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Temperature Function of Birefringence and Structural Changes in Carbazole Crystal

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With a modified quarter-wave Sénarmont compensator, exact measurements of the optical path difference have been carried out in (010) plates of carbazole, $C_{12}H_9N$, in the temperature range $20 < T < 190$°C. At a temperature near 155°C distinct anomaly has been found corresponding to crystal-to-crystal phase transformation. The birefringence changes are discussed in terms of temperature dependence of density and orientation of molecules in the unit cell due to thermal expansion of the crystal.

1 INTRODUCTION

Papers that contribute to the problem of the influence of temperature on birefringence of molecular crystals$^{1-4}$ indicate that this crystal property shows a relatively great sensitivity to structural changes that may occur in the crystal lattice. So far the main interest in such measurements was devoted to visualization and characterization of phase transformations of the type crystal-to-crystal even in cases where very small enthalpy change takes place. However, it may be also of interest to study the linear temperature behaviour of birefringence in terms of thermal expansion and/or other effects that may occur in the lattice while the crystal is heated. Changes of birefringence have lately been discussed for anthracene and phenanthrene[5] from the point of view of thermal expansion. It was assumed[5] that the thermal coefficient of birefringence, $\mathrm{d}B/\mathrm{d}T$, is proportional to the thermal coefficient of the path difference, $\mathrm{d}R/\mathrm{d}T$. As a matter of fact, there is no proportionality between these two quantities but rather a linear relationship[7] (cf. equation (1) in this paper). With this point of view, and using data given in,[2,5] and the thermal expansion coefficient perpendicular to the cleavage plane, $\beta_\perp = 12 \cdot 10^{-5}$ deg^{-1}, taken from the paper of Ryzhenkov *et al.*[25] we will find that in anthracene the thermal expansion accounts for only about 60% of the observed effect in birefringence measurements.

Recently, it has been shown on an example of fluorene crystal[6] that also some change of molecular orientation with respect to the frame of the unit cell should be taken into consideration. Basing on these ideas we will try in this paper to separate both effects while interpreting the experimental results for carbazole crystal.

Similarly as in fluorene, carbazole molecules take special positions in the orthorhombic crystal structure, space group Pnma with $Z = 4$ molecules in the unit cell:[8] the molecular symmetry plane, which is perpendicular to the carbon skeleton of the molecule, coincides with the symmetry plane of the crystal. Therefore, the symmetry restrictions allow for a change of molecular orientation with only one degree of freedom, corresponding to a small rotation about long molecular axis, L, which is perpendicular to the symmetry plane. This greatly facilitates the interpretation of the experimental results.

2 EXPERIMENTAL

Commercial carbazole was purified by means of subsequent crystallizations from ethanol followed by sublimation at reduced air pressure. Final product was again crystallized from ethanol while cooling the solution which gave thin, colorless and transparent plates of the thickness of about 0.1 mm, suitable for measurements of the optical path difference. The orientation of plates was (010).

The optical path difference, or retardation, R, was measured in the temperature interval $20 < T < 190$°C by means of a modified quarter-wave Sénarmont compensator elaborated in[9] and shortly described in.[7] The

TABLE 1

Crystallographic and physical data for carbazole crystal

Crystallographic axes,[8] in Å	Optical orientation[a]	Refractive indices[b]	Thermal expansion coeff.[10], in 10^{-6} deg^{-1}
a 7.77_2	X	n_1 1.560	β_1 122
b 19.18_2	Z	n_2 2.057	β_2 55
c 5.72_5	Y	n_3 1.726	β_3 46

[a] Optical sign positive.

[b] For $\lambda = 546$ nm, acc. to[9]

temperature was controlled with an accuracy of 0.3°C. The estimated accuracy of optical path difference measurements reached 1.5 nm. Structural data of carbazole and certain physical constants are presented in Table I. Thermal expansion coefficients have been determined by means of an X-ray method using a Bond diffractometer.[10]

3 RESULTS AND DISCUSSION

In all investigated samples of carbazole a deviation from linear relationship was observed between the retardation, R, and temperature T, starting about 156°C. Typical behaviour of $R(T)$ is shown in Figure 1. The anomaly corresponds to the phase transformation that was first observed in calorimetric investigations by Robinson and Scott,[11] and is of the crystal-to-crystal type. It has also been found in[11] by means of X-ray diffraction that the orthorhombic symmetry of the low-temperature phase does not change on transformation. This is in accordance with our observations concerning the extinction directions: they do not change in the whole temperature region.

