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Density Functional Theory Investigation of the Conformational Energy Landscape of Cyclohexane

Priyanka Madhukar
Department of Chemistry, University of Rajasthan, Jaipur 302004, India

Nisha Rajput
Department of Chemistry, University of Rajasthan, Jaipur 302004, India

Pinky Saini
Department of Chemistry, University of Rajasthan, Jaipur 302004, India

S.G. Kalane
Department of Chemistry, Late Pundalikrao Gawali Arts & Science Mahavidyalaya, Shirpur Jain, Dist. Washim, Maharastra, India

Devendra Kumar Mahawar
Department of Chemistry, University of Rajasthan, Jaipur 302004, India
devendramahawar@gmail.com

Abstract
The conformational landscape of cyclohexane was investigated using Density Functional Theory (DFT) at the B3LYP/def2-TZVP level. Four characteristic structural forms—chair, twist-boat, boat, and half-chair—were examined using geometry optimization, vibrational-frequency analysis, thermochemical calculations, and frontier-molecular-orbital analysis. The chair structure was found to be the global minimum, with an electronic energy of −235.818410 Hartree. Relative electronic energies of 6.237, 7.187, and 11.380 kcal mol^{-1} were obtained for the twist-boat, boat, and half-chair structures, respectively. Vibrational analysis identified the chair and twist-boat as minima, whereas the boat and half-chair exhibited one imaginary frequency at −98.85 and −234.49 cm^{-1}, respectively, consistent with first-order saddle points. Zero-point and thermal corrections did not alter the conformational ordering. The calculated chair–twist-boat Gibbs free-energy difference was 5.943 kcal mol^{-1}, in close agreement with the experimentally established magnitude of approximately 5.5 kcal mol^{-1}. Structural analysis showed that the chair minimizes angular and torsional distortion, whereas greater geometrical distortion accompanies the higher-energy stationary points. Frontier-orbital analysis revealed a systematic decrease in the HOMO–LUMO gap from 8.982 eV for the chair to 8.615 eV for the half-chair. The results demonstrate that electronic energy, thermochemistry, molecular geometry, vibrational analysis, and frontier-orbital properties provide complementary descriptions of cyclohexane conformational behavior.
Keywords: *Cyclohexane, conformational analysis, DFT, twist-boat, ring inversion.*

1. Introduction

Conformational analysis provides a molecular-level description of the spatial arrangements accessible to a molecule through rotation or deformation without changing its covalent connectivity. It is particularly important for cyclic compounds, in which ring closure couples the motions of individual bonds and restricts the accessible geometries. Cyclohexane is a classical and exceptionally useful model for investigating these effects because its six tetrahedral carbon atoms can adopt several distinct three-dimensional arrangements with substantially different energies.

The conformational behavior of cyclohexane was historically central to the development of modern stereochemistry. Recognition that the six-membered ring need not be planar led to the puckered chair and boat representations, which subsequently became fundamental to the description of cyclic molecular structure. Modern conformational analysis distinguishes the chair, twist-boat, boat, and half-chair geometries and identifies them as different regions or stationary points on the conformational energy surface. Computational and experimental studies have established the chair as the lowest-energy form and the twist-boat as a higher-energy local minimum, while boat and half-chair structures occur at higher-energy regions of the conformational landscape[9].

The exceptional stability of the chair conformation arises from its favorable three-dimensional geometry. It maintains C–C–C angles close to the preferred tetrahedral geometry while minimizing unfavorable eclipsing interactions. The boat structure experiences greater torsional and nonbonded strain, including the well-known flagpole interaction, whereas twisting the boat relieves part of this strain and gives rise to the twist-boat minimum. An additional important characteristic of the chair conformation is the presence of axial and equatorial positions. Six bonds are axial and approximately parallel to the principal molecular axis, while six are

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equatorial and extend around the perimeter of the ring. During ring inversion, the two chair structures interconvert and the axial and equatorial positions exchange. This process is commonly referred to as the cyclohexane ring flip. Ring inversion consequently proceeds through a series of puckered structures rather than by rotation about an isolated C–C bond.

Experimental spectroscopic studies have directly established the twist-boat as a real conformational species and measured the free-energy difference between the chair and twist-boat forms. A value of approximately 5.5 kcal mol^{-1} for this gas-phase free-energy difference is widely reported[10-12].

