The Microwave Spectrum, Dipole Moment, and Conformation of Bicyclo[3.1.0]hexane

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Abstract: The microwave spectrum of bicyclo[3.1.0]hexane has been studied in the range 26.5–40.0 GHz (R band) with a Hewlett–Packard Model 8400 Stark-modulated microwave spectrometer. The rotational constants (MHz) for the ground vibrational state have been determined to be $A = 5542.955 \pm 0.014$, $B = 4236.818 \pm 0.007$, and $C = 3127.040 \pm 0.007$ from a least-squares fit to 22 lines including both a- and c-type low-J R-branch transitions. Model calculations indicate that the data are consistent with the boat conformation of the molecule. From the analysis of the Stark effect, the dipole moment components have been determined to be $|\mu_a| = 0.093 \pm 0.001$ D and $|\mu_c| = 0.168 \pm 0.002$ D yielding a total dipole moment $\mu = 0.192 \pm 0.003$ D.

There has been considerable research activity in recent years concerning the determination of the conformations and low-frequency vibrational modes of ring molecules by far-infrared, Raman, and microwave spectroscopy.[1,2] Part of this activity has concerned the low-frequency vibrations and conformations of some analogs of bicyclo[3.1.0]hexane.[3-7] These have included 6-oxabicyclo[3.1.0]hexane,[3,4] 3-oxabicyclo[3.1.0]hexane,[5,7] 3,6-dioxabicyclo[3.1.0]hexane,[5,6] and the parent hydrocarbon, bicyclo[3.1.0]hexane.[5] There have also been several nmr[8,9] and dipole moment[10] studies as well as an X-ray diffraction[11] investigation of derivatives of bicyclo[3.1.0]hexane, all of which have been consistent with the boat conformation as the stable form for these molecules. The similarity of the far-infrared spectra of the bicyclo[3.1.0]hexane analogs[3,5] was offered as indirect evidence that all four existed in the same conformation. Microwave studies of 6-oxabicyclo[3.1.0]hexane[4] and 3,6-dioxabicyclo[3.1.0]hexane[6] as well as a determination of the dipole moment of the latter in benzene solution (2.50 D)[5] clearly indicated the boat form for these molecules. Subsequently, a microwave study of 3-oxabicyclo[3.1.0]hexane was found to be consistent with the boat conformation.[7]

Since bicyclo[3.1.0]hexane was the parent hydrocarbon for this series of molecules, it was desirable to obtain direct evidence of the conformation and consequently this microwave study was undertaken. Of further interest, due to its small magnitude, would be a

reliable value of the electric dipole moment which may be compared to the dipole moments of other slightly polar molecules. This may be obtained by analysis of the Stark effect in the microwave spectrum and is not subject to some of the difficulties which may arise in determining small dipole moments by other techniques.[12]

Experimental Section

The bicyclo[3.1.0]hexane used in this study was a portion of the same sample used in the previous far-infrared study and was synthesized from cyclopentene by the Simmons–Smith procedure.[13,14] The sample was purified by distillation through a column packed with glass helicies. A gas chromatogram and nmr spectrum revealed an impurity of ∼0.5% cyclopentene. The sample was used without further purification.

The microwave spectrum was obtained with a Hewlett–Packard Model 8400C Stark modulated spectrometer operating in the R-band region (26.5–40.0 GHz). Due to the small dipole moment of bicyclo[3.1.0]hexane, it was not practical to run fast scans of the spectrum, which have proved so useful in the past for the initial assignment of "large" molecules.[15] The intensity (or lack thereof) of the spectrum required packing the waveguide in Dry Ice which increased the intensity of the ground state spectrum by depopulating vibrationally excited states and also increased the intensity of the low-J transitions. It was also necessary to use a high amplifier gain and consequently a long time constant to obtain an acceptable signal-to-noise ratio so that rather slow sweeping of the spectrum was required (50–100 MHz/hr). The Stark effect measurements were made using methylacetylene ($\mu = 0.7835$ D) and carbonyl sulfide ($\mu = 0.7152$ D) as standards to calibrate the Stark cell. The calibration measurements were made at each voltage setting used in the experimental measurements and on the same day, as near as possible in time to the experimental measurements in order to minimize drift.

