

## QUANTUM CHEMICAL STUDIES ON THE STRUCTURE AND VIBRATIONAL SPECTRA OF 2-PYRROLIDINONE

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### ABSTRACT

A systematic study on the structural characteristics of the 2-pyrrolidinone (2-py) has been investigated using different methods at different basis sets, where in all cases the twist form was found to be the only minimum exist. A complete vibrational analysis conducted for the twist ( $C_1$ ) 2-pyrrolidinone (2-py) molecule based on the experimental infrared spectra and Raman spectra in the 100 - 4000  $\text{cm}^{-1}$  region, and the potential energy distribution obtained from the normal coordinate analysis, as well as the wave numbers calculated using the B3LYP/6-31G(d) level with their scaled wave numbers. A good correlation was found between the calculated and the experimental wave numbers.

**Keywords:** Quantum studies , Vibrational spectra , 2-pyrrolidone

### INTRODUCTION

The conformational analysis of saturated five-membered rings has been the subject of experimental [Laane J (1972); Legon, A.C (1980); Strauss, H.L. (1983) ; Adams, W. J., et al.(1970) ; Geise, H.J.,et al. (1969); Engerholm, G. G., et al. (1969); Cadioli, B., et al. (1993)] and theoretical studies [Cadioli, B., et al. (1993) ; Cremer, D., et al.(1975); Dabado, J.A., et al. (1994); Han S.J., et al. (1996)]. These rings can invert their conformation passing through different envelope and twist forms, in a movement that has certain characteristics of rotation, where the atoms move perpendicularly to the ring without contributing to the angular momentum. This motion was given a name pseudorotation [Kilpatrick, J. E., et al. (1947)]. 2-pyrrolidinone, which belong to such systems, may have the envelope and twist structures expected of stable conformations (see Fig. (1)). A potential energy surface scanning for 2-py was theoretically investigated in order to detect these two conformations, using different quantum mechanical levels of computation and to investigate the influence of the

different computational levels on molecular geometry. A detailed vibrational assignment of 2-py molecule was reported [Mc Dermott, D.P. (1986)] based on the assumption of a  $C_s$  symmetry of the the 2-py molecule and the measured liquid and gas phase IR and Raman was discussed on this assumption. Based on the conformational study of 2-py in this work, where the 2-py was found to have a  $C_1$  twist structure, we initiate a vibrational assignment reinvestigation with the aid of theoretical calculations.

## METHODS OF CALCULATIONS

For a systematic study on the structural characteristics of the 2-pyrrolidinone (2-py), several calculations using the semiempirical methods were performed with the hyperchem program [Hyperchem 8, Hypercube, Inc.]. Also, MP2 and DFT calculations were performed with the Gaussian 03 program [Gaussian 03 program, Gaussian Inc. Walling ford CT 2004]. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [Pulay, P., (1969)]. The 6-311G(d,p) basis set, as well as the corresponding ones with diffuse functions were employed with the Møller-Plesset perturbation method [Møller, C. and Plesset, M.S., (1934)] to the second order (MP2(full)) as well as with the density functional theory by the B3LYP method.

## RESULTS AND DISCUSSION

### Molecular Structure of 2-pyrrolidinone

#### Conformational preference and Ring Puckering

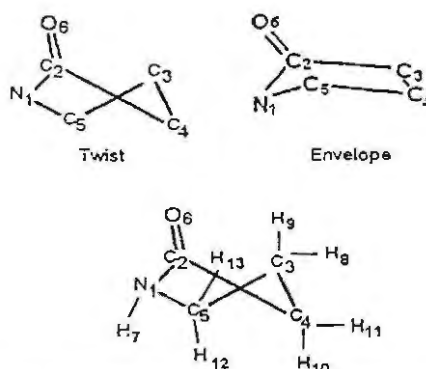


Fig. (1) : The expected conformations for 2-pyrrolidinone and their atomic numbering order.

The semiempirical methods; INDO, MINDO3, MNDO, MND/d, AM1 and RM1, showed only one stationary point, at which molecule has overall a planar structure. This result is not reasonable and does not satisfy the expected structural configuration. The Semi-empirical PM3 method, on the other hand, resulted in only one stationary point representing a structure in which the five membered ring has an envelope form where

the N-atom with the two adjacent C- atoms ( at the two sides of N-atom ) of the ring forming a plane in which the N-atom is an apex. The four carbons (  $C_2-C_3-C_4-C_5$  ) forming another plane, and the interplaner angle was calculated to be about 13 degrees. The hydrogen atom of the N-H group is about 21 degrees out-of-the plane of N-atom with the two adjacent carbons. The envelope structure which has equatorial hydrogen was found to be more stable than that with axial hydrogen by about 3.22 Kcal/mol ( -1271.16 and -1267.94 Kcal/mol). The optimized envelope form has a dipole moment value of 3.52 D (which is far from that experimentally reported (3.96 D) [De Smet, K., (1996) ]. The MP2 with full electron correlations as well as the density functional theory, DFT, using the B3LYP (the hybrid Exchange-Correlation Functional defined by Becke, to contains an exchange functional that consists of : 20% - Hartree-Fock Exchange, 8% - Slater Exchange, and 72% - Becke Exchange, plus a correlation functional that consists of 19% VWN#5 Correlation and 81% - LYP Correlation [Lee, C., (1993)] employing different basis sets (including diffuse functions) with different size were also used to carry out a conformational search and optimize the obtained molecular conformations of 2-pyrrolidinone. All the MP2 as well as DFT methods resulted in only one stationary point representing a structure in which the five membered ring has a twisted structure ( see Fig. (1) ). No other stationary points corresponding to the envelope or the planar structure could be detected as a global minimum and confirmed by vibrational analysis.

