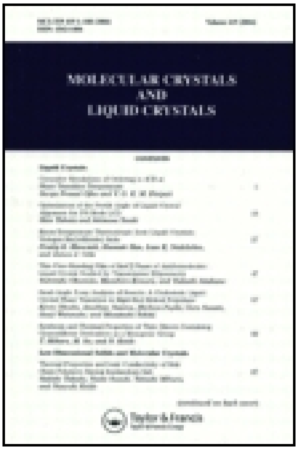

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Study of Orientation and Order of Non-mesogenic Solutes in Liquid Crystalline Matrix by Infrared Spectroscopy

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To cite this article: P. Chingduang , S. Bualek , O. Phaovibul & B. Schrader (1986): Study of Orientation and Order of Non-mesogenic Solutes in Liquid Crystalline Matrix by Infrared Spectroscopy, Molecular Crystals and Liquid Crystals, 132:1-2, 131-141

To link to this article: http://dx.doi.org/10.1080/00268948608079534

Mol. Cryst. Liq. Cryst., 1986, Vol. 132, pp. 131–141
0026-8941/86/1322-0131/$20.00/0

Printed in the United States of America

Study of Orientation and Order of Non-mesogenic Solutes in Liquid Crystalline Matrix by Infrared Spectroscopy†

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(*Received November 27, 1984, in final form April 15, 1985*)

The orientation and order of molecules of solutions containing a non-mesogenic solute, n-alkylbenzenes and halobenzenes, in the nematic solvent N-(p-ethoxybenzylidene)-p'-n-butylaniline, EBBA, were investigated by the measurement of the intensity of the absorption bands in the infrared region of both homogeneous and homeotropic aligned samples. The results show that the decrease of the nematic-isotropic transition temperature, T_c, depends on the size and shape of the non-mesogenic guest molecules. Increasing length of the flexible end chain (n-alkyl group) of the n-alkylbenzene homologous series decreases T_c of the mesomorphic mixture. Increasing the size of the atomic radius of the halogen atom of the halobenzene homologous series also decreases T_c of the mixture. Since the order parameter of host molecules depends on the cell preparation, the order parameter of the dissolved n-alkylbenzenes and halobenzenes was evaluated for a constant solvent order. Plotting these results against the number of C-atoms of the alkyl side chain shows an odd-even effect. The order parameter of halobenzene guest molecules decreases slightly with increasing radius of the halogen atom.

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†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

INTRODUCTION

The order parameter, S, of nematic liquid crystal, which was deduced by Maier and Saupe as $S = 1/2 < 3\cos^2\theta - 1 >$ (where θ is the angle between the major molecular axis and the preferred direction of nematic phase) can be determined by several methods.[1] Infrared dichroism is one such technique that can be conveniently carried out for determining the order parameter of pure nematic liquid or mixtures of nematogenic or non-nematogenic solutes in nematic solvents.[2-6] There are two methods for sample preparation used in the determination of the order parameter, leading to either homogeneous or to homeotropic molecular alignment. For homogeneous alignment, absorbance $A_\parallel$ and $A_\perp$ for plane polarized light with the electric vector parallel and perpendicular to the preferred axis of nematic phase, resp., are measured. The dichroic ratio R, defined as $R = A_\parallel/A_\perp$, for a particular absorption band at a fixed temperature is then used to calculate the order parameter from the following equation:[1]

$$S = \frac{R-1}{R+2}\,\frac{1}{\frac{1}{2}(3\cos^2\alpha - 1)} \qquad (1)$$

where α is the angle between the transition moment and the molecular axis. This is reduced to

$$S = (R-1)/(R+2) \qquad \text{where } R > 1 \qquad (2)$$

for a band whose transition moment is parallel to the major molecular axis (parallel transition moment) and

$$S = 2(1-R)/(R+2) \qquad \text{where } R < 1 \qquad (3)$$

for a band whose transition moment is perpendicular to the long molecular axis (perpendicular transition moment). For homeotropic alignment, no polarizer is needed. The ratio of absorbances of a particular band at a fixed temperature in nematic phase, A_N, to that of the isotropic phase, A_{ISO} (extrapolated from isotropic phase, dashed lines in Figure 3), is defined as the dichroic ratio $R' = A_N/A_{ISO}$. In this case, the order parameter can be calculated from the following formula:[6]

$$S = (1 - R')\,\frac{1}{\frac{1}{2}(3\cos^2\alpha - 1)} \qquad (4)$$

which is simplified to

$$S = 1 - R' \qquad \text{where } R' < 1 \tag{5}$$

for parallel transition moment and

$$S = 2(R' - 1) \qquad \text{where } R' > 1 \tag{6}$$

for perpendicular transition moment.

