MICROWAVE ROTATIONAL SPECTRUM, ELECTRIC DIPOLE MOMENT AND GEOMETRY OF 2-BICYCLO[3.1.0] HEXANONE

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ABSTRACT

We report the microwave rotational spectrum of 2-bicyclo[3.1.0] hexanone in its vibrational ground state and in vibrationally excited states associated with the bending mode $\nu_{\rm B}$ of the five-membered ring. Variation of the rotational constants with $\nu_{\rm B}$ allows the conclusion that the five-membered ring is effectively planar although the mode $\nu_{\rm B}$ is governed by an asymmetric potential energy function. Measurement of the Stark effect in a number of transitions leads to the components $\mu_a = 3.28 \pm 0.02$ D and $\mu_b = 1.81 \pm 0.2$ D of the electric dipole moment.

INTRODUCTION

2-Bicyclo[3.1.0] hexanone results formally from the addition of a methylene group to the C=C bond of cyclopent-2-enone. The ring conformation, the nature of the ring bending vibration and the electric dipole moment of the latter molecule have been investigated in detail by using the techniques of microwave and far-infrared spectroscopy [1, 2]. Clearly, the investigation of 2-bicyclo[3.1.0] hexanone in a similar manner will reveal the effects that addition of a methylene group to cyclopent-2-enone has on these properties. Moreover, the corresponding isomeric pair, cyclopent-3-enone [3, 4] and 3-bicyclo[3.1.0] hexanone [5], have been investigated in detail and thus the present investigation completes a detailed analysis of four closely related molecules.

Accordingly, we report here the microwave rotational spectrum of 2bicyclo[3.1.0] hexanone in order to obtain information about the molecular conformation and the bending vibration of the five-membered ring. We have also measured the electric dipole moment of the molecule by means of the Stark effect.

EXPERIMENTAL

The sample of 2-bicyclo[3.1.0] hexanone was prepared according to the following scheme

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Tosyl chloride was added to cyclohexane-1,4-diol in pyridine to yield 4tosyloxycyclohexanol. The crude product was dissolved in acetone and acetic acid before addition of chromium trioxide. The mixture was stirred for half an hour, keeping the temperature between 15°C and 20°C. When all the 4-tosyloxycyclohexanol had dissolved, 4-tosyloxycyclohexanone was extracted with ether and dried over MgSO₄. The product was recrystallized from light petroleum. In the final stage of the synthesis, 4-tosyloxycyclohexanone in dioxan was added to a 50% dispersion of sodium hydride in oil. The mixture was refluxed for 3 h under nitrogen, then allowed to cool. 2-Bicyclo[3.1.0] hexanone was extracted and purified. Its purity and identity were confirmed through GLC and ¹H-NMR and ¹³C-NMR spectra.

Microwave rotational spectra were observed with a Hewlett-Packard 8460A spectrometer which employs Stark modulation at 33.33 kHz. Spectra were recorded in the frequency range 12–40 GHz with sample pressures in the range 10–50 mtorr at room temperature. The calibration of the spacing between the absorption cell walls and the central electrode necessary in the Stark effect measurements was carried out using the $J = 2 \leftarrow 1$ transition of ${}^{12}CH_{3}{}^{12}C\equiv {}^{12}CH$ [6] or the $J = 2 \leftarrow 1$ of ${}^{16}O{}^{12}C{}^{32}S$ [7].

RESULTS

Ground state rotational spectrum and assignment

2-Bicyclo[3.1.0] hexanone is an asymmetric rotor with an asymmetry parameter $\kappa = -0.39$. The rotational spectrum is very rich, showing strong μ_{a} , R-branch transitions accompanied to higher frequency by a series of vibrational satellites which was assigned as a progression in the bending mode of the five-membered ring, this being predicted to be the lowest energy vibration associated with the molecule. Transitions of the μ_a , Q-branch and μ_b , Q-branch type were also observed. The assignment of the spectrum involved the initial identification of a few μ_a , R-branch transitions by means of their Stark effects after approximate predictions in terms of a reasonable assumed geometry based on bond lengths and bond angles taken from the isomer 3-bicyclo[3.1.0] hexanone [5]. An initial set of ground state rotational constants was then readily obtained from the frequencies of these transitions by a least-squares analysis in the rigid rotor approximation. The constants so obtained were then used to predict the frequencies of higher $J \mu_a$, R- and Q-branch and μ_b , Q-branch transitions and further assignments accordingly made. Transitions allowed by μ_c were evidently too weak to be observed.