The potential energy curve was calculated by determining the structural total electronic energy corresponding to the structure formed by systematic variation of the  $C_2-C_3-C_4-C_5$  dihedral angle (see atomic numbering order in Fig. (1)). The DFT/B3LYP/6-311G(d,p) level of computation was employed, since it produced the closest value of dipole moment compared to the experimentally determined value [De Smet, K., (1996)]. The calculated total electronic energy values were plotted against the dihedral angle and shown in Fig. (2) .

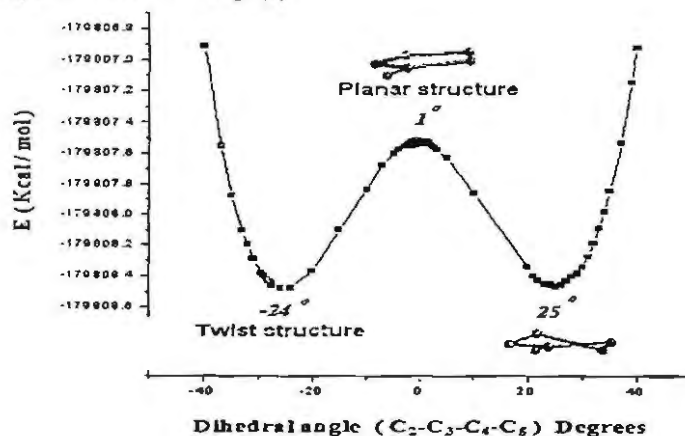


Fig. (2) : The potential energy curve of 2-pyrrolidinone as a result of the variation of the  $C_2-C_3-C_4-C_5$  dihedral angle from DFT/ B3LYP/6-311G(d,p) basis set level.

As shown in the potential energy curve Fig. (2) there is only one global minimum at a ring-twist angle of 25 degrees, and at a total energy of -179808.47 Kcal/mol. Also, there is one saddle point at dihedral angle of about 1.0 degree. No local minima was detected which may indicate the possible existence of other conformations. Trials were also continued to obtain a structure for the other expected envelope conformation for the molecule, by applying restraints of different ring twist-angles other than C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub>-C<sub>5</sub> dihedral angle of the skeleton, using the same level of computation in a geometry optimization process, but no stable conformations were detected.

The structure of the molecule at the saddle point have nearly a quasi-planar ring structure showing one negative frequency which indicated that we are dealing with a first order stationary point. The quasi-planar form was found to be more energetic (~ 1 Kcal/mol) than the twist form Fig. (2).

#### Ground State Structural Parameters of 2-pyrrolidinone

The optimized molecular bond lengths, bond angles, dihedral angles and atomic charge densities of 2-pyrrolidinone as obtained from different methods of computation are given in Table (1).



Table (1) : Selected structural parameters of 2-pyrrolidinone as obtained From the different methods of computations.

method	MP2(full)		DFT		Sum of Covalent Radii (Å)	Experimentally determined values	
	6-311 G(d,p)	6-311++ G(d,p)	6-311G(d,p)	6-311++ G(d,p)		ED [Takeshima, T. et al.,]	X-ray[Muller, G.,et al. ]
<b>Bond length</b>							
N <sub>1</sub> -C <sub>2</sub>	1.3565	1.3740	1.3711	1.3702	1.47 (1.29 for N=C) <sup>Gillespie, R.J.</sup>	1.384	1.345(2)
N <sub>1</sub> -C <sub>5</sub>	1.4480	1.4539	1.4561	1.4579	1.47	1.463	1.454(1)
N <sub>1</sub> -H <sub>7</sub>	0.9938	1.0105	1.0086	1.0091	1.02	-	-
C <sub>2</sub> -C <sub>3</sub>	1.5196	1.5252	1.5326	1.5304	1.54	1.532	1.514(2)
C <sub>2</sub> =O <sub>6</sub>	1.1905	1.2187	1.2122	1.215	1.28	1.219	1.225(1)
C <sub>3</sub> -C <sub>4</sub>	1.5322	1.5304	1.5368	1.5376	1.54	1.536	-
C <sub>3</sub> -H <sub>8</sub>	1.0868	1.0961	1.0951	1.0952	1.09	1.109	-
C <sub>3</sub> -H <sub>9</sub>	1.0816	1.0906	1.0899	1.0899	1.09	1.109	-
C <sub>4</sub> -C <sub>5</sub>	1.5370	1.5369	1.5458	1.5458	1.54	1.555	1.524(2)
C <sub>4</sub> -H <sub>10</sub>	1.0827	1.0915	1.0907	1.0906	1.09	1.109	-
C <sub>4</sub> -H <sub>11</sub>	1.0848	1.0934	1.0927	1.0927	1.09	1.109	-
C <sub>5</sub> -H <sub>12</sub>	1.0886	1.0982	1.0982	1.0977	1.09	1.109	-
C <sub>5</sub> -H <sub>13</sub>	1.0833	1.0923	1.0927	1.0923	1.09	1.109	-
<b>Bond angle</b>							
C <sub>2</sub> -N <sub>1</sub> -C <sub>5</sub>	113.9	113.8	114.9	114.8		113.9	113.8(1)
C <sub>2</sub> -N <sub>1</sub> -H <sub>7</sub>	119.1	119.1	119.8	119.9		122.8	123.4(1)
C <sub>5</sub> -N <sub>1</sub> -H <sub>7</sub>	123.4	123.5	123.6	123.6		122.8	122.2(1)
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	106.2	106.5	106.5	106.8		107.1	108.2(1)

