

FTIR and Laser Raman Spectra, Vibrational Assignments and *Ab-initio* Calculations of 6-Hydroxypurine

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The FTIR and Raman spectra of 6-hydroxypurine were recorded and all the 36 ($25a' + 11a''$) normal modes of vibrations are assigned assuming C_s point group symmetry. A complete vibrational analysis is proposed based on predictions from *ab-initio* 3-21G calculations. The vibrational assignments are supported by potential energy distribution (PED) calculations.

INTRODUCTION

Purine and its derivatives are find applications in biological and pharmaceutical fields and they are the building blocks of RNA and DNA¹. The purine rings also presented in many natural products. In this paper a complete vibrational analysis is proposed using *ab-initio* calculation. *Ab-initio* vibrational analyses beyond the normal mode of approximation are becoming increasingly common for polyatomic molecules. These data can be very valuable in vibrational assignments, conformational analyses, structural determinations, predicting harmonic force constants and relative intensities in infrared and Raman spectra².

EXPERIMENTAL

The pure sample of 6-hydroxy purine was obtained from Aldrich Chemical Company (Milwaukee, WI, USA). The FTIR spectrum was recorded on Perkin-Elmer spectrophotometer by the KBr disc technique. The laser Raman spectrum has been recorded at room temperature with 514.5 nm line of an Ar⁺ laser for excitation operating at 200 mw of power. The structure of the molecule along with internal coordinates are given in Fig. 1.

Ab-initio Calculations: Using the 3-21G basis set, the Gaussian 88 program³ was used to perform the *ab-initio* calculations. The calculated structural parameters as determined with the 3-21G basis set are given in Table-1 and they are found to be comparable with previously reported values⁴. The results of the *ab-initio* calculations reported here are expected to be $\pm 1^\circ$ for the angular parameters but small differences are expected for bond lengths.

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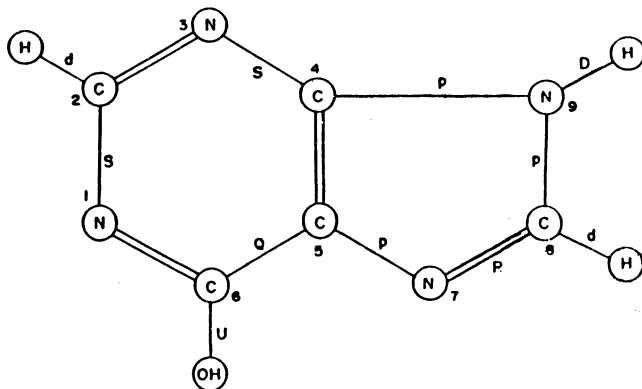
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TABLE-1
CALCULATED STRUCTURAL PARAMETERS OF 6-HYDROXYPURINE AND ITS
COMPARISON WITH THE LITERATURE VALUES

Bond	Calculated with 3-21G basis set	Ref. 4
N ₁ C ₂ ^a	1.3529	1.3642
C ₂ N ₃	1.3041	1.2997
N ₃ C ₄	1.3408	1.3548
C ₄ C ₅	1.3691	1.3710
C ₅ C ₆	1.4351	1.4248
C ₆ N ₁	1.4195	1.4266
C ₅ N ₇	1.3968	1.3918
N ₇ C ₈	1.2896	1.2904
C ₈ N ₉	1.3904	1.3954
N ₉ C ₄	1.3520	1.3553
C ₆ O ₁₀	1.2088	1.2117
C ₁₀ H ₁₁	1.0266	0.9715
C ₂ H ₁₂	1.0807	1.0626
N ₉ H ₁₃	0.9963	0.9952
C ₈ H ₁₄	1.0591	1.0634
C ₂ N ₁ C ₆ ^b	126.09	126.03
N ₁ C ₂ N ₃	123.71	122.65
C ₂ N ₃ C ₄	114.60	114.30
N ₃ C ₄ C ₅	127.21	127.38
C ₄ C ₅ C ₆	119.90	119.76
C ₅ C ₆ N ₁	108.46	109.87
N ₉ C ₄ C ₅	107.20	106.16
C ₄ C ₅ N ₇	109.37	109.75
C ₅ N ₇ C ₈	106.07	105.92
N ₇ C ₈ N ₉	112.30	111.31
C ₈ N ₉ C ₄	107.12	106.87
N ₁ C ₆ O ₁₀	119.94	118.75
C ₆ O ₁₀ H ₁₁	112.41	112.05
N ₁ C ₂ H ₁₂	122.80	112.09
C ₄ N ₉ H ₁₃	112.95	113.62
N ₇ C ₈ H ₁₄	122.26	121.50

a: Bond length in Å, b: Bond angle in degree

Normal Coordinate Analysis: In order to obtain a complete description of the molecular motions involved in the normal modes of the title compound, the normal coordinate analysis has been carried out using the *ab-initio* calculations and Wilson's FG matrix mechanism⁵ utilizing the software (FORTRAN IV) by Schachtschneider⁶ with suitable modifications. The force constant matrix in



$$\angle CCC = \alpha, \angle CNC = \beta, \angle COH = \gamma, \angle HCN = \psi, \angle NCN = \phi, \angle NCC = \delta, \angle CNH = \theta$$

