High-resolution infrared spectra of bicyclo[1.1.1]pentane ☆

M.A. Martin [a], A. Perry [a], T. Masiello [b], K.D. Schwartz [a], J.W. Nibler [a,*], A. Weber [c], A. Maki [d], T.A. Blake [e]

[a] Department of Chemistry, Oregon State University, Corvallis, OR 97332-4003, USA
[b] Department of Chemistry and Biochemistry, California State University, East Bay, Hayward, CA 94542, USA
[c] Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
[d] 15012 24th Ave., S.E., Mill Creek, WA, 98012, USA
[e] Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352, USA

ARTICLE INFO

ABSTRACT

Infrared spectra of bicyclo[1.1.1]pentane (C_5H_8) have been recorded at a resolution (0.0015 cm^{-1}) sufficient to resolve for the first time individual rovibrational lines. This initial report presents the ground state constants for this molecule determined from the detailed analysis of three of the ten infrared-allowed bands, v_{14}(e′) at 540 cm^{-1}, v_{17} (a″$_2$) at 1220 cm^{-1}, v_{18}(a″$_2$) at 832 cm^{-1}, and a partial analysis of the v_{11}(e′) band at 1237 cm^{-1}. The upper states of transitions involving the lowest frequency mode, v_{14}(e′), show no evidence of rovibrational perturbations but those for the v_{17} and v_{18} (a″$_2$) modes give clear indication of Coriolis coupling to nearby e′ levels. Accordingly, ground state constants were determined by use of the combination-difference method for all three bands. The assigned frequencies provided over 3300 consistent ground state difference values, yielding the following constants for the ground state (in units of cm^{-1}): B_0 = 0.2399412(2), D_J = 6.024(6) × 10^{-8}, D_{JK} = −1.930(21) × 10^{-8}. For the unperturbed v_{14}(e′) fundamental, more than 3500 transitions were analyzed and the band origin was found to be at 540.34225(2) cm^{-1}. The numbers in parentheses are the uncertainties (two standard deviations) in the values of the constants. The results are compared with those obtained previously for [1.1.1]propellane and with those computed at the *ab initio* anharmonic level using the B3LYP density functional method with a cc-pVTZ basis set.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

The properties of molecules with great Bayer ring strain have in recent years been at the focus of much attention of organic and quantum chemists. Among these molecules are the cyclopropanes, cyclobutanes, propellanes and others. All of these molecules contain carbon rings, the smaller of which exhibit the greatest amount of strain [1–6]. Except for the smallest members of these families, most have not been examined by high-resolution spectroscopic methods. Only cyclopropane (C_3H_6) has been extensively studied [7], as it is commercially available and is stable in spite of the ring strain caused by the small 60° C—C—C angles.

Other interesting small cyclic molecules, such as cubane (C_8H_8) [8], [1.1.1]propellane (C_5H_6) [9], bicyclo[1.1.1]pentane (C_5H_8) [10], and spiropentane are not commercially available and must be synthesized. Such molecules exhibit high symmetry and, in the case of propellane, very unusual chemical bonding. These features make them of special interest for structural investigations by X-ray, neu-

tron, and electron diffraction methods and, in particular, by high-resolution spectroscopic techniques of the free molecules in the gaseous state at low pressures. Comparisons of moments of inertia, interatomic bond lengths, and interbond angles obtained by diffraction, spectroscopic, and theoretical methods have been discussed at length in several publications that point out the great importance of accurate structural and spectroscopic data [11–13]. In addition to structural parameters, high-resolution spectroscopic studies yield many other standard molecular parameters such as the B, D, v, α, ζ, x, k, ... coefficients for the various vibrational states, as well as less common vibration–rotation interaction terms. Furthermore, band intensities can give information about the electronic environment in which the atomic nuclei execute their vibrational motions. Many of these molecular constants can be calculated by *ab initio* methods, which can be used as a guide for the analysis of vibration–rotation spectra and, conversely, can be improved through comparisons with experimentally determined parameters. In this paper, we present the results of such studies for bicyclo[1.1.1]pentane and offer comparisons with [1.1.1.]propellane. The D_{3h} structures of these molecules are shown in Fig. 1 and both are appealing for study since they are small enough for high level *ab initio* calculations and are symmetric top rotators so that detailed spectroscopic analysis is readily feasible.
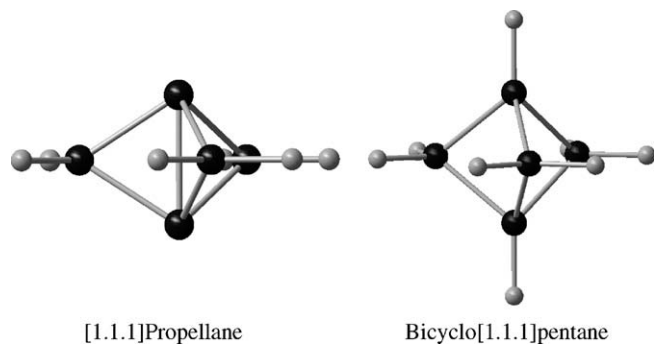
Fig. 1. Structural arrangements for [1.1.1]propellane and bicyclo[1.1.1]pentane. Both molecules possess the symmetry of the D_{3h} point group.