method	MP2(full)		DFT		Sum of Covalent Radii (Å)	Experimentally determined values	
	6-311 G(d,p)	6-311++ G(d,p)	6-311G(d,p)	6-311++ G(d,p)		ED [Takeshima, T.et al.,]	X-ray[Muller, G.,et al. ]
N <sub>1</sub> -C <sub>2</sub> -O <sub>6</sub>	126.3	126.1	126.1	125.9		-	125.3(1)
C <sub>3</sub> -C <sub>2</sub> -O <sub>6</sub>	127.6	127.4	127.4	127.3		-	126.5(1)
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	104.1	104.1	104.6	104.6		-	105.2(1)
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	102.9	103.1	103.9	103.9		103.6	-
N <sub>1</sub> -C <sub>5</sub> -C <sub>4</sub>	101.5	101.6	102.2	102.3		103.0	104.0(1)
<b>Dihedral Angle</b>							
C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	-7.8	-7.6	-5.5	-5.4			
C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub> -O <sub>6</sub>	171.4	171.7	173.6	173.7			175.3(1)
H <sub>7</sub> -N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	-167.1	-166.9	-170.8	-170.8			-175.8(1)
N <sub>1</sub> -C <sub>5</sub> -C <sub>4</sub> -C <sub>3</sub>	-32.9	-32.3	-27.3	-26.9			-19.8
N <sub>1</sub> -C <sub>2</sub> -C <sub>5</sub> -H <sub>7</sub>	-158.3	-158.3	-164.7	-164.8			-
C <sub>2</sub> -N <sub>1</sub> -C <sub>3</sub> -O <sub>6</sub>	179.2	179.3	179.1	179.1			-
H <sub>7</sub> -N <sub>1</sub> -C <sub>2</sub> -O <sub>6</sub>	12.1	12.4	8.2	8.3			3.9(2)
C <sub>2</sub> -N <sub>1</sub> -C <sub>5</sub> -C <sub>4</sub>	26.2	25.7	21.2	20.9			-
H <sub>7</sub> -N <sub>1</sub> -C <sub>5</sub> -C <sub>4</sub>	-175.4	-175.9	-174.0	-174.3			-172.8(1)
<b>Atomic Charge</b>							
N <sub>1</sub>	-0.518	-0.295	-0.406	-0.174			
C <sub>2</sub>	0.526	0.342	0.335	0.136			
C <sub>3</sub>	-0.269	-0.316	-0.277	-0.264			
C <sub>4</sub>	-0.218	-0.317	-0.252	-0.309			
C <sub>5</sub>	0.034	-0.242	-0.044	-0.288			

method	MP2(full)		DFT		Sum of Covalent Radii (Å)	Experimentally determined values	
	6-311 G(d,p)	6-311++ G(d,p)	6-311G(d,p)	6-311++ G(d,p)		ED [Takeshima, T.et al.,]	X-ray[Muller, G.,et al. ]
O <sub>6</sub>	-0.486	-0.474	-0.353	-0.372			
H <sub>7</sub>	0.238	0.329	0.223	0.296			
H <sub>8</sub>	0.131	0.179	0.138	0.170			
H <sub>9</sub>	0.139	0.184	0.142	0.177			
H <sub>10</sub>	0.112	0.152	0.124	0.150			
H <sub>11</sub>	0.117	0.157	0.129	0.160			
H <sub>12</sub>	0.101	0.139	0.118	0.150			
H <sub>13</sub>	0.109	0.161	0.122	0.162			
E (Kcal/Mol)	-178805.99	-178809.51	-179911.40	-179916.23			
μ(Debye)	4.401	4.691	3.969	4.350			
Ring twist angle (Degrees)	29.28	28.34	24.94	24.54			

Comparative graphs of bond lengths, bond angles and dihedral angles, as well as the charge densities obtained from the different levels of computations are presented in Fig. (3). Generally it was found that, theoretically predicted values of the optimized bond lengths are slightly larger than the corresponding experimental values. This may be attributed to fact that the performed theoretical calculations that belong to isolated molecules in the gaseous phase and the experimental results belong to molecules in the solid state. Comparing different parameters of 2-py obtained from B3LYP with that obtained from MP2, were found the data of the former was larger than the later. However, the B3LYP calculated values correlate well with the experimentally determined data. The bond lengths and bond angles are nearly the same by the two approaches. The charge density on the different atoms for the 2-pyrrolidinone molecule especially N<sub>1</sub>, C<sub>2</sub> and C<sub>5</sub> are strongly affected using different approaches. The charge density on the nitrogen atom as example is highly affected by the addition of the diffused function, where its value obtained by the MP2(full)/6-311G(d,p) was found to be (-0.52) and decreased to a value about (-0.3) when adding a diffused function to the basis set used, (see Fig. (3d)). No definite trend for the change for atomic charge density values can be deduced, when the different approaches are used.

