

Radical-substituted allenes as high-spin species and subunits of organic ferromagnets

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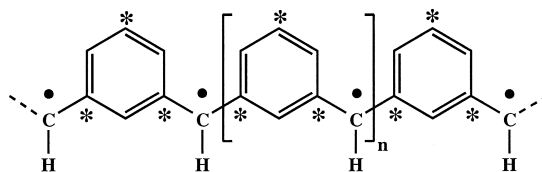
Abstract

Allenes, substituted with radicalic groups (CH_2^\bullet , NH_2^+ , $\text{HN}-\text{O}^\bullet$) at the terminal carbon atoms, have been investigated theoretically by ab initio methods. It is shown that the 1,3-dimethyleneallene and the 1,3-diaminoallene dication are molecules with triplet ground states due to the formation of carbene-like triplet state structures. In contrast, the closed-shell singlet state and the triplet state are degenerate for the 1,3-dinitroxideallene due to orthogonally arranged and hence decoupled π -electron systems. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The presence of degenerate MOs in a molecular system is an important requirement for the existence of a high-spin ground state. Theoretical and experimental investigations of high-spin π -systems have

mainly been focused on alternant non-classical polymers [1,2], e.g.

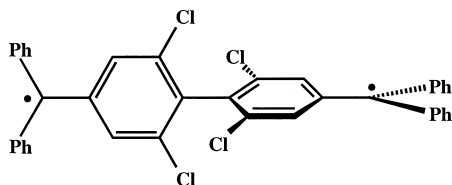


In this case, the presence of a band of half-filled degenerate states follows from the molecular topology as a consequence of the Coulson–Rushbrooke–Longuet–Higgins (CRLH) theorem [3–7] and its generalization [8,9].

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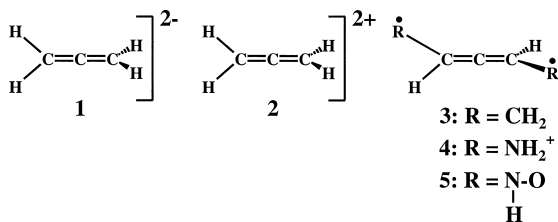
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Another class of narrow-band high-spin organic polymers investigated theoretically [10] and experimentally (oligomers) [11] are compounds in which conjugated π -systems as the elementary units (EUs) are linked (nearly) orthogonally to each other due to steric hindrance (e.g., poly(9,10-anthrylene)polyanions). The overlap between the interacting singly occupied MOs is reduced to zero in the case of an orthogonal arrangement of the orbitals at adjacent EUs. Here, the barrier of the π -conjugation is caused by the geometry of the system. An molecule with a triplet ground state experimentally studied is the 2,6,2',6'-tetrachlorobis(diphenylmethyl)-biphenyl in which the two triphenylmethyl fragments are arranged nearly orthogonally to one another [12,13]:



The principle of orthogonally arranged singly occupied orbitals is also known from systems containing metal ions [14] and from carbenes [15].

Another class of compounds with perfect orthogonally arranged π -electron systems are the allenes and possibly reductively (1) and oxidatively (2) doped allenes and allenes substituted with two spin carrying groups (3–5).



Formally, the electronic structure of allene can be considered as a system consisting of two π -bonds. The MO scheme in HMO approximation is shown in Fig. 1.

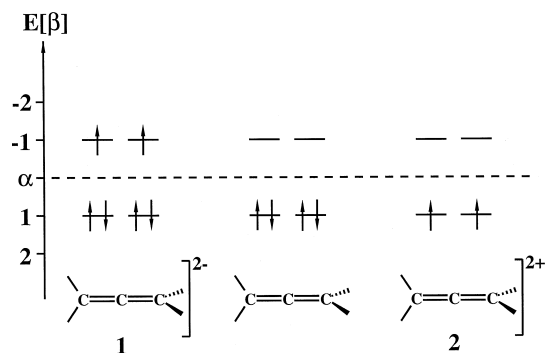


Fig. 1. MO scheme for allene, and its dianion (1) and dication (2) in HMO approximation.

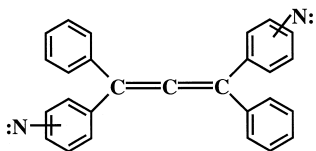
The HOMO and LUMO are degenerate, hence the twofold reductively or oxidatively doped species could have a triplet ground state.

