

Microwave Spectrum, Molecular Geometry, Ring Bending Potential Function, and Electric Dipole Moment of 3-Bicyclo[3.1.0]hexanone

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Abstract: The rotational spectrum in the vibrational ground state of 3-bicyclo[3.1.0]hexanone and in each of the states $\nu_B = 1$ through to $\nu_B = 5$ associated with the bending mode of the five-membered ring has been observed and analyzed to give rotational constants. Rotational constants have been derived likewise for the vibrational ground states of the isotopic species $[^{13}\text{C}_1]$ -, $[^{13}\text{C}_2]$ -, and $[^{13}\text{C}_6]$ -3-bicyclo[3.1.0]hexanone studied in natural abundance and the species $[^{18}\text{O}]$ -3-bicyclo[3.1.0]hexanone after isotopic enrichment. r_s coordinates for the substituted atoms were therefore obtained and, if the assumptions of $r_s(\text{C}=\text{O}) = 1.210 \text{ \AA}$ (as in cyclopent-3-enone) and of coplanarity of the atoms O, C₃, C₂, and C₄ are made, the principal axis coordinates of the remaining heavy atom (C₅) can be established. The following, essentially r_s , structure for the heavy atom skeleton of 3-bicyclo[3.1.0]hexanone then results: $r(\text{C}_1-\text{C}_6) = 1.510 (3) \text{ \AA}$, $r(\text{C}_1-\text{C}_5) = 1.519 (1) \text{ \AA}$, $r(\text{C}_1-\text{C}_2) = 1.534 (5) \text{ \AA}$, $r(\text{C}_2-\text{C}_3) = 1.529 (6) \text{ \AA}$, $\tau = 66.9 (3)^\circ$, $\phi = 18.8 (1)^\circ$, $\angle \text{C}_6\text{C}_1\text{C}_5 = 59.8 (1)^\circ$, $\angle \text{C}_1\text{C}_6\text{C}_5 = 60.4 (2)^\circ$, $\angle \text{C}_5\text{C}_1\text{C}_2 = 108.9 (2)^\circ$, $\angle \text{C}_2\text{C}_3\text{C}_4 = 104.1 (5)^\circ$, $\angle \text{C}_1\text{C}_2\text{C}_3 = 110.6 (6)^\circ$. From Stark effect measurements, the values reported for the electric dipole moment components are $\mu_a = 2.93 \pm 0.07 \text{ D}$, $\mu_B = 0$ (by symmetry), $\mu_c = 1.22 \pm 0.11 \text{ D}$, and $\mu_{\text{total}} = 3.17 \pm 0.07 \text{ D}$. The far-infrared spectrum of 3-bicyclo[3.1.0]hexanone observed in the range $50\text{--}150 \text{ cm}^{-1}$ allows the fundamental and hot bands associated with the bending mode of the five-membered ring to be assigned. A one-dimensional treatment of this mode in terms of the reduced ring bending coordinate Z establishes that the observed spectrum for the bending mode is best described by the potential energy function (cm^{-1}) $V(Z) = 9.74(Z^4 + 2.70Z^3 + 15.5Z^2)$.

Introduction

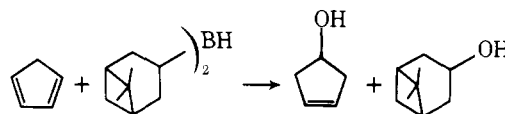
3-Bicyclo[3.1.0]hexanone can be envisaged as formed by addition of a methylene group to the $\text{C}=\text{C}$ double bond of cyclopent-3-enone. The molecular geometry, the form of the ring bending vibration, and the electric dipole moment of the latter substance have been studied in considerable detail^{1,2} through the techniques of microwave and far-infrared spectroscopy. Clearly, a similar investigation of 3-bicyclo[3.1.0]hexanone will reveal the effects on these various properties of the addition of the methylene group to cyclopent-3-enone. Moreover, the detailed conformation, whether boat or chair, will be established and a comparison with bicyclo[3.1.0]hexane itself and the 3-oxa, 6-oxa, 3,6-dioxa, and 6-thia analogues will be possible. Such a comparison is of interest because these molecules have all been shown to exist in the boat conformation in the gas phase by microwave,³⁻⁷ far-infrared,^{8,9} Raman,¹⁰ and gas-phase electron diffraction¹¹ techniques and, in particular, the angles ϕ and τ (see Figure 1) are in the case of all four molecules close to 40 and 64° , respectively. The extent to which the angles and the form of the ring-bending potential function are altered by the increased angle strain imposed on the five-membered ring by replacing CH_2 or O at the 3 position by a $\text{C}=\text{O}$ can then be ascertained.

