Novel Ferrocene Diesters with Liquid-Crystal Properties

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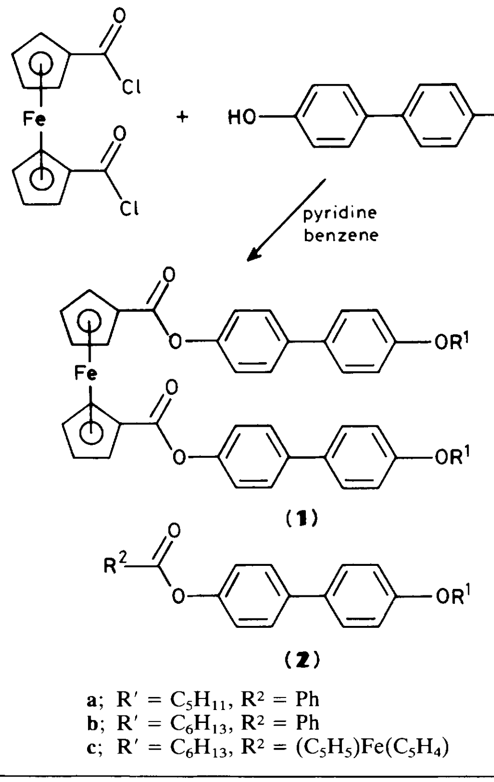
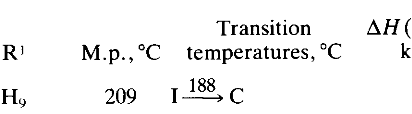
A series of bis-(4-alkoxy-4'-biphenyl)ferrocene 1,1'-diesters (**1**) has been synthesized; three compounds in this homologous series exhibit liquid-crystal phases.

Compounds which display liquid-crystal properties typically possess a rod- or disc-like core and long, flexible alkyl chains. Liquid-crystal compounds containing transition metals have recently attracted special attention because the transition-metal centre offers the appealing prospects of imparting unique optical, magnetic and electrical properties as well as enforcing various well-defined molecular geometries.[1,2]

We report the preparation and melting properties of a series of 1,1'-ferrocene diesters (**1**) which are characterized by the presence of two mesogenic groups joined by the kinked ferrocene core.[3,4] The synthesis of orange crystalline (**1a**—**h**) was accomplished by coupling readily available 1,1'-ferrocene diacid chloride[5] with various 4-alkoxy-4'-biphenols.[6] All these new compounds exhibited appropriate ^{1}H and ^{13}C n.m.r., i.r., and h.r.m.s. data.



(**1**)



(**2**)

a; R' = C_5H_{11}, R^2 = Ph
b; R' = C_6H_{13}, R^2 = Ph
c; R' = C_6H_{13}, R^2 = $(C_5H_5)Fe(C_5H_4)$

Table 1. Melting properties of ferrocene diesters.

Compound	R^1	M.p., °C	Transition temperatures, °C	ΔH (melting), kJ/mol
(**1a**)	C_4H_9	209	$I \xrightarrow{188} C$	69
(**1b**)	C_5H_{11}	167	$I \xrightarrow{140} S_c \xrightarrow{129} C$	51
(**1c**)	C_6H_{13}	181	$I \xrightarrow{139} S_c \xrightarrow{132} C$	56
(**1d**)	C_7H_{15}	180	$I \xrightarrow{146} C$	60
(**1e**)	C_8H_{17}	183	$I \xrightarrow{145} C$	52
(**1f**)	C_9H_{19}	169	$I \xrightarrow{141} C$	41
(**1g**)	$C_{10}H_{21}$	161	$I \xrightarrow{146} C$	64
(**1h**)	$C_{11}H_{23}$	163	$I \xrightarrow{141} S_a \xrightarrow{132} C$	56
(**2a**)	C_5H_{11}	142	$C \xrightarrow{129} S_c \xrightarrow{139} I^a$	27
(**2b**)	C_6H_{13}	127	$C \xrightarrow{127} S^b \xrightarrow{142} I^a$	35
(**2c**)	C_6H_{13}	153	$I \xrightarrow{80} C$	44

[a] Thermotropic transition. [b] Phase to be identified.

The Table summarizes the phase transition temperatures and enthalpy data [determined by differential scanning calorimetry (D.S.C.)] for the various ferrocene esters. The compounds (**1b**, **c** and **h**) with R^1 = C_5H_{11}, C_6H_{13} and $C_{11}H_{23}$, respectively, were found to form monotropic mesophases over an 8—10 °C range. Under examination by a polarizing microscope the other compounds in the series were found to crystallize directly from the liquid phase upon cooling. Although the three liquid-crystal compounds display strikingly similar transition temperatures, preliminary polarizing-microscopic investigations suggest that (**1b**) and (**1c**) form a smectic C phase whereas (**1h**) exhibits a smectic A phase.[7] It is interesting to note that this change in phase behaviour follows the gap in which the C_7—C_{10} compounds do not form liquid crystals, apparently because the isotropic melts do not supercool to an adequate extent (see Table 1).

In order to probe the influence of the ferrocenyl unit on the observed liquid-crystal behaviour we prepared similarly the benzoate derivatives (**2a**, **2b**) and the monoferrocenyl ester (**2c**). The benzoates were also found to form a mesophase [smectic C for (**2a**)] over a remarkably similar temperature range to that of the ferrocenyl diesters (**1b**, **c** and **h**). However, the presence of only one mesogenic group on ferrocene as in (**2c**) failed to induce liquid-crystal behaviour. It appears, therefore, that the ferrocene unit attenuates the liquid-crystal forming tendency of the alkoxybiphenyl group. Attachment of two such groups to the ferrocene core, however, is sufficient to restore liquid-crystal properties. At present, we do not know whether these molecules adopt a 'U' (shown) or the seemingly more likely 'S' geometry. Efforts are underway to address this point, to elucidate further the structural requirements for metallocene-based liquid crystals, and to extend their liquid-crystal range.

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References

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