

# DFT study of Oxidation Initiation for Different Compound in Gasoline

Na Li, Jun Long, Yi Zhao, Zhiping Tao, and Zhenyu Dai

**Abstract**—A DFT study of oxidation initiation reaction for same carbon number but different type hydrocarbon compound in gasoline was performed. Firstly, the homolytic dissociation energies of the C-H bond in various hydrocarbon molecules were calculated and the C-H active site which was most likely to be attacked by oxygen molecules was obtained. Then, the reaction barrier of oxidation initiation reaction for different gasoline hydrocarbon molecules was compared. Furthermore, frontier orbital theory was used to analyze the chain initiation mechanism. It was found that the symmetry and energy gap of the HOMO orbitals of gasoline hydrocarbon molecules and the LUMO orbitals of oxygen molecule are the decisive factors in the oxidation initiation reaction. The results indicate that the reaction barrier of the olefin is much lower than other hydrocarbons. On the other hand, the energy gap between the HOMO orbital of 2, 4-hexadiene and the LUMO orbital of the oxygen is much lower than other molecules just followed by 1-hexene.

**Index Terms**—Gasoline, oxidation, chain initiation reaction, molecular simulation.

## I. INTRODUCTION

During its usage in the automobile engine, gasoline molecules are able to react with the oxygen in the vehicle engine. The formed oxidation products could continue to form sticky gum [1]-[4] and further generate carbon deposit inevitably [5]-[8]. The deposit could stick to the metal surfaces of engine parts, such as oil nozzle, intake valve, along the fuel system, from the tank to the combustion chamber. For example, if the gasoline molecule could form sticky gum in the oil tank, filter or pipeline, it will affect the oil supply seriously. The formed sticky gum would precipitate in the spark plug under high temperature. Then it will continue to react to produce carbon deposit which will cause short circuit. Deposition in the intake and exhaust valves will lead to coke, which could result in valve closure lax. Deposition in the cylinder head and piston will result in cylinder poor heat radiation and even increase combustion knock tendency. It can be seen that gasoline with poor stability will affect the normal work of the engine [9]-[12]. But how different classes molecules in gasoline begin to form the deposit. Based on the study of oxidation mechanism of hydrocarbon, it is found that the oxidation of hydrocarbon molecules follows the free radical chain reaction mechanism, which contains chain initiation, chain propagation and chain termination. The existing literature [13]-[15] shows that the deposit mechanism is as follows.

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Chain initiation:  $\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HOO}\cdot$

Chain propagation:  $\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$

$\text{ROO}\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$

$\text{ROOH} \rightarrow \text{RO}\cdot + \cdot\text{OH}$

$\text{RO}\cdot + \text{RH} \rightarrow \text{ROH} + \text{R}\cdot$

$\cdot\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}\cdot$

Chain termination:  $\text{R}\cdot + \cdot\text{R} \rightarrow \text{R-R}$

$\text{ROO}\cdot + \cdot\text{OOR} \rightarrow \text{ROOOOR}$

The traditional study is mainly using the macroscopic test to find active components in gasoline which could generate sediment. They did not explain the nature of the reaction details. As free radical chain reaction would produce a large number of free radical intermediates, it is very difficult to obtain the thermodynamic and kinetic data for the reaction of free radicals by means of experiment measurements [16]-[20]. Therefore, we use molecular simulation techniques to reveal the information of the molecular level which cannot be given through the macroscopic test.

Revealing the essence of the oxidation reaction of gasoline molecules can provide an important theoretical basis for the study of the stability of gasoline and the development of effective antioxidant additives. The present work intends to study the difficulty of oxidation chain initiation of different classes molecules in gasoline. For this purpose, reaction barrier of several chain initiation reactions have been calculated by density functional theory (DFT) calculation. DFT is a quantum mechanical method to study the electronic structure of multi electron systems. The classical methods of electronic structure theory are based on the complex multi electron wave function. DFT is to replace the wave function with the electron density as the basic quantity. In addition, various molecular parameters like energy of the frontier molecular orbitals (HOMO, the highest occupied molecular orbital and LUMO, the lowest unoccupied orbital) in energy optimized geometry were also analyzed by DFT calculation.

