THE RELATIONSHIP OF MOLECULAR STRUCTURE TO MESOMORPHISM IN SOME AROMATIC ESTERS OF DIPHENOLS

by

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CHAPTER I

INTRODUCTION

Matter exists principally in three distinct states - crystalline solid, isotropic liquid, and gas. Individual units in both the liquid and gaseous state are more or less mobile, while in the crystalline solid state these units are held in the rigid, three dimensional configuration of a crystalline lattice. Consequently, the crystalline solid is regarded as the most highly ordered of the three states of matter.

Heating a crystalline solid increases the thermal vibrations and the ordered arrangement begins to break down. The solid passes from the highly organized crystalline state to the disorganized isotropic liquid.

In 1888, Friedrich Reinitzer discovered that, on melting cholesteryl benzoate, the solid collapsed to form a turbid liquid which, on further heating, gave the normal, transparent, isotropic liquid.[1] This turbid liquid exhibited properties of both liquid and crystalline forms of matter; the substance was both birefringent (a property of crystals) and fluid.

Although Reinitzer is credited with discovering the liquid crystalline phenomenon, Lehmann[2] was first to suggest the name "liquid crystals", and to describe their properties. Later, Friedel[3,4] proposed the term "mesomorphs" or "mesophases" for substances that were neither isotropic liquids nor crystalline solids. Since both terminologies are generally accepted, the terms liquid crystal and mesomorph, or liquid crystallinity and mesomorphism, will be used interchangeably throughout this thesis.

Active interest in liquid crystals persisted until the 1930's. Thereafter, few papers were published until the 1950's when interest once again flourished. Renewal of work in this area was perhaps unavoidable for it has been estimated that one out of every 200 organic compounds is liquid crystalline.[5]

Compounds that exhibit liquid crystallinity vary widely in their chemical constitution, but all contain similarly rigid, rod-shaped, and highly polarizable molecules.

Liquid crystals may be categorized as thermotropic or lyotropic. Both are produced from crystalline solids with the molecular structural characteristics indicated above, thermotropically by melting, lyotropically by addition of solvent.

When the mesomorphic state is produced thermotropically, the crystalline solid melts to the mesophase. At some higher temperature, the mesophase undergoes transition to the isotropic liquid.

$$\text{CRYSTALS} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{MESOPHASE} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{ISOTROPIC LIQUID}$$

This change from phase to phase is thermodynamically first order and reversible. Cooling the isotropic liquid first gives the liquid crystalline state, then the crystalline solid. Although a transition from the mesomorphic to crystalline state is commonly accompanied by supercooling, all mesomorphic transitions always occur at the same temperature; if not, the purity of the specimen is suspect.

In the production of a lyotropic mesophase, the action of solvent on solute has a disruptive effect analogous to the melting process. The result is a turbid material with a consistency varying between that of a waxy substance and a freely flowing liquid. Thus, when certain compounds are treated with solvent, a state arises that is neither a true crystalline solid nor a true isotropic liquid. These are, in fact, liquid crystals. The addition of excess solvent causes true isotropic solution while evaporation of solvent first gives the liquid crystalline state, then the crystalline solid.

In general, lyotropic mesomorphism has not been as thoroughly investigated as thermotropic mesomorphism; nevertheless, literature on the subject is quite extensive.[6-10]

Thermotropic and lyotropic liquid crystals that exhibit more than one mesophase are termed polymesomorphous. If the mesomorphic transition occurs reversibly above the melting point of a thermotropic liquid crystal, it is enantiotropic. If the transition is below the melting point, it is termed monotropic.

Thermotropic liquid crystals are generally classified as either smectic, nematic or cholesteric. An unusual exception to this is the mesophase of di-isobutyl silanediol which does not fit any of these classifications.[11]

The term smectic was coined by Friedel[12] from the Greek word "smectos" meaning grease or slime. The highly ordered smectic structure is stratified with the long axes of the molecules in a parallel arrangement normal to the planes of the layers (Figure 1a). Molecules are mobile in two directions and may rotate about one axis.

The smectic mesophase may adopt different "textures" depending on a number of variables.[13] Apparently, there exist at least seven of these textures- smectic A,B,C,D,E,F and G.[14] Only the more common textures will be briefly outlined.

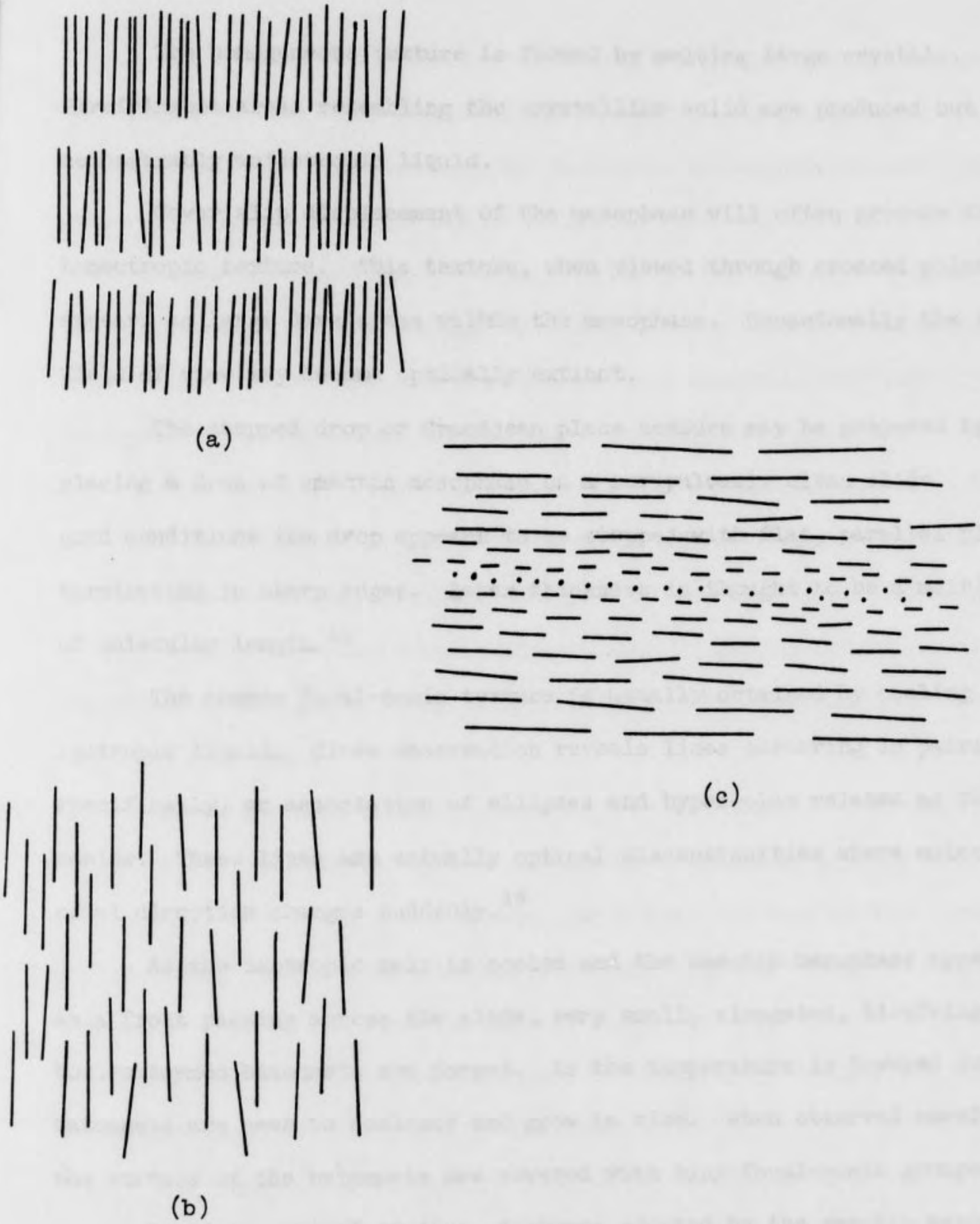


Figure 1. Molecular Structure of Mesomorphic Liquids. a) Smectic, b) Nematic, c) Cholesteric

The homogeneous texture is formed by melting large crystals. Birefringent areas resembling the crystalline solid are produced but are demonstrably anisotropic liquid.

Cover slip displacement of the mesophase will often produce the homeotropic texture. This texture, when viewed through crossed polaroids, appears as large dark areas within the mesophase. Occasionally the entire field of view may become optically extinct.

