Available online at www.sciencedirect.com

ScienceDirect

Journal of Molecular Spectroscopy 248 (2008) 153–160

Journal of MOLECULAR SPECTROSCOPY

www.elsevier.com/locate/jms

High resolution infrared spectroscopy of [1.1.1]propellane

Robynne Kirkpatrick [a], Tony Masiello [b], Narumol Jariyasopit [a], Alfons Weber [c], Joseph W. Nibler [a,*], Arthur Maki [d], Thomas A. Blake [b], Timothy Hubler [b]

[a] *Department of Chemistry, Oregon State University, Room 101, Gilbert Hall, Corvallis OR 97332-4003, USA*
[b] *Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352, USA*
[c] *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*
[d] *15012 24th Avenue, S.E., Mill Creek, WA 98012, USA*

Received 24 November 2007; in revised form 27 December 2007
Available online 8 January 2008

Abstract

The infrared spectrum of [1.1.1]propellane has been recorded at high resolution (0.002 cm^{-1}) with individual rovibrational lines resolved for the first time. This initial report presents the ground state constants for this molecule determined from the analysis of five of the eight infrared-allowed fundamentals $\nu_9(\text{e}')$, $\nu_{10}(\text{e}')$, $\nu_{12}(\text{e}')$, $\nu_{14}(\text{a}_2'')$, $\nu_{15}(\text{a}_2'')$, as well as of several combination bands. In nearly all cases it was found that the upper states of the transitions exhibit some degree of perturbation but, by use of the combination difference method, the assigned frequencies provided over 4000 consistent ground state difference values. Analysis of these gave for the parameters of the ground state the following values, in cm^{-1}: $B_0 = 0.28755833(14)$, $D_J = 1.1313(5) \times 10^{-7}$, $D_{JK} = -1.2633(7) \times 10^{-7}$, $H_J = 0.72(4) \times 10^{-13}$, $H_{JK} = -2.24(13) \times 10^{-13}$, and $H_{KJ} = 2.25(15) \times 10^{-13}$, where the numbers in parentheses indicate twice the uncertainties in the last quoted digit(s) of the parameters. Gaussian *ab initio* calculations, especially with the computed anharmonic corrections to some of the spectroscopic parameters, assisted in the assignments of the bands and also provided information on the electron distribution in the bridge-head carbon–carbon bond.

Keywords: Propellane; High-resolution infrared spectrum; Ground state structure and rotational constants; Ab initio DFT study; Anharmonic frequencies

1. Introduction

In recent decades, organic chemists have been very successful in creating interesting strained ring compounds, many of which were thought previously to be incapable of existence. The syntheses of these substances were accomplished not only on the basis of the intuition and expertise of the chemists, but were often made possible by the guidance given by the predictions of quantum theoretical calculations. Examples include molecules of unusual shapes that are grouped together under the collective names cubanes, prismanes, propellanes [1], fenestranes, paddlanes, rotanes, and other appellations evocative of the molecule's three-dimensional structures [1–6]. All of these molecules contain carbon rings, the smaller of which exhibit great amounts of strain [7–9]. This strain can be the cause of instability that not only makes the syntheses of these molecules difficult, but also complicates their investigation by physical methods due to their propensity to undergo facile rearrangement, decompose, or polymerize. A number of these molecules are sufficiently exotic and intriguing that they form "A Potpourri of Pathologies" [10]. Despite this, many derivatives of these compounds have been synthesized in recent years and found to be useful in both their monomeric and polymeric forms [11].

The structures of the basic geometric element of these classes of molecules are of considerable interest and some have been investigated by X-ray and electron diffraction techniques. However, very few have been subjected to investigations by high-resolution spectroscopy in the gas

---

[*] Corresponding author. Fax: +1 541 737 2062.
E-mail address: Niblerj@chem.orst.edu (J.W. Nibler).

0022-2852/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2007.12.009

phase. An exception is cubane, which has been studied by one of us (Maki) using high-resolution laser infrared spectroscopy [12]. A cube-edge C–C distance of 1.565(4) Å was deduced, a value that is somewhat larger than the result of 1.551(5) Å determined for crystalline samples by X-ray studies [13]. This is not atypical; structural data for crystals by neutron or X-ray diffraction methods often differ significantly from those obtained for free molecules in the gaseous state using electron diffraction or high-resolution spectroscopic techniques [14,15]. As discussed by Hargittai and Hargittai [16], the differences between the various structures reported for different phases and methods are significant since they have bearing on the interpretation of experimental data and consequently on our understanding of chemical bonding.

