THE MESOMORPHIC PHASE TRANSITION TEMPERATURES OF

THE UNSYMMETRICAL 1,4-PHENYLENE ESTERS

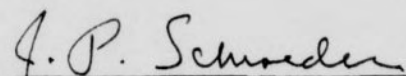OF THE 4-n-ALKOXYBENZOIC ACIDS

by

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CHAPTER I

INTRODUCTION

The normal melting process occurs at a specific temperature, characteristic of every substance, when the constituent molecules of the solid have sufficient vibrational kinetic energy to overcome the net attractive forces binding the crystal lattice. The resulting phase change involves a transition from the highly ordered environment of the solid to the isotropic liquid.

From X-ray diffraction studies,[1] the isotropic liquid has been found to possess some short range molecular ordering. The absence of any long range order prevents the liquid from exhibiting properties of the solid state, particularly those properties which are characteristically associated with crystalline anisotropy. However birefringence and some other anisotropic properties are shown by the melts of certain organic compounds.

The phenomenon was first observed by Reinitzer[2] in 1888 with esters of cholesterol and Lehmann[3] in 1890 with ammonium oleate and p-azoxyphenetole. Both men found that the substances melted sharply at specific temperatures to give cloudy liquids which, when heated further, cleared suddenly at characteristic temperatures to yield the normal liquid. The melts were also found to be birefringent in thin films when viewed with crossed polaroids - a property previously found only in crystalline solids.

To describe this new combination of solid and liquid traits, Lehmann coined the name "Fliessende Krystalle," that is, liquid crystals. Although

ordered fluid is more precise, the term liquid crystal persists and is
commonly accepted. Mesomorphism is synonymous with liquid crystallinity
and a liquid crystalline state is called a mesophase. The literature
contains a variety of reviews on the mesomorphic state.[4-9]

This introduction will entail only a general survey of mesomor-
phism with special consideration only to topics relevant to the theme of
this thesis.

There are three principle manifestations of the mesomorphic state:
the smectic, nematic, and cholesteric mesophases. Although these are the
most common, a notable exception is the mesophase of diisobutyl silanediol
which cannot be classified.[10]

The smectic mesophase is the most highly ordered and least stable
form of the mesomorphic state, consisting of a laminar pattern of parallel
molecules with their major axes perpendicular to the sheet plane (Fig. 1a).
Each molecule is free to rotate about its major molecular axis or move
laterally within its sheet, but not to cross between sheets. Each sheet
is free to move, in mass, between its companions. This structure was first
postulated by Friedel[11] based on his observations and later corroborated
by X-ray work.[12-14]

The smectic phase can adopt several textures or appearances depend-
ing on the nature of the compound and techniques used to observe the
mesomorphic birefringence. Smectic liquids are very viscous and this
property accounts for the homogeneous texture, where the mesophase retains
the same appearance and boundaries as existed in the solid before melting.
Movement of the sample, e.g., by displacement of the cover slide, reveals
that it is actually liquid.
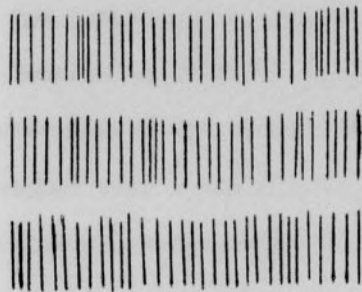
a) The Smectic Mesophase
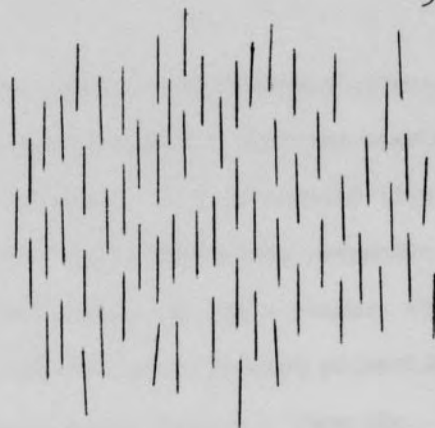
b) The Nematic Mesophase
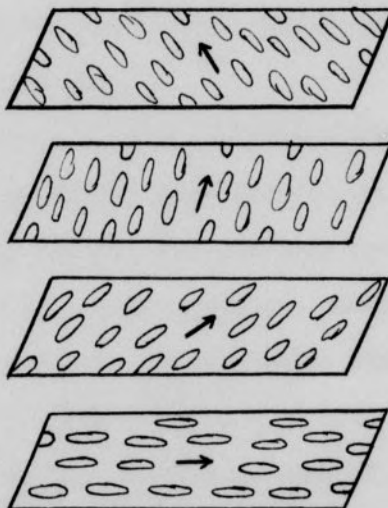
c) The Cholesteric Mesophase

Figure 1. Molecular Alignment in the
Mesomorphic Liquid

The homoeotropic texture arises when there is no preferred orientation imposed by original solid or mounting procedures. When the sample is between meticulously clean cover slips or when a drop of smectic liquid is stretched over a small hole, the molecules align themselves perpendicular to the glass-mesophase or air-mesophase interface. This renders the viewing field of the microscope optically extinct using crossed polaroids.

The third smectic texture is the focal conic texture. Here the layers in the smectic liquid are distorted, crimped, and folded by molecular and mechanical movement producing a pattern of interconnecting lines and ellipses.

The smectic state is the only mesophase which has been found to be polymesomorphic, that is, to exhibit two or more distinct phases of the same type in a single compound.

The nematic mesophase is less regimented that the smectic and often appears alone, but when a smectic phase does occur, a nematic phase often follows at a higher temperature. The molecules are arranged in an imbricated pattern with their major axes parallel. Each molecule has three degrees of translational freedom and may rotate about its major axis but not about its minor axes. (Fig. 1b).

This description is the short range view of the nematic liquid as suggested by Friedel's work[11] and is generally accepted. The overall view of the nematic is subject to controversy. A large body of evidence compiled from light diffusion[15], alternating electric field effects[16], and scintillation effects[17,18] in nematic melts seems to support the so-called Swarm Theory of Bose[19], Ornstein and Kast.[20] They suggest that the nematic liquid is composed of swarms of about 10^5 molecules. Within each swarm

all the molecules are aligned with their major axes more or less parallel but with the resultant axis of each swarm randomly oriented. Interswarm liquid is composed of independent molecules whose alignments gradually change from one swarm to the next. The molecules constantly exchange in and out of swarms and from swarm to swarm.

An alternate view is provided by Zocher[21] who proposed the Distortion Hypothesis. He contends that no swarms exist but rather the molecular orientation gradually changes from any given region of the liquid to the next.

Some attempts have been made to show the compatibility of the two theories[17] and it has been found that identical results are obtained from both theories in nuclear magnetic resonance experiments.[22]

The majority of data indicates the preferability of the Swarm Theory although Chatelain[15] points out that, based on more recent studies, the actual structure of the nematic liquid is probably intermediate between the two models.

There have been a variety of attempts at constructing mathematical concepts which relate physical properties to molecular order in the liquid crystalline phases.[23-27] Recently, attempts have been made to interpret nematic molecular order in terms of the behavior or rigid rods.[28-30]

The nematic phase can also exist in several textures. The homogeneous texture is similar to the analogous smectic texture, but has a much lower viscosity. The nematic liquid may also display an optically extinct homoeotropic texture, distinguishable from its smectic analog again by lower viscosity and by minute flashes of light caused by momentary variation in molecular orientation as a result of Brownian Movement. A

third form is the centered texture in which differently oriented regions, appearing as bands, meet at points in the liquid to form a dot or center. The most common nematic texture is the threaded texture. The optical field appears as brightly colored regions, randomly crossed by dark winding threads. The threads represent optical discontinuities in the melt but their exact nature is uncertain.

The last general manifestation of liquid crystals is the cholesteric mesophase, so named because its particular properties were first observed with esters of cholesterol and, in fact, steroid structures predominate in generating this phase.

The most commonly agreed upon model for the cholesteric mesophase is one comprised of sheets of molecules. The major molecular axes are within the plane of the layer in an imbricated parallel alignment. From each layer to the next, the direction of the major molecular axes is pitched slightly in a regular manner to form an overall helical array (Fig. 1c). A unique property of the cholesteric mesophase is its potent optical rotatory power.

The cholesteric phase exhibits a focal conic and a homoeotropic texture and, in addition, a plane texture which appears as brilliantly colored regions under the polarizing microscope. This texture also produces brilliant irridescence from reflected light.

The cholesteric and nematic mesophases have been shown to be intimately related. Friedel[31] found that dextro-rotatory and laevo-rotatory cholesteric isomers produced nematic racemic mixtures. Friedel[11,12], and more recently Sackmann and coworkers[32], found that mixtures of an optically active nematic compound and a racemic nematic or non-mesomorphic compound

produced cholesteric mesophases. Sackmann also points out that the cho-
lesteric phase so obtained became nematic when subjected to strong magnetic
fields. A cholesteric and a nematic mesophase are never found together
in any one substance. Occurrence of one eliminates the possibility of the
other except in the previously mentioned case of magnetic field effects.

The mesomorphic phenomenon can be visualized as a stepwise melting
process, with directional molecular ordering disappearing a dimension at
a time. The three dimensionally ordered solid, by overcoming major attrac-
tive forces, passes to the two dimensionally ordered smectic liquid. At
a higher temperature, lateral interactions, which maintain the smectic
ordering, are overcome and the liquid passes to a nematic or cholesteric
phase. Finally, at a still higher temperature, the residual lateral and
terminal forces are overcome and the one dimensionally ordered nematic
or cholesteric phase passes over to the complete disorder of the isotropic
liquid. In passing through any transition, the molecular interactions of
the next phase may be so small that the phase does not occur at all. For
example, a compound may melt directly to a nematic phase or a smectic
phase may pass directly to the isotropic liquid. The extreme case of this
behavior is the normal melting process where a molecule lacks the pre-
requisites for mesomorphism and the solid passes directly to isotropic
liquid at the melting point.

A mesomorphic transition which occurs reversibly above the melting
point is termed enantiotropic. Transitions occurring below the melting
point in the supercooled liquid are monotropic transitions.

There are three criteria for judging the probability of a compound
displaying mesomorphic properties. First, the molecule must possess a

rigid, linear, rod-shaped geometry with a relatively high length to width ratio. Second, the molecule must contain constituent units with high permanent or induced dipole moments. And third, the molecule must contain polarizable constituent units.

There are many compounds which contain both polar and polarizable groups but which do not show liquid crystalline properties due to the lack of the linear, rodlike molecular geometry required for anisotropy in the liquid. Likewise, molecules which satisfy the geometric requirements, but lack polar and polarizable groups, fail to be mesomorphic because intermolecular attractive forces are insufficient to maintain fluid structuring.

The positioning of the constituent units influences the existence and stability of a compound's mesophase. The general configuration of a mesomorphic compound is shown in Figure 2. Polarizable and polar groups will tend to enhance mesomorphic stability and their effect is most efficient when located terminally (X) or centrally (Y) in the molecule.

Various attempts at compiling efficiency tables for central and terminal substituents have not been successful because the actual effect a group has on the mesomorphic properties is a combination of factors such as conjugative effects, dipole interactions, and polarizability effects. Every molecular system will be influenced differently by each of these factors.

