Journal of Molecular Spectroscopy **196,** 283–289 (1999)
Article ID jmsp.1999.7882, available online at http://www.idealibrary.com on IDEAL®

Microwave Spectrum and Molecular Conformation of (*E*)-Benzaldehyde Oxime

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Received December 14, 1998; in revised form April 19, 1999

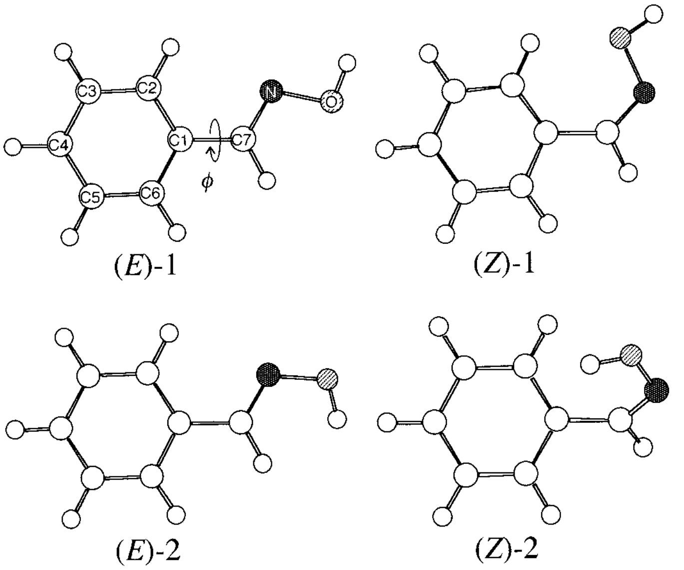
The microwave spectrum of (*E*)-benzaldehyde oxime, C_6H_5—CH═NOH and C_6H_5—CH═NOD, has been observed in the frequency range from 26.5 to 40.0 GHz. The spectrum of the ground vibrational state was assigned and fitted to the Watson's *A*-reduced Hamiltonian to obtain these rotational and centrifugal distortion constants: $A = 5183.13(29)$ MHz, $B = 895.367(3)$ MHz, $C = 763.819(3)$ MHz, $\Delta_J = 0.019(3)$ kHz, and $\Delta_{JK} = 0.204(7)$ kHz for the normal species, and $A = 5158.4(23)$ MHz, $B = 869.44(2)$ MHz, $C = 744.34(2)$ MHz, $\Delta_J = 0.023(2)$ kHz, and $\Delta_{JK} = 0.193(7)$ kHz for the deuterated species. The values of the ΔI $(= I_c - I_a - I_b)$ obtained for the normal and deuterated species were $-0.295(6)$ and $-0.28(5)$ a.m.u. Å^2, respectively. The molecular conformation of this molecule was a planar one in which the values of the dihedral angles, CCNO and CNOH, were almost 180° and 180°, respectively.

1. INTRODUCTION

Benzaldehyde oxime (C_6H_5—CH═NOH), which is the prototype of the aromatic oximes, has two geometrical isomers, *syn* form in which the C(═N)—H and N—O bonds are in the eclipsed position ((*E*)-isomer) and *anti* form in which the C(═N)—H and N—O bonds are in *anti* orientation ((*Z*)-isomer), as shown in Fig. 1. The (*Z*)-isomer gradually inverts into (*E*)-isomer at ambient temperature. The (*E*)- and (*Z*)-isomers of benzaldehyde oxime in solution were identified by NMR study (*1*). The molecular structure of (*E*)-benzaldehyde oxime in the solid phase was determined at 100 K by X-ray diffraction (*2*). The CCCN dihedral angle, ϕ, between the planes of the phenyl group and the oxime moiety was reported to be about 20°. Sauvaitre has recorded the IR and Raman spectra of benzaldehyde oxime in the gas phase as well as in solution and solid (*3*) and assigned the observed spectra by the normal coordinate analysis, assuming the planar conformation. Our interest was in the conformation of benzaldehyde oxime related to the dihedral angle, ϕ, in the vapor phase. In this work, we determined the molecular constants and the molecular conformation of (*E*)-benzaldehyde oxime in the vibrational ground state by the microwave spectroscopy.

