"CHEMICAL PORTRAIT" OF FULLERENE MOLECULES

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Chemical activity of fullerene molecules is associated with a partially radical character of these molecules caused by the presence of effectively unpaired electrons (EUE). Values of the total number of N_D and partial distribution N_{DA} of EUE over the atoms in a singlet state of molecules C_{60} and C_{70} have been calculated. "Chemical portraits" of molecules are presented, and N_{DA} values are proposed to be used as indicators for chemical activity of atoms and to predict thereby the position of favorable atom-atom contacts in addition reactions with participation of these molecules. Bases of "computational synthesis" procedures for fullerene C_{60} derivatives are exemplified by initial phases of its fluorination.

Keywords: quantum chemistry, chemical activity, fullerene C_{60} and C_{70}, computational synthesis.

Present ideas of chemical activity of fullerenes, mostly of C_{60} molecule, come to two basic statements. The first is that fullerene behaves like an electron-deficient polyalkene [1, 2], and not like an electron-enriched aromatic molecule as was originally supposed [3]. Rigid localization of double bonds in the molecule, confidently shown experimentally, is explained [1, 2] by the presence of pentagon molecules in the structure precluding π-electrons from conjugation. However, the electronic mechanism by which the pentagon structures localize double bonds remains entirely obscure.

The second statement concerns selectivity of the chemical activity of molecules. The opinions on this point have divided. Some researchers incline to that the molecule has 30 equivalent reaction centers (by the number of double bonds) due to which most chemical reactions are not selective [2]. It is, however, difficult to reconcile this statement with the presence of primary derivatives of C_{60}, hydrides and halides, mostly of a specific stoichiometric composition, for example, $C_{60}H_{36}$, $C_{60}Hal_{24}$, $C_{60}Hal_{36}$, $C_{60}Hal_{48}$ [4, 5]. Moreover, in obtaining the metallofullerenes, it has been established from the very beginning [1, 6] that transition metals are forming an octahedron surrounding for the internal C_{60} nucleus. Thus the idea of atom-local selectivity (regioselectivity) of the molecule has appeared. The extension of this approach to organic derivatives of fullerene has led to a model suggested by Wudle [2, 7] the core of which is a structural factor — pyracyclene fragment responsible for each elementary act of addition. In the author's opinion [2], localization of molecule the chemical activity within the fragment is caused by its pentagons. The presence of six such fragments in the structure of the C_{60} molecule made it possible to explain the formation of organic pseudo-octahedron covalent derivatives, fullerene stars with added products of different complexity [8].

Attempts to give the quantum chemical (QC) description of C_{60} derivatives have been made repeatedly (see, for example, detailed works [9-11] and references therein). These computations, however, were aimed not so much at understanding the nature of the molecule chemical activity as at the confirmation of stability of reaction products. All computations have been made in the approximation of full covalent pairing (the approximation of closed shells) of C_{60} molecule electrons, which *a priori*, as it is shown below, exclude from consideration just those of its properties which are

associated with the presence of "excess"* electrons in the molecule and lead to chemical activity.

An alternative option in the consideration of the chemical activity of fullerenes based on the analysis of the main feature of their molecules — partial exclusion of excess electrons from the covalent pairing — has been recently proposed in [14]. Partially radical character of the molecules of fullerenes is displayed by the presence in it of EUE [15-17]. For the determination of both the total number of N_D EUE and its partial distribution among the atoms of N_{DA} molecule it was proposed in the work [14] to use UHF solution of the quantum chemical problem for the singlet state of molecules. The analysis of instability of this solution with respect to a purely spin (PS) singlet state has revealed the following regularities [14].

1. With the presence of EUE in the system the energy of UHF state is usually higher, and in the case of C_{60} molecule this excess makes 6%.

2. The wave function of UHF state at even number of electrons determines the function of the singlet PS state to good accuracy (in case of C_{60} to 10^{-2}%).

The UHF solution, therefore, conforms to the physical reality, at the same time presenting a unique possibility to reveal and determine the numerical EUE parameters by spin characteristics of this state.