## II. COMPUTATIONAL DETAILS

Computational results were performed with density functional theory (DFT) by Dmol<sup>3</sup> module in the Material Studio 8.0 software developed by Accelrys Inc. Geometry optimizations of all gasoline molecules were carried out with the generalized gradient approximation (GGA-PBE) functional of DFT employing basis set DNP. SCF calculations were converged tightly (SCF tolerance:  $1 \times 10^{-6}$  Ha; energy:  $1 \times 10^{-5}$  Ha; max force: 0.0002 Ha/nm; max displacement:  $5 \times 10^{-4}$  nm). Transition state search protocol was chosen Complete LST/QST method.

### III. MODEL COMPOUNDS

Gasoline is a volatile mixture of hydrocarbons that is used in spark-ignition (SI) engines. It is a complex mixture composed of olefins, paraffins, naphthenes and aromatic hydrocarbons (C4-C12), whose boiling points is in the 30-220°C range. At the same time, it also contains traces impurity atoms, such as sulfur, nitrogen, and metals [21]. The molecular composition of gasoline determines whether it is stable or not.

But how to select the model compound? The carbon number distribution of main components in gasoline pool was analyzed. It can be concluded in Fig. 1 that C6 hydrocarbon is the component with the highest content.

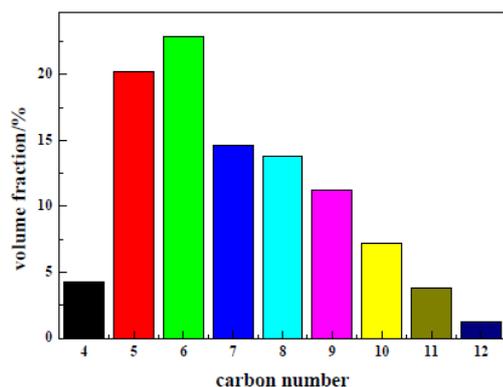


Fig. 1. Carbon number distribution of main compound in gasoline pool.

So in this work, different classes of C6 hydrocarbon molecules in gasoline are selected as the model compounds, as shown in Fig. 2.

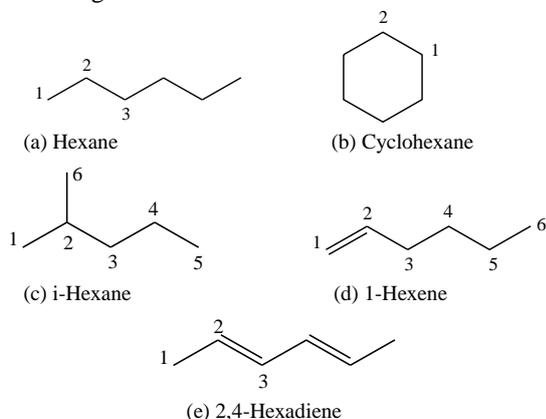
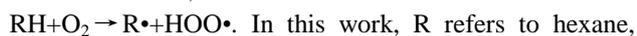


Fig. 2. Structure of model compounds in gasoline.

### IV. RESULTS AND DISCUSSION

#### A. Determination of the C-H Active Site

The essence of formation of carbon deposit from gasoline molecules is chain free radical reaction mechanism<sup>[22]</sup>. Free radical chain reaction contains chain initiation, chain transfer and chain termination steps. Oxidation reactions can produce free radicals. The first step of chain initiation reaction is that the gasoline molecules were attacked by oxygen molecule. Due to the steric hindrance, not the C-C bond but the C-H bond in the molecule was attacked by the oxygen molecule. Then it can generate free radicals R• and hydrogen peroxide free radicals HOO•, as shown below:



cyclohexane, i-hexane, 1-hexene or 2, 4-hexadiene respectively.

As in Table I, the homolytic dissociation energies of the C-H bond in different position of five compounds were calculated. The value of the homolytic dissociation energies determine which site of C-H was most likely to be attacked by oxygen molecules. The site with the minimum homolytic dissociation energy is the most vulnerable to be attacked by oxygen. It can be seen from the data, The active sites of C-H in the 5 compounds most likely to be attacked by oxygen respectively were C-H(2), C-H(1), C-H(2), C-H(3) and C-H(1). The data shows that, compared with the C-H bond in primary carbon position of and C-H bond in secondary carbon position, the homolytic dissociation energy of the C-H bond in the tertiary carbon position is the lowest. For the olefin molecules, the homolytic dissociation energy of the C-H bond in the  $\alpha$  position of C=C bond is the lowest.

