

Coriolis analysis of several high-resolution infrared bands of bicyclo[1 1 1]pentane-d₀ and -d₁ [☆]

A. Perry ^a, M.A. Martin ^a, J.W. Nibler ^{a,*}, A. Maki ^b, A. Weber ^c, T.A. Blake ^d

^a Department of Chemistry, Oregon State University, Corvallis, OR 97332-4003, United States

^b 15012 24th Avenue, S.E., Mill Creek, WA 98012, United States

^c Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

^d Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88 Richland, WA 99352, United States

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ABSTRACT

High-resolution infrared absorption spectra have been analyzed for two bicyclo[1 1 1]pentane isotopologues, C₅H₈ (-d₀) and C₅H₇D (-d₁), where in the latter the D-atom replaces a hydrogen on the C₃ symmetry axis such that the molecular symmetry is reduced from D_{3h} to C_{3v}. Two (a₂') parallel bands, ν₁₇ and ν₁₈, of bicyclopentane-d₀ were studied and the former was found to be profoundly affected by Coriolis coupling with the nearby (e') perpendicular band, ν₁₁. Weaker coupling was observed between the ν₁₈ band and the nearby ν₁₃(e') band, for which fewer transitions could be assigned. For bicyclopentane-d₁, the ν₅ parallel band was also studied along with the nearby ν₁₅(e') band to which it is coupled through a similar type of Coriolis resonance. For both isotopologues, quantum calculations (B3LYP/cc-pVTZ) done at the anharmonic level were very helpful in unraveling the complexities caused by the Coriolis interactions, provided that care is taken in identifying the effect of any Coriolis resonances on the theoretical values of α_B and q rovibrational parameters. The ground state B₀ constants were found to be 0.2399412(2) and 0.2267506(11) cm⁻¹ for the -d₀ and -d₁ isotopologues. The difference yields an R_g substitution value of 2.0309(2) Å for the position of the axial H atom relative to the -d₀ center of mass, a result in good accord with a corresponding R_a value of 2.044(6) Å from electron diffraction data. For both isotopologues, the theoretical results from the quantum calculations are in good agreement with all corresponding values determined from the spectra.

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1. Introduction

Our previous work on bicyclo[1 1 1]pentane (C₅H₈) was devoted to the determination of the ground state constants of this molecule from measurements on three different fundamental vibrations, ν₁₄(e') at 540 cm⁻¹, ν₁₇(a₂') at 1220 cm⁻¹, and ν₁₈(a₂') at 832 cm⁻¹, as well as some transitions from a partially analyzed ν₁₁(e') band at 1232 cm⁻¹. [1] In the course of this work it was found that the upper state levels of the ν₁₄ band are unperturbed but the ν₁₇(a₂') and ν₁₈(a₂') bands showed evidence of strong and weak Coriolis interactions with nearby levels of the ν₁₁(e') and ν₁₃(e') fundamentals, respectively. The present work deals with these Coriolis interactions in order to not only determine the constants of the upper states of the ν₁₇(a₂') and ν₁₈(a₂') bands but also to deduce rovibrational parameters for the less intense ν₁₁ and ν₁₃(e') bands.

[☆] Based in part on an undergraduate honors thesis of M. Martin, University Honors College, Oregon State University.

* Corresponding author. Fax: +1 541 737 2062.

E-mail addresses: niblerj@orst.edu, niblerj@chem.orst.edu (J.W. Nibler).

In addition, the mono-deuterated isotopologue (C₅H₇D) of bicyclopentane was synthesized (with the D atom on the C₃ symmetry axis) and its infrared spectrum recorded at a resolution of 0.002 cm⁻¹ to provide additional information on the properties of the bicyclopentane species. (Henceforth for brevity we will omit the specifier [1 1 1] and use bicyclopentane-d₀ and bicyclopentane-d₁ (or -d₀ and -d₁) to designate the normal (C₅H₈) and deuterated (C₅H₇D) species, respectively.) This work on bicyclopentane is an outgrowth of our earlier work on [1 1 1]propellane [2–4] and provides experimental data to better understand the bonding and molecular properties of these small ring-strained molecules. All three molecules are symmetric tops and their structures are shown in Fig. 1.

This work has benefitted from earlier investigations of the vibrational infrared and Raman spectra of bicyclopentane-d₀, -d₁, and -d₂ reported by the Wiberg group [5,6]. Although done at relatively low resolution, infrared spectra obtained at 0.06 cm⁻¹ resolution did show some unresolved J, K rotational structure, from which approximate upper and ground state B-values were obtained for the ν₁₇ and ν₁₈ modes of bicyclopentane-d₀ and -d₂ [6]. The current 30-fold improvement in spectral resolution gives a much more complete view of the individual J, K lines, hence this

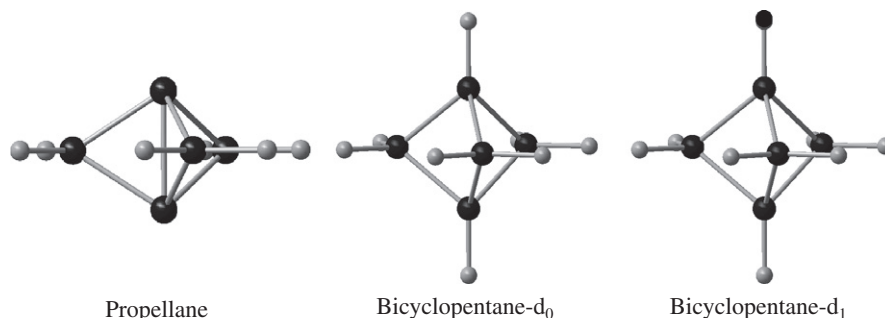


Fig. 1. Structural arrangements for [111]propellane, bicyclo[111]pentane-d₀, and bicyclo[111]pentane-d₁. The first two structures possess the symmetry of the point group D_{3h} , while the symmetry of the -d₁ isotopologue is C_{3v} .

