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Synthetic Methods to Ferrocenomesogens containing a Pendent Ferrocenyl Group

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Introduction

Ferrocene behaves much like a three dimensional arene and is useful for incorporating a metal atom into a molecule that requires a certain degree of structural rigidity such as a liquid crystal.[1] The ferrocenyl unit is not only useful for modifying the shape of a molecule; in addition the metal atom with its large electron density can be used to modify the physical properties such as colour, polarisability and magnetism. Following the publication in 1976 of the first examples of ferrocene derivatives with liquid-crystalline properties (type **A**) [2]and more notably since 1988 when the first liquid crystals based on a disubstituted ferrocene were synthesized (type **B**),[3] there has been a growing interest in these compounds amongst chemists. The majority of ferrocenyl-containing liquid crystals or ferrocenomesogens (as we have named them) prepared so far belong to one of the structural types **A**, **B** or **C**. Although the synthesis of derivatives with interesting new shapes continue to be exciting, a systematic approach to structure-liquid crystal activity which will allow meaningful predictions has become necessary.

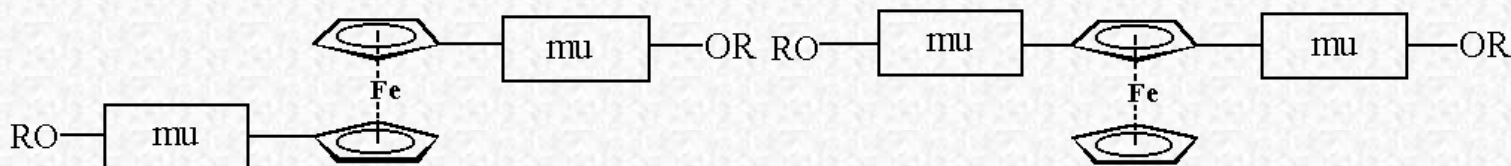General Structural Geometries of Ferrocenomesogens
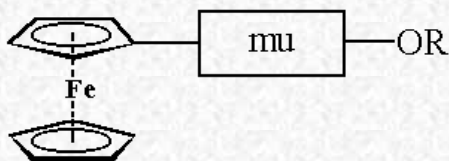
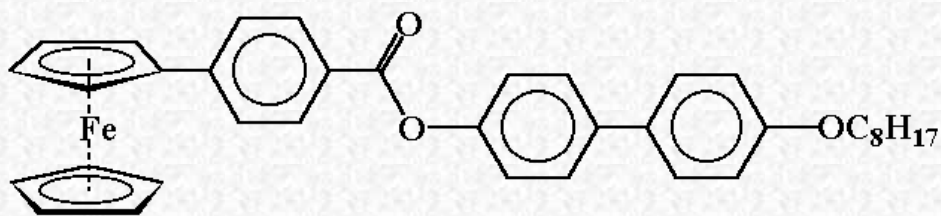L-shape: 1-substitution
A
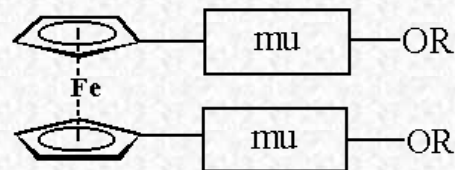
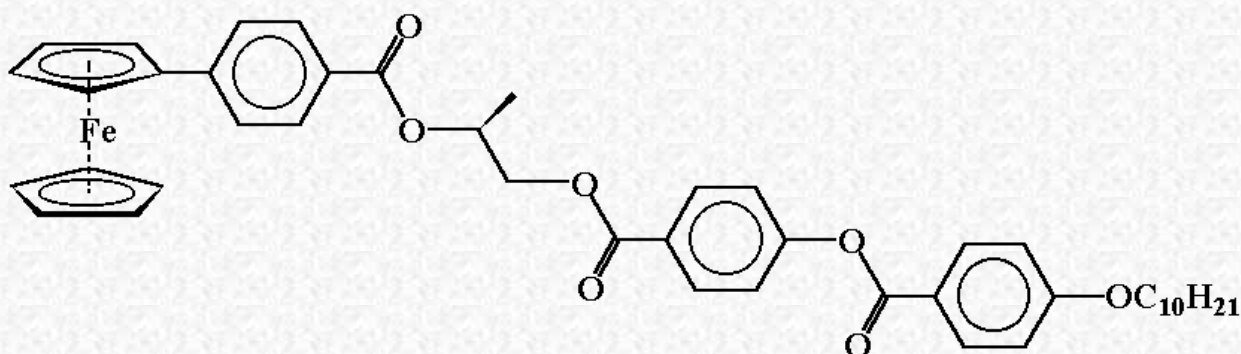U-shape: 1,1'-disubstitution
B