Great similarity of partial N_{DA} distributions and free valence over the atoms of C_{60} and Si_{60} [14] molecules makes it necessary to take N_{DA} as a characteristic of the chemical activity of the bound atom. Hence, it is proposed that N_{DA} is used as the main parameter selecting atoms of the molecule by the degree of chemical activity and, thereby, to predict the position of the most favorable atom-atom contacts in the addition reaction involving C_{60} and C_{70} molecules. In this work, the approach based on selection of the most active atoms of the molecule by the maximum N_{DA} value is illustrated by an example of initial phases of C_{60} fluorination reactions.

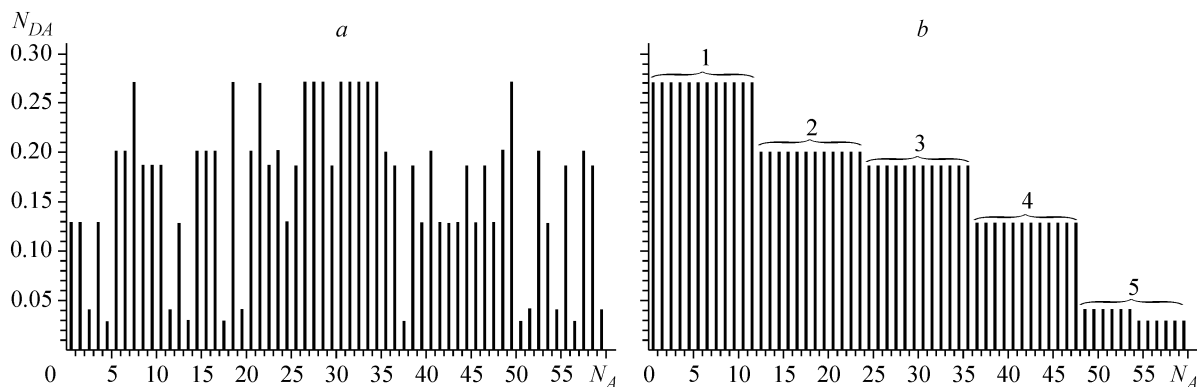## "CHEMICAL PORTRAITS" OF C_{60} AND C_{70} MOLECULES

N_D and N_{DA} values have been found for fixed interatomic distances corresponding to equilibrium structures of UHF solution for C_{60} and C_{70}** molecules. Calculations were made using a half-empirical method AM1 of the software CLUSTER-Z1 [18]. Fig. 1 shows the N_{DA} distribution over the atoms of C_{60} molecule. The map of N_{DA} in Fig. 1a conforms to the picture taken from the output file of the computation and complies, in general, with the random numbering of atoms. It is well seen in the figure that this value on different atoms is different and changes within broad enough limits from zero to 0.32. However, if to redistribute N_{DA} over atoms merely in descending order, then distribution becomes ordered, that is shown in Fig. 1b, in which five groups of 12 atoms in each with the equal value of N_{DA} within each group are clearly seen. The atoms of each group make six equal pairs within which two atoms are coupled by a short bond C–C and have equal in value but opposite in sign spin density. Therefore, it is possible to imagine that in the structure of C_{60} molecule the same five-pair C_{10} configuration is repeated six times (one pair from each group). As distributing the atoms among six fragments according to N_{DA} distribution in Fig. 1a, we really obtain in Fig. 1b six practically identical five-pair configurations of C_{10} that are naphthalene cores (Fig. 2a). Fig. 2b presents C_{60} molecule as $6 \cdot C_{10}$ allowing for the grouping of atoms. This can be considered as the "chemical portrait" of C_{60} molecule in a singlet UHF state, which quite unexpectedly validates the assumption of just this formation of C_{60} molecule from carbene chains C_5 [19, 20].

The "color spectrum" of the N_{DA} distribution map over the molecule atoms or of the relevant map of the chemical activity of its atoms is determined by a difference between N_{DA} values for atoms of different groups and makes the ground for

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*The term "excess electrons" widely used to describe the electron structure of diradicals [12, 13] is introduced to denote the fact that the number of valence electrons of each atom from fullerene molecules is by a unit larger than the number of attached atoms.

**In accord with [14], N_D and N_{DA} are determined as $N_{DA} = \sum_{i \in A} \sum_{B=1}^{NAT} \sum_{j \in B} D_{ij}$ and $N_D = \sum_A N_{DA}$, where D_{ij} is an element of a spin density matrix in the singlet UHF state.

