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Far-Infrared Spectra and Ring-Puckering Potential Energy Function of Bicyclo[3.1.0]hexan-3-one

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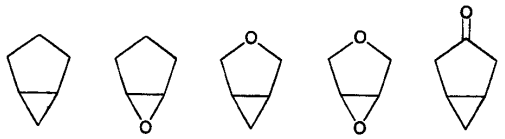
The far-infrared spectrum of the ring-puckering vibration of bicyclo[3.1.0]hexan-3-one has been recorded and analyzed. Ten closely spaced bands with a band origin at 86.4 cm^{-1} were observed. Kinetic energy expansions were calculated for this molecule and also for bicyclo[3.1.0]hexane, 6-oxabicyclo[3.1.0]hexane, 3-oxabicyclo[3.1.0]hexane, and 3,6-dioxabicyclo[3.1.0]hexane, and these expansions along with published data were utilized to calculate the asymmetric one-dimensional ring-puckering potential energy functions for each. For bicyclo[3.1.0]hexan-3-one the function is $V\,(cm^{-1}) = (2.99 \times 10^5)x^4 + (0.39 \times 10^5)x^2 + (1.58 \times 10^5)x^3$, where x is the puckering coordinate in Å. The experimental results were compared to molecular mechanics calculations in each case.

Introduction

In the 1970s the far-infrared,[1] Raman,[2] and microwave spectra[3–7] of bicyclo[3.1.0]hexane (I) and several of its analogs (II–V) were investigated. Each of these molecules has a single-



I II III IV V

minimum asymmetric ring-puckering potential energy function, as determined from its low-frequency vibrational spectra.[1,2] Microwave studies[3–7] have shown each of these molecules to have boat conformations with the five-membered ring puckered toward the three-membered ring. The dihedral angles of puckering determined[5,7] for molecules I–V were found to be 35°, 40°, 42°, 41°, and 19°, respectively.

The fundamental ring-puckering frequencies of molecules I–IV range from 195 cm^{-1} for IV to 241 cm^{-1} for I whereas for bicyclo[3.1.0]hexan-3-one (V) this was assigned[7] at 78 cm^{-1}. Molecule V also differs from the other molecules in that its ring-puckering progression was assigned with the lowest observed puckering frequency attributed to the $0 \rightarrow 1$ transition. Each of the other molecules, however, showed a clear decrease in cm^{-1} for transitions originating from higher states. We recently initiated a jet-cooled fluorescence excitation study of V (following paper).[8] This, together with the spectral inconsistencies of this molecule with the other four, has prompted us to reinvestigate the far-infrared spectrum of this molecule. Our results are reported here.

Experimental Section

The sample of bicyclo[3.1.0]hexan-3-one was provided by Professor Pat Mariano, who had synthesized it in his laboratory. A reaction procedure is described elsewhere.[7] The proton NMR and gas-phase mid-infrared spectra confirmed the identity and purity of the sample.

The gas-phase far-infrared spectra were recorded on a Bomem DA3.002 interferometer using 2 Torr of sample in a 20 m Wilks cell with polyethylene windows which had been deformed by pounding to eliminate fringing patterns. A liquid-helium-cooled germanium bolometer served as the detector. Typically 2000 scans at 0.25 or 0.50 cm^{-1} resolution were recorded. A globar or mercury source and mylar beam splitters were employed to record the far-infrared spectra in the different spectral regions: 12.5 μm for the 40–200 cm^{-1} region and 25 μm for the 20–125 cm^{-1} region.

Results and Discussion

A. Far-Infrared Spectrum. Figure 1 shows the far-infrared spectrum recorded for bicyclo[3.1.0]hexan-3-one (V). This is quite similar to that reported by Bevan and co-workers.[7] Ten closely spaced bands can be seen in the 77 to 87 cm^{-1} region, and the observed frequencies are presented in Table 1. In the previous study[7] the $v = 0 \rightarrow 1$ transition was assigned to the 77.6 cm^{-1} band with increasing frequency in the progression although the authors recognized that the transitions could go in the opposite direction. From the band intensities alone it is somewhat difficult to conclude which band is the $0 \rightarrow 1$ fundamental. However, as described in the following paper,[8] from hot bands in the fluorescence excitation spectrum, we can clearly determine that the 86.4 cm^{-1} band and not the 77.6 cm^{-1} one is the fundamental. Table 1 thus presents the correct, revised assignment which, in fact, is more consistent with the assignments for molecules I–IV where the ring-puckering sequences progressed from high to low frequency. The spacing between the far-infrared bands decreases regularly until the spectrum appears to stop abruptly at 77.1 cm^{-1}. At this point it is quite likely that the higher transitions do not occur at significantly lower frequencies and may begin to increase in frequency. They may then be obscured by the stronger bands arising from the lower states.