TABLE I: HOMOLYTIC DISSOCIATION ENERGIES OF C-H BOND AT DIFFERENT POSITION IN MODEL COMPOUNDS(UNIT: kJ/mol)

C-H	hexane	cyclohexane	i-hexane	1-hexene	2,4-hexadiene
1	551.13	499.61	463.66	581.25	377.46
2	519.32	514.31	429.92	554.90	483.73
3	520.93	—	444.15	441.11	485.76
4	—	—	443.09	514.26	—
5	—	—	461.80	511.20	—
6	—	—	461.75	540.99	—

#### B. Reaction Barrier Calculations

In section A, the C-H active site which was most likely to be attacked by oxygen molecules was obtained. Then transition state search was performed for these five reactions. The structures of reactants, transition states and products are shown in Table II. Then the detailed mechanism can be seen.

In addition, the reaction barrier of oxidation initiation reaction for different gasoline hydrocarbon molecules was compared. As can be seen from Fig. 3, compared with other gasoline molecules, the chain initiation reaction barrier of mono olefin and conjugated dienes is much lower than other molecules. It indicates that olefins especially conjugated contribute to initiate the chain reaction. It may be related to the higher stability of the formed allylic radicals [23] in order to make the next oxidation steps carried out further. In addition, the reaction barrier of i-hexane is lower than hexane and cyclohexane. It is indicated clearly i-paraffin is easier to initiate free radical reaction than n-paraffin. Further analysis, the activity of oxidation reaction of the tertiary C-H of i-hexane is higher than the primary and second C-H. When the oxygen molecule attacks the tertiary C-H, lower energy is needed to produce the corresponding alkyl radical and peroxy radical.

The basic reason that affects the oxidation stability of gasoline is its chemical composition, mainly depending on the molecular structure. From the point of view of the reaction chemistry, the macroscopic phenomena can be explained in terms of the basic reaction mechanism at the molecular level with molecular simulation technique so as to solve the problem in essence.

TABLE II: REACTION STRUCTURE OF DIFFERENT GASOLINE HYDROCARBON

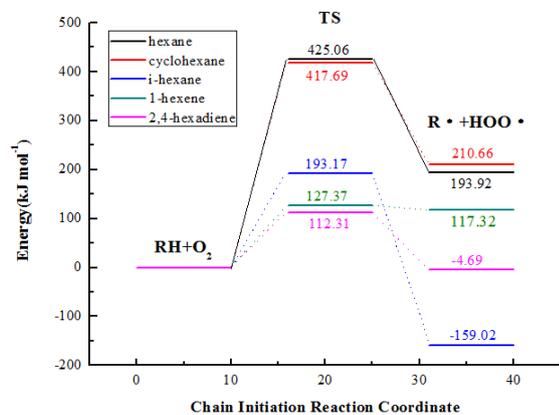
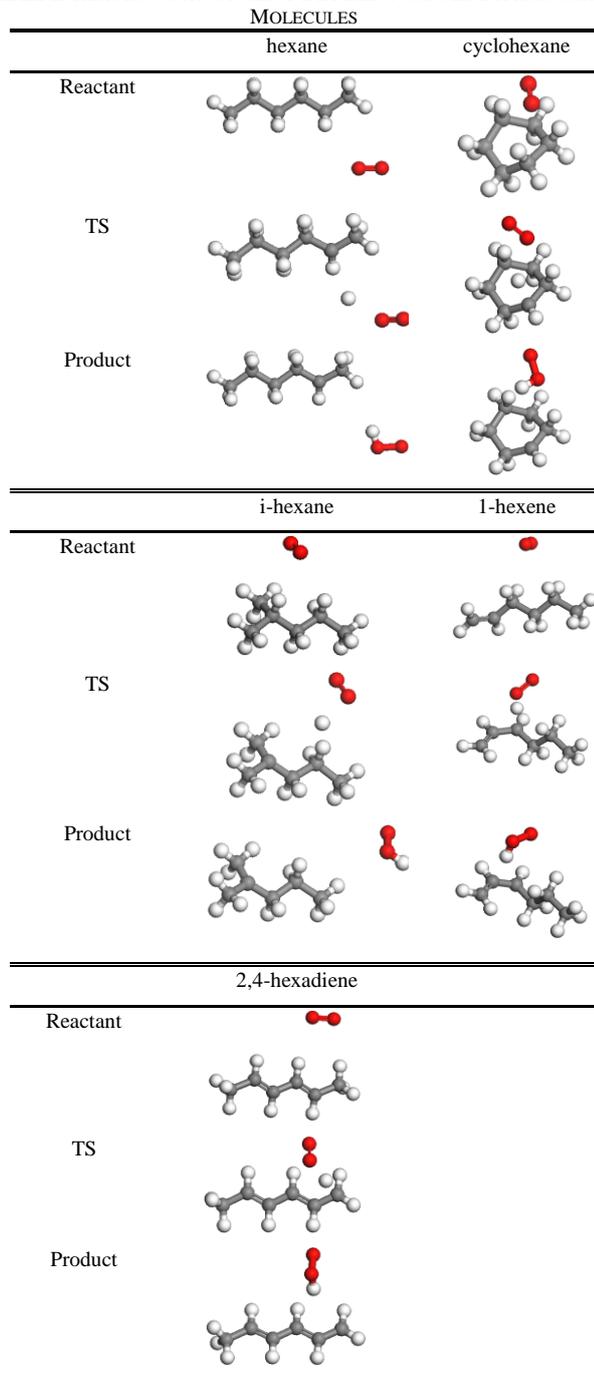


