# Magnetic anisotropy of liquid crystals based on lanthanide mesogenic complexes

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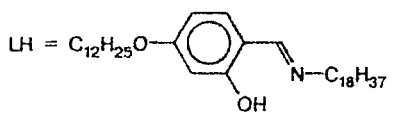
The values of magnetic anisotropy of smectic A-phases for a number of lanthanide complexes $(LH)_2LM(NO_3)_2$, where M = Nd, Eu, Gd, Tb, Dy, Ho, and Er, and LH is a Schiff's base), were measured. These values are two orders of magnitude larger than those normally found for diamagnetic liquid crystals and are well correlated with magnetic birefringence constants and molecular magnetic anisotropy of nonmesogenic lanthanide diketonates.

**Key words:** magnetic anisotropy, lanthanides, liquid crystals.

The anisotropy of electric and magnetic properties of liquid crystals is an important characteristic determining the behavior of these systems in electric or magnetic fields.[1,2] Significant opportunities for the variation of anisotropic characteristics of mesophases were provided by the synthesis of metal-containing mesogens.[3,4] The presence of a metal atom in a mesogenic molecule significantly changes the magnetic, electric, and optical properties of liquid crystals. Thus many liquid-crystal calamites based on rare earth element complexes[5] exhibit record-breaking magnetic susceptibilities among liquid crystals; Dy and Tb complexes with Schiff's bases and β-aminovinyl ketones demonstrate high anisotropies of the magnetic susceptibility.[6—10] However, no single-crystal samples of these compounds have been grown so far and no data on their structures have been obtained.

In this work, we studied magnetic susceptibility and the anisotropy of magnetic susceptibility of the liquid-crystal phase of a series of mesogenic complexes of lanthanides based on 4-alkoxy-*N*-alkyl-2-hydroxybenzaldimine (LH) of the general formula $(LH)_2LM(NO_3)_2$, where M = Nd, Eu, Gd, Tb, Dy, Ho, Er.




## Experimental

All compounds were synthesized by a procedure described previously[5] and characterized by the data of elemental analysis and NMR and IR spectroscopy. Mesogenic properties were studied using a differential scanning calorimeter (the temperatures and heats of phase transitions)[10] and a polythermal polarization microscope (the texture of the mesomorphic phase and phase transition temperatures). The temperatures of the phase transition of the crystal phase into the smectic $S_A$ phase ($T_{c-s}$) and from the smectic phase into the isotropic phase ($T_{s-i}$) are listed in Table 1.

The magnetic susceptibility and its anisotropy were studied using an original magnetometer that we designed, whose operation is based on the measurement of the charge that passes through the receiving coils as the sample (placed in a glass capillary with a diameter of ~3 mm) moves between two points of fixation in the magnetic system gaps. The magnetic field intensity in the gaps was 1.2 T. The transfer of a sample from one fixation point to the other changes the sign of the magnetic flux through the receiving coils and, correspondingly, generates a current pulse in these coils. The system for temperature measurement and control was mounted directly on the sample holder and moved together with the sample. The instrument was calibrated using precise weighed portions of substances with known magnetic susceptibilities. The calibration characteristic proved to be close to linear for $\chi$ ranging from $-0.9 \cdot 10^{-6}$ cm$^3$ g$^{-1}$ to $170 \cdot 10^{-6}$ cm$^3$ g$^{-1}$. (Detailed description of the instrument will be published elsewhere.) Checking measurements of the magnetic susceptibility anisotropy of known diamagnetic liquid crystals gave $\Delta\chi \approx 30 \cdot 10^{-6}$ cm$^3$ mol$^{-1}$, which is in good agreement with published data.[11]

The complete cycle of measurements included heating of a sample to a temperature several degrees above the $T_{s-i}$ value and cooling it at a rate of 0.3 °C min$^{-1}$. The results obtained for the Tb complex at cooling rates of 0.03 and 0.3 °C min$^{-1}$ coincided to within the error of the measurements. During the first heating in the specified temperature range, the magnetic susceptibility of all samples varied according to the Curie law, $\chi = \mu^2_{eff}/(8T)$, where $\chi$ is the molar magnetic susceptibility, $\mu_{eff}$ is the effective magnetic moment, and $T$ is temperature (K). The values $\mu_{eff} = \mu_i$ corresponding to the first heating cycle and $\chi = \chi_i$ at $T = T_{s-i}$ for all samples are presented in Table 1.

