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## Molecular Crystals and Liquid Crystals

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### Cyano-Alkyl Diaryl Compounds: Preparation and Liquid Crystal Properties

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## Cyano-Alkyl Diaryl Compounds: Preparation and Liquid Crystal Properties

S. IGNASIAK and M. J. RAFUSE

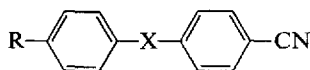
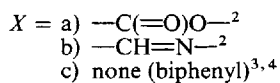
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Cyano-alkyl Schiff bases and cyano-alkyl esters were synthesized and homologous and isomeric eutectic mixtures with nematic phases near room temperatures were prepared. Isomeric Schiff base mixtures decomposed via exchange reactions whereas isomeric ester mixtures produced stable low voltage nematogens.

### INTRODUCTION

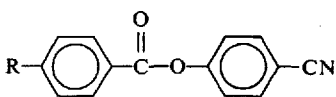
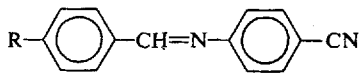
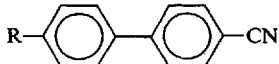
With the introduction of the field effect display<sup>1</sup> using nematic liquid crystals, there has been increased emphasis upon the investigation of nematic liquid crystals with positive dielectric anisotropy. Nematic compounds exhibiting positive dielectric anisotropy are generally those with a strong on-axis dipole. To be useful in many display applications the materials used must not only exist in the nematic phase around room temperature, but also be able to operate at low turn-on voltages and resist degradation in an electric field. Recently a number of cyano-alkyl diaryl compounds of Type I have been described in the literature.<sup>2,3,4</sup>



Type I

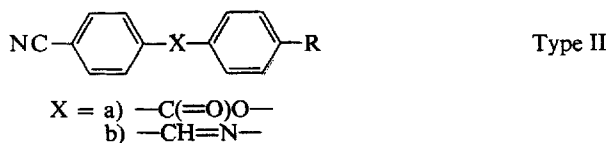
Mixtures of some of these positive dielectric anisotropic materials exhibit a room temperature nematic phase with a low turn-on voltage in field effect displays as listed in Table I.

TABLE I  
Low threshold voltage mixtures

|  | Threshold<br>V (rms) | Nematic<br>Range (°C) | Ref. |
|--|----------------------|-----------------------|------|
| Type Ia  |                      |                       |      |
| <br>R = <i>n</i> -heptyl and <i>n</i> -butyl (2:1)    | 0.9                  | 25–50                 | 2    |
| Type Ib  |                      |                       |      |
| <br>R = <i>n</i> -hexyl and <i>n</i> -propyl (2:1)    | 1.1                  | –30 <sup>a</sup> –62  | 2    |
| Type Ic  |                      |                       |      |
| <br>R = <i>n</i> -pentyl and <i>n</i> -heptyl (56:44) | 1.1                  | 0.5–37                | 3, 4 |

<sup>a</sup> Phase diagrams of similar mixtures indicate +30°C to be the lower limit of the stable nematic.

During our evaluation of materials for use in field effect displays, we discovered the instability of the Schiff base materials such as used in the mixture of Type Ib (Table I). Consequently, we undertook to synthesize the geometrical isomers of these compounds to yield the cyano-alkyl diaryl compounds of Type II wherein the end groups are interchanged with the hope that these compounds might prove more stable.



It was hoped that mixtures of these compounds would not only have stable nematic phases around room temperature and have low turn-on thresholds in field effect displays, but would also be more stable to chemical and electrical degradation. To this end a homologous series of Schiff bases (Type IIb) and one ester (Type IIa) were synthesized and the nematic behavior of mixtures of homologues and mixtures of isomers was investigated.

## EXPERIMENTAL

All compounds were recrystallized to constant melting point and identified by m.p. and infrared spectrum. All melting points were determined in glass capillaries in a Mel-Temp apparatus. All infrared spectra were determined on a Perkin-Elmer model 337 recording spectrophotometer. Microanalysis data are presented in Table II.