Groups frequently found in liquid crystalline compounds are listed in Table 1. The mesomorphism of carboxylic acids is a particularly interesting situation. Dimerization by hydrogen bonding produces a molecule, with the COOH groups centrally located, which is sufficiently
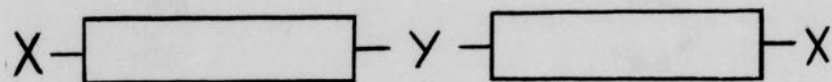
Figure 2. A General Structure for a
Mesomorphic Compound

TABLE 1

COMMON TERMINAL AND CENTRAL GROUPS

Terminal Groups	Central Groups
$-OR$	$\diagup C = C \diagdown$
$-COOR$	$\diagup C = N \diagdown$
$-NO_2$	$N = N$
$-Cl$	$N = N \nearrow^{O}$
$-Br$	$-C \equiv C-$
$-I$	$-C \diagup^{O \cdots H-O} \diagdown_{O-H \cdots O} C-$
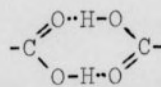
long to exhibit mesomorphism where normally not expected. For example, the 4-n-alkoxybenzoic acids[33] are mesomorphic whereas their esters, which are incapable of dimerization, have molecules too short to be liquid crystalline (Fig. 3). This is one of the few instances where intermolecular hydrogen bonding actually enhances mesomorphism. In general, any group that introduces very strong intermolecular attractions into a system, which are not neutralized by intramolecular interactions[34], will increase the melting point to such an extent that mesomorphic tendencies may be submerged.[35]

The 1,4-phenylene unit is a particularly desirable central group because of its polarizable aromatic bonding, rigidity and ease of incorporation. Most liquid crystalline compounds contain at least one 1,4-phenylene unit. Mesophase stability increases with increasing numbers of such units in the molecule. For example, the 4'-n-alkoxybiphenyl-4-carboxylic acids[36,37] have higher transition temperatures[38] than their shorter analogs, the 4-n-alkoxybenzoic acids.[33]

Phenylene units also introduce the possibility of lateral substitution on the molecular skeleton. It has been found that lateral substitution of any kind tends to destabilize a mesophase by increasing molecular width, forcing the molecules apart and thus lessening intermolecular attractions.

Terminal substitution of a polar group will enhance mesomorphic stability, particularly in the nematic phase. Gray[40] states that, although no consistent terminal group efficiency order prevails in the literature, replacement of a terminal hydrogen by any constituent will increase nematic stability. This statement should be qualified to the
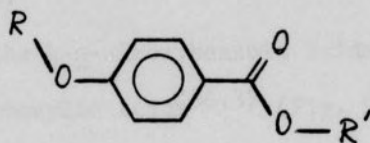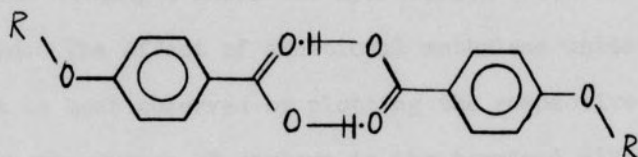
Figure 3. 4-n-Alkoxybenzoic Acid and Ester

extent that the constituent group can not be extremely bulky and thereby greatly increase the molecular width.

Terminal alkoxy (RO-) substitution is notable. Many homologous series of mesomorphic compounds have been prepared in which the bulk of the molecule remains unchanged while the hydrocarbon chain of the alkoxy group is lengthened. The effect of additional methylene units on mesomorphic properties is best observed by plotting the respective transition temperatures versus the number of carbons in the terminal alkyl chains. The same approach is used for other homologous series of liquid crystals containing hydrocarbon chains.

Typical examples are the 4-n-alkoxybenzoic acids[33] (Fig. 4) and the 4'-n-alkoxybiphenyl-4-carboxylic acids[36,37] (Fig. 5). All transition temperatures except the unpredictable melting points form approximately smooth curve relationships when plotted as described above.

The determinant factor in the capriciousness of the melting points is the complexity and unpredictability of crystalline packing in the solid state. An X-ray study of the 4-n-alkoxybenzoic acids has been done by Bryan[41,42] and it explains in terms of solid state crystal packing why, for example, the first two members are non-mesomorphic and why nematic and smectic properties arise in later members. The physical arrangement of the molecules in the crystal lattice determines the efficiency of the intermolecular attractive forces which, in turn, determines the temperature (kinetic energy) required to overcome them.

For most mesomorphic homologous series, a plot of the nematic-isotropic transition temperature versus terminal carbon chain length is characterized by relatively high transition temperatures for very short
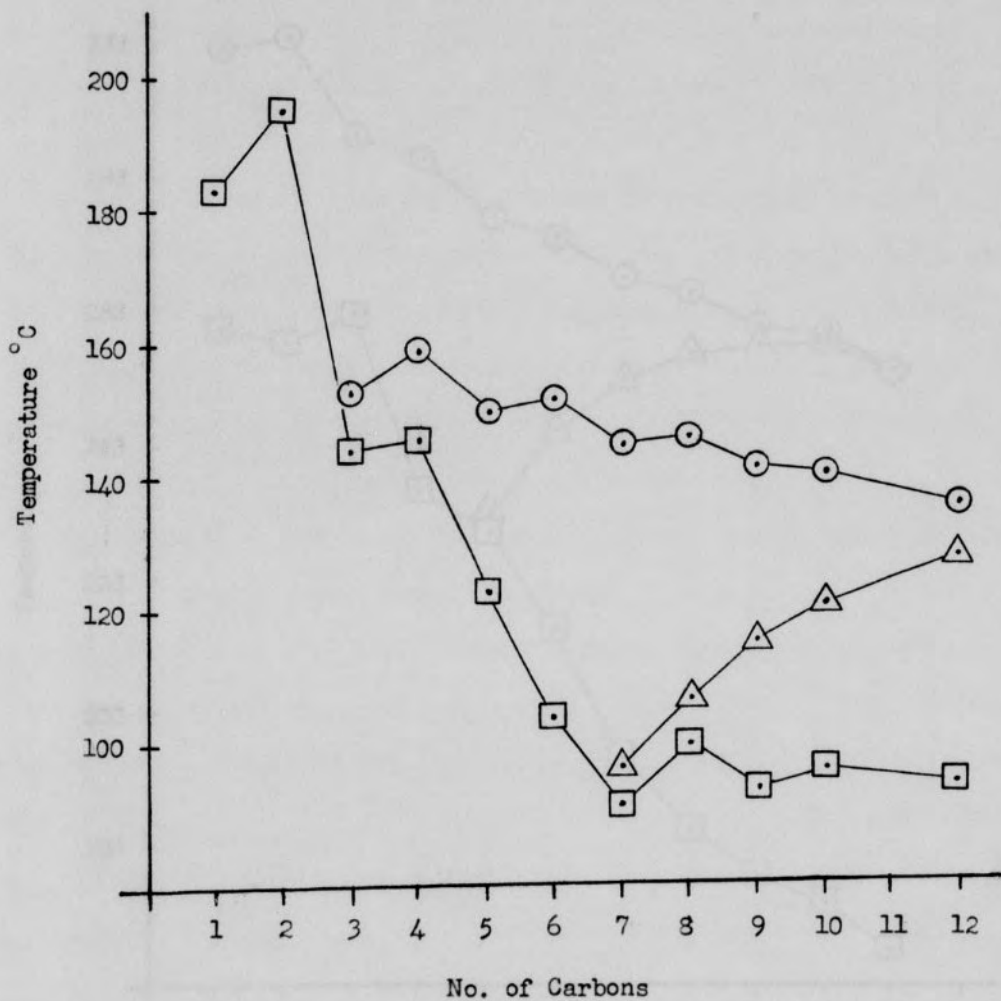
Figure 4. Mesomorphic Phase Transition Temperatures
of the 4-n-Alkoxybenzoic Acids

Melting Point ⊡
Nematic → Isotropic ⊙
Smectic → Nematic △

15
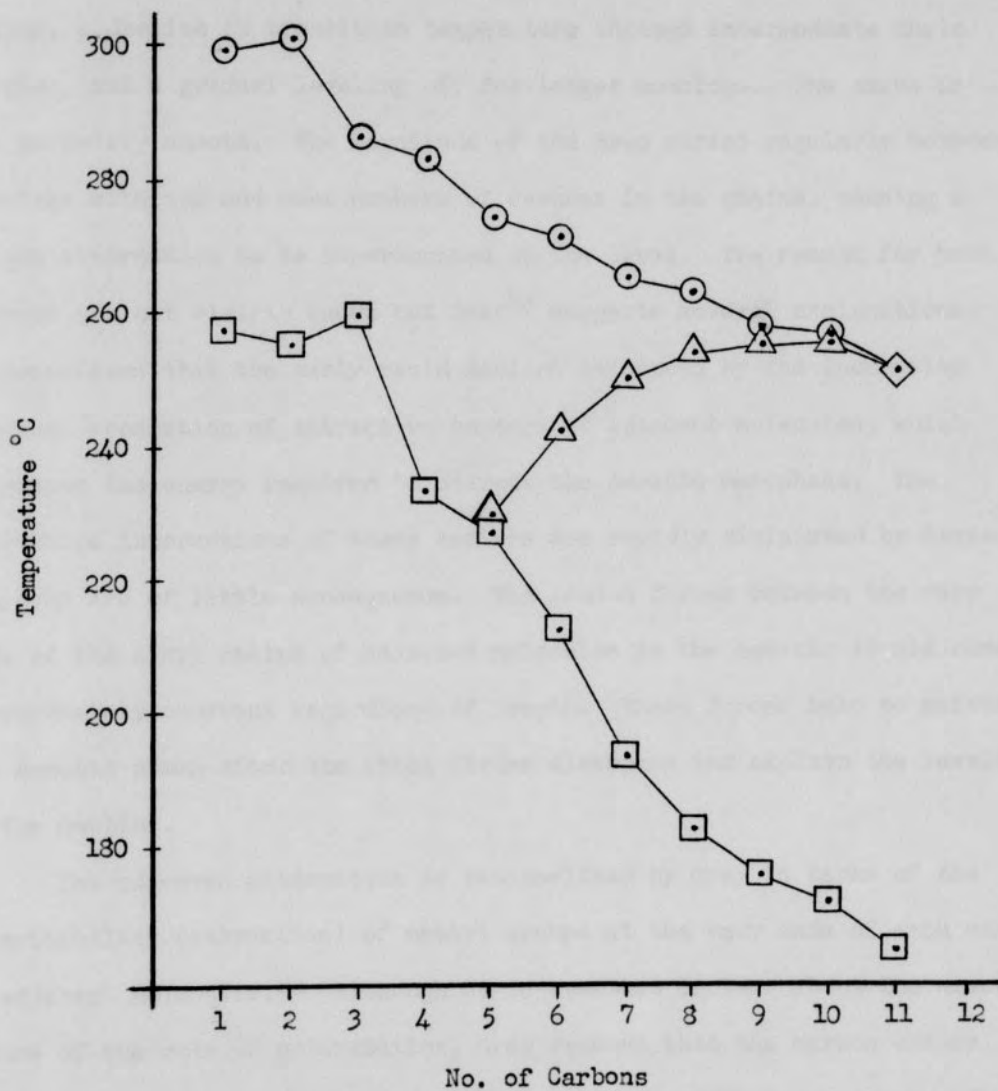
Figure 5. Mesomorphic Phase Transition Temperatures
of the 4'-n-Alkoxybiphenyl-4-Carboxylic Acids

Melting Point ⊡
Nematic → Isotropic ⊙
Smectic → Nematic △
Smectic → Isotropic ◇

chains, a decline in transition temperature through intermediate chain
lengths, and a gradual leveling off for longer homologs. The curve is
not perfectly smooth. The magnitude of the drop varies regularly between
homologs with odd and even numbers of carbons in the chains, causing a
slight alternation to be superimposed on the curve. The reason for both
effects are not clearly known but Gray[43] suggests several explanations.
He postulates that the early rapid decline is caused by the increasing
physical separation of attractive centers of adjacent molecules, which
decreases the energy required to disrupt the nematic mesophase. The
attractive interactions of these centers are rapidly diminished by distance
and soon are of little consequence. The London forces between the very
ends of the alkyl chains of adjacent molecules in the nematic liquid remain
approximately constant regardless of length. These forces help to maintain
the nematic phase after the other forces disappear and explain the leveling
of the decline.