The structures and spectral properties of molecules in the gas phase also offer the most direct test of the results of quantum calculations, which often depend on the choice of basis sets and the computational model employed. Structure comparisons have been the usual yardstick, but now spectroscopic parameters, e.g., v, B, C, D, H, α, ζ, x, and various coupling terms, can provide valuable additional tests, since such parameters can be computed with reasonable accuracy using cubic and quartic potential energy terms available from Gaussian and other computational programs. Importantly, high-resolution methods can give accurate experimental values for these spectroscopic parameters, provided that the spectral analysis can be done. Often, initial theoretical estimates of the various anharmonic couplings are needed before the analysis of congested spectra for the deduction of rotational and other constants can be accomplished. Combining the analysis of observed spectra with quantum theoretical calculations is a symbiotic “bootstrap” technique to arrive at a reliable end result. For example *ab initio* calculations of parameters such as v, ΔB, ΔC, and $C\zeta$ were used to predict rovibrational transitions that aided in the initial assignment of spectral lines of low J and K value.

The present work focuses on the smallest member of the propellane family, [1.1.1]propellane, whose structure is shown in Fig. 1a, along with that of the related molecule, bicyclo[1.1.1]pentane (Fig. 1b). (For brevity, the [1.1.1] notation will henceforth be dropped.) A recent major review provides excellent detailed descriptions of propellane and similar molecules [11]. Predicted to be stable by preliminary quantum theoretical studies, propellane was first synthesized in 1982 by Wiberg and Walker [17]. In contrast to bicyclopentane, propellane appears to have a central bond that joins the bridge-head carbon atoms. This unusual inversion of the bridge-head carbon bond in Fig. 1a away from the common tetrahedral arrangement shown in Fig. 1b has been the subject of much discussion. [18–21].

In their comprehensive work dealing with the vibrational spectra of gaseous propellane and its fully deuterated isotopomer, Wiberg and coworkers were unable to resolve individual rovibronic features since their infrared spectra were recorded at a resolution of 0.06 cm^{-1} and their Raman spectra were recorded at a resolution of 2 cm^{-1} [22]. However, from partially-resolved infrared band structure, they were able to deduce a value for the B rotational constant that Hedberg and Hedberg [23] combined with their electron diffraction data to obtain the values 1.596(5) Å and 1.525(2) Å for the bridge-head (axial–axial) and pyramidal (axial–equatorial) C–C bond lengths, respectively.

Previously, Wiberg et al. [24–26] had studied the bicyclopentane molecule. Two different electron diffraction structures for this species were reported, by Chiang and Bauer [27] and Almenningen, et al. [28]. According to Almenningen the axial–equatorial C–C bond length of bicyclopentane (Fig. 1b) is 1.557(2) Å, somewhat larger than the analogous bond length in propellane. The axial–axial distance in bicyclopentane, however, is much larger, 1.874(4) Å, and indicates the absence of a bond. In the context of the times that these studies were undertaken, they constituted an important source of information that, coupled with quantum theoretical calculations, gave information about the quadratic force fields, normal coordinates, and dipole moment derivatives for these molecules, and allowed some conclusions to be drawn regarding the similarities and dissimilarities of their chemical bonding not only with respect to one another, but also with respect to cyclopropane, which may be considered to be their predecessor molecule. Other work dealt with the photoelectron spectroscopy of propellane [29–36], *ab initio* calculations of its NMR spectra [37–39], and a new theoretical study of its vibrational spectrum and structure [40].

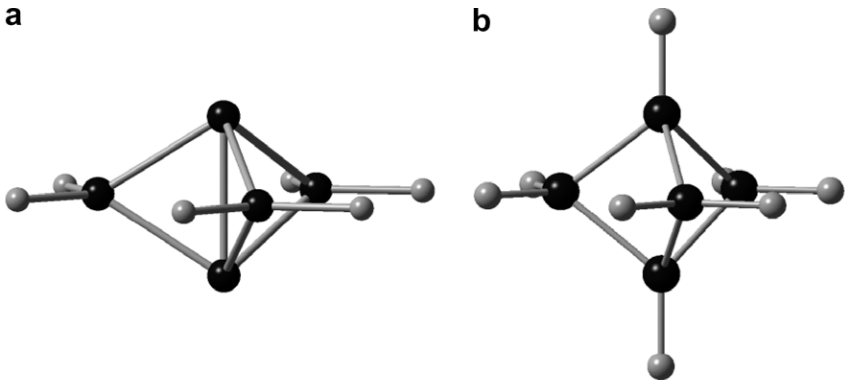

Fig. 1. D_{3h} structural arrangements for [1.1.1]propellane (a) and bicyclo[1.1.1]pentane (b).