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Structural conformations, tautomerization and vibrational spectral study of 6-amino-1-methylpurine with density functional theoretical calculations

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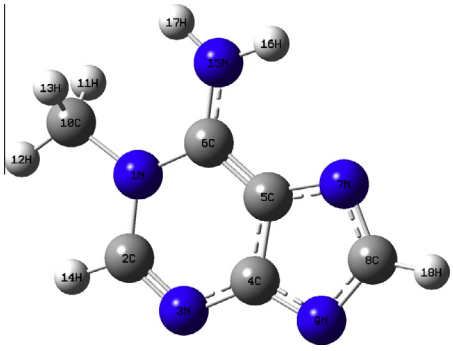
HIGHLIGHTS

- The calculated vibrational values are in good agreement when they are compared with IR and Raman experimental data.
- Amine–imine tautomerism is studied in detail.
- The NBO analysis has been performed to elucidate the intra molecular interaction and delocalization.

GRAPHICAL ABSTRACT



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ABSTRACT

The FT-IR and FT-Raman spectra of 6-amino-1-methylpurine (AMP) have been recorded in the region 4000–400 cm^{-1} and 3500–50 cm^{-1} respectively. The optimized geometry, frequency and intensity of the vibrational bands of AMP have been obtained by DFT level of theory using B3LYP method with 6-311++G(d,p) basis set. A complete vibrational assignment aided by the theoretical harmonic frequency analysis has been proposed. Purines, including substituted purines and their tautomers, are the most widely occurring nitrogen-containing heterocyclic in nature. Purines and pyrimidines make up the two groups of nitrogenous bases, including the two groups of nucleotide bases. Two of the four deoxyribonucleotides and two of the four ribonucleotides, the respective building-blocks of DNA and RNA, are purines. The calculated vibrational values are in good agreement when they are compared with IR and Raman experimental data. Amine–imine tautomerism of 6-amino-1-methyl purine is studied in detail. In agreement with experimental results, it was found that imine tautomer is more stable than amine tautomer.

Introduction

A purine is a heterocyclic aromatic organic compound. It consists of a pyrimidine ring fused to an imidazole ring. Purines, including substituted purines and their tautomers, are the most widely occurring nitrogen-containing heterocycle in nature [1]. Purines and pyrimidines make up the two groups of nitrogenous bases, including the two groups of nucleotide bases. Two of the four deoxyribonucleotides and two of the four ribonucleotides, the respective building-blocks of DNA and RNA, are purines. Prominent purines (derivatives) include caffeine acids are adenine and guanine. In DNA, adenine and guanine form hydrogen bonds with their complementary pyrimidines, thymine and cytosine. Purine is

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also a component in Adenosine triphosphate (ATP) which stores and transports chemical energy within cells.

Also, 6- and 9-substituted purine derivatives are evaluated for their antitumour and antiviral activity, as cardiovascular agents and for their use as hepadnaviride-active avtiviral agents [2]. Literature survey reveals that to the best of our knowledge no DFT with 6-311G++ (d, p) basis set calculations of 6-amino-1-methyl purine (AMP) has been reported so far. It is, therefore thought worthwhile to make a comprehensive vibrational analysis using both experimentally observed IR and Raman wavenumbers and theoretically calculated vibrational spectra.

Experimental details

The pure sample of AMP is obtained from Lancaster chemical company, UK and used as such without any further purification to record FT-IR and FT-Raman spectra. The room temperature Fourier transform IR spectrum of the title compound is measured in the 4000–400 cm^{-1} region at a resolution of ± cm^{-1} using BRUKER IFS-66V Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter and globar arc source.

The FT-Raman spectrum is recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory. The FT-Raman spectrum is recorded in the 3500-50 cm^{-1} stokes region using the 1064 nm line of Nd:YAG laser for the excitation operation at 200 mW power. The reported wave numbers are expected to be accurate within ±1 cm^{-1}.

Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN 09 program are subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering, [3–5]

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i\left[1 - \exp\left(-\frac{hcv_i}{K_b T}\right)\right]}$$

where v_0 is the exciting frequency in cm^{-1}, v_i the vibrational wave number of the ith normal mode, h, c and k_b are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities (see Tables 1 and 3).

Results and discussions

6-Amino-1-methyl purine (AMP) or 1-methyl adenine ($C_6H_7N_5$) is a yellow crystalline powder with Molecular weight – 149.15 g/mol and melting point 214 °C. For AMP, amino and methyl groups are substituted in the N6 and N1 position respectively. Fig. 1 shows the optimized molecular geometry of AMP. Figs. 2 and 3 show the FT-IR and FT-Raman spectra of the title compound. Normally, Adenine exists in two amino tautomeric forms N9-H and N7-H. However, Nowak et al. [6] have reported that, in low temperature inert environment, the N9-H tautomer dominates and they have recorded the infrared spectra of adenine in argon (Ar) and nitrogen matrices. Pivovarov et al. have analyzed the structure of 1-methyl adenine in an argon matrix [7]. The advantage of matrix isolated spectra is that, intermolecular hydrogen bondings present in solid state samples are reduced to a minimum. The matrix spectra can be directly compared with calculated anharmonic frequencies. Molecules of AMP have two labile protons. The title compound exhibit amine-imine tautomerism character. The total number of prototropic tautomers is four (Figs. 4–7). Figs. 4–6 correspond to imine tautomers with the second proton localization at the N_7 or

Table 1
Optimized geometrical parameters of 6-amino-1-methylpurine obtained by DFT method with 6-311++G(d,p) basis set.

Parameters bond length	Value (Å)		Bond angle	Value (Å)	
	DFT/6-311++G(d,p)	Exp.[a]		DFT/6-311++G(d,p)	Exp.[a]
N1–C2	1.408	1.338	C2–N1–C6	120.16	–
N1–C6	1.383	1.349	C2–N1–C10	119.28	–
N1–C10	1.470	–	C6–N1–C10	120.54	118.8
C2–N3	1.303	1.332	N1–C2–N3	125.30	–
C2–H14	1.079	–	N1–C2–H14	114.63	–
N3–C4	1.376	1.342	N3–C2–H14	120.06	–
C4–C5	1.429	1.382	C2–N3–C4	115.92	110.8
C4–N9	1.352	1.376	N3–C4–C5	121.92	126.9
C5–C6	1.385	1.409	N3–C4–N9	129.09	–
C5–N7	1.378	1.385	C5–C4–N9	108.97	–
C6–N15	1.35	–	C4–C5–C6	120.47	–
N7–C8	1.360	1.312	C4–C5–N7	109.49	110.7
C8–N9	1.379	1.367	C6–C5–N7	130.03	132.3
C8–H18	1.075	–	N1–C6–C5	116.19	–
C10–H11	1.091	–	N1–C6–N15	121.10	119.0
C10–H12	1.086	–	C5–C6–N15	122.70	–
C10–H13	1.091	–	C5–N7–C8	102.02	103.9
N15–H16	1.007	–	N7–C8–N9	116.47	113.8
N15–H17	1.002	–	N7–C8–H18	122.03	–
			N9–C8–H18	121.49	–
			C4–N9–C8	103.03	105.9
			N1–C10–H11	110.86	–
			N1–C10–H12	108.71	–
			N1–C10–H13	110.85	–
			H11–C10–H12	108.22	–
			H11–C10–H13	109.87	–
			H12–C10–H13	108.22	–
			C6–N15–H16	116.72	–
			C6–N15–H17	124.46	–
			H16–N15–H17	118.81	–

[a] Exp. Ref. [5].