Calculation of UV/VIS absorption spectra of liquid crystals and dye molecules An INDO MO approach

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Calculation of UV/VIS absorption spectra of liquid crystals and dye molecules

An INDO MO approach

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The electronic transitions in the UV/VIS range of liquid crystals and stilbene dyes, which are of commercial and applicational interest, have been studied theoretically by a semi-empirical INDO (intermediate neglect of differential overlap) CI (configuration interaction) approach. Experimentally obtained polarized UV/VIS spectra of the systems investigated can be reproduced with reliable accuracy by the theoretical model. Measured and calculated $\pi-\pi^*$ transitions differ frequently by less than 30 nm. The main absorption bands are strongly polarized parallel to the principal molecular axis.

1. Introduction

Since the first applications of liquid-crystalline materials in the early seventies the commercial interest in this field of research has steadily increased. Besides the common display applications with very fast switching times and high resolution, it can be expected that liquid crystals will also be used as a carrier material in a rather new field of research, i.e. the examination of non-linear optical properties of organic molecules. These compounds contain an extended conjugated aromatic moiety. Asymmetric substituted stilbene derivatives are of great utility as chromophores in second harmonic generation because of their large hyperpolarizibility and large ground state dipole moment [1–3]. A theoretical insight into the electronic structure properties, which have a pronounced influence on the desired material parameters, for example non-linear optical properties, is required for further experimental investigations.

The aim of this paper is the theoretical evaluation of the key electronic quantities of liquid-crystalline materials and dyes containing different aromatic units such as simple benzene rings or more complex biphenyl, tolane or stilbene systems. The compounds investigated are listed in table 1. In our view there is a need for the estimation of dipole moments in the electronic ground state, the calculation of the electronic transition energies together with the associated band intensities as well as the direction of the transition moment relative to macroscopic parameters such as the orientation of the director. Both groups of materials, liquid crystals and stilbene dyes, show strong absorptions in the UV/VIS range, which are very sensitive to changes in the electronic

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Table 1. Acronyms and chemical structure of all of the compounds investigated.

Compound	Structure
PCH5	C_5H_{11} —(H)—(O)— CN
NCS3	C_3H_7 —(H)—(O)— NCS
ECCP-CN	C_3H_7 —(H)—(H)— C_2H_4 —(O)— CN
5CB	C_5H_{11} —(O)—(O)— CN
5OCB	$C_5H_{11}O$ —(O)—(O)— CN
T-33FF	C_3H_7 —(O)—(O)—(O)— C_3H_7; F F
T-3FF3	C_3H_7 —(O)—(O)—(O)— C_3H_7; F F
PTP502FF	C_5H_{11} —(O)— C≡C —(O)— OC_2H_5; F F
ANS	O_2N —(O)— = —(O)— NH_2
DANS	O_2N —(O)— = —(O)— $N(CH_3)_2$
HHNS	O_2N —(O)— = —(O)— $O(CH_2)_6OH$

environment. This suggests an investigation of the modifications in these material parameters as a function of different chemical substituents and the position of these groups in the aromatic framework, both experimentally and theoretically.

In this context it is a central question as to whether or not these changes in material properties can be estimated by the methods of molecular quantum chemistry. At present the available computational facilities allow the investigation of larger organic systems. Thus ionization potentials, electronic transition energies, molecular geometries and charge distributions, can be reproduced, quite often with remarkable accuracy. *Ab initio* calculations cannot be used because of the large number of atomic centres in the organic molecules investigated. Therefore, semi-empirical molecular orbital models have to be employed. In the present work we adopt a model hamiltonian based on the intermediate neglect of differential overlap approximation (INDO). The

latter method, which was originally designed to reproduce one-electron properties such as ionization potentials and electronic transition energies for organic compounds containing transition metal atoms, allows us to investigate molecules including 80 atoms with reliable accuracy. The capability of the INDO/MO method is described in [4–7], and will be demonstrated here by comparing the known experimental spectra of all the compounds with the calculated data. Up to now only a few spectra of liquid crystals and stilbene dyes have been compared with model calculations [6–12]. Therefore we felt it necessary to perform a more detailed numerical evaluation of the UV/VIS spectra. Previously we have shown [13] that the adopted INDO/MO model is of reliable accuracy to reproduce electronic spectra of π-compounds containing different aromatic substructural elements which are also partially found in the present model systems.