2. EXPERIMENTAL SECTION

(*E*)-Benzaldehyde oxime with 98% purity obtained from Aldrich Chemical Company, Inc. was further purified by vacuum distillation. The deuterated species (C_6H_5—CH═NOD) was synthesized by refluxing a mixture of C_6H_5—CH═NOH and D_2O for 24 h. The product was identified by its mass spectrum and the yield of the deuterated species was ca. 50%. The microwave spectrum was observed in the frequency range from 26.5 to 40.0 GHz with



(*E*)-1 (*Z*)-1

(*E*)-2 (*Z*)-2

FIG. 1. Four possible molecular conformations with atom numbering of (*E*)- and (*Z*)-isomers of benzaldehyde oxime. The CCCN dihedral angle ϕ is defined to be zero when the molecular conformation is planar.

0022-2852/99 $30.00

TABLE 1

Principal Geometric Parameters and Relative Energies for Benzaldehyde Oxime Calculated at MP2/6-31G(*d*, *p*) Level of Theory[a]

	Conformer			
	(*E*)-1	(*E*)-2	(*Z*)-1	(*Z*)-2
Bond Lengths (Å)				
C1-C2	1.399	1.399	1.401	1.400
C1-C6	1.403	1.402	1.408	1.404
C1-C7	1.465	1.465	1.468	1.479
C2-C3	1.394	1.394	1.398	1.399
C3-C4	1.398	1.398	1.395	1.395
C4-C5	1.395	1.395	1.396	1.398
C5-C6	1.394	1.394	1.391	1.393
C7-N	1.291	1.292	1.295	1.297
N-O	1.409	1.387	1.408	1.392
C2-H	1.082	1.082	1.077	1.083
C3-H	1.083	1.083	1.083	1.083
C4-H	1.083	1.083	1.083	1.082
C5-H	1.083	1.083	1.083	1.083
C6-H	1.084	1.084	1.084	1.084
C7-H	1.089	1.096	1.086	1.084
O-H	0.966	0.976	0.966	0.976
Bond Angles (°)				
C2-C1-C6	119.54	119.65	118.93	119.45
C2-C1-C7	121.92	121.64	125.48	121.36
C6-C1-C7	118.54	118.71	115.60	119.16
C1-C2-C3	119.80	119.70	119.61	119.96
C2-C3-C4	120.59	120.61	121.13	120.32
C3-C4-C5	119.69	119.73	119.47	119.85
C4-C5-C6	119.93	119.91	119.77	120.03
C1-C6-C5	120.45	120.40	121.09	120.38
C1-C7-N	120.72	121.00	133.34	128.12
C7-N-O	109.92	115.95	113.11	116.64
C1-C2-H	119.36	119.32	120.23	119.86
C2-C3-H	119.57	119.53	119.12	119.61
C3-C4-H	120.12	120.11	120.25	120.06
C4-C5-H	120.19	120.21	120.31	120.08
C5-C6-H	120.09	120.01	119.73	120.25
N-C7-H	120.04	121.19	110.75	113.10
N-O-H	101.75	108.03	101.17	108.02

	Conformer			
	(*E*)-1	(*E*)-2	(*Z*)-1	(*Z*)-2
Dihedral Angles (°)				
C2-C1-C7-N (ϕ)	0.00	-0.06	0.02	49.85
C1-C7-N-O	179.99	180.00	0.00	1.29
C6-C1-C2-C3	0.00	-0.03	0.01	0.62
C1-C2-C3-C4	0.00	0.03	-0.01	0.08
C2-C3-C4-C5	0.00	-0.02	0.01	-0.61
C3-C4-C5-C6	0.00	0.02	-0.02	0.44
C1-C6-C5-C4	0.00	-0.02	0.02	0.26
C2-C1-C6-C5	0.00	0.03	-0.02	-0.79
C6-C1-C2-H	180.00	180.00	180.00	-177.25
C1-C2-C3-H	-180.00	-180.00	-180.00	-179.55
C2-C3-C4-H	180.00	180.00	180.00	179.99
C3-C4-C5-H	180.00	180.00	-180.00	-179.50
C4-C5-C6-H	-180.00	-180.00	-180.00	-179.83
C2-C1-C7-H	180.00	179.95	-179.98	-131.14
C7-N-O-H	-179.98	0.00	180.00	9.01
Relative Energy Difference (kcal/mol)[b]				
ΔE	0.00	4.68	1.82	6.16
Rotational Constants (MHz)				
A	5188.52	5170.70	4140.60	3871.87
B	895.25	895.91	1105.69	1131.50
C	763.51	763.60	872.66	946.64
Dipole Moment (D)				
μ_a	-1.21	2.14	1.18	4.70
μ_b	-0.03	2.87	0.00	0.54
μ_c	0.00	0.00	0.00	-0.33

[a] Atom numberings are shown in Fig. 1.