TABLE II  
Elemental analyses<sup>a</sup>

| Compound   | C                             | H              | N                |
|--|-------------------------------|----------------|------------------|
| <i>p</i> -Cyanobenzylidene- <i>p</i> - <i>n</i> -methylaniline | 81.79<br>(81.68) <sup>b</sup> | 5.49<br>(5.59) | 12.72<br>(12.71) |
| <i>p</i> -Cyanobenzylidene- <i>p</i> - <i>n</i> -ethylaniline  | 82.02<br>(82.02)              | 6.02<br>(6.02) | 11.96<br>(11.98) |
| <i>p</i> -Cyanobenzylidene- <i>p</i> - <i>n</i> -propylaniline | 82.22<br>(82.33)              | 6.49<br>(6.51) | 11.28<br>(11.20) |
| <i>p</i> -Cyanobenzylidene- <i>p</i> - <i>n</i> -butylaniline  | 82.41<br>(82.32)              | 6.92<br>(6.87) | 10.68<br>(10.58) |
| <i>p</i> -Cyanobenzylidene- <i>p</i> - <i>n</i> -pentylaniline | 82.57<br>(82.37)              | 7.29<br>(7.31) | 10.14<br>(10.11) |
| <i>p</i> -Cyanobenzylidene- <i>p</i> - <i>n</i> -hexylaniline  | 82.72<br>(82.83)              | 7.64<br>(7.55) | 9.65<br>(9.59)   |
| <i>p</i> -Cyanophenyl- <i>p</i> - <i>n</i> -butylbenzoate      | 77.40<br>(77.23)              | 6.13<br>(6.15) | 5.01<br>(4.92)   |
| <i>p</i> -Cyanophenyl- <i>p</i> - <i>n</i> -heptylbenzoate     | 77.79<br>(77.70)              | 6.53<br>(6.64) | 4.77<br>(4.80)   |
| <i>p</i> - <i>n</i> -Pentylphenyl- <i>p</i> -cyanobenzoate     | 78.47<br>(78.31)              | 7.21<br>(7.10) | 4.36<br>(4.42)   |

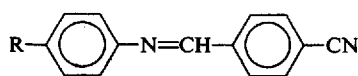
<sup>a</sup> Analyses performed by Galbraith Laboratories, Knoxville, Tennessee.

<sup>b</sup> The weight per cent found appears in parentheses.

*p*-Cyanobenzylidene *p*-*n*-alkylanilines were obtained by reacting *p*-cyano-benzaldehyde with a *p*-*n*-alkylaniline in refluxing benzene. Water was separated from the reaction mixture with a Dean-Stark trap. The alkylanilines which were not commercially available were synthesized from the phenylalkane via the acetophenone and acetanilide intermediates.<sup>5</sup> The yields and melting points for the Schiff bases synthesized are given in Table III.

TABLE III

Schiff base syntheses



| R      | Yield <sup>a</sup> (%) | MP (°C) | Clearing point (°C)   |
|--------|------------------------|---------|-----------------------|
| Methyl | 77                     | 141.5   |                       |
| Ethyl  | 93                     | 72.5    | 50 Metastable nematic |
| Propyl | 87                     | 66-68   | 75 Stable nematic     |
| Butyl  | 90                     | 79-80   | 60 Metastable nematic |
| Pentyl | 81                     | 71      | 71 Metastable nematic |
| Hexyl  | 93                     | 63-65   | 65 Metastable nematic |

<sup>a</sup> The reaction solvent was benzene in all cases

*p*-Cyanophenyl *p*-*n*-alkylbenzoates The previously reported *n*-butyl- and *n*-heptylbenzoates were prepared by the reaction of the appropriate alkylbenzoyl chloride prepared by the method of Zaki and Fahim<sup>6</sup> with *p*-cyanophenol in benzene in the presence of pyridine. The melting points are given in Table IV.

TABLE IV

Melting behavior of cyano-alkyl esters

|  |       | MP (°C) | CP (°C)   |
|--|-------|---------|-----------|
| <i>p</i> -cyanophenyl- <i>p</i> - <i>n</i> -heptylbenzoate (A) |       | 40      | 54        |
| <i>p</i> -cyanophenyl- <i>p</i> - <i>n</i> -butylbenzoate (B)  |       | 60-61.5 | (42)      |
| <i>p</i> - <i>n</i> -pentylphenyl- <i>p</i> -cyanobenzoate (C) |       | 88-94.5 | —         |
| Mixtures   | Ratio | MP (°C) | CP (°C)   |
| Homologous:  |       |         |           |
| A:B  | 2:1   | 25      | 50 Ref. 2 |
| Isomeric:  |       |         |           |
| A:B  | 1:1   | 45      | 63        |
| B:C  | 1:1   | 41-52   | 56        |
| A:B:C  | 1:1:1 | >21     |           |
|  | 2:1:1 | >21     | 51-52     |
|  | 4:1:1 | ~21     | 54        |

*p*-Pentylphenyl *p*-*n*-cyanobenzoate was prepared by the reaction of *p*-cyanobenzoyl chloride with *p*-*n*-pentylphenol in benzene in the presence of pyridine. Its melting point is given in Table IV.

