

AN ABSTRACT OF THE THESIS OF
Matthew A. Martin for the degree of Honors Baccalaureate of Science in Chemistry
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Bicyclo[1.1.1]pentane

Abstract Approved: _____
Joseph Nibler

The strained carbon ring, bicyclo[1.1.1]pentane, was synthesized by a reaction between 1-(phenylsulfanyl)bicyclo[1.1.1]pentane, prepared from propellane, and Raney nickel. Infrared spectra were recorded at a resolution of 0.0015 cm^{-1} , a resolution significantly better than previous measurements, 0.06 cm^{-1} . A single fundamental band was analyzed to determine the ground state and excited state vibrational constants. Over 2300 transitions of the A_2'' band, ν_{18} , were fit to a root mean squared deviation of 0.00016 cm^{-1} , giving the ground state and excited state constants (cm^{-1}): $B_0 = 0.2399418(3)$, $D_0^J = -0.601(4) \times 10^{-7}$, $D_0^{JK} = 0.13(1) \times 10^{-7}$, $\nu_{18} = 832.92903(3)$, $\Delta B_{18} = -2.08394(10) \times 10^{-3}$, and $\Delta C_{18} = -0.2514(1) \times 10^{-3}$, where the numbers in parenthesis indicates twice the uncertainty. The rovibrational parameters were then compared to parameters for an analogous normal mode of [1.1.1]propellane, ν_{18} . Parameters from both molecules were in good accord with values predicted by ab initio calculations.

Key Words: High resolution spectroscopy, bicyclopentane, propellane, strained

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High Resolution Spectroscopy of Bicyclo[1.1.1]pentane

by

Matthew A. Martin

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I understand that my project will become part of the permanent collection of Oregon
State University, University Honors College. My signature below authorizes release of
my project to any reader upon request.

Matthew A. Martin, author

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High Resolution Spectroscopy of Bicyclo[1.1.1]pentane

Introduction:

The synthesis and chemistry of small, strained carbon rings provides an ideal meeting point for physical and organic chemistry. The molecule bicyclo[1.1.1]pentane, Fig. 1, (henceforth the [1.1.1] will not be used) and its derivatives have fascinated chemists since Wiberg et al. synthesized it in 1964 [1]. A particularly interesting derivative, [1.1.1]propellane, previously thought to be unstable due to an inverted tetrahedral carbon, was then synthesized in 1982 [2].

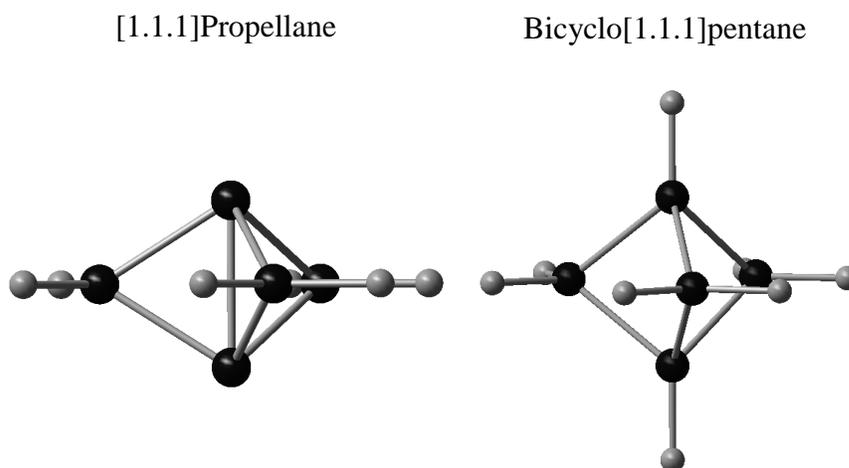


Fig. 1. Models of [1.1.1]propellane and bicyclo[1.1.1]pentane showing D_{3h} symmetry.

Physical chemists have an interest in bicyclopentane, propellane, and similar derivatives because of the high molecular symmetry, interesting geometry, and small number of atoms, making high level ab initio calculations possible. Wiberg offered initial, low resolution spectroscopic, analysis of both bicyclopentane [3] and propellane

[4] following the publication of the synthesis. The high resolution infrared spectrum of propellane has been analyzed by our lab at Oregon State University [5] and the ground state, as well as many excited state rovibrational constants have been determined to considerable accuracy.

High resolution spectra of a molecule in the gas phase at low pressure most accurately reveal properties of a lone molecule. Analysis of the high resolution spectra leads to the accurate determination of rovibrational parameters (e.g. ν , B , D) which can then be compared to the parameters predicted by ab initio calculations. The rovibrational parameters determined for bicyclopentane can also be compared to parameters previously determined for propellane, leading to a further understanding of the structural differences between the two molecules. Comparison of experimentally determined rovibrational constants for propellane with constants determined from Gaussian03 calculations provide a basis for similar comparisons for bicyclopentane.

Comparisons between the two analogues are also of importance. The significant difference between bicyclopentane and propellane is the lack of the bridgehead carbon bond in bicyclopentane. However, as found in this work, the readiness of bicyclopentane derivatives to reform that central bond exhibits the surprising stability of the highly strained bond. The uniqueness of the bond owes to the inverted tetrahedral geometry displayed by the bridgehead carbon. Although the current work does not deeply explore the nature of the bond, it is the foundation for the interesting comparisons made between the two molecules.