The odd-even alternation is rationalized by Gray in terms of the
polarizability (attraction) of methyl groups at the very ends of each chain
on adjacent molecules.[44] Although he is somewhat unclear about the exact
nature of the role of polarization, Gray reasons that the carbon chains
assume a cog wheel type of conformation rather than the lower energy zig-
zag conformation found in long chain n-alkanes (Fig. 6). There are a
variety of physical explanations for this conformational preference but
the most convincing argument is that the particular geometry of the cog
wheel alkyl chain allows rationalization of the observed alternation while
the zig-zag does not. As shown in Figure 7, depending on whether the
chain length is even or odd, the cog wheel form presents two different

Zig-Zag
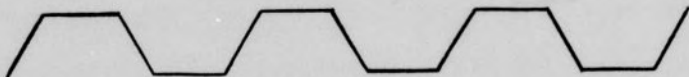
Cog-Wheel

Figure 6. Two Conformations of a Hydrocarbon Chain
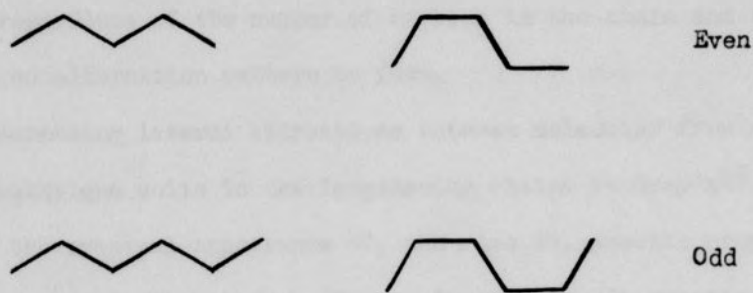
Figure 7. Orientations of Even and Odd Chain
Lengths for Hydrocarbon Conformers

orientations of the end methyl group. The two orientations of these methyl groups will alternately affect the magnitude of the residual terminal attractions between adjacent molecules. Since the residual attractions slightly counteract the larger destabilizing effects of long chains, two degrees of counteraction will occur, depending on the orientation (no. of carbons) of the chains, and thus a minor alternation in the major curve will result. The zig-zag conformation presents only one orientation regardless of the number of carbons in the chain and therefore cannot cause an alternation pattern to form.

The increasing lateral attractions between molecules from additional polarizable methylene units in the lengthening chains is Gray's[45] interpretation of the eventual appearance of, and rise in, smectic properties on ascending an homologous series. Except for monotropic smectic phases, the solid now melts to form a smectic mesophase which at a higher temperature undergoes a smectic-nematic transition. As the chains lengthen, the temperature curve of the latter transitions rises and eventually merges with the nematic-isotropic curve in longer homologs so that only a smectic mesophase occurs. The smectic mesophase eventually also declines in stability with increasing chain lengths due to the inability of the lateral forces to maintain the growing bulk of the molecule in the smectic strata and ultimately the smectic phase is so destabilized that the melts of very long homologs cease to be anisotropic and mesomorphic properties disappear.

Purpose of This Investigation

For both fundamental and practical applications, it is desirable to have at hand a mesomorphic compound which has high thermal stability,

a low melting point, and a wide liquid crystalline range. For example, the larger the liquid crystalline temperature range of a compound, the more detailed and valuable is the information that can be obtained from it on the molecular changes involved in passing through the mesomorphic state.[46] p-Azoxyanisole has a nematic range of only 17°C but has been a prime source of liquid crystalline basic research because of its ease of procurement. There are a variety of compounds with much longer mesophases but they are either prohibitively expensive or difficult to prepare. One of the many practical applications of liquid crystals has been their use as stationary liquid phases in gas-liquid chromatography.[47-52] Here a thermally stable compound, with a low melting point and wide nematic range, provides more efficient separations.[50]

Since the same forces which stabilize a nematic phase and extend its range also tend to raise the melting point, few compounds have been found which combine all the sought after properties.

In the past, the favored properties were achieved by using a binary mixture of pure compounds, at least one of which was mesomorphic.[53-55] This procedure takes advantage of the usual melting point depression exhibited by most mixtures of crystalline compounds. At the same time, if the mesomorphic properties of the mixture are disrupted less than the melting point is lowered, a low melting, wide temperature ranged nematic system may be achieved. Unfortunately, mixtures themselves present several disadvantages. The transitions usually occur over a significant temperature range; the process of finding a suitable mixture is tedious; and exact duplication of a useful composition is difficult. A single, pure mesomorphic compound is thus a still more desirable system. This

investigation was initiated with the objective of finding just such a compound or compounds.

Previous studies of binary nematic mixtures have shown that, although melting points may vary significantly, the nematic-isotropic transition temperatures vary less the more the two components resemble each other in molecular size, shape, polarity, and mesomorphic behavior.[53,54] It was reasoned that by modifying half of a suitable molecule to that of another similar molecule, a hybrid or "intramolecular mixture" would result. The hybrid should have a lower melting point than either parent, but a nematic-isotropic transition temperature intermediate between the two, as in a 1:1 mixture of the pure components. In effect, the desirable qualities of a mixture would be achieved without the inconveniences.

The symmetrical 1,4-phenylene bis(4'-n-alkoxybenzoates) (Fig. 8, R=R') have been shown to be highly stable compounds with relatively low melting points and wide nematic ranges.[56-59] This system is well suited for the type of modification required. By the simple use of acids with unlike alkoxy groups, the "intramolecular mixture" can be achieved. For example, the unsymmetrical ester with R=methyl and R'=n-octyl should have about the same melting point and nematic environment as a 1:1 mixture of the symmetrical esters with R=R'=methyl and R=R'=n-octyl.

Twenty-eight unsymmetrical esters were prepared representing the possible binary combinations of the symmetrical esters from R=R'=methyl to R=R'=n-octyl.

In referring to particular esters from this point on, the following nomenclature is used. A double number is assigned to every compound signifying the number of carbon atoms in the alkoxy chains at each end of the

molecules. The external hydrocarbon is 4,5 and top-center, 2,3;4-methyl 3,4;5,6 and so on. When 6,7 and 7,6 are equivalent, to avoid confusion, the earliest chain number is written first.
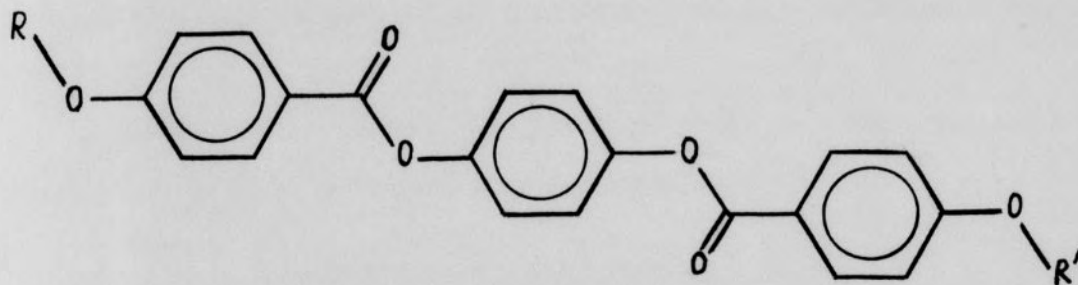
Figure 8. 1,4-Phenylene Bis(4'-n-Alkoxybenzoate)

molecule. For example, R=R'=methyl is 1,1 and R=n-pentyl, R'=n-heptyl is 5,7 and so on. Since 5,7 and 7,5 are equivalent, to avoid confusion, the smaller chain number is written first.

CHAPTER II

EXPERIMENTAL

Transition temperature determinations were made optically, using a Reichert "Thermopan" Polarizing Microscope equipped with a Kofler Micro Hot Stage. All melting points are corrected.

Thermal analysis was used for obtaining preliminary transition temperatures using a Perkin-Elmer Differential Scanning Calorimeter, model DSC-1B.

Elemental microanalyses were performed by Dr. Kurt Eder, Laboratoire Microchimique, École de Chimie, Geneva, Switzerland.

Preparation of 4-n-Alkoxybenzoic Acids

The procedure used was adapted from that of Gray and Jones.[60] Typically 16.6 g (100 mmoles) ethyl 4-hydroxybenzoate, 55.3 g (400 mmoles) anhydrous K_2CO_3, 110 ml cyclohexanone, and 160 mmoles of the appropriate n-alkyl bromide were refluxed in a 500 ml Erlenmeyer flask for 1-3 hours. Because of the low solubility and bulk of the K_2CO_3, vigorous stirring was required to maintain adequate dispersion. After cooling, the cyclohexanone solution was decanted and the remaining solid washed three times with about 50 ml ether. The ether washes were concentrated, combined with the decantate and the mixture distilled at aspirator vacuum. The viscous, dark liquid residue and 84 ml of 10% ethanolic KOH were refluxed for 1 hour. If a heavy precipitate formed and fouled the stirrer, the mixture was vacuum filtered and the filtrate returned for completion of the reaction. After

cooling, the mixture was poured into 800 ml cold water, any filtered solid added, and the solution acidified with 6N HCl. The precipitated product was vacuum filtered, washed with water, air dried, and recrystallized from benzene. The acids exhibited the following transition temperatures: 4-n-propoxybenzoic acid, m.p. 145°, nematic-isotropic 156° (lit.[33], 145°, 154°); 4-n-hexyloxybenzoic acid, m.p. 109°, nematic-isotropic 155° (lit.[33], 105°, 153°); 4-n-heptyloxybenzoic acid, m.p. 94°, smectic-nematic, 99°, nematic isotropic 146° (lit.[33], 92°, 98°, 146°). The 4-ethoxy, 4-n-butoxy, and 4-n-octyloxybenzoic acids were obtained commercially.

Preparation of 4-n-Alkoxybenzoyl Chlorides

A mixture of the appropriate 4-n-alkoxybenzoic acid, a thirteen-fold molar excess of thionyl chloride, and several drops of anhydrous pyridine as a catalyst were refluxed with stirring for 1 hour. The excess thionyl chloride was then distilled and the last traces removed at aspirator vacuum on a steam bath. A calcium chloride drying tube was used at all stages of the preparation to protect the product from moisture. The residual 4-n-alkoxybenzoyl chloride was used without further purification. 4-Methoxybenzoyl chloride and 4-n-pentoxybenzoyl chloride were obtained commercially.

Preparation of 4-Hydroxyphenyl 4'-n-Alkoxybenzoates

The appropriate 4-n-alkoxybenzoyl chloride was slowly poured into a vigorously stirred, saturated solution of hydroquinone in anhydrous pyridine (ca. 3 ml pyridine per gram of hydroquinone, a five-fold molar excess). The reaction mixture was stirred at room temperature for 20-24 hours, then poured (with stirring) into a sufficient volume of 2.2 N HCl

to dissolve the hydroquinone, neutralize the pyridine, and precipitate the product (ca. 11 ml per mmole of original 4-n-alkoxybenzoyl chloride). The light tan precipitate was collected by vacuum filtration, washed with water, and slurried for 1 hour in a saturated aqueous NaHCO$_3$ solution to remove unreacted acid (at least 10 ml solution per mmole original acid chloride). The tan solid was collected by vacuum filtration and dried overnight at 100°C. The heptyloxy and octyloxy products required pre-heating of the slurry solutions to 90°-95° just prior to hot filtration due to the low solubility of the respective sodium alkoxybenzoate salt in cold water. The crude products were used in the next step without further purification but were later recrystallized from ethanol and water. The properties of these products are presented in Table 2.

