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New Nematogenic β-Diketones for Synthesis of Lanthanidomesogens

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Abstract—A series of new β-diketones containing in their structure cyclohexane and benzene ring was obtained. The effect of the terminal substituents in the molecules of β-diketones on their liquid crystal and optical properties was studied. The absorption spectra of all β-diketones practically do not overlap with the emission spectrum of polymer PFO but have good overlapping with that of PVC. The obtained compounds are promising ligands for synthesis of liquid crystal adducts of lanthanide β-diketonates with the Lewis bases, polyfunctional luminescent materials.

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The problem of preparation of liquid crystals (LC) oriented by weak magnetic fields has been intensively discussed in the last decades [1, 2]. The main advantage of the use of magnetic field to manipulation of LC is the possibility of their orientation in any direction and stability of the cell caused by the absence of electrochemical reactions. In a number of works such liquid crystals were shown to possess large anisotropy of magnetic susceptibility. To achieve this into the structure of LC ions of Cu(II), Ni(II), Fe(III), and lanthanides(III) were introduced. The latter turned out to be the most effective due to the known high anisotropy of magnetic susceptibility of ions Dy(III), Tb(III), Ho(III), Eu(III) and Er(III), exceeding that of conventional LC by 2–3 orders of magnitude. At the same time, complexes of lanthanides with organic ligands have a high luminescence quantum yield caused by electron transitions between the 4*f* levels, and a narrow emission band that provide wide possibilities for their application in optoelectronics [3–6].

The most important problem for practical use is the preparation of defect-free optical medium with the molecules of the lanthanide complexes oriented along one axis. Such a uniform medium [7] must provide maximum efficiency of luminescence. In this case the regulation of the polarization degree, including that by the use of magnetic fields, opens new possibilities for the use of these media for wide range of optoelectronic devices. However, almost all lanthanide complexes LCs obtained so far, are smectics whose orientation is hindered by their high viscosity. In this sense must obviously be promising LC compounds of lanthanides having nematic mesophase, which is known to be the least viscous of all types of mesophases and is capable of being oriented by weak magnetic fields [8, 9].

In the lanthanide complexes, the excitation energy transfer onto the emitting ion (the antenna effect) is provided by the organic ligands coordinated to the lanthanide ion (for example, β-diketones, Lewis bases) [10]. Nowadays, a large number of β-diketones is already examined, which are LC materials or may impart LC properties to complexes on their basis. Earlier, the first samples of thermostable nematic adducts of the lanthanide β-diketonates with the Lewis bases have been obtained in our group [11], which showed regulated polarized luminescence. One of possible ways of application of these complexes can be their use as components of luminescent composite materials (emitters) on the basis of LC conducting polymers. However, for the earlier obtained nematic

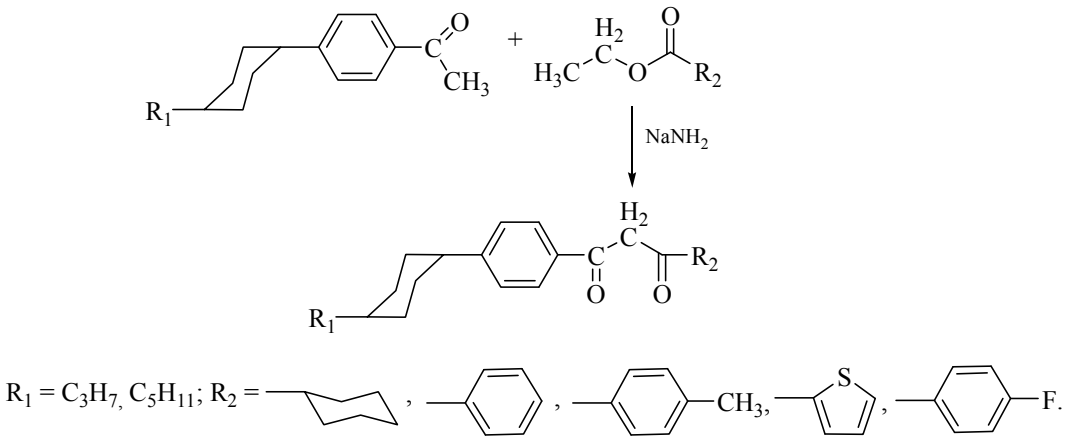


Fig. 1. Scheme of synthesis of β-diketonates.

adducts of lanthanides it was restricted by weak overlapping of the emission spectra of commercial conducting polymers used in these devices, and the absorption spectra of the complexes. The absorption spectra of the lanthanide adducts directly depends on the optical characteristics of the ligands (β-diketones). That is why the preparation of β-diketones with absorption in a wide range of wavelengths and having the structure that would supply complexes with nematic properties is an important problem. This would give a possibility to choose the components in the composite (polymers, complexes) to provide effective energy transfer and maximum luminescence yield.