**Mixtures** The binary, ternary and quaternary mixtures were prepared by combining the compounds in molar ratios by weight, melting them together with mixing and recooling to freeze the mixtures. The lower limit of the stable nematic phase was determined by melting the solid mixtures thus prepared. Metastable phases were determined by the freezing behavior on cooling.

## DISCUSSION

### Schiff base preparation and properties

The production of the alkyylaniline Schiff bases proceeded smoothly in high yield. Attempts to synthesize the isomeric Schiff bases (Type I) from alkylbenzaldehydes and *p*-aminobenzonitrile under similar conditions proceeded in low yields.<sup>7</sup> This coupled with the higher melting points (C-I transition) for the Type II Schiff bases indicates that the equilibrium favors the formation of the Schiff base to a greater degree when the alkyl group is on the amine. The implication is that the Schiff bases made from alkyylanilines are more resistant to hydrolysis than those made from alkyl benzaldehydes.

The melting point behavior of the homologous series of Type II Schiff bases is presented in Figure 1. The N-I transition temperatures display the

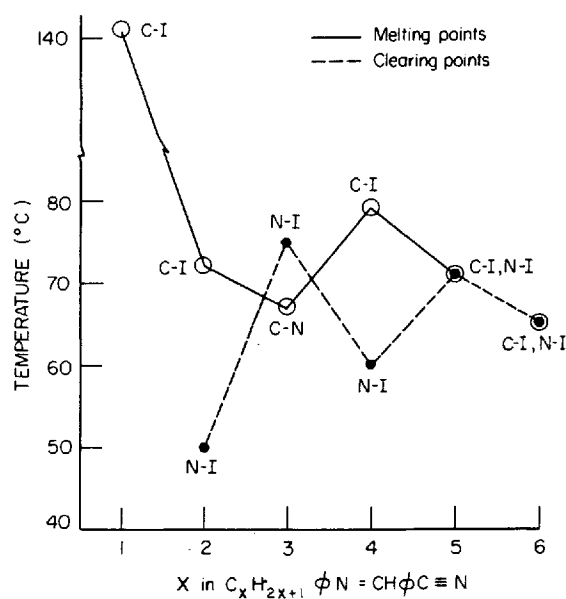


FIGURE 1 Melting behavior of cyanobenzylidene-alkylanilines

well known alternation effect.<sup>8</sup> With the exception of *p-n*-propylaniline *p*-cyanobenzaldehyde the nematic phases are metastable. Of the six compounds synthesized all except the methyl derivative had melting points below 80°C. These five compounds were used to make mixtures to explore the effectiveness of mixtures in producing stable liquid crystals with nematic phases embracing room temperature.

#### Mixtures of alkyylaniline Schiff bases

Obtaining lower crystal to nematic transition temperatures by synthesizing new single components usually results in lowered nematic to isotropic transitions as well. However, when a lowered C-N temperature is attained by mixing several similar compounds, the N-I temperature is often only slightly affected. That is, the N-I transition of the mixture remains at a temperature close to that for the individual components while the C-N transition may display a large decrease in temperature. This was found to be true for mixtures of homologous Schiff bases and for mixtures of homologous and isomeric ester compounds. Although true also for mixtures of isomeric cyano Schiff bases, their instability rendered them useless.

#### Phase diagrams

In order to determine at what composition eutectic mixtures might be expected with binary mixtures of the Type II Schiff base materials, phase diagrams were prepared for two binary systems. The phase diagram for mixtures of *p*-cyanobenzylidene *p-n*-hexylaniline and *p*-cyanobenzylidene *p-n*-butylaniline is shown in Figure 2. That for *p*-cyanobenzylidene *p-n*-propylaniline and *p*-cyanobenzylidene *p-n*-hexylaniline is shown in Figure 3. In Figure 2 the eutectic composition is observed at the 1:1 mole composition. In Figure 3 it is closer to 2:1, that is, 65 mole% of the propylaniline and 35% of the hexylaniline. With both of these mixtures it should be noted that the phase boundary lines are smooth curves and that the eutectic points are located in broad basins. Since the slope of the transition curves is small near the eutectic points, a small change in composition will not change the transition temperature by many degrees. The phase diagrams aid in determining the extent of the stable nematic phase which might otherwise be thought to be larger for a particular mixture if it supercooled before freezing. They also indicate the composition which will provide the nematic mixture with the lowest stable C-N point and the magnitude of the effect that a change in composition will have on a transition temperature.

