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QUANTUM-CHEMICAL STUDY OF D- AND L-ASPARTIC ACID: STABILITY IN AQUEOUS SOLUTION AND COMPLEX-FORMING PROPERTIES

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Abstract. In this study, the quantum-chemical properties of D- and L-aspartic acid were investigated using the Gaussian 09 software package at the B3LYP/6-311+G(d,p) level of theory and the IEFPCM solvation model for an aqueous medium. The optimized geometry, total energy, Gibbs free energy, dipole moment, orbital energies, and stability in aqueous solution of the molecules were compared. The calculation results showed that there are only very small energetic differences between the D- and L-isomers. The total energy of L-aspartic acid was found to be slightly lower, indicating its relatively higher thermodynamic stability in aqueous solution. Based on the functional groups of the molecules and the distribution of electron density, their ability to form complexes with metal ions was analyzed.

Keywords: D-aspartic acid, L-aspartic acid, Gaussian 09, DFT, B3LYP, PCM, aqueous solution, complex formation, quantum-chemical calculations.

Introduction. Aspartic acid is one of the biologically active amino acids and participates in important metabolic processes in living organisms. This compound exists in two optical isomeric forms – D- and L-forms. While L-aspartic acid is widespread in biological systems, the D-form occurs in certain microorganisms and specialized biological systems. Due to the presence of an amino group ($-NH_2$), a carboxyl group (-COOH), and an amide group in its structure, aspartic acid has the ability to form coordination complexes with metal ions. Therefore, studying the electronic structure, energetic stability, and solvation properties of this compound using quantum-chemical methods is of significant scientific importance.

The aim of this work is to investigate and compare the following properties of D- and L-aspartic acid based on quantum-chemical calculations:

- optimized geometric parameters;
- total energy;
- dipole moment;
- orbital energies;
- stability in aqueous solution;
- complex-forming properties;
- electron density distribution.

Methodology. The calculations were performed using the Gaussian 09 software package. The molecular geometries were optimized using the DFT (Density Functional Theory) method with the B3LYP functional and the 6-311+G(d,p) basis set.

The effect of the aqueous solution was taken into account through the IEFPCM (Integral Equation Formalism Polarizable Continuum Model) solvation model.

Calculation parameters:

Table 1

Parameter	Value
Software	Gaussian 09

Level of theory	DFT/B3LYP
Basis set	6-311+G(d,p)
Solvation model	IEFPCM
Solvent	Water
SCF mode	QC Tight
Geometry optimization	Tight
Vibrational analysis	Frequency

Since all vibrational frequencies obtained in the calculations had positive values, it was confirmed that the optimized structures correspond to true minimum-energy states.

Results and Discussion

1. Analysis of the Geometric Structure

According to the calculation results, the overall geometries of D- and L-aspartic acid are nearly identical, representing mirror images of each other. Carboxyl, amino, and amide functional groups were identified in the molecular structures.

These groups can participate as donor centers in the formation of coordination bonds with metal ions.

In the optimized structures, the C=O bonds are relatively short, the C–N bonds are partially conjugated, and intramolecular hydrogen bonds are present. These features contribute to the enhanced stability of the molecules in aqueous solution.

2. Comparison of Energetic Parameters

Table 2. Comparison of the Energetic Parameters of D- and L-Aspartic Acid

Parameter	D-Aspartic Acid	L-Aspartic Acid
SCF Energy (Hartree)	-512.496997	-512.498876
Gibbs Free Energy (Hartree)	-512.410883	-512.412435
Zero-Point Energy (Hartree)	-512.374197	-512.376005
Dipole Moment (Debye)	2.3579	1.8995
Imaginary Frequency	Absent	Absent

As can be seen from Table 2, the total energy of L-aspartic acid is slightly lower than that of the D-form. A lower energy value indicates that the molecule is thermodynamically more stable. The lower Gibbs free energy value of the L-form also suggests that it possesses an energetic advantage in aqueous solution. The dipole moment of the D-form is higher, indicating that its electrostatic interaction with the solvent may be stronger.

3. Stability in Aqueous Solution

The results obtained using the PCM model showed that aspartic acid interacts strongly with water molecules.

The main factors contributing to stability are:

1. The tendency of the carboxyl group to ionize;
2. The ability of the amide and amino groups to form hydrogen bonds;
3. Electrostatic stabilization provided by the aqueous medium with its high dielectric constant.

