5840 *J. Org. Chem.* **2001,** *66,* 5840−5845

Molecular Structure and Conformation of Cyclopropylbenzene As Determined by ab Initio Molecular Orbital Calculations, Pulsed-Jet Fourier Transform Microwave Spectroscopic, and Gas-Phase Electron Diffraction Investigations

Quang Shen,*,† Christopher Wells,† Marit Traetteberg,‡ Robert K. Bohn,§
Amanda Willis,⊥ and Joseph Knee||

Departments of Chemistry, Colgate University, 13 Oak Drive, Hamilton, New York 13346, Norwegian University of Science and Technology, NTNU, N-7491 Trondheim, Norway, University of Connecticut, Storrs, Connecticut 06269, Mt. Holyoke College, South Hadley, Massachusetts 01075, and Wesleyan University, Middletown, Connecticut 06459-0180

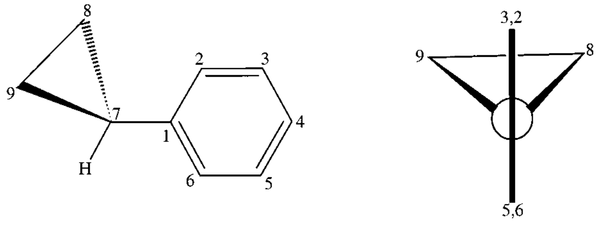
mshen@mail.colgate.edu

Received March 16, 2001

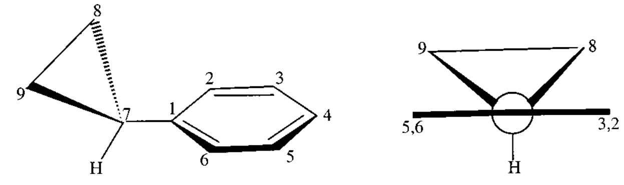
Ab initio computational, microwave spectroscopic, and electron diffraction techniques have been used to study the gas-phase structure of cyclopropylbenzene. Theoretical calculations at the HF, B3LYP, and MP2 levels for basis sets 6-31G(d) and 6-311G(d) have been carried out. Both MP2 and B3LYP calculations showed the bisected form to be lower in energy (245/157 and 660/985 cal mol^{-1}, respectively, for basis sets 6-311G(d)/6-31G(d)). Rotational constants for the bisected form of the parent and eight singly substituted ^{13}C isotopic species were obtained. The selection rules of the observed rotational transitions and the facts that eight (rather than six) singly substituted ^{13}C isotopers are observed and assigned and that seven of the compound's nine carbon atoms lie in the molecule's symmetry plane required the molecule to exist in the bisected conformation. No transition from the perpendicular form was observed in the pulsed-jet microwave experiment. Gas-phase electron diffraction data were collected at a nozzle-tip temperature of 265 K. Least squares analyses were carried out using ED data alone and with the inclusion of microwave rotational constants. The principal structural results (r_g and $\angle_\alpha$) obtained from the combined ED/MW least-squares analysis are $r(C-H)_{av} = 1.093(6)$ Å, $r(C^7-C^8)_v = 1.514(20)$ Å, $r(C^8-C^9)_d = 1.507(26)$ Å, $r(C^7-C^1) = 1.520(25)$ Å, $r(C-C)_{Ph} = 1.395(1)$ Å, $\angle C^1C^7C^8 = 119.6(17)°$, $\angle C^2C^1C^7 = 122.5(25)°$, $\angle C^1C^2C^3 = 120.9(35)°$, $\angle HC^8C^9 = 116.7(20)°$, $\angle HCC_{Ph} = 120.0°$ (assumed).

Introduction

The molecular structure and conformation of cyclopropylbenzene has been the subject of many investigations because of the possible interaction between the π-system of the phenyl ring and the Walsh orbitals in the three-membered ring.[1−12] For example, the bisected form (see Figure 1) maximizes the donor−acceptor interaction between the HOMO of the cyclopropyl group and the LUMO of the phenyl π-system. The consequence of this interaction (donation of electron from the cyclopropyl group to the π-system) is the lengthening of the vicinal C−C bonds relative to the distal C−C bond in the three-membered ring. In the perpendicular conformation cyclopropylbenzene would enhance the interactions of the cyclopropyl LUMO and the HOMO of the π-system and



Bisected form τ = 0°



Perpendicular form τ = 90°

Figure 1. Molecular diagram with atom numbering of the bisected and perpendicular forms of cyclopropylbenzene.

---

† Colgate University.
‡ Norwegian University of Science and Technology.
§ University of Connecticut.
⊥ Mt. Holyoke College.
|| Wesleyan University.