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**Table 1.** Phase transition temperatures and characteristics of the magnetic properties of the mesogenic $(LH_2)LM(NO_3)_2$ complexes

| M | $T_{c-s}$ | $T_{s-i}$ | $\mu_i$ | $\mu_{or}$ | $\chi_i$[a] | $\chi_{or}$[b] | $(\chi_{or} - \chi_i)$[b] | $\Delta\chi_{min}$[b] |
|---|---|---|---|---|---|---|---|---|
| | °C | | $\mu_B$ | | $10^{-6}$ cm$^3$ mol$^{-1}$ | | | |
| Nd | 100.0 | 161.0 | 3.50 | 3.60 | 2540 | 3420 | 260 | 390 |
| Eu | 112.5 | 156.0 | 3.45 | 3.50 | 2490 | 3040 | 160 | −480[c] |
| Gd | 112.0 | 149.5 | 7.80 | 7.80 | 17890 | 19700 | 50 | 75 |
| Tb | 96.0 | 149.0 | 9.55 | 9.80 | 27010 | 32870 | 1980 | 2970 |
| Dy | 130.3 | 147.0 | 10.45 | 10.55 | 32250 | 34750 | 1130 | 1695 |
| Ho | 129.2 | 146.0 | 10.55 | 10.65 | 32960 | 35340 | 980 | 1470 |
| Er | 127.0 | 146.0 | 9.55 | 9.65 | 27310 | 29050 | 440 | −1320[c] |

[a] $T = T_{s-i}$. [b] $T = T_{c-s}$. [c] Assuming that $\Delta\chi < 0$ (see the text).

## Results and Discussion

When samples are cooled in the vicinity of $T_{s-i}$, the $\chi$ and $\mu_{eff}$ values markedly increase (Fig. 1). With allowance for the data of polarization polythermal microscopy for $T_{s-i}$, one can conclude that in a narrow temperature range near $T_{s-i}$ the sample, which is initially nonoriented, orients itself so that its axis of the largest magnetic susceptibility arranges along the magnetic field. This orientation occurs only during cooling of the sample and does not occur during heating, due to the high viscosity of the mesophase. This is a typical behavior of smectic phases.

As the temperature decreases further, the variation of the magnetic susceptibility again follows the Curie pattern but with a different, higher, $\mu_{eff}$ value.

During the subsequent cycles of sample heating and cooling, the results obtained for the first cooling are completely reproduced: during heating, the magnetic susceptibility follows the Curie pattern with higher $\chi$ and $\mu_{eff}$ values, which decrease in the vicinity of $T_{s-i}$ to reach their initial values corresponding to the lower curves in Fig. 1. During cooling, the $\chi$ and $\mu_{eff}$ values again increase near $T_{s-i}$ and then follow the upper curves.

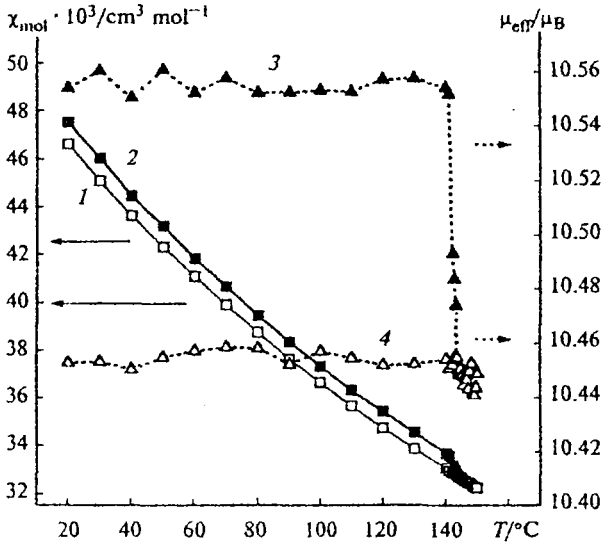


**Fig. 1.** Temperature dependences of the $\chi_{mol}$ (*1*, *2*) and $\mu_{eff}$ (*3*, *4*) values for the $(LH)_2LDy(NO_3)_2$ complex during the initial heating (*1*, *4*) and cooling (*2*, *3*) of the sample.