Assignment of the Spectrum

The spectrum is quite similar in many respects (intensity excepted) to the spectra previously reported for 6-oxabicyclo[3.1.0]hexane[4] and 3,6-dioxabicyclo[3.1.0]hexane,[6] in that the stronger lines are c-type Q branches for a highly asymmetric rotor. These are ${}^{c}Q_{1,0}$ and ${}^{c}Q_{1,-2}$ transitions, many of which exhibit first-order Stark effects. The assignment of $K_{-1} \rightarrow$

(1) C. S. Blackwell and R. C. Lord, "Vibrational Spectra and Structure," J. R. Durig, Ed., Marcel Dekker, New York, N. Y., 1973, and references cited therein.

(2) J. Laane, "Vibrational Spectra and Structure," J. R. Durig, Ed., Marcel Dekker, New York, N. Y., 1973.

(3) L. A. Carriera and R. C. Lord, *J. Chem. Phys.*, **51**, 2735 (1969).

(4) W. J. Lafferty, *J. Mol. Spectrosc.*, **36**, 84 (1970).

(5) R. C. Lord and Thomas B. Malloy, Jr., *J. Mol. Spectrosc.*, **46**, 358 (1973).

(6) R. A. Creswell and W. J. Lafferty, *J. Mol. Spectrosc.*, **46**, 371 (1973).

(7) Thomas B. Malloy, Jr., *J. Mol. Spectrosc.*, in press.

(8) P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965); P. K. Freeman, F. A. Raymond, and M. F. Grostic, *ibid.*, **32**, 24 (1967); P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *ibid.*, **33**, 1448 (1968).

(9) S. Winstein, E. C. Frederick, R. Baker, and Y. Lin, *Tetrahedron*, **58**, 621 (1966).

(10) J. J. McCullough, H. B. Henbest, R. J. Bishop, G. M. Glover, and L. E. Sutton, *J. Chem. Soc.*, 5496 (1965).

(11) M. F. Grostic, D. J. Duchamp, and C. G. Chidester, *J. Org. Chem.*, **36**, 2929 (1971).

(12) See, for example, the comparison of the dipole moment of cyclohexene (0.331 D), determined from the microwave spectrum, L. H. Scharpen, J. E. Wollrab, and D. P. Ames, *J. Chem. Phys.*, **49**, 2368 (1968), to those determined by other techniques (0.28–0.76 D).

(13) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

(14) R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

(15) See, for example, T. Ikeda, R. Kewley, and R. F. Curl, Jr., *J. Mol. Spectrosc.*, **44**, 459 (1972), and references cited therein.

$K_{-1} + 1$ Q branches for several values of J beginning with $J = 9$ then allowed us to predict the positions of the weaker a-type $^aQ_{0,-1}$ and $^aQ_{+2,-1}$ lines, and these were subsequently found. Since the Q-branch assignment fixes only two linear combinations of the three rotational constants, it was then necessary to find the somewhat weaker R-branch transitions. One is then faced with the problem that only very few c-type R-branch transitions with appreciable intensity are predicted in the range of the spectrometer. Many more a-type transitions, with somewhat greater line strengths, are expected but are weak due to the small a component of. the dipole moment. The Q-branch fit allows one, however, to fix, quite closely, the frequency difference between certain R-branch transitions, among these the $3_{30} \leftarrow 2_{20}$ and $3_{31} \leftarrow 2_{21}$ transitions, and this facilitated their assignment. This turned out to be more fruitful than the more common procedure of looking for lines with resolved Stark effects since the Stark lobes were not prominent in some of the somewhat noisy survey scans. This assignment allowed the prediction of the positions of the remaining low-J R-branch transitions. In Table I are indicated

