The Microwave Spectrum, Structure, Dipole Moment and Quadrupole Coupling in 1-Pyrrolidinecarboxaldehyde

Sung Guen Lee,[a] Ki Woon Hwang,[a] Robert K. Bohn,[a,*] Kurt W. Hillig II[b] and Robert L. Kuczkowski[b]

[a]Department of Chemistry, University of Connecticut, Storrs, CT 06268, and [b]Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, U.S.A.

The microwave spectrum of 1-pyrrolidinecarboxaldehyde (1-formylpyrrolidine) has been assigned and analyzed at room temperature and in a cold, pulsed molecular beam. The ground state has been characterized by its rotational constants, centrifugal distortion constants, nitrogen quadrupole coupling constant and dipole moment. Rigid rotor rotational constants for the lowest energy vibrationally excited state are also reported. All the data are consistent with the presence of only one conformational isomer which has the 5-membered ring in an envelope conformation with the nitrogen atom at the flap position and the formyl group directed equatorially. The bond from the nitrogen atom to the formyl group lies about 37° out of the plane of the other two N−C bonds.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Structural studies of amides provide consistent and overwhelming evidence that the bonds about the central N−C=O group are coplanar. Planar bonding frameworks have been determined in many gaseous amides, including formamide (H_2NCHO),[1–3] acetamide (H_2NCOCH_3),[4] N-methylformamide (CH_3HNCHO),[5] N,N-dimethylformamide [$(CH_3)_2NCHO$],[6] N-methyl-acetamide ($CH_3HNCOCH_3$),[7] fluoroacetamide (H_2NCOCH_2F), urea ($H_2N)_2CO$[9] and the peptide links in many proteins.[10] The planarity is a consequence of the resonance interaction between the carbonyl group and the nitrogen electron lone pair. The structures of a number of N-containing five-membered ring compounds have been determined and, in each case, the bonding about the N atom is pyramidal. Examples include the unsubstituted compound pyrrolidine[11,12] (H axial), N-chloropyrrolidine[13] (Cl both equatorial and axial, with the equatorial con-

former more stable by 0.7 kcal mol⁻¹), N-methyl-pyrrolidine[13,14] (CH_3 equatorial), and N-cyano-pyrrolidine[15] (CN equatorial). In each of these pyrrolidines, the ring has an envelope conformation with the N atom at the flap position (out of the plane of the four ring-C atoms). The barrier to pseudorotation within the 5-membered ring is relatively high in each of these with the exception of N-cyanopyrrolidine, which has a vibrationally excited state lying less than 4 cm⁻¹ above the ground state.[15]

The coplanarity of the bonds about an N−C=O group also means that the carbonyl group is coplanar with an adjacent bond. Even in compounds in which the carbonyl group is adjacent to an atom with non-planar bonding, the carbonyl group is usually eclipsed with an adjacent bond. A survey of electron diffraction structural studies[16] of free molecules indicates that in compounds containing C=O groups bonded to saturated C atoms, the C=O group is almost always *syn*-eclipsed with an adjacent

---

*To whom correspondence should be addressed.

bond. A ^{13}C NMR study[17] of 1-pyrrolidinecarbox-aldehyde in solution reveals five separate ^{13}C resonances, indicating non-equivalent atoms. Therefore, the aldehyde group cannot lie in the symmetry plane of the pyrrolidine ring in an envelope configuration.

From the above studies it is clear that a nitrogen atom in a saturated 5-membered ring norm-

Table 1. Microwave spectrum of the ground and first vibrationally excited state of 1-pyrrolidinecarboxaldehyde.