S-shape: 1,1'-disubstitution
B

T-shape: 1,3-disubstitution
C

## Examples of Monosubstituted Ferrocenomesogens

(Loubser and Imrie, 1997)

(Loubser and Imrie, 1994)

Our research efforts have concentrated on the synthesis and characterization of monosubstituted ferrocenomesogens (type **A**) in which the ferrocenyl unit is pendent rather than being centre-piece in the molecule.[4,5] The general structure representing the compounds in our first series consists of three sections; the pendent ferrocenyl moiety, the core of the liquid crystal Z and the terminal alkoxy chain. The size and shape of Z was modified by varying (a) the number of phenyl rings (i), (b) the linking group Y, (c) lateral substitution X and (d) the number of carbon atoms, n in the terminal chain. With a view to extending the range of monosubstituted ferrocenomesogens, it was decided to synthesize molecules where j = 2 and for this, it was necessary to synthesize 4-substituted biphenylferrocenes. It was also decided to introduce a new linking unit into the general structure, the ether linkage (ie. Y = O). For this, a synthesis of ferrocenylphenylaryl ethers was required.

General Structure of the First Series of Ferrocenomesogens
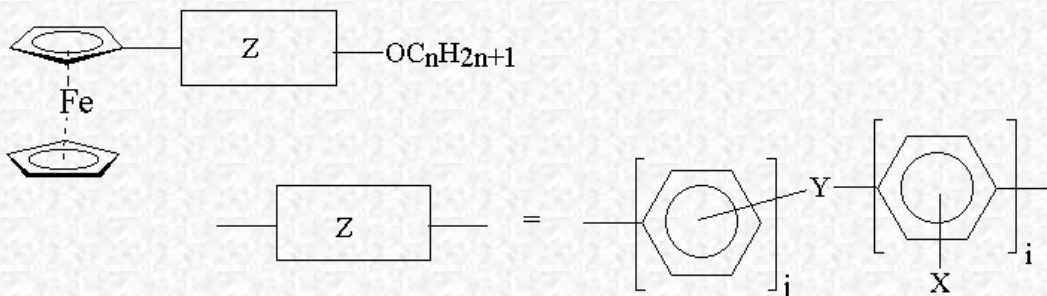

n = 5, 8, 9, 10, 12, 14

j = 1; i = 1 or 2; X = H or F

Y = -COO-, -OOC-, -COOPhCOO-

# The Synthesis of 4-Substituted Ferrocenylbiphenyl Compounds

We have recently reported the use of a modified Suzuki cross-coupling procedure for the synthesis of 4-substituted phenylferrocenes.[6] Iodoferrocene was reacted with a series of 4-substituted phenylboronic acids in the presence of a base and catalyst to provide a range of 4-substituted phenylferrocenes. By replacing the iodoferrocene with 4-bromophenylferrocene, the same reaction provides 4-substituted ferrocenylbiphenyl compounds. The isolated yields of the ferrocenylbiphenyl products were good-to-excellent in most cases (Table 1). Experience in the previous Suzuki work on substituted phenylferrocenes had shown that yields could be improved significantly by heating reactions involving electron-deficient arylboronic acids. The result in Table 1 (entry 5) supports that conclusion.

