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Spontaneous site reorientation in a mixed molecular crystal: Tetracene in benzoic acid

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Absorption and fluorescence spectra of tetracene in a benzoic acid host crystal at 1.5 K are presented. The fluorescence zero-phonon line is shifted by more than 800 cm^{-1} to the red of the maximum of the 120 cm^{-1} broad absorption origin. This shift is attributed to a lateral site reorientation of the guest upon excitation, permitted by the difference in size between the tetracene and the benzoic acid dimer it replaces. In addition, other features in the fluorescence spectrum are ascribed to proton tautomerization occurring in the host dimers in the vicinity of the guest. These features disappear upon deuteration of the host acid protons, while the magnitude of the red shift is virtually unchanged.

I. INTRODUCTION

The electronic spectra of dilute mixed molecular crystals at low temperatures usually consist of sharp zero-phonon lines (zpl's $\sim 1\text{ cm}^{-1}$ FWHM) corresponding to the vibronic transitions of the guest molecules. Each of these lines is generally followed by a more or less diffuse phonon sideband, whose width and structure depend upon the details of the interactions between the guest molecules and the host lattice. These interactions can be characterized^{1,2} on the basis of the strength of the linear electron-phonon coupling, which is a measure of the displacement of the equilibrium lattice position of the guest upon electronic excitation,¹ and the degree of lattice distortion caused by the substitution of a guest molecule in the host. While the effects of these two processes on electronic spectra are not entirely independent of each other, in general, the strength of the linear electron-phonon interaction is responsible for the relative intensities of the zpl and phonon sideband (as well as the general shape of the latter). The effect of lattice distortion is to introduce fairly sharp features, arising from pseudolocal modes, into the phonon sideband.

In contrast to many systems in fluid solution, where reorientation of solvent molecules in the field of the excited solute during the lifetime of the excited state contributes to the red shift of the highest energy fluorescence band with respect to absorption,³ spontaneous reorientation in a crystal is prevented by the constraints imposed by the crystal structure. In this case, the position of the zpl is governed by the total crystal field of the host at the impurity site, and is the same in absorption and emission.¹ This is an advantage in the spectral analysis of many mixed crystals showing multiple site origins, such as various aromatic hydrocarbons in polyphenyl hosts.⁴⁻⁶ An anomaly in this respect has been reported by Kruse and Small^{5,7} for the system of tetracene (TC) in a *p*-terphenyl host. In their experiments, they observed emission from site origins absent in absorption upon excitation into phonon bands built on the absorption origins. This "other site" emission, which increased in intensity with increasing phonon energy, was at the expense of intensity of the absorption origins. This was interpreted⁷ as "phonon-assisted site

relaxation," where excitation of pseudolocalized modes sufficiently distorts the lattice around the impurity site to allow the TC to alter its orientation. A phenomenon intimately related to this has been observed in crystals of pentacene in benzoic acid (BZA) by Olson *et al.*^{8,9} They report nonphotochemical hole burning in this system, where excitation into the unburned absorption band results in the production of "antiholes," sites that appear in absorption outside of the original inhomogeneous profile. This was attributed⁹ to proton tautomerization in the host material, assisted by the excitation of pentacene, which then altered the crystal field at the pentacene site. While in pentacene/BZA structural reorganization of the host has been assigned responsibility for the appearance of antiholes, this can be considered an extreme of the tetracene/*p*-terphenyl case; whereas in the latter, no trace of the phonon-induced sites were observed in absorption, the antiholes in the former persisted for more than 5 min.

In this paper, we report the results of experiments performed on TC molecules in a BZA host crystal, where we observe spontaneous site reorientation resulting in a shift of over 800 cm^{-1} between absorption and emission origins. Furthermore, we attribute certain spectral features as resulting from proton tautomerization occurring in the host. We discuss these results in light of other mixed crystal investigations.

