



Spherical conformational landscape shed new lights on fluxional nature of cyclopentane and its derivatives, confirmed by their Raman spectra



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ABSTRACT

A detailed conformational analysis of cyclopentane and its derivatives were performed using DFT ω b97xd/6-311+G(d,p) level of theory. Intrinsic Reaction Coordinate (IRC) computations augmented with frequency computations were used to figure out a way to assemble four pseudorotational platforms into a final hyper-surface which can elaborately describe the vibrational pattern in Raman spectra of five membered ring compounds. The spherical conformational landscape represents two concentric ring coordinates for twisting and bending pathways in cyclopentane and its derivatives. The two ring coordinates work hand-in-hand to support the very intrinsic property of this molecule, its fluxional nature, coded intricately into the D/G band region ($1100\text{--}1600\text{ cm}^{-1}$) of its Raman spectrum. This fluxional nature seems to cope with almost any rigidity imposed by either temperature or structural restrictions. The same rationale was also used to resolve a hyper-surface for the fused five membered rings, octahydropentalenes. Further investigations are needed to shed light on the so called sugar pucker conformational wheels in DNA, **B** and **A** helices.

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1. Introduction

The first complete pseudorotational model for conformational analysis of cyclopentane was introduced by Lipnick et al. [1], in which a full cast of 20 conformers were arranged in a conformational wheel [2,3] to describe cyclopentane vibrations. Further attempts [4–19] to separate these conformers based on either energy or vibrational patterns [20,21] mostly proved unsuccessful. Some 37 years later Laane et al. [22], provided a precise energy for *twist* and *bent* conformers [7] showing how close the two conformers are in energy and vibrations. Along with a fully assigned vibrational spectrum even for some deuterated forms of cyclopentane in all, solid, liquid and gas phases. More recently Leutwyler et al. [23] have used femtosecond Raman spectroscopy [24,25] to analyze rotational constant and estimate the bond lengths in both *twist* and *bent* conformers with $\pm 0.001\text{ \AA}$ accuracy [22]. They were even able to measure cyclopentane external rotation effect [26–28] on its soft radial pseudorotational motion which they found it 1000 times smaller than what they expected.

The main defect in Lipnick's original conformational wheel model, still unresolved, is the lack of any distinction between conformers. And in fact the conformers are closely related and similar [29], referred to by Leutwyler et al. as the fluxional nature [30–33] of cyclopentane molecule. Whether the twisting and bending coordinates for cyclopentane and some of its derivatives are orthogonal, as proposed by Laane et al., is the main question to be addressed in this paper. Classifying these twenty conformers into separate conformational platforms plays a key role in answering such questions.

2. Methods

To study conformational fluctuations in small cycloalkanes, Hartree-Fock, and most local density functional methods, slightly over estimate the barriers mostly due to their inability to account for van der Waals attractions in *twist* conformations [34,35]. While some density functional methods, in particular ω b97xd, yield results that are both comparable and similar to those obtained by correlational methods. The ω b97xd (used in this paper) can also reliably result in accurate van der Waals considerations. Moreover vibrational frequencies of density functional methods [36,37] are in good agreement with experimental data. Vibrational modes of the bare carbonic skeletons were considered for simplicity and clarity of interpretations.