(1) Galli, C. *Magn. Reson. Chem.* **1989**, *27*, 214.
(2) Castan, P.; Lopez, A.; Martino, R. *Tetrahedron* **1979**, *35*, 1093.
(3) Shundo, K.; Okamoto, T. *Tetrahedron* **1977**, *33*, 1717.
(4) Shundo, K.; Kobayashi, T.; Utsunomiyu, C. *Tetrahedron* **1977**, *33*, 1721.
(5) Prius, I.; Verhoeven, J. W.; DeBoer, T.; Worrell, C. *Tetrahedron* **1977**, *33*, 127.
(6) Parr, W. J.; Schaefer, T. *J. Am. Chem. Soc.* **1977**, *99*, 1033.
(7) Sorriso, S.; Stefani, F.; Semiprini, E.; Flamini, A. *J. Chem. Soc., Perkin Trans.* **1976**, *2*, 4.374.
(8) Martinelli, L.; Mutha, S. C.; Ketcham, R.; Strait, L. A.; Cavestri, R. *J. Org. Chem.* **1972**, *37*, 2278.
(9) Closs, G. L.; Klinger, H. B. *J. Am. Chem. Soc.* **1966**, *87*, 3265.
(10) DeBoer, J. S. A. M.; Loopstra, B. O.; Stam, C. H. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 537.
(11) Drumright, R. E.; Mas, R. H.; Merola, J. S.; Tanko, J. M. *J. Org. Chem.* **1990**, *55*, 4098.
(12) Jason, M. E.; Kurzweil, P. R.; Leonard, K. E. *J. Org. Chem.* **1986**, *51*, 2550.

10.1021/jo010293u CCC: $20.00

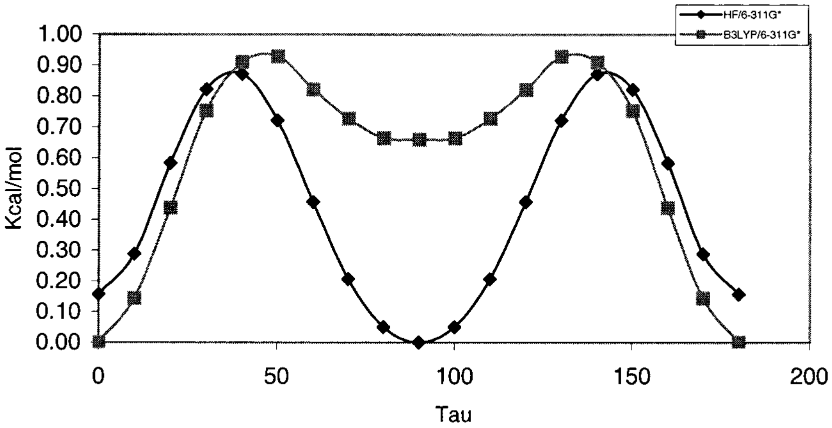


Figure 2. Potential function as a function of the torsional angle (τ) obtained from ab initio molecular orbital calculations.

result in the donation of the electron from the π-system to the cyclopropyl group, which incidentally is a weak π-acceptor.

The solid-state structure of cyclopropylbenzene[10] has been reported, and the molecule was found to adopt the bisected conformation with the vicinal bonds longer than the distal bond (1.520 vs 1.502 Å). Molecular mechanics calculations[11] showed that the bisected form was 1.1 kcal mol^{-1} lower in energy than the perpendicular form. An NMR investigation[9] found the bisected form to be 1.4 kcal mol^{-1} lower in energy than the perpendicular form, and the rotational barrier was determined in a later study[6] to be 2.0 kcal mol^{-1} in CS_2 solution. Calculations at the CNDO/2 level[7] showed that the most stable conformer had the cyclopropyl group and the phenyl ring orthogonal to one another.

No gas-phase molecular structure determination or ab initio molecular orbital calculations of cyclopropylbenzene has been reported. We have therefore initiated microwave, gas-phase electron diffraction and ab initio molecular orbital calculation investigations to elucidate the structure and conformation of cyclopropylbenzene.

Experimental Section

A commercial sample of cyclopropylbenzene (99%) was obtained from Aldrich Chemical Co. GC−MS analysis did not reveal any significant impurities, and the sample was used without purification. Electron diffraction data were collected using the Oslo Balzers apparatus using a nozzle tip temperature of 304 K. The electron wavelength was 0.05866 Å, as calibrated against the diffraction pattern for benzene. Four plates from each of the two camera distances (500.12 and 250.12 mm) were selected for analysis. Optical densities were measured and the usual data reduction procedures were carried out[13] and were interpolated at integral values of q [$(40/\pi)\sin(\theta/2)$] where θ is the scattering angle.

