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PYROELECTRIC PROPERTIES OF CHIRAL SMECTIC PHASES

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Résumé. — On a mesuré la réponse pyroélectrique des cristaux liquides ferroélectriques (L-p-décyl-*oxy*-, L-p-nonyloxybenzylidène *p'*-amino cinnamate de méthyl-2 butyle et mélange) à des impulsions thermiques de durées de 2×10^{-4} et 3×10^{-8} s. A partir des données obtenues on a calculé les variations du coefficient pyroélectrique $\gamma(T)$ en fonction de la température. La dispersion de γ et de la polarisation spontanée P_s en fonction de la fréquence a été obtenue et est en accord avec les mesures de dispersion de la susceptibilité diélectrique pour des fréquences dans la gamme 10^4 - 2×10^5 Hz. On a mesuré le temps de relaxation de la polarisation spontanée (τ) et on a trouvé une divergence de τ près de la température de transition smectique C-smectique A. On a aussi montré que des impuretés dipolaires ont une influence visible sur les valeurs de γ^{\max} et de P_s^{\max} pour les cristaux étudiés.

Abstract. — The temperature dependences of the pyroelectric coefficient $\gamma(T)$ of ferroelectric liquid crystalline L-p-decyloxy- and L-p-nonyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate and their mixture were calculated from the measurements of their responses to heat pulses with durations of 2×10^{-4} and 3×10^{-8} s.

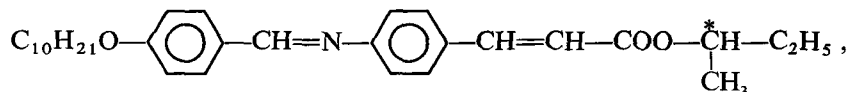
The frequency dispersion of γ and the spontaneous polarization P_s was discovered which is consistent with the corresponding dispersion of dielectric permittivity over a frequency range 10^4 - 2×10^5 Hz. The direct measurements of the relaxation time for spontaneous polarization (τ) were performed and sharp increase in τ near the SmC-SmA phase transition was observed. The effect of dipolar admixtures on γ^{\max} and P_s^{\max} was also discussed.

1. Introduction. — Pyroelectricity is one of the most characteristic features of ferroelectric crystals. This is also true for ferroelectric liquid crystals discovered by R. Meyer [1]. The first attempt to observe the pyroelectric effect has been made in [2], where the value of the pyroelectric coefficient

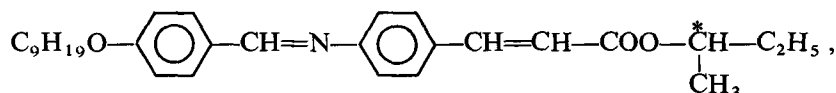
$$\gamma = \frac{dP_s}{dT} \quad (1)$$

of L-p-decyloxybenzylidene-*p'*-amino-2-methylbutyl cinnamate (L-DOBAMBC) has been measured at some arbitrary temperatures for the smectic C and H phases (in eq. (1) P_s and T are spontaneous polarization and temperature).

The aim of our paper is to investigate the temperature behaviour and frequency dispersion of γ and P_s over a whole range of existence of a ferroelectric phase for DOBAMBC



its nonyloxy-homologue (NOBAMBC)



and their mixture, as well as to study the effect of dipolar admixtures on $\gamma(T)$ and $P_s(T)$ of DOBAMBC.

2. Experimental. — A liquid crystal (LC) layer of thickness $d = 200 \mu$ was placed between two SnO_2 -coated glass plates. Homogeneous (but at the same

time mosaic) orientation was achieved using rubbing technique. Samples were polarized by external voltages of 50-200 V which caused untwisting of the

helical structure. The voltage was applied at $T = 95^\circ\text{C}$ (the smectic A phase in all the cases) during the cooling from the isotropic to the chiral smectic C phases. The pyroelectric coefficient $\gamma(T)$ was calculated from the measurements of responsivity (S) of the layer to heat pulses of a Nd-glass laser. Laser radiation ($\lambda = 1.06 \mu$) was absorbed by special dye (a dithiyne Ni-complex with an absorption maximum at $\lambda = 1.1 \mu$) dissolved in a liquid crystal. Concentration of the complex did not exceed the value of 0.5 wt %, and optical density at $\lambda = 1.06 \mu$ was equal to 1.4-1.7. We used both the unmodulated neodymium laser pulse under free-running condition (*long pulse*) and single giant Q-switched laser pulse (*short pulse*). The measurement apparatus is shown schematically in figure 1a, b.