Table 1. Yield of ferrocenylbiphenyl compounds from the reaction of 4-bromophenylferrocene with arylboronic acids
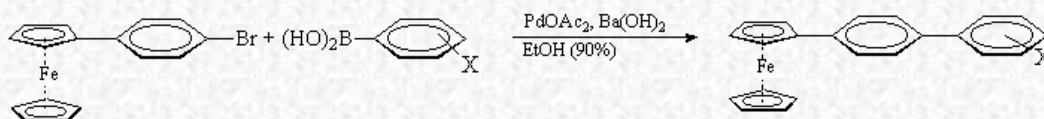
Entry	X	4-Bromophenylferrocene (mmol)	Time (days)	Yield (%)[a]
1	4-OCH$_3$[b]	1.5	14	93
2	4-CH$_3$[b]	1.5	14	88
3	4-OC$_8$H$_{17}$[b]	1.5	14	65
4	4-Ph[b]	1.5	14	79
5	4-CHO[c]	3.0	21	50
6	4-CHO[b]	3.0	32	13
7	4-CHO[b]	3.0	1	10
8	4-F[b]	3.0	14	89
9	4-COCH$_3$[c]	3.0	14	14
10	4-CH$_2$Ph[c]	1.5	14	70

[a]Yield is based on the amount of 4-bromophenylferrocene as starting material. [b]Typical procedure. To 90% ethanol, which was degassed by nitrogen bubbling for 48h, deaerated by the freeze-thaw method (3 cycles) and degassed by nitrogen bubbling for another 24 h was added the substituted arylboronic acid (2 equiv.), 4-bromophenylferrocene (1 equiv.), barium hydroxide (1.4 equiv.) and palladium acetate (0.3 equiv.) under nitrogen. The reaction mixture was then vigorously shaken for 30 min. prior to stirring under nitrogen. [c]Same procedure as for b with the exception that the reaction mixture was intermittently heated under reflux (7 x 7h).
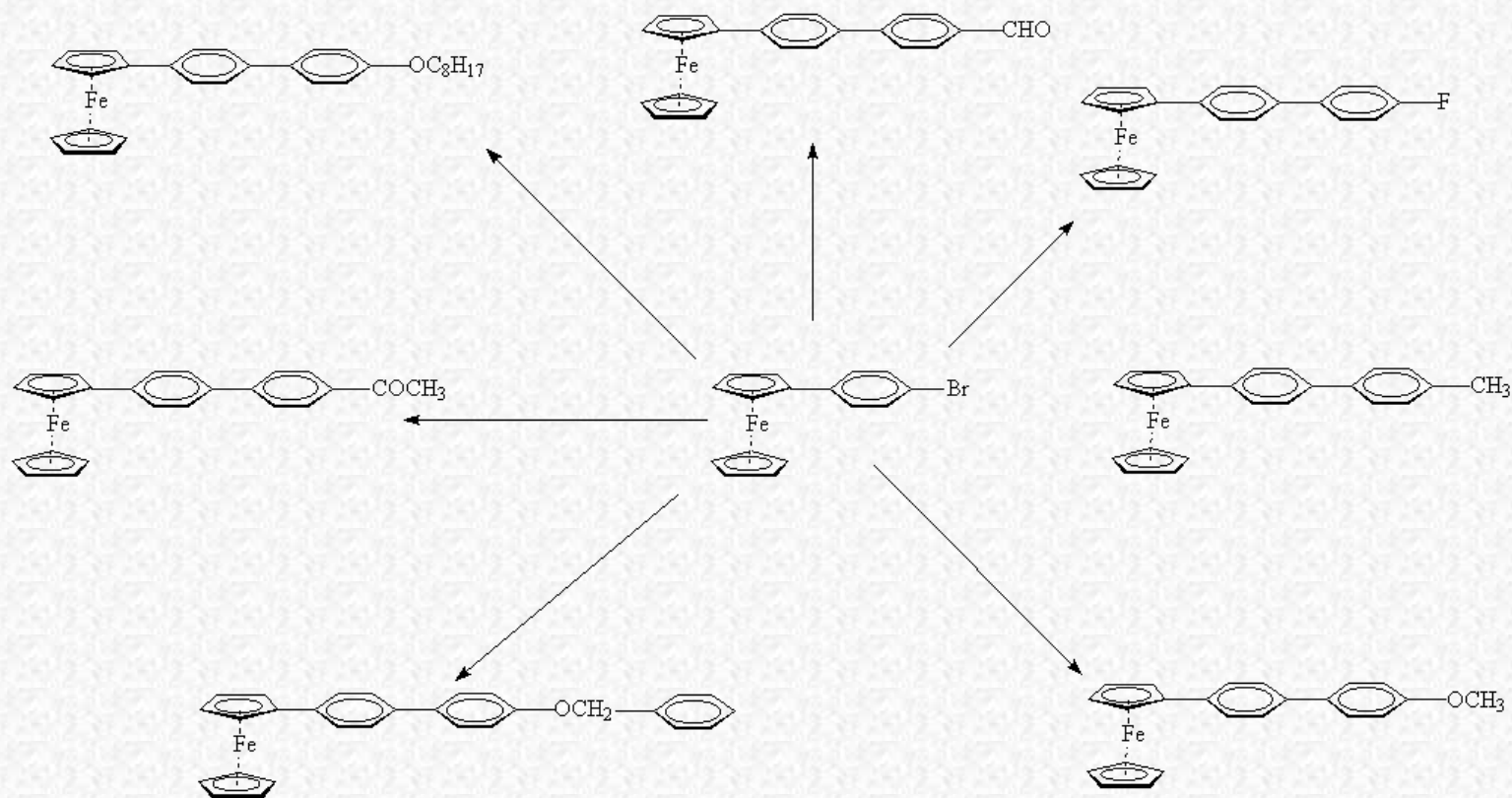
Biphenylferrocene derivatives synthesized by the modified Suzuki method

