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SPECTROSCOIC INVESTIGATIONS OF 2-HYDROXY-4-METHYL PYRIMIDINE HYDROCHLORIDE

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ABSTRACT

The vibrational frequencies of 2-hydroxy-4-methyl pyrimidine were calculated using Gaussian 03 software package and the fundamental modes are assigned. The calculated frequencies are in agreement with the reported experimental values. The calculated geometrical parameters are compared with the geometrical parameters of similar derivatives. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non linear optics.

Key words: Pyrimidine, Hyperpolarizability, HF Calculations, Methyl.

INTRODUCTION

N-Heterocyclic molecules like pyrimidine, uracil and cytosine show a great importance as they play a central role in the structure and properties of nucleic acids[1-3].The vibrational spectra of some disubstituted pyrimidines have been reported by Singh *et al.*[4] Yadav *et al.*[5] reported the FTIR spectroscopic study of 2-hydroxy-4-methyl pyrimidine hydrochloride. Kartha[6] interpreted the spectra of 4-methyl- and 5-methyl-pyrimidine and the 2-X pyrimidines have been studied by several authors[7]. In this work, we have calculated the vibrational frequencies of the title compound by using HF method and compared it with the IR bands observed by Yadav et al.[5].

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COMPUTATIONAL DETAILS

Calculations of the title compound were carried out with Gaussian03 program[8] using the HF/6-31G* basis set to predict the molecular structure and wave numbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wave number values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation[9]. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set[9]. The absence of imaginary wave number on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The spectral assignment was aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes. The optimized geometrical parameters are given in Table 1.

Table 1: Optimized geometrical parameters

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C_1–N_2	1.3277	A(2,1,6)	125.6	D(6,1,2,3)	0.26
C_1–N_6	1.3219	A(2,1,9)	117.5	D(6,1,2,15)	-46.7
C_1–O_9	1.3405	A(6,1,9)	116.9	D(9,1,2,3)	-179.9
N_2–C_3	1.3324	A(1,2,3)	117.1	D(9,1,2,15)	133.2
C_3–C_4	1.3834	A(1,2,15)	90.9	D(2,1,6,5)	-0.1
C_3–H_7	1.0705	A(2,3,4)	121.7	D(9,1,6,5)	180.0
C_4–C_5	1.3961	A(2,3,7)	116.4	D(2,1,9,14)	0.4
C_4–H_8	1.0698	A(4,3,7)	121.9	D(6,1,9,14)	-179.7
C_4–H_{16}	2.9842	A(7,3,15)	99.8	D(1,2,3,4)	-0.3
C_5–N_6	1.3353	A(3,4,5)	117.2	D(1,2,3,7)	179.6
C_5–Cl_{10}	1.4962	A(3,4,8)	121.4	D(1,2,15,4)	85.4
O_9–H_{14}	0.9525	A(5,4,8)	121.5	D(1,2,15,16)	-121.8
C_{10}–H_{11}	1.0808	A(5,4,15)	94.1	D(2,3,4,5)	0.5
C_{10}–H_{12}	1.0829	A(8,4,15)	82.3	D(2,3,4,8)	179.1

Cont…

Bond lengths (Å)		Bond angles (º)		Dihedral angles (º)	
C_{10}–H_{13}	1.0825	A(4,5,6)	120.4	D(7,3,4,5)	-179.5
H_{15}–Cl_{16}	1.2960	A(4,5,10)	123.0	D(7,3,4,8)	-0.8
		A(6,5,10)	116.6	D(7,3,15,16)	-56.7
		A(1,6,5)	118.0	D(3,4,5,6)	-0.4
		A(1,9,14)	112.5	D(3,4,5,10)	179.5
		A(5,10,11)	111.8	D(8,4,5,6)	-179.1
		A(5,10,12)	109.7	D(8,4,5,10)	0.8
		A(5,10,13)	109.9	D(15,4,5,6)	97.5
		A(11,10,12)	109.0	D(15,4,5,10)	-82.6
		A(11,10,13)	109.1	D(5,4,15,2)	-89.2
		A(12,10,13)	107.3	D(8,4,15,2)	149.6
		A(2,15,4)	35.4	D(4,5,6,1)	0.2
		A(2,15,16)	179.9	D(10,5,6,1)	-179.6
		A(3,15,16)	162.1	D(4,5,10,11)	1.9
		L(4,15,16,2,-2)	207.2	D(4,5,10,12)	-119.1
				D(4,5,10,13)	123.2
				D(6,5,10,11)	-178.2
				D(6,5,10,12)	60.8
				D(6,5,10,13)	-56.9

RESULTS AND DISCUSSION

The calculated scaled wave numbers, IR and Raman bands and their assignments are given in Table 2. For pyrimidines[7], υCH is expected in the region 3020-3120 cm^{-1} and the pyrimidine ring stretching modes are expected in the region 1250-1590 and 985 ± 10 cm^{-1}. Pyrimidines absorb strongly at 1600-1500 cm^{-1} due to C = C and C = N ring stretching vibrations[10]. The CH in-plane and out-of-plane deformation bands of the pyrimidine ring are expected in the regions[11,12] 1500 - 1000 cm^{-1} and 1000 - 750 cm^{-1}. Singh *et al.*[4] reported the C-N stretching mode in the region 1650-1400 cm^{-1}, and Yadav *et al.*[13] assigned this mode at

1560 cm^{-1} in disusbtituted pyrimidine.