The intensity data were analyzed using a least squares procedure outlined by Gundersen and Hedberg[14] using elastic scattering and phase shift factors calculated by Ross, Fink and Hilderbrandt.[15]

Microwave Spectroscopy. A few drops of cyclopropylbenzene (bp 174 °C) were placed in the carrier gas line just before the mirror-mounted room-temperature nozzle, which pulsed at 5 Hz. About 3 atm of first-run Ne (~75% Ne, ~25% He) was used as the carrier gas so the sample composed only about 0.1% of the gas in the jet. Some spectra were obtained with 2 atm Ar as the carrier gas. Microwave spectra were observed on the pulsed-jet Fourier Transform spectrometer[16] at Wesleyan of the Southern New England Microwave Consortium[17] in the region between 6 and 18 GHz. Most of the a-type transitions of the parent isotopomer could be seen in a single pulse. The b-type transitions of the parent were generally an order of magnitude less intense than the a-type transitions, which means the dipole moment component in the direction of the b principal axis is much smaller than the dipole moment along the a axis. Signal averaging was required for a-type transitions of the ^{13}C isotopomers observed in natural abundance, whereas the b-type transitions of ^{13}C isotopomers were not measured. Transitions were observed as Doppler doublets, and line widths in the power spectrum ranged from 10 to 20 kHz with uncertainties in the reported frequencies estimated to be less than 2 kHz.

Data Analysis. Theoretical Calculations. Ab initio molecular orbital calculations at the HF, B3LYP, and MP2 levels and with basis sets 6-31G(d) and 6-311G(d) were carried out with the GAUSSIAN98 program.[18] In all calculations complete geometry optimization of the bisected and perpendicular forms were carried out. At the HF level of theory the perpendicular form was found to be 63/157 cal mol^{-1} (6-31G(d)/6-311G(d)) lower in energy than the bisected form, while the B3LYP and MP2 calculations showed the bisected form to be favored over the perpendicular by 985/660 and 157/245 cal mol^{-1}, respectively. The optimized geometries from the MP2 and B3LYP calculations are shown in Table 1.

The torsional potential function about the $C^1{-}C^7$ bond has been calculated at 10° intervals from 0° to 90° for the HF and B3LYP calculations and 30° intervals for the MP2 calculations. Complete geometry optimization, with the exception of the $C^1{-}C^7$ dihedral angle, was carried out in each of these calculations, and the relative energies are presented in Table 2 and Figure 2.

Microwave Spectroscopy. Because p-cyclopropylbenzaldehyde unambiguously displayed rotational spectra of the bisected conformation of the cyclopropylbenzene fragment,[19] the bisected conformation was first sought for cyclopropylben-

---

(13) Andersen, B.; Seip, H. M.; Strand, T. G.; Stolevik, R. *Acta Chem. Scand.* **1969**, *28*, 224.

(14) Gundersen, G.; Hedberg, K. K. *J. Chem. Phys.* **1969**, *51*, 2500.

(15) Ross, A. W.; Fink, M.; Hilderbrandt, R. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, 1992; Vol. C.

(16) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33.

(17) Hight-Walker, A. R.; Lou, Q.; Bohn, R. K.; Novick, S. E. *J. Mol. Struct.* **1995**, *346*, 187.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

Table 1. Structural Parameters Obtained by ab Initio Calculations for Bisected (τ $C^6C^1C^7H = 0°$) and Perpendicular (τ $C^6C^1C^7H = 90°$) Conformers of Cyclopropylbenzene

	MP2/6-31G(d)		B3LYP/6-31G(d)		B3LYP/6-311G(d)	
	0°	90°	0°	90°	0°	90°
C1−C2	1.4037	1.4013	1.4042	1.4017	1.4019	1.3992
C2−C3	1.3949	1.3958	1.3940	1.3956	1.3915	1.3931
C3−C4	1.3968	1.3968	1.3966	1.3962	1.3939	1.3933
C4−C5	1.3957	1.3968	1.3950	1.3962	1.3922	1.3934
C5−C6	1.3956	1.3959	1.3953	1.3956	1.3928	1.3930
C6−C1	1.4019	1.4013	1.4025	1.4017	1.4002	1.3993
C1−C7	1.4856	1.4932	1.4919	1.5011	1.4906	1.5001
C7−C8	1.5119	1.5065	1.5186	1.5113	1.5173	1.5096
C7−C9	1.5119	1.5065	1.5186	1.5113	1.5173	1.5095
C8−C9	1.4980	1.5046	1.5009	1.5098	1.5006	1.5098
$C-H_{av}$	1.0870	1.0871	1.0871	1.0873	1.0843	1.0845
C1−C2−C3	120.80	120.67	120.99	120.92	120.99	120.91
C2−C3−C4	120.35	120.08	120.40	120.12	120.41	120.13
C3−C4−C5	119.40	119.71	119.26	119.55	119.26	119.55
C4−C5−C6	120.15	120.08	120.20	120.12	120.21	120.14
C5−C6−C1	121.04	120.67	121.21	120.92	121.21	120.90
C6−C1−C2	118.27	118.80	117.95	118.38	117.92	118.38
C1−C7−C8	121.18	120.18	121.85	121.28	121.85	121.36
C1−C7−C9	121.18	120.17	121.85	121.29	121.88	121.37
C1−C7−C15	114.06	114.90	113.35	114.00	113.38	113.83
H−C−H	114.44	114.59	114.12	114.26	114.37	114.47
C2−C1−C7	122.10	120.59	122.59	120.80	122.59	120.79
C6−C1−C7	119.63	120.59	119.51	120.80	119.50	120.80
ΔE (kcal mol^{-1})	0.0	+0.157	0.0	+0.985	0.0	+0.660

