

A quantum chemical study of the interaction of carboxylic acids with DMSO

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3 **A Quantum chemical study of the interaction of carboxylic acids with DMSO**

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12 **ABSTRACT**

Quantum chemical computational methods, which use quantum mechanics and molecular dynamics theory, have developed rapidly in the past few decades, and quantum chemical computation has penetrated almost all fields of chemistry. Hydrogen bonds are ubiquitously common weak intermolecular interactions. Moreover, the bonding mechanism of hydrogen bonds is considered to be different from that of chemical bonding. Because of the difficulty of experimental studies, a more accurate calculation of hydrogen bonding from theory is a more convenient and direct method to understand hydrogen bonding. Density functional theory (DFT) is the most widely used general function in quantum chemical calculations, giving accurate results for most chemical systems. In this paper, the geometries of the hydrogen-bonded dimer complex of acetic acid and DMSO was structurally optimized and potential energy surface was determined. The geometries of four related hydrogen-bonded dimer complexes were fully optimized using the M06-2X/6-311++G (3d, 2p) exchange-correlation functional with DFT-D3(BJ) empirical dispersion correction. We found that hydrogen bonding is a mixture of electrostatic interactions and covalent bonding, and that hydrogen bonding is a kind of force with different percentages of electrostatic and covalent character, rather than a special force independent of chemical bonding. Thus, more clearly defining our inherent classification of forces between substances provides a new perspective for our future study of weak interactions such as hydrogen bonding.

30 **Keywords:** quantum chemistry, hydrogen bonding natures, acetic acid, dimethylsulfoxide

INTRODUCTION

Today's high-performance computers allow for the ground-state DFT geometry optimization of molecules with about 100 atoms in a single day. According to Moore's law, in 25 years the computing power will increase by a factor of 106 [1], and algorithms will improve, so advances in experimental chemistry will not be comparable to advances in computing power. Quantum chemical computing will become an essential tool for studying chemical problems, even surpassing experimental observations, and by 2050, chemical research methods will be very different. Therefore, it is crucial to focus current research and future efforts on theory development. Many chemical processes and biological systems operate based on weak intermolecular interactions [2], so weak intermolecular interactions have been of particular interest in chemistry [3-20], for example, in the field of gas chromatographic separations using capillary columns, where weak intermolecular interactions play an irreplaceable role [21]. We found that hydrogen bonding plays a critical role in the retention time of acetic acid(AA) when using gas chromatography to analyze short-chain fatty acids (SCFAs) dissolved in dimethyl sulfoxide (DMSO) [22]. Hydrogen bonding is a frequent weak intermolecular interaction, similar to chemical bonding in that it is directional and saturated, while the bond energy of hydrogen bonding is much smaller than that of chemical bonding. The bonding mechanism of hydrogen bonds is different from chemical bonds in that hydrogen bonds are a special type of the intermolecular force, dipole-dipole. The formation of hydrogen bonds involves electron donors and electron acceptors, where the electron acceptors must be positively charged hydrogen atoms [5]. A more accurate calculation of hydrogen bonding from theory is an obvious way to understand hydrogen bonding, since experiments can be a complicating factor.

Liu *et al.* performed AIMD calculations on the structure of hydrogen bonds in liquid water [23], Dereka *et al.* investigated (HF)₂ hydrogen bonding using quantum chemical calculations combined with experimental methods [24], and Alkorta *et al.* described non-covalent interactions in detail using quantum chemical calculations [25]. However, the definition of hydrogen bonding still seems to be vague.

The focus of this paper is to present the research methods of quantum chemistry and its utility for studying hydrogen bonds. The hydrogen-bonded dimer complexes were fully optimized using the M06-2X/6-311++G (3d, 2p) exchange-correlation function with Basis set superposition error (BSSE) [26] of DFT-D3(BJ) empirical dispersion correction [27]. The hydrogen bonding in the active site was determined using the electrostatic potential (ESP) results of the molecule; a quantum-chemical explanation of hydrogen bonding was derived using molecular orbital theory (MO) [28, 29]; confirmation of the directionality of hydrogen bonding was determined using a potential energy surface scan; estimates and comparisons of the energy of intermolecular hydrogen bonds in the geometries of the related 2 hydrogen-bonded dimer complexes (Formic Acid(FA)-DMSO and Trifluoroacetic acid (TFA)-DMSO) were determined using the M06-2X/6-311++G (3d, 2p) exchange-correlation function with DFT-D3(BJ) empirical dispersion correction. Based on the

69 above calculations, we propose a supplement to the traditional understanding of hydrogen bonding.