Table I. Rotational Lines Used in the Determination of the Rotational Constants (MHz) for Bicyclo[3.1.0]hexane

		a-type			c-type	
Transition	Obsd, MHz	Obsd − calcd, MHz	Transition	Obsd, MHz	Obsd − calcd, MHz	
$4_{04} \leftarrow 3_{03}$	26748.10	+0.07	$3_{12} \leftarrow 2_{02}$	27362.41	+0.07	
$4_{14} \leftarrow 3_{13}$	26577.31	+0.09	$3_{22} \leftarrow 2_{12}$	29339.37	+0.05	
$4_{31} \leftarrow 3_{21}$	38546.16	−0.04	$3_{21} \leftarrow 2_{11}$	27973.74	+0.06	
$4_{13} \leftarrow 3_{12}$	30312.35	+0.07	$3_{31} \leftarrow 2_{21}$	31646.75	−0.04	
$4_{23} \leftarrow 3_{22}$	29075.87	+0.03	$3_{30} \leftarrow 2_{20}$	31316.32	+0.02	
$4_{22} \leftarrow 3_{21}$	31750.60	+0.09	$4_{13} \leftarrow 3_{03}$	37079.70	−0.01	
$4_{32} \leftarrow 3_{31}$	30114.15	+0.07	$4_{23} \leftarrow 3_{13}$	38238.34	0.00	
$5_{05} \leftarrow 4_{04}$	32940.86	−0.05	$4_{22} \leftarrow 3_{12}$	36354.53	−0.06	
$5_{15} \leftarrow 4_{14}$	32886.70	+0.01				
$5_{14} \leftarrow 4_{13}$	36619.53	−0.03				
$5_{24} \leftarrow 4_{23}$	35797.67	−0.09				
$5_{33} \leftarrow 4_{32}$	37504.15	−0.11				
$5_{42} \leftarrow 4_{41}$	37840.80	−0.02				
$5_{41} \leftarrow 4_{40}$	38078.61	−0.06				

$$A = 5542.96$$
$$B = 4236.82$$
$$C = 3127.04$$
$$\kappa = -0.0812771$$

the 14 a-type and 8 c-type R-branch transitions which were then used to determine the rigid rotor constants. The lines are quite sharp and for the most part are accurate to ±0.05 MHz. The probable errors in the rotational constants determined by least-squares fitting to the lines in Table I are ±0.01 MHz or less. The Q-branch transitions, which proved to be so useful in the initial assignment, are rather high J lines and were not included in the final fit for determining the rigid rotor constants in order to minimize the effect of centrifugal distortion.

Stark Effect and Dipole Moment

In order to determine the dipole moment of bicyclo-[3.1.0]hexane, a search was made for lines which exhibited second-order Stark effects. The $4_{22} \leftarrow 3_{12}$ transition was satisfactory and the $|M| = 3$ and 2 lobes

were followed from 2000 V/cm to ∼4000 V/cm in 200-V/cm steps. At 4000 V/cm the $|M| = 1$ lobe is less than 2 MHz from the zero-field line and the $|M| = 0$ lobe has not yet appeared. Consequently, only the $|M| = 3$ and 2 lobes were used. Examination of the dependence of the second-order Stark effect on the dipole moment components calculated in the standard manner[16] revealed, however, that the Stark effect for the $4_{22} \rightarrow 3_{12}$ transition was very insensitive to the a component. It was possible, however, to set an upper limit of 0.17 D on the magnitude of μ_c. In order to determine the smaller a component it was necessary to measure the Stark effect of a transition with nearly degenerate energy levels coupled by μ_a. This severely limits the choice of transitions. The $3_{31} \leftarrow 2_{21}$ transition was found to be suitable, the 2_{21} level being ∼467 MHz from the 2_{20} level and the 3_{31} level ∼136 MHz from the 3_{30} level. The interaction between the latter pair is the more important in determining the Stark effect for the transition. The necessary coefficients for the degenerate Stark effect for this transition were then calculated using a computer program originally written by R. A. Beaudet with modifications by W. H. Kirchhoff. In Table II are indicated the dipole mo-

