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Ab Initio Conformational Analysis of *trans*-Cyclohexene

Richard P. Johnson* and Kenneth J. DiRico

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

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Introduction

The constraint of trans-disubstituted carbon–carbon double bonds in progressively smaller rings engenders large incremental increases in strain and reactivity.[1] *trans*-Cyclooctene is an isolable substance,[2] while the next smaller homologue *trans*-cycloheptene has been seen only by low temperature NMR spectroscopy.[3] Flash spectroscopic experiments have provided the only direct experimental evidence for the existence of *trans*-cyclohexenes, which have been postulated as transient intermediates in many photoreactions.[4] *trans*-Cyclopentene is presumably highly strained and has received very little serious consideration.[5]

Early force field and ab initio computational studies on *trans*-cyclohexene considered only a single chairlike conformation.[6,7] During the course of an ab initio computational study on *trans*-cyclohexenones, we located two distinct conformational minima, best described as chair and twist-boat.[8] At about the same time there appeared reports of a stochastic MM3 (92) conformational search, complementary HF/6-31G* optimizations[9], and semiempirical calculations[10] which led to the same conclusion for *trans*-cyclohexene. In these studies, only the minima were located.

Strained π bonds and especially transition states for π bond rotation are not adequately described at the Hartree–Fock (HF) level because of their substantial diradical character. Two configuration SCF (TCSCF) methods which mix $(\pi)^2$ and $(\pi^*)^2$ configurations provide an optimal wavefunction for these unusual species.[11] We describe here results of a TCSCF/6-31G* study on trans-cyclohexene in which the three relevant minima and three connecting transition states have been located at the TCSCF/6-31G* level.[12] For highly strained species such as these, the barriers to π bond rotation may be of the same magnitude as those for conformational interconversion. Our calculations provide the most complete analysis to date of the conformations of *trans*-cyclohexene and their potential for interconversion, both with the cis isomer and with each other.

Computational Methods

Structures were initially constructed and minimized at the HF/3-21G level with SPARTAN.[13] Successive TCSCF/3-21G and TCSCF/6-31G* geometry optimizations were then performed with GAMESS.[14] In all cases, the TCSCF wave function included one orbital of A symmetry and one of B symmetry; these correspond to π and π^* molecular orbitals. In several cases, TCSCF convergence problems required initial use of MCSCF(2,2) methods to obtain a converged wave function. Analytic hessian calculation and frequency analysis were performed at the TCSCF/3-21G level. Further TCSCF/6-31G* optimization afforded only minor changes in structures and energetics. All optimizations were restricted to C_2 symmetry; vibrational frequency analysis showed this was not an artificial constraint since all stationary points showed the expected number of imaginary frequencies.

The TCSCF methodology was calibrated by calculation of the π bond rotational barrier in ethylene.[11a] TCSCF/6-31G* optimization of both D_{2h} and D_{2d} structures for ethylene yielded total energies of −78.06026 and −77.95571 hartrees, respectively. This gives a predicted enthalpic barrier of 65.6 kcal/mol, which is in excellent agreement with experiment.[15] Thus, we have confidence that our predicted barriers should be accurate to within a few kcal/mol.

Results of Calculations

Scheme 1 provides the most concise pictorial summary of this work. All structures shown are from TCSCF/6-31G* optimizations. Relative energies (kcal/mol) in Scheme 1 are given at the TCSCF/6-31G* level, corrected with zero point differences calculated at the TCSCF/3-21G level. Total and relative energies calculated at all levels are given in Table 1. The HF/3-21G energies for **2** and **3** are ca. 10 kcal/mol above the TCSCF values; this is readily attributed to the biradical character in the

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Scheme 1. Structures and Relative Energies (kcal/mol) for *trans*-Cyclohexene Conformers and Transition States