Fig. 1. N_{DA} distribution over the atoms of C_{60} molecule: *a* is the result corresponding to a random numbering of atoms , *b* is the ordered distribution.
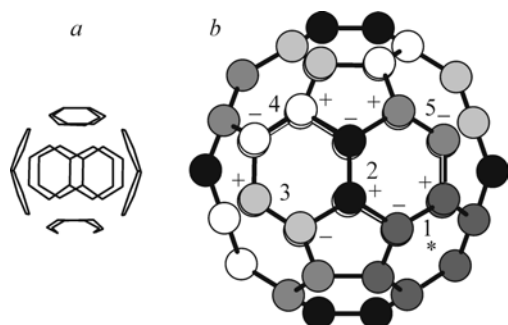
Fig. 2. "Chemical portrait" of C_{60} molecule. The figures correspond to numbers of groups in Fig. 1*b*. Plus and minus denote the sign of spin density.
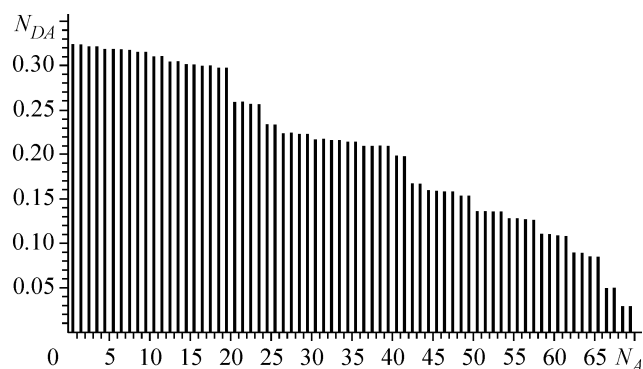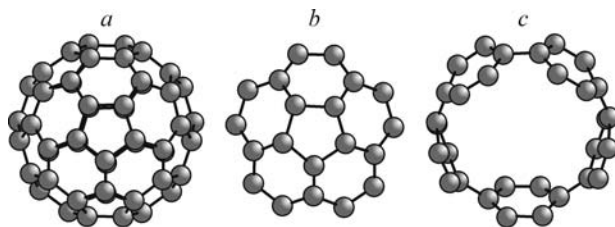

Fig. 3. Ordered N_{DA} distribution over the atoms of C_{70} molecule.

the atom-local selectivity of the molecule chemical activity. Thus, the atoms of group 1 forming two hexagons on the opposite ends of the molecule (Fig. 2*b*) have the absolute priority in the initial steps of reactions of addition to C_{60} molecule.

Fig. 3 shows the N_{DA} distribution map of C_{70} molecule over atoms. It reveals that the "chemical portrait" of the molecule is less colorful than that of C_{60}. Nevertheless, like in the previous case, N_{DA} distribution has a clearly expressed group structure. However, this structure complexity indicates that, unlike C_{60}, it is impossible to distinguish in C_{70} molecule the only one basic structural element by multiplying which it is possible to build a molecule. The space symmetry D_{5h} prompts decomposition of the molecule structure into three five-member ring cycles shown in Fig. 4*b* and *c*. A common structural element for all the cycles is hexagon C_6. In two 20-atom cycles I (Fig. 4*b*) hexagons are conjugated forming the contour of a five-petal flower. In the third 30-atom cycle II (Fig. 4*c*) five hexagons form a closed sparse "chain-bracelet" being coupled with each other by a single bond.

From the viewpoint of the space structure symmetry D_{5h}, hexagons within each cycle are identical. But this conclusion contradicts the complicated group structure of the N_{DA} map. Indeed, projecting the N_{DA} values on the space structure of the cycles (Fig. 5), we find out that this takes place only for cycle II. In cycle I**,** the symmetry with respect to N_{DA} distribution is not higher than C_{2v}, and hexagons forming the cycle are not identical. Both cycles I, indeed, are identical at that. Paying attention to N_{DA} values within the cycle, we note that the maximum values of N_{DA} are concentrated in the ring "belt-bracelet" II. Therefore, this zone contains atoms with the maximal chemical activity.