The purpose of the present study is to investigate the effect of structure of the solute molecules on their orientational order in a nematic matrix of equally ordered. The systems studied were homologous series of n-alkylbenzenes and halobenzenes in the nematic solvent, EBBA. Furthermore, results obtained from homogeneous and homeotropic alignment are compared.

EXPERIMENTAL

A. Materials

Solvent: N-(p-Ethoxybenzylidene)-p'-n-butylaniline, EBBA, prepared in our laboratory (nematic range 35–79°C), was used as the solvent throughout this study.

Solutes: The solutes are n-alkylbenzenes, $C_6H_5-C_nH_{2n+1}$, where $n = 3 - 10$ and halobenzenes, C_6H_5-X, where $X = Cl$, Br and I. These compounds were purchased from Fluka and E. Merck Company and purified by distillation as necessary.

B. Instruments

Infrared spectrophotometers, Perkin-Elmer Model 180 (resolution 2 cm^{-1} at wave number 700 cm^{-1}), interfaced with the central computer and Perkin-Elmer Model 683 equipped with the Data Station 3500 (resolution 2.5 cm^{-1} at 1100 cm^{-1}) were used for this study. An aluminium wire grid polarizer (Cambridge Physical Sciences) was placed at the entrance slit of PE 180 whereas this was placed in the sample compartment of PE 683 for the polarization measurements of the homogeneous sample. Averaged spectra were obtained by the multiscanning method. Phase transitions of the solutions containing a non-mesogenic solute in EBBA were observed on a heating stage microscope, Mettler model FP 52.

C. Preparation of samples and measurement of infrared spectra

The homogeneous molecular alignment was achieved by rubbing of NaCl (and KBr) cells on a fine tissue paper for about 100 times and confirmed for its homogeneity between two crossed polaroids. The absorbance $A_{\parallel}$ and $A_{\perp}$ of some selected bands were taken at various temperatures. The order parameters were then determined from these bands by using Eq. (2) or (3). The clearing temperature was taken to be the temperature at which the order parameter is extrapolated to zero.

Coating a very thin film of lecithin on NaCl plates induced the homeotropic molecular alignment of the sample. Absorbances of selected bands were measured at various temperature up to 10°C above the clearing point. T_c was determined from the intercept of the linear decrease of the absorbance with the non-linear curve (see Figure 3). The linear range above T_c was extrapolated to the low temperature region (dashed line) so that A_{ISO} at different temperature could be read out. The order parameter was then calculated by Eqs. 5 or 6. One band was used to determine the order parameter of EBBA, *viz.* at 841 cm^{-1}, which is due to the γ (C-H) vibration of disubstituted benzene, perpendicular transition moment. This band gives the highest value of order parameter of the solvent. The absorption band

TABLE I

Nematic-isotropic transition temperature (in °C) of solutions containing a non-mesogenic solute in EBBA (mole fraction 0.15)

	Temperature (°C) observed by		
		IR(±0.5°C)	
Solute	microscope*	homeotropic alignment	homogeneous alignment
propylbenzene	52.2 - 56.0	51	50
butylbenzene	45.0 - 49.5	46	48
pentylbenzene	46.4 - 49.0	48	47
hexylbenzene	43.9 - 47.4	44	45
heptylbenzene	43.9 - 50.3	45	47
octylbenzene	44.2 - 48.5	45	46
nonylbenzene	43.9 - 48.4	–	46
decylbenzene	– –	–	46
chlorobenzene	57.2 - 59.1	56	55
bromobenzene	51.3 - 53.8	51	52
iodobenzene	48.1 - 51.7	49	49

*The temperature range is from the first appearance of the isotropic droplets to the complete change to the isotropic phase.

chosen for calculating the order parameter of the solutes is at 701 cm^{-1} for n-alkylbenzenes and at 686 cm^{-1} for halobenzenes, which corresponds to the C-C-C out of plane bending of monosubstituted benzene,[7] perpendicular transition moment. All samples contained solutes at a mole fraction of 0.15 and the spacers were 10 μm thick.