Table II. Stark Coefficients $(\Delta\nu/E^2) \times 10^6$ (MHz cm²/V²) and Dipole Moment Components of Bicyclo[3.1.0]hexane

Transition	$|M|$	Exptl	Calcd
$4_{22} \leftarrow 3_{12}$	3	+0.468 ± 0.024	+0.469
	2	+0.209 ± 0.006	+0.208
$3_{31} \leftarrow 2_{21}$	2	Each of 3_{31} and 2_{21} interact with	
	1	another level with a μ_a	
		connector	
$|\mu_a|$ = 0.093 ± 0.001 D			
$|\mu_c|$ = 0.168 ± 0.002 D			
μ_{tot} = 0.192 ± 0.003 D			

ment components determined from the analysis of the Stark effect for these two transitions. The values $|\mu_a| = 0.093 \pm 0.001$ D and $|\mu_c| = 0.168 \pm 0.002$ D yield a total dipole moment $\mu = 0.192 \pm 0.003$ D.

Table III indicates the dipole moments of some selected hydrocarbons for the purpose of comparison. All of these cited are dipole moments determined for the molecules in the gas phase from microwave studies. The rather wide range (0.083–0.67 D) should prove fruitful as test cases for future theoretical considerations.

Model Calculations and Conformation

While it would be desirable to be able to do a complete structural determination by isotopic substitution,[17] the weakness of the spectrum precludes observation of different isotopic species in natural abundance and the cost and synthetic difficulties in preparing isotopically enriched samples are great. Alternatively, judicious choice of some structural parameters from similar molecules allows one to determine some of the salient features of the structure, in this case, the conformation. In general, the assumption of the invari-

(16) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

(17) For a description of the types of molecular structure which may be obtained from microwave data see, for example, W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Wiley-Interscience, New York, N. Y., 1970.
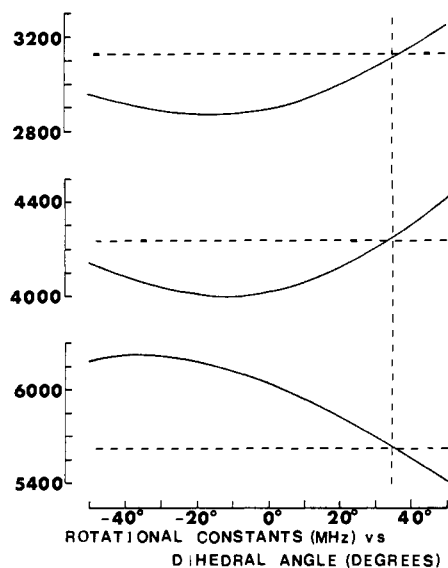
Figure 1. Calculated rotational constants as a function of $\tau = 180° - \angle(1245)-(234)$ for bicyclo[3.1.0]hexane. Positive values correspond to the boat conformation and negative values to the chair conformation.

Figure 2. Projection in the molecular symmetry plane. The orientation of the a and c principal axes is indicated as well as the value of τ.

Table III. Dipole Moments of Some Selected Hydrocarbons

Molecule	μ, D	Ref
Propane	0.083	a
Propene	0.364	b
Bicyclo[1.1.0]butane	0.67	c
Methylcyclopropane	0.139	d
Methylenecyclopropane	0.402	e
Methylenecyclobutane	0.514	f
Methylenecyclopentane	0.60	g
Cyclopropene	0.454	h
Cyclobutene	0.132	i
Cyclopentene	0.22	j
Cyclohexene	0.331	k
Bicyclo[3.1.0]hexane	0.192	This work