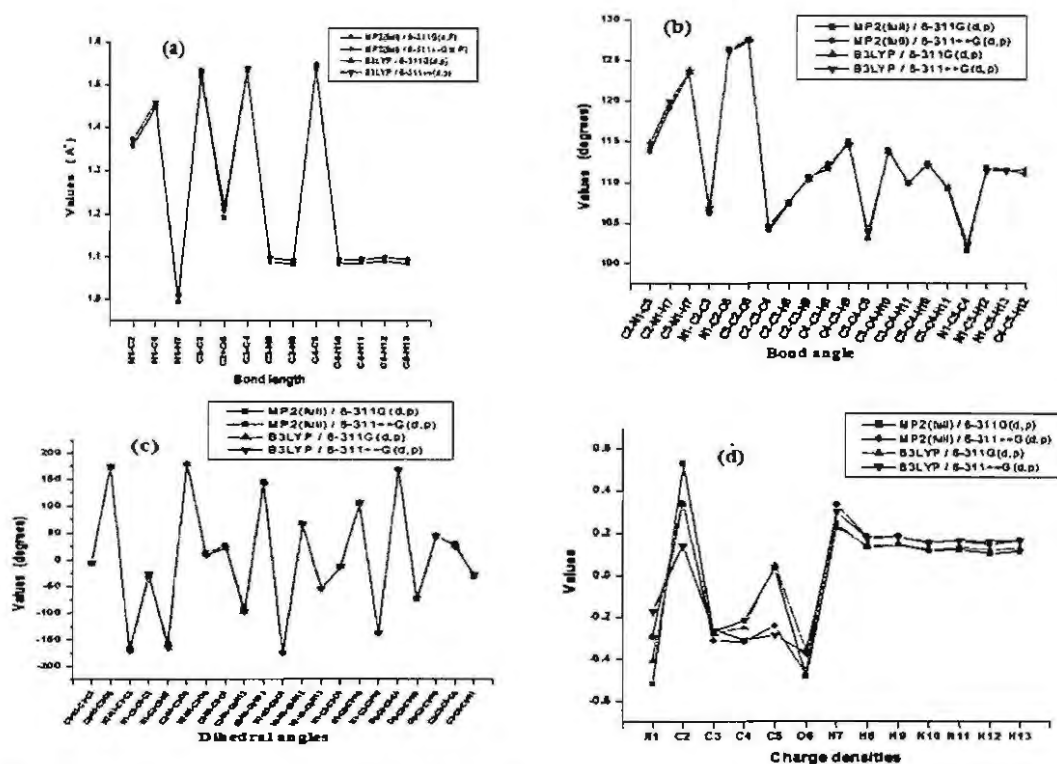


Fig. (3) : Comparative graphs of the results obtained from theoretical MP2 and DFT approaches for 2-pyrrolidinone molecule. (a) bond length; (b) bond angle; (c) dihedral angle; (d) charge densities differences



The optimized bond lengths of 2-py as seen from Table (1) showed that the bond lengths  $r_{N_1-C_2}$  and  $r_{N_1-C_5}$  have values of 1.3711 Å and 1.4561 Å respectively. These values are less than the bond length value for a pure undisturbed N-C single bond (1.47 Å), as estimated from the sum of the covalent radii of the N and C atoms. At the same time, these two bond-length values are much longer than 1.29 Å, the bond length value for a C=N double bond. However, the  $N_1-C_2$  is slightly shorter than  $N_1-C_5$  as a result of the effect of the C=O bond adjacent to  $N_1-C_2$ .

The  $N_1-H_7$  bond length Table (1) was found to be 1.0086 Å, which is slightly longer than the unperturbed N-H bond length for pyrrolidine molecule (1.000 Å) [El Defrawy, A. M., (2008); El-Gogary, T.M. and Soliman, M.S., (2001)] and slightly shorter than the normal unaffected N-H bond (1.02 Å). Moreover, the results indicated that the nitrogen atom of the NH- group in 2-pyrrolidinone, exhibits a trigonal planar structure more than the expected pyramidal geometry. This is attributed to the effect of the interaction with the carbonyl group and can be attributed to a certain population of hybridization [Gillespie, R.G., et al. (1970); Gaedt, K., (1998)]. This is also revealed from the resulted in value for the dihedral angle  $N_1-C_2-C_5-H_7$  (164.74 degrees). This led to an out-of-plane angle of the N-atom from the plane of the  $C_2-C_5-H_7$  atoms of a value of 9.48 degree. This value is lower than the corresponding angle in case of pyrrolidine molecule (37.8 degrees) [El Defrawy, A. M., (2008); El-Gogary, T.M. and Soliman, M.S., (2001)] and much lower than the normal out-of-plane angle for saturated nitrogen atom. On the other hand, The  $C_2$ - atom of the carbonyl group exhibit the expected trigonal planar structure (179.1° for the  $C_2-N_1-C_3-O_6$  dihedral angle)

The calculated value for the carbonyl group,  $C_2=O_6$ , was found to be 1.212 Å. This value is slightly higher than the calculated value for cyclopentanone molecule (1.182 Å) using the same level of computation which reflect the interaction of the N-H group with the carbonyl group. The  $N_1-C_2-O_6$  and  $C_3-C_2-O_6$  angles were found to be 126.1° and 127.3° respectively.

The electrostatic potential isosurface for 2-py molecule as obtained from the B3LYP/6-311G(d,p) method of calculation is shown in Fig. (4). This Figure shows that the centers are capable accepting protons or could be attacked by an electrophile. The calculated atomic charges Table (1) indicated that the Hydrogen atom attached to the nitrogen atom is the highest positively charged hydrogen atom in the molecule. This indicates that it is the highest acidic H-atom in the molecule. The hydrogen atoms,  $H_8$  and  $H_9$  which are directly attached to  $C_3$ , the carbon atom adjacent to the carbonyl group (see Fig. (1)), have charge densities of (+0.1382 and +0.1418). These values are higher than the corresponding values for the two H-atoms  $H_{12}$  and  $H_{13}$  which are directly attached to  $C_5$ , the carbon atom adjacent to the N-H group (+0.1184 and +0.1223) as well as the two H-atoms  $H_{10}$  and  $H_{11}$  which are directly attached to  $C_4$  (+0.123 and +0.129) respectively. These theoretically predicted structural parameters Table (1), are in good agreement with the experimental data [Takeshima, T., et al. (2007); Muller, G., et al. (1996)].