Transition	(Unsplit freq.)/MHz	(Obs-Calc)/MHz	Obs/MHz	(Obs-Calc)/MHz
$3_{13}-2_{12}$	9988.7557	−.0020		
$3_{03}-2_{02}$	10481.9415	.0001		
$3_{22}-2_{21}$	10584.6089	.0037		
$2_{12}-1_{01}$	10809.2268	.0002		
$3_{12}-2_{11}$	11148.0738	.0004		
$2_{20}-2_{11}$	12444.6676	.0016		
$4_{14}-3_{13}$	13290.5762	−.0011		
$2_{21}-2_{12}$	13579.2070	−.0017		
$4_{04}-3_{03}$	13860.8977	−.0003		
$4_{23}-3_{22}$	14092.6520	.0000		
$4_{22}-3_{21}$	14344.5140	.0001		
$4_{13}-3_{12}$	14831.2919	−.0003		
$5_{15}-4_{14}$	16571.6304	.0002		
$5_{05}-4_{04}$	17155.4030	−.0012		
$5_{24}-4_{23}$	17583.5118	.0030		
$5_{33}-4_{32}$	17718.9787	.0030		
$5_{32}-4_{31}$	17741.5146	−.0053		
$5_{23}-4_{22}$	18068.7680	.0002		
$5_{14}-4_{13}$	18483.0750	−.0002		
$6_{16}-5_{15}$	10930.33	.15	19887.68	.22
$6_{06}-5_{05}$	20368.89	.04	20422.28	.14
$6_{25}-5_{24}$	21053.03	−.06	21107.59	.33
$6_{24}-5_{23}$	21851.92	−.09	21907.53	.22
$6_{15}-5_{14}$	22091.47	−.04	22142.22	.19
$7_{17}-6_{16}$			23133.26	.20
$7_{07}-6_{06}$	23520.18	.02	23582.88	.09
$7_{26}-6_{25}$	24497.63	.00	24560.96	.22
$7_{16}-6_{15}$	25642.48	−.05	25701.06	.02
$7_{25}-6_{24}$	25670.13	−.09	25734.36	.12
$8_{18}-7_{17}$	26231.28	.04		
$8_{08}-7_{07}$			26708.07	.01
$8_{27}-7_{26}$	27913.86	.02	27985.96	.09
$8_{17}-7_{16}$	29120.81	−.02	29187.03	−.06
$9_{19}-8_{18}$	29477.93	.09	29563.83	−.21
$8_{26}-7_{25}$	29491.28	−.10		
$9_{09}-8_{08}$	29738.00	.02	29820.73	.02
$9_{28}-8_{27}$	31299.38	.18	31380.14	.01
$9_{37}-8_{36}$	31927.69	.15	32054.28	−.04
$9_{18}-8_{17}$	32512.54	−.02	32586.40	.03
$10_{110}-9_{19}$	32569.23	.06	32755.14	−.07
$10_{010}-9_{09}$	32841.35	.02	32934.51	.04
$9_{27}-8_{26}$	33285.69	−.02	33365.43	−.08
$10_{29}-9_{28}$	34652.50	.34	34741.93	−.07
$10_{37}-9_{36}$			36325.80	−.17
$10_{28}-9_{27}$	37030.65	−.11	37117.61	−.09
$11_{210}-10_{29}$	37972.55	.18	38070.88	−.33

ally has its bonds directed pyramidally. It is also clear that a nitrogen atom which is part of an amide group has its bonds coplanar. The nitrogen atom in 1-pyrrolidinecarboxaldehyde simultaneously exists in both environments. This study was initiated to determine the conformation of 1-pyrrolidinecarboxaldehyde and to examine the coplanarity of the bonds about the nitrogen atom.

