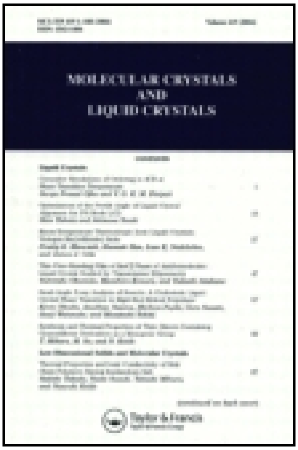

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# Liquid Crystalline Bridge Substituted Schiff Bases

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# Liquid Crystalline Bridge Substituted Schiff Bases[†]

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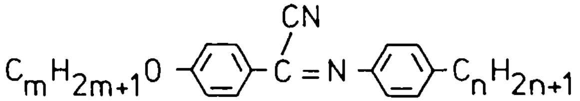
The preparation and mesomorphic behaviour of some imidoyl cyanides is reported. Their general formula is:



They are yellow stable compounds. Due to the strongly nonplanar conformation they show lower clearing temperatures than the analogous Schiff bases. However their melting points are in general higher. Consequently only monotropic nematic behaviour is observed. The dielectric anisotropy is small positive.

## INTRODUCTION

During the last years much effort has been devoted to the synthesis of new liquid crystalline materials, preferably around room temperature[1]. By now it is realized that mesomorphic molecules are not necessarily planar. Nevertheless the

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[†] Presented at the Fourth International Liquid Crystal Conference in Kent, Ohio, August 21-25, 1972.

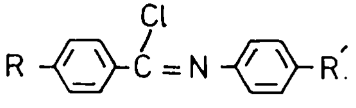
conformation is an important factor for mesomorphic behaviour. This has been demonstrated in a study of *ortho* methyl substituted Schiff bases[2]. Introduction of the *o*-methyl group leads to a depression of the melting point as well as of the clearing temperature $T_c$. In this case the introduction of steric hindrance is coupled with a broadening of the molecule.

More recently Young, Aviram and Cox [3] studied the behaviour of chloro and methyl bridge substituted stilbenes. These nonplanar stilbenes show significantly lower melting points than their planar analogues, while liquid crystalline properties are preserved. The interesting point in this case is that the steric hindrance resulting in a twisted molecule was introduced without appreciable broadening[4]. This can easily be seen from inspection of a molecular model.

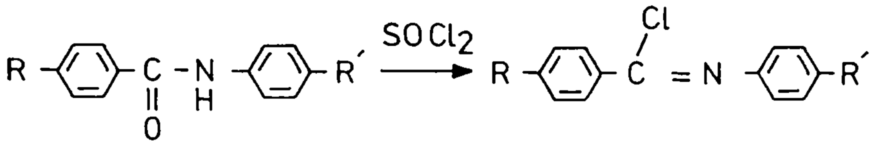
Obviously it would be interesting to study the possibilities for bridge substitution in the Schiff bases. Analogous to the above results one would expect these bridge substituted Schiff bases to have lower melting and clearing points than their nonsubstituted analogues. Furthermore bridge substitution will influence the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the dielectric constants parallel and perpendicular to the long molecular axis respectively. The sign and magnitude of $\Delta\epsilon$ is of importance for the display applications of the various electro-optic effects in nematic liquid crystals.

## RESULTS

A rather unfamiliar class of bridge substituted Schiff bases are the imidoyl chlorides, with the general formula



Their preparation is described in an excellent review by Bonnett [5]. Starting with the anilides these compounds are obtained by reaction with phosporus pentachloride or with thionyl chloride:



Unfortunately these compounds are unstable and hydrolyze readily in moist air. Some of them show nematic behaviour†. Substitution of the chlorine atom in a

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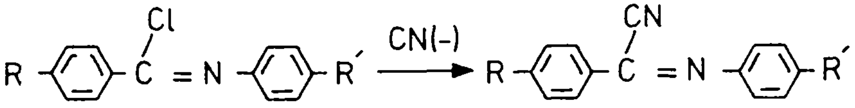
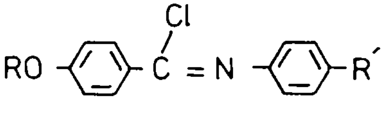
† Due to their instability they were not investigated systematically. In the following compounds nematic behaviour was observed $R = -OC_2H_5$, $R' = -C_5H_{11}$ mp 47° $T_c$ 48°
$R = -OC_4H_9$, $R' = -C_5H_{11}$ mp 37° $T_c$ 42°
$R = -OC_4H_9$, $R' = -OC_4H_9$ mp 62° $T_c$ 80°

nucleophilic reaction, for example by a cyano group is easily realized by a reaction with potassium cyanide at room temperature[8]:



We prepared imidoyl chlorides with the following general formula



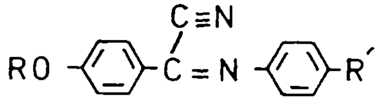
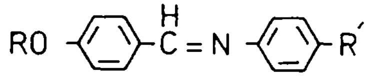
These compounds were used immediately without further purification for the preparation of the corresponding cyanides. The cyanides turned out to be yellow and quite stable compounds. Usually they could be undercooled, making it possible to detect monotropic nematic behaviour. The melting points and clearing temperatures determined with a Reichert Thermopan polarizing microscope are shown in Table 1. In Figure 1 the clearing temperatures of substituted and unsubstituted compounds are compared as a function of the number of carbon atoms in R or R'. The assumed structures were confirmed by the elemental analyses which are given in Table 2. The IR and NMR measurements were in accordance with the known data[6,7] for this class of compounds. In figure 2 $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are given for a nematic mixture of equimolecular amounts of compound no. *5* and no. *9* (mp 40°, $T_c$ 24°). The dielectric constants were derived from capacity measurements of a sample aligned by a magnetic field. The capacities were determined at a frequency of 1592 Hz with a Wayne-Kerr B 642 autobalance bridge.

## DISCUSSION

The expectation that the clearing temperatures of the imidoyl cyanides would be lower than those of the unsubstituted analogues is born out quite clearly (see Table 1 and Fig. 1). This forms an indication that the introduction of a cyano group in the bridge does indeed lead to an even more nonplanar conformation than in the case of the Schiff bases [2]. From UV spectra the conclusion can be drawn that the cyano group increases the extent of conjugation in the molecule at the same time causing steric hindrance to coplanarity [6]. Unfortunately the expectation that the melting points would be lower than those of the analogous Schiff bases is not born out. Generally they are in fact higher. A simple explanation for this result is not available.

The dielectric measurements of a mixture of compound no. *5* and no. *9* (see Figure 2) give a small positive dielectric anisotropy ($\Delta\epsilon \sim 0.6$). This can be com-

TABLE 1

|  | | | | |  | |
|---|---|---|---|---|---|---|
| no. | R | R' | mp (°C) | $T_c$ (°C) | mp (°C)[a] | $T_c$ (°C)[b] |
| 1 | $CH_3$ | $C_4H_9$ | 66 | −36 | 21 | 46 |
| 2 | $CH_3$ | $C_5H_{11}$ | 66 | 0 | 40 | 63 |
| 3 | $CH_3$ | $C_6H_{13}$ | 38 | −10 | 35 | 54 |
| 4 | $C_2H_5$ | $C_4H_9$ | 52 | 1 | 35 | 79 |
| 5 | $C_2H_5$ | $C_5H_{11}$ | 58 | 24 | 63 | 90 |
| 6 | $C_2H_5$ | $C_6H_{13}$ | 50 | 16 | 40 | 80 |
| 7 | $C_4H_9$ | $C_3H_7$ | 80 | – | – | – |
| 8 | $C_4H_9$ | $C_4H_9$ | 61 | −8 | 8 | 75 |
| 9 | $C_4H_9$ | $C_5H_{11}$ | 62 | 23 | 28 | 85 |
| 10 | $C_4H_9$ | $C_6H_{13}$ | 58 | 16 | 26 | 77 |
| 11 | $C_5H_{11}$ | $C_3H_7$ | 52 | 1 | – | – |
| 12 | $C_5H_{11}$ | $C_4H_9$ | 46 | – | 52 | 69 |
| 13 | $C_5H_{11}$ | $C_5H_{11}$ | 50 | 12 | 29 | 77 |
| 14 | $C_4H_9$ | $OC_4H_9$ | 78 | 56 | $125^+$ | $121^+$ |

Compounds no. 7 and 12 crystallized before $T_c$ was reached

a Data from ref. 13
b Data from ref. 14

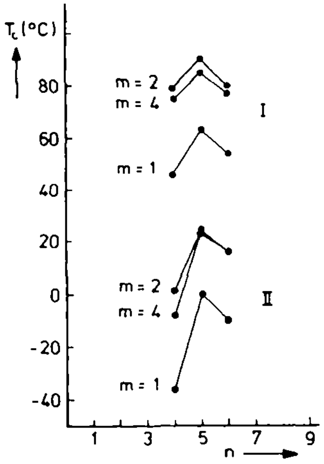
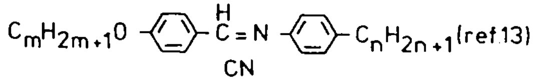
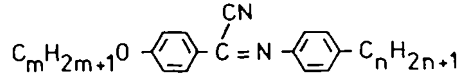


FIGURE 1 Clearing temperature versus number of carbon atoms n in the alkyl chain.