From the linear part of the curve, i.e. in the temperature interval $20 < T < 156$°C, we have from Figure 1 a constant slope amounting to

$$\left(\frac{\mathrm{d}R_{13}}{\mathrm{d}T}\right)_{\mathrm{exp}} = -5.48\ \mathrm{nm}\cdot\mathrm{deg}^{-1}$$

where R_{13} denotes the retardation of a plate with n_1 and n_3 parallel to its plane. At room temperature (20°C) the thickness, t_0, and R_0 amount to

$$t_0 = 7.4\cdot 10^4\ \mathrm{nm}, \qquad R_0 = 12284\ \mathrm{nm}.$$

The temperature coefficient of the birefringence, $\mathrm{d}B_{13}/\mathrm{d}T$, can be calculated according to the formula[7]

$$\frac{\mathrm{d}B_{13}}{\mathrm{d}T} = \frac{\mathrm{d}R_{13}}{\mathrm{d}T}\cdot\frac{1}{t_0} - \frac{R_0}{t_0}\beta_{\perp} \tag{1}$$

where $\beta_{\perp}$ is the temperature expansion coefficient across the plate

$$\left(\frac{\mathrm{d}B_{13}}{\mathrm{d}T}\right)_{\mathrm{exp}} = -8.31\cdot 10^{-5}\ \mathrm{deg}^{-1} \tag{2}$$

The contribution of the second term of the right-hand side of (1) in our case amounts to $-0.91\cdot 10^{-5}\ \mathrm{deg}^{-1}$ and cannot be neglected in comparison to the value of the first term, $-7.4\cdot 10^{-5}\ \mathrm{deg}^{-1}$.

We will discuss the physical factors that may be responsible for the observed function of birefringence by means of Lorentz-Lorenz formula written for