[b] Total energy of (*E*)-1 conformer is -399.680239 hartrees.

100 kHz square-wave Stark-modulated spectrometer at room temperature. The sample was flowed in the waveguide at the pressure of ca. 0.01 Torr. The microwave source employed was a phase-locked YIG-tuned GaAs oscillator (WJ 5610-302FD), using a signal generator (HP 8672A) as a standard frequency oscillator.

3. *AB INITIO* CALCULATIONS

The *ab initio* molecular orbital calculations have been performed at the MP2/6-31G(*d*, *p*) level of theory (*4*, *5*) using the Gaussian 94 program package (*6*). The structural optimizations of the (*E*)- and (*Z*)-isomers of benzaldehyde oxime were carried out by varying the dihedral angle, ϕ, which was the torsional angle of the phenyl group, in steps of 30° between $\phi = 0°$ and 90°. The most stable conformation of each isomer in this molecule was the planar one in which the dihedral angle CNOH was nearly 180° (see (*E*)-1 and (*Z*)-1 in Fig. 1) and the energy differences between the planar conformer and the one with $\phi = 90°$ were 4.6 and 3.0 kcal mol^{-1} for the (*E*)- and (*Z*)-isomers, respectively (see Fig. 2). Then the full optimizations were performed for both isomers; the optimized structures were almost planar. We found two more stable conformations; one was the (*E*)-isomer in which CNOH = 0° (see (*E*)-2 in Fig. 1) and the other was the (*Z*)-isomer in which $\phi = 50°$ and CNOH = 9° (see (*Z*)-2 in Fig. 1). The most stable conformation was (*E*)-1. The optimized parameters, relative energy differences, rotational constants, and the components of the dipole moment in the principal axis system for four conformations of benzaldehyde oxime are summarized in Table 1.

TABLE 2

Observed Transition Frequencies (MHz) of (*E*)-Benzaldehyde Oxime for the Normal and Deuterated Species