**Fig. 4**. Structural elements of C_{70} molecule.
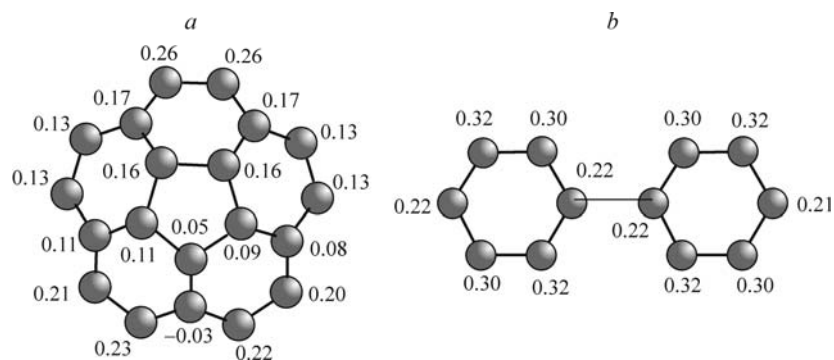
Fig. 5. N_{DA} distribution over the atoms of five-member cycles of C_{70} molecule: *a* is cycle I, *b* is cycle II.

BASES OF THE QUANTUM CHEMICAL SYNTHESIS OF FULLERENE DERIVATIVES. SYNTHESIS OF C_{60} FLUORIDES

Using N_{DA} as a quantitative indicator of the chemical activity of atoms, it is possible to make a "computational synthesis" of the derivatives of C_{60} and C_{70} molecules under the conditions of set chemical reactions. Well known reactions of hydration and fluorination of fullerenes in vapors of the corresponding gases are simplest from the computational viewpoint [4, 5]. Let us exemplify the methods for such a synthesis by the initial phase of fluorination of C_{60} molecule.

When starting the computation, a pair of atoms from group 1 coupled by a short bond C_F–C_F, with maximum N_{DA} values (see reference atoms in Fig. 6*a*) is selected. Fluorine molecule is placed near this pair of atoms and a full optimization of the joint structure in the singlet state is performed. Fluorine molecule turned out to willingly join to fullerene molecule in all cases. However, two products of reaction are possible, depending on the orientation of the fluorine molecule axis relative to the selected bond C_F–C_F. If the fluorine molecule axis is parallel to C_F–C_F bond, then the computation results in the final product $C_{60}F_2$ (I, Fig. 6*b*). If the orientation of the F_2 molecule axis in respect to C_F–C_F bond deviates from the parallel, even so slightly as is shown in Fig. 6*a*, then the complex $C_{60}F_1 + F_1$ (II + F_1, Fig. 6*c*) is formed.
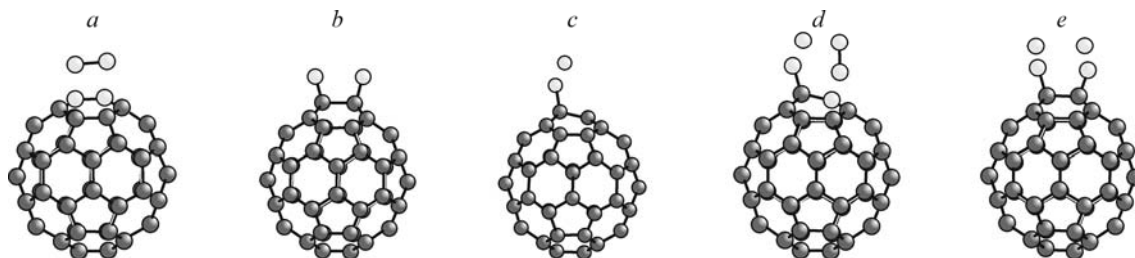

