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Theoretical and Microwave Spectroscopic Characterization of Cyclobutenone: Planar or Puckered?

Michael J. Carrillo, Dinesh Marasinghe, Erik B. Feeley, Kristin M. Sobie, Rourke J. Zarzycki, Kevin Carter-Fenk, Christopher J. Fenk, and Michael J. Tubergen*

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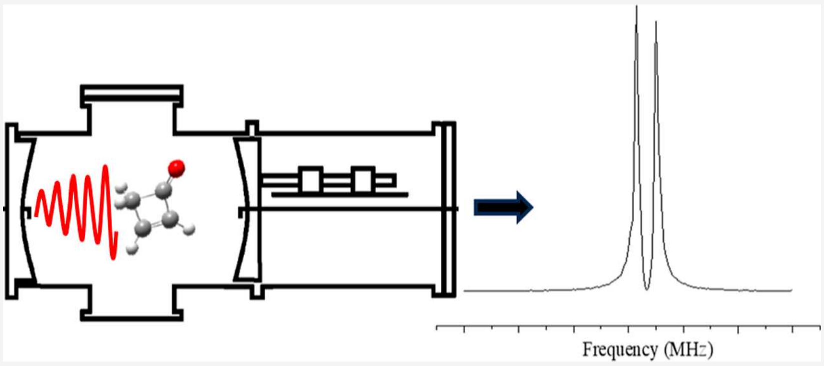

ABSTRACT: Cyclobutenone was characterized by high-resolution Fourier transform microwave spectroscopy for the first time. High-level, first-principles quantum chemical calculations at the B3LYP, CISD, MP2, and CCSD levels of theory were implemented to better understand the molecular structure and obtain model rotational and centrifugal distortion constants to aid in spectral assignment, and the results at the different levels of theory are compared. The assignment of the experimental spectrum provided fits of 2.7 kHz using Watson *A*-reduced and Watson *S*-reduced Hamiltonians. No tunneling splittings were observed, suggesting that cyclobutenone is not undergoing ring-puckering tunneling.

1. INTRODUCTION

Cyclobutane is a cyclic four-membered ring that belongs to the cyclic alkane family. It is one of the most ring-strained cyclic alkanes (26.3 kcal/mol), second only to cyclopropane (27.5 kcal/mol).[1] Ring strain favors a planar ring conformation with D_{4h} symmetry for cyclobutane, but torsional forces cause the heavy-atom ring to exist in two energetically equivalent nonplanar (puckered) conformations with a D_{2d} symmetry as shown in Figure 1. Spectroscopic studies of cyclobutane reported tunneling splittings that arise from its symmetric double well potential, which has an inversion barrier estimated to be 371−518 cm^{-1} and a puckering angle of 29.5°.[2,3] When cyclobutane is monosubstituted with a functional group (e.g., $-OH$, $-NH_2$, $-CN$, $-COOH$), the group may be axial and/or equatorial.[4−12] Monosubstitution also eliminates the symmetric double well potential, and tunneling splittings are not observed for these species. When a cyclobutane derivative has a π-bond involving a ring carbon, the ring may have either a puckered or planar orientation, as observed with cyclobutanone and cyclobutene, respectively.[13−15] There are not enough experimental data for cyclic, four-membered rings with two π-bonds, such as cyclobutenone, to predict if the preferred ring structure is planar, quasi-planar, or puckered.

Synthesizing cyclobutenone (c-bone) has been attempted since the 1950s.[16−18] Cope and co-workers first reported c-bone as a byproduct in their synthesis with the observation of two carbonyl bands in their infrared spectra.[17] Vogel and co-workers expanded on this by isolating c-bone from the pyrolysis of cyclobutenone dimethyl ketal, which, if treated with aqueous acid, would produce a mixture of 3 cyclobutyl compounds, which provided evidence that c-bone could be isolated from the Cope experiment.[16,17,19] In 1971, Sieja et al. successfully synthesized c-bone by two independent routes from allene and ketene.[18] Since then, there have been more complex synthetic routes for the synthesis of c-bone.[20,21]

High-resolution Fourier transform microwave (FTMW) spectroscopy is a gas phase technique that provides the most precise structural information about the molecule of interest.