Bicyclopentane exhibits D_{3h} symmetry and consists of three equatorial $-(CH_2)$ groups and two axial $-(CH)$ groups. The bond length between an axial carbon and an

equatorial carbon has been found to be 1.557(2) Å and that between two axial carbons to be 1.874(4) Å [6]. The bond lengths were also determined for propellane by electron diffraction and were used, at the time, to help determine if there existed a bond between the bridgehead carbons of propellane. Hedberg and Hedberg used the value of the B rotational constant found by Wiberg in combination with electron diffraction data, finding the axial-axial bonds and equatorial-axial bonds to be 1.596(5) Å and 1.525(2) Å, respectively [7]. Most importantly, for spectroscopic purposes, this constrained the possible symmetries of the molecule to D_{3h} or D_3 .

The synthesis of bicyclopentane and propellane engaged organic chemists and a flurry of activity produced many unique, and geometrically interesting, strained carbon rings. Strained carbon rings like the propellanes, cubanes, prismanes, rotanes, and others not only find a use as an exercise in complex synthesis but they also appear to have practical uses. Consideration of the unique shape of the bicyclopentane cage suggests that it could be used as a space filling polymer. A review of bicyclopentane by Levin, et. al., listed several other uses of bicyclopentane and its derivatives owing to the unique cage shape [8]. The challenge the organic chemist faces is manipulating the bridgehead bond in order to incorporate bicyclopentane into and onto various molecules without disrupting the geometry.

In this work, bicyclopentane and propellane were synthesized from commercial available chemicals. A single fundamental infrared band was analyzed in order to determine the ground state rotational and vibrational constants of bicyclopentane. The constants determined from the high resolution spectrum were then compared with constants predicted using ab initio calculations and previous, low-resolution works. The

band chosen for analysis, ν_{18} , is a parallel band with few perturbations, allowing very accurate ground state constants to be determined, an essential step to further analysis of more complex spectra bands.

Experimental

Synthesis

Propellane served as the precursor to bicyclopentane and it was prepared using the procedure reported by Mondanaro and Dailey [9], which was a refinement of the procedure reported by Michl and co-workers [10]. Into a solution of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane in ether, under argon, was added dropwise a 1.6 M solution of methyl lithium at -78°C , in a 1:1.2 molar ratio. The propellane was then converted to 1,3-diiodobicyclopentane using the method reported by Alber and Szeimies [11]. A molar equivalent of iodine was dissolved in a 5:1 pentane to ether mix and then dripped into the crude solution while it was irradiated by an incandescent lamp. After this step the solution was then exposed to the air.

Two methods for the synthesis of bicyclopentane were attempted. In the first method, it was thought that a reaction with tributyltin hydride irradiated with a fluorescent lamp would remove iodine from the axial carbons and replace it with hydrogen. Surprisingly, monitoring by ^1H NMR showed that the 1,3-diiodobicyclopentane instead reformed the bridgehead carbon bond and the reaction produced propellane.

A second attempt was made using a reaction of propellane noted by Wiberg [12]. A new solution of propellane in ether was synthesized as previously noted and to the crude solution of propellane was added, dropwise, a slight excess of thiophenol, suggested by Wiberg to react with propellane with 98% yield. This produced a solution of 1-(phenylsulfanyl)bicyclo[1.1.1]pentane and thiophenol. Freshly prepared Raney nickel was added to the solution and allowed to react. The reactions were constantly

monitored by ^1H NMR and both the presence of the thioester derivative and the subsequent formation of bicyclopentane were observed. Bicyclopentane was thought to be partially in the vapor above the solution and 2.42 torr of gas was transferred to a glass infrared cell using a vacuum line. Upon spectroscopic analysis it was determined that 19.8% (0.48torr) of the gas was bicyclopentane with the remaining either isopentane (1.54 torr) or benzene (0.4 torr). The benzene is expected from cleavage on the benzene side of the thioester bond and the isopentane from the decomposition of bicyclopentane.

All NMR used to confirm the presence of bicyclopentane was done at Oregon State University on the Bruker AC 300 MHz NMR.

Spectroscopy

The point group of bicyclopentane is D_{3h} and the $3N - 6 = 33$ normal modes can be represented as: $\Gamma_{\text{bicyclopentane}} = 5a_1' (\text{R}) + 2a_2' + 7e' (\text{IR, R}) + a_1'' + 3a_2'' (\text{IR}) + 4e'' (\text{R})$. There are three modes which have a_2' and a_1'' symmetry that have inactive fundamental transitions in both the Raman scattering and infrared absorption spectra. The ten bands which have e' and a_2'' symmetry are active in the infrared spectrum and the 16 bands with a_1' , e' , or e'' symmetry are all Raman active. Following the initial synthesis of bicyclopentane, Wiberg et al., recorded both infrared and Raman data and made initial band assignments [3]; Table 1 displays those assignments and the corresponding *ab* initio values we calculated using the Gaussian03 program [13].

Our high resolution spectra were taken using the Bruker 125 FTIR spectrometer at Pacific Northwest National Laboratory. The spectrometer used a Globar light source and had an evacuated path length, except for the absorption cell which was filled with

1.07 torr of bicyclopentane. There were 448 single-sided interferograms collected, including both backwards and forwards

scans, and boxcar apodization was used. A resolution of 0.0015cm^{-1} was achieved with a 25.6m White cell and an MCT detector.

The spectrum was calibrated with a NIST OCS gas sample. Fig. 2 shows a comparison between the resolution achieved by previous studies (0.06cm^{-1}) and the current study [3].

