

# Solvent Influence on the Electronic Absorption Spectra of B<sub>3</sub> Vitamin in Ternary Solutions

VIORREL-PUIU PAUN<sup>1\*</sup>, CRISTINA MARCELA RUSU<sup>2</sup>, MARICEL AGOP<sup>3</sup>

<sup>1</sup>Politehnica University of Bucharest, Physics Department, Faculty of Applied Sciences, 313 Splaiul Independentei, 060042, Bucharest, Romania

<sup>2</sup>“Al. I. Cuza” University, Faculty of Physics, 11 Carol I Rd., 700506, Iași, Romania

<sup>3</sup>“Gheorghe Asachi” Technical University, Physics Department, 59A Dimitrie Mangeron Rd., 700050, Iasi, Romania

*The spectral shifts in the visible electronic absorption spectra of B<sub>3</sub> in water-ethanol mixtures were correlated with the macroscopic parameters (refractive index and electric permittivity) of the solvents. The contributions of the intermolecular interactions upon the spectral shifts as a function of the solvent macroscopic parameters were expressed by multiparameter regressions. The dependence of the wave number in maximum vibronic band of B<sub>3</sub> vitamin on the solvent macroscopic parameters demonstrates the prelevance of the orientation interactions in the studied solutions. Some electro-optical parameters and global descriptors of B<sub>3</sub> vitamin were computed by Spartan program. In present, the assimilation of the B<sub>3</sub> vitamin copolymeric compounds in medicine and cosmetics must fulfill the complexity of the biological issues that result from using them. We note that the B<sub>3</sub> vitamin can be incorporated in the polymeric structures to improve its functions.*

*Keywords: solvents effects, absorption spectra, B<sub>3</sub> vitamin*

In the pharmaceutical nomenclature, B<sub>3</sub> vitamin (also known as nicotinic acid or pyridine-3-carboxylic acid) is an organic compound with the formula C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, a derivative of pyridine with a carboxyl group (COOH) at the 3-position, water-soluble and colorless. It helps the digestive system functions promoting a healthy appetite and nerves, lowering LDL cholesterol. An important role of the vitamin B<sub>3</sub> is that of a mild vasodilator - an action that results in the widening of the diameter of blood vessels leading to a greater blood flow along the arterial or venous systems.

The electronic absorption spectra of organic molecules are modified in solvation processes. When the spectrally active molecules (B<sub>3</sub>) pass from the gaseous phase to the liquid phase all spectral characteristics such as the intensity, frequency or shape of the absorption spectra undergo changes. The modifications induced by a solvent in the electronic absorption spectra of molecules can offer information on the interactions between the spectrally active molecule and the solvent molecules. The universal and specific interactions will be taken into account in the expression frequency shift. Attempts to evidence some empirical relations between the spectral characteristics and macroscopic parameters of the solvent were made in the first stage of the research on the intermolecular interactions. Intermolecular interactions were described in some kinetic or cell models [1-6]. These models based on statistical [7-13] and dielectrical [14] approach neglected the specific interactions. In order to take them into account, a supplementary term has been added to those resulting from theoretical treatment [15-17].

## Experimental part

On the basis of the relations established by different models, there can be estimated the contribution of each type of interaction between the spectrally active molecule and the solvent molecules. Usually, the supply of the specific interactions is expressed by semi-empirical terms dependent on the local distribution of the electronic

charges in the interacting molecules [18]. In Bakhshiev theory [2], the total shift measured in the electronic absorption spectra is expressed by relation of type (1):

$$\tilde{\nu} = \tilde{\nu}_0 + C_1 \cdot f(\epsilon) + C_2 \cdot f(n) \quad (1)$$

In relation (1)  $\tilde{\nu}(\text{cm}^{-1})$  is the wave number in the maximum electronic absorption band,  $\tilde{\nu}_0(\text{cm}^{-1})$  has the significance of the wave number in the maximum electronic absorption band recorded for the gaseous phase

of the spectrally active molecule,  $f(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2}$  and  $f(n) = \frac{n^2 - 1}{n^2 + 2}$  are the solvent functions which depend on the electric permittivity or refractive index. The  $f(\epsilon)$  function expresses the contributions of the orientation interaction to the total spectral shift and  $f(n)$  expresses the contributions of dispersive-induction-polarization interactions to the spectral shift. Taking into account the specific interactions, a supplementary term must be added to equation (1), obtaining the relation (2):

$$\tilde{\nu} = \tilde{\nu}_0 + C_1 \cdot f(\epsilon) + C_2 \cdot f(n) + \Delta\tilde{\nu}_{\text{sp.int.}} \quad (2)$$

Computational methods [7] are used to decide which terms are given a dominant contribution to the total spectral shift.