METHODS OF QUANTUM CHEMISTRY

In classical mechanics, Newton's second law describes the motion of macroscopic objects. In quantum mechanics, Schrödinger proposed the fluctuation equation to describe the state of motion of microscopic particles, which became the most fundamental equation of quantum mechanics and the theoretical basis of quantum chemical calculations [30, 31]. The time-independent Schrödinger equation can be written as:

$$75 \quad \hat{H}\Psi = E\Psi \quad (1)$$

Where \hat{H} is a Hamiltonian operator and includes all possible interactions within that system. Ψ is the wave function of the system containing all measurable information. E is the energy of the system and the eigenvalue of the Schrödinger equation. On this basis, the traditional Hartree-Fock equation [32] or the DFT method [33-35] both seek approximations to solve the Schrödinger equation.

81 **Molecular modeling:** Molecular modeling is simply the theoretical methods and computational techniques used to model or simulate the behavior of molecules [36]. Each model is an approximate solution of the Schrödinger equation, which includes theoretical approaches and basis sets. The rapid development of computer technology and rapid advances in density general function theory and molecular dynamics theory have made theoretical calculations a powerful tool for studying intermolecular forces. In 1998, the Nobel Prize in Chemistry honored quantum chemists Pople and Kohn for their contributions to quantum chemistry. Pople's approach to quantum chemical calculations and Kohn's density functional theory are significant milestones in computational chemistry. Mhamad Chrayteh *et al.* used second-order perturbation theory (MP2), where aldehyde hydrogen atoms strongly interact with water oxygen atoms, in the case of di- and tri-hydrates [37]. Chen Jun *et al.* used density flooding theory (DFT) and molecular dynamics (MD) simulations to study the hydration mechanism of kaolinite surfaces [38]. Bilonda and Mammino performed calculations of intramolecular hydrogen bonding in matter using different theoretical approaches and basis sets [39]. Quantum chemical calculations played an essential role in all these studies.

96 Theoretically, the use of higher-level theoretical methods and more sophisticated basis sets can lead to more accurate computational results. However, this can also make the computation costly or even unattainable. Ultimately, a trade-off between computational cost and computational accuracy needs to be made when choosing molecular simulations. In this paper, the trend or qualitative forecast of hydrogen bonding in the AA-DMSO hydrogen-bonded dimer complex was found using the Gaussian16 quantum chemistry package [40] in the DFT calculations because the quantitative structure is not predicted.

RESULTS OF QUANTUM CHEMICAL CALCULATIONS OF HYDROGEN BONDING

Hydrogen bonding sites - Electrostatic natures: The carboxyl group in AA is a combination of two functional groups connected to a single carbon atom, the hydroxyl group (-OH) and the carbonyl group (=O). This combination imparts unique natures to each functional group, including polarity, high electronegativity, and weak acidity. These functional groups are capable of hydrogen bonding by providing and accepting protons [41] and will produce strong hydrogen bonds with the polar non-protic solvent DMSO. Quantum chemical computations provide a good characterization of the intermolecular interactions and the sites of action. In this paper, structure-optimization and frequency calculations were performed separately for the AA molecule and the DMSO molecule using the M062X/6-311++G(3d,2p) [42, 43] method and the DFT-D3BJ [27] dispersion correction, which includes NBO [44] analysis and characterization of the hydrogen bonding sites between the solvent AA molecule and the DMSO molecule. The absence of imaginary frequencies is the end of the structural optimization-stable structure.