Fig. 6. Addition of fluorine molecule to fullerene C_{60}: *a* is the initial geometry; light atoms in the C_{60} structure are reference ones; *b* is the final product **I**, $C_{60}F_2$; *c* is the final product **II**, $C_{60}F_1$, and free fluorine atom F_1; the obtained complex corresponds to the initial configuration *a*. The initial configuration (*d*) and the final product (*e*) of $(C_{60}F_1 + F_1) + F_2$ reaction.
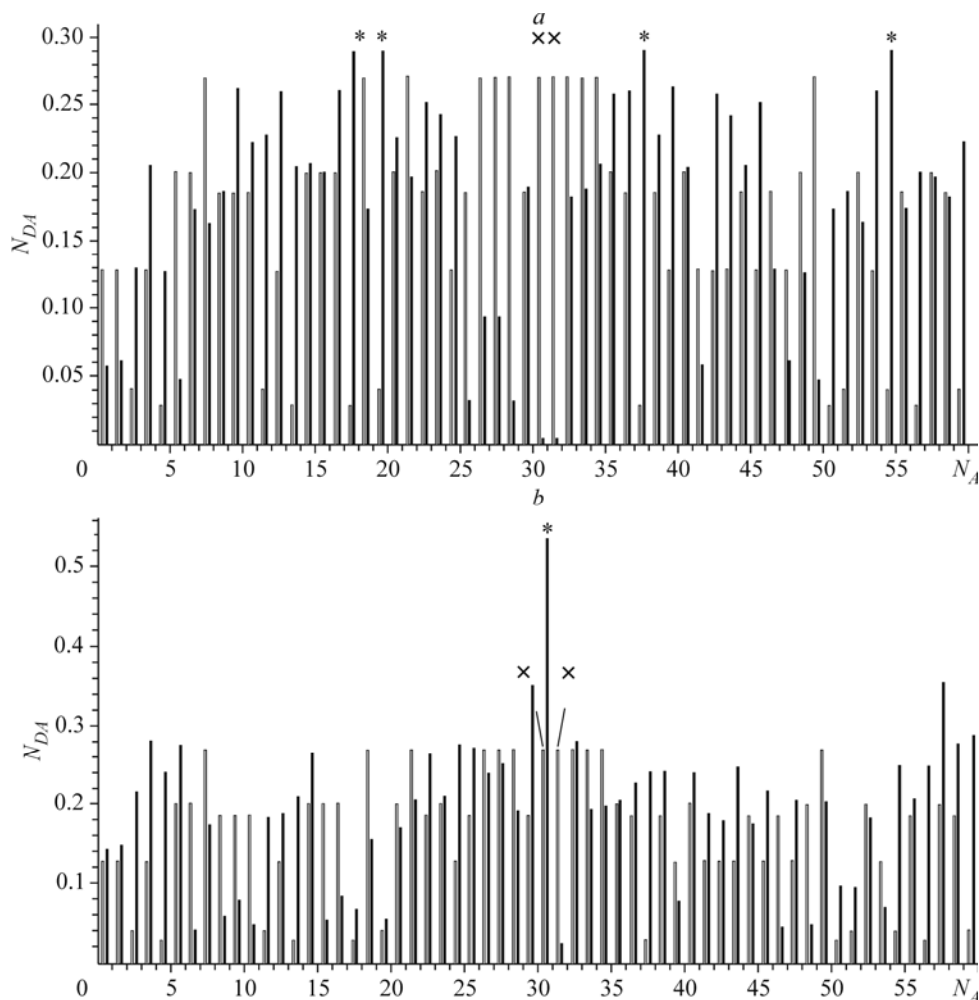
Fig. 7. N_{DA} distribution map for $C_{60}F_2$ (*a*) and $C_{60}F_1$ (*b*) products.