Observed frequencies of the assigned rotational transitions (shown in Table 1) were fitted in the semi-rigid approximation using the Watson-type analysis for centrifugal distortion [8] to give the rotational and centrifugal distortion constants displayed in Table 2.

Vibrational satellites

Each μ_a , *R*-branch transition is accompanied to high frequency by an extended vibrational satellite progression, as exemplified by the $7_{3,5}-6_{3,4}$ transition shown in Fig. 1. This progression, assigned to the bending mode v_B of the five-membered ring, originates at $v_B = 0$ and continues with successive excitation of this mode. Such an assignment is readily justified by a consideration of the related molecules 3-bicyclo[3.1.0]hexanone [5], cyclopent-2-enone [1], and cyclopent-3-enone [3, 4]. Observed rotational transition frequencies and their differences from those calculated in an analysis similar to that applied to the ground state are recorded in Table 3. For the states, $v_B = 1$ to 4, the number of transitions was insufficient for a full analysis and therefore frequencies were first corrected for the centrifugal distortion contribution appropriate to the corresponding transition in the ground state and a rigid rotor analysis applied. Rotational constants so determined are included in Table 2.

Relative intensity measurements [9] for a number of rotational transitions lead to the approximate value of $110 \pm 20 \text{ cm}^{-1}$ for both the vibrational separations $v_{\rm B} = 1 \leftarrow 0$ and $2 \leftarrow 1$.



Fig. 1. The $7_{3,3}-6_{3,4}$ transition of 2-bicyclo[3.1.0]hexanone showing the vibrational satellite progression in the mode $\nu_{\rm B}$.

Observed and	calculated rota	tional frequencies ((MHz) for the vibra	tional ground state	of 2-bicyclo[3,	1.0]hexanone	
Transition	Obs. froq.	Ohs. – calc.	Contrifugal distortion contribution	Transition	Obs, freq.	Obs. — calc.	Centrifugal distortion contribution
μa, R-branch				μ_a , Q-branch			
3,,1-2,0	15352.69	-0,15	-0.06	14,11-14,12	29049.91	-0.03	-1.64
3,,-2,,	14620.76	0,07	-0.05	16, 13-15,13	32006.89	-0.02	-2.07
43	17988,25	0.03	-0.05	16, 11-16, 11	30388,34	0.00	-2.20
41,3, .	17646.42	-0,06	-0,05	17, 17, 17, 14	33539.23	0.07	-2.82
41.3-91.3			0.07	18,13-18,14	31330.07	0.02	2.69
4,,,3,,	20834,62	0.01	-0.10	19,11-19,11	15620.21	0,09	0.39
51, -41,	21863.45	0.08	-0.10	20, 14-20, 14	31770.68	0,01	2.91
5, -4,			-0.14	21,21,	13580.26	0.04	1.20
5.1-4.2	26223,37	0'00	-0.16	24.16-24.17	30748.16	-0.02	-1.78
5.,-4,,	26402,80	-0,12	0,37	26.16-25.17	22948.10	0,01	1,68
5, -4,	24778,36	0,03	-0.20	26 _{10.16} -26 _{10.17}	14264.84	0.02	3.74
6.,5,,	26084.38	-0.03	-0.16	27 27	20376.02	0.02	3.69
61, -51,	26010,36	-0'05	-0.16	28 10. 16 - 28 10. 10	26960.49	0.02	2.48
61.5-51.4	29234,91	0.08	-0,23	29 to 10 - 29 to 10	33467.56	-0,06	-0.06
e, -5,	31362,04	-0.03	-0.26	30 _{11,19} -30 _{11,20}	24192,44	0.00	5.60
63,453,4	28370,16	0.15	-0.22	3111.20-3111.11	31163.37	0.05	3,50
6,5, .			0.30	32 _{11,20} -32 _{13,21}	21044.10	0,00	9,06
6,,,5,,	30046,39	0.11	-0,40	33,1,11-33,1,11	28262.76	0.00	7,95
6,,5,,			-0.41	34 n. 21 - 34 n. 22	17711.01	0.03	12.43
7.,,6.,	30169.83	-0'04	-0.25	35, 23-35, 23	24879.49	0.00	12.90
71.7-61.6	30140,81	0.07	-0.25	36,0, 20-36,0,4	32625.96	0,03	10.63
71,0-01,1	33227.05	0.01	0,34	3814.24-3814.24	28980.38	0.01	17.47
72, -02,	36150,09	0.04	-0.40	3911.24-3916.31	17643.69	0.00	21.96
7.,-6,,			-0.45	40,11,140,11,16	25074.75	0.01	24.37
76.	34420,99	00'0	-0.42				
8°."-7°.	34269.52	-0.05	-0,37	μ _b -Q branch			
8,7, ,	34258,69	-0.05	-0.37	364.21-3611.20	31872.83	-0,01	-23,32
8, ,7	37200.31	0.06	-0.48	37 14, 20 - 37 10, 24	33132.45	60'0-	-15.41
9,8, 1	38376,62	-0,02	-0.62	37 11.21 - 37 14.20	36464.56	-0.04	-41.42
				38,4,24-38,19,28	36466,94	0,01	8.45
				3811,23-3814,24	34291.09	0.06	34.95
				4016, 24-4010, 16	37683.86	0.04	-49.21

