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# Origin of the Conformational Mobility for 4-Tetrahydropyranone: An *ab Initio* MO Study

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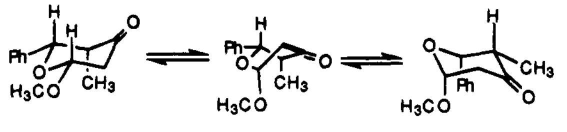
Studies by the *ab initio* MO methods indicate a rather flat ring system and a small barrier for ring inversion in 4-tetrahydropyranone (4-THPN). The crystal structure of *syn*-6-(*p*-bromophenyl)-2-methoxy-5-methyl-4-THPN determined by X-ray diffraction supports the flattened ring structure predicted by the *ab initio* calculations. The relationship between the endocyclic torsional angle $\phi$ and the bond length C−X (X = O, N, C, and S) in a 4-X-cyclohexanone system was studied by *ab initio* MO methods. The size of $\phi$ is in the order of 4-THPN ($\phi = 44.5°$) < 4-piperidinone ($\phi = 47.1°$) < cyclohexanone ($\phi = 49.1°$) < 4H-thiopyran-4-one ($\phi = 53.6°$). The flattening of the ring is inversely proportional to the C−X bond distance.

## Introduction

Recently we reported a computational study of the conformations of 4-tetrahydropyranones (4-THPN).[1] It was found that the diaxial conformer **1a** is more stable than the diequatorial form **1e** by $\sim$0.5 kcal/mol according to molecular mechanics. Although such a small energy difference by MM2 should not be taken literally, it did indicate that there is little energy difference between these two conformers. This finding was important since **1e** had been assumed by Danishefsky to be the only conformer,[2] which formed the basis for the interpretation of the diastereofacial selectivity ("100% axial attack") in hydride reduction of 4-THPNs using the Cieplak model.[3] If our computational results were reasonable, the interpretation for the origin of the $\pi$-facial selectivity needs to be revised. The observed product stereochemistry could have come from equatorial attack on **1a**.



**1e** **1t** **1a**

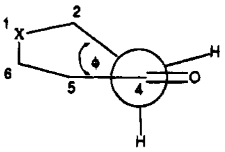
In order to evaluate the quality of the predictions of the molecular mechanics, we have performed variable temperature NMR studies[4] and obtained the crystal structure of a bromo derivative of **1** (*vide infra*). The X-ray diffraction analysis shows that the phenyl and the methoxy groups in **1** assume the diequatorial orientation in the crystal. However, a rapid equilibrium among all conformers occurs in solution.[4] In order to understand the divergence of the experimental results we have performed *ab initio* calculations on related six-membered-ring ketones. In this report, we will show that the 4-tetrahydropyranones have a flattened ring system. Consequently, the barrier for ring inversion is small and the population of the diaxial isomer is substantial in solution. Both the flattened ring and the substantial population of **1a** can have significant consequences on the $\pi$-facial selectivity of **1**.

## Computational Methods

*Ab initio* calculations were performed with the GAUSSIAN 92 program[5] implemented on the IBM mainframe ES/9000-480 computer. All initial conformations were generated by interactive computer graphics[6] and then were fully optimized with the 3-21G, and the 6-31G* basis sets. Harmonic frequencies were calculated for each conformer at the 6-31G* level. The optimized structures other than the transition states for ring inversion have all positive frequencies, which is an indication of true minima on the 6-31G* potential surface. The barrier for ring inversion was studied by constraining the endocyclic CC(=O)CC torsion angle in cyclohexanone or the endocyclic C2C3C4C5 torsion angle in THP at 0 °C.

## Results and Discussion

**A. Conformational Trend in Six-Membered-Ring Compounds: Comparison of Computational and Experimental Results.** The calculated total and relative energies (in parentheses) for the chair and the twist conformers and the ring inversion barrier of cyclohexanone, THP, and 2-hydroxy-4-THPN are listed in Table 1 along with the experimental values when they are available. The calculated structures (6-31G*) are shown in Figure 1. For convenience of the discussion, the endocyclic torsional angle $\phi$, which has direct consequence on $\pi$-facial selectivity, is defined as shown below.



$\phi = \tau_{2,3,4,5}$

It involves the four consecutive carbon atoms around the

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(2) Danishefsky, S.; Langer, M. E. *J. Org. Chem.* **1985**, *50*, 3672. We thank Professor Danishefsky for sending us detailed experimental procedures.