The N_{DA} distribution map for compounds I and II is shown in Fig. 7*a* and *b*. The background in both figures is the N_{DA} map of C_{60} molecule where initial reference atoms are marked with crosses. As seen from the figures, as a result of the addition of fluorine atoms, a substantial redistribution of N_{DA}, in comparison with the initial distribution in C_{60} molecule, occurs, different in both considered cases. In the first case, as seen from the figure, N_{DA} is fully extinguished on reference atoms 31 and 32, and atoms 18, 20, 38, and 55, marked by asterisks, become the most chemically active ones. In the second case (Fig. 7*b*), atom 31 which is the pair to the initial reference atom 32, that has added fluorine atom, prevails in the N_{DA} map (Fig. 6*c*). The obtained picture certainly evidences the readiness of C_{60} molecule to complete the reaction with participation of just this atom paired to the already used reference atom. Following this instruction and maintaining the configuration of the II + F complex, another fluorine molecule is added, as shown in Fig. 6*d*. As a result of the optimization of this complex structure, the outcome of which in this case does not depend on the mutual orientation of fluorine molecule axes in relation to C_F–C_F bond, we obtain a new complex $C_{60}F_2 + 2F$ (III + 2F, Fig. 6*e*). The geometry and electronic properties of molecule III are totally identical to those of molecule I, which is proved by the full identity of N_{DA} maps. Therefore, irrespective of whether the addition reaction of fluorine molecule to fullerene proceeds in one stage (Fig. 6*b*) or in two stages (see Fig. 6*e*), the same final product $C_{60}F_2$ forms. Obviously, the two-stage character of the reaction ought to prevail in practice, since, first, the cases of parallel orientation of the fluorine molecule axis relative to C_F–C_F bond occur surely less often comparing to non-parallel orientation; and, second, single fluorine atoms formed in the two-stage process are much more active than molecular fluorine.
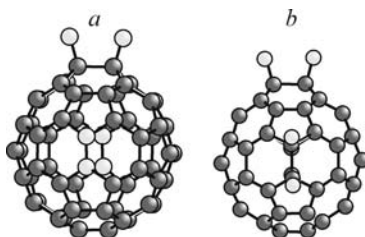
Fig. 8. The initial configuration (*a*) and the final product (*b*) of $C_{60}F_2 + F_2$ reaction. Two pairs of atoms with maximum N_{DA} values are shown in a lighter color.

Passing to the next step of the reaction, note that atoms 18, 20, 38, and 55 of $C_{60}F_2$ molecule are marked out in the N_{DA} map. These atoms form two pairs of short C_F–C_F bonds symmetrically arranged in the equatorial plane of the molecule relative to the primary reference atoms (Fig. 8*a*). One of these pairs is chosen as the reference point to consider the next addition of fluorine molecule. The procedure of this step completely repeats the above one. Finally, $C_{60}F_4$ molecule forms, shown in Fig. 8*b*.

Thus, performing the synthesis of $C_{60}X_{2n}$ (X = H, F) derivatives as a series of successive steps $C_{60}X_{2k} + X_2$, $k = n - 1$ and being guided in the addition of the atoms of each following molecule X_2 by maximum values of N_{DA} on the atoms of the preceding $C_{60}X_{2k}$ derivatives, the synthesis of hydrides and fluorides of C_{60} was performed with a change in k value from 1 to 30 [21]. The obtained results allow us to understand many features in the chemical formation of the families of these derivatives to explain quantitative differences in their synthesis and answer a number of questions arising in the course of the laboratory synthesis [21]. In particular, it is shown that absolute nullification of N_{DA}, appearing as k reaches the value 24 for C_{60} fluorides, naturally explains the break in the corresponding series of the chemical synthesis on $C_{60}F_{48}$ molecule [4, 5].

CONCLUSION

The reported here analysis of the chemical activity of fullerene molecules is based on the use of a quantitative feature inherent in these molecules, the presence of EUE representing that part of valence electrons which is not involved in covalence pairing. To determine the number EUE N_D and their partial contribution distribution over atoms N_{DA}, it is proposed to use the UHF solution of the quantum chemical problem for the singlet state of molecules. The N_{DA} map of distribution over the atoms supplements the structural description of fullerene molecules with the "chemical portrait." Thus in terms of N_{DA} distribution, C_{60} molecule is a configuration of six naphthalene fragments $6 \cdot C_{10}$. This result can be viewed as one of quantitative arguments in favor of the statement about the formation of fullerene from the linear carbene C_5 chains [19, 20]. A similar approach to C_{70} molecule has made it possible to state that the molecule consists of three five-member ring structures, whose basic element is a hexagon C_6. Mutually different hexagons are conjugated in two identical rings and form the five-petal-flower-like structure. In the third structure, five identical benzene rings are bound by singe bonds forming an openwork "bracelet."

The very character of N_{DA} makes one consider this value as a characteristic of the chemical activity of the bonded atom. It is suggested in the paper that N_{DA} is used as the main parameter selecting the molecule atoms by the degree of chemical activity. This approach opens opportunities for a broad "computational synthesis" of fullerene derivatives. The bases of such a synthesis have been illustrated here by the example of initial phases in the reactions of C_{60} fluorination. Currently this synthesis has been realized in hydration of C_{60} [21] as well as in obtaining its derivatives as a result of addition of various amines [22-25], including primary amines that are terminal groups of star-shaped fullerene-containing polymers [22, 23].

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