3-Bicyclo[3.1.0]hexanone is also important in its role as the basic skeleton for the well-known terpenes thujone and isothujone, since both of these can be envisaged as generated by substitution of a methyl group and an isopropyl group for hydrogen at the 1 and 4 positions, respectively, of the parent molecule. The considerable discussion¹² of the conformations of thujone and isothujone would be greatly aided were the detailed molecular geometry and the ring bending potential function of their basic skeleton known. In fact, we have investigated under low resolution the broad-band rotational spectra of these terpenes¹³ and have shown that the molecules have boat conformations very similar in detail to that established below for 3-bicyclo[3.1.0]hexanone and to the other bicyclo[3.1.0]hexane systems mentioned.

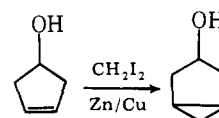
For the reasons outlined above, we have now investigated the microwave rotational spectrum of 3-bicyclo[3.1.0]hexanone in sufficient detail to determine an essentially r_s structure of its heavy atom skeleton and have recorded its far-infrared spectrum in order to provide information about the ring bending potential energy function. From the former spectrum we have also measured the electric dipole moment of the molecule.

Experimental Section

3-Bicyclo[3.1.0]hexanone was prepared from cyclopentadiene according to the following scheme. The dialkylborane resulting from the *in situ* hydroboration of α -pinene was reacted with cyclopentadiene to give Δ^3 -cyclopentenol by the method of Hess and Brown.¹⁴



Addition of a methylene group to the double bond of Δ^3 -cyclopentenol to give 3-bicyclo[3.1.0]hexanol was achieved through reaction with methylene iodide in the presence of a zinc/copper couple, as described by Winstein and Sonnenberg.¹⁵



Finally, 3-bicyclo[3.1.0]hexanol was oxidized to the corresponding ketone using the dipyridinechromium(VI) oxide reagent.¹⁶

The isotopically substituted species $[^{18}\text{O}]$ -3-bicyclo[3.1.0]hexanone was prepared through the reaction of excess acidified H_2^{18}O (98% ^{18}O) with 3-bicyclo[3.1.0]hexanone for a few minutes at room temperature, followed by distillation of the organic compound from the mixture under vacuum at dry ice temperature to give a product containing $\sim 90\%$ of ^{18}O . The enriched water was conveniently acidified by condensing with it sufficient HCl gas to produce 10^{-4} M aqueous hydrogen chloride solution.

Microwave rotational spectra were observed with a Hewlett-Packard 8460A spectrometer which employs Stark modulation at

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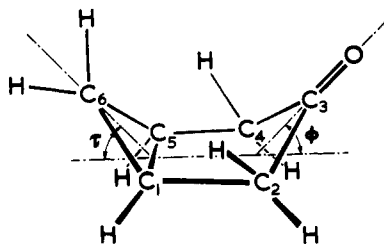


Figure 1. The ring numbering scheme and the definition of the dihedral angles $\phi = 180^\circ - \angle(C_2C_3C_4 - C_1C_2C_4C_5)$ and $\tau = 180^\circ - \angle(C_1C_5C_6 - C_1C_2C_4C_5)$.

33.33 kHz. Absorption cell temperatures were in the range 20 to -30°C .

The far-infrared spectrum of 3-bicyclo[3.1.0]hexanone was obtained in the region $150\text{--}50\text{ cm}^{-1}$ at room temperature and the vapor pressure of ~ 2 Torr (≈ 250 Pa) using a Michelson interferometer (RMC Model FS520) in conjunction with a Fourier transformation of the digitalized interferograms. A 5-m brass light pipe with an effective optical path length of ~ 6 m was used as an absorption cell.¹⁷ The spectrum finally used was an average of data computed from several interferograms.