To generate the former, a copy of the high resolution spectrum was convolved using a Gaussian linewidth of 0.06cm^{-1} and is displayed as the bold line. The lower resolution spectrum shows individual *J*-peaks but the *K*-structure is only visible at the higher resolution obtained recently.

Table 1: List of fundamental band frequencies along with frequencies predicted using ab initio calculations for bicyclopentane

Mode		Exp. ^a	<i>Ab initio</i> ^b
$A_{1'}$	ν_1	2976.1	3092.1
	ν_2	2886.9	3042.1
	ν_3	1509.2	1553.1
	ν_4	1106.6	1118.9
	ν_5	897.9	907.5
$A_{2'}$	ν_6		3094.5
	ν_7		967.0
E'	ν_8	2976.1	3099.8
	ν_9	2886.9	3036.7
	ν_{10}	1455.8	1503.5
	ν_{11}	1231.8	1259.3
	ν_{12}	1097.9	1117.1
	ν_{13}	886.2	897.6
	ν_{14}	539.8	541.2
$A_{1''}$	ν_{15}		1003.6
$A_{2''}$	ν_{16}	2986.1	3086.6
	ν_{17}	1219.7	1252.4
	ν_{18}	832.0	844.4
E''	ν_{19}		1216.3
	ν_{20}		1143.8
	ν_{21}	1006.4	1029.2
	ν_{22}	769.4	773.8

^a Ref. [3]

^b Anharmonic values calculated using Gaussian03 Anharm option

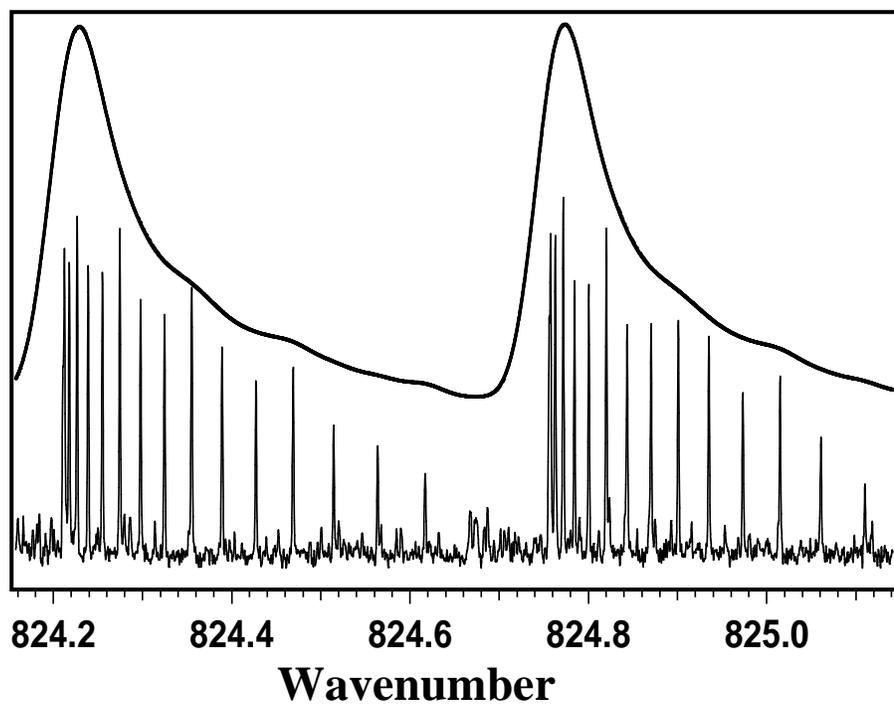


Fig 2. Comparison of spectra high resolution (0.0015 cm^{-1}) with previous spectra at 0.06 cm^{-1} .

Analysis

Bicyclopentane, like propellane, is an oblate symmetric top where two moments of inertial, I_A and I_B , are equal and less than the last moment, I_C . The rotational term values for non-degenerate vibrational states are given as:

$$F(J, K) = B_v J(J+1) + (C_v - B_v)K^2 - D_v^J J^2 (J+1)^2 - D_v^{JK} J(J+1)K^2 - D_v^K K^4 + H_v^J J^3 (J+1)^3 + H_v^{JK} J^2 (J+1)^2 K^2 + H_v^{KJ} J(J+1)K^4 + H_v^K K^6 \pm \delta_{3K} \Delta_3 [J(J+1)][J(J+1)-2][J(J+1)-6]. \quad (1)$$

The transition energy (ν) is calculated from Eq. 1 for an oblate symmetric top, where the transition selection rules for a parallel band are $\Delta J = \pm 1$ and $\Delta K = 0$:

$$F(J+1, K) - F(J, K) = 2B_v(J+1) - 4D_v^J (J^3 + J^2 + J + 1) - 2D_v^{JK} (J+1)K^2 + 2H_v^J (J+1)^3 (4+6J+3J^2) + 4H_v^{JK} (16J^3 + 3J^2 + 3J + 1)K^2 + 2H_v^{KJ} (J+1)K^4 \quad (2)$$

From Eq. 2 it is seen that not all of the rovibrational constants can be determined by this band analysis; specifically, C_v , D_v^K , and H_v^K cannot be determined. The undetermined constants all depend exclusively on K , which, by the selection rules, does not change for a transition.

The constants C_v and B_v are dependent on the moments of inertia around the primary symmetry axis (z) and an axis perpendicular to the z axis, respectively. The total angular momentum is quantized by J and K is the projection of that angular momentum onto the principal symmetry axis, the axis intersecting the two bridgehead carbons.