Transition							C_6H_5-CH=NOH		C_6H_5-CH=NOD	
J'	K'_{-1}	K'_{+1}	←	J	K_{-1}	K_{+1}	Obsd.	Obsd. – Calcd.	Obsd.	Obsd. – Calcd.
17	2	16		16	2	15	27826.70	0.04		
17	13	4		16	13	3	28227.50	-0.10		
17	11	7		16	10	6			27459.0	-0.04
17	10	8		16	10	7	28238.20	-0.01	27463.1	0.01
17	9	9		16	9	8	28244.30	0.09	27468.6	0.08
17	8	10		16	8	9	28252.50	-0.07	27476.1	0.01
17	7	10		16	7	9	28264.80	-0.02	27487.2	0.03
17	6	11		16	6	10	28283.90	-0.02	27504.4	-0.05
17	5	12		16	5	11			27534.3	-0.08
17	4	14		16	4	13			27576.0	0.00
17	4	13		16	4	12			27606.1	-0.03
17	1	16		16	1	15	28507.95	-0.04		
17	2	15		16	2	14	29200.20	0.04		
18	1	18		17	1	17	28223.20	-0.04		
18	2	17		17	2	16	29417.60	0.03		
18	13	5		17	13	4	29890.00	0.14		
18	12	6		17	12	5	29893.00	-0.06	29072.9	-0.01
18	11	7		17	11	6	29897.10	-0.02	29076.6	0.02
18	10	8		17	10	7	29902.40	0.00	29081.4	0.03
18	9	9		17	9	8	29909.50	0.00	29087.8	0.00
18	8	10		17	8	9	29919.40	-0.02	29096.8	0.02
18	7	11		17	7	10	29933.95	0.00	29109.9	-0.03
18	6	14		17	6	13	29956.60	0.00	29130.5	0.03
18	5	13		17	5	12			29166.4	0.02
18	3	16		17	3	15	29978.50	-0.01	29158.5	0.02
18	4	15		17	4	14	30044.50	0.08	29211.7	0.02
18	4	14		17	4	13	30098.60	-0.02	29256.3	-0.05
18	1	17		17	1	16	30065.20	-0.04		
18	3	15		17	3	14	30501.80	-0.02		
18	2	16		17	2	15	30916.40	0.00		
19	1	19		18	1	18	29759.30	-0.03		
19	0	19		18	0	18	29829.57	0.00		
19	2	18		18	2	17	31002.10	-0.02		
19	14	6		18	14	5			30684.0	-0.08
19	13	7		18	13	6	31552.40	-0.04	30686.8	-0.02
19	12	7		18	12	6	31556.10	-0.08	30690.3	0.08
19	11	8		18	11	7	31560.90	-0.03	30694.5	-0.02
19	10	9		18	10	8	31567.10	-0.02	30700.1	-0.03
19	9	10		18	9	9	31575.40	-0.06	30707.7	0.02
19	8	11		18	8	10	31587.20	0.09	30718.2	-0.03
19	7	12		18	7	11			30733.7	0.00
19	1	18		18	1	17	31605.80	-0.02		
19	6	13		18	6	12	31630.90	-0.09	30758.0	0.10
19	3	17		18	3	16	31632.35	-0.02		
19	5	14		18	5	13	31678.80	0.10	30800.7	-0.04
19	5	15		18	5	14	31674.60	0.07	30797.5	0.02
19	4	15		18	4	14	31806.40	-0.01	30912.9	-0.09
19	4	16		18	4	15	31728.20	0.02	30848.4	-0.01
19	3	16		18	3	15	32281.10	-0.02		
19	2	17		18	2	16	32618.20	-0.01		
20	1	20		19	1	19	31293.70	0.01		
20	0	20		19	0	19	31348.80	-0.09		
20	2	19		19	2	18	32580.40	-0.04		
20	1	19		19	1	18	33132.20	0.02		
20	14	6		19	14	5			32300.8	0.04
20	13	7		19	13	6	33215.60	0.26	32303.9	-0.04
20	12	8		19	12	7	33219.78	0.10	32307.9	0.03
20	11	10		19	11	9	33225.20	0.00	32312.9	0.02
20	10	11		19	10	10	33232.50	0.09	32319.4	0.00
20	9	12		19	9	11	33242.10	-0.02	32328.2	0.01
20	8	13		19	8	12	33255.70	-0.01	32340.5	0.01
20	7	14		19	7	13	33275.60	-0.06	32358.6	0.06
20	3	18		19	3	17	33281.10	0.01		
20	6	15		19	6	14	33306.80	0.04	32386.7	0.02
20	5	16		19	5	15	33357.15	0.03	32432.5	0.00
20	5	15		19	5	14	33363.70	-0.05	32437.7	0.01
20	4	16		19	4	15	33522.70	-0.04	32577.0	-0.05
20	4	17		19	4	16	33412.50	0.06	32485.8	-0.01
20	3	17		19	3	16	34066.90	-0.04		
20	2	18		19	2	17	34304.10	-0.03		
21	1	21		20	1	20	32826.70	0.08		
21	2	20		20	2	19	34152.80	0.03		

