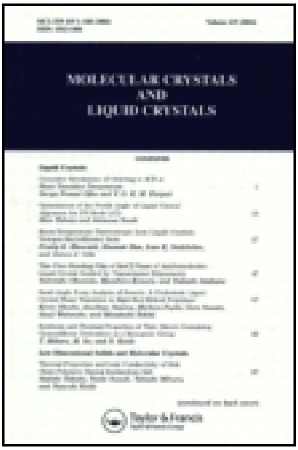

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Smectic Polymorphism and Molecular Shape-the Orthogonal Phases

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To cite this article: J. W. Goodby (1981): Smectic Polymorphism and Molecular Shape-the Orthogonal Phases, Molecular Crystals and Liquid Crystals, 75:1, 179-199

To link to this article: http://dx.doi.org/10.1080/00268948108073613

*Mol. Cryst. Liq. Cryst.*, 1981, Vol. 75, pp. 179–199
0026-8941/81/7504-0179 $06.50/0

Printed in the United States of America

# Smectic Polymorphism and Molecular Shape—the Orthogonal Phases

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*(Received February 23, 1981; in final form April 6, 1981)*

A method has been developed that can be used to describe the volume of space occupied by a given molecule with a known conformational structure as it rotates about a defined axis. The packing requirements of these volumes of revolution have been utilized in the prediction of phase formation, particularly of the B and E phases. Conclusions indicate that the subtle balance between steric and dipolar properties of a mesogen determine the phase types ultimately exhibited by the material.

## INTRODUCTION

The degree of smectic polymorphism exhibited by various smectogens is becoming increasingly complex as knowledge concerning the mesophase modifications continues to expand. Moreover, the discovery of new phase types,[1,2] coupled with detailed investigations of the structures of known phases,[3,4] have led to a void in our present comprehension of the true nature and origins of smectic polymorphism. Early investigations of the structures of various smectic modifications tended to assume that the constituent molecules had either a lath-like or a cylindrical shape.[5] This gave rise to a variety of interpretations of phase formation,[6,7] in terms of rod-like particles packing together coupled with dipolar interactions.

For example, in McMillan's[8] theory of the smectic C phase, the constituent molecules are assumed to have a relatively symmetrical structure, and are depicted as being of a cylindrical shape. The molecules are also expected to have strong dipole moments associated with certain functional groups (e.g. —COO—, —CH=N—, etc.) or atoms (e.g. O, N, etc.). These dipolar groups are situated, for the purposes of the theory, towards the ends of the rod-like molecule, and hence called "outboard terminal dipole moments." Provided that molecular rotation is "frozen out," it is then predicted that the alignment of these dipoles produces the necessary torque within the system to activate the drive for tilting of the molecules within their layers in order to form a smectic C phase, see Figure 1.

Later investigations, particularly by Wulf,[9] have contradicted the ideas of the molecular particles being merely cylinders, and have suggested instead that they are of a "zig-zag" type of steric shape. Thus concluding that it is the steric packing requirements of these "zig-zag" molecular shapes that can help to produce the necessary tilting within the layers to form a smectic C phase, as shown in Figure 2.

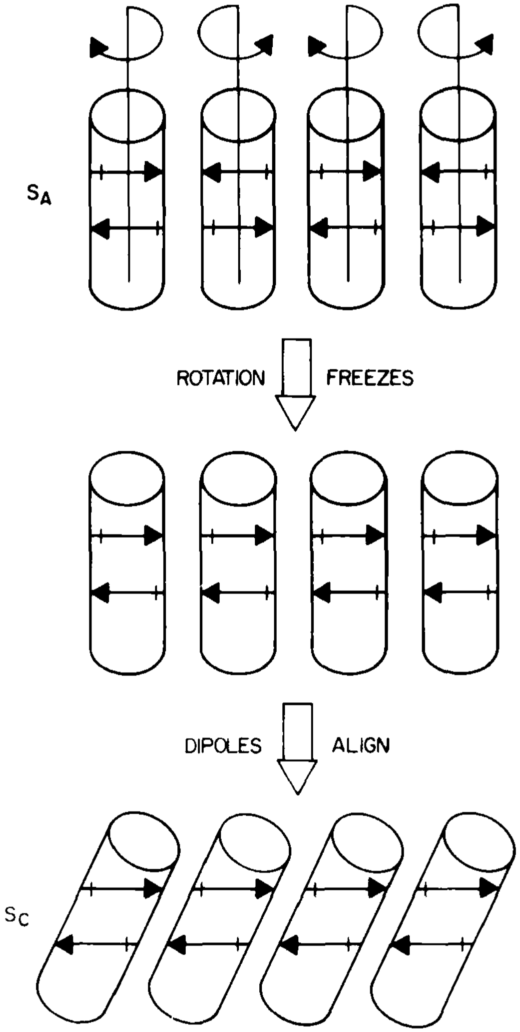


FIGURE 1 McMillan's Dipolar Model of the Smectic C Phase.