Preparation of The Unsymmetrical 1,4-Phenylene Esters of The 4-n-Alkoxybenzoic Acids

A solution of one gram of the appropriate 4-hydroxyphenyl 4'-n-alkoxybenzoate in a minimum volume of anhydrous pyridine (ca. 15-30 ml) was stirred into a three-fold molar excess of the appropriate, freshly prepared 4-n-alkoxybenzoyl chloride. The reaction was allowed to proceed for 18-24 hours. A calcium chloride drying tube was used at all times to protect the acid chloride reactant from moisture. The reaction was ter-minated by pouring the dark mixture into 200 ml of stirred, ice-cooled, 2.0 N hydrochloric acid. This amount is sufficient to neutralize the pyridine solvent and precipitate the product. After several minutes of stirring, the light brown precipitate was collected by vacuum filtration, washed with water, and slurried in 200 ml of a saturated aqueous NaHCO$_3$

TABLE 2

4-HYDROXYPHENYL 4'-n-ALKOXYBENZOATES

$$RO-\text{C}_6\text{H}_4-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{C}_6\text{H}_4-OH$$
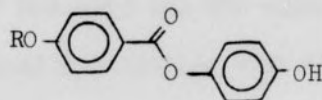
R	Recrystn. Solvent	% Yield	Melting Point, °C	% C Calcd.	Found	% H Calcd.	Found
CH_3	EtOH-Water	84	154-156[a]	-		-	
C_2H_5	EtOH-Water	89	163-164	69.76	69.75	5.46	5.14
n-C_3H_7	EtOH-Water	90	135-136	70.78	70.75	5.92	6.11
n-C_4H_9	EtOH-Water	88	143-144	71.31	71.55	6.34	6.58
n-C_5H_{11}	EtOH-Water	80	119-120	71.98	71.66	6.71	6.50
n-C_6H_{13}	EtOH-Water	66	115-116	72.59	72.54	7.05	6.88
n-C_7H_{15}	EtOH-Water	86	111-113	73.15	73.24	7.37	7.42
n-C_8H_{17}	EtOH-Water	85	108-111	73.66	73.30	7.65	7.27

[a]Lit., 150°-152°C [57]

solution for 4 hours to remove the excess acid. The product was collected by vacuum filtration, washed with water, and dried overnight at 100°C.

For all products involving the use of heptyloxy- and octyloxybenzoic acids, the $NaHCO_3$ slurry was preheated to 90°-95°C to dissolve the relatively insoluble sodium salt of the acid and the slurry filtered hot. In all cases the filtrates were eventually acidified with 6N HCl and the excess acids recovered for later reuse.

The crude product was dissolved in an appropriate solvent, treated with Norite, and recrystallized twice from about 20 ml of the solvent. For subsequent recrystallizations, 60-100 ml of a mixture of the original solvent and hexane was used; or hexane alone for the three highest homologs. Recrystallization was continued to constant phase transition temperatures. The properties of these products are found in Table 3.

It should be noted here that the esters 1,5; 2,4; 2,6; 2,7; and 2,8 refused to crystallize but rather repeatedly precipitated out of the solvent as white powders. Except for the 1,5 ester, after five reprecipitations, the melting point ranges of these compounds were still on the order of several degrees. The reported transition temperatures remained constant over the last two precipitations for all. Esters 2,3 and 2,5 behaved similarly but after two precipitations formed crystals and recrystallized normally.

It is postulated that in the synthesis of the intermediate 4-hydroxy-phenyl 4'-n-alkoxybenzoates, some symmetrical esters were also formed. Since the intermediates were used without recrystallization, the symmetrical ester carried over to contaminate the respective unsymmetrical esters. Either the 4-hydroxyphenyl 4'-ethoxy and 4'-n-pentoxybenzoates formed more of the symmetrical esters that the others, or the crystallizing behavior

TABLE 3

UNSYMMETRICAL 1,4-PHENYLENE ESTERS
OF 4-<u>n</u>-ALKOXYBENZOIC ACIDS
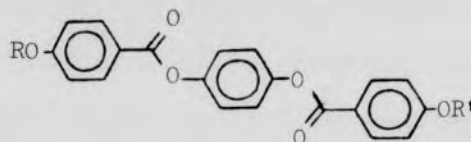
No.	Recrystn. Solvent	% Yield	Nematic Range, °C	% C Calcd.	% C Found	% H Calcd.	% H Found
1,2	Dioxane	81	213-295	70.40	70.12	5.14	5.31
1,3	Dioxane	67	167-277	70.93	70.69	5.46	5.75
1,4	EtOAc	75	134-266	71.41	71.83	5.75	5.79
1,5	Dioxane	56	137-253	71.87	72.10	6.03	6.03
1,6	EtOAc	54	125-244	72.30	72.44	6.29	6.31
1,7	EtOAc	66	127-234	72.71	72.48	6.54	6.42
1,8	EtOAc	62	125-229	73.09	73.25	6.77	6.52
2,3	Dioxane	81	198-278	71.42	70.86	5.75	5.78
2,4	Dioxane	77	150-270	71.87	71.56	6.03	6.22
2,5	Dioxane	69	150-251	72.30	72.52	6.29	6.29
2,6	EtOAc	81	134-248	72.71	72.08	6.54	6.74
2,7	EtOAc	84	127-240[a]	73.09	73.49	6.77	6.68
2,8	EtOAc	74	124-235	73.45	73.49	6.99	6.82
3,4	EtOAc	82	151-248	72.30	72.20	6.29	6.55
3,5	EtOAc	59	126-236	72.71	72.79	6.54	6.87
3,6	EtOAc	78	114-230	73.09	73.17	6.77	7.02
3,7	EtOAc	67	120-222	73.45	73.33	6.99	7.20
3,8	EtOAc	71	128-216	73.79	74.18	7.19	7.25
4,5	EtOAc	75	140-229	73.09	73.68	6.77	6.79
4,6	EtOAc	75	117-226	73.45	73.74	6.99	7.05
4,7	EtOAc	67	114-218	73.79	74.02	7.19	7.27
4,8	EtOAc	72	121-214	74.11	73.87	7.39	7.27
5,6	EtOAc	62	123-215	73.79	73.27	7.19	7.12
5,7	EtOAc	69	108-210	74.11	74.14	7.39	7.19
5,8	EtOAc	74	116-207	74.41	74.39	7.57	7.60
6,7	Hexane	74	118-206	74.41	74.77	7.57	7.54
6,8	Hexane	66	107-202[b]	74.70	74.18	7.74	7.84
7,8	Hexane	57	121-198[c]	74.97	74.82	7.91	7.59
5,5	EtOAc	78	145-222[d]	73.45	73.36	6.99	7.17

[a]A second preparation of 2,7 from recrystallized intermediate gave a Nematic range of 130°-235°C.
[b]Smectic → Nematic Transition 106°C
[c]Smectic → Nematic Transition 114°C
[d]This symmetrical ester had not been previously synthesized.

of 2,2 and 5,5 are very similar to the crystallizing behavior of the unsymmetrical esters synthesized with them, but in either case, it is apparent that, even after constant transition temperatures were achieved, some symmetrical ester is still affecting the transition temperatures of the aforementioned powdery esters. Being a mixture, the melting points would be lower and with a wider range, and the nematic-isotropic transition temperatures would be intermediate between their true value and that of the symmetrical contaminant. In these two cases, that would make the reported melting points low and the nematic-isotropic temperatures high. This hypothesis is strengthened by the fact that ester 2,7 was resynthesized from recrystallized 4-hydroxyphenyl 4'-n-heptyloxybenzoate and formed needles after two crystallizations. The melting point was higher and the nematic-isotropic temperature was lower. Because of this, in all tables after Table 3 and all Figures, the transition temperatures of 2,7 are those of the second product.

Differential Thermal Analysis

DTA thermograms were used to determine preliminary transition temperatures and to locate any monotropic mesomorphic transitions which might have gone unnoticed by optical methods. Agreement with transition temperatures obtained optically was on the order of $\pm 5^{\circ}C$.

CHAPTER III

RESULTS AND DISCUSSION

The behavior of the new unsymmetrical 1,4-phenylene esters can be interpreted in several ways. By fixing the length of one of the alkoxy chains and then varying the length of the other, eight homologous series are formed. A symmetrical ester appears once in each series where the variable chain length equals the constant chain length. Within the eight series, each unsymmetrical ester appears twice. For example, the ester 2,4 will be in both the ethoxy series and the n-butoxy series. These homologous series are referred to by a roman numeral corresponding to the number of carbons in the constant chain, for example, the series of esters with a constant n-propoxy are in series III and so on. The interrelation of all the unsymmetrical and symmetrical esters is shown by the grid in Figure 9. The symmetrical esters form the diagonal while the eight series lie horizontally and vertically in parallel rows.

The literature values for the nematic ranges of the symmetrical esters are listed in Table 4. The fact that Dewar and Goldberg[57,58] did not find smectic mesophases for esters 6,6; 7,7; and 8,8 while in this investigation esters 6,8 and 7,8 did show smectic behavior, casts doubt on the accuracy of their values for these compounds. It is for this reason that, in subsequent tables and all transition temperature plots, the values of Arora and coworkers[59] are used for these three esters. The transition temperature versus chain length plot of the symmetrical phenylene esters is shown in Figure 10. The combined transition temperatures of the symmetrical

and unsymmetrical esters, arranged in homologous series, are listed in Table 5 and plotted in Figures 11-18.

Taken individually, each series' transition temperature plot behaves as would be expected. That is, in progressing from short to long alkoxy chains, the nematic-isotropic transition temperature is lowered and eventually smectic properties arise. The melting points display their usual eccentricity but a noticeable trend is evident which is not as apparent in other homologous series. The melting point, instead of simply tending to decrease with increasing chain length, has a maximum or near maximum value at the symmetrical member. Moving away from the particular symmetrical homolog, either to longer or shorter chains, the melting point declines. This trend is especially clear in series I through V. In series VI through VIII, the spread of the melting point values from maximum to minimum does not vary beyond normal scattering, so that the trend is not obvious.

The dissymmetry of the molecule is the probable reason for the melting point behavior. The more the lengths of the two alkoxy chains on a molecule differ, the more difficult it is for efficient crystal packing to occur in the solid state; and thus the lower the temperature (kinetic energy) required to break up the lattice.

The dissymmetry does not have a similar effect on the nematic mesophases of these esters for, as previously mentioned, their behavior is typical of that found in most homologous series transition temperature plots. Evidently, the dissymmetry has no appreciable influence and only the separation of attractive centers by increasing chain length is of consequence. This can be observed by comparing the transition temperatures of isomeric esters, that is, those esters with the same molecular weight.

	I	II	III	IV	V	VI	VII	VIII
VIII	1,8	2,8	3,8	4,8	5,8	6,8	7,8	8,8
VII	1,7	2,7	3,7	4,7	5,7	6,7	7,7	7,8
VI	1,6	2,6	3,6	4,6	5,6	6,6	6,7	6,8
V	1,5	2,5	3,5	4,5	5,5	5,6	5,7	5,8
IV	1,4	2,4	3,4	4,4	4,5	4,6	4,7	4,8
III	1,3	2,3	3,3	3,4	3,5	3,6	3,7	3,8
II	1,2	2,2	2,3	2,4	2,5	2,6	2,7	2,8
I	1,1	1,2	1,3	1,4	1,5	1,6	1,7	1,8
	I	II	III	IV	V	VI	VII	VIII

Figure 9. Interrelation of Homologous Series
of Symmetrical and Unsymmetrical
1,4-Phenylene Esters

TABLE 4

SYMMETRICAL 1,4-PHENYLENE ESTERS
OF 4-n-ALKOXYBENZOIC ACIDS[a]

No.	Nematic Range, °C
1,1	213-297[b]
2,2	226-287
3,3	175-249
4,4	153-241
5,5	145-222[c]
6,6	121-211[d]
7,7	121-198[e]
8,8	118-192[f]

[a]Tabulated values from reference 57 and 58 except where noted.