The stepped drop or Grandjean plane texture may be prepared by placing a drop of smectic mesophase on a scrupulously clean slide. Under good conditions the drop appears to be stepped with flat, parallel planes terminating in sharp edges. Layer thickness is thought to be a multiple of molecular length.[15]

The common focal-conic texture is usually obtained by cooling the isotropic liquid. Close observation reveals lines occurring in pairs, specifically, an association of ellipses and hyperbolas related as focal-conics. These lines are actually optical discontinuities where molecular axial direction changes suddenly.[16]

As the isotropic melt is cooled and the smectic mesophase appears as a front passing across the slide, very small, elongated, birefringent bodies termed batonnets are formed. As the temperature is lowered further, batonnets are seen to coalesce and grow in size. When observed carefully, the surface of the batonnets are covered with tiny focal-conic groups.

Based on optical studies, textures adopted by the smectic mesophase are consistent with a parallel arrangement of molecules in layers. Early X-ray studies by de Broglie and Friedel[17,18] support such an arrangement. Thus, in terms of molecular order, smectic mesophases are probably more similar to crystalline solids than to isotropic liquids.

The nematic mesophase is less ordered than the smectic mesophase and is not as well characterized. Although the nematic mesophase has a parallel molecular arrangement, the molecules are mobile in three directions and may rotate about one axis (Figure 1b). For this reason nematic liquids give diffuse X-ray patterns similar to the isotropic liquid.[19,20]

Due to light scattering, thick sections of nematic liquids appear turbid to the naked eye, but when placed in a magnetic field and viewed along the lines of force, the nematic liquid appears clear.

The fact that molecules of a nematic mesophase are oriented by electric and magnetic fields[21,22] indicates a lesser degree of order than the smectic structure, which is much less affected.[23] In an electric field, nematic molecules align perpendicular to the electrical lines of force and in a magnetic field molecular alignment is parallel to the magnetic flux lines.

There are four nematic textures. Friedel used the term nematic to describe the thread-like texture frequently obtained on cooling the isotropic liquid or heating the crystalline solid. Threads of the threaded and schlieren textures have no definite shape and may disappear from a mesophase without a trace. In the schlieren texture, black dots are threads viewed on end. Like the lines in the smectic focal-conic texture, these threads are optical discontinuities.

The homogeneous texture is similar to the homogeneous smectic texture in that large birefringent areas corresponding exactly to the large crystalline areas are produced. The nematic homogeneous texture is different in that the melt is in rapid and continuous motion.

The nematic mesophase also exhibits a homeotropic texture. As in the analogous smectic texture, dark areas are produced by molecular alignment perpendicular to the supporting surface. However, complete homeotropy is seldom attained.

The smectic and nematic mesophases are sometimes distinguishable by the texture adopted from cooling the isotropic liquid. While the smectic mesophase frequently manifests itself in the form of batonnets, the nematic structure returns as freely floating "droplets" that are spherical and show a cross. The arms of the crosses appear to be parallel to the cover slide, but movement of the slide to an angle normal to the original position has no effect. Apparently, this is indicative of either a spherical structure with molecules radiating from a nuclear point in the center of the drop or a molecular arrangement along concentric circles.[24]

The optical discontinuities of the threaded and Schlieren textures, the discrete areas of the homogeneous texture, and the light scattering properties of the nematic mesophase are all consistent with an imbricated structure where the molecules maintain a parallel arrangement without layers.

Two theories have been proposed to explain the structure of the nematic liquid - the swarm theory and the continuum theory. The swarm theory was first proposed by Bose in 1909.[25,26] Later, in 1918, Ornstein and Zernicke,[27] published a detailed mathematical study supporting the swarm theory.

The swarm theory holds that molecules in a nematic liquid tend to form aggregates or swarms consisting of approximately 10^5 molecules.

Molecules lie parallel or nearly parallel within the swarms, but orientation of individual swarms is random. Interaction between swarms is small and molecules are free to move from swarm to swarm.

The light scattering phenomenon of nematic liquids is strong evidence in support of the swarm theory. Even in an external field, strong light scattering is still observed, presumably because the swarms are not homogeneously oriented. The effect of an external field on the nematic mesophase is much greater than that on the smectic mesophase since the moment (length x charge) would be larger for a swarm than for a single molecule.

The continuum theory was developed by Zocher[28] and Oseen.[29] In essence, the continuum theory assumes that at every point in the undisturbed liquid there is a preferred orientation of the molecules, and although this orientation varies continuously with position, the orienting influences of the container walls and external forces cannot be ignored.

Unlike the swarm theory, the continuum theory is not confined to the nematic mesophase, but applies to smectic and cholesteric mesophases as well. Albeit both theories have gained widespread support and have been the subject of much controversy, the swarm theory is the more widely accepted.

The last general form of thermotropic mesomorphism is termed cholesteric because the mesophase is shown primarily by cholesteryl derivatives. The cholesteric mesophase is also frequently referred to as twisted nematic since its molecular arrangement corresponds to a twisted nematic structure where molecular axial direction is no longer continuous but changes gradually with each plane (Figure 1c).

Friedel[12] suggested that the cholesteric mesophase may be regarded as a special case of the nematic mesophase. A single compound may exhibit both smectic and nematic or smectic and cholesteric mesophases, but never both a nematic and a cholesteric mesophase. It has also been found that certain mixtures of dextrorotatory and levorotatory cholesteric isomers exhibit typically nematic properties.[30] Furthermore, cholesteric mesophases are aligned by electric and magnetic fields much in the same way as nematic liquids.

In addition to the homeotropic texture, the cholesteric mesophase exhibits the focal-conic texture and the intensely irridescent and highly optically active Grandjean plane texture. The highly organized molecular arrangement of the cholesteric mesophase accounts for the intense irridescence of the plane texture while the twisted helical pattern of cholesteric molecules explains the observed high optical activity perpendicular to the molecular axial direction.[12,31]

Since liquid crystallinity is found in aromatic, aliphatic, and multi-ring compounds, it is difficult to define explicitly a characteristic molecular structure capable of exhibiting mesomorphism. However, it can be stated that molecules which form liquid crystals all have certain features in common. First, molecules should be rather long, lath shaped or flat. Molecules which have a comparatively small length/breadth ratio are structurally unsuitable because of their difficulty in adopting a parallel arrangement. Second, the molecules should be rigid along their long axes so as to maintain their rod-like nature. And third, the presence of highly polarizable and strongly dipolar groups seems important. For these reasons, mesomorphic compounds frequently incorporate aromatic rings and unsaturated linkages.

An example of a typical molecular structure for a mesomorphic compound with some common terminal (A) and central (B) groups are presented in Table 1. Generally, mesomorphic thermal stability is likely to be high when dipolar groups are terminally (A) or centrally (B) located, and low when substitution is along the side of the molecule.

First attempts at correlating molecular structure and liquid crystallinity were undertaken by Vorlander and Lehmann soon after Reinitzer's discovery in 1888. Their objectives were simply to define the relationship between the type of mesophase exhibited (smectic, nematic or cholesteric), the mesomorphic transition temperature and the subsequent effect of altering the chemical constitution.

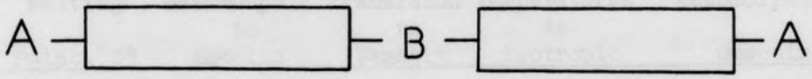
Examination of the homologous series of dimeric 4-n-alkoxybenzoic acids (Table 2) reveals that relatively minor changes in chemical constitution lead to marked variations in melting point. The addition of methylene groups into the alkoxy chain clearly results in a general trend toward lower melting points, but from homolog to homolog the effect is essentially unpredictable.

Although certain trends are observed, the melting points of organic compounds are largely unpredictable. Roughly speaking, the melting point of high molecular weight or strongly dipolar compounds is high, and that of low molecular weight or weakly dipolar compounds is low.

The melting process occurs when sufficient thermal energy is applied to weaken the intermolecular dipole-dipole interactions, induced dipole-dipole interactions, and Van der Waals attractive forces between molecules. These forces are dependent on the way the molecules are

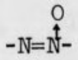
TABLE 1

COMMON CENTRAL AND TERMINAL GROUPS IN LIQUID CRYSTALLINE COMPOUNDS



Central Groups (B)

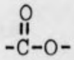
$-N{=}N-$

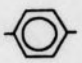

$-N{=}\overset{\overset{O}{\uparrow}}{N}-$

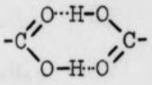
$-CH{=}CH-$

$-CH{=}N-$

$-C{\equiv}C-$


$-\overset{\overset{O}{\|}}{C}-O-$





Terminal Groups (A)

$CH_3(CH_2)_n^-$

$NC-$

n-alkyl-O-

n-alkyl-OOC-

O_2N-

$F-$

$Cl-$

$Br-$

$I-$

H_2N-

$CH_3-O-(CH_2)_n^-O-$

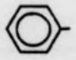
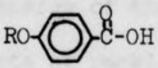


TABLE 2

4-n-ALKOXYBENZOIC ACIDS



R	Melting Point, °C[a]	Mesomorphic Transition Temperatures[b]			Mesomorphic Range, °C	
		to Smectic	to Nematic	to Isotropic	Smectic	Nematic
CH_3	184	-	-	184	-	-
C_2H_5	196	-	-	196	-	-
C_3H_7	145	-	145	154	-	9
C_4H_9	147	-	147	160	-	13
C_5H_{11}	124	-	124	151	-	27
C_6H_{13}	105	-	105	153	-	48
C_7H_{15}	92	92	98	146	6	48
C_8H_{17}	101	101	108	147	7	39
C_9H_{19}	94	94	117	143	23	26
$C_{10}H_{21}$	97	97	122	142	25	20
$C_{12}H_{25}$	95	95	129	137	34	8
$C_{16}H_{33}$	85	85	-	132.5	47.5	-
$C_{18}H_{37}$	102	102	-	131	29	-

[a] Reference 32.

