Synthesis and liquid crystalline behavior of a series of ferrocene 1,1′-bis-azino-derivatives

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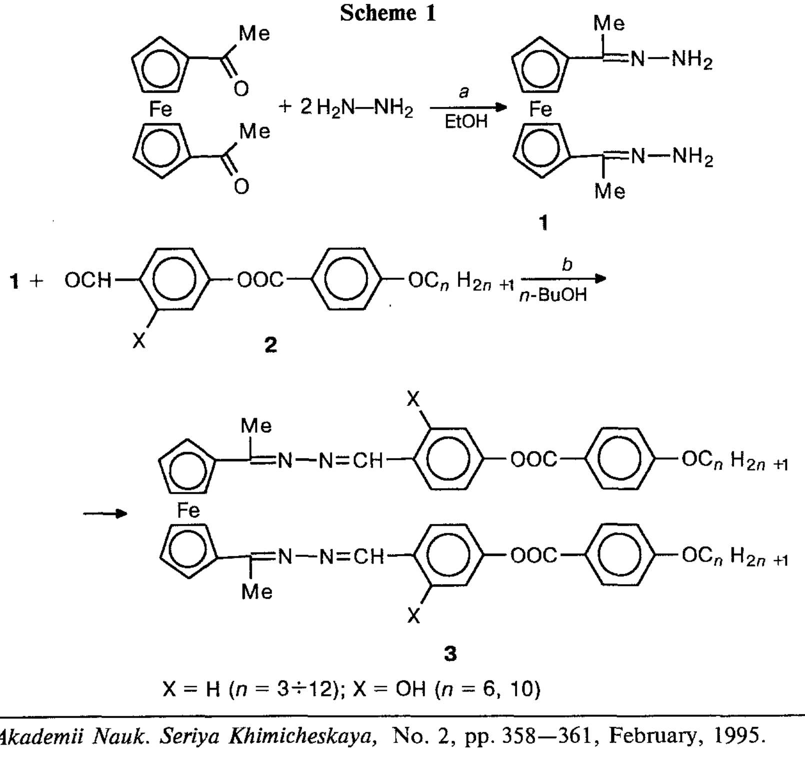
A series of liquid-crystalline ferrocene derivatives, Fe{C_5H_4—$C(CH_3)$=N—N=CH—$C_6H_3(X)$—OOC—C_6H_4—OC_nH_{2n+1}}$_2$ (X = H, OH; n = 3 to 12), were obtained by the condensation of 1,1′-bishydrazondiacetylferrocene with *p*-alkoxybenzoyloxybenzaldehides. According to DSC and polythermic microscopy, all of the compounds exhibit an enantiotropic nematic mesophase in the 150—230 °C temperature range. A polycrystalline transition precedes the nematic transition. The liquid crystalline properties of the obtained compounds were investigated with respect to the number of carbon atoms in the terminal alkyl chain and the terminal hydroxyl group. The composition and structure of the obtained compounds were determined by elemental analysis and IR and NMR spectroscopy.

Key words: liquid crystals, ferrocene, metallomesogenes.

Introducing a metal atom directly into the molecule of a liquid crystal gives rise to new physical properties,[1,2] which is the reason for the increasing interest in metallomesogenes. Up to now, metallocene-containing liquid crystals[3—10] have drawn less attention, although the synthesis and investigation of organometallic mesogenes has been of considerable interest. In a continuation of our investigations on the synthesis of ferrocene-containing mesogenes and the correlation between structural factors and the mesomorphic properties

Scheme 1



X = H (n = 3÷12); X = OH (n = 6, 10)

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Table 1. The elemental analysis data and the yields of compounds **3**

X	*n*	Found/Calculated (%)			Molecular formula	Yield (%)
		C	H	N		
H	3	69.22 69.39	5.73 5.59	6.65 6.74	$C_{48}H_{46}N_4O_6Fe$	83
"	4	69.84 69.92	5.77 5.88	6.15 6.52	$C_{50}H_{50}N_4O_6Fe$	85
"	5	70.23 70.41	6.04 6.15	6.17 6.32	$C_{52}H_{54}N_4O_6Fe$	80
"	6	70.76 70.88	6.27 6.40	6.03 6.12	$C_{54}H_{58}N_4O_6Fe$	72
"	7	71.49 71.32	6.67 6.64	5.97 5.94	$C_{56}H_{62}N_4O_6Fe$	81
"	8	71.58 71.73	6.85 6.86	5.83 5.77	$C_{58}H_{66}N_4O_6Fe$	77
"	9	71.79 72.12	7.03 7.07	5.73 5.61	$C_{60}H_{70}N_4O_6Fe$	89
"	10	72.28 72.49	7.17 7.28	5.71 5.45	$C_{62}H_{74}N_4O_6Fe$	73
"	11	72.69 72.83	7.45 7.46	5.46 5.31	$C_{64}H_{78}N_4O_6Fe$	77
"	12	72.98 73.17	7.54 7.64	5.12 5.17	$C_{66}H_{82}N_4O_6Fe$	86
OH	6	68.27 68.48	6.25 6.19	5.87 5.92	$C_{54}H_{58}N_4O_8Fe$	69
"	10	70.01 70.30	6.97 7.06	5.19 5.29	$C_{62}H_{74}N_4O_8Fe$	78