I. 
$C_mH_{2m+1}O-C_6H_4-CH=N-C_6H_4-C_nH_{2n+1}$ (ref.13)

II 
$C_mH_{2m+1}O-C_6H_4-C(CN)=N-C_6H_4-C_nH_{2n+1}$

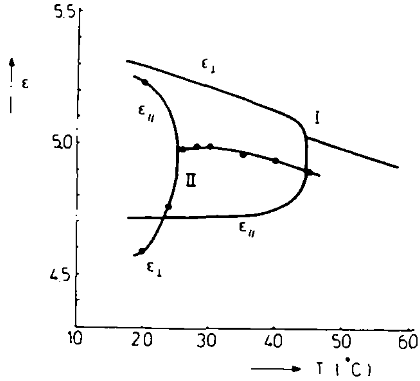


FIGURE 2 Dielectric constants of MBBA (curve I, ref. 9) and an equimolecular mixture of compound no. 5, and no. 9, (curve II)

pared with the small negative anisotropy of e.g. MBBA ($\Delta\epsilon \sim -0.5$)[9]. At an angle of 55° with the long molecular axis a dipole moment contributes equally to $\epsilon_\parallel$ and $\epsilon_\perp$[10]. As the dipole moment of the alkoxy group is directed mainly perpendicularly to this axis, this means that the dipole moment of the bridge in the imidoyl cyanides contributes mainly to $\epsilon_\parallel$. Consequently the angle between the bridge dipole and the long molecular axis must be less than 55°. This can be understood from a vector addition of the two carbon-nitrogen dipoles. This contrasts with the situation in MBBA where this angle must be somewhat more than 55°. Secondly we find that the average or isotropic dielectric constant is hardly different from that of MBBA. Although this comparison is not completely justified because the different *p*-substituents of the mixture and of MBBA it indicates that the cyano group in the imidoyl cyanides is only weakly polar. This supposition is confirmed by the weak intensity of the cyano bond in the IR spectrum, due to conjugation of the cyano group[6].

In conclusion we found that imidoyl cyanides do not show useful nematic ranges. In a next attempt the same ideas as described above were applied to the stilbenes. This has lead to the preparation of a number of *p,p*'-disubstituted α-cyano stilbenes[11] and a large negative dielectric anisotropy[12].

## EXPERIMENTAL

As an example of the preparation of the imidoyl chlorides the following procedure was used. A mixture of 8.5 g (0.02 mole) of *p*-pentyloxy, *p*'-propyl benzanilide and 8.5 ml (0.07 mole) of thionylchloride was refluxed for two hours. After cooling 40 ml of petroleum ether was added to the reaction mixture. This

TABLE 2

Elemental Analyses

| Compound No. | %C calc. | %C found | %H calc. | %H found | %N calc. | %N found |
|---|---|---|---|---|---|---|
| 1 | 78.03 | 77.86 | 6.90 | 7.03 | 9.58 | 9.56 |
| 2 | 78.40 | 78.51 | 7.24 | 7.42 | 9.15 | 9.11 |
| 3 | 78.72 | 78.62 | 7.55 | 7.72 | 8.75 | 8.85 |
| 4 | 78.40 | 78.20 | 7.24 | 7.39 | 9.15 | 9.06 |
| 5 | 78.72 | 78.47 | 7.55 | 7.70 | 8.75 | 8.78 |
| 6 | 79.00 | 79.02 | 7.84 | 7.79 | 8.38 | 8.38 |
| 7 | 78.72 | 78.79 | 7.55 | 7.51 | 8.75 | 8.70 |
| 8 | 79.00 | 78.82 | 7.84 | 7.77 | 8.38 | 8.16 |
| 9 | 79.25 | 79.30 | 8.11 | 8.16 | 8.03 | 7.88 |
| 10 | 79.50 | 79.44 | 8.35 | 8.52 | 7.72 | 7.53 |
| 11 | 79.00 | 78.85 | 7.84 | 8.06 | 8.38 | 8.40 |
| 12 | 79.25 | 79.14 | 8.11 | 8.30 | 8.03 | 8.02 |
| 13 | 79.50 | 79.41 | 8.35 | 8.51 | 7.72 | 7.59 |
| 14 | 75.44 | 75.47 | 7.42 | 7.58 | 7.99 | 8.04 |

Elemental analyses were carried out under the supervision of W.J. Buis at the Micro-Analytical Department of the Institute for Organic Chemistry T.N.O., Utrecht, The Netherlands.

mixture was then cooled in dry ice-acetone. The resulting precipitate was filtered off and taken up in petroleum ether. The anilide did not dissolve and was filtered off. The solvent was evaporated in vacuo. The yield of imidoyl chloride was 5.7 g (64%). The procedure used for the preparation of the imidoyl cyanides was similar to that described in the literature [8]. They were recrystallized from petroleum ether.

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