Experimental

1-Pyrrolidinecarboxaldehyde was obtained from Aldrich Chemical Co. and was vacuum distilled prior to use. Its IR and ^{1}H NMR spectra gave no evidence of impurities. Microwave spectra were recorded between 18–40 GHz for the room temperature vapor at about 60 microns Hg pressure in a Hewlett-Packard 8460A Stark-modulated spectrometer. Lines are fairly broad and no quadrupole splittings from the ^{14}N nucleus were resolved. Vibrational satellite spectra were evident, and the ground state and most intense excited state transitions were assigned and measured to an accuracy of about 0.1 MHz. Spectra in the range 8–18.5 GHz were recorded with a Fourier transform (FT) cavity microwave spectrometer equipped with a Bosch fuel injector pulsed nozzle gas source.[18,19] Since 1-pyrrolidinecarboxaldehyde has low volatility, a sample of liquid was placed in a reservoir just upstream from the nozzle and heated to 110 °C. Argon at 1–1.5 atm swept the vapor above the warm liquid through the pulsed nozzle. 1-Pyrrolidinecarboxaldehyde comprised 1–2 % of the flowing gas. Timing of the gas and microwave pulses was coordinated to eliminate Doppler splitting of the transitions. The lines have full widths at half-maximum of 25 kHz, and quadrupole splittings were resolvable. The frequencies are estimated to be accurate to 2 kHz.

Results

Spectral assignment. Survey scans between 18 and 40 GHz revealed a-type R-branch pile-ups with spacings of 3530 MHz. Model calculations suggested that the $K_{-1} = 0$, 1 and 2 lines should be split out from the pile-ups. These were found and assigned. All the lines measured in the room temperature gas (24 for the ground state and 25 for the first vibrationally excited state) are a-type. Attempts to measure b- and c-type transi-

tions under these conditions failed due to the extremely rich and frequently unresolved vibrational satellite pattern. The observed frequencies and assignment are shown in Table 1. This assignment accounts for all the more intense lines in the spectrum as well as all the unresolved pile-ups. There is no evidence for any other conformer.

Further measurements on the ground state species were made on the Fourier transform pulsed gas beam spectrometer. The quadrupole coupling constants for formamide[20] ($\chi_{aa} = 1.960$ and $\chi_{bb} = 1.888$ MHz) were used to estimate the quadrupole splittings of 1-pyrrolidinecarboxaldehyde. The observed and calculated patterns of components were so similar that the assignment was straightforward. The quadrupole splittings (54 well-resolved components from 16 transitions) were analyzed and quadrupole coupling constants determined. The derived quadrupole coupling constants are $\chi_{aa} = 1.747(2)$ and $\chi_{bb} = 2.500(3)$ MHz. The rms deviation between observed and calculated splittings is 2.2 kHz. The quadrupole coupling data and results are summarized in Table 2.

The hypothetical unsplit frequencies were determined for 19 transitions, 16 a-type and 3 b-type. Three of these transitions were not included above in the quadrupole coupling analysis because the splittings were not well enough resolved. Nevertheless, the unsplit frequencies could still be accurately determined. The rotational constants and four centrifugal distortion constants (Watson's S reduction, I^r representation) were then determined using all observed frequencies in the least-squares fit weighted inversely according to their estimated uncertainties (Table 1). Introduction of a fifth centrifugal distortion constant, d_2, did not improve the fit and its uncertainty was as large as its small magnitude; it was therefore omitted. No satellite lines were visible in the FT spectra because of the low temperature (ca. 1 K) of the gas in the pulsed beam. The spectrum of the vibrationally excited species was fitted by a rigid rotor model since the accuracy of measurement of the transition frequencies did not warrant a more detailed analysis (Table 1). Relative intensity measurements to estimate the vibrational frequency could not be made due to spectral congestion and overlapping transitions. The final rotational and centrifugal distortion constants are listed in Table 3.

Table 2. ^{14}N Quadrupole coupling in 1-pyrrolidinecarboxaldehyde.

