Another Look at the Mechanism of the Concerted 1,3-Dipolar Cycloaddition of Fulminic Acid to Acetylene†

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The transition structure and energy barrier for the concerted addition of fulminic acid to acetylene, a prototypical 1,3-dipolar cycloaddition, have been determined using various molecular orbital and density functional theory methods (MP2, CCSD(T), G2(MS), G2(CC), CASSCF/CASPT2, and B3LYP) with the aim of obtaining accurate energetics and finding an economical but reliable approach for treating larger substituted systems. Although the activation energy is not particularly sensitive to the geometries employed, it is strongly dependent on the treatment of dynamical electron correlation. The approximate G2(MS) appears to be an efficient and reliable treatment. Both CCSD(T) and CASPT2 results agree with each other, suggesting that the energy barrier for the HCNO + HCCH addition amounts to about 14 kcal/mol. The electronic mechanism of the cycloaddition has also been probed further using DFT descriptors, as well as an analysis of the CAS-LMO-CI wave functions. The hardness profile along the minimum energy path shows a minimum in the saddle region, but the position of its minimum is somewhat shifted toward the product side compared to the maximum in energy profile. The variation of the coefficients of the excited configurations in the CAS wave function along the reaction path suggests that the transition state does correlate with a substantial electron movement from the O to the N of HCNO. The O thus behaves as a new bond acceptor center and the C as a new bond donor, in contrast with a picture previously derived from either the net charges distribution, or the motion of the centroids of Hartree−Fock based localized orbitals accompanying the nuclear approach of both reaction partners, or a spin-coupled valence bond analysis.

1. Introduction

Since the systematic classification of Huisgen[1] in the early sixties, the 1,3-dipolar cycloaddition (referred to hereafter as 13DC) emerged as a general and powerful method for the synthesis of five-membered rings.[2] Owing to the large number of possible combinations of several heteroatoms to form either the dipoles or the dipolarophiles, the potential of the 13DC in heterocyclic syntheses is enormous. As a result, several theoretical studies using molecular orbital methods[3−5] have been devoted to its mechanism. Although most of the ab initio calculations assumed or favored a concerted mechanism, some other studies have suggested a stepwise biradical mechanism (for a comprehensive review, see ref 5). That is in fact the case for the addition of fulminic acid to acetylene (HCNO + HCCH), which is a prototypical 13DC.[6−9] Nevertheless, available ab initio quantum chemical studies on this reaction have apparently not allowed the controversy to be resolved. The main difficulty lies in the fact that, for such a problem involving a singlet open-shell biradical species, a construction of very high-level wave functions, including massive electron correlation with extended one-electron basis functions, is really needed. Although some studies were performed using a multireference treatment,[8,9] the basis sets employed, having only minimal (STO-3G) and split-valence (4-31G) quality, are rather too small to yield reliable energetics. As a consequence, even for the concerted reaction path whose transition-state structure is well characterized, the energy barrier of the HCNO + HCCH reference reaction is not well established yet. The reported values varied in fact from 8 to 29 kcal/mol.[6−10] The most recent MP4/6-311G(d,p) calculations[10] gave an estimate of 7.8 kcal/mol.

In view of such a lack of accurate activation parameters on this prototype 13DC, we set out to determine them using more reliable methods. In addition, the present study also provides us with an assessment of the current quantum chemical procedures and thereby a necessary

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calibration for further use in the study of the regioselectivity and stereoselectivity of the 13DC involving much larger substituted systems. It is not our intention here to make any additional comment on the concerted–stepwise mechanism debate, and we rather confine ourselves in the concerted approach. In this context, we attempt to have another look at the corresponding mechanism making use of the two recently proposed analyses, namely, the configuration interaction treatment based on localized molecular orbitals (CI-LMO-CAS)[11,12] and the reactivity descriptors based on density functional theory such as hardness and softness in both global and local senses.[13−18] These analyses bring about some additional insights into the electronic reorganization and the regioselectivity of the addition.

2. Methods and Results

Calculated results are presented hereafter in three separate sections including the determination of the energy barrier, a CI-LMO-CAS analysis, and a hardness profile. For the sake of convenience, details of the corresponding methods will be outlined at the beginning of each section.