TABLE 2—*Continued*

Transition							C_6H_5-CH=NOH		C_6H_5-CH=NOD	
J'	K'_{-1}	K'_{+1}	←	J	K_{-1}	K_{+1}	Obsd.	Obsd. – Calcd.	Obsd.	Obsd. – Calcd.
21	15	6		20	15	5	34871.35	0.09		
21	14	7		20	14	6	34874.45	-0.11	33917.7	-0.01
21	13	8		20	13	7	34878.55	-0.04	33921.4	0.04
21	12	9		20	12	8	34883.50	-0.09	33925.9	0.00
21	11	10		20	11	9	34889.90	-0.06	33931.7	0.03
21	10	11		20	10	10	34898.25	-0.04	33939.2	-0.01
21	9	12		20	9	11	34909.50	-0.02	33949.4	0.03
21	3	19		20	3	18	34924.10	-0.01	33976.6	0.12
21	8	13		20	8	12	34925.25	0.00	33963.6	-0.01
21	7	14		20	7	13	34948.35	-0.02	33984.5	-0.02
21	6	15		20	6	14	34984.60	-0.19	34017.4	0.00
21	5	16		20	5	15	35052.00	-0.09	34077.5	-0.02
21	5	17		20	5	16	35042.00	0.17	34069.5	0.01
21	4	17		20	4	16	35248.80	-0.04	34249.6	-0.01
21	4	18		20	4	17	35096.70	0.04	34123.4	-0.02
21	3	18		20	3	17	35855.60	-0.01		
21	2	19		20	2	18	35972.80	0.05		
22	16	7		21	16	6	36530.60	-0.07		
22	15	8		21	15	7	36533.90	0.08		
22	14	9		21	14	8	36537.80	0.21		
22	13	10		21	13	9	36542.15	-0.05	35539.1	-0.01
22	12	11		21	12	10	36547.90	-0.03	35544.3	-0.01
22	11	12		21	11	11	36555.20	-0.04	35550.9	-0.03
22	10	13		21	10	12	36564.80	0.00	35559.6	0.02
22	9	14		21	9	13	36577.75	0.05	35571.3	0.04
22	8	15		21	8	14	36595.85	0.07	35587.7	0.08
22	7	16		21	7	15	36622.40	0.02	35611.7	0.03
22	7	15		21	7	14	36622.40	0.00		
22	6	17		21	6	16	36664.00	0.18		
22	6	16		21	6	15			35649.5	-0.16
22	5	18		21	5	17	36728.75	0.13	35708.4	-0.02
22	5	17		21	5	16	36743.95	-0.21	35720.6	0.00
22	4	19		21	4	18	36780.20	-0.04	35760.7	-0.03
22	4	18		21	4	17	36986.00	0.13	35931.8	0.04
22	3	20		21	3	19	36560.95	0.00	35572.0	-0.09
22	3	19		21	3	18	37643.15	-0.02		
22	2	21		21	2	20	35719.45	0.03		
22	2	20		21	2	19	37622.65	-0.05		
22	1	21		21	1	20	36154.70	0.06		
23	6	17		22	6	16	38346.20	-0.04		
23	16	7		22	16	6			37145.3	-0.01
23	15	8		22	15	7	38196.60	-0.06	37148.6	0.04
23	14	9		22	14	8			37152.5	0.05
23	13	10		22	13	9	38206.15	-0.04	37157.2	0.00
23	12	11		22	12	10	38212.70	-0.02	37163.0	-0.12
23	11	12		22	11	11	38221.00	-0.05	37170.7	0.03
23	10	13		22	10	12	38231.90	-0.06	37180.5	-0.04
23	9	14		22	9	13	38246.70	0.01	37193.8	-0.07
23	8	15		22	8	14	38267.35	-0.01	37212.6	0.03
23	7	16		22	7	15	38297.80	-0.02	37240.1	-0.01
23	7	17		22	7	16	38297.80	0.01		
23	6	18		22	6	17	38345.20	0.05		
23	6	17		22	6	16			37283.7	-0.05
23	5	18		22	5	17			37367.3	-0.03
23	5	19		22	5	18			37349.2	-0.06
23	4	19		22	4	18			37624.6	0.07
23	4	20		22	4	19			37397.2	0.04
23	3	21		22	3	20	38191.20	-0.01	37161.8	0.01
24	15	10		23	15	9			38765.8	-0.07
24	14	10		23	14	9			38770.3	0.03
24	13	11		23	13	10			38775.6	-0.05
24	12	12		23	12	11			38782.4	0.05
24	11	13		23	11	12			38790.9	-0.01
24	10	14		23	10	13			38802.1	-0.02
24	9	15		23	9	14			38817.3	0.04
24	8	16		23	8	15			38838.5	-0.02
24	7	17		23	7	16			38869.9	0.09
24	6	19		23	6	18			38918.5	0.00
24	5	20		23	5	19			38991.9	0.00
24	5	19		23	5	18			39018.2	-0.01
24	4	20		23	4	19			39328.8	0.05
24	4	21		23	4	20			39032.1	0.01