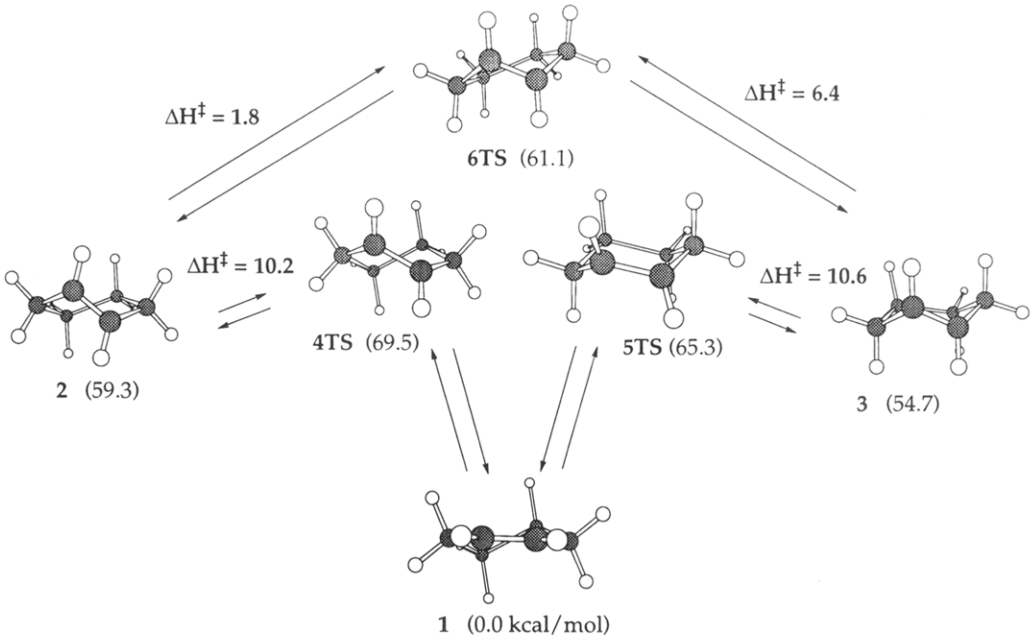

Table 1. Energetics of *trans*-Cyclohexene Conformers and Transition States[a,b]

structure	HF/3-21G	TCSCF/3-21G	TCSCF/6-31G*	ZPVE[c]
cyclohexene (**1**) (half-chair)	−231.72915 (0.0)	−231.75773 (0.0)	−233.04672 (0.0)	98.1
twist-boat *trans*-cyclohexene(**2**)	−231.61802 (69.7)	−231.66434 (58.6)	−232.95076 (60.2)	97.2
chair *trans*-cyclohexene (**3**)	−231.62798 (63.5)	−231.67309 (53.1)	−232.95872 (55.2)	97.6
twist-boat π bond transition state (**4TS**)	*d*	−231.64305 (72.0)	−232.93072 (72.8)	94.8 [$\nu_I = -895.8$ cm^{-1}]
chair π bond transition state (**5TS**)	*d*	−231.65007 (67.6)	−232.93794 (68.3)	95.1 [$\nu_I = -872.8$]
chair to twist-boat transition state (**6TS**)	−231.61671 (70.6)	−231.66434 (62.3)	−232.94794 (62.0)	97.2 [$\nu_I = -200.5$]

[a] Total energies in hartrees. Relative energies (kcal/mol) are given in parentheses. [b] All structures were optimized within C_2 symmetry at the computational level cited. [c] In kcal/mol, calculated at the TCSCF/3-21G level with unscaled frequencies. [d] HF level calculation is not appropriate for this species.

Table 2. Selected Structural Data from TCSCF/6-31G* Optimizations

structure	double bond length, Å	dihedral angle H−C=C−H, deg	dihedral angle C−C=C−C, deg
1	1.341	1.7	−0.316
2	1.381	174.6	88.1
3	1.382	176.6	84.0
4TS	1.478	132.6	60.7
5TS	1.482	129.3	55.2
6TS	1.376	173.5	91.2

trans structures. Selected geometric parameters are collected in Table 2.