The difference between the values obtained for the oriented ($\chi_{or}$) and isotropic phases ($\chi_i$), measured at $T = T_{c-s}$ (see Table 1), is related to the magnetic anisotropy ($\Delta\chi = \chi_\parallel - \chi_\perp$) by the expression

$$\chi_{or} - \chi_i = 2 \cdot P(H) \cdot \Delta\chi/3, \qquad (1)$$

where indices $\parallel$ and $\perp$ correspond to the parallel and perpendicular directions with respect to the director $\bar{n}$ (the direction of the predominant orientation of the longer axes of molecules) and $P(H)$ is the degree of orientational order of the system in the magnetic field $H$:

$$P(H) = \langle 3 \cdot \cos^2\theta - 1 \rangle/2,$$

where $\theta$ is the angle between the director $\bar{n}$ and the magnetic field. Averaging is carried out over all the possible directions of the directors of ordered (characterized by the order parameter $S$) macroscopic areas

$$\langle \cos^2\theta \rangle = \frac{\int \cos^2\theta \cdot \exp[-(W/kT)] \cdot d\cos\theta}{\int \exp[-(W/kT)] \cdot d\cos\theta}. \qquad (2)$$

The energy of a local orientationally correlated group (domain) in a magnetic field: $W \propto -\Delta\chi \cdot H^2 \cdot \cos^2\theta$.

In the absence of a magnetic field, a macroscopic sample is a combination of nonoriented areas with different directions of the director $\bar{n}$; therefore, $P(H) = 0$. In a completely oriented system, $P(H) = 1$ at $\Delta\chi > 0$ or $P(H) = -1/2$ at $\Delta\chi < 0$. The former case corresponds to $\chi_{or} = \chi_\parallel$, while for the latter case, $\chi_{or} = \chi_\perp$. Hence, to find the lower limit $\Delta\chi = \Delta\chi_{min}$, the $\chi_{or} - \chi_i$ values in the penultimate column in Table 1 must be multiplied by a factor equal to 1.5 or 3, depending on the sign of $\Delta\chi$. This factor can only increase if one takes into account the possibility of incomplete orientation (*e.g.*, due to wall effects). Full orientation of nematics is normally attained in the 0.1—0.2 T fields. Full orientation of typical diamagnetic smectics A with

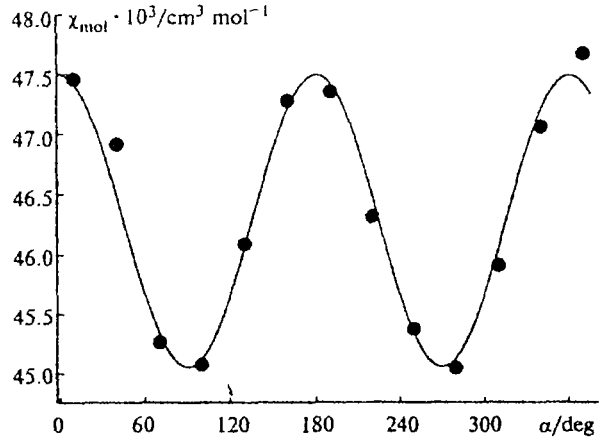


**Fig. 2.** The $\chi_{mol}$ value for the $(LH)_2LDy(NO_3)_2$ complex as a function of the α angle between the directions of the predominant orientation and the magnetic field at 21 °C.