II. EXPERIMENTAL

Dilute crystals of TC in *h*-BZA and *d*-BZA (substitution of acid proton) were grown by standard Bridgman techniques from zone refined benzoic acid and sublimed tetracene. The actual concentration was governed by the limited solubility of the guest, most of which zone refined out during crystal growth. In the most concentrated crystals, from pieces taken nearest the top of the boule, an optical density (OD) of ~ 0.7 ($\sim 1.5\text{ mm}$ crystal thickness) at the peak of the 0-0 absorption band was the maximum obtainable. The crystals were cleaved parallel to the *ab* plane, oriented using a polarizing microscope, and mounted in a variable temperature cryostat. Transmission spectra were recorded using a filtered filament lamp as a source. Fluorescence and

FIG. 1. Transmission spectrum of TC in *h*-BZA. The vibration frequencies (in cm^{-1}) are measured from the maximum of the 0-0 at 4833 Å to the maximum of the band labeled. The sloping baseline is due to the characteristics of the filament lamp used. The resolution is $\sim 0.8 \text{ cm}^{-1}$.

excitation spectra were obtained using a Moletron DL200 dye laser, pumped by a Moletron UV-12 N_2 laser. All spectra were recorded using a SPEX 1704 monochromator and an EMI 9816 photomultiplier. Fluorescence signals were processed via an EG&G LG105/N linear gate and stretcher module, whose output was averaged by computer and displayed on a x - y plotter. Fluorescence lifetimes were estimated by observing the decay of the fluorescence on a Tektronix R712 transient digitizer. Deuterated BZA was prepared by multiple refluxes of BZA in D_2O , as described by Olson *et al.*⁹ All experiments were performed with the crystals at $\sim 1.5 \text{ K}$.

III RESULTS

A. Transmission spectrum

The transmission spectrum for a TC/*h*-BZA crystal at 1.5 K is presented in Fig. 1. The peak positions cor-

respond to a 0-0 band and most of the strong and medium vibrations in the TC spectrum.⁵ However, the linewidth of the asymmetric 0-0 is $\sim 120 \text{ cm}^{-1}$ (FWHM) as compared to $\sim 2 \text{ cm}^{-1}$ for TC in a *p*-terphenyl host (the instrumental resolution in this experiment is $\sim 0.8 \text{ cm}^{-1}$). The absence of any sharp features (e.g., zpl's) initially leads one to conclude that this is a glass-like system, where broad inhomogeneous lines are standard.¹⁰ However, as will be seen, this interpretation is rather unlikely. The transition is strongly polarized in this host, with the absorbance ratio parallel and perpendicular to the host crystalline *a* axis of ~ 7 , similar to that observed for pentacene in BZA.¹¹ Replacement of the acidic proton by a deuteron shifts the maximum of the 0-0 by $+20 \text{ cm}^{-1}$, also comparable to that observed by Olson *et al.*⁹ in the pentacene system. This was attributed by them to lattice expansion of the BZA upon deuteration.^{9,12}

B. Fluorescence

1. *h*-BZA

The laser excited fluorescence spectrum of this crystal is shown in Fig. 2. The spectrum appears as a series of "sharp" zpl's (only strongly visible in the 0-0) followed by broad ($\sim 150 \text{ cm}^{-1}$) phonon sidebands. As in the absorption spectrum, the vibrational frequencies correspond well to those in *p*-terphenyl.⁵ This spectrum resembles that obtained in a fluorescence line-narrowing (FLN) spectrum of TC in a methanol: ethanol glass¹⁰; however, there are several striking differences. Comparing Figs. 1 and 2, we see that the sharp feature at 5035 Å in fluorescence is shifted by $\sim 830 \text{ cm}^{-1}$ to the red from the maximum of the 0-0 in absorption at 4833 Å. (While there is some uncertainty in the assignment of the zpl due to its absence, the red shifts quoted here are overestimated by no more than 70 cm^{-1}). This is in marked contrast to all other reported low temperature mixed-solid spectra. The position and shape of the emission spectrum is independent of the wavelength of excitation within the 0-0 and 0+310 absorption profile. In fact, the fluorescence excitation spectrum of the emission zpl is essentially identical to the absorption

FIG. 2. Ungated fluorescence spectrum of TC in *h*-BZA. The vibration frequencies (in cm^{-1}) are measured from the zpl at 5035 Å. Excitation was at 4833 Å, the maximum of the absorption 0-0.

