Ene-heterocyclic/Aromatic Schiff Bases as Potential Mesogens

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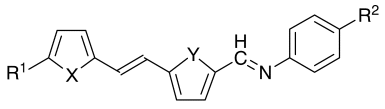
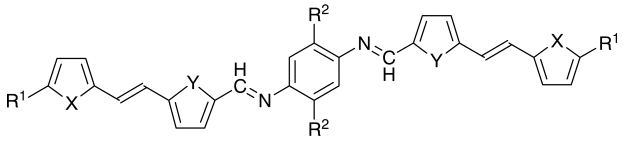
The condensation of aromatic mono- and di-amines with alkenyl furanic and/or thiophenic aldehydes gave a series of Schiff bases, some of which displayed liquid crystal properties.

The recent synthesis of well-defined conjugated oligomers bearing furan and/or thiophene heterocycles and a terminal aldehyde function,[11] prompted us to investigate the possibility of using the latter reactive site to build structures possessing interesting properties. In the present context the specific feature sought was related to mesomorphicity and, therefore, applications related to the liquid crystal domain.

The simple aldehyde/amine condensation was chosen for this study which involved, on the one hand, various dimeric alkenyl heterocyclic precursors and, on the other hand, several primary aromatic mono- and di-amines bearing different substituents. The resulting Schiff bases, obtained in high yields, had therefore the general structures shown below. Spectroscopic and elemental analyses confirmed the validity of each expected structure.



R^1 = H, CH_3; R^2 = alkyl, CN, NO_2, Br, ester; X, Y = O, S



R^1, R^2 = H, CH_3; X, Y = O, S

Scheme 1

A thorough inspection of the thermal and morphological properties of all these compounds was then conducted using DSC and optical microscopy, both applied in successive heating–cooling cycles. This enabled first of all the assessment of the primary features related to the melting and crystallization and then a thorough search for mesophases. Only a limited number of structures displayed mesogenic properties.

Among the monofunctional imines, only those bearing a thiophene ring attached to the CH=N moiety and, at the same time, a 4-cyano substituent (a well-known mesophase enhancer) on the aromatic ring showed the appearance of a nematic monotropic feature. The introduction of a methyl group at the C5 position of the outside heterocycle raised the mesophase stability and led to enantiotropic behaviour.

Most of the Schiff bases prepared with difunctional aromatic amines exhibited a clear-cut mesomorphism, but the high melting temperatures of some of them induced problems related to chemical stability.

Techniques used: FTIR, ^{1}H NMR, UV–VIS, mass spectrometry, elemental analysis, DSC, optical microscopy

References: 14

Fig. 1: Monotropic nematic texture of sample **7** at 86 °C

Fig. 2: Enantiotropic nematic phase of sample **11** at 171 °C, on heating

Fig. 3: DSC heating profile of sample **11**

Fig. 4: DSC heating profile of sample **24** after cooling from the melt

Table 1: Structures of the synthesized Schiff bases

Table 2: Thermal properties of the Schiff bases resulting from the reaction with monofunctional amines

Table 3: Thermal properties of the Schiff bases resulting from the reaction with bifunctional amines

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References cited in this synopsis

11 C. Coutterez and A. Gandini, *Polymer*, 1998, **39**, 7009.

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