[b] Reference 33.

packed in the crystalline lattice; something which is difficult to predict with any degree of accuracy. Although the molecules arrange themselves so that the potential energy of the system will be minimized, the subtle and unpredictable aspects of packing all exert an influence on the melting point. The exact molecular arrangement in the crystalline lattice will determine the lateral and planar attractive forces, all of which must weaken sufficiently for the compound to melt. For this reason, variations in the melting points of a homologous series are observed. Thus, the melting point is dependent not only on the chemical constitution but on the crystalline structure as well.[34]

The mesomorphic state arises when melting occurs in stages. The weaker crystalline bonds are broken, first giving some degree of movement before additional thermal energy can overcome the tendency of the molecules to line themselves up. Mesophase-mesophase and mesophase-isotropic transitions involve a much less profound decrease in the state of order than does the conversion of a crystalline solid to liquid. These transitions may, therefore, have a more direct relationship to chemical constitution than to melting point.

When a smectogenic crystal melts, primarily the end-to-end attractive forces are weakened, allowing free movement of the strata. Lateral cohesive forces must then be strong enough to prevent molecules from sliding out of the strata and producing the nematic structure. Thus, strong lateral and weak end-to-end attractive forces are desirable in the production of a smectic mesophase.

A stratified mesophase is most likely to arise from a layered crystalline lattice,[35] while either an imbricated or a layered crystalline lattice can give rise to a nematic mesophase.[36] Although both may produce the mesomorphic state on melting, their presence does not guarantee that the compound will be liquid crystalline. If the intermolecular binding forces in the crystal are very strong, then the melting point may be high enough that the parallel orientation is not maintained when the crystal melts. The solid then passes directly to the isotropic liquid.

The solid-nematic transition is more complex than the solid-smectic transition. Molecules of a nematogenic crystal lie parallel in a fixed geometric array. At the solid-nematic transition, the lateral, planar, and terminal cohesions all weaken sufficiently so that only the parallel order remains. Nematic mesomorphism is then favored by strong head-to-tail and weak lateral attractive forces.

On ascending a homologous series of liquid crystalline compounds the nematic-isotropic transition temperatures usually decrease (Table 2). The smectic-nematic transition temperatures rise quickly at first then more slowly. In other series the smectic-isotropic transition temperatures may rise to an early maximum then fall gradually. Inspection of Table 2 shows that the lower homologs are typically nematic and, as the chain lengthens smectic mesomorphism is followed by nematic. Then, in higher members, only smectic liquid crystallinity is observed.

Increasing the alkyl chain length must, therefore, have the effect of increasing the lateral or side-to-side attractive forces between molecules. Gray[37] suggests that the addition of methylene groups increases the intermolecular lateral attractive forces because of the polarizability of the added groups and decreases the end-to-end attractive forces by increasing separation of dipolar and polarizable units. Lateral attractive forces may also be enhanced by the reinforcement of dipoles operating across the long axes of the molecule. For these reasons the smectic mesophase is most likely observed in the long chain members of a homologous series.

One would think that a regular change in chemical constitution, such as the addition of a methylene group, would induce a regular change in intermolecular attractions, resulting in a regular trend in mesomorphic transition temperatures. If the transition temperatures in Table 2 are plotted against alkyl chain length, a smooth curve is indeed obtained.[38]

It should be noted, however, that the mesophase-isotropic transition temperatures for the odd numbered homologs are typically lower than those of the even (Table 2). Gray[39] suggests that the addition of a methylene group to an <u>odd</u> numbered alkyl chain increases the polarizability of the molecule. According to Gray, if the alkyl chain adopts the cog wheel rather than the common zigzag conformation, the addition of a methylene group to the alkyl chain that results in an even number of carbon atoms increases the length of the molecule along its major axis. Conversely, the addition of a methylene group that results in an odd number, makes an angle of approximately 70° to the molecular axial direction. The polarizability of the molecule, therefore, increases most on passing from an odd to an even number of atoms.

Terminal and lateral attractive forces and their relative strengths will finally determine if a compound will exhibit mesomorphic behavior. If these forces have the proper relative magnitudes so that melting occurs in stages, then a compound will be liquid crystalline. The relative extent of these attractive forces is again dependent on the chemical constitution.

For certain practical applications, such as display devices,[40] stationary phases in gas-liquid chromatography,[41-44] and solvents for NMR[45] and ESR,[46] it is highly desirable to have stable liquid crystalline compounds which exist at or near room temperature and which are mesomorphic over broad temperature ranges. Unfortunately, the molecular requirements necessary for nematic mesomorphism also increase the stability of the crystalline lattice, resulting in high melting points.

Early successes in obtaining the favored properties involved Schiff bases where a high degree of molecular dissymmetry is a key factor.[47] Schiff bases incorporate the C=N linkage which gives color and renders the molecule unstable toward thermal, hydrolytic and oxidative processes. More stable systems that exhibit nematic mesophases at low temperatures include substituted azoxybenzenes,[48-50] stilbenes,[51] and tolanes.[52] Aromatic esters are known to be relatively stable, and terminally substituted p-phenylene dibenzoates (Figure 2), which include both an ester linkage and the p-phenylene group, have been shown to exhibit broad mesomorphic ranges.[53,54]

The p-phenylene group is particularly amenable to inclusion in liquid crystalline systems; it is polarizable, rigid, and easily incorporated. Its presence enhances the mesomorphic stability and introduces the possibility of lateral substitution along the molecular skeleton. Moreover, the preferred conformation of these groups should be one in which the aromatic rings are coplanar and trans to each other (Figure 2). Thus, terminally substituted p-phenylene dibenzoates possess all the necessary features (rigidity, rod shape, polar terminal and internal groups) known to favor mesomorphism.

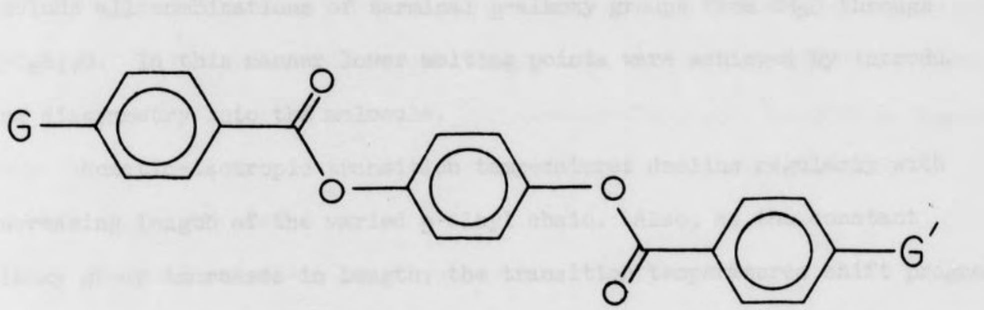


Figure 2. Configuration of Terminally Substituted p-Phenylene Dibenzoates.

In this system, (Figure 2) the effects of terminal alkoxy substitution (R and R'=n-alkoxy) on mesomorphism have been studied by a number of investigators.[53-55] The most notable and indeed the most comprehensive of these studies, was conducted by Haut, Schroeder and Schroeder.[55] By varying one terminal n-alkoxy substituent while holding the other constant, these workers synthesized twenty-eight unsymmetrical esters ($R \neq R'$) to include all combinations of terminal n-alkoxy groups from CH_3O through n-$C_8H_{17}O$. In this manner lower melting points were achieved by introducing dissymmetry into the molecule.

Nematic-isotropic transition temperatures decline regularly with increasing length of the varied n-alkyl chain. Also, as the constant alkoxy group increases in length, the transition temperatures shift progresively to lower and lower temperatures. Both results are analogous with those obtained for the homologous series of 4-n-alkoxybenzoic acids. Again the effect of increasing the alkyl chain length causes a decrease in the thermal stability of the nematic mesophase as a result of a decrease in rigidity and polarity of the molecule.