2.1. Energy Barrier. Ab initio quantum chemical calculations of structures and energies were carried out with the aid of the Gaussian 94 set of programs[19] and the MOLCAS program.[20] Geometrical parameters of both reactants and the transition structure (TS) were optimized using both second-order perturbation theory (MP2) and coupled-cluster theory (CCSD(T)) of the molecular orbital (MO) approach and the hybrid B3LYP functionals of density functional theory (DFT) in conjunction with both 6-31G and 6-31G(d) basis sets. It turns out that there is no need for geometry optimization using larger basis functions. On the contrary, improved estimates for the energy barrier were subsequently obtained using single-point electronic energy calculations with either the larger 6-311++G(d,p), 6-311+G(2df,2p), and 6-311++G(2df,2p) basis sets or the atomic natural orbital (ANO) basis set with various optimized geometries. On one hand, we have considered the performance of two modified G2 schemes[21,22] in which the higher level electronic energies are approximated from lower level calculations through an additivity scheme. Thus, the electronic energies are defined as follows:

$$E[\mathrm{G2M(MS)}] = E[\mathrm{CCSD(T)/6\text{-}31G(d)}] + E[\mathrm{MP2/6\text{-}311{+}G(2df,2p)}] - E[\mathrm{MP2/6\text{-}31G(d)}] \quad (1)$$

and

$$E[\mathrm{G2M(CC)}] = E[\mathrm{CCSD(T)/6\text{-}311{+}{+}G(d,p)}] + E[\mathrm{MP2/6\text{-}311{+}{+}G(2df,2p)}] - E[\mathrm{MP2/6\text{-}311{+}{+}G(d,p)}] \quad (2)$$

Whereas the G2M(MS) procedure (1) is based on either B3LYP or MP2 geometries, the G2M(CC) method (2) is based on CCSD(T)/6-31G(d) geometries. The additivity scheme G2(MS) will be of use in our following work on the 13DC of substituted dipoles and dipolarophiles.

On the other hand, due to the fact that the TS might exhibit a certain biradical character, a multiconfigurational treatment was applied using the complete active space self-consistent field (CASSCF) method, followed by a second-order peturbation theory (CASPT2) treatment. A CASSCF/CASPT2 combination has been shown to be a reliable approach for systems containing a significant biradical character.[23] For the latter computations, CCSD(T)-optimized geometries were employed in conjunction with both 6-31G(d,p) and ANO basis sets. The contraction scheme[24] of the ANO basis is (10s6p3d/3s2p1d) for C, N, and O and (7s3p/2s1p) for H. The ANO basis was constructed in the real spheric harmonic representation. To ensure that all the electrons participating in the bond reorganization are included in the CASSCF wave functions, we have first considered the active space comprising six electrons in six orbitals (denoted as CASSCF(6,6)) and progressively enlarged it to CASSCF(8,8), CASSCF(10,10), and CASSCF(12,12). In any case, all of the reactant π electrons, as well as the forming σ bonds in the TS, are incorporated. In the two latter active spaces, two distinct sets of orbitals having different symmetry were also considered, namely, the sets of (5a′ + 5a″) and (6a′ + 4a″) in CASSCF(10,10) and the sets of (6a′ + 6a″) and (7a′ + 5a″) in CASSCF(12,12). It turns out that although in each case the difference in CASSCF energies obtained from both sets of orbitals is significant (up to 5 kcal/mol on the barrier height), the difference in CASPT2 energies becomes much smaller (being less than 0.5 kcal/mol). This indicates the crucial role played in this case by the dynamical electron correlation.

Selected geometrical parameters of the TS obtained from four distinct levels of theory are compared in Figure 1. As would be expected, there are noticeable fluctuations in the bond distances and angles in going from one to another level, especially for those belonging to the fulminic acid moiety. In fact, it is known that the HCNO geometry constitutes a difficult case for MO methods.[25] Even though a bent or a linear structure could be found with a given method, the energetic consequence is minimal, amounting only to a few hundred cal/mol. At