**Fig. (4):** Mapping of the 3D electrostatic potential isosurface for 2-pyrrolidinone molecule as obtained from B3LYP/6-311G(d,p) calculations at a contour value of 0.25 vibrational assignment

In order to obtain a complete description of the molecular motions involved in the fundamental modes of 2-pyrrolidinone, a normal coordinate analysis has been carried out. The force field in Cartesian coordinates was obtained with the Gaussian 03 program at the DFT/B3LYP level with the 6-31G(d) basis set. The internal coordinates used to calculate the **G** and **B** matrices are given in Fig. (5) with the atomic numbering shown in Fig. (1). By using the **B** matrix [Guirgis, G.A., (2000)], the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, scaling factors of 0.89 for CH stretches, 0.87 for C=O stretch and with 0.91 for all other coordinates were applied, along with the geometric average of scaling factors for interaction force constants, to obtain the fixed scaled force field and resultant wavenumbers. A set of symmetry coordinates was used Table (3) to determine the corresponding potential energy distributions (P.E.D.s). A comparison between the observed and calculated wave numbers, along with the calculated infrared intensities, Raman activities, depolarization ratios and potential energy distributions are listed in Table (2).

The vibrational spectra of 2-Pyrrolidinone as obtained from the infrared and Raman measurements of 2-pyrrolidinone in its standard state (the pure liquid state at room temperature) have been reported [Schrader, B. and Meier, W., (1978)] and shown in Fig. (6). A detailed vibrational assignment of 2-py molecule was reported [Mc Dermott, D.P., (1986)] based on the assumption of a  $C_s$  symmetry of the the 2-py molecule and the measured liquid and gas phase IR and Raman was discussed on this assumption. Based on the conformational study of 2-py in this work, where the 2-py was found to have a  $C_1$  twist structure, a detailed vibrational assignment can be made rather straight forward. This can be done based on the predicted frequencies and the Raman depolarization ratio using the B3LYP/6-31G (d) level of calculation, which with only three scaling factors can predict the observed fundamentals of the  $C_1$  twist 2-py remarkably well. The agreement between the predicted and the observed frequencies is good enough when taking into consideration the significantly strong intermolecular interaction in the liquid phase.



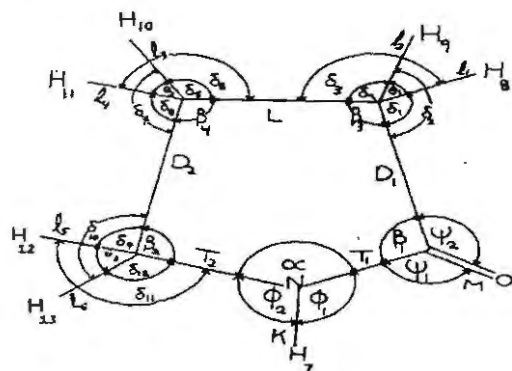


Fig. (5) : Definition of the internal coordinates of 2-pyrrolidinone

2-pyrrolidinone molecule is a five membered heterocyclic molecule containing a total of 13 atoms (4 carbons, 7 hydrogens, one nitrogen and one oxygen). Such system possesses 39 degree of freedom, and has a total of 33 fundamental modes of vibrations ( $3n-6$ ). These modes represent different possibilities of the internal motion of atoms relative to each other and they have different vibrational frequencies very characteristic of the molecule. In addition to these 33 normal modes, there are three rotational as well as three translational modes. 2-pyrrolidinone has a total of 43 molecular internal coordinates. These coordinates are those involved to describe the different 33 fundamental modes of vibration of the molecule.

The five membered ring moiety of 2-pyrrolidinone has five internal coordinates corresponding to the five bonds of the ring. See Table (2). Therefore, a five stretching fundamental vibrations of the ring in which their highest amplitude of the vibrational motion should be observed for these five internal coordinates. In addition to these fundamentals there is one more skeletal fundamental stretching mode should be detected as a result of a vibrational mode, which is a responsibility of a stretching motion of the C=O (carbonyl group) internal coordinate. Therefore, we are dealing with six stretching modes for the 2-py molecular skeleton and as indicated in Table (2). These ring stretching modes ( $\nu_{16}$ ,  $\nu_{21}$ ,  $\nu_{22}$ ,  $\nu_{23}$ ,  $\nu_{25}$ ) are observed at 1229, 995, 920, 980 and 810  $\text{cm}^{-1}$  respectively where the mode  $\nu_{25}$  represents ring breathing with a PED 51% from the  $S_{26}$  symmetry coordinate Table (2).

The carbonyl group is contained in a large number of different class of compounds, for which a strong absorption band due to the C=O stretching vibration is observed in the region 1850-1550  $\text{cm}^{-1}$  [Socrates, G., (1981)]. For the 2-py molecule, the mode C=O stretch was observed in the IR spectra at 1671  $\text{cm}^{-1}$  and it was theoretically predicted by the B3LYP/6-31G(d) at 1713  $\text{cm}^{-1}$ , whereas this mode was observed at 1660  $\text{cm}^{-1}$  in the Raman spectrum. Two modes  $\nu_{28}$  and  $\nu_{31}$  were assigned to C=O out of plane and C=O in plane bend respectively with the mode  $\nu_{28}$  (C=O out of plane bend) showing considerable mixing with contribution from modes  $\nu_{29}$ ,  $\nu_{23}$  and  $\nu_{16}$  with 21%, 12% and 11% respectively.

