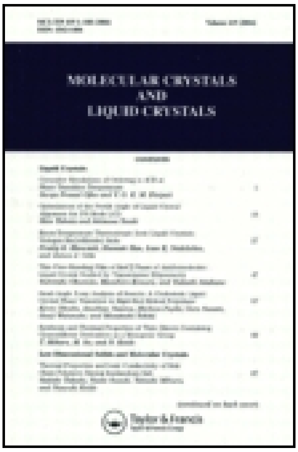

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Ferrocene Mesogens: Polymorphism, Molecular Properties and Temperature Stability

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FERROCENE MESOGENS: POLYMORPHISM, MOLECULAR PROPERTIES AND TEMPERATURE STABILITY

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Abstract The Mossbauer spectroscopy, polarization microscopy, differential scanning calorimetry and X-ray photoemission spectroscopy were used to study of structure peculiarities, dynamical and orientational properties and thermal stability of ferrocene mesogens with general formula $Fe(C_5H_4C(CH_3)=N-N=CHC_6H_4COOC_6H_4OC_nH_{2n+1})_2$ where n = 8, 10, 12. The obtained data were compared with those for nonmesomorphic derivatives of ferrocene and organic liquid crystals.

INTRODUCTION

Metallomesogens (MM) - metalloorganic compounds and metal complexes of organic ligands - combine the variety of metal-based coordination chemistry with unusual properties exhibited by liquid crystals (LC).

The presence of metal atom opens many exiting possibilities comparatively to the corresponding organic LC's and hence new properties are then accessible[1,2]. For instance, the incorporation of d-metals (such as Fe) brings with it features such as para- (or ferro-) magnetism. For this reason the investigations such properties of MM's, which determine their differences from corresponding organic LC's are necessary.

In this paper we report the results of complex study of structure peculiarities, electron and coordination structure, dynamical and orientational properties and thermal destruction mechanism of ferrocene mesogens with general formula $Fe(C_5H_4C(CH_3)=N-N=CHC_6H_4COOC_6H_4OC_nH_{2n+1})_2$ where n = 8, 10, 12 (abbreviated as FLCn). The compounds are a Shiff bases of ferrocene and exhibit nematic phase above 140 °C.

In the case of FLCn's it is possibly to use all possibilities of Mossbauer spectroscopy. This technique provides for direct insight into the chemistry of LC molecule as well as its dynamics[3] and naturally becomes one of the main instrument for such study.

The other actual problem for MM - to receive and fix the glassy mesophases of these compounds at room temperature (usually the transition "solid-mesophase" observed at essentially more high temperatures). Early we had showed such possibility for organic LC[4]. The extension of the LC-phases to low temperature regime is very important as for better understanding of this state as for possible practical applications of MM.

EXPERIMENTAL

Phase transformation behaviour of these compounds was obtained with a polarizing microscope equipped with a heating plate. Differential scanning calorimetry (DSC) measurements were obtained with a Du Pont Instrument calorimeter. Indium was used to calibrate the temperature scale and the enthalpy values. X-ray photoemission spectroscopy was also used as a complementary method for study the thermal destruction mechanism of these compounds.

The Mossbauer spectra (MS) were taken on standard constant acceleration spectrometer with a source of ^{57}Co(Cr) in the temperature range of 90 - 300 K. MS were fit with Lorenzian line-shapes using standard programs. The asymmetry of quadrupole splitting lines (A), recoil free fraction (f'), quadrupole splitting (QS), and isomer shift (IS) were all obtained from the computer fits of the data.

RESULTS AND DISCUSSION

Polymorphism

For study of polymorphism of ferrocene mesogens the polarization microscopy, DSC and Mossbauer spectroscopy were used.

It was shown that the formation of one or another metastable mesophase by a given FLCn species is essentially dependent on the temperature history of the sample. On Fig.1 calorimetry curves for FLC8 cooled from solid phase (upper curve) and nematic phase (lower curve) to liquid nitrogen temperature are presented.

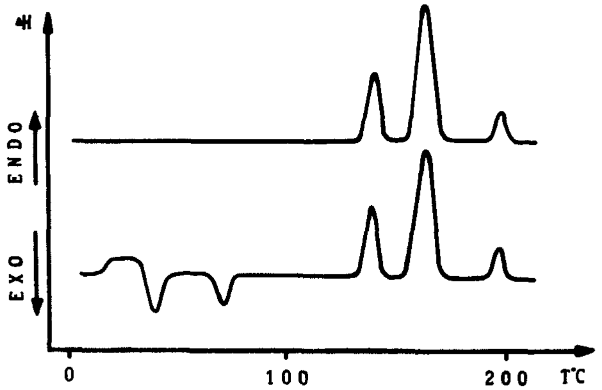

FIGURE 1 Calorimetry curves for FLC8.

The scheme of phase transitions depending from thermal history proposed for FLC8 from microscopical, calorimetry and MS investigations is given on Fig.2.

