

## Triboluminescence, a new tool to investigate fracture-initiation time of crystals under stress

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**Abstract.** The present paper reports that triboluminescence (TBL) does not appear at the instant of impact of the load but a certain time lag is required for its appearance which depends on the value of the stress applied to the crystal. Since TBL appears in sugar crystals during the creation of new surfaces, the fracture-initiation time of the crystal has been taken to be the delay time in observing TBL pulse after the application of stress. The dependence of fracture-initiation time,  $t_f^\sigma$ , of crystals on the stress,  $\sigma$ , may be expressed as  $t_f^\sigma = t_0 \exp(-a\sigma)$ , where  $t_0$  and  $a$  are constants. The values of the lattice energy, and the change in lattice energy per unit stress, of sugar crystals have been calculated from TBL measurements and they have been found to be  $21.2 \text{ kcal mole}^{-1}$  and  $0.41 \times 10^{-8} \text{ kcal mole}^{-1} \text{ dyne}^{-1} \text{ cm}^2$  respectively.

**Keywords.** Triboluminescence; luminescence; high pressure phenomena; fracture.

### 1. Introduction

Considerable interest has been shown in the investigation of fracture of solids in the last three decades to close the gap between the theoretical and experimental values of the strength of solids. As a matter of fact, several mechanisms of fracture and various formulae for the strength of solids have been given (Nadai 1950, Bartenev *et al* 1958, Irwin 1958, Drucker and Gilman 1963, Stock and Pratt 1965). One of the methods to investigate the fracture of solids is to study the fracture-initiation time of crystals under stress (Hsiao 1963, Bartenev and Zuev 1964, Zhurkov *et al* 1969). In the present paper, an attempt has been made to investigate the fracture-initiation time of sugar crystals under stress from their triboluminescence (TBL) which is the phenomenon of emission of light during the fracture of a crystal.

### 2. Experimental

Good crystals of sugar were chosen from the commercial cane sugar (specific rotation  $64^\circ$  of an arc at  $29^\circ \text{ C}$ ). The measurements of the fracture-initiation time of the crystals under stress were made with the help of an arrangement shown

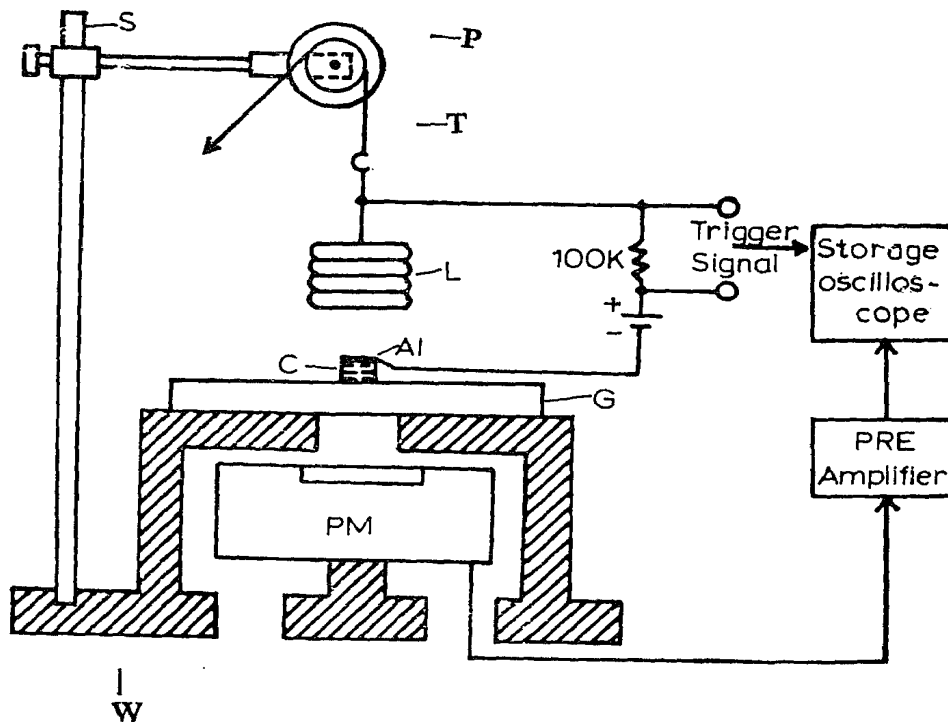


Figure 1. Experimental arrangement for studying time dependence of TBL in crystals. S—stand, P—pulley, T—thread, L—Load, Al—aluminium foil, C—crystal, G—glass plate, PM—photomultiplier tube, and W—wooden base.