RESULTS AND DISCUSSION

Nematic-isotropic transition temperature (T_c) of solutions containing an alkylbenzene or halobenzene in EBBA (mole fraction 0.15) are listed in Table I as observed by a heating stage microscope and also as obtained by extrapolation of the IR measurements for homogeneous and homeotropic techniques. Clearing points of the mixture decrease as the solute molecules are longer in the alkylbenzene series or larger in the case of the halobenzenes.

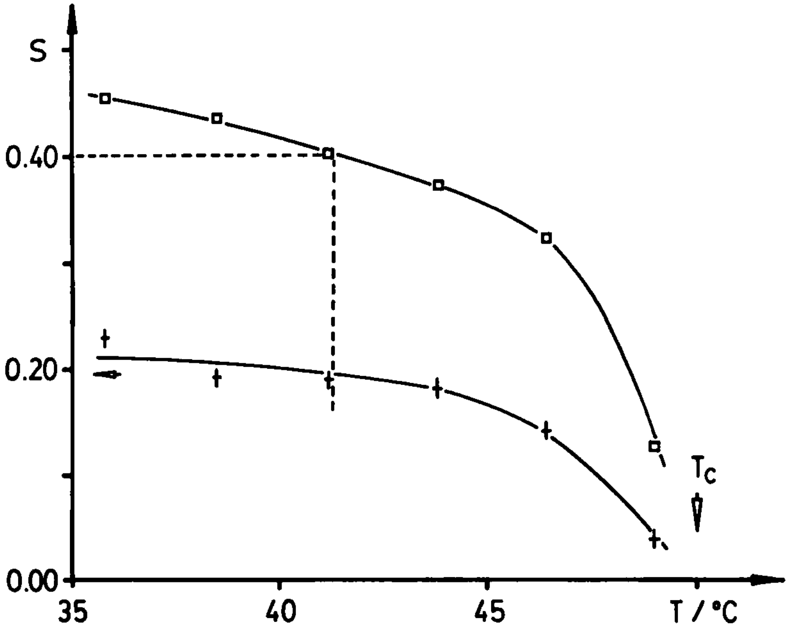

FIGURE 1 Temperature dependence of the order parameter of n-propylbenzene in EBBA (mole fraction 0.15) for homogeneous alignment, □ = solvent, + = solute.

3.1 n-Alkylbenzenes

3.1.1 Homogeneous samples

Solutions of n-alkylbenzenes (mole fraction 0.15) in EBBA have been studied in homogeneous alignment. A typical result of the temperature dependence of the order parameter is shown in Figure 1 for propylbenzene. The upper curve shows the order parameter of the solvent as calculated using band at 841 cm^{-1} (□) and the lower curve shows the order parameter of the solute as calculated using band at 701 cm^{-1} (+). Similar results were obtained for other solutes with varying alkyl end groups.

Since homogeneous molecular alignment depends on sample preparation, the order parameter thus varies from sample to sample. In order to compare results, the order parameter of the solutes were taken at a constant value of the order parameter of the solvent, namely at $S_{\mathrm{solvent}} = 0.4$ (dashed line). These values are shown in Figure 2 where they are plotted against the number of C-atom of the solute end chain. A clear odd-even effect can be observed in this series. The results reveal that alkylbenzenes with odd number of C-atoms have higher order than those of even number. This can be explained in a similar way as previously described by Marcèlja,[8] i.e. the odd number of C-atoms at the alkoxy group deviates from the main molecular axis and therefore the ordering of the molecules in the nematic matrix is lower than those of even number. The results obtained in the present work for odd number of C-atom in alkylbenzenes are equivalent to the even number of C-atom in alkoxyazoxybenzene series as studied by Marcèlja because of the absence of the O-atom. Deviation of S by odd-even effect from the nearly horizontal line (Figure 2) reveals that as the side chain becomes longer the orientation of the solute molecules remains essentially unchanged. This suggests that the configuration of the solute end chain (up to 10 C-atoms) are all trans otherwise the trend of S should decrease with increasing number of carbon atoms.