FIG. 3. Spectrum a is the ungated fluorescence of TC/*h*-BZA in the region of the emission 0-0, with excitation at 4833 Å. Note the shoulders at 29 and 58 cm^{-1} to the blue of the zpl. Spectrum b is the same region but with the fluorescence gated 30 ns after the excitation pulse. The ungated fluorescence 0-0 of TC/*d*-BZA is shown in c, with excitation at the maximum of the absorption 0-0. The solid triangles in b and c are Gaussian profiles having widths of 20 and 29 cm^{-1} , respectively. The spectrometer resolution in all three spectra is $\sim 1 \text{ cm}^{-1}$.

spectrum. This is also contrary to many FLN studies of organic molecules in glasses where the zpl's follow the laser frequency, owing to the photoselection of a narrow range of molecules within the laser bandwidth. However, such studies were performed using resonant excitation,¹⁰ while in our case the emission system is nonresonant with the excitation. In this event, the FLN characteristics are dependent on correlations in the inhomogeneous distributions between the state excited and the emitting state.¹³ We shall return to this point later in the discussion.

Upon excitation into the $0 + 310 \text{ cm}^{-1}$ absorption band, there is no detectable emission in the region of the absorption 0-0. We rule out the possibility of reabsorption on the basis of emission in this region being absent in a crystal whose maximum OD was 0.1. We also observe two features that appear as shoulders 29 and 58 cm^{-1} to the blue of the emission 0-0 zpl, as shown in Fig. 3(a). These shoulders have the same excitation spectra as the zpl, and have lifetimes of ~ 10 and ~ 3 ns, respectively; this is compared to ~ 20 ns for the zpl, which is essentially the same as for TC in *p*-terphenyl.¹⁴ By gating the fluorescence later in the decay, it was possible to obtain spectra free of these shoulders [Fig. 3(b)].

From this, we estimate the width of this zpl at 20 cm^{-1} , for a Gaussian line shape. This is several times wider than for pentacene in the same host.⁹ We observe no buildup of the fluorescence in response to a laser pulse, as viewed on the transient digitizer, within the time response of our detection system ($\sim 1 \text{ ns}$). We note further that the polarization behavior in emission is the same as in absorption.

2. *d*-BZA

The 0-0 region of the ungated spectrum of TC/*d*-BZA is shown in Fig. 3(c). The entire spectrum is shifted by 85 cm^{-1} to the blue, relative to the *h*-BZA spectrum. Note that the shoulders which are present in the *h*-BZA spectrum are absent in this crystal. The width of the zpl is 29 cm^{-1} , substantially broader than in the protonated host. However, the shape of the phonon side band is essentially identical in the two hosts. In contrast to pentacene/BZA,⁹ we observe no obvious shortening of the fluorescence lifetime with host deuteration. The features in both hosts are independent of crystal and sample history.

IV. DISCUSSION

A. Origin of the fluorescence red shift

It is at first tempting to attribute this shift to proton tautomerization of the BZA dimers in the immediate vicinity of the guest site, as has been cited for the appearance of antiholes in the pentacene/BZA system.⁹ However, there are several important differences. Perhaps the most striking of these is that replacement of the acid proton with a deuteron shifts the TC emission origin by only 85 cm^{-1} or $\sim 10\%$ of the total red shift, while it reduces the hole burning in the pentacene system by a factor of 100. The second difference is that whereas the nonphotochemically induced site farthest removed from the unburned pentacene origin is $\sim 130 \text{ cm}^{-1}$, the bluest shoulder in the TC/*h*-BZA crystal is still $\sim 800 \text{ cm}^{-1}$ to the red of the absorption maximum. The lack of even a qualitative similarity in actual behavior makes it unlikely that these two processes proceed via the same mechanism.

It seems more reasonable to suggest a site relaxation of the TC molecule upon excitation. For crystals of aromatic molecules, it has been shown^{6,15} that the actual orientation of a ground state molecule is largely determined by repulsive interactions between C-H σ electrons, while electrostatic and dispersive interactions between π systems are much less sensitive to position. It has been suggested,⁶ though, that these π interactions between guest and host play a larger role in the excited state. While these observations were explicitly directed towards rotational orientation, it is not unreasonable to consider them equally valid for translational orientations as well.