Centrifugal distortion of the molecule is taken into account by the quartic D_v^X and sextic H_v^X terms. The final term in Eq. 1 accounts for a small splitting observed when $K = 3$; the Δ_3 term is the splitting constant and δ_{3K} is Kroneker's Delta, which ensures the splitting term is only applied to transitions where K is three. For a given constant, e.g. B_v , ν is replaced by the normal mode referenced and ν_0 indicates the ground state.

The high resolution spectra showed generally well resolved bands, with many thousands of sharply defined transitions. As the initial step in the analysis of these, a single parallel band, ν_{18} at 832.9 cm^{-1} , was analyzed to find the ground state and excited state constants. There were 2317 transitions fit, ranging from $J = 0 - 59$ and $K = 0 - 49$, with a root mean squared (RMS) deviation of 0.00016 cm^{-1} . The ground state parameters and the parameters for ν_{18} are given in Table 2.

Discussion

Synthesis

Synthetic routes to bicyclopentane have been reported but there was not one using propellane as a precursor. The preparation of propellane had been done in this lab for a previous publication [5, 14] and because of experience synthesizing that molecule and its derivative, 1,3-diiodobicyclopentane, they were considered possible precursors to bicyclopentane. The synthesis of propellane and subsequent synthesis of the diiodo compound produced a crude solution containing the diiodo, pentane, and ether. The solvents were allowed to evaporate and left the diiodo compound, a yellow solid. A yield was never calculated but appears, from the consumption of I_2 during the conversion from propellane, to be around 60%.

Initially, it was thought that 1,3-diiodobicyclopentane could be reacted with tributyltin hydride ($SnBu_3H$) to produce bicyclopentane. Small, microscale reactions were conducted in NMR tubes with C_6D_6 in order to monitor the progress of the conversion. A solution of the diiodo compound with $SnBu_3H$ showed no decrease in the peak corresponding to the diiodo (δ 2.195, 6H). A second solution was created consisting of the diiodo, $SnBu_3H$, and a trace amount of AIBN, a radical initiator, which was then exposed to a 75W incandescent lamp for 16 hours. The peak corresponding to the diiodo compound was almost completely absent and there was another peak present at δ 1.82 (6H), obscured by the peaks from $SnBu_3H$. The chemical shift given by Wiberg for propellane occurred at δ 2.06 [12] and the two for bicyclopentane occurred at δ 1.84 (6H) and δ 2.44 (2H) [8]. A corresponding peak did not appear where it would be expected, δ

2.44, for bicyclopentane and thus, it is suspected, that the reaction with SnBu_3H simply converted the diiodo compound back to propellane.

A second synthesis of propellane was undertaken and the crude solution of propellane was then reacted directly with thiophenol. ^1H NMR confirmed the synthesis of bicyclo[1.1.1]pentyl phenyl sulfide [12]. Although symmetric synthesis of bicyclopentane from the diiodo compound failed because of reversion to propellane, by going through a thioester intermediate a single proton was already affixed to one bridgehead carbon. The thioester was then removed by reaction with Raney nickel, a hydrogenation catalyst. After 30 minutes of reaction time, a preliminary ^1H NMR was taken and peaks were seen at 1.83 (6H) and 2.32 (2H). A HSQC spectrum, Fig. 3, was taken and showed a coupling

between the carbon at 73.5ppm and the hydrogen at 1.83ppm, both values similar to literature values. Accordingly, a large scale sample was allowed to react with Raney nickel overnight. The resultant sample was frozen in liquid nitrogen and, on warming, the initial volatile products were used for the infrared spectroscopy.

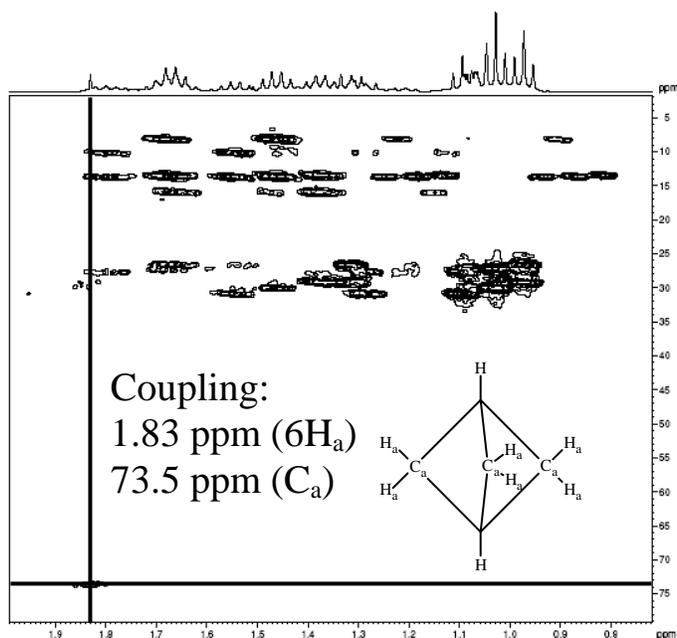


Fig. 3. HSQC showing the coupling between the equatorial carbons (C_a) and the equatorial hydrogens (H_a)

Spectroscopy

High level ab initio calculations done for bicyclopentane provided an ideal starting point for spectral analysis of ν_{18} . Although the calculations are not perfect they provided adequate ground state and excited state constants (e.g. B_0 and ΔB_{18}) from which transitions could begin to be assigned.

The process of transition fitting begins at low J values in the P and R branches, shown in Fig 4.