[b] 222°-300°C[56] ; m.p. only 212°C[61]

[c]This thesis

[d] 124°-213°C[59]

[e]Monotropic Nematic → Smectic Transition 110°C ; Nematic Range 122°-199°C[59]

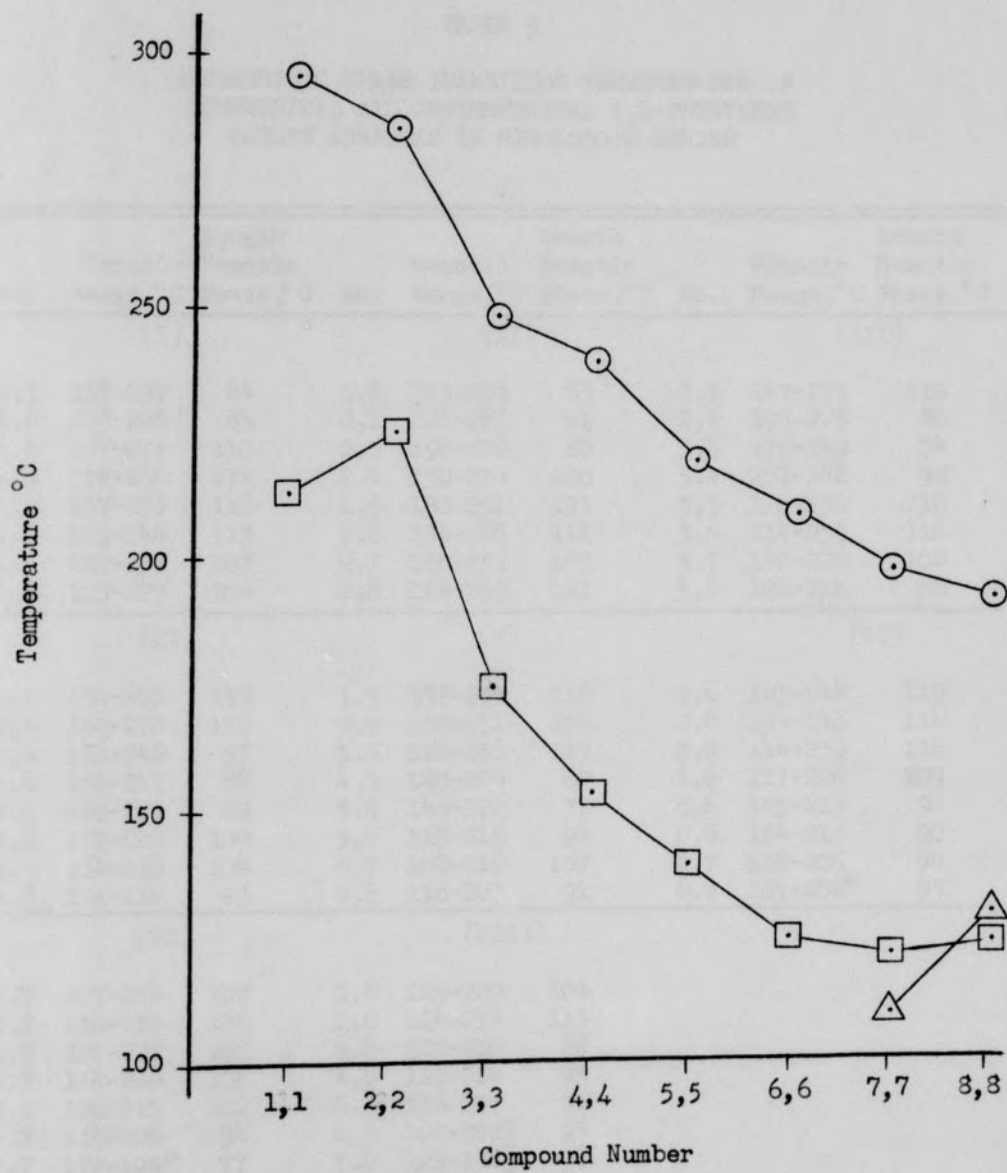[f]Solid → Smectic Transition 122°C ; Nematic Range 126°-195°C[59]

Figure 10. Mesomorphic Phase Transition Temperatures
of the Symmetrical 1,4-Phenylene Esters

Melting Point ▣
Nematic → Isotropic ⊙
Smectic → Nematic △

TABLE 5

MESOMORPHIC PHASE TRANSITION TEMPERATURES OF
SYMMETRICAL AND UNSYMMETRICAL 1,4-PHENYLENE
ESTERS ARRANGED IN HOMOLOGOUS SERIES

No.	Nematic Range, °C	Length Nematic Phase, °C	No.	Nematic Range, °C	Length Nematic Phase, °C	No.	Nematic Range, °C	Length Nematic Phase, °C
(I)			(II)			(III)		
1,1	213-297	84	1,2	213-295	83	1,3	167-277	110
1,2	213-295	83	2,2	226-287	61	2,3	198-278	80
1,3	167-277	110	2,3	198-278	80	3,3	175-249	74
1,4	134-266	132	2,4	150-270	120	3,4	151-248	97
1,5	137-253	116	2,5	150-251	101	3,5	126-236	110
1,6	125-244	119	2,6	134-248	114	3,6	114-230	116
1,7	127-234	107	2,7	130-235	105	3,7	120-222	102
1,8	125-229	104	2,8	124-235	111	3,8	128-216	88
(IV)			(V)			(VI)		
1,4	134-266	132	1,5	137-253	116	1,6	125-244	119
2,4	150-270	116	2,5	150-251	101	2,6	134-248	114
3,4	151-248	97	3,5	126-236	110	3,6	114-230	116
4,4	153-241	88	4,5	140-229	89	4,6	117-226	109
4,5	140-229	89	5,5	145-222	77	5,6	123-215	92
4,6	117-226	109	5,6	123-215	92	6,6	124-213	90
4,7	114-218	104	5,7	108-210	102	6,7	118-206	94
4,8	121-214	93	5,8	116-207	91	6,8	107-202[a]	95
(VI)			(VIII)					
1,7	127-234	107	1,8	125-229	104			
2,7	130-235	105	2,8	124-235	111			
3,7	120-222	102	3,8	128-216	88			
4,7	114-218	104	4,8	121-214	93			
5,7	108-210	102	5,8	116-207	91			
6,7	118-206	94	6,8	107-202[a]	95			
7,7	122-199[b]	77	7,8	121-198[c]	77			
7,8	121-198[c]	77	8,8	126-195[d]	69			

[a] Solid → Smectic Transition 106°C
[b] Monotropic Nematic → Smectic Transition 110°C
[c] Solid → Smectic Transition 114°C
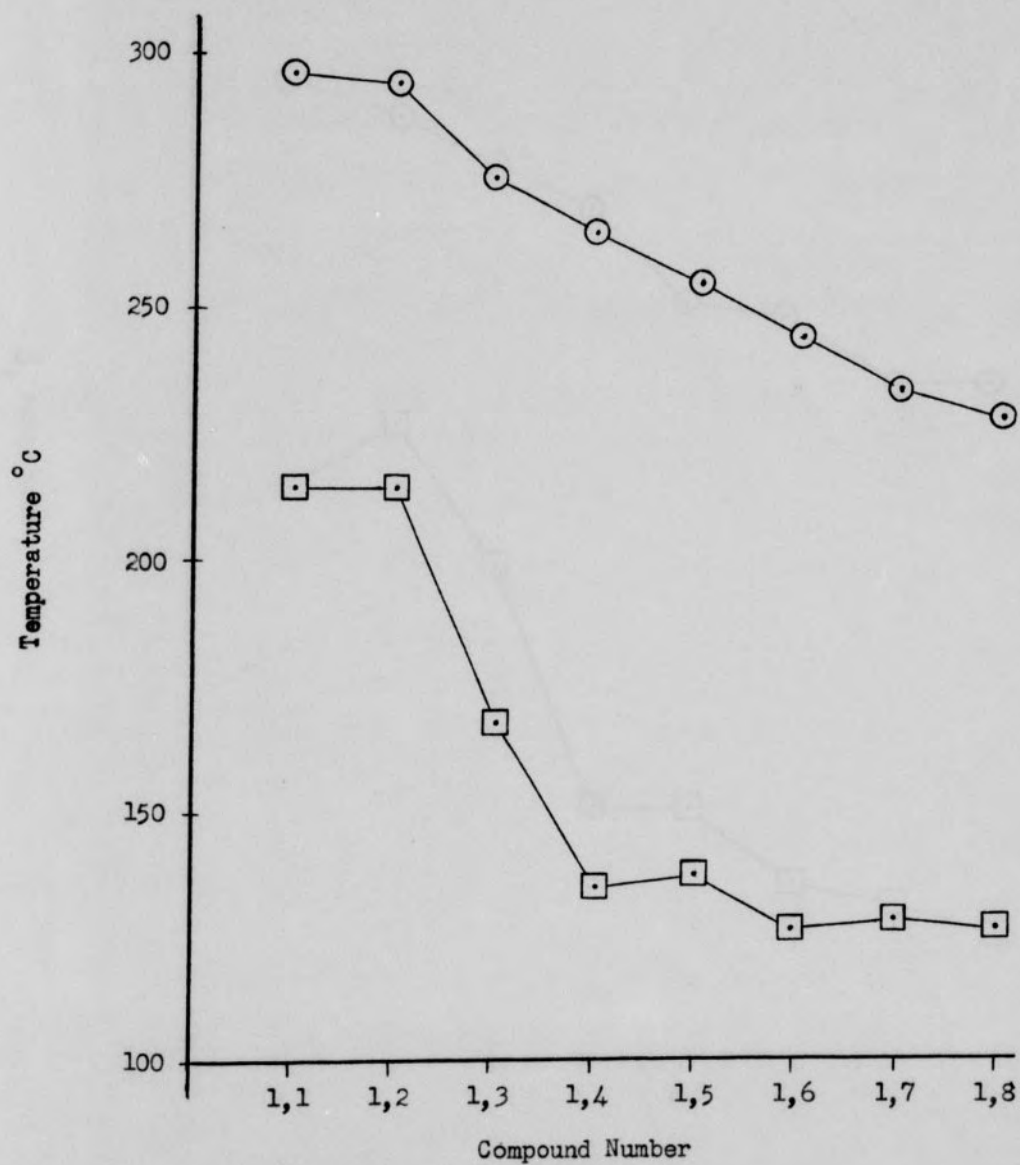[d] Solid → Smectic Transition 122°C

Figure 11. Mesomorphic Phase Transition
Temperatures for Series I

Melting Point ⊡
Nematic → Isotropic ⊙
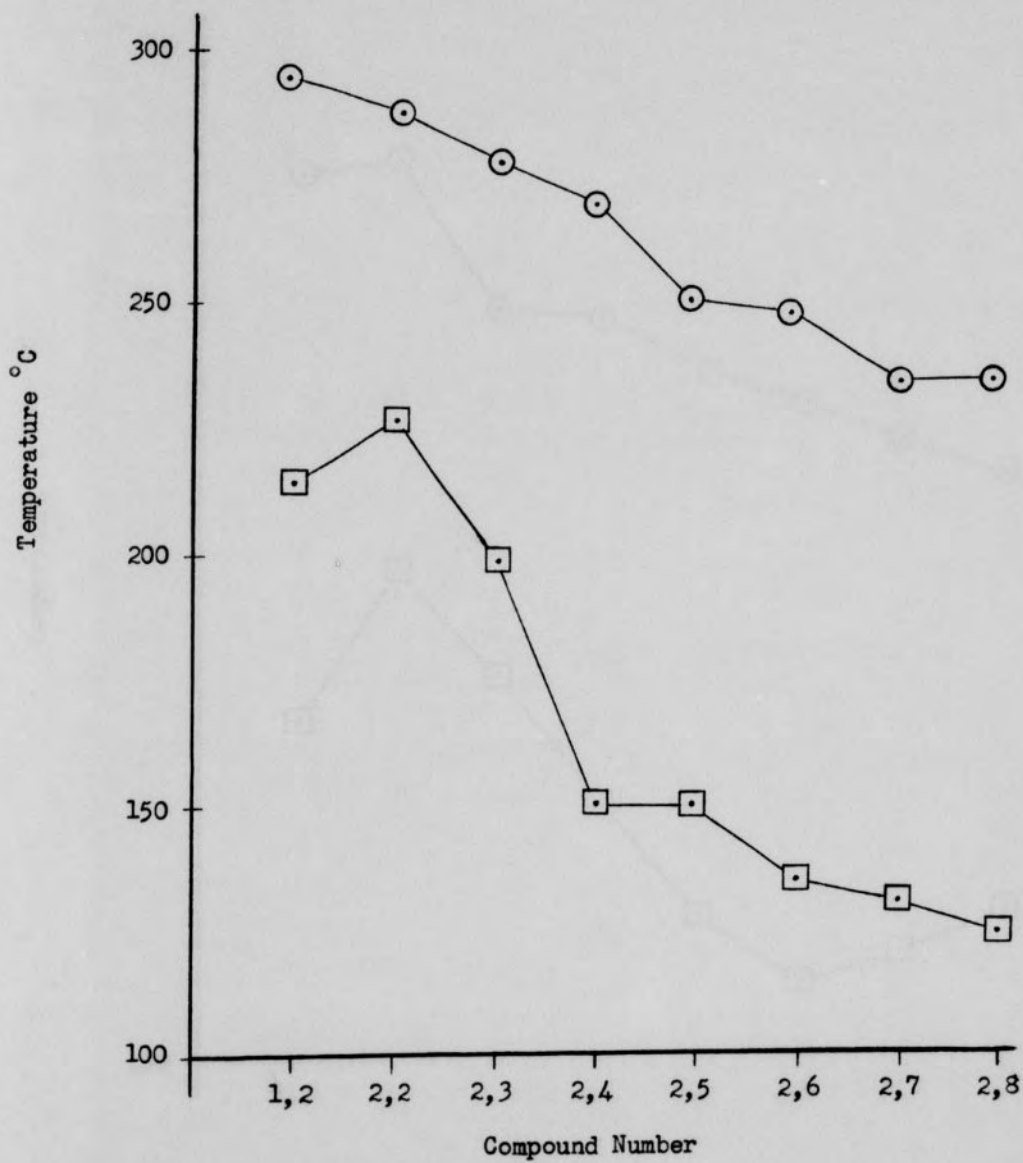
Figure 12. Mesomorphic Phase Transition
Temperatures for Series II