It has been shown[56,57] that replacement of the alkoxy end groups by substituents such as Cl, NO_2 or CN does not destroy the mesomorphism of this system. In a recent study by Schroeder and Bristol,[57] it was found that relatively small, polar, terminal groups (CN, NO_2, COOMe, halogen, EtO, MeO, Me) give the highest melting points while large, relatively nonpolar, long chain alkoxy groups give the lowest. The nematic-isotropic transition temperatures are similarly affected by end group size and polarity. Small polar groups located terminally give the highest values and more bulky, nonpolar groups give the lowest. Of the 63 presently known substituted p-phenylene dibenzoates, 56 of them are nematic. These results suggest that even more drastic alterations in chemical constitution are possible without destroying the mesomorphism of the system.

Bulky groups located terminally are not nearly as deleterious as the same bulk located laterally. The 3-halo derivatives of the 4-n-dodecyloxybenzoic acids will serve to illustrate this effect (Table 3). Inspection of Table 3 reveals that the 3-halo substituent lowers both the nematic and smectic thermal stabilities. As the size of the halo substituent increases, both the smectic-nematic and nematic-isotropic transition temperatures decrease, and in the bromo derivative, liquid crystallinity is completely eliminated.

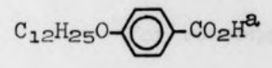
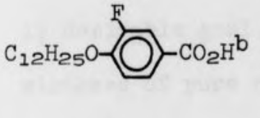
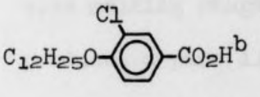
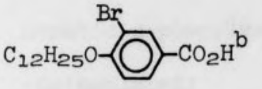
Lateral substitution decreases the length/breadth ratio resulting in a loss of geometric anisotropy. Molecular breadth, of course, increases as the size of the halo substituent increases. This increase in the width of the molecule forces it farther and farther apart from neighboring molecules and in doing so decreases the lateral, intermolecular cohesive forces. Both the smectic and nematic mesophases depend more or less on these cohesive forces to maintain a parallel orientation of molecules.

Now if the substituent group introduces a dipole into the molecule, then the lateral and terminal attractive forces may be enhanced. This will, however, depend on the total polarizability of the parent molecule. If the increase in polarizability is substantial, an increase in the induced dipole and dispersion forces will result, and the breadth increasing effect will be diminished.[58]

Thus, the introduction of a substituent into the side position has two opposing effects: (1) a decrease in lateral attractions because of

TABLE 3

LATERALLY SUBSTITUTED 4-n-DODECYLOXYBENZOIC ACIDS

	Transition Temperatures, °C	
	Smectic-Nematic	Nematic-Isotropic
	129	137
	113	114.5
	(88)[c]	101.5
	-[d]	-[d]

[a] Reference 33.

[b] Reference 59.

[c] Monotropic transition.

[d] Not mesomorphic.

the increased width of the molecule and (2) an enhancement of lateral attractive forces from the increased polarity and polarizability. Although effect (1) generally predominates, there are cases where mesomorphic stability is greater for laterally substituted than for unsubstituted compounds.[60]

Purpose of this Investigation

For reasons outlined earlier, the preparation of liquid crystalline materials with wide mesomorphic ranges spanning room temperature is a highly desirable goal. Early investigations in this direction employed binary mixtures of pure compounds[61,62] but, because mixtures typically exhibit wide melting ranges and because useful compositions are difficult to reproduce, a pure liquid crystalline compound is still more desirable.

The original purpose of this study was to prepare low melting, nematic p-phenylene dibenzoates and related esters. Three approaches were contemplated:

(1) Alteration of the central p-phenylene group. Dewar and Goldberg[63] studied the role of this group and the effects of its replacement by 1,4-bicyclo[2.2.2]octylene and 1,4-cyclohexylene. However, there is only one reference[54] to simple substitution of the central p-phenylene unit, so this appeared to be a fruitful area to explore.

(2) Alteration of the benzoate groups by substitution. Although many terminal substituents have been studied, some have not and there have been no reports of lateral substitution.

(3) The use of cinnamate rather than benzoate and of m-phenylene rather than p-phenylene groups. Neither of these approaches has been previously reported.

Although the original objective was maintained throughout the project, it became clear as the work progressed that the effects of lateral substitution were particularly interesting. Accordingly, special emphasis was placed on this area of the research.

CHAPTER II

EXPERIMENTAL

Preliminary mesomorphic and polymorphic transition temperatures as well as normal melting points were determined using a Thomas-Hoover melting point apparatus. Subsequent optical determinations were made using a Reichert "Thermopan" polarizing microscope equipped with a Kofler micro hot stage. The instrument had been calibrated against pure melting point standards.

Where applicable, polymorphic transitions were checked using a Perkin-Elmer differential scanning calorimeter, model DSC-1B. IR spectra were obtained on a Perkin-Elmer model 457 grating infrared spectrophotometer using the KBr pellet technique.

Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Satisfactory analytical data (±0.4% for C and H) were obtained for all products.

Preparation of Substituted Benzoic Acids

The 3,4-dimethyl, _p_-cyano, _tert_-butyl, isopropyl (Eastman), 3,5-dimethyl (Aldrich), _p_-methoxy (MCB), _n_-hexyloxy and _n_-octyloxy (Frinton) acids were available as commerical products.

_p_-_n_-Butylbenzoic acid was prepared by hydrolysis of _p_-_n_-butylbenzonitrile. In a 50 ml round bottom flask were placed 0.8 g of _p_-_n_-butylbenzonitrile and 10 ml of a mixture containing 20% NaOH, 66% water and 14% ethanol. After refluxing mildly overnight, the reaction mixture was diluted and acidified with hydrochloric acid. The crude product was collected by filtration, washed with water, and dissolved in 100 ml of 15% aqueous NaOH solution. The acid was precipitated with dilute hydrochloric acid, washed with water, dried and dissolved in 45 ml of 95% ethanol. The solution was treated with Norit and filtered hot through Celite. As excess ethanol was evaporated, 10 ml of distilled water was gradually added to the flask so that crystallization was from essentially a 50/50 mixture. The acid crystallized as white needles, mp 98° nematic-isotropic transition at 112° (lit. 102, 112°[64]; 98, 112°[65]). The p-n-butylbenzonitrile reactant was provided by Dr. J. P. Schroeder. Hydrolysis of the nitrile using a 30% aqueous solution of NaOH was found to proceed with much less facility than the above described synthesis. p-Methoxycinnamic acid was also available as a commercial product (Aldrich).

Preparation of Substituted Benzoyl and Cinnamoyl Chlorides

p-Methoxy (Eastman) and p-nitrobenzoyl chloride (Eastman, practical) were purchased. The others were prepared from the corresponding acids by treatment with a fifteen molar excess of thionyl chloride. To a 50 ml round bottom flask containing the appropriate acid, $SOCl_2$ and several drops of anhydrous pyridine as catalyst were introduced. The flask was attached to a reflux condenser fitted with a $CaCl_2$ drying tube and the contents refluxed mildly with stirring for 45 minutes. The excess $SOCl_2$ was then distilled and the last traces removed with an aspirator. The residual acid chloride was used without further purification.

Preparation of Substituted Hydroquinones

Hydroquinone (MCB), 2,5-dichlorohydroquinone, methylhydroquinone (Eastman), chlorohydroquinone, bromohydroquinone (Eastman, practical) and resorcinol (Fisher) were purchased. However, the bromohydroquinone was found to be impure, mp 100-120 (lit[66] 110-111°). Material sublimed from the commercial product and recrystallized several times from various solvents also melted over a wide range. A thorough search of the literature[67-72] yielded a plausible synthetic route involving bromination of hydroquinone with dioxane dibromide,[67] a mild brominating agent.

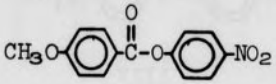
To 25 g of dioxane, distilled from CaH_2, was added, with cooling, 49.5 g of bromine. The mixture quickly solidified into yellow-orange crystals of dioxane dibromide. To the solid mass was added 50 ml of cold petroleum ether and the slurry stirred briefly. The yellow-orange product was collected on a porous funnel, dried briefly by pulling air through the sample, and stored in an air-tight container.