Table 2. Torsional Potentials from ab Initio Calculations for Cyclopropylbenzene; Relative Energies in kcal mol^{-1}

rotation (deg)	HF/6-31G(d)	HF/6-311G(d)	B3LYP/6-31G(d)	B3LYP/6-311G(d)	MP2/6-31G(d)	MP2/6-311G(d)
0	0.063	0.157	0.0	0.0	0.0	0.0
10	0.207	0.289	0.157	0.144		
20	0.521	0.584	0.502	0.439		
30	0.778	0.822	0.866	0.753	0.954	1.029
40	0.847	0.872	1.073	0.910		
50	0.709	0.722	1.295	0.929		
60	0.458	0.458	1.067	0.822	0.684	0.797
70	0.213	0.207	1.010	0.728		
80	0.050	0.050	0.979	0.665		
90	0.0	0.0	0.985	0.660	0.157	0.245

zene itself. Ab initio molecular orbital calculations[20] at the HF/6-31G(d) level predicted a model with the $4_{04}-3_{03}$ transition expected in the 8100−8200 MHz range and the $4_{14}-3_{13}$ transition about 300 MHz below and the $4_{13}-3_{12}$ about 400 MHz above the $4_{04}-3_{03}$ line. An intense line was observed at 8145.7895 MHz, tentatively assigned to $4_{04}-3_{03,}$ and scans for the other two revealed intense lines at 7867.8375 and 8523.5098 MHz. A rigid rotor fit to those three lines gave reasonable rotational constants that were used to predict frequencies of other transitions, which were easily found. Twenty-three transitions were measured and fit to a standard deviation of 1.7 kHz, comparable to the experimental error. The measured frequencies are displayed in Table 3, and the fitted spectroscopic parameters, three rotational constants and two centrifugal distortion constants, are given in Table 4. In scanning for the lines, many weaker lines were observed at frequencies below the parent isotopomer's lines in patterns expected for ^{13}C isotopomers. Isotopic substitution near the center of mass shifts frequencies downward very little, while substitution at the ends of the molecule causes larger frequency shifts. Seven to ten transitions of each isotopomer were measured. The assignment of these lines is also shown in Table 3 with the isotopomers listed in order from substitution nearest the center of mass to farthest away. The lines were then fit varying only the three rotational constants while holding the two centrifugal distortion constants fixed to the values determined for the parent isotopomer. The standard deviations of the fits are all appropriately small. Spectroscopic constants for the isotopomers are given in Table 4. Details of microwave spectroscopy are described in Townes and Schawlow's monograph.[21] The rotational temperature of the gas in the pulsed-jet drops to just a few K.

Electron Diffraction. All amplitudes of vibration needed for electron diffraction analysis for the bisected and perpendicular forms of cyclopropylbenzene were calculated from the force fields obtained from the B3LYP/6-31G(d) calculations, using the program ASYM40[22] after applying a factor of 0.9 to the ab initio force constant values.

The geometrical parameters chosen to define the structure of cyclopropylbenzene are $r(C-H)_{av}$, $r(C^7-C^8)_v$, $r(C^1-C^7)$, $r(C^1-{}^2)_{Ph}$, $\angle C^1C^7C,^8$ $\angle C^2C^1C,^7$ $\angle HC^8C,^9$ τ $C^6C^1C^7H$ (0.0° = bisected, and 90° = perpendicular). The C−C bonds in the cyclopropyl group are not the same, and the C−C bonds of the phenyl ring are not all identical. The following assumptions are made: (a) the distal bond length $[r(C^8-C^9)_d]$ is 0.018 Å shorter than the vicinal one $[r(C^7-C^8)_v]$, (b) all of the calculated differences between the phenyl C−C bonds [i.e., $r(C^1-C^2)$ is longer than $r(C^2-C^3)$ and $r(C^3-C^4)$ (see Table 1)] from the B3LYP/ 6-311G(d) calculations are maintained, (c) $\angle C^2C^1C^7$ is larger than $\angle C^6C^1C^7$ by 2.37°, (d) all C−H bonds are identical, and (e) all ∠CCH angles in the phenyl group = 120°. Table 5 summarizes the actual geometrical parameter differences used in the analyses.