[a] D. R. Lide, *J. Chem. Phys.*, **33**, 1514 (1960). [b] D. R. Lide and D. E. Mann, *ibid.*, **27**, 868 (1957). [c] M. D. Harmony and K. Cox, *J. Amer. Chem. Soc.*, **88**, 5049 (1966). [d] R. G. Ford and R. A. Beaudet, *J. Chem. Phys.*, **48**, 4671 (1968). [e] V. W. Laurie and W. M. Stigliani, *J. Amer. Chem. Soc.*, **92**, 1485 (1970). [f] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **49**, 3031 (1968). [g] J. R. Durig, Y. S. Li, and L. A. Carreira, *ibid.*, **57**, 1896 (1972). [h] P. H. Kasai, R. J. Meyers, D. F. Eggers, and K. B. Wiberg, *ibid.*, **30**, 512 (1959). [i] H. Kim and W. D. Gwinn, *ibid.*, **42**, 3728 (1965). [j] G. W. Rathjens, *ibid.*, **36**, 2401 (1962); S. S. Butcher and C. C. Costain, *J. Mol. Spectrosc.*, **15**, 40 (1965). [k] Reference 12.

ance of bond distances among similar molecules is a better assumption than invariance of bond angles. The assumption of the bond distances in bicyclo[3.1.0]-hexane is sufficient to allow the other structural parameters (other than the hydrogen atom parameters) to be determined by reproducing the experimentally determined rotational constants. In Table IV are indicated the assumed bond distances and hydrogen atom parameters. The remaining parameters consist of the $C_2C_3C_4$ angle (α) and the angles $\beta = \angle(C_1C_5C_6)-(C_1C_2C_4C_5)$ and $\tau = 180° - \angle(C_1C_2C_4C_5)-(C_2C_3C_4)$.

Two approaches have been followed in order to demonstrate that the rotational constant data do, in fact, determine the conformation and that the structures derived are self-consistent for the series of bicyclo-[3.1.0]hexane analogs. In the first of these, it is noted that the quantity $2P_b = I_a + I_c - I_b$ depends only on
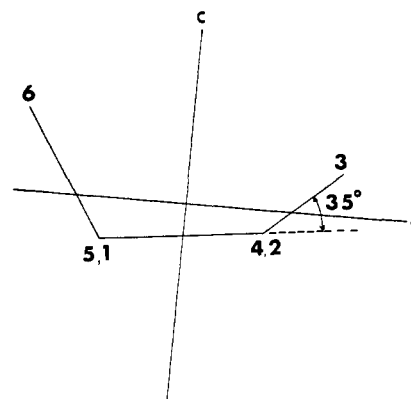
Table IV. Structural Parameters Used to Calculate the Rotational Constants for Bicyclo[3.1.0]hexane Analogs

	A	B	C	D
r_{12}, Å	1.53	1.53	1.513	1.513
r_{23}, Å	1.53	1.41	1.53	1.41
r_{15}, Å	1.513	1.513	1.471	1.471
r_{16}, Å	1.513	1.513	1.436	1.436
$r_{1H} = r_{6H}$, Å	1.082	1.082	1.082	1.082
$r_{2H} = r_{3H}$, Å	1.092	1.092	1.092	1.092
$\angle HC_2H = HC_3H$	109°28'	109°28'	109°28'	109°28'
$\angle HC_6H$	116°	116°		

the atomic masses and the distance of the atoms from the symmetry plane. It is almost independent of β and τ and the $\angle C_2C_3C_4$ was adjusted to reproduce the experimental value (a conversion factor of 5.05376 $\times$ 10^5 MHz amu Å^2 was used in computing moments of inertia[17]). The $C_2C_3C_4$ angle (108.5°) was then kept fixed, β was fixed at 116°, and the rotational constants calculated for a grid of values of the angle τ. As τ varied, the methylene hydrogens, assumed to share a common bisector with the adjacent ring angles, were moved to preserve the H–C–H angle and the common bisector. The resulting values of the rotational constants as a function of τ are plotted in Figure 1, where positive values of τ correspond to the boat conformation and negative values of τ to the chair conformation. As may be seen from the figure, a value of +35° for τ (Figure 2) best reproduces the experimental rotational constants shown as dashed horizontal lines in Figure 1. As may also be seen, the calculated values of the rotational constants for the negative values of τ (chair conformation) are clearly not consistent with the experimental values.