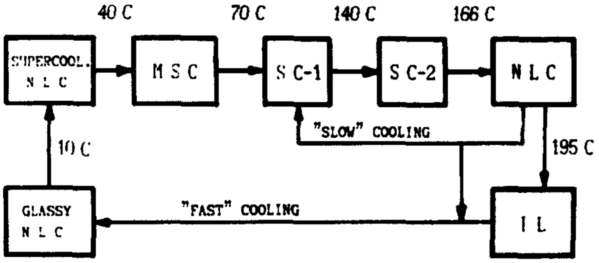

FIGURE 2 The scheme of phase transitions for FLC8.

It was shown that such behaviour is common for all FLCn's under investigation. All the compounds were shown to possess solid state polymorphism with one metastable and, at least, two stable solid phases within the range from an ambient temperature to an nematic LC-phase melting temperature. For all these compounds the glassy nematic phase arises with a glass-transition point close to the ambient temperature.

Mossbauer investigations

The Mossbauer spectra consisted of quadrupole doublets of Lorenzian lines with the following Mossbauer parameters: IS = 0.80±0.02 mm/s, QS = 2.30±0.02 mm/s (at 95K). The values are similar to those for the ferrocene and its derivatives[5]. The analysis of temperature dependence of the Mossbauer effect probability f' were made for ferrocene, its nonmesomorphic derivatives and FLCn's.

FLCn's as other metalloorganic compounds may be regarded as molecular crystals. For this case $f' = f'_M f'_L$[6], were f'_M and f'_L are , respectively, the "molecular" and the "lattice" contribution to f', i.e. probabilities of the fact that absorption of gamma-quanta by the system would excite neither intramolecular vibrations (Fe atom vibrations around the center of gravity of the FLCn molecule) nor intermolecular vibrations (vibrations of FLCn molecule as a whole).

A calculation based on vibration spectra shown that for ferrocene and its derivatives the molecular contribution f'_M is weakly dependent on temperature and $f' = 0.8 \cdot f'_L$[7]. Therefore the $f'(T)$ dependence is determined mainly by $f'_L(T)$ characterizing the dynamical properties of the molecules of the compounds studied, as mentioned above.

The "lattice" contribution to f' in the case of molecular crystals may be adequately described by Debye's model of solids. Therefore, using the high-temperature approximation of f'_L:

$$\ln f'_L = - 6RT / k(\Theta^*_D)^2 \qquad (1)$$

where Θ^*_D - the effective Debye temperature and taking into account the correlation

$$\ln f'_L = - \langle X^2_\gamma \rangle / \lambda\!\!\!^-{}^2 \qquad (2)$$

where $\lambda\!\!\!^-$ is reduced wave length of the gamma-quantum and

$\langle X_\gamma^2\rangle$ - the mean square amplitude of vibrations of molecule in the direction of gamma-quanta propagation, it is possible to estimate Θ_D^* and $\langle X_\gamma^2\rangle$ for compounds studied from experimental dependencies of ln $f'(T)$.

The experimental data $f'(170K)/f'(77K)$ and the values of $\langle X_\gamma^2\rangle$ estimated from the equation (2) for ferrocene, its nonmesomorphic derivatives and FLCn compounds are given in the Table I.

A greater temperature dependence f' for FLCn's, as compare to ferrocene and diacetylferrocene (DAF) reflects the differences in dynamical properties of these compounds. These differences apparently arise from the connection of the long-chain mesogenic substitutes which results to the most "loose" molecular packing because of steric hindrances. Such "loose" molecular packing weaken intermolecular bonds in FLCn's and results to increase of vibration amplitude of molecules $\langle X_\gamma^2\rangle$.

TABLE I Temperature dependencies of f' and $\langle X^2\rangle$ values for FLCn's and nonmesomorphic compounds.

Compound	Phase	$\frac{f'(170K)}{f'(77K)}$	$\langle X^2\rangle\cdot10^{18}sm^2$	
			77K	170K
DAF*	Solid	0.72	0.5	1.1
F*	Solid	0.60	0.8	1.8
FLC8	Solid	0.46	1.2±0.1	2.7±0.2
	Glassy NLC	0.32	1.9±0.2	4.1±0.3
FLC10	Solid	0.50	1.1±0.1	2.4±0.2
	Glassy NLC	0.43	1.3±0.2	3.0±0.3
FLC12	Solid	0.35	1.6±0.1	3.5±0.2
	Glassy NLC	0.32	1.7±0.2	3.9±0.3

* - data were taken from V.Ya.Rochev et al.[8]

It can see from the Table I the $\langle X_\gamma^2\rangle$ values for glassy LC phase lower than those for solid phase of FLCn compounds. From these data it is evidently that the dynamical properties of the FLCn's lattice in solid phase and glassy LC phase are really different.

In our investigations we observed the deviation of ln $f'(T)$ dependence from linear behaviour near 250K even in the crystal phase of FLCn's. Clearly this deviation must be associated with excitation of additional degrees of freedoms corresponding to phase or relaxation transitions. It is logical to propose that such peculiarity for FLCn's associated with the "defreezing" of mobility of its hydrocarbon chains above 250K. Our preliminary solid-state PMR experiments also fixed appearance of new movement form at this temperature.