A double-beam oscilloscope was used when the long pulse produced the pyroelectric effect. In this case, electric time constants for both the pyroelectric layer and photomultiplier controlled a radiation pulse were chosen to be equal to $\tau_{el} \approx (1-2) \cdot 10^{-5}$ s, that is, τ_{el} was much longer than the duration of a separate peak but much shorter than duration of a pulse envelope ($\tau_{env} \approx (2-3) \cdot 10^{-4}$ s). Typical oscillograms of pyroelectric response to unmodulated laser pulse and the corresponding control pulse from a photomultiplier are shown in figure 1c. The radiation power was determined from the pulse energy, measured by a calorimeter, and the form of the envelope. When the short-circuit regime was provided by a proper choice of load resistor ($R_L \leq 10^5$ ohm) the pyroelectric coefficient can be calculated from formula [3] :

$$\gamma(T) = \frac{S(T) \cdot \rho \cdot c(T) \cdot d}{\eta \cdot R_L} \quad (2)$$

Here, ρ and $c(T)$ are LC density ($\approx 1 \text{ g} \cdot \text{cm}^{-3}$) and heat capacity taken from [4], $\eta \approx 0.7$ is an absorbed part of incident power with account taken of multiple reflections from plates. The temperature was controlled to an accuracy of 0.1°C . All the measurements were performed on slow cooling the samples at a rate of 0.2-0.3 grad/min. With increasing the polarizing voltage the pulse pyroelectric signal (and calculated value for γ) reached saturation. This saturation values were plotted on experimental curves for $\gamma(T)$.

When the pyroelectric effect was produced by a giant pulse of duration $\tau_Q = 3 \times 10^{-8}$ s (at half-width), we used a single-beam storage oscilloscope with a differential amplifier. Signal from a photomultiplier calibrated in incident power was registered by one of the input channels. Pyroelectric signal from a liquid crystal cell was passed through a delay line (delay time was 2.5×10^{-7} s) and delivered to the second channel. Typical oscillogram is shown in figure 1d. For $R_L = 300$ ohm the electric time constant of a cell was small enough to provide the short-circuit regime and the same formula (2) was used to calculate the pyroelectric coefficient.