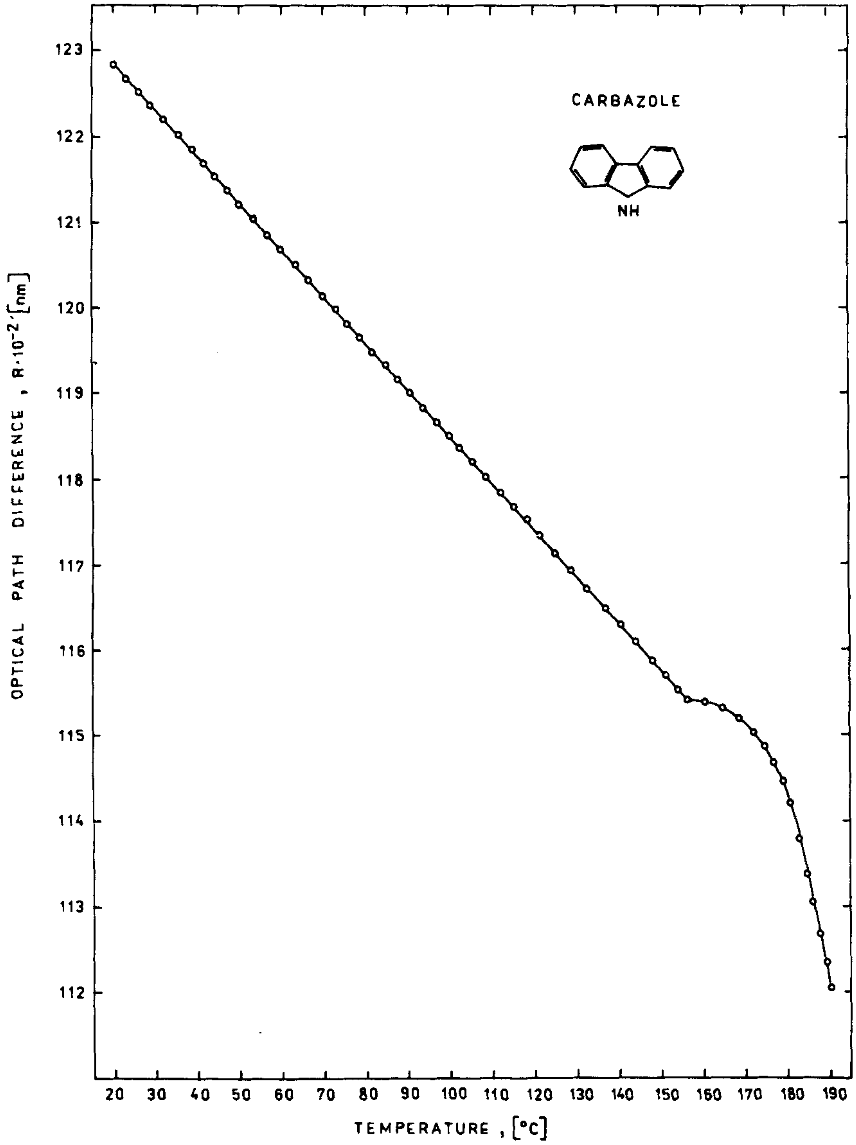

FIGURE 1 Optical path difference vs. temperature for a crystal of carbazole, $C_{12}H_9N$. Birefringence of crystal plate $B_{13} = n_3 - n_1$, $\lambda = 546$ nm. Accuracy of the measurement of the optical path difference ± 1.5 nm.

anisotropic medium. This allows for simple although not very rigorous calculation of molecular polarizabilities from optical data and for a description of microscopic changes in the crystal lattice. In spite of contemporary efforts to construct a more exact theory of the local electric field in molecular crystals, no equations are presently available that can yield unique and reasonable solutions for what is called "polarizability of a molecule within the crystal" in an anisotropic approximation. This leant us to apply approximate relationships of Lorentz-Lorenz type, supported by some new arguments. The amount of angular shift of molecules resulting from this calculation, presented in 3.1, will be confronted with a direct consideration on lattice distortion due to thermal expansion and given in 3.2.

3.1 Lorentz-Lorenz formula for anisotropic medium

This formula written for each principal direction of the optical indicatrix separately, $i = 1, 2, 3$, is of the form

$$\frac{n_i^2 - 1}{n_i^2 + 2} = \frac{4}{3}\pi\frac{1}{V}\Gamma_i \tag{3}$$

where V is the volume of the unit cell and Γ_i its polarizability in the corresponding direction. Equation (3) which is based on the assumption that the local electric field is of the form

$$F_i = \tfrac{1}{3}(n_i^2 + 2)E_i \tag{4}$$

has been used among others by Bunn and Daubeny[12,13] with good results to calculate the principal refractive indices of molecular crystals from known crystal structure and bond polarizabilities of constituent molecules. In spite of critical voices objecting some oversimplification of the form of local field used[14] the consistency of such calculations may be illustrated with some new arguments. As a matter of fact, instead of rotational ellipsoid so far used for bond polarizabilities in calculations of the polarizability of a free molecule[12,13] we can introduce new values of bond polarizabilities in a full anisotropic approximation as given by Le Fèvre.[15] Basing on his data the polarizabilities of five molecules have been calculated and are presented in Table II.

The polarizability of the unit cell, Γ, may be written in the following way

$$\Gamma = \sum_{k=1}^{\sigma} \Gamma_k = \sum_{k=1}^{\sigma} A_k \alpha A_k^T \tag{5}$$

where α is the polarizability tensor of the molecule and A_k is the orientation matrix of the k-th molecule and A_k^T means A_k transposed. Matrices A_k can

TABLE II

Molecular polarizabilities and structural information of five crystals composed of planar hydrocarbon molecules

Molecule	Polarizability in 10^{-24} cm^3 α_L	α_M	α_N	Symmetry, structure and orientation of indicatrix
Benzene	11.19	11.19	7.38	orthorhombic[16]
Naphthalene	19.61	17.58	11.61	monoclinic[17,21]
Anthracene	28.01	23.97	15.84	monoclinic[18,21]
Phenanthrene	27.01	24.99	15.84	monoclinic[19,21]
Fluorene	24.75	23.00	14.77	orthorhombic[20]

be obtained from A_1, given in structural data, by means of symmetry operations, B_k, inherent in the factor symmetry group of the crystal