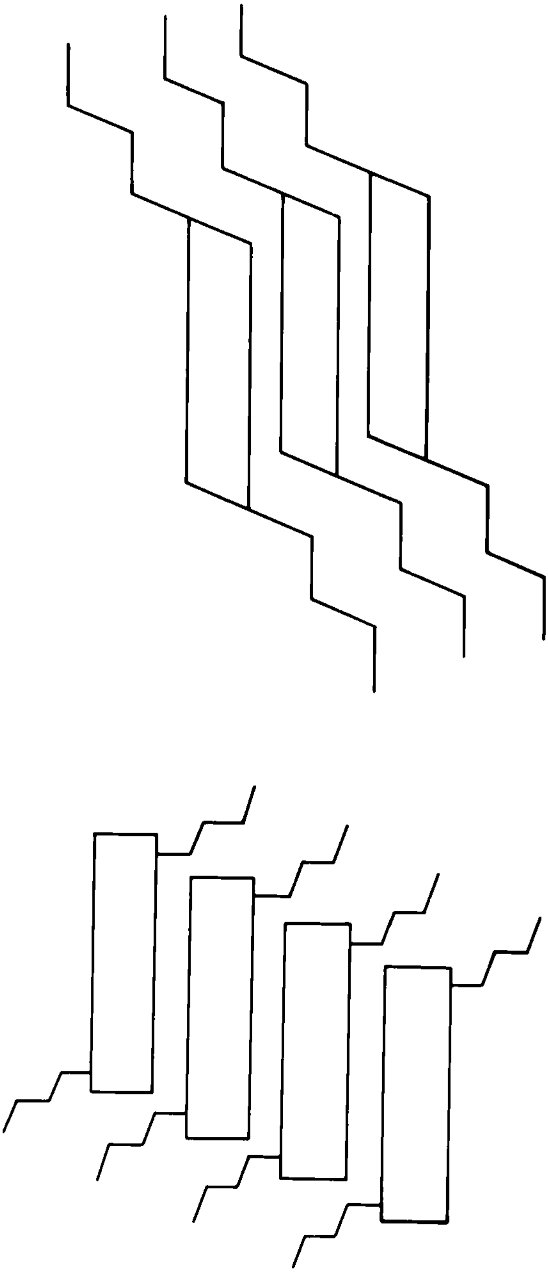


FIGURE 2 Wulf's Steric Model of the Smectic C Phase.

However, major problems can arise with these theories that involve either, dipolar couplings between adjacent molecules, and/or steric packing requirements of flat lamellar molecular shapes, and these can be listed as follows:

### (1) Molecular rotation

In order to utilize dipolar interactions or packing requirements of flat lamellar structures for the purpose of predicting phase formation, it is necessary to presume that the molecules have a restricted rotational freedom about their molecular long axes. These restrictions extend, in the extreme,[8] to the total freezing out of all rotational motion, and at the least to a time dependent alignment of those properties which are cited as the cause of certain types of phase formation,[10] e.g., dipolar interactions.

However, it has been known for a number of years that even in the most ordered, orthogonal smectic modification, the E mesophase that the molecules are oscillating very rapidly through large angles about their molecular long axes (periodicity $10^{11}$ $s^{-1}$).[11] Furthermore, even in the B phase the molecules are rotating about their molecular long axes, albeit in a coordinated way, very quickly.[12] This type of motion is expected to continue into the smectic A and nematic phases as well, with the rotation becoming free, and uncoordinated.

The assumption that in a $S_A$—$S_C$—$S_B$ mesophase sequence that the molecules rotate in both the A and B phases quite rapidly, but that this motion is restricted or even frozen out in the C phase is difficult to comprehend. Therefore, for these theories[8,9] to remain applicable to the C phase, in this type of situation the molecules must *all* rotate in the *same* direction and in a coordinated fashion with either their dipoles or their molecular shapes well-aligned, see Figure 3, in order to retain their interactions.

However, in states that are as disorganized, as the $S_A$, $S_C$ or even the $S_B$ phases are, it is difficult to imagine that this motion will occur in a harmonius way over an extended distance. A tentative solution to this problem could be that conglomerations of molecules will form small domains, where this type of motion and interaction can occur on a time dependent basis.

### (2) Effects of molecular structure

Numerous studies have shown that small changes in molecular structure of a given mesomorphic system can radically alter the smectic polymorphism observed.[5,13-16] Yet, it is also known that some basic molecular frameworks prefer to exhibit certain phase types, for example, cyano-smectogens usually exhibit orthogonal phases but only rarely tilted phases. Experimental evidence shows that the influence of molecular structure on the incidence and temperature range of liquid crystal phases is an important, complex, and sub-

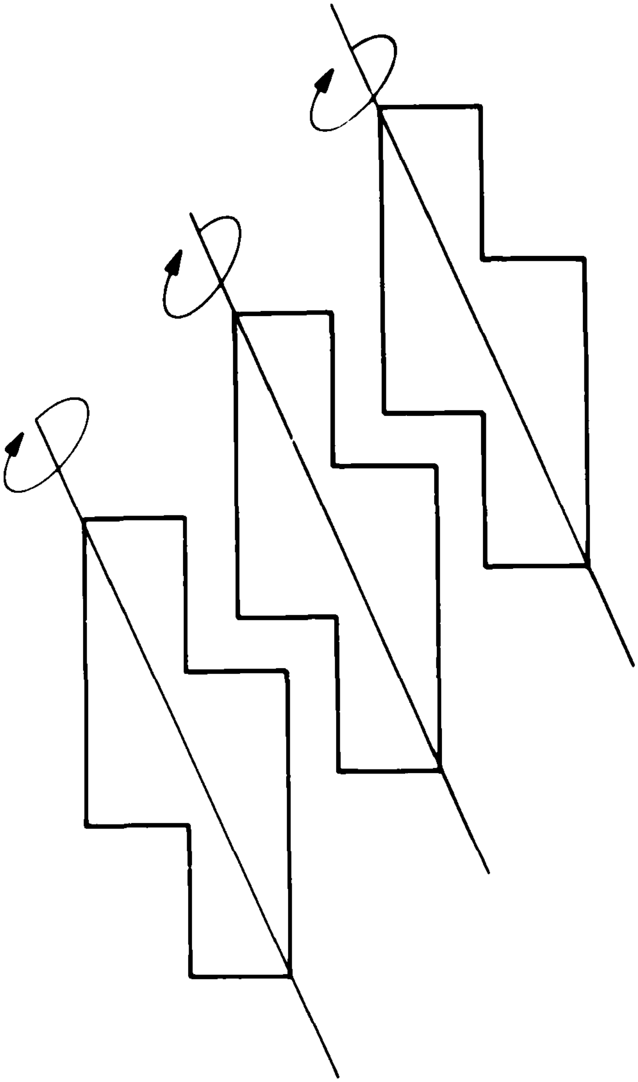


FIGURE 3 Combined interactions in a rotating model.

tle topic. For example, some of the effects incurred by merely extending a terminal carbon chain are shown in Figure 4 for the *n*-butyl 4′-*n*-alkoxybiphenyl-4-carboxylates.[13] Increases in the terminal alkoxy chain produce injections of different types of tilted smectic phase when passing from the *n*-hexyloxy member to the *n*-octyloxy homologue. Whilst current theories concerning the nature of the smectic polymorphic modifications attempt to be all embracing, it is apparent from studies of the effects of small changes in molecular struc-