The ground state of allene is a closed-shell singlet state with D_{2d} structure. A triplet excited state 3A_2 with a planar and angular structure (C_{2v} symmetry) has been located ~ 48 kcal/mol above the singlet ground state (ab initio result [16]).

Upon reductive or oxidative doping, the electronic structure of allene should be changed and a triplet ground state could result. The singlet–triplet splitting is mainly determined by the exchange integral. In the case of two orthogonal orbitals at one atom (the overlap integral is zero), the exchange integral should have a relatively large value (~ 0.5 eV). Therefore, the singlet–triplet splitting should be relatively large in favour of the triplet ground state for these species.

In a preliminary communication [17], we have investigated twofold reductively (1) and oxidatively (2) doped allenes. For the allene dianion (1), the orthogonal structure of the undoped allene is not preserved regardless of the state multiplicity. The angular C_2 structure of the triplet state shows close similarities to the triplet state structures of carbenes. Nevertheless, the ground state of the allene dianion is a closed-shell singlet one. In contrast, for the most stable triplet state of the allene dication (2) a D_{2d} structure has been found as referring geometry. The most stable closed-shell singlet state is characterized by a D_{2h} structure. Although both π -subsystems are positioned orthogonally to one another in the triplet state structure, a closed-shell singlet ground state has been found.

Allenes being substituted with radical carriers on both terminal carbon atoms have been investigated neither experimentally nor theoretically up to now. As only exception, in a recent publication [18] it has been shown experimentally that the ground state of 1,3-di-*p*-(*m*-nitrenophenyl)-substituted allenes is a high-spin one (quintet) or this state is degenerate with a closed-shell singlet state:



The aim of this paper is to present the results of quantum-chemical investigations on the structures and ground state multiplicities of 1,3-disubstituted allenes **3**–**5**. These species could be applied as EUs

of narrow-band high-spin polymers with ferromagnetically interacting electrons in the half-filled band.

2. Computational methods

All species described herein have been optimized on ab initio RHF/ROHF level with the basis set 6-31G*. CISD calculations including all singly and doubly substituted electronic configurations have been carried out on the basis of these optimized geometries; for the heavy atoms, the 1σ molecular orbitals and their virtual analogues have been omitted.

Furthermore, all systems investigated have been treated multiconfigurally by CASSCF geometry optimizations with the basis set 6-31G*. The active space consisted of six molecular orbitals of the types π , σ_π and σ_n being occupied by six electrons. All species described in this communication have been found to refer to minimum structures due to frequency analyses performed on the basis of the RHF/ROHF optimized geometries.

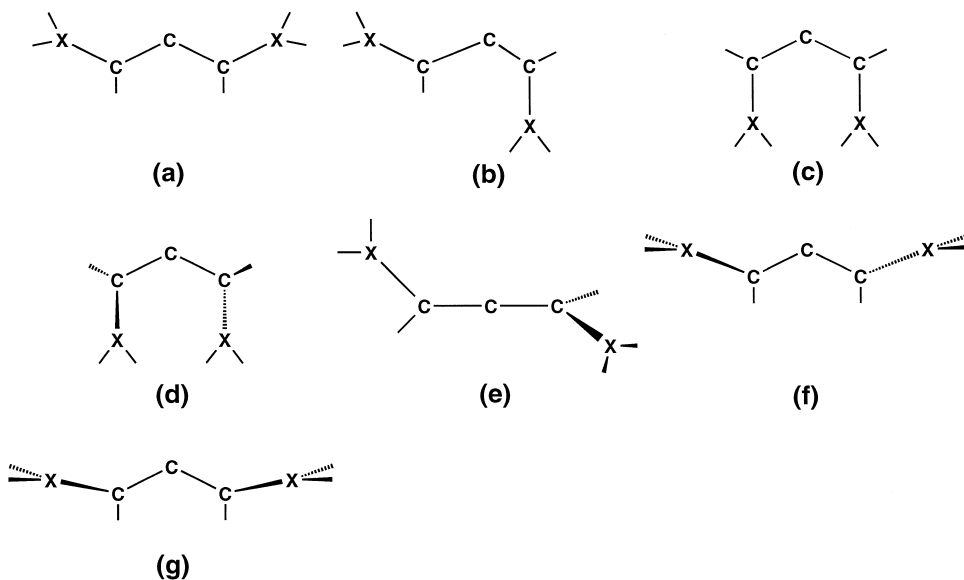


Fig. 2. Principal structures of **3** (X = C) and **4** (X = N).