in figure 1. In this arrangement, the crystal was placed on a clean transparent glass plate mounted on a wooden platform with a hole. Below the hole, an RCA IP28 photomultiplier tube was mounted separately. An HP181A storage oscilloscope was used to record the transient TBL pulses. An impulsive technique was employed for the crushing of the crystals, in which a fixed load was dropped on the crystal from different heights with the help of a pulley of negligible friction.

Triboluminescence appears in sugar crystals during the creation of new surfaces. Hence the fracture-initiation time of the crystal under stress has been taken to be the delay time in observing TBL pulse after the application of stress. The following arrangement was used to measure the delay time.

The crystal was covered with a thin aluminium foil which was connected to one terminal of an 1.5 V battery through a resistance (100 k $\Omega$ ). The other terminal of the battery was connected to the metallic load to be dropped. When the dropped load touched the aluminium foil on the crystal, the trigger pulse appears across the resistance of 100 k. This pulse is used to trigger the oscilloscope. The triboluminescence intensity is monitored by the photomultiplier whose output is fed to the Y-input of the oscilloscope. The delay in the appearance of the TBL pulse is taken as fracture-initiation time. Thus the fracture-initiation time of the crystals under different stresses could be determined. The response time of the combined detector-amplifier-oscilloscope system is  $5 \times 10^{-6}$  second.

The size of the crystals used in the present investigation was  $5 \times 4 \times 3$  mm<sup>3</sup>. The crystals were always crushed into crumbled masses by dropping a load of 800 gm from different heights, along their *c* direction of the crystallographic axis. For each stress, five experiments were carried out and the deviation in the fracture-initiation time was estimated to be  $\pm 5\%$ . The mean values of the fracture-initiation time determined from TBL measurements for different heights are shown in table 1.

**Table 1.** Estimation of stress at impact from TBL measurements.

Height through which the load is dropped (cm)	Mass of the dropped load (gm)	Integrated value of TBL intensity (arb. units)	Stress at impact estimated from TBL measurement (kg/cm <sup>2</sup> )	Fracture-initiation time (milliseconds)
0.5	800	15.8	220	1.20
1.0	800	19.5	300	0.70
2.0	800	30.0	340	0.50
3.0	800	46.0	368	0.40
4.0	800	70.0	396	0.35
5.0	800	80.0	424	0.30

The estimation of the stress at impact of the load on the crystals, was made with the help of a calibration curve between integrated value of TBL intensity and statical stress (Das *et al* 1972, Das and Chandra 1974). For the measurement of the integrated TBL intensity the output of the photomultiplier tube was coupled to a sensitive ballistic galvanometer. The integrated TBL intensity was measured in terms of the deflection of the galvanometer, for the load of 800 gm dropped from different heights and for different heavy loads applied statically on the crystal with almost zero velocity. At a given height through which the load of 800 gm was dropped and at a given statical stress, five experiments were carried out. The deviation obtained in the measurement of TBL intensity was  $\pm 5\%$ .

Figure 2 shows the calibration curve between the integrated value of TBL intensity and the statical stress. In table 1, the calculated values of applied stress in the load-drop technique are given.

### 3. Results and discussion

Figure 3 shows the oscillogram of TBL pulse of a sugar crystal. The variation of intensity ( $I$ ) of TBL, with time in sugar crystals for different heights from which load is dropped on the crystal, has been shown in figure 4. It is seen that TBL does not appear at the instant of the impact of the load. The (delay) time between the impact of the dropped load and the appearance of TBL decreases with increasing applied stresses. The rate of rise of TBL (*ie.*, the slope of the  $I$  versus time curve) is higher for higher crushing heights and lower for lower values of crushing height. The TBL intensity reaches a maximum, and the position of maximum shifts towards longer time values for higher values of the crushing height.