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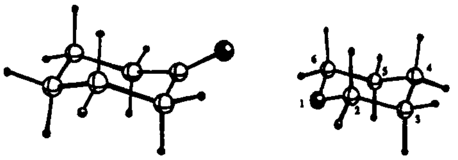
**Table 1. Gaussian 92 Compound Energies, au (kcal/mol)**

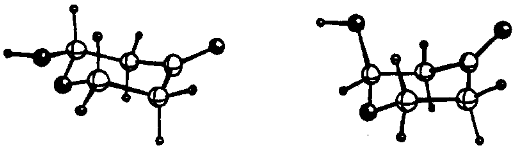
| conformation | 3-21G//3-21G | 6-31G*//3-21G | 6-31G*//6-31G* | exp (kcal/mol)[7,8] |
|---|---|---|---|---|
| | | Cyclohexanone (**2**) | | |
| chair | −306.1916217 (0.00) | −307.9045971 (0.00) | −307.9059163 (0.00) | 0.0 |
| twist | −306.1852887 (3.97) | −307.8985319 (3.81) | −307.8997880 (3.85) | |
| barrier | −306.1826603 (5.62) | −307.8985633 (3.79) | −307.8995844 (3.97) | 4.0 ± 0.1 |
| | | Tetrahydropyran (**3**) | | |
| chair | −268.5256008 (0.00) | −270.0154349 (0.00) | −270.0179072 (0.00) | 0.0 |
| twist | −268.5175789 (5.03) | −270.0056675 (6.13) | −270.0084758 (5.92) | |
| barrier | −268.5079881 (11.05) | −269.9991809 (10.20) | −270.0016963 (10.17) | 10.1 ± 1.2 |
| | | 2-Hydroxy-4-THPN (**4**) | | |
| chair[a] | | | | |
| (axial-OH) | −416.2509141 (0.00) | | −418.5789945 (0.00) | |
| (eq-OH) | −416.2454384 (3.44) | | −418.5767289 (1.42) | |
| twist[a] | −416.2453278 (3.51) | | −418.5746557 (2.72) | |
| barrier | | | | |
| (eq-OH) | −416.2375006 (8.42) | | −418.5713429 (4.80) | |
| (axial OH) | −416.2443783 (4.10) | | −418.5743297 (2.93) | |

[a] Data from ref 1.



Cyclohexanone **2** THP **3**

φ = 49.0 (52.7)[12a] 51.3



**4e** **4a**

2-Hydroxy-4-THPN, equatorial-OH axial-OH (reference 1)

φ = 43.3 47.1

**Figure 1.** Optimized structures (6-31G*) for cyclohexanone (**2**), THP (**3**), and 2-hydroxy-4-THPN (**4**).

carbonyl carbon. By comparing the structures in Figure 1, a trend in the torsional angle φ becomes obvious. First, all the structures in Figure 1 have smaller values of φ than a normal cyclohexane ring. The endocyclic torsional angle in the ring of cyclohexane is about 55° (gas-phase electron diffraction and low-temperature X-ray structure).[9] *Ab initio* calculations at various levels of theory (STO-3G, DZ, and DZP) agree with this value.[10] The calculated and experimental values for the torsional angle φ of cyclohexanone are 49° (6-31G*, Figure 1) and 52.7° (microwave),[11] respectively. The calculated φ involving the C2C3C4C5 of the THP cycle is 51° (Figure 1). Although we have not found experimental values for THP itself, two X-ray diffraction studies show an average φ value of 52.7° for the crystals of the 2-phenoxy derivatives of THP.[12] Thus, the incorporation of a sp² carbon atom in the cyclohexane cycle will cause a flattening of the ring and the incorporation of an oxygen atom causes a flattening of the part of the ring involving the C2C3C4C5 torsional angle, φ.

Second, the ring-flattening effect appears to be additive, i.e., 4-THPN is flatter than either cyclohexanone or THP. The calculated torsional angles φ of 2-hydroxy-4-THPN are only 43° for the equatorial OH isomer and 47° for the axial OH isomer. The calculated flattening of the 4-THPN ring system (Figure 1 and Table 2) is supported by the X-ray structure of the bromo derivative of 4-THPN (**5**) (Figure 2 and Table 2).[13] The torsional angles (φ) in this crystalline compound are 37.4° (C2C3C4C5) and −42.0° (C3C4C5C6). The conformation of this compound in the crystalline state is diequatorial.