$$A_k = B_k A_1 B_k^T, \qquad k = 1, 2, \ldots \sigma \tag{6}$$

with σ molecules in the unit cell. Unit cell polarizabilities referred to the principal axes of the indicatrix, XYZ, are given for the five crystals in Table III. In principle, in this system of axes all non-diagonal terms of Γ should vanish. Small values of Γ_{13} in monoclinic crystals point out to some inaccuracies in determination of optical directions on (010), however, the misorientation does not exceed 2°. Refractive indices calculated from (3) are compared with experimental values in Table IV. It is worthwhile to mention here that the calculations refer to the wavelength $\lambda = 589$ nm. Therefore, it is possible to obtain a better agreement with experimental data for naphthalene, anthracene, phenanthrene and fluorene, taking into account the dispersion of refractive indices. For similar molecular crystals it ranges from 0.01 to 0.03 for a wavelength interval 546–589 nm.[22] From Table IV we can see that the discrepancies do not exceed 3 per cent and are comparable with experimental errors which may be found while viewing n_i values reported by different authors.[22]

Concluding, we may observe that using Le Fèvre's anisotropic bond polarizabilities for a free molecule and molecular orientation from structural

TABLE III

Unit cell polarizabilities in 10^{-24} cm^3 referred to the principal axes of the indicatrix, *XYZ*

Crystal	Γ_{11}	Γ_{22}	Γ_{33}	Γ_{13}
Benzene	37.09	37.95	43.99	0
Naphthalene	25.59	33.00	39.00	0.22
Anthracene	34.63	45.07	55.86	−0.07
Phenanthrene	36.02	45.64	54.03	0.46
Fluorene	69.82	81.26	99.00	0

TABLE IV

Comparison of calculated and experimental values of principal refractive indices in crystals

Crystal	n_i	Calculated	Experimental	λ (nm)	Literature
Benzene	n_X	1.525	1.544	589	23
	n_Y	1.539	1.550		
	n_Z	1.646	1.646		
Naphthalene	n_X	1.508	1.525	546	21
	n_Y	1.696	1.722		
	n_Z	1.871	1.945		
Anthracene	n_X	1.522	1.556	546	21
	n_Y	1.725	1.786		
	n_Z	1.976	1.959		
Phenanthrene	n_X	1.529	1.548	546	21
	n_Y	1.710	1.724		
	n_Z	1.893	1.920		
Fluorene	n_X	1.547	1.578	546	21
	n_Y	1.660	1.663		
	n_Z	1.858	1.919		

data we are able to get an idea about optical properties of crystals which is compatible with experimental data. But it is not the accurate values of molecular polarizabilities of primary importance here but rather the geometrical compatibility between the macroscopic and microscopic properties of the crystal.

As no polarizability is known for carbon-nitrogen bond that participates in the structure of carbazole molecule, we can proceed this procedure in the reverse direction, i.e. we may look for unit cell polarizabilities from refractive indices. In XYZ system of axes we have

$$\Gamma = \begin{pmatrix} 65.88 & 0 & 0 \\ 0 & 80.99 & 0 \\ 0 & 0 & 105.66 \end{pmatrix} \cdot 10^{-24}\,\mathrm{cm}^3$$

From known orientation of LMN axes of the first molecule in abc axes

$$A_1 = \begin{pmatrix} 0 & -h & -(1-h^2)^{1/2} \\ 1 & 0 & 0 \\ 0 & -(1-h^2)^{1/2} & h \end{pmatrix}, \tag{7}$$

where

$$h = \cos(M, a) = \cos\theta = 0.4815, \tag{8}$$

the principal polarizabilities of carbazole molecule are

$$\alpha_L = 26.42, \qquad \alpha_M = 21.88, \qquad \alpha_N = 14.84 \cdot 10^{-24}\,\mathrm{cm}^3 \tag{9}$$

L is the longest in-plane molecular axis, N is normal to the plane of the molecule, and M completes the right-handed system of axes.