2. Electronic transitions in organic molecules

For the theoretical evaluation of the electronic absorption behaviour of molecules the wavefunctions ϕ_0 and ϕ_i of the electronic ground and the single excited states have to be described using a MO LCAO approximation in an atomic orbital basis. Since electronic excitation processes involve an interaction of the charged electron with the fluctuating electric field of the electromagnetic radiation, it is expected that the absorption depends on common localization properties of ϕ_0 and ϕ_i in the z direction, which is the principal direction of the oscillating electric vector. Of course, an electronic transition is only possible if the direct product of the ground state wavefunction, that of the excited state and the dipole moment operator, contains the totally symmetric representation. For a given excitation the transition probability is usually character-ized by the oscillator strength $f_{0,i}^{(r)}$, which is related to the integrated intensity of the absorption band; here r represents the electron position vector [14]. The macroscopic expression for the intensity of an absorption band, the extinction coefficient ε, can be deduced from the square of the transition moment on a microscopic level. The description of molecular quantities by quantum chemical methods underlies some principle restrictions, i.e. there exists a compromise between the complexity of the systems studied and the accessible theoretical accuracy. For the calculation of electronic spectra on the basis of one-determinantal ground state calculations in a MO basis the configuration interaction method is widely employed [15]. Using a CI procedure in combination with a semi-empirical model hamiltonian an evaluation of the electronic absorption spectra of large organic molecules becomes possible. The liquid crystals and dye molecules examined consist of more than 30 atoms and contain aromatic substructures such as benzene or more extended conjugated systems (see table 1). The principal absorption bands are due to π–π^* transitions in the benzene analogous part of the molecule. In pure benzene three π–π^* transitions in the low energy range are observed; the strongest band with twofold degeneracy is the spin and symmetry allowed $^1A_{1g} \rightarrow {}^1E_{1u}$ transition at 180 nm. A smaller intensity shows the spin allowed but dipole forbidden $^1A_{1g} \rightarrow {}^1B_{1u}$ transition around 203 nm. The $^1A_{1g} \rightarrow {}^1B_{2u}$ transition at 256 nm is symmetry forbidden and is, therefore very weak [16]. These benzene-like transitions are roughly conserved in the model systems studied, but they are influenced by the conjugation length and the different substituents in the π frames.

Experimental UV/VIS spectra show, in general, broad absorption bands. The main reasons which cause this broadening are the interactions of the chromophore with the solvent environment, different vibrational transitions accompanying the electronic

absorption, collisional broadening and Doppler broadening. Therefore, transitions separated by less than 10–20 nm are frequently not resolvable. In a complex conjugated aromatic molecule like the biphenyl or stilbene systems examined a large number of excited states can exist within a rather small energy interval. This leads to close lying transition energies, which cannot be separated in the experiment. Depending on the localization properties of the wavefunctions of the configurations participating in the electronic transitions, we find shifts in the electronic transition energies which are controlled and influenced by the position of the chemical substituents in the corresponding π systems.

3. Computational considerations

Common structural parameters of the systems considered such as bond lengths and angles were taken from the literature [17–20]. Special conformational features have to be assumed; multiple quantum NMR studies on deuteriated 5CB (see table 1 for the chemical structures) in the nematic phase show a torsional angle of 32° between the two benzene moieties [21]. This value was used in the calculations of 5CB, 5OCB, T33FF and T3FF3. Small deviations of 10° in the torsional angle do not have a strong influence on the calculated electronic excitation spectra. The lack of steric hindrance in PT5O2FF makes the all-coplanar structure of the isolated aromatic rings in the tolane framework possible [20]. In order to allow for a reliable comparison between the measured and the theoretical absorption spectra it is necessary to adopt experimental data from idealized dilute solutions [22] as the CI calculations refer, of course, to isolated molecules in the gas phase at zero temperature. In the subsequent CI calculations a 15×15 array has been used; this means that 15 occupied and 15 unoccupied states were considered. Model calculations have shown that this is a reliable compromise between the necessary computational time and the observed accuracy and stability of the numerical results. Subsequently we discuss the calculated transition energies for the systems summarized in table 1. For a better comparison with spectroscopic data a gaussian distribution with a peak halfwidth of 20 nm has been assumed, starting from the numerical value of the calculated peak maxima (see table 2). The deviations between the calculated transition energies and experiment are less than 5 per cent; for the associated oscillator strengths both quantities differ by less than 30 per cent.