The corresponding parameters from the X-ray analysis of **5** are listed in Table 2 along with the *ab initio* (6-31G*) parameters for **4e**. Keeping in mind that the 4-bromophenyl and the methyl groups in **5** are replaced with hydrogen atoms in **4e**, the pyranone skeletons compare

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(11) (a) Dillen, J. Geise, H. J. *J. Mol. Struct.* **1980**, *69*, 137. For molecular mechanics calculations, see: (b) Allinger, N. L.; Chen, K.; Rahman, M.; Pathiaseril, A. *J. Am. Chem. Soc.* **1991**, *113*, 4505. (c) Navio, P. F.; Molina, J. M. *J. Mol. Struct.* **1990**, *222*, 387. For a X-ray structure of *tert*-butylcyclohexanone, see: (d) Lectard, A.; Lichnot, A.; Metras, F.; Gaultier, J.; Hauw, C. *Cryst. Struct. Commun.* **1975**, *4*, 527.

(12) (a) Jones, P. G.; Sheldrick, G. M.; Kirby, A. J.; Glenn, R. *Z. Kristallogr.* **1982**, *161*, 253. (b) Jones, P. G.; Sheldrick, G. M.; Kirby, A. J.; Glenn, R.; Ramaswamy, P.; Halstenberg, M. *Z. Kristallogr.* **1982**, *159*, 265.

(13) **X-ray crystallographic analysis of *syn*-6-(*p*-bromophenyl)-2-methoxy-5-methyl-4-THPN (5)**: $C_{13}H_{15}O_3Br$, orthobromic, space group *Pbca*, $a = 9.195(3)$ Å, $b = 31.103(6)$ Å, $c = 9.091(3)$ Å, $Z = 8$, MW = 299.2 g/mol, $\mu$(Mo Kα) = 33.5 cm$^{-1}$ , $d_c = 1.53$ g/cm³. A clear colorless crystal, which showed sharp extinction under crossed polarizers, was selected from a batch of crystals grown from a solution in ethanol. Unit cell dimensions and intensity data were measured using Mo Kα radiation ($\lambda = 0.71069$ Å) at 293 K on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Three control reflections monitored every 250 measurements showed no significant variation in intensity over the course of the data collection. A total of 2655 unique reflections were collected using the $\omega/2\theta$ method out to $2\theta = 50.00°$ ($\sin\theta/\lambda = 0.5947$). Of these, 1493 reflections had non-zero intensities and 1043 had $F_0 > 1.5\sigma(F_0)$, which were used in the structure analysis and refinement. Empirical absorption corrections were applied using information from $\psi$-scans. The structure was solved using a combination of direct and difference Fourier methods and refined (154 variable parameters) by a full-matrix least-squares procedure. Hydrogen atom parameters were included in the structure factor calculations but were not refined. Anisotropic refinement for all non-hydrogen atoms converged to $R = 0.091$ and $R_w = 0.079$ and "goodness of fit" = 2.34. The weighting of scheme used was $w = [\sigma(F_0)^2 + (0.015F_0)^2]^{-1}$, where $\sigma(F_0)$ for each reflection was estimated from counting statistics. The maximum shift/esd for any parameter in the final least-squares refinement cycle was 0.01. A final difference Fourier synthesis showed no significant residual electron density. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

**Table 2. Structural Parameters from the X-ray Diffraction Analysis of *syn*-(6-*p*-Bromophenyl)-2-methoxy-5-methyl-4-THPN (5)[13] and from *ab Initio* (6-31G*) Calculations for 2-Hydroxy-4-THPN (4e)**

| | **5** (X-ray) | **4e** (6-31G*) |
|---|---|---|
| | Torsional Angles (deg) | |
| O1−C2−C3−C4 | −44.7 | −50.3 |
| C2−C3−C4−C5 | 37.4 | 42.7 |
| C3−C4−C5−C6 | −42.0 | −43.3 |
| C4−C5−C6−O1 | 57.1 | 51.8 |
| C5−C6−O1−C2 | −69.4 | −63.9 |
| C6−O1−C2−C3 | 61.2 | 63.0 |
| | Bond Distances (Å) | |
| C2−O1 | 1.42 (2) | 1.40 |
| C2−O7 | 1.39 (2) | 1.37 |
| C2−C3 | 1.51 (2) | 1.52 |
| C3−C4 | 1.50 (2) | 1.52 |
| C4−O8 | 1.21 (2) | 1.19 |
| C4−C5 | 1.50 (2) | 1.52 |
| C6−O1 | 1.42 (1) | 1.40 |
| C5−C6 | 1.53 (2) | 1.53 |
| | Bond Angles (deg) | |
| C6−O1−C2 | 110.3 (1.1) | 113.6 |
| O1−C2−O7 | 107.0 (1.2) | 108.6 |
| O1−C2−C3 | 111.2 (1.3) | 110.9 |
| C3−C2−O7 | 107.6 (1.3) | 108.2 |
| C2−C3−C4 | 113.4 (1.3) | 111.3 |
| C3−C4−C5 | 117.0 (1.3) | 114.6 |
| C3−C4−O8 | 122.2 (1.6) | 122.6 |
| C5−C4−O8 | 120.8 (1.6) | 122.8 |
| C4−C5−C6 | 107.6 (1.2) | 110.5 |
| C5−C6−O1 | 111.0 (1.1) | 110.7 |