The separation of the universal and specific interactions permits to estimate the strength of each type of interactions acting in the solution. A great value of the regression coefficient shows that the interaction expressed by this parameter is dominant in the spectral shift [19].

Some models of ternary solutions were developed [20, 21] and their applicability to different kind of spectrally active molecules was analyzed.

In order to explain the solvatochromic effects some electro-optical parameters and global reactivity descriptors were calculated. Some parameters such as the dipole moment, polarizability, molecular orbital HOMO and LUMO energies, chemical hardness, chemical potential and electronegativity were computed.

\* email: paun@physics.pub.ro

By using Koopman theory, the frontier orbital energies are given by [22]:

$$\begin{aligned} I &= -E_{\text{HOMO}} \\ A &= -E_{\text{LUMO}} \end{aligned} \quad (3)$$

The concept of absolute electronegativity and absolute hardness are defined by [23-26]:

$$\begin{aligned} \chi &= \frac{I + A}{2} \\ \eta &= \frac{I - A}{2} \end{aligned} \quad (4)$$

The chemical potential is related to the free energy corresponding to one molecule when it is into condensed state:

$$\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \quad (5)$$

Electrophilicity index is considered as a measure of stabilization in energy when the system acquires an additional electronic charge.

These molecular properties are correlated with the reactivity and biological activity of B<sub>3</sub> vitamin.

B<sub>3</sub> vitamin was provided by Sigma Aldrich Co. Solvents ethanol and water were used for achieving ternary solutions of B<sub>3</sub> vitamin.

The ternary solutions are made of two miscible solvents in variable molar concentrations and a solute – spectrally active molecule (B<sub>3</sub>) vitamin, in a very low concentration.

The refractive index of the solvents was measured at room temperature at  $\lambda = 589.2$  nm with an Abe refractometer and electric permittivity was approximated by using formula:

$$\epsilon_{\text{mix}} = \frac{\epsilon_1 \cdot x_1 + \epsilon_2 \cdot x_2}{100} \quad (6)$$

where  $x_1$ ,  $x_2$  and  $\epsilon_1$ ,  $\epsilon_2$  are the volumetric fraction of the solvents in the ternary solutions, dielectric constants, respectively.

The electronic spectra of ternary solutions was recorded with a Shimadzu 1700 UV spectrophotometer with a data acquisition system.

## Results and discussions

In the solutions with polar components, the orientation forces play an important role on the spectral shifts. The dispersive interactions are due to the instantaneous molecular dipole moments. In dipolar solutions, a dipolar

molecule can be oriented by the electric field created by the neighboring molecules and the local reactive electric field induces an additional dipole moment. The orientation-induction interactions determine the spectral shifts which can be expressed by functions of electric permittivity and refractive index of solvents. Specific interactions of the hydrogen bond type or electron transfer can act between some parts of molecules [21]. B<sub>3</sub> vitamin is a dipolar molecule and can participate both in universal interaction (orientation, induction) and in the specific interactions in protic solvents, in which its carboxyl group can participate to hydrogen bonding with the hydroxyl proton.

The pair of solvents used for this study (ethanol and water) are able to make hydrogen bonds with the carboxyl group of B<sub>3</sub> vitamin. The volumetric fractions of the protic solvents and the wave number in the ICT visible electronic band in ternary solutions B<sub>3</sub>+ethanol+water are given in table 1.

The dependences  $\bar{\nu}$  vs.  $f(\epsilon)$  and  $\bar{\nu}$  vs.  $f(n)$  for ternary solutions evidence a great contribution of the orientation-induction interactions and of the specific interactions to the solvation energy.