In Fig. 1, the different colors on the molecular surface correspond to the qualitative size of the surface electrostatic potential (ESP). Regions colored in red indicate the ESP is negative: electrons concentrate more in these locations and positively charged particles have stronger interactions. Regions colored in blue indicate the ESP is positive: negatively charged particles more favorably interact in these locations [45]. The maximum positive ESP value of the AA molecule concentrates in the upper portion of the carboxyl functional group (-OH), while the upper region of the S=O in the DMSO molecule has a negative ESP value; these two regions produce hydrogen bonding [46]. Using the ESP results, the AA molecule and DMSO molecule follow the placement of Fig. 1.

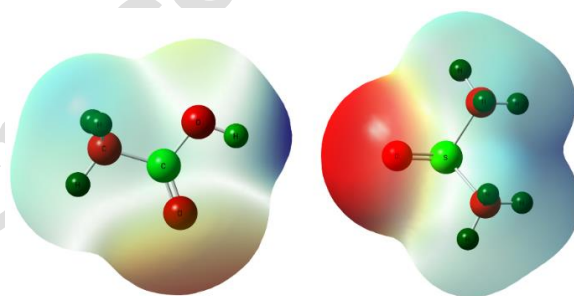


Fig. 1. The hydrogen bonding site of AA with DMSO

ESP has been a popular function for revealing electrostatic interactions between substances [47]. We chose the FA-DMSO hydrogen-bonded dimer complex, which is similar to the AA-DMSO hydrogen-bonded dimer complex. We performed ESP computations, and the results were in concordance with the results of Rohmann's study [48]. We also performed ESP calculations for hydrogen-bonded dimer complexes of AA with N-methyl-pyrrolidone (NMP) and AA-dimethylformamide (DMF) (Fig. 2), both of which are polar, non-protic solvents with similar dipole moments to DMSO [49]. The results and hydrogen bonding interaction sites are consistent with the results of Mu [50] and Safonova [51] *et al.* ESP accurately shows the hydrogen bonding

135 action sites and effectively illustrates the electrostatic nature of hydrogen bonding.

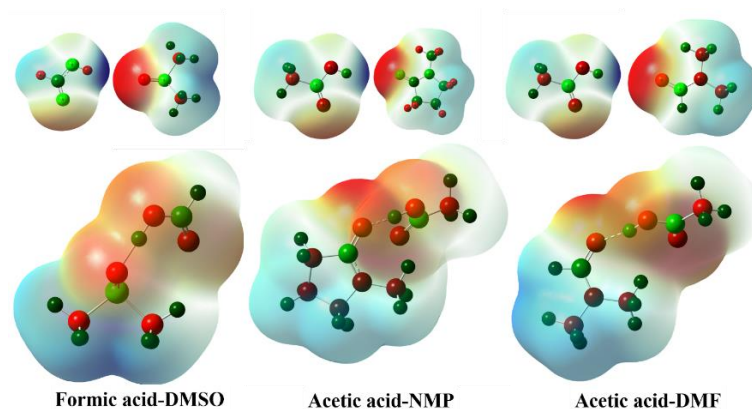


Fig. 2. Hydrogen bonding sites for similar hydrogen-bonded dimer complex of AA and DMSO

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Covalent nature of hydrogen bonds: HOMO/LUMO Interaction: HF is a typical hydrogen bonding system, and the structure-optimized geometry of the (HF)₂ hydrogen bonding system according to previous reports [52-54] and using the computations of section 0 is shown in Fig. 3(b). The angles of F-H...F-H are $\theta_1 = 113^\circ$ and $\theta_2 = 7.6^\circ$, and the four atoms not in a straight line, which matches the action site characterized by the ESP results of HF. However, the angle of action does not follow the results of the ESP (Fig. 3 (a)), and our computations are consistent with the studies of Řezac [54] and Howard [55].