Table 1

Symmetry, total energies E_{total} (in a.u.) and relative energies $\Delta E_{\text{rel}} (= E - E_{\text{scs(a)}})$ with respect to the energy of the closed-shell singlet state of structure (a), Fig. 2, in kcal/mol of the singlet closed-shell states (scs), the singlet open-shell states (sos) and the triplet states (t) of **3**, calculated by means of ab initio RHF/ROHF/CISD and CASSCF[6, 6], respectively

Structure	State	Symmetry	RHF/ROHF/CISD		CASSCF[6, 6]		
			E_{total}	ΔE_{rel}	E_{total}	ΔE_{rel}	c^2
(a)	scs, 1A_1	C_{2v}	-193.21842	0	-192.74675	0	0.891
	sos, 1B_1	C_{2v}	-193.20903	5.9	-192.73735	5.9	0.850
	t, 3B_1	C_{2v}	-193.23552	-10.7	-192.76638	-12.3	0.881
(b)	scs, 1A	C_1^a	-193.21288	3.5	-192.74371	1.9	0.838
	sos, $^1A'$	C_s	-193.21007	5.2	-192.73316	8.5	0.902
	t, $^3A'$	C_s	-193.23389	-9.7	-192.76458	-11.2	0.882
(c)/(d)	scs(d), 1A	C_2	-193.21393	2.8	-192.74616	0.4	0.843
	sos(c), 1B_1	C_{2v}	-193.20126	10.8	-192.72871	11.3	0.849
	t(d), 3B	C_2	-193.23229	-8.7	-192.76346	-10.5	0.881
(e)	scs, 1A	C_2	- ^b	- ^b	-192.74395	1.8	0.446/0.440
	t, 3B	C_2	-193.22670	-5.2	-192.75647	-6.1	0.862

c^2 = square of the mixing coefficient(s) of the major configuration(s) of the state.

^aNonplanar structure.

^bState cannot be characterized on RHF level.

The calculations have been performed by using the program package GAMESS-UK [19].

3. Results and discussion

3.1. 1,3-dimethyleneallene (**3**)

The 1,3-dimethyleneallene (**3**) is the simplest species with two spin carriers separated by cumulative double bonds. Formally, it can be considered as consisting of two orthogonally arranged allyl radicals. The HMO scheme is characterized by degenerate NBMOs, hence the ground state should be a triplet one. The whole variety of possible chain-like structures of **3** has been investigated, ring structures

have been omitted since they can be considered as being less important as appropriate building block for polymers with high-spin ground states. The principal structures of the system are depicted in Fig. 2 ($X = C$).

In Table 1, the total (E_{total}) and relative energies (E_{rel}) of the various electronic states of the different structures of **3** shown in Fig. 2 are collected.

The ground state is a triplet one with the structure of type (a). Its ‘loose geometry’ is typical for triplet states [20] and is either ~ 12.3 kcal/mol more stable than the closed-shell singlet state and 18.2 kcal/mol more stable than the open-shell singlet state with similar structures of type (a) on CASSCF[6, 6] level. It is obvious that all structures that apply for a given electronic state differ only

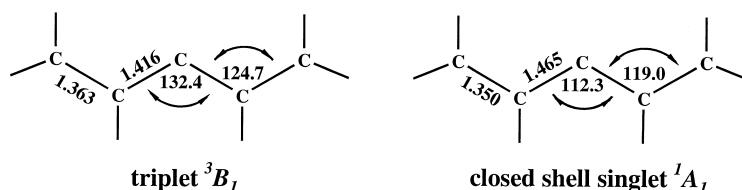


Fig. 3. Optimized geometries of the triplet ground state 3B_1 and the lowest-lying closed-shell singlet state 1A_1 of **3**; data from CASSCF[6, 6] optimizations; bond lengths in Å, bond angles in deg.