Melting Point ⊡
Nematic → Isotropic ⊙
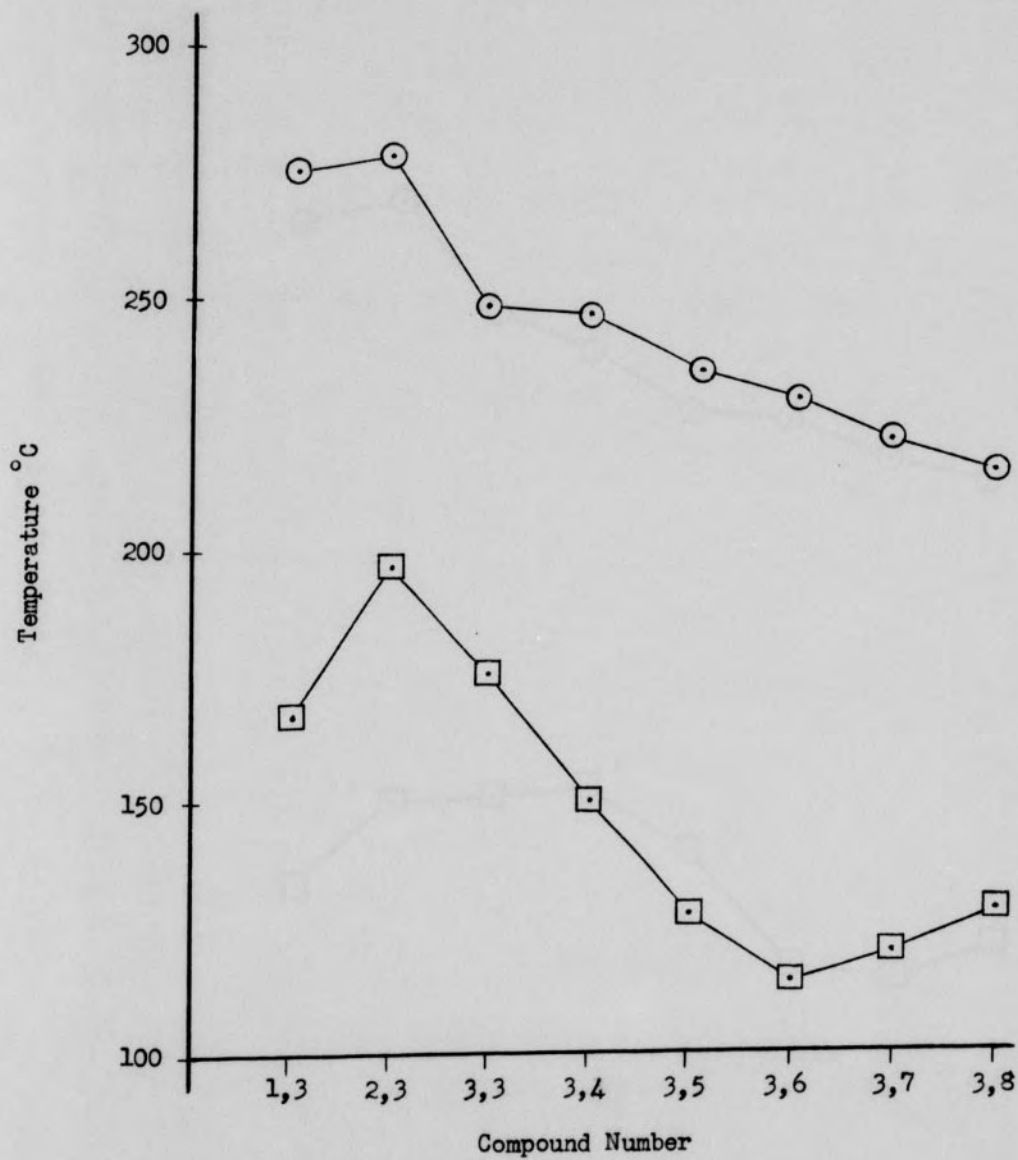
Figure 13. Mesomorphic Phase Transition
Temperatures for Series III

Melting Point ⊡
Nematic → Isotropic ⊙
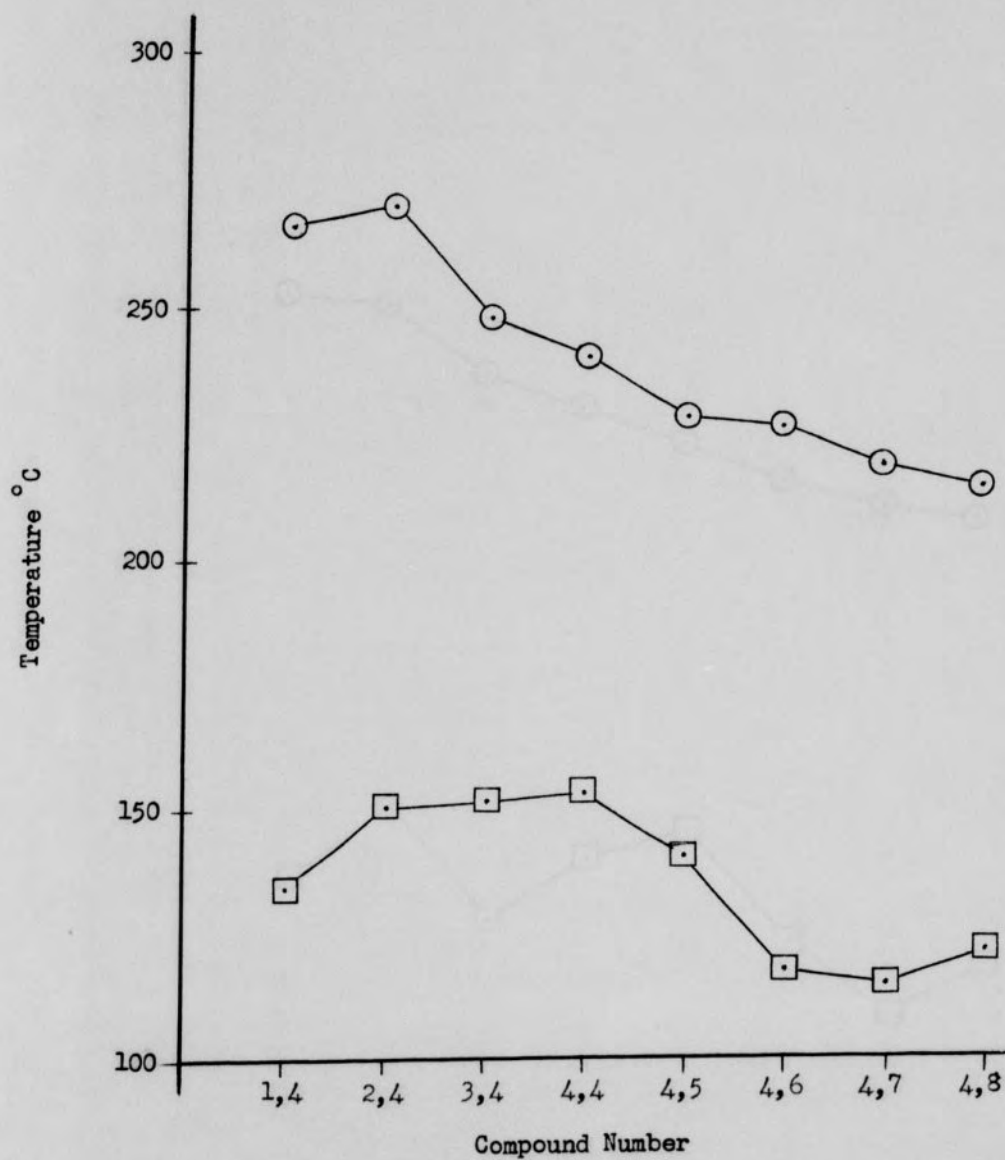
Figure 14. Mesomorphic Phase Transition
Temperatures for Series IV

Melting Point ▢
Nematic → Isotropic ⊙
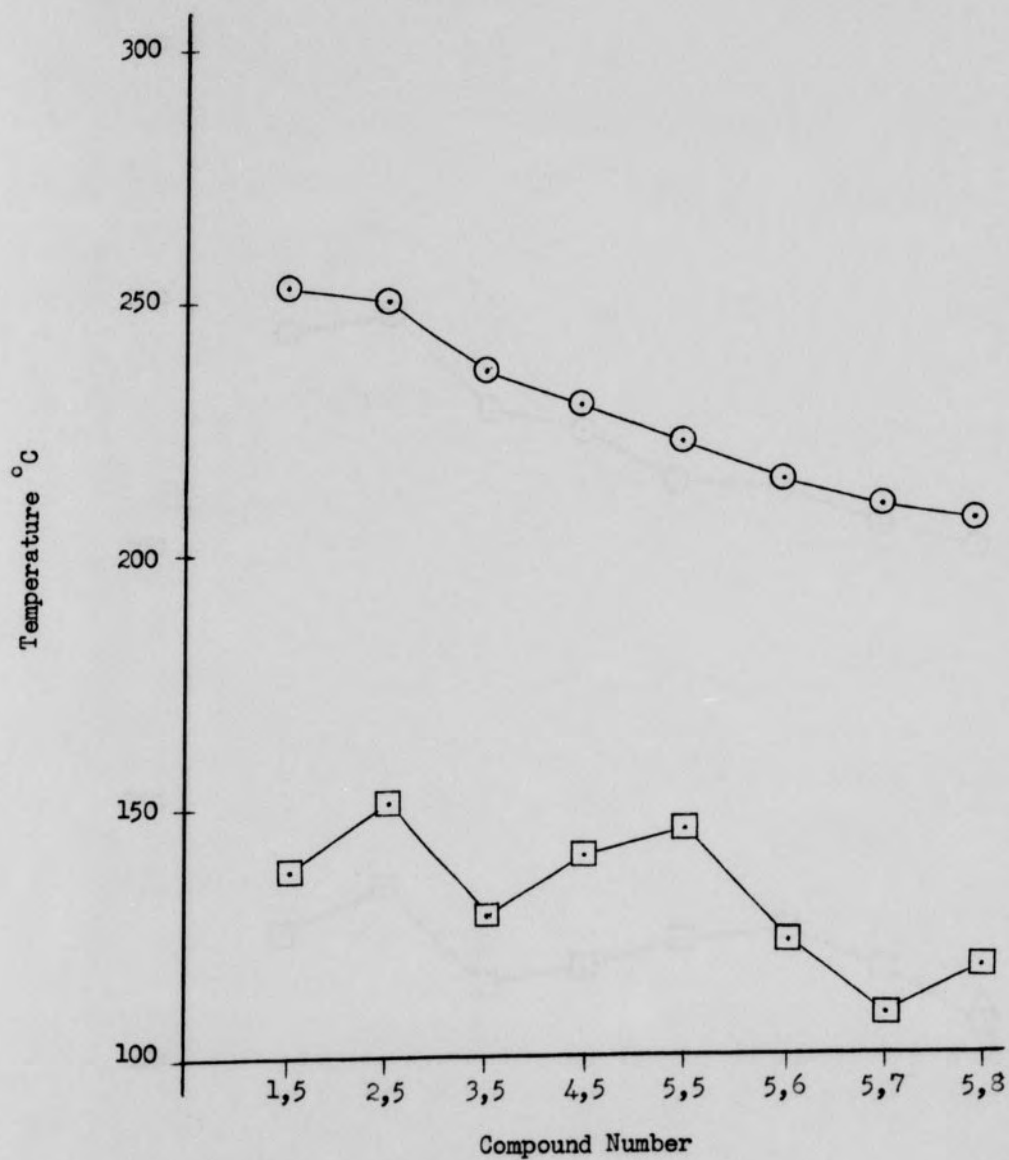
Figure 15. Mesomorphic Phase Transition
Temperatures for Series V