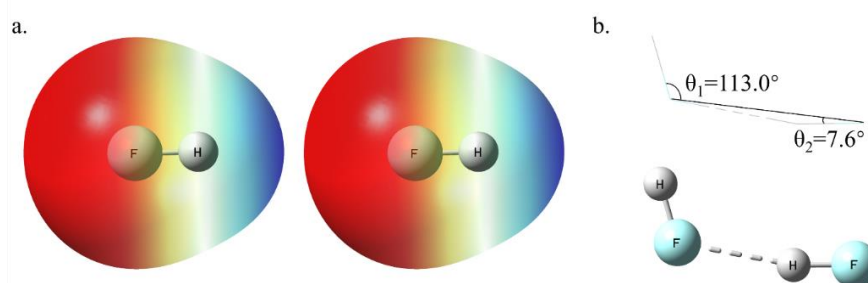


Fig. 3. Hydrogen bonding of (HF)₂

147 a. Site and direction of (HF)₂ interaction presumed by ESP, b. Hydrogen bonding angle of (HF)₂

150 Frontier molecular orbital theory, which incorporates highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) calculations, is an important indicator for chemical reactions [56]. The formation of covalent bonds is the redistribution of electrons in the orbitals of frontier molecules when satisfying certain conditions [57, 58]. Following the arrangement of the AA-DMSO hydrogen-bonded dimer complex according to the hydrogen bonding sites, we used the calculation method in section 0 for structure optimization and frequency calculations. During the mapping of its molecular orbitals, we were able to determine the covalent natures of the AA-DMSO hydrogen bonding: the redistribution of electrons in the AA molecule

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LUMO+3 (Fig. 4(a)) and the DMSO molecule HOMO-1 (Fig. 4(c)) forms HOMO-4 in the AA-DMSO hydrogen-bonded dimer complex (Fig. 4(b)).

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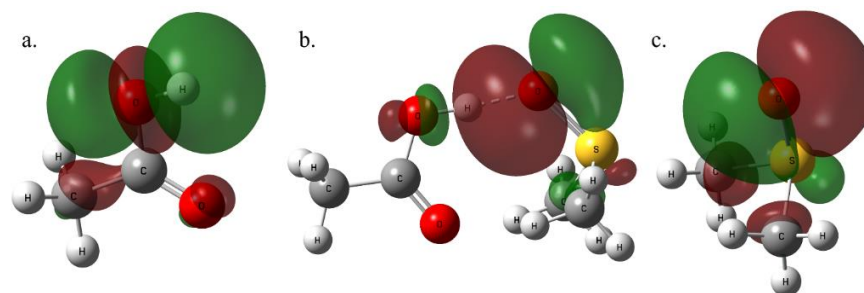


Fig. 4. Hydrogen bonding associated molecular orbitals of the AA-DMSO hydrogen-bonded dimer complex

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a. LUMO+3 of the AA molecule, b. HOMO-4 of the AA- DMSO hydrogen-bonded dimer complex c. HOMO-1 of DMSO molecule

165 According to the above results, we cannot explain the hydrogen bonding energy by van der Waals gravity and chemical bonding gravity alone [59], nor can we explain the hydrogen bonding angle of $(\text{HF})_2$ by electrostatic interactions alone, since the van der Waals force is also an electrostatic interaction, and electrostatic interactions will only place the four atoms of $(\text{HF})_2$ in a straight line. 168 The results of Wolters [60] for hydrogen bonding between compounds containing halogens and our quantum chemical calculations indicate the involvement of covalent bonds in the hydrogen bonding interaction. 171

Directionality of hydrogen bonding: Potential energy surface (PES) determination is one of the central concepts in quantum chemical calculations. According to the Born-Oppenheimer approximation, a PES is a mathematical or graphical relationship between the energy of a molecule 174 (or collection of molecules) and its geometry [61], and we can represent the energy of a system as a function of geometric coordinates. We performed a PES scan of the AA-DMSO hydrogen-bonded dimer complex using the calculation method in Section 0. In order to obtain the surface in three-dimensional space to identify the directionality of the hydrogen bonds, the quantum chemical calculation selects only two variables: the hydrogen bond length L and its angle θ (Fig. 5(a)), so 177 the energy E of the system is a function of L and θ . 180