Quantum-chemical calculations[1, 2] provide a complementary approach by allowing the energies and structures of individual stationary points to be determined. In the present work, DFT calculations were employed to investigate the energetic, structural, vibrational, thermochemical, and electronic characteristics of the principal cyclohexane conformations. The objective was to establish the conformational energy ordering and relate the calculated differences to molecular geometry and strain.

2. Computational Methodology

Initial geometries of the chair, twist-boat, boat, and half-chair structures of cyclohexane were constructed using Avogadro[13] and subjected to preliminary geometrical relaxation. The resulting Cartesian coordinates were subsequently used for quantum-chemical calculations with the ORCA program[7, 8]. ORCA is a general-purpose quantum-chemical package supporting DFT and a wide range of electronic-structure methods.

All calculations reported here were performed using the B3LYP[3-5] exchange-correlation functional with the def2-TZVP[6] basis set. The B3LYP formulation combines Becke exchange with correlation treatment based on the Lee–Yang–Parr functional framework, while def2-TZVP is a triple-ζ valence basis set with polarization functions developed within the Karlsruhe def2 basis-set family.

Geometry optimizations were performed for the selected conformational structures, followed by vibrational-frequency calculations. The frequency calculations were used both to obtain thermochemical corrections and to characterize the nature of each stationary point. A structure with no imaginary frequencies was assigned as a minimum, whereas a structure with one imaginary frequency was considered a first-order saddle point, subject to confirmation that the associated normal mode corresponds to the expected conformational coordinate.

Electronic energies, zero-point energies (ZPE), and Gibbs free energies were obtained from the calculations. Relative electronic and Gibbs free energies were defined with respect to the chair structure according to

$$\Delta E_i = E_i - E_{\text{chair}}$$

and

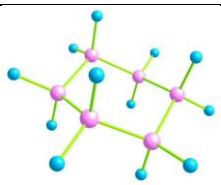
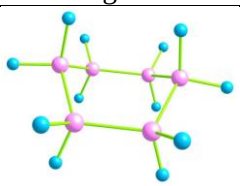
$$\Delta G_i = G_i - G_{\text{chair}}$$

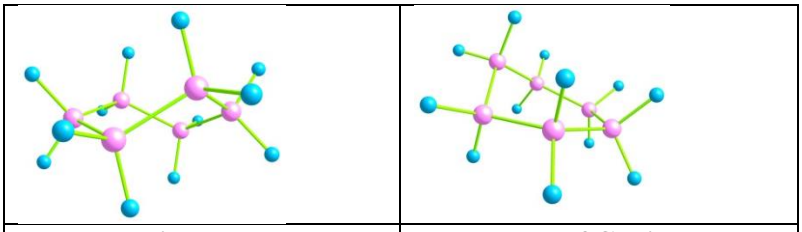
HOMO and LUMO energies, HOMO–LUMO gaps, and dipole moments were also evaluated. No explicit solvent model was used in performing calculations; accordingly, the present results are treated as gas-phase B3LYP/def2-TZVP calculations.

3. Results and Discussion

3.1. Structural Parameters and Conformational Strain

The geometry optimisation calculations of Avogadro designed initial geometries of various conformations have been performed at B3LYP/def2-TZVP level. The final optimized geometries of each conformer is shown in Figure 1.

	
Chair	**Boat**



Twisted Boat	Half Chair

Figure 1. Optimized chair, Boat, Twisted Boat and Half Chair conformations of cyclohexane calculated at the B3LYP/def2-TZVP level.

The optimized structural parameters are summarized in Table 1.

Table 1. Selected optimized structural parameters

Conformation	C–C (Å)	C–H axial (Å)	C–H equatorial (Å)	C–C–C (°)	C–C–C–C dihedral (°)
Chair	1.531	1.096	1.093	111.4	54.93
Twist-boat	1.529–1.542	1.093–1.095	1.092–1.093	110.89–112.15	30.75–64.19
Boat	1.531–1.553	1.094	1.092–1.093	111.25–111.49	0.3–52.9
Half-chair	1.525–1.557	1.091–1.096	1.091–1.093	109.6–118.09	7.05–69.9

The chair structure exhibits a relatively regular carbon framework. Its C–C bond length of 1.531 Å and C–C–C angle of 111.4° indicate that the tetrahedral character of the carbon centers is substantially preserved. The C–C–C–C dihedral angle of 54.93° reflects the characteristic puckered chair geometry.

The twist-boat retains relatively favorable bond angles, with C–C–C angles of 110.89–112.15°, but exhibits a broader range of torsional angles. This reflects the ring twisting required to alleviate unfavorable interactions in the boat geometry. The structure consequently retains some torsional strain but is sufficiently relaxed to constitute a local minimum.