Fig. 1. The structure of 6-hydroxypurine along with internal coordinates

Cartesian coordinates has been calculated by the Gaussian -88 software with 3-21G basis set and subsequently transformed into a force constant matrix in internal coordinates by considering non-redundant internal coordinates. Initially all scale factors were kept at 1.0 to produce the pure *ab-initio* calculated wavenumbers. Subsequently 0.940 and 0.839 are used for scaling the wavenumbers of in-plane and out-of-plane vibrations respectively. A set of in-plane and out-of-plane vibrational modes of 6-hydroxy purine was proposed from the normal coordinate analysis based on empirical force field using the structural parameters of a related system and adjusted by least square refinement process. The comparison of those values with *ab-initio* force field are given in Table-2.

Vibrational Assignments: The 36 ($25a' + 11a''$) normal modes of vibrations are assigned by assuming that the molecule belongs to C_s point group symmetry. In Table-3 a summary of the vibrational assignments for both in-plane (a') and out-of-plane (a'') modes is given. The present vibrational assignments are mostly based on the PED calculations.

(a) Force Constants

It is interesting to compare the *ab-initio* predicted constants with the empirical constants for the title compound (Table-2). The N—H and C—H diagonal force constants are in close agreement, whereas the O—H and C—N force constants differ. Similarly the off-diagonal interaction terms are also found varying. These variations are due to the change in the structural parameters. A comparison of these parameters could provide some interesting trends and help to understand better the bonding in the molecule. As expected there is no double bond force constant since the electrons are delocalized in the double bond region.

(b) Vibrational Analysis

The stretching modes of O—H, N—H and C—H normally appear in this region. In the case of C—H stretching, two modes are expected one each from

TABLE-2
 COMPARISON OF THE *AB-INITIO* PREDICATED FORCE CONSTANTS WITH
 EMPHERICAL FORCE CONSTANTS VALUES (IN THE UNITS OF
 $\text{mdyne } \text{\AA}^{-1}$, mdyne rad^{-1} AND $\text{mdyne } \text{\AA}^{-1} \text{rad}^{-2}$)

Character of Constants	Scaled <i>ab-initio</i> force constants	Empirical force constants
Stretch		
N ₉ —H	6.2238	6.2054
C ₆ —O	6.0855	5.9732
O—H	6.9676	6.5609
C ₂ —H	5.7291	5.6929
C ₂ —N ₁	5.7348	5.8611
C ₅ —N ₇	5.4140	5.6517
C ₈ —H	5.6603	—
(C ₄)C ₈ —N ₉	5.3561	—
(C ₆)C ₄ —C ₅	5.6814	5.6385
Bend		
C ₂ N ₁ C ₆	0.5391	0.4793
N ₁ C ₂ N ₃	0.4419	0.4621
C ₄ C ₅ C ₆	0.3147	0.4982
C ₅ C ₆ N ₁	0.7653	—
N ₉ C ₄ C ₅	0.3017	0.3416
C ₄ C ₅ N ₇	0.5532	—
C ₄ N ₉ C ₈	0.2967	0.3103
N ₇ C ₈ N ₉	0.3529	0.3855
N ₁ C ₆ O ₁₀	0.5301	—
C ₆ OH	0.9811	1.8377
N ₁ C ₂ H	0.3729	—
C ₄ N ₉ H	0.4051	—
Stretch-stretch		
C ₂ HC ₂ N ₁	0.1938	—
C ₆ O OH	0.0971	0.1302
C ₄ C ₅ C ₅ N ₇	0.2219	—
N ₉ H C ₈ H	0.1806	—
N ₉ H C ₈ N ₉	0.1006	0.1757
C ₈ H C ₈ N ₉	0.5133	—
C ₄ N ₉ C ₈ N ₉	0.5261	2.9750
C ₄ C ₅ C ₅ C ₆	0.4385	—
Stretch-bend		
C ₄ C ₅ C ₅ C ₆ N ₁	0.1130	—
C ₂ H N ₁ C ₂ N ₃	0.0749	0.0654
C ₂ N ₁ C ₅ C ₆ N ₁	0.0622	0.0781
C ₆ O C ₅ C ₆ N ₁	0.1839	—
N ₉ H C ₄ N ₉ C ₈	0.1028	—
Bend-bend		
C ₂ N ₁ C ₆ C ₄ C ₅ C ₆	0.0431	0.0614
C ₄ C ₅ N ₇ C ₄ N ₉ C ₈	0.0517	0.0908
C ₆ OH C ₅ C ₆ N ₁	0.0037	—
N ₁ C ₂ H.C ₅ C ₆ N ₁	0.0054	—
C ₄ N ₉ H N ₇ C ₈ N ₉	0.0151	0.0316