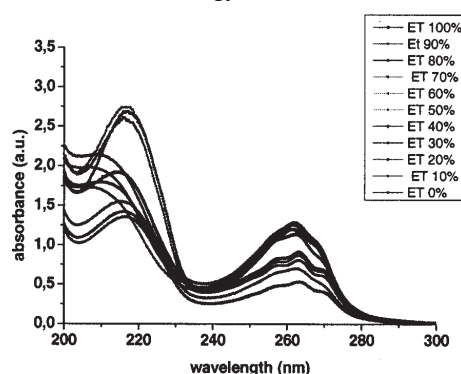


Fig. 1 Electronic absorption spectra of B<sub>3</sub> vitamin in ethanol-water mixtures

Multiparameter equations are:

$$\text{UV: } \bar{\nu} = 41377 + 572 \cdot f(\epsilon) - 17922 \cdot f(n) + 2519 \cdot \delta(\text{ppm}), R^2 = 0,98045$$

$$\text{VIZ: } \bar{\nu} = 24671 + 3775 \cdot f(\epsilon) - 4679 \cdot f(n) + 841 \cdot \delta(\text{ppm}), R^2 = 0,96847 \quad (7)$$

Contribution of the specific interactions between the protic solvents and solvate molecule was approximated by the distance from the first bisecting and the line containing points corresponding to protic solvents in the plane ( $\bar{\nu}_{\text{calc}}$ ,  $\bar{\nu}_{\text{exp}}$ ).

The values from table 2 show that in UV region, the dispersion interactions–induction-polarization are prevalent followed by specific interactions; in the visible region

No.	Ethanol (%)	n	$\epsilon_{\text{mixture}}$	$f(n) = \frac{n^2 - 1}{n^2 + 2}$	$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2}$	$f(\epsilon, n) = \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}$	$\bar{\nu}$ (cm <sup>-1</sup> )	$\bar{\nu}$ (cm <sup>-1</sup> )
1	100	1.3618	24.5	0.2216	0.8867	0.6651	37908	26998
2	90	1.3628	30.06	0.2222	0.9064	0.6842	37908	27012
3	80	1.3627	35.62	0.2221	0.9202	0.6981	37936	27130
4	70	1.3615	41.18	0.2215	0.9305	0.7090	37951	27159
5	60	1.3595	46.76	0.2204	0.9384	0.7180	37965	27174
6	50	1.357	52.30	0.2190	0.9447	0.7257	37994	27189
7	40	1.349	57.86	0.2146	0.9498	0.7352	38052	27248
8	30	1.347	63.42	0.2135	0.9541	0.7406	38081	27307
9	20	1.343	68.98	0.2112	0.9577	0.7465	38139	27307
10	10	1.336	74.54	0.2073	0.9608	0.7535	38226	27322
11	0	1.332	80.1	0.2051	0.9634	0.7583	38256	27337

**Table 1**  
PHYSICAL PARAMETERS OF THE SOLVENTS AND WAVE NUMBERS IN THE MAXIMUM OF UV-Vis band for TERNARY SOLUTIONS OF B<sub>3</sub> VITAMIN

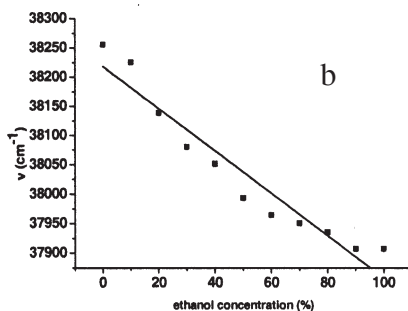
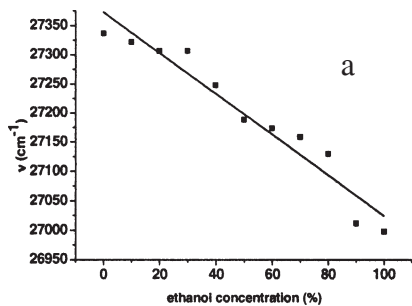


Fig. 2. Linear correlations between  $\bar{\nu}$  and ethanol concentrations for UV (a) and Vis (b)