4. Results and discussion

Different types of liquid-crystalline and stilbene compounds containing aromatic substructures like benzene rings (PCH5, NCS3, ECCP-CN), biphenyl (5CB, 5OCB) and terphenyl units (T-33FF, T-3FF3), tolane (PTP5O2FF) and stilbene groups (ANS, DANS, HHNS) were investigated (see table 1) in order to examine the influence of the substituents and the conjugation lengths on the spectral quantities. The polarized absorption spectra of all liquid-crystalline compounds except ECCP-CN are known [22], for ECCP-CN only an unpolarized spectrum is available [23] just as for the stilbene dyes ANS and HHNS.

4.1. *Calculated dipole moments*

Large ground state dipole moments improve the bulk orientation of DC poled polymer films containing side chain polymers, which consist of liquid-crystalline moieties and, for example, stilbene units like the compounds investigated. Therefore,

Table 2. Comparison of the measured and calculated main absorption wavelengths of all liquid crystal compounds investigated.

Compound	Measured [19, 20] λ/nm	Calculated λ/nm
PCH5	198	180, 185
	235	245, 246
NCS3	207, 238	189, 243
	272, 284	250, 256
ECCP-CN	199	177, 185
	235	233, 239
5CB	200	180
	220	245, 247
	282	277
5CB$_{gas}$	195	180
	220	245, 247
	275	277
5OCB	202	176, 194
	225	245
	298	278
T-33FF	205	184
		246
	287	289
T-3FF3	205	182
		246
	283	290
PTP502FF	198	179
	292, 311	273

using our INDO MO approach the ground state dipole moments were calculated (see table 3) and as expected, the values for the dipole moment depend on the position of polar substituents in the π system. For this discussion it turned out to be convenient to employ labels in the interpretation of electronic modifications caused by the attached ring substituents, which have their roots in descriptive chemistry. Aliphatic moieties such as long saturated alkyl chains show a negligible contribution to the value of the dipole moment (for example, PCH5 and ECCP-CN). Different positions of polar

Table 3. Calculated dipole moments and conjugation lengths *l*.

Compound	μ/D	μ/D (exp [24])	l/Å
PCH5	4·3		6·8
NCS3	6·5		8·4
ECCP-CN	4·5		6·8
5CB	4·7		12·4
5OCB	4·4		13·8
T-33FF	3·8		15·5
T-3FF3	3·5		15·5
PTP502FF	11·3		13·7
ANS	8·7	6·5	16·7
DANS	8·7	7·1	16·7
HHNS	8·2		16·7

groups at the aromatic rings perpendicular to the principal molecular axis do not lead to large changes in the total dipole moment (T-33FF and T-3FF3). The introduction of so-called donor and acceptor groups leads to a rapid increase in the dipole moment. This can be seen, for example, in the case of compound PTP502FF in comparison to 5OCB, T-33FF and T-3FF3 as well as for the different stilbene dyes. In the latter case the large distance between the more electron withdrawing group and the donor moiety is responsible for the large dipole moment of about 8·5 D. The values of the dipole moment for the stilbenes investigated do not differ strongly because of the common basic structural element; comparison with experimental data shows a satisfying agreement [24].