The BZA crystal is comprised of stacks of plane parallel dimers.¹⁶ This crystal can be viewed as a "bifunctional apolar" host in the sense that each BZA dimer has two different types of region in terms of polarizability: a "softer," aromatic outer region sepa-

rated by a "harder," more localized carboxyl-hydrogen-bonding region. The term "apolar" refers to the fact that, while at distances large compared to molecular dimensions, this hard core is apolar, when considering smaller distances, the dipole approximation is at best limited,¹⁷ and one must consider many terms in the multipole expansion.¹⁵ Consequently, the interactions between the guest π electrons and the host crystal field could conceivably be more important in this type of crystal. Upon substitution of a pentacene molecule for a BZA dimer, the C-H σ repulsions are probably responsible for the ultimate orientation of the guest, owing to the fact that pentacene is roughly the same size as the host species it replaces. TC, however, being $\sim 4/5$ as long as pentacene is most likely less restrained by these repulsions in its orientation with respect to the long axis of the BZA dimer, due to reduced interaction with other stacks. By this reasoning, the guest π -electron interactions with the host are thus permitted a greater weight in determining the site orientation; as a result, it would not be surprising if the TC molecule were to laterally shift its position in the site upon electronic excitation. We therefore attribute this red shift in fluorescence to such a spontaneous reorientation process. This differs from the effect observed by Kruse and Small^{5,7} in that their reorientation required phonon assistance, presumably to overcome a rotational barrier, while, in the BZA host, this process occurs even when exciting on the red edge of the absorption band.

That the excited state equilibrium position must be different from that in the ground state is obvious from the fact that there is a shift at all. If the molecules were randomly distributed in the sites, then the excited state orientation would correspond to one of the ground state configurations and the spectra would overlap. At present, it is difficult to assign orientations to the two states, although on the basis of charge cloud expansion with excitation one is inclined to place the excited state more towards the middle of the site, with the ground state occupying a position closer to the edges. A more thorough analysis of this reorientation requires a detailed calculation of the guest-host interactions.

At first sight, the $\sim 800\text{ cm}^{-1}$ shift appears rather large for a site reorientation process. However, this is only a few times larger than the site splittings observed for TC in various hosts. For example, one site for TC in benzophenone¹⁸ is shifted by $\sim 350\text{ cm}^{-1}$ from the lowest energy origin. While this crystal is polar, it still lacks the comparatively large regions of differing polarizability in BZA (the hydrogen-bonding network in BZA is approximately the same size as a phenyl ring).¹⁶ In fact, the lowest energy phonon-induced emissive site of TC in nonpolar *p*-terphenyl is $\sim 188\text{ cm}^{-1}$ to the red of the absorption origins.^{5,7}

To interpret this shift as other than a lateral reorientation requires either the introduction of structural disorder or specific complex formation. Rotational reorientation would require vacancies at host sites adjacent to each guest at the time of crystal growth, which, provided the TC is a substitutional guest, seems rather unlikely. Indeed, given the good crystal quality, as

evinced by extinction under the polarizing microscope, the strongly polarized absorption and emission characteristics, and the fact that a crystal containing TC and pentacene in BZA shows both the broad absorption and red-shifted emission of TC and sharp lines due to pentacene, we are rather hard pressed to find any evidence of structural disorder. We are inclined to exclude complex formation on several grounds. While BZA dimers are known to quench the fluorescence from solutions of naphthalene and related compounds,¹⁹ presumably due to exciplex formation, the emissive state of TC in BZA is extremely luminescent, and the comparatively well-resolved fluorescence spectrum is not characteristic of these complexes, which are generally dissociative in the ground state.²⁰ Whereas we cannot *a priori* rule out the formation of TC dimers, which then form an excimer upon excitation, the notion of the exclusive dimer formation during crystal growth seems unstatistical, in addition to the aforementioned dissociative nature of the excimer ground state. Consequently, our interpretation of a lateral site reorientation appears the most plausible.