Fig. 3. Transition-state search results.

### C. Molecular Orbital Energy Level Calculations

According to the frontier orbital theory, for the two

molecules reaction A and B, when the frontier orbitals are symmetry adapted, LUMO orbital energy level of A (or B) and HOMO orbital energy level of B (or A) more closely, the electron transfer reaction is more likely to happen. In the reaction,  $RH+O_2 \rightarrow R\cdot+HOO\cdot$ , the oxygen molecule obtains electrons because of its higher electronegativity. And gasoline molecules donate electrons. Therefore, LUMO orbital of oxygen molecule and HOMO orbitals of gasoline molecules should be further analyzed. The energy gap of the HOMO orbitals and LUMO orbital is the essential factor that affects the difficulty of chain initiation reaction.

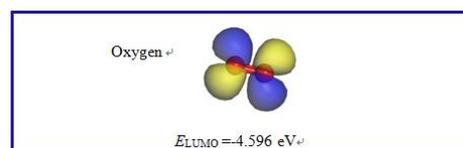


Fig. 4. LUMO orbital and energy level of oxygen molecule.

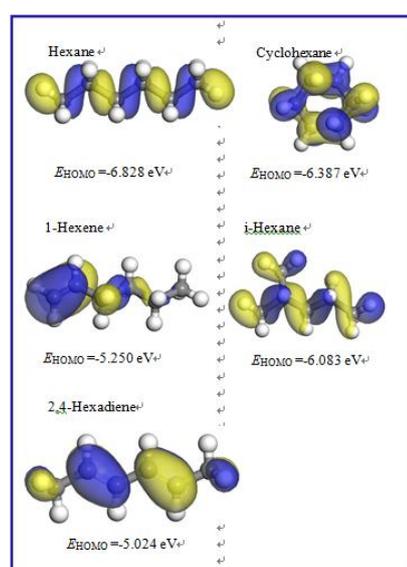


Fig. 5. HOMO orbitals and energy level of gasoline molecules.

Electron distribution in LUMO and HOMO energy levels for the energy optimized neutral oxygen molecule and gasoline molecules are shown in Fig. 3 and Fig. 4. Generally, higher the value of  $E_{HOMO}$  is, stronger is the electron donating ability of the molecules. Whereas, the lower value of  $E_{LUMO}$  signifies the molecule to be susceptible to accept electrons. And the two reactant molecules with lower absolute values of the energy gap exhibits easier for electron transfer, moreover the chemical reactions are more likely to occur.