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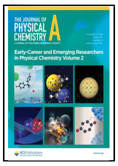

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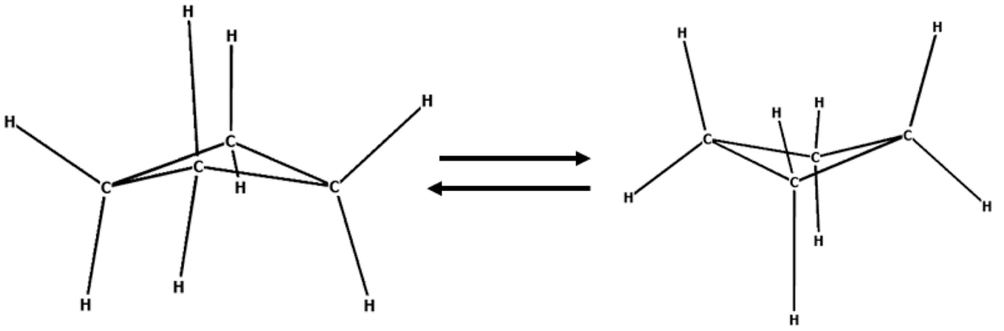

Figure 1. Ring puckering tunneling of cyclobutane.

Previous spectroscopic studies of the halocyclobutanes (X = F, Cl, Br), deuterated cyclobutane, and cyanocylobutane reported the observation of axial and equatorial conformers, with the equatorial conformation being more stable.[4,6,7,22−25] Only the equatorial conformer was observed for aminocyclobutane,[9,10] cyclobutanecarboxylic acid chloride,[26] and cyclobutanol.[5,8] Besides the conformational analysis of cyclobutyl derivatives, MW spectroscopy can also help understand the ring puckering of cyclobutyl rings like cyclobutane-d_1,[12] cyclobutanone,[14] and cyclobutene.[13,15] In this article, we report the MW spectrum of c-bone for the first time, which we have used to determine the ring conformation. This study may also aid the understanding of the effect of ring-puckering tunneling in the MW spectrum of cyclobutanecarboxylic acid.[11]

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

High-level quantum chemical and ab initio calculations were carried out using Gaussian 16[27] on the Owens cluster at the Ohio Supercomputer Center. The Becke three-parameter Lee−Yang−Parr exchange−correlation (B3LYP), second-order Møller−Plesset perturbation theory (MP2), configuration interaction singles and doubles (CISD), and coupled cluster singles and doubles (CCSD) levels of theory were employed by using the aug-cc-pVTZ basis set. The B3LYP exchange−correlation calculation has a fairly dense grid that is pruned from a base grid of 99 radial and 590 angular points. Harmonic and anharmonic frequency vibrational calculations were used to calculate the modeled centrifugal distortion constants. Since the centrifugal distortion constants from the harmonic and anharmonic calculations were essentially the same, the anharmonic values are the only ones reported below.

C-bone was prepared following the procedure reported in *Organic Syntheses.*[19] 3-Oxocyclobutanecarboxylic acid was mixed with dichloromethane to dissolve the acid. It was then stirred gently and mixed with anhydrous magnesium sulfate and mercury(II) oxide. The reaction was carried out under argon. The heterogeneous mixture was stirred at 250−300 rpm and brought to vigorous reflux (oil bath temperature 46 °C) for 5 to 10 min to ensure freely flowing solids. Bromine was then carefully added dropwise, and the mixture was stirred for 6 h. After completion, the reaction mixture is cooled and filtered through a pad of Celite and silica gel with the aid of additional dichloromethane. The clear, colorless filtrate was then placed in a 1 L separatory funnel and washed with saturated aqueous sodium bicarbonate. The combined milky aqueous washes were back-extracted with dichloromethane. The combined organic extracts were washed with water and then brine. The solution was dried over approximately 5 g of magnesium sulfate, filtered, and concentrated under reduced pressure (25 °C, 100 to 30 mmHg) to give the crude bromide as a clear, pale yellow liquid. The 3-bromocyclobutenone was then mixed with tri-*n*-butylamine and stirred for 1 h at ambient temperature to produce c-bone. Purified c-bone was isolated by distillation and immediately used for spectroscopic analysis. The ^{1}H NMR spectrum, recorded using a Bruker AV 400 MHz spectrometer, was used to confirm the synthesis of c-bone.