It is seen from figure 5 that the plot of  $\log t_f^\sigma$  versus stress,  $\sigma$ , is a straight line with a negative slope, which suggests the relation

$$t_f^\sigma = t_0 \exp(-\alpha\sigma); \quad (1)$$

where  $t_f^\sigma$  is the fracture-initiation time under stress,  $\sigma$  and,  $t_0$  and  $\alpha$  are constants. The physical significance of the constants  $t_0$  and  $\alpha$  in eq. (1) will become clear from the following consideration of the thermofluctuation mechanism of fracture of solids (Bartenev 1955, Zhurkov 1965).

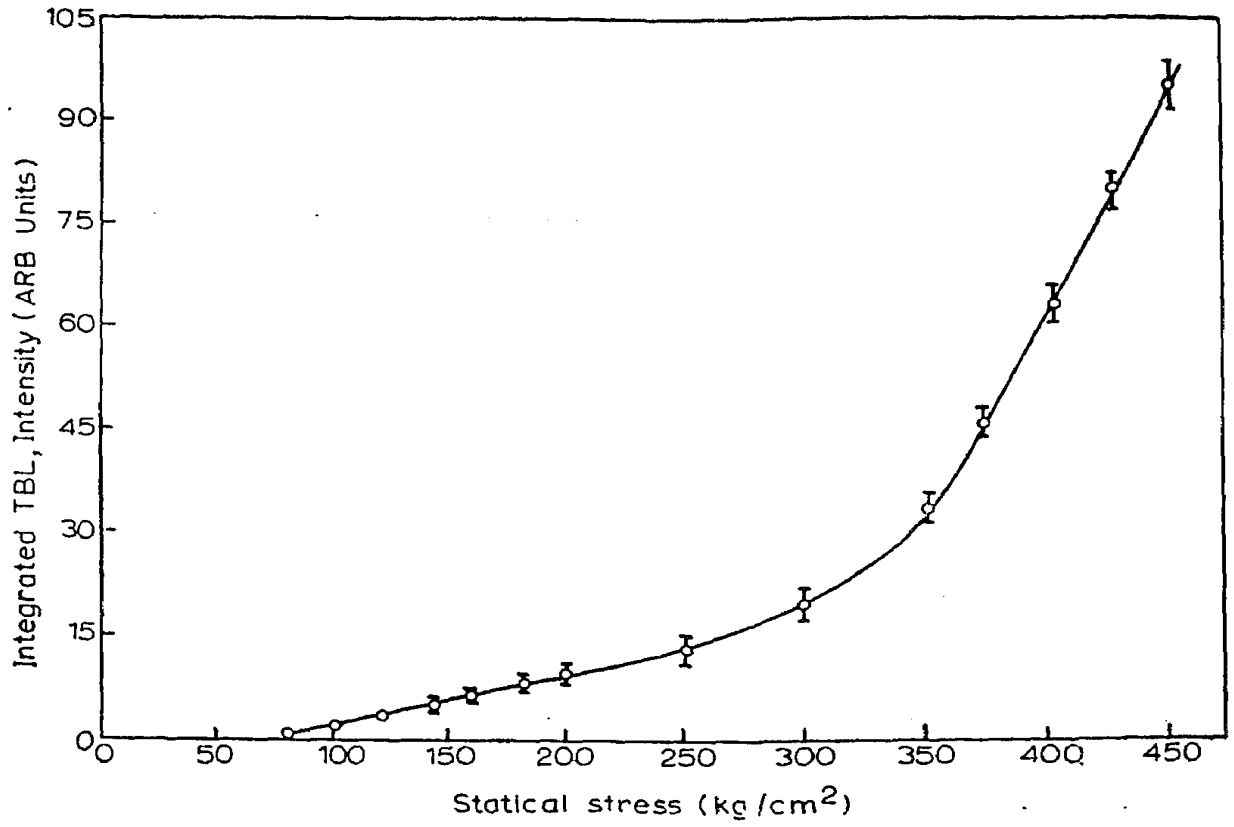


Figure 2. Calibration curve of integrated value of TBL intensity,  $I_0$  versus statical stress,  $\sigma$ .