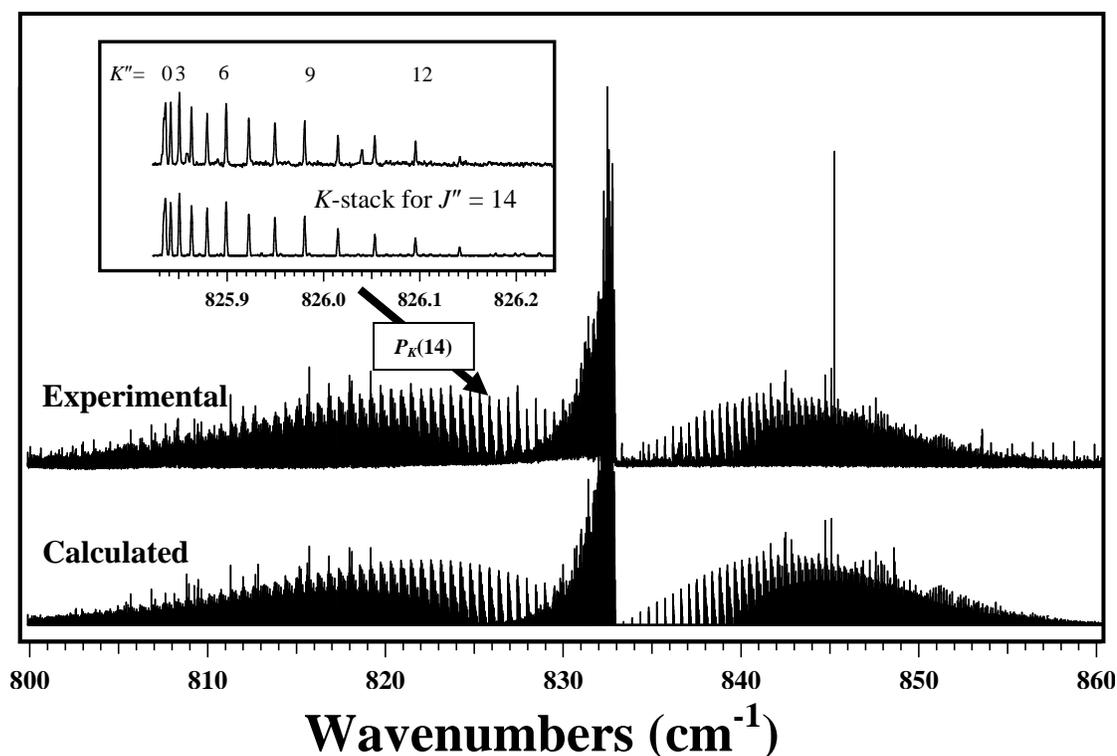


Fig. 4. A comparison of the calculated and experimental spectra showing the excellent fit for all branches. . The inset shows fine K substructure for the $J'' = 14$ P -stack

Generally, for a parallel band, the R -branch will display the cleanest transitions because it lacks the interference from the tail of the Q -branch that extends into the P -branch. Initial transitions were assigned to K -stacks associated with $J' < 10$. Generally, it was observed

that the individual lines for $K = 0$ and 1 were not resolved and thus transitions were assigned from $K = 2$ to $K = J$. Assignment of transitions was helped by the intensity enhancement of the lines where K is an integer multiple of three (3p). This enhancement is the result of hydrogen nuclear spin weights which are $K = 3p$ (96) and $K \neq 3p$ (80). The nuclear spin weights for $K = 0$ are 56 (J even) and 40 (J odd) [15]. Initially, the only constants being fit were the band origin, ν_{18} , B_0 , and ΔB_{18} ; in an iterative process, further constants were added as dictated by the fitting residuals.

The lines of the Q -Branch are more congested than the simple, expanded pattern in the P and R branch levels. However, once reasonable constants had been determined using transitions from the P and R branches, the Q -branch transitions could be confidently assigned. These fit the model very well, except for lines at high J where $J \approx K$,

which showed a small discrepancy, Fig 5. The first noticeable discrepancy for the $J = K$ lines is at $J = 27$ and the difference between the predicted transition and the observed increases from 0.0004 cm^{-1} to 0.0015 cm^{-1} as J increases. At very high J , where the intensity of the Q -branch is almost into the noise, a small perturbation (0.0004 cm^{-1}) is also noticed for lines where $J = K + 1$. These perturbations are not visible in the other two branches because at such high J and K values the intensity of the line is insufficient to distinguish the transition from the noise. The cause of the perturbation is believed to be a

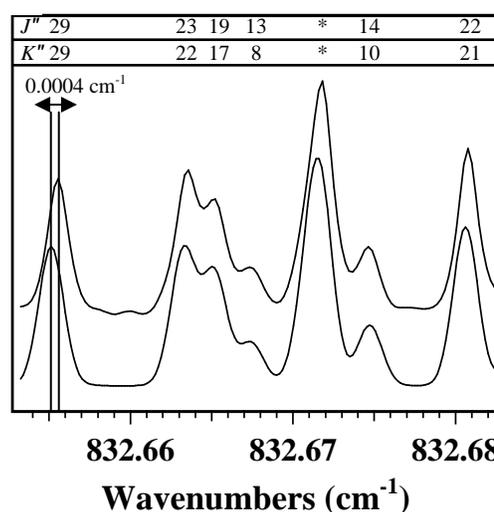


Fig. 5. An example of the Coriolis interaction with ν_{13} perturbing the $J = K = 29$ line. (*) Note: This is a stack of several unresolved transitions.