4.2. Calculated absorption spectra of liquid crystals

The values of the strongest absorption bands obtained from experimental work [22, 23] and the calculated ones are compared in table 2. The influence of the substituents in the aromatic core on the position of the main absorption band becomes evident from the data. To achieve a visualization of the calculated absorption spectra and to simplify a comparison with the experimental and the calculated absorption peaks of three representative compounds (PCH5, 5CB and T-33FF) were taken as the origin of a gaussian function with an assumed halfwidth of 20 nm. Always three gaussian fitted curves are presented in figures 1, 2 and 4. The curves labelled by $\diamond$ represent a parallel polarization of the transition moment relative to the principal molecular axis which is defined by a straight line through the aromatic core. The curves with $\square$ refer to perpendicular polarization, i.e. in the direction of the short molecular axis and the third curves represent an unpolarized spectra. The intensities displayed correspond to the calculated oscillator strengths. Figure 1 shows the calculated polarized spectra of PCH5, quite similar in structure is NCS3. In both cases two main bands appear as we have mentioned, i.e. the $^1A_{1g} \rightarrow {}^1E_{1u}$-like transition at lower wavelengths and the $^1A_{1g} \rightarrow {}^1B_{1u}$-like transition closer to the visible region [22].
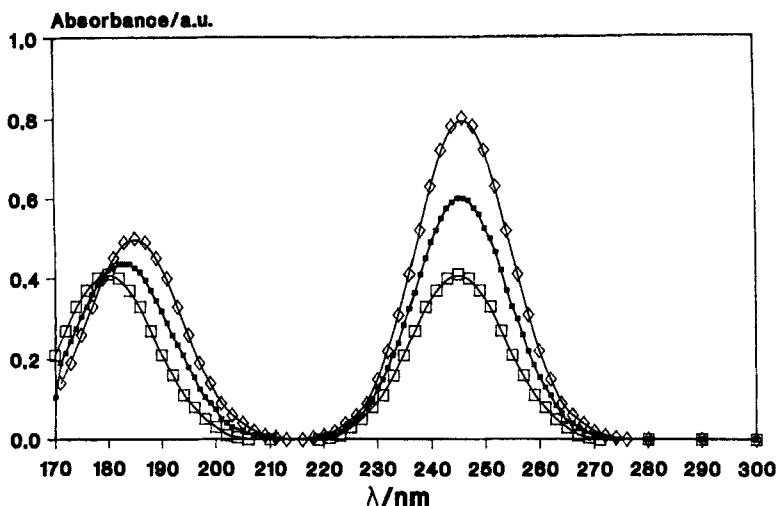

Figure 1. Calculated polarized UV absorption spectra of PCH5, $\diamond$ represents parallel, $\square$ refers to perpendicular polarization to the principal molecular axis, the small rectangles represent an unpolarized spectrum.

Substitution of the cyano group in PCH5 with the isothiocyanato group in NCS3 leads to a red shift, which can be explained by a simple increase of the conjugation length and a bathochromic effect of the more electropositive sp^2-hybridized sulphur atom attached to the unsaturated system. A direct comparison of the experimental and calculated results (see table 2) gives a satisfying agreement. Another analogous liquid crystal molecule is the more complex ECCP-CN with a very large aliphatic substituent. The experimental spectra of the chemically related compounds PCH5 and ECCP-CN are quite similar. Although the size of the π system is the same as in PCH5, the calculation shows that the different aliphatic groups influence the shape of the spectra, resulting in a small blue shift.

Typical representatives of cyanobiphenyl containing liquid crystal compounds are 5CB and 5OCB. Both systems differ in that 5OCB contains an ether group while in 5CB a direct linkage of the aliphatic group to the aromatic frame exists (see table 1). In comparison to simple π systems (for example PCH5: 246 nm) the band with the strongest oscillator strength is shifted to longer wavelengths (5CB: 277 nm; 5OCB: 278 nm). In both molecules this band is also strongly parallel polarized with a large oscillator strength. In contrast to simple aromatic systems, like PCH5 and related compounds, another absorption band appears around 245 nm (see figure 2). As we have mentioned electronic transitions are affected by interactions with the solvent. The present quantum chemical model calculations refer always to an isolated molecule in the gas phase. So the comparison of the unpolarized gas phase spectra of 5CB (see figure 3) with the calculated data should show a better agreement and indeed only a negligible difference of 2 nm for the main absorption band exists. Unfortunately only one gas phase spectrum is available, so a more general statement concerning the accuracy of the semiempirical MO model employed can be made only after further investigations, but the general trend of the computational results is consistent with the experimental data. The deviations between theoretical and experimental spectra are small, they may have their origin in intermolecular interactions and the simplified all-valence hamiltonian which is based on several approximations. But also modifications
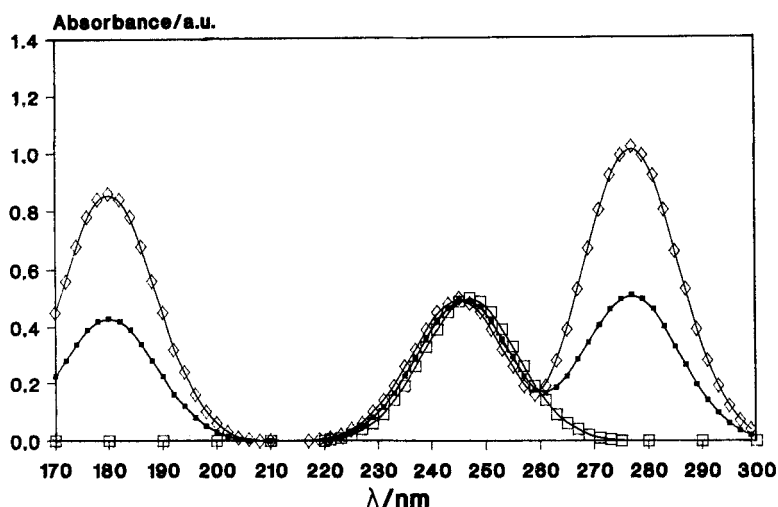