It should be noted that the existence of a metastable chair form cannot be ruled out on the basis of the microwave data alone; indeed, weak rotational transitions corresponding to this conformer could easily be missed. However, the far-infrared data are consistent with a single stable conformer for bicyclo[3.1.0]hexane but do
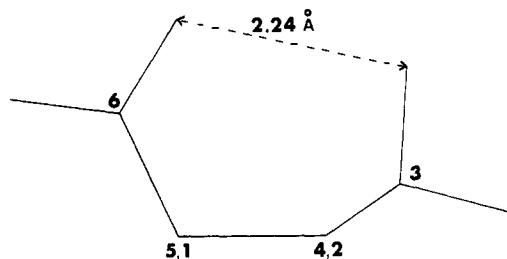
Figure 3. Projection in the molecular symmetry plane indicating the distance between the endo hydrogens on atoms 3 and 6.

not yield directly the identity of this conformer.[5] In this case, the far-infrared and microwave studies are truly complementary.

Tables IV and V summarize the assumed structural

Table V. Structural Parameters Varied to Reproduce the Rotational Constants for Bicyclo[3.1.0]hexane Analogs

Molecule	$\alpha,^a$ deg	$\tau,^b$ deg	$\beta,^c$ deg
Bicyclo[3.1.0]hexane	108.5	35	(116)
3-Oxabicyclo[3.1.0]hexane	111.5	42	(116)
6-Oxabicyclo[3.1.0]hexane	108.5	40	(116)
3,6-Dioxabicyclo[3.1.0]hexane	112	41	(116)

^{a} $\alpha = \angle 234°$; α was chosen to reproduce $2P_b = I_a + I_c - I_b$. ^{b} $\tau = 180° - \angle(1245)-(234)$; τ was varied to reproduce the experimental rotational constants for the given value of α and β assumed equal to 116°. ^{c} $\beta = \angle(165)-(1245)$; β was fixed at 116°.

parameters and the values of α and τ which best reproduce the rotational constants for bicyclo[3.1.0]hexane, 3-oxabicyclo[3.1.0]hexane, 6-oxabicyclo[3.1.0]hexane, and 3,6-dioxabicyclo[3.1.0]hexane. Of particular note are the similarity of the C_2-C_3-C_4 angles (111.5 and 112°) and the $C_2C_3C_4$ angles (108.5° for both bicyclo[3.1.0]hexane and the 6-oxa derivative) which were varied to reproduce $2P$. There is also an interesting trend in the values of τ derived for the four molecules. The three oxygen-containing molecules have values of τ ranging from 40–42° while the hydrocarbon has a smaller value of 35°. There are rather large uncertainties in the values of τ derived from the rotational constants, primarily due to the rather arbitrary assumption of $\beta = 116°$, since the values of these angles are rather highly correlated. It is primarily the distance between atoms 3 and 6 to which the rotational constants are sensitive. Although the uncertainties in τ are rather large, this smaller value of τ for bicyclo[3.1.0]hexane is undoubtedly due to a real difference in the structure of this molecule compared to the other three. This is illustrated in Figure 3 where the distance between the endo hydrogens on atoms 3 and 6 is indicated as 2.24 Å for $\tau = 35°$ compared to 2.4 Å as the sum of the van der Waals radii. For $\tau = 40°$ this distance would be 2.09 Å. Of the four molecules, this small transannular distance between protons is possible only in the case of the hydrocarbon. Previously, Creswell and Lafferty pointed out that for $\tau = 41°$, which best reproduced the rotational constant data, the oxygen–oxygen distance in 3,6-dioxabicyclo[3.1.0]hexane was 2.66 Å compared to a sum of van der Waals radii of 2.8 Å.[6] It is thus seen that this smaller value of τ for bicyclo[3.1.0]hexane is quite consistent.