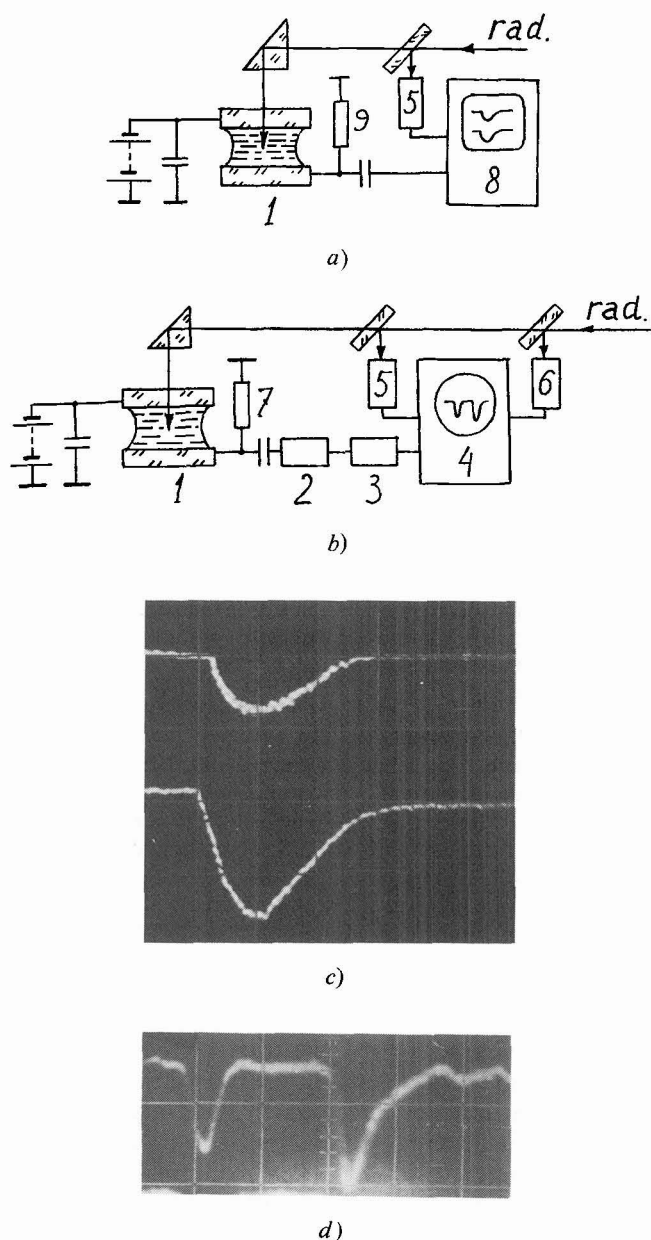


FIG. 1. — Experimental apparatus for detection of pyroelectric response of liquid crystals : a) to unmodulated Nd-glass laser pulse, $\tau_{env} = (2-3) \cdot 10^{-4}$ s (long pulse), b) to Q-smithed laser pulse, $\tau_Q = 3 \times 10^{-8}$ s (short pulse). 1. LC cell, 2. amplifier, 3. delay line, 4. storage oscilloscope, 5. photomultiplier for laser pulse detection, 6. photomultiplier for synchronization, 7. load resistor, $R_L = 300$ ohm, 8. dual-beam storage oscilloscope, 9. load resistor $R_L = 10^5$ ohm. c) oscillogram obtained using a long pulse : above, pyroelectric response of LC cell (vertical scale 10 mV/div), below, response of photomultiplier (vertical scale 10 W/div). Horizontal scale : 100 $\mu\text{s}/\text{div}$. d) oscillogram, obtained using a short laser pulse : the first pulse, response of photomultiplier (vertical scale 3×10^4 W/div), the second pulse, pyroelectric response of LC layer (vertical scale 2 mV/div). Horizontal scale 100 ns/div.

3. Results and discussion. — The temperature behaviour of the pyroelectric coefficient for DOBAMBC calculated from the LC responsivity to a long ($\tau_{env} = 3 \times 10^{-4}$ s) and short ($\tau_Q = 3 \times 10^{-8}$ s)

pulses is illustrated by curves (a) in figures 2 and 3, respectively. Curves (b) in the same figures illustrate the temperature behaviour of the spontaneous polarization calculated from $\gamma(T)$ upon integrating with respect to the temperature :

$$P_s(T) = \int_{T_c}^{T_c - T} \gamma(T) dT . \quad (3)$$

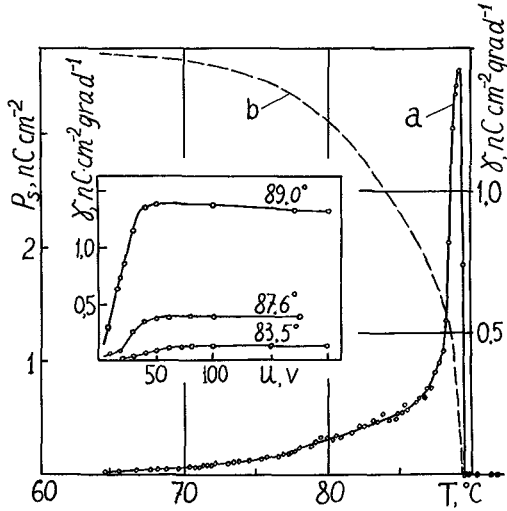


FIG. 2. — Pyroelectric coefficients $\gamma(T)$ versus temperature for DOBAMBC, calculated from pyroelectric response to a pulse with $\tau_{env} = 3 \times 10^{-4}$ s (a), and spontaneous polarization $P_s(T)$ (b), calculated from the curve $\gamma(T)$.

Insert : pyroelectric coefficient versus the polarizing voltage.