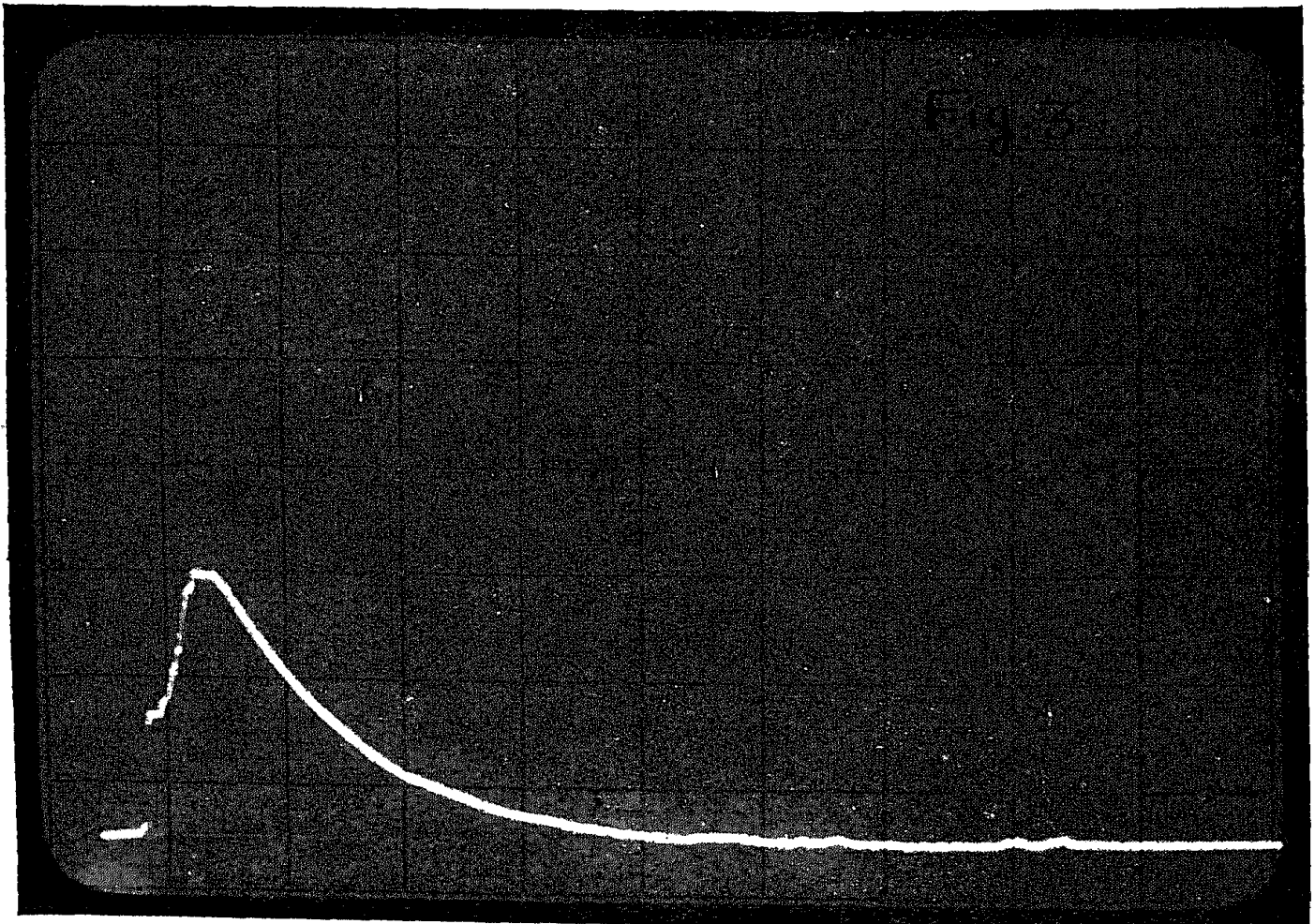


Figure 3. Oscillogram of TBL pulse of a sugar crystal.