Coriolis coupling with the ν_{13} band at 886 cm^{-1} and future work will include an analysis of this band with inclusion of an appropriate Coriolis coupling term.

At the high resolution of the measurements, a second perturbation is seen in the spectra. A splitting of the $K = 3$ lines caused by the Δ_3 centrifugal distortion interaction can be seen at high J ; at low J the two lines are unresolved so their intensities simply add. The Δ_3 splitting term in Eq. 1 is only resolved after $J' = 45$ with relative spin weights of 56:40 or more simply 7:5. At higher J values, the line intensity, given by the Hönl-London factor [16], drops to 14% of the most intense R -branch peak. Nevertheless, thirteen split $K = 3$ lines were measured and fit (5 from the R -branch and 8 from the P -branch) with a residual of 0.00040 cm^{-1} . The Δ_3 splitting exists in both the ground state and the excited state, Fig. 6, but, the ground state splitting is generally much smaller than the excited state splitting so it was assigned to be zero. We note that splitting would also occur for the $K = 6, 9 \dots$ transitions but the magnitude of these would be much too small to be resolved.

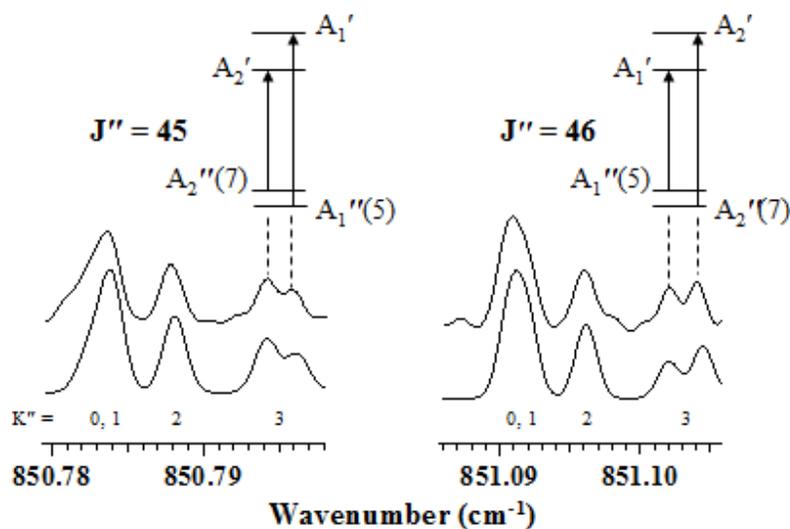


Fig. 6. An example of the $K = 3$ splitting observed and the associated nuclear spin weights.

The parameters, deduced from the analysis are shown in Table 2, along with those obtained from ab initio calculations. Gaussian03 was used to calculate both the harmonic and anharmonic rovibrational constants using the B3LYP density functional method and a cc-pVTZ basis set [13]. For these high level calculations, the computer time was appreciable (17 hours and 8 days, 7 hours for the harmonic and anharmonic calculations, respectively, on a personal computer with 1 CPU). Of greatest interest for comparison are the values for ν_0 , B_0 , ΔB , C_0 , ΔC , and the quartic centrifugal distortion constants: D_0^J , D_0^{JK} , and D_0^{JK} . The experimental band origin given in Table 2 for ν_{18} (832.9 cm^{-1}) is in reasonable accord with the ab initio anharmonic frequency (824.7 cm^{-1}). The harmonic frequency (844.4 cm^{-1}) is predicted and is higher than the anharmonic frequency, as is the usual case. Although the anharmonic frequency does not accurately pinpoint the band origin, it does a more than sufficient job of assisting in the assignment of all the fundamentals of the molecule. The accuracy of the ab initio calculations appears best in the prediction of values for which there is a high J dependence. For example, the B_0 constant agrees exceptionally well, within 0.6%, and the D_0^J term is within 1.3%. The sextic terms do not match, but those terms were only marginally determined experimentally, transitions at much higher J and K will be needed to more accurately predict those terms.

Table 2

Experimental and ab initio parameters for the ground state and an excited state of bicyclopentane and propellane. Twice the standard errors are given in parenthesis.

Ground State parameters (cm ⁻¹)	Bicyclopentane		Propellane ^a	
	Experimental	Gaussian03	Experimental	Gaussian03
B_0	0.2399418(3)	0.2387	0.28755833(14)	0.2866
C_0	—	0.2058	—	0.1918
$D_J \times 10^7$	0.601(4)	0.609	1.1313(5)	1.147
$D_{JK} \times 10^7$	-0.130(13)	-0.190	-1.2633(7)	-1.285
$D_K \times 10^7$	—	-0.038	—	0.425
$H_J \times 10^{12}$	—	0.0447	0.072(4)	0.089
$H_{JK} \times 10^{12}$	0.25(29)	-0.419	-0.224(13)	-0.916
$H_{KJ} \times 10^{12}$	4.2(7)	0.646	0.225(15)	1.685
$H_K \times 10^{12}$	—	-0.261	—	-0.809
$\Delta_3 \times 10^{12}$	—	-0.002	—	—
Excited State Parameters (cm ⁻¹)	Bicyclopentane ν_{18}		Propellane ν_{15}	
	Experimental	Gaussian03	Experimental	Gaussian03
ν	832.92903(3)	—	612.31698(2)	—
$\nu_{\text{anharmonic}}$	—	824.7	—	564.9
ν_{harmonic}	—	844.4	—	601.4
$\Delta C \times 10^3$	-0.2514(1)	-0.259	-0.34361(3)	-0.338
$\Delta B \times 10^3$	-2.08400(9)	-2.17	-0.17923(2)	-0.045
$\Delta D_J \times 10^6$	0.07288(8)	—	0.007535(7)	—
$\Delta D_{JK} \times 10^6$	-0.2268(2)	—	-0.015002(18)	—
$\Delta D_K \times 10^6$	0.1536(2)	—	0.008933(14)	—
$\Delta H_J \times 10^{10}$	-0.03270(19)	—	-0.001332(17)	—
$\Delta H_{JK} \times 10^{10}$	0.1698(7)	—	0.003753(40)	—
$\Delta H_{KJ} \times 10^{10}$	-0.2486(11)	—	-0.003446(70)	—
$\Delta H_K \times 10^{10}$	0.1133(7)	—	0.001031(34)	—
$\Delta_3 \times 10^{12}$	-0.102(5)	—	—	—