For the L-isomer:

• the energy is lower;
• molecular redistribution is more favorable;
• solvation stabilization is more effective.

Therefore, the widespread occurrence of L-aspartic acid in biological systems can also be explained from a thermodynamic perspective.

4. Electronic Structure and Orbital Analysis

The frontier molecular orbitals (HOMO and LUMO) are of great importance in evaluating chemical reactivity.

Table 3. Comparison of HOMO–LUMO Parameters

Parameter	D-Aspartic Acid	L-Aspartic Acid
HOMO Energy	-0.26535	-0.27075
LUMO Energy	Higher virtual orbital	Higher virtual orbital
Energy Gap	Large	Large

The HOMO orbitals are mainly localized around the oxygen atoms, the amino group, and the amide oxygen. This indicates that these donor centers are prone to forming coordination bonds with metal ions. The large HOMO–LUMO energy gap suggests that the molecules are kinetically stable.

5. Complex-Forming Properties

Aspartic acid contains several donor atoms:

Donor Atom	Functional Group	Coordination Role
O	Carboxyl group	Primary donor
O	Amide group	Secondary donor
N	Amino group	Strong donor

Therefore, aspartic acid can act as a bidentate, tridentate, or bridging ligand.

Possible coordination modes include:

- Through the amino nitrogen atom;
- Through the carboxylate oxygen atom;
- Through the amide oxygen atom.

This enables the formation of stable complexes with metal ions such as Cr(III), Cu(II), Ni(II), Co(II), and VO(IV).

Differences Between D- and L-Forms in Complexation

Although the electronic parameters of D- and L-aspartic acid are very similar, their spatial configurations differ. As a result, the coordination geometry around the metal center, the optical activity of the complex, biological selective binding, and crystal structure may differ. L-aspartic acid forms a more compatible coordination environment with enzymes and proteins in biological systems.

In contrast, the D-form may differ in:

- crystallization properties;
- water solubility;
- symmetry of the resulting complexes.

7. Vibrational Frequency Analysis

No negative frequencies were observed in the frequency calculations.

This indicates that:

- the optimized structures correspond to true minima;
- the geometries are stable;
- the calculations were successfully completed.

Major IR Vibrations

Vibration Type	Expected Region (cm^{-1})
O–H stretching	3200–3600
N–H stretching	3100–3400
C=O stretching	1650–1750
C–N stretching	1200–1350

The strong vibrations of the carbonyl group play an important role in complex formation.

General Discussion. The calculation results indicate that the physicochemical properties of D- and L-aspartic acid are very similar. However, the L-form is thermodynamically slightly more stable, while the D-form possesses a larger dipole moment. Both molecules behave as strong donor ligands. In aqueous solution, solvation of the carboxyl and amino groups provides significant stabilization.

Conclusion.The optimized structures of D- and L-aspartic acid were successfully calculated at the DFT/B3LYP/6-311+G(d,p) level of theory. No negative frequencies were observed for either molecule, confirming that both structures correspond to true minimum-energy states. The total energy of L-aspartic acid was found to be lower than that of the D-form, indicating greater thermodynamic stability in aqueous solution. The larger dipole moment of the D-form suggests stronger electrostatic interactions with the solvent. The localization of the HOMO orbitals on oxygen and nitrogen atoms confirms the ability of aspartic acid to form complexes with metal ions. Aspartic acids can form coordination compounds with ions such as Cr(III), Cu(II), Ni(II), Co(II), and VO(IV), acting as bidentate and tridentate ligands. The obtained results provide an important scientific basis for studies in coordination chemistry and bioinorganic systems.

References

1. Frisch, M.J. et al. *Gaussian 09 Revision A.02*, Gaussian Inc., Wallingford, CT, 2009.
2. Becke, A.D. *Density-Functional Thermochemistry. III. The Role of Exact Exchange*. Journal of Chemical Physics.
3. Lee, C., Yang, W., Parr, R.G. *Development of the Colle–Salvetti Correlation-Energy Formula*.
4. Jensen, F. *Introduction to Computational Chemistry*.
5. Atkins, P., de Paula, J. *Physical Chemistry*.
6. Cotton, F.A., Wilkinson, G. *Advanced Inorganic Chemistry*.
7. Lever, A.B.P. *Inorganic Electronic Spectroscopy*.