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The ring-puckering potential energy function and theoretical calculations for silacyclopent-2-ene-d_0 and 1,1-d_2 and the difluoro and dichloro derivatives

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Abstract

High level *ab initio* and DFT calculations have been carried out for silacyclopent-2-ene and its 1,1-d_2, 1,1-difluoro, and 1,1-dichloro derivatives. The previously published far-infrared spectra of the ring-puckering vibration, which had been interpreted to be characteristic of a rigid planar molecule, have been reanalyzed for the hydride and 1,1-d_2 derivative. Both the spectra and the theoretical calculations show the molecule to have a small barrier to planarity. The experimental data analyzed with a Gaussian barrier produce a barrier of 49 cm^{-1} as compared to a value of 47 cm^{-1} computed using the CCSD/6-311++G(d,p) basis set. The experimental value for the deuteride was determined to be 41 cm^{-1} from the one-dimensional approximation. All MP2 and DFT computations for the 1,1-difluoro derivative predict a planar structure whereas the MP2 computation when used with triple-ζ basis set predicts a barrier of 13 cm^{-1} for the chloride. Vibrational frequencies were also computed for these molecules and compared to experimental results for the characteristic frequencies for these types of molecules.

Keywords: Silacyclopent-2-ene; Ring-puckering; Far-infrared spectra; Potential energy function; *Ab initio* and DFT calculations

1. Introduction

For more than thirty years we have been investigating the potential energy surfaces governing the large-amplitude vibrations of non-rigid molecules. Both ground and excited electronic states have been studied and both experimental and theoretical methods have been applied. Some of this work has been summarized in several reviews [1–7]. Among these studies has been the investigation of "pseudo-four-membered" rings, which are five-membered rings containing one double bond each. We showed already in 1967 that molecules such as cyclopentene behaved like four-membered rings for the ring-puckering vibration since the two atoms joined by the rigid double bond moved together as one single atom [8]. Therefore, in general, the ring puckering vibration in both four- and five-membered rings can be represented by a potential function of the form

$$V = ax^4 + bx^2, \tag{1}$$

where x is the puckering coordinate as previously defined [1–7] and where a and b are potential energy constants. As we have shown [1–7], angle strain for these molecules contributes primarily a positive quartic (x^4) term but also contributes to some extent to the quadratic term (x^2). Torsional forces typically make a negative contribution to the b term so that the sign of b is determined by the competing angle strain and torsional forces.

The pseudo-four-membered rings previously studied are shown below. These fall into two groups characterized by C_{2v} and C_s symmetry, respectively, at their planar forms.

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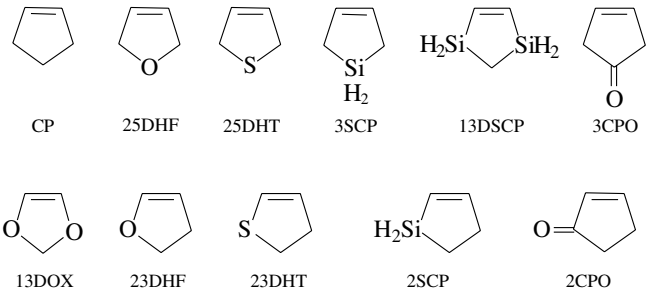

In the symmetric group of molecules cyclopentene (CP) is puckered with a barrier to planarity of 232 cm^{-1} arising from the two CH_2–CH_2 torsional interactions [8–11]. 2,5-Dihydrofuran (25DHF) [12], 2,5-dihydrothiophene (25DHT) [13], and 3-cyclopentenone (3CPO) [14] are all planar with positive *a* and *b* constants in Eq. (1) as these have no CH_2–CH_2 torsional interactions and angle strain dominates. Silacyclopent-3-ene (3SCP) [15,16] and 1,3-disilacyclopent-4-ene (13DSCP) [17] each have two –SiH_2–CH_2– interactions, which are much weaker than the CH_2–CH_2 interactions, and thus make significantly less negative contribution to the *b* term in Eq. (1). For 3SCP this weaker torsional force almost exactly cancels out the angle strain contribution to the quadratic coefficient and a very nearly perfect quartic oscillator potential energy results. Bell in 1945 postulated that four-membered rings should have quartic potential energy functions [18], but 3SCP is the only molecule known to be close to this prediction. 13DSCP is similarly planar and has mostly a quartic potential energy function. However, there is a small positive *b* constant indicating that the torsional forces are a little bit weaker and/or the angle strain is a little bit greater.