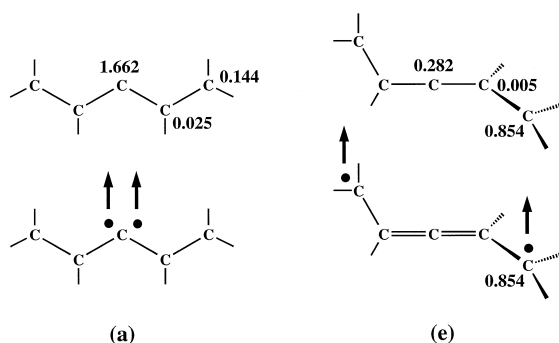


Fig. 4. Distribution of the spin population (Mulliken's formalism, on the basis of the ROHF optimized geometries) of the triplet ground state 3B_1 , structure type (a), and the triplet state 3B , structure type (e), of **3** and the corresponding Lewis structures.

slightly with respect to their total energies. Orthogonality of both π -fragments does only occur in structure (e) (symmetry C_2). For the closed-shell singlet state, this structure refers to a linear combination of the two closed-shell singlet configurations $10a^2 8b^2$ and $9a^2 9b^2$. This structure is 1.8 kcal/mol less stable than the closed-shell singlet state with structure (a) and is also less stable than the triplet state with an orthogonal structural arrangement by 7.9 kcal/mol on CASSCF[6, 6] level. Thus, ground state structures with an orthogonality of both π -fragments have been found neither for the triplet nor the closed-shell nor the open-shell singlet states.

The geometric structures of either the triplet ground state of type (a) and the most stable closed-shell singlet state of type (a) are given in Fig. 3.

The geometric and electronic structures of the different states as well as the singlet–triplet splitting of **3** are very similar to those of carbene [21] and substituted carbenes [15,20,22]. The ab initio optimized and experimentally determined C–C–C bond angles of triplet carbenes are in the range between 130° and 136° , whereas the corresponding angles of

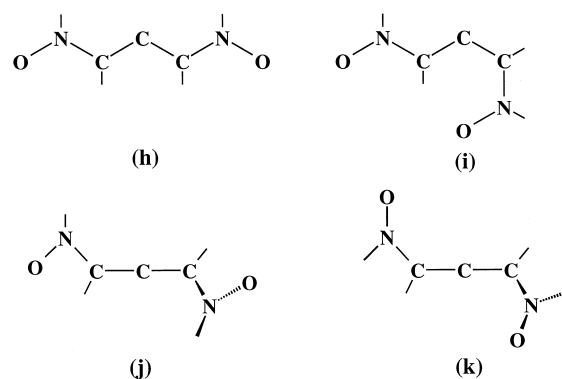


Fig. 6. Energetically most important structures of 1,3-dinitrooxideallene **5**.

singlet carbenes are $\sim 105^\circ$. The singlet–triplet splitting of carbene is ~ 10 kcal/mol in favour of the triplet state [21].

The close similarity of the triplet ground state of 1,3-dimethyleneallene to triplet carbenes can be proved by the investigation of the distribution of the spin population in the triplet state of the angular structure (a) and the orthogonal structure (e) shown in Fig. 4 together with the corresponding Lewis structures.

Whereas most of the spin density is localized in the orthogonal orbitals at the central carbon atom of the carbene-like structure (a), the unpaired electrons are localized in either subsystems of the orthogonal allene-like structure (e).

Obviously, for the 1,3-dimethyleneallene it is more advantageous to stabilize the triplet states by formation of an angular planar carbene-like structure than by decoupled π -subsystems due to an orthogonal allene-like molecular structure.

In summary, either the geometric and the electronic structure of the triplet ground state of 1,3-dimethyleneallene correspond to divinylcarbene.

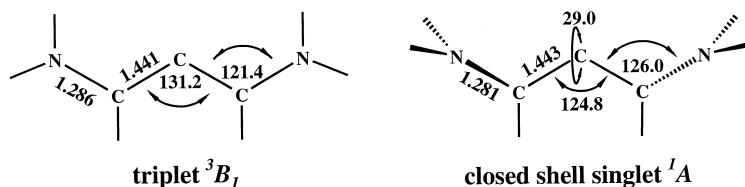


Fig. 5. Optimized geometries of the triplet ground state 3B_1 and the lowest-lying closed-shell singlet state 1A of **4**; data from CASSCF[6, 6] optimizations; bond lengths in Å, bond angles and dihedral angle (NC_1C_3N) in deg.