The boat structure has C–C–C angles within a comparatively narrow range, but its dihedral angles extend to approximately 0.3°. Such near-eclipsed torsional geometry is consistent with increased torsional strain. The nonbonded distance between two flagpole hydrogens has been found to be 2.32 Å. This close approach between hydrogen atoms at the two ends of the boat, flagpole interaction, further contributes to its higher energy.

The half-chair exhibits the greatest structural distortion, with C–C–C angles ranging from 109.6 to 118.09° and dihedral angles from 7.05 to 69.9°. Its broad geometrical distribution is consistent with the substantial deformation required to move the ring away from the favorable chair geometry toward the conformational transition region.

Thus, the calculated structural parameters support the energetic ordering and demonstrate that the major conformational energy differences arise from changes in ring puckering, angular distortion, and torsional relationships rather than from large changes in the intrinsic C–C or C–H bond lengths.

3.2. Optimized Structures and Energetic Ordering

The calculated energetic properties of the four principal cyclohexane structures are presented in Table 2.

Table 2. Calculated energetic and thermochemical properties of cyclohexane conformations

Conformation	E_{elec} (Hartree)	ZPE (Hartree)	E + ZPE (Hartree)	G (Hartree)	ΔE (kcal mol^{-1})	ΔG (kcal mol^{-1})
Chair	−235.818410	0.16985435	−235.6485558	−235.6773305	0.000	0.000
Twist-boat	−235.808471	0.16981591	−235.6386549	−235.6678597	6.237	5.943
Boat	−235.806957	0.16967092	−235.6372857	−235.6657878	7.187	7.243
Half-chair	−235.800276	0.16961595	−235.6306597	−235.6596983	11.380	11.064

The chair structure has the lowest electronic energy and is therefore the reference structure for the relative-energy analysis. The calculated electronic-energy ordering is

$$\boxed{\text{Chair} < \text{Twist} - \text{boat} < \text{Boat} < \text{Half} - \text{chair}}$$

with the twist-boat, boat, and half-chair lying 6.237, 7.187, and 11.380 kcal mol^{-1} above the chair, respectively.

The calculated values establish the familiar energetic hierarchy of cyclohexane. The chair structure is strongly favored, whereas the twist-boat represents a higher-energy stationary point. The boat lies only 0.950 kcal mol^{-1} above the twist-boat:

$$\Delta E_{\text{boat}-\text{twist}-\text{boat}} = 7.187 - 6.237 = 0.950 \text{ kcal mol}^{-1},$$

indicating that twisting the boat geometry produces substantial strain relief.

The calculated energy landscape is consistent with established theoretical descriptions in which the chair is the lowest-energy minimum, the twist-boat is a second minimum, and the boat and half-chair correspond to higher-energy stationary points.[9]

3.3. Vibrational Analysis and Stationary-Point Character

Vibrational analysis provides an essential distinction between the calculated minima and saddle points.

Table 3. Vibrational characterization of the calculated structures

Conformation	Imaginary frequency (cm^{-1})	Stationary-point assignment
Chair	None	Minimum
Twist-boat	None	Minimum
Boat	−98.85	First-order saddle point
Half-chair	−234.49	First-order saddle point

The chair and twist-boat structures possess no imaginary frequencies and are therefore consistent with minima on the calculated potential-energy surface. In contrast, both the boat and half-chair structures exhibit exactly one imaginary frequency, consistent with first-order saddle points.

Visualization of the corresponding normal modes shows collective deformation of the carbon framework. The −98.85 cm^{-1} mode of the boat and −234.49 cm^{-1} mode of the half-chair are associated with ring-puckering motions rather than localized C–H stretching. These modes are therefore consistent with conformational deformation of the cyclohexane ring.

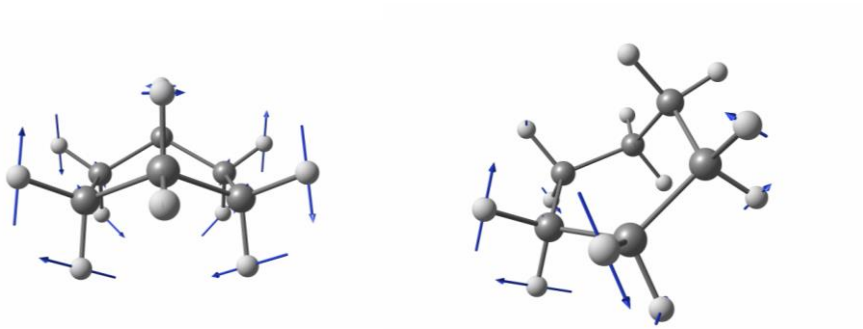


Figure 2. Calculated imaginary-frequency modes of the boat (−98.85 cm^{-1}) and half-chair (−234.49 cm^{-1}) stationary points. The displacement patterns correspond to collective deformation of the cyclohexane carbon framework.