Results

Ground State Rotational Spectrum and Assignment. 3-Bicyclo[3.1.0]hexanone is a nearly prolate asymmetric rotor molecule having $\kappa = -0.74$. Model calculations using a reasonable assumed geometry indicated that the rotational spectrum would be dominated by strong R-branch transitions allowed by the major component of dipole moment μ_a , with μ_a , Q branch transitions, and various transitions allowed by the minor component μ_c as weaker features. The component of dipole moment μ_b is restricted by symmetry to a value of zero. Each low J , μ_a , R branch transition consists of a ground-state component accompanied to low frequency by a regularly spaced vibrational satellite series which was assigned as a progression in the bending mode of the five-membered ring system, this being predicted as the lowest energy mode associated with the molecule. Spectral assignments were straightforwardly secured from the Stark effects of low J transitions and an initial set of rotational constants for the vibrational ground state was readily obtained from a least-squares analysis of μ_a , R branch transitions in the rigid rotor approximation. From these rotational constants the frequencies of higher J , μ_a , Q branch transitions and μ_c , R and Q branch transitions were predicted and further assignments accordingly made. Transitions allowed by μ_c were, in general, weaker than those allowed by μ_a and of those of the former type only certain Q branch transitions were accurately measured. Low J , μ_c , R branch transitions were unfortunately sufficiently weak and sufficiently often overlaid, partly or wholly, by stronger lines that their measurement was considered unprofitable in con-

nection with improving the rotational constants. Such transitions could, however, be observed at the predicted frequencies. The measured frequencies of the assigned rotational transitions were subjected to a Watson¹⁸ type first-order centrifugal distortion analysis to give rotational constants, moments of inertia, and the quantity $P_b = \frac{1}{2}(I_a + I_c - I_b)$, which are shown in Table I together with the concomitantly determined centrifugal distortion constants. (The observed and calculated frequencies are available in Table S1 as supplementary material.)

Vibrational Satellites. The close chemical relationship between 3-bicyclo[3.1.0]hexanone and its precursor cyclopent-3-enone suggests that the lowest energy vibrational state in the former molecule will be that associated with the bending of the five-membered ring, as is the case in the latter molecule. Thus, one expects and observes a regularly spaced vibrational satellite progression to accompany each low J , R branch in 3-bicyclo[3.1.0]hexanone also but in this case it occurs to low, rather than high, frequency of the vibrational ground-state transition. The observed frequencies of rotational transitions in states of the ring bending mode (ν_B) having vibrational quantum numbers $\nu_B = 1$ through to $\nu_B = 5$ (available as supplementary material Table S2) were used to obtain the spectroscopic constants for these states included in Table I. The constants in Table I result from a rigid rotor analysis of transition frequencies after these had been corrected for centrifugal distortion as appropriate to the corresponding ground-state transitions. This approach was necessary because an insufficient number of transitions and transition types for a centrifugal distortion treatment was measured for the vibrational satellites. From Table I it is clear that the quantity $P_b = \frac{1}{2}(I_a + I_c - I_b)$ is sensibly independent of the state of excitation of the ring bending mode. Moreover, when we collect together this quantity for several related molecules, as in Table II, several interesting conclusions become apparent once it is accepted that P_b depends only on the perpendicular distances of the atoms from the ac plane and the atomic masses and is therefore almost independent of the dihedral angle ϕ (see Figure 1) of the five-membered ring. First, the similarity of P_b values suggests that each molecule has heavy atoms disposed about the ac plane in a similar manner and that this plane is a symmetry plane in each case. Secondly, substitution of O and S for CH_2 at the 6 position of bicyclo[3.1.0]hexane presumably leaves the distances of the atoms from the ac plane essentially unchanged while substitution of O and $\text{C}=\text{O}$ for CH_2 at the 3 position of bicyclo[3.1.0]hexane leads to a small increase and a small decrease, respectively, in the breadth of the five-membered ring. Thirdly, the addition of CH_2 to the $\text{C}=\text{C}$ double bond of cyclopent-3-enone to form 3-bicyclo[3.1.0]hexanone does not greatly change the disposition of the atoms about the ac plane. Fourthly, the small increase of P_b per quantum of excitation of the ring bending mode of