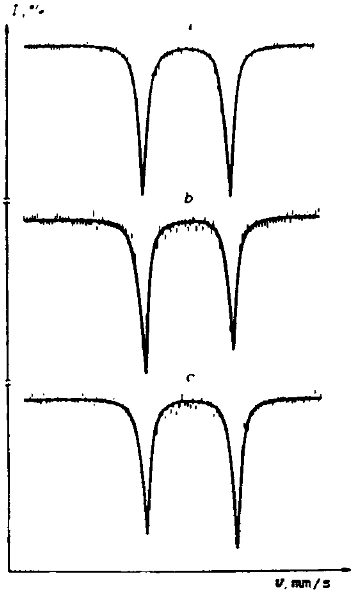

FIGURE 3 Mossbauer spectra of FLC10 "fast" cooled from nematic phase in the absence of a magnetic field (a), in the magnetic field directed parallel (b) and perpendicular (c) to a gamma-quanta beam.

The FLCn molecules were aligned in nematic phase by the external magnetic field of 6.7 kG. Figure 3 presents the Mossbauer spectra of FLC10 "fast" cooled from the NLC phase to the temperature of liquid nitrogen in the absence of a magnetic field (a) as well as in the magnetic field directed

parallel (b) and perpendicular (c) to a gamma-quanta beam. Similar data were obtained for other compounds under study. As one can see from Fig.3 , the orientation in a magnetic field results in the appearance of QS line asymmetry A, indicating alignment of FLCn molecules in NLC phase. From the character of angular dependence of $A(\theta)$, where θ is the angle between the magnetic field direction and that of the gamma-quanta beam, we concluded that the sign of the principal component V_{zz} of the electric field gradient tensor is positive for FLCn's as well as for ferrocene.
From the analysis of angular dependencies of $A(\theta)$ and $f'(\theta)$ according to D.L.Uhrich[9] we obtain the additional parameters, characterizing dynamical properties of FLCn molecules in the ordered glassy NLC phases: the orientational order parameter S, intramolecular E_M and lattice E_L contributions to the nuclear vibrational anisotropy. Table II compares these data with those for some other LC-systems.

TABLE II Parameters obtained from Mossbauer spectroscopy of LC compounds oriented by a magnetic field.

LC compound	S	E_M	E_L
FLC8	0.27±0.05	0.11±0.04	-0.04±0.05
FLC10	0.21±0.08	0.04±0.04	-0.07±0.05
N8+FLC10*	0.36±0.05	-0.02±0.04	-0.10±0.05
BBOA+FLC10**	0.67±0.08	0.13±0.04	-0.12±0.05

* - data were taken from V.G.Bekeshev et al.[10]
** - data were taken from V.G.Bekeshev et al.[11]

It follows from the Table II that order parameter S = 0.2-0.3 for individual FLCn's is essentially increases under introduction their into nematic (N8) and especially smectic (BBOA) LC-matrix. This effect arise from the additional orienting influence exerted by the LC-matrix and shows that FLCn's may be used as a good molecular labels under investigations of the organic LC by Mossbauer spectroscopy.

The small values of E_M imply that intramolecular vibrations are nearly isotropic, which is typical for disubstituted derivatives of ferrocene[9]. The values of E_L are in good agreement with available data for other LC systems. The negative sign at E_L means that molecular motion parallel to the orienting field possesses less freedom than when it is normal to the magnetic field in the glassy LC phase.

Thermal stability

The problem of thermal stability of MM is very important under study their dynamical and structural properties. In particular, under x-ray study of the structure of LC phase some of the ferrocene mesogens authors [12] had the experience difficulties caused by thermal destruction of studying compounds in LC phase. The FLCn's studied in our experiments were stable in the whole temperature range. However, it has been found that under multiple heating in air to the temperature corresponding isotropic phase give rise to destruction of FLCn compounds. In order to understand the mechanism of thermal destruction we obtain Mossbauer and X-ray photoemission spectra for initial compounds and for intermediate and final products of FLC10 destruction. From the analysis of these data we conclude that under multiple heating in air FLCn's results in broking of Fe-C bonds and arising of active forms of Fe^{2+} which turn into Fe^{3+} with forming of high disperse Fe oxides.

CONCLUSIONS

Mossbauer (Fe^{57}) spectroscopy, calorimetry and X-ray photoemission spectroscopy were used for study of molecular structure, dynamical properties, solid phase polymorphism and thermodestruction mechanism of nematic ferrocene mesogens. It was shown that all these compounds show the solid state polymorphism with one metastable and, at least, two stable solid phases. The scheme of phase transitions depending from thermal history was proposed for FLC8.

The heating of FLCn's at the temperature of isotropic phase results in broking of Fe-C bonds and arising of Fe^{3+} ions as high disperse oxides.

According to Mossbauer data the intermolecular bonds in FLCn's are essentially weaker in comparison with ferrocene and its nonmesomorphic derivatives.

The FLCn molecules are aligned by external magnetic field with the order parameter S = 0.2-0.3 for individual compounds, S = 0.36 for their solutions in nematic solvent and S = 0.67 for their solutions in smectic-B solvent. It shows that the FLCn's may be used as a good molecular labels for study of the organic LC's by Mossbauer spectroscopy.

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