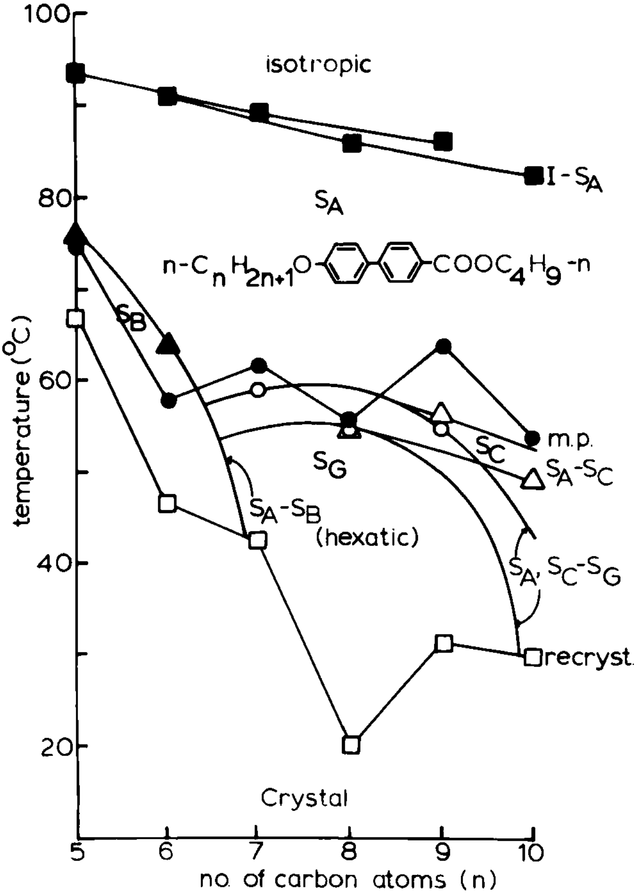


FIGURE 4 Plot of transition temperatures against the number of carbon atoms (*n*) in the *n*-alkoxy chain of the *n*-butyl 4′-*n*-alkoxybiphenyl-4-carboxylates. Key: ■, I—$S_A$; ▲, $S_A$—$S_B$; O, $S_A$ or $S_C$—$S_G$; △, $S_A$—$S_C$; ●, crystal-mesophase; □, mesophase-crystal on cooling.

ture on the incidence of certain phases, that no theory has a general application to any one phase.

It is apparent, particularly from studies comparing how the structures of various mesogenic materials effect smectic polymorphism, that there is a subtle balance between molecular structure, molecular packing requirements, dipolar interactions, and orbital overlap which predetermines the phase types observed.

In the formation of the smectic phases the proximity of approach of the nearest neighboring molecule is an important factor to be considered. In the A and C phases the molecules are assumed to be rotating freely about their long axes,[12] and therefore the volume ascribed by the molecule in space as it rotates is an important quantity for calculating the closest distance of approach of two molecules for this motion to remain uncoordinated. In the formation of the other phases this volume of space will be interpenetrated as the molecular rotations become more coordinated, however, the packing requirements of these volumes can help to predict the phase sequence observed.

Thus, in the following sections a simple method of determining the molecular swept-out volume is given. These volumes are then used to examine the formation of the B and E phases and the I—$S_{AB}$ transition.[5]

## RESULTS AND DISCUSSION

### (1) Calculation of the molecular rotational volume

In its simplest form the calculation of the shape of a molecule as it rotates about its long axis can be made by projecting the molecular structure of the mesogen onto a flat surface. This involves the drawing out of the molecular structure in its all *trans* conformation (other conformations can be used if required) by use of the known bond lengths and bond angles; this requires that bonds sticking out of the plane must be projected back into it as though the molecule is flat. This provides the simple "$\sigma$" bond framework of the molecule. The molecule can then be given more "shape" by the addition of van der Waals radii associated with the electrons of each atomic center, as shown in Figure 5 for methyl 4′-*n*-octyloxybiphenyl-4-carboxylate.

The flat molecular projection can now be placed on cartesian axes of arbitrary location. The positions of all the atomic centers can be related directly to these axes, and the position of the long axis can now be made either by;

(a) arbitrary placement of a line through the mass points

(b) assuming the mass of the hydrogen atom is negligible and that the masses of the oxygen, carbon, and nitrogen atoms are approximately equal, therefore by using the locations of their centers in a least squares fit the equation of a line through the atomic centers can be produced (see Figure 5)

(c) noting the positions of all of the molecular centers by means of the cartesian axes and fitting them into a program to determine the minimum moment of inertia of the molecular centers about a given line.

Once the equation of the line has been determined it can be drawn on the graphical description of the mesogen, see Figure 5. This line depicts the molecular long axis of the molecule in the desired conformational structure. If the molecule is allowed to rotate about this long axis then a representation of the volume ascribed in space by this motion can be derived by using the axis as a plane of reflection. Thus, by reflecting mass centers across this line it is possible to project the shape of the molecule rotated through an angle of 180° about

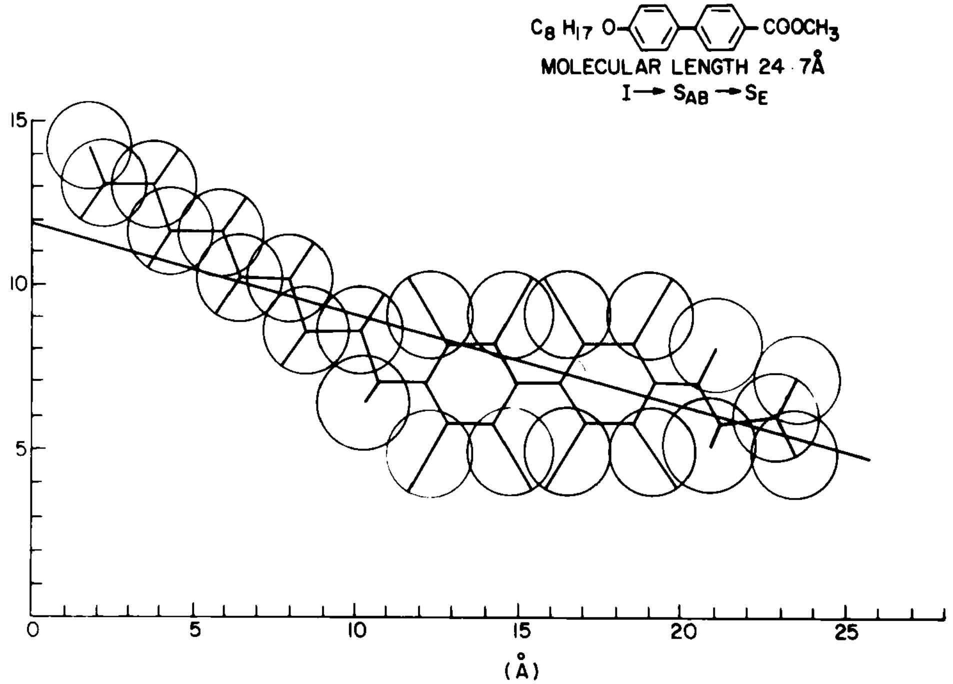


FIGURE 5 The molecular shape of methyl 4'-*n*-octyloxybiphenyl-4-carboxylate in its all *trans* conformation.