In the present work a series of new β-diketones was prepared (Fig. 1) having in their structure cyclohexane and benzene rings. As the second terminal substituent different cyclic functional groups were used.

All β-diketones have been prepared by the method of Adams and Hauser [12] (Fig. 1). The composition and the structure of the products were proved by NMR spectroscopy, mass spectrometry, and elemental analysis.

The identification of liquid crystal properties was performed using the data of polarization optical microscopy (POM) (the types of mesophases and the temperatures of the phase transition were established from the textures) and differential scanning calorimetry (DSC) (variation of enthalpy and of the temperatures of phase transition). The textures of the nematic phase visible in polarization microscope are shown in Fig. 2. The temperatures of the phase transitions found by the POM method were then compared with the data of DSC (see the table). As evident from the table, the results of the two methods coincide.

The DSC curve (Fig. 3) is given for nematic β-diketone **IV** (see the table) possessing enantiotropic mesomorphism. On the curve two peaks are clearly seen corresponding to transitions Cr–N (94°C) and N–I (109°C) upon heating. Upon cooling, the effect of overcooling is observed with crystallization at 65°C.

Analysis of the obtained data shows that LC properties are manifested in β-diketones having in their structure substituent R_2 containing the benzene ring. The elongation of the molecule by the longer alkyl chain in R_1 results in the appearance of the enantiotropic mesomorphism (compound **II** in the table).

In order to investigate the possibility of the use of the lanthanide compounds prepared on the basis of β-diketones in luminescent composite materials, we have measured the absorption spectra of β-diketones in solution (Fig. 5) and compared them with the emission

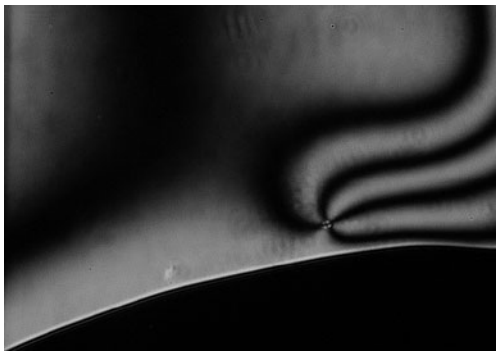
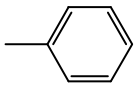
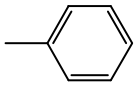
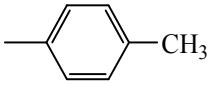
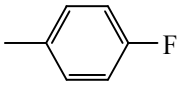
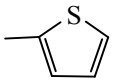


Fig. 2. Schliren texture of the nematic phase of 1-phenyl-3-[4-(4-propylcyclohexyl)phenyl]propandione at T = 100°C, 96-fold magnification.

Thermodynamic parameters of phase transition

Comp. no.	R_1	R_2	Phase transition	Phase transition temperatures, °C	ΔT, °C	Phase transition enthalpies, kJ mol^{-1}
I	C_3H_7		Cr → I	103		–
			I → N[a]	93		
II	C_5H_{11}		Cr → N	61	32	9.45
			N → I	93		11.45
III	C_3H_7		Cr → I	115		23.55
			I → N[a]	103		–
IV	C_3H_7		Cr → N	94	15	–
			N → I	109		35.34
V	C_3H_7		Cr → I	110		25.67
VI	C_5H_{11}		Cr → I	104		27.74

[a] Monotropic mesophases.

spectra of the known commercial conducting polymers (Fig. 4), PVC [poly(*N*-vinylcarbazole)] and PFO [poly-(9,9-dioctylfluorene)] used in optoelectronic devices. The absorption spectra of all β-diketones practically do not overlap with the emission spectrum of polymer PFO but have good overlapping with that of PVC. Maximum overlapping of the spectra was observed for the β-diketone having the thiophene ring (compound **VI** in the table). Also, rather good overlapping of the spectra was observed for β-diketones with substituents having the benzene rings (compounds **I–IV** in the table).

Therefore, new β-diketones, which are promising ligands for preparation of liquid crystal lanthanide complexes, were synthesized and their LC properties characterized. In the obtained series, depending on the type of the substituent in the β-diketone, the maxima of the absorption spectra vary in the wavelength range from 330 to 370 nm making it possible to increase the degree of overlapping of the absorption spectra of the lanthanide complexes with the emission spectra of conducting polymers thus expanding the opportunities for the use of the lanthanide compounds on the basis of the obtained ligands in luminescent film composite materials.

