Synthesis of substituted 1-acyl-1´-biphenylylferrocenes. Crystal structures of 4-bromo-4´-ferrocenylbiphenyl and 1-(4´-cyanobiphenyl-4-yl)-1´-((*S*)-3-methylpentanoyl)ferrocene

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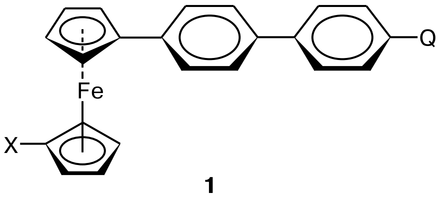
Acylation of 4-bromo- and 4-cyano-4´-ferrocenylbiphenyl with alkanoyl chlorides afforded the corresponding 1-acyl-1´-biphenylylferrocenes in ~20% yields. X-ray diffraction study of the above-mentioned bromo derivative and 1-(4´-cyanobiphenyl-4-yl)-1´-((*S*)-3-methylpentanoyl)ferrocene demonstrated that these ferrocenylbiphenyl derivatives crystallize in noncentrosymmetric space groups.

Key words: acylation, ferrocenylbiphenyls, X-ray diffraction study, nonlinear optics.

Ferrocene-containing derivatives that belong to materials exhibiting nonlinear optical and liquid-crystalline properties have been extensively studied in recent years.[1,2] These compounds have attracted attention due to both specific properties of the ferrocenyl group (an easily polarizable electron donor having a three-dimensional sandwich structure) and the fact that ferrocene derivatives are more readily accessible than other organometallic compounds. The introduction of a ferrocenyl substituent into a molecule of an organic compound can result in materials possessing new magnetic and electrochemical properties, which can be controlled by modifying the groups bound to ferrocene and employing the ability of the latter to undergo reversible redox transformations.[2,3]

With the aim of preparing such nonlinear optical and liquid-crystalline materials, we developed procedures for the synthesis of compounds **1**.



1

X = $C_nH_{2n+1}CO$, H; Q = Br, CN

Molecules **1** contain an electron-donating (ferrocenyl) group and an electron-withdrawing (Q) group at the opposite sides of the π-conjugated system giving rise to a charge-transfer system favorable for the manifestation of nonlinear optical effects. The biphenyl moiety and the cyclopentadienyl ring bound thereto impart a rod-like shape to the molecule, and the substituent X can contain a flexible alkyl chain. Hence, compounds **1** can exhibit also liquid-crystalline properties provided that a rod-like fragment is sufficiently long and the molecule is flexible. Actually, a number of ferrocenyl-containing liquid-crystalline materials involve the biphenylyl group as the mesogenic fragment, which is linked to the ferrocenyl moiety either directly[4] or through a spacer that provides flexibility of the rigid conjugated system.[5] Most studies were devoted to the latter type of ferrocenyl-containing mesogens, the carboxy group often serving as the spacer.[6] 4-Ferrocenylbiphenyl derivatives remain poorly studied. Only one class of such compounds, *viz.*, Schiff bases Fc—C_6H_4—C_6H_4—CH=N—C_6H_4—OC_nH_{2n+1} (n = 5, 8, 14), possessing liquid-crystalline properties is known.[4]

Earlier,[7] we have synthesized 4-substituted 4´-ferrocenylbiphenyls (including, compounds **2a** and **3a**; Scheme 1) and studied the molecular and crystal structures of these compounds. In the present study, we found optimum conditions for the synthesis of compounds **1** containing the acyl group as the substituent X and established the structures of 4-bromo-4´-ferrocenylbiphenyl and 1-(4´-cyanobiphenyl-4-yl)-1´-((*S*)-3-methylpentanoyl)ferrocene by X-ray diffraction analysis.

1-Acyl-1´-biphenylylferrocenes can further be modified and used as precursors for new liquid-crystalline and nonlinear optical materials.

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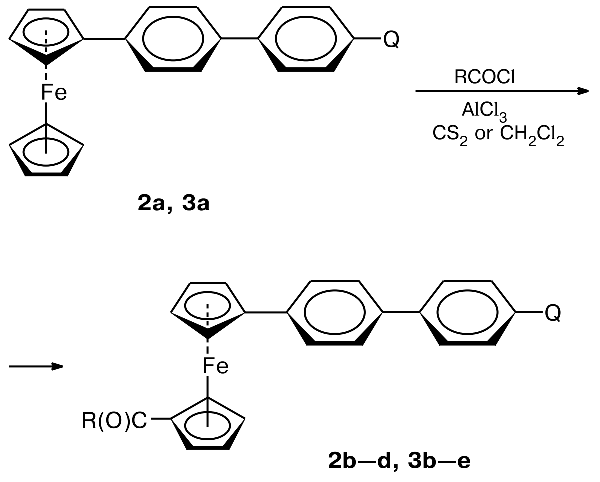
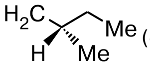
Scheme 1



2a, 3a

2b—d, 3b—e

Q = Br (**2a**), CN (**3a**),
Q = Br, R = n-C_7H_{15} (**2b**), n-$C_{10}H_{21}$ (**2c**), n-$C_{17}H_{35}$ (**2d**),
Q = CN, R = Me (**3b**), n-C_7H_{15} (**3c**),
n-$C_{10}H_{21}$ (**3d**),  (**3e**)

Results and Discussion

Compounds **1** were synthesized by acylation of the corresponding ferrocenylbiphenyls (see Scheme 1) taking into account the known fact that arylation of substituted ferrocenes gave unsatisfactory results.[8]

With the aim of searching for the optimum acylation conditions, we examined the influence of the solvent, the reagent ratio, and the reaction time on the yield of 1-acyl-1′-biphenylylferrocenes. The results of this investigation are given in Table 1.