the long axis on top of the original molecular projection, as shown in Figure 6. This composite shape will then represent the cross-sectional area of the volume of space occupied by the molecule as it rotates about its long axis.

Methods (b) and (c) produce a swept out volume of rotation which has a radius of rotation that is a minimum. That is if the rotational volume of the molecule is contained within a cylinder, so that the molecule just touches the sides of the cylinder, then the diameter of the cylinder will be a minimum. Thus, if these cylinders are closely packed together in layers side by side the effective volume occupied by the molecules, with freedom of rotation, will also be a minimum.

### (2) Packing requirements in the orthogonal B and E phases

Once having determined the shape of the cross-sectional area of the molecule as it rotates about a known long axis, these shapes can be used to investigate the packing requirements of the mesogen under consideration.

Firstly, it should be noted that a great number of smectic B materials have one, or only short, terminal alkyl chains and often without terminal outboard dipole moments associated with them. This is in stark contrast to the situation

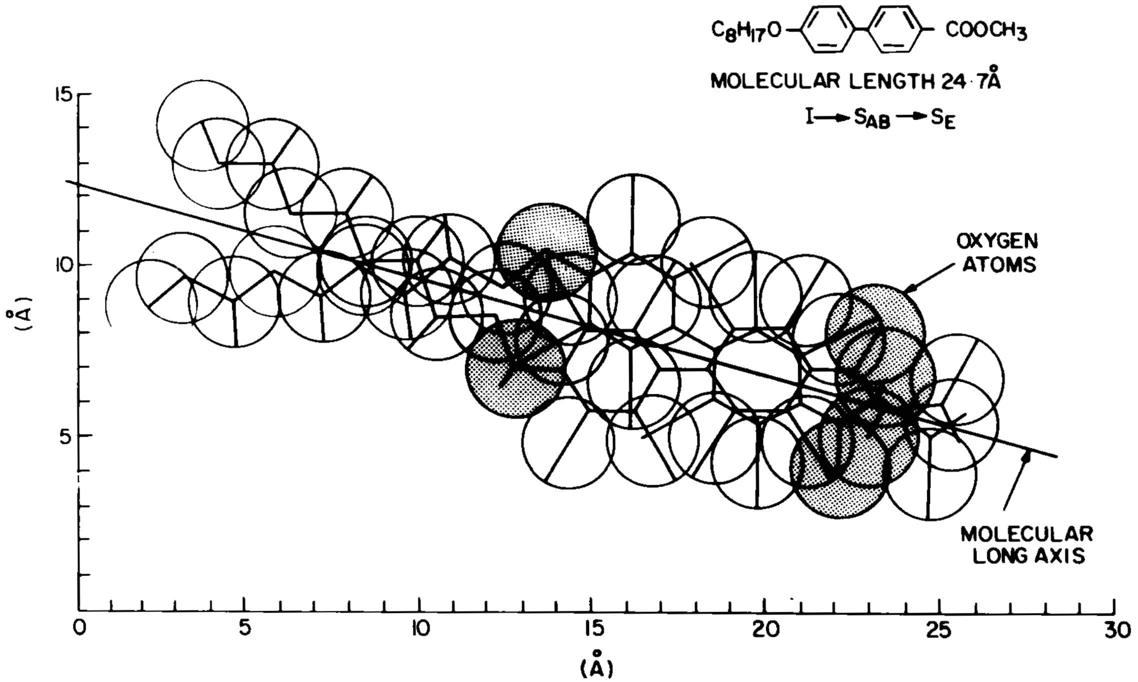


FIGURE 6 The rotational molecular shape of methyl 4′-*n*-octyloxybiphenyl-4-carboxylate.

for smectic C and other tilted mesophase materials. The majority of compounds that exhibit the orthogonal B phase have a distorted molecular structure that is often bent or curved. From experimental observations[5] it appears that the more distorted the molecular structure is, the more the formation of the B phase is favored. Thus, within the constraints of a liquid crystal system, it appears that the more unsymmetrical the molecular structure is, the more likely will be the chances of forming B phases. This again contrasts with the picture for the C phase, for which the required molecular structure deviates only slightly from that of the most symmetrical structure.[21]

A typical shape of a molecule as it rotates in space about its long axis is shown in Figure 6 for methyl 4′-*n*-octyloxybiphenyl-4-carboxylate ($S_A$, $S_B$ and $S_E$ phases).[13] The A phase, however, is extremely short-lived and the transition from the isotropic liquid is effectively straight to the B phase with the transition being classed as the I-$S_{AB}$ type. In the homologous series of the n-alkyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid, only the first three members (methyl, ethyl and *n*-propyl) exhibit B phases.[13] The A to B transition temperatures fall dramatically as the ester chain length increases. Therefore, it could be proposed that the methyl ester must have a molecular structure more suited to forming a $S_B$ phase than the other two esters.

### (a) Packing Arrangements of Two Molecules

The shape of the volume of revolution for methyl 4′-*n*-octyloxybiphenyl-4-carboxylate is of a tumble-boy type. As the ester chain is increased this shape becomes more symmetrical. Most of the compounds studied so far which have strong $S_B$ characteristics have rotational molecular shapes of the tumble-boy variety. These shapes are stylized in Figure 7.