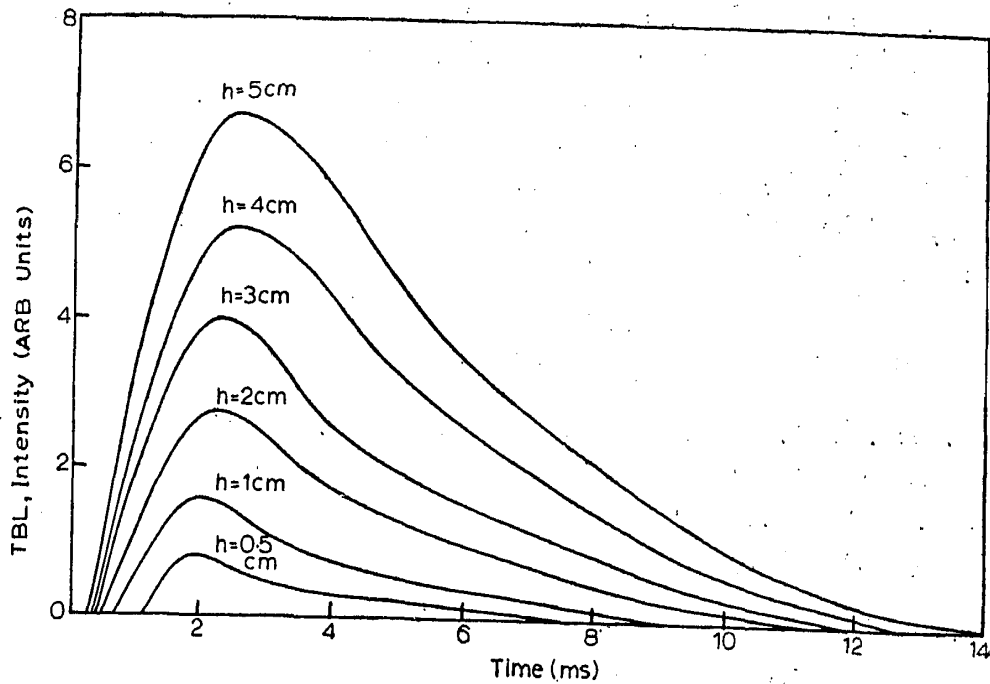


Figure 4. Variation of intensity,  $I$ , of TBL with time in sugar crystals for different values of  $h$ .

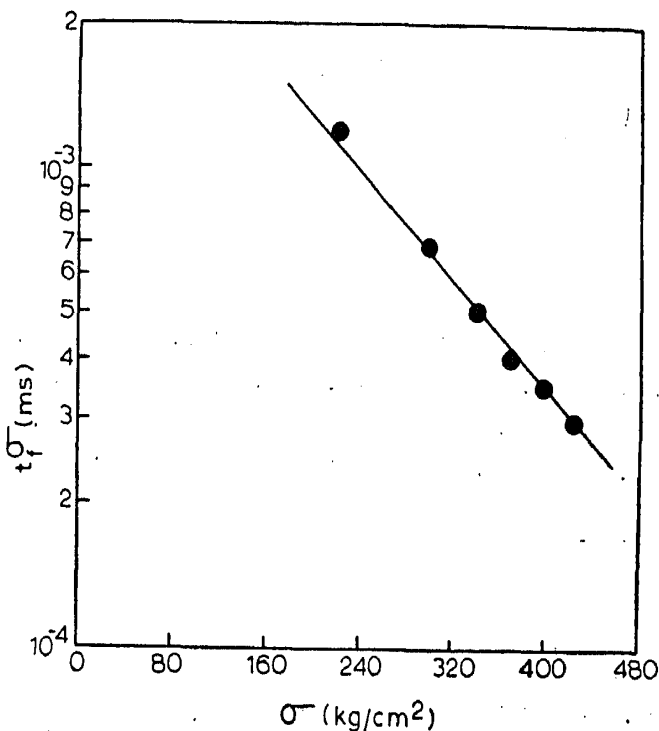


Figure 5.  $\log t_f^\sigma$  plotted against applied stresses  $\sigma$ .