B. Vibrational Hamiltonian and Kinetic Energy. As in our previous work,[9–11] we utilized the one-dimensional Schrödinger equation in terms of the ring-puckering coordinate x

$$\mathcal{H}(x)\,\Psi(x) = E\,\Psi(x) \qquad (1)$$

with

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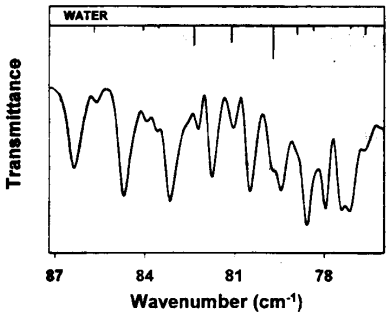


Figure 1. Far-infrared spectra of bicyclo[3.1.0]hexan-3-one vapor: path length, 20 m; vapor pressure, 2 Torr; resolution, 0.25 cm^{-1}. The positions and relative intensities of the water vapor bands are marked.

TABLE 1: Observed and Calculated Vibrational Frequencies (cm^{-1}) for the Ring-Puckering Transitions of Bicyclo[3.1.0]hexan-3-one

	frequency		
transition	obs	calc[a]	Δ
0 → 1	86.4	86.4	0.0
1 → 2	84.8	84.8	0.0
2 → 3	83.1	83.2	−0.1
3 → 4	81.8	81.8	0.0
4 → 5	80.6	80.6	0.0
5 → 6	79.5	79.5	0.0
6 → 7	78.6	78.6	0.0
7 → 8	77.9	77.9	0.0
8 → 9	77.5	77.5	0.0
9 → 10	77.1	77.2	−0.1

[a] $V\ (cm^{-1}) = (2.99 \times 10^5)x^4 + (0.39 \times 10^5)x^2 + (1.58 \times 10^5)x^3$.

$$\mathcal{H}(x) = (-\hbar^2/2)\ \partial/\partial x\ g_{44}(x)\ \partial/\partial x + V(x) \qquad (2)$$

to determine the quantum states for a ring-puckering potential energy function $V(x)$. Here, $g_{44}(x)$ represents the reciprocal reduced mass function for the ring-puckering coordinate x. The computational and vector methods utilized for calculating $g_{44}(x)$ have previously been presented for several types of molecules,[12−16] and these were modified to carry out the calculations for the bicyclic molecules studied here. The $g_{44}(x)$ expansions calculated for molecules I−V are presented in Table 2. The table lists the expansion coefficients both for the "nontranslated" case, for which $x = 0$ corresponds to the planar five-membered ring conformation, and also for the translated case, where $x = 0$ corresponds to the energy minimum determined from microwave work. The availability of these kinetic energy expansions allowed us to determine the dimensioned potential energy parameters for each of these molecules, for which only reduced (dimensionless) functions had been calculated previously.

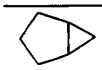
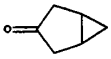
C. Potential Energy. The far-infrared spectrum observed for V can readily be fit with an asymmetric single-minimum potential energy function of the form

$$V = ax^4 + bx^2 + cx^3 \qquad (3)$$

where a, b, and c are potential energy constants. Utilizing our computational methods, which we have previously described,[9−11,17,18] we determined the parameters to be $a = 2.99 \times 10^5\ cm^{-1}/Å$, $b = 0.39 \times 10^5\ cm^{-1}/Å^2$, and $c = 1.58 \times 10^5\ cm^{-1}/Å^3$.