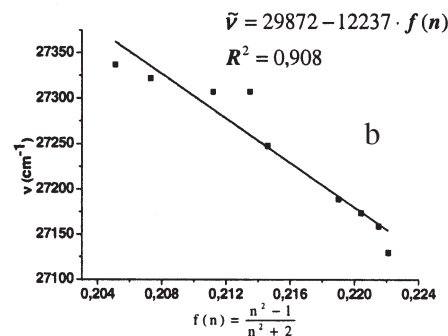
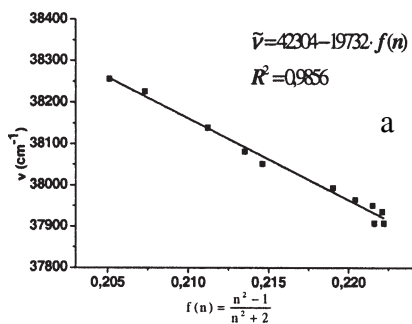


Fig. 3. Linear correlations between  $\bar{\nu}$  and  $f(n) = \frac{n^2-1}{n^2+2}$  for UV (a) and Vis (b)

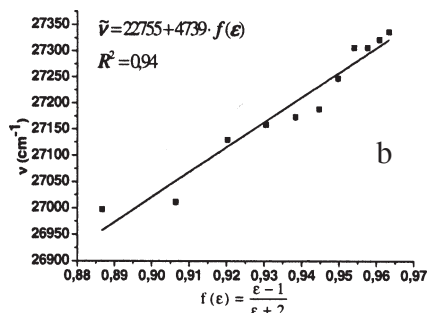
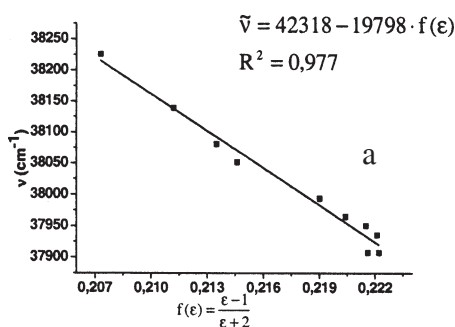


Fig. 4. Linear correlations between  $\bar{\nu}$  and  $f(\epsilon) = \frac{\epsilon-1}{\epsilon+2}$  for UV (a) and Vis (b)

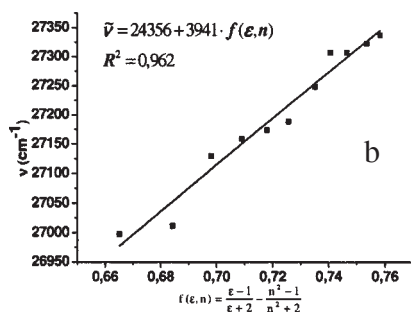
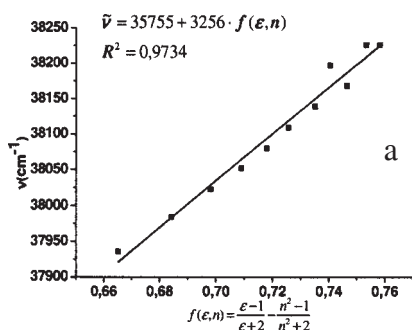


Fig. 5. Linear correlations between  $\bar{\nu}$  and  $f(\epsilon, n) = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{n^2-1}{n^2+2}$  for UV (a) and Vis (b)

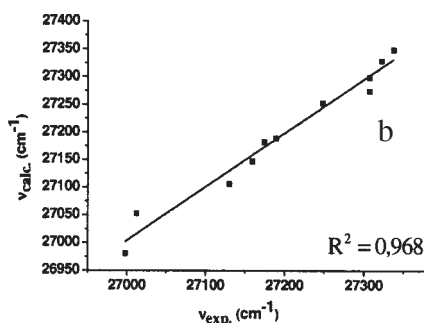
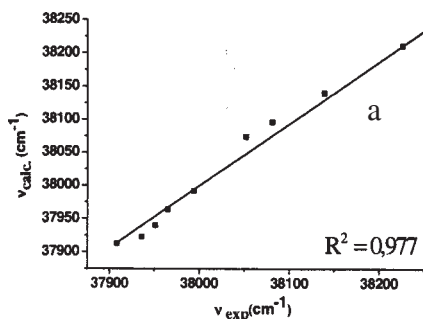


