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The molecular structure and the puckering potential function of silacyclobutane as determined by gas electron diffraction and relaxation constraints from ab initio calculations

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Abstract

Gas electron diffraction is applied to determine the geometric parameters of the silacyclobutane molecule using a dynamic model where the ring puckering was treated as a large amplitude motion. The structural parameters and the parameters of the potential function were refined taking into account the relaxation of the molecular geometry estimated from ab initio calculations at the MP2/6-311+G(d, p) level of theory. The potential function has been described as $V(\varphi) = V_0[(\varphi/\varphi_e)^2 - 1]^2$ with the following parameters $V_0 = 0.82 \pm 0.60$ kcal/mol and $\varphi_e = 33.5 \pm 2.7°$, where φ is a puckering angle of the ring.

The geometric parameters at the minimum $V(\varphi)$ (r_a in Å, $\angle_\alpha$ in degrees and uncertainties given as three times the standard deviations including a scale error) are: $r(\mathrm{Si–H_{ax}}) = 1.467(96)$, $r(\mathrm{Si–H_{eq}}) = 1.468(96)$, $r(\mathrm{Si–C}) = 1.885(2)$, $r(\mathrm{C–C}) = 1.571(3)$, $r(\mathrm{C–H}) = 1.100(3)$, $\angle\mathrm{CSiC} = 77.2(9)$, $\angle\mathrm{HSiH} = 108.3$, $\angle\mathrm{SiCH_{eq}} = 123.5(16)$, $\angle\mathrm{SiCH_{ax}} = 111.9(16)$, $\angle\mathrm{CC_5H_{eq}} = 118.4(24)$, $\angle\mathrm{CC_5H_{ax}} = 112.3(24)$, $\angle\mathrm{HC_3H} = 107.7$, $\angle\delta(\mathrm{HSiH}) = 6.6$, $\angle\delta(\mathrm{HC_3H}) = 7.0$, where the tilts δ, $\angle$HSiH, and $\angle\mathrm{HC_3H}$ are estimated from ab initio constraints. The structural parameters are compared with those obtained for related compounds.

Keywords: Silacyclobutane; Electron diffraction; Ab initio calculations; Ring puckering; Normal coordinate analysis

1. Introduction

After silacyclobutane (SiCB) was synthesized for the first time in 1967 by Laane [1] two excellent comprehensive investigations of its vibrational spectra [2,3] have been published. In 1971 the microwave spectrum of this molecule was observed and the vibrational–rotational interaction and ring puckering vibration had been studied [4]. The complete molecular structure of SiCB, however, has been studied for the first time in 1975 [5]. Subsequent systematic investigations on various 1,1-disubstituted [6–12] and monosubstituted [13–17] silacyclobutanes have evidently shown that the previously given Si–C and C–C bond distances in SiCB are not in accord with the correlation that has been found between these bonds and the electronegativity of the substituent for the derivatives mentioned above [12,13].

This non-conformity has prompted us to reinvestigate the structure of SiCB utilizing the aid of the quantum mechanical calculations and improved procedures for processing electron diffraction data. The determination of an accurate structure of SiCB is of particular importance because it is the parent molecule for the silacyclobutane series and thus the reference for all these derivatives. Table 1 compares the most prominent geometric parameters of some silacyclobutanes, which have been previously studied.

One of the main reasons for investigating SiCB and its derivatives is to systematically explore the effects of substitution on the geometry and the puckering motion within this class of strained silicon compounds, which have a wide range of applications in chemistry and technology. Such

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Table 1
Some important parameters in various silacyclobutane derivatives of the type $(CH_2)_3SiX_2$

Parameter	X=H [5]	X=H (this work)	X=CH_3 [8]	X=C≡CH [12]	X=Cl [7]	X=F [10]
r(Si–C), Å	1.895(2)	1.885(2)	1.885(2)	1.874(2)	1.860(3)	1.836(3)
r(C–C), Å	1.607(6)	1.571(3)	1.563(4)	1.563(2)	1.557(4)	1.574(8)
XSiX (°)	115.6(90)	108.3[a]	109.9(47)	106.5(6)	105.2(8)	106.9(5)
CSiC (°)	80.8(5)	77.2(9)	79.2(11)	79.2(6)	81.1(10)	82.7(6)
φ_e, (°)	33.6(2)	33.5(27)	29.7(45)	30.0(15)	25.9(26)	25(2)

[a] Value obtained from the ab initio constraints using approximations (3, 4).

methodical study may provide valuable information that allows predicting some chemical and physical properties of analogous compounds.