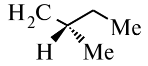
Acylation afforded a mixture of acyl derivatives containing also the starting ferrocenylbiphenyl. All acyl derivatives exhibit similar chromatographic mobilities on Al_2O_3, which prevents their isolation and leads to losses in the chromatography and crystallization. In all cases, only heteroannularly substituted acylation products were isolated. Their yields were, on the average, 20 %.

According to TLC data, acylation gave rise to heteroannular isomers as the main products. This results is consistent with the fact that the biphenyl fragment bearing the Br atom or the CN group exhibits electron-withdrawing properties with respect to the ferrocenyl fragment and deactivates the substituted C_5H_4 ring of ferrocenylbiphenyl to a greater extent than the C_5H_5 ring. In 4-ferrocenyl-4′-nitrobiphenyl (**4**), the nitro group completely inhibits the reaction. The starting nitro compound was recovered in 54% yield due to partial decomposition in the course of the reaction in boiling carbon disulfide.

Acylation was performed using carbon disulfide and dichloromethane as the solvents. As can be seen from Table 1, carbon disulfide has no advantages over dichloromethane. The highest yield of 1-acyl-1′-biphenylylferrocene was achieved in the reaction performed in the presence of a twofold excess of $AlCl_3$ for 13—15 h.

Study of compounds **2b—d** and **3c,d** demonstrated that they do not form liquid-crystalline phases in spite of the presence of long alkyl chains. Presumably, the main reason is the insufficient length of the rigid rod-like fragment in the molecules of the compounds under consider-

Table 1. Reaction conditions and results of acylation of ferrocenylbiphenyls **2a**, **3a**, and **4**

Reaction conditions			Reaction product			
Ratio $Fc(C_6H_4)_2Q$: RCOCl : $AlCl_3$	Solvent	t/h	Compound	Q	R	Yield (%)
1.0 : 1.0 : 1.4	CH_2Cl_2	20.5	**2b**	Br	C_7H_{15}	21[a]
1.0 : 1.0 : 1.4	CS_2	2.5	**2b**	Br	C_7H_{15}	26
1.0 : 1.0 : 1.6	CS_2	5	**2c**	Br	$C_{10}H_{21}$	17
1.0 : 1.1 : 2.0	CH_2Cl_2	22.5	**2c**	Br	$C_{10}H_{21}$	27
1.0 : 1.0 : 1.6	CS_2	2.5	**2d**	Br	$C_{17}H_{35}$	17
1.0 : 1.1 : 2.0	CH_2Cl_2	15	**3b**	CN	Me	22
1.0 : 1.0 : 1.4	CH_2Cl_2	5	**3c**	CN	C_7H_{15}	10[b]
1.0 : 1.1 : 2.0	CH_2Cl_2	14	**3d**	CN	$C_{10}H_{21}$	35
1.0 : 1.1 : 2.0	CS_2	4.5	**3d**	CN	$C_{10}H_{21}$	16[c]
1.0 : 1.1 : 2.0	CH_2Cl_2	13	**3e**	CN	 H_2C Me H Me	27
1.0 : 1.0 : 1.7	CS_2	3	**4a**	NO_2	C_7H_{15}	0[d]

[a] The starting compound **2a** was recovered in 17% yield.
[b] The starting compound **3a** was recovered in 28% yield.
[c] The starting compound **3a** was recovered in 18% yield.
[d] The starting 4-ferrocenyl-4′-nitrobiphenyl (**4**) was recovered in 54% yield.

ation, *i.e.*, the ratio of the length of the biphenyl fragment to the "thickness" of the ferrocene fragment is unfavorable for stabilization of the mesophase.

With the aim of searching for approaches to the construction of nonlinear optical materials (*i.e.*, the materials that crystallize in a noncentrosymmetric space group), we studied the structures of compound **2a** and chiral acyl derivative **3e** by X-ray diffraction analysis. It should be noted that X-ray diffraction analysis of compounds **3a** and **4** has demonstrated[7] that they crystallize in a centrosymmetric space group and, consequently, do not possess nonlinear optical activity. However, it is known that a compound can be crystallized in a noncentrosymmetric space group by varying the donor or acceptor substituents.[9]

X-ray diffraction data showed that compounds **2a** and **3e** crystallize in the noncentrosymmetric space groups $P2_1$ (**2a**) and $P1$ (**3e**).