Structure **1** is the well-known half-chair conformation of *cis*-cyclohexene[12] while **2** and **3** are the twist-boat and chair conformers, respectively, for *trans*-cyclohexene.[9,10] The two transition states for π bond rotation to **1** are shown as **4TS** and **5TS**, while **6TS** is the transition state for conformational interconversion between chair and twist-boat.

We first consider the relative energetics and most likely pathways available to these reactive species. Our calculations concur with earlier studies[9,10] in predicting that the chair conformer **3** should be the lowest energy form of *trans*-cyclohexene. The chair to twist-boat energy difference is about the same as that for the corresponding conformers of cyclohexane. This structure permits a fully trans double bond while still minimizing other forms of strain. Chair structure **3** is predicted to be 54.7 kcal/mol above *cis*-**1**; this value agrees well with previous estimates.[6,7,9,10] Relevant experimental data come from a recent study by Caldwell and co-workers who used photoacoustic calorimetry to measure a trans−cis isomerization energy of either 44.7 ±5 or 47.0 ±3 kcal/mol for 1-phenylcyclohexene.[4b,10]

Trans isomer **3** has two available reaction paths: π bond rotation to **1** which has a predicted barrier of 10.6 kcal/mol, and interconversion with the twist-boat conformer, with a barrier of 6.4 kcal/mol. In the opposite direction, twist-boat conformer **2** has a 10.2 kcal/mol barrier for π bond rotation, but a barrier of only 1.8 kcal/mol for isomerization to **3**. Thus, within its short lifetime, prior to π bond rotation, **3** should undergo a rapid, but conformationally biased, interconversion with **2**, while **2** should easily convert to **3**. Caldwell and co-workers[4g] have measured a 12.1 kcal/mol barrier for trans to cis isomerization of 1-phenylcyclohexene. In principle, phenyl substitution should diminish the barrier, thus our predicted barrier of 10.6 kcal/mol appears to be a few kcal/mol too low.

The structures of **2** and **3** show only slightly elongated π bonds (Table 2) which are substantially pyramidalized. Thus, while the H−C=C−H dihedral angles for **2** and **3** are close to 180°, the C−C=C−C angles are nearly orthogonal. For the π bond transition states **4TS** and **5TS**, these values show a clear progression toward **1**.

Efforts with a TCSCF/3-21G wave function to locate a minimum corresponding to *trans*-cyclopentene (**7**) have been unsuccessful to date. Simple extrapolation from the present results, as well as data on larger ring homologues,[1,10] suggest that if it exists, the π bond strain energy of **7** should be >70 kcal/mol. Nevertheless, we believe it is possible that a shallow minimum exists for **7**, and we are continuing efforts to locate this structure.

Conclusions

Our calculations support the existence of two conformational minima for *trans*-cyclohexene. This result is in agreement with other recent studies.[9,10] However, we find that the twist-boat structure **2** is of sufficiently higher energy and has such a small barrier to conformational change that it may not play a significant role in the chemistry of these strained species. In each case, π bond rotation has a predicted barrier of ca. 10 kcal/mol, and rotation should lead to **1** since there appear to be no other low energy minima for cyclohexene.[12]

We believe the value of this conformational analysis may lie in the eventual ability to "tune" these processes by ring substituents or other structural modifications, much as has been done for cyclohexanes. *trans*-Cyclohexenones are potential intermediates in cyclohexenone photochemistry[16] and we are currently studying the role of conformational control in trans-intermediates as one explanation of the diverse photochemical reactions of cyclohexenones. We are also studying the unusually large secondary kinetic isotope effects (k_H/k_D for vinyl deuterium) that have been observed for trans to cis isomerization in phenylcyclohexene.[4g]

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Supplementary Material Available: Cartesian coordinates (Å) for TCSCF/6-31G* stationary points calculated in this research (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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