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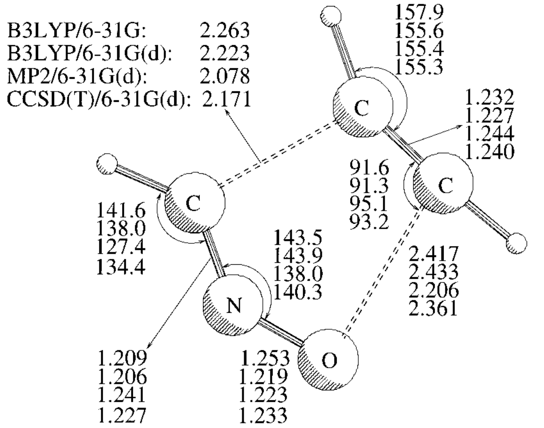

Figure 1. Selected geometrical parameters of the transition structure for the concerted 1,3-dipolar cycloaddition of fulminic acid to acetylene at four different levels of theory. Bond lengths are given in angstroms, and bond angles are in degrees.

all the levels of theory considered, the intermolecular distance *r*(C−C) is confirmed to be shorter than the *r*(C−O), in agreement with earlier studies.[3−10] We note, however, that the ratio *r*(C−C)/*r*(C−O) is about 0.92−0.94 in the present B3LYP, MP2, and CCSD(T) cases, whereas it amounts to 0.98 and 0.89 in Hartree−Fock and BLYP calculations, respectively, with a similar basis set.[7,10] This is remarkable in view of the fact that in the five-membered cyclic product, the C−C bond is actually longer than the C−O. The more advanced formation of the C−C bond arises presumably from a stronger interaction of the corresponding p-orbital lobes. Apparently, the B3LYP functional tends to yield a slightly earlier TS, as compared with both MO treatments. A similar observation has recently been made for the Diels−Alder reaction of formaldehyde to butadiene.[26]

The classical energy barrier for the fulminic acid plus acetylene addition derived from various theoretical models and geometries are summarized in Table 1. A number of important results can thus be noted:

(1) The energy barrier is not quite sensitive to the one-electron functions employed in either MO or DFT calculations. When d functions on heavy atoms are incorporated, a further basis set extension does not appear to induce a variation larger than 1 kcal/mol.

(2) In contrast, the electron correlation is far more important. The large difference of up to 7 kcal/mol between both CCSD and CCSD(T) energy barriers again points out the crucial role of triple substitutions in the evaluation of this quantity.

(3) Taking the CCSD(T) value as the reference, for a given basis set and geometry, the MP2 value is underestimated, whereas the B3LYP value turns out to be similar. Nevertheless, such a similarity should be regarded with caution at this stage. More cases should be considered before a general trend could be identified in the behavior of DFT methods.

(4) The change of energy barrier with respect to the geometry is found to be marginal. When the coupled-cluster treatment is utilized, the choice of a set of geometry employed for single-point energy computations is no longer an important factor. It is pleasant that the CCSD(T)/6-31G(d) method yields practically the same energy barrier using four distinct and rather different geometries, as seen in Figure 1. A similar trend has also been detected for the Diels−Alder cycloaddition.[26,27] It is apparent that the saddle regions of these reactions are pretty shallow in such a way that a large geometrical fluctuation only induces a small change in relative energies. It is needless to say that any generalization of such characteristics would be beneficial for the study of larger systems.

Table 1. Energy Barrier of the Addition of Fulminic Acid to Acetylene using Different Levels of Theory and Geometries

geometry	method	energy barrier[a] (kcal/mol)
B3LYP/6-31G	B3LYP/6-31G	12.4
	MP2/6-31G(d)	9.8
	CCSD(T)/6-31G(d)	13.5
	MP2/6-311+G(2df,2p)	9.9
	G2(MS)	13.6
B3LYP/6-31G(d)	B3LYP/6-31G(d)	13.4
	MP2/6-31G(d)	9.1
	CCSD(T)/6-31G(d)	13.4
	MP2/6-311+G(d)	9.5
	CCSD/6-311++G(d)	19.0
	CCSD(T)/6-311++G(d,p)	13.8
MP2/6-31G(d)	MP2/6-31G(d)	9.6
	CCSD(T)/6-31G(d)	13.3
CCSD(T)/6-31G(d)	MP2/6-31G(d)	10.2
	CCSD(T)/6-31G(d)	13.8
	MP2/6-311++G(d,p)	10.4
	CCSD/6-311++G(d,p)	20.2
	CCSD(T)/6-311++G(d,p)	14.2
	MP2/6-311++G(2df,2p)	10.3
	G2(CC)	14.1
	CASSCF(8,8)/6-31G(d,p)	25.5
	CASSCF(8,8)/CASPT2/6-31G(d,p)	13.0
	CASSCF(10,10)/6-31G(d,p)	24.1
	CASSCF(10,10)/CASPT2/6-31G(d,p)	13.2
	CASSCF(12,12)/6-31G(d,p)	19.5
	CASSCF(12,12)/CASPT2/6-31G(d,p)	13.4
	CASSCF(12,12)/CASPT2/ANO	13.8