The frequency results are particularly important for the interpretation of the boat and half-chair. Their higher energies alone would not establish transition-state character; the presence of a single imaginary frequency provides the required stationary-point evidence.

3.4. Zero-Point Energy and Gibbs Free Energy

The zero-point energies of the four structures differ only slightly, ranging from 0.16961595 to 0.16985435 Hartree. Consequently, ZPE correction does not alter the energetic ordering.

The approximate ZPE-corrected relative energies are 0.00, 6.21, 7.07, and 11.23 kcal mol^{-1} for the chair, twist-boat, boat, and half-chair, respectively. Thus, the chair remains the lowest-energy structure after inclusion of zero-point vibrational contributions.

The Gibbs free-energy data lead to the same ordering:

$$\boxed{\text{Chair} < \text{Twist} - \text{boat} < \text{Boat} < \text{Half} - \text{chair}}$$

with relative Gibbs free energies of 0.000, 5.943, 7.243, and 11.064 kcal mol^{-1}, respectively.

The chair–twist-boat free-energy difference,

$$\Delta G_{\text{TB}-\text{Chair}} = 5.943 \text{ kcal mol}^{-1},$$

is particularly significant. Experimental spectroscopic measurements have established a chair–twist-boat free-energy difference of approximately 5.5 kcal mol^{-1} in the gas phase. The

calculated value therefore agrees reasonably well with the experimental magnitude, differing by approximately 0.44 kcal mol^{-1}.

3.5. Frontier Molecular-Orbital Analysis

The calculated frontier-orbital properties are given in Table 4.

Table 4. HOMO, LUMO, HOMO–LUMO gap, and dipole moment

Conformation	HOMO (eV)	LUMO (eV)	HOMO–LUMO gap (eV)	Dipole moment (D)
Chair	−8.029871	0.951862	8.981733	0.00000
Twist-boat	−8.025517	0.831859	8.857376	0.00050
Boat	−7.962931	0.788592	8.751523	0.04518
Half-chair	−7.903609	0.711039	8.614648	0.00511

The HOMO energy becomes progressively less negative from the chair to the half-chair:

$$-8.0299 \rightarrow -8.0255 \rightarrow -7.9629 \rightarrow -7.9036 \text{ eV}.$$

Conversely, the LUMO energy decreases from 0.9519 eV for the chair to 0.7110 eV for the half-chair. These changes result in a systematic narrowing of the HOMO–LUMO gap:

$$8.9817 > 8.8574 > 8.7515 > 8.6146 \text{ eV}.$$

The chair therefore has the largest calculated frontier-orbital gap, whereas the half-chair has the smallest. The HOMO and LUMO plots provide a complementary visualization of how the frontier electronic structure changes as the ring geometry is distorted.

The systematic reduction in the HOMO–LUMO gap is consistent with changes in the electronic structure accompanying conformational distortion. Nevertheless, the HOMO–LUMO gap should not be interpreted as a direct measure of thermodynamic stability. In fact, the half-chair provides