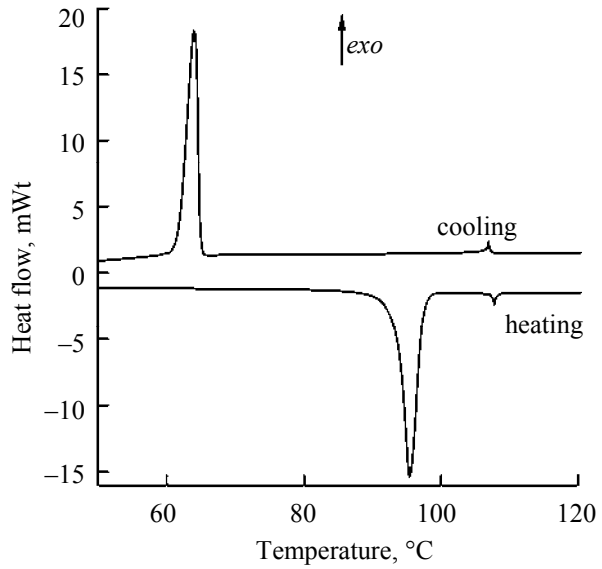


Fig. 3. DSC curve for β-diketone **IV**.

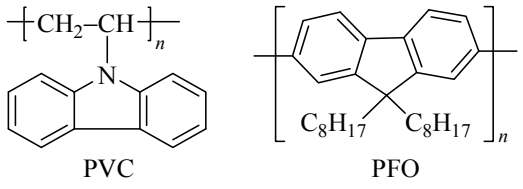


Fig. 4. Structures of polymers PVC and PFO.

EXPERIMENTAL

Textures and the phase transition temperatures were determined on a polarization microscope Boetius equipped with the temperature unit and on a differential scanning calorimeter Mettler-Toledo DSC 821. The accuracy of temperature measurement ±0.1°C. ^{1}H NMR spectra were registered on a Bruker Avance 300 spectrometer (300 MHz) in $CDCl_3$.

Synthesis of β-diketones. To the solution of ketone (0.05 mol) in dry ether (100 ml) cooled to 0°C the suspension of sodium amide (0.1 mol) in toluene (50%) was added. After stirring of the suspension obtained for 20 min, 0.1 mol of ester was added dropwise. The obtained mixture was refluxed for 6 h. The colorless solution turned brown. Then, to the reaction mixture 20 ml of water was added, and the mixture was neutralized with HCl solution (2 M) to pH = 7. The ether layer was several times washed with water, solvent was removed, and the residue was dried over P_2O_5. The obtained product was twice crystallized from ethanol.

1-Phenyl-3-[4-(4-propylcyclohexyl)phenyl]propane-1,3-dione. Yield 53.5 %. *m/z*: 347 (M^+). ^{1}H NMR spectrum, δ, ppm: 0.91–0.96 m (3H, CH_3), 1.06–1.56 m (9H, CH_2), 1.88–1.95 m (4H, C_6H_{10}), 2.51–2.60 m (1H, C*H*C_6H_4), 4.62 s (0.1H, keto = CH_2), 6.86 s (0.9H, enol = CH), 7.33 d (1H, C_6H_5, J = 8.1 Hz), 7.47–7.59 m (3H, OCC_6H_5), 7.92 d (2H, C_6H_5, J = 8.4 Hz), 7.99 d (2H, C_6H_5, J = 9.0 Hz), 16.95 s (0.8H, enol OH; keto:enol = 1:9). Found, %: C 82.64; H 8.15. $C_{24}H_{28}O_2$. Calculated, %: C 82.72; H 8.10.

1-Phenyl-3-[4-(4-pentylcyclohexyl)phenyl]propane-1,3-dione. Yield 42.8%. *m/z*: 375 (M^+). ^{1}H NMR spectrum, δ, ppm: 0.89–0.94 m (3H, CH_3), 1.01–1.56 m (13H, CH_2), 1.88–1.95 m (4H, C_6H_{10}), 2.51–2.60 m (1H, C*H*C_6H_4), 4.62 s (0.1H, keto = CH_2), 6.85 s (0.9H, enol = CH), 7.32 d (1H, C_6H_5, J = 8.4 Hz), 7.47–7.59 m (3H, OCC_6H_5), 7.92 d (2H, C_6H_5, J = 8.4 Hz), 7.98–8.00 m (2H, C_6H_5), 16.95 s (0.8H, enol OH; keto:enol = 1:9). Found, %: C 82.97; H 8.62. $C_{26}H_{32}O_2$. Calculated, %: C 82.94; H 8.57.