3.1.2 Homeotropic sample

An example of the temperature dependence of absorbance for a homeotropic alignment is shown in Figure 3 for butylbenzene. As described in the experimental part, the data obtained from Figure 3 were used to calculate the order parameter of both solvent and solute. These are shown in Figure 4 as a function of temperature. The order parameter of the solutes read at $S_{\mathrm{solvent}} = 0.4$ and plotted against the

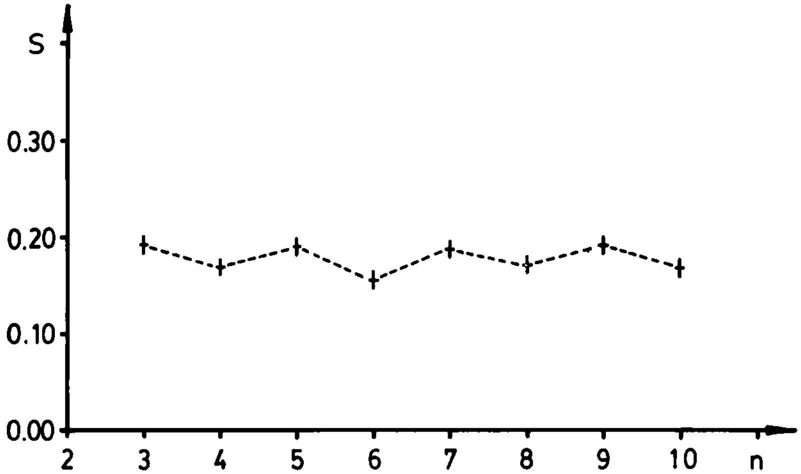

FIGURE 2 Order parameters of n-alkylbenzene taken at S(solvent) = 0.4 plotted as a function of the number of C-atoms of the solute alkyl side chain, for homogeneous alignment.

number of C-atoms of the alkyl side chain is given in Figure 5. The alternation of S according to odd and even number of C-atom is not as clear as those obtained by the homogeneous method. The results shows that there is a trend for longer alkylbenzene molecule to have higher order than the shorter one. This might be due to the interaction of the alkyl group with the non-polar part of the lecithin molecules. The order parameters obtained from homeotropic method is in general found to be higher than those from homogeneous alignment but the data points are more scattered (compare Figure 1 and 4). This may arise from the linear extrapolation (dashed lines in Figure 3). A small deviation in these lines may cause large error in calculation of order parameter. In addition, the quantity of lecithin coated on NaCl plates could not be quantitatively controlled. This may be another reason why the reproducibility of the results is rather poor, even though the sample was checked between crossed polaroids to be completely dark prior the measurements.

3.2 Halobenzenes

The order parameter of the solutes in the halobenzene series taken at a constant $S_{solvent}$ = 0.4 are plotted (Figure 6) against the atomic radii of the halogen for homogeneous alignment. Measurement of