The Synthesis of Ferrocenylphenylaryl ethers

Instead of having a terminal ferrocenylbiphenyl unit as part of the ferrocenomesogen, it was of considerable interest to us to change this unit to a ferrocenylphenylaryl ether group. We took note of an article written by Theil[7] entitled "Synthesis of Diaryl Ethers: A Long-Standing Problem has been solved." This article directed us to a new method of synthesizing diaryl ethers using cheap reagents and mild reaction conditions.[8,9] The reactions of 4-ferrocenylphenol and substituted arylboronic acids provided ferrocenylphenylaryl ethers in yields in the range of 25-50% according to the substituent on the boronic acid. Again, yields were lower generally when the substituents on the boronic acid were electron-withdrawing.

Table 2. Yield of ferrocenylphenylaryl ethers from the reaction of 4-ferrocenylphenol and substituted arylboronic acids
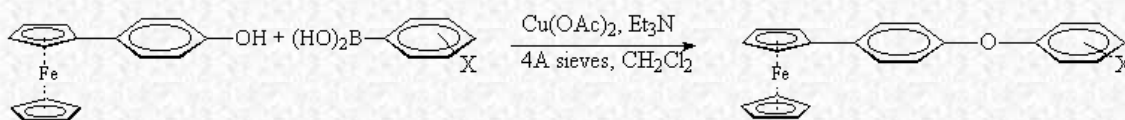

Substituent X	Yield (%)[a]
4-CH$_3$[b,c]	49
4-OCH$_3$[b,c]	41
3,4,5-(OCH$_3$)$_3$[b,c]	42
4-OCH$_2$Ph[b,c]	46
4-H[b,c]	51
4-OC$_8$H$_{17}$[b,c]	21
4-F[b,c]	34

3-F[b,c]	27
4-Br[b,c]	19
4-COCH$_3$[b,c]	32
4-CHO[b,c]	26
4-CHO[b,d]	34
4-OCF$_3$[b,c]	28
4-CF$_3$[b,c]	2
3-NO$_2$[b,d]	10

a Yield is based on the amount of 4-ferrocenylphenol as starting material. [b]Typical procedure. 4-Ferrocenylphenol (1 equiv.), anhydrous copper acetate (1 equiv.), the substituted arylboronic acid (1.2 equiv.), powdered 4 D molecular sieves, and distilled triethylamine (5 equiv.) were added to anhydrous dichloromethane. The reaction mixture was allowed to stir at room temperature for 168 h. [c]Reactions were carried out using 4-ferrocenylphenol (200 mg). [d]Reactions were carried out using 4-ferrocenylphenol (approx. 1 g).