Rotational constants (MHz) and principal moments of inertia (amu A^2)^a for the $v_B = 0$ to $v_B = 4$ states and the centrifugal distortion constants (MHz) for the ground state of 2-bicyclo[3.1.0]hexanone

	$v_{\rm B} = 0$	1	2	3	4
A_v	4537.710(8)	4530.43(3)	4525,33(7)	4520.3(1)	4515.8(1)
B_n	2818,290(3)	2822.302(3)	2824.966(4)	2827.55(1)	2829.96(1)
C_v	2055.289(3)	2056,253(3)	2056.334(5)	2056.30(2)	2056.01(2)
I_a^{v}	111.3725	111.5514	111.6772	111.8014	111.9128
I,Ū	179.3201	179.0652	178.8963	178,7328	178,5806
Ĭ,	245.8905	245.7752	245.7655	245.7696	245.8043
Δ_J	0.00024(3)			-	
Δ_{JK}	0.00097(5)				
Δ_{R}	-0.00040(10)				
δ	0.000038(3)				
δ _K	0.00034(3)				

^aConversion factor, BI = 505 376 MHz amu A^2 .

Stark effect and electric dipole moment

The frequency shifts $\Delta \nu$ of the $M_J = 1$ Stark component of the $4_{2,2}-3_{2,1}$, $6_{3,4}-5_{3,3}$ and $7_{3,5}-6_{3,4}$ transitions and the $M_J = 2$ Stark component of the $5_{2,3}-4_{2,2}$ and $4_{2,2} \leftarrow 3_{2,1}$ transitions in 2-bicyclo[3.1.0] hexanone were found to be linear functions of E^2 , where E is the strength of the applied electric field. It was possible to measure $\Delta \nu$ over an appreciable range of E values for these components in unencumbered regions of the spectrum. The corresponding Stark coefficients $\Delta \nu/E^2$ are given in Table 4.

The displacements $\Delta \nu$ depend on each of the three components, μ_a , μ_b and μ_c , of the electric dipole moment since none can be set to zero by symmetry considerations. Consequently, we attempted to determine all three components simultaneously by a least-squares fit to the five Stark coefficients given in Table 4. The resulting values of μ_a , μ_b and μ_c were respectively 3.28 ± 0.02 D, 1.81 ± 0.2 D and a small imaginary value of μ_c with a very large error. Inspection of the equations of condition confirmed that the observed Stark coefficients are insensitive to the value of μ_c and this was accordingly set to zero in a final analysis which gave the results for μ_a , μ_b and calculated $\Delta \nu/E^2$ values shown in Table 4. Such an approach is further justified by geometrical arguments (see below) which indicate that μ_c will be close to zero.