Least squares refinements of the electron diffraction data using the bisected model gave agreement with an *R* factor of 6.5%. There is no observable difference in the intensity and

---

(19) True, N. S.; Bohn, R. K.; Chieffalo, A.; Radhakrishnan, J. *J. Phys. Chem.* **1983**, *87*, 4628.

(20) *MacSpartan*; Wavefunction, Inc.: Irvine, CA 92715.

(21) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; Dover: New York, 1975.

(22) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

Table 3. Assigned Rotational Transitions (MHz) of Cyclopropylbenzene and Each of Its Singly Substituted ^{13}C Isotopoers

transition	parent	^{13}C1	^{13}C2	^{13}C6	^{13}C7	^{13}C3	^{13}C5	^{13}C4	^{13}C8/9
				a-Type Transitions					
$3_{03}-2_{02}$	6131.064								
$4_{04}-3_{03}$	8145.7895	8145.015	8134.7761	8120.9328	8100.5438	8086.5762	8063.036	8038.6852	8031.1552
$4_{14}-3_{13}$	7867.8375	7866.9391	7854.7958	7840.3664	7824.173	7807.6443	7787.2652	7766.4157	7761.2618
$4_{13}-3_{12}$	8523.5098	8523.0808	8517.9965	8506.1134	8475.666	8468.6325	8437.7702	8405.4713	8394.281
$4_{23}-3_{22}$	8203.3871	8202.7404	8194.384		8157.5538		8120.1694		8084.9742
$4_{22}-3_{21}$	8265.8972	8265.3869	8259.0748		8219.424	8210.7335			8143.3792
$4_{32}-3_{31}$	8220.4593								
$4_{31}-3_{30}$	8221.3692								
$5_{05}-4_{04}$	10136.961	10135.9004	10121.6923	10103.7828	10080.8544	10061.5019	10033.8886	10005.389	9996.5502
$5_{15}-4_{14}$	9823.9606	9822.8125		9789.1185	9769.4859		9723.3332	9697.733	9691.4254
$5_{14}-4_{13}$	10641.5089	10640.9409	10634.1384	10619.09	10581.8412	10572.4432	10534.4383	10494.6751	10480.8582
$5_{24}-4_{23}$	10246.3471	10245.5182		10218.392		10174.4877	10142.3893	10109.0879	10098.8512
$5_{23}-4_{22}$	10369.7308	10369.1694	10362.4295			10301.9507	10264.772	10226.0427	10214.2273
$5_{33}-4_{32}$	10280.4818								
$5_{32}-4_{31}$	10283.6564								
$6_{06}-5_{05}$	12101.2995								
$8_{08}-7_{07}$	15950.4789								
$9_{09}-8_{08}$	17843.2678								
				b-Type Transitions					
$3_{22}-2_{11}$	15518.0959								
$3_{21}-2_{12}$	16042.0082								
$4_{14}-3_{03}$	10605.7014								
$5_{15}-4_{04}$	12283.8718								
$6_{16}-5_{05}$	13920.551								

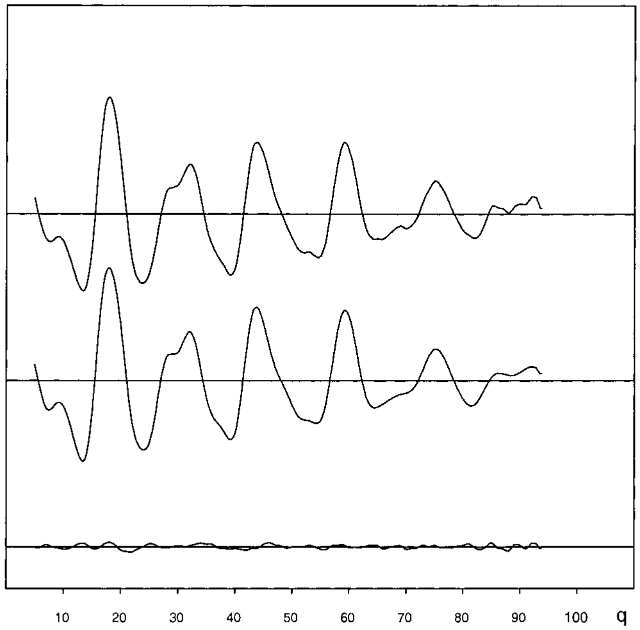


Figure 3. Intensity curves for cyclopropylbenzene. Difference curve is experimental minus theoretical for the bisected form.