Transition	Fitted Unsplit Frequency/MHz	$F' \leftarrow F''$	Splitting Obs/MHz	(Obs-Calc)/MHz
$3_{13}-2_{12}$	9988.7557	3–3	1.4963	−.0001
		3–2	0.1343	.0031
		2–2	−2.0177	−.0015
		4–3	−0.0957	−.0014
$3_{03}-2_{02}$	10481.9415	2–2	−1.0065	−.0007
		4–3	−0.0565	.0040
		2–1	0.0125	−.0028
		3–2	0.1105	.0020
		3–3	0.7625	−.0024
$3_{22}-2_{21}$	10584.6089	2–1	−0.4349	.0018
		4–3	−0.1249	−.0001
		3–2	0.4351	−.0017
$2_{12}-1_{01}$	10809.2268	1–1	−1.4998	−.0012
		3–2	−0.2148	.0012
		2–1	0.6232	−.0019
		2–2	1.1512	.0020
$3_{12}-2_{11}$	11148.0738	3–3	−0.6708	−.0006
		2–1	−0.2298	.0020
		4–3	−0.0118	.0030
		3–2	0.1302	−.0033
		2–2	1.0172	−.0011
$2_{20}-2_{11}$	12444.6676	1–1	−0.1136	.0010
		3–3	−0.0346	−.0018
		2–2	0.1154	.0009
$4_{14}-3_{13}$	13290.5762	3–3	−2.1002	−.0012
		5–4	−0.0622	.0013
		4–4	1.6658	−.0001
$2_{21}-2_{12}$	13579.2070	2–2	−1.4990	−.0004
		3–2	−0.9350	.0020
		1–2	−0.6270	−.0020
		2–3	−0.1310	.0023
		3–3	0.4320	.0038
		2–1	0.6200	−.0051
		1–1	1.4980	−.0006
$4_{04}-3_{03}$	13860.8977	5–4	−0.0677	−.0010
		4–3	0.1363	.0010
$4_{23}-3_{22}$	14092.6520	3–2	−0.1380	−.0009
		5–4	−0.0680	.0018
		4–3	0.1910	−.0009
$4_{13}-3_{12}$	14831.2919	3–2	−0.1009	.0002
		5–4	−0.0149	.0002
		4–3	0.0821	−.0005
$5_{15}-4_{14}$	16571.6304	6–5	−0.0494	.0001
		4–3	0.0226	.0019
		5–4	0.0576	−.0019
$5_{24}-4_{23}$	17583.5118	6–5	−0.0468	.0012
		5–4	0.1132	−.0012
$5_{33}-4_{32}$	17718.9787	6–5	−0.0657	−.0036
		5–4	0.1763	.0036
$5_{32}-4_{31}$	17741.5146	4–3	−0.1096	.0053
		6–5	−0.0586	−.0028
		5–4	0.1544	−.0025
$5_{14}-4_{13}$	18483.0750	6–5	−0.0170	.0034
		5–4	0.0720	−.0034

$$\chi_{aa} = 1.747(2)^a \text{ MHz}$$
$$\chi_{bb} = 2.500(3) \text{ MHz}$$
$$\chi_{cc} = -4.247(4) \text{ MHz}$$

[a] 1 standard deviation

Table 3. Rotational Constants for 1-pyrrolidinecarboxaldehyde.

	Ground State	Excited State
A/MHz	6097.2012(24)	6066.9(4)
B/MHz	1957.5059(4)	1961.503(4)
C/MHz	1570.7053(4)	1575.757(4)
D_J/MHz	0.000185(4)	
D_{JK}/MHz	0.000357(18)	
D_K/MHz	0.0019(5)	
d_1/MHz	−0.000013(4)	
$\varkappa$	−0.829092	−0.82822

Table 4. Structural Parameters (Å and °) for 1-pyrrolidinecarboxaldehyde.

Assumed		Determined	
C−C	1.55	θ(flap)	32
C−N	1.46	φ(pyramid)	37
N−C(HO)	1.385	τ(C−N−C=O)	0
C=O	1.22		
C−H	1.10		
∠CCC	105.5		
∠CNC	108.5		
∠HCH	109.5		
Ring plane of symmetry			

Fig. 1. Definition of flap angle, θ, and the nitrogen pyramid angle, φ, in 1-pyrrolidinecarboxaldehyde.

