Quantum mechanics/molecular mechanics studies on the intrinsic properties of typical ester oil molecules

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Abstract

The molecular structure of lubricating oil affects its lubrication properties, catalytic and hydrolytic stability, and anti-wear properties. Based on the idea of material genomics, researchers are trying to find the correlation between structural characteristics and functional performances of lubricating oil, but the correlation can only explore the influence weight of structural parameters on performance, it is also very important to research the influence mechanism. In this study, through quantum mechanics/molecular mechanics calculations, (i) the spatial configurations of four typical ester lubricants with different chain length structures were studied, (ii) effects of active functional groups and charge distribution on the properties of the ester lubricants were discussed, and (iii) electronic transition and molecular orbital contributions were compared. The calculated results are expected to provide considerable support for theoretical research on the anti-wear and anti-oxidation mechanisms of ester lubricants and assist the rapid design, development and application of lubricating materials.

1. Introduction

In material genetic engineering, multi-scale material simulation plays an increasingly important role in exploring the microscopic mechanism of materials, predicting new materials and properties, and simulating material properties in extreme environments [1–5]. At the same time, computational simulation has gradually emerged as a powerful tool that aids in experiments to explain certain phenomena and understand the microscopic mechanism of materials [6]. Ester lubricant is one of the synthetic lubricating oils with best comprehensive performance and the earliest development and applications [7]. The effect of structural differences of ester lubricant on its lubrication performance, catalytic and hydrolytic stability, friction and wear performance, and other behaviors, however, has not been extensively studied up to now. Quantum mechanics/molecular mechanics calculation is an effective method, which can combine with modern analytical instruments and avoid the uncertainty associated with the use of empirical methods and provide a scientific basis for the development and application of high-end ester lubricants. Unfortunately, quantum mechanics/molecular mechanics calculations of lubricating materials are rarely reported.

A series of ester-based oils, with diverse physical and chemical properties, can be prepared with the basic principle of molecular design. Based on the number and molecular structure of ester groups, ester lubricants include diesters, polyol esters, aromatic carboxylic acid esters, and composite esters. Different types of esters have different performances and corresponding lubricating mechanisms.

As early as 1947, Bried et al [8] studied the chemical stabilities, low-temperature fluidities, and viscosity temperature properties of 34 diester-based oils with different structures. However, to date, the exploration of ester oil is still at the macro level of basic synthesis, physical and chemical properties tests, and service
performance tests. The quantum mechanics calculation has been successfully applied in calculating the molecular orbitals, electronic density of states, and energy band structures from the microcosmic angles. Thus, it is possible to elucidate the microstructure of materials and analyze their macroscopic properties to progress the basic theory of materials [9–13]. A more detailed understanding of the structure-performance relationship of ester-based oil underpinning designs, under specific working conditions, is of profound significance in the search of a new base oil in the future.

Therefore, this study explores numerous molecular models for four typical ester lubricants, and optimal energy configurations were obtained through structural optimizations. Furthermore, the molecular energy, polarity, orbital distribution, electronic density, energy band structure, and other aspects were simulated for different chain length structures. According to the calculation results, the influence of the bonding properties, chemical activities, molecular orbitals, and electronic structures of ester oil molecules on their service properties was analyzed. This research is of great significance for improving service performance and guiding the development and application of ester lubricants.

2. Calculation methodology

Molecular models of ester lubricants can be established in Materials Studio (MS). However, the establishment process first requires structural optimizations of ester lubricants by using the Forcite package [14] and the DMol 3 package [15]. After the geometric optimization, it uses the DMol 3 package to calculate the anticipated parameters for a single molecule. Simultaneously, the cell is built by amorphous cell packaging. Next, structural and dynamic optimizations by the Forcite package are conducted again, and the molecular configuration with minimum energy is selected to calculate the expected parameters.

In this study, four typical ester lubricants—diester, pentaerythritol ester, trimethylolpropane ester, and trimellitate—are selected for the calculations. The general structure of these ester lubricants is shown below, where R denotes the length of carbon chains (R = C4–C10). Figure 1 shows the corresponding molecular models.
3. Results and discussions

3.1. Molecular structure characteristics of ester lubricants

3.1.1. Total energy

The total energy of molecules is an important parameter to determine its state, related to the number of atoms and the electronic structure [16]. The higher the energies and total number of free electrons, the greater is the total energy. The variation in the total molecular energy of each ester lubricant is listed in table 1. The total energies of the diesters is the largest and that of pentaerythritol esters is the smallest. The total energies of the trimethylolpropane esters and trimellitates are equal. The total molecular energy can reflect the stability of molecules, and the calculation results reflect the thermal stability and hydrolysis stability of ester oil to a certain extent.

3.1.2. Dipole magnitude

The dipole moment is also an important physical property, which is often used to judge the spatial configurations of molecules [17]. Figure 2 compares the dipole magnitudes of the four lubricants in the order of increasing chain length. The results show that all four lubricating oil molecules are polar, with the diester being the most polar. The dipole magnitudes of the diester and trimellitate vary only slightly with increasing R, i.e. increasing chain length; however, the dipole magnitude of the trimethylolpropane ester increases with increasing R. Lastly, the dipole magnitude of the pentaerythritol ester changes with increasing R. It is generally believed that the lubricant with high dipole moment has better lubricity than the lubricant with the same viscosity [18]. Therefore, dipole moment is one of the important structural parameters of lubricating oil.