It can be seen from Fig. 4 and Fig. 5, the LUMO orbital of oxygen molecule and the HOMO orbitals of gasoline molecules are all symmetry adapted. Therefore, the energy gap should be further contrast to depend which gasoline molecule is easier to be attacked by the oxygen molecule.

The LUMO orbital energy of oxygen molecule and the HOMO energy level of hydrocarbon molecules were subtracted, and the absolute values are plotted then. As shown in Fig. 6, the energy gap between LUMO orbital of oxygen molecule and HOMO orbitals of different classes of gasoline molecules is in order. It is clear that the gap of 1-Hexene and 2,4-hexadiene is much lower than other molecules. In other words, electrons in HOMO orbitals of the two molecules are much easier to transfer into the LUMO orbital of the oxygen molecule. This provides further explanations why the reaction

energy barrier is significantly lower. In addition, for alkanes, the energy gap of i-Hexane is lower than Hexane and cyclohexane due to the presence of tertiary carbon.

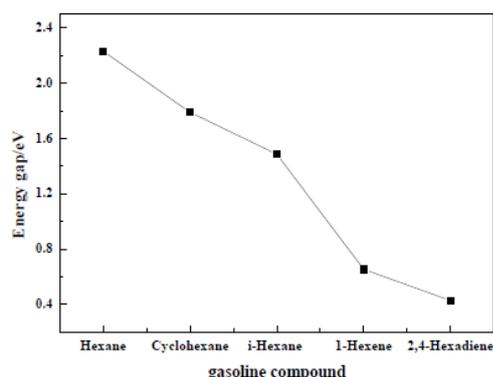


Fig. 6. Energy gap between gasoline molecules and oxygen molecule.

## V. CONCLUSION

Using molecular simulation, the difficulty level of different classes of gasoline molecules attacked by the oxygen molecule to initiate the chain initiation reaction is investigated. We demonstrate that olefin molecules, especially conjugated ones are the most likely to carry out chain initiation reactions to initiate the oxidation reaction. Thus, the reaction barrier of the chain initiation step of conjugated hydrocarbon is the lowest which may be related to the higher stability of the formed allylic radicals.

On the other hand, electron distribution in LUMO and HOMO energy levels for the energy optimized oxygen molecule and gasoline molecules are calculated. It can be seen that LUMO orbital of oxygen molecule and the HOMO orbitals of gasoline molecules are all symmetry adapted. And the two reactant molecules with lower absolute values of the energy gap exhibits easier for electron transfer, thus the chemical reactions are more likely to occur. It can be seen that the gap between the HOMO orbital of 2, 4-hexadiene and the LUMO orbital of the oxygen is much lower than other molecules just followed by 1-hexene. In other words, electrons in HOMO orbitals of 2, 4-hexadiene are much easier to transfer into the LUMO orbital of the oxygen molecule. This provides further explanations why the reaction energy barrier is significantly lower.

The work provides a solid theoretical basis for the gasoline quality upgrading. Under the premise of ensuring octane number, it is better to reduce the olefin content, especially the content of conjugated diene. Thus the oxidation stability of gasoline could be significantly improved. In addition, the work performance of SI engine could be further improved, such as emissions reduction, fuel consumption reduction, work efficiency improvement and so on.

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## REFERENCES

[1] T. B. Brooks, "The chemistry of gasolines-particularly with respect to gum formation and discoloration," *Industrial and Engineering Chemistry*, vol. 18, no. 11, pp. 1198-1203, 1926.