A high-resolution jet-cooled molecular beam cavity-based FTMW spectrometer with a 2.5 kHz frequency resolution was used to obtain the MW spectrum of the c-bone in the 9−22 GHz frequency range. The instrument is described in detail elsewhere.[28] The sample was placed in a reservoir nozzle and carried into the Fabry−Perot resonator with Ar gas at a 1.5 atm backing pressure, which produced a supersonic jet expansion in the vacuum chamber. Each gas pulse is 800 μs and is followed by a 0.2 μs microwave irradiation pulse. The heterodyne detection circuit is closed after an additional 2 μs delay, and the signal is digitized at 100 MHz for 400 μs.

3. RESULTS AND DISCUSSION

3.1. Molecular Structure. The modeled molecular structure of c-bone, see Figure 2, at different levels of theory can be found in Table 1. Modeled spectroscopic constants are

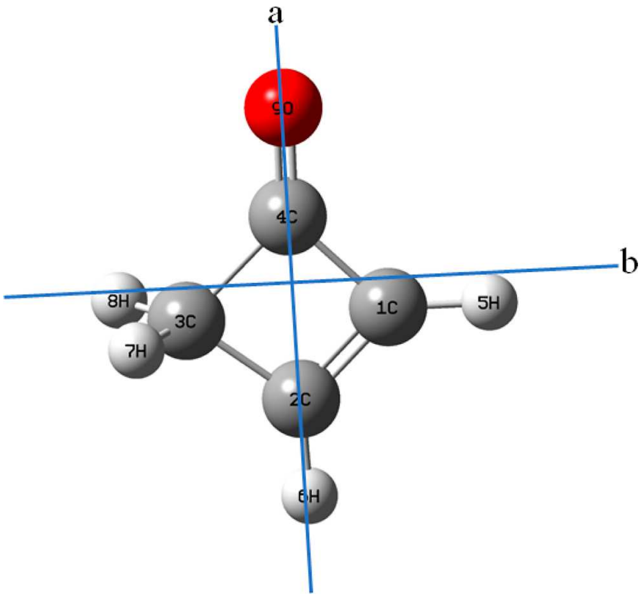

Figure 2. Modeled structure of cyclobutenone at the MP2/aug-cc-pVTZ level.

Table 1. Molecular Structure Parameters of Cyclobutenone Calculated Using B3LYP, MP2, CISD, and CCSD Methods

parameter	B3LYP[a]	MP2[a]	CISD[a]	CCSD[a]
$r(C_1{-}C_2)$ (Å)	1.343	1.353	1.334	1.347
$r(C_2{-}C_3)$ (Å)	1.522	1.520	1.516	1.526
$r(C_3{-}C_4)$ (Å)	1.565	1.560	1.545	1.557
$r(C_4{-}O_9)$ (Å)	1.197	1.205	1.185	1.197
$r(C_4{-}C_1)$ (Å)	1.491	1.493	1.486	1.496
$r(C_1{-}H_5)$ (Å)	1.080	1.080	1.072	1.080
$r(C_2{-}H_6)$ (Å)	1.080	1.081	1.073	1.080
$r(C_3{-}H_7)$ (Å)	1.091	1.090	1.082	1.090
$r(C_3{-}H_8)$ (Å)	1.091	1.090	1.082	1.090
$\angle(C_2{-}C_1{-}C_4)^\circ$	91.6	91.0	91.4	91.3
$\angle(C_2{-}C_1{-}H_5)^\circ$	134.2	134.2	134.4	134.3
$\angle(C_1{-}C_2{-}C_3)^\circ$	96.7	96.8	96.6	96.6
$\angle(C_1{-}C_2{-}H_6)^\circ$	132.2	132.0	132.3	132.3
$\angle(C_4{-}C_1{-}H_5)^\circ$	134.2	134.7	134.3	134.3
$\angle(C_1{-}C_4{-}C_3)^\circ$	89.2	89.6	89.4	89.4
$\angle(C_1{-}C_4{-}O_9)^\circ$	136.7	136.4	136.6	136.5
$\angle(C_3{-}C_2{-}H_6)^\circ$	131.0	131.2	131.1	131.1
$\angle(C_2{-}C_3{-}C_4)^\circ$	82.4	82.6	82.6	82.7
$\angle(C_2{-}C_3{-}H_7)^\circ$[b]	116.5	116.3	116.3	116.3
$\angle(C_4{-}C_3{-}H_7)^\circ$[c]	115.0	114.6	114.8	114.7
$\angle(C_3{-}C_4{-}O_9)^\circ$	134.1	134.0	134.0	134.0
$\angle(H_7{-}C_3{-}H_8)^\circ$	109.5	110.0	109.8	110.0
$\angle(C{-}C{-}C{-}C)^\circ$	0	0	0	0
$\angle(C{-}C{-}C{-}O)^\circ$	180	180	180	180
$c(H_7$ & $H_8)$ (Å)	±0.892	±0.893	±0.886	±0.893