According to the absolute reaction rate theory, the effect of stress on elastic deformation and viscous flow may be related to a comprehensive activation process as a consequence of the movement of the whole or a segment of a molecule, from one equilibrium state to the next (Hsiao 1959, Hsiao and Ting 1965). If  $U$  is the potential energy barrier between two equilibrium states in unstressed crystal, then the frequency with which cross-overs occur is proportional to  $\exp(-U/RT)$ ; where  $R$  is universal gas constant and  $T$  is absolute temperature of the crystal. After the application of a stress,  $\sigma$ , to the crystal, the energy barrier becomes  $(U - \beta\sigma)$  in the direction of the applied stress, and  $(U + \gamma\sigma)$  in the opposite

direction, where  $\beta$  and  $\gamma$  are constants depending upon the modification of the energy barrier. Thus the rate of reformation of broken elements will be  $k_r = \omega_r \exp [-(U + \gamma\sigma)/RT]$  and the rate of rupturing of unbroken elements  $k_b = \omega_b \exp [-(U - \beta\sigma)/RT]$ ; where  $\omega_r$  and  $\omega_b$  are respectively frequencies of motion associated with their reformation and breakage processes. For a large value of  $\sigma$ ,  $k_r$  will be much smaller compared to  $k_b$ . Therefore the rate of accumulation of ruptured bonds may be written as

$$k_b = \omega_b \exp \left\{ - \left( \frac{U - \beta\sigma}{RT} \right) \right\}. \quad (2)$$

It has been shown that the fracture-initiation time of a stressed solid is completely determined by the rate of accumulation of the ruptured bonds, and the fracture-initiation time,  $t_f^\sigma$  and the rupture rate,  $k_b$ , at equal stress and temperature are related by the equality (Zhurkov 1965)

$$t_f^\sigma \cdot k_b = \text{const.} \quad (3)$$

Thus,  $t_f^\sigma$  may be written as

$$t_f^\sigma = \frac{\text{const.}}{\omega_b} \exp \left( \frac{(U - \beta\sigma)}{RT} \right); \quad (4)$$

or

$$t_f^\sigma = \tau_0 \exp \left( \frac{U}{RT} \right) \exp (-\beta\sigma/RT); \quad (5)$$

where

$$\tau_0 = \frac{\text{const.}}{\omega_b} \quad (6)$$

The parameter,  $\tau_0$ , is equal to the reciprocal of the natural oscillation frequency of atoms in solids and its value has been found to be of the order of  $10^{-13}$  second for most of solids (Zhurkov 1965, Zhurkov *et al* 1969).

The above equation is compared with eq. (1) and we get

$$t_0 = \tau_0 \exp (U/RT) \quad (7)$$

and

$$a = \beta/RT \quad (8)$$

As the value of  $a$  can be determined from the plot of  $\log t_f^\sigma$  versus  $\sigma$  (figure 5) the value of  $\beta$  can be calculated using eq. (8). The value of  $\beta$  thus calculated is  $0.41 \times 10^{-8}$  kcal mole<sup>-1</sup> dyne<sup>-1</sup> cm<sup>2</sup> for sugar crystals. The order of the value of  $\beta$  calculated from TBL measurements agrees with that obtained from studies on fracture, which is  $1.5 \times 10^{-8}$  kcal mole<sup>-1</sup> dyne<sup>-1</sup> cm<sup>2</sup> for polycrystalline silver (Zhurkov 1965) and  $3.2 \times 10^{-8}$  kcal mole<sup>-1</sup> dyne<sup>-1</sup> cm<sup>2</sup> for polymers (Bartenev 1965).

Equation (5) may be written as

$$U = RT \ln (t_f^\sigma/\tau_0) + \beta\sigma. \quad (9)$$

The values of all the factors on the right hand side of eq. (9) are known and thus by substituting them the value of  $U$  is found to be 21.2 kcal mole<sup>-1</sup> for sugar

crystals. The potential energy barrier,  $U$ , is physically interpreted as the lattice energy of the crystal (Zhurkov *et al* 1969).

The fracture-initiation time of the crystal decreases with increasing values of the applied stress, whereas the TBL intensity increases with increasing values of the applied stress. Such a trend is to be expected based on eq. (3), and it is suggested that the rate of accumulation of ruptured bonds is responsible for the phenomenon of TBL.

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