- [2] T. Donal, J. W. Flood, Hladky, and Graham Edgar, "Chemical nature of gum-forming constituents in gasoline," *Industrial and Engineering Chemistry*, vol. 25, no. 11, pp. 1234-1239, 1933.
- [3] J. M. Nagpal, G. C. Joshi, J. Singh, and K. Kumar, "Studies on the nature of gum formed in cracked naphthas," *Oxid Commun.*, vol. 21, no. 4, pp. 468-477, 1998.
- [4] E. L. Walters, H. B. Iminor, and D. L. Yabroff, "Chemistry of gum formation in cracked gasoline," *Industrial and Engineering Chemistry*, vol. 41, no. 8, pp. 1723-1729, 1949.
- [5] Gabriela de la Puente and Ulises Sedran, "Formation of Gum Precursors in FCC Naphthas," *Energy & Fuels*, vol. 18, pp. 460-464, 2004.
- [6] J. M. Nagpal, G. C. Joshi, and J. Singh, "Gum forming olefinic precursors in motor gasoline. A model compound study," *Fuel Sci Technol Int*, vol. 12, no. 6, pp. 873-894, 1994.
- [7] G. Christopher, Kabana, S. Botha, C. Schmucker *et al.*, "Oxidative stability of middle distillate fuels. Part 1: Exploring the Soluble macromolecular oxidatively reactive species (SMORS) mechanism with jet fuels," *Energy & Fuel*, vol. 25, pp. 5145-5157, 2011.
- [8] P. Singer and J. R. Iñe, "On the mechanism of deposit formation during thermal oxidation of mineral diesel and diesel/biodiesel blends under accelerated conditions," *Fuel*, vol. 133, pp. 245-252, 2014.
- [9] M. Kinoshita, A. Saito, S. Matsushita, H. Shibata, and Y. Niwa, "Study of deposit formation mechanism on gasoline injection nozzle," *Proceedings of SAE Paper*, vol. 19, pp. 355-357, 1998.
- [10] J. M. Nagpal, G. C. Joshi, and S. N. Rastogi, "Stability of cracked naphthas from thermal and catalytic processes and their additive response. Part II. Composition and effect of olefinic structures," *Fuel*, vol. 74, no. 5, pp. 720-724, 1995.
- [11] P. Lacey, S. Gail, J. M. Kientz *et al.*, "Internal fuel injector deposits," *Proceedings of SAE Paper 2011-01-1925*.
- [12] A. Tanaka, K. Yamada, T. Omori, *et al.*, "Inner diesel injector deposit formation mechanism," *Proceedings of SAE Paper*, 2013-01-2661.
- [13] C. E. Frank, "Hydrocarbon Autoxidation," *Chemistry Reviews*, vol. 46, no. 1, pp. 155-169, 1950.
- [14] J. L. Reyes-Gavilan, P. Odorisio, *NLGI Spokesman*, vol. 64, no. 11, pp. 22-33, 2001.
- [15] J. Pfaendtner and L. G. Broadbelt, "Mechanistic modeling of lubricant degradation. 2. The autoxidation of decane and octane," *Industrial & Engineering Chemistry Research*, vol. 47, no. 9, pp. 2897-2904, 2008.
- [16] J. Nicholas *et al.*, "Use of measured species class concentrations with chemical kinetic modeling for the prediction of autoxidation and deposition of jet fuels," *Energy & Fuels*, vol. 21, pp. 530-544, 2007.
- [17] R. Epping, S. Kerkering, and J. T. Andersson, "Influence of different compound classes on the formation of sediments in fossil fuels during aging," *Energy & Fuels*, vol. 28, 5649-5656, 2014.
- [18] B. D. Batts and A. Z. Fathoni, "A literature review on fuel stability studies with particular emphasis on diesel oil," *Energy & Fuels*, vol. 5, pp. 2-21, 1991.
- [19] F. Pradelle, S. L. Braga *et al.*, "Gum formation in gasoline and its blends: A review," *Energy & Fuels*, vol. 29, pp. 7753-7770, 2015.
- [20] S. M. Martin, J. R. W. A. Gruse, and A. Lowy, "Distribution of gum-forming constituents in cracked gasoline," *Industrial and Engineering Chemistry*, vol. 25, no. 4, pp. 381-386, 1933.
- [21] J. M. Nagpal, G. C. Joshi, J. Singh *et al.*, "Gum forming olefinic precursors in motor gasoline, a model compound study," *Fuel Science and Technology International*, vol. 12, no. 6, pp. 873-894, 1994.
- [22] J. Pfaendtner and L. J. Broadbelt, "Mechanistic modeling of lubricant degradation. 1. Structure-reactivity relationships for free-radical oxidation," *Ind. Eng. Chem. Res.*, vol. 47, no. 9, pp. 2886-2896, 2008.
- [23] C. C. Rita *et al.*, "Effect of mono-olefins and diolefins on the stability of automotive gasoline," *Fuel*, vol. 85, pp. 1860-1865, 2006.



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