The hydroxyl OH group provides three normal vibrations, υOH, δOH and γOH, of which not only the stretching vibration but also the out-of-plane deformation are good group vibrations[7]. *Ab initio* calculations give the υOH mode at 3590 cm^{-1}. The moderate to strong absorption at 1350 ± 40 cm^{-1} in the spectrum of phenols is assigned to δOH mode[14]. In the present case, the band at 1190 cm^{-1} in IR and 1191 cm^{-1} in HF is assigned as δOH mode. The OH out-of-plane deformation is assigned at 504 cm^{-1}, which is expected in the range 685 ± 115 cm^{-1} for phenols[7].

Table 2: Calculated (scaled) vibrational wave numbers and band assignments

$\upsilon_{(HF)}$ cm^{-1}	IR intensity	Raman activity	$\upsilon_{(IR)}$ cm^{-1}	Assignments
3590	149.29	97.92	3460	υOH
3053	7.31	112.78	3038	υCH
3035	7.05	66.14	3010	υCH
2946	17.14	59.01	2949	υ_{as}Me
2932	7.47	86.43	2900	υ_{as}Me
2867	8.38	146.02		υ_{s}Me
2601	26.24	322.61		υHCl
1599	300.70	11.88	1581	υRing
1561	264.55	11.61	1556	υRing
1476	54.84	2.741		υRing
1459	25.13	11.22		δ_{as}Me
1458	12.23	18.03		δ_{as}Me
1445	294.92	0.12	1426	υRing
1414	12.02	11.69	1403	δ_{s}Me
1321	37.36	4.40		υRing
1256	100.00	2.02	1250	υC-OH
1191	153.00	0.48	1190	δOH

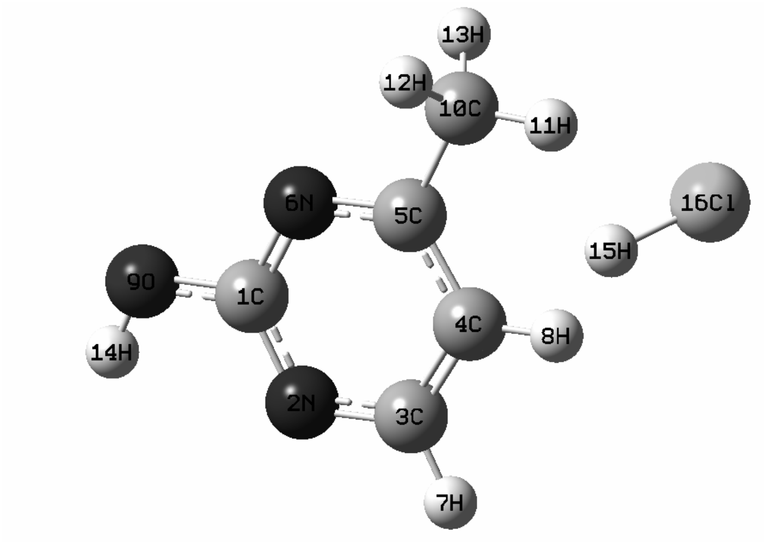
Cont…

$\upsilon_{(HF)}$ cm^{-1}	IR intensity	Raman activity	$\upsilon_{(IR)}$ cm^{-1}	Assignments
1147	16.20	7.69	1158	υRing
1083	17.26	3.59		υCC
1081	17.83	1.73		ρMe
1032	5.57	1.95	1035	δCH
1031	27.13	2.02	1026	ρMe
980	6.58	15.36		γCH
934	18.04	3.30	925	δRing
856	57.33	0.76		γCH
817	45.04	0.04	837	γRing
745	4.33	14.09	761	Ring breath
635	10.27	0.43	611	γRing
583	0.54	6.08	588	δRing(X)
533	8.86	6.94	530	δRing(X)
504	198.96	2.57	512	γOH
466	10.97	0.41		δRing
465	7.28	1.30		γRing(X)
298	8.59	0.52		tMe
217	6.17	1.02		γRing(X)
205	2.34	2.81		γRing(X)
119	60.57	18.77		δClH
74	79.47	39.33		γClH
52	0.53	0.69		tMe
31	0.45	3.90		tRing
14	4.18	4.51		tRing
8	6.25	4.52		tClH

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-twisting; rocking; ω -wagging; Me- methyl; Ring-Pyrimidine ring; t-torsion; subscripts:

as – asymmetric, s- symmetric; experimental frequencies are taken from reference [5].