The results for 1,3-dioxole (13DOX) would appear to be out of line with the other molecules in that it has a 325 cm^{-1} barrier to planarity even though it has no CH_2–CH_2 torsional interactions [19]. However, the non-planarity of the molecule can readily be explained by the anomeric effect resulting from the presence of the –O–CH_2–O– arrangement in the molecule. Details for this have been reported [19,20].

Among the asymmetric molecules 2,3-dihydrofuran (23DHF) [21,22] and 2,3-dihydrothiophene (23DHT) [23,24], each have one CH_2–CH_2 torsional interaction which produces a barrier to planarity and a puckered structure. The barriers are 93 and 430 cm^{-1}, respectively. The larger value for 23DHT reflects the fact that the presence of the "soft" sulfur atom in the ring gives rise to less angle strain. 2-Cyclopentenone [25] (2CPO) is rigid and non-planar due to conjugation between the C=O and C=C groups. However, in its $S_1(n,\pi^*)$ electronic excited state it becomes much more floppy [26], and in its $T_1(n,\pi^*)$ state it actually takes on a puckered structure [27,28].

This brings us to silacyclopent-2-ene which has been difficult to understand since we first reported its far-infrared spectrum in 1970 which seemed to be indicative of a very rigid potential energy function characteristic of large angle strain or positive torsional forces [29]. At that time we postulated that the silicon d orbital interactions with the C=C π orbitals could result from a type of conjugation which would tend to keep the ring rigid. In 1988 we studied the far-infrared spectra of the 1,1-d_2 isotopomer of 2SCP and this appeared to confirm this rigid potential energy function [30]. This led us to synthesize 13DSCP with the hope of seeing great ring rigidity due to the presence of two silicon atoms next to the double bond. Its far-infrared spectra, however, only showed a very modest increase in the stiffness of this ring [17]. Until our present study, we had not been able to reconcile this apparent enigma. As the results from 2SCP have continued to seem perplexing, we have reexamined the interpretation of the 2SCP and 2SCP-d_2 spectra and also carried out high level *ab initio* calculations to better understand why the results for these molecules appeared to be out of line with all the others. Our reinterpretation of the data and the results of the theoretical calculations will be presented here.

2. Experimental

No new experimental data are presented in this work, although the original spectra were reexamined and reassigned. The experimental conditions and results were published previously [29,30].

3. Computations

Ab initio second-order Møller-Plesset (MP2), coupled cluster theory with single and double excitation (CCSD), and density functional theory (DFT) using the Gaussian 03 program [31] were employed to study the structure of silacyclopent-2-ene in its planar and non-planar forms. The structures of the difluoro and dichloro derivatives were optimized at the MP2 level, and their frequencies were calculated. The vibrational frequencies of silacyclopent-2-ene, its 1,1-d_2 isotopomer, and the dihalo derivatives were computed using density functional theory (DFT) with the B3LYP hybrid functional using different basis sets. Because changing the basis sets used for the DFT treatments produced different results for the stable configurations of silacyclopent-2-ene, the 6-311++G(d,p) basis set, which predicted a slightly puckered structure for silacyclopent-2-ene in agreement with the results obtained from the coupled cluster theory computations, was used to calculate the vibrational frequencies for the difluoro and dichloro derivatives.

The MP2 theory using different basis sets was utilized to locate the stable conformation of silacyclopent-2-ene and the results are shown in Table 1. Smaller basis sets, which lack the diffuse and polarization functions, predicted the molecule to be totally planar. A barrier of about 50 cm^{-1}, however, was predicted when larger basis sets were used. However, for DFT calculations, even the triple-ζ basis set, predicted a planar structure for silacyclo-