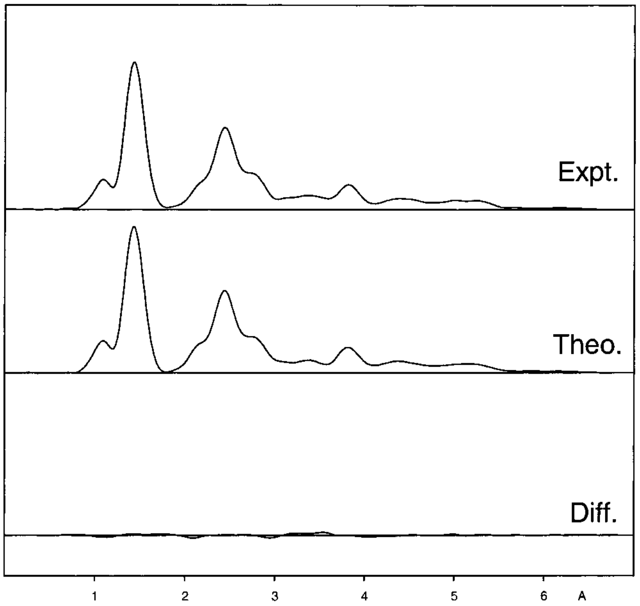


Figure 4. Radial distribution curves for cyclopropylbenzene. Difference curve is experimental minus theoretical for the bisected form.

RD curves as those showed in Figures 3 and 4. The final geometrical parameters obtained for this model are summarized in Table 5. Rotational constants of the parent and eight ^{13}C isotopic species are known. These eight isotopic species are the ones where one of the carbon atoms in cyclopropylbenzene is replaced by a ^{13}C atom. There are nine carbon atoms in cyclopropylbenzene, but in the bisected form ^{13}C substitution on C_8 and C_9 give identical molecules. Standard corrections to the rotational constants (B_o to B_z) and to the bond distances (r_g to r_z)[23] for each of these nine molecules are calculated using force field obtained from ab initio calculation. A combined ED/MW analysis was carried out for the pure bisected model. In these analyses constraint (a) was removed as the result of the inclusion of the rotational constants. Excellent agreements were obtained for both the electron diffraction and microwave data as indicated by the intensity and radial curves shown in Figures 3 and 4 and in the B_z values revealed in Table 5, respectively. The final results for the combined analysis are summarized in Table 5.

Discussion

Figure 2 clearly showed that the energy differences between the bisected and perpendicular forms are sensitive to the level of theory of calculation. Both HF and MP2 calculations gave a small difference (~200 cal mol^{-1}) between these two forms. HF/6-31G(d) calculation favored the perpendicular form while the bisected form is predicted to be more stable in MP2/6-31G(d) and B3LYP/6-31G(d) calculations. DFT calculations indicate that the energy difference between the perpendicular and bisected forms is about 1 kcal mol^{-1}. This difference is more

---

[23] Hilderbrandt, R. L.; Weiser, J. D. *J. Mol. Struct.* **1973**, *13*, 27.

Table 4. Rotational Constants, Second Moments, and Centrifugal Distortion Constants of Cyclopropylbenzene and Its ^{13}C Isotopomers.

rotational constant	parent	^{13}C1	^{13}C2	^{13}C6	^{13}C7	^{13}C3	^{13}C5	^{13}C4	^{13}C8/9
A (MHz)	4228.7369(4)[a]	4226.15(4)	4190.07(2)	4170.11(11)	4215.10(3)	4166.43(3)	4193.80(2)	4225.39(4)	4207.57(3)
B (MHz)	1108.1111(1)	1108.0905(2)	1107.9552(1)	1106.6538(4)	1101.8516(1)	1101.6445(2)	1097.0567(1)	1092.2242(2)	1090.4263(2)
C (MHz)	943.9661(1)	943.8275(2)	941.9146(1)	939.9710(4)	938.7546(1)	936.1569(3)	934.2059(1)	932.2520(2)	931.9663(2)
P_{aa} (uÅ^2)	435.97015	435.977	436.034	436.568	438.558	438.648	440.567	442.603	442.815
P_{bb} (uÅ^2)	99.40824	99.480	100.511	101.086	99.792	101.196	100.405	99.502	99.457
P_{cc} (uÅ^2)	20.10240	20.104	20.103	20.105	20.105	20.102	20.101	20.103	20.655
D_J (kHz)	0.039(1)	[0.039][b]	[0.039]	[0.039]	[0.039]	[0.039]	[0.039]	[0.039]	[0.039]
D_{JK} (kHz)	0.13(1)	[0.13]	[0.13]	[0.13]	[0.13]	[0.13]	[0.13]	[0.13]	[0.13]
number of lines	23	10	8	7	8	8	9	8	10
SD (kHz)	1.7	2	1	3.5	1	1.7	1.1	1.7	1.4

[a] Numbers in parentheses are 1 SD in the last printed digit. [b] Values in square brackets were held fixed at the values determined for the parent isotopomer.