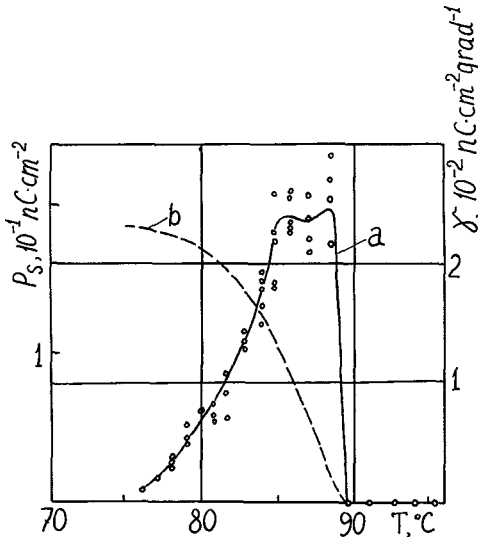


FIG. 3. — $\gamma(T)$ (a) and $P_s(T)$ (b) for DOBAMBC, obtained using a short pulse with $\tau_0 = 3 \times 10^{-8}$ s.

The curves $\gamma(T)$ and $P_s(T)$ calculated for NOBAMBC and a mixture of DOBAMBC and NOBAMBC (1 : 1) are similar to those for pure DOBAMBC and are not shown in figures. The maximum values of $\gamma(T)$ and $P_s(T)$ obtained for both long and short pulses are given in table I.

In the case of long pulses, near the phase transition we have measured rather high values of the pyroelectric coefficient, $\gamma \approx 2 \times 10^{-9}$ C.cm⁻² grad⁻¹, comparable with the corresponding values for traditional pyroelectrics. At temperatures 65-70 °C very small value of $\gamma \approx 2 \times 10^{-11}$ C.cm⁻² grad⁻¹ agrees well with data of paper [2]. The maximum polarization, $P_s = 4 \times 10^{-9}$ C.cm⁻² is in good agreement with data of papers [5-7].

In the case of short pulses, even near the phase transition to the smectic A phase we have obtained the values of $\gamma \approx (2-3) 10^{-11}$ C.cm⁻² grad⁻¹ which is two orders of magnitude less than those for long pulses. We have assumed that this discrepancy was due to the inequality $\tau_Q \ll \tau_D$ where τ_D is a Debye relaxation time of the dipoles responsible for the spontaneous polarization. We have evaluated τ_D [8] as the product of τ_Q and the ratio between the steady-state (for long pulses) and dynamic (for short pulses) values of the pyroelectric coefficient and obtained $\tau_D \approx 10^{-5}-10^{-6}$ s. Thus, on the assumption, there has to be observed a dispersion of P_s , γ and also dielectric permittivity (ϵ) over the frequency range $f \approx 10^4-10^6$ Hz.

Such a dispersion of $\epsilon(f)$ did is observed in DOBAMBC (it has not been found in [9] due to a lower accuracy of the measurements). The experimental curves are shown in figure 4 for two tempe-

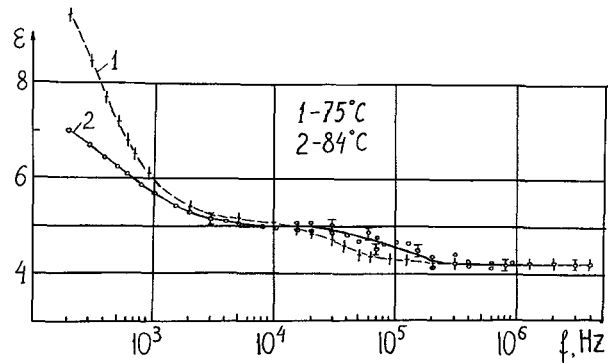


FIG. 4. — Frequency dependence of dielectric constant ϵ for DOBAMBC.

TABLE I

Material	T_c	$\tau_{env} = (2-3) 10^{-4}$ s		$\tau_Q = 3 \times 10^{-8}$ s	
		γ_{max} , C.cm ⁻² grad ⁻¹	P_s , C.cm ⁻²	γ_{max} , C.cm ⁻² grad ⁻¹	P_s , C.cm ⁻²
DOBAMBC	89.4°	1.5×10^{-9}	3.7×10^{-9}	2.7×10^{-11}	1.9×10^{-10}
NOBAMBC	89.4°	1.7×10^{-9}	3.5×10^{-9}	3.0×10^{-11}	2.1×10^{-10}
DOBAMBC+NOBAMBC (1 : 1)	90.1°	2.2×10^{-9}	3.4×10^{-9}	2.8×10^{-11}	2.4×10^{-10}

ratitudes. The dispersion of ε takes place at frequencies 10^4 - 2×10^5 Hz which agree with those expected from the τ_D value. The dispersion frequencies decrease sharply with decreasing temperature due to the increase in τ_D . That is why the dynamic pyroelectric coefficient decreases sharply near the transition from the smectic C to smectic H phase, figure 3a.