If a molecule that has a tumble-boy rotational shape becomes in close proximity to another similar molecule then at transition to a $S_B$ phase these molecules must pack closely together. It is known that the separation of the molecular centers in the B phase is extremely small,[22,23] therefore the intermolecular separation is of a magnitude whereby the space occupied by one of the molecules is partly shared by its nearest neighbor, i.e., the rotational molecular volumes are interpenetrable. In this close-packed situation, however, molecular rotation is still permitted provided it is of a coordinated nature.

Therefore, even though the rotational swept-out volumes are interpenetrated, as the molecules move closer together in order to coordinate their rota-

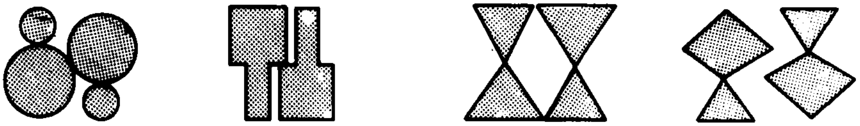


FIGURE 7 The rotational molecular shapes of materials which strongly favor smectic B properties.

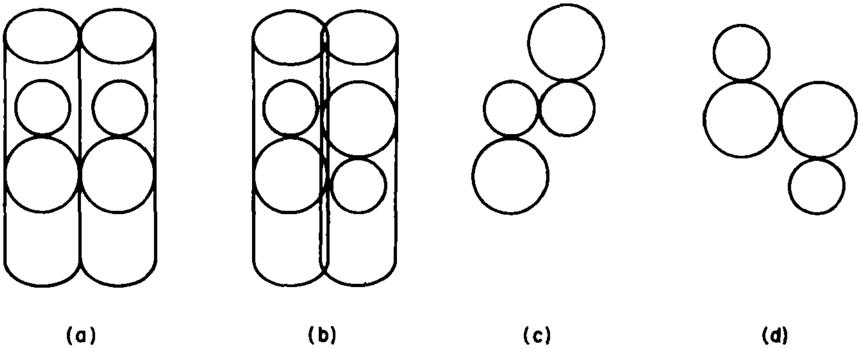


FIGURE 8 The packing arrangements of the tumble-boy rotational swept-out molecular volumes.

tional motions and form this close-packed arrangement they must pass through a situation where for some molecules the volumes themselves are closely packed. Thus, the packing arrangements of these volumes can be used to aid the prediction of the phase type formed.

Consider the packing arrangements of the tumble-boy shapes as shown in Figure 8. It can be seen that the tilted arrangements (c) and (d) will be relatively unstable and create very large tilt angles in the phase. The packing arrangement with all the molecules the same way up (a) produces a more stable arrangement, but does not fill space efficiently. Packing arrangement (b) however, shows very close packing of the molecules so that they even interpenetrate each others cylindrical volume of space without interfering with each others rotational motion. This can be seen more clearly in Figure 9 for methyl 4′-*n*-octyloxybiphenyl-4-carboxylate where the predicted phase type would certainly be orthogonal.

### (b) Packing Arrangements in a Hexagonal Matrix

Having described the situation for two molecules close-packed together these ideas can be extended to groups of molecules. Consider the addition of one molecule to the closely-packed pair. The next molecule can pack closely either the right way up or upside down, see Figure 10, the two positions are equivalent.

The packing arrangement of a trio of molecules forms the basis for packing in the hexagonal net. Remembering that the molecular motion in the B phase is coordinated and thus the swept out volumes are interpenetrable; the molecules can be packed together in a very "stylised" way in order to alleviate some of the coordinated motion in certain directions. The optimum packing arrangement for the tumble-boy shapes is in rows, see Figure 11. Rotation can then occur in a well-coordinated way along the rows, but in a less well defined fashion across the rows. This is due to the sharing of space by the tumble-boy

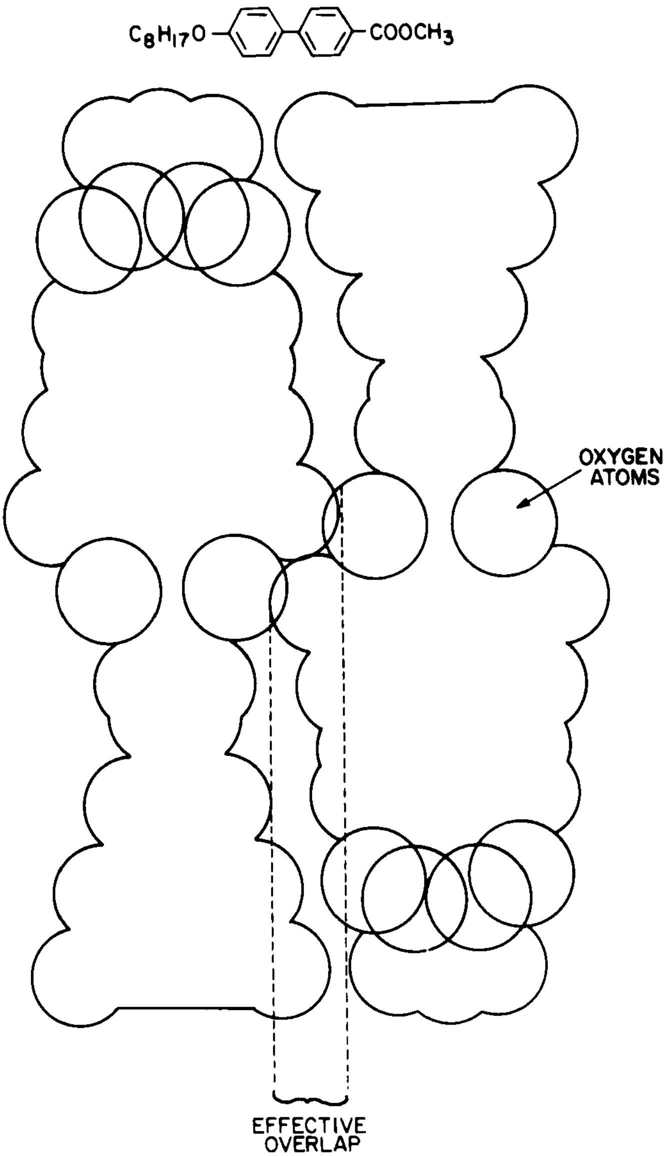


FIGURE 9 The packing arrangement of two methyl 4′-*n*-octyloxybiphenyl-4-carboxylate molecules.