We will assume in what follows that the polarizabilities are constant, in particular that they do not depend on temperature. This assumption seems to be reasonable and was assumed also in other papers.[5] Lately only very small influence of temperature has been reported for liquid crystals.[24]

If we assume at a first approximation that also unit cell polarizabilities are independent on temperature, we can write basing on Eq. (3) the following expression for the temperature coefficient of refractive indices

$$\frac{\mathrm{d}n_i}{\mathrm{d}T} = -\frac{2}{9}\pi\frac{(n_i^2 + 2)^2}{n_i}\frac{\Gamma_i}{V}\left(\sum_i \beta_i\right) \tag{10}$$

For carbazole β_i have been measured by means of diffractometric method[10] and found to be constant in the temperature range $20 < T < 120°\mathrm{C}$. From Eq. (10) it follows that

$$\frac{\mathrm{d}n_1}{\mathrm{d}T} = -15.1 \cdot 10^{-5}\,\mathrm{deg}^{-1}, \qquad \frac{\mathrm{d}n_3}{\mathrm{d}T} = -20.9 \cdot 10^{-5}\,\mathrm{deg}^{-1},$$

and

$$\frac{\mathrm{d}B_{13}}{\mathrm{d}T} = -5.8 \cdot 10^{-5}\,\mathrm{deg}^{-1}.$$

This figure differs significantly from experimental value, $-8.31 \cdot 10^{-5}\,\mathrm{deg}^{-1}$, and clearly Γ_i cannot be assumed to be independent on temperature. The contribution of the term

$$\frac{\mathrm{d}\Gamma_{13}}{\mathrm{d}T} = \pm 8(\alpha_M - \alpha_N)\,h\,\frac{\mathrm{d}h}{\mathrm{d}T} \tag{11}$$

can be evaluated graphically. Figure 2 shows a plot of $(B_{13})_{\mathrm{calc}} = f(\theta)$ from which we can read $\mathrm{d}\theta/\mathrm{d}T = -0.16\,\mathrm{min} \cdot \mathrm{deg}^{-1}$. Direct calculation according to Eq. (5)–(7) and (11) yields

$$\frac{\mathrm{d}\theta}{\mathrm{d}T} = -0.164\,\mathrm{min} \cdot \mathrm{deg}^{-1} \tag{12}$$

Therefore, we see that the change of density is accompanied by a small angular shift of molecules. The sign of $\mathrm{d}\theta/\mathrm{d}T$, indicating the direction of reorientation of molecules, is uniquely determined by sign of $\mathrm{d}B_{13}/\mathrm{d}T$.

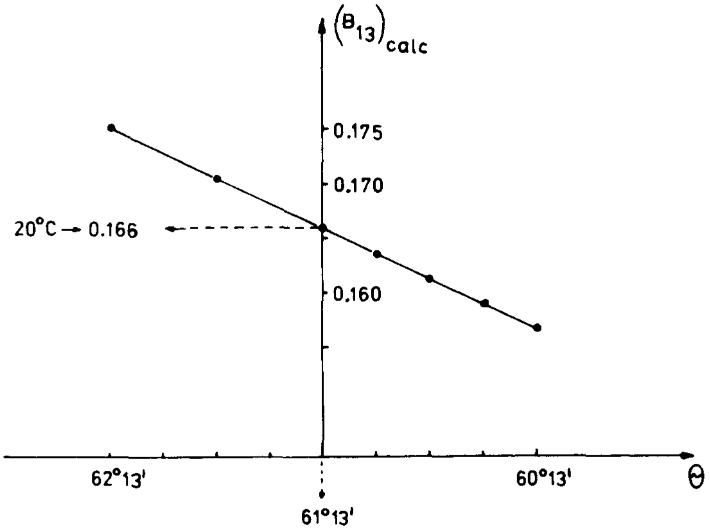

FIGURE 2 Calculated birefringence B_{13} vs. the angle θ between molecular axis M and crystal axis a.

3.2 Angular shift of a vector due to thermal expansion

Consider a vector $m||M$ whose end points are: atom N, and the projection C' of the corresponding carbon atom of the five-membered ring of carbazole molecule, Figure 3. Thus m is situated on (010) plane and so are its position vectors, $R^{(i)}$, $i = 1, 2$. The change of temperature $\Delta T = 1$ deg causes a uniform deformation so that the ends of m will shift by vectors $r^{(i)}$. We have to calculate $d\theta/dT$, i.e. the change of orientation of m for a unit change of temperature.