Molecular structure. Since the molecule has 16 atoms and no symmetry except in certain assumed conformations, only a rough structure determination is possible from assignment of a single isotopic species. Since the ring structures in pyrrolidine[11,12] and its N-chloro-,[13] N-methyl-[13,14] and N-cyano-[15] derivatives have been reported to have the envelope conformation with the N atom at the flap position, the same conformation was assumed for 1-pyrrolidinecarboxaldehyde. Reasonable bond lengths and angles were also assumed (listed in Table 4) and the structure was refined by least-squares methods allowing the flap angle, θ, of the 5-membered ring envelope (Fig. 1), the pyramid angle, φ, of the bonds around the nitrogen atom (Fig. 1), and the torsion of the CHO group to vary. The deviation of the exocyclic N−C(HO) bond from the assumed symmetry plane of the pyrrolidine ring was also considered, but the molecule's rotational con-
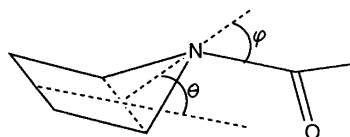
stants are not sensitive to this parameter and no preferred value could be determined. Using a variety of different starting models, the refined C−N−C=O torsional angle deviated from planarity by less than 6°. Therefore, we conclude that the C−N−C=O angle is essentially zero (*syn*-planar). In all of the refinements the flap angle was in the range between 31 and 32° and the pyramid angle at the N atom was between 36 and 38°. A reasonable structural model which fits the microwave spectrum is summarized in Table 4 and drawn in Fig. 2. There are certainly other structures which can fit the microwave spectrum but it is highly unlikely that the bonding about the N atom can be coplanar or that the carbonyl group is significantly twisted from a *syn*-planar conformation with an adjacent ring N−C bond.

A structural parameter particularly sensitive to the planarity of the bonding about the N atom is P_{cc}, the second moment which measures deviations of atom positions from the *ab* principal axis plane (Fig. 2). The observed value is quite small, viz. 9.35 amu Å². If the bonding about the N atom is constrained to be planar, the flap angle must decrease to bring about agreement between the calculated and observed P_{cc} values. However, this lengthens the molecule along the *a*-axis such that there is not agreement between calculated and observed P_{aa} values, for example, for any reasonable set of bond lengths and angles. Therefore, the observed P_{cc} value provides strong evidence in support of a non-planar bonding configuration about the nitrogen atom.

Table 5 presents a summary of flap angles of the pyrrolidine ring and the pyramid angles at the nitrogen atom in the pyrrolidine derivatives whose structures have been studied. The sum of the three bond angles about the nitrogen atom is also shown. For coplanar bonding the sum would be 360°, and for tetrahedral bonding the sum would be 328.5°. The flap angle is smallest in compounds with axial substituents or unsaturated equatorial substituents which can have resonance
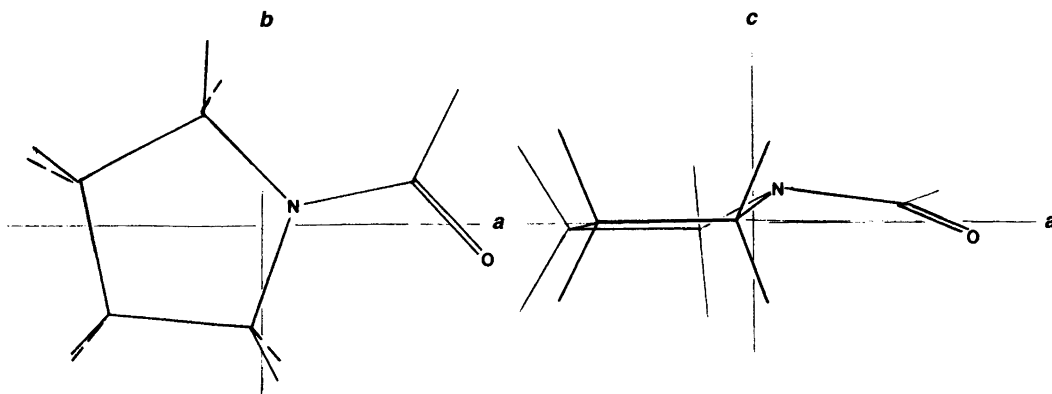
Fig. 2. Structure of 1-pyrrolidinecarboxaldehyde: Left: Projection onto *ab* plane. Right: Projection onto *ac* plane.

interactions with the nitrogen lone pair. Apparently, steric interactions between the axial substituent and the ring favor flattening the ring.