The stability of the boat form over that of the chair conformation is apparently due to the fact that, in contrast to cyclohexane analogs, in the chair form, the hydrogen on atom 1 (or 5) is eclipsed by one of the methylene hydrogens on atom 2 (or 4). On the other hand, in the boat form, this hydrogen on atom 1 (or 4) is staggered between the two adjacent methylene hydrogens. Thus, in bicyclo[3.1.0]hexane, a balance is struck in achieving the preferred staggered conformation about the 1–2 (and 4–5) bond while maintaining a reasonable contact distance between the endo hydrogens on atoms 3 and 6.

The second approach to adjusting the parameters α, β, and τ to reproduce the rotational constants assumes that the boat conformation has been established as the stable form and then proceeds using a linear least-squares iteration on α, β, and τ, simultaneously. The procedure used is "diagnostic least squares"[18] which avoids some of the difficulties encountered in ordinary least squares and is briefly outlined below. The reader is referred to ref 18 for a more complete description and for examples of other types of applications.

The values of α, β, and τ were initially estimated as 110 ± 3, 116 ± 5, and $40 \pm 10°$ for each of the four bicyclo[3.1.0]hexane analogs where the uncertainties were estimated as 90% confidence limits (Table VI). These parameters were used to define a new set of parameters which have equal uncertainties

$$z_j = \Delta p_j / \sigma_j \qquad (1)$$

where Δp_j = the correction to the jth adjustable parameter and σ_j = the length of the uncertainty interval for the jth parameter/3.290 (i.e., 90% confidence). The Jacobian matrix elements are computed

$$J_{ij} = (\partial x_i / \partial z_j) = \sigma_j (\partial x_i / \partial p_j) \qquad (2)$$

where x_i = ith experimentally determined quantity. The derivatives of the rotational constants with respect to α, β, and τ were obtained numerically for each of the four molecules.

In ordinary linear least squares the matrix of coefficients of the normal equations $\mathbf{J^tJ}$ (t denotes matrix transpose) is inverted and used to compute the shifts in the parameters

$$\mathbf{z} = (\mathbf{J^tJ})^{-1} \mathbf{J^t \Delta x} \qquad (3)$$

where Δx is the error vector (obsd − calcd).

If the number of adjustable parameters, p_j, exceeds the number of experimentally determined quantities, x_i, or if some linear combinations of the parameters are not well determined by the experimental data, then $\mathbf{J^tJ}$ may be singular or nearly so. In this case, the matrix inversion leading to eq 3 may not be possible. However, as pointed out by Curl,[18] some linear combinations of the parameters are determined by the data. The matrix of coefficients of the normal equations may be diagonalized by an orthogonal transformation, $\mathbf{T}$.

$$\mathbf{T^tJ^tJT} = \Lambda \qquad (4)$$

As a result of the parameter scaling (eq 1), the size of a particular eigenvalue reflects how well determined is that linear combination of z_j described by the corresponding

(18) R. F. Curl, Jr., J. Comput. Phys., 6, 367 (1970), and references cited therein.

Table VI. Parameters Varied in Least-Squares Iteration Procedure for Bicyclo[3.1.0]hexane Analogs·

Molecule	Assumed values and estimated uncertainties			"Improved" values		
	α, deg	τ, deg	β, deg	α, deg	τ, deg	β, deg
Bicyclo[3.1.0]hexane	110 ± 3	40 ± 10	116 ± 5	107.9	38.0	117.0
3-Oxabicyclo[3.1.0]hexane	110 ± 3	40 ± 10	116 ± 5	111.3	40.7	115.5
6-Oxabicyclo[3.1.0]hexane	110 ± 3	40 ± 10	116 ± 5	108.6	40.7	115.7
3,6-Dioxabicyclo[3.1.0]-hexane	110 ± 3	40 ± 10	116 ± 5	112.8	39.3	116.1

eigenvector. The shifts in the original parameters are then computed from

$$\Delta p_j = \sigma_j \sum_k T_{jk} \frac{1}{\lambda_k} \sum_l \sum_m T_{lk} J_{ml} \Delta x_m \qquad (5)$$

where m runs up to the number of experimentally determined quantities, l runs up to the number of adjustable parameters, k runs over only those values for which $\lambda_k > \sigma^2$, and σ^2 = the variance of the experimentally determined quantities.