The functional form of eq 3 was selected to minimize the number of adjustable parameters, but the energy minimum for this function at $x = 0$ does not correspond to the planar conformation, which has usually been the case. Since the energy minimum has been reported[7] to be at 19° (0.09 Å), we place the minimum at this value by translation of the potential energy function by $x = x_0 + t$, where $x_0 = 0$ corresponds to the planar conformation and t is the magnitude of the translation. The translated function is shown in Figure 2. Since all translated functions produce the same eigenvalues, the magnitude of t cannot be confirmed or determined from the far-infrared data. Table 1 compares the frequencies calculated from the potential energy function to those observed. The fit can be seen to be excellent. The potential function shows the boat conformation

TABLE 2: Reduced Masses (u) and Kinetic Energy Coefficient[a] (Multiplied by 10^{-2} in Units of $u^{-1}\ Å^{-k}$) of Bicyclo[3.1.0]hexane and Its Analogs (NT, Nontranslated Coordinate; T, Translated Coordinate)

	μ	$g_{44}^{(0)}$	$g_{44}^{(1)}$	$g_{44}^{(2)}$	$g_{44}^{(3)}$	$g_{44}^{(4)}$	$g_{44}^{(5)}$	$g_{44}^{(6)}$
 T:	155	0.644	-1.075	-3.577	-3.350	18.90	92.54	90.85
NT:	134	0.747	-0.232	-1.977	1.205	-20.34	2.600	90.85
T:	165	0.606	-1.248	-3.585	-0.724	30.33	103.7	89.10
NT:	136	0.736	-0.257	-1.972	1.367	-19.94	2.675	89.10
T:	137	0.730	-1.586	-4.630	0.498	52.01	159.7	130.7
NT:	111	0.898	-0.320	-2.078	1.640	-29.28	4.487	130.7
T:	138	0.724	-1.545	-4.418	0.018	48.07	153.7	128.1
NT:	112	0.890	-0.355	-2.076	1.872	-28.75	4.655	128.1
 T:	341	0.293	-0.475	-1.422	1.483	-0.869	5.737	21.54
NT:	310	0.322	-0.194	-1.861	1.930	-0.947	5.380	21.54

[a] The form of the kinetic energy expansion is

$$g_{44}(x) = \sum_{k=0}^{6} g_{44}^{(k)}(x - a)^k.$$

The subscripts $i,j = 1-3$ for g_{ij} are reserved for the rotations.

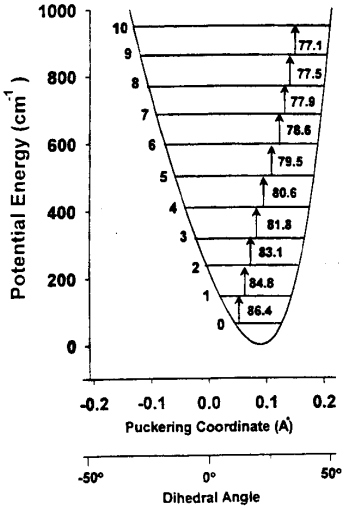


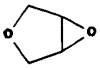
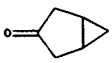
Figure 2. Ring-puckering potential energy function and observed transitions for bicyclo[3.1.0]hexan-3-one. The function has been translated so that $x = 0$ corresponds to the planar conformation and the energy minimum corresponds to a dihedral angle of 19°.

to be about 200 cm^{-1} lower in energy than the planar form and about 600 cm^{-1} lower than the chair conformation with the same dihedral angle in the opposite direction.

The calculation of the reciprocal reduced mass expansions $g_{44}(x)$ (Table 2) for bicyclo[3.1.0]hexan-3-one (V) and also for molecules I–IV allowed us to carry out the potential energy calculations in dimensioned form for each of these molecules. The calculations were carried out both for a fixed reduced mass model [$g_{44}(x) = g_{44}(0)$] and for the full expansion. Since the accuracy of the latter is dependent on the microwave value of the dihedral angle of puckering, some uncertainty in the dimensioned parameters may result. The dimensioned potential energy coefficients are presented in Table 3 for both models along with the average deviation Δ between the observed and calculated frequencies for that calculation. For bicyclo[3.1.0]hexan-3-one both calculations give excellent frequency agreement. This is also the case for the other molecules although molecule II has only five observed frequencies so that its potential energy parameters are determined with considerably less certainty. The poorest frequency fit, with or without the expansion terms, is for III where the average deviation is 1.0 cm^{-1} for its eight observed frequencies.