If we define a dimensionless matrix

$$D = \beta \cdot \Delta T \tag{13}$$

we can write the translations of N and C' as follows

$$r^{(i)} = D \cdot R^{(i)}, \qquad i = 1, 2 \tag{14}$$

The components of translations perpendicular to m are

$$\begin{aligned} r_{\perp}^{(i)} &= \left\{(r^{(i)})^2 - \frac{1}{m^2}(m^T D R^{(i)})^2\right\}^{1/2} \\ &= \left\{(D_{11}R_1^{(i)})^2 + (D_{33}R_3^{(i)})^2 - \frac{1}{m^2}[D_{11}R_1^{(i)}m_1 + D_{33}R_3^{(i)}m_3]^2\right\}^{1/2} \end{aligned} \tag{15}$$

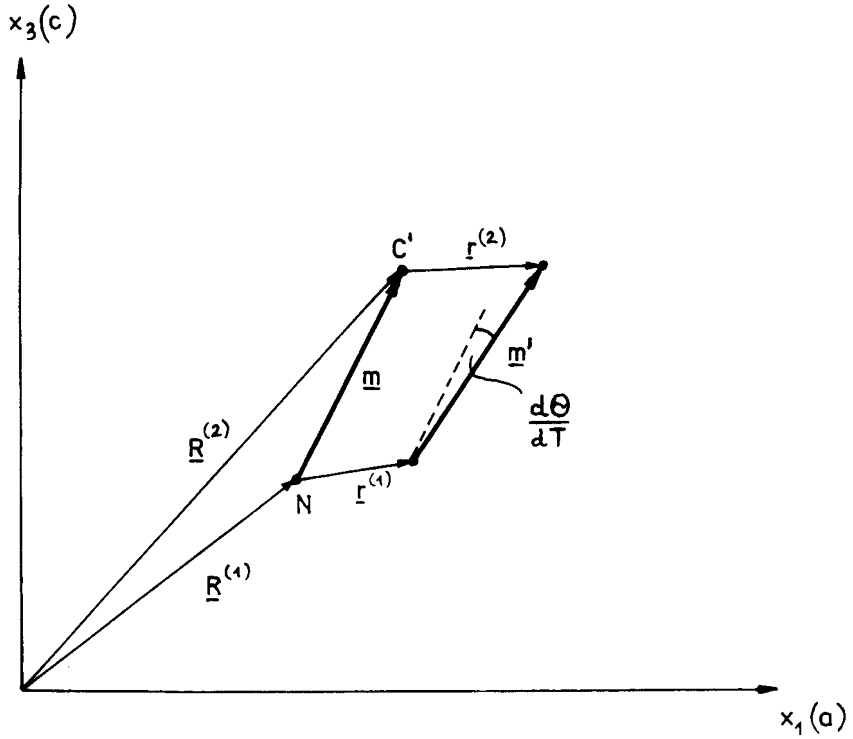

FIGURE 3 Angular shift of a vector due to thermal expansion. Comments in text.

Therefore, the angle of rotation of m equals to

$$\sin\theta \cong \theta = \frac{r_{\perp}^{(1)} - r_{\perp}^{(2)}}{m} \tag{16}$$

Using the crystal structure data[8] we can find for carbazole crystal

$N(1.844, 0, 1.343)$ and $C'(2.874, 0, 3.251)$ Å

so that

$$R^{(1)} = (2.104, 0, 1.857)$$
$$R^{(2)} = (3.134, 0, 3.765)$$
$$m = (1.030, 0, 1.908)\ \text{Å}.$$

From Eq. (15) and (16) we obtain

$$\frac{d\theta}{dT} = -31.8 \cdot 10^{-6}\ \text{rad} \cdot \text{deg}^{-1} = -0.11\ \text{min} \cdot \text{deg}^{-1} \tag{17}$$

This result is quite near to Eq. (12).

4 CONCLUDING REMARKS

We have shown on an example of carbazole that the temperature function of birefringence in the linear region can be explained quantitatively by means of two effects, both due to thermal expansion of the lattice. These are:

i) A volume effect causing the "dilution" of concentration of molecules while the lattice expands. In carbazole this effect is responsible for 70 per cent contribution in dB_{13}/dT.

ii) Small shift of orientation of molecules of the order of magnitude 10 seconds of arc per one deg.

The two cooperative effects probably correspond to the two kinds of anharmonicity of molecular motions: the former to translational, and the latter to librational vibrations.

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