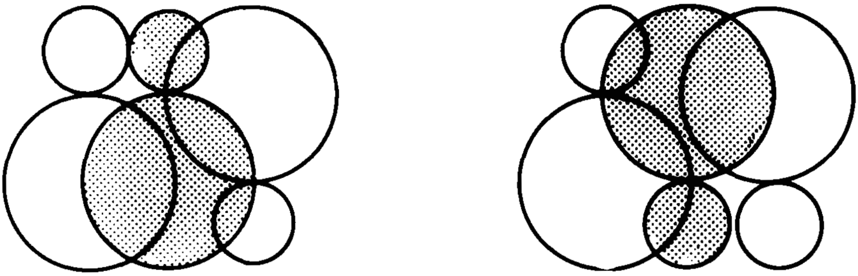


FIGURE 10 Build-up of the hexagonal close-packed matrix in the B phase.

shapes occuring across the rows in head to tail arrangements. When the heads are the same way up, i.e. along the rows, there has to be a greater interpenetration of each others space and hence the rotational motion is well-coordinated. This type of packing may occur in small domains but it will become random over large areas.

### (c) The $S_B$ to $S_E$ Phase Transition

In a hexagonally close-packed net of molecules which have tumble-boy rotational shapes, transition to the E phase can occur via a contraction across the rows in which the molecules have head to tail arrangements, as shown in Figure 12.

Thus, the utilization of the remaining space available, i.e., that between the head to tail arrangements of these volumes aids the drive to form an orthorhombically close-packed matrix. In this case the molecules will no longer be able to rotate freely or coordinately but will only oscillate as this remaining free space is occupied.

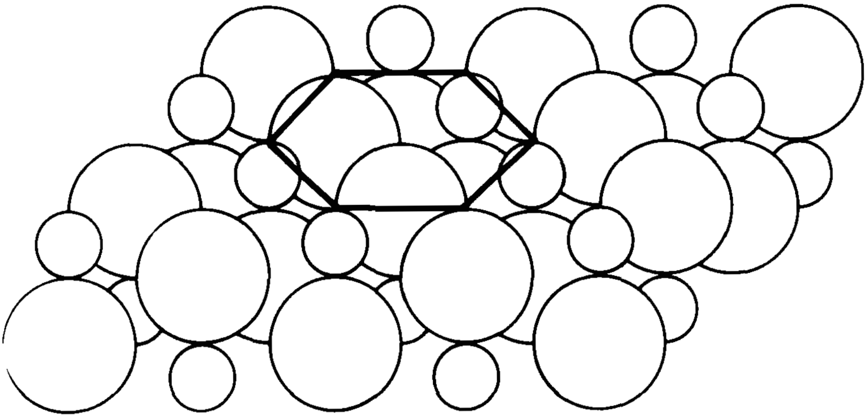


FIGURE 11 Packing in the hexagonal net of the B phase.

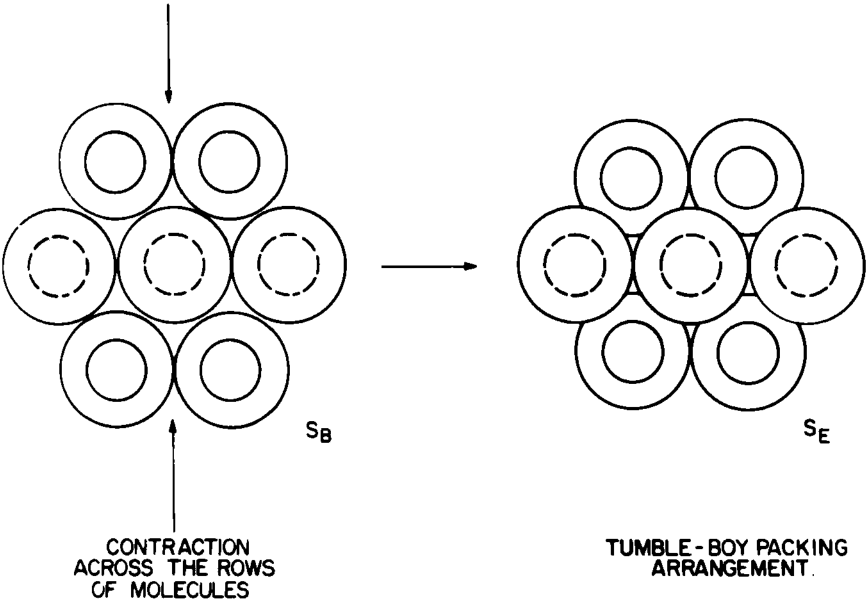


FIGURE 12 Compression across the rows in the B phase can form the orthorhombic close packed net of the E phase.

### (3) The interpenetration of rotational volumes

It has been shown[22,23] for some materials which exhibit B and E phases that the separation of the molecular centers is very small. For example, in the smectic B phase of ethyl 4-(4′-ethoxybenzylideneamino) cinnamate the molecular separation is of the order of 4.8–5 Å.[22] The width of a benzene ring (across its sides) is of the order of 6.6–6.8 Å, thus indicating that the molecules must have a coordinated rotation in the B phase of this material.

For a separation of 4.8–5 Å for the molecular centers in the B phase, coordinated motion can only occur when the edge of one molecule is presented to the side of its nearest neighbor and the two molecules rotate in opposite directions. Many descriptions of this motion assume that the molecule is of a flat blade-like shape[24] whereas in the real situation they are of a bent or distorted shape. For example, Coates and Gray[5] investigated the properties of substituted and unsubstituted ω-phenylalkyl esters of 4-(4′-phenylbenzylideneamino) cinnamic acid. They found that as the internal carbon chain was extended so the terminal phenyl ring was displaced from the long axis of the rest of the molecule for odd values of the carbon atoms in the chain, see Figure 13. Substituent groups were added onto the phenyl ring to emphasize this effect. Their results show an odd-even alternation effect for the A to B transition temperatures, but instead of being a relatively small effect it is in fact quite