1-*p*-Tolyl-3-[4-(4-propylcyclohexyl)phenyl]propane-1,3-dione. Yield 46.5%. *m/z*: 361 (M^+). ^{1}H NMR spectrum, δ, ppm: 0.92–0.97 m (3H, CH_3), 1.03–1.56 m (9H, CH_2), 1.89–1.95 m (4H, C_6H_{10}), 2.44 s (3H, CH_3), 2.51–2.60 m (1H, C*H*C_6H_4), 4.58 s (0.1H, keto = CH_2), 7.28–7.35 m (4H, C_6H_5), 7.9–7.94 m (4H, C_6H_5), 16.95 s (0.9H, enol OH; keto:enol = 1:9).

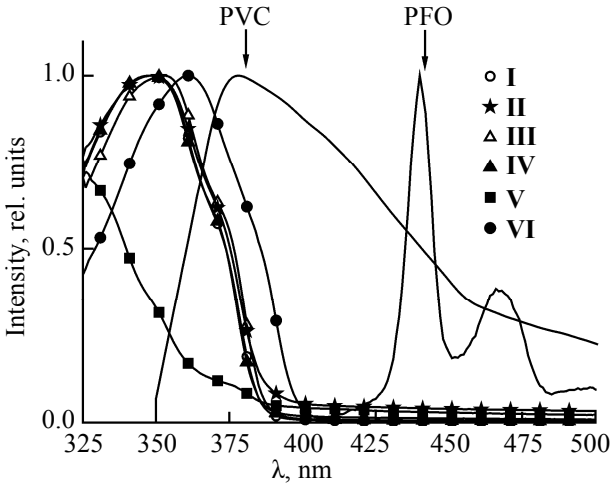


Fig. 5. Absorption spectra of β-diketones in solution and emission spectra of polymers PVC and PFO. λ_{max}, nm = 348 (**I, II, IV**), 353 (**III**), 326 (**V**), and 361 (**VI**).

Found, %: C 82.81; H 8.36. $C_{25}H_{30}O_2$. Calculated, %: C 82.83; H 8.34.

1-(4-Fluorophenyl)-3-[4-(4-propylcyclohexyl)-phenyl]propane-1,3-dione. Yield 42.7%. *m/z*: 366 (M^+). $C_{24}H_{27}FO_2$. ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, CH_3, J = 7.2 Hz), 1.01–1.56 m (9H, CH_2), 1.87–1.93 m (4H, CH_2), 2.50–2.59 t (1H, C*H*C_6H_4), 4.59 s (0.1H, keto = CH_2), 6.79 s (0.9H, enol = CH), 7.14–7.19 m (2H, FC_6H_4), 7.31–7.34 m (2H, FC_6H_4), 7.90 d (2H, J = 8.4 Hz), 7.99-8.03 m (2H, OCC_6H_4), 16.95 s (0.9H, enol OH; keto:enol = 1:9).

1-Cyclohexyl-3-[4-(4-propylcyclohexyl)phenyl]-propane-1,3-dione. Yield 40.3 %. *m/z*: 354 (M^+). ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, CH_3, J = 7.2 Hz), 1.01–1.54 m (15H, CH_2), 1.70–1.96 m (8H, CH_2), 2.27–2.37 m (1H, COC_6H_{11}), 2.48–2.59 t (1H, C*H*C_6H_4) 4.11 s (0.1H, keto = CH_2), 6.16 s (0.9H, enol = CH), 7.27–7.30 m (2H, C_6H_4), 7.80–7.83 m (2H, C_6H_4), 16.36 s (0.9H, enol OH; keto:enol = 1:9). Found, %: C 81.24; H 9.66. $C_{24}H_{34}O_2$. Calculated, %: C 81.31; H, 9.67.

1-Thienyl-3-[4-(4-pentylcyclohexyl)phenyl]propane-1,3-dione. Yield 44.2%. *m/z*: 382 (M^+). ^{1}H NMR spectrum, δ, ppm: 0.89–0.94 m (3H, CH_3), 1.01–1.56 m (13H, CH_2), 1.88–1.95 m (4H, C_6H_{10}), 2.51–2.60 m (1H, C*H*C_6H_6), 4.53 s (0.1H, keto = CH_2), 7.15–7.18 m (1H, C_4H_3S), 7.27–7.34 m (2H, C_6H_4), 7.61–7.63 m (1H, C_4H_3S), 7.80–7.82 m (1H, C_4H_3S), 7.87–7.90 m (1H, C_4H_3S), 16.95 s (0.8H, enol OH; keto:enol = 1:9). Found, %: C 75.21; H 7.84. $C_{24}H_{30}O_2S$. Calculated, %: C 75.35; H 7.90.

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