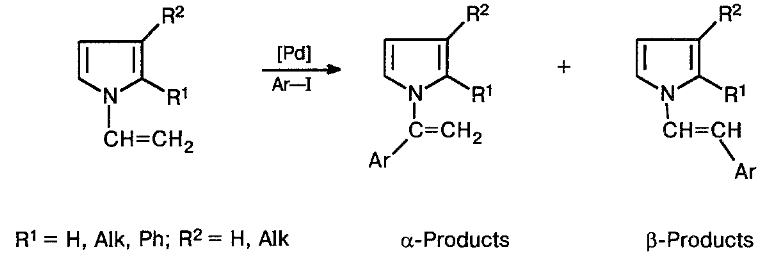
Scheme 1



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Metallomesogen with a large magnetic anisotropy

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The anisotropy of the electrical and magnetic features of liquid crystals determines their properties and behavior. The expected attractive features of metallomesogens of rare-earth elements are the large values of their magnetic moments, and, more important, their large magnetic anisotropy. Now we report the synthesis (analogous to that previously published[1]), measurements of static magnetic susceptibility in powders and solid melts, and the magnetic birefringence in solutions of mesogenic compounds $L(LH)_2M(NO_3)_2$, where LH is $C_7H_{15}O{-}C_6H_3(OH){-}CH{=}N{-}C_{16}H_{33}$, and M is La^{3+}, Gd^{3+}, or Dy^{3+}. The composition was determined on the basis of elemental analysis. The following phase transition points (°C), mesophase types (determined using a polarization microscope and the DSC method), and magnetic susceptibilities (25 °C), (measured using the Faraday method) ($\chi_g \cdot 10^6/\mathrm{cm}^3\ \mathrm{g}^{-1}$) are C 92 S_X 128 S_A 149 I (−0.7) for $L(LH)_2La(NO_3)_2$; C 128 S_A 146 I (15.9) for $L(LH)_2Gd(NO_3)_2$; C 140 S_A 142 I (29.6) for $L(LH)_2Dy(NO_3)_2$; where C is crystalline, S_A is smectic, and I is isotropic phase, respectively.

The magnetic susceptibilities of these compounds and their temperature dependences are typical of diamagnetic (La) and paramagnetic (Gd, Dy) lanthanides. Using the differences between the measured susceptibility (${}^{c}\chi_g \cdot {}^{c}m$) of the complexes and those expected[2] (${}^{m}\chi_g \cdot {}^{m}m$) for the metal ions (M) one can determine independently the number of ligands (n) in the $L_nM(NO_3)_2$ complex:

$${}^{c}\chi_g{}^{c}m = {}^{m}\chi_g{}^{m}m + n{}^{L}\chi_g{}^{L}m,$$

where χ_g is the specific susceptibility, and m is its mass. The values $n \cong 3.1$ and 3.2 for Gd and Dy complexes, respectively, are in good agreement with the elemental analysis.

The measurements of magnetic birefringence of solutions of the complexes in CCl_4 demonstrates that this effect is not molecular (Cotton—Mouton effect) even for the minimum concentration of the complex (*ca.* $2 \cdot 10^{-4}$ *M*), but it results from the structurization of the solutions (formation of associates). Neglecting the pecu-

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liarities of the effect observed for birefringence (the non-quadratic dependence of the effect, exceeding the molecular effect by 4 orders of magnitude), note that it is proportional to the magnetic anisotropy of supramolecular structures $\Delta\chi$, at least a weak magnetic field. The molar constants of the effect of magnetic birefringence[3] ${}^{m}P_0 \sim \Delta\alpha\Delta\chi$ approximated to a zero magnetic field are equal to $6.3 \cdot 10^{-11}$, $7.3 \cdot 10^{-11}$, $1.5 \cdot 10^{-7}$ cm^3 mol^{-1} for La, Gd and Dy derivatives, respectively.

The similar chemical properties of rare-earth ions, along with the IR and NMR data for solutions and for the condensed phase suggest that the solutions of the complexes studied have the same structure, and, hence, the same anisotropy of electronic polarizability ($\Delta\alpha$) of their objects. Thus the ratio of the anisotropy for the magnetic susceptibilities of the associates, and, in the approximation of axial symmetry, of the remaining complexes ($\Delta\chi_m$) is approximately equal to the ratio of the ${}^{m}P_0$ constants: $\Delta\chi_m(\mathrm{La})/\Delta\chi_m(\mathrm{Gd})/\Delta\chi_m(\mathrm{Dy}) \cong 1/1.2/2.4 \cdot 10^3$. Analogous results were obtained for solutions of the complexes in chloroform and benzene. The liquid crystal complexes of diamagnetic lanthanum and paramagnetic ($S = 7/2$, $\mu_{\mathrm{eff}} = 7.9$ M.B.) gadolinium (in S state), which have similar compositions and structures, possess magnetic anisotropy typical of mesogenes. The paramagnetic complex of Dy is characterized by magnetic anisotropy, significantly exceeding the anisotropy of known organic and metal-containing mesogenes.

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Palladium-catalyzed condensation of symmetrical diaryliodonium salts with phenylacetylene in aqueous media

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It is known that the condensation of terminal acetylenes with aryl halides proceeds the most efficiently if palladium complexes and copper (I) halides in the presence of base are used simultaneously.[1,2]

We found that in the presence of 1 mol. % of $PdCl_2(PPh_3)_2$, 2 mol. % of CuI, and 2 eq. of Bu_3N phenylacetylene reacts easily with diaryliodonium salts in DMF at ambient temperature to afford substituted tolans in quantitative yields, *e.g.*, *m*-nitrotolan was obtained in 94 % yield.

$$(m\text{-}NO_2C_6H_4)_2IHSO_4 + 2\,PhC{\equiv}CH \longrightarrow$$

$$\longrightarrow 2\,PhC{\equiv}CC_6H_4NO_2\text{-}m$$

It should be noted that both of the aryl groups of the iodonium salt are involved in the cross-coupling. The diaryliodonium salt evidently interacts with phenylacetylene at the first stage, and the resulting aryl iodide reacts with phenylacetylene (see Ref. 3).

K_2CO_3 can be successfully used instead of Bu_3N if the reaction is carried out in aqueous DMF (DMF : H_2O = 9 : 1)[3]. In this case, the yield of *m*-nitrotolan reaches 96 %.

One can avoid using organic solvents and carry out the reaction in water in the presence of K_2CO_3 and a catalytic amount of Bu_3N.

$(m\text{-}NO_2C_6H_4)_2IHSO_4$ (0.5 mmol), phenylacetylene (1.3 mmol), $PdCl_2(PPh_3)_2$ (0.01 mmol), CuI (0.02 mmol), Bu_3N (0.1 mmol), K_2CO_3 (2 mmol), and H_2O (2 mL) were placed into a flask equipped with a magnetic stirrer and a reflux condenser under Ar. The reaction mixture was stirred at

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