Table 5. Structural Results From Least Squares Analyses of Electron Diffraction Data and Combined Electron Diffraction and Microwave Spectroscopic Data for Cycloproylbenzene[a]

	ED		ED/MW	
	r_{ij}	l_{ij}	r_{ij}	l_{ij}
$r(C-H)_{av}$	1.095(5)	0.079(5)	1.093(6)	0.078(6)
$r(C_8-C_9)$	1.509(10)[b]	0.051	1.507(26)	0.045
$r(C_7-C_8)$	1.523(10)[b]	0.051(6)	1.514(20)	0.045(5)
$r(C_1-C_7)$	1.505(25)	0.051	1.520(25)	0.045
$r(C_1-C_2)$	1.407(2)	0.042(3)	1.405(1)	0.039(4)
$r(C-C)_{ph}$	1.397(2)	0.042(3)	1.395(1)	0.039(4)
$\angle C_6C_7C_8$	119.6(10)		119.6(17)	
$\angle C_2C_1C_7$	122.7(10)		122.5(25)	
$\angle C_1C_2C_3$	121.1(10)		120.9(35)	
$\angle HC_8C_9$	117.4(21)		116.7(20)	
$\angle(HCC)_{ph}$	120 (assumed)		120 (assumed)	

Amplitudes of Vibration (l_{ij})

	ED	ED/MW
$C_1\cdots C_3$	0.053(7)	0.051(5)
$C_2\cdots C_7$	0.0639	0.0639
$C_1\cdots C_8$	0.066(17)	0.076(25)
$C_1\cdots C_4$	0.057(56)	0.061(10)
$C_5\cdots C_7$	0.089(9)	0.0899(11)
$C_5\cdots C_8$	0.135(55)	0.21(13)
$C_2\cdots C_8$	0.145	0.152(33)
$C_3\cdots C_8$	0.144	0.144
$C_5\cdots C_8$	0.135	0.21(13)
$C_4\cdots C_7$	0.0894	0.11(6)
$C_4\cdots C_8$	0.117(47)	0.14(8)

B_z[c]	B_z (calc)	ΔB_z	B_z	B_z (calc)	ΔB_z
	parent			^{13}C3	
4237.75000	4237.38200	0.36816	4175.18000	4175.93100	−0.75098
1108.24000	1107.94800	0.29150	1101.76000	1101.56000	0.19971
943.96000	943.72810	0.23187	936.15000	936.03650	0.11353
	^{13}C1			^{13}C5	
4235.16000	4234.66600	0.49414	4202.66000	4203.09400	−0.43408
1108.22000	1107.87600	0.34363	1097.18000	1097.03500	0.14551
943.83000	943.53960	0.29041	934.20000	934.11680	0.08319
	^{13}C2			^{13}C4	
4198.94000	4199.47400	−0.53418	4234.42000	4233.86000	0.55957
1108.08000	1107.76900	0.31104	1092.35000	1092.21200	0.13770
941.91000	941.70450	0.20544	932.24000	932.11690	0.12305
	^{13}C6			^{13}C8/9	
4178.85000	4179.38500	−0.53516	4216.54000	4216.10200	0.43848
1106.78000	1106.47700	0.30273	1090.54000	1090.53800	0.00208
939.97000	939.75820	0.21179	931.98000	931.92460	0.05542
	^{13}C7				
4224.09000	4223.36900	0.72119			
1101.98000	1101.62700	0.35327		SD = 0.36924	
938.75000	938.44630	0.30371			

[a] Distances (r_g) in angstroms and angles ($\angle_\alpha$) in degrees; parenthesized values are 2σ which include estimates of systematic errors. [b] A fixed difference is assumed. [c] B_z values are converted from microwave rotational constant (B_{obs}) values reported in Table 4 and $\Delta B_z = B_z - B_z(calc)$

consistent with the microwave experiments where only the bisected form is observed.

At least three features of the observed microwave spectra unambiguously identify the observed conformer as the bisected form without reference to the numerical values of the spectral parameters. First, spectra of eight ^{13}C isotopomers are observed with the spectrum of that isotopomer most shifted from the parent about twice as intense as the others. This pattern is consistent only with the bisected form. In considering the possibility of bisected, asymmetric, or perpendicular structures, the asymmetric structure would display nine different isotopomers, and the perpendicular structure would display six. In the asymmetric structure, all isotopomers would exist at about 1.1% of the parent in accordance with natural abundance. For the perpendicular structure, three of the six possible isotopomers would have twice the intensity of the other three since there are equivalent pairs of C atoms in three positions (ortho and meta in the ring and the remote pair of three membered ring C atoms). Only the bisected form would display the observed spectra pattern of eight isotopomers with the isotopomer with single substitution at the C position farthest from the center of mass (C_8 and C_9 atoms in the three-membered ring) having intensity twice the other isotopomers because of equivalent C atoms.