Wiberg et al. [14] have studied the vibrational spectrum of the bicyclo[1.1.1]pentane as well as the intensities of the infrared transitions of this parent (-d_0) molecule and its mono (-d_1) and dideutero (-d_2) isotopomers, with the D-atoms located on the principal C_3 symmetry axis [15]. (For brevity, we henceforth omit the d_0 and [1.1.1] specifiers for bicyclopentane and propellane.) Values for most of the infrared and Raman active vibrational fundamentals of the parent compound and the two isotopomers were reported. Band contours of the infrared bands of the parent compound and its symmetric top d_1 and d_2 isotopomers were recorded at a resolution of 0.25 cm^{-1}, which aided in making the vibrational assignments. At a higher resolution of 0.06 cm^{-1}, infrared spectra of the v_{17} and v_{18} rovibrational bands of the parent d_0 and d_2 isotopomers of bicyclopentane were partially resolved and this was sufficient to give reasonable estimates of the I_B inertial constants. An electron diffraction study by Almenningen et al. [16] provided structural data which were in good accord with the spectroscopic I_B value for bicyclopentane. A normal coordinate analysis and ab initio calculations at the MP2/6-31G* level were also performed by Wiberg and coworkers. When scaled, the vibrational frequencies were in fair agreement with the measured values, as were the calculated moments of inertia of the d_0 and d_2 isotopomers with the I_B values determined from the band analyses. Tables 1 and 2 present the diffraction and spectroscopic results, along with ab initio results we obtained using anharmonic methods and a larger basis set than in previous calculations.

Much higher resolution spectroscopic measurements are currently possible than in the earlier work on bicyclopentane and on propellane. In view of the particular chemical interest of

the latter, we recently reexamined its spectrum at a resolution of about 0.002 cm^{-1} and reported some of our results in two previous publications [17,18]. The detail revealed in that case by the 30-fold increase in resolution over that available for the earlier studies [19] prompted us to also reinvestigate the infrared spectra of bicyclopentane (C_5H_8) as well as of monodeuterated bicyclopentane-d_1 (C_5H_7D) with C_{3v} symmetry. We report here for the C_5H_8 molecule upper state constants for the unperturbed $v_{14}(e')$ band, along with ground state constants obtained from the combination-difference analysis of the combined data sets of the $v_{14}(e')$, $v_{17}(a_2'')$, and $v_{18}(a_2'')$ fundamental bands. These parameters are compared to analogous results obtained for propellane and to ab initio values computed at the anharmonic level. For the $v_5(a)$ 1216 cm^{-1} band of bicyclopentane-d_1 and the $v_{17}(a_2'')$ and $v_{18}(a_2'')$ upper states of bicyclopentane, evidence for Coriolis interactions with nearby e states was seen and the analysis of this effect and the parameters for these states will be given in a subsequent paper.

Table 2
Fundamental modes of bicyclopentane (cm^{-1}).

Mode		Ab initio results[a]		Experiment[b]
		Harmonic	Anharmonic	
a_1'	1	3092	2950	2976
	2	3042	2906	2887
	3	1554	1500	1509
	4	1119	1096	1107
	5	908	888	898
a_2'	6	3095	2952	
	7	969	954	
e'	8	3100	2956	2976
	9	3037	2888	2887
	10	1504	1492	1456
	11	1259	1226	1232
	12	1117	1093	1098
	13	898	874	886
	14	542	538	540
a_1''	15	1004	977	
a_2''	16	3087	2952	2976
	17	1252	1221	1220
	18	844	825	832
e''	19	1216	1186	
	20	1144	1113	
	21	1029	1005	1006
	22	774	748	769

[a] This work, B3LYP/cc-pVTZ calculations using Gaussian 03 with Anharm/Vibrot options.
[b] Ref. [15].

Table 1
Experimental and ab initio structural parameters for bicyclopentane and propellane.

Parameter[a]	Unit	Bicyclopentane			Propellane		
		Electron diffraction[a]	Ab initio B3LYP/cc-pVTZ[b]		Electron diffraction[ba]	Ab initio B3LYP/cc-pVTZ[b]	
		(R_a)	(R_e)	(R_0)	(R_a)	(R_e)	(R_0)
C_{ax}–C_{eq}	Å	1.557(2)	1.554	1.562	1.522(2)	1.515	1.524
C_{ax}–C_{ax}	Å	1.874(4)	1.876	1.886	1.592(5)	1.568	1.577
C_{eq}–H	Å	1.107(4)	1.09	1.095	1.100(5)	1.082	1.088
H–C–H	°	111.7(18)	111.6	111.4	116.0(19)	115.1	115
C_{ax}–H	Å	1.107(4)	1.088	1.097			
I_B	amu-Å^2	70.38	69.87	70.67	58.82	58.19	58.87
I_C	amu-Å^2	81.77	80.94	81.94	87.22	86.89	87.91
B	cm^{-1}	0.2395	0.2413	0.2387	0.2866	0.2897	0.2863
C	cm^{-1}	0.2062	0.2083	0.2058	0.1933	0.194	0.1918

[a] Thermal-average (R_a) parameters from Refs. [16,29]. (R_e) and (R_0) refer to parameters for the equilibrium and ground state structures. The uncertainties in the last digits are given in parentheses.
[b] This work, using Gaussian 03 with Anharm/Vibrot options.