Fig. 6. Linear dependence between  $\bar{\nu}_{calc}$  for UV (a) and Vis (b)

Type of interaction	UV	Vis
$C_1 \cdot f(\epsilon)$	7.73%	65.62%
$C_2 \cdot f(n)$	55.91%	18.77%
$C_3 \cdot \delta(\text{ppm})$	36.34%	15.59%

**Table 2**  
PERCENTAGE CONTRIBUTIONS OF INTERACTIONS TO THE TOTAL SPECTRAL SHIFT

**Table 3**  
COMPUTED VALUES OF SOME ELECTRICAL PROPERTIES AND GLOBAL DESCRIPTORS FOR B<sub>3</sub> IN GROUND STATE

No.	Property	B <sub>3</sub>
1.	Heat of formation (kJ/mol)	-221.50
2.	Dipole moment (Debye)	3.42
3.	Polarizability (a.u.)	48.884
4.	E <sub>HOMO</sub> (eV)	-10.719
5.	E <sub>LUMO</sub> (eV)	-0.925
6.	Gap energy ( $\Delta E$ ) (eV)	9.794
7.	Electronegativity (eV)	5.822
8.	Hardness (eV)	4.897
9.	Chemical potential	-5.822
10.	Index of electrophilicity (eV)	3.46

**Table 4**  
COMPUTED VALUES OF SOME ELECTRICAL PROPERTIES AND GLOBAL DESCRIPTORS FOR TERNARY SOLUTIONS OF B<sub>3</sub>

No.	Property	B <sub>3</sub>
1.	Heat of formation (kJ/mol)	-78.969
2.	Dipole moment (Debye)	4.16
3.	Polarizability (a.u.)	54.96
4.	E <sub>HOMO</sub> (eV)	-10.538
5.	E <sub>LUMO</sub> (eV)	-1.326
6.	Energy gap ( $\Delta E$ ) (eV)	9.212
7.	Electronegativity (eV)	5.932
8.	Hardness (eV)	4.606
9.	Chemical potential	-5.932
10.	Index of electrophilicity (eV)	3.819

orientation interactions are dominant. The coefficient C<sub>1</sub> is positive demonstrating that the orientation forces determine a spectral shift to lower wavelengths. The coefficient C<sub>2</sub> is positive, suggesting that the universal interactions determine a spectral shift to high wavelength. Consequently, the dispersive and specific interactions determine a decrease of the wavelength (UV range) in the maximum of  $\pi \rightarrow \pi^*$  band; on the other hand, in the visible range, the orientation interactions dominate and determine a spectral shift towards lower wavelengths.

The behaviour of pyridine 3- carboxylic acid and its absorption spectra were studied in different solvents [27-30]. Some properties as the dipol moment, the polarizability, the energies of HOMO, LUMO orbital etc. can be estimated by using molecular program [31].

The optimized geometry of B<sub>3</sub> was made using a RHF/PM3 as illustrated in figure 7.

The electrical parameters and the global descriptors of B<sub>3</sub> in the ground state, obtained by using Spartan program are listed in table 3.

Between B<sub>3</sub> vitamin and the protic solvents there can be achieved both intermolecular and intramolecular hydrogen bonds, as shown in figure 8.

The chemical reactivity and the stability of the system (ternary solutions) were compared with those from binary solutions (B<sub>3</sub>+water and B<sub>3</sub>+ethanol) tabulated in table 4.

Higher reactivity is demonstrated by the hardness as seen from the values contained in tables 4 and 5. In accordance with the principle of maximum hardness which postulates that the system is more reactive as the hardness is lower, it can be observed that molecular structure from ternary solutions is more reactive than binary solutions.