Trends of bond angles about the N atom are also clear. Axial substituents favor sharply pyramidal bonding configurations about the N atom. The pyramid angle, φ, would be 54.8° in a tetrahedral structure and is more peaked in pyrrolidine and the axial conformer of *N*-chloropyrrolidine. The pyramid angle is flatter in all of the equatorially substituted pyrrolidines and flattest (37°) in 1-pyrrolidinecarboxaldehyde, the compound with the greatest resonance interaction between the substituent and the N atom. However, even this structure is far from planar.

None of the observed transitions have perturbations which are not explained by the above analysis. We conclude that pseudorotation in the 5-membered ring of 1-pyrrolidinecarboxaldehyde is hindered by a substantial potential barrier.

Dipole moment. Stark field measurements on a few transitions near 12 GHz were first attempted on the room temperature vapor with the Hewlett-Packard spectrometer. The richness of the vibrational satellite pattern and the weakness of the transitions prevented successful analysis. Stark shifts in the cold, pulsed beam of the FT spectrometer were easily measurable but the analysis was complicated by the presence of quadrupole

Table 5. Some geometric parameters in pyrrolidine derivatives (°).

Compound Method	H−P[a] ED[b]	CH₃−P[a] ED[c]	Cl−P[a] ED[c]	CN−P[a] MW[d]	CHO−P[a] MW[e]
Equatorial substitution					
θ(flap)		42	45	24	32
φ(pyramid)		49	53	46	37
Sum of N					
bond angles		333	329	337	344
Axial substitution					
θ(flap)	39		36		
φ(pyramid)	−61		−59		
Sum of N					
bond angles	319		322		

[a]H−P is pyrrolidine, CH₃−P is *N*-methylpyrrolidine, etc. [b]Ref. 12. [c]Ref. 13. [d]Ref. 15. [e]This work.

as well as electric field perturbations. Electric fields available on the FT spectrometer with its Stark plates separated by about 30 cm, up to about 700 V cm⁻¹, are not large enough to reach the strong-field limit in which the quadrupole moment and rotational angular momentum are uncoupled. Quadrupole corrections to the Stark levels were calculated according to eqn. (1).[21]

$$E_q^{(1)} = \frac{eQq_j \, [32M_J^2 - J(J+1)][3M_I^2 - I(I+1)]}{4J(2J-1)I(2I-1)} \quad (1)$$

These corrections assume that the off-diagonal elements of the quadrupole Hamiltonian can be ignored. The corrections are only semi-quantitatively correct but they allowed the hypothetical quadrupole-unsplit Stark shifts to be estimated. These unsplit frequencies were plotted vs. the square of the electric field and the slopes determined. Nine components of three transitions were analyzed. The data and results are summarized in Table 6. The dipole moment lies predominantly along the a-axis [μ_a = 4.24(2) D] with a smaller b-component [μ_b = 1.28(3) D] and a still smaller c-component [μ_c = 0.60(6) D]. The total dipole moment [μ_T = 4.47(7) D] is comparable to, but larger than, that of N,N-dimethylformamide [μ_T = 3.85(2) D].[6] The larger magnitude of the dipole moment in 1-pyrrolidinecarboxaldehyde is consistent with a more polar, non-planar configuration of the bonds about the nitrogen atom. Also, the small c-axis dipole moment component is consistent with the carbonyl group lying close to the ab-plane, i.e., essentially syn-planar with one of the ring N−C bonds.