[a] At the level indicated and corrected for zero-point energies, Δ(ZPE) = 1.3 kcal/mol.

(5) The difference between energy barriers derived from the G2(MS) and G2(CC) methods is also very small. Use of the 6-311++G(d,p) basis set instead of the smaller 6-31G(d) in the additivity scheme (1) contributes only 0.5 kcal/mol to the relative energy. In a systematic comparison of substituted compounds, such small variations in energy barriers are expected to be canceled out, and the smaller basis set could thus be employed for their reliable evaluation. Overall, the CCSD(T) and G2 treatments predict a barrier height of about 14 kcal/mol.

(6) The CASSCF methods tend to substantially overestimate the barrier, irrespective of the active space. It seems, however, that the barrier is somewhat reduced upon extension of the active space. The overestimation is no doubt due to the fact that mainly nondynamical correlation energies are included in CASSCF wave functions. Results listed in Table 1 suggest that the CASPT2 barriers tend to converge to a value of 13−14 kcal/mol, which is comparable to the CCSD(T) result mentioned above.

(7) Taking all the calculated values into account, in particular the G2 and CASPT2 results, we would suggest that the classical energy barrier of the HCNO + HCCH

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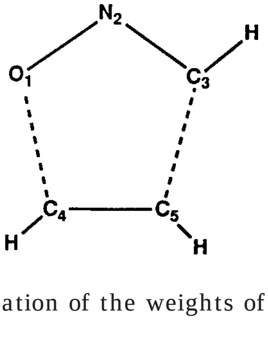
cycloaddition is about 13−14 kcal/mol, which is much larger than the most recent MP4 value of 7.8 kcal/mol.[10] As far as we are aware, no experimental result is available yet, even for substituted systems.

2.2. An Analysis of the CI-LMO-CAS Wave Function. The electronic mechanism of the 13DC was investigated in detail in the late seventies by Leroy and coworkers.[3,4] In following the motion of the charge centroids of the Boys localized orbitals (LMO) of the supersystems along the minimum energy reaction paths, the electronic reorganization, the bond donor and bond acceptor centers, and thereby the formation mechanism of the new bonds have been identified. In establishing the migration direction of the electron pairs, this approach is quite successful in rationalizing and predicting the regioselectivity and the effect of substituents in a large number of 13DCs. However, there have been some difficulties in interpreting the regioselectivity of nitrile oxides (RCNO), whose simplest member is actually fulminic acid. To probe further this mechanistic problem, a multiconfigurational wave function has been constructed for the transition state structure of fulminic acid to acetylene; the transition-state geometry was determined with a CASSCF method using the 6-31G(d) basis set. For the CASSCF calculation, a five-orbital active space corresponding to three p-orbitals on the molecular plane of the HCNO moeity of the reaction system and two p-orbitals on the molecular plane of the acetylene moiety were chosen. All excited configurations in the active space were generated. The CI-LMO-CAS analysis was carried out following a method described elesewhere.[11,12] In brief, it involves the following steps: (1) A five-orbital, six-electron CASSCF calculation is initially performed to obtain a starting set of orbitals for the localization procedure. (2) After completion of the CASSCF procedure, the CASSCF-optimized orbitals are subjected to the Boys localization procedure.[28] The resulting localized orbitals are thus very atomic in nature. (3) By using the localized MOs as a basis, a (50 × 50) configuration interaction wave function is constructed to generate the electronic structures and their relative weights in the ground-state wave function. The CI-LMO-CAS calculations were performed with the GAMESS program.[29]