Table I. Rotational Constants (MHz), Moments of Inertia ($\text{amu } \text{\AA}^2$), and the Quantity $P_b = \frac{1}{2}(I_a + I_c - I_b)$ for the $\nu_B = 0$ to $\nu_B = 5$ States and the Quartic Centrifugal Distortion Constants (MHz) for the Ground State of 3-Bicyclo[3.1.0]hexanone

	$\nu_B = 0$	1	2	3	4	5
A	5356.835 (1)	5370.7	5383.6	5397.3	5410.6	5422.7
B	2461.202 (1)	2458.384	2455.578	2452.835	2450.242	2447.863
C	2037.243 (1)	2034.577	2031.991	2029.560	2027.387	2025.572
I_a	94.342 27 ^a	94.0991	93.8733	93.6356	93.4049	93.1964
I_b	205.337 07	205.5725	205.8073	206.0375	206.2555	206.4560
I_c	248.068 59	248.3936	248.7098	249.0077	249.2745	249.4979
P_b	68.536 90	68.4601	68.3879	68.3029	68.2119	68.1192
Δ_J	0.000 545 (8)					
Δ_{JK}	-0.002 200 (5)					
Δ_K	0.005 80 (4)					
δ_J	-0.000 029 6 (2)					
δ_K	0.000 154 (6)					

^a Conversion $BI = 505\,376\text{ MHz amu } \text{\AA}^2$.

Table II. The Quantity $P_b = \frac{1}{2}(I_a + I_c - I_b)$ (amu Å²) for 3-Bicyclo[3.1.0]hexanone and Related Molecules

molecule	$\nu_B = 0$	$\nu_B = 1$	$\nu_B = 2$	$\nu_B = 3$	$\nu_B = 4$	$\nu_B = 5$
bicyclo[3.1.0]hexane ^a	66.754					
6-oxabicyclo[3.1.0]hexane ^b	66.3889	66.5358	66.7088			
3-oxabicyclo[3.1.0]hexane ^c	61.334	61.477	61.627			
3,6-dioxabicyclo[3.1.0]hexane ^d	61.4759	61.5871				
6-thiabicyclo[3.1.0]hexane ^e	65.8816	66.0289	66.141			
3-bicyclo[3.1.0]hexanone	68.5369	68.4601	68.3879	68.3029	68.2119	68.1193
cyclopent-3-enone ^f	65.2818	65.1780	65.0864	65.0039	64.9284	64.8586

^a Reference 3. ^b Reference 5. ^c Reference 4. ^d Reference 6. ^e Reference 7. ^f Reference 1.

the oxa and thia analogues of bicyclo[3.1.0]hexane distinguishes these molecules from 3-bicyclo[3.1.0]hexanone and cyclopent-3-enone, for which P_b decreases. This suggests some significant difference in the ring bending modes between these two groups.

Isotopic Species and Heavy-Atom Geometry. The assignment of the rotational spectrum of the isotopically enriched species [¹⁸O]-3-bicyclo[3.1.0]hexanone was straightforward and followed that of the most abundant species. For the species [¹³C₁]-, [¹³C₂]-, and [¹³C₃]-3-bicyclo[3.1.0]hexanone, studied in their abundances of 1.1, 2.2, and 2.2%, respectively, advantage was taken of the Stark modulation properties of a nearly prolate asymmetric rotor in order to effect assignment. Such molecules, when subjected to a sufficiently small Stark electric field, exhibit a rotational spectrum in which the only features modulated are the effectively degenerate pairs of transitions $(J+1)_{K-1=J} \leftarrow J_{K-1=J}$ and moreover such features appear with a characteristically symmetrical Stark effect pattern.¹ One therefore seeks this feature associated with a given $J+1 \leftarrow J$ transition and a given isotopic species in that spectral region predicted on the basis of the model structure which satisfactorily reproduces the rotational constants of the most abundant isotopic variety. An additional constraint on the assignment of transitions to ¹³C species is a correct and temperature-independent intensity relative to the corresponding transitions of the most abundant species. Further assignments were made subsequently at high electric fields on the basis of Stark effect patterns, relative intensities, and frequencies.