Second, the plane of symmetry of the perpendicular form is the *ac* principal axis plane. Therefore, by symmetry, this conformer has a zero dipole moment along the *b* principal axis, allowing transitions with *a*- and *c*-type selection rules but forbidding the observation of *b*-type transitions. Conversely, the plane of symmetry of the bisected conformer is the *ab* principal axis plane requiring a zero dipole moment in the *c* direction, allowing transitions with *a*- and *b*-type selection rules but forbidding the observation of *c*-type transitions. The observed transitions are *a*- and *b*-type compatible only with the bisected form.

Third, a second moment remains constant with isotopic substitution if the substituted atom lies in a plane of symmetry. Note in Table 4 that P_{cc} is constant (variation only over the very small range of 0.004 uÅ^2) among the parent and seven of the eight isotopomers. Therefore, all of atoms C^1 through C^7 lie in a symmetry plane, and only C^8/C^9 lie outside that plane. This pattern is only consistent with the bisected conformer. C^1, C,^{4} and C^7 are the only carbon atoms lying in a plane of symmetry in the perpendicular form, and if the structure were asymmetric, all isotopomers would have different P_{cc} values.

Since the microwave spectrum of the parent isotopomer as well as every singly substituted ^{13}C isotope was observed and assigned, it is possible to determine a full substitution structure of the carbon skeleton.[24] Unfortunately, C^1, the ipso carbon atom, lies close to the center of mass of the molecule so that the rotational data is insensitive to its location. As a result bond lengths and bond angles involving that atom are poorly determined and unreliable. Also, the *A* constants for the ^{13}C isotopers were not determined as accurately as the other rotational constants, which contributes uncertainty to the substitution structure.

Attempts to find any transitions attributable to a perpendicular conformer were made, but none was observed. This does not rule out the existence of a stable perpendicular conformer at higher energy than the observed bisected conformer, however. In the expansion of the gas pulse from the nozzle, it has been observed that conformational populations present in the gas in the reservoir before expansion are only preserved in the expanded gas if the barriers separating the conformers are quite large, i.e., about 1 kcal mol^{-1}.[25] Since the internal rotation barrier separating the perpendicular conformer from the bisected form is calculated to be less than 1 kcal mol^{-1}, any perpendicular conformer would be expected to relax into the bisected form in the pulsed-jet spectrometer during the gas expansion. It appears that the microwave experiment is consistent with all of the calculations since none of them shows a barrier larger than 1 kcal mol^{-1}.

Electron diffraction data alone cannot shed any light on the issue of whether the energy difference between the bisected and perpendicular forms is large or small because the difference in the distance distributions between these two forms are too small to be distinguished in an ED experiment. A pure bisected form gave excellent agreement with the experimental data. In terms of molecular structure, the differences in the vicinal and distal C$-$C bond lengths expected for the bisected form are reproduced but unfortunately with very large error limits, even with the incorporation of the rotational constants from the parent and eight isotopic species. Nevertheless the calculated structure (B3LYP/6-311G-(d)) is well within the error limits of the experimental values. For example, $r(C^1-C^2)$ 1.403(2)/1.402 Å, $r(C^2-C^3)$ 1.395(2)/1.391 Å, $r(C^1-C^7)$ 1.520(25)/1.491 Å, $r(C^7-C^8)$ 1.514(20)/1.517 Å, $\angle C^1C^2C^3$ 120.9(35)/120.99°, $\angle C^2C^3C^4$ 120.5(35)/120.41°, $\angle C^1C^7C^8$ 119.6(17)/121.8°, and $\angle C^2C^1C^7$ 122.5(25)/122.59°. The gas-phase structure and conformation agree with the solid-state results.[10] The bisected form was observed in both states, and the distal [1.507-(20)/1.502] and vicinal bond [1.514(20)/1.520] bond lengths are comparable. The C$-$C bond lengths in cyclopropyl benzene did not vary much from their parent compounds, i.e., cyclopropane (1.514(1) Å)[26] and benzene (1.399(1) Å).[27]

Supporting Information Available: Correlation matrix is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010293U

---

[24] Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.

[25] Ruoff, R. S.; Klots, T. D.; Emilsson, T.; Gutowsky, H. S. *J. Chem. Phys.* **1990**, *93*, 3142.

[26] Yamamoto, S.; Nakata, M.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1985**, *89*, 3298.

[27] Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243.