[a] aug-cc-pVTZ basis set was used. [b] $\angle(C_2{-}C_3{-}H_8)$ is identical. [c] $\angle(C_4{-}C_3{-}H_7)$ is identical.

compared in Table 2. For c-bone the modeled bond lengths from the B3LYP, MP2, and CCSD were found to be $r_{C_1-C_2}$ = 1.343 to 1.353 Å, $r_{C_2-C_3}$ = 1.522 to 1.526 Å, $r_{C_3-C_4}$ = 1.557 to 1.565 Å, $r_{C_4-C_1}$ = 1.491 to 1.496 Å, r_{C-H} = 1.091 Å, and the vinyl r_{C-H} = 1.080 Å. The CISD-calculated values were found to deviate little from the values shown above: $r_{C_1-C_2}$ = 1.334 Å, $r_{C_2-C_3}$ = 1.516 Å, $r_{C_3-C_4}$ = 1.545 Å, $r_{C_4-C_1}$ = 1.486 Å, r_{C-H} = 1.082 Å, and vinyl r_{C-H} = 1.073 Å. The $\angle C_2{-}C_1{-}C_4$ angle is calculated to be between 91.0 and 91.6°; the $\angle C_2{-}C_3{-}C_4$ angle to be between 82.4 and 82.7°; and the $\angle C_1{-}C_2{-}C_3$ angle to be between 96.6 and 96.8°. These ring angles are smaller than those reported for cyclobutanone and cyclobutene.[13−15] The dihedral angles $C_1{-}C_2{-}C_3{-}C_4$ and $C_2{-}C_3{-}C_4{-}O_5$ were found to be 0.0 and 180°, respectively, indicating that all levels of theory predict a planar ring structure.

Since little experimental structural information on c-bone was found, a comparison to other cyclic four-membered rings must be made in order to provide a more detailed understanding of its bond lengths and bond angles. Vogelsanger and co-workers assigned the MW spectrum of cyclobutane-d_1.[12] They used deuterated cyclobutane instead of normal cyclobutane because of the absence of a permanent electronic dipole moment in the normal species. This species was also studied to avoid the tunneling splittings arising from the symmetric double well minima that are observed in more symmetric deuterated species. Cyclobutane-d_1 was found to exist in the equatorial and axial conformations with bond lengths, bond angles, and torsion of r_{C-C} = 1.555 Å, r_{C-H} = 1.091 Å, $\angle C_{eq}{-}C_{eq}{-}C_{eq}$ = 130.60° ($\angle C_{ax}{-}C_{ax}{-}C_{ax}$ = 120.08°), and τ = 28.58°, where τ represents the ring puckering angle.[12] For cyclobutene, Kim and Gwinn[13] reported bond lengths to be r_{C-C} = 1.523 Å, r_{C-H} = 1.09 Å, and the vinyl r_{C-H} = 1.08 Å, while the bond angle is $\angle H{-}C{-}H$ = 110°. For cyclobutanone, the $r_{C_1-C_2}$ = 1.527 Å and $r_{C_2-C_3}$ = 1.556 Å, while the bond angles are $\angle C_2{-}C_1{-}C_2$ = 93.1°, $\angle C_1{-}C_2{-}C_3$ = 88.0°, and $\angle C_2{-}C_3{-}C_2$ = 90.9°.[14,15] The bond lengths and bond angles from the B3LYP, MP2, and CCSD model molecular structures for c-bone show good agreement with the values determined from the MW experiments on these related species. Microwave experiments on c-bone will help us identify which computational model is better for structural and rotational spectral predictions.