^a Ref [14]

The rovibrational constants for the excited state (expressed as $\Delta B_{18} = B_{18} - B_0$) are only predicted for the band origin, ΔB_{18} , and ΔC_{18} . Generally, the ab initio constants are in good agreement with those determined experimentally (within 5%). Both ΔB_{18} , and ΔC_{18} are negative, indicating that the I_B and I_C moments of inertia increase in the excited vibrational state. This is a general phenomenon; excitation of vibrations usually tends to extend all bonds and moves all atoms away from the center of mass, Fig 7.

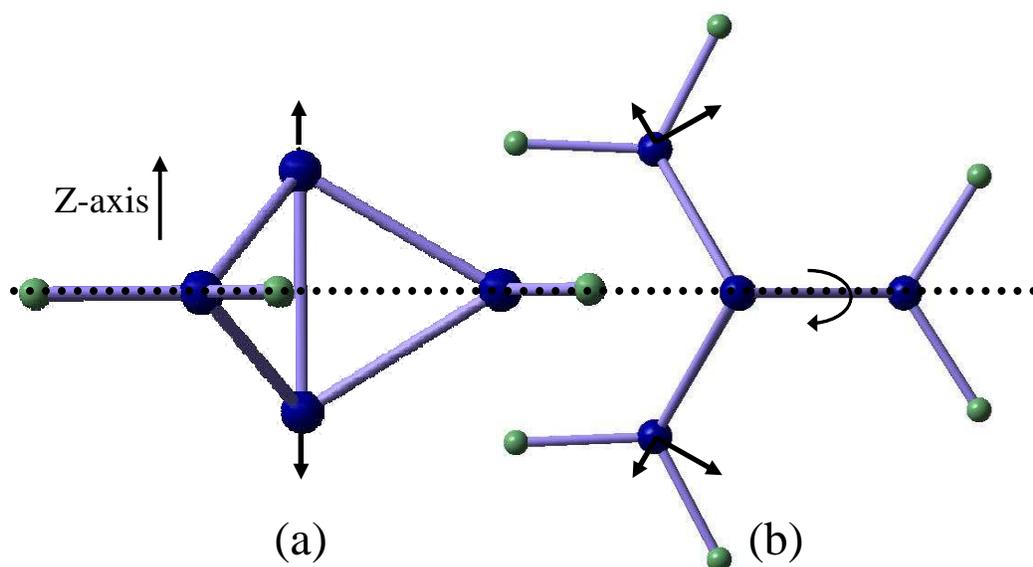


Fig. 7. The movement vectors of the axial carbons and the equatorial $-\text{CH}_2$ groups. The representation (b) is propellane (a) rotated 90° around the y-axis, represented by the dotted line.

It is interesting to consider the predicted splitting constant for the $K = 3$ levels in the ground state. During band analysis the ground state splitting constant (Δ_3'') was fixed at zero and it was only the upper state constant (Δ_3') was allowed to vary. The ab initio calculations predict a value of $-0.216 \times 10^{-14} \text{ cm}^{-1}$ for the Δ_3'' splitting term, two orders of magnitude less than the Δ_3' splitting constant determined experimentally. The small value

predicted from the ab initio calculations indicates that fixing the ground state splitting at zero had a negligible effect on the constants reported.

Specific structural parameters (bond lengths and bond angles) for bicyclopentane cannot be determined from analysis of a single fundamental band of a molecule. A full determination of the five structural parameters would require a study of five isotopomers. Nevertheless, structural comparisons can still be drawn between bicyclopentane and propellane. Included in Table 2 are the rovibrational constants determined experimentally and from ab initio calculations for propellane [5, 14]. The ground state constant, B_0 , is inversely proportional to the moment of inertia about an axis perpendicular to the primary symmetry axis. The value for B_0 is noticeably different for propellane (0.2876 cm^{-1}) [5] than bicyclopentane (0.2399 cm^{-1})—a consequence of molecular geometry. In bicyclopentane, the lack of the axial carbon bond increases the distance between the axial carbons. This, plus the two axial H atoms contribute to the larger I_B value for bicyclopentane.