Bromination of hydroquinone with dioxane dibromide was attempted several times with apparent oxidation or formation of a quinhydrone. The following preparation was successful: Hydroquinone was recrystallized from a benzene/ether mixture after treatment with Norit. Freshly recrystallized hydroquinone (2.2 g) and 50 ml of absolute ether were added to a 150 ml three neck flask and the mixture stirred until solution was complete. The flask was fitted with a dropping funnel containing 5.0 g of dioxane dibromide dissolved in 100 ml of absolute ether. The flask was placed in an ice bath and, when the contents had reached 0°, the dioxane dibromide solution was allowed to run in over a period of 40 minutes. (After 30 minutes the dioxane dibromide solution separated into two layers; apparently a characteristic phenomenon of this mixture. The dioxane dibromide solution was shaken occasionally in an attempt to prevent this separation and mix the contents.) After the dioxane dibromide had been added, the ice bath was removed and the contents were allowed to warm to 18° over a period of 40 minutes. At this point the reaction was quenched by the addition of 25 ml of distilled water. The reaction mixture was transferred to a separatory funnel and the lower water layer drawn off. The ether layer was washed with an additional 25 ml of water before drying over anhydrous Na_2SO_4. After drying overnight, the ether solution was filtered through a cotton plug and the solvent evaporated on a rotary evaporator. A thick, brown oil remained, which was extracted with 150 ml of benzene and filtered to remove the unreacted hydroquinone. The benzene solution was treated with Norit, filtered, then placed on a hot plate and allowed to boil. Heptane was gradually added as the benzene distilled so that a heptane solution was ultimately attained. The product precipitated from the hot solution when a volume of 125 ml was reached. It was recovered by decantation and, after recrystallization from 150 ml of heptane, melted at 110-112°.

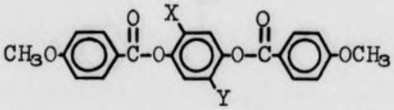
Preparation of Compound I (Figure 3)

In a 50 ml Erlenmeyer flask, 0.51 g (0.0037 mole) of p-nitrophenol was dissolved in 10 ml of dry pyridine with stirring. After addition of 1.25 g (0.0073 mole) of anisoyl chloride and brief stirring, the flask was stoppered. A precipitate was observed within one minute. The reaction mixture was allowed to stand overnight and was then poured into 100 ml of

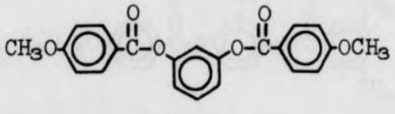
Figure 3. Esters Synthesized in this Study



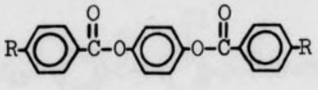
I



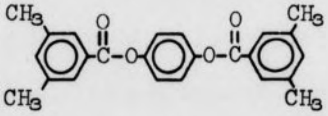
II a X = CH_3, Y = H
b X = Br, Y = H
c X = Cl, Y = H
d X = Cl, Y = Cl



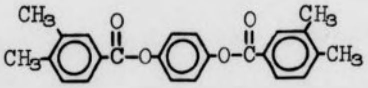
III



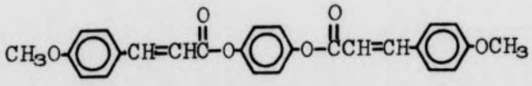
IV a R = <u>i</u>-propyl
b R = <u>tert</u>-butyl
c R = CN
d R = NO_2



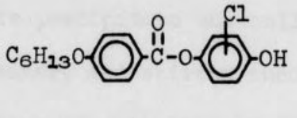
V



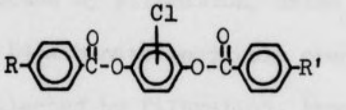
VI



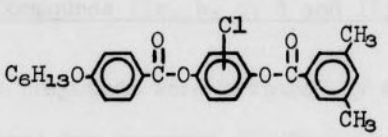
VII



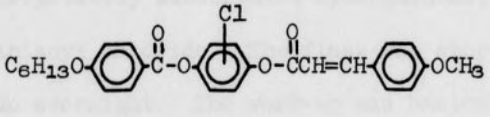
VIII



IX a $R = R' = \underline{n}\text{-}C_6H_{13}O$
b $R = \underline{n}\text{-}C_6H_{13}O$, $R' = \underline{n}\text{-}C_4H_9$
c $R = \underline{n}\text{-}C_6H_{13}O$, $R' = \underline{n}\text{-}C_8H_{17}O$



X



XI

distilled water. The white precipitate was collected on a Hirsch funnel, transferred to a 250 ml beaker, and stirred successively for 30 minutes each with two 100 ml portions of saturated aqueous $NaHCO_3$ solution. The insoluble solid was collected by filtration, dried and stirred with 100 ml of ethanol to remove any bicarbonate-insoluble o-anisic acid. The ethanol-insoluble product was collected by filtration, treated with Norit, filtered hot through Celite and recrystallized from 25 ml of 95% ethanol.

Preparation of Compounds IIa, b, c, d and III (Figure 3)

Method A. These compounds were prepared by essentially the same procedure as that outlined for compound I. To a pyridine solution of resorcinol, or the appropriately substituted hydroquinone, was added a four molar excess of anisoyl chloride. The flask was stoppered and the reaction allowed to run overnight. The work-up was basically the same as that outlined for compound I.

It should be noted that compound IIb synthesized from commercial bromohydroquinone melted over a wide range (167-180°). Since the carbon-hydrogen analysis was good, the presence of isomers was suspected. In the commercial anisoyl chloride used, there was evidence for ortho-anisoyl chloride being present. This could react in the same fashion as the para-isomer to give a mixture of isomers in the final product and, thus, a wide melting range. A base-catalyzed hydrolysis of compound IIb gave only para-anisic acid as product. A thin layer chromatogram on silica gel in several solvents and mixtures of solvents gave one spot. A reaction of pure para-anisoyl chloride with commercial bromohydroquinone also gave a product with a wide melting range. Synthesis of compound IIb using bromohydroquinone prepared as previously outlined gave a good carbon-hydrogen analysis, but the product, after recrystallization from ethyl acetate, melted over two distinct temperature ranges (162.5-164, 168.5-170). A DSC trace gave two endothermic peaks with relative intensities of 1:2. The temperatures at which these peaks occurred (163° and 172°) corresponded very closely with those obtained with the hot stage microscope. Cooling the sample and then reheating in the DSC gave a single sharp peak at 177.5° with a weak shoulder on the low temperature side. This behavior suggests that more than one crystalline modification (polymorphism) is present in compound IIb. Recrystallization from a different solvent or simply heating a compound will sometimes convert one polymorph to another and, indeed, material recrystallized from ethanol gave mainly one peak at 177.5°.

The reaction of anisoyl chloride with 2,5-di-*tert*-butylhydroquinone gave three products, but since none were liquid crystalline, they were not examined further.

Method B. An alternate procedure using classic Schotten-Baumann conditions was also tried. In a 50 ml Erlenmeyer flask were placed a magnetic stirring bar, 8 ml of water and 2.0 g of NaOH. The mixture was stirred until the NaOH dissolved. To this solution was added 0.0010 mole of resorcinol, or the appropriately substituted hydroquinone, and stirring was continued until the phenol had dissolved. After cooling to room temperature, 0.0040 mole of anisoyl chloride was added and the mixture stirred for one hour or until a precipitate separated. The insoluble product was collected by suction on a Hirsch funnel, then washed with water and dried. In general, yields were lower for this method than for method A. In both methods, excess acyl chloride could be recovered (as the acid) by treating the alkaline filtrate with excess hydrochloric acid.

Compounds IIa-IId were prepared by both method A and method B.

Preparation of Compounds IVa, b, c and d, V, VI and VII (Figure 3)

Compound IVa was prepared from hydroquinone and a four molar excess of p-isopropylbenzoyl chloride by method B above. Compounds IVb-VII were prepared by reacting hydroquinone with a four molar excess of the appropriate acyl chloride in accordance with the conditions outlined for compound I. Compound V melted at different temperatures depending on the solvent chosen for recrystallization. From 95% ethanol small white needles melting at 156-158.5° were obtained. The same material recrystallized from cyclohexane gave a melting point of 170-172.5°. After standing atop a warm drying oven for two weeks, the melting point was again taken. Surprisingly, the compound began melting at 156°, then no further melting was observed until the temperature reached 170.5° where the compound again began melting and melted until 172.5°. Compound VII formed deeply colored by-products and required washing with acetone for their removal.