of these compounds,[8–10] we prepared a new series of compounds of this type, *viz.*, the 1,1′-bisazine ferrocene derivatives, according to Scheme 1.

Stage *a* occurs when a weak solution of diacetylferrocene is treated with a large excess of hydrazine. The condensation of dihydrazone (**1**) with substituted resorcyl (X = H) and salicyl (X = OH) aldehydes (**2**) resulted in mesogene ferrocene derivatives (**3**). The structures of compounds **3** were confirmed by elemental analysis (Table 1) and the IR and ^{1}H NMR spectra. The hydroxy derivatives (X = OH) are feasible complex formation reagents for the synthesis of heteronuclear mesogenes.[8,9] They are also useful for elucidation of the effect of the OH group on the mesomorphic properties of the ferrocene derivatives of this series.

The mesomorphic properties and the mesophase types were studied by polarization polythermic microscopy and differential scanning calorimetry (DSC). All of the compounds of the obtained homologous series possess an enantiotropic nematic phase (Table 2), which was identified by the characteristic marble and schlieren textures. Apparently, in compounds **3** with X = H, the polycrystalline transition $K_1 \rightarrow K_2$, which is absent in the hydroxy-substituted analogs, takes place before the transition into the nematic state. The character of the dependence of the transition temperature on the hydrocarbon chain length (Fig. 1) together with the shape of the DSC thermogram are in agreement with this suggestion and rule out the assignment of the $K_1 \rightarrow K_2$ peak to the melting of impurities. The shape of the DSC peaks or their absence are also indicative of the purity of the compounds obtained and the absence of the monosubstituted products.

The dependence of the phase transfer temperature on the number of carbon atoms in the terminal chain of

Table 2. The temperatures of the phase transitions (°C) of compounds **3**

X	*n*	$K_1 \rightarrow K_2$	$K_2 \rightarrow N$	$N \rightarrow i$	Interval of mesophase, ΔT/°C
H	3	173	208	236	28
"	4	163	201	230	29
"	5	160	188	210	22
"	6	149	171	217	46
"	7	140	167	201	34
"	8	130	164	206	42
"	9	126	156	183	27
"	10	120	161	193	32
"	11	114	158	185	27
"	12	112	152	180	28
OH	6	—	212	225	13
"	10	—	187	199	12

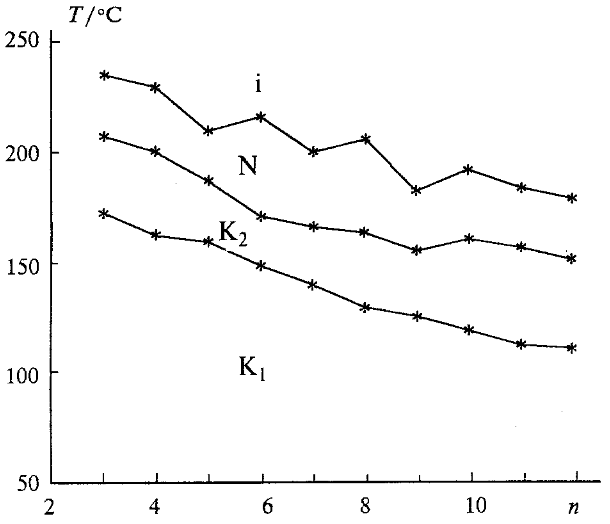
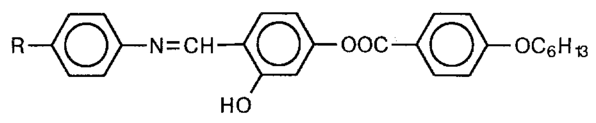


Fig. 1. The dependence of the phase transition temperatures on the number of carbon atoms of compounds **3**.

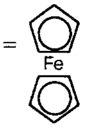
the obtained mesogene ferrocene derivatives (see Fig. 1) is typical of homologous series of liquid crystals[11] (alternation of the clarification temperatures, the tendency of all of the phase transfer temperatures to decrease when the length of the terminal chain increases).