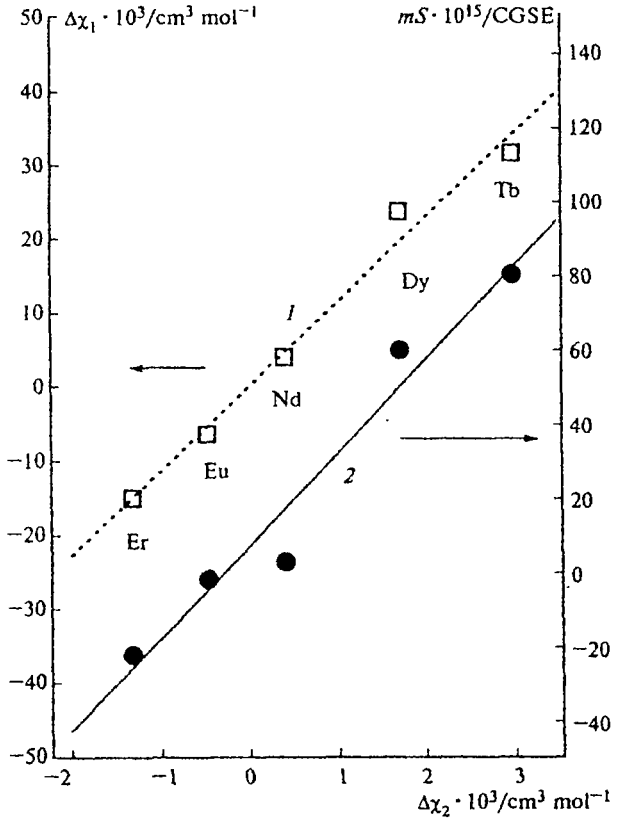


**Fig. 3.** Correlations between the $\Delta\chi_1$ values for the mesophases of the $(LH)_2LM(NO_3)_2$ complexes and $\Delta\chi_2$ (*1*, $r = 0.991$) and the birefringence constants (*2*, $r = 0.979$) for the $(DMP)_3M(\gamma\text{-pic})_2$ complexes. The reasoning for choosing the negative sign are given in the text.

$\Delta\chi = 20 \cdot 10^{-6}$ cm$^3$ mol$^{-1}$ requires,[12] due to high viscosity, magnetic fields equal to ~2—3 T in the vicinity of $T = T_{s-i}$. However, in the case of the paramagnetic mesophases studied here, the $\Delta\chi$ values are at least an order of magnitude greater and, hence, a field intensity of 1.2 T should be quite sufficient to ensure the maximum orientation.

The magnetometer used makes it possible to perform direct measurement of the anisotropy of magnetic susceptibility of a sample oriented preliminarily by a magnetic field and then cooled. Previously,[10] it has been found that mesogenic complexes of lanthanides are vitrified on cooling with retention of texture. Figure 2 presents the variation of magnetic susceptibility of a sample containing a Dy complex, prepared in this way as a function of the angle α between the directions of the predominant orientation and the magnetic field.

The values $\Delta\chi = \chi(\alpha = 0°) - \chi(\alpha = 90°)$, measured in this way for Dy and Er complexes, differ insignificantly from the $\Delta\chi$ values found from the measurement $\chi_{or} - \chi_i$ with allowance for relation (1).

Thus, the anisotropy of mesophases of several lanthanide complexes exceeds the anisotropy of known diamagnetic liquid crystals by one to two orders of magnitude.

The $\Delta\chi$ values measured for the complexes under study are well correlated with the magnetic birefringence constants (the Cotton—Mouton effect) and the molecular magnetic anisotropy for a number of nonmesogenic dipivaloylmethanate complexes of lanthanides with γ-picoline ($(DPM)_3M(\gamma\text{-pic})_2$)[13,14] (Fig. 3). The sign $\Delta\chi < 0$ for the Er and Eu complexes was chosen by analogy with the data for the corresponding diketonates.[14] The relative magnetic anisotropy $\Delta\chi$ in the lanthanide series is known to be highly sensitive to the symmetry of the crystal field, *i.e.*, to the structure of the coordination unit.[13] The correlation found here opens up the way for looking for an analogy between the structures and the directions of the main magnetic axis of the mesogenic compounds that we synthesized and those of diketonates. In addition, it points to a similarity of the structures of the coordination units in the mesogenic complexes studied.

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