Molecular conformation and geometry

While insufficient information is available from the present investigation for a complete determination of the molecular geometry of 2-bicyclo[3.1.0]hexanone, it is nevertheless possible to draw conclusions about the effective

Transition	Centrifugal	$v_{\mathbf{B}} = 1$		υ _B = 2		$v_{\rm B} = 3$		υ _B = 4	
	distortion contribution	Obs. freq.	Diff. ^a	Obs. freq.	Diff. ^a	Obs. freq.	Diff. ^a	Obs. freq.	Diff. ^a
4 _{1.3} -3 _{1.3}	-0.07	20516.56	0,02	I	I	I	I	ſ	1
4.,3,	-0.10	20865.35	-0,03	ł	1	1	I	I	1
5, -4,	-0.14	25058,56	0.03	25065,30	0.03	25070.87	-0,08	I	I
5, -4, .	-0.16	26257.88	0.03	26279.50	00'0	26300.25	0.09	I	I
6,5,	-0.23	29246.71	0,08	ł	I	*	I	ł	I
6, ⁵ .	-0.26	31395.93	-0.02	31416,13	00'0	31435.07	-0,01	32451.91	0,05
6,5,	-0.22	ł	j	28398,31	0,01	I	1	j	ł
65	0.30	29692.37	-0.06	29710,01	0.03	29726.33	0.03	ł	1
6,5,	-0.40	30088.16	-0.03	ł	I	1	ł	I	ł
6,5, ,	-0.41	29918.84	0.10	29940.84	0,03	29961.80	0.08	ł	1
7	0.25	30183.26	-0.05	I	I	ł	1	I	1
7, ,6, ,	-0.25	30155.04	-0.02	I	1	l	ł	1	ł
76.	-0.34	33237,16	0.05	1	1	I	I	ł	i
7, -6,	-0.40	36178.14	0.00	36192.88	0,04	36206.08	0.05	36216.87	-0'03
7, -6,	-0.45	36698.66	-0.02	36735.05	0.03	36769.88	60.0-	36801.89	-0.02
7, -6,	-0.42	34453.21	0,03	34470.28	-0,18	34486.23	-0.05	34499.34	0.01
8, -7,	-0.37	34286.14	-0.07	34287.23	0.04	1	1	1	ł
81, 1-71, 7	0.37	34274.88	0.11	ł	I	I	ł	ł	I
^a Difference effective rigi	between observed d rotor value.	frequency afte	er first corre	eting for the e	c.d. contribu	ution appropri	ate to grou	nd state and c	alculated

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TABLE 3

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Transition	M_J	Experimental	Calculated
4, -3, .	1	62.04	
********	2	-262.2	-259.3
5, -4.,	2	-33.19	33.56
6, -5, ,	1	23.58	23.91
7,6,	1	4.19	4.24
3,3 3,4	$ \mu_{\alpha} = 3.27 \pm 3.27$	0.02 D	
	$ \mu_b = 1.81 \pm$		
	$ \mu_{c} = 0.00$ (assumed, see text)	

Second order Stark coefficients $(\Delta \nu/E^2 \times 10^6)$ (MHz cm² V⁻²) and electric dipole moment components of 2-bicyclo[3.1.0]hexanone

conformation of the five-membered ring and, with reasonable assumptions about bond lengths and angles, we show that the ground rotational constants are consistent with an effectively planar conformation.

The conformation of 2-bicyclo[3.1.0] hexanone can be discussed in terms of the dihedral angles τ and ϕ defined in Fig. 2. The angle τ appears to be a transferrable property for molecules based on bicyclo[3.1.0] hexane [10] and hence we assume the value 66.9° from the closely related 3-bicyclo[3.1.0] hexanone [5]. Discussion of the conformation of 2-bicyclo-[3.1.0] hexanone then reduces to a discussion of the conformation of the five-membered ring.

The variation of the rotational constants $(g_v - g_0)$, where g = A, B or C, with v_B establishes that the five-membered ring is effectively planar. It is readily seen from Fig. 3, which shows plots of $|g_v - g_0|$ versus v_B , that points corresponding to $v_B \ge 1$ lie on a smooth curve but those for the state with $v_B = 0$ do not. This behaviour, which is also apparent in the vibrational satellite progression shown in Fig. 1, is characteristic of a ring bending mode governed by a double-minimum potential energy function with a barrier to the planar ring that is very low [11]. In the present case, where the potential function must be asymmetric, this behaviour is also consistent with a single minimum function that exhibits an inflection near to the zero point level. We conclude, therefore, that the five-membered ring is effectively planar, with a potential function having a small perturbation acting



Fig. 2. Definition of the dihedral angles τ and ϕ in 2-bicyclo[3.1.0]hexanone.