The introduction of a side chain OH group into compounds **3** (X = OH) results in a significant increase in the temperatures of the K → N and N → i transitions (compare entries 4 and 11, 8 and 12 in Table 2). In this case, the low temperature limit of the mesophase increases to a greater extent than the high temperature limit, which leads to narrowing of the mesophase temperature range. This behavior of the phase transition temperatures can be explained by the formation of a chelate cycle with an intramolecular hydrogen bond (ν(OH) ~2800 cm^{-1}). First, this leads to greater coplanarity of the benzene rings[12] and, therefore, to a higher density of the crystal packing (the temperature of the K → N transition increases accordingly). Second, the conjugation of the π-system increases, which causes an increase in the anisotropy of the polarisation of the molecule, which determines the thermal stability of the mesophase characterized by the N → i transition temperature. In ferrocene-containing Shiff bases synthesized earlier by us,[9] the thermal stability of the mesophase is also increased when side OH groups are introduced. However, at the same time, the K → N temperature decreases, contrary to the data reported in Ref. 12 and to that for the azine derivatives studied in the present work. This can be associated with the characteristic features of the crystal packing.

To decide if the chelate cycle with the hydrogen bond is retained during the transitions to the nematic and isotropic phases, we studied the IR spectra of the ferrocene-containing Shiff's base with the hydroxyl group and its analog with the methoxy group instead of the ferrocene group of the general structure **4**:



4

R = CH_3O (K 109 N 249 i); R =  (K 170 N 203 i)

The positions of the valent vibration bands of the O—H (~2800 cm^{-1}) and C=N (1620 cm^{-1}) groups do not change during the transitions from the crystal to the nematic and isotropic states, which indicates the retention of the intramolecular hydrogen bond during phase transitions and the validity of our conclusions.

Experimental

The temperature of the phase transitions and the mesophase types were determined on a polarizing microscope equipped with a Boetius thermotable. IR spectra were recorded on a Specord 75IR spectrophotometer in KBr cuvettes; the measurements of the temperature dependences were carried out in a melt between KBr glasses. ^1H NMR spectra were obtained on a Varian HA-100 spectrometer. The detailed description of the synthesis is given for one of the compounds that differs with respect to the terminal hydrocarbon radical.

1,1′-Bis(hydrazonato)ferrocene (1). A solution of diacetylferrocene (13.45 g, 0.05 mmol) in 100 mL of EtOH was added dropwise over a period of 6 h to hydrazine (32 g, 1 mol, 10-fold excess) with stirring at 50 °C. After the addition was completed, the mixture was heated for an additional 1 h. Then part of the solvent was removed in the vacuum of an aspirator. After cooling the mixture, the precipitated brownish-red crystals were recrystallized from EtOH to give 5.3 g (39 %) of a product with m.p. 163 °C. IR (CCl_4), ν/cm^{-1}: 3360, 3200 (N—H), 3115 (C—H_{Fc}), 3045 (CH_3), 1590 (C=N), 465, 505 (Fc). ^1H NMR ($CDCl_3$), δ: 1.92 (s, 3 H, Me); 4.10, 4.46 (m, 4 H, Fc); 5.04 (m, 2 H, NH_2).

1,1′-Bis[4-(4′-dodecyloxybenzoyloxy)benzylideneazinaceto]ferrocene (3). Compound **1** (0.06 g, 0.2 mmol) was boiled in 10 mL of *n*-BuOH with 4-dodecyloxybenzoyloxyrezorcyl aldehyde (0.17 g, 0.4 mmol). After cooling, an orange residue precipitated, which was recrystallized from *n*-BuOH. IR (CCl_4), ν/cm^{-1}: 3110 (C—H_{Ar}), 1720 (C=O), 1600 (C=N), 480, 535 (Fc). ^1H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, CH_2Me); 1.28 (m, 16 H, CH_2CH_2); 1.48 (m, 2 H, $OCH_2CH_2CH_2$); 1.82 (m, 2 H, OCH_2CH_2); 2.39 (s, 3 H, FcCMe); 4.02 (t, 2 H, OCH_2); 4.45 (s, 2 H, Fc); 4.83 (s, 2 H, Fc); 6.91 (d, 2 H, Ph); 7.22 (d, 2 H, Ph); 7.79 (d, 2 H, Ph); 8.08 (d, 2 H, Ph); 8.39 (s, 1 H, CH=N).

Elemental analysis data and the yields of compounds **3** are given in Table 1.

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