Summary. The microwave spectrum of 1-pyrrolidinecarboxaldehyde has been observed for the room temperature vapor and for a cold, pulsed beam. Rotational constants and centrifugal distortion constants for the ground state and rigid rotor rotational constants for the lowest energy vibrationally excited species are reported. The dipole moment and quadrupole coupling constants have been determined. All of the data are consistent with a single conformational isomer with the formyl substituent, approximately eclipsed with a *syn* CN bond, occupying an equatorial position on a nitrogen with pyramidal bonding. There is no evidence for other conformers.

Table 6. Dipole moment of 1-pyrrolidinecarboxaldehyde.

Transition	$\|M\|$	Stark Shift /MHz/(V/cm)²/10⁻⁵	Obs − Calc
3_{03}–2_{02}	0	−3.71	−0.00
	1	−0.71	−0.04
	2	8.43	−0.03
4_{14}–3_{13}	0	−1.60	−0.08
	1	0.03	0.02
4_{13}–3_{12}	0	0.50	−0.01
	1	−0.41	0.02
	2	−3.24	0.01
	3	−7.96	−0.01
μ_a /D	4.24(2)		
μ_b /D	1.28(3)		
μ_c /D	0.60(6)		
μ_d /D	4.47(7)		

References

1. Kurland, R. J. and Wilson, E. B. *J. Chem. Phys. 27* (1957) 585.
2. Kukolich, S. G. and Nelson, A. C. *Chem. Phys. Lett. 11* (1971) 383.
3. Brown, R. D., Godfrey, P. D. and Kleibömer, B. *J. Mol. Spectrosc. 124* (1987) 34.
4. Kitano, M. and Kuchitsu, K. *Bull. Chem. Soc. Jpn. 46* (1973) 3048.
5. Elzaro, R. A. and Schwendeman, R. H. *Symposium on Molecular Structure and Spectroscopy*, Ohio State University, Ohio 1973, Paper CC6.
6. Elzaro, R. E., Brittain, A. H., Thompson, H. B. and Schwendeman, R. H. *Symposium on Molecular Structure and Spectroscopy*, Ohio State University, Ohio 1973, Paper CC7.
7. Kitano, M. and Kuchitsu, K. *Bull. Chem. Soc. Jpn. 46* (1973) 384.
8. Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct. 22* (1984) 287.
9. Brown, R. D., Godfrey, P. D. and Storey, U. I. *J. Mol. Spectrosc. 58* (1975) 445.

10. Kennard, O. and Watson, D. G. *Mol. Struct. Dimensions 1* (1970) 343.
11. Caminati, W., Oberhammer, H., Pfafferott, G., Filgueira, R. R. and Gomez, R. R. *J. Mol. Spectrosc. 106* (1984) 217.
12. Pfafferott, G., Oberhammer, H. and Boggs, J. E. *J. Am. Chem. Soc. 107* (1985) 2305.
13. Pfafferott, G., Oberhammer, H. and Boggs, J. E. *J. Am. Chem. Soc. 107* (1985) 2309.
14. Caminati, W. and Scappini, F. *J. Mol. Spectrosc. 117* (1986) 184.
15. Su, C. F. and Harmony, M. D. *J. Mol. Spectrosc. 112* (1985) 328.
16. Bohn, R. K. In: Sutton, L. E., Ed., *Diffraction Studies of Molecular Structure,* Specialist Periodical Reports of the Chemical Society, London 1977, Chap. 2.
17. Llinares, J., Faure, R., Vincent, E. J. and Elguero, J. *Spectrosc. Lett. 14* (1981) 423.
18. Hillig, K. W., II, Matos, J., Scioly, A. and Kuczkowski, R. L. *Chem. Phys. Lett. 133* (1987) 359.
19. Balle, T. J. and Flygare, W. H. *Rev. Sci. Instrum. 52* (1981) 33.
20. Kukolich, S. G. and Nelson, A. C. *Chem. Phys. Lett. 11* (1971) 383.
21. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra.* In: Weissberger, A., Ed., *Techniques of Chemistry,* Wiley-Interscience, New York 1984, Vol. XVIII.