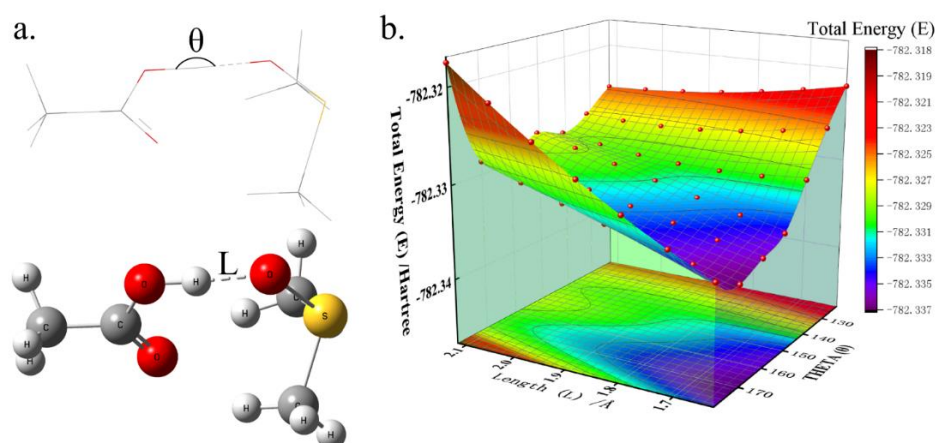


Fig. 5. Hydrogen bonding and three-dimensional PES of the AA-DMSO hydrogen-bonded dimer complex

- 183 a. Hydrogen bond length L and angle θ of the AA-DMSO hydrogen-bonded dimer complex
 b. Hydrogen bonding PES of the AA-DMSO hydrogen-bonded dimer complex

186 Fig. 5(b) shows the 3D PES of the system energy variation with hydrogen bond length L and angle θ . When the angle θ tends to 180° and the bond length L tends to 1.6 \AA , the energy of the AA-DMSO hydrogen-bonded dimer complex decreases, indicating that the AA-DMSO hydrogen-bonded dimer complex is more stable and the hydrogen bond strength is stronger [62-65], further
 189 indicating the hydrogen bond is directional.

Directionality is an essential indicator of covalent bonds. The strength of covalent bonds between atoms is strongly dependent on an angle [66]. The three-dimensional PES of the AA-DMSO
 192 hydrogen-bonded dimer complex demonstrate the directionality of hydrogen bonds and also indicate that hydrogen bonds have covalent nature.

Estimates of the Energy of Intermolecular Hydrogen Bonds: Estimates of the energy of
 195 intermolecular hydrogen bonds can be characterized in several ways, of which the binding energy (BE) is one of the most important quantities. The BE, as used herein, is equivalent to the "interaction energy" between two monomers in complex geometry. Quantum chemistry has
 198 become a routine and reliable method for estimating the BE of various hydrogen bonds [67]. For example, a study evaluated the performance of DFT generalized functions in calculating the binding energy of furan clusters. The results showed that the functionals M05-2X and M06 are
 201 recommended for further affordable investigations of the furan clusters [68].

In this section, the geometries of all three hydrogen-bonded dimer complexes (

204 Table 1) were fully optimized using the M06-2X exchange-correlation functional with DFT-D3(BJ) empirical dispersion correction. For fully characterizing hydrogen bond interactions, we have utilized many other quantum chemical calculations in addition to BEs, such as the hydrogen bond length, the NPA charges of the atoms at the ends of the hydrogen bonds, and ESP.

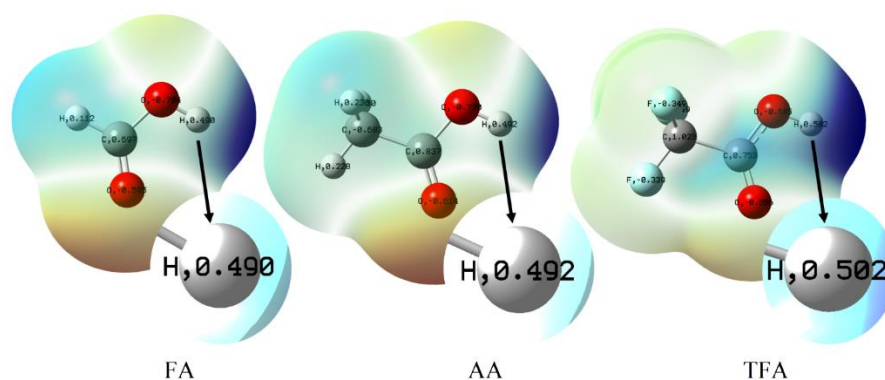


Fig. 6. ESP for FA, AA, and TFA and the NPA charge of the hydrogen atoms of FA, AA, and TFA involved in hydrogen bonding