Preparation of Compound VIII (Figure 3)

A saturated solution of 14.75 g (0.10 mole) of chlorohydroquinone in 50 ml of dry pyridine was prepared in a 125 ml Erlenmeyer flask and cooled in an ice bath. A solution of 4.09 g (0.017 mole) of p-n-hexyloxybenzoyl chloride in 40 ml of dry pyridine was also cooled in an ice bath and then slowly added to the saturated solution of chlorohydroquinone. A $CaCl_2$

drying tube was attached to the flask and the contents were allowed to react overnight. The reaction mixture was poured into 300 ml of 2N HCl and the resulting slurry was cooled and stirred for 30 minutes. The acid wash was decanted and replaced by 250 ml of saturated aqueous $NaHCO_3$ solution. The contents were warmed and stirred for two hours, then cooled in an ice bath until the oily precipitate stiffened. The $NaHCO_3$ solution was then decanted and replaced by a second 250 ml $NaHCO_3$ wash. This mixture was warmed and stirred for one hour, then cooled and the supernatant liquid decanted. After washing the gummy residue with water, 75 ml of 95% ethanol was introduced and the mixture stirred for 20 minutes. Filtration gave compound IXa as the insoluble by-product. Compound VIII was precipitated from the ethanol by the addition of 150 ml of distilled water. There were two forms of material present: a white crystalline product and an amber oil on the bottom of the beaker. The supernatant liquid was decanted into a separatory funnel and extracted with three 50 ml portions of ether. The oil and solid material were also extracted with ether. The ether extracts were combined and washed with water, then aqueous $NaHCO_3$ solution, then with water again. The ether solution was dried over anhydrous Na_2SO_4, treated with Norit and filtered through Celite. The ether was evaporated on a rotary evaporator, leaving a thick, amber oil in the flask. To the flask was added sufficient 90-120° ligroin to dissolve the oily material. The volume was reduced to 20 ml before allowing the flask to cool for several hours. Scratching induced immediate crystallization of compound VIII.

Preparation of Compounds IXa, b, c, X and XI (Figure 3)

Typically a solution of 0.001 mole of compound VIII in 10 ml of dry pyridine was added to a 50 ml round bottom flask containing the appropriate acid chloride. A $CaCl_2$ drying tube was then attached and the mixture was allowed to react overnight. Work-up was the same as that described in Method A. p-Methoxycinnamoyl chloride apparently reacts with pyridine to form a stable and highly colored compound. When pyridine alone is added to p-methoxycinnamoyl chloride, a violent reaction occurs with formation of a highly colored (red-amber) solid material. For this reason, compound XI was prepared in benzene.

A summary of the data for these compounds will be found in Table 4.

TABLE 4

DATA FOR ESTERS PREPARED IN THIS WORK[a]

Compound[b]	Recrystn Solvent	% Yield	Melting Range, °C	Nematic Range, °C	%C Calc.	%C Found	%H Calc.	%H Found
I	EtOH	94	165-166	_____[c]	61.53	61.43	4.07	4.08
IIa	EtOH/Acetone (70/30)	96	169-170	170-250[d]	70.39	70.58	5.15	5.21
IIb	EtOAc	94	162.5-164, 168.5-170[e]	170-249.5[f]	57.78	58.12	3.75	3.69
IIc	EtOAc	97	165-166.5	166.5-254[g]	64.00	64.12	4.16	4.28
IId	Dioxane	94	234.5-236	_____[h]	59.07	58.91	3.61	3.55
III	EtOH	92	137-138	_____[c]	69.83	69.78	4.80	4.83
IVa	EtOH	8	160.5-161.5	_____[c]	77.59	77.84	6.51	6.66
IVb	EtOAc	58	202-204	_____[c]	78.12	78.18	7.02	7.02
IVc	Dioxane	74	329.5-331.5	331.5-353.5	71.74	71.54	3.29	3.30
IVd	Dioxane	55	260-262	262-281[i]	58.83	58.89	2.96	3.10
V	EtOH	73	156-158.5, 170.5-172.5[e]	_____[c]	76.97	76.88	5.93	6.01
VI	Acetone	16	207-208	_____[c]	76.97	77.02	5.93	5.98
VII	Dioxane	64	209-214	214-(337)[j]	72.54	72.30	5.16	5.05
VIII	Ligroin	53	109-112	_____[c]	65.41	65.43	6.08	5.94
IXa	EtOH/Dioxane	47	86-121[e]	121-169.5	69.48	69.23	6.76	6.68
IXb	Pentane	8	70-78	78-158	70.77	70.72	6.55	6.55
IXc	Hexanes	52	75-77	77-161.5	70.26	70.50	7.12	7.28
X	MeOH	30	96.5-102.5	_____[c]	69.91	69.70	6.09	6.00
XI	Ligroin	49	119-167	167-238	68.42	68.18	5.75	5.72

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[a] All data in this table are for compounds prepared by method A.

[b] Compounds VII, VIII, IXb, IXc, X and XI are apparently mixtures of isomers.

[c] Not liquid crystalline.

[d] Monotropic smectic transition observed at 126°.

[e] Apparently more than one crystalline modification exists for this compound.

[f] Monotropic smectic transition observed at 130°.

[g] Monotropic smectic transition observed at 127.5°.

[h] Monotropic isotropic-nematic transition at 215°.

[i] Mp 260° and nematic-isotropic transition temperature 266° have been previously reported.[56]

[j] Decomposition begins.

CHAPTER III

RESULTS AND DISCUSSION

In an effort to present an organized discussion of a fairly large number of compounds which vary structurally, in some cases quite markedly, this section will follow the compound order set forth in Figure 3. This is not necessarily the order in which the compounds were prepared and should not be construed to be any relative order of mesomorphic tendencies.

Compound I

Low melting liquid crystalline materials with wide nematic ranges spanning room temperature are of great technological importance. Many recent studies in this direction include the 1,4-phenylene ester system.[53-57,64] The majority of these investigations, however, involve relatively large molecules (three phenylene rings) with dissymmetry being introduced by various terminal or lateral substituents. Generally, esters with three phenylene rings have higher crystal-nematic transition temperatures than do systems containing only two. 4-Alkoxyphenyl 4-alkyloxycarbonyloxybenzoates,[73] 4-substituted phenyl 4-n-hexyloxybenzoates[74] and, in general, many 4,4'-disubstituted phenyl benzoates[75,76] have been recently prepared and found to have relatively low crystal-nematic transition temperatures. These studies use unsymmetrical long chain terminal substituents to achieve lower melting points.

It was pointed out earlier that when the transition temperatures for a homologous series, e.g., the p-n-alkoxybenzoic acids, are plotted against the number of carbon atoms in the alkyl chain, regular declines in the melting point and nematic-isotropic transition temperature occur. Since the melting characteristics of a compound are largely determined by the intermolecular attractive forces in the crystalline lattice, then separating the centers of charge by increasing the alkyl chain length could produce lower melting materials. Further increasing the alkyl chain length might lead to still lower melting points, but past studies have shown that chain lengths of eight or more carbon atoms result in an increase of the ratio of lateral to terminal attractions and the appearance of smectic behavior. Additional increases in the chain length would then result in increased smectic thermal stability and shorter nematic ranges. Although relatively low melting substituted phenyl benzoates have been obtained by unsymmetrical terminal substitution with alkoxy chains, none have nematic ranges spanning room temperature.

Since there appeared to be little work involving substitution of relatively compact and polar groups into these shorter molecules, this seemed to be an interesting area to explore briefly. Compound I is unsymmetrical and contains relatively compact and polar MeO and NO_2 groups in terminal positions. In the p-phenylene dibenzoate system, these groups give high melting points (262° and 222° for compounds IVd and IV, R = MeO[53]) and high nematic-isotropic transition temperatures (281° and 300°, respectively).

As shown by the data in Table 4, compound I has a relatively high melting point and is not liquid crystalline. Although I is substantially lower in molecular weight than a system containing three phenylene rings, the presence of highly polar terminal groups has the deleterious effect of increasing the melting point to a relatively high 166°, thus submerging any low temperature liquid crystallinity which may exist. Unfortunately, this compound does not supercool below 133°. It is possible that a nematic mesophase might be formed below this temperature.

Now, replacing terminal alkyl chains with compact groups represents a rather dramatic decrease in the length/breadth ratio of the molecule. The resulting loss in geometric anisotropy is apparently the dominant factor accounting for the absence of liquid crystallinity in I. This is evidenced by the fact that IVd, a similar but longer molecule, is mesomorphic.

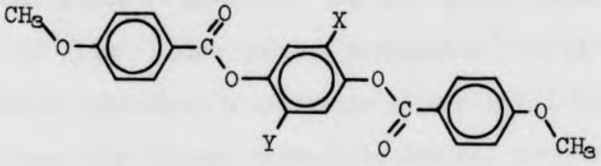
From these results one may conclude that ester systems containing only two phenylene rings terminally substituted by compact and relatively polar groups are not likely to be mesomorphic. However, more work is needed in this area before any quantitative and more complete qualitative relationships between size and polarity of substituent groups and mesomorphism can be established.