The observed frequencies for the vibrational ground state of the various isotopic species of 3-bicyclo[3.1.0]hexanone studied (available as supplementary material, Table S3) were analyzed using a rigid rotor least-squares procedure after the centrifugal distortion corrections appropriate to the parent molecule had been subtracted from the observed frequencies, a procedure necessitated by the small number of observed transitions of the isotopically substituted species. Rotational constants and inertial data so obtained are displayed in Table III. The quantity P_b is essentially identical for the parent

Table III. Rotational Constants^a (MHz) and Moments of Inertia (amu Å²) of Isotopically Substituted Species of 3-Bicyclo[3.1.0]hexanone

	[¹³ C ₁]	[¹³ C ₂]	[¹³ C ₃]	[¹⁸ O]
<i>A</i>	5318.89 (5)	5263.48 (4)	5315.48 (4)	5344.44 (5)
<i>B</i>	2443.072 (6)	2459.186 (8)	2418.246 (2)	2347.101 (6)
<i>C</i>	2021.074 (6)	2023.861 (9)	2013.600 (2)	1960.129 (7)
<i>I_a</i>	95.0153 ^b	96.0155	95.0762	94.5610
<i>I_b</i>	206.8608	205.5054	208.9845	215.3193
<i>I_c</i>	250.0532	249.7088	250.9814	257.8279
<i>P_b</i>	69.1038	70.1094	68.5366	68.5348

^a The figures in parentheses are standard errors generated in the least-squares analysis of transition frequencies and pertain to the last figure quoted for each rotational constant. ^b Conversion $BI = 505\,376$ MHz amu Å².

Table IV. r_s Coordinates (Å) of Atoms in 3-Bicyclo[3.1.0]hexanone^a

atom	<i>a</i>	<i>b</i>	<i>c</i>
C _{1,5}	1.1914 (5)	±0.7595 (8)	−0.331 (2)
C _{2,4}	−0.259 (3)	±1.2573 (6)	−0.324 (2)
C ₆	1.7087 (2)	0.0 (by symmetry)	0.8681 (4)
O	−2.2282 (1)	0.0 (by symmetry)	0.3459 (9)

^a The figures in parentheses refer to the errors in the coordinates and follow from those quoted for the rotational constants in Table III.

molecule, the [¹⁸O], and the [¹³C₆] species, as required if *ac* is a plane of symmetry of the molecule.

Given the accurate ground state, effective moments of inertia of the isotopic species in Table III and those of the parent molecule (Table I), the r_s coordinates of the atoms C₆, C₁, C₂, and O referred to the principal inertial axis system of the parent species can be calculated by means of Kraitchman's equations in a form appropriate to a nonplanar asymmetric rotor:^{19–21}

$$\alpha^2 = \frac{\Delta P_\alpha}{\mu} \left(1 + \frac{\Delta P_\beta}{I_\alpha - I_\beta} \right) \left(1 + \frac{\Delta P_\gamma}{I_\alpha - I_\gamma} \right)$$

in which $\Delta P_\alpha = \frac{1}{2}(-\Delta I_\alpha + \Delta I_\beta + \Delta I_\gamma)$, α , β , and γ are to be permuted cyclically among *a*, *b*, and *c*, and the quantity $\mu = \Delta m M / (M + \Delta m)$ is the reduced mass for the isotopic substitution which leads to changes Δm and ΔI in the mass *M* and the moments of inertia *I* of the parent species. The r_s coordinates thus calculated are given in Table IV. It should be noted that each of these exceeds 0.2 Å and is therefore well determined, according to Costain's criterion.²⁰

In order to obtain a complete r_s structure for the heavy atom skeleton of 3-bicyclo[3.1.0]hexanone the r_s coordinates of the atom C₃ are required. It was not possible to detect the [¹³C₃] species in natural abundance and no isotopic synthesis was attempted. The procedure then to follow is to calculate the coordinates of C₃ by assuming that the atoms O, C₃, C₂, and C₄ are coplanar and that $r(\text{C}=\text{O}) = 1.210 \pm 0.002$ Å, which is the r_s distance determined in the precursor molecule cyclopent-3-enone,¹ and standard C–H distances and angles. On so doing the result is $a(\text{C}_3) = -1.084$ (6), $b(\text{C}_3) = 0.000$, $c(\text{C}_3) = -0.048$ (3) Å, and, using these with the r_s coordinates of Table IV, the essentially r_s geometry of the heavy atom skeleton displayed in Table V is generated.