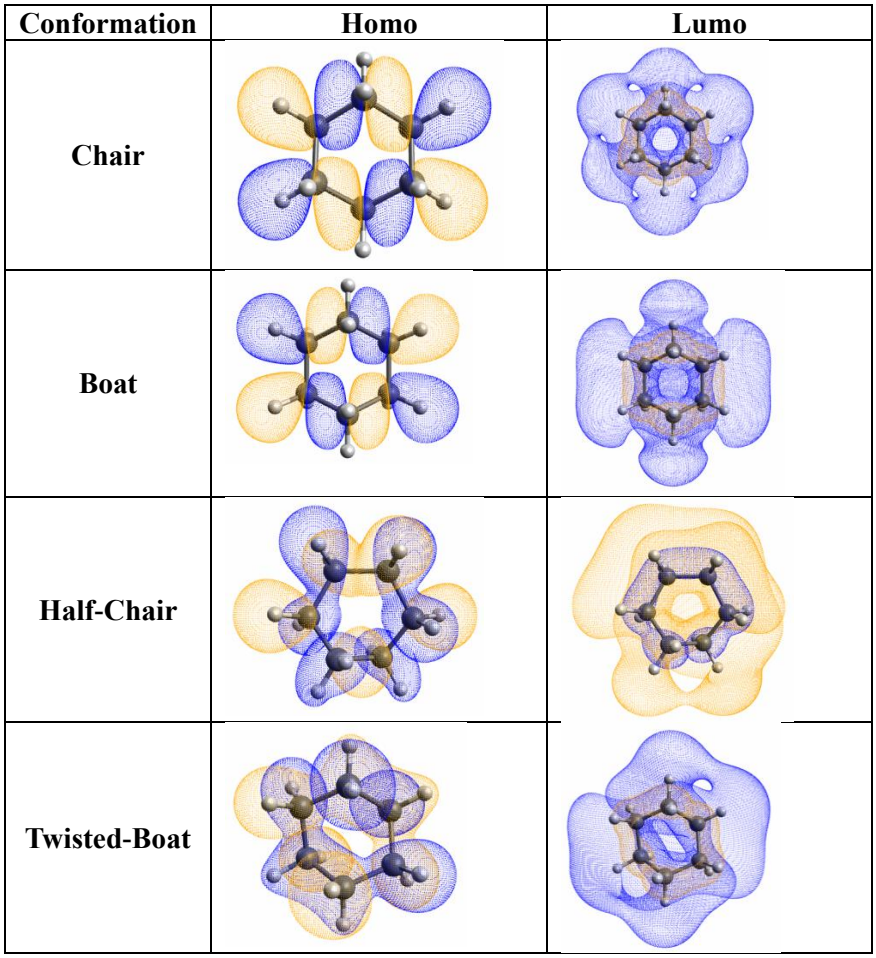


Figure 3. Calculated HOMO and LUMO distributions for the chair, twist-boat, boat, and half-chair structures of cyclohexane at the B3LYP/def2-TZVP level.

a clear example: it has the smallest HOMO–LUMO gap but the highest conformational energy. The frontier-orbital gap therefore represents an electronic-structure descriptor rather than a direct criterion for conformational preference.

3.6. Dipole-Moment Analysis

The calculated dipole moments are extremely small for all structures. The chair has a dipole moment of 0 D, while the twist-boat, half-chair, and boat have values of 0.00050, 0.00511, and 0.04518 D, respectively. The essentially zero dipole moment of the chair is consistent with the high symmetry and cancellation of local bond-dipole contributions in unsubstituted cyclohexane. The somewhat larger value calculated for the boat reflects its lower symmetry and more asymmetric charge distribution. Nevertheless, even the largest value remains very small, confirming that all four structures are effectively nonpolar. These electronic properties are consistent with, but do not determine, the conformational energy ordering.

3.7. Conformational Interconversion and Energy Landscape

The calculated stationary points provide a coherent representation of the cyclohexane conformational landscape:

$$\text{Chair} \rightarrow \text{Half} - \text{chair}^{\ddagger} \rightarrow \text{Twist} - \text{boat} \rightarrow \text{Boat}^{\ddagger} \rightarrow \text{Twist} - \text{boat} \rightarrow \text{Half} - \text{chair}^{\ddagger} \rightarrow \text{Chair}$$

The chair represents the global minimum, whereas the twist-boat corresponds to a higher-energy local minimum. The boat and half-chair are higher-energy first-order saddle points based on their single imaginary frequencies. The calculated boat–twist-boat energy separation of 0.950 kcal mol^{-1} is consistent with the established description of the boat as a saddle point between two twist-boat minima. Literature studies likewise place the twist-boat several kcal mol^{-1} above the chair and the boat approximately 1 kcal mol^{-1} above the twist-boat region. The half-chair lies substantially higher than the twist-boat and represents the more strongly distorted stationary region associated with chair–twist-boat interconversion. The present calculations therefore reproduce the essential topology of the established cyclohexane conformational energy surface.