Assuming that other binary mixtures would exhibit the same "basin eutectic" the other eight binary mixtures were prepared in a 1:1 mole ratio.

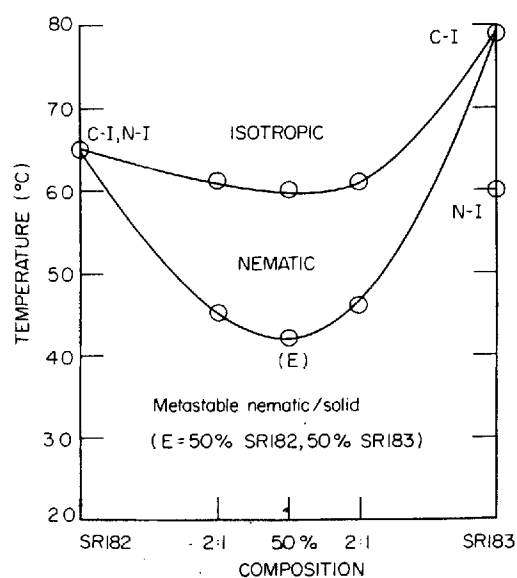


FIGURE 2 Phase diagram for *p*-cyanobenzylidene-*p*-*n*-hexylaniline (SR182) and *p*-cyanobenzylidene-*p*-*n*-butylaniline (SR183).

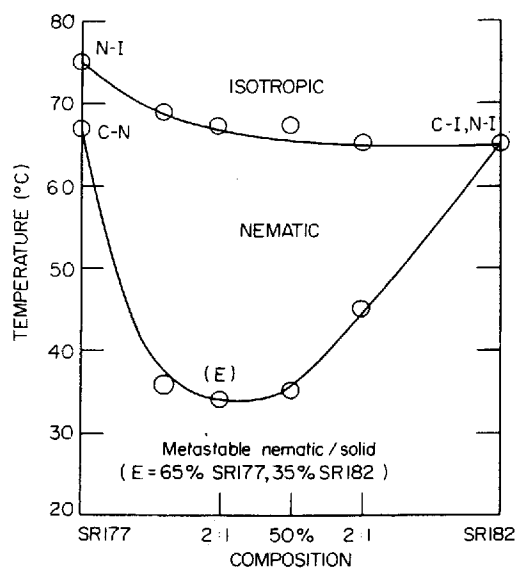
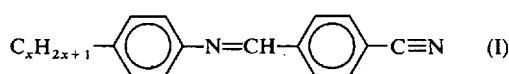


FIGURE 3 Phase diagram for *p*-cyanobenzylidene-*p*-*n*-propylaniline (SR177) and *p*-cyanobenzylidene-*p*-*n*-hexylaniline (SR182).



TABLE V  
Equimolar mixtures



|                     | Values of $x$ in Structure I | Stable Nematic Range ( $^{\circ}\text{C}$ ) |
|---------------------|------------------------------|---|
| Binary Mixtures     | 2-3                          | 45-63.5 (18.5)                              |
|                     | 2-4                          | 42-58 (16)                                  |
|                     | 2-5                          | 40-60 (20)                                  |
|                     | 2-6                          | 40-56 (16)                                  |
|                     | 3-4                          | 59-68 (9)                                   |
|                     | 3-5                          | 35-70 (35)                                  |
|                     | 3-6 (see Figure 3)           | 35-67 (32)                                  |
|                     | 4-5                          | 65-66 (1)                                   |
|                     | 4-6 (see Figure 2)           | 42-60 (18)                                  |
|                     | 5-6                          | 53-67 (14)                                  |
| Ternary Mixtures    | 2-3-4                        | 33-62 (29)                                  |
|                     | 2-3-5                        | $\sim 25-64.5$ ( $\sim 39.5$ )              |
|                     | 2-3-6                        | $\sim 25-61$ ( $\sim 36$ )                  |
|                     | 2-4-5                        | 38-60 (22)                                  |
|                     | 2-4-6                        | $\sim 25-56$ (31)                           |
|                     | 2-5-6                        | 33-62 (29)                                  |
|                     | 3-4-5                        | 42-67.5 (25.5)                              |
|                     | 3-4-6                        | $\leq 29-63.5$ ( $\sim 34.5$ )              |
|                     | 3-5-6                        | 42- $\sim 64$ ( $\sim 22$ )                 |
| Quaternary Mixtures | 2-3-4-6 <sup>a</sup>         | 15-61.5 (46.5)                              |
|                     | 2-4-5-6                      | $\sim 25-56$ ( $\sim 31$ )                  |