TABLE 3
Observed and Calculated Rotational Constants, Δ*I*, and Centrifugal Distortion Constants of Benzaldehyde Oxime

C_6H_5-CH=NOH

	Obs.[a]	Theor.[b]						
		(*E*)-1				(*E*)-2	(*Z*)-1	(*Z*)-2
ϕ (deg)		0	30	60	90	0	0	50
A (MHz)	5183.13(29)	5188.52	5140.90	5080.98	5025.17	5170.70	4140.60	3871.87
B (MHz)	895.367(3)	895.25	896.23	888.50	883.83	895.91	1105.69	1131.50
C (MHz)	763.819(3)	763.51	768.86	774.22	779.08	763.60	872.66	946.64
Δ_J (kHz)	0.019(3)							
Δ_{JK} (kHz)	0.204(7)							
ΔI (uÅ^2)[d]	–0.295(6)	0.00	–4.89	–15.50	–23.69	0.00	0.00	–43.31

C_6H_5-CH=NOD

	Obs.[a]	Theor.[c]			
		(*E*)-1	(*E*)-2	(*Z*)-1	(*Z*)-2
ϕ (deg)		0	0	0	50
A (MHz)	5158.4(23)	5162.24	5126.02	4101.93	3821.42
B (MHz)	869.44(2)	869.23	875.51	1075.76	1123.36
C (MHz)	744.34(2)	743.96	747.79	852.25	940.92
Δ_J (kHz)	0.023(2)				
Δ_{JK} (kHz)	0.193(7)				
ΔI (uÅ^2)[d]	–0.28(5)	0.00	0.00	0.00	–45.02

[a] Errors in parentheses are 2.5 times the standard deviation referring to the last significant digit..

[b] Obtained from the *ab initio* calculations at the MP2/6-31G(d, p) level of theory. The geometry of conformers (*E*)-1, (*E*)-2, (*Z*)-1 and (*Z*)-2 was calculated from an unconstrained minimization (see Table 1).

[c] Estimated by using the optimized structure of normal species.

[d] $\Delta I = Ic - Ia - Ib$

4. RESULTS AND DISCUSSION

The microwave spectrum of C_6H_5—CH=NOH in the 26.5–40.0 GHz frequency region, observed with the Stark field of 100 Vcm^{-1}, revealed *K* structures of *a*-type *R* branch appearing with frequency intervals of 1660 MHz. The assignment of the spectral lines ascribed to $K_{-1} = 0$, 1, and 2 were confirmed by observing their Stark behavior and the shapes of the spectral lines at the Stark fields of 1600, 2000, and 2200 Vcm^{-1}, respectively. The intensities of these lines were all weak. The spectral bunches for the deuterated species were observed with intervals of 1620 MHz and were not overlapped with the spectrum of normal species. The intensities of the absorption lines for the deuterated species were weak since the sample was a mixture of normal and deuterated molecules. Therefore, the assignment of the spectral lines for the deuterated species was limited to high *K* lines. The total number of the spectral lines observed and assigned to *a*-type *R*-branch transitions in the ground vibrational states were 117 for normal and 103 for deuterated species (see Table 2).

In the spectral bunches for normal and deuterated species, many absorption lines attributed to the vibrational satellites were observed. In this study, however, the analysis of the

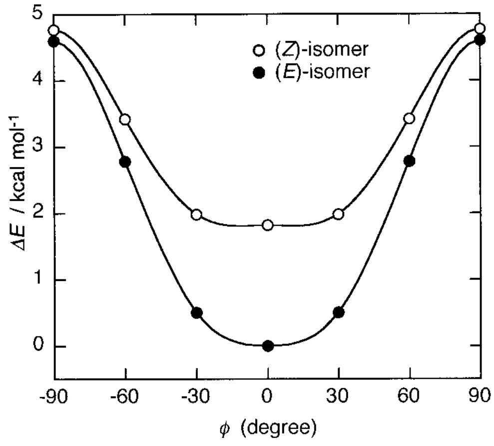


FIG. 2. The torsional potential curve of (*E*)- and (*Z*)-benzaldehyde oxime as a function of the dihedral angle ϕ calculated from the MP2/6-31G(*d*, *p*) *ab initio* MO calculations.