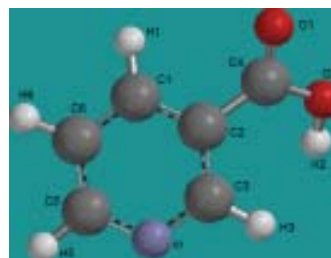


Fig.7. Optimized geometry of B<sub>3</sub> vitamin (PM3 method)



Fig. 8. Possible intermolecular hydrogen bonds formed between B<sub>3</sub>-water-ethanol (red -oxygen atoms, gray-carbon atoms, white-hydrogen atoms, blue-nitrogen atom, broken yellow line- hydrogen bonds)

**Table 5**  
GLOBAL DESCRIPTORS FOR BINARY SOLUTIONS OF B<sub>3</sub>

No.	Molecular complex	$\chi$ (eV)	$\eta$ (eV)	$\mu$ (eV)	$\omega$ (eV)
1.	B <sub>3</sub> +water	5.5725	4.91	-5.5725	3.161
2.	B <sub>3</sub> + ethanol	5.5345	4.9055	-5.5345	3.121

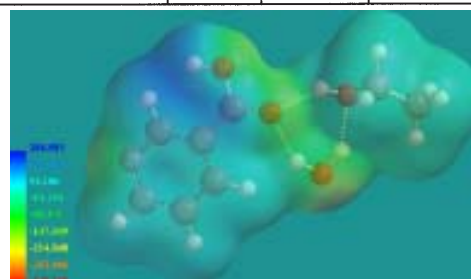


Fig. 9. Molecular electrostatic map of molecular complex B<sub>3</sub>-water-ethanol

Because the electrophilicity index is considered a measure of the stability of the system, we can say that the ternary solution is more stable than the binary solutions.

Electrophilicity quantify the tendency of molecules to accept electrons from a donor. The higher electrophilicity index is, a greater ability to attract electrons the molecules have.

The electrostatic potential is the energy of interaction of a point positive charge (an electrophile) with the nuclei and electrons of a molecule. Negative electrostatic potentials (fig. 9) indicate areas that are prone to electrophilic attack. Colours towards red indicate negative values of the electrostatic potential, while colors towards blue indicate positive values of the potential.

The surface colour reflects the magnitude and polarity of the electrostatic potential. Gray, violet and blue colours correspond to a negative electrostatic potential - regions of the molecule susceptible to electrophilic attack.

The HOMO and LUMO orbitals are commonly known as Frontier Orbitals and were found to be extremely useful in explaining chemical reactivity. Electrophilic attacks were shown to correlate very well with atomic sites having high density of the HOMO orbital, whereas nucleophilic attacks correlated very well with atomic sites having high density of the LUMO orbital (fig. 10).

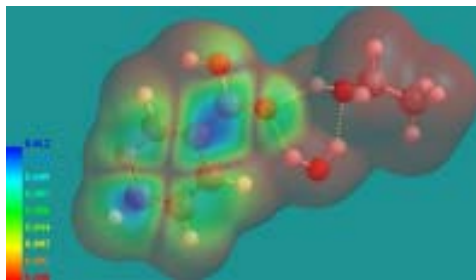


Fig. 10. LUMO map plotted by Spartan

LUMO map: by convention, colour blue indicates a high concentration of orbitals, while the colours to red indicate a low concentration. LUMO orbitals map is important because it shows the potential areas where nucleophilic attack will occur. In the case of carbon atoms there is observed an electrophilicity characteristic. The intense red region shows where there will be most likely nucleophilic attack.

A good electrophile is characterized by a high electronegativity and a low hardness, so that, the ternary solutions formed between B<sub>3</sub>-water-ethanol is a better electrophile than binary solutions B<sub>3</sub> + water or B<sub>3</sub> + ethanol (tables 4 and 5).

Finally, in accordance with the author [32-33], we can say that is important to embed B<sub>3</sub> vitamin in copolymers in order to improve product quality cosmetics and pharmaceutical industry.

## Conclusions

The study regarding solvent effects on the electronic absorption spectra recorded in ternary solutions can contribute to estimate each type of interactions.

The Bakhshiev theory for pure liquids could be applied to the ternary solutions made of two pure solvents (water and ethanol) and spectrally active molecules (B<sub>3</sub> vitamin) at very low concentrations. It was introduced an empirical term in order to estimate the specific interactions.

The linear correlations between  $\bar{\nu}_{calc}$ ,  $\bar{\nu}_{exp}$  permit to estimate the contributions of each type of intermolecular interactions to the total spectral shift computed in a given mixture.

The computational method PM3 gives the values of some parameters for ternary solutions such as dipole moment, polarizability, total energy, molecular orbital HOMO, LUMO energies and some global descriptors such as electronegativity, hardness, chemical potential, electrophilicity index.

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