It is appropriate here to comment on the short-lived shoulders to the blue of the emission zpl in the *h*-BZA crystal. In view of the magnitudes of the shifts (29 and 58 cm^{-1}) from the zpl and the fact that they are absent in the *d*-BZA host, it is reasonable to attribute them to the production of different hydrogen-bonding configurations of the host dimers in the immediate neighborhood of the TC upon excitation. With regard to the magnitude of the shifts, Clemens *et al.*²¹ have recently observed multiple origins in the spectrum of thioindigo in BZA, whose splittings are on the order of 35 cm^{-1} , which they interpret as being due to different host tautomers. This lends further support to our assignment of these shoulders. A possible mechanism for this excitation-assisted tautomerization is analogous to one proposed by Olson *et al.*⁹ for pentacene. The shift of the TC molecule releases several hundred cm^{-1} into the local lattice, which, if coupled to the proper vibrational modes of the BZA dimers could assist in hydrogen-bond tautomerization. This would effectively "scramble" the protons around the TC site, which were initially in their lowest energy configurations, giving rise to a finite number of different TC site energies and hence to different emission frequencies, three of which are observed in the emission spectrum. A possible contributing factor is that the site relaxation alters the total crystal field at the protons in the nearest neighbor BZA dimers to the extent that the original hydrogen-bond configuration is no longer that of lowest energy, the energy supplied by the TC shift being sufficient to overcome the potential barrier between the initial and new energy minimum (or minima). Another possible mechanism, also similar to one suggested by Olson *et al.*,⁹ requires a certain amount of lattice relaxation around the TC to occur, as described in the work of Craig and co-workers²² for excimer and photodimer formation, *before* the TC lateral site shift occurs. This local motion of the BZA heavy atom framework then assists in the tautomerization of the protons, as Graf *et al.*²³ have recently demonstrated. In this mechanism, the protons rearrange before or dur-

ing TC reorientation. It is also possible that any of these three processes assists in the recovery of the initial proton configuration after deexcitation of the TC.

Experimentally, all three emissive states appear to be formed simultaneously, rather than sequentially, in light of their nanosecond time-scale lifetimes and no apparent build up in the fluorescence of the other species. (It is worth noting here that the 29 cm^{-1} shoulder is also observed on the 1385 cm^{-1} vibration in emission.) Independent of the actual mechanism, deuteration of the BZA simplifies the spectrum to the extent that there is apparently only one emitting species, presumably by increasing the barrier height or width⁹ for tautomerization. This interpretation is lent further credence by the fact that the highest energy fluorescence shoulder in *h*-BZA is only 25 cm^{-1} to the red of the zpl in *d*-BZA. This is very close to the difference between absorption origins in the two hosts. On this basis, we attribute this shoulder to the lowest energy proton configuration prior to the TC shift.

B. Absorption and emission line shape

Before proceeding with the discussion, it will be useful to briefly review some of the results from the theory of linear electron-phonon coupling.^{24,27} In general, the spectrum in the region of the electronic origin consists of a narrow zpl followed by a broad multiphonon sideband. At low temperature, the weight P_r of the r -phonon process is given by²⁴

$$P_r = \frac{S^r}{r!} e^{-S}, \quad (1)$$

where S is the Huang-Rhys²⁵ factor, which characterizes the strength of the electron-phonon interaction, the most probable phonon process being that which is nearest the numerical value of S . When S is less than unity, the zpl dominates the spectrum. As S becomes large, multiphonon processes become more probable and the intensity of the zpl decreases in comparison with the phonon sideband. When $S \geq 10$, the zpl is no longer visible, and one speaks of being in the strong coupling regime. It is also common in the literature^{10,28} to describe the coupling strength by the Debye-Waller (DW) factor, which is the ratio of the integrated intensity of the zpl (I_{zpl}) to that of the entire 0-0 band (I_{tot}). At low temperature, this is given by²⁶

$$\frac{I_{\text{zpl}}}{I_{\text{tot}}} = e^{-S}. \quad (2)$$

The sidebands due to one phonon processes should reflect the frequency spectrum of the mixed crystal, which includes the density of host phonon states, as well as any features due to localized or pseudolocalized modes.^{4,27} The appearance of a given mode is also weighted by the extent to which it is influenced by changes in the impurity electronic state.²⁷ The general shape of the multiphonon sideband is the sum of the r -phonon processes weighted by Eq. (1), where the shape of the r th phonon contribution is the result of convoluting the one-phonon spectrum r times with itself.²⁴ From this, we can see that both the relative intensity of the zpl and the width of the phonon sideband depend on the value of S .

FIG. 4. Comparison of absorption (black circles) and emission (solid line) origins. The zero of energy is chosen at the maximum of the absorption. The dashed lines denote the position of the half-maximum points in absorption, and show the strong asymmetry of the curve. Note the similarity between the high energy side of absorption and low energy side of emission (both of which are to the right of 0 in this figure).