3.2. Spectral Analysis.

Ab initio models predict that c-bone has a strong dipole moment, 3.3−3.6 D, along the *a*-axis (as shown in Figure 2). The model values, excluding CISD, for *B* + *C* were used to predict the $1_{01}{-}0_{00}$ rotational transition between 9135 and 9163 MHz. The $1_{01}{-}0_{00}$ rotational transition was found experimentally at 9127.735 MHz (as shown in Figure 3). The *B* + *C* values from the B3LYP/aug-cc-pVTZ (9160.67 MHz), MP2/aug-cc-pVTZ (9135.50 MHz), and CCSD/aug-cc-pVTZ (9163.30 MHz) levels were the closest to the experimental value. Morales[29] and Etim[30] calculated rotational constants for c-bone using MP2/6-

Table 2. Spectroscopic Parameters of Cyclobutenone

parameter	experimental	B3LYP[a]	MP2[a]	CISD[a]	CCSD[a]
A (MHz)	12548.258(14)	12642.575	12605.073	12819.048	12632.402
B (MHz)	5307.560(3)	5323.561	5308.903	5417.019	5325.621
C (MHz)	3820.178(3)	3837.109	3826.598	3900.871	3837.679
D_J (kHz)	0.7(4)	0.564			
D_{JK} (kHz)	6.4(4)	6.65			
D_K (kHz)	1.30[b]	1.30			
d_1 (kHz)	−0.197(9)	−0.195			
d_2 (kHz)	−0.0834[b]	−0.0834			
$\lvert\mu_a\rvert$ (D)		3.3	3.3	3.6	3.4
$\lvert\mu_b\rvert$ (D)		0	0	0.1	0.1
$\lvert\mu_c\rvert$ (D)		0	0	0	0
N[c]	9				
rms (kHz)[d]	2.7				

[a] aug-cc-pVTZ basis set was used. [b] Fixed using the calculated value from Table 4. [c] Number of transitions included in the fit. [d] Root mean square deviation of the fit.

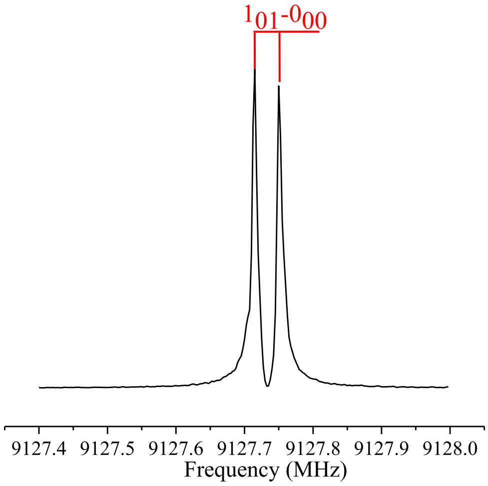

Figure 3. $1_{01}-0_{00}$ rotational transition averaged at 25 shots with a Doppler splitting of 35 kHz.

31G(d′) and G4 models. The rotational constants at the MP2/6-31G(d′) level are A = 12468.4, B = 5260.8, and C = 3789.7 MHz;[15] the G4 model constants are A = 14561.9, B = 3249.2, and C = 2656.5 MHz.[30] The $B + C$ values from these calculations are 9050.5 and 5905.703 MHz respectively, indicating that the 6-31G(d′) basis set may be sufficient to model the rotational spectra of small, rigid species.