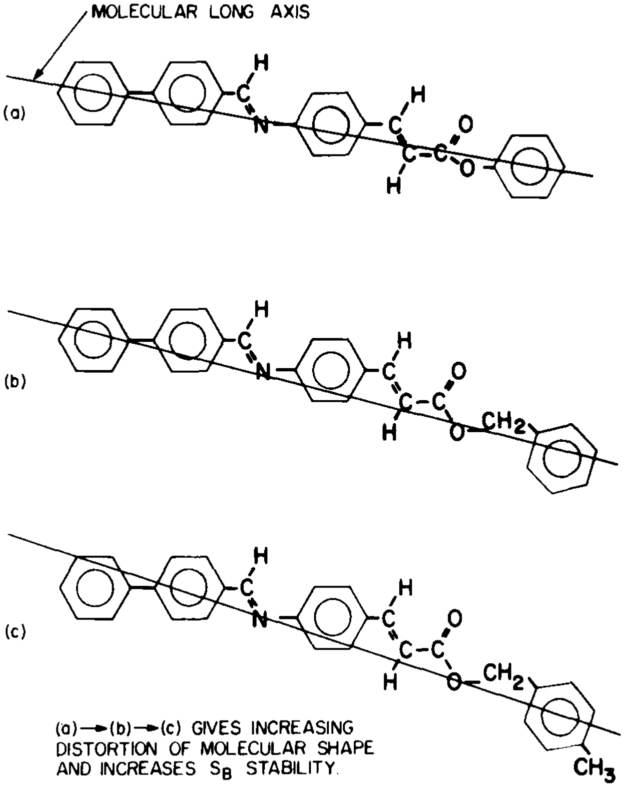


FIGURE 13 Distortion of the molecular shape in the substituted and unsubstituted ω-phenyl esters of 4-(4′-phenylbenzylideneamino) cinnamic acid.

dramatic. The odd members exhibit I—$S_{AB}$ transitions whilst the even members exhibit a normal N,A,B,E sequence. The temperature range of the B phase is elevated by approximately 30° for the odd members with respect to the even members.

As the internal chain increases so the terminal phenyl ring moves in and out of line with the rest of the molecule. Thus, the B phase is preferred when the ring is out of line and the molecular structure is bent.

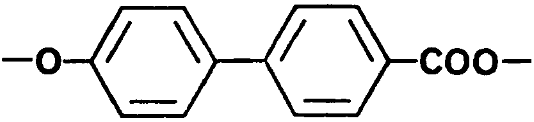
The more bent the structure is then the greater is the "cylindrical" volume occupied by the molecule when it rotates about its long axis, and also, the greater is the volume to share with its nearest neighbors. This gives rise to a greater stability of the B and E phases.

Distortion of molecular shape can aid the interpenetration of the swept-out volumes by increasing the amount of volume there is to share and by having holes or spaces within the molecular envelope that can be utilized in close packing arrangements by its nearest neighbors.

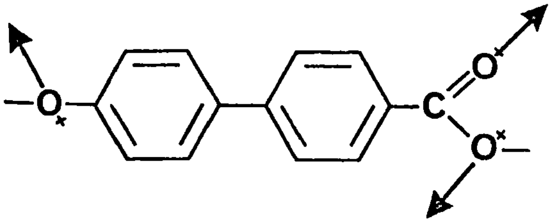
### (4) Dipolar effects

Dipolar effects play a large part in the formation of most phase types, for example, in the C phase there is a delicate balance of dipolar effects that can help stabilize the phase.[25–27]

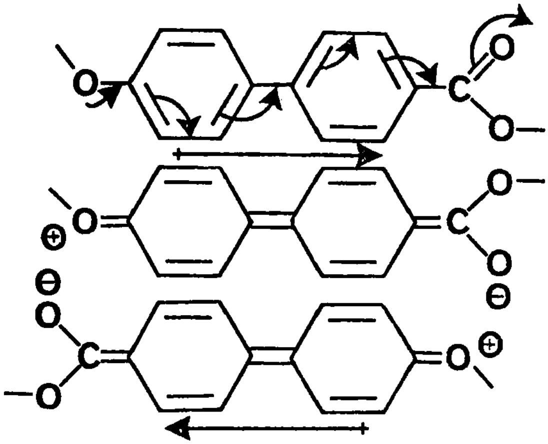
There are a number of ways of treating dipolar interactions and their origins. If we consider just the 4′-oxy-biphenyl-4-carboxylate system



then we have permanent dipole moments associated with the lone pair orbitals on the oxygen atoms which are directed across the molecular long axis and are



often referred to as "terminal outboard dipole moments." These dipoles will exist even in an isolated molecule, but when two such structures approach each other in a head to tail arrangement we can also obtain induced dipoles formed by mesomeric relay through the $\pi$ cloud of electrons, as shown below.



Thus we have the attracting force of two opposite poles coupled with dipoles running in opposite directions along the molecular long axis. This will obviously aid an alternating head to tail packing arrangement.

It is interesting to note that if the alkoxy oxygen atom is removed then there is a loss of mesomorphic properties as well. Therefore there may be a Leonard-Jones potential energy-well associated with the permanent dipolar effects which prevents the phase collapsing to a solid. At long distances, there is an attraction between the oppositely charged species, but as these approach there is a strong repulsive effect from the electronegative oxygen atoms. For example, 4-*n*-hexyl 4′-*n*-pentylbiphenyl-4-carboxylate does not exhibit any mesophases whilst the analogous 4-*n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (650BC) exhibits A, B and E phases.

The polarizability of the molecular structure is another important factor to be considered in phase formation. Removal of the source of the mesomeric relay (in this case the alkoxy oxygen atom) or the insertion of a group or atom which prevents this relay thus producing isolated dipoles will depress the liquid crystal properties of the system in some cases.

As two molecules approach each other and pack together side by side, the best packing arrangement will have an effect on the strength of the dipolar interactions. The larger the separation of the dipole moments by steric factors the weaker the interaction will be, and this will ultimately influence the smectic polymorphism observed. However, as the packing arrangements change by interpenetration of the rotational volumes giving a tighter packing situation, so the relative positions of the dipole moments change. Therefore, there will be a subtle change in the strength of the dipolar interactions as the phase "condenses" which may promote the formation of other types of smectic phase.