Table 2

Symmetry, total energies E_{total} (in a.u.) and relative energies ΔE_{rel} ($= E - E_{\text{scs}(f)}$, with respect to the energy of the closed-shell singlet state of structure (f), Fig. 2, in kcal/mol) of the singlet closed-shell states (scs), the singlet open-shell state (sos) and the triplet state (t) of **4**, calculated by means of ab initio RHF/ROHF/CISD and CASSCF[6, 6], respectively

Structure	State	Symmetry	RHF/ROHF/CISD		CASSCF[6, 6]		
			E_{total}	ΔE_{rel}	E_{total}	ΔE_{rel}	c^2
(f)	scs, 1A	C_2	-225.80014	0	-225.28426	0	0.933
(g)	scs, $^1A'$	C_s	-225.80042	-0.2	-225.28177	1.6	0.941
(a)	sos, 1B_1	C_{2v}	-225.78623	8.7	-225.27764	4.2	0.892
	t, 3B_1	C_{2v}	-225.82812	-17.6	-225.32201	-23.7	0.917

c^2 = square of the mixing coefficient of the major configuration of the state.

3.2. 1,3-diaminocarbene dication (**4**)

From all possible structures which were investigated (corresponding to those of 1,3-dimethylenallene in Fig. 2, X = N), only those with a 'loose' geometry (a) or (f), respectively, refer to the most stable states of either multiplicity. The total and relative energies of these species are summarized in Table 2.

The ground state is a triplet one which is significantly more stable than the closed-shell singlet state of structural type (f) (23.7 kcal/mol, CASSCF[6, 6]) and the open-shell singlet state of structural type (a) (27.9 kcal/mol, CASSCF[6, 6]). Thus, in comparison to the 1,3-dimethylenallene, the singlet–triplet splitting is considerably increased. This is in line

with the general findings for substituted carbenes: π -acceptor substituents stabilize the triplet state in relation to the singlet state, π -donor substituents favour the singlet state [15,23–25].

A triplet ground state of carbenes can be stabilized by both electronic as well as steric effects of substituents [23]. Bulky substituents should favour a larger C–C–C valence angle by steric effects and therefore promote a triplet ground state.

The triplet and open-shell singlet state structures of type (a) are planar with C_{2v} symmetry, in the most stable closed-shell singlet state structure (f) the amino groups are arranged orthogonally with respect to the C–C–C plane (see Fig. 5). The C–C–C valence angle in the triplet ground state structure of type (a) is similar to that of triplet carbenes.

Table 3

Symmetry, total energies E_{total} (in a.u.) and relative energies ΔE_{rel} ($= E - E_{\text{scs}(h)}$) with respect to the energy of the closed-shell singlet state of structure (h), Fig. 6, in kcal/mol) of selected closed-shell singlet states (scs), open-shell singlet states (sos) and triplet states (t) of **5**, calculated by means of ab initio RHF/ROHF/CISD and CASSCF[6, 6], respectively

Structure	State	Symmetry	RHF/ROHF/CISD		CASSCF[6, 6]		
			E_{total}	ΔE_{rel}	E_{total}	ΔE_{rel}	c^2
(h)	scs, 1A_1	C_{2v}	-375.11793	0	-374.35633	0	0.858
(i)	sos, $^1A''$	C_s	-375.11109	4.3	-374.34777	5.4	0.957
(j)	scs, 1A	C_2	– ^a	– ^a	-374.37459	-11.5	0.647/0.185
	t, 3B	C_2	-375.14675	-18.1	-374.37600	-12.3	0.905
(k)	scs, 1A	C_2	– ^a	– ^a	-374.36830	-7.5	0.459/0.451
	t, 3B	C_2	-375.13920	-13.3	-374.36980	-8.5	0.911

c^2 = square of the mixing coefficient(s) of the major configuration(s) of the state.

^aState cannot be characterized on RHF level.