3.1.3. Molecular orbital

Molecular orbital refers to a single-electron wave function in molecules, which plays an important role in the analysis of molecular interactions, chemical activities, and the shape and composition of a molecular orbital [19, 20]. In this study, molecular orbital calculations of the four types of ester lubricants has been carried out.

Table 1. Comparison of total energies of four ester lubricants.

| Carbon chain | Total energy/\text{Ha} | Total energy/\text{Ha} | Total energy/\text{Ha} | Total energy/\text{Ha} |
|--------------|------------------------|------------------------|------------------------|------------------------|
|              | (Diester)              | (Pentaerythritol Ester)| (Trimethylolpropane Ester) | (Trimellitate) |
| R = C4       | -849.3501              | -1579.6072              |                       | -1273.3604              | -1268.6358              |
| R = C5       | -927.8918              | -1736.6687              |                       | -1391.1671              | -1386.4501              |
| R = C6       | -1006.4316             | -1893.7579              |                       | -1508.9738              | -1504.2577              |
| R = C7       | -1084.9723             | -2050.8466              |                       | -1626.7832              | -1622.0682              |
| R = C8       | -1163.5139             | -2207.9254              |                       | -1744.5895              | -1739.8794              |
| R = C9       | -1242.0545             | -2365.0151              |                       | -1862.3936              | -1857.6902              |
| R = C10      | -1320.5968             | -2522.0857              |                       | -1980.2204              | -1975.4995              |
(1) Diester

The highest occupied molecular orbital (HOMO) of the diester is located on the ester group, while the lowest unoccupied molecular orbital (LUMO) is located on the positively charged center. This configuration means that the activity of the molecular surface is more concentrated in the ester group (figure 3).

(2) Pentaerythritol ester

The HOMO of pentaerythritol ester is located on the ester group of two symmetrical long chains, and the LUMO is located on the positively charged center. This configuration indicates that the surface activity is more concentrated on the ester group of the two symmetrical long chains than other parts of the molecule. (figure 4).
Figure 6. HOMO-LUMO energy of Trimellitate.

Figure 7. Changes in active functional groups of diesters with increasing chain length.

Figure 8. Mapping of electrostatic potentials on the surfaces of electron density diagrams.
Trimethylolpropane ester

The HOMO of pentaerythritol ester is mainly located on the ester group of two long chains; however, for a few molecules, it is located on the ester group of the other long chain. The LUMO is mainly located between the carbon atom of the ester group and the carbon atom connected to the ester group (figure 5).

Trimellitate

Unlike the other three ester lubricants, trimellitates have a phenyl group directly connected to the carbon atom of the carbon-oxygen double bond of the ester group. The HOMO and LUMO of trimellitate are located on the ester and phenyl groups, respectively, indicating that the conjugated carbon atom orbitals constitute the frontier orbitals of trimellitic esters [21] (figure 6).

Among these molecules, the HOMO has the highest energy and the smallest binding energy; therefore, it is the most active and susceptible to change. Meanwhile, the LUMO has the lowest energy among all the unoccupied orbitals, and has the greatest tendency to accept electrons. Therefore, these two orbitals determine the electronic gain and loss and transfer abilities of molecules. These orbitals also determine the spatial orientations in intermolecular reactions and other important chemical properties. Our analysis reveals that the activity at the ester group in the molecular structure is highest in the ester lubricants. When lubricating metal to ensure good friction performance, a solid lubricating film is adsorbed on the metal surface. However, when the phenyl ring is linked to the ester group, the active site is a conjugated structure. Meanwhile, considering diesters as an example, the HOMO and LUMO regions are gradually concentrated and its color gradually deepens with increasing chain length, leading to better anti-wear performance (figure 7). This conclusion can be verified from the literature [22].

3.1.4. Electrostatic potential

The electrostatic potential energy can directly reflect the characteristics of molecular charge distribution and predict the possible chemical properties of molecules. Figure 8 shows the electrostatic potentials of the four
different types of ester lubricants. From the figure, the deepest part of region 1 is the carbon-oxygen double bond (C=O). In the process of lubrication by the ester oil, metal ions (Fe²⁺/Cu²⁺) are easily produced owing to wear and corrosion effects. The C=O is more likely to combine with these metal ions and reduce the lubricating performance. Unlike the other three esters, electrons around the C=O of trimellitate are delocalized on the phenyl group because the C=O in the molecular structure forms a conjugated system with the phenyl group [23, 24].

The hydrolytic stability of the ester lubricating oil is also one of its important properties. During hydrolysis, H⁺ attacks the C=O bond. If the space occupied by the substituent on the carbonyl carbon is large, it will delay the formation of a tetrahedral structure, which in turn delays hydrolysis [25]. As seen from figure 8, diester is the easiest to hydrolyze, difficulty of hydrolysis of pentaerythritol ester and trimethylolpropane ester are equivalent, and trimellitate is the most difficult to hydrolyze. The direct connection of the phenyl ring and the carbonyl carbon in trimellitate blocks the attack of water molecules on the carbonyl carbon and delays hydrolysis.

