to form wide  $S_B$  and/or  $S_E$  ranges, often at the expense of the  $S_A$  phase. With only very few exceptions, orthogonal phases are always found. This supports our idea that, quite generally, permanent dipoles are needed to obtain a tilted phase. For the  $S_A-S_C$  transition, this idea has been promoted on both experimental grounds<sup>21</sup> and theoretically.<sup>8</sup> Because of the rotational freedom of the molecules,<sup>23</sup> interactions between permanent and induced dipoles must be involved,<sup>8(b)</sup> as the interactions between permanent dipoles average out. In order to produce a tilt, the dipoles should be located outside the molecular center ("outboard") and be directed off axis. More generally, the presence of dipole moments seems to promote smectics with liquid layers at the expense of the more highly ordered  $S_B$  and  $S_E$  phases observed in nonpolar compounds. The two exceptions in Table V refer to the  $S_H$  phase of CBC53, which is a very highly ordered crystalline phase, and, more interestingly, to compound no. 8. In this latter case, the occurrence of the tilted  $S_C$  phase could be related to the presence of two permanent dipoles, in spite of the fact that they compensate internally giving an overall zero dipole moment. The results of Table V contradict somewhat the conjecture of Goodby,<sup>24</sup> that  $S_B$  behavior is favored by an unsymmetrical molecular structure.

A peculiar effect of the x-ray diagrams in the  $S_B$  phase of the CBC series is the presence of a second reflection at large Bragg angles. From the indexing given, we interpret this as being due to interlayer correlation, leading, in fact, to a bilayer structure. The absence of  $00l$  reflections with  $l=2n+1$  ( $n$  integer) indicates an ABAB... type of packing with equivalent half-layers. Thus, the centers of molecules in next-nearest neighbor layers are on top of each other. Such interlayer correlations have been observed in aligned  $S_B$  phases by Leadbetter *et al.*<sup>25</sup> The observation in powder patterns is rare, though briefly mentioned in one case by Doucet and Levelut.<sup>26</sup> Since the work on the CBC series was completed, we have observed it in several other  $S_B$  phases of compounds with a cyclohexane ring. A relatively strong interlayer coupling could result from a less dense packing of the alkyl chains of compounds having a relatively bulky saturated ring as compared with substances with only benzene rings. As discussed by Doucet,<sup>27</sup> the combination of a benzene ring and an alkyl chain is an almost perfect match from the point of view of packing. Additional support for this explanation can be derived from the x-ray results of Reiffenrath and Schneider<sup>14</sup> on some substituted *bibicyclo*(2, 2, 2)octanes. In their case, the two or three rings at large Bragg angles can be interpreted as resulting from an  $S_B$  phase with layer correlation of the type AAA...

The above results clearly show that, in the CBC series, we are dealing with crystalline  $S_B$  phases, to be distinguished from hexatic  $S_B$ . As far as information is available, most of the higher ordered phases mentioned in Table V seem to be crystalline. Conse-

quently, the possible role of the polarity of the molecules in connection with the hexatic  $S_B$  phase is not yet clear.

The scheme of Table I provides a rather complete summary of the information available on the various smectic phases. In addition to the difference in tilt direction between  $S_F$  and  $S_I$ , it has been found, in one case, that  $S_F$  possesses only limited positional order and  $S_I$  true 2D long-range positional order.<sup>28</sup> Also the (im)miscibility of the corresponding  $G$  and  $G'$ , respectively  $H$  and  $H'$ , phases has not yet been established.<sup>29</sup> There is no doubt that all phases in the lower two lines of Table I ( $B, G, E, H$ ) are crystalline. Nevertheless, the molecules still possess considerable freedom, as is evident, for example, from the relaxation of the dielectric permittivity. In that respect one could call them *lamellar plastic crystals*.

#### ACKNOWLEDGMENTS

The authors wish to thank F. van der Horst and W. J. Soppe (University of Groningen) for technical assistance.