Following the trend of the B_0 constant, the centrifugal distortion constants in propellane are also larger than their counterparts in bicyclopentane. In Eq. 1 B_0 and D_0^J can be isolated to illustrate that D_0^J is a correction to B_0 : $E \approx [B_0 - D_0^J J(J+1)]J(J+1)$. Structurally, the D_0^J term results from a change in the moment of inertia I_B as rotation occurs around an axis perpendicular to the primary axis of symmetry. The movement vectors of the atoms associated with an increase of angular momentum (an increase in J) around the axis perpendicular to the axis of symmetry are shown in Fig 10. For both propellane and bicyclopentane the distortion will increase I_B , decreasing B_0 . This implies that D_0^J should be positive, as observed. It is interesting that D_0^J is larger for propellane

than for bicyclopentane. It would seem counter intuitive that propellane, an already highly strained molecule, would undergo a more radical distortion of the atomic framework when compared to bicyclopentane. Consideration of the anharmonicity of the axial carbon bond, perhaps, can explain the deviation from expected behavior. It is not unreasonable that it would be harder to compress the axial bond than to extend it. In contrast the potential energy for bicyclopentane may be more harmonic so the band extension with increasing J would be less. A similar rationalization might also explain the large D_0^{JK} and D_0^K values for propellane.

Part of our interest in bicyclopentane stems from a desire to better understand the unique bonding found in propellane. The vibrational motion of ν_{18} is of interest because it is analogous to vibrational motion in the ν_{15} band in propellane, a band which has already undergone high resolution analysis. The normal modes are both motion along the primary symmetry axis: the carbons, in propellane, and the $-(CH)$ groups in bicyclopentane; the opposing motion is the movement of the hydrogen atoms on the equatorial $-(CH_2)$ groups.

We note that the ν_{18} mode of bicyclopentane is 832 cm^{-1} , higher than the analogous A_2'' mode in propellane (612 cm^{-1}). In both cases the normal mode vibration involves the movement of the axial carbons with respect to the equatorial carbons. It might be expected that propellane, with its rigid frame from the central bond, would resist the motion and would thus have a higher force constant and frequency. However, we note for both molecules that there is a higher frequency $-(CH_2)$ wagging mode of A_2'' symmetry that will mix with ν_{18} (and ν_{15}). The higher frequency of ν_{18} might be a result of significantly different mixing in that molecule.

Most striking is the intensity difference exhibited by the similar modes in the two molecules. In propellane, ν_{15} is the most intense band in the infrared spectrum and the predicted intensity from the ab initio calculations has a relative value of 128. The analogous ν_{18} mode in bicyclopentane is quite weak and the predicted relative intensity is only 3.8. As a rationalization of this unusual feature, we note that the bond between axial carbons in propellane distributes electron density along the primary symmetry axis and in bicyclopentane the majority of the electron density is around the cage made by the – (CH₂) groups. Movement of the axial carbons with respect to the equatorial carbons produces an instantaneous dipole moment in the molecule that makes the transition IR active. Clearly movement of the electron density in propellane creates a much bigger oscillating dipole moment than the corresponding motion in bicyclopentane. Since the absolute intensity of an infrared transition goes as the square of the oscillating dipole moment, it appears that the electron density associated with the axial carbon bond greatly enhances the intensity of the ν_{15} vibration in propellane.

Bicyclopentane provides a wonderful tool for the further analysis of the unique bonding found in propellane. The two molecules differ by the addition of two hydrogens and the loss of the central bond; a change which analysis indicates does produce noticeable differences in the rovibrational parameters. The ab initio calculations did a generally excellent job of predicting both the transition locations and rovibrational parameters for both molecules. As ab initio computations improve, initial band analysis will be made easier by more accurate initial parameter estimate and as spectroscopic tools improve, band analysis will yield more demanding tests of the theoretical calculations.

BIBLIOGRAPHY

1. K.B. Wiberg, D.S. Connor, *J. Am. Chem. Soc.* **88** (1966), pp. 4437–4441.
2. K.B. Wiberg and F.H. Walker, *J. Am. Chem. Soc.* **104** (1982), pp. 5239–5240.
3. K.B. Wiberg, R.E. Rosenberg, and S.T. Waddell, *J. Phys. Chem.* **96** (1992), pp. 8293-8303.
4. K.B. Wiberg, W.P. Dailey, F.H. Walker, S.T. Waddell, L.S. Crocker and M. Newton, *J. Am. Chem. Soc.* **107** (1985), pp. 7247–7257.
5. R. Kirkpatrick, T. Masiello, N. Jariyasopit, A. Weber, J.W. Nibler, A. Maki, T.A. Blake, T. Hubler, *J. Mol Spectrosc.* **248** (2008), pp. 153-160.
6. A. Almennigen, B. Andersen and B.A. Nyhus, *Acta Chem. Scand.* **25** (1971), pp. 1217–1223.
7. L. Hedberg and K. Hedberg, *J. Am. Chem. Soc.* **107** (1985), pp. 7257–7260.
8. M.D. Levin, P. Kaszynski and J. Michl, *Chem. Rev.* **100** (2000), pp. 169–234.
9. K.R. Mondanaro and W.P. Dailey, *Org. Synth.* **75** (1998), pp. 98.
10. Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, 53, 4593.
11. F. Alber and G. Szeimies, *Chem. Ber.* **125** (1992), pp. 757–758.
12. K.B. Wiberg and S.T. Waddell, *J. Am. Chem. Soc.* **112** (1990), pp. 2194-2216.
13. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford, CT (2004).

14. R. Kirkpatrick, T. Masiello, N. Jariyasopit, J.W. Nibler, A. Maki, T.A. Blake, A. Weber, *J. of Mol Spectrosc.* **253** (2009), pp. 41-50.
15. A. Weber, *J. Chem. Phys.* **73** (1980), pp. 3952-3972.
16. G. Herzberg, *Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Polyatomic Molecules* **vol. II**, van Nostrand Reinhold Co., New York, NY (1962) p. 434.