The molecular structure of compound **3e** is shown in Fig. 1. The unit cell of acyl derivative **3e** contains two crystallographically independent molecules (**A** and **B**), which are related by a pseudocenter of symmetry, except for the substituents at the chiral carbon atom (Fig. 2). In both molecules, the cyclopentadienyl rings of the ferrocene moiety adopt a nearly eclipsed conformation. The

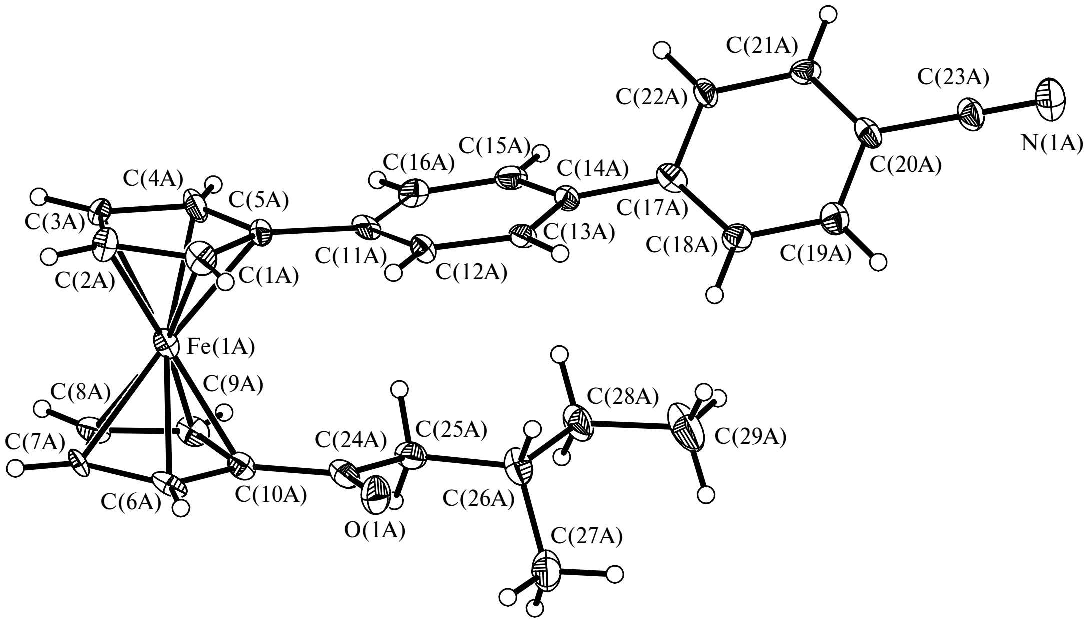


Fig. 1. One of two crystallographically independent molecules (**A**) of compound **3e** with displacement ellipsoids drawn at the 30% probability level.

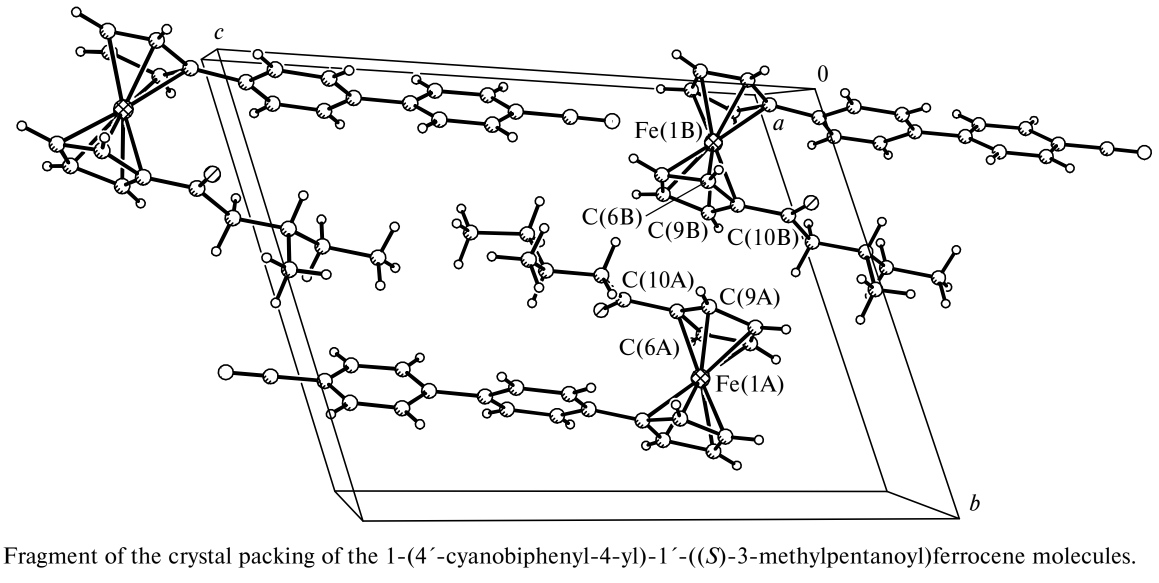


Fig. 2. Fragment of the crystal packing of the 1-(4′-cyanobiphenyl-4-yl)-1′-((*S*)-3-methylpentanoyl)ferrocene molecules.

C(10)—Cnt^1—Cnt^2—C(5) pseudotorsion angle is close to 11° (Cnt^1 and Cnt^2 are the centroids of the Cp rings bound to the acyl group and the biphenyl-4-yl fragment, respectively). The biphenyl fragment and the acyl group are located at the same side of the ferrocene moiety, *i.e.*, the molecule in the crystal adopts a U-shaped conformation.