Stark Effect and Electric Dipole Moment. The Stark shifts of the $M_J = 1$ lobe of the $3_{1,3} \leftarrow 2_{1,2}$ transition and the $M_J = 1, 2$, and 3 lobes of the $4_{1,4} \leftarrow 3_{1,3}$ transition of 3-bicyclo[3.1.0]hexanone were found to be linear functions of E^2 , where *E* is the strength of the applied electric field, and also to be observable in unencumbered regions of the spectrum. The second-order Stark coefficients $\Delta\nu/E^2$ shown in Table VI were therefore conveniently measured for these lobes and the dipole moment components $\mu_a = 2.93 \pm 0.07$ D and $\mu_c = 1.22 \pm 0.11$ D (with μ_b constrained to zero for symmetry reasons) consequently determined by a least-squares fit to the coefficients. The resulting value for the electric dipole moment is $\mu_{\text{total}} =$

Table V. Molecular Geometry of 3-Bicyclo[3.1.0]hexanone

	bond lengths/Å	angles/deg
r_s quantities ^a	$r(C_1-C_6) = 1.510 (3)$	$\tau^a = 66.9 (3)$
	$r(C_1-C_5) = 1.519 (1)$	$\phi^a = 18.8 (1)$
	$r(C_1-C_2) = 1.534 (5)$	$\angle C_6C_1C_5 = 59.8 (8)$
		$\angle C_1C_6C_5 = 60.4 (2)$
quantities assuming $r(C=O) = 1.210 (2)^b$	$r(C_2-C_3) = 1.529 (6)$	$\angle C_2C_3C_4 = 104.1 (5)$
		$\angle C_1C_2C_3 = 110.6 (6)$

^a $\tau = 180^\circ - \angle(C_1C_6C_5 - C_1C_5C_4C_2)$ and $\phi = 180^\circ - \angle(C_2C_3C_4 - C_1C_2C_4C_5)$ (see Figure 1). ^b If $r(C=O)$ is assumed as 1.210 (2) Å, the a , b , and c coordinates of C_3 can be calculated and hence the remaining geometry evaluated (see text).

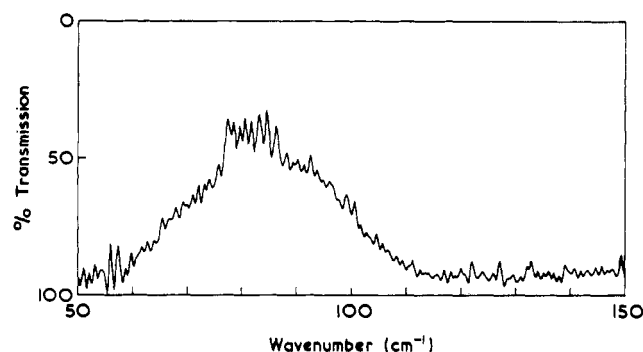
Table VI. Second-Order Stark Coefficients ($\Delta\nu/E^2 \times 10^4$)(MHz cm² V⁻²) and Dipole Moment Components of 3-Bicyclo[3.1.0]hexanone

transition	$ M $	exptl	calcd
$3_{1,3}-2_{1,2}$	1	0.418	0.418
$4_{1,4}-3_{1,3}$	1	0.0214	0.0247
	2	0.187	0.186
	3	0.454	0.454
	$ \mu_a = 2.93 (7) \text{ D}$		
	$ \mu_c = 1.22 (11) \text{ D}$		
	$ \mu_{\text{tot}} = 3.17 (7) \text{ D}$		

$3.17 \pm 0.07 \text{ D}$. The Stark absorption cell calibrations necessary for the determination of $\Delta\nu/E^2$ values were carried out using the $J = 1 \leftarrow 0$, $K = 0$ transition of propyne in conjunction with the value $\mu = 0.7835 \text{ D}$ for this molecule measured by Muentner and Laurie.²²