<sup>a</sup> Threshold  $\sim 1$  volt (rms)

In Table V are listed the ten binary mixtures with the stable nematic ranges obtained. Ten ternary 1:1:1 mole ratio systems and two quaternary 1:1:1:1 mole ratio mixtures were also prepared and listed in Table V. The widest stable nematic range was obtained with an equimolar mixture of the ethyl-, propyl-, butyl-, and hexylaniline Schiff bases (15 to 61.5 $^{\circ}\text{C}$ ).

Phase diagrams for the ten ternary systems (Figures 4 and 5) were prepared using a triangle to represent the possible combinations of three materials. The single components are represented by the apices of the triangle and the binary mixtures are located along the sides of the triangle. The 1:1:1 mole ratio mixtures are represented at the center-point of the triangle. The temperatures at the apices are the melting points of the single compounds. The lower limit of the nematic phase is listed for the binary mixtures and the 1:1:1 ternary mixture. The transition temperatures would form hills and valleys if projected out of the plane of the triangle. Based on the broad eut-

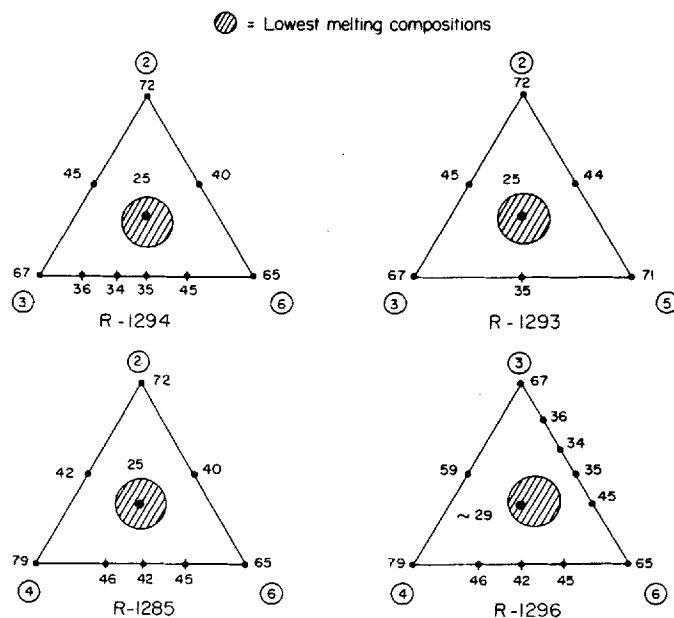


FIGURE 4 Ternary phase diagrams. Encircled numbers at apices represent  $x$  in  $C_xH_{2x+1}(C_6H_4)N=CH(C_6H_4)CN$ .

ectics observed for binary mixtures the ternary eutectics are assumed to be broad. The region of the lowest stable nematic phase was approximated from the transition temperatures available for each group of three compounds. In seven out of ten cases the ternary eutectic was located close to the 1:1:1 mole ratio. In two cases binary systems were lower melting than a ternary system indicating that the addition of another component will not always lower the melting point.

#### Mixtures of isomeric *p*-cyano Schiff bases

In addition to the mixtures of members of a homologous series of Schiff bases previously described mixtures were also prepared by combining a Schiff base with its isomer. It was reasoned that by combining compounds which are identical (except for the arrangement of atoms in the central link) materials would be obtained with electro-optic properties essentially unchanged but with lowered melting points. On mixing isomers of cyano Schiff bases expanded nematic ranges were obtained; however, the initial extension of the nematic range was gradually lost as a result of an exchange reaction which produced the high-melting, insoluble dicyano Schiff base.<sup>9</sup>