Figure 2. Calculated polarized UV absorption spectra of 5CB, ◇ represents parallel, □ refers to perpendicular polarization to the principal molecular axis, the small rectangles represent an unpolarized spectrum.
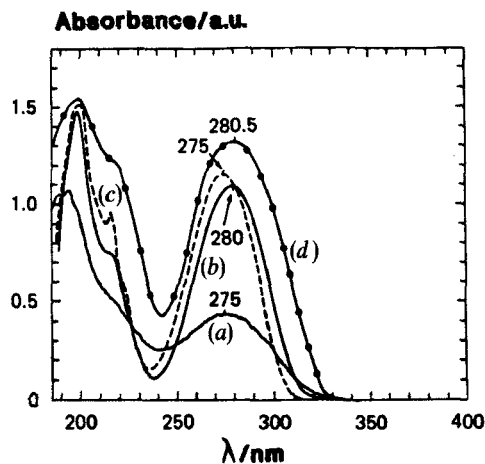
Absorbance/a.u.

Figure 3.   Unpolarized spectra of 5CB in the gas phase and in different solvents measured using a Perkin–Elmer Lambda-9 spectrometer. (*a*) Vapour phase, (*b*) in CH_3CN, (*c*) in hexane, (*d*) isotropic phase.
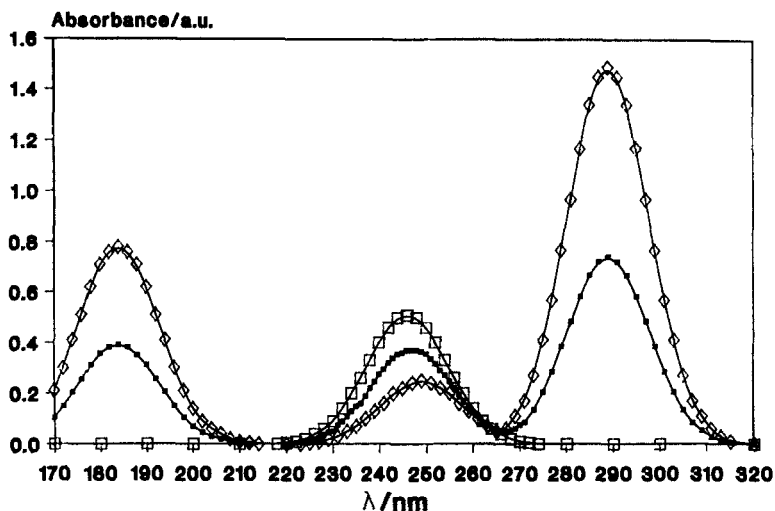

Figure 4.   Calculated polarized UV absorption spectra of T33FF, $\diamond$ represents parallel, $\square$ refers to perpendicular polarization to the principal molecular axis, the small rectangles represent an unpolarized spectrum.