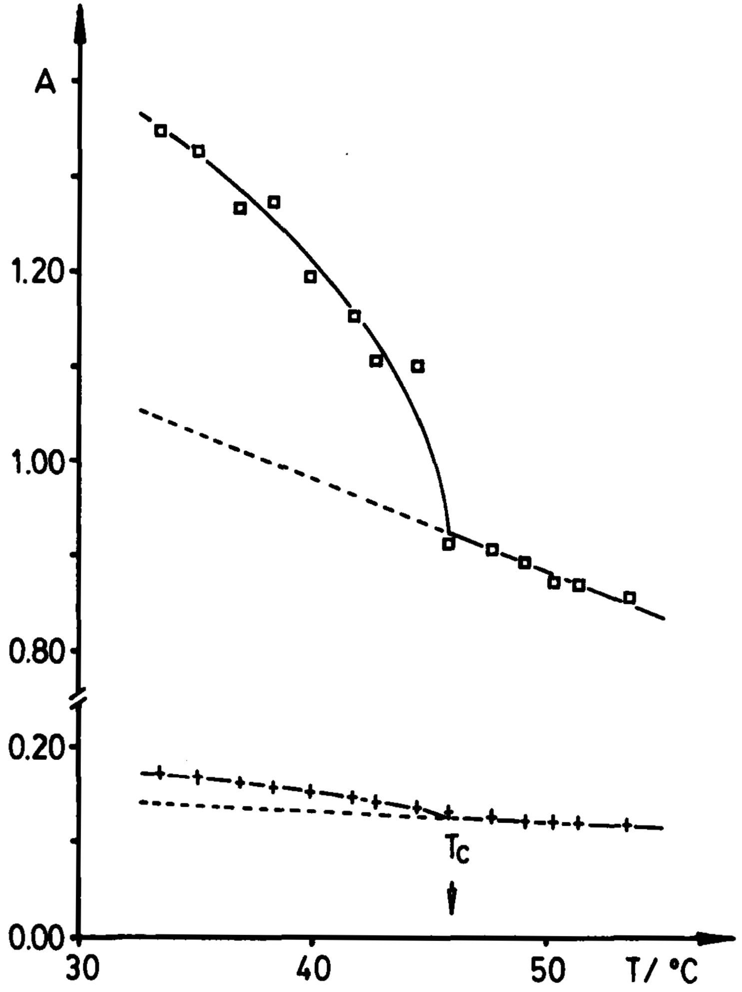

FIGURE 3 Temperature dependence of absorbance of a homeotropic sample of n-butylbenzene in EBBA (mole fraction 0.15) □ = solvent, + = solute.

the order parameter using homeotropic technique were also carried out for this series but the results were even less reproducible than the first series. Smearing of lecithin on NaCl cell either once or twice gave greatly different results. This might be due to some interaction between the halobenzene and lecithin. Therefore the homeotropic results for this series is not presented. The results in Figure 6 indicate slight decrease in the ordering of solute molecules as the size of the substituent halogen atom increases. As would be expected, the pack-

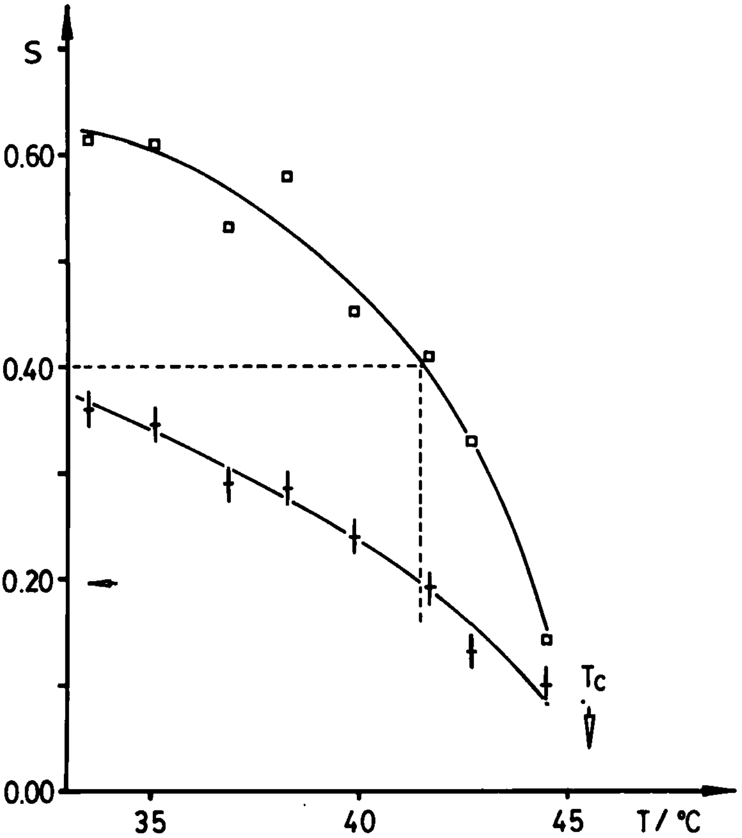

FIGURE 4 Temperature dependence of order parameters of both solvent (□) and solute (+) calculated from the data in Figure 3, for homeotropic alignment.

ing of increasingly larger globular molecules within the nematic matrix should cause less ordering.