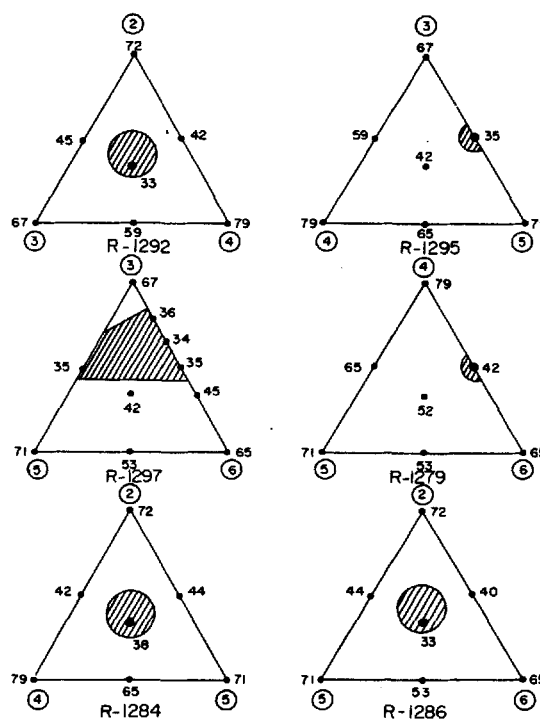


FIGURE 5 Ternary phase diagrams.

The mixture of the propylamine Schiff base (41 %) (Type IIb) with the propylbenzaldehyde Schiff base (59 %) (Type Ib) had an initial nematic range of 24 to 72°C. The individual components have C–N transitions at 67 and 60°C respectively. Thus, a drop in the stable nematic transition temperature of approximately 40°C was achieved. However, after three days the mixture became a solid with a C–I transition of over 100°C with no liquid crystal phase. The dicyano compound, *p*-cyanobenzylidene *p*-aminobenzonitrile, was isolated from the solid and identified by comparison of melting point, thin-layer chromatogram and infrared spectrum with those of the previously synthesized material. When *p*-ethoxybenzylidene *p*-aminobenzonitrile (Type Ib) and its isomer (Type IIb) were mixed in equal quantities, the dicyano compound was again isolated after the mixture was warmed to its melting point to keep it fluid. Whether the end groups of the *p*-cyano Schiff base compounds were alkyl or alkoxy, the result of mixing two isomers was the same—precipitation of the dicyano compound. This behavior of mixtures of isomers illustrates the instability of the *p*-cyano Schiff bases. In this case the

reversible condensation reaction can be driven in an undesirable direction by the precipitation of the high melting insoluble dicyano compound. The ease with which the exchange reaction can occur with all Schiff bases should be considered in the formulation of mixtures of Schiff bases. Since it is extremely difficult to get rid of all traces of water, a careful consideration must be given not only to the stability of the parent Schiff bases in a mixture but also the effect of any exchange products on the properties of the mixture.

#### Mixtures of *p*-cyano-diaryl esters

Although the mixture of isomers of *p*-cyano Schiff bases did yield nematic liquid crystals with desirable temperature ranges, the instability of these mixtures rendered them of little use. It was expected that other more stable compounds which have an unsymmetrical central link would also provide the same gains in stable nematic range without the problem of decomposition via exchange reaction. One such unsymmetrical central link is the ester group. The increased stability of ester-linked compounds compared with Schiff bases is well known, since esters are more stable to hydrolysis than Schiff bases. To explore this possibility, three binary and three ternary mixtures were formulated from two Type Ia esters and one Type IIa ester. The melting behavior of these mixtures is presented in Table IV. The various three-part mixtures containing isomeric esters have wider nematic ranges than the two-part mixtures. This demonstrates that adding an isomeric cyano ester to a two-part mixture of homologous esters can increase the nematic range.

To test the stability of these mixtures of isomers, they were subjected to several heating and cooling cycles. There was no evidence of decomposition of the isomeric ester mixtures and no loss of the nematic phase. The esters do not hydrolyze and recombine to form the dicyano ester as did the Schiff bases to form the dicyano derivative. The mixture of esters does supercool and for those mixtures whose melting points are near room temperature, it is difficult to determine the C-N point precisely. However, the isomeric mixture in the 4:1:1 mole ratio solidifies more slowly at 0°C than the other ester mixtures and melts more quickly at room temperature.

#### CONCLUSIONS

The cyanobenzylidene Schiff bases appear to be more stable than the cyano-aniline Schiff bases with mixtures of their homologs yielding liquid crystals with nematic ranges approaching room temperature. The formation of ne-

matic liquid crystals with improved temperature ranges upon mixing cyano-benzylidene Schiff bases with cyanoaniline Schiff bases followed by decomposition to yield the dicyano Schiff base illustrates the instability of these compounds. When the ester linkage replaces the  $\text{—CH=N—}$  link, mixtures of isomers are stable.

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