The MP2/aug-cc-pVTZ level provided the closest prediction of the $1_{01}-0_{00}$ rotational transition, and this model was used to predict the remaining transitions. SPCAT and SPFIT were used to predict and fit the rotational spectrum of c-bone.[31] PGOPHER was used as a visual device to compare the simulated and experimental spectra.[32] Only 9 strong rotational transitions are found within the 9−22 GHz frequency region of our spectrometer; the frequencies of the experimental rotational transitions are given in Table 3.

Table 3. Experimental Rotational Transitions of c-Bone

J'	Ka′	Kc′	J''	Ka″	Kc″	ν_{EXP}/MHz	$\Delta\nu$/kHz[a]
1	0	1	0	0	0	9127.735	0.0
6	2	4	6	2	5	11019.221	−1.4
9	3	6	9	3	7	11539.695	2.9
4	1	3	4	1	4	14748.203	−5.0
2	1	2	1	1	1	16768.048	−3.3
2	0	2	1	0	1	18048.980	1.6
10	3	7	10	3	8	18192.701	−1.6
2	1	1	1	1	0	19742.804	1.7
5	1	4	5	1	5	21819.583	3.6

[a] $\Delta\nu = \nu_{\mathrm{EXP}} - \nu_{\mathrm{CALC}}$.

The rotational spectrum of c-bone was fit using both the Watson S-reduction and Watson A-reduction Hamiltonians. Fitting the nine rotational transitions to the A, B, and C rotational constants and the quartic centrifugal distortion constants D_J, D_{JK}, and d_1 using the S-reduction Hamiltonian gives a 5.6 kHz rms fitting error. Previous literature has shown that model centrifugal distortion constants arising from the B3LYP level are generally in agreement with experimentally determined centrifugal distortion constants.[33] Centrifugal distortion constants for both the S- and A-reduction calculated at the aug-cc-pVTZ level are given in Table 4. The nine rotational transitions were then fit to A, B, C, D_J, D_{JK}, and d_1 with the D_K and d_2 constants fixed to the model values. The RMS error was reduced to 2.7 kHz.

Table 4. Modeled Centrifugal Distortion Constants from the B3LYP/aug-cc-pVTZ Level of Theory

parameter	symmetric reduced	parameter	asymmetric reduced
D_J (kHz)	0.564	Δ_J (kHz)	0.731
D_{JK} (kHz)	6.65	Δ_{JK} (kHz)	5.64
D_K (kHz)	1.30	Δ_K (kHz)	2.13
d_1 (kHz)	−0.195	δ_J (kHz)	0.195
d_2 (kHz)	−0.0834	δ_K (kHz)	3.62

The Watson A-reduction Hamiltonian was also used to fit A, B, C, Δ_J, Δ_{JK}, and δ_J to the experimental spectrum. A preliminary fit with Δ_K and δ_K fixed to 0.0 gave an rms error of 5.6 kHz; when Δ_K and δ_K are included and fixed at the ab initio values, the rms error is reduced to 2.7 kHz. The best-fit values for these final S-reduction and A-reduction fits are given in Table 5. The two fits converge to almost the same values for A, B, and C. The fitted values for the D_{JK} and d_1 (or Δ_{JK} and δ_J) distortion constants are also in good agreement with the ab initio values, although the fitted values for D_J and Δ_J are both 24% larger than the model values.

Table 5. Comparison of the Final S-Reduction and A-Reduction Fits

parameter	S-reduction	parameter	A-reduction
A (MHz)	12548.248(14)	A (MHz)	12548.256(14)
B (MHz)	5307.560(3)	B (MHz)	5307.567(3)
C (MHz)	3820.178(3)	C (MHz)	3820.171(3)
D_J (kHz)	0.7(4)	Δ_J (kHz)	0.9(4)
D_{JK} (kHz)	6.4(9)	Δ_{JK} (kHz)	5.4(4)
D_K (kHz)	1.30[a]	Δ_K (kHz)	2.13[a]
d_1 (kHz)	−0.197(9)	δ_J (kHz)	0.197(9)
d_2 (kHz)	−0.0834[a]	δ_K (kHz)	3.62[a]
rms (kHz)[b]	2.7	rms (kHz)[b]	2.7

[a] Fixed using the calculated value from Table 4. [b] Root mean square deviation of the fit.