The relative weights of the various electronic configurations along the intrinsic reaction coordinate (IRC)[30] are shown in Figure 2. It can be seen from Figure 2 that the weight of configuration 18 decreases progressively from the reactant side to the product side, whereas the weight of configuration 16 increases in the same direction. Both configurations 18 and 16 correspond to the distributions O1(2)N2(1)C3(1)C4(1)C5(1) and O1(1)N2(2)C3(1)C4(1)-C5(1), respectively, where the values in brackets are the numbers of electrons in the atomic-like localized orbitals. The subscription of atoms is as follows:



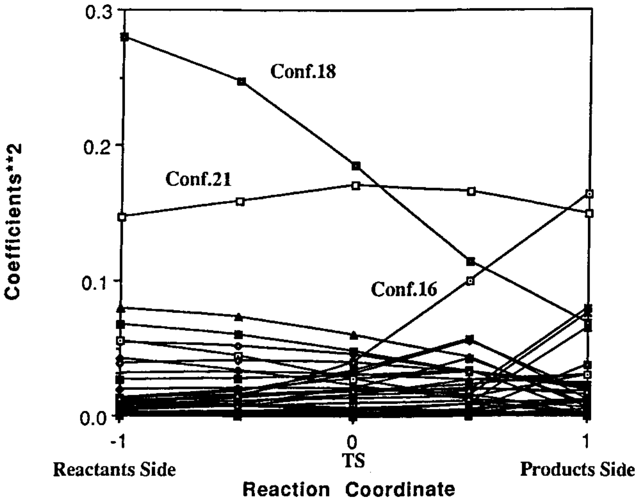


Figure 2. The square of CI coefficients of the LMO-CI along the IRC path for the HCNO + HCCH addition. See text for the definition of the configurations 16 and 18.

From the variation of the weights of both configurations 18 and 16 along the reaction pathway, the reaction mechanism can be characterized by a charge transfer (electron movement) from the O1 atom to the N2 atom. Such a mechanism corresponds to the previous discussion of the ratio *r*(C3−C5)/*r*(O1−C4) at the transition-state structure: *r*(C3−C5)/*r*(O1−C4) < 1 at the transition structure and *r*(C3−C5)/*r*(O1−C4) > 1 at the cyclic product. At the transition-state structure, the weight of configuration 18 is larger than that of configuration 16. This implies that in the concerted addition, via a biradical coupling, the formation at the transition state of the new O1−C4 bond proceeds less readily than that of the other new C3−C5 bond. That is due to a difference in electron repulsion between O1(2)−C4(1) and C3(1)−C5(1). That is to say, when the reaction of the intermolecular HCNO + HCCH system occurs through the concerted mechanism, the intramolecular mechanism occurs through a charge transfer (an electron migration) from the O1 atom to the N2 atom in the fulminic acid moiety.

Due to the fact that within a cycloaddition the electron movement is cyclic by nature, the electron flow is therefore moving forward from the N atom to the C atom, finally making the C atom a new bond donor center. This picture is thus in clear contrast with the one derived earlier by considering the net charges or the cyclic motion of the electron pairs identified by the Boys localized orbitals obtained from HF wave functions. In fact, the O atom is the most negatively charged[5] and was shown to act as a bond donor center, whereas the C atom behaves as a bond acceptor.[3,4] Needless to say, such a new view implies an important change in the understanding of the regioselectivity of fulminic acid and its derivatives with respect to hetero-dipolarophiles.

2.3. An Analysis using DFT Reactivity Descriptors. A further attempt has been made to understand the reaction mechanism by using DFT-based reactivity descriptors, such as Fukui function, hardness, and local

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softness. It is now well known that these reactivity desciptors provide new and efficient avenues for the interpretation of reaction mechanisms.[13] Recently, we have proposed[14−18] a simple approach to interpret the regiochemistry of cycloaddition reactions using the local softness and local hard and soft acids and bases (HSAB) principle. Although in the present case there is no regioselectivity as both carbon atoms of HCCH are identical, it is rather clear from our earlier discussion and other studies that one of the atoms of HCNO is expected to act as a bond donor to form a new intersystem bond, whereas the other acts as a bond acceptor. To verify it further, we have calculated the DFT-based local reactivity parameters for HCNO.