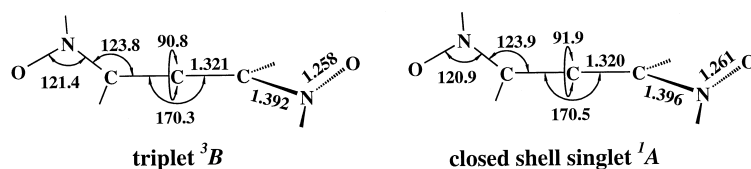


Fig. 7. Optimized geometries of the lowest-lying triplet state 3B and the lowest-lying closed-shell singlet state 1A of **5**; data from CASSCF[6,6] optimizations; bond lengths in Å, bond angles and dihedral angles (NC₁C₃N) in deg.

The geometric and electronic structure of the triplet ground state correspond to di-protonated di-formimidylcarbene.

3.3. 1,3-dinitroxideallene (**5**)

For 1,3-dinitroxideallene, the number of geometric structures to be investigated is considerably higher than for the species discussed before. A selection of all possible structures according to the energies of the referring states is shown in Fig. 6.

In contrast to the species **3** and **4**, the allene-like structures (j) and (k) with orthogonally arranged π -electron systems refer to the most stable states regardless of the multiplicity (both closed-shell singlet states refer to linear combinations of two closed-shell singlet configurations). In Table 3, the total and the relative energies of the most stable states of either multiplicity are given.

As can be seen from Table 3, the most stable triplet state is almost degenerate with the most stable closed-shell singlet state. Both states refer to the structural type (j). Carbene-like structures cannot be

stabilized in triplet states. Surprisingly, the triplet state with the structure of type (h) does not refer to a minimum state but to a transition state and is thus not compiled in Table 3.

In Fig. 7, the optimized geometries of the triplet and the closed-shell singlet states with orthogonally arranged π -subsystems are shown.

It seems that triplet states with a carbene-like structure cannot be stabilized due to the large electronegativity of both the nitrogen and oxygen atoms of the substituents. Thus, the unpaired electrons are fixed particularly at the oxygen atoms and are unavailable to be localized at the central carbon atom of the allene fragment what would favour carbene-like triplet state structures. This can be seen from the distribution of the spin population, Fig. 8, which can be expressed by the referring Lewis structure.

4. Conclusions

Whereas for 1,3-dimethyleneallene (**3**) and 1,3-aminoallene-dication (**4**) the triplet ground state is significantly stabilized in relation to a closed-shell singlet state, the triplet ground state of 1,3-dinitroxideallene (**5**) is almost degenerate with a closed-shell singlet state.

For the investigated allenes being substituted with two spin carrying groups, there are two possible ways for stabilizing triplet states energetically with respect to the closed-shell singlet states:

(1) Carbene-like planar angular structures might favour a triplet ground state. Both unpaired electrons are localized mainly at the central carbon atom of the allene fragment. The bonds between the terminal carbon atoms of the allene fragment and the substituents are formal double bonds. Hence, the vinyl and the protonated formimidyl groups as π -acceptor substituents stabilize the triplet state in relation to the

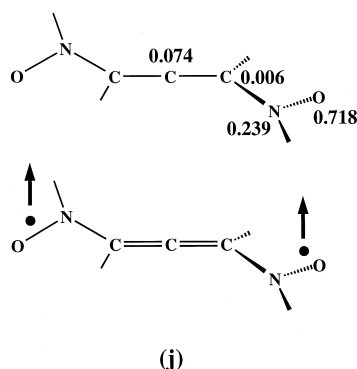


Fig. 8. Distribution of the spin population (Mulliken's formalism, on the basis of the ROHF optimized geometry) of the triplet state 3B of **5** and the corresponding Lewis structure.

singlet state in the case of 1,3-dimethyleneallene and 1,3-diaminoallene-dication.

(2) Orthogonally arranged decoupled π -subsystems stabilize the triplet state. The unpaired electrons are mostly localized in either π -subsystem due to the orthogonally arranged singly occupied MOs. This type of distribution of the spin population is supported by substituents containing strongly electronegative atoms which may fix the unpaired electrons. This kind of stabilization has been found in the most stable triplet state of 1,3-dinitroxideallene. However, this did not lead to a significantly stabilized triplet ground state.

Acknowledgements

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