TABLE-3
OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) ALONG WITH PED FOR
NORMAL MODES OF 6-HYDROXYPURINE

Species	Observed FTIR	Observed Raman	Calculated	Assignments/ % PED
In-plane				
—	—	3980 w	—	(3721 + 251)
a'	—	3731 w	3823	O—H Stretching (98)
a'	3543 vs	3592 w	3630	O—H Stretching(96)
a'	3361 w	3378 m	3379	N—H Stretching (99)
a'	3330 w	3340 w	3351	N—H Stretching (94)
a'	3120 w	3124 w	3120	C—H Stretching (99)
a'	3010 w	3014 w	3007	C—H Stretching (96)
—	2907 m	2907 m	—	(1288 + 619)
—	1817 m	—	—	(1008 + 809)
a'	1697 vs	1695 ms	1690	C—N Stretching (89)
a'	1619 m	1590 m	1612	C—C Stretching (84)
a'	1488 w	—	1476	C—C Stretching (88)
a'	1454 ms	—	1448	C—N Stretching (84)
a'	1421 ms	1421 ms	1418	C—N Stretching (81)
a'	1407 ms	1400 w	1400	C—N Stretching (84)
a'	1316 s	1312 w	1311	C—O Stretching (86)
a'	1288 s	1302 w	1286	N—H in-plane bending (80)
a'	1246 m	1234 w	1244	C—OH in-plane bending (86)
a'	1207 s	—	1204	O—H in-plane bending (79)
a'	1186 s	1186 m	1182	C—H in-plane bending (74)
a'	1112 m	1110 m	1104	C—H in-plane bending (77)
a'	1091 ms	—	1089	C—OH in-plane bending (76)
a'	1008 w	—	996	C—C—C in-plane bending (80)
a'	—	976 s	964	C—C—C in-plane bending (76)
a'	809 m	—	812	ring-in-plane bending (72)
a'	690 m	—	684	C—O in-plane bending (75)
a'	523 w	524 m	518	N—C—N in-plane bending (68)
a'	469 m	—	461	N—C—N in-plane bending (66)
Out of Plane				
a''	917 w	910 w	902	N—H out-of-plane bending (64)
a''	779 w	790 ms	784	C—H out-of-plane bending (66)
a''	739 m	731 m	744	C—H out-of-plane bending (62)
a''	714 vs	707 m	701	O—H out-of-plane bending (56)
a''	672 m	670 m	665	C—C—C out-of-plane bending (57)
a''	619 m	609 m	602	C—C—N out-of-plane bending (60)
a''	585 m	—	578	C—N out-of-plane bending (58)
a''	—	379 m	384	C—O out-of-plane bending (54)
a''	—	348 m	340	C—OH out-of-plane bending (57)
a''	—	305 vs	296	C—OH out-of-plane bending (55)
a''	—	251 m	242	N—C—N out-of-plane bending (56)
—	—	148 m	—	lattice vibrations

vs, very strong; s, strong; ms, medium strong; m, medium, w, weak.

pyrimidine and imidazole respectively and they are found at 3120 and 3010 cm^{-1} in FTIR and 3124 and 3014 cm^{-1} in the Raman spectrum. Apart from these bands some bands observed should involve these C—H stretching modes, but may also correspond to overtones or combination modes. The O—H, N—H stretching vibrations observed in this study are of their characteristic regions.^{7, 8}

The FTIR and Raman peaks observed in the intermediate regions (1600–1300 cm^{-1}) are mainly due to C—C, C—N and C—O stretching vibrations^{9, 10}. Accordingly the title compound has shown the peaks at 1488, 1454 and 1316 cm^{-1} in FTIR for C—C, C—N and C—O group stretching modes respectively. The Raman counterparts for these regions are presented in Table-3.

The strong IR band at 1288 cm^{-1} and the weak Raman band at 1302 cm^{-1} are assigned to N—H in-plane bending vibrations in agreement with the PED calculations. The assignments made for other in-plane bending vibrations shown in Table-3 are in good agreement with the literature^{11, 12}

All the out-of plane vibrations belong to the a'' symmetry block. The C—C—C and C—C—N out-of-plane bending vibrations are identified at 672 and 610 cm^{-1} in FTIR. The Raman counterparts of these modes are found at 670 and 609 cm^{-1} respectively. These assignments are supported by the potential energy distribution values.

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