Far Infrared Spectrum and Ring Bending Potential Energy Function. The far-infrared spectrum of 3-bicyclo[3.1.0]hexanone in the region 50–150 cm⁻¹ is shown in Figure 2. The signal to noise ratio is limited by the low vapor pressure of the compound. The bending mode of the five-membered ring in 3-bicyclo[3.1.0]hexanone should be its lowest in energy with the $\nu_B = 1 \leftarrow 0$ transition at 80–90 cm⁻¹, by analogy with the precursor cyclopent-3-enone. The band in Figure 2 is assumed to consist of a series of Q branches associated with the fundamental and hot bands $\nu_B = n + 1 \leftarrow n$ of the mode ν_B projecting from an unresolved background of the overlapping P and R branches. The Q branch at 77.56 cm⁻¹ is assigned to $\nu_B = 1 \leftarrow 0$ and those at higher wavenumber successively to the hot bands, as shown in Table VII. This assignment follows that in cyclopent-3-enone, for which the shape of the band is very similar. On the other hand, the shapes and positions of the corresponding bands in bicyclo[3.1.0]hexane and its oxa analogues^{8–10} are quite different, with the Q branches all occurring in the range 200–250 cm⁻¹ (rather than 77–100 cm⁻¹) and converging to lower wavenumber as ν_B increases. This, taken together with the geometrical result that the dihedral angle ϕ is 18.8° in 3-bicyclo[3.1.0]hexanone but ~40° in bicyclo[3.1.0]hexane and its oxa analogues,^{3–6} suggests a vibration in the present case like that of the planar precursor cyclopent-3-enone and supports the assignment of Table VII. Such a conclusion is also consistent with the behavior of the rotational constants as a function of ν_B which is similar to that in cyclopent-3-enone but different from that in the oxabicyclo[3.1.0]hexanes.

Once the assignment of Table VII is made, a one-dimensional potential energy function for the ring bending vibration can be derived from the observed spectrum. We have assumed a one-dimensional Hamiltonian of the form^{9,10,23–25}

**Figure 2.** Far-infrared spectrum of gaseous 3-bicyclo[3.1.0]hexanone in the range 50–150 cm⁻¹.**Table VII.** Observed and Calculated Positions (cm⁻¹) of Q Branch Absorptions for the Fundamental and Hot Bands of the Ring Bending Mode (ν_B) of 3-Bicyclo[3.1.0]hexanone

transition $\nu_B = n + 1 \leftarrow n$	obsd	calcd ^a
1 \leftarrow 0	77.56	77.59
2 \leftarrow 1	78.62	78.59
3 \leftarrow 2	79.78	79.67
4 \leftarrow 3	80.74	80.82
5 \leftarrow 4	81.84	82.00
6 \leftarrow 5	83.28	83.22
7 \leftarrow 6	84.80	84.70
8 \leftarrow 7	86.46	86.49
9 \leftarrow 8		91.29
10 \leftarrow 9		97.18

^a Using the potential energy function $V/\text{cm}^{-1} = 9.74(Z^4 + 2.698Z^3 + 15.512Z^2)$.

$$H = A[P_Z^2 + W(Z)]$$

where A is a scaling factor with the dimension of energy, Z is the reduced ring puckering coordinate, and both Z and the momentum P_Z are dimensionless. The potential energy $V(Z) = AW(Z)$ can then be expressed in the usual manner as a simple anharmonic function

$$V(Z) = A(Z^4 + BZ^3 + CZ^2)$$

where B and C are reduced potential constants. The Hamiltonian matrix was set up in a truncated harmonic-oscillator basis (50 functions proved sufficient) and diagonalized to obtain the vibrational energy levels. The required matrix elements of the reduced quantum mechanical operators P_Z and Z in the harmonic oscillator basis are readily derived from the commutation relations.²⁶ The ring bending potential function (cm⁻¹)

$$V(Z) = 9.74(Z^4 + 2.70Z^3 + 15.5Z^2)$$

was then obtained by fitting the observed vibrational transition wavenumbers using an iterative least-squares procedure devised by Lees.²⁷ The wavenumbers calculated using this function are also displayed in Table VII.