reasonably well between the theory and the experiment. Because of the three substituents on **5**, its structure is more distorted from a standard chair conformation than the 2-hydroxypyranone **4e**. The result is a still flatter ring system.

The consequence of a flat ring becomes apparent when the ring-inversion barriers are considered. Theoretical predictions for the barriers of ring-inversion at the 6-31G* level of theory are in excellent accord with the experimental values. The calculated barrier for ring inversion in cyclohexanone is 3.97 kcal/mol (Table 1), and the reported experimental (NMR) value was 4.0 kcal/mol.[7] The calculated barrier for THP ring inversion is 10.17 kcal/mol, and the reported experimental value was 10.1 ± 1.2 kcal/mol.[8] The energy required for ring-flip in 2-hydroxy-4-THPN is only 2.93 kcal/mol according to calculations using the 6-31G* basis set. Judged by the quality of the calculated barriers for cyclohexanone and THP ring inversion, confidence can be placed upon the computational results for the 2-hydroxy-4-THPN. Thus, the ring-inversion barrier for the phenyl-substituted 4-THPNs, such as **4**, should be even lower. It is not surprising that there is a rapid equilibrium among conformational isomers even at low temperatures.[4]

**B. Direct Relationship between the Endocyclic Torsional Angle $\phi$ and the C−X Distance in 4-X-Cyclohexanone Systems.** It is easy to understand why the incorporation of an $sp^2$ carbon atom into a six-membered cycle flattens the ring since the $sp^2$ carbon is trigonal planar.[14] However, the reasons why an oxygen atom causes the flattening of the ring are less obvious. It has been suggested that the difference between the C−O and the C−C bond lengths (1.40 Å for C−O vs 1.53 Å for C−C) might be responsible for this distortion.[15]

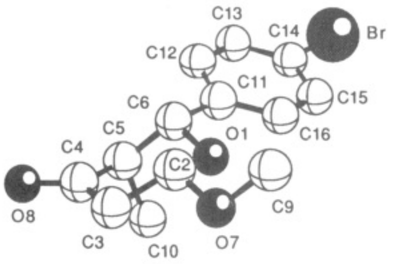

**Figure 2.** X-ray structure of *all-cis*-2-(*p*-bromophenyl)-6-methoxy-5-methyl-4-THPN (**5**). Hydrogen atoms are omitted for clarity. The torsional angles, $\phi$, are 37.4° (C2C3C4C5) and −42.0° (C3C4C5C6).

To explore the relationship between the endocyclic torsional angle $\phi$ and the bond lengths C−X in a 4-X-cyclohexanone, we have carried out *ab initio* calculations on the nitrogen and sulfur analogs of 4-THPN (Table 3). The bond lengths are in the order of C−O < C−N < C−C < C−S, and the flattening of the ring is in the same order: 4-THPN ($\phi = 44.5°$) < 4-piperidinone ($\phi = 47.1°$) < cyclohexanone ($\phi = 49.1°$) < 4H-thiopyran-4-one ($\phi = 53.6°$). Thus the 4-THPN with the shortest bond (C−O = 1.40 Å) has the flattest ring and the 4*H*-thiopyran-4-one with the longest bond (C−S = 1.81 Å) has the most puckered ring.

**C. Why High Ratio of Axial Attack Occurs in a Flattened Ring?** The flattening or puckering of the ring measured by $\phi$ is of significant interest in that it directly influences the diastereofacial selection in nucleophilic addition to the carbonyl group.[16,17] A small $\phi$ indicates a flat ring, which suffers from high axial nucleophilic attack.[16,17] Currently, there are two explanations for the experimental observation. When Anh first summarized the ring-flattening rule more than 20 years ago, he attributed the preferential axial attack on flat rings to the antiperiplanarity of the nucleophile and the Cα−H bond in the transition state.[16] Based on their *ab initio* calculations, Anh believes that the nucleophile should be in the antiperiplanar orientation relative to the Cα−H bond, i.e., stereoelectronic control. This antiperiplanarity cannot be achieved when nucleophilic attack occurs in a puckered ring. More recently, Houk explained the difference in nucleophilic additions on a flattened ring or on a puckered ring emphasizing the torsional strain during an equatorial attack.[17] The equatorial attack on a puckered ring does not suffer from as much torsional strain as it would on a flattened ring. Therefore puckered rings give more equatorial attack product and flattened rings lead to more axial addition.

