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SYNTHESIS OF SCHIFF BASES FORMING THE FIRST ROOM TEMPERATURE FERROELECTRIC LIQUID CRYSTAL - THE MORA SERIES

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Abstract: Condensation of chiral S-4-(6-methyl)octyloxy-2-hydroxybenzaldehyde (S-4-O-(6-methyl)octylresorcylaldehyde) with 4-alkylanilines (the MORA series, 3) gives low-melting Schiff bases showing chiral smectic C phases at or slightly above room temperature. The previously known MBRA series (4'-O-(2-methyl)-butyl-resorcylidene-4-alkylanilines, 1) has been extended by MBRA 4 and 12, both showing low-temperature smectic phases. Bis (S,S-4'-(2-methylbutyloxy-2-hydroxybenzylidene)-2-chloro-1,4-phenylenediamine shows a cholesteric blue phase between 174 and 175 °C.

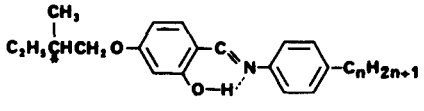
INTRODUCTION

The fact that smectic C phases of certain chiral compounds are ferroelectric[1] has stimulated

much work. The experimental investigations have almost exclusively concerned DOBAMBC and HOBACPC.[2-8] However, these compounds melt around 70 °C, and efforts are being made to obtain room temperature ferroelectrics.

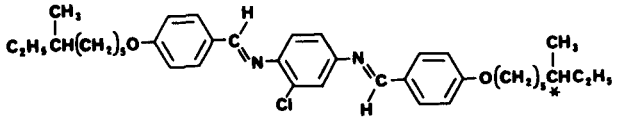
Symmetry properties and experimental evidence for the existence of ferroelectricity in chiral smectic C phases have been discussed by Meyer.[9]

Optically active S-4-O-(2-methyl)butyl-resorcylidene-4'-alkylanilines (1) (in this paper referred to as the MBRA series) have recently been described (MBRA 7-10).[10] Of these MBRA 8 shows the lowest lying smectic C phase, namely between 29 and 54 °C.[11] In 1971 Helfrich and Oh[12] described a double Schiff base of 2-chloro-1,4-phenylenediamine with S-4-(6-methyl)octyloxybenz-aldehyde (2) exhibiting a S_C phase between 29 and 94.4 °C, but of course they could not realize at that time that this compound should be ferroelectric.



1 MBRA n

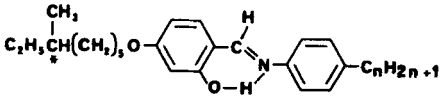
1a n=4, 1b n=8, 1c n=12



2

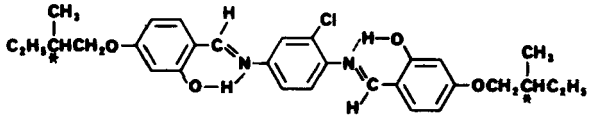
RESULTS

We have considered the MBRA family of compounds, and extended the MBRA series by MBRA 4 and 12, in order to decrease the melting points. We have also made hybrid compounds, viz the new MORA series, which are S-4-(6-methyl)octyl-resorcylidene-4'-alkylanilines (3), and a Schiff base with S-4-(2-methyl)butyl-2-hydroxybenzaldehyde and 2-chloro-1,4-phenylenediamine (4).



3 MORA n

3a n=4, 3b n=8, 3c n=12



4

Of particular interest in this work is the MORA 8 compound which is ferroelectric at room temperature. The S_C phase not only shows a very broad range, almost 80 degrees, but also especially strong supercooling, down to about -40 ^{o}C, extending the range to well above 100 degrees, which is certainly remarkable for a pure compound.

MBRA 4 also gives a room temperature liquid crystal phase, which is unfortunately not ferro-

electric although the compound shows two different smectic phases which have not yet been identified.

The other compounds, except MBRA 12, all show S_C phases which are readily supercooled below room temperature.

Another notable feature of these compounds is the increased stability due to hydrogen bonding between the hydroxy group and the nitrogen atom which is depicted in structures 1, 3 and 4. The strong intramolecular hydrogen bonding, also noted by Ostrovskii et al.[10], is confirmed by NMR spectroscopy as a downfield shift of the hydroxyl proton (δ = 13-14).

We have also investigated bis (S,S-4'-(6-methyl)-octyloxybenzylidene)-2-chloro-1,4-phenylenediamine (2), first described by Helfrich and Oh[12], and confirmed that this compound really gives a ferroelectric phase.[13] The dissymmetry in the molecule, due to the chlorine atom, is noted in the NMR spectrum which shows the two imine protons to be chemically non-equivalent ($\Delta\delta$ = 0.04).

The last of the above mentioned hybrids, bis (S,S-4'-(2-methyl)butyloxy-2'-hydroxybenzylidene)-2-chloro-1,4-phenylenediamine (4), is rather high-melting and shows a cholesteric and a narrow-range blue phase on heating and an additional smectic phase (probably S_C) on cooling. The blue phase is not detected in the DSC measurements but is clearly shown in a polarization microscope.

Melting points and transition temperatures are given in Table 1.

TABLE 1 Transition temperatures (°C); S_1 and S_2 are unidentified smectic phases

Compound	X	S_1	S_2	S_C	S_A	Ch	Bl.Ph.	I
1a	····	18	·	·	43	·		69
1b			28	57	·	·		64
1c				41	·	·		70
2			35	·	93	·		145
3a			35	·	62	·		70
3b	·····	12		·	·	·		97
3c			35	·	·	·		93
4					146	174		175

CHEMICAL

The optically active precursor to S-4-(6-methyl)octyloxy-2-hydroxybenzaldehyde is S-1-bromo-6-methyloctane which has earlier been obtained by tedious, stepwise elongation of S-1-bromo-2-methylbutane.[14] We applied the direct elongation with copper-catalysed reaction[15] of S-2-methylbutylmagnesium bromide and 1,4-dibromobutane to give the optically active S-1-bromo-6-methyloctane in 28 % yield. The bromide was purified on a 50 cm column (approximately 50 plates). The method is a convenient route to other long haloalkanes by using other terminal dihaloalkanes. The 4-alkoxy-2-hydroxybenzaldehydes were

then obtained by the Williamson ether synthesis.

4-Octyl- and 4-dodecylaniline were obtained by acylation of acetanilide and subsequent reduction and hydrolysis.

Finally the Schiff bases were prepared from equimolar amounts of aldehyde and amine in refluxing ethanol. The compounds were recrystallized from ethanol or ethyl acetate and dried in high vacuum until constant transition temperatures were obtained.

The molecular structures of all compounds were confirmed by high resolution NMR spectroscopy (270 MHz). The Schiff bases were examined by DSC measurements and polarization microscopy.

Synthetic improvements on, and extension of, the MBRA and MORA series are under way.

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