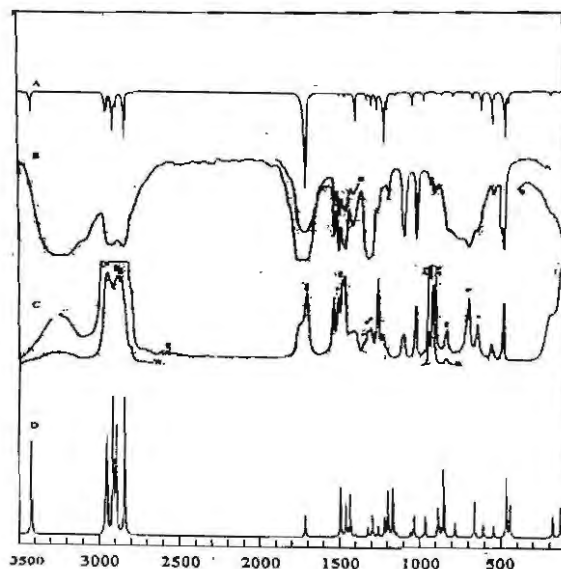


Fig. (6) Comparison of experimental [Schrader, B. and Meier, W., (1978)] and Calculated (B3LYP/6-31G\*) infrared spectra of 2-py molecule: (A) simulated infrared spectrum; (B) observed infrared spectrum. (C) observed Raman spectrum. (D) Simulated Raman spectrum.

The structure of 2-pyrrolidinone including three  $-\text{CH}_2-$  groups, and consequently there are six C-H internal coordinates should be responsible for six different fundamental modes of vibrations. These are the modes  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$ ,  $\nu_6$  and  $\nu_7$  as indicated in Table (2). These modes are showing a PED% more than 50% except for mode  $\nu_5$  and  $\nu_6$  for the  $\beta$ - $\text{CH}_2$  sym. stretch where there is a mixing of the modes with a contribution of 47%  $S_5$ , 24%  $S_6$  and 14%  $S_4$  for the mode  $\nu_5$ , while for the mode  $\nu_6$  the contributions are 43%  $S_6$ , 32%  $S_5$  and 18%  $S_3$  Table (2). In addition to these fundamentals there is one more fundamental should be arisen as a result of the stretching motion of the characteristic N-H internal coordinates. This is the  $\nu_1$  mode as indicated in Table(2). The difference between the predicted frequency  $3421 \text{ Cm}^{-1}$  for this mode and that observed ( $3250 \text{ Cm}^{-1}$ ) in the IR spectra could be explained on the basis of the strong intermolecular interaction in the liquid phase compared to the gas phase theoretically predicted frequency Table (2). Two modes  $\nu_{27}$  and  $\nu_{29}$  observed at  $680 \text{ Cm}^{-1}$  and  $540 \text{ Cm}^{-1}$  in the IR spectrum were assigned to ring deformation modes with both of the two modes show a considerable mixing with three other modes Table (2).

The structure of 2-pyrrolidinone molecule have three  $-\text{CH}_2-$  groups. For each one of these groups, there are five angle deformation internal coordinates Fig. (5). These five coordinates, of each  $-\text{CH}_2-$  group, are responsible for four angle-deformation fundamental vibrations (one of them is redundant): one  $-\text{CH}_2-$  scissoring, one  $-\text{CH}_2-$  wagging, one  $-\text{CH}_2-$  twisting, and one  $-\text{CH}_2-$  rocking vibrational modes. Modes  $\nu_9$ ,  $\nu_{10}$  and  $\nu_{11}$  were assigned as  $\text{CH}_2$  deformations modes Table (2) and these modes appear to



be pure modes to a considerable extent as observed from their PED values Table 2). Most of the rest of  $\text{CH}_2$  deformation modes as the  $\text{CH}_2$  twist,  $\text{CH}_2$  rock and  $\text{CH}_2$  wag involve extensive mixing with significant contributions from other symmetry coordinates as observed from their PED values in Table (2).

On the other hand, the N-H bond makes two angle- deformation internal coordinates with the ring bonds. These two internal coordinates are responsible for two fundamental angle deformation modes of this N-H bond with the ring: one for in-plane, and the other for out-of-plane angle- deformation fundamental vibrations, the  $\nu_{13}$  and  $\nu_{30}$  modes as described in Table (2). By investigating the IR and Raman spectra in this study, and by comparing it to the most comprehensive vibrational study [Mc Dermott, D.P. (1986)], It was observed that some bands were not existing in the previous assignment. In the  $2800 \text{ Cm}^{-1}$  region two bands at  $2885$  and  $2840 \text{ Cm}^{-1}$  were not previous reported are assigned to  $\nu_6$  and  $\nu_7$  modes respectively. Another band  $1140 \text{ Cm}^{-1}$  is assigned as  $\beta$ -  $\text{CH}_2$  twist ( $\nu_{19}$ ) where this band was not assigned previously. In the  $800 \text{ Cm}^{-1}$  region, a band at  $850 \text{ Cm}^{-1}$  is assigned to  $\nu_{24}$  as  $\alpha$ -  $\text{CH}_2$  rock is not reported in ref. [Mc Dermott, D.P. (1986)].

Another mode according to ref [Mc Dermott, D.P. (1986)] was observed at  $740 \text{ Cm}^{-1}$  and was assigned as N-H out of plane bend, but in our results this mode is assigned at  $490 \text{ Cm}^{-1}$  with a PED 58%  $S_{30}$  and with a 12% contribution from mode  $S_{52}$  Table(2). For the rest of the modes, there was a good agreement between the vibrational assignment of ref [Mc Dermott, D.P. (1986)] and this work.

