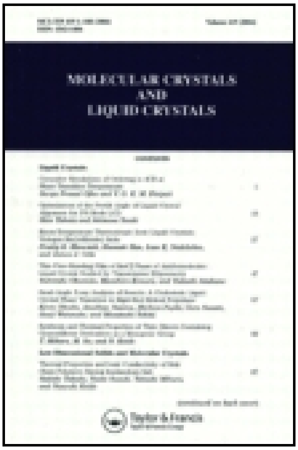

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Ke-Qing Zhao [a] , Pin Hu [a] , Hong-Bo Xu [a] , Wen Wan [b] , Zhong-Yuan Zhou [b] & Liang-Fu Zhang [b]

[a] Department of Chemistry, Sichuan Normal University, Chengdu, 610066, P.R. China

[b] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, P.R. China

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Synthesis and Crystal Structure of Mono-Substituted Ferrocene-Containing Liquid Crystals

KE-QING ZHAO[a*], PIN HU[a], HONG-BO XU[a], WEN WAN[b], ZHONG-YUAN ZHOU[b] and LIANG-FU ZHANG[b]

[a]*Department of Chemistry, Sichuan Normal University, Chengdu, 610066, P.R. China and* [b]*Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, P.R. China*

Ten mono-substituted ferrocene-containing liquid crystals, which containing Schiff base or ester group, were prepared and their mesogenic behaviors were investigated. Two molecular structures were analyzed by X-ray. 4-ferrocenylphenyl 3'-chloro-4'-(2-methylbutyloxy)-benzoate, triclinic crystal system, P1 space group, a=12.035(2)Å, b=14.402(3)Å, c=15.137(3)Å, α =103.07(3)°, β = 102.01(3)°, γ = 96.70(3)°, Z=4, 8141 independent reflections, R=0.0528, Rw=0.1724. 4-ferrocenylphenyl 3'-chloro-4'-decanyloxybenzoate, triclinic crystal system, $P\bar{1}$ space group, a= 11.663(2)Å, b=11.729(2)Å, c=22.005(4)Å, α=76.10(3)°, β =87.56(3)°, γ = 77.89(3)°, Z=4, 7935 independent reflections, R=0.0784, Rw=0.2265.

Keywords: liquid crystals; ferrocene derivatives; arylation; phase transfer catalysis; molecular structure

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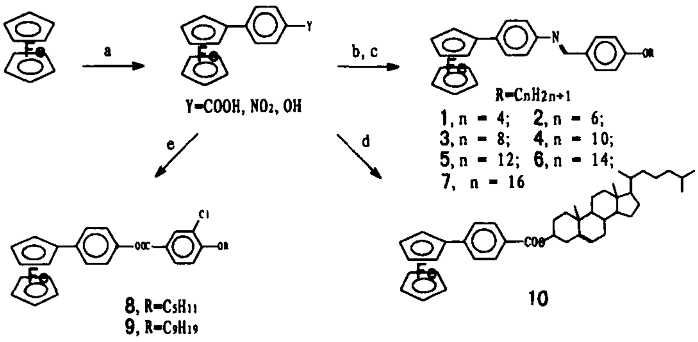
* Corresponding author: Email: kexiang@mail.sc.cninfo.net Tel/Fax: +86–28–4764743.

INTRODUCTION

The incorporation of metals into structures of low molar mass liquid crystals, hoping to acquire novel physical properties, is now a well established area of materials chemistry. Ferrocene-containing complexes, which possess special thermal and chemical stability, have been widely used as the building blocks of thermal liquid crystalline, non-linear optical materials and magnetic materials[1-8]. Here we report the synthesis and characterization of a serials of new mono-substituted ferrocene-containing liquid crystalline. Scheme 1 lists the synthesis route of these compounds.



SCHEME 1 Reagents and conditions: a, CTMAB, Y-C_6H_4-$N_2^+Cl^-$, Et_2O/H_2O,0°-5°C. b, Y = NO_2, Sn/HCl, EtOH. c, HCl, $H_{2n+1}C_nO$-C_6H_4-CHO. d, $(COCl)_2$, then ChOH, Et_3N. e, Et_3N, RO-C_6H_3(Cl)-COCl.

EXPERIMENT

Chemicals and Instruments:

All chemicals are commercial products without further purification.

NMR spectra were recorded on a Brucker ACE-200 spectrometer. IR spectra were recorded on Nicolet Magna-IR 500 Spectrometer, Series II. The transition temperatures of these compounds were determined with a polarizing microscope equipped with a heating stage and from thermograms recorded on a differential scanning calorimeter (Perkin-Elmer 7 Series).

Synthetic Procedure.

General method for the synthesis of 4-substituted phenylferrocene (the synthesis of *p*-nitrophenylferrocene as example).

p-nitrophenylferrocene

14g(0.1mol) *p*-nitroaniline, was dissolved in the mixture of 30ml water and 30ml concentrated hydrochloride acid and cooled to 0°~5°C. The solution of 7g sodium nitrite in 20ml water was slowly added with stirring in 1h. The diazonium salt was kept in low temperature for use.

9.5g(0.05mol) ferrocene was dissolved in 100ml ethyl ether, 1g of cetyltrimethyl ammonium bromide(CTMAB) added. The diazonium salt was added in 1h with stirring. After reaction finished, ethyl ether was distilled out. The mixture was filterated, washed with water, and water vapor distillated to get out of un-reacted ferrocene. The residue was re-crystallized from petroleum ether to get *p*-nitrophenylferrocene 13.5g (70%). mp 169.5-170.0°C.

^{1}H NMR($CDCl_3$, TMS), δ (ppm): 4.0(s, 5H, C_5H_5), 4.5(d, 2H, C_5H_4), 4.7(m, 2H, C_5H_4), 7.5(d, J_{HH}=8.8Hz, 2H, C_6H_4), 8.1(d, J_{HH}=8.8Hz, C_6H_4). ^{13}C NMR($CDCl_3$, TMS), δ (ppm): 67.2, 70, 70.6, 81.7, 123.8, 125.9, 145.5, 148.2. IR(KBr), cm^{-1}: 1596, 1507, 1341, 846.

p-aminophenylferrocene

This intermediate was prepared by the reduction of p-nitrophenylferrocene with tin in ethanol solution of hydrochloride acid. Yield, 76%, mp157-159°C. ^{1}H NMR($CDCl_3$, TMS), δ (ppm): 3.6(s, 2H, NH_2), 4.0(s, 5H, C_5H_5), 4.2(m, 2H, C_5H_4), 4.5(m, 2H, C_5H_4). IR(KBr), cm^{-1}: 3437, 3350, 1621, 1529, 1454, 1288, 819.

Fc-C_6H_4-N=CH-C_6H_4-OC_nH_{2n+1}, compound **1~7**.

0.28g(1mmol), *p*-aminophenylferrocene, and 1mmol *p*-alkoxylbenzaldehyde were dissolved in 50ml ethanol and refluxed overnight. After cooling, the precipitate was collected through filtration and crystallized from petroleum ether(60°-80°C) to get orange solids.
Yield: 90%. ^{1}HNMR($CDCl_3$, TMS), δ (ppm): 1.0(t, 3H, CH_3), 1.4~2.0(m, $(CH_2)_{n-2}$), 3.7~3.9(m, 2H, OCH_2), 4.0(s, 5H, C_5H_5,), 4.3, 4.6(d, 4H, C_5H_4), 6.8(d, 2H, C_6H_4), 7.2(d, 2H, C_6H_4), 7.5(d, 2H, C_6H_4), 7.9(d, 2H, C_6H_4).

The preparation of *p*-hydroxyphenylferrocene and *p*-hydroxycarbonyl-pheneylferrocene has similarity with the experimental procedure of *p*-nitrophenylferrocene.
p-hydroxyphenylferrocene, yield, 47%, mp, 163.5-164.0°C.
^{1}H NMR($CDCl_3$, TMS), δ (ppm): 4.0(s, 5H, C_6H_4), 4.25(s, 2H, C_5H_4), 4.54(s, 2H, C_5H_4), 4.62(s, 1H, OH), 6.7(d, J_{HH}=8.2Hz, 2H, C_6H_4), 7.3(d, J_{HH}=8.2Hz, C_6H_4). IR(KBr), cm^{-1}: 3516, 3104, 1619, 1540, 1268, 1109, 830.

4-ferrocenylphenyl 3'-chloro-4'-(2-methylbutyloxy)benzoate, **8**.
The preparation of **8** and **9** was realized by the reaction of benzoyl chloride with *p*-hydroxyphenylferrocene in the presence of triethylamine.
^{1}H NMR($CDCl_3$, TMS), δ (ppm): 7.4, 7.2(4H, C_6H_4), 8.4, 8.1, 6.9(3H, C_6H_3), 4.7, 4.4, 4.1(9H, Fc), 5.3, 0.6-2.0(OR)
IR(KBr), cm^{-1}: 2921, 2850, 1737, 1270, 1194.
4-ferrocenylphenyl 3'-chloro-4'-decanyloxybenzoate, **9** has similar spectra data with compound **8**.

p-hydroxycarbonylphenylferrocene, yield, 64.2%, mp,240°C(dec.)
^{1}H NMR($CDCl_3$, TMS), δ (ppm): 3.8(s, 5H, C_5H_5), 4.18(m, 2H, C_5H_4), 4.50(m, 2H, C_5H_4), 7.3(d, J_{HH}=8.4Hz, 2H, C_6H_4), 7.8(d, J_{HH}=8.4Hz, 2H, C_6H_4). IR(KBr), cm^{-1}: 3600-3200, 1593, 1507, 1341, 1105, 848, 472.

Cholestryl *p*-ferrocenylbenzoate, **10** was prepared by the reaction of *p*-ferrocenylbenzoyl cloride with cholesterol in presence of triethylamine. Yield: 80%. ^{1}H NMR($CDCl_3$, TMS), δ (ppm): 7.8(d, 2H, C_6H_4), 7.2(d, 2H, C_6H_4), 4.3, 4.8, 4.0(s, 9H, Fc), 5.4, 4.85, 2.5, 0.6~2.0(m, 33H, Ch). IR(KBr), cm^{-1}: 2943, 2867, 1713, 1243.

X-ray Crystallographic Analysis.

Diffraction data were measured at 298K on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo Ka radiation. Cell parameters were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the basis of an experimental Ψ rotation curve. The refinement procedure was by a full-matrix least-squares method, including all the non-hydrogen atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and a C-H distance of o.1nm; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Computing programs are from the NRCC SDP VAX package. Crystallographic data of compound **8** and **9** are listed on Table 1.

TABLE 1, X-ray Single Crystal Parameters of Compound **8** and **9**
[**8**: Fc-C_6H_4-OOC-C_6H_3(Cl)(OC_5H_{11}),
9: Fc-C_6H_4-OOC-C_6H_3(Cl)(OC_9H_{19})].

Empirical formula	$C_{28}H_{27}ClFeO_3$ **8**	$C_{32}H_{35}ClFeO_3$ **9**
Formula weight	502.80	558.90
Temperature	293(2)K	
Wavelength	0.71073Å	
Crystal system	Triclinic	Triclinic
Space group	$P1$	$P\bar{1}$
Unit cell dimensions	a = 12.035(2) Å	a=11.663(2)Å
	b = 14.402(3) Å	b=11.729(2)Å
	c = 15.137(3)Å	c=22.005(4)Å
	α =103.07(3)°	α =76.10(3)°
	β =102.01(3)°	β =87.56(3)°
	γ =96.70(3)°	γ =77.87(3)°
Volume z	2462.4(9)Å^3 4	2856.6(10)Å^3 4
Density(calculated)	1.356Mg/m^3	1.300 Mg/m^3
Absorption coefficient	0.748mm^{-1}	0.652
F(000)	1048	1176
Crystal size	0.28X 0.26 X 0.20 mm	0.28X0.26X0.20mm
Θ range for data collection	1.47 to 25.54 °	2.02 to 25.47°
Limiting indices	$-14\leqslant h\leqslant 14$,	$-13\leqslant h\leqslant 13$,
	$0\leqslant k\leqslant 17$,	$-13\leqslant k\leqslant 14$,
	$-18\leqslant l\leqslant 17$	$0\leqslant l\leqslant 26$

Reflection collected	8141	7935
Independent reflections	8141(R_{int} = 0.0000)	7935(R_{int} = 0.0000)
Absorption correction	Semi-empirical	
Max. and min. Transmission	0.8648 to 0.8179	1.000 and 0.384
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8141/19/1202	7935/50/720
Goodness-of-fit on F2	1.308	0.662
Final R indices[I>2 δ (I)]	R1 = 0.0528, WR2 = 0.1724	R1=0.0784 wR2=0.2265
R indices (all data)	R1 = 0.0621 WR2 = 0.1862	R1=0.1132 wR2=0.2884
Extinction coefficient	0.0000(11)	0.0119(13)
Largest diff. Peak and hole	0.443 and -0.293 eÅ^{-3}	0.630 and -0.382

RESULTS AND DISCUSSION

Synthesis.

The arylation reaction of ferrocene with diazonium salt leads to arylferrocene[9]. But in most cases the yield is low when aryl contains functional group. To improve the yield, the reaction conditions for the preparation of *p*-ferrocenylbenzoic acid were optimized in this lab.

Ferrocene dissolved in ethyl ether reacted with the diazonium salt of *p*-aminobenzoic acid in different pH mediates. In strong acid solution, the reaction got the highest yield. The yield in hydrochloric acid was 42.7%, and in sodium hydrogen carbonate solution, 5.8%, and in sodium hydroxide, no product.

In presence of phase transfer catalysts, the yield of ferrocenylbenzoic acid was improved. In hydrochloric acid solution, for cetyltetramethylammonium bromide, tetradecylpyridinium bromide, and tetrabutylammonium bromide, the yield was 62.4%, 59%, and 56.0% respectively. So the phase transfer catalyzed ferrocene arylation reaction has apparent improvement in yield[9].

Mesophases

The mesogenic behaviors of the ten synthesized complexes have been studied through DSC and polarizing microscopic photography. The results listed on Table 2. The textures of these compounds were assigned according literature[10]. The Schiff bases complexes **1~7** show smectic phase and the transition temperature stead lowers as the number (n) of carbon increases. When $n=16$, this compound shows nematic phase. The ester compounds **8** and **9** are nematic liquid crystals and compound **10** has monotropic cholesteryl phase as it contains a cholestryl group in its molecular structure.

TABLE 2, Mesophase, Transition Temperature(°C) and Enthalpy Changes(Δ H) of the Synthesized Mono-substituted Ferrocen-containing liquid crystals.

Compound	Mesophase behavior(Δ H, KJ/mol)[a]
1	C -173(9.24)-S-186(29.06)-Iso
2	C-145(31.39)--S-149(40.80)-Iso
3	C-125(35.31)-S-144(41.63)-Iso
4	C-118(32.13)-S-131(40.76)-Iso
5	C-103(35.41)-S-107(13.42)-Iso
6	C-76(35.13)-S-106(21.46)-Iso
7	C-50(9.78)-S-54(40.46)-N-76(13.57)-Iso
8	C-114.4(25.75)-N-121.5(0.59)-Iso
9	C-122(28.16)-N-139(2.138)-Iso
10	C-145(35.60)-I I-137(2.126)-Ch-124(23.9)-C

[a] C: crystal, Iso: isotropic, S: Smectic, N: nematic, Ch: cholesteryl.

X-ray Crystal Results

The single crystals of two complexes have been obtained and tested. Figure 1 and 2 are the molecular structures and molecular packing in crystal lattice of compound **8** and **9**. The molecular structures of 8 and 9 show that the phenyl rings connected to ferrocene are almost parallel to the cyclopentadiene rings and the other phenyl in the molecular are twisted or perpendicular to the ferrocenyl. In the crystal lattice, there are four molecules in each unite cell and compound **8** all placed in the order of head (ferrocenyl) to head. While, compound **9**, 3 molecules out of 4 are head to tail and 1 molecule in the order of head to head. Compound **9** seems in higher order in layer arrangement than compound **8**. The layer arrangement of molecules in crystal can change into nematic phase when heated[11].

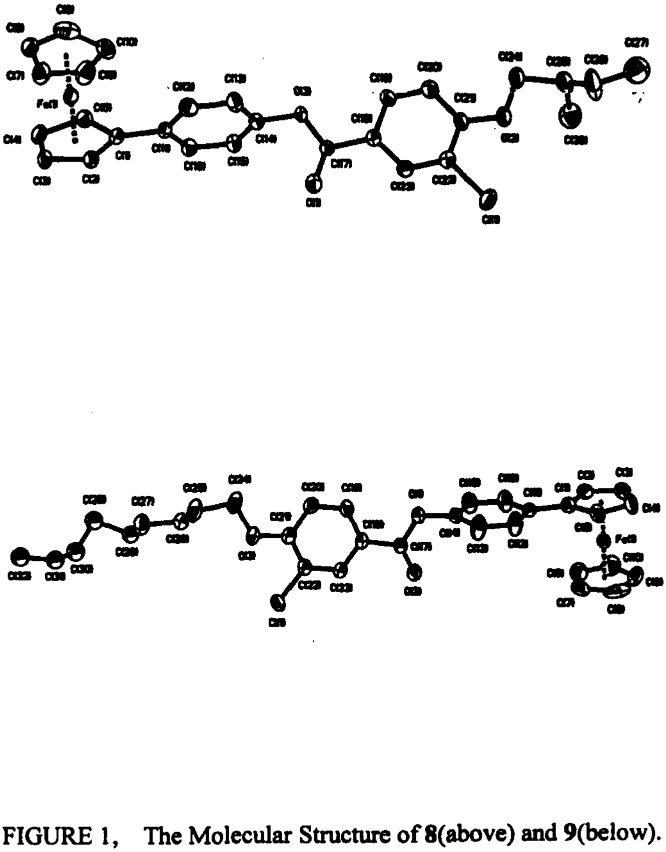


FIGURE 1, The Molecular Structure of **8**(above) and **9**(below).

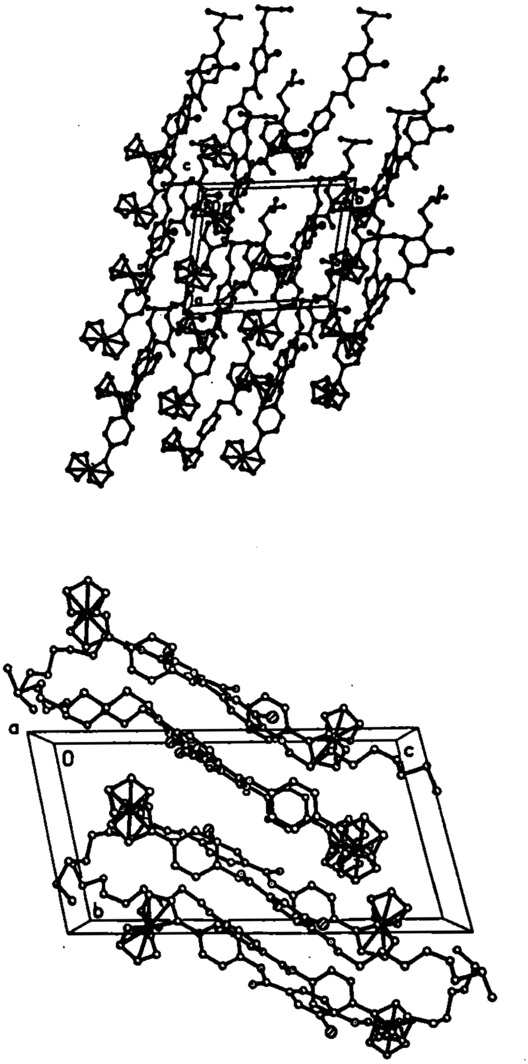


FIGURE 2, Molecular Packing in Crystal Lattice, **8**(above) and **9**(below).

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