TABLE 4

Structural Parameters of (*E*)-Benzaldehyde Oxime Derived by the Scaling of the Whole *Ab Initio* Geometry for the Reproduction of the Observed Rotational Constants[a]

	fitted	residual [b]		fitted	residual [b]
C1-C2	1.3997(2)	0.0006	C2-C1-C6	119.57(2)	0.03
C1-C6	1.4028(3)	0.0003	C2-C1-C7	121.92(1)	0.00
C1-C7	1.4652(5)	-0.0002	C6-C1-C7	118.51(2)	-0.03
C2-C3	1.3942(5)	-0.0002	C1-C2-C3	119.79(1)	-0.01
C2-H	1.0822(2)	0.0003	C2-C3-C4	120.56(2)	-0.03
C3-C4	1.3984(3)	0.0003	C3-C4-C5	119.72(2)	0.03
C3-H	1.0833(1)	0.0005	C4-C5-C6	119.93(1)	0.00
C4-C5	1.3959(2)	0.0006	C1-C6-C5	120.42(2)	-0.03
C4-H	1.0824(4)	-0.0001	C1-C7-N	120.69(2)	-0.03
C5-C6	1.3939(5)	-0.0002	C7-N-O	109.88(2)	-0.02
C5-H	1.0829(2)	0.0003	C1-C2-H	119.39(2)	0.03
C6-H	1.0845(1)	0.0005	C2-C3-H	119.56(1)	-0.01
C7-N	1.2908(3)	0.0003	C3-C4-H	120.10(2)	-0.02
C7-H	1.0895(1)	0.0005	C4-C5-H	120.22(2)	0.03
N-O	1.4094(4)	0.0000	C5-C6-H	120.09(1)	0.00
O-H	0.9663(2)	0.0003	N-C7-H	120.07(2)	0.03
			N-O-H	101.72(2)	-0.03

[a] Errors in parentheses are estimated from the uncertainties (3σ) of the scaling factor for the cartesian coordinates. Bond lengths are in angstroms and angles are in degrees.

[b] Differences between the fitted values and the theoretical (*ab initio*) ones.

vibrational satellites could not be performed since the absorption lines for low K transitions in the excited vibrational states were too weak to be measured and assigned.

The observed frequencies of the absorption line were fitted to obtain the rotational and centrifugal distortion constants, using Watson's A-reduced Hamiltonian (*7*). Table 3 shows the molecular constants in the ground vibrational state obtained along with those calculated by *ab initio* MO method.

The values of the ΔI $(=I_c - I_a - I_b)$ obtained experimentally were $-0.295(6)$ and $-0.278(2)$ u Å^2 for the normal and deuterated species, respectively. These two values meant that the molecular conformation of this molecule was planar or almost planar. The result of the *ab initio* calculation of C_6H_5—CH═NOH was consistent with this experimental result. In Table 3, the rotational constants for deuterated species estimated by assuming the planar conformation of C_6H_5—CH═NOH optimized at the MP2/6-31G(d, p) level of theory also agreed with the experimental ones. Although it was concluded that (*E*)-benzaldehyde oxime had the planar structure, two rotational isomerisms of this molecule might be possible in respect to the rotation around the N–O bond, i.e., (*E*)-1 and (*E*)-2 as shown in Fig. 1. To elucidate the orientation of the hydroxyl group, the r_s coordinates of the hydrogen atom bonded to the oxygen atom were calculated from the moments of inertia, I_b and I_c, of normal and deuterated species by the Kraitchman's equations (*8*) on the condition of the planar molecular conformation ($\Delta I = 0$). The values of a- and b-coordinate were determined to be 4.105(4) and 0.70(4) Å, respectively (errors in parentheses were 2.5 times the standard deviation). The calculated coordinates of the hydrogen atom were $a = 4.113$ Å for (*E*)-1 and $a = 3.416$ Å for (*E*)-2 conformers on the basis of the *ab initio* calculation. The former value was consistent with the experimental one. Therefore, the observed molecular conformation was concluded to be (*E*)-1 as shown in Fig. 1.

In this study the observed absorption lines were only assigned to the a-type transitions. The calculated dipole moment component (see Table 1) shows that the (*E*)-1 conformer has only μ_a component and so the b-type lines of this conformer may not be expected to be observed.