Fig. 3. Variation of the rotational constants $|g_v - g_o|$ (g = A, B and C) with the vibrational quantum number v_B .

Fig. 4. Calculated variation of rotational constants A, B and C with ϕ in 2-bicyclo-[3.1.0]hexanone when $r(C_1-C_2) = 1.470$ A (see Fig. 2 and text). Dashed lines indicate the observed values of A_0 , B_0 and C_0 .

predominantly on the zero-point level. Such a conclusion requires that μ_c is small or zero, as assumed in the preceding section.

The ground state rotational constants provide additional support for the conclusion that the five-membered ring is effectively planar. We assume all but two of the parameters required to define the geometry shown in Fig. 2 from standard values and the appropriate quantities of 3-bicyclo[3.1.0]hexanone [5], and bicyclo[3.1.0] hexane [12], as indicated in Table 5. The only parameters not assumed are those that are least predictable, that is $r(C_1-C_2)$ and the angle ϕ . We can set a probable upper limit to $r(C_1-C_2)$ of 1.529 Å, as assumed for $r(C_2-C_3)$ from 3-bicyclo[3.1.0] hexanone (Table 5) and a lower limit of 1.470 Å, as for the corresponding C-C bond of trans acrolein which is presumably shortened as a result of conjugation. Plots of $g_0 = A_0, B_0$ and C_0 versus ϕ were then made for various values of $r(C_1 - C_2)$ in the above range. The example when $r(C_1-C_2) = 1.470$ Å is shown in Fig. 4, in which the observed values of A_0 , B_0 and C_0 are also indicated. The value of ϕ thus obtained is 22 ± 8° but when larger values of $r(C_1-C_2)$ are used in a similar manner a much larger range of ϕ values results. We conclude therefore that the best value for $r(C_1-C_2)$ is 1.470 Å, under the above assumptions, and that the five-membered ring is undergoing large amplitude bending in the zero point state which, if governed by an asymmetric potential energy

Assumed bond lengths (A) and angles (degrees) for 2-bicyclo[3.1.0]hexanone

Quantity	Value	Source
Three-membered ring $r(C_1 - C_6) \doteq r(C_5 - C_6)$ $r(C_1 - C_5)$	1.510 1.519 66.9	3-bicyclo[3.1.0]hexanone ^a 3-bicyclo[3.1.0]hexanone ^a 3-bicyclo[3.1.0]hexanone ^a
all $r(C-H)$ $\angle C_6C_5H = \angle C_1C_5H = \angle C_4C_5H$	1.082 118.3	bicyclo[3.1.0]hexane ^b 3-bicyclo[3.1.0]hexanone ^a
Five-membered ring $r(C_1 - C_3)$	see text	
r(C ₂ C ₃)	1.529	
r(C ₃ C ₄)	1.541	standard value
$r(C_4 - C_5)$	1.534	↓ o
$\angle C_2 C_1 C_5 = \angle C_1 C_5 C_4$	108.9	o l
all other ring angles fixed by ring C–C distances and $\angle C_2C_1C_5 = \angle C_1C_5C_4^c$ all $r(C-H)$ \angle HCH	1.092 109.44	bicyclo[3.1.0]hexane ^b bicyclo[3.1.0]hexane ^b
Carbonyl group r(C=O)	1.210	3-bicyclo[3.1.0]hexanone ^a

^aRef. 5. ^bRef. 12. ^cAngles assumed independent of ϕ .

function with a low barrier or an inflection, slightly favours the bent form, leading to a small positive effective value of ϕ .

The above results, for $r(C_1-C_2)$ and ϕ can be rationalized if we assume that the cyclopropyl ring in 2-bicyclo[3.1.0] hexanone behaves like a π -bond in the 1-5 position. Conjugation across the C_1-C_2 bond then leads to a value of $r(C_1-C_2)$ similar to that in *trans*-acrolein, for example, and would tend to favour a planar five-membered ring.

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