While the absence of a resolved absorption zpl would seem to indicate much stronger electron-phonon coupling in this orientation, this is probably not the case. From Fig. 4, where the two spectra are superimposed, we see that the widths of the two origins are comparable, and that the high energy side in absorption and low energy side in emission have essentially the same shape. The DW factor calculated from the emission spectrum is 0.18 ($S=1.7$), which is slightly larger than that for pentacene in BZA.²⁸ The electron-phonon coupling appears larger in this spectrum due to the large inhomogeneous width of the zpl, which is also consistent with the actual site configuration being determined by dispersive and electrostatic interactions between guest and host, rather than C-H σ -electron repulsions, as discussed in Sec. A, above. It can be seen from the foregoing discussion that in order for the absorption spectrum to reflect stronger electron-phonon coupling, the TC molecule in the absorbing state would have to couple with much lower frequencies than the emitting state. While this is not inconceivable, given that the absorbing state is in a different site orientation, the strong asymmetry of the absorption profile leads us to conclude that this is unlikely. The half-width of the blue side of the TC origin is almost twice as large as the red side, while in cases of very strong coupling, the line shape is expected to be Gaussian.^{24,29} In fact, using a simple model of a single interacting lattice mode of 35 cm^{-1} (corresponding roughly to one of the low frequency modes in the BZA crystal Raman spectrum),³⁰ where each member in the progression including the zpl was a Gaussian function having a 50 cm^{-1} width and weighted by Eq. (1),³¹ with $S=1.7$, the main features (asymmetry, width, etc.) in the absorption spectrum in Fig. 4 are

well described. While this is not intended as a quantitative fit, it does illustrate the fact that in cases where the zpl is broad enough, it will not be resolvable from the phonon sideband, even with moderately weak electron-phonon coupling. It is also on the basis of this asymmetry and similarity to emission phonon sideband that we exclude the possibility of the total absorption width being entirely due to inhomogeneous broadening. For TC in BZA, this unusually large width in absorption could be due to inhomogeneous causes (as a result of the lack of very rigid site constraints) and/or homogeneous processes (e.g., if the site shift upon excitation is indeed very fast).

We remark here that recovery of the original site orientation after return to the ground state appears to be very rapid. Preliminary nanosecond pump-probe experiments failed to detect residual population in the excited state site orientation at times > 40 ns. While the pulse powers used (~ 0.5 mW, average) are rather low (compared to those used in hole burning studies),⁹ we estimate the quantum efficiency for site reorientation to be very high (assuming that the TC radiative properties are only weakly dependent on orientation), and hence detectable in this type of experiment. However, a very rapid recovery rate is consistent with the apparent speed with which the original site shift occurs.

There remain a number of unanswered questions about this system. Among them are:

- (i) What precisely are these different site orientations, and how fast are the interconversion processes?
- (ii) By which mechanism is the TC excitation coupled to the host tautomerization, and what is the recovery rate of the original proton configuration?

Further experiments are currently in progress in an attempt to answer these questions about this novel phenomenon.

V. SUMMARY

We have presented spectra of TC in a BZA host, crystal, where the origin of fluorescence is shifted by > 800 cm^{-1} from that of absorption. This is attributed to a site reorientation of the guest in the host crystal field upon excitation. The shift is rationalized in terms of the relaxed restraints imposed on the TC due to C-H σ -electron repulsions with the host molecules, by virtue of the comparatively smaller size of the guest. This, in turn, permits the guest π -electron interactions a greater role in determining the TC orientation, which changes in response to the altered electron distribution upon guest excitation. The width of the emission zpl (~ 20 cm^{-1} in *h*-BZA) tends to support this idea of relaxed restraints. The lack of a resolved absorption zpl is ascribed to being probably due to an unusually large width resulting from either inhomogeneous or homogeneous causes. The absence of a buildup of fluorescence in time-resolved experiments places an upper limit of ~ 1 ns on the lifetime of the absorbing orientation after excitation. Deuteration of the host acid proton affects the site orientation and hence the shift by a negligible amount, while eliminating other emitting

species, which are interpreted as arising from proton tautomerization occurring in BZA dimers adjacent to the excited TC molecule.

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