3.2. The electronic structure characteristics of ester lubricants
3.2.1. Energy band structure
Band gap is the energy difference between the valence band maximum and conduction band minimum [26] and is also known as an energy gap. A larger band gap signifies greater difficulty for electrons to be excited from the valence band to the conduction band. In this study, the energy gaps of the four ester lubricants are calculated and shown in figure 9. Except for the diester, the energy gaps of the ester lubricants are between 2.70 eV and 3.25 eV, and show no significant variations with increasing chain lengths. The energy gaps of diesters with different chain lengths are all ∼5 eV, which indicates that the electrons in the diesters are more difficult to excite to the conduction bands, except when R = C7. At this chain length, the energy gap is only 1.756 eV. For this lubricant, electrons can easily obtain energy and jump to the inverted band with appropriate energy excitations, such as high temperature, which destabilizes the whole system.

3.2.2. Density of states
The bonding mechanism can be elucidated by investigating the density of states (DOS), and this mechanism is central to the modern electronic structure theory [27, 28]. DOS is the number of states (number of vibrational modes) in the unit frequency interval, expressed as:
In addition, the distributions and compositions of energy-level orbitals can be reflected by calculating the partial DOS (PDOS).

(5) Diester

In figure 10, the electronic state energy of the diester molecule increases gradually at approximately $-2$ eV with increasing chain length. In the PDOS (figure 11), the energy level of the diester is mainly composed of p- and s-orbitals.

(6) Pentaerythritol ester

The peak of DOS near the Fermi level of pentaerythritol ester becomes very sharp with increasing chain length, as shown in figure 12. The diagram of the PDOS indicates that the energy levels at $-1$ eV are composed mainly of p-orbitals, and those at $-3$ eV are composed of p- and s-orbitals (figure 13).

(7) Trimethylolpropane ester

$$g(w) = \lim_{\Delta \omega \rightarrow 0} \frac{\Delta n}{\Delta \omega}$$  \hspace{1cm} (1)
For trimethylolpropane ester, the electronic state energy decreases at $-1$ eV and increases at $-3$ eV with increasing chain length (figure 14). This result is different from that of the pentaerythritol ester. However, the distribution of energy-level orbitals is similar. The energy levels at $-1$ eV are composed mainly of p-orbitals, and those at $-3$ eV are composed of p- and s-orbitals (figure 15).

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(8) Trimellitate

The electronic density of trimellitate at approximately $-2$ eV increases with increasing chain length (figure 16). The valence and conduction bands of the energy level are composed of p- and s-orbitals (figure 17). Through the preliminary analysis of the DOS of ester oil, the contribution and distribution of molecular orbitals can be determined. Combined with the molecular orbital of reaction compounds, the bonding
mechanism can be elucidated, which provides a scientific explanation for the oxidation and nitration of ester lubricants. However, there is almost no research on the DOS of lubricating oils. This paper provides a new idea for analysis and research.

4. Conclusions

In this study, four typical ester lubricants are considered. The molecular energies, orbital distributions, electron densities, and band structures of different chain length structures are simulated, and the results show that:

- The total energy of diesters is the largest and that of pentaerythritol esters is the smallest. The calculation results reflect the stability of ester oil to a certain extent; All four lubricating oil molecules are polar, and the polarity of the diester is maximum. The dipole magnitudes of diester and trimellitate change slightly with increasing chain length; however, with increasing chain length, the dipole magnitude of trimethylolpropane ester increases and that of the pentaerythritol ester changes.

- The activity of the ester group is the highest in the molecular structure of the ester lubricants. However, when the phenyl ring is linked to the ester group, the active site is a conjugated structure. Meanwhile, the HOMO and LUMO regions are gradually concentrated and their colors gradually deepen with increasing chain length, leading to better anti-wear performance.

- The electrostatic potentials of the ester lubricant molecules, except trimellitate, show that the negative charges were concentrated in the C=O bonds. This result indicates that the C=O combines easily with metal ions, thus reducing the lubricating ability. The negative charge of trimellitate was concentrated in the conjugated system formed by the phenyl ring and C=O. The hydrolytic stabilities of ester lubricants are as follows: diester is the most easily hydrolyzed, followed by pentaerythritol ester, trimethylolpropane ester, and trimellitate. Pentaerythritol and trimethylolpropane esters have equivalent hydrolytic stabilities.

- The energy gaps for the diesters are all ~5 eV, except for R = C7, while the that of the other three lubricants are between 2.70 eV and 3.25 eV. The valence and conduction bands are composed of p- and s-orbitals. The DOS provides a basis for identifying the oxidation bonding mechanism.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest statement

All authors declare that: (i) no support, financial or otherwise, has been received from any organization that may have an interest in the submitted work; and (ii) there are no other relationships or activities that could appear to have influenced the submitted work.

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