No spectroscopic splittings were observed for any of the c-bone rotational transitions; therefore, the possibility of tunneling between equivalent ring-puckering energy minima is excluded. Also, the rotational and centrifugal distortion constants are close to their calculated values, indicating that other large-amplitude vibrational motions do not significantly affect the spectrum or structure.

3.3. Is c-Bone Planar?

The c-bone model structures all have a planar heavy-atom structure with H_7 and H_8 equidistant below and above the plane [MP2 model values: −0.893 and 0.893 Å]; the corresponding distances from the other ab initio models are given in Table 1. The dihedral angles for all models along the $C_1-C_2-C_3-C_4$ are 0 and 180° for the $C_2-C_3-C_4-O_5$ dihedral.

The inertial defect, $\Delta_0 = I_{cc} - I_{aa} - I_{bb}$, where I_{aa}, I_{bb}, and I_{cc}, are the inertial moments along the a-, b-, and c-inertial axes, has often been used to characterize planar molecular structures. Using the experimental data for c-bone, we calculate Δ_0 = −3.202 uÅ^2. For a planar molecule, Δ_0 is expected to have a small positive value; $\Delta_0 < 0$ for nonplanar molecules.[34] The small negative value is consistent with a structure that is close to planarity, with only two hydrogen atoms falling out of plane.

Δ_0 was found to be −0.109 uÅ^2 for cyclopropenone[35] (no hydrogen atoms out of plane), −6.393 uÅ^2 for cyclobutene[13] (4 hydrogen atoms out of plane), and −9.98 uÅ^2 for cyclobutanone[14] (6 hydrogen atoms out of plane). The value of Δ_0 for c-bone falls on the clear trend toward increasingly negative values for the inertial defect of these planar ring systems with increasing numbers of out-of-plane hydrogen atoms.

Second moments, P_{cc}, provide a more reliable metric for planarity and planes of symmetry.[36,37] Equation 1 gives the second moment along the *c*-axis

$$P_{cc} = \Sigma m_i c_i^2 = \frac{1}{2}(I_{aa} + I_{bb} - I_{cc}) \tag{1}$$

where m_i are the atomic masses and c_i are the atomic *c*-coordinates. The theoretical value of P_{cc} calculated from the MP2 model structure is 1.608 uÅ^2, and it is nearly identical to the value calculated from the experimentally determined moments of inertia (1.601 uÅ^2). The heavy atoms of c-bone lie in the *ab*-plane, with the *c*-axis perpendicular to the heavy-atom plane. The MP2-modeled structure is in excellent agreement with the experiment.

4. CONCLUSIONS

The pure rotational spectrum of c-bone was recorded by high-resolution FTMW spectroscopy for the first time. High-level, first-principles calculations at the B3LYP, MP2, CISD, and CCSD levels of theory were used to provide guidance for spectral assignment and detailed molecular structure information. It was determined that the MP2/aug-cc-pVTZ level modeled the structure better than did the B3LYP, CISD, and CCSD levels of theory. Watson *S*-reduced and *A*-reduced Hamiltonians fit the rotational transitions equally well, and experimental second moments were used to determine a planar ring structure. No tunneling splittings arising from ring-puckering tunneling were observed, and there is no evidence of other large-amplitude vibrations.

AUTHOR INFORMATION

Corresponding Author

Michael J. Tubergen − *Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States;* orcid.org/0000-0002-5646-0300; Phone: 330-672-7079; Email: mtuberge@kent.edu

Authors

Michael J. Carrillo − *Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States;* orcid.org/0000-0001-6060-4664

Dinesh Marasinghe − *Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States*

Erik B. Feeley − *Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States*

Kristin M. Sobie − *Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States*

Rourke J. Zarzycki − *Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States*

Kevin Carter-Fenk − *Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States;* orcid.org/0000-0001-8302-4750

Christopher J. Fenk − *Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpca.3c05510

Notes

The authors declare no competing financial interest.

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