It should be noted that the *apparent* dispersion in polarization at frequencies of 10^2 - 10^3 Hz [7, 9] measured by the Sawyer-Tower method [6, 7, 9] is due to the slow process of untwisting the helix and does not involve any information about dipolar relaxation times. According to our measurements, the spontaneous polarization is independent of frequency up to the frequencies of about 10^4 Hz, and the measurements of pyroelectric signals using our long pulses give the steady-state values for γ and P_s .

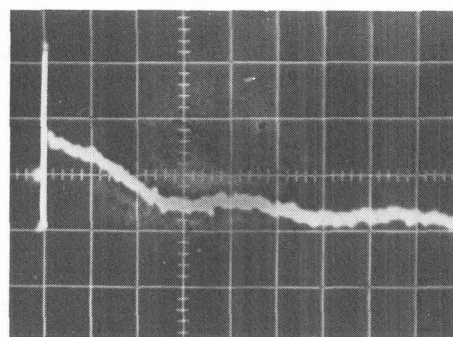
We have also performed for the first time the direct measurements of the relaxation time for spontaneous polarization of DOBAMBC. According to the theoretical analysis there has to be observed an exponential decay of pyroelectric response to a short heat pulse when the finite relaxation time (τ) takes place. The time constant for pyroelectric response (under conditions of short-circuit regime and large thermal time constant of the layer) is equal to the relaxation time of the spontaneous polarization.

Sharp peak of the oscillogram, shown in figure 5a, reproduces the giant laser pulse and is caused by the *fast* component of P_s which is due probably to the rotation of LC molecules around their long axes.

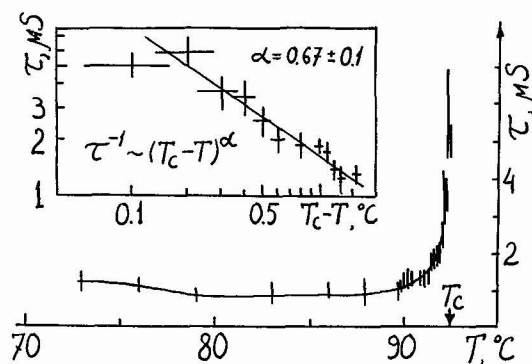
The time constant of the slow decay (τ) agrees well with τ_D evaluated earlier. The sharp increase in τ near the phase transition from SmC to SmA phase (Fig. 5b) reminds the behaviour of the soft mode in solid ferroelectrics. The critical index for this temperature dependence was shown to be $\alpha = 0.67 \pm 0.1$.

We have also made an attempt to observe the pyroelectric effect without any external voltage. In this case, the spontaneous polarization could be caused by surface phenomena. To this effect, we used cells made of glass plates with thin metal electrodes absorbing laser light. After heating the electrode by a giant laser pulse a thermal front was transferred into a liquid crystal layer and caused the pyroelectric voltage across the electrodes. Incident light can be directed to both the front and rear surfaces of the cell. The *surface* dynamic pyroelectric coefficients were shown to be of the same order of magnitude as the volume ones and have different signs at opposite surfaces. This experiment indicates that near electrodes there are thin oriented LC layers with a finite spontaneous polarization. The layer thickness probed in such a method by a pulse of duration $\tau_D \sim 10^{-7}$ s is of about 0.1μ [10].

