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# Low-Melting Nematic 4,4′-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines

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# Low-Melting Nematic 4,4′-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines†

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A series of 4,4′-bis-(alkylbenzal)-2-chloro-1,4-phenylenediamines were prepared and their mesomorphic behavior characterized. All homologues showed nematic behavior with broad mesophases and rather low-melting points. The mesomorphic behavior is compared with that obtained from the 4,4′-bis-(alkoxybenzal)-1,4-phenylenediamine series[1] and the 4,4′-bis-(alkoxybenzal)-2-chloro-1,4-phenylenediamine series.[2]

## INTRODUCTION

The synthesis of nematic liquid crystals with low-melting points and broad mesophases are of great importance to researchers involved in developing various electrooptic liquid crystal displays. In search of such materials it was noted that the 4,4′-bis-(alkoxybenzal)-1,4-phenylenediamine series showed rather broad mesophases[1] and that substitution of a chlorine atom on the central aromatic ring[2] was effective in reducing the melting points while maintaining a broad mesophase range. Similar results had also been obtained for substituted phenyl 4-benzoyloxbenzoates.[3]

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In light of this, it seemed of interest to substitute alkyl chains for alkoxy ones in the substituted phenylenediamine series in an effort to get a further reduction in the melting point (as had been shown by Gray).[4] Therefore a series of 4,4′-bis-(alkylbenzal)-2-chloro-1,4-phenylenediamines was synthesized. For completeness the series of 4,4′-bis-(alkoxybenzal)-2-chloro-1, 4-phenylendiamines was also synthesized. Portions of this series had been prepared earlier by Arora *et al.*[2] The results are presented below together with comments on the relation between molecular structure and mesomorphic behavior.

## EXPERIMENTAL

### A Preparation of Materials

1 *Preparation of 2-chloro-1,4-phenylenediamine* 2-Chloro-1,4-phenylenediamine was prepared by neutralizing the dihydrochloride (Aldrich Chemical Company) 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° to 64.5°C (lit. 64°C).

2 *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 mole of the diamine with 0.02 mole of the appropriate *p*-alkoxybenzaldehyde (obtained commercially from Eastman Organic Chemicals) at 80°C for $\frac{1}{2}$ hour. The product was isolated and recrystallized several times from absolute ethanol. The recrystallizations were continued until a reproducible mesophase was evident.

3 *Preparation of p-alkylbenzaldehydes* The *p*-alkylbenzaldehydes were prepared[5] by adding 0.2 mole of the appropriate alkylbenzene to a mixture of 63.4 grams titanium tetrachloride in 100 ml of carbon disulfide (maintained below 10°C). As the temperature was kept below 10°C, 22 grams of dichloromethyl methyl ether (hazardous chemical) 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% $NaHCO_3$, 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 was vacuum distilled. Typical yields were 30% to 40%:

| | |
|---|---|
| *p*-propylbenzaldehyde | (78°C, 0.5 mm) |
| *p*-butylbenzaldehyde | (80°C, 0.4 mm) |
| *p*-amylbenzaldehyde | (105°C, 0.5 mm) |
| *p*-hexylbenzaldehyde | (112°C, 0.4 mm) |
| *p*-heptylbenzaldehyde | (119°C, 0.5 mm) |
| *p*-octylbenzaldehyde | (128°C, 0.5 mm) |

### 4 *Preparation of 4,4′-bis-(alkylbenzal)-2-chloro-1,4-phenylenediamines*

4,4′-Bis-(alkylbenzal)-2-chloro-1,4-phenylenediamines were prepared by heating 0.01 mole of the diamine with 0.02 mole of the appropriate *p*-alkylbenzaldehyde at 80°C for ½ hour. The product was recrystallized several times in absolute ethanol or isopropyl alcohol until a constant mesomorphic range was obtained. A Perkin-Elmer differential scanning calorimeter model #DSC-1B was used to determine mesomorphic transition temperatures.

Some of the compounds were analyzed for elemental composition with the following results (calculated values are 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).

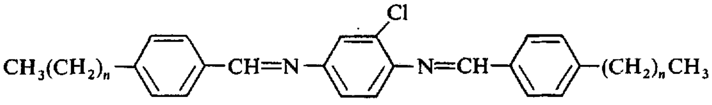
## RESULTS AND DISCUSSION

The results of the 4,4′-bis-(alkylbenzal)-2-chloro-1,4-phenylenediamine series are shown in Table I. It is interesting to compare this series with the 4,4′-bis(alkoxybenzal)-2-chloro-1,4-phenylenediamine series (Table II) and the unsubstituted phenylenediamine series reported by Gray *et al*[1] (Table III).