Thickness of the samples used throughout this work was 10 μm because thicker samples gave too high absorbance and hence too high noise of the solvent band at 841 cm^{-1} ($A > 1.3$). However, by averaging 20 scans in order to reduce the noise level, the value of $S_{solvent}$ has been observed to be about 0.1 lower than for the sample of 30 μm thickness. This is certainly because of the surface effect. However, the value of S_{solute} which was taken at $S_{solvent} = 0.4$ remains approximately the same within the range of experimental error.

The present work reports the value of order parameter of the solutes taken from the normalized nematic environment, i.e. at $S_{solvent}$

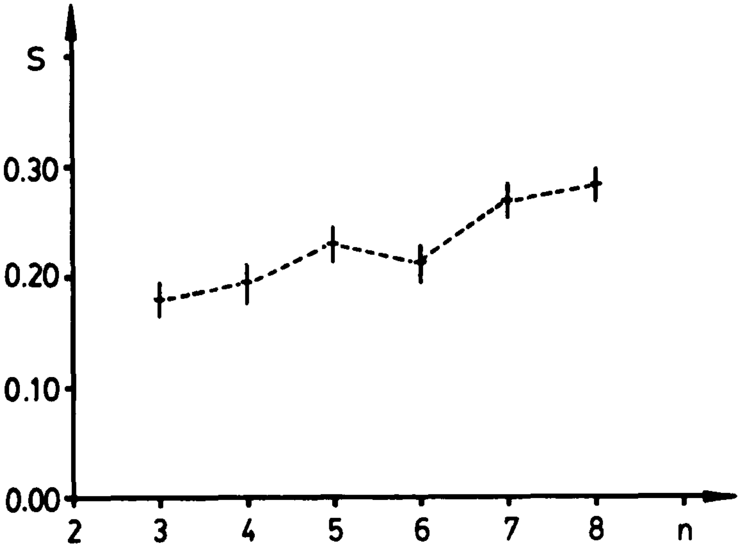

FIGURE 5 Order parameters of n-alkylbenzene taken at S(solvent) = 0.4 plotted as a function of the number of C-atoms of the solute alkyl side chain, for homeotropic alignment.

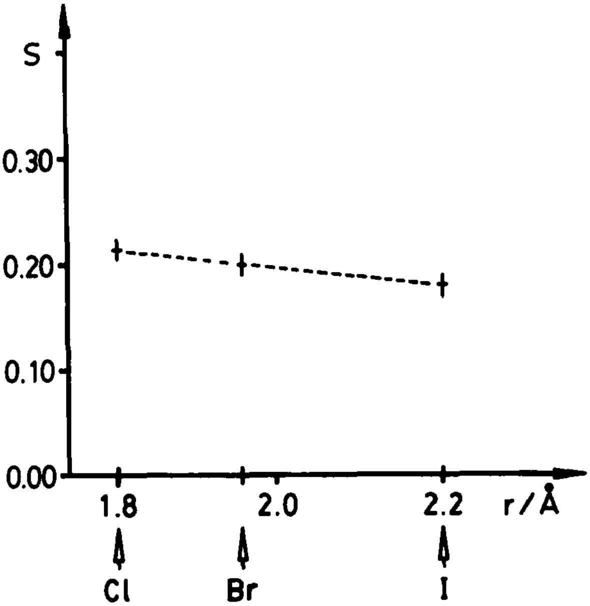

FIGURE 6 Order parameters of halobenzenes in EBBA (mole fraction 0.15) taken at S(solvent) = 0.4, plotted against the atomic radii of the halogen atoms, for homogeneous alignment.

= 0.4, in order to see the influence of the solute structure on their orientation. A few assumptions were made for the calculation of the order parameter. First, equation (3) or (6) are based on the assumption that the direction of the transition moment is exactly perpendicular to the long axis of the molecule. Second, the order parameter D[9] were not taken into account since the molecular structure of both solute and solvent studied could be regarded as non-planar molecules. Third, no internal field[1] correction was made.

Acknowledgment

The authors wish to thank the Volkswagen Foundation for the financial support. We are indebted to Dr. E. H. Korte and Dr. P. Limcharoen for valuable discussions. We also thank Dr. Prapin Wilairat for correcting the manuscript.

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