- <sup>1</sup>See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
- <sup>2</sup>See, for example, A. J. Leadbetter, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979), Chap. 13.
- <sup>3</sup>J. Doucet, Ref. 2, Chap. 14.
- <sup>4</sup>(a) R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, *Phys. Rev. Lett.* **46**, 1135 (1981); (b) J. W. Goodby, *Mol. Cryst. Liq. Cryst.* **72**, 95 (1981).
- <sup>5</sup>J. J. Benattar, F. Moussa, M. Lambert, and C. Germain, *J. Phys. Lett.* **42**, L-67 (1981).
- <sup>6</sup>G. W. Gray, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979), Chap. 12.
- <sup>7</sup>W. L. McMillan, *Phys. Rev. A* **4**, 1238 (1971).
- <sup>8</sup>(a) W. L. McMillan, *Phys. Rev. A* **8**, 1921 (1973); (b) B. W. van der Meer and G. Vertogen, *J. Phys. Colloq.* **40**, C3-222 (1979).
- <sup>9</sup>D. Demus and L. Richter, *Textures of Liquid Crystals* (VEB, Leipzig, 1978).
- <sup>10</sup>D. Demus (private communication).
- <sup>11</sup>R. Eidenschink, M. Römer, and F. V. Allen, *Proc. Symp. Am. Chem. Soc. (Las Vegas, 1982)*.
- <sup>12</sup>M. Hanack, *Conformation Theory* (Academic, New York, 1965), p. 31.
- <sup>13</sup>R. Skubatz, *Diplomarbeit*, Halle, 1978.
- <sup>14</sup>V. Reiffenrath and F. Schneider, *Z. Naturforsch. Teil A* **36**, 1006 (1981).
- <sup>15</sup>J. Schnuppe, *Diplomarbeit*, Halle, 1980.
- <sup>16</sup>A. Ludwig, *Diplomarbeit*, Halle, 1976.
- <sup>17</sup>H. Müller and W. Haase, 12. Arbeitstagung Flüssigkristalle, Freiburg (1982).
- <sup>18</sup>D. Demus, K. H. Kölz, and H. Sackmann, *Z. Phys. Chem. (Leipzig)* **249**, 217 (1972).
- <sup>19</sup>D. Demus, H. Demus, and H. Zäschke, *Flüssige Kristalle in Tabellen* (VEB, Leipzig, 1974).
- <sup>20</sup>I. C. Lewis and C. A. Kovac, *Mol. Cryst. Liq. Cryst.* **51**, 173 (1979).
- <sup>21</sup>W. H. de Jeu, *J. Phys.* **38**, 1265 (1977).
- <sup>22</sup>(a) H. Zäschke, *Wiss. Z. Univ. Halle* **29**, 35 (1980); (b) H. -J. Deutscher, H. -M. Vorbrod, and H. Zäschke, *Z. Chem.* **21**, 9 (1981).
- <sup>23</sup>A. J. Dianoux and F. Volino, *J. Phys.* **40**, 181 (1979).
- <sup>24</sup>J. W. Goodby, *Mol. Cryst. Liq. Cryst.* **75**, 179 (1981).
- <sup>25</sup>A. J. Leadbetter, J. C. Frost, and M. A. Mazid, *J. Phys. Lett.* **40**, L-325 (1979).
- <sup>26</sup>J. Doucet and A. -M. Levelut, *J. Phys.* **38**, 1163 (1977).
- <sup>27</sup>J. Doucet, *J. Phys. Lett.* **40**, L-185 (1979).
- <sup>28</sup>P. A. Gane, A. J. Leadbetter, J. J. Benattar, F. Moussa, and M. Lambert, *Phys. Rev. A* **24**, 2694 (1981).
- <sup>29</sup>P. A. C. Gane, A. J. Leadbetter, and P. G. Wrighton, *Mol. Cryst. Liq. Cryst.* **66**, 247 (1981).