The preliminary investigations have been also performed of the effect of dipolar admixtures on the values of $\gamma(T)$ and $P_s(T)$ for DOBAMBC. Two admixtures were used with large transverse (DC)

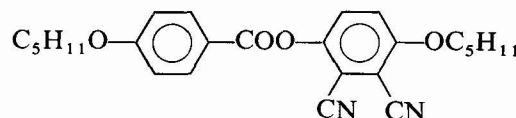


a)

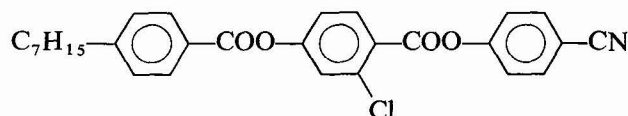


b)

FIG. 5. — a) Oscillogram of pyroelectric response of DOBAMBC to giant pulse at the temperature near the T_c . Vertical scale : 2 mV/div, horizontal scale : 1 μ s/div. b) Temperature dependence of relaxation time of DOBAMBC, calculated from the response decay.



and large longitudinal (CC)



molecular dipole moment.

The curves of $\gamma(T)$ for DOBAMBC doped with CC (4.4 %) measured by means of a long (γ_1) and short (γ_2) pulses are shown in figure 6. The value for γ_1 is not strongly affected by the admixture. However, it seems to be a new phase transition at $T^* = 75$ °C where $\gamma_1(T)$ changes by a jump and $\gamma_2(T)$ changes its sign. Above and below T^* an electric field affects on the pyroelectric response in different manner. At $T > T^*$ the response reaches saturation with increasing polarizing voltage (U) just as for pure DOBAMBC (insert in figure 2), at $T < T^*$ the function $\gamma(U)$ can have fractures and even change sign.

The dependences of γ^{\max} and P_s^{\max} on concentration of each of the two admixtures in DOBAMBC are

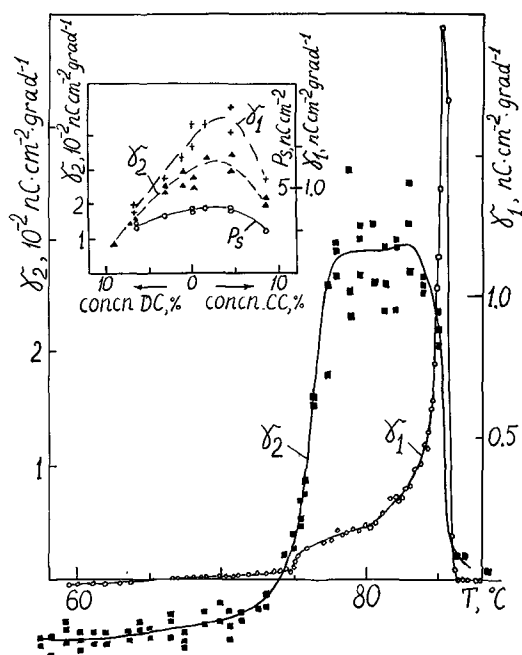


FIG. 6. — Temperature dependence of the pyroelectric coefficient of a mixture of DOBAMBC and CC (4.4 %). $\gamma_1(T)$ was obtained for $\tau_{\text{env}} = 2 \times 10^{-4}$ s, $\gamma_2(T)$ — for $\tau_{\text{env}} = 3 \times 10^{-8}$ s. Insert — dependence of spontaneous polarization P_s and maximum pyroelectric coefficients for mixtures of DOBAMBC + DC and DOBAMBC + CC on concentration of DC and CC.

given in figure 6 (insert). Curves γ_1 and γ_2 refer to the long pulse ($\tau_{\text{env}} = 2 \times 10^{-4}$ s) and short pulse ($\tau_{\text{env}} = 3 \times 10^{-8}$ s) measurements, respectively. All the curves pass through a maximum at the concentration of CC (with longitudinal dipole) of about 1-5 %. At present, we have no explanation for this effect.

In conclusion, we have measured the temperature dependences of the pyroelectric coefficient for DOBAMBC, NOBAMBC and their mixture and, for the first time, obtained the high value of $\gamma \approx 2 \times 10^{-9}$ C.cm $^{-2}$ grad $^{-1}$. In addition, we have discovered a frequency dispersion of γ and P_s over a range of 10^4 - 2×10^5 Hz which correlated with the dispersion of ϵ . For the first time, we have performed the direct measurements of the relaxation time τ for polarization of LC and discovered sharp increase in τ near the phase transition from SmC to SmA phase which is similar to the behaviour of the soft mode in solid ferroelectrics. The influence of dipolar admixtures on pyroelectric properties of DOBAMBC has been also detected.

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