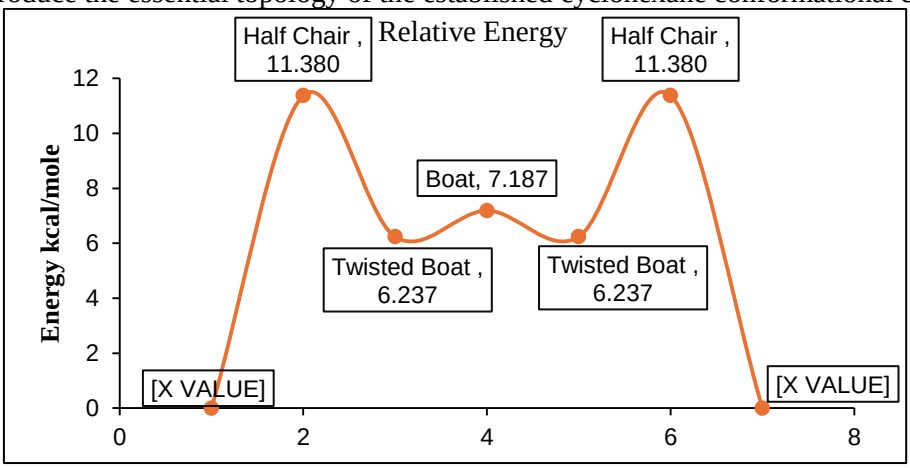


Figure 4. Relative electronic energies of the chair, twist-boat, boat, and half-chair conformational structures of cyclohexane calculated at the B3LYP/def2-TZVP level, with the chair conformer used as the zero-energy reference.

3.8. Comparison with Literature

Table 5. Comparison of present results with representative literature values

Quantity	Present calculation	Representative literature value
Chair relative energy	0.000 kcal mol^{-1}	0.0 kcal mol^{-1}
Twist-boat relative electronic energy	6.237 kcal mol^{-1}	~5.5–7 kcal mol^{-1}
Twist-boat relative Gibbs free energy	5.943 kcal mol^{-1}	~5.5 kcal mol^{-1}
Boat relative energy	7.187 kcal mol^{-1}	~7 kcal mol^{-1}
Half-chair relative energy	11.380 kcal mol^{-1}	~10.8–12 kcal mol^{-1}

The present results are consistent with the established experimental and theoretical description of cyclohexane[4]. Spectroscopic measurements established the twist-boat as an accessible

conformational species and yielded a chair–twist-boat free-energy difference of approximately 5.5 kcal mol^{-1}. High-level ab initio calculations have independently identified the chair as the lowest-energy minimum and the twist-boat as a second minimum, with higher-energy stationary points associated with the conformational interconversion pathway[9].

The calculated Gibbs free-energy difference of 5.943 kcal mol^{-1} is particularly close to the experimental value. The approximately 0.44 kcal mol^{-1} difference is reasonable given that the present value derives from a B3LYP/def2-TZVP thermochemical calculation, whereas experimental measurements represent experimentally accessible thermodynamic quantities under specific conditions.

The present boat and half-chair energies also fall within the range of conventional literature estimates. The agreement is primarily qualitative and should not be interpreted as an exact benchmark because different studies may report electronic energies, enthalpies, free energies, or transition-state barriers.

3.9. Conclusion

The present B3LYP/def2-TZVP calculations provide a consistent description of the conformational landscape of cyclohexane. The chair structure was identified as the global minimum, with the twist-boat representing a higher-energy local minimum, while the boat and half-chair structures were characterized as first-order saddle points by their single imaginary vibrational frequencies. The calculated relative electronic energies of the twist-boat, boat, and half-chair were 6.237, 7.187, and 11.380 kcal mol^{-1}, respectively, relative to the chair. These values are consistent with the established conformational preference of cyclohexane for the chair geometry.

The energetic ordering was preserved after zero-point and thermal corrections, with relative Gibbs free energies of 5.943, 7.243, and 11.064 kcal mol^{-1} for the twist-boat, boat, and half-chair, respectively. The calculated chair–twist-boat Gibbs free-energy difference of 5.943 kcal mol^{-1} is in close agreement with the experimentally reported value of approximately 5.5 kcal mol^{-1}. The structural analysis further showed that the chair minimizes angular and torsional distortion, whereas the higher-energy structures exhibit progressively greater geometrical deformation.

The frontier-orbital analysis revealed a systematic decrease in the HOMO–LUMO gap from 8.982 eV for the chair to 8.615 eV for the half-chair, demonstrating that conformational distortion influences the electronic structure. However, the HOMO–LUMO gap should be regarded as a complementary electronic descriptor rather than a direct measure of thermodynamic stability. Overall, the study demonstrates that the combined analysis of molecular geometry, electronic energy, vibrational frequencies, thermochemistry, and frontier orbitals provides a coherent theoretical description of cyclohexane conformational behavior and the origin of its pronounced chair preference.

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