Table (2): Calculated<sup>a</sup> and observed frequencies (cm<sup>-1</sup>) for 2-pyrrolidinone twisted (C<sub>1</sub>) form

Vib. No.	Approx. description	B3LYP	Fixed scaled	IR int.	Raman act.	dn ratio	infrared	Raman	P.E.D. <sup>c</sup>
								liquid	
v <sub>1</sub>	N-H stretch	3627	3421	24.5	122.1	0.27	3250	3250	100S <sub>1</sub>
v <sub>2</sub>	β-CH <sub>2</sub> <i>assym</i> stretch	3137	2959	21.9	78.6	0.61	2970	2971	80S <sub>2</sub>
v <sub>3</sub>	β-CH <sub>2</sub> <i>assym</i> stretch	3126	2949	19.1	85.9	0.38	2948	2950	71S <sub>1</sub> +16S <sub>1</sub> +11S <sub>1</sub>
v <sub>4</sub>	α-CH <sub>2</sub> <i>assym</i> stretch	3089	2914	50.9	124.7	0.20	2910	2917	53S <sub>1</sub> +23S <sub>7</sub> +12S <sub>7</sub> +11S <sub>1</sub>
v <sub>5</sub>	β-CH <sub>2</sub> <i>sym</i> stretch	3075	2901	13.1	57.9	0.58	2900	2892	47S <sub>1</sub> +24S <sub>1</sub> +14S <sub>1</sub>
v <sub>6</sub>	β-CH <sub>2</sub> <i>sym</i> stretch	3063	2890	14.2	95.3	0.17	2885	2892	43S <sub>1</sub> +32S <sub>7</sub> +18S <sub>1</sub>
v <sub>7</sub>	α-CH <sub>2</sub> <i>sym</i> stretch	3011	2840	68.5	123.2	0.21	2840	2840	69S <sub>7</sub> +30S <sub>1</sub>
v <sub>8</sub>	C=O stretch	1837	1713	415.3	8.5	0.56	1671	1660	81S <sub>7</sub> +11S <sub>3</sub>
v <sub>9</sub>	α-CH <sub>2</sub> def.	1564	1491	3.9	17.1	0.56	1490	1490	93S <sub>9</sub>
v <sub>10</sub>	β-CH <sub>2</sub> def.	1527	1457	5.2	11.3	0.72	1461	1461	69S <sub>16</sub> +25S <sub>11</sub>
v <sub>11</sub>	β-CH <sub>2</sub> def.	1500	1431	3.3	13.9	0.73	1435	1438	73S <sub>11</sub> +25S <sub>19</sub>
v <sub>12</sub>	α-CH <sub>2</sub> wag.	1462	1395	38.5	0.8	0.62	1377	1370	30S <sub>12</sub> +30S <sub>13</sub> +17S <sub>23</sub>
v <sub>13</sub>	NH-in plane def.	1383	1319	9.9	2.9	0.75	1301	1301	22S <sub>13</sub> +19S <sub>12</sub> +18S <sub>13</sub> +15S <sub>13</sub>
v <sub>14</sub>	β-CH <sub>2</sub> twist	1353	1291	15.6	6.1	0.65	1284	1283	21S <sub>16</sub> +20S <sub>11</sub> +16S <sub>12</sub> +13S <sub>13</sub>
v <sub>15</sub>	β-CH <sub>2</sub> wag.	1319	1258	21.0	3.0	0.67	1262	1261	33S <sub>11</sub> +26S <sub>13</sub> +15S <sub>14</sub>
v <sub>16</sub>	Ring def.	1277	1218	78.6	5.1	0.62	1229	1225	13S <sub>16</sub> +13S <sub>13</sub> +10S <sub>11</sub> +18S <sub>11</sub>
v <sub>17</sub>	α-CH <sub>2</sub> twist	1254	1196	20.1	11.9	0.72	1190	1190	44S <sub>17</sub> +20S <sub>11</sub> +15S <sub>19</sub>
v <sub>18</sub>	β-CH <sub>2</sub> wag	1222	1166	1.1	12.4	0.67	1169	1169	22S <sub>15</sub> +25S <sub>16</sub> +13S <sub>12</sub> +11S <sub>21</sub>
v <sub>19</sub>	β-CH <sub>2</sub> twist	1198	1142	4.2	1.0	0.68	1140	1140	31S <sub>19</sub> +30S <sub>11</sub> +20S <sub>17</sub>
v <sub>20</sub>	β-CH <sub>2</sub> rock	1105	1054	0.4	1.3	0.75	1070	1065	38S <sub>20</sub> +19S <sub>11</sub> +18S <sub>12</sub>
v <sub>21</sub>	Ring def.	1085	1035	16.1	4.7	0.75	995	995	30S <sub>21</sub> +17S <sub>16</sub> +12S <sub>13</sub>
v <sub>22</sub>	Ring def.	1010	964	10.6	4.1	0.74	920	920	48S <sub>22</sub> +16S <sub>18</sub> +12S <sub>29</sub>
v <sub>23</sub>	Ring def.	926	883	0.8	5.0	0.12	890	890	15S <sub>23</sub> +20S <sub>11</sub> +13S <sub>23</sub> +10S <sub>21</sub>
v <sub>24</sub>	α-CH <sub>2</sub> rock	916	874	2.0	1.2	0.75	850	845	30S <sub>24</sub> +28S <sub>11</sub> +21S <sub>20</sub> +10S <sub>12</sub>
v <sub>25</sub>	Ring breathing	892	851	3.7	11.6	0.10	810	810	51S <sub>25</sub> +18S <sub>21</sub> +18S <sub>29</sub>
v <sub>26</sub>	β-CH <sub>2</sub> rock	818	780	5.6	2.1	0.27	730	720	32S <sub>26</sub> +19S <sub>19</sub> +12S <sub>11</sub> +12S <sub>27</sub>
v <sub>27</sub>	Ring def.	695	663	7.7	4.4	0.31	680	680	49S <sub>27</sub> +21S <sub>1</sub>
v <sub>28</sub>	C=O out of plane	637	608	23.5	1.4	0.57	625	625	41S <sub>28</sub> +21S <sub>28</sub> +12S <sub>21</sub> +11S <sub>14</sub>

<sup>a</sup>B3LYP/6-31G(d) calculations, scaled frequencies, infrared intensities (Km/mol), Raman activities (Å<sup>4</sup>/u), depolarization ratios(dp) and potential energy distributions(P.E.D.s).