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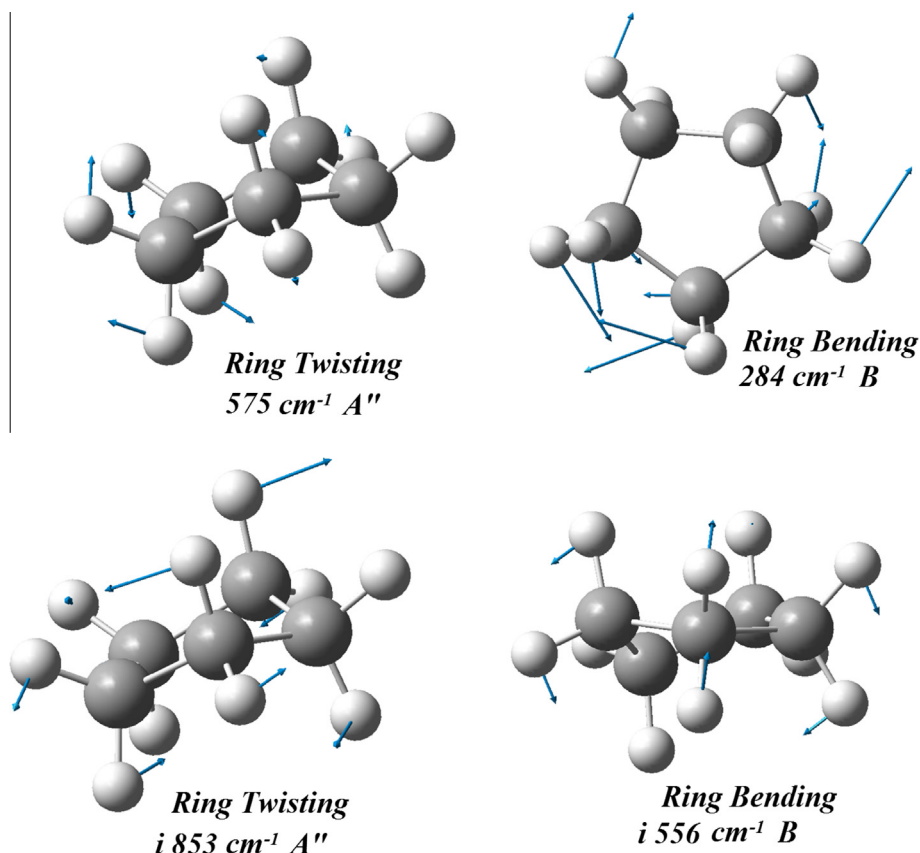


Fig. 1. Ring vibrations for both bent (left column) and twist conformers (right column).

The geometries and vibrational computations were done at ob97xd/6-311+G(d) level [38–40], using Gaussian g09 package [39]. Larger basis sets like $6-311+G(d,p)$ proved no better accuracy. In fact the cc-pVTZ basis sets were slightly better, some basic conformers and those with methyls were in some cases studied with cc-pVTZ basis set. But there has to be a compromise between computational method, time and resources.

The computations also provide facts on skeletal ring vibrations that are responsible for conformational paths, but the reproduction of full Raman spectra through computations must be used with much more account on ro-vibrational modes and also with more elaborate consideration of polarizabilities to yield insights on the hyper-surface patterns of Raman spectrum observed specially in solid phase. However through a close inspection of Raman spectra, an area called D/G band region appears promising. The area certainly reveals patterns of disturbance in fluxional nature of pseudorotation, in good agreement with the spherical conformational landscape model. Thus making the model a reliable tool to further study cyclopentane derivatives.

3. Results and discussion

Before designing a spherical conformational landscape, a ring flipping process was investigated in cyclopentane. It led us to the conclusion that two main classes of conformers and their mirror images are involved. Even though it's a totally different process in cyclopentane, compared to classical ring flipping in cyclohexane, they bear strong similarities as well (supplementary info). And this is the exact point where wheel conformational models for cyclopentane fail to explain. Finally the twenty conformers were divided into four classes of five interconverting conformers each.

The ordering of twenty conformers in Lipnick's original scheme [41] is ultimately correct, yet placing them in a wheel model [42–49] is so confusing that no correlation can be inferred to help one categorize them into groups.

For cyclopentane the ring flipping process helps one categorize the conformers into four conformational platforms¹ namely B, B_m , T and T_m , where B stands for *bent*, T for *twist* and *m* indices for mirror images. Then IRC computations were used, that upon restricting conformers to locked symmetries, produced important ring vibrations. These vibrations involved both real in platform and imaginary out of platform frequencies, of ring twisting nature for *bent* conformers and of ring bending nature for *twist* conformers (Fig. 1).

The rate of conversion and populations on each platform could be determined at least qualitatively and after all a detailed picture of a ring flipping process began to emerge out of the chaos in the conformational wheel (the highlighted path, in yellow, Fig. 2 bottom panel). The final step to get the spherical conformational landscape model was the intimate relationship between the *twist* (T/T_m) and *bent* (B/B_m) platforms that helps to assume not an orthogonal relationship but rather a parallel one. So the *twist* conformers were all put on an inner ring.

One interesting aspect of cyclopentane pseudorotational motion is the lack of any hybrid structure between the *bent* and *twist* forms except for a somehow disordered *bent* structure that can either flip to the next *bent* form in its own class of conformers or to two *twist* forms, with opposite curls, in inner *twist* ring

¹ Conformational platform or conformational landscape is best described by a group of rapidly inter-converting conformers chosen based on their similar energies or their shared vibrational mode through their energy path, in and out of the platform.

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