The absolute value of ΔI of (*E*)-benzaldehyde oxime ($-0.295(6)$ u Å^2) was slightly larger than that of the related compound, benzaldehyde (-0.1199 u Å^2) (*9*). This suggests that there may be some large-amplitude motion around the C–C single bond, which is supported by the calculated vibrational frequency of the torsional motion around the C–C single bond, 78 cm^{-1} (HF/6-31G(d, p), no scaling).

The molecular conformation of this compound in the solid state is tetramer (*2*). Each molecule is slightly distorted with the dihedral angle, ϕ, of ca. 20°. This conformation may be due to an intermolecular hydrogen bond between the nitrogen and the hydrogen atom of the hydroxyl group. However, in the gas phase, the molecular structure might become planar because of no intermolecular interaction. This molecule may have the

TABLE 5

Comparison of *r*(C—C), *r*(C═N), and ∠CCN of (*E*)-Benzaldehyde Oxime and Related Compounds[a]

	r(C–C)[b]	*r*(C=N)	∠CCN
C_6H_5–CH=NOH[c]	1.465(1)	1.291(1)	120.69(2)
C_6H_5–CH=NCH_3[d]	1.460(11)	1.286(8)	126.5(16)
CH_3–CH=NOH[e]	1.508(8)	1.264(4)	118.1(10)
CH_3–CH=NCH_3[f]	1.511(5)	1.278(4)	121.4(7)

Rotational Constants (MHz)

	C_6H_5–CH=NOH			C_6H_5–CH=NOD		
	Obs.	Calc.[g]	Obs.-Calc.	Obs.	Calc.[g]	Obs.-Calc.
A	5183.13(29)	5183.14	-0.1	5158.4(23)	5156.9	1.5
B	895.367(3)	895.529	-0.162	869.44(2)	869.50	-0.06
C	763.819(3)	763.597	0.222	744.34(2)	744.05	0.29

[a] Bond lengths are in angstroms and angles are in degrees. Errors in parentheses are 3 times the standard deviation referring to the last significant digit..

[b] The C–C single bond distance.

[c] This work (r_0 structure).

[d] Reference (10). Determined by gas-phase electron diffraction (r_a structure).

[e] Reference (11). Determined by microwave spectroscopy (r_s structure).

[f] Reference (12). Determined by gas-phase electron diffraction (r_g and $\angle_\alpha$).

[g] Caluculated from the derived structural parameters in Table 4.

conjugation interaction between the phenyl ring and the oxime moiety. The planar conformation of (*E*)-benzaldehyde oxime in the gas phase is consistent with that of *N*-benzylidenemethylamine (C_6H_5—CH═NCH_3) determined by gas-phase electron diffraction (*10*).

Table 4 shows the structural parameters of (*E*)-benzaldehyde oxime derived by the scaling of the whole *ab initio* geometry (Cartesian coordinates in the principal axis system) of (*E*)-1 conformer for best reproduction of the observed rotational constants of the normal species. Since the values of the theoretical rotational constants were in good agreement with the observed ones, the values of the derived structural parameters were almost equal to the theoretical values. Table 5 lists the structural parameters, *r*(C—C), *r*(C═N), and ∠CCN, of (*E*)-benzaldehyde oxime and related compounds, (*E*)-acetaldehyde oxime (CH_3—CH═NOH) (*11*), *N*-benzylidenemethylamine (*10*), and *N*-methylethylideneimine (CH_3—CH═NCH_3) (*12*). The *r*(C—C) and *r*(C═N) of (*E*)-benzaldehyde oxime and *N*-benzylidenemethylamine were shorter and longer than those of (*E*)-acetaldehyde oxime and *N*-methylethylideneimine, respectively. These might be due to the conjugation interaction between the phenyl group and the substituent. The CCN angles in the aromatic compounds were larger than those in (*E*)-acetaldehyde oxime and *N*-methylethylideneimine. This may be ascribed to the effects of steric repulsion between the lone pair electrons on the nitrogen atoms and the phenyl groups.

ACKNOWLEDGMENT

We thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institutes, for the use of the NEC HSP and Gaussian 94 program (Revisions C.2 and E.2).

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