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Thermotropic Behavior of Ferrocenecarboxaldehyde and some Ferrocene Schiff's Base Derivatives

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Thermotropic Behavior of Ferrocenecarboxaldehyde and Some Ferrocene Schiff's Base Derivatives

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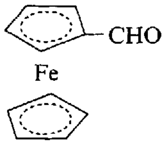
The state of ferrocenecarboxaldehyde between 43.5° and 123.5° has been characterized as a non-birefringent, highly viscous phase having the following enthalpies and entropies of transition: 43.5°: 3.0 kcal/mole, 9.5 cal/deg·mole; 123.5°: 0.6 kcal/mole, 1.6 cal/deg·mole. Several *p*-substituted phenyl Schiff's bases of ferrocenecarboxaldehyde were synthesized and examined together with various other ferrocene derivatives. All exhibited normal crystal melting behavior.

1 INTRODUCTION

Ferrocenecarboxaldehyde, **1**, is one of the most useful starting materials for the synthesis of many ferrocene derivatives. Its preparation was described almost simultaneously in 1957 by two groups.[1,2] Graham and coworkers[2] report that "ferrocenecarboxaldehyde exhibits a liquid crystalline state between 45° and 124.5°" but no further mention of this is made in the ensuing ferrocene literature. This largely neglected observation is intruiging since compounds having terminal groups at an approximately 90° angle to their long molecular axis are not expected to be capable of forming liquid crystal phases.[3]



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We have carried out an investigation of **1** using differential thermal analysis (DTA), differential scanning calorimetry (DSC), and polarized light microscopy and have found what we believe to be interesting thermal behavior. In addition, several new Schiff's base derivatives of **1** have been synthesized.

2 RESULTS AND DISCUSSION

A sample of ferrocenecarboxaldehyde, prepared by the reaction of ferrocene with *N*-methylformanilide and phosphorus oxychloride,[1,2] was found from DSC measurements to have a calculated purity[4] of 99.6%. Determination of the melting point of **1** in the usual manner, either between cover slips on the Fisher–Johns hot stage or in a capillary tube using a stirred oil bath showed only sharp melting at 123.0–123.5°(corr.). In contrast, DTA measurements showed the presence of an endothermic transition at 43.5°, in addition to the previously determined melting point, and indicated that the lower temperature transition was the major calorimetric event. DSC† gave the following enthalpies and entropies of transition: *43.5° transition*; 3.0 kcal/mole, 9.5 cal/deg.mole; *123.5° transition*; 0.6 kcal/mole, 1.6 cal/deg.mole. Heating and cooling cycles determined that the 123.5° transition was readily reversible but *the lower temperature transition was subject to supercooling*. The cooling curves eliminated the possibility of artifacts such as the polymerization of **1**, loss of solvent of crystallization, or decarbonylation.

Careful examination of **1** under the polarizing microscope (100 × magnification, N_2 atmosphere) revealed that at 43.5°, the reddish-brown birefringent crystals undergo a sharp transition involving loss of birefringence. For purposes of discussion we shall term the phase occurring between 43.5° and 123.5° the intermediate phase. Use of different samples and various types of cover slip and sample preparation gave the same results. The intermediate phase appears identical to the crystalline state from which it is formed except for lack of birefringence. It is only when *substantial pressure is applied to the microscope cover slip that the intermediate phase is observed to be a viscous material possessing considerable resistance to flow*. No further change is observed upon further heating until at 123.5°, the material undergoes another first-order transition to give the mobile, isotropic liquid.

The 80° temperature range of the intermediate phase indicates a substantial degree of stability. The high viscosity may be explained in terms of plastic

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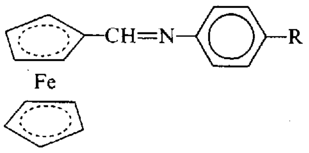
† The work was done on a Perkin–Elmer DSC 1B through the courtesy of Dr. Ivan Haller. The estimated precision was ±5%.

crystals[5] which have low yield stresses and involve molecules with considerable rotational freedom in the crystal lattice or in terms of an isotropic liquid crystal, which would indeed be unique. X-ray studies should afford more definitive evidence.[6]

The unusual thermal behavior of ferrocenecarboxaldehyde made it of interest to examine some condensation products with aromatic amines, since diaryl azomethines constitute a large and important class of mesogens. Accordingly, the new Schiff's bases shown in Table I were prepared and their thermal behavior determined by polarized light microscopy and DTA.

TABLE I

Physical data for Schiff's bases of ferrocenecarboxaldehyde[a]



R	m.p., °C
H	78–80
n-C_4H_9	63–64
n-C_5H_{11}	59–60
OCH_3	108–109
OC_5H_{11}	86–87
OC_6H_{13}	82–84

[a] All compounds gave correct elemental analyses.

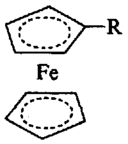
None showed any of the thermal characteristics of the parent organometallic aldehyde; only a single crystal-to-isotropic liquid point was observed as indicated by the entries in the Table. Molecular models indicate these ferrocene Schiff's bases to be almost L-shaped and deviations from overall molecular colinearity are well known to result in the absence of mesogenicity.

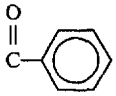
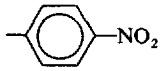
Several other ferrocene derivatives, kindly supplied by Prof. Rosenblum[7] were examined and the results, normal melting of the crystal, are given in Table II.

We see no reason why the unique phase behavior of ferrocenecarboxaldehyde should not occur in other metallocene derivatives and further studies are warranted.

TABLE II

Physical data for some ferrocene derivatives[a]



R	m.p., °C
COOH	205–208
$\mathrm{CH{=}CHCOOH}$	187–189
$\mathrm{C{\equiv}CH}$	54–55
$\mathrm{C{\equiv}C}^{b}$	246–249
	108–109
	115–116
	170–172
—HgBr	198–201

[a] Ref. 7.
[b] Diferrocenylacetylene

Acknowledgements

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6. An X-ray study is in progress with Dr. A. de Vries at the Liquid Crystal Institute, Kent State University.
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