Melting Point ⊡
Nematic → Isotropic ⊙
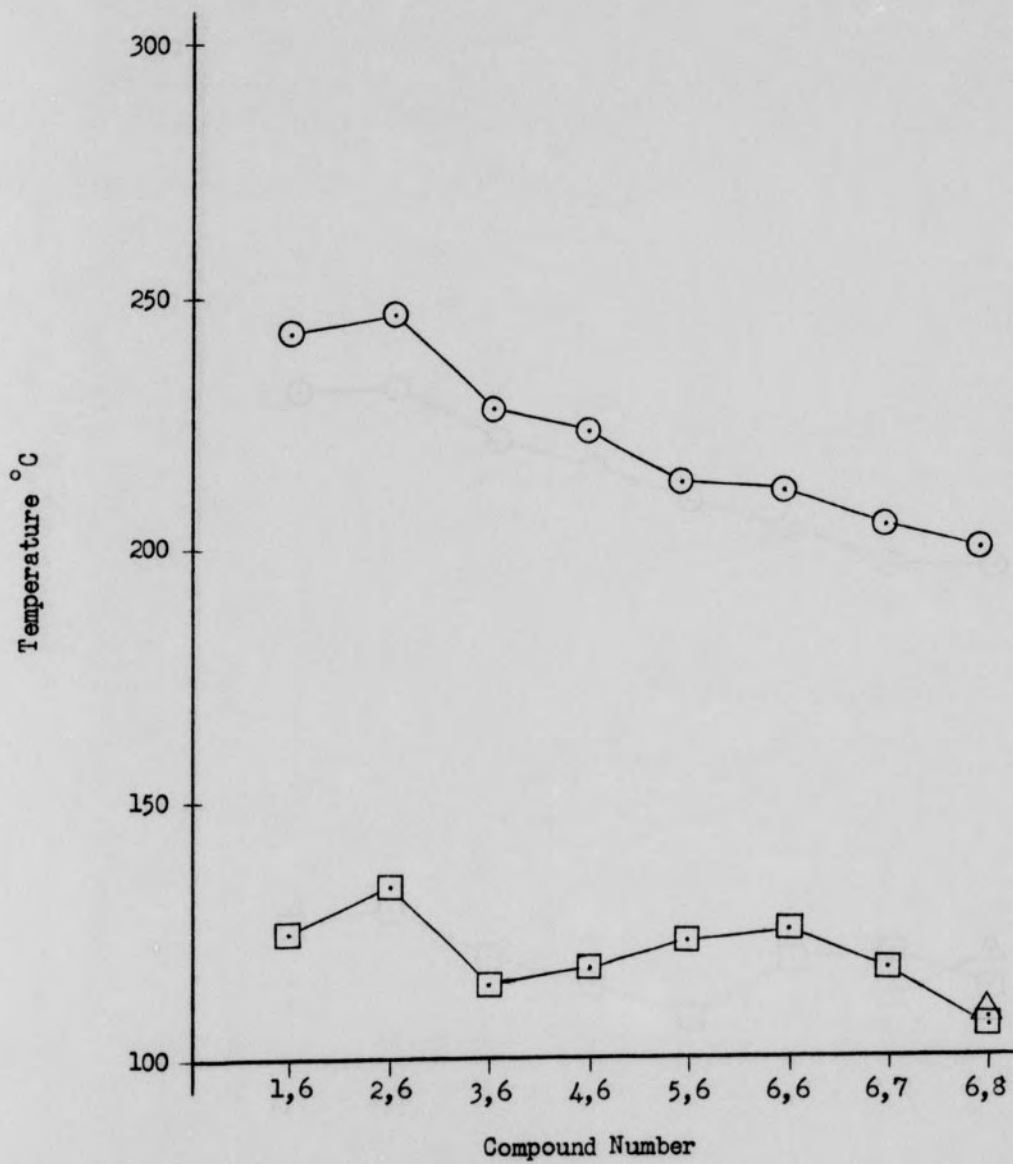
Figure 16. Mesomorphic Phase Transition
Temperatures for Series VI

Melting Point ⊡
Nematic → Isotropic ⊙
Smectic → Nematic △
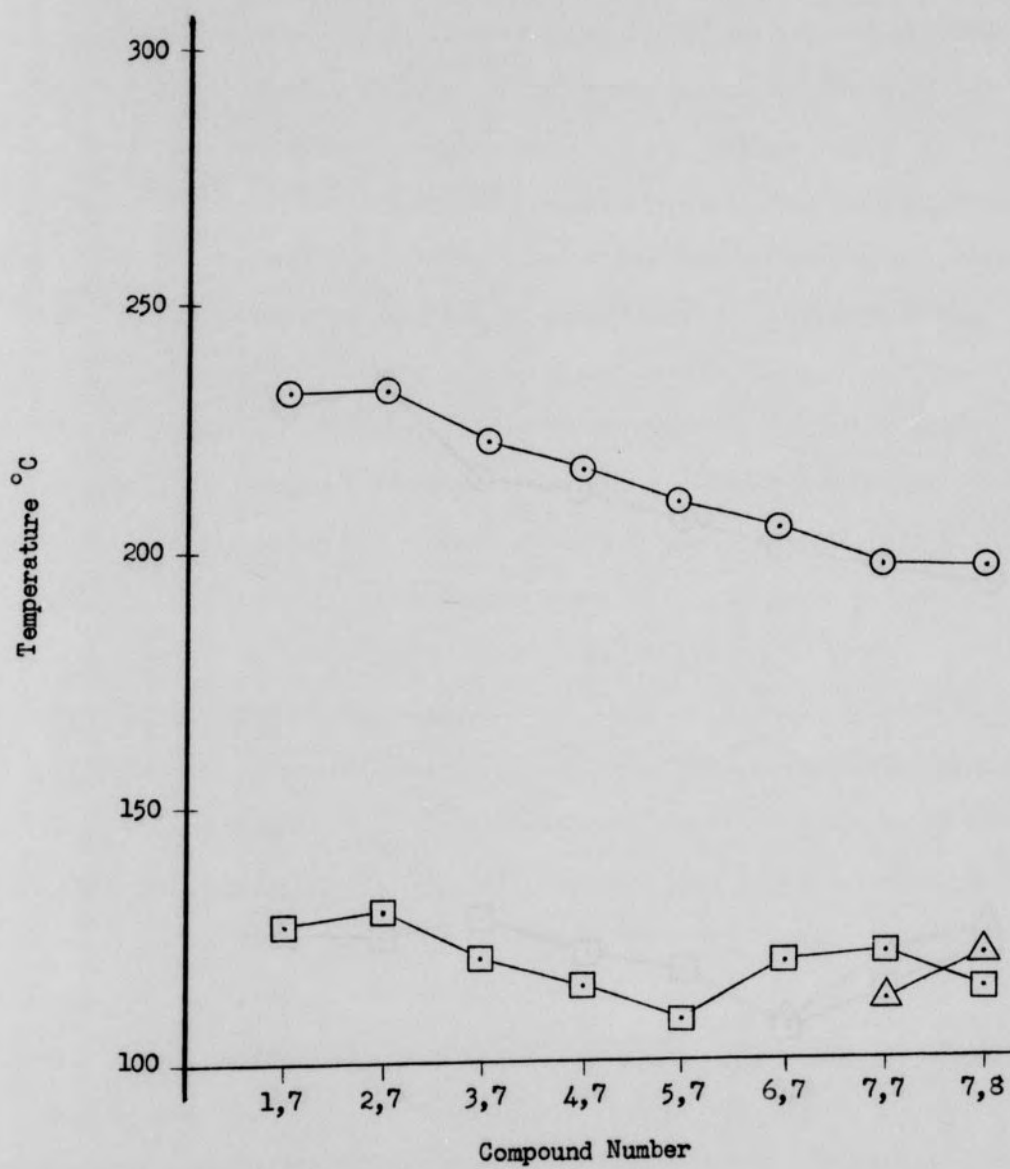
Figure 17. Mesomorphic Phase Transition
Temperatures for Series VII

Melting Point ▫
Nematic → Isotropic ⊙
Smectic → Nematic △

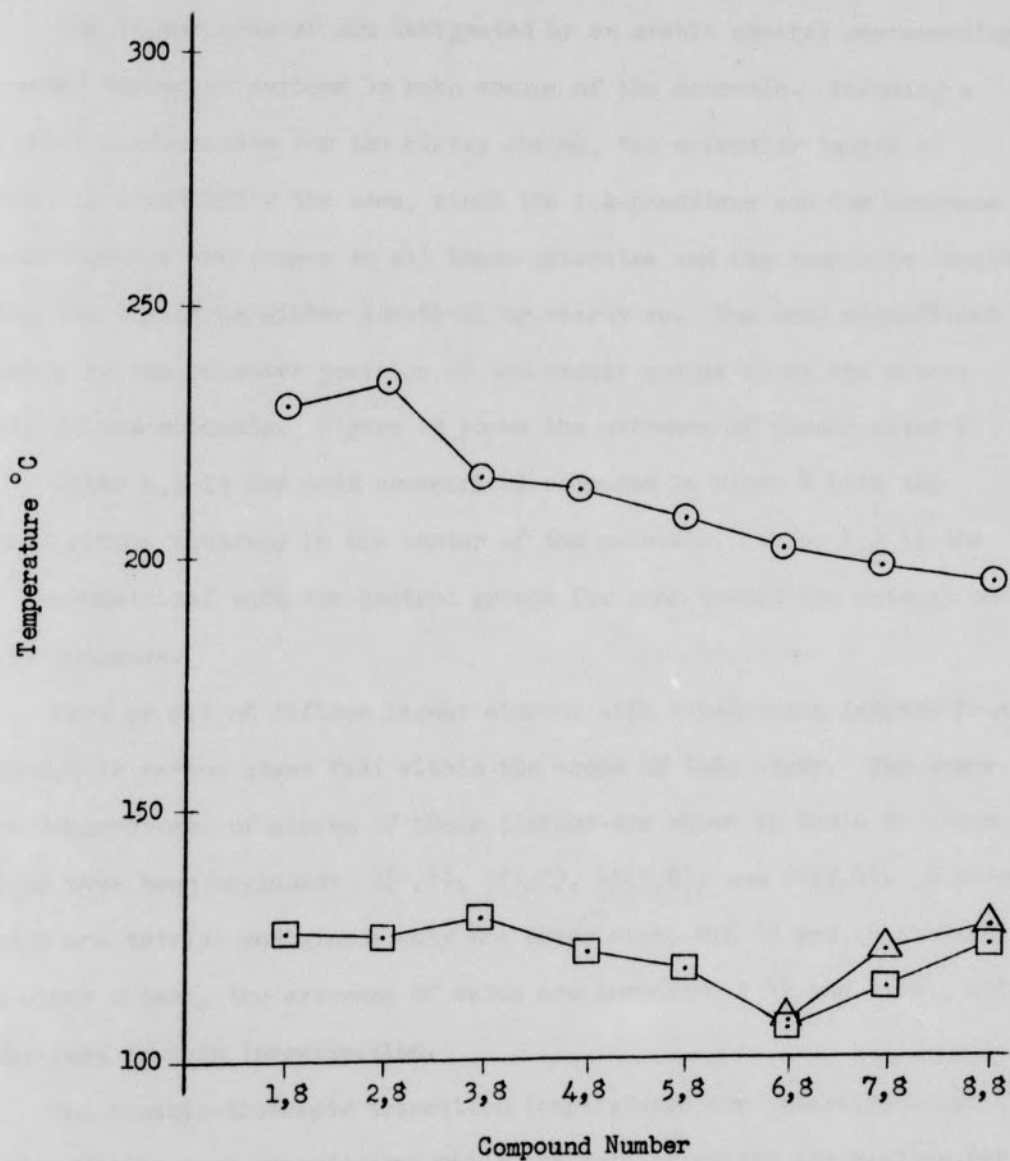Figure 18. Mesomorphic Phase Transition
Temperatures for Series VIII