However, in the search for the origin of the axial preference displayed by small nucleophile, we feel that the steric effect, which is the most important factor in the outcome of $\pi$-facial selectivity, seems to have been overlooked. It is generally agreed that a bulky nucleophile gives preferentially equatorial attack and that the reason for this is the steric interactions between the

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(14) For an early observation of the flattened 4,4-diphenylcyclohexanone, see: Lambert, J. B.; Carhart, R. E.; Corfield, P. W. R. *J. Am. Chem. Soc.* **1969**, *91*, 3567.

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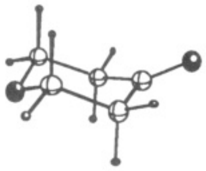
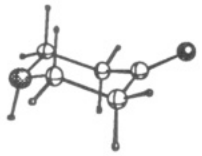
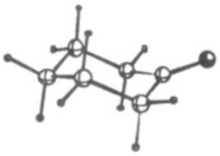
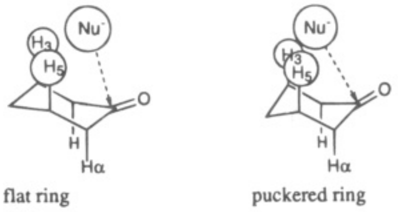
**Table 3. Structural (6-31G*) Relationship between the Bond Length C−X (Å) and the Endocyclic Torsional Angle ($\phi$) in 4-X-Cyclohexanone System**

| Entry | X | Structure | # | Name | C-X (Å) | $\phi$ (°) | $\angle_{612}$ |
|---|---|---|---|---|---|---|---|
| 1 | O |  | **6** | 4-THPN | 1.40 | 44.5 | 113.2 |
| 2 | N-H (axial) |  | **7a** | 4-Piperidinone | 1.45 | 47.1 | 112.7 |
| 3 | N-H (eq.) |  | **7e** | 4-Piperidinone | 1.45 | 45.2 | 112.3 |
| 4 | $CH_2$ |  | **2** | Cyclohexanone | 1.53 | 49.1 | 111.1 |
| 5 | S |  | **8** | 4H-thiopyran-4-one | 1.81 | 53.6 | 97.7 |

nucleophile and the 3,5-diaxial substituents.[18] The trajectory of a nucleophilic attack on an acyclic carbonyl compound has been recognized as extremely important.[19] As shown in Figure 3, when the cyclohexanone ring is puckered or flattened, the optimal trajectory of the attacking nucleophile is also changed. The result of the ring-flattening is that the trajectory of the axial attack moves away from the 3,5-diaxial substituents. Consequently, less steric interaction is experienced by the nucleophile. The result of ring-puckering has the opposite effect, i.e., more steric interaction between the nucleophile and the 3,5-disubstituents (Figure 3). Consequently, equatorial attack is favored. In our opinion, the "flattening rule (the more flattened the ring, the more axial attack)" described by Anh should be the result of all three factors described above. The order of their relative importance should be steric > torsional > stereoelectronic.



flat ring puckered ring

**Figure 3. Axial attack on a flattened cyclohexanone ring suffers less steric hindrance at optimal trajectory.**

## Summary

*Ab initio* calculations reveal a direct relationship between the C−X distance and the endocyclic torsional angle $\phi$ in 4-X-cyclohexanones—the $\phi$ angle decreases as the C−X bond length becomes shorter. Thus, the following order of $\phi$ is found: 4-THPN ($\phi = 44.5^\circ$) < 4-piperidinone ($\phi = 47.1^\circ$) < cyclohexanone ($\phi = 49.1^\circ$) < 4*H*-thiopyran-4-one ($\phi = 53.6^\circ$). A small $\phi$ indicates a flatter ring. A flattened ring reduces the barrier for ring inversion and the difference in energy between axial and equatorial additions on the basis of nucleophile trajectory. Consequently, the high ratio of axial vs equatorial attack

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in the hydride reduction of 4-THPN can be explained on the basis of its conformation and structure.

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**Supplementary Material Available:** The *Z*-matrices for conformations of **2**, **3**, and structures **6**–**9** (6-31G*) and details of X-ray structure determination of **5** (11 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.