The definitions of molecular hardness, Fukui function, and local softness can be found elsewhere.[31−34] In the present study, local softnesses are calculated by using the finite difference technique[33,34] and applying the DFT-B3LYP procedure in conjunction with 6-31G(d,p) basis functions.

For its part, molecular hardness is approximated as[31] $\eta = (\mathrm{IE} - \mathrm{EA})/2$. Assuming bond donation ability as electron donation ability, we can look at the s^- values (softness for electrophilic attack) for the C and O atoms of HCNO, which are 0.95 and 0.86 (in au), respectively. Thus, this descriptor also indicates the C atom as a more likely bond donor, in line with the picture derived above from the CI-LMO-CAS analysis.

We have also extended our study to examine how hardness of the supersystem changes when the reactants approach each other along the reaction coordinate (RC). More precisely, our intention is to examine whether η goes through a minimum when energy goes through a maximum (TS) along the RC. A hardness profile can simply be defined[18,35,36] as the change in the hardness of a species along the RC. Global hardness has been estimated from the finite difference formula, and the vertical IE and EA values were evaluated at each point of the RC by the ΔSCF procedure using B3LYP electronic energies. Figure 3 shows the variation of energy and η along the RC near the transition-state structure. It is obvious from Figure 3 that η does go through a minimum along the RC, but the point of minimum does not coincide with the point of maximum in energy. Rather, η attains its minimum value more toward the product side in comparison to the maximum in energy profile. The two extrema are separated by 0.05 au along the intrinsic reaction path. It appears that there is also some kind of reverse Hammond behavior for the hardness in which the position of the hardness minimum is determined by the corresponding values of the reactants or products rather than by the position of the energy stationary points. In this specific case, the hardness of the cycloadduct seems to be lower than that of the reactants; as a consequence, the hardness minimum lies closer to that of the adduct. In any case, it is interesting to notice that a hardness profile can be defined in the same notion as an energy profile. It should be mentioned that although the present case is not exhaustive to allow any generalization on this matter, it would be helpful to initiate further research in this direction.

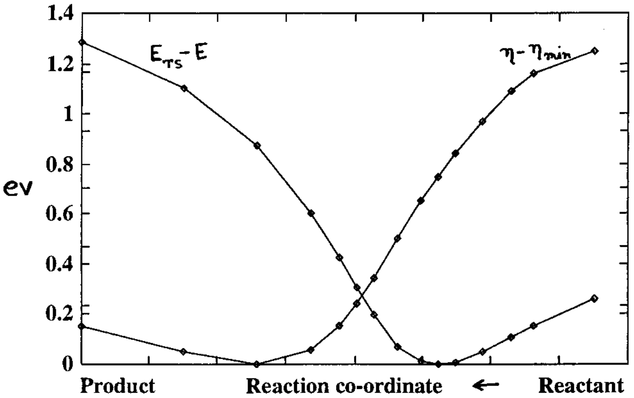

Figure 3. Energy and hardness profiles along the IRC path of the HCNO + HCCH addition.

In summary, we have determined in the present theoretical study an energy barrier of 13−14 kcal/mol for the prototype 13DC of fulminic acid to acetylene. In contrast with earlier views, we have also found that *the oxygen (O) atom can better be regarded as a bond acceptor center and the carbon (C) as a bond donor*.

After submission of this paper, we became aware of a theoretical study on the same reaction of fulminic acid plus acetylene,[37] using in particular a spin-coupled valence bond (SC-VB) approach to the electronic reorganization of the 13DC. The results reported in ref 37 show some similarities but also some important differences with ours. On one hand, in agreement with our results, these authors obtained an energy barrier of 13.5 kcal/mol (12.2 kcal/mol without ZPE corrections) from CASSCF(6,6)/CASPT2/6-31G(d) computations. On the other hand, The SC-VB analysis appeared to confirm the earlier views in which the O atom behaves as a new bond donor and the C atom as a bond acceptor, in clear contrast with our CI-LMO-CAS analysis. In view of the discrepancy, further studies are certainly necessary to clarify this essential issue regarding the electronic mechanism and thereby the regioselectivity of nitrile oxides.

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