<sup>b</sup>scaled frequencies with scaling factors of 0.89 for CH and stretches, 0.87 for C=O stretch and 0.91 for all other modes.

<sup>c</sup>symmetry coordinates with P.E.D contribution less than 10% are omitted

Table (3) Symmetry coordinates of 2- pyrrolidinone.

Description	Symmetry Coordinate <sup>a</sup>
N-H stretch	$S_1 = K$
$\beta$ -CH <sub>2</sub> assym.stretch	$S_2 = l_1 - l_2 + l_3 - l_4$
$\beta$ -CH <sub>2</sub> assym.stretch	$S_3 = l_1 - l_2 - l_3 + l_4$
$\alpha$ -CH <sub>2</sub> assym.stretch	$S_4 = l_5 - l_6$
$\beta$ -CH <sub>2</sub> sym.stretch	$S_5 = l_1 + l_2 - l_3 - l_4$
$\beta$ -CH <sub>2</sub> sym.stretch	$S_6 = l_1 + l_2 + l_3 + l_4$
$\alpha$ -CH <sub>2</sub> sym.stretch	$S_7 = l_5 + l_6$
C = O stretch	$S_8 = M$
$\alpha$ -CH <sub>2</sub> def.	$S_9 = 4\theta_3 - \delta_{10} - \delta_{12} - \delta_9 - \delta_{11}$
$\beta$ -CH <sub>2</sub> def.	$S_{10} = 4\theta_1 - \delta_2 - \delta_4 - \delta_1 - \delta_3 + 4\theta_2 - \delta_6 - \delta_8 - \delta_5 - \delta_7$
$\beta$ -CH <sub>2</sub> def	$S_{11} = 4\theta_1 - \delta_2 - \delta_4 - \delta_1 - \delta_3 - 4\theta_2 + \delta_6 + \delta_8 + \delta_5 + \delta_7$
$\alpha$ -CH <sub>2</sub> wag.	$S_{12} = \delta_{10} + \delta_9 - \delta_{12} - \delta_{11}$
NH-in plane def.	$S_{13} = \Phi_1 - \Phi_2$
$\beta$ -CH <sub>2</sub> twist	$S_{14} = \delta_2 - \delta_4 - \delta_1 + \delta_3 + \delta_6 - \delta_8 - \delta_5 + \delta_7$
$\beta$ -CH <sub>2</sub> wag.	$S_{15} = \delta_2 - \delta_4 + \delta_1 - \delta_3 + \delta_6 - \delta_8 + \delta_5 - \delta_7$
Ring def.	$S_{16} = T_1 - T_2 - D_1 + D_2$
$\alpha$ -CH <sub>2</sub> twist	$S_{17} = \delta_{10} - \delta_{12} - \delta_9 + \delta_{11}$
$\beta$ -CH <sub>2</sub> wag	$S_{18} = \delta_2 - \delta_4 + \delta_1 - \delta_3 - \delta_6 + \delta_8 - \delta_5 + \delta_7$
$\beta$ -CH <sub>2</sub> twist	$S_{19} = \delta_2 - \delta_4 - \delta_1 + \delta_3 - \delta_6 + \delta_8 + \delta_5 - \delta_7$
$\beta$ -CH <sub>2</sub> rock	$S_{20} = \delta_2 + \delta_4 - \delta_1 - \delta_3 - \delta_6 - \delta_8 + \delta_5 + \delta_7$
Ring def.	$S_{21} = T_1 + T_2 - D_1 - D_2$
Ring def.	$S_{22} = 4L - T_1 - T_2 - D_1 - D_2$
Ring def.	$S_{23} = \delta_{10} - T_2 + D_1 - D_2$
$\alpha$ -CH <sub>2</sub> rock	$S_{24} = \delta_{10} + \delta_{12} - \delta_9 - \delta_{11}$
Ring breathing	$S_{25} = T_1 + T_2 + D_1 + L + D_2$
$\beta$ -CH <sub>2</sub> rock	$S_{26} = \delta_2 + \delta_4 - \delta_1 - \delta_3 + \delta_6 + \delta_8 - \delta_5 - \delta_7$
Ring def.	$S_{27} = 4\alpha - \beta_1 - \beta_3 - \beta_4 - \beta_2$
C=O out of plane	$S_{28} = \Gamma_4$
Ring def.	$S_{29} = \beta_1 - \beta_2 + \beta_3 - \beta_4$
N-H out of plane	$S_{30} = \Gamma_3$
C=O in plane bend	$S_{31} = \Psi_1 - \Psi_2$
Ring twist	$S_{32} = \Gamma_1 + \Gamma_2$
Ring puckering	$S_{33} = \Gamma_1 - \Gamma_2$

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## الملخص العربي

## دراسات كيميائية كمية على تركيب وطيف الاهتزاز ل ٢-بيرووليدينون

اسم الباحث

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تم دراسة التركيب الفراغى لمركب ٢-بيرووليدينون باستخدام الطرق المختلفة لحسابات ميكانيكا الكم لتعيين المدرات الجزئية . وتم تحليل طرق الاهتزاز له بناءً على النتائج العملية لطيف الأشعة تحت الحمراء وطيف ارامان فى المنطقة ما بين ١٠٠-٤٠٠٠ سم<sup>-1</sup>، ودراسة توزيع طاقة الوضع الناتجة من تحليل محاور الإهتزاز ، و قيم الأعداد الموجية الناتجة من B3LYP/6-31G(d) مع تلك المقاسة عملياً. وقد وجد توافق ما بين قيم الأعداد الموجية المقاسة عملياً وتلك المحسوبة نظرياً.