If the index k runs over all the possible values (*i.e.*, all the $\lambda_k > \sigma^2$), then keeping in mind that one may invert J^tJ by diagonalizing, inverting the eigenvalues, and then performing the inverse of the transformation indicated in eq 4, it is seen that eq 5 and 3 are equivalent. The difference comes when one or more $\lambda_k \leq \sigma^2$, for then that eigenvector is not used in computing the parameter shifts.

In the case of each of the four bicyclo[3.1.0]hexane analogs, one of the three eigenvalues was smaller than the estimated variance and only the two eigenvectors corresponding to the larger eigenvalues were used as indicated in eq 5. A new set of rotational constants was computed with the adjusted parameters. The improved values of α, β, and τ for each molecule are indicated in Table VI. After this one cycle of the linear least-squares iteration, the rms deviation of the rotational constants has decreased from $\sim$60 to $\sim$7.5 MHz.

The residual rms deviation is due to the fact that by excluding the summation over the one value of k for which $\lambda_k < \sigma^2$, one has effectively fit the three rotational constants for each molecule with two adjustable parameters. The two adjustable parameters are linear combinations of the three original parameters α, β, and τ. A second iteration yields changes of the order of 0.01° in α, β, and τ and changes of the order of 0.1–1.0 MHz in the calculated rotational constants. This is well within the noise level of the calculations.

Illustrated by the values of β and τ (Table VI) is that which was stated earlier concerning the correlation of the values of these two angles. The value of τ derived for bicyclo[3.1.0]hexane in this fashion is 38°, somewhat greater than by the other procedure, but this is some-
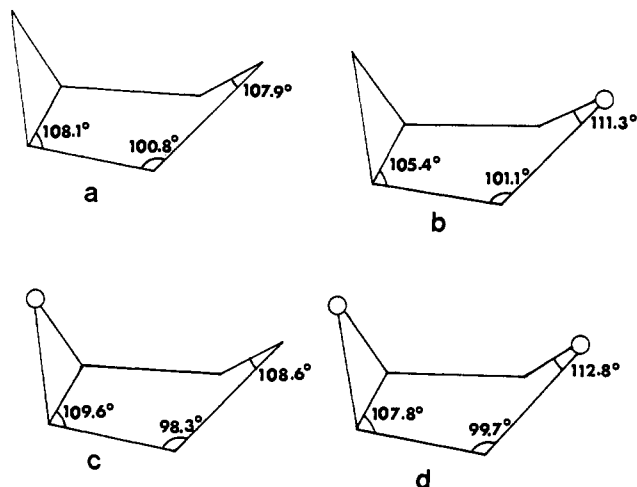

Figure 4. Ring angles for the structures which reproduce the rotational constants: (a) bicyclo[3.1.0]hexane, (b) 3-oxabicyclo[3.1.0]hexane, (c) 6-oxabicyclo[3.1.0]hexane, (d) 3,6-dioxabicyclo[3.1.0]hexane.

what compensated by an increase of $\sim$1° in β so that the H–H transannular contact distance is 2.20 Å for this structure. In contrast, the values of τ for the other molecules ranged from 39.3 to $\sim$40.7° while β ranged from 115.5 to 116.1°. The values of α were within 0.6° of the values derived previously by fitting $2P_b$.

While the value of τ is highly correlated with β, this is not true of the other bond angles. Assuming uncertainties of ±0.01–0.02 Å in the assumed bond distances and ±5° in the values of β and τ yields uncertainties of typically ±2–3° in the other ring angles. The values of some of the ring angles for the structure derived by the least-squares iteration are shown in Figure 4. It is noted that all the angles in the five-membered ring are near their "unstrained" values with the exception of the C_1–C_2–C_3 and $C_2C_4C_5$ angles which are $\sim$10° smaller. Examination of the angles indicates that the ring strain is similar in these molecules.