Compounds IIa-d

The effects of lateral substitution have been illustrated and discussed in some detail in the introduction to this thesis. In most cases, substituents which occupy positions along the side of the long molecule decrease the thermal stabilities of both the smectic and nematic mesophases. Therefore, any substitution leading to an increase in molecular breadth will decrease the mesomorphic thermal stabilities as well as lower the melting point. Compounds IIa-d, for the most part, are no exception. Table 5 shows that nematic-isotropic transition temperatures are indeed much lower

TABLE 5

LATERAL SUBSTITUENT EFFECTS FOR ESTERS IIa-d



Substituents(X,Y)	H,H	Cl,H	Br,H	Me,H	Cl,Cl
Melting Point(°C)	222[a]	166.5	(164,170)[b]	170	236
Nematic-Isotropic Transition Temperature(°C)	300[a]	254	249.5	250	(215)[c]
Nematic Range(°C)	78	87.5	79.5	80	-
Smectic-Nematic Transition Temperature(°C)	-	(127.5)[d]	(130)[d]	(126)[d]	-
Δt(H-X)Nematic-Isotropic Transition Temperature(°C)	-	-46	-50.5	-50	-85
Sum of Van der Waals Radii of X and Y (Å)	2.16	2.88	3.03	3.08	3.60
Increase in Mol Breadth Relative to H,H(Å)	-	0.72	0.87	0.92	1.44

[a] Reference 53.

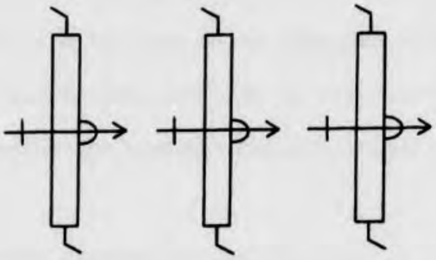
[b] Apparently more than one crystalline modification exists for this compound.

[c] Monotropic isotropic-nematic transition.

[d] Monotropic nematic-smectic transition.

(43-82°) for the laterally substituted than for the corresponding unsubstituted compound. This decrease is directly attributable to an increase in breadth of 0.72Å over the unsubstituted compound.

It is interesting to speculate why the chloro, bromo and methyl substituted esters (IIa-c) show smectic mesophases. It is well known that a substituent which introduces a crosswise dipole into a linear molecule is likely to enhance the lateral attractive forces, resulting in increased smectic behavior. In compounds IIa-c, the lateral attractions may be enhanced by the reinforcement of dipoles. These dipoles, which operate across the long axes of the molecule, should reinforce and increase the lateral attractions. This would appear to be a good argument since the unsubstituted ester shows no smectic behavior. However, one should bear in mind that the substituted molecules are now separated more than the parent compound and, on this basis, a reduction in smectic behavior might be expected. Although the effects of lateral substitution will vary from one system to another, the molecular geometry of compounds of series II is such that the full breadth increasing effect of the substituent group is felt and a reduction in smectic thermal stability should occur.



The fact that IIa-c show smectic mesophases is anomalous in another respect. Compound IXa, which is also laterally substituted, shows <u>no</u>

smectic mesophase even when supercooled to 54°. Replacement of the chloro substituent in IXa with a methyl group also gives a compound that shows no smectic mesomorphism.[54] Now, compounds IIa-c and IXa are similar structurally, the principal difference being that IXa has longer terminal alkyl groups than does IIa-c. From past experiences with homologous series of liquid crystalline compounds, longer chain lengths are known to favor smectic behavior. It would then not be illogical to assume that IXa should show a smectic mesophase. This seemingly enigmatic behavior could be explained by assuming that the parent compound for series II esters and IXa could not be supercooled adequately and that the mesophase is stable only at temperatures which are too low to be obtained without crystallization. However, this would not explain why IXa is not smectic at 54°, a temperature which is far below the nematic-smectic transition temperatures of IIa-c.

A more plausible explanation may be that in IIa-c the dipolar effect dominates over the breadth increasing effect of the lateral substituent. Thus, the lateral cohesions are increased and an increase in smectic thermal stability results. Although the same effect is present in IXa, there is the additional factor of the bulky end groups. These groups can enhance the lateral attractions weakly when close approach of molecules is possible. When it is not, as in IXa (because of the Cl group), these groups contribute little or nothing to the lateral cohesions. In fact, their presence may be detrimental because of their great bulk.

The melting points of the chloro, bromo and methyl substituted compounds (IIa-c) are lower but that of the dichloro compound IId is 23° higher than the melting point of the corresponding unsubstituted compound.

The higher melting point for IId may be attributed to an increase in molecular weight and an increase in intermolecular attractive forces with no loss in symmetry.

It should be pointed out that IIb melted over two distinct temperature ranges encompassing 7.5°. Although there is evidence to show that IIb is polymorphous, there may be some question as to its purity. But comparison with similarly substituted compounds, e.g., IIa and IIc, shows that melting point and nematic-isotropic transition temperatures for IIb are of the proper relative magnitude. For example, it is well known that within a particular liquid crystalline system, a decline in melting point and mesomorphic transition temperatures is likely to occur on passing from laterally substituted fluoro to chloro, chloro to bromo, and bromo to iodo.[77] Comparison of IIb with IIc shows that a decline of 4.5° in the nematic-isotropic transition temperature has indeed occurred. This value is very acceptable. The increase in molecular breadth on passing from chloro to bromo is about 0.15Å. On passing from chloro to dichloro (IIc to IId) the increase is about 0.72Å with a decline of 39° in the nematic-isotropic transition temperature. This represents a decline in transition temperature of 54° for each Ångstrom unit increase in molecular breadth. On this basis, a decline of 8.1° in the nematic-isotropic transition temperature should occur on passing from chloro to bromo (IIc to IId). The fact that a decline of only 4.5° is observed is probably due to the increased polarizability of the larger bromo group, which would enhance the intermolecular cohesions and result in a more stable nematic phase.

Compound III

Much work has been done in attempts to relate molecular structure to mesomorphism, but these studies have centered around the effects of terminal or lateral substituents. Now, the large majority of liquid crystalline compounds have rod-shaped structures; such structures favor the parallel orientation of molecules in the mesophase. Dewar and Goldberg[63] have studied the effects of replacing 1,4-phenylene units in the 1,4-phenylene dibenzoate system with 1,4 bicyclo[2.2.2]octylene and trans-1,4-cyclohexylene units. Although these units maintain the linearity of the system, molecules containing the 1,4-cyclohexylene group are more flexible and a decrease in rigidity results. This decrease leads to a decline in nematic thermal stability.

Replacement of the 1,4-phenylene unit by these saturated groups also represents a significant decrease in the overall polarizability of the system. The polarizable π electrons of the benzene rings induce strong intermolecular Van der Waals attractions. In compound III, the total aromaticity and rigidity of the system remain unchanged relative to its 1,4-phenylene analog, but the linearity of the molecule has been somewhat disrupted. Models show that III is wider than IId, even when the more linear cis configuration is adopted, but is certainly no wider than cholesteryl benzoate. Yet, III exhibits no liquid crystallinity whatsoever. The significance of this result should be emphasized. The 1,4-phenylene analog (IV, R = MeO[53]) melts at 222° to a nematic mesophase which is stable to 300°. Compound III melts at 138° to isotropic liquid. I.e., the simple change of the central group from 1,4- to 1,3-phenylene lowers the melting point 84° and the nematic-isotropic transition temperature at least 162°.

This is a striking example of the effects of molecular symmetry on melting point and of molecular linearity on mesomorphism.

Compounds IVa-d

These compounds illustrate the effects of end group bulk and polarity on melting points and nematic-isotropic transition temperatures. Compounds IVa and b are not mesomorphic, while the more compact methyl-terminated ester (IV, R = CH_3)[57] has a nematic range of 4.5°. The bulk of the i-Pr and t-Bu groups inhibit the close approach of adjacent molecules and, being relatively nonpolar, they contribute very little to intermolecular attraction. For these reasons, IVa and b are not mesomorphic.

Compounds IVa-d are all symmetrical. Symmetry will favor high melting temperatures, but the strong intermolecular attractive forces induced by the polar terminal groups in IVc and d result in higher melting temperatures and greater mesomorphic thermal stability.

Compounds V and VI

Up to this point, lateral substitution has been on the central ring, but in this case, substituents occupy side positions on both terminal benzene rings. Compounds V and VI are isomeric, the only difference being two methyl groups occupying either the 4,4' or 5,5' positions. Now, both compounds have a great deal of symmetry associated with them, but V is the wider molecule. This probably accounts for the higher melting point of VI. Both compounds melt at fairly high temperatures and this may be one reason why they are not liquid crystalline.

Compound VI is similar to IV, R = CH_3[57] where methyl groups in the 3 and 3' positions are not present. This compound has a nematic-isotropic transition temperature of 236°. Since compound VI has a relatively high melting point of 208°, it is not too surprising that a methyl group introduced into the 3 and 3' positions, so that the width of the molecule is increased, destroys mesomorphism altogether.

Compound VI is approximately equal in width to IIa-c and is certainly no wider than IId. Therefore, it is not the width alone that is responsible for the absence of liquid crystallinity. More than likely it is a combination of the increased width and the absence of polar groups.