Based on the analysis of the vibrational analysis that has been carried out by Durig et al. [11] it was concluded that the C–C bond in silacyclobutane should be much shorter than it was given in the earlier electron diffraction work [5]. Later, based on the analysis of experimental and theoretical structural data of 1-monosubstituted derivatives of SiCB, the same conclusion has been made by M. Dakkouri [12,13] who suggested the reinvestigation of this molecule.

The SiCB molecule is excellently appropriate for studying the puckering motion in the four-membered rings by means of vibrational spectroscopy [2,3,16]. According to these data SiCB has a puckered conformation with a puckering angle between the CSiC and CCC planes of about $35.9 \pm 2°$ [2], and the barrier height to puckering $440 \pm 3\ cm^{-1}$ [2]. On the other hand, this motion makes an accurate determination of the SiCB by gas electron diffraction (GED) rather sophisticated because the ring puckering obviously needs to be treated as a large amplitude motion (Fig. 1).

Moreover, it has been shown in the GED study of 1, 1-dichlorosilacyclobutane [7] that the changes of the geometric parameters during the ring puckering can become significant so that they should be included in an accurate structural analysis.

In the present work, the molecular structure and the potential function governing the ring puckering motion in SiCB have been determined using a dynamic model, which takes into account the relaxation of geometric parameters estimated from ab initio calculations.

Thus, using the new GED experimental data for SiCB as well as the ab initio force field for the calculations of amplitudes and vibration corrections, we anticipate obtaining more reliable structural results. We also intend to utilize these GED for the determination of the potential function of the puckering motion in SiCB and compare it with the spectroscopic data.

2. Experimental and data reduction

The most probable reason for the inconsistency of the SiCB geometry obtained in the previous investigation [5] is that the substance contained some impurities originating from decomposition products. SiCB possesses a high reactivity and can easily undergo various radical reactions including slow polymerization during the storage even at room temperature. Therefore, we paid a special attention to ensure the purity of the SiCB sample and kept the sample at low temperature before performing the GED experiment. The sample of SiCB was synthesized at the University of Ulm (Germany) by the treatment of 1,1-dichlorosilacyclobutane with lithium aluminum hydride according to the method of Laane [1]. Following the advice of Prof. L.E. Guselnikov (Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow) the SiCB sample was distilled twice in vacuum and placed in glass ampoules, which were previously evacuated and heated for the purpose of drying and degassing. The ampoules designed for recording the GED data were sealed under vacuum and immediately placed into a vessel with liquid nitrogen where they were kept until the beginning of GED experiment. The ampoule with the sample of SiCB was broken directly inside the GED unit when the pressure in the system has achieved the typical low limits for recording GED patterns. The electron diffraction patterns were recorded at the Moscow State University on an EG-100A unit with accelerating voltage of 60 kV, and a nozzle temperature of 25 °C for two nozzle-photoplate distances of 495 and 197 mm. The electron diffraction photographs were recorded on Kodak Scientific Imaging Film SO-163 and processed with the Agfa Duoscan HiD scanner in Tübingen (Germany) using the method described in Ref. [18]. The total scattering intensity curves were obtained by applying the program SCAN3 and utilizing the two-dimensional algorithm [19]. The electron wavelength was calibrated by the inner gas standard method [20]. Benzene was used as a standard and its structural parameters were taken from Ref. [21]. As to our estimations, the scale error did not exceed 0.07%. Three photographic films for each camera distance were analyzed with the scanner method and averaged to obtain the total scattering intensities in intervals of s corresponding to 3.0–18.2 and 10.2–32.0 $Å^{-1}$ with the step $\Delta s = 0.2\ Å^{-1}$, for the long and short camera distances, respectively. The experimental $sM(s)$ and the differences curves corresponding to the final model (Table 2) are shown in Fig. 2.