in the solvent lead to smaller changes in the measured absorption spectra of 5CB (see figure 3). In table 3 the extension of the conjugated system in all of the compounds are listed. The net length includes the interatomic distances of all the participating centres. As expected the increase in the conjugation length results in a decrease of the transition energies corresponding to a red shift of the absorption bands. The terphenyl derivatives T-33FF and T-3FF3 investigated show the expected behaviour (see figure 4). In both cases the position of the lateral fluorine atoms does not influence the magnitude and oscillator strength of the main absorption bands. The intensities and the shape of the absorption bands are quite similar. One additional band as in the case of the biphenyl

compounds appears again around 245 nm. Another absorption spectrum similar to the latter is realized in the tolane derivative PT502FF (see table 1) which includes a similar π extension, like 5OCB. Especially the value of the main absorption band around 273 nm is conserved. One main difference between the experimental spectra and the calculated ones can be seen from a comparison of the absorption profile of the spectra. In the measured spectra the $^1A_{1g} \rightarrow {}^2E_{1u}$-like transition at lower wavelengths (for example in 5CB around 200 nm) shows in most cases a larger oscillator strength than the $^1A_{1g} \rightarrow {}^1B_{1u}$-like transition (5CB: 282 nm), but the opposite intensity ratio has also been observed experimentally [22]. The calculated spectra show that in all of the liquid-crystalline molecules examined the $^1A_{1g} \rightarrow {}^1B_{1u}$-like transition is stronger than the $^1A_{1g} \rightarrow {}^1E_{1u}$-like transition. But as we have mentioned the computational error in the oscillator strength is about 30 per cent. Another general computational result is the better agreement between experimental data and calculated ones for transitions with lower energies (see table 2). The mutual difference increases with increasing transition energies. This behaviour found for the far UV transitions may be caused by the limited size of the CI matrix.

4.3. Calculated absorption spectra of stilbene dyes

All of the stilbene compounds examined (see table 1) show a very broad absorption range (FWHM up to 80 nm) with large molar extinction coefficients in their experimental VIS absorption spectra. Despite the very broad shape of the absorption band there is only one electronic transition responsible for that absorption. The calculations show that this transition is polarized parallel to the principal molecular axis of the aromatic framework. This can also be verified experimentally by doing dichroism measurements [25]. A comparison of our measured spectra and data taken from the literature [26] with the calculated results show good agreement (see table 4). Further investigations indicate that the position of the absorption maxima depends strongly on the solvent. This observation can be used to estimate the hyperpolarizibility via solvatochromic experiments or more accurately via frequency doubling [27]. But the strong broadening of the visible absorption band suggests that the energy gap between the ground and excited states is very sensitive to intermolecular interactions or changes and fluctuations in the electronic environment of the molecule. The values of the absorption maxima in the different stilbenes vary in a range of 50 nm; the calculated ones are closer together. This can be explained by the dye–solvent interaction based on the different electronic properties of the amino or ether groups. The conjugation length is not affected by the different donor substituents and is nearly identical (see table 3) for all stilbene compounds. Therefore, the deviations in the absorption maxima (see table 4) can be traced back to the different donor properties of the amino and the ether

Table 4. Comparison of the measured and calculated main absorption wavelengths of the stilbene compounds.

Compound	Measured [25, 26] λ/nm	Calculated λ/nm
ANS	402	423
DANS	420	430
HHNS	370	395

functionality, respectively. The introduction of the amino function instead of the ether group results in a red shift of the visible band. The calculated values show a reasonable agreement with experiment and an improved accuracy in comparison to former investigations [8].

5. Conclusions

We have calculated the electronic transition energies in the UV/VIS range for eight commerical liquid crystals and three stilbene dyes by using a semiempirical INDO MO method. It has been possible to evaluate the polarized absorption spectra with reliable accuracy. The influence of different substituents has been demonstrated. The position of these substituents or the π conjugation length affects directly the range, the shape and the intensity profile of the absorption bands. The electronic transitions polarized parallel to the aromatic framework are more sensitive to changes in the molecular structure. The principal transition in the systems investigated polarized perpendicular is located in the range between 240–250 nm. In most of the cases all transitions with large oscillator strengths are strongly polarized parallel to the principal molecular axis. The comparison of the theoretical data with experiment shows sufficient agreement both for the transition energy and the direction of the band polarization. A prediction of the spectral quantities of UV/VIS absorbing materials for further experiments, for example in non-linear optics or for future applications, is possible with reliable accuracy and should simplify the proper design of new materials.

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