For bicyclo[3.1.0]hexan-3-one the far-infrared spectra extend about 800 cm^{-1} above the energy minimum whereas for each of the other four molecules the data extend up to 1000–1500 cm^{-1}. Thus, the potential functions can reliably be determined no further than the experimental data allow. Each of these functions is asymmetric, and there is the possibility that a second minimum with a chair conformation might exist at higher energies. For each potential function originally determined in reduced form,[1,2] there is no second energy minimum except for II for which a shallow minimum (above the experimental data) of a few cm^{-1} was calculated. Our functions calculated with fixed reduced masses or with expansions are similar. Utilizing the expansions, only for II do we get the best frequency fit with a potential function that has a second minimum. Since the experimental data do not extend to this region of the potential energy, the existence of a shallow minimum corresponding to the chair conformation cannot be proved or disproved. Figure 3 shows a comparison between the potential energy functions calculated for the five molecules of interest here, with each function translated to the reported value of the energy minimum. As pointed out by Malloy,[5,6] the preference of these molecules for the boat over the chair conformation arises primarily from the fact that the boat form minimizes the eclipsing between the methylene hydrogens, present in all molecules at carbon atoms 2 and 4, and the single hydrogen atoms at carbon atoms 1 and 5 which are part of both ring systems. Since a similar interaction is present in all of these molecules, it is not surprising that the dihedral angles of molecules I–IV are similar. The lower dihedral angle of V apparently arises from the increased angle strain introduced by the sp^2 hybridization of the carbon atom of the carbonyl group. Increased angle strain favors the planar conformation. On the other side of the ketone molecule the three-membered ring is

TABLE 3: Potential Energy Coefficients of Bicyclo[3.1.0]hexane and Its Analogs

	No Expansion (×10⁵)				Expansion (×10⁵)			
	a(cm⁻¹/Å⁴)	b(cm⁻¹/Å²)	c(cm⁻¹/Å³)	Ave. Δ	a(cm⁻¹/Å⁴)	b(cm⁻¹/Å²)	c(cm⁻¹/Å³)	Ave. Δ
	12.77	1.44	7.86	0.4	13.70	1.44	8.06	0.3
	9.77	1.22	6.56	0.2	8.93	1.19	6.27	0.8
	12.92	1.41	7.38	1.0	9.30	1.29	6.17	1.0
	10.81	0.90	5.51	0.8	9.93	0.88	5.25	0.5
	2.76	0.39	1.52	0.1	2.99	0.39	1.58	0.0

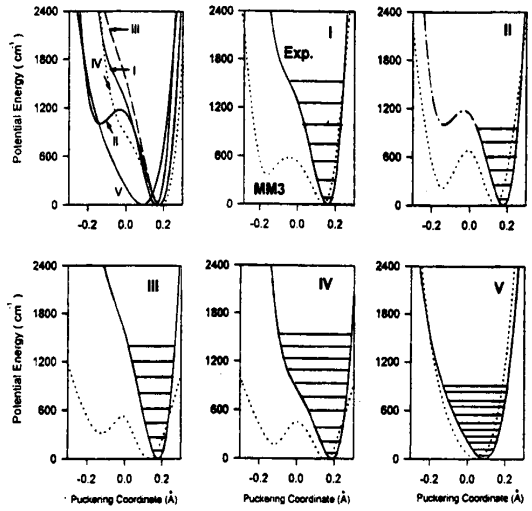


Figure 3. Comparison of potential energy functions for bicyclo[3.1.0]-hexan-3-one and its analogs (upper left) and comparison between the experimental functions and MM3 calculations for molecules I−V.

reported[7] to be out of the plane of the five-membered ring by 67°, not unlike the 64° reported for the other molecules.[5,6]

D. Molecular Mechanics Calculations. We also carried out MM3 molecular mechanics calculations[19] for the conformational energy of each molecule as a function of its ring-puckering coordinate and compared these to our experimental results. Figure 3 also presents these results. For molecule V studied here the MM3 energy minimum is at 11° as compared to the experimental value of 19°. For the other molecules the MM3 minimum is typically 8°−10° lower than the reported microwave value and MM3 also predicts a second minimum for the chair conformation. With the possible exception of the 6-oxabicyclo[3.1.0]hexane (II) molecule discussed above, the experimental potential functions have no second minima. Thus, the force constants inherent in the molecular mechanics program do a fairly good job of predicting the dihedral angles for the boat structures and identifying these to be the lowest energy conformations. However, the energies of the planar and chair conformations are predicted by MM3 to be too low.

Conclusion

The experimental potential energy functions for the five molecules are shown in Figure 3. Except for V, which is nearly planar because of its higher angle strain, the other molecules have inflections (or minor barriers) very near the planar conformations at $x = 0$. This is quite satisfying, since the position of each inflection point is affected both by the microwave value of the dihedral angle and by the kinetic energy expansion calculated in the present work. The planar structures represent critical points in the potential functions where the angle strain is at a minimum and where for molecules I and II the methylene−methylene torsional interactions are at a maximum, and it is expected that the shapes of these functions change more rapidly in this region.

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