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Liquid Crystals: Low Melting Nematic 4, 4'-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines

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LIQUID CRYSTALS: LOW MELTING NEMATIC 4,4'-(ALKYLBENZAL)-2-CHLORO-1,4-PHENYLENEDIAMINES

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

by Herbert S. Cole, Jr. M.S. 1973

By Herbert S. Cole, Jr. (Student's Signature)

Approved by [Signature]
Thesis Advisor

Approved by [Signature]
Committee of Graduate Studies

Date 6/6/73
ACKNOWLEDGEMENT

The author wishes to thank Dr. John Sowa for helpful guidance during the course of this work.

I would also like to express my appreciation to Dr. Siegfried Aftergut and the General Electric Company for support and encouragement throughout this program.
TABLE OF CONTENTS

List of Figures ...................................................... v
List of Tables ....................................................... vi
Abstract .............................................................. vii
Introduction ......................................................... 1
Experimental .......................................................... 14

I. Preparation of Materials ........................................ 14
   a. Preparation of 2-Chloro-1,4-Phenylenediamine .......... 14
   b. Preparation of 4,4'-Bis-(Alkoxybenzal)-2-Chloro-1,4-Phenylenediamines .......... 14
   c. Preparation of p-Alkylbenzaldehydes ................. 15
   d. Preparation of 4,4'-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines .......... 16

II. Detection of Mesomorphic Behavior ............................ 17

Results and Discussion ............................................ 18
Summary .............................................................. 31
Bibliography ........................................................ 32
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Schematic Representation of the Three Types of Liquid Crystals</td>
<td>5</td>
</tr>
<tr>
<td>2.</td>
<td>Mesomorphic Behavior vs. Chain Length for 4'-n-Alkoxybiphenyl-4-Carboxylic Acids</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>Mesomorphic Behavior vs. Chain Length for the 4,4'-Bis-(Alkoxybenzal)-2-Chloro-1,4-Phenylenediamine Series</td>
<td>21</td>
</tr>
<tr>
<td>4.</td>
<td>Mesomorphic Behavior vs. Chain Length for the 4,4'-Bis-(Alkoxybenzal)-1,4-Phenylenediamines</td>
<td>22</td>
</tr>
<tr>
<td>5.</td>
<td>Mesomorphic Behavior vs. Chain Length for the 4,4'-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines</td>
<td>26</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Mesomorphic Behavior of the 4,4'-Bis-(Alkoxybenzal)-2-Chloro-1,4-Phenylenediamines</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>III</td>
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<td>25</td>
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</table>
ABSTRACT

Several homologues of the 4,4'-bis-(alkoxybenzal)-2-chloro-1,4-phenylene series were synthesized and their mesomorphic behavior characterized. Furthermore a new series of liquid crystalline compounds, 4,4'-bis-(alkylbenzal)-chloro-1,4-phenylenediamines, have been synthesized and the mesomorphic behavior characterized up to the C₈ carbon chain length. All homologues showed nematic behavior with broad mesophases and particularly low melting points.
INTRODUCTION

Since the initial discovery of liquid crystals (1), researchers have studied in great detail the relation between molecular structure and mesomorphic or liquid crystalline behavior. Prominent workers in the field included Reinitzer (1), Lehmann (2), Vorlander (3), and Weygand (4). The melting points and clearing points of known liquid crystalline compounds from these early workers was compiled and discussed with relation to molecular structure by Kast (5). More recently Brown et al (6), Saupe (7) and Gray (8) have given general reviews of mesomorphic behavior.