Compounds VII-XI

These compounds will be considered as a group because all, except IXa, are believed to be mixtures of isomers. The use of mixtures is a common technique for lowering the melting point of mesomorphic materials.[61,62,78] In addition to being mixtures, all except VII have a bulky lateral chloro substituent and IXb, IXc, X and XI have two different end groups, at least one of which is a long alkyl chain. These, too, are familiar techniques for inducing melting point depression.[55] It is not surprising, therefore, that the lowest melting products are in this group.

The unsymmetrical compounds IXb, IXc, X and XI were prepared by reacting VIII with the appropriate acyl halide. Compound VIII was prepared by the nucleophilic displacement of the chloro group from p-n-hexyloxybenzoyl chloride by excess chlorohydroquinone. This can occur with either oxygen atom of chlorohydroquinone. Therefore, VIII is probably a mixture of two compounds: one with the chlorine atom ortho to the ester linkage and one with the chlorine atom in the meta position. It is also probable that more of the meta isomer is formed because of inductive effects and steric factors. Formation of the ortho isomer is less favored because attack by the oxygen of chlorohydroquinone is sterically hindered by the bulky chloro group in the ortho position. Also, because of the inductive effect of the chloro group, the nucleophilicity of the closest oxygen atom is decreased.

This could explain, in part, why yields for these unsymmetrical esters are lower than, for example, yields for esters IIa-c. In the synthesis of compounds IIa-c an excess of acyl halide was used, while in the preparation of VIII an excess of chlorohydroquinone was employed. In the synthesis of VIII, this excess will surely favor formation of the meta isomer for the reasons just discussed. The subsequent reaction of the resulting monoester (mainly ortho-chlorophenol) with an acyl halide to give the unsymmetrical diester should proceed with difficulty and, therefore, in low yield. The synthesis of IIa-c involve the same overall process, but competition between the two different hydroxyl groups in chlorohydroquinone for reaction with acyl halide is probably less selective when the latter is present in excess. As a result, yields are higher.

Regardless of which isomer is favored, it is probable that a mixture of two isomers is present in VIII. When VIII is treated with the appropriate acyl halide to produce the unsymmetrical diesters IXb, IXc, X and XI, the isomerism is carried forward into the final product. Since these compounds are mixtures, they have wide melting ranges. It is well known that when two miscible mesomorphic compounds are mixed, their melting points and mesomorphic transition temperatures are depressed. The extent to which the mesomorphic transition temperatures are depressed depends on the molecular structures of the components. If these are very different, mesomorphism may be eliminated altogether. But, if the two compounds are similar, as is the case here, mesomorphism may persist to a high temperature.

For the reasons just outlined, nearly all the esters in this series exhibit wider melting ranges than expected for pure single compounds. These compounds were recrystallized repeatedly until a constant melting point and nematic-isotropic transition temperature were obtained. In addition, they gave analyses within ± 0.25% and ± 0.16% for carbon and hydrogen, respectively. Also, comparison with other liquid crystalline compounds that are similar in structure reveals that the transition temperatures are of the proper relative magnitude. Thus, it is believed that the broad melting ranges are the result of isomerism rather than extraneous impurities.

In VII, there is the possibility of three isomers, cis-cis, cis-trans, and trans-trans, being present, since the commercial p-methoxycinnamic acid used in its preparation is not specified as being either cis or trans. It is unlikely, however, that a significant amount of the cis isomer is present. The melting point agrees with that of the trans isomer (174°) and a DSC trace shows no peak for the cis isomer (lit[79] m.p. 66°). However, the trans acid is known to be sensitive to both light and heat with apparent isomerization to the cis form.

Now, in the preparation of esters VII and XI both the acid and the acid chloride were exposed to light and heat. Melting point and mesomorphic transition determinations required the use of heat and light. Thus, it is possible that a significant amount of the cis isomer is present in these two products. If cis-trans isomerism were obtained in XI, a mixture of four isomers would be present (ortho-cis and trans, meta-cis and trans).

As a result of the double bond in the central linkage unit, compounds VII and XI have very long, rigid, rod-shaped structures. Such structures favor mesomorphism. In addition, the polarizable, π cloud of the double bonds may contribute to the intermolecular cohesions. Thus, VII and XI exhibit very high mesophase stability (337° and 238°, respectively) and relatively high crystal-nematic transition temperatures.

The effects of lateral substitution have already been discussed and it is clear that lower melting points have been attained in this manner. All the unsymmetrical esters except for X are liquid crystalline. Compound X not only has a central lateral substituent but also has terminal substituents in the 3 and 5 positions. The increase in breadth in X is apparently just too great for mesomorphism to survive.

Because these compounds are unsymmetrical, there is the chance for positional isomerism with respect to the lateral chloro substituent. Unsymmetrical molecules generally have lower melting points and lower mesomorphic thermal stability than their symmetrical analogs. In addition, the presence of the lateral chloro substituent depresses the melting point and transition temperatures still further. But in some of the unsymmetrical esters, e.g., IXb and c, the position of the chloro group relative to the terminal substituents is less important than in others. Although compounds IX b and c are unsymmetrical, they are not nearly so unsymmetrical as esters X and XI. Thus, positional isomers based on the chloro group in compounds X and XI are very different in molecular structure when compared to those from IXb and c.

Three effects have been used to achieve lower melting points: (1) dissymmetry, (2) the presence of a bulky, lateral chloro substituent and (3) the presence of positional isomers. The combination of these effects in IXb and c results in materials having relatively low melting points (78° and 77°, respectively) with retention of relatively high nematic thermal stability (158° and 161°, respectively). These are the lowest melting p-phenylene dibenzoates synthesized to date. Although these compounds are still too high melting to be of practical interest, their high mesomorphic thermal stability suggests that this chemically stable system might survive still more drastic structural variations and remain mesomorphic. Mixtures containing these compounds should be even lower melting, with nematic mesophases that are stable at or near room temperature.

CHAPTER IV

SUMMARY

Although 1,4-phenylene ester systems containing only two phenylene rings terminally substituted by long alkyl or similar groups are mesomorphic, terminal substitution with compact, polar groups (MeO and NO_2) into this system is likely to result in complete disappearance of mesomorphism and higher melting points. Because these groups are smaller, a substantial decrease in the length/breadth ratio of the molecule results. This decrease, coupled with the higher melting points resulting from the high polarity of these groups, is sufficient to eliminate mesomorphism altogether. In the 1,4-phenylene dibenzoate system, these groups give still higher melting points and mesomorphic transition temperatures. Bulky, relatively nonpolar i-Pr and t-Bu groups, because they inhibit the close approach of adjacent molecules, eliminate liquid crystallinity.

The effects of lateral substitution in the 1,4-phenylene dibenzoate system are analogous to those obtained for other systems where the breadth increasing effect is fully exercised. Both the melting points and mesomorphic transition temperatures are depressed in IIa-c. In this system, the effects are additive. Thus, for di-lateral substitution of the central ring (IId), the depression in nematic-isotropic transition temperature is nearly twice that for the corresponding mono-substituted compound (IIc). Lateral substituents located on terminal rings also lower the melting point, but because the compounds studied were not liquid crystalline, the extent of the effect on mesomorphic transition temperatures could not be ascertained.

Replacement of the central ring in the 1,4-phenylene dibenzoate system with a 1,3-phenylene ring results in a molecule which, although no wider than cholesteryl benzoate, is not liquid crystalline. It is apparent that not only is a rigid and polarizable molecule necessary, but also a linear structure if liquid crystallinity is to survive in this system.

Replacement of benzoate units with cinnamate groups gives higher melting points and mesomorphic transition temperatures. These temperatures are lowered if dissymmetry is introduced into the molecule. Dissymmetry coupled with lateral substituent effects, gives still lower melting materials. In unsymmetrical esters containing a lateral substituent, an isomeric mixture is possible. Although no quantitative estimates were made, the extent to which this affects the melting point is probably dependent on the degree of dissymmetry involved.

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BRISTOL, DAVID WILLIAM. The Relationship of Molecular Structure to Mesomorphism in some Aromatic Esters of Diphenols.
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Various aromatic esters of diphenols representing some major structural variations of the 1,4-phenylene dibenzoate system have been synthesized and their mesomorphic transition temperatures determined. The possibility of obtaining low melting liquid crystalline materials by using dissymmetry, lateral substitution, cinnamate rather than benzoate end groups, and *m*-phenylene rather than *p*-phenylene central groups was explored.

It was found that cinnamates and molecules which contain compact, polar groups located in terminal positions give the highest melting points and mesomorphic transition temperatures while very bulky, non-polar *i*-Pr and *t*-Bu groups eliminate liquid crystallinity altogether. The phase transition temperatures are lowered in symmetrical molecules containing one central side substituent. Unsymmetrical, laterally substituted molecules give still lower melting points. Molecules containing *m*-phenylene central groups, or an ester system with only two phenylene rings terminally substituted by small polar groups, do not exhibit mesomorphic behavior.