The Cp^1—Ar^1—Ar^2 ring system (Ar = C_6H_4) is nonplanar. The dihedral angles between the planes of the Cp^1 and Ar^1 rings and the Ar^1 and Ar^2 rings are 10.6(6)° and 40.2(3)°, respectively. All aromatic rings are planar (the rms deviations are 0.001—0.013 Å). The rings of the Cp^1—Fe—Cp^2 fragment are virtually coplanar. The angles between the Cp^1 and Cp^2 planes are 1.8(8)° and 3.4(8)° for the crystallographically independent molecules **A** and **B**, respectively.

Analysis of the crystal packing of molecules **3e** showed that all intermolecular distances in the crystal correspond to usual van der Waals contacts. The adjacent planes of the Cp rings, *viz.*, C(6A)...C(10A) and C(6B)...C(10B), of the ferrocenyl fragments of two independent molecules are coplanar (the angle between these planes is 1.2(8)°) (see Fig. 2). The shortest distances C(6A)...C(9B), C(9A)...C(6B), and C(10A)...C(10B) are 3.649(14), 3.640(14), and 3.561(5) Å, respectively. The independent molecules are related by a pseudocenter of symmetry and are arranged in a head-to-tail fashion due apparently to dipole-dipole interactions, with the resulting antiparallel orientation of the dipole moments. This character of the molecular packing is unfavorable for generation of strong nonlinear optical effects because it leads to mutual compensation of the contributions of molecular hyperpolarizability to the nonlinear optical susceptibility of the crystal.

The crystal structure of compound **2a** also contains two independent molecules **A** (Fig. 3) and **B**, which differ only in the conformation of the Cp^1—Ar^1—Ar^2 and Cp^1/Cp^2 ring systems. The angles between the planes of the Cp^1 and Ar^1 rings and the Ar^1 and Ar^2 rings are 7.9(4)° and 18.7(2)° for the molecule **A** and 0.8(3)° and 14.2(3)° for the molecule **B**, respectively. The C(10)—Cnt^2—Cnt^0—C(5) pseudotorsion angle (Cnt^0 is the centroid of the unsubstituted Cp ring) is 13° and 20° in the molecules **A** and **B**, respectively. In the crystal of compound **2a**, the molecules **A** and **B** are also related by a pseudocenter of symmetry and are arranged in a head-to-tail fashion.

The crystal packing of the 4-bromo-4´-ferrocenylbiphenyl molecules (**2a**) is shown in Fig. 4. All intermolecular distances correspond to usual van der Waals contacts, except for the Br(1A)...H(5A´)—C(5A´) [$1 - x$, $-0.5 + y$, $1 - z$] contact characterized by the parameters of 2.79 Å, 3.695(7) Å, and 153°. This contact occurs between two molecules **A**.

The bond lengths in molecules **2a** and **3e** have standard values**[10]** and correspond to the bond lengths in 4-cyano-4´-ferrocenyl- and 4-ferrocenyl-4´-nitrobiphenyls **3a** and **4**, which we have studied earlier.

X-ray diffraction study demonstrated that crystallization in a noncentrosymmetric space group can be achieved by varying the substituent in compounds **1**. The introduction of a chiral group having a particular configuration necessarily results in a homochiral structure. One would expect that this modification of the molecules not only will allow one to prepare noncentrosymmetric crystals but also will give rise to the optimum (from the viewpoint of nonlinear optical activity) molecular packing.

Experimental

All experiments were carried out at 20 °C under argon using the standard Schlenk technique. The compounds synthesized were purified by column chromatography on Al_2O_3 (Brockmann activity II). The course of the reactions was monitored by TLC on Silufol plates. Anhydrous $AlCl_3$ was purified by sublimation in a vacuum of a water-aspirator pump at 150—170 °C.

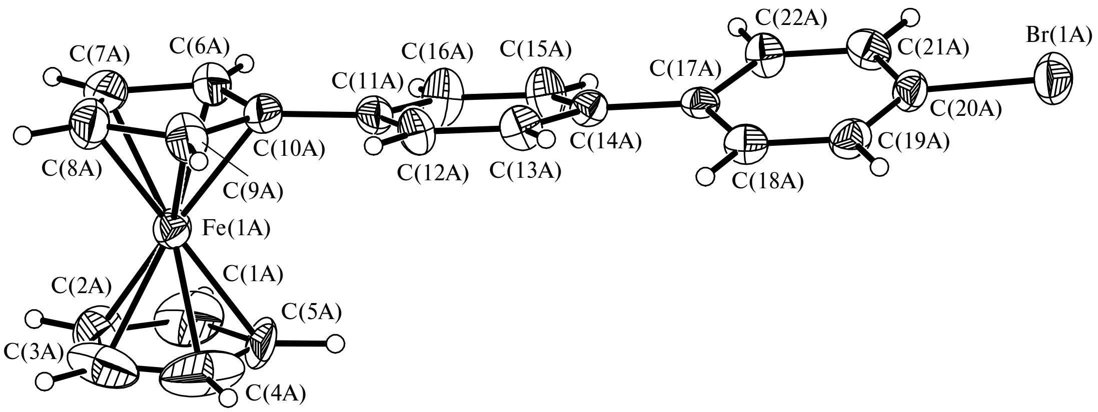


Fig. 3. One of the crystallographically independent molecules (**A**) of compound **2a** with displacement ellipsoids drawn at the 30% probability level.

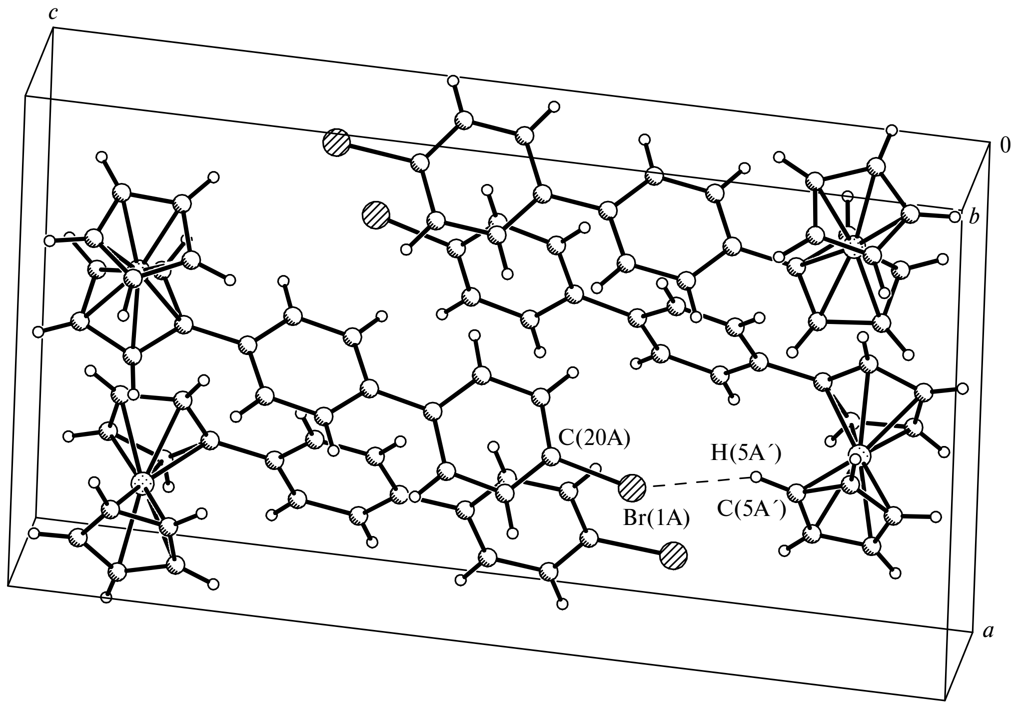


Fig. 4. Fragment of the crystal packing of the 4-bromo-4´-ferrocenylbiphenyl molecules.

Dichloromethane was distilled over CaH_2. Carbon disulfide was kept over P_2O_5 and distilled.

The ^1H NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz) in $CDCl_3$.

1-(4´-Bromobiphenyl-4-yl)-1´-octanoylferrocene (2b). ***A.*** A mixture of aluminum chloride (0.19 g, 1.4 mmol), dichloromethane (35 mL), and octanoyl chloride (0.17 mL, 0.16 g, 1 mmol) was stirred for 3.5 h until $AlCl_3$ nearly completely dissolved. The resulting solution of the acylating reagent was added dropwise to a stirred solution of compound **2a** (0.42 g, 1 mmol) in CH_2Cl_2 (15 mL) for 2 h. The reaction mixture was stirred for 3.5 h, kept without stirring for 15 h, and poured onto ice. Then concentrated HCl (8 mL) and $CHCl_3$ (20 mL) were added. The organic layer was separated, washed with water to the neutral reaction, dried with $MgSO_4$, and filtered. The solvent was removed *in vacuo* and the residue was chromatographed on Al_2O_3. The starting compound **2a** was eluted with a 1 : 2 benzene—light petroleum mixture in a yield of 0.07 g (17%). Crude product **2b** was eluted in a yield of 0.15 g with a 3 : 1 benzene—light petroleum mixture. Then the crude product was twice recrystallized from light petroleum (70/100). The yield of 1´-(4´-bromobiphenyl-4-yl)-1-octanoylferrocene (**2b**) was 0.12 g (21%), m.p. 132—134 °C. Found (%): C, 66.41; H, 5.95; Fe, 10.16. $C_{30}H_{31}BrFeO$. Calculated (%): C, 66.32; H, 5.75; Fe, 10.28. ^1H NMR, δ: 0.88 (t, 3 H, Me); 1.26 (m, 8 H); 1.57 (m, 2 H, $\underline{CH_2}CH_2CO$); 2.38 (t, 2 H, CH_2CO); 4.37 (m, 4 H); 4.65 and 4.68 (both m, 2 H each); 7.44—7.57 (m, 8 H, C_6H_4—C_6H_4).

B. A mixture of $AlCl_3$ (0.19 g, 1.4 mmol), octanoyl chloride (0.17 mL, 0.16 g, 1 mmol), and carbon disulfide (18 mL) was stirred for 1 h and then a solution of compound **2a** (0.40 g, 1 mmol) in CS_2 (7 mL) was added. The dark-cherry reaction mixture was stirred for 2.5 h. Compound **2b** was isolated as described above. The yield of compound **2b** was 0.14 g (26%), m.p. 130—133 °C.

1-(4´-Bromobiphenyl-4-yl)-1´-undecanoylferrocene (2c). ***A.*** A mixture of $AlCl_3$ (0.18 g, 1.35 mmol), undecanoyl chloride (0.17 g, 0.84 mmol), and CS_2 (7 mL) was stirred for 15 min, and a solution of compound **2a** (0.35 g, 0.84 mmol) in CS_2 (15 mL) was added. The reaction mixture was stirred for 5 h and then worked up as described for **2b**. The acylation product was chromatographed on Al_2O_3. The starting compound **2a** was eluted with a 1 : 1 benzene—light petroleum mixture. Compound **2c** was eluted with a 3 : 2 benzene—light petroleum mixture and twice recrystallized from light petroleum (70/100). Compound **2c** was isolated in a yield of 0.085 g (17%) as pale-red crystals, m.p. 127—130 °C. Found (%): C, 67.86; H, 6.24. $C_{33}H_{37}BrFeO$. Calculated (%): C, 67.71; H, 6.37. ^1H NMR, δ: 0.87 (t, 3 H, CH_3); 1.22 (m, 14 H); 1.51 (m, 2 H, $\underline{CH_2}CH_2CO$); 2.39 (t, 2 H, CH_2CO); 4.36 (m, 4 H), 4.64 and 4.68 (both m, 2 H each); 7.46—7.52 (m, 6 H, Ar); 7.55—7.57 (m, 2 H, Ar).

B. A mixture of $AlCl_3$ (0.32 g, 2.4 mmol), undecanoyl chloride (0.27 g, 1.3 mmol), and CH_2Cl_2 (8 mL) was stirred for 20 min. Then a solution of compound **2a** (0.50 g, 1.2 mmol) in CH_2Cl_2 (23 mL) was added. The reaction mixture was stirred for 8.5 h and then kept without stirring for 14 h. Compound **2c** was isolated by column chromatography on Al_2O_3 and recrystallized from light petroleum (70/100). The yield was 0.19 g (27%), m.p. 127—130 °C.

1-(4´-Bromobiphenyl-4-yl)-1´-stearoylferrocene (2d). A mixture of compound **2a** (0.40 g, 1 mmol), stearoyl chloride (0.30 g, 1 mmol), and aluminum chloride (0.21 g, 1.6 mmol) in carbon disulfide (20 mL) was stirred for 2.5 h. The reaction mixture was worked up as described for **2b**. The oily product was chromatograped on Al_2O_3 using a 2 : 1 benzene—light petroleum mixture as the eluent. After removal of the solvent, the residue (0.28 g) was recrystallized from light petroleum. The yield of compound **2d** was 0.11 g (17%), m.p. 111—113 °C. Found (%): C, 70.32; H, 7.63; Br, 12.02. $C_{40}H_{51}BrFeO$. Calculated (%): C, 70.28; H, 7.52; Br, 11.69. ^{1}H NMR, δ: 0.88 (t, 3 H, Me); 1.26 (m, 28 H); 1.57 (m, 2 H, $\underline{CH_2}CH_2CO$); 2.38 (t, 2 H, CH_2CO); 4.37 (m, 4 H); 4.65 and 4.68 (both m, 2 H each); 7.44—7.57 (m, 8 H, C_6H_4—C_6H_4).

1-Acetyl-1´-(4´-cyanobiphenyl-4-yl)ferrocene (3b). Aluminum chloride (0.40 g, 3.0 mmol) was added to a solution of acetyl chloride (0.13 g, 1.7 mmol) in CH_2Cl_2 (7 mL). The reaction mixture was stirred for 35 min. Then a solution of compound **3a** (0.55 g, 1.5 mmol) in CH_2Cl_2 (20 mL) was added. The reaction mixture was stirred for 15 h and worked up as in the synthesis of **2b**. The crude product was twice chromatographed on Al_2O_3 using a 1 : 1 light petroleum—$CHCl_3$ mixture as the eluent. The solvent was distilled off and the residue was twice recrystallized from a CH_2Cl_2—hexane mixture. Compound **3b** was isolated in a yield of 0.14 g (22%) as dark-red crystals, m.p. 162—164 °C. Found (%): C, 74.25; H, 4.88; N, 3.38. $C_{25}H_{19}FeNO$. Calculated (%): C, 74.09; H, 4.72; N, 3.46. ^{1}H NMR, δ: 2.13 (s, 3 H, Me); 4.37, 4.39, 4.62, and 4.69 (all m, 2 H each); 7.50—7.56 and 7.70 (both m, 4 H each, C_6H_4).

1-(4´-Cyanobiphenyl-4-yl)-1´-octanoylferrocene (3c). A mixture of aluminum chloride (0.18 g, 1.4 mmol), dichloromethane (20 mL), and octanoyl chloride (0.17 mL, 0.16 g, 1 mmol) was stirred for 1.5 h. The resulting solution of the acylating reagent was added dropwise to a stirred solution of compound **3a** (0.36 g, 1 mmol) in CH_2Cl_2 (20 mL) for 2 h. The reaction mixture was stirred for 3 h and worked up as described for **2b**. Chromatography in benzene gave the starting compound **3a** in a yield of 0.10 g (28%) and then the acylation product. This was recrystallized from a mixture of light petroleum with a small amount of benzene. Compound **3c** was isolated in a yield of 0.05 g (10%) as red crystals, m.p. 129—131 °C. Found (%): C, 76.35; H, 6.34; N, 2.81. $C_{31}H_{31}FeNO$. Calculated (%): C, 76.08; H, 6.38; N, 2.86. ^{1}H NMR, δ: 0.84 (t, 3 H, Me, ^3J = 6.4 Hz); 1.22 (m, 8 H); 1.51 (m, 2 H, $\underline{CH_2}CH_2CO$); 2.38 (t, 2 H, CH_2CO, ^3J = 7.2 Hz); 4.36, 4.38, 4.63, and 4.68 (all m, 2 H each); 7.49—7.55 and 7.70 (both m, 4 H each, C_6H_4).

1-(4´-Cyanobiphenyl-4-yl)-1´-undecanoylferrocene (3d). *A.* Under the conditions of acylation of **3b**, compound **3a** (0.57 g, 1.6 mmol) was acylated with undecanoyl chloride (0.37 g, 1.8 mmol) in the presence of $AlCl_3$ (0.43 g, 3.2 mmol) and chromatographed on Al_2O_3. An admixture of the starting nitrile

Table 2. Crystallographic data and details of X-ray diffraction study for compounds **2a** and **3e**

Parameter	**2a**	**3e**
Molecular formula	$C_{22}H_{17}FeBr$	$C_{29}H_{27}FeNO$
Molecular weight	417.12	461.37
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P1$
T/K	293(2)	120(2)
λ/Å	0.71073	0.71073
Z	4	2
a/Å	11.014(2)	5.9327(10)
b/Å	7.6230(15)	12.379(2)
c/Å	20.781(4)	16.601(3)
α/deg	90	105.984(4)
β/deg	94.19(3)	98.529(4)
γ/deg	90	102.194(4)
V/Å^3	1740.1(6)	1117.6(3)
d_{calc}/g cm^{-3}	1.592	1.371
Absorption coefficient μ/mm^{-1}	3.162	0.697
F(000)	840	484
Scanning mode	θ/2θ	ω (0.3° step)
θ Scan range/deg	2—27	2—29
Number of measured reflections	7624	10300
Number of independent reflections	5538	9430
R_{int}	0.0233	0.0316
Absorption correction	ψ Scan	SADABS[11]
T_{min}/T_{max}	0.627/0.964	0.631/0.962
Number of parameters in refinement	433	577
GOOF	0.925	0.943
Number of reflections with $I \geq 2\sigma(I)$	3487	5180
Convergence of refinement based on reflections with $I \geq 2\sigma(I)$	R_1 = 0.0299	R_1 = 0.0578
Convergence of refinement based on all reflections	wR_2 = 0.0651	wR_2 = 0.1093
Flack parameter	0.099(9)	0.05(3)

3a was eluted with a 3 : 1 light petroleum—Et_2O mixture. Compound **3d** was eluted with a 2 : 1 light petroleum—Et_2O mixture and recrystallized first from a mixture of light petroleum (70/100) with a small amount of benzene and then from an acetone—hexane mixture. Compound **3d** was isolated in a yield of 0.29 g (35%) as red needle-like crystals, m.p. 120—122 °C. Found (%): C, 76.91; H, 6.94; N, 2.87. $C_{34}H_{37}FeNO$. Calculated (%): C, 76.83; H, 7.02; N, 2.63. ^1H NMR, δ: 0.86 (t, 3 H, CH_3, ^3J = 6 Hz); 1.21 (m, 14 H); 1.50 (m, 2 H, $\underline{CH_2}CH_2CO$); 2.38 (t, 2 H, CH_2CO, ^3J = 8 Hz); 4.36, 4.38, 4.63, and 4.68 (all m, 2 H each); 7.49—7.55 and 7.68—7.73 (both m, 4 H each, C_6H_4).

B. A mixture of $AlCl_3$ (0.40 g, 3.0 mmol), undecanoyl chloride (0.34 g, 1.7 mmol), and carbon disulfide (8 mL) was stirred for 20 min. Then a solution of nitrile **3a** (0.55 g, 1.5 mmol) in CS_2 (40 mL) was added. The reaction mixture was stirred for 4.5 h and quenched by pouring onto a mixture of ice and concentrated HCl as described for compound **2b**. Chromatography of the acylation product afforded the starting nitrile **3a** in a yield of 0.10 g (18%) and compound **3d**. The latter was recrystallized first from a mixture of light petroleum (70/100) with a small amount of benzene and then from an acetone—hexane mixture. The yield of compound **3d** was 0.13 g (16%), m.p. 120—122 °C.

1-(4´-Cyanobiphenyl-4-yl)-1´-((*S*)-3-methylpentanoyl)ferrocene (3e). (*S*)-3-Methylpentanoyl chloride (0.34 g, 2.5 mmol) was added to a suspension of aluminum chloride (0.60 g, 4.5 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for 1 h. Then a solution of compound **3a** (0.84 g, 2.3 mmol) in dichloromethane (30 mL) was added. The dark-cherry reaction mixture was stirred for 13 h. The oily product was twice chromatographed on Al_2O_3 using a 1 : 1 hexane—CH_2Cl_2 mixture as the eluent. The product thus obtained was twice recrystallized from a mixture of light petroleum (70/100) with a small amount of benzene. Compound **3e** was isolated in a yield of 0.25 g (27%) as red needle-like crystals, m.p. 88—90 °C. Found (%): C, 75.44; H, 6.18; N, 3.01. $C_{29}H_{27}FeNO$. Calculated (%): C, 75.50; H, 5.90; N, 3.04. ^1H NMR, δ: 0.84 (t, 3 H, Me, ^3J = 8 Hz); 0.87 (d, 3 H, Me, ^3J = 8 Hz); 1.17, 1.32, 1.91, 2.24, and 2.42 (all m, 1 H each); 4.36 and 4.38 (both m, 2 H each); 4.61 and 4.63 (both m, 1 H each); 4.68 (m, 2 H); 7.50—7.55 and 7.67—7.73 (both m, 4 H each).

Reaction of 4-ferrocenyl-4´-nitrobiphenyl with octanoyl chloride in the presence of $AlCl_3$. Octanoyl chloride (0.06 mL, 0.3 mmol) was added to a suspension of aluminum chloride (0.07 g, 0.5 mmol) in CS_2 (10 mL). The reaction mixture was stirred for 1 h. Then a solution of 4´-ferrocenyl-4-nitrobiphenyl (**4**) (0.13 g, 0.3 mmol) in CS_2 (25 mL) was added. The reaction mixture was stirred at 20 °C for 2 h, refluxed with stirring for 1 h, and then worked up as described for compound **2b**. Column chromatography on Al_2O_3 (benzene—light petroleum, 2 : 1) yielded 0.07 g (54%) of 4-ferrocenyl-4´-nitrobiphenyl (**4**).

X-ray diffraction study. Crystals of 1-(4´-cyanobiphenyl-4-yl)-1´-((*S*)-3-methylpentanoyl)ferrocene (**3e**) suitable for X-ray diffraction analysis were grown by gradual addition of hexane to a solution of **3e** in toluene. Crystals of 4-bromo-4´-ferrocenylbiphenyl (**2a**) were grown analogously from a benzene—hexane mixture. X-ray diffraction data for compounds **2a** and **3e** were collected on a four-circle automated Siemens P3/PC diffractometer and a SMART CCD 1000 diffractometer, respectively. The crystallographic data and details of X-ray diffraction study for compounds **2a** and **3e** are given in Table 2.

The structures of **2a** and **3e** were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters against F^2_{hkl}. The X-ray diffraction data for the crystals of compound **3e** were processed with the use of the SAINT program.[12] The final refinement was carried out by the full-matrix least-squares method with anisotropic thermal parameters. The coordinates of the hydrogen atoms were calculated geometrically and refined using the riding model.

All calculations were carried out using the SHELXTL program package[13] on an IBM PC.

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References

1. C. Imrie, P. Engelbrecht, C. Loubser, and C. W. McCleland, *Appl. Organomet. Chem.*, 2001, **15**, 1.
2. G. G. A. Balavoine, J. C. Daran, G. Iftime, P. G. Lacroix, E. Manoury, J. A. Delaire, I. Maltey-Fanton, K. Nakatani, and S. Di Bella, *Organometallics*, 1999, **18**, 21.
3. R. Deschenaux, M. Schweissguth, M. T. Vilches, A. M. Levelut, D. Hautot, G. J. Long, and D. Luneau, *Organometallics*, 1999, **18**, 5553.
4. C. Imrie, P. Engelbrecht, C. Loubser, C. W. McCleland, V. O. Nyamori, R. Bogardi, D. C. Levendis, N. Tolom, J. van Rooyen, and N. Williams, *J. Organomet. Chem.*, 2002, **645**, 65.
5. C. Imrie, C. Loubser, P. Engelbrecht, C. W. McCleland, and Y. Zheng, *J. Organomet. Chem.*, 2003, **665**, 48.
6. K. P. Reddy and T. L. Brown, *Liq. Cryst.*, 1992, **12**, 369.
7. D. A. Lemenovskii, M. V. Makarov, V. P. Dyadchenko, A. E. Bruce, M. R. M. Bruce, S. A. Larkin, B. B. Averkiev, Z. A. Starikova, and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 583 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 607].
8. A. N. Nesmeyanov, E. G. Perevalova, N. A. Simukova, T. V. Nikitina, and P. D. Reshetov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1961, 77 [*Bull. Acad. Sci. USSR, Div. Chem.* 1961 (Engl. Transl.))].
9. J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press Inc., New York, 2002.
10. F. H. Allen, O. Kennard, D. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.
11. G. M. Sheldrick, *SADABS*, *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen (Germany), 1996.
12. *SMART V5.051 and SAINT V5.00*, *Area Detector Control and Integration Software*, Bruker AXS Inc., Madison (WI-53719, USA), 1998.
13. G. M. Sheldrick, *SHELXTL-97*, *V5.10*, Bruker AXS Inc., Madison (WI-53719, USA), 1997.

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