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# Mesomorphic Derivatives Of Ferrocene

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# MESOMORPHIC DERIVATIVES OF FERROCENE

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Abstract The first series of ferrocene derivatives exhibiting mesomorphic properties (substituted N-(p-benzoyloxybenzylidene) anilines 1a and 1b) has been synthesized for application in Mössbauer spectroscopy.

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During the past ten years, Mössbauer spectroscopy has become a very useful technique for the study of solid state by means of heavy metal nuclei such as $^{57}Fe$, $^{61}Ni$, $^{67}Zn$, $^{119}Sn$... Lately, its utilization in structural studies of ordered systems such as smectic liquid crystals has undergone remarkable development (1).

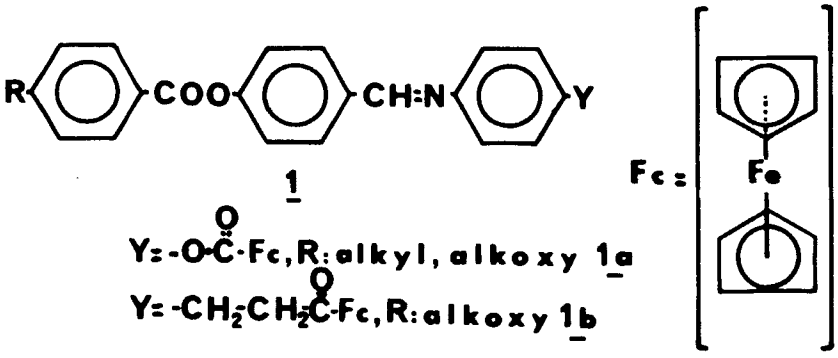
Hitherto, only non-mesomorphic "Mössbauer markers" have been used, for example : diacetylferrocene (2) and tin-containing compounds (3)(4) dissolved in smectic phases. The principal limitation of these "markers" appears to be absence of mesophases and low solubility.

Besides, by such a method, the results concerning the preponderating constituent can be

only indirect and their interpretation is often difficult *.

Consequently, we felt that is was highly desirable to undertake the preparation of stable and easily synthesized liquid crystals, incorporating appropriate Mössbauer metal atome and having relatively low melting points.

Ferrocenes appeared to correspond the best to the requirements : they are chemically stable, and readily synthesized. Yet, it was quite difficult to conceive a mesogenic organic structure containing a voluminous group such as ferrocene, perpendicular to the molecular axis which would yield the desired mesophases (6).




1

Y= -O-C(=O)-Fc, R: alkyl, alkoxy 1a

Y= -CH2CH2C(=O)-Fc, R: alkoxy 1b

* To our knowledge, only one mesomorphic compound, suitable for Mössbauer experiments, has been reported to date. This substance, prepared by YOUNG (5) is a Schiff base with trimethyltin group which exhibited two smectic phases in the 165-173° C range.

On the basis of other studies, we were led to consider Schiff bases of type 1, which surprisingly tolerate large Y groups without losing their mesomorphic properties. So, we have synthesized a new series of mesomorphic derivatives of 1, containing a ferrocenyl group which have the desired properties. The melting points and transition temperatures of these compounds, determined with a differential scanning calorimeter (Perkin-Elmer DSC-2), are given in Table I ([N-4(4'-alkyl, alkoxybenzoyloxy)benzylidene]p-aminophenyl ferrocenecarboxylates 1a), and Table II ([N-4(4'-alkoxybenzoyloxy)benzylidene]1-ferrocenyl-3-(p-aminophenyl)-1-propanones 1b).

The mesophases have been identified by the examination of their texture under the polarizing microscope (Panphot Leitz) with heating stage. The textures of the nematic phases are "schlieren" with threads.

Among these new compounds, only p-alkoxy 1a derivatives exhibit stable nematic phases.

The synthesis of the Schiff bases was carried out by reaction of the corresponding p-benzoyloxybenzaldehydes 2 (0,1 mmole) prepared according to ref. (7) with p-aminophenylferrocenecarboxylate 3b (0,1 mmole-m.p.149-150°C, ethanol) or 1-ferroecenyl-3-(p-aminophenyl)-1 propanone 4b (0,1 mmole-m.p. 128-129°C, benzene/cyclohexane 1/1) in absolute ethanol at reflux (70-80 % - orange crystals - after recrystallization in absolute ethanol).

3b and 4b were obtained by catalytic reduction ($H_2$, Pd-C 5 %, ethanol) of ester 3a and

and chalcone 4a respectively prepared according to ref. (8) (34 %; m.p. 140°C, ethanol) and according to ref. (9) (65 %; m.p. 195°C, methoxy-ethanol).

The study of other mesomorphic derivatives of 1 is in progress.

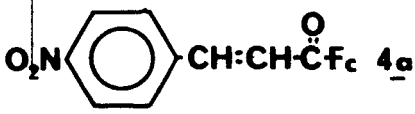
We thank Professors P.G. De GENNES and J. JACQUES for helpful discussions.

TABLE I Transition temperatures of alkyl, alkoxy 1a

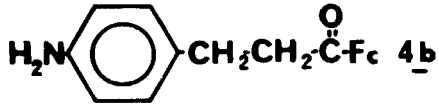
| | C | N | I |
|---|---|---|---|
| $n^{C_5H_{11}}$ | 182 | [155] | |
| $n^{C_6H_{13}}$ | 164 | [143] | |
| $n^{C_8H_{17}}$ | 152 | [135] | |
| $n^{C_8H_{17}O}$ | 153 | 167 | |
| $n^{C_{10}H_{21}O}$ | 143 | 159 | |

TABLE II Transition temperatures of alkoxy 1b

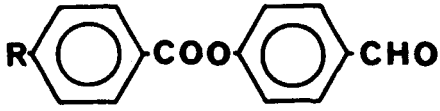
| | C | N | I |
|---|---|---|---|
| $n^{C_8H_{17}O}$ | 137 | [112] | |
| $n^{C_{10}H_{21}O}$ | 135 | [107] | |



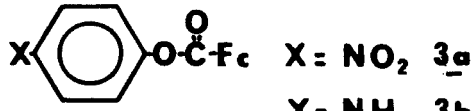

4a




4b




2




X = $NO_2$ 3a

X = $NH_2$ 3b

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