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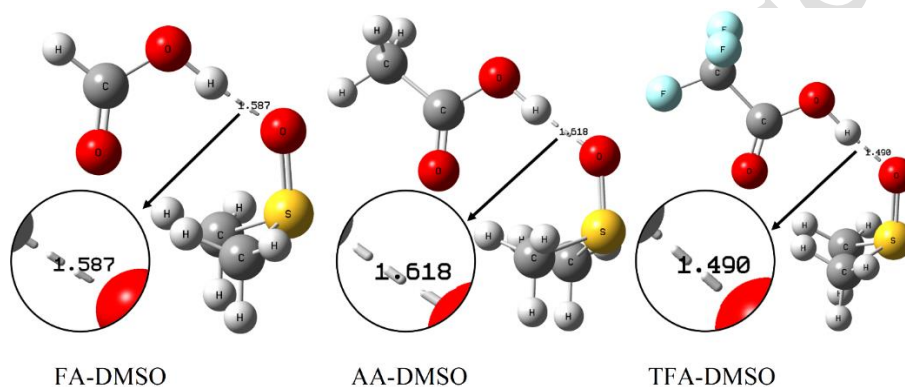


Fig. 7. Hydrogen bond lengths of FA—DMAO, AA-DMSO, and TFA-DMSO

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Table 1. NPA charges of hydrogen bond atoms, hydrogen bond length, and energy

Project	FA-DMSO	AA-DMSO	TFA-DMSO
NPA charge (H atom)*	0.490	0.492	0.502
NPA charge (O atom)*	-1.015	-1.015	-1.015
Hydrogen bond length (Å)	1.587	1.618	1.490
Hydrogen bond BE (kJ/mol)	-61.743	-59.079	-73.955

*NPA charge (H atom) is the NPA charge of the hydrogen atoms of FA, AA and TFA involved in hydrogen bonding.

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*NPA charge (O atom) is the NPA charge of the oxygen atoms of DMSO involved in hydrogen bonding.

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Using correlations between various well-known hydrogen bond-related quantum chemical calculations and estimated BE values, we have shown that each of these quantum chemical calculations has its own ability to characterize the strength of hydrogen bond interactions. Our

222 calculations have revealed that the higher the NPA charge difference of the hydrogen bond terminal
atoms, the shorter the bond length. Additionally, larger hydrogen bond energy is observed with
lower electron density of the electron acceptor as determined by ESP. We found from the strong
225 hydrogen-bonded dimeric complexes that the electron acceptor of the hydrogen atom all contain
atoms or groups of atoms with high electronegativity.

CONCLUSION

In the work presented here, we have performed DFT calculations for the AA-DMSO hydrogen-
228 bonded dimer complex using ESP, HOMO/LUMO, PES, and estimated and compared the energy
of hydrogen bonds of four related hydrogen-bonded dimer complexes. The quantum chemical
calculations have revealed the natures of hydrogen bonding in the AA-DMSO hydrogen-bonded
231 dimer complex: electrostatic interaction is the main factor in the generation of hydrogen bonds,
and the ESP can characterize the site of action of hydrogen bonds; the redistribution of electrons
in molecular orbitals provides hydrogen bonding with a significant degree of chemical bonding
234 character, which is one of the reasons why the hydrogen bonding energy is between chemical
bonding and van der Waals forces, and the directionality of hydrogen bonding revealed by PES,
and estimates of the energy of intermolecular hydrogen bonds is also consistent with this finding.
237 Different interactions link the atoms in a compound, and these links do not have a clear
demarcation line, but can be considered a mixture of multiple interactions. Therefore, on the
premise that hydrogen bonding is a mixture of electrostatic interactions and covalent character,
240 further in-depth study of the percentage of each interaction force is of more practical research
significance than classifying hydrogen bonds.

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