Applying Vibrational Spectroscopy to the Study of Nucleobases – Adenine as a Case-Study

Rui P. Lopes, Rosendo Valero, John Tomkinson, M. Paula M. Marques, and Luís A. E. Batista de Carvalho

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Table S1 – Calculated (isolated molecule and condensed phase) and measured (asymmetric unit) geometric parameters for adenine.

Dihedrals	[a]Isolated Molecule	[b]Condensed Phase		[c]Asymmetric Unit	
		I	II	I	II
H10-N6-C6-C5	171.0	-178.0	-180.0	179.3	-179.0
H10-N6-C6-N1	-10.0	2.1	0.4	0.0	0.0
H11-N6-C6-C5	10.9	2.1	-0.9	-0.8	1.0
H11-N6-C6-N1	-170.1	-177.8	179.5	180.0	-180.0
N6-C6-N1-C2	-178.6	-179.9	-179.1	-179.8	-179.2
N6-C6-C5-C4	178.6	180.0	-179.9	-178.8	-179.8
N6-C6-C5-N7	-1.8	0.7	-0.2	-0.2	-0.7
C6-C5-C4-N9	179.8	179.9	179.1	178.6	179.0
C6-C5-C4-N3	0.0	-0.6	-1.3	-2.5	-2.3
C6-C5-N7-C8	-179.7	179.6	-179.2	-178.3	-179.1
C6-N1-C2-N3	-0.2	0.4	-0.7	-0.5	0.0
C6-N1-C2-H	179.9	-178.6	179.9	179.4	180.0
N1-C2-N3-C4	-0.1	-0.9	-0.8	-1.2	-0.8
N1-C6-C5-C4	-0.3	0.0	-0.3	0.4	1.2
N1-C6-C5-N7	179.3	-179.3	179.4	179.1	-179.7
C2-N3-C4-C5	0.2	1.0	1.8	2.8	2.1
C2-N3-C4-N9	-179.6	-179.7	-178.8	-178.7	-179.5
C2-N1-C6-C5	0.4	0.1	1.2	0.9	-0.2
N3-C4-N9-H	-0.2	4.9	5.4	1.2	1.8
N3-C4-C5-N7	-179.7	178.9	178.9	178.6	178.4
N3-C4-N9-C8	179.7	-178.8	-179.0	-178.8	-178.3
C4-C5-N7-C8	-0.1	0.3	0.5	0.4	0.0
C4-N9-C8-H	-179.9	178.0	178.3	-179.7	179.4
C4-N9-C8-N7	0.1	-0.5	-0.2	0.3	-0.5
C4-N3-C2-H	179.8	178.1	178.6	178.8	179.2
C5-N7-C8-N9	0.0	0.2	-0.2	-0.4	0.3
C5-N7-C8-H	-180.0	-178.3	-178.6	179.6	-179.6
C5-C4-N9-H	180.0	-175.6	-175.1	-180.0	-179.5
C5-C4-N9-C8	-0.1	0.7	0.5	0.0	0.5
N7-C8-N9-H	180.0	175.6	175.2	-180.0	179.4
N7-C5-C4-N9	0.1	-0.6	-0.6	-0.3	-0.3
H-N9-C8-H	0.0	-5.9	-6.3	0.2	-0.6

Angles	[a]Isolated Molecule	[b]Condensed Phase		[c]Asymmetric Unit	
		I	II	I	II
H10-N6-C6	118.0	119.1	118.9	120.0	120.1
H11-N6-C6	119.3	121.8	122.0	120.0	120.0
H10-N6-H10	119.6	119.1	119.1	120.0	120.0
N6-C6-N1	118.9	119.2	119.2	117.9	119.7
N6-C6-C5	122.3	124.4	124.5	123.5	122.4
C6-N1-C2	118.3	120.4	120.3	117.7	118.4
N1-C2-N3	128.9	128.0	128.2	129.3	129.0
N1-C2-H	115.2	115.8	115.6	115.4	115.5
N1-C6-C5	118.9	116.4	116.3	118.6	117.9
N3-C2-H	115.9	116.2	116.1	115.4	115.5
C2-N3-C4	111.1	112.0	111.8	110.6	111.0
N3-C4-C5	126.9	126.0	126.0	127.2	127.9
N3-C4-N9	128.6	127.8	127.8	128.2	127.6
C4-C5-C6	115.8	117.2	117.3	116.7	115.8
C4-N9--H	125.8	125.2	125.3	126.2	126.7
C4-N9-C8	106.7	106.2	106.2	107.6	106.6
C4-C5-N7	111.5	109.6	109.7	111.4	111.6
C5-N7-C8	103.9	104.6	104.5	103.2	103.1
C5-C4-N9	104.4	106.2	106.1	104.6	104.5
N7-C8-H	125.2	124.7	124.9	123.3	123.0
N7-C8-N9	113.5	113.4	113.5	113.3	114.1
C8-N9-H	127.5	128.5	128.3	126.2	126.7
N9-C8-H	121.4	121.9	121.6	123.4	122.9

Bond Lengths	[a]Isolated Molecule	[b]Condensed Phase		[c]Asymmetric Unit	
		I	II	I	II
H10-N6	100.7	104.4	104.6	86.0	86.0
H11-N6	100.7	104.3	104.1	86.0	86.0
N6-C6	135.6	132.4	132.5	134.3	134.9
C6-N1	134.5	135.4	135.3	137.1	136.8
C6-C5	141.1	141.3	141.2	139.0	142.1
N1-C2	134.4	132.8	132.7	134.4	135.1
C5-C4	139.9	139.4	139.4	139.7	138.1
C2-N3	133.7	132.7	132.6	134.4	132.1
C4-N3	133.9	133.7	133.7	133.9	135.0
C2-H	108.8	110.0	110.0	93.0	93.0
C5-N7	138.6	137.0	137.0	137.5	137.8
C4-N9	137.8	135.9	135.7	135.7	136.7
N7-C8	131.1	131.5	131.5	132.9	130.4
N9-C8	138.1	135.5	135.5	135.3	135.7
C8-H	108.2	109.3	109.1	93.0	93.0
N9-H	100.9	106.5	106.9	85.9	86.1

H-bonding: Condensed Phase[b]

		I		
(N)-H----X	(N)-H	H----X	(N)-----X	<(N-H----X)
N6-H10----N7	104.4	200.6	304.8	174.6
N6-H11----N1	104.3	203.4	305.5	166.7
N9-H----N3	106.5	186.0	291.2	168.8
		II		
N6-H10----N7	104.6	197.7	302.0	174.8
N6-H11----N1	104.1	208.3	310.2	165.6
N9-H----N3	106.9	181.9	287.7	169.7

H-bonding: Asymmetric Unit[c]

		I		
N-H----X	N-H	H----X	(N)------X	<(N-H----X)
N6-H10----N7	86.0	219.4	305.3	176.8
N6-H11----N1	86.0	222.8	305.6	161.6
N9-H----N3	85.9	202.0	286.4	166.9
		II		
N6-H10----N7	86.0	221.2	307.2	178.0
N6-H11----N1	86.0	217.5	299.9	160.6
N9-H----N3	86.1	204.6	289.1	166.5

[a]At the DFT B3LYP/6-31G** level of theory.
[b]With the PWSCF/LDA methodology. **I** and **II** refer to the two adenine molecules in the asymmetric unit.
[c]Geometric parameters obtained from X-ray diffraction data [31]