Melting Point ▣
Nematic → Isotropic ⊙
Smectic → Nematic △

The isomer classes are designated by an arabic numeral representing the total number of carbons in both chains of the molecule. Assuming a cog wheel conformation for the alkoxy chains, the molecular length of isomers is essentially the same, since the 1,4-phenylene and two benzoate "center" groups are common to all these molecules and the composite lengths of the two chains is either identical or nearly so. The only significant variable is the relative position of the center groups along the entire length of the molecule. Figure 19 shows the extremes of isomer class 8.

Ester 4,4 is the most symmetrical compound in class 8 with the central groups squarely in the center of the molecule. Ester 1,7 is the most unsymmetrical with the central groups far over toward the methoxy end of the molecule.

Part or all of fifteen isomer classes with total chain lengths from 2 through 16 carbon atoms fall within the scope of this study. The transition temperatures of eleven of these classes are shown in Table 6. Four classes have been excluded: 2(1,1), 3(1,2), 15(7,8), and 16(8,8). Classes 2 and 3 are trivial containing only one ester each, but 15 and 16 contain many other esters, the extremes of which are compounds 1,14 and 1,15 , not synthesized in this investigation.

The nematic-isotropic transition temperatures are generally about the same within each isomer class while the melting points are maximum for the symmetrical member and tend to be lower for the most unsymmetrical. Fluctuation of these tendencies is probably due to the same effects which cause alternation in the homologous series plots, that is, chain orientations, but this is complicated here by dissymmetry factors. Particularly eccentric in both the isomer classes and homologous series are the
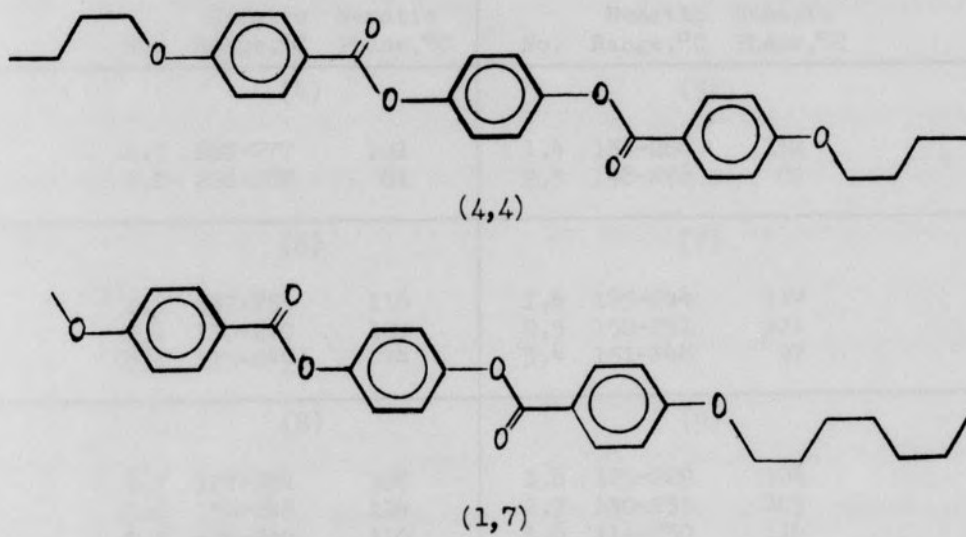
Figure 19. Dissymmetry Extremes
for Isomer Class 3

TABLE 6

MESOMORPHIC PHASE TRANSITION TEMPERATURES OF SYMMETRICAL AND UNSYMMETRICAL 1,4-PHENYLENE ESTERS ARRANGED IN ISOMER CLASSES

No.	Nematic Range, °C	Length Nematic Phase, °C	No.	Nematic Range, °C	Length Nematic Phase, °C
	(4)			(5)	
1,3	167-277	101	1,4	134-266	132
2,2	226-287	61	2,3	198-278	80
	(6)			(7)	
1,5	137-253	116	1,6	125-244	119
2,4	150-270	120	2,5	150-251	101
3,3	175-249	74	3,4	151-248	97
	(8)			(9)	
1,7	127-234	107	1,8	125-229	104
2,6	134-248	114	2,7	130-235	105
3,5	126-236	110	3,6	114-230	116
4,4	153-241	88	4,5	140-229	89
	(10)			(11)	
2,8	124-235	111	3,8	128-216	88
3,7	120-222	102	4,7	114-218	104
4,6	117-226	109	5,6	123-215	92
5,5	145-222	77			
	(12)			(13)	
4,8	121-214	93	5,8	116-207	91
5,7	108-210	102	6,7	118-206	94
6,6	124-213	89			

No.	Smectic Range, °C	Nematic Range, °C	Length Nematic Phase, °C
		(14)	
6,8	106-107	107-202	95
7,7	110[a]	122-199	77

[a]Monotropic

transition temperatures of esters containing methoxy and ethoxy chains. This situation may be the result of the inability of these short chains to shield adjacent molecular chains from the polarizing effects of their own alkoxy oxygen atoms. The ethoxy group in particular behaves this way in both the symmetrical and unsymmetrical series. The member containing an ethoxy chain has the highest or next to highest melting point and nematic-isotropic transition temperature in the homologous series plots. This phenomenon is observed for many homologous series and is probably magnified here by the contamination problem mentioned earlier in the experimental section.

The length of the nematic mesophase within the homologous series is shortest for the symmetrical ester. The position of the longest nematic mesophase is somewhat dependent on the erratic behavior of the melting points, but does tend to occur early in each series, where the nematic-isotropic transition temperature is near the maximum and the melting point is either rapidly dropping, as in series I, II, and III, or is low to begin with, as in series IV through VIII.

Within the isomeric classes, the most symmetrical ester has the shortest nematic mesophase. The most unsymmetrical esters tend to have the longest nematic mesophases although the trends are not as clear due to the incompleteness of some of the classes. For example, class 13 encompasses esters 6,7 through 1,12, but 4,9 through 1,12 were not synthesized in this study. From the behavior of other shorter, more completely investigated classes, it seems that the more unsymmetrical the ester, the wider is its nematic range. Presumably, this is because the increased dissymmetry lowers the melting point (disrupts the crystal lattice) more

than it does the nematic-isotropic transition temperature (disrupts the nematic mesophase).

The maintenance of the nematic stabilities, despite inherent dissymmetry, recalls the earlier reasoning concerning the "intramolecular mixture." It would be of interest to compare the transition temperatures of equimolar mixtures of the symmetrical esters with the transition temperatures of the analogous unsymmetrical compounds, for example, a mixture of 1,1 and 2,2 versus the 1,2 ester. Unfortunately, no studies of this type have yet been done. Estimation of the mixture transition temperatures should be possible since, as mentioned in the introduction, mixtures of very similar mesomorphic compounds exhibit mesomorphic transition temperatures which are linearly proportional to the composition.[53,54] With this in mind, it does not seem unreasonable to assume that for a 1:1 mixture of any two symmetrical esters (differing in structure only by chain lengths), the nematic-isotropic transition temperature should be about the average of those for the pure components.

Table 7 contains the observed nematic-isotropic transition temperatures of the unsymmetrical esters ("intramolecular mixtures") and the hypothetical nematic-isotropic transition temperature of the appropriate symmetrical ester mixture, calculated as explained above. Extended discussion would be futile without the actual mixture temperatures but correlations are good, suggesting that nematic mesophase stability in the unsymmetrical esters is determined primarily by the average separation of the polar centers of adjacent molecules. Dissymmetry is also a factor since the poorest correlations in Table 7 are for the most unsymmetrical esters, with abnormally low transition temperatures. The compounds 1,6;

TABLE 7

NEMATIC→ISOTROPIC PHASE TRANSITION TEMPERATURES
FOR UNSYMMETRICAL 1,4-PHENYLENE ESTERS
AND HYPOTHETICAL 1:1 MIXTURES OF
ANALOGOUS SYMMETRICAL ESTERS

No.	Unsymm. Trans. Temp.	Mixture Trans. Temp.
1,2	295	292
1,3	277	273
1,4	266	269
1,5	253	260
1,6	244	255
1,7	234	248
1,8	229	246
2,3	278	268
2,4	270	264
2,5	251	254
2,6	248	250
2,7	235	243
2,8	235	241
3,4	248	245
3,5	236	234
3,6	230	231
3,7	222	224
3,8	216	222
4,5	229	232
4,6	226	227
4,7	218	220
4,8	214	218
5,6	215	218
5,7	210	210
5,8	207	208
6,7	206	206
6,8	202	204
7,8	198	197

1,7; and 1,8 demonstrate this trend most effectively. However, based on actual mixture data for the 4,4'-dialkoxyazoxybenzenes,[52] the calculated transition temperatures are probably too high since the straight line assumption made here fails slightly when the mixed symmetrical compounds differ by such extreme alkoxy chain lengths.

Due to insufficient data, very little can be said about the behavior of the smectic mesophase within the scope of this investigation. The smectic-nematic transition temperatures of the incomplete isomer class 14 are similar. It would be interesting to see if the entire class yields a smectic mesophase. Much is dependent on the melting points here, but since increasing dissymmetry lowers the melting point, it is reasonable to expect smectic properties in them. If the melting points of shorter classes are depressed sufficiently, it is possible smectic properties may appear in the most unsymmetrical members.

Only four homologous series transition temperature plots contain smectic-nematic transitions. Series VIII is the only one to have three in a row and it is strange that the smectic-nematic curve seems to be prematurely leveling off. Whether or not this is a minor fluctuation remains to be seen.

Summary

The original purpose of this research was to synthesize a variety of unsymmetrical 1,4-phenylene esters in an attempt to produce liquid crystalline compounds with wider mesomorphic ranges and lower melting points than had been previously found in the symmetrical analogs. The results bear out the initial assumptions in that dissymmetry disrupts the

ability of the ester molecules to pack efficiently in the solid state crystalline lattice to a greater extent than it affects the anisotropy and molecular interactions in the nematic liquid. The melting points are, therefore, lowered much more than are the nematic-isotropic transition temperatures. Within the context of both the homologous series and the isomer classes, the more unsymmetrical members possess lower melting points and wider ranged nematic mesophases than do their symmetrical parents.

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