Table 1
Frequencies and intensities of the fundamental modes of bicyclo[111]pentane-d₀.

Mode	Experiment ^a		Theory ^b		Relative intensity	
			Harmonic	Anharmonic	Raman	IR
a_1'	1	2976	3092	2950	436 vs	...
	2	2887	3042	2906	370 s	...
	3	1509	1554	1500	5.2 vw	...
	4	1107	1119	1095	36 vs	...
	5	898	908	888	6.6 s	...
a_2'	6	–	3095	2952
	7	–	969	954
e'	8	2976	3100	2956	131 vs	72 vs
	9	2887	3037	2888	1.3 s	83 vs
	10	1456	1504	1492	5.3 vw	0.4 m
	11	1231.41	1259	1226	6.3 w	1.9 w
	12	1098	1117	1093	0.9	0.3 w
	13	886.5	898	874	4.3	0.4 w
	14	540.34	542	537	0.3 w	0.2 w
	15	–	1004	975
a_2''	16	2976	3087	2952	...	138 vs
	17	1219.89	1252	1221	...	37 s
	18	832.93	844	825	...	3.8 m
e''	19	–	1216	1186	0.2	...
	20	–	1144	1112	1.7	...
	21	1006	1029	1005	18 m	...
	22	769	774	747	5.9 m	...

^a Ref [6], Table (VII). Values in boldface are from reference 1 and from this study.

^b This work, B3LYP/cc-pVTZ calculations using Gaussian 09 with Anharm/Vibrot options. Anharmonic frequencies in bold italics are obtained from Gaussian and include correction for Fermi resonance. The qualitative experimental intensities (vw, w, m, s, vs), where available, are taken from Ref. [5].

reinvestigation was done in order to obtain accurate values for the various constants that characterize the intra-molecular properties. We here account for the Coriolis perturbations that afflict the upper state levels of the ν_{17} and ν_{18} transitions as well as their counterparts (ν_5 , ν_{15}) in bicyclo[111]pentane-d₁. The mode numbering for the fundamentals of bicyclo[111]pentane-d₀ and bicyclo[111]pentane-d₁ is given in Tables 1 and 2, along with wavenumber and approximate intensity values reported by Wiberg et al. [6]. Also given in the Tables are the corresponding values we have calculated in the anharmonic approximation using the Gaussian 09W program (method B3LYP, basis cc-pVTZ, options Anharm/Vibrot) [7].

2. Experimental

2.1. Synthesis

The synthesis of bicyclo[111]pentane-d₀ was described in [1] and was modified slightly for the synthesis of bicyclo[111]pentane-d₁. In

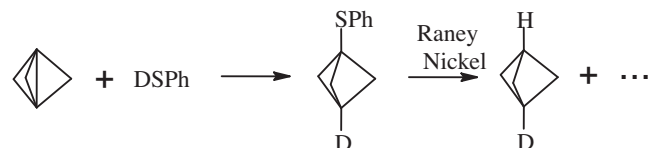
Table 2
Frequencies and intensities of the fundamental modes of bicyclo[111]pentane-d₁.

Mode	Experiment ^a		Theory ^b		Relative intensity	
			Harmonic	Anharmonic	Raman	IR
a_1	1	2975	3090	2952	232 vs	65 vs
	2	2886	3045	2905	384 s	4.0 s
	3	2223	2281	2201	92 s	39 s
	4	1501	1552	1498	6.0vw	0.0
	5	1217.33	1250	1218	0.1	36 s
	6	1086	1099	1077	38 vs	0.0 w
	7	892	905	886	5.4 m	0.0
	8	823	834	815	0.0	3.9 m
a_2	9	–	3095	2951
	10	–	1004	975
	11	–	969	954
e	12	2975	3100	2956	131 vs	72 vs
	13	2886	3037	2888	1.3 s	83 s
	14	1456	1504	1490	5.3 m	0.4 m
	15	1210.31	1238	1206	4.0 m	1.2
	16	1144	1171	1142	3.3 m	0.5 m
	17	1104	1142	1110	3.1 m	0.0
	18	–	1105	1079	5.3	0.1
	19	955	967	941	10 s	0.1 w
	20	798	808	784	1.3 w	0.2
	21	–	721	705	7.4	0.2
	22	538	540	535	0.3 w	0.2 w

^a Ref [6], Table (VII). Values in boldface are from this study.

^b This work, B3LYP/cc-pVTZ calculations using Gaussian 09 with Anharm/Vibrot options. Anharmonic frequencies in bold italics are obtained from Gaussian and include correction for Fermi resonance. The qualitative experimental intensities (vw, w, m, s, vs), where available, are taken from Ref. [5].

both cases, the propellane precursor, prepared using the method reported by Mondanaro and Dailey [8], was reacted with a slight excess of thiophenol (HSPH) to produce phenyl bicyclo[111]pentyl sulfide.



For the -d₁ synthesis, shown above, the thiophenol was deuterated at the sulfur position by three exchanges with D₂O (99.8%), yielding DSPH with a deuteration level estimated from NMR spectra to be in excess of 75%. Subsequent reaction with propellane yielded the mono-deuterated phenyl bicyclo[111]pentyl sulfide with the deuterium and the phenyl sulfide group in the axial positions.

After subsequent aqueous workup and treatment with Raney nickel as outlined in [1], the volatile products were collected at

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