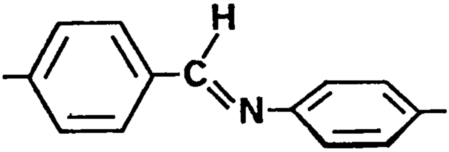
### (5) Internal molecular disposition

The overall molecular shape solely in its all *trans* conformation has only been used to describe molecular packing arrangements so far. The packing arrangements and the swept-out volumes of revolution of a molecule are dependent entirely on the structural conformation of the molecular species.

Although many structural studies have been made, particularly those using neutron scattering and NMR techniques involving perdeuteriated and selectively deuteriated mesogens, little has been reported concerning the actual shape of a molecule as it rotates about its long axis.

There are two possibilities for changing the molecular shape, firstly, twisting of the conformational structure, and secondly, different parts of the molecule rotating at different rates. Both of these will add to the complexity of the overall molecular motion.

For example, recent proposals[20,28] suggest that aromatic Schiff's base materials may be twisted about this linkage, so that the planes of the two benzene rings are at an angle to each other as shown below:



This type of arrangement could help the packing requirements of the B phase and other ordered smectic phases (even tilted phases), see Figure 14, by allowing the cores of two molecules to pack closer together than if they were just flat bent lamellar shapes. The rotation of the cores in this case may be occurring at different rates with respect to the rotations of the terminal alkyl chains.

Similarly, McDonnell and Gray[29] have indicated that there is a possibility that materials which contain the cyclohexyl ring system may change their overall shape with temperature. The cyclohexane ring can undergo conformational changes of structure from the boat form, through the twisted boat, to the chair and these types of change could also effect the stability of the phase types exibited.

### (6) Problems arising with the rotational shape theory

There are numerous problems with this simple concept of molecular volumes and fitment of dipoles and shape together. The more important aspects can be listed as follows:

(a) The molecular long axis has no need to pass through the mass atoms to give the least moment of inertia about this line. It is more likely that the long axis will run closer to the axis of the molecular core. However, the simple drawing out of the molecule as a flat projection does allow the long axis to be placed in an arbitrary position apart from the calculated direction. Therefore a family of rotational shapes can be examined if so desired.

(b) The molecule does not necessarily have to have an all *trans* conformation. Again *cis* or *gauche* conformations can be coped with in the original molecular projection.

(c) The volumes of rotation must be interpenetrable in the ordered phases because of the tight packing arrangements of the molecules. Although the formation of tilted or orthogonal phases can possibly be predicted, once formed subsequent phase formation is difficult to forecast.

(d) The dipolar interactions are difficult to quantify for these shapes and therefore the effect they have on phase formation is in itself difficult to determine.

(e) The change in volume at the A to B transition is relatively small indicating the molecular separation even in the A phase is very narrow. Therefore, some but not all the molecules in the A phase also have their molecular swept-out rotational envelopes substantially interpenetrated.

(f) The method used to determine the molecular long axis depends on producing a flat projection of the molecule under consideration when in fact it has three-dimensional bulk. However, detailed calculations can give the equation of the axis in three-dimensional space providing a better approximation to the rotational shape.

(g) The rotational swept-out volumes determined by this method produce a molecular shape that is given its "fullness of body" by the van der Waals radii of the paired electron clouds of each atom. These clouds are represented by the molecular shapes in an almost solid form which they are not, and it should be

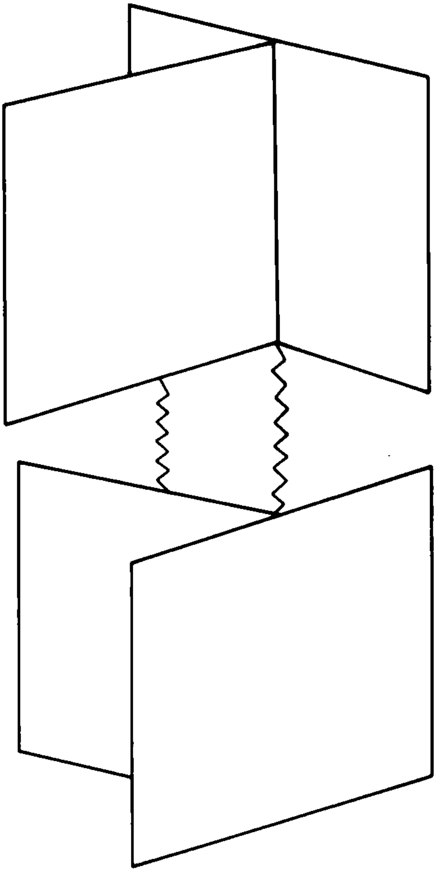


FIGURE 14 Two twisted molecules pack closer together in the B phase because of mutual utilization of the same space.

remembered that they too are of a deformable nature. This would produce a molecular shape with a strong skeleton ("$\sigma$" bond framework) with a pliable, fleshy, outer covering (van der Waals radii and $\pi$ cloud electrons).

## CONCLUSIONS

A method of determining the shape of a molecule as it rotates about its long axis has been described. The resultant rotational shapes have been used to show how formation of the B and E phases can occur *via* a drive to obtain a tighter packing arrangement.

Although the determination of rotational shape is easy to perform for a particular material, it does have inherent problems in its conception and limited usage. However, it still provides useful information concerning factors which favor the formation of certain phases. The concept, although in its initial stages, does show potential for further development. The absolute molecular configuration and the position of the molecular long axis can be varied for an individual molecule giving a variety of rotational volumes which in turn can give a number of different packing arrangements. The stability of certain packing arrangements, with regard to dipolar and other structural features, can aid the prediction of the formation of certain phase types for a given molecule.

The incidence and formation of smectic phase types appears to be dependent on a number of factors which can be listed as follows:

(a) Rotational molecular shape

(b) Interpenetration of the volumes of revolution

(c) Actual flat lamellar shape

(d) Twisted and conformational shape

(e) Dipolar considerations involving mesomeric relay—induced dipole moments

(f) Dipole moments (permanent)—attractive and repulsive

(g) Directional dipoles occurring across or along the axis of the molecule resulting from induced dipole moments

(h) The rotational disposition of each phase

(i) The balance between packing arrangements and the positions of the dipole moments

(j) The relative overlap of the "$\pi$" cloud electrons and the "$\sigma$" bond framework of neighboring molecules.

## Acknowledgment

The author wishes to thank Professor G. W. Gray for many helpful discussions.

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