The asymmetric stretching modes[7,15] of CH_3 are expected in the range 2905-3000 cm^{-1} and the symmetric CH_3 stretching vibrations in the range of 2860-2870 cm^{-1}. The first of these results from the asymmetric stretching of δ_{as}Me mode, in which two C-H bonds of the methyl group are extending while the third one is contracting. The second arises from the symmetrical stretching δ_sMe in which all the three of the C-H bonds extend and contract in phase. The asymmetrical stretching modes of the methyl group are calculated to be 2946, 2932 and symmetrical mode at 2867 cm^{-1}. The asymmetrical deformations of the methyl group are expected in the region[7] 1400-1485 cm^{-1} and band calculated at 1459, 1458 cm^{-1} are assigned as these modes. In many molecules, the symmetric deformation of CH_3 is expected in the region[7] 1380 ± 25 cm^{-1} and the HF calculation give this mode at 1414 cm^{-1}. The rocking modes[7] of the methyl group is reported in the range 970 ± 70 cm^{-1} and in the neighborhood of 1045 cm^{-1} The methyl torsions[7] are assigned in the region 185 ± 65 cm^{-1}.



The C_1–O_9 bond length 1.3405 Å is less than the average distance of 1.362 found among phenols[16], which is due to the presence of N_2 and N_3 atoms in the ring. Sundaraganesan *et al.*[17] reported the range of the bond lengths C_5–N_6 as 1.318-1.327, C_1–N_6 as 1.324-1.352, C_1–N_2 as 1.324-1336, N_2–C_3 as 1.318-1337, C_3–C_4 as 1.384-1.395, C_4–C_5 as 1.384-1.403 and C_3–H_7 as 1.069-1.079 Å theoretically for pyrimidine derivatives. In the present case, the corresponding values are 1.3353, 1.3219 , 1.3277, 1.3324, 1.3834, 1.3961 and 1.0705 Å. For the title compound, HF calculations give the bond angles A(2,1,6) =125.6 , A(1,2,3) =117.1 , A(2,3,4) =121.7 , A(3,4,5)= 117.2 , A(4,5,6) = 120.4 and A(5,6,1) = 118.0°, whereas the corresponding reported values are in the range 126.7-127.1, 115.8-116, 123.0-123.5, 114.6-115, 123.4-123.8 and 115.0-115.9°[17] .

Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research[18]. The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectrum. The first hyperpolarizability (β_0) of this novel molecular system is calculated using DFT method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry[19].

The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_{i} \mu_I F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \ldots \quad \ldots(1)$$

where E_0 is the energy of the unperturbed molecule, F^i is the field at the origin, μ_i, α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyper polarizabilities, and second hyperpolarizibilites, respectively. The calculated first hyperpolarizability of the title compound is 1.35×10^{-30} esu, which is comparable with the reported values of similar derivatives[20] and experimental evaluation of this data is not readily available. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

REFERENCES

1. V. K. Kumar and V. Balachandran, Indian J. Pure Appl. Phys., **39**, 623 (2001).
2. B. S. Yadav, V. Kumar, V. Singh and B. S. Semwal, Indian J. Pure Appl. Phys., **37**, 34 (1999).
3. V. K. Kumar and R. R. Sany, Indian J. Pure Appl. Phys., **40**, 252 (2002).
4. D. N. Singh, I. D. Singh and R. A. Yadav, Indian J. Phys., **76B**, 307 (2002).
5. B. S. Yadav, P. Yadav, P. Kumar and Vaishali, Asian J. Chem., **20**, 273 (2008).
6. A. B. Kartha, Spectrochim. Acta, **38A**, 859 (1982).

7. N. P. G. Roeges, A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures, Wiley, New York (1994).
8. M. J. Frisch, et al. Gaussian 03, Revision C.0*2,* Gaussian Inc:Wallingford, (2004).
9. J. B. Foresman, E. Frisch, in Frisch, E., (Ed.), Exploring Chemistry with Electronic Structure Methods, A Guide to Using Gaussian, Gaussian, Pittsburg PA (1996).
10. G. Socrates, Infrared Characteristic Group Frequencies, Wiley-Interscience, New York (1980).
11. B. S. Yadav, M. K. Yadav and A. K. Pandir, Acta Cinec. Indica, **26**, 47 (2002).
12. B. S. Yadav and V. Singh, Spectrochim. Acta, **55A**, 1267 (1999).
13. B. S. Yadav, M. K. Singh and A. Gupta, Oriental J. Chem., **18**, 501 (2002).
14. G. Varsanyi and P. Sohar, Acta Chim. Acad. Sci. Hung., **74**, 315 (1972).
15. N. B. Colthup, L. H. Daly and S. E. Wiberly, Inroduction to Infrared and Raman Spectroscopy, Ed. 3, Academic Press, Boston (1990).
16. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, J. Chem. Soc. Perkin Trans., **2**, S1 (1987).
17. N. Sundaraganesan, K. S. Kumar, C. Megathan and B. D. Joshua, Spectrochim. Acta, **65A**, 1186 (2006).
18. M. Tommasini, C. Castiglioni, M. Del Zoppo and G. Zerbi, J. Mol. Struct., **480**, 179 (1999).
19. D. A. Kleinman, Phys. Rev., **126**, 1977 (1962).
20. H. T. Varghese, C. Y. Panicker, V. S. Madhavan, S. Mathew, J. Vinsova and C. Van Alsenoy, J. Raman Spectrosc. Doi:10.1002/jrs.2265.

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