Synthesis of New Ferrocenomesogens

One of the objectives of the work was to observe the effect of introducing the ferrocenylbiphenyl- and ferrocenylphenylaryl ether unit into ferrocenomesogens. With this goal in mind, a series of Schiff bases, series I and series II were synthesized. The compounds of series I were synthesized by the reaction of 4'-formyl-4-biphenylferrocene with a series of n-alkoxyanilines. The compounds where n=8 and n=14 exhibit enantiotropic smectic and nematic phases, whereas the compound where n=5 exhibits a monotropic nematic phase. The liquid crystal domains in all cases are relatively short and the usual effect of chain lengthening in relation to the lowering of clearing temperatures is observed. Replacement of 4'-formyl-4-biphenylferrocene by 4-(4-formyl)phenoxyphenylferrocene in the reactions with the n-alkoxyanilines provided the corresponding Schiff base derivatives of series II in good yield. The compounds where n=5 and n=14 were prepared and in both cases, they exhibit normal melting behaviour.
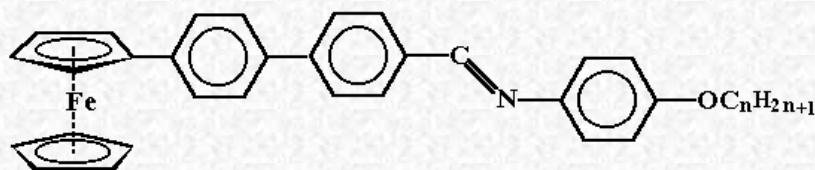
Liquid Crystalline Series I
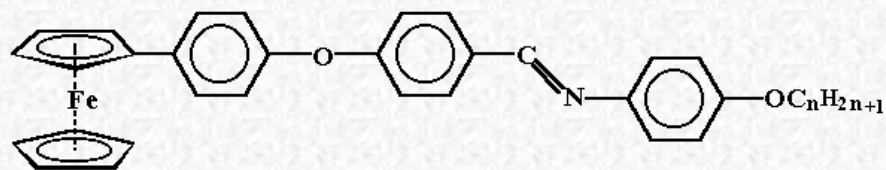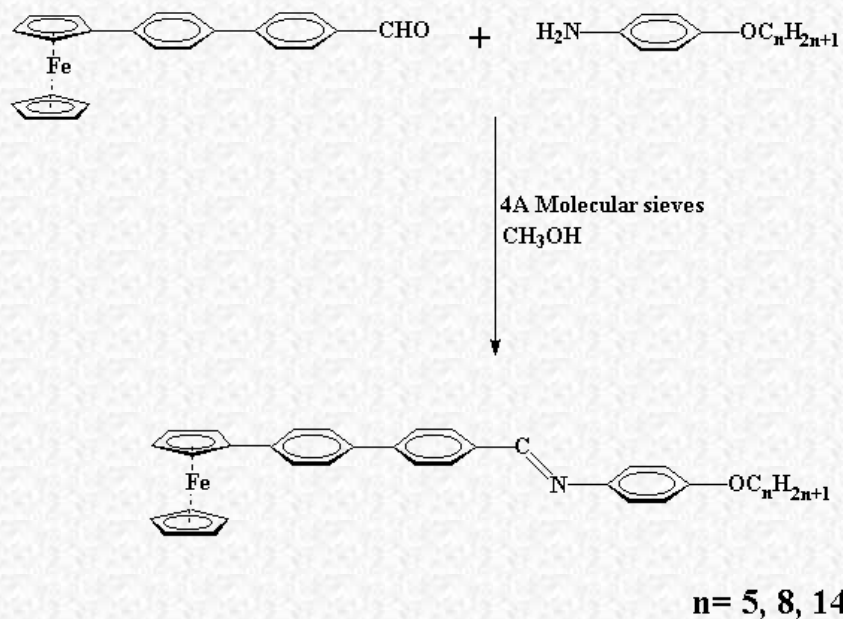
n= 5, 8, 14

Non-liquid Crystalline Series II

n= 5, 14

Synthesis of Series I Compounds

n= 5, 8, 14

Conclusion

Long rigid molecules containing bulky pendent ferrocenyl moieties are useful for stabilizing nematic liquid crystal phases. Small alterations to the molecules which give rise to kinks in the molecular structure inhibit liquid-crystalline behaviour. Further work is in progress to establish other factors that could affect the liquid crystal properties of monosubstituted ferrocenomesogens. Modern synthetic methods are being used for the elaboration of the ferrocenyl-phenyl group.

References

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