All of the phenylenediamine derivatives exhibit broad mesomorphic temperature ranges. Further, the 4,4′-bis-(alkylbenzal)-2-chloro-1,4-phenylenediamine series shows four homologues which melt below 50°C. Specifically, the $C_7$ homologue was nematic from 36 to 133°. This 97° mesophase is the broadest range nematic material reported to date with a melting point below 40°.

TABLE I

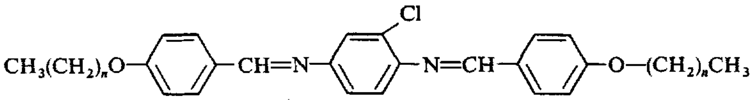
4,4′-Bis-(Alkylbenzal)-2-Chloro-1,4-Phenylenediamines



| | Transition Temperatures (°C) | |
|---|---|---|
| *n* | C → N | N → I |
| 0 | 139 | 197 |
| 1 | 111 | 170 |
| 2 | 85.5 | 185 |
| 3 | 50 | 152 |
| 4 | 42 | 153 |
| 5 | 38 | 131 |
| 6 | 36 | 133 |
| 7 | 39 | 125 |

TABLE II

4,4′-Bis-(Alkoxybenzal)-2-Chloro-1,4-Phenylenediamines



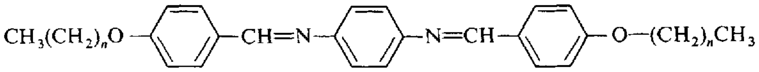
| | Transition Temperatures (°C) | | | |
|---|---|---|---|---|
| *n* | C → Sm | C → N | Sm → N | N → I |
| 0 | — | 135 (131) | — | 277 (275.5) |
| 1 | — | 133 | — | 276 |
| 2 | — | 110 | — | 237 |
| 3 | — | 79 | — | 228 |
| 4 | — | 97 (96.8) | — | 203 (205) |
| 5 | — | 96 (100) | — | 197 (199) |
| 6 | — | 80 | — | 183 |
| 7 | — | 60 (59) | — | 181 (179) |
| 8 | (71) | — | (96) | (172) |
| 9 | 66 (66) | — | 112 (112) | 166 (166) |

Values in parenthesis reference 2.

It is interesting to compare melting points and clearing points for the three homologous series. In going from the unsubstituted alkoxy series to the substituted series we see a large decrease in these points. The chlorine positioned on the central aromatic ring has a broadening effect on the molecule, which results in decreased intermolecular attractions.[4] These decreased intermolecular attractions thus result in lower melting and clearing points. Another factor to be considered is the effect of molecular geometry as shown

TABLE III

4,4′-Bis-(Alkoxybenzal)-1,4-Phenylenediamines[1]



| | Transition Temperatures (°C) | | | |
|---|---|---|---|---|
| *n* | C → Sm | C → N | Sm → N | N → I |
| 0 | — | 214.5 | — | >330 |
| 1 | — | 202.5 | — | >330 |
| 2 | — | 193 | — | 313 |
| 3 | — | 186.5 | — | 297.5 |
| 4 | 171.5 | — | 175 | 271 |
| 5 | 169.5 | — | 189 | 259.5 |
| 6 | 164.5 | — | 202.5 | 245 |
| 7 | 160 | — | 209 | 238 |
| 8 | 150.8 | — | 211.5 | 228 |
| 9 | 145.5 | — | 212 | 222 |
| 11 | 137 | — | 208 | 209 |

by Arora *et al.*[6] Steric and repulsive interactions tend to cause a twist about the two C—N single bonds and substitution on the central aromatic ring leads to a larger twist than in the unsubstituted molecule. This larger twist tends to reduce the ratio of lateral-to-terminal polarizabilities (or anisotropic polarizability), thus reducing the thermal stability.

Replacement of the alkoxy groups by alkyl shows a further reduction in the melting and clearing points although the molecular breadth is unchanged. This decreased thermal stability is attributed to a reduced polarizibility of the molecule and numerous examples of this have been shown by others.[7,8]

The comparison of these homologous series further enhances the notion that for low-melting mesogens one must reduce the anisotropy of the polarizability. Here we have shown that it is also possible to maintain a broad mesophase range in addition to obtaining relatively low-melting points.

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