Initially it was recognized that there were three possible states of matter, namely the solid state, the isotropic liquid and the gaseous state. The solid state can be composed of a regular three-dimensional array of molecules or ions or it can be amorphous where the regular arrangement is absent and there exists a random
arrangement of molecules. Most solids exhibit a crystalline arrangement of molecules and we shall focus our attention on them. When a solid crystal is heated, the thermal vibrations increase with increasing temperature and when the molecules are no longer able to maintain themselves in a regular arrangement the solid begins to melt to an isotropic liquid. In the case of inorganic molecules where strong interionic attractions exist this melting temperature is quite high (typically about 500°C). With organic compounds the weaker intermolecular cohesive forces break at lower temperatures and give rise to much lower melting points (even below room temperature). This breaking of intermolecular or ionic attractions usually occurs over very small temperature ranges and gives rise to sharp melting points, therefore it is not surprising that melting points are used for the identification of pure substances. At higher temperatures random attractions are minor and vaporization occurs. The boiling point and melting point of an organic compound are quite reproducible providing there has been no decomposition.
In 1888 Reinitzer (1) prepared a series of esters of cholesterol in which he noticed strange melting phenomena. Upon heating cholesteryl benzoate he observed a sharp melting transition at 145.5° but the melt was optically opaque and did not clear until 178.5°. Initial characterization showed the opaque fluid possessed both crystalline and liquid behavior. When a thin film was placed between crossed polarizers the fluid matter exhibited anisotropic optical properties. Lehmann (2) found similar observations for p-azoxyphenetole.

\[ H_5C_2O - \begin{array}{c} \text{N= N} \\ \text{O-C}_2H_5 \end{array} \]

This molecule contains two aromatic rings held together by a rigid bridging group. This elongated molecule has intermolecular attractions which differ at the terminal ends and the lateral portion of the molecule. This is a different arrangement than we have with more spherically shaped molecules where the lateral and terminal attractions are nearly identical. As the
temperature is raised, the weaker intermolecular attractions (i.e. the terminal intermolecular forces) will break down. On the other hand the lateral forces remain intact and hence the molecules can slide in layers over one another. This fluidic substance still possesses long-range molecular order, and hence constitutes a fourth state of matter namely, the liquid crystalline or mesomorphic state. This mesomorphic state is generally exhibited by long, rod-shaped organic molecules that contain dipolar and polarizable groups. The mesophase exists over specific temperature ranges below which exists the solid state and above which exists the isotropic liquid. This discussion is restricted to thermotropic mesophases; a discussion of lyotropic mesophases can be found in ref. 9.

After extensive optical studies on mesomorph ic materials, Friedel (10) discovered three main types of mesomorphic states which he designated as smectic, nematic and cholesteric. Figure 1 shows schematically these three distinct types of molecular ordering.
FIGURE 1

SMECTIC

NEMATIC

CHOLESTERIC

Schematic Representation of the Three Types of Liquid Crystals
The smectic mesophase consists of a turbid, highly viscous state. The term smectic is derived from the Greek word "smectos" meaning soaplike. In this state the molecules are arranged in layers with the long molecular axes of the molecules parallel to each other. These layers can slide in two directions.

In the nematic (threadlike) state the liquid is a turbid, mobile fluid with the long axes of the molecules parallel to each other. The molecules are mobile in three directions due to a different ratio of lateral to terminal intermolecular attractions.

The cholesteric mesophase is generally found in derivatives of cholesterol. The structure consists of parallel, monomolecular layers in which the direction of the long axes of molecules in a given layer is slightly displaced from the direction of the axes of molecules in an adjacent layer. This displacement from one layer to another results in a helical structure.

In this thesis we are only concerned with smectic and nematic behavior and their relationships to molecular structure. Gray (8) has shown that when
the mesomorphic transition temperatures for a homologous series of compounds are plotted against the number of carbon atoms in the terminal alkyl chain, certain smooth curve relationships occur. These relationships, in fact, can be used as a criterion of purity for the homologous series since departures from these smooth curve trends are usually due to impurities. Mesomorphic transition temperatures are extremely sensitive to trace amounts of impurity, melting points and clearing points can be depressed much more than transition temperatures in ordinary compounds.

Figure 2 is a plot of mesomorphic transition temperature vs. alkoxy chain length for the homologous series of 4'-n-alkoxybiphenyl-4-carboxylic acids (11). This figure shows that for relatively short chain homologues we have purely nematic behavior. As the chain length is increased, the overall polarizability of the molecule is increased (11), but the terminal intermolecular attractions decrease because of the greater length between the highly polarizable aromatic rings.
FIGURE 2

Mesomorphic Behavior vs. Chain Length for 4'-n-Alkoxybiphenyl-4-Carboxylic Acids (11).
This causes the layers to slip over one another and gives rise to smectic behavior. For very long chain lengths the lateral intermolecular attractions are very large with respect to the terminal intermolecular attractions and purely smectic behavior is obtained. Furthermore, we see that the nematic to isotropic transition temperatures fall along two distinct lines such that a smooth curve of the even numbered carbon chains lies below the curve for the odd numbered ones. This regular alternation has been accounted for by Gray (8) on the basis of molecular conformations. If we assume a cog-wheel (eclipsed) conformation and start adding methylene groups in the chain we see that the separation of the polarizable groups is being increased by different amounts:

- for even we have $X$
- for odd we have $Y = (\cos 70^\circ) (X)$
For the odd numbered case the decrease in terminal strength has a \( \cos 70^\circ \) factor and results in a larger increase in polarizability when going from an odd member to an even member of the series. Hence on this basis we can explain the fact that clearing points of the even numbered chains lie on a curve above the odd numbered members of the alkoxy series. Similarly for ester or hydrocarbon terminal groups the clearing points of the odd numbered chains lie on a curve above the even numbered members of the series. As this chain length is increased, the contribution of each successive methylene group becomes smaller and the regular alternation from odd to even becomes negligible.

The effects of lateral substitution on the meso-phase should also be considered. For example, a halogen or other bulky group on the aromatic ring of the series described in Figure 2 would tend to force the long molecules further apart and reduce the lateral inter-molecular attractions on the basis of steric factors.
There would also be an increase in polarizability of the molecule and this could reinforce the lateral and terminal intermolecular attractions. However, the overall effect is generally a decrease in lateral strength and a decrease in smectic and nematic thermal stabilities. The above can be summarized by the following:

(1) For mesomorphic behavior we require a long, rigid molecule with polarizable groups.

(2) Short terminal chains give nematic behavior whereas increasing chain length tends to favor smectic behavior.

(3) By increasing the breadth of the molecule the thermal stability can be reduced for nematic as well as smectic behavior.

During the past decade, a primary goal of researchers in this field has been the synthesis of liquid crystals of low thermal stability such that the mesophase would include room temperature. The primary
motivation for this effort has been the possibility of commercial applications of nematic liquid crystals in the electro-optic display field (12). To date three such single component materials have been found to exhibit liquid crystalline behavior at room temperature, \( N-(p\text{-methoxybenzylidene}) \) \( p\text{-n-butylaniline} \) (13), \( \text{dL-4-}(2\text{-methylhexyl})\text{-4'\text{-ethoxy-}}\alpha\text{-chloro-trans-stilbene} \) (14), and \( p,p'\text{-di-n-butylazoxybenzene} \) (15). However, the mesophase of these compounds do not occur over large enough temperature ranges to make them applicable for electro-optical display devices where variable operating temperatures are required. One method of achieving extended temperature ranges has been through the use of mixtures (16). For example, Fishel and Hsu report that a 1:1 mole mixture of \( N-(p\text{-methoxybenzylidene}) \) \( p\text{-n-butylaniline} \) and \( N-(p\text{-propoxybenzylidene}) \) \( p\text{-n-heptylanilne} \) are nematic between \(-36^\circ\text{ to } +57^\circ\), however they do not rule out the possibility of a supercooled state which is usually observed with nematic liquid crystals.
Another approach has been attempted in this thesis which involves the preparation of liquid-crystalline compounds with a broader range of mesomorphic behavior. It had been shown by Gray (8) that substitution leading to an increase in molecular breadth would decrease the smectic and thermal stabilities. Therefore substituted phenylenediamines appeared to be of particular interest.

To further study the effects of molecular structure on mesomorphic behavior a series of 4,4′-bis-(alkoxybenzal)-2-chloro-1,4-phenylenediamines were synthesized. Portions of this series had been synthesized earlier by Arora, et al (17). Evaluation of this series led to the synthesis of a new homologous series namely 4,4′-bis-(alkylbenzal)-2-chloro-1,4-phenylenediamines. This series showed broad nematic mesophases and particularly low melting points.
I. Preparation of Materials

a. Preparation of 2-Chloro-1,4-Phenylenediamine

2-Chloro-1,4-phenylenediamine was prepared by neutralizing the dihydrochloride (Aldrich Chemicals) in aqueous solution followed by extraction with benzene. The benzene layer was filtered and taken to dryness to yield the free diamine which melted 64 - 64.5°C (lit. 64°C) (15).

b. Preparation of 4,4'-Bis-(Alkoxybenzal)-2-Chloro-1,4-Phenylenediamines

The 4,4'-bis-(alkoxybenzal)-2-chloro-1,4-phenylenediamines were synthesized by heating 0.01 moles of the diamine with 0.02 moles of the appropriate p-alkoxybenzaldehyde (obtained commercially from Eastman Organic Chemicals) at 80°C for 1/2 hour. The product was isolated and recrystallized several times from absolute ethanol. The recrystallizations were continued until a reproducible mesophase was evident.
c. Preparation of p-Alkylbenzaldehydes

The p-alkylbenzaldehydes were prepared (ref. 25) by adding 0.2 moles of the appropriate alkylbenzene to a mixture of 63.4 g. titanium tetrachloride in 100 ml of carbon disulfide (maintained below 10°C). While keeping the temperature below 10°C, 22 g. of dichloromethyl methyl ether was added dropwise over the course of 10 minutes with strong agitation. After an additional 10 minutes of mixing at room temperature the reaction mixture was poured over ice. The product was then extracted into ether and washed with distilled water, 5% NaHCO₃, and again with water. The ether was removed from the organic layer and the residue steam distilled. The product was then extracted into ether, isolated, the ether removed and the product vacuum distilled. Typical yields were 30-40%.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling Point, Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-propylbenzaldehyde</td>
<td>(78°C, 0.5 mm.)</td>
</tr>
<tr>
<td>p-butylbenzaldehyde</td>
<td>(80°C, 0.4 mm.)</td>
</tr>
<tr>
<td>p-amylbenzaldehyde</td>
<td>(105°C, 0.5 mm.)</td>
</tr>
<tr>
<td>p-hexylbenzaldehyde</td>
<td>(112°C, 0.4 mm.)</td>
</tr>
<tr>
<td>p-heptylbenzaldehyde</td>
<td>(119°C, 0.5 mm.)</td>
</tr>
<tr>
<td>p-octylbenzaldehyde</td>
<td>(128°C, 0.5 mm.)</td>
</tr>
</tbody>
</table>
d. Preparation of 4,4'-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines

4,4'-Bis-(alkylbenzal)-2-chloro-1,4-phenylene-diamines were prepared by heating 0.01 moles of the diamine with 0.02 moles of the appropriate p-alkylbenzaldehyde at 80°C for 1/2 hour. The product was isolated and recrystallized several times in absolute ethanol or isopropyl alcohol until a constant mesomorphic range was obtained. Liquid crystals are known to supercool and remain in this state for extended periods of time. To avoid this problem, the compounds were recrystallized at -15°C where necessary to insure that a true melting point was obtained.

Some of the compounds were analyzed for elemental composition with the following results, calculated values in parenthesis:

4,4'-Bis-(methylbenzal)-2-chloro-1,4-phenylenediamine: C, 75.96(76.50); H, 5.44(5.50); N, 8.15(8.12).

4,4'-Bis-(ethylbenzal)-2-chloro-1,4-phenylenediamine: C, 76.54(77.25); H, 6.53(6.18); N, 7.19(7.48).

4,4'-Bis-(propylbenzal)-2-chloro-1,4-phenylenediamine: C, 77.95(77.60); H, 6.89(6.71); N, 6.98(6.97).
4,4'-Bis-(hexylbenzal)-2-chloro-1,4-phenylenediamine: C, 79.43(79.05); H, 8.36(8.05); N, 5.79(5.77).

4,4'-Bis-(heptylbenzal)-2-chloro-1,4-phenylenediamine: C, 80.15(79.20); H, 8.55(8.38); N, 5.28(5.44).

II. Detection of Mesomorphic Behavior

The transition temperatures of the compounds prepared were determined by several methods. A Rinco Instrument Company melting point apparatus was used to visually inspect the melting and clearing points. In addition, a Perkin-Elmer Differential Scanning Calorimeter Model #DSC-1B was used to confirm the transition temperatures.

All of the liquid crystals synthesized were shown to rotate the plane of polarized light (a known property of mesomorphic materials) (ref. 8) by placing a few crystals of the sample between microscope slides and the sandwich warmed above the melting point but below the clearing point and inspecting between crossed polarizers.
RESULTS AND DISCUSSION

The results of the 4,4’-bis-(alkoxybenzal)-2-chloro-1,4-phenylenediamine series are shown in Table I. It is interesting to compare this series with the unsubstituted phenylenediamine series examined by Gray, et al (18). Table II summarizes his results.

These results are further shown in Figures 3 and 4. As predicted the melting points for the substituted phenylenediamines are much lower than the unsubstituted compounds. With the chlorine positioned on the central aromatic ring, the overall breadth of the molecule is increased which in turn weakens the lateral intermolecular attractions even though the overall polarizability of the molecule in the lateral direction is increased. Another indication of decreased lateral attractions is that smectic behavior in the substituted phenylenediamine series does not occur until the C_9 alkyl chain length is reached whereas the unsubstituted series shows smectic behavior at C_5. With the substituted series
TABLE I

Mesomorphic Behavior of the 4,4'-Bis-(Alkoxybenzal)-2-Chloro-1,4-Phenylenediamines

\[
\begin{align*}
H_3C - (CH_2)_n - O - & \quad CH = N - \quad N = CH - O - (CH_2)_n - CH_3 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>n</th>
<th>SOLID → SMECTIC</th>
<th>SOLID → NEMATIC</th>
<th>SMECTIC → NEMATIC</th>
<th>NEMATIC → ISOTROPIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>135 (131)</td>
<td>-</td>
<td>277 (275.5)</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>133</td>
<td>-</td>
<td>276</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>110</td>
<td>-</td>
<td>237</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>79</td>
<td>-</td>
<td>228</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>97 (96.8)</td>
<td>-</td>
<td>203 (205)</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>96 (100)</td>
<td>-</td>
<td>197 (199)</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>183</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>60 (59)</td>
<td>-</td>
<td>181 (179)</td>
</tr>
<tr>
<td>8</td>
<td>(71)</td>
<td>-</td>
<td>(96)</td>
<td>(172)</td>
</tr>
<tr>
<td>9</td>
<td>66 (66)</td>
<td>-</td>
<td>112 (112)</td>
<td>166 (166)</td>
</tr>
</tbody>
</table>

Values in parenthesis reference 17.
TABLE II

Mesomorphic Behavior of the 4,4' Bis(-Alkoxybenzal)-1,4-Phenylenediamines

\[ \text{H}_3\text{C}-(\text{CH}_2)_n\text{-O} \begin{array}{c}
\text{CH} = \text{N} \\
\text{N} = \text{CH} \\
\text{O-(CH}_2)_n\text{-CH}_3
\end{array} \]

Transition Temperatures (°C)

<table>
<thead>
<tr>
<th>n</th>
<th>SOLID (\rightarrow) SMECTIC</th>
<th>SOLID (\rightarrow) NEMATIC</th>
<th>SMECTIC (\rightarrow) NEMATIC</th>
<th>NEMATIC (\rightarrow) ISOTROPIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>214.5</td>
<td>-</td>
<td>&gt; 330</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>202.5</td>
<td>-</td>
<td>&gt; 330</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>193</td>
<td>-</td>
<td>313</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>186.5</td>
<td>-</td>
<td>297.5</td>
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<td>228</td>
</tr>
<tr>
<td>9</td>
<td>145.5</td>
<td>-</td>
<td>212</td>
<td>222</td>
</tr>
<tr>
<td>11</td>
<td>137.5</td>
<td>-</td>
<td>208</td>
<td>209</td>
</tr>
</tbody>
</table>
FIGURE 3

Mesomorphic Behavior vs. Chain Length for the 4,4'-Bis(Alkoxybenzal)-2-Chloro-1,4-Phenylenediamine Series.
Mesomorphic Behavior vs. Chain Length for the 4,4'-Bis-(Alkoxybenzal)-1,4-Phenylenediamines (18).
the ratio of lateral to terminal intermolecular attractions remains more favorable for nematic behavior with increasing chain length. Furthermore we see that the odd even alternation of the clearing point is more pronounced in the substituted series. With weaker lateral intermolecular attractions, the contribution of each additional methylene group has more influence on the relative strength of the terminal forces. The unsubstituted series having stronger lateral attractions receives less of a contribution from the addition of a methylene group.

The melting point curves for the two series are more difficult to explain. In the unsubstituted phenylenediamines we see a regular decrease in melting point with increasing chain length. However the chlorophenylenediamine derivatives show a melting point minimum at the C₄ and C₈ chain lengths. This effect cannot be attributed to impurities. Impurities would also alter the clearing points, but Figure 3 shows that the latter fall on a smooth curve. It should be mentioned that melting points of mesomorphic compounds do not always
show smooth curve relationships and in fact others have also seen melting point minimums. For example, Arora, Fergason and Taylor (19) studied a series of 2-methyl-1, 4-phenylene-bis-(p-n-alkoxybenzoates) (C₆ - C₁₈) and showed a similar dip at the C₈ chain length. They also prepared the unsubstituted series and although there were irregular melting points beyond C₁₀, they showed no minimum at the C₈ carbon. It appears that the steric factor present in the laterally substituted compounds causes a change in the packing density of the molecules in the crystalline state. The C₄ and C₈ carbon chains and to a lesser degree the C₃ and C₇ carbon chains pack more loosely and hence have weaker intermolecular attractions.

To better evaluate the steric effects of the laterally substituted series, a new series, 4,4' bis-(alkylbenzal)-chloro-1, 4-phenylenediamines were synthesized. Their properties are shown in Table III.

Figure 5 shows the effect of chain length on the mesomorphic behavior. In comparing the alkyl series with the alkoxy series (Figure 3), we see a strong decrease in
TABLE III

Mesomorphic Behavior of the 4,4'-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines

<table>
<thead>
<tr>
<th>Alkyl Group</th>
<th>Transition Temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NEMATIC</td>
</tr>
<tr>
<td>N = C - C H</td>
<td>SMECTIC</td>
</tr>
<tr>
<td></td>
<td>ISOTROPIC</td>
</tr>
<tr>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>197</td>
</tr>
<tr>
<td>1</td>
<td>170</td>
</tr>
<tr>
<td>2</td>
<td>185</td>
</tr>
<tr>
<td>3</td>
<td>152</td>
</tr>
<tr>
<td>4</td>
<td>131</td>
</tr>
<tr>
<td>5</td>
<td>133</td>
</tr>
<tr>
<td>6</td>
<td>125</td>
</tr>
</tbody>
</table>

\[
H_3C - (C_2H_5)_m - CH = N - (C_6H_4)(C_2H_5) - C H_3
\]
Mesomorphic Behavior vs. Chain Length for the 4,4'-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines
the thermal stability of the alkyl derivatives. Steinstrasser (20) showed that p,p'-disubstituted phenyl p-benzoyloxybenzoates showed broad nematic mesophases although the lowest melting point achieved was 89°C. In a more recent publication Van Meter (21) and Klanderman showed that substitution on the central aromatic ring by a chlorine atom lowered the melting points but kept the mesophase broad. One compound (I) studied

![Chemical Structure](image)

reportedly was nematic between 39 - 104.5°C. They also stated that this compound has the largest range (yet obtained) for any single component liquid crystal with a crystal to nematic transition below 40°. However, the C₆, C₇ and C₈ bis alkyl derivatives reported in Table III all show lower melting points and broader mesophases than I. The C₇ derivative which is
nematic between 32 - 133°C represents the lowest melting (chlorophenylenediamine) derivative synthesized to date. The 101° temperature range over which the mesophase exists makes it a potentially significant material for electrooptical display applications.

The further depression of the melting points for the alkyl series can be attributed to the absence of the oxygen linkage at the ends of the molecule. The C - O bond in the alkoxy series has a dipole moment that contributes to the polarizability of the lateral forces of the molecule as well as the terminal forces. The effect of this is to strengthen the lateral and terminal forces and hence give more thermal stability to the crystalline phase. Further we see that the addition of each successive methylene group in the alkyl series shows a more pronounced effect on the odd-even alternation of the clearing points. With less polarizability at the ends of the molecule, the terminal methyl group contributes more to the polarizability of the molecule and in the case of the even numbered carbons will contribute less than the odd numbered carbon atoms. Therefore in the
case of the alkyl derivatives (Figure 5) it is the odd numbered carbon atoms which fall on a line above the even numbered carbon atoms.

The melting points are again more difficult to explain. In the alkoxy series there was a melting point depression at the C\textsubscript{3} and C\textsubscript{4} as well as the C\textsubscript{7} and C\textsubscript{8}. The alkyl series shows a depression at the C\textsubscript{4} chain length which however is not as pronounced as with the alkoxy series. The original explanation of this depression was made exclusively on the basis of steric considerations, however after evaluating the alkyl series, the results suggest that the oxygen atom was somewhat responsible for the melting point depressions in the alkoxy series. At the present there is insufficient understanding of the relationship between melting point and molecular structure.

In summation we can say that the reduction in melting temperatures is due to a net overall decrease in polarizability of the molecule but by providing a substitution on the central phenylenediamine ring we are able to maintain a favorable ratio of intermolecular forces and yield broad mesomorphic behavior.
The significance of this new series of compounds is found in the following. The broad mesophase is useful for making mixed liquid crystals with even broader operating ranges. For example, an equimolar mixture of the $C_6$ and $C_8$ derivatives was nematic between $20 - 127^\circ$. This represents a significant improvement over known literature temperature ranges. Further for a nematic liquid crystal to exhibit the electro-optic effect of dynamic scattering (22, 23) it must possess a negative dielectric anisotropy, where $\Delta \varepsilon = \varepsilon_{11} - \varepsilon_\perp$. The chlorine substituent on the central aromatic ring should increase the perpendicular component and in turn increase the magnitude of the overall negative dielectric anisotropy. A larger negative dielectric anisotropy may be useful for different electro-optic effects (24).
SUMMARY

A new series of liquid crystalline compounds, 4,4'-bis-(alkylbenzal)-2 chloro-1, 4-phenylenediamines, have been synthesized. The mesomorphic behavior has been characterized for the series up to the C\textsubscript{8} carbon chain length. All homologues show nematic behavior and are characterized by broad mesophases and particularly low melting points. The C\textsubscript{7} homologue which is nematic between 32° - 133°C has potential use for electro-optic display applications where large operating temperature ranges are required. Further eutectic mixtures can be made to lower the melting point and further broaden the mesophase. For example, an equimolar mixture of the C\textsubscript{6} and C\textsubscript{8} derivatives was nematic between 20 - 127°C.
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