Apart from using the preferred assignment, we also checked alternatives, especially the completely reversed case having $\nu_B = 1 \leftarrow 0$ at 86.46 cm⁻¹ and the hot bands following successively to lower wavenumbers. Actually, it was possible to obtain convergence in this case as well giving

$$V(Z) = 6.83(Z^4 + 12.6Z^3 + 42.4Z^2)$$

with a root mean square deviation of 0.56 cm⁻¹ for the eight frequencies compared with 0.11 cm⁻¹ for the preferred assignment. This assignment seems unlikely in view of the arguments rehearsed above.

Discussion

The essentially r_s structure of 3-bicyclo[3.1.0]hexanone given in Table V clearly corresponds to the boat form, with the angle $\phi = 18.8^\circ$ and the angle $\tau = 66.9^\circ$ (see Figure 1). Thus the boat form has now been established as the predominant conformation in the gas phase for all of the bicyclo[3.1.0]hexane analogues so far studied. It is of interest to note that in all other bicyclo[3.1.0]hexane analogues studied the angle τ has been taken as 64° together with reasonable bond distances and angles in order to obtain the angle ϕ by fitting the rotational constants of each molecule. The value found for τ in 3-bicyclo[3.1.0]hexanone (66.9°) is very close to this value and presumably adds weight to the conclusions that ϕ lies in the range $35\text{--}50^\circ$ in all other cases. Thus it appears that while the dihedral angle τ between the three- and five-membered rings is sensibly invariant in these molecules, the angle ϕ for the five-membered ring is considerably smaller in 3-bicyclo[3.1.0]hexanone than for other members of the series. It has been pointed out that the preference for the boat conformation in these molecules arises from the fact that the hydrogen atom on carbon atom 1 (or 5) is staggered between the hydrogens of carbon atom 2 (or 4). In the case of 3-bicyclo[3.1.0]hexanone the replacement of a tetrahedral carbon atom at position 3 by a trigonal (carbonyl) carbon atom in the five-membered ring on its formation from bicyclo[3.1.0]hexane increases the ring-angle strain. The ring will therefore tend to become planar in order to relieve such strain and movement in this direction occurs but in so doing sacrifices some of the above-mentioned staggering until a new balance occurs when $\phi = 18.8^\circ$.

The remaining details of the molecular geometry can be compared with the precursor molecule cyclopent-3-enone and with cyclopropane. The addition of a CH_2 group to the $\text{C}=\text{C}$ double bond of cyclopent-3-enone to give 3-bicyclo[3.1.0]hexanone causes a change from trigonal to tetrahedral environments in the carbon atoms at positions 1 and 5 in the latter molecule. Consequently, the $\text{C}=\text{C}$ bond lengthens from 1.338 Å to 1.519 Å for the corresponding single bond, the $\text{C}_1\text{--C}_2$ bond lengthens from 1.509 Å to 1.534 Å (i.e., from essentially an $\text{sp}^2\text{--sp}^3$ length to an $\text{sp}^3\text{--sp}^3$ length), while the angle $\text{C}_5\text{C}_2\text{C}_1$ decreases from 112.43° to 108.94° and the angles $\text{C}_1\text{C}_2\text{C}_3$ and $\text{C}_2\text{C}_3\text{C}_4$ increase accordingly. It should be noted that the values $r(\text{C}_1\text{--C}_6) = 1.510$ Å, $r(\text{C}_1\text{--C}_5) = 1.519$ Å, $\angle\text{C}_1\text{C}_6\text{C}_5 = 60.38^\circ$, and $\angle\text{C}_6\text{C}_1\text{C}_5 = 59.81^\circ$ are close to the values $r(\text{C--C}) = 1.513$ Å and $\angle\text{CCC} = 60^\circ$ found in cyclopropane.

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Supplementary Material Available: Measured and calculated rotational transition frequencies for the ground state (Table S1), for excited states of the ring bending mode (Table S2), and for the ground state of four singly substituted isotopic species (